

SCIENCE AND CONSERVATION FOR MUSEUM COLLECTIONS



edited by
Bruno Fabbri

NARDINI EDITORE

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INTRODUCTION

HOW THE IDEA OF A BOOK WAS BORNE

In the years 2009 and 2010 a long refreshing course for restorers of Syrian Directorate General of Antiquities and Museums was made at the Archaeological Museum in Damascus, Syria. The course was organized and managed by the Institute of Science and Technology for Ceramics (ISTEC), of the Italian National Research Council (CNR), which has its main office in Faenza, in collaboration with a private Syrian organization. In particular, CNR-ISTEC planned and managed the scientific program, while the Syrian organization mainly devoted itself to the logistic problems.

The course included the study and conservation of a lot of different types of artefacts and materials, which were taken into account from a theoretical and practical point of view. The lessons were partly given by personnel of CNR-ISTEC, but for the main part of the lessons, especially the practical ones, it was necessary to contact external private professionals. A total of more than twenty experts contributed to the success of the enterprise.

During the progress of the course, a common difficulty emerged for all the teachers, due to the lack of suitable didactic material for the trainees. In fact, there are many publications at disposal, but they generally are mono-thematic and a high number of books would be necessary in order to cover all the subjects of a course. In addition, it was not possible to utilize books in Italian language, so that all the experts had to prepare the suitable documentation for their own speciality in English language. Due to this situation, the idea was borne that it would have been possible to re-arrange and complete this didactic material and to realize a book, of which the main characteristics were to be poly-thematic, in English language, and including about fifteen types of archaeological materials, sometime very different from each other.

CONTENT OF THE BOOK

The book takes into consideration archaeological artefacts made out of the most common materials, like stones (both natural and artificial), mosaics, ceramics, glass, metals, wood and textiles. But all these important materials are accompanied by less diffuse artefacts and materials, like clay tablets, goldsmith artefacts, icons, leather and skin objects, bones and

ivory, coral and mother of pearl. Each type of artefact and/or material is treated from at least four different points of view:

- Composition and processing technology
- Alteration and degradation causes and mechanisms
- Procedures for conservative intervention
- Case study and/or examples of conservative intervention

In this way, the importance of science and diagnostics in the field of conservation emerges, together with the fact that it is not possible to avoid scientific analyses of the archaeological finds if one wants to achieve the best results from the conservation point of view. In addition, it becomes clear that the choice of the conservation systems is strictly connected to the results of the analyses.

Of course, the high number of materials and the great difference between their conservation problems would require a great number of pages, if they were treated in a deep way. Such a solution is not practical and not economic, therefore the solution was to treat all the subjects in a not deep, but complete and precise way. As a consequence, the book is subdivided into chapters devoted to different materials, together with two transversal chapters: one devoted to the general principles of the preventive conservation and the other one to the description of the most useful analytical techniques. In such an approach, special reference has been made to the needs of the museums and to the use of non-invasive analytical techniques.

THE TARGET

Due to its general features, the book is mainly addressed to students and young restorers or conservation scientists all around the world, because it is written in English. The book can be usefully read by expert professionals too, because nobody knows everything and the experts often need to learn something of the materials not included in their specific knowledge. All these people will find the essential on a lot of different ancient materials, all that is necessary to face up to specialist mono-thematic publications. After reading this book, they will be able to choose what really they need in order to become experts of new types of artefacts.

Of course, the reading of this book needs the knowledge of the English language, even though at a not very high level, because the text is written in a simple English form. This was possible because it mainly deals with technical items, which can be often described

with simplicity. We hope that not too many errors will be discovered when reading the book, while the reader will discover that the lecture is very easy.

The English language facilitates the reading by people of all the world, while the digital publication of the book makes its diffusion cheaper, allowing to avoid its printing and the subsequent distribution by mail.

THE AUTHORS

As said before, the training course for restorers in Syria had many experts, and each one of them treated only the materials of his competence. Therefore, all these experts were contacted in order to ask them to collaborate for realizing this book. In addition, some other experts were contacted in order to increase the subjects treated in the book or to substitute those already contacted experts who were not in condition to collaborate. At the end, 24 experts accepted to contribute with their experience for obtaining a good product, because these contributors have very different experiences and activities. As it is shown from the list reported in the following Table 1, all they are Italian experts, or work in Italy, so that the book can be seen as an example of the Italian vision in the conservation of Cultural Heritage.

In order to appreciate the variety of the authors, it can be observed that many of them work in public institutions, while others are professionals. Another difference comes from their sector of activity: about half of them are restorers, while the others are conservation scientists, and they have a particular experience in studying materials and degradation processes. In this way, all the aspects of each material treated in the book could be faced.

As a consequence of what said above, each chapter of the book generally results from the contribution of two or more collaborators, but each author remains the responsible of what he wrote. For this reason, the contributions of the authors are detailed in the table following (Table 2).

Table 1 – List of the experts who collaborated to the realization of the book.

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Table 2 – Detail of the contributions of each author to the book.

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DE NUNTIIS Paola	<i>1.1.1 – 1.2 – 1.3 – 1.4.2 – 1.4.3 – 1.4.4 – 1.5 – 1.7</i>
PALLA Franco	<i>1.1.2 – 1.4.1</i>
PONTI Fabio	1.6
CHAPTER 2 – STONE ARTEFACTS	
ABU AYSHEH Moh'd	<i>2.1 – 2.6 – 2.7.1</i>
AMATO Francesca	<i>2.2 – 2.3.1 – 2.3.2</i>
MACCHIAROLA Michele	<i>2.3.3 – 2.3.4 - 2.4 – 2.7.2</i>
MAMBELLI Roberto	2.5
CHAPTER 3 – MOSAICS	
ABU AYSHEH Moh'd	<i>3.1 – 3.2 – 3.3 – 3.4 – 3.5.1</i>
MACCHIAROLA Michele	3.5.2
CHAPTER 4 – CERAMICS	
AGNINI Elena	<i>4.4 – 4.6.2</i>
BANDINI Giovanna	<i>4.6.1</i>
FABBRI Bruno	<i>4.1 – 4.2 – 4.5.1 – 4.5.2</i>
GUALTIERI Sabrina	<i>4.3 – 4.5.1</i>
CHAPTER 5 – CLAY TABLETS	
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CHAPTER 6 – GLASS	
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AMATO Francesca	6.1 – 6.2
FABBRI Bruno	6.5.2
MACCHIAROLA Michele	6.3

CHAPTER 7 – METALS	
AMATO Francesca	7.1 – 7.2
FABBRI Bruno	7.5
MARIANI Bruna	7.3 – 7.4.1 – 7.4.2
PINTO FOLICALDI Barbara	7.4.3 – 7.4.4
CHAPTER 8 – GOLDSMITH ARTEFACTS	
AMATO Francesca	8.2 – 8.3
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INGUI' Giuseppe	9.3 – 9.4 – 9.5 – 9.6
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CHAPTER 10 – ICONS	
MALTSEVA Daria	10.1 – 10.2 – 10.3 – 10.4
CHAPTER 11 – TEXTILE FINDS	
PERTEGATO Francesco	11.1.1 – 11.1.2 – 11.1.3 – 11.2 – 11.3 – 11.4
PALLA Franco	11.1.4
CHAPTER 12 – LEATHER AND ANIMAL SKIN OBJECTS	
SCIANNA Nicolangelo	12.1 – 12.2 – 12.3 – 12.4 – 12.5 – 12.6 – 12.7
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CRISTOFERI Elena	13.1 – 13.2 – 13.3.1 – 13.3.2
FABBRI Bruno	13.3.3
CHAPTER 14 – ANALYTICAL TECHNIQUES	
FABBRI Bruno	14.1.2 – 14.1.4 – 14.3.1 – 14.4.3
GUALTIERI Sabrina	14.2.3 – 14.8
MACCHIAROLA Michele	14.2.1 – 14.2.2 – 14.4.1 – 14.4.2 – 14.6 – 14.7
PALLA Franco	14.9
RUFFINI Andrea	14.1.1 – 14.1.3 – 14.3.2 – 14.3.3 – 14.3.4 – 14.3.5 – 14.3.6 – 14.5
SIANO Salvatore	14.3.7

1 – PREVENTIVE CONSERVATION

1.1 Introduction

1.1.1 The concept of preventive conservation

Since the XIX century the problem of artwork conservation has become a growing concern due to environmental changes (air pollution) and, in confined environments, increased public enjoyment.

The following is a brief summary of the milestones in the development of the concept of ‘Preventive Conservation’:

- In the late 1960s, the science of conservation developed as a result of cultural heritage damage caused by floods in Florence and Venice.
- In 1963, *C. Brandi* proposed a new concept of restoration as “*protection, hazard removal and ensuring favourable conditions*”.
- The *Carta del Restauro di Venezia* (1964) used terms such as: “*systematic maintenance, preservation of the environment, no separation of the monument from its environment, restoration as a exceptional process*”.
- In “Problems of Preservation” (1973), *G. Urbani* presented a “conservation program” focused on the relationship between heritage and environment.
- In the 1970s, ICCROM (International Centre for the Study of the Preservation and Restoration of Cultural Property) defined preventive conservation as a discipline encompassing a series of actions required to enhance the conservation status of a monument over time.
- In 1987, the ICR (Italian Central Institute for Restoration) proposed the “Carta del Rischio” (Risk Charter) for cultural heritage, with the aim of creating a computerized database to simplify access to information on risk factors for materials, their conservation status, environmental aggression, and maintenance.

Artistic heritage is subject to deterioration: over time materials lose their ability to respond and adapt to different environmental parameters (natural and man-made damage). Degradation is a cumulative process evolving in a non-linear and irreversible fashion. The same causes may produce different effects depending on the type of object and its previous

history. The combination of different causes, past or present, produces synergistic effects. The aging of materials is an irreversible process that cannot be stopped, but only accelerated by inadequate conservation or neglect, or slowed by protecting objects or artefacts from the harmful effects of degradation agents.

Prevention begins with knowledge. The aim of this chapter is to identify key simple steps to achieve preventive conservation addressing the increasing difficulties of cultural heritage due to changing environmental social and cultural conditions: prolonged exposure, outdoor and indoor air pollution, transfers of works of art, and the presence of visitors. The presence of large uncontrolled numbers of visitors in museums, for example, can compromise works of art. Each visitor is a source of particles, gases and heat affecting the museum environment. One visitor in an exhibition hall produces:

- 50-100 g/h of water vapour
- 100 watt/h of heat
- 50 ml/h of carbon dioxide
- 0.2 g/h dust (microorganism, fibres of clothing, organic fragments)

Numerous rules and recommendations are available, both at national and international level, concerning the conservation of artworks. The literal application of recommendations is not sufficient, and the procedures to follow must be assessed on a case-by-case basis. In other words, the rules are “indications” that must be interpreted and modelled explicitly to each object, knowing its nature and history.

The involvement of all museum staff and visitors will be essential to prolong the existence of the works entrusted to them.

1.1.2 Preventive conservation program and climatic history

A crucial step in a cultural heritage preventive conservation program is to define the compatibility of environmental parameters, particularly in the indoor environment. In order to stop or to slow the rate of artefact deterioration, attention focuses on:

- research on the climatic history of the artefact related to the characteristics of materials, and any previous restorations and the current state of conservation/degradation;
- analysis of specific environmental parameters which the works of art are exposed to;
- determining the capacity of the environment to preserve artefacts;
- identifying the parameters [temperature, relative humidity, radiation inside the visible

range (UV/lumen ratio), air speed] that the corrective action must provide;

- analysing the particulate matter both on surfaces and in environmental aerosol.

In addition to planning a methodology for environmental analysis, useful to yield information on hazardous conditions for the artefacts, it is important to pay attention to possible health risks for operators and users of cultural assets stored in confined environments.

To describe the climatic history of an artefact, it is particularly important to fill in a specific detection form that accompanies the traditional cataloguing card. The *detection form* will summarize:

- the last location of the object;
- notes on conservation;
- environmental measurements;
- monitoring equipment;
- deterioration events.

1.2 International standards and guidelines

There are many national and international documents (standards, guidelines, technical standards and not) for the conservation of works of art. Some are general, others are rough guidelines often written by people with no scientific training and background, so that their application and compliance are complicated by myriad laws, standards, guidelines and rules, which sometimes contradict each other. Some of those rules are derived from regulations drawn up for other areas outside cultural heritage, and there are difficulties of comprehension, both for user understanding and the basic knowledge of the subject matter. Not just the literal application of the recommendations must be assessed, but also the procedures to follow in each specific case. The responsibility then goes back into the hands of those appointed by the museum curator or director to take concrete action to tackle the various conservation issues, selecting and critically adapting the many documents currently available.

The choice of procedures for preventive conservation requires multidisciplinary expertise that is normally achieved by a university science degree at least. Currently, however, the options for preventive conservation are the prerogative of staff in the cultural heritage

sector primarily persons with training in art history. So training should be modified to include a significant scientific component.

The head of the museum must be aware of the importance of preventive conservation, and organize training and transfer of advanced concepts to the staff through basic training courses. The implementation of conservation practices requires staff to be educated on the principles and procedures in a understandable and simple way.

This section surveys the international law, standards and guidelines to show the different approaches. Each country has special institutions working to define various standards based on experience in the specific area. They are technical standards with protocols that define goals, procedures and limits. In Italy the national body in charge of unifying all the national standards is UNI.

Recently, an agreement between UNI and the Ministry of the Cultural Heritage has allowed experts in the field of cultural heritage to draw up specific regulations for operators in the sector. At supranational level the European agency is CEN (European Committee for Standardization) and regulations are made at international level by ISO (International Organization for Standardization). They are private organizations with voluntary membership. Once published, standards are not free but must be purchased, also through websites. There are numerous UNI regulations on cultural property, specifically those dealing with environmental monitoring, measurement methods, analysis and reference values for storage (Table 1.1).

In addition to the technical rules in Italy national legislation has established regional standards for accessibility to the regional museum systems, and hence to financial contributions (D.M. 10/05/2001, Atto di indirizzo sui criteri tecnico-scientifici e sugli standard di funzionamento e sviluppo dei musei, Art. 150, comma 6, D.Lgs. n. 112 del 1998).

At European level a working group “Environment” of CEN/TC 346/WG4 has been set up. At international level reference is made to ISO-11799 (2005) “Information and documentation - document storage requirements for archive and library materials”.

Mention should also be made of the major international conservation institutions such as UNESCO, ICOM, ICCROM, the Canadian Conservation Institute, the Institute for Cultural Heritage of the Netherlands, the European Confederation of Conservators-Restorers’ Organizations, and others.

Societies that do not work exclusively in the cultural heritage field, but must be taken into consideration include: the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE), and National Information Standards Organization (NISO, USA). Particularly useful for our field are the ASHRAE Handbook: “Applications 2003 – Museum, Libraries and Archives”, ANSI/NISO Z39.79-2001 “*Environmental Conditions for Exhibiting Library and Archival Materials*”, NISO TR01-1995 “*Environmental Guidelines for the Storage of Paper*”.

Table 1.1 - UNI standards dealing with environmental monitoring for Cultural Heritage.

UNI	TITLE
UNI 10586, 1997	Documentation - Climatic conditions for storage of graphic documents and characteristics of lodging
UNI 10829, 1999	Works of art of historical importance - Ambient conditions for conservation - measurement and analysis
UNI 11131, 2005	Cultural Heritage - Field measurement of air humidity
UNI EN 15757, 2010 (<i>ex UNI 10969, 2002</i>)	Conservation of Cultural Property - Specifications for temperature and relative humidity to limit climate-induced mechanical damage in organic hygroscopic materials
UNI EN 15758, 2010 (<i>ex UNI 11120, 2004</i>)	Conservation of Cultural Property - Procedures and instruments for measuring temperatures of the air and the surfaces of objects

1.3 Environment-material interaction

1.3.1 Atmospheric aerosol

Air pollution is no longer confined to cultural heritage located outdoors, but also affects the inside of buildings (up to 40% of the outdoor pollution) and, hence, museums, rooms and showcases. Dust, vapors and gases produced by traffic and other human and natural activities can be trapped inside, but also transformed. It is therefore necessary to understand what happens in the atmosphere and what is meant by atmospheric aerosol. The atmospheric dispersion of particles in liquid or solid phase is called atmospheric aerosol. The fraction of airborne particles of biological origin (for instance fungal spores) is called bio-aerosol.

The atmosphere is constituted by 78.1% N₂, 20.9% O₂, 0.1% Ar; the remaining 0.1% consists of several trace gases: CO₂ (360 ppm), CH₄ (2 ppm), N₂O (0.3 ppm), CFC (3 ppb), O₃ (0.1 ppm), NO₂ (0.1 ppm), C₆H₆ (0.1 ppb). The gas concentration can be expressed in weight (mass/volume; $\mu\text{g}/\text{m}^3$) or in volume (volume/volume; % = percentage; ppm = part per million; ppb = part per billion).

The natural sources of aerosol include: land, ocean, volcanoes, fires, forests, pollen and fungal spores. Those of human industry are transport, power plants, agriculture, deforestation and waste. Gas (CO, SO₂, NO_x, VOC) and dust (heavy metal, carbon compounds, polycyclic aromatic hydro-carbons) in the urban atmosphere cause serious damage to health, but the threshold levels utilized for health are not applicable to cultural heritage.

Pollutants can be divided into:

- primary, produced directly from the sources, like SO₂ produced by thermal power plants, industry and traffic, or NO₂ produced by traffic, power stations, industry, agriculture and livestock;
- secondary, formed in the atmosphere by reaction between primary pollutants and the primary constituents of the atmosphere. We speak of homogeneous reactions when reactions occur in the same gas phase, while heterogeneous reactions occur between gas and liquid (water droplets) or gas and solid (solid particles).

Polluting particles differ in shape (fractals of diesel, spherical particles of carbon), size and composition. Figure 1.1 shows the distribution of diameters idealized for different types of aerosol. Urban aerosol is characterized by small size and high concentration, unlike bio-aerosol that has a low concentration and large size.

Figure 1.2 shows the dynamic evolution of an airborne system. Rainout is the process that determines the removal of particles from the atmosphere as they are absorbed by water droplets or by ice. The process is called washout when the droplets fall to the ground incorporating particles encountered on the way. The particles can act as condensation nuclei around which droplets or ice crystals are formed. Coalescence is the process by which droplets containing particles merge during contact or impact to form a single drop.

Wet deposition includes all the processes used to capture pollutants in the atmosphere due to the interaction of water in liquid or solid phase (rainout and washout). Dry deposition indicates the different processes (chemical, biological, physical) that occur in the absence

of rainfall and are continuous in time. The result is the removal of pollutants from the atmosphere, but this is followed by their enrichment in soil, water bodies and on cultural heritage surfaces. The removal efficiency of aerosols from the atmosphere by rain depends on their size and the distance between the clouds and the Earth’s surface. Fog droplets can absorb six times more aerosol than that absorbed by drops of rain.

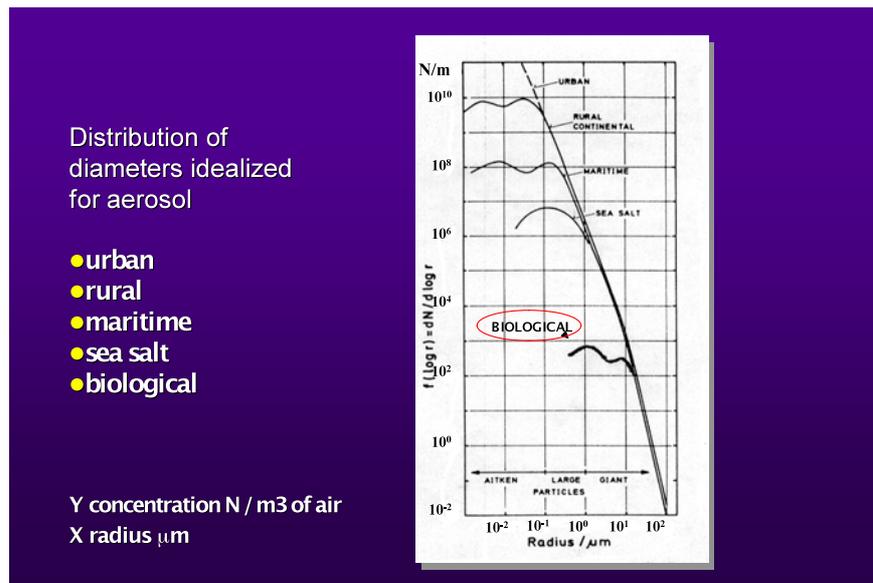


Figure 1.1 – Particle size distribution for different types of aerosol.

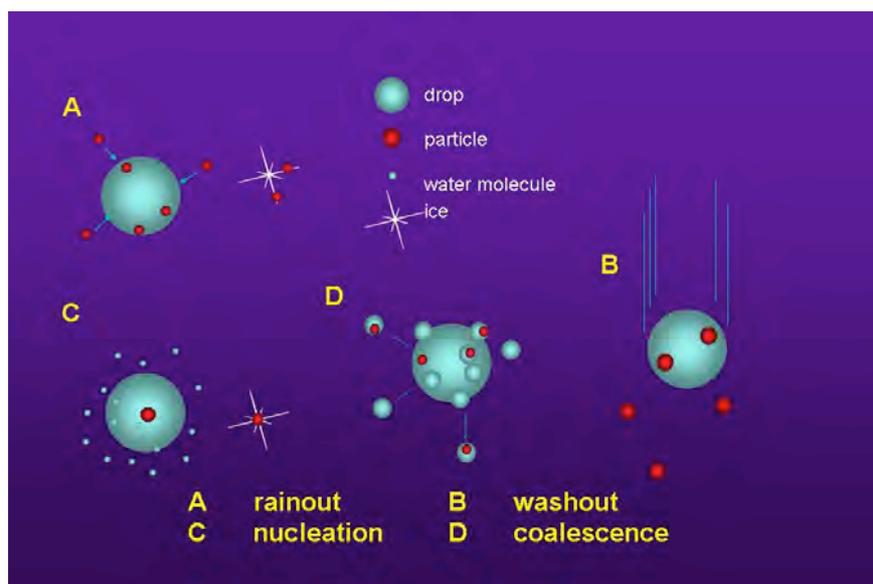


Figure 1.2 – Dynamic evolution of an airborne system.

The factors determining the amount of dry deposition are turbulence, the chemical and physical properties of pollutants and the nature of their surface. Figure 1.3 shows the components that allow ideal particles to float in the air.

The transport of air masses is influenced by meteorological parameters: turbulence and atmospheric stability, wind, horizontal movements, thermal gradient for vertical movements.

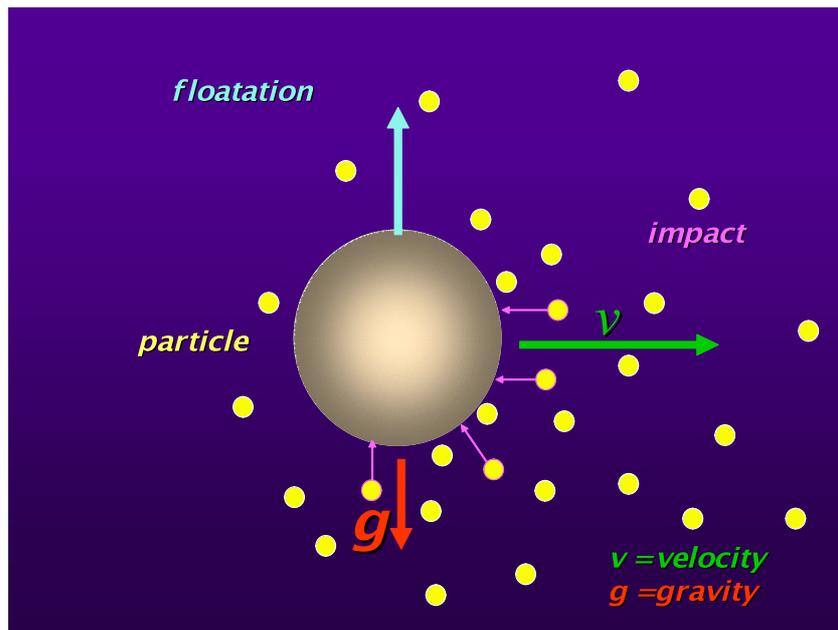


Figure 1.3 – Forces acting on airborne particles.

The efficiency of capture of a surface is given by the number of particles captured from the surface per unit of particles deposited, depending on the characteristics of the surface, i.e. composition, porosity, if wet or dry, smooth or rough.

1.3.2 Biological aerosol as a potential deteriorating agent

Atmospheric aerosol is a suspension of liquid, solid or multiple-phases of condensed matter ranging from 0.001 to 100 μm approximately in size. Particle size is determined by the formation processes and subsequent atmospheric chemical and physical transformations.

On the basis of the size-distribution, aerosol is divided into three categories:

- nuclei mode (0.005 to 0.1 μm)
- accumulation mode (0.1–2 μm)
- coarse mode (>2 μm).

Biological aerosol or bio-aerosol is a fraction of organic aerosol including dead or alive (e.g., bacteria, fungi, virus) fragments, or by-products of biological activities, such as semi-volatile organic compounds and micro-molecules. Bio-aerosol can range from: single spores (fungus spores), pollen grains (emitted by in flowering vegetation), algae, bacteria, virus, biological aggregates, materials produced by biological activity or attached to non-biological particles. Aerosol of biological origin (cells, fractions of cell, organic matter of different origin: animal, plant and microbial) forms a significant portion of atmospheric aerosol, sometimes reaching close to 50% of all aerosol particles.

Biological materials account for 25%-40% in weight of airborne particulate. Bio-aerosol is also called Primary Biological Aerosol Particles (PBAP). PBAP-PM10 mass is dominated by fungal spores, plant debris is also important. The contribution of PBAP is very small in winter, but may reach 5% of PM10 or more when vegetation is active. The annual emission factor based on total vegetation land area is 24 kg/km². The annual European emissions are more than 200,000 tons.

Bio-deterioration can be defined as the irreversible loss of value and/or information of works of art as a consequence of attack by living organisms. The action of the airborne microorganisms produces not only an anti-aesthetic effect but also the progressive loss or transformation of the physical and chemical properties of the materials.

Successful colonization by any biological community on organic and inorganic materials depends on the composition of the material, its state of conservation and the existence of favourable environmental and climatic conditions (temperature, humidity, natural and artificial radiation, ventilation, and inorganic and organic pollutants). The relative intensity of the biological attack on different materials is shown in Table 1.2.

The sources of bioaerosol are outdoor and indoor. Outdoor sources are mainly Primary Biological Aerosol (PBA) from natural sources present in the environment and secondly anthropogenic bioaerosol. Indoor sources include PBA incoming from outdoors and Secondary Biological Aerosol generated from colonies growing on materials and surfaces present in the indoor environment. A large quantity of dust (organic and inorganic particles and fibres) is transported by visitors and staff and deposited in the indoor environment.

Biological particles are mainly transported through the air circulation and secondly by contact between objects. Many materials can act as good substrate for the growth of colonies when water is available.

Table 1.2 – Intensity of the biological attack on different materials.

Micro-organism	Auto-trophic Bacteria	Hetero-trophic Bacteria (Actinomycetes)	Fungi	Algae (Cyanobacteria)	Lichens	Mosses
Organic Material						
<i>Wood</i>	-	**	***	+	+	-
<i>Paper</i>	-	**	***	-	-	-
<i>Textiles</i>	-	*	**/**	-	-	-
<i>Parchment</i>	-	*	**/**	-	-	-
<i>Painting</i>	-	*	**/**	-	-	-
<i>Synthetic material</i>	-	*	**	-	-	-
Inorganic Material						
<i>Stone</i>	**	*	*	***	***	**/**
<i>Mural painting</i>	*	*	**	***	*	+
<i>Glass</i>	*	-	-	*	*	-
<i>Metal</i>	*	-	-	*	+	-

Legend: - = absent; + = rare; * = occasional; ** = common; *** = frequent.

Re-suspension of the viable biological particles in the indoor environment plays an important role for the rapid spread of pathogens. The biological particles are deposited onto surfaces by some important physical processes:

- gravitational deposition,
- impact due to air movements,
- thermophoresis (gradient of temperature from air and surface),
- electrophoresis (electric particle charge in relation to the surface electric charge).

The conditions of deposition are strictly related to the particle features and to the kind of physical process. Gravitational deposition mostly involves large particles whereas thermophoretic deposition mostly involves small particles.

Several methods have been developed to analyze and measure airborne biological particles to identify them by their morphological, physical and chemical characteristics.

Many devices are in use for sampling airborne particles. Each is best suited for a limited particle size range and all operate on a few basic principles. Bioaerosol samplers are often similar to the instruments used for the collection of other kinds of airborne particles. The treatments and assay methods differ and require special procedures depending on whether the material is viable or non-viable. No devices are currently available for automatic

measurement of bioaerosol. Figure 1.4 shows the different devices for sampling airborne particles:

- *gravitational settling* (non volumetric): a simple Petri dish with culture media (Figure 1.4, left);
- *suction*: a volumetric sampler for morphological identification of viable and non-viable particles (Figure 1.4, centre);
- sampler for cultural identification of viable particles (Figure 1.4, right).

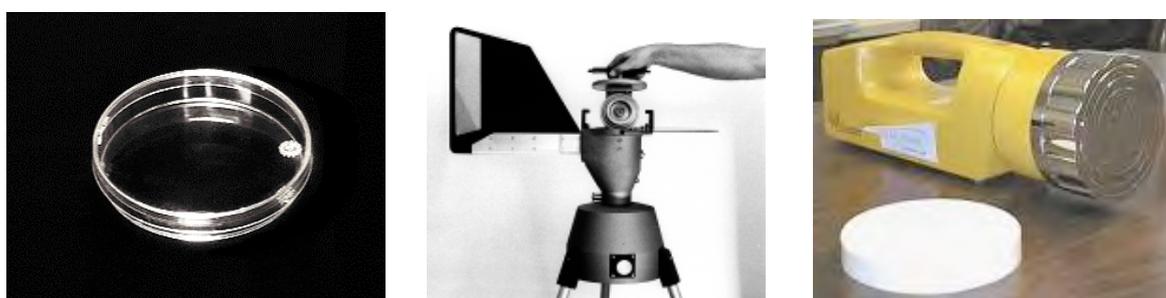


Figure 1.4 – Different devices for sampling airborne particles: *gravitational settling* (left), *Hirst sampler* for morphological identification of particles (centre), *SAS (Surface Air System) sampler* for cultural identification of viable particles.

Airborne micro-organisms are always present in the air of open and closed spaces. Continuous monitoring of humidity and air temperature is important to prevent biological attacks. Equal importance is given to the calculation of the dew-point temperature that will disclose the presence of water on surfaces, structures and objects due to condensation of water vapour. Figure 1.5 shows some examples of biodeterioration of cultural heritage: details of damage and biodeteriogens as colonies and magnified by SEM or OM microscopy.

1.3.3 The pollution factor

The deterioration of stone has increased dramatically in the urban environment during the last century. The degradation of materials depends on different parameters like relative humidity, temperature, radiation, mechanical stress and pollution. The effects of multi-pollutants on construction materials are studied using three different approaches:

- analysis of damage on monuments,

- simulation in a microclimatic room,
- exhibitions in the field on different materials in different places.

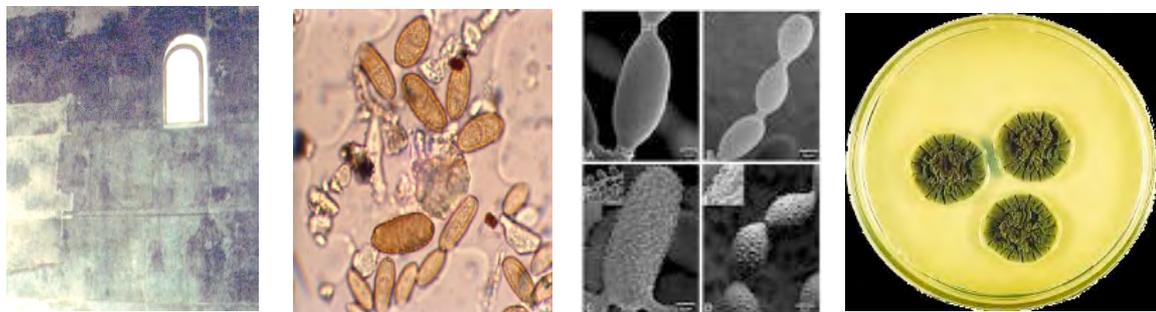
Deuteromycete: *Aspergillus* sp.Deuteromycete: *Cladosporium* sp.*Alternaria**Aspergillus-Penicillium**Cladosporium**Curvularia**Stemphylium**Epicoccum*

Figure 1.5 – Images of fungi that cause major damage to cultural heritage: colonies on Petri dish and samples observed by OM (colour) and SEM (black and white).

The types of degradation are recognizable as white areas and black areas on marble and limestone monuments (Figure 1.6). The white areas are characterized by washout, while the black areas are due to formation of an alteration crust. The white areas are located on surfaces wetted by rainwater and subjected to intense runoff. The black areas are located on surfaces wetted by rainwater, but protected from runoff. There are also grey areas that are surfaces completely protected from rainwater.



Figure 1.6 – Degradation on marble, white areas and black areas

The stone surface in the white area is eroded and thinned by the mechanical action of rain water. In addition the stone dissolves due to acid attack. In polluted areas gaseous pollutants, mainly SO_2 and NO_x , are deposited slowly in the absence of precipitation (dry deposition, see paragraph 1.3.1). Rain normally has a cleaning effect due to carbonic acid dissolved in the rain. The wet deposition on stone surfaces is related to the phenomenon of acid rain.

The black areas are the areas where the products of interaction between atmospheric deposition and materials accumulate (black crusts), by studying the layers of alteration the alteration mechanisms that occur on monuments as a result of multi-pollutant areas can be identified. SO_2 is oxidised to SO_3 and H_2SO_4 originates during raining that determines the dissolution of CaCO_3 from the stone material and the formation of gypsum (70% vs 1% contained in the white areas). The process of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) formation is called sulphatation. Figure 1.7 shows optical and electron microscopy images of black areas.

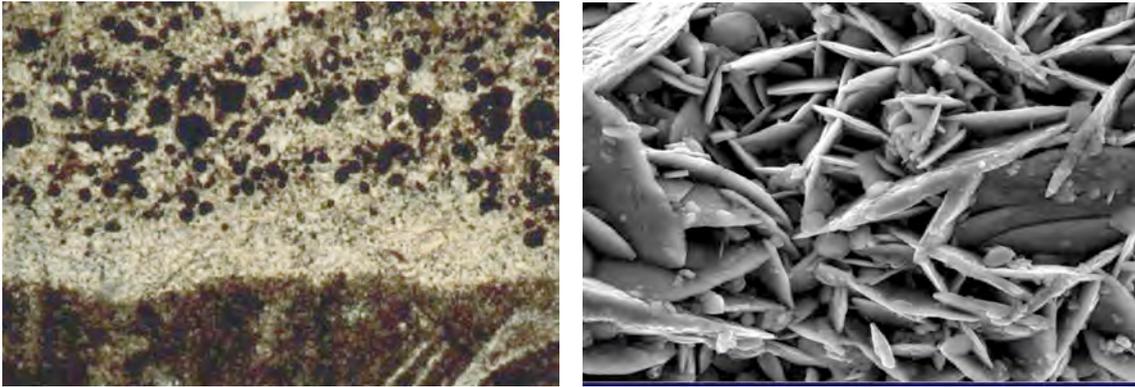


Figure 1.7 – Magnification of the black area at optical (left) and scanning electron (right) microscope.

The lamellar crystals of gypsum give a greater porosity to the new surface. Carbon particles are also trapped between the slats of gypsum crystals and give the crust a typical black colour. In hydraulic mortars gypsum reacts with the hydrate silicates and determines the formation of Thaumasite and Ettringite, whose crystalline structure favours swelling and fracturing of the original material resulting in severe damage.

Very often some of the effects of degradation are misinterpreted; for example the black patinas of biological origin are mistaken for black crusts (e.g. fungal melanin, lichens, algae, cyanobacteria). Black biological patinas can be found in places with frequent presence of run-off, where the formation of black crusts is impossible, and in places where the drying and aging of the cyanobacteria that colonize the rocks lead to a darkening of the surface, mainly due to chemical changes (e.g. chlorophyll). The interaction between anthropogenic and biogenic deposits further complicates the situation of materials. Bioaerosol is often sticky, so the following deposit is easily retained. In highly polluted areas it may be difficult to detect microbial infections, even if present.

1.3.4 Degradation factors of artwork materials

Two degradation factors affect works of art. The first regards the type of materials, the second the damage: physical, chemical and biological damage.

Materials can be divided into two main categories:

- a) inorganic materials, such as metals, alloys, ceramics, glass, stone and mortar,
- b) organic materials, such as paper, wood, leather, rubber, plastics, paintings and textiles.

Inorganic materials

Inorganic materials are the part of heritage generally least susceptible to deterioration in museums, archives and historic buildings, but also subjected to slow but inexorable aging.

The main environmental hazards are:

- climate: inadequate relative humidity, temperature and light,
- pollution by gas and dust: deposition of aerosols on surfaces from internal and external sources, corrosion, formation of crystalline structures on the surface, oxidation and carbonation,
- microbiology: formation of bacterial and algal coatings under conditions of high water availability and light surfaces.

Inorganic materials are theoretically more tolerant than organic substances to the limit values of relative humidity, light and temperature but their relative waterproofing, with the exception of stone, marble and plaster, causes the formation of water condensation (dew) on the surface of materials. Water condensation and dust deposited on the surface can lead to aggressive chemical reactions with dissolution of the substrate. In these cases frequent dusting and climate control are recommended.

Outdoor urban pollution (particles and gases) is particularly aggressive against these materials due to the chemical reactions that frequently generate crystalline products that can grow within the microscopic gaps producing fissures, fractures and detachments.

Organic materials

Organic materials constitute a substantial part of the cultural property in museums, archives and historical buildings. They are the materials most vulnerable to deterioration and show the following types of damage:

- Paintings: discolouration, cracks, soiling,
- Textiles: reduced strength, colour change and fading,
- Paper: embrittlement, discolouration and stains,
- Wood: breakage, decomposition and sputtering surface,
- Leather: weakening and surface sputtering,
- Rubber and polymers: embrittlement and discolouration.

Environmental hazards

The main environmental hazards are:

- Climate: relative humidity, temperature and light are all important factors that must be

monitored in museums. The restriction of fluctuations in relative humidity is important for the preventive conservation of organic materials. Light and ultraviolet radiation should be monitored for photosensitive materials.

- Pollution by gas and dust: deposition aerosols on surfaces from internal and external sources. Aerosol lifted by visitors and floor-cleaning machines, corrosion, formation of patinas that reduce readability, oxidation, suitable substrate development of different biological forms. Monitoring results show that the indoor and outdoor museum pollutant concentrations depend on the type of building and its use.
- Microbiology: fungal attacks on objects displayed in glass cases or placed in storage with high humidity are very frequent in museums. The presence of bacteria may be an additional risk.

Control of environmental conditions

It is important to control environmental conditions to avoid the attack of deposited bioaerosol. However, attention should be paid to avoid overdrying materials, using water as a structural medium like wet sand sculpture (i.e. paper). Experience suggests that RH should never fall below 40% or exceed 65%. Rapid excursions (within 30 minutes) of relative humidity have little impact on wood and books, but prints are more sensitive if not adequately protected.

More dangerous are cyclical RH fluctuations in the 24 hours that allow the wood to enter into equilibrium with the environment resulting in shrinkage and swelling, which may detach the painted surface.

The physical deterioration of artwork is due to radical changes in materials through the action of hygrothermal cycles, while chemical deterioration occurs mainly on the surface. These problems are added to biological deterioration that is caused by all the physical and chemical processes induced by the growth of microorganisms deposited on the surfaces.

Relative humidity influences:

- size and shape (RH high = bulge = biodeterioration; RH low = shrinkage = cracks and breaks)
- the speed of deteriogenic chemical reactions
- biodeterioration sources.

Air Pollution can:

- cause the loss of surface material

- encourage the development of microorganisms
- leave traces of pollutants on surfaces
- change the appearance of objects

Temperature can:

- promote chemical reactions
- accelerate the physical processes
- encourage the expansion of materials
- alter colour pigments
- increase the surface temperature of objects

Vibration and noise can cause:

- damage or destruction of crystals and unstable glass
- detachment of unstable parts

1.4 Microclimate and monitoring

1.4.1 Explorative and continuous monitoring

The correct preservation of historical and artistic heritage in the site where the works of art are conserved requires monitoring of potential interactions between the environment and works of art. For this purpose a continuously working external meteorological unit should be installed for the complete monitoring of climatic parameters such as temperature, humidity, wind speed and direction, and barometric pressure.

Generally, the measurement in an indoor environment can be divided into two steps:

- *Explorative monitoring*: First a short-term measurement is made using portable equipment to identify the area/s for detecting the environmental parameters and eventually for microbiological sampling. At the same time a technical-information form is filled in for each environment (including information acquired during the *documentation* action).
- *Continuous monitoring*: After having identified the location to monitor environmental parameters, continuous monitoring can be performed by instruments, establishing the most appropriate schedule.

Both *Explorative and Continuous monitoring* can survey the temperature and relative humidity, lighting, amount of ultraviolet radiation and surface temperature in relation to the timing and modality of access to cultural assets. Long-term measurements can be

carried out by sensors, connected to the equipment by cable or by a cordless system.

Considering the complexity of the process involved in artwork deterioration, a range of parameter variations that could be “acceptable”, and a narrower range that could be “optimal” can be devised. Finally, internal parameters can be recorded by a wireless network for data storage (using a local computer or a remote processing centre) and must be compared to the external climatic parameters recorded simultaneously. The results allow proper conservation to be planned for cultural heritage preserved in that environment.

1.4.2 Analyzed parameters and analysis systems

The indoor environment can be characterized by physical parameters. These parameters are measured using specific equipment and standard procedures. The main physical parameters to be measured in a museum are: temperature, relative humidity, ventilation and radiation (natural or artificial). Secondly, vibration, dust and airborne particles must be monitored.

Temperature

Depends on the object under consideration and not its history, and varies with the temperature of adjacent structures (thermal equilibrium), measured with different types of thermometer and expressed in Celsius degrees (°C). The different operating principles of thermometers are: liquid (mercury and alcohol), gas, metal deformation (hygrothermograph), electrical resistance (Pt100), thermocouple and infrared. Related to the concept of temperature is that of heat. Heat flow is the quantity of heat, i.e. the amount of energy entering or leaving the body in a process of heat exchange. Heat flow is achieved through conduction, convection and radiation. Items at different temperatures, will slowly tend to reach equilibrium. The thermal insulation of buildings helps to limit heat exchange during winter to the outside and during summer internally.

Relative humidity

Relative humidity expresses the ratio between the amount of water vapour in the air and the amount that, at the same temperature, would be needed as steam condenses into water droplets. Humidity is the parameter that most affects biodeterioration, which generally occurs when values exceed 65%. Low relative humidity must be considered equally as dangerous as excessive moisture (water becomes part of the structure of the material, cellulose fibres in paper or wood). If dehydrated, these materials lose their elasticity.

Relative humidity is not evenly distributed in an environment, but is related to the distribution of temperature. Where significant differences in temperature occur, such as close to walls, doors, windows and heat sources, there will be marked variations of relative humidity.

Humidity and temperature measurements

Both humidity and temperature can be measured by several types of instruments based on different operating principles:

- hair hygrometer (RH) Lambrecht,
- mechanical thermohygrometer,
- pocket digital thermometer,
- thermohygrometer with mini-datalogger (2 sensors T - RH, 32.000 store data, Tinytag),
- Assman psychrometer.

The control of relative humidity values is a high priority activity compared to controlling lighting and temperature. Continuous measurement data are essential to the diagnosis. The choice of instrumentation and management measures is extremely important.

Illumination

Illumination is the amount of light radiation striking the surface. All exhibition premises are equipped with natural or artificial lighting. Some light sources are harmful to conservation of works of art. Radiation useful for viewing the work is visible, but the other components of both natural and artificial light are harmful because they are still energetic.

The damage caused by light includes:

- colour changes and fading
- cracking
- failure of media
- yellowing

In addition, warm air forms movements involving dust and biological particles, which are then deposited on a cool surface. Illuminance, radiance, luminance, ultraviolet radiation must be measured. It is very important to pay attention to where the sensor is positioned, the action of sunlight entering through windows and artificial lighting. The intensity of light should be monitored and measured before the final placement of objects. Often aesthetic criteria of construction and engineering take precedence over those of

conservation. Ignition systems to environmental presence can be useful to extend the life of an object and save energy and money when the number of visitors is low. In choosing artificial lighting the “colour temperature” and “tone” characterizing each type of lamp must be taken into account. The choice of light source should consider both the amount of light reaching the object and the quality of light (emission spectrum). The choice of the lamp should be evaluated taking into account the characteristics given in the product data sheets. The following types of lamps are available:

- incandescent lamps
- halogen light bulbs
- discharge lamps
- fluorescent
- LED (light emitting diode)
- fibre optics.

Ventilation

Ventilation in the exhibition halls is essential to have a uniform distribution of temperature and humidity but should not be excessive (not exceeding 0.1 meters per second) and should be made with filtered air to limit the movement and deposition of dust. The same treatment should be reserved for store rooms, often underestimated. Precision instruments such as the hot wire anemometer should be used to measure air flow.

Dew point

The dew point or dew temperature is the temperature to which air should be warmed to condense it into dew. The dew point temperature is not a parameter measured directly but calculated by measuring the air temperature and relative humidity. The measurement of dew point serves to highlight condensation on surfaces.

Monitoring systems

Monitoring systems with sensors linked by radio to a data-logger are currently available to manage the timing of measurements, data storage and transmission of data to a local computer or a remote processing center (Figure 1.8). They are advantageous because:

- installing the system is less costly because it is cable-free
- the choice of sensor location is less constrained and sensors can be repositioned in case of a change in exhibition environments
- distance network transmission is rapidly expanding.



Figure 1.8 – Monitoring instruments: thermohygrometers (left) and photo radiometers (right).

1.4.3 Macroenvironments

Macroenvironments are understood as the museum itself and its rooms. The buildings that house museums and archives can be divided into three categories:

- Buildings constructed ad hoc with air conditioning systems regulating temperature, relative humidity and ventilation. If well managed, the risk of physical chemical and biological damage processes is very small. Possible problems derive from the incorrect detection of climate parameters due to a plant design not suitable for museums.
- Buildings constructed ad hoc with no air conditioning, built in different eras and with different criteria (historic buildings, museums dating back to the late 1880s) with various microclimatic situations. Possible problems are that temperature can be adjusted, while humidity is adjusted only in dehumidification.
- Buildings or premises used for other purposes (convents, schools, housing, etc.) and later adapted. Possible problems include poor or inadequate insulation, and management of heating shared with other institutions with different needs.

Often, due to lack of space, highly diverse and less appropriate environments (humidity, no ventilation, poorly lit, etc.) are used with different climatic conditions, which often facilitate the deterioration of materials.

The same building may have different environmental situations depending on:

- location of the rooms (basement, intermediate floors, roofs) and their exposure,
- presence or absence of windows and skylights,
- intended use of the rooms (exhibition rooms, lockers, study rooms, offices etc.).
- type of heating, cooling or air conditioning, type of lighting,

- presence and activities of staff and visitors.

In buildings without air conditioning, into which unfiltered air is blown, two other factors have an impact on the retention of materials: chemical and biological pollution which differ in relation to the location of the museum. Industrialization and urbanization of the area in which the museum is located and its proximity to the sea or parks determine the prevalence of certain chemical or biological compounds.

Degradation processes are also supported by:

- significant fluctuations of temperature and moisture due to incorrect adjustment,
- the quantity of material present in the rooms,
- the presence of capillary rise of water resulting in high relative humidity,
- poor ventilation of the rooms, promoting condensation,
- interruption of use of air drying, forced air heating or air conditioning systems,
- exceptional events (floods, water leaks, broken plumbing, heating, sanitation ...)

The objects in museums experience vibrations whose frequency can damage their structure, especially if large and placed at high levels in urban buildings close to roads with heavy traffic such as buses, or railways and airports. The remedy is to design shock absorber supports. Noise and vibration in museums can cause damage or destruction of crystals or glass in unstable conditions, the detachment of unstable parts and disturb visitors.

Store rooms are very important places in museums because many objects remain there for a long time waiting to be exhibited or lent to other museums. Different types of material require different levels of temperature and relative humidity conditions that entail the preparation of different storage environments. Frequent inspections are necessary to control the environment and the conditions of objects. Continuous microclimatic monitoring is therefore important to filter the incoming air, schedule regular cleaning, check that there is adequate air circulation and there are no damp patches on walls, ceilings or floors, check if windows are covered and if the works in storage are protected from dust, perform periodic aerobiological sampling, especially if the rooms are humid (RH > 65%), and monitor the presence of insects.

Light in store rooms should be managed as follows:

- ✓ artificial light and natural light will not enter,
- ✓ the lighting will be used only when necessary,

- ✓ the lighting level must be high when it is necessary to examine the objects,
- ✓ a level of 500 to 600 lux is required to see the details of the surfaces, but only for a few minutes.

1.4.4 Microenvironments

Microenvironments are understood as showcases, showcases and climaboxes (Figure 1.9). Objects in museums are protected, especially from dust, by containers called showcases, display cases and climaboxes. Showcases are equipped with doors that open normally, sometimes dust-tight but not air-tight. Caskets are inspected only by designated staff. Climaboxes are containers built to protect a single artwork by adjusting the internal RH.

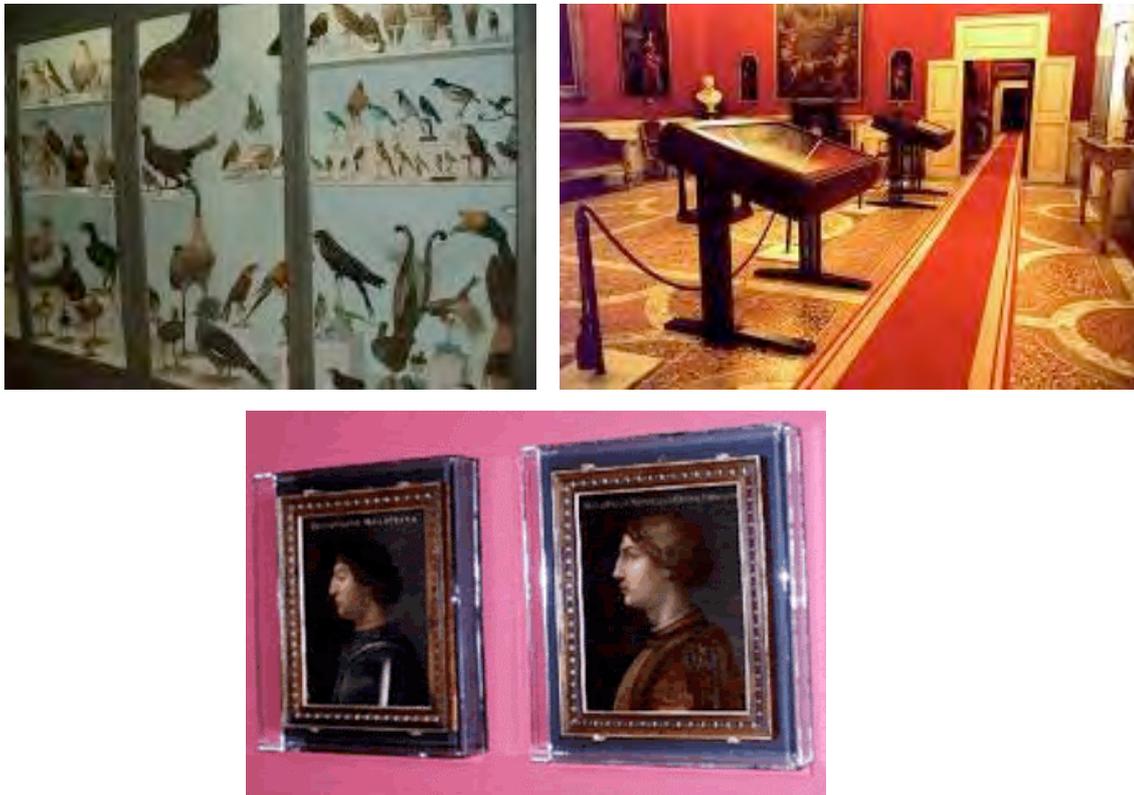


Figure 1.9 – Microenvironments: showcases, caskets and climaboxes.

Temperature, relative humidity, lighting, air pollutants and parasites should be tested even in small containers using passive systems. Relative humidity can be controlled and measured inside the containers using desiccant substances such as silica gels without cobalt

salts or PROSORB and ART SORB, respectively, which are used for relative humidity from 40% to 60% and 60% to 80%. The relative humidity can also be controlled using organic materials like cotton.

Temperature, relative humidity, illuminance and air pollutants should be tested in the box using electronic instrumentation allowing the insertion of sensors inside the containers without having to make changes to the structures, or *humidity indicator cards* that can be inserted in the glass case and show the maximum value of moisture reached, or small instruments with digital display to put inside windows.

Light is controlled by measuring illuminance (lux) and UV ($\mu\text{watt}/\text{m}^2$). It is better to have external lights for the container to avoid warming, changes in RH at the time of start-up and shut down, and trapping insects attracted by light inside the containers.

Pollutants can be controlled by minimizing the entry of air using building materials in the container with low or zero emission of pollutants, inserting substances to purify the air inside the window.

If the container is well sealed, insects will not enter, but in any case it will be important to lay traps for insects and put filters in the openings.

If necessary, showcases, display cases and climaboxes may be equipped with active systems for humidity control and internal pressure, but these are recommended for use only when absolutely necessary due to their high purchase and maintenance costs.

The choice of suitable materials ensures better preservation of objects placed inside windows and showcases. The design of the windows should be taken as a priority consideration for a better visibility and enjoyment of the exhibits, also from an academic point of view. Placing artwork in a showcase with the wrong microclimate means accelerating the processes of deterioration and aging.

1.5 Handling works of art

Handling works of art for exhibitions is the most risky type of event to the integrity of the transferred works.

For this reason many institutions lend their paintings only if they receive a declaration of

conformity on the environmental conditions of the rooms used for temporary exhibitions. Based on the microclimatic monitoring conducted in the rooms, the declaration ensures that the conditions required by the lender are respected (in percentage terms) and therefore in compliance with requests. Figure 1.10 shows an example of a declaration of conformity processed by ISAC-CNR before a recent temporary exhibition.

Damage can be provoked by unsuitable micro-climatic conditions, manipulation, and mechanical stresses (for instance landing aircraft). The first and most important problem is to maintain the micro-climatic conditions of the original location. Operationally, we can split the transfer into the following steps: preparation work and transport, stay at the temporary exhibition, preparation for return and transport, and relocation in the place of origin.

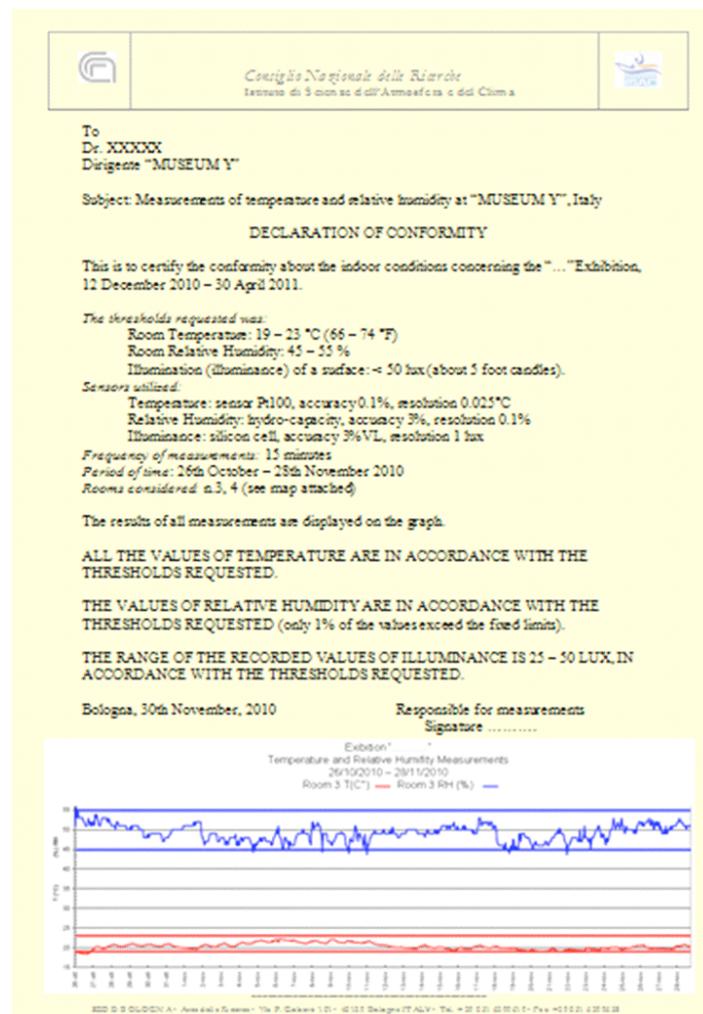


Figure 1.10 – Declaration of conformity, example of a document utilized by ISAC-CNR for a recent exhibition.

Is important to ensure constant temperature and humidity conditions throughout all phases of the transfer, making sure that:

- all packaging operations take place in the same environment in which the artwork is kept,
- boxes and packaging material have been acclimatized in the same environment for at least a day,
- filling materials sensitive to atmospheric moisture, such as paper, cardboard and rags are used. A new generation of desiccant materials (such PROSorb) is available able to keep a certain percentage of relative humidity within certain limits of volume and characteristics of cases and time spent,
- the conditions within the package are recorded throughout the duration of transport, inserting, in agreement with the carrier, a micro datalogger capable of continuously monitoring temperature and humidity inside the case (Figure 1.11).



Figure 1.11 – Instruments for measuring temperature and humidity inside the storage case during transportation: Tinytag and Black Box.

Acclimatization phase

Once the objects reach their destination, it is essential for the boxes to be placed promptly in a room with characteristics similar to those of local shows, to mitigate the differences in temperature and humidity between the external environment and the interior of the packaging. Then objects can be unpackaged, the datalogger retrieved and the data downloaded, and the objects arranged in their final place of exhibition.

During the construction of an exhibition, pictures and tables should not be placed in contact with the wall (an air gap of 3 cm for small items and 5 cm for large objects must be left), or in the vicinity of jets of air circulation. At least one measurement of illumination should be made on the objects, and solar radiation prevented from reaching the artwork during the exhibition. Finally continuous monitoring of temperature and relative humidity is essential to ensure the providers of compliance with the materials during the exhibition.

Documentation

Before and after the exhibition forms and reports should be prepared to be sent to supplier museums. The documentation before the exhibition should collect information essential to the safe movement of works and for the organization that takes care of the transfer. The cards must contain information on the host structure and the state of conservation of the material provided.

The documentation after the exhibition should give provider museums information on repackaging and acclimatization procedures of the works after the return, and provide a declaration of compliance stating the artworks was conserved within the required limits.

Despite the large amount of national and international attention to the issue of preventive conservation, we are still far from having reached standard storage conditions to be observed for many types of cultural heritage. It is not uncommon to receive requests for compliance with limits for conservation of material that differ from those reported by the rules and recommendations available today. Table 1.3 lists several international recommendations for painted panels.

1.6 Exhibition criteria

In working out some guidelines in order to realize a museum better, one becomes quickly aware of how wide the existing material on the subject and how great the risk of making repetitive any form of method suggested and examined. But simply putting ourselves in the shoes of the visitor and imagining how we would like space and exhibition were organized in a museum, everything suddenly becomes clearer and we have no more doubts about what we would find in order to understand at the highest level the value of what we visit and enjoy the emotions that it sends.

Table 1.3 – Recommendations for painted panels.

MUSEUM	T °C	RH %	MUSEUM	T °C	RH %
Great Britain	< 25	45 - 65	France	16 - 20	50 - 60
Great Britain	17 - 23	45 - 65	Austria	20 - 22	50 ?
Great Britain	18 - 24	40 - 60	Spain	20 - 24	50 - 60
USA	20 - 21	45 - 55	The Netherlands	15 - 25	53 - 57 ?
USA	19 - 25	45 - 55	Vatican	18 - 20	55 - 60
USA	16 - 26	45 - 60	Milan	19 - 20	50 - 60
USA	< 25	45 - 55	Modena	15 - 20	50 - 60
USA	19 - 23	45 - 55	Parma	15 - 20	50 - 60
Canada	18 - 22	45 - 55	Pesaro	16 - 22	50 - 60
Ireland	18 - 22	50 - 60	Florence	15 - 20	50 - 60
France	< 22	45 - 55	Naples	19 - 24	50 - 60
UNI (IT) 10829	19 - 24	50 - 60			

All this must always happen in the greatest possible respect to the protection and conservation of exhibits. The ever-present risk in who designs is that, being a creative person, he tends to indulge in forms of leadership that threaten to steal the scene to the actors, which in this case are the exhibits. Therefore the goal to be centered is the creation of an environment that enhances and facilitates the understanding of what is on display, and does not detract attention or compete with the artwork that is exhibited.

The most important elements that make work at the best the “machine” of the exhibition, when used carefully, and that ensure a good level of protection and preservation of the artworks, are:

- the quality of the light and how it is used; the light also affects the microclimate of the environment;
- the materials, including their colours, that make up the container which houses artefacts, as well as its structure;
- the space with its implications made of sizes and distances;
- the meaning of the route, both physical and mental, that is not only a space to walk in a while, but it will be the place to find the events of history represented in the objects;

- the chronological route, as a tape that accompanies the succession of objects, and the mutual influence of the artworks;
- the technology that currently offers opportunities for consultation and interaction until recently unimaginable.

1.6.1 The light

The light allows us to see the objects, but can also damage and alter the microclimate of the environment and its choice is extremely delicate because it involves not only the quality of exposure and the creativity of the designer, but also affects the same preservation of works. That's just the first dilemma to face: natural or artificial light?

Usually people who visit an exhibition tend to prefer natural light, but natural light is not stable, because it depends on: prevailing weather conditions, season, time of day when the visit takes place, kind of opening to the outside of the space that hosts the artworks. So, according to these variables natural light requires a series of measures for diminishing or increasing it. These actions have costs that far outweigh the savings derived from the non-use of artificial light.

The artificial light, conversely, can be configured by programming its intensity as a function of the sensitivity of the object exposed, so avoiding any effects that might damage it. In addition, it can be modulated so as to amplify or mitigate the contrast between artwork and background, depending on whether it deals with painting rather than sculpture, black and white photo rather than colour photo, modern art with sharp colour tones rather than classical art with soft and delicate effects.

As light affects the fruition quality of the artwork is obvious, just think of distracting reflections from light created when investing pictures and paintings (especially if protected by glass) and how much the direct light from a spotlight wisely addressed may enhance the three-dimensional shapes of a statue or a sculpture in general. Although it is always risky to generalize, in most cases we can say that, in the presence exhibitions of paints is preferable to use diffuse light coming from above, while in the presence of marble statues and groups, a well-designed use of direct light can help to better enjoy the plasticity of forms. Do not forget that, illuminating an object rather than another, we influence the visitor's attention and, in a sense, we accompany him on a precise chronological or logical sequence that can be variously motivated. For example, if we want that a sculpture is

observed before another one, it will be sufficient to put an ignition device that automatically sends a beam of light on it first and then on the next.

The use of ignition devices using photoelectric cells, which are activated when the visitors are arriving, allows to highlight the object so avoiding being distracted by other nearby objects, and addressing the focus where we want and when we want it to happen, with a substantial energy saving. In addition, the lighting of a lamp placed for the benefit of a object, which applies only to the passage of the visitor and turns off on in absence of visitors, greatly limits the warming of the room, reducing the risk of damage to the exhibits.

The use of fibre optics, as well as that of the LED light sources, currently provides us with great opportunities and variety of action, without any infrared and ultraviolet emissions that are filtered upstream, and without generation of heat.

In conclusion we can say that the artificial light, with its greater flexibility, can be better controlled than the natural one, both for the prevention of the risk of damage and alteration of the artworks and for the role of emphasis and guidance that can play within the space of a museum.

1.6.2 Materials and colours

Material and colours are strongly linked to each other, and together inextricably interact with light: let us think how much the visual and emotional effect of a monument or an archaeological site changes if lit by yellow sodium lamps rather than white neon lights. To fully evaluate the importance of lighting in relation to colour, just remember that in absence of light all colours are equal, i.e. blacks.

The materials, intended as constructive elements, can be used and treated in endless ways that can alter their appearance. If we think of a few of them (glass, aluminum, steel, copper, white plaster, brick, concrete, wood, marble, ceramic tiles), immediately for each of them we imagine a different colour or we have a different and exclusive feeling. We could go on much longer, but that is enough to make us immediately aware that imagining a single object on display on a background made from time to time with one of the materials listed, we shall experience a different feeling for each scenario imagined.

The same goes for colours: white, ivory, cream, pink, orange, yellow, light and dark green, light and dark blue, brown, dark red, light gray, dark gray, black. Every background

combined with a same object increases or decreases its apparent brightness, making us a different effect, forcing us to focus our attention in a different way; it relaxes us or excites us, it saddens us or exalts us. This interplay of material and colour is a crucial point for the design of interior exhibition space, and should be used in a wise way to enhance the story that we want to tell with our exposure and for the emotional journey in which we want to lead the visitors.

Intense colours, used as a background, will impose their own personality to the whole environment, and thus risk to attract attention and visual energy, while a soft background with an average capacity of reflectance (where the white colour has the highest reflectance factor and black the lowest) will be more restful to the eye of the visitor and will be less protagonist and less competitive in comparison with the exhibited objects.

Please note that in dealing with the component “building material” of the building museum, we limit ourselves to his perception experienced from “within”, that is as it appears from the internal space and how it interacts with the artworks exhibited in it. It is obvious that the building seen from the outside, with its constructive materials, enters a totally different dynamics, that is the report with the outer space represented from the city with its many components and conditionings, something that would take us off topic and would require an analysis of different kind. The close connection between the building material with its own capacity to reflect and return in different way the amount of light received, and the effect this has on the artwork exhibited and the human eye, provides another starting point in designing museum spaces.

The halls and paths that are home to the artworks will be treated differently from the transition and disengagement spaces between an exhibition area and the other, allowing the visitor to reduce “the stress of visiting a museum” and allowing the eye to rest and to loosen the concentration every time you are in an area not strictly dedicated to the contemplation of objects.

1.6.3 Space, sizes and distances

The concept of the exhibition space for the museum is linked inseparably with that of the exhibition that we will face later. Instead, in this area you want to emphasize, again according to the principles of conservation and prevention of damage to the artworks, the importance of calculating the average contemporary influx of visitors and the relative size of the space needed to accommodate them. The method can start from the tie given by a

space that already exists and that can not be changed, or from the case when we are in condition to design the same space. In the first case we will speak about the control of the influx, kept within the limits tolerated by the space, acting in such a way that overcrowding does not seriously affect the microclimate of the room. In the second case we will ensure that the areas destined to the observation of the artwork are sufficient as it regards size and comfort, so that the object can be seen and understood without causing any damage to it.

A preliminary feasibility study, performed on homogeneous museums to ours for type of host city, population, tourism, geographic latitude and longitude, average educational level of population and type of exhibition occurred, will give us a reliable estimate of peak flow throughout the year and we will not be unprepared to cope with any periods of great affluence.

All this will contribute to the planning and staging of the “ideal museum” to which we must always strive for, although we will never be able to reach it. The “ideal museum” is the space that guarantees both the “perfect preservation” of an artwork and its “perfect enjoyment” by the visitor.

Proxemics is the discipline that studies the space and distance in relationships between people and their impact in their reports and communications. Proxemics can help us in sizing flows and spaces in the exhibition halls, taking into account the four interpersonal areas defined and codified by the anthropologist Edward T. Hall:

- the intimate distance (0-45 cm),
- the personal distance (45-120 cm) for the interaction between friends,
- the social distance (1.2-3.5 m) for communication between acquaintances,
- the public distance (over 3.5 m) for public relations.

These parameters can help us in defining the space to be devoted to the placement of an artwork, in relation to the number of visitors expected to admire it contemporaneously, as well as with reference to relations between them, that is if they are among foreigners, friends, colleagues or otherwise. All this is clearly designed to put who visit an exhibition in a comfortable situation, and it determines, together with the other factors considered, the success or failure of an exhibition.

We all have fixed in our memory, if only once we happened to live it, the hasty visit that we were allowed to do to the “Mona Lisa” by Leonardo in the halls of the Louvre in Paris. Moreover, after queuing up to admire her, the visit was also disturbed by the reflections of

light present on the glass placed for her protection. Therefore, it can be argued that, as partial compensation for a long wait, then we should at least have a comfortable and rewarding visit to the opera, or, however, to a faster visit should not match exhausting expectations. Putting the visitor in a state of “stress due to visiting the museum” discourages him in the desire to the approach to culture, frustrating those persons which with their accurate work of research, seek to bring to the attention of all the excellence of the creativity and sensitivity of human beings.

1.6.4 Physical and mental path

The path in a museum exhibition is a narrative space and, as such, must follow the logic and timing of the narrative language. All this interacts with the specific four-dimensional architecture, where the three spatial dimensions are combined with the fourth dimension represented by time, which becomes the instrument of exploitation and creation of the real architectural space.

The visitor must be enabled to move in the museum path following the narrative logic that the designer of the exhibition wants to transmit, as we must move within a book, reading the lines in succession, and turn the pages in sequence. An improper arrangement of the exhibits or a wrong indication of the way to follow would have the same effect as a book read by jumping carefully from one line to another and from one page to another. If the viewer was forced to move in a illogical way, or he freely chose a wrong succession of reading, he will read a story different from that we want to communicate, or worse, will not be able to grasp the full meaning of the narrative.

Let us imagine getting close to that classical marvel that is the Acropolis of Athens; let us examine the map and we immediately understand how the path can guide and limit the fruition of what appear to our view (Figure 1.12).

Following the path uphill to the entrance, we see that, now in its final stretch, it proceeds in the direction of the Temple of Athena Nike, with the entrance of the Propylaia on the left. Arriving near the Temple, the path turns almost 165 degrees to the left, leaving behind the Temple, and giving us the surprise of the Propylaea this time on our right; then finally, with an additional curve on the right, we are at the front of the Propylaea, which, once crossed, will reveal to us the Parthenon and other wonders. In this case the path has literally animated the works, showing them to us in various perspectives. The Greek

masters with this sublime work show us what is meant by path, i.e. a place of surprises and unexpected events, never with a dead time of transfer from one space to another.

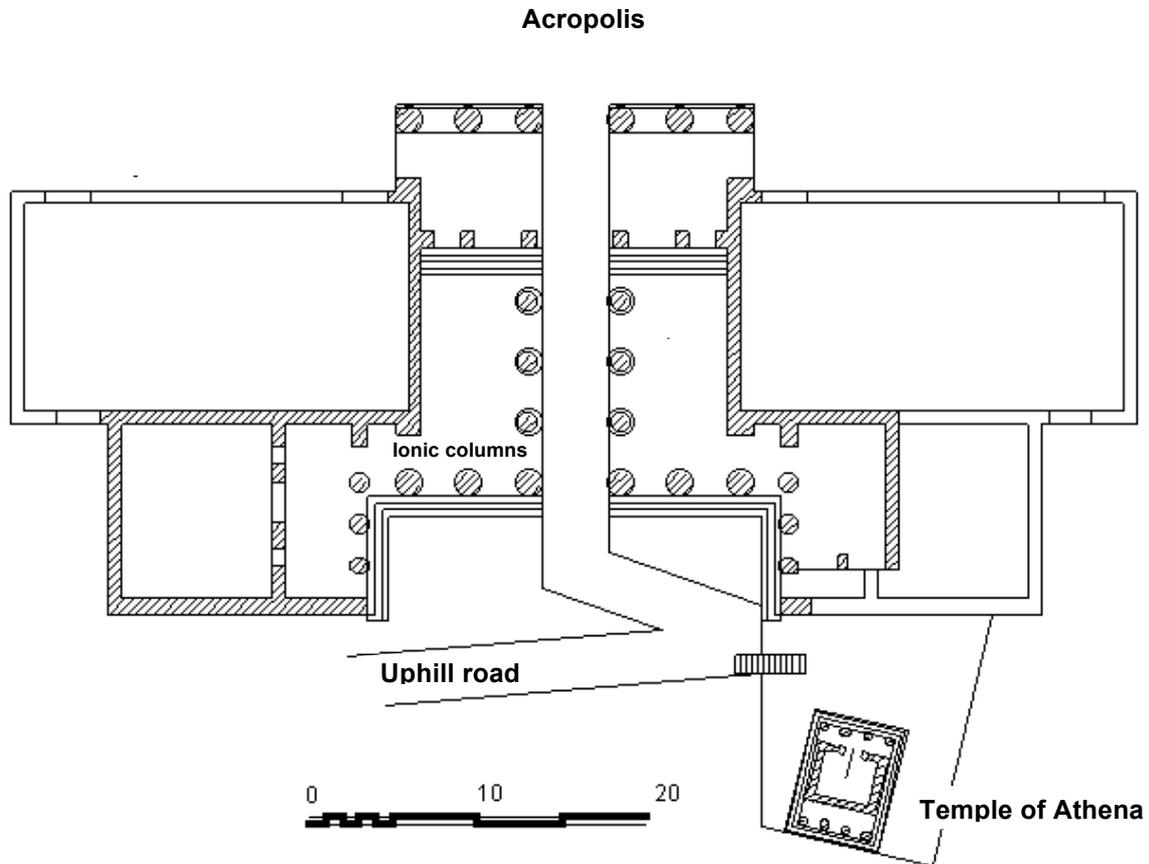


Figure 1.12 – Map of the entrance to the Acropolis of Athens.

Let us imagine, now, to be in a room where the statues on display depict the various emperors of ancient Rome, and that we want to associate with each one of them a brief history of the events during their reign, showing how these events have taken place and also how they affected the techniques of creative arts.

The importance of a correct reading of the works in chronological order is evident. Let's suppose that you have a room that does not have enough space to exhibit artworks in linear sequence in a single row, but for reasons of space must exhibit works in two symmetrical rows (Figure 1.13).

Without a proper indication, the visitor is undecided about which path to follow among the many possible, with the risk of "reading" the show in a disordered or wrong manner.

With proper use of light indicators or through explanatory graphs or just a simple

numerical sequence, we will put the visitor in condition to follow without doubt the right path to “read our story”.

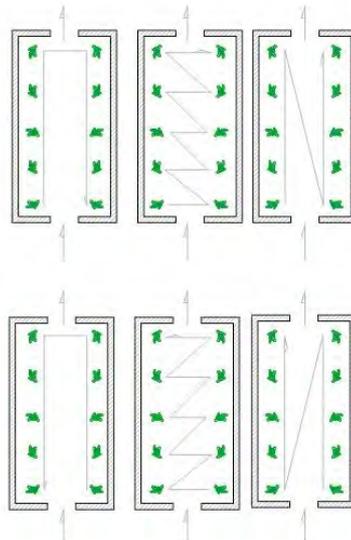


Figure 1.13 – Solutions for the path when the artworks are exhibited in parallel rows.

1.6.5 The time as a chronological tape

The concept of time that we examine in this context is similar to a chronological journey of the artworks shown, which also has a vision of what is happening while the artworks are realized. If, for example, we are admiring a classical Greek artwork dated 480 BC, which was found away from the motherland, undoubtedly is of help for better understanding the artwork, making us more excited, to know that:

- in that year the most dramatic of the Persian wars took place, in which Leonidas with 300 Spartan warriors faces the huge army of Xerxes at Thermopylae,
- the destruction of Athens had then favoured the reconstruction of the Acropolis with the criteria of the classicism contained and anticipated in the object that we are admiring.

So it is essential to place the artwork in a specific historical-temporal context, accompanied by information about what had happened before, what was happening at that moment and what would have happened immediately afterwards, in historical, political, social and artistic terms.

Other information that can enrich the visitor’s knowledge relates to all the work of the experts which has preceded the exhibition which is visited:

- how and by whom a specimen has been found,
- what technique has been used to restore the specimen, and what was its original context.

The framing of the artwork, as part of the world view that prevailed when it was made, makes us better understand its value. The value of a work can be represented by:

- its capacity to fix the more typical and representative characters of the history of taste when he saw the light,
- its subversive and revolutionary potentiality to undermine these characters, and to propose major turning points in the artistic communication process.

This is definitely one of the most demanding and important tasks to face by who organizes an exhibition; completeness and clarity of the framework will determine the final quality of work.

1.6.6 Technology

The current level of evolution of technology is opening up huge opportunities for museum exhibition, because it is a fundamental support in the preservation of the artworks thanks to the possibilities reached in monitoring and tele-control of the climate, and in the lighting and security. But technology also adds potentialities really striking in the interactive fruition of artworks.

The architectural and urban reconstruction with 3D graphics of some archaeological sites leaves very surprised, and with interactive information you can reach the ideal level of knowledge exchange with the visitor to a museum.

A monitor placed next to the specimen on display, which contains the data previously mentioned, mostly with reference to the historical-temporal context, will allow the visitor to access information that most interests him, putting him in a position to choose whether to deepen the historical aspect rather than the political or artistic one relative to the artwork visited, or to know the history of its discovery or to view a virtual reconstruction of its original appearance and the context in which it lived.

Over the millennia, which have written his history, man has changed infinite forms of expression and communication of his emotions, but their substance has not changed.

Therefore, a correct guide to follow in our work is to ensure that those coming after can find what we would want to find for us.

1.7 MUSA Project: intermuseum network for conservation of artistic heritage

The MUSA project's watchword is “preventive conservation”. The MUSA project stemmed from the need to conserve exhibits in the best possible condition in museums, art galleries, libraries, churches and underground archaeological sites. Unfortunately objects are not “naturally” preserved but tend to deteriorate. So it is very important to survey the quality of the air “enveloping” works of art displayed in museums controlling the physical, chemical and biological parameters of the air by target analysis campaigns and with the aid of microclimatic instrumentation. In addition, the project was stimulated by recent legislation establishing the standards and targets of quality that museums, libraries and historical archives will have to achieve in the near future, in particular the Italian Ministerial decree dated 10/05/2001.

The MUSA project (www.isac.cnr.it/musa) set up a network exploiting the Internet and wireless communication technology to monitor buildings containing works of art using a remote-controlled system. The experimental phase, lasting about two years, finished on 31/12/03 and involved three pilot sites. Thirty museums in the Emilia–Romagna region (Italy) were involved in the project (Figure 1.14), which ended at the end of the year 2009.

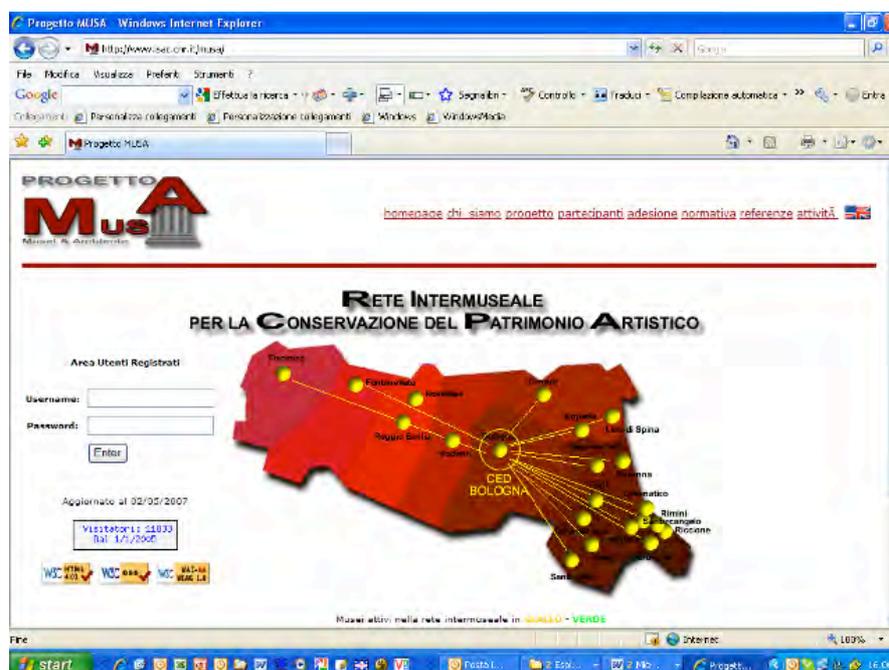


Figure 1.14 – Web page of the MUSA project.

The network offers museum curators and technical staff a practical means of tackling preservation of cultural heritage by automatically measuring the physical parameters of peripheral sites. The parameters measured are those fixed in the cited decree:

- Temperature and Relative Humidity for physical parameters,
- Bacterial, Fungal and Total Microbial load for biological parameters, expressed as Colony Forming Units per cubic meter of air (CFU/m³).

The aerobiological measurements are carried out with the Andersen sampler (6 stages) in different seasons and in rooms with risk situations.

The main philosophy of the MUSA project is to verify the resistance of various types of materials in relation to the environmental conditions. The system will be particularly useful for those sites without conservation experts to report situations at risk or ongoing hazards. All parameters monitored are transmitted in real time from the peripheral sites to a central archive (database) providing analyses and forecasts on the trend of environmental conditions. The participating museums periodically received clear reports with recommendations for easy application:

- to rationalize and optimize restoration,
- meet the requirements of the microclimate monitoring systems to access credit and loans,
- certification of the showrooms at temporary exhibitions,
- undertake a process of optimization of energy requirements.

The system is implemented through:

- a telematic network exchanging data and information from and to the museum sites connected,
- local use of wireless communication technology for environmental data,
- real time transmission and reception of data via internet communication technology from the museums to the Data Management Centre and vice versa.

A simulation of a remote-controlled system: every museum in the world transmit for instance T and RH data by an automatic system to the data management centre in Italy that will provide analyses and forecasts on the trend of environmental conditions sending reports, graphs, alarm messages and restoration procedures. Alarm messages indicate the possible micro-environmental risk situations that might occur (or are already present) for the preserved works of art. The recovery procedures suggest recovery actions to achieve optimal parameters for the proper storage of artwork materials. Another important form of

help offered to the museums is to check the correct operation of remote equipment and when necessary, provide remote assistance and notify any abnormalities.

The graphic interface of the database consists of a website, a useful tool for connecting remote sites with the operation centre (CNR-ISAC). The Data Management Centre collects and archives all the data of the individual museums that can be requested via the web anytime and anywhere with network connection.

In conclusion, project's last phase was concentrated on the study of relations between materials and biological and physical parameters and the search for the threshold within which works of art must be maintained for their optimal conservation in relation to their constituent materials. The research project conducted by ISAC-CNR in Bologna for about 10 years has become a service available to anyone anywhere in the world ([MUSARTIS®](http://www.musartis.it) PEGASOFT: Art Care Innovation. www.musartis.it).

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2 - STONE ARTEFACTS

2.1 What conservation means

2.1.1 Strategy for conservation

Conservation is a duty of protection that each one of us has in relation to the environment, its cultural heritage, its diversity and identity respect to other ethnic groups, religions and social status.

Generally it means to promote and contribute to conservation of material and immaterial works: our culture and our custom, our art that have been passed down and that we must deliver to the future generation. This is achieved through steps involving the materials constituting the artifacts and the environment conservation.

We must know the materials, their behavior, their interactions with the environment to having correct vision of the specific conservative needs.

In principle there are three times correlated with the conservation of artifacts:

- ancient, where the knowledge of the materials was of great relevance to workers and artists;
- intermediate, characterized by the exchange of books, collections and museums;
- modern, where it exceeds the traditional materials and traditional methods with the study of the dynamics of degradation and the behavior of ancient materials and synthetic ones used for the restoration.

The requirements of knowledge regarding modern treatments are: thorough knowledge of the constituent materials, knowledge of the 'excursus vitae' of the artifact; knowledge of conservation and awareness of the treatments received by the artifacts over the years.

Based on the knowledge mentioned before, derived from the interpretation of data and intersection from scientific analytical processes and research of historical sources, we can develop the most advantageous strategy for conservation.

In any type of artistic work, there are technological or restoration operations that involve the use of natural and synthetic materials, traditional or innovative, always with

interactions or physical or chemical contact with the materials constituting the artifacts. They are typical of the type of each work of art.

2.1.2 Preliminary studies

Preliminary study allows us to understand and have full and complete knowledge of the work of art to be restored. This study is summarized in a number of preliminary researches concerning the publications that cover the issue of interest, findings, architectural components and archaeological sites to be retained; historical photos and archival reports and/or techniques on any conservative intervention made in the past. The preliminary study also includes:

- graphic survey: plans, sections, any significant relief in scale 1:1, paintings of areas of particular interest;
- photographic survey: general photographs, photographic survey of the conservation condition before the restoration, photos documenting particular areas to be studied carefully.

The survey (two-dimensional and/or three-dimensional) must be finalized to the knowledge of the work of art, assuming, for example, that our reference unit for a wall structure is ashlar stone.

The use of non-destructive investigation methodologies is useful for the analysis on sight, the photographic and reflectographic relief, which contribute significantly to the knowledge of the areas and materials and are able to highlight the differences just perceptible or completely invisible to naked eye, and often help in the identification of significant restorations, various states of degradation, etc..

The most significant parameters through which to articulate the visual observation are: geometry of the object, types of materials, colors, size and performance, size and characteristics of the eventual joints of mortar in the interstices, composition, iconography, conservation status and points of sampling.

There are various non-destructive methods for the relief of the color in terms of both quality and quantity: the traditional relief and digital photography using *band kodak* as a color reference, for a more faithful reproduction of the areas concerned. The method of visual comparison relies on the comparison between the colors under consideration and a set of standard samples, such as the *Munsell book of color* (1488 samples of color); the

instrumental relief is based on the elaboration of the measure of diffuse reflectance from the surface of the sample.

2.1.3 Morphologies of alteration and degradation

THE ITALIAN STANDARD UNI 11182/2006

This Italian standard provides the definitions of terms used to indicate the different forms of alteration and micro-organisms visible macroscopically. The document permits the detection of the state of conservation of the stone surface and the definition of the causes, while the extent of the alteration will be detected later by diagnostics. In this context, *alteration* is a modification of the material that does not necessarily imply a deterioration of characteristics in conservative terms, while *degradation* is a modification of the material that involves a deterioration of characteristics in conservative terms. We list below the terms of alteration and degradation with their definition.

- *Absence*: loss of three-dimensional elements (in the arms of a statue, in a loop, mosaic floor tiles).
- *Alveolization*: presence of cavities of variable shape and size, such alveoli, often interrelated and uneven distribution.
- *Biological colonization*: presence, macroscopically detected, of micro and/or macro-organisms (algae, mosses and lichens).
- *Biological patina*: thin and homogeneous layer, consisting primarily of micro-organisms of varying texture, color and adhesion to the substrate (Figure 2.1).
- *Boundary of migration*: limit of the migration of water, usually upwards, which is manifested by the formation of efflorescence and/or loss of material. It is generally accompanied by change of color saturation in the area below.
- *Casting*: tracks vertically performed; frequently they are several in parallel.
- *Chromatic alteration*: natural variation of the parameters that define the color of the material. It generally covers the entire surface of the materials concerned; when the alteration occurs in a localized area, it is preferable to use the term *stain*.
- *Crust*: modification of the surface layer of stone, of variable thickness, generally hard, distinguishable from the underlying parts for the morphological characteristics and often in color. It can also detach spontaneously from substrate that generally appears disrupted and/or powder.

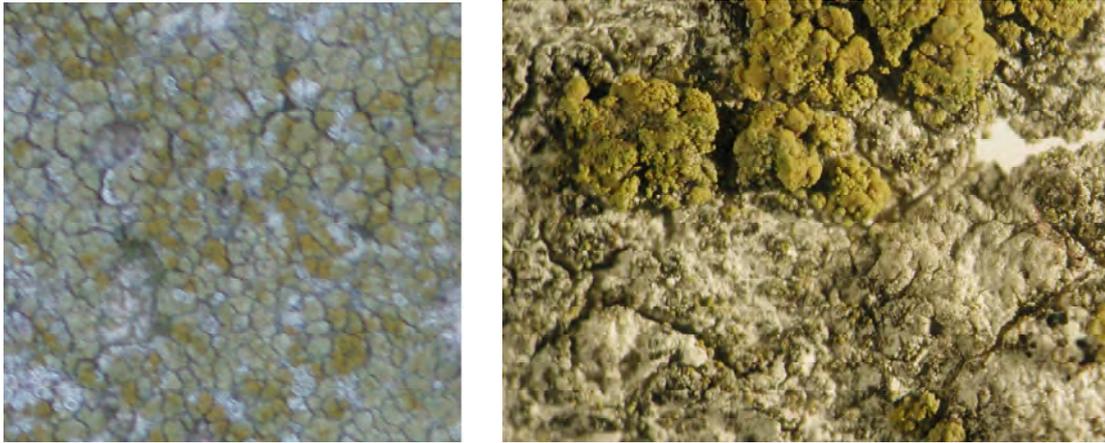


Figure 2.1 – Biological patina on a building in Rimini: macrophoto on the left and microphoto on the right.

- *Deformation*: change in shape that involves the entire thickness of the material.
- *Differentiated degradation*: loss of material from the surface, indicating the heterogeneity of the texture and structure; in the case of plaster can take a characteristic form similar to a small rose.
- *Disintegration*: de-cohesion with the fall of material in form of powder, or tiny fragments. Sometimes the term ‘pulverization’ is used as a synonymous.
- *Efflorescence*: formation and appearance of crystalline powder, usually white, on the surface.
- *Encrustation*: stratiform compact deposit, generally adherent to the substrate. The deposit is defined *concretion* when it is preferentially developed in a direction not coinciding with that of the stone surface and takes the form of stalactite or stalagmite.
- *Erosion*: removal of material from the surface which in most cases is compact.
- *Exfoliation*: formation of one or more laminar portions, called ‘sheets’, with very reduced thickness and sub-parallel between them.
- *Film*: superficial layer of transparent or semitransparent substances, which are consistent with each other and unrelated to the stone material (for example protective film, film with aesthetic function, etc.).
- *Fracture or slot*: discontinuity in the material that implies the mutual displacement of the parties. In the case of incomplete fracture, in Italy we use the term *cricca*; when the phenomenon occurs in the glassy coating of ceramic materials, we use the term *cavillo*.
- *Graffiti vandalism*: affixing of colored paint on the surface of the work.

- *Lacuna (gap)*: discontinuity with loss of material, for example part of a plaster or a painting, piece of ceramic body or ceramic coating, mosaic tiles, etc.
- *Patina*: natural modification of the surface; it is not connected to particular phenomena of degradation and is perceived as a variation of the original color of the material.
- *Pitting*: Degradation that occurs with the formation of blind holes, numerous and close together. The holes mainly have cylindrical shape with a maximum diameter of a few millimeters (Figure 2.2).



Figure 2.2 – Pitting in mosaic tesserae.

- *Posting*: a) mortar: discontinuity between layers of plaster, both among themselves and with respect to the substrate, that usually preludes to the fall of the layers themselves; b) ceramics: discontinuity between coating and ceramic body or between two coatings.
- *Stain*: localized color variation of the stone surface (especially marbles); it is related to the presence of foreign material (water, oxidation products of metallic materials, organic substances, paints, and microorganisms).
- *Superficial deposit*: accumulation of materials of various nature, such as dust, soil, guano, on the surface. The deposit has variable thickness, generally poor coherence and poor adhesion to the material below.
- *Presence of vegetation*: presence of herbaceous plants (higher plants).
- *Swelling*: localized lifting of the material surface, variable in shape and texture depending on the state of conservation.

DOCUMENTATION OF THE CONSERVATION STATE

The morphologies of alteration and degradation must be graphically represented by thematic tables, also the constituent materials must be marked in such a way that helps in

understanding and interpreting the conservation status of an artifact prior to conducting any intervention. So is important and fundamental the graphic and photographic documentation of conservation status of the artifact before conservative intervention.

The diagnostics along with the archival documents are to be considered our point of departure for a project of conservation and without which it is not possible to perform a correct conservative intervention.

The thematic charts of conservation status are the identity card of the artifact and this should highlight the types of materials, morphology of deterioration and alteration and their location.

2.1.4 The principles of conservation

In principle, every intervention of conservation can be divided into three main phases: cleaning, consolidation and protection; not necessarily all three are present and not always the sequence of execution is the one cited above. Reasons of safety for the artifact sometimes recommend its pre-consolidation before cleaning it. Generally the conservative intervention terminates with its detailed documentation.

CLEANING

Cleaning is the removal of materials, unrelated or not, in different state of aggregation and of different nature (crust, concretion, patinas, deposits, vegetal and animal organisms) which disrupt or prevent the enjoyment of any aesthetic or material level of the artifact.

In fact its action or a too vigorous cleaning may also remove historical patinas, reducing the artifact to a mere material object, deprived of its past. Often enough in recent times, a thorough cleaning was carried out that affected the work, such as a polychrome surface. This is an outdated view of cleaning, the “renewal” of a surface; today, cleaning means “thinning” of the surface patina of an artifact. The purpose of cleaning, in terms of conservation, is to remove what is harmful to the stone: soluble or insoluble salts, layers of various materials intentionally used and not suitable or no longer functional, infesting vegetation, dirt, etc., respecting the upper layer of the artifact. And this should occur without producing harmful substances for the conservation of the materials, or micro abrasion on the surfaces.

The main cleaning methods can be grouped into: physical, chemical and mechanical (see paragraph 2.5). Before performing the cleaning operations, the following preliminary operations should be made:

- detailed analysis of the consistency of the materials,
- analysis of reaction products,
- pre-consolidation (reversible) if there is a need.

Water is among the most common solvents for cleaning operations, although in some cases it is incompatible with certain substrates, because most artistic materials are insoluble in water (metals, stones, textiles, organic materials). In addition, because many substances are conveyed by water, this last can operate equally well in their removal.

CONSOLIDATION AND PROTECTION

The term “consolidation” indicates a treatment designed to improve the cohesion and adhesion between the constituents of a artifact. Consolidation must restore the structural continuity of the material and recover the primary characteristics of matter, or at least bring them close to their initial values. It must not exaggerate in the continuity, or block the existing porosity. Of course all of this while respecting the meaning of the artifact and its iconographic aspect. The consolidation should bring benefits to the structure of the material, but without exceeding in this, otherwise you can get imbalances and very dangerous tensions in the structure. Consolidation should not alter the appearance of the materials of the artwork (increasing the reflectivity, colour saturation) and respect the characteristics of the materials.

The inorganic consolidants have considerable affinity with the stone, as regards the physical properties, and they last more than the organic materials, but the improve of mechanical properties induced by inorganic consolidants is much lower. With inorganic consolidants you can not weld cracks whose walls are distant less than 50-100 microns. This is because the hardening of the inorganic compounds is too rapid; in addition there may be the clogging of the pores near the surface. Difficulties in penetration there are also for organic consolidants, in particular those with large polymer molecules. The distribution of the consolidant within the stone also depends on the concentration of the solution, the type of solvent, the contact time, pressure and temperature of the working environment.

Each material undergoes processes of transformation caused by environmental imbalance. The protection interventions are designed to make these transformations less likely or

slower. The protection offered by chemicals is to reduce the penetration of water inside the porous structure, making the surface and the walls of the pores hydrophobic; consequently are reduced all the phenomena that develop in the presence of water, such as transport and crystallization of salts and the phenomenon of freezing/thawing.

DOCUMENTATION OF THE CONSERVATIVE INTERVENTION

Finally, it is of fundamental importance the graphic and photographic documentation of the various conservative interventions performed on an artifact. The graphical documentation can be done through tables showing the themes and highlighting the areas of intervention and the type of intervention performed.

You must make an extensive photographic documentation during the operations for the conservation and restoration; at the end of each work, there must be a report, which is a technical-scientific summary of what was done to the artifact, with lots of graphic and photographic documentation. In addition the results of the work must be made public, with conferences, scientific meetings and subsequent publication, so that the work is found to be consultable from interested persons and not. This documentation helps the restorer to apply the most appropriate methodologies to obtain excellent results. In addition, it will be of paramount importance to perform other conservative interventions in the future.

2.2 Natural stones

2.2.1 Definition

Natural stones can be divided into three groups depending on their origin:

- *Igneous rocks*: very hard rocks deriving from the solidification of a magma inside the earth's crust or a lava on the earth's surface, with different structures (micro or macro crystalline, porphyritic or vitreous), often intensely coloured and with a precious aspect, such as basalt, porphyry, granite and diorite.
- *Sedimentary rocks*: formed from deposited material, more or less tender, such as sandstone, limestone, gypsum and tuff.
- *Metamorphic rocks*: deriving from a re-crystallization in solid state of pre-existent rocks due to heavy change of temperature and/or pressure, more or less tender, sometimes easily workable. Included in this group are all types of marble, white and not. Marble is a

metamorphic rock with carbonate composition (calcite and/or dolomite) deriving from metamorphism (contact or regional) of pure carbonate rocks.

A rock as building material (mainly for ornamental functions) is chosen according to its aesthetic (for example color) and technical (for example workability) properties.

Over the centuries sedimentary rocks (limestone, sandstone, clays, etc.) were mainly used either as building materials either as raw material for producing mortars and ceramic products. In fact these rocks are easily available and simple to be extracted.

Also marbles (metamorphic rocks) were often used as ornamental stone, while the use of other rocks is less frequent due to hard supplying, difficult working and other.

In a limestone, three principal components can be identified, which are used to classify the different types of limestone:

- granules (framework)
- micrite (matrix, granules < 30 micron)
- cement (carbonate crystals due to chemical precipitation).

The most complete and used classification for limestone (and dolomite) is Folk classification (Figure 2.3), that takes into account both the nature of the principal components and the texture of the rock.

%	Allochemical granules		Allochemical granules		Allochemical granules < 1%	Rocce di scogliera e di bioerma
	Sparite calcite	micrite > sparite	Allochemical granules			
Intraclasts >	INTRASPARITE	INTRAMICRITE	Intraclasti MICRITE CONTENENTE INTRACLASTI		MICRITE, o in presenza di chiazze spatiche, DISMICRITE	BIOLITITE
> 25% di ooidi	OOSPARITE	OOMICRITE	Ooidi MICRITE CONTENENTE OOIDI			
< 25% di ooidi rapporto volumetrico bioclasti/ peloidi	3:1 BIOSPARITE	BIOMICRITE	Bioclasti MICRITE FOSSILIFERA			
da 3:1 a 1:3	BIOPELSPARITE	BIOPELMICRITE	Peloidi MICRITE CONTENENTE PELOIDI			
< 25% di intraclasti			granuli allochimici più diffusi			
1:3	PELSPARITE	PELMICRITE				

Tab. 4. Classificazione dei calcari in base allo schema di Folk (1959, 1962). I nomi delle rocce sono riportati in lettere maiuscole.

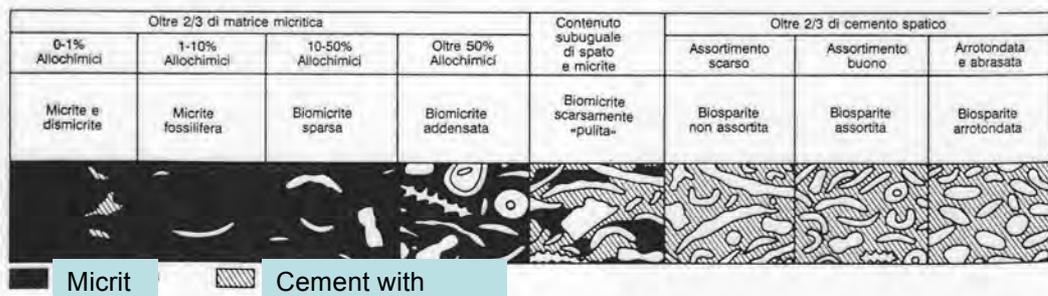


Figure 2.3 – FOLK classification of limestone.

2.2.2 Sculpture

One of the characteristics that the sculptor wants to find in the stone is the compactness, ie, the block must have the same resistance in all directions, in order not to have breaks along eventual lines of weakness. Some natural defects, such as the so-called “hairs of the marble”, which were often unexpected and which forced the sculptor to abandon the block, are to be avoided.

There are three groups of tools, which are commonly used for sculpture (Figure 2.4):

- 1) chisels of various forms (beams, gouge, cuneo), beaten with clubs to remove splinters;
- 2) drills, used for making holes,
- 3) abrasives (natural pumice, emery), used for polishing the surface.

Large pointed chisels are used to give the first roughing to the block. Shapes are outlined with a scalpel (“gradina”), whose end has three teeth, which leaves characteristic signs, known as “tracks”, with round or squared section, and with various types of abrasive.

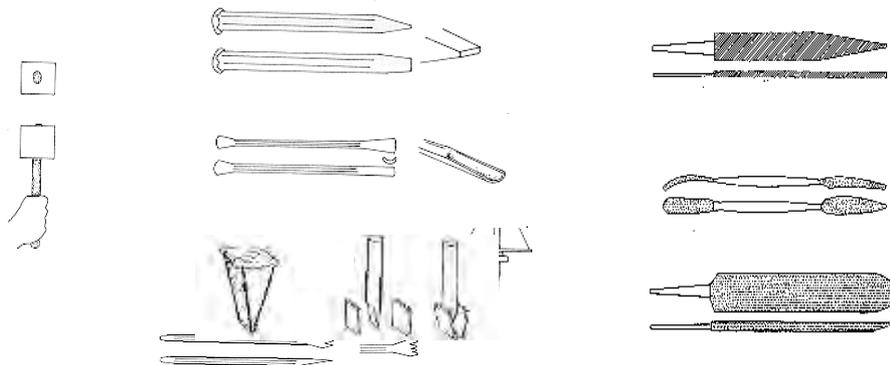


Figure 2.4 – Tools for sculpture.

USING A MODEL

The preparation of a model is not strictly necessary; the sculptor can in fact carve the block directly, without making any prior preparation. But it has often been used because, once the material has been removed, there is no turning back.

The model can be graphic, sometimes with four main views (front, rear and two sides), or three-dimensional in plaster or terracotta. It may be of equal size to the sculpture that the artist want to achieve, or smaller. It often happened that the artist made the model and then the workshop prepared the sculpture. The degree of completeness of the model varied, depending on whether there was an intervention of the artist on the final sculpture. The use

of a model allowed the series production, which was very important for example in the Hellenistic and Roman period. To produce a large number of replicas, a sort of semi-industrial system was organized: parts of the statues were made by different craftsmen and assembled later with metal nails. The execution of the most important parts, like the face, was realized by the artist. Unfortunately, sometimes the parts coming from different workshops have different colours.

The use of a model requires the “counting of points”. This technique was firstly used in ancient Greece, which invented the use of the plumb line. The distances between the wire and the surface of the model were reported on the block, where the sculptor drill holes as deep as the distances measured. The stone in excess was removed with the chisel until the desired surface.

In the Renaissance, graduated instruments were used to calculate the points. Leon Battista Alberti, in the book “De Statue” speaks of a “definitor”, a graduated circle fixed to the top of the model, in a horizontal position, with a turning arm (Figure 2.5). To detect a point, you turn the arm from which a plumb cable drops. This cable touches the surface of the model and then it is possible to report three measures: 1) the angle marked by the turning arm above the graduated circle, 2) the distance between the centre of the circle and the point of contact of the plumb, 3) the distance between the point to be noted and the pavement. In the case of large cavity that cannot be reached by the cable, a straight horizontal arm is used, that starts from the plumb cable. Vasari, in the book “Vite”, speaks about a simpler but more used technique: a combination of a vertical and a horizontal arm.



Figure 2.5 – The “definitor” system by Leon Battista Alberti for the sculpture.

2.2.3 Painting and polishing

In antiquity the stone was coloured directly or, more often, on the preparation of plaster. In the fifth century BC in Greece the “ganosis” was diffused, that consists in coating with wax. In the Middle Ages only a few parts of the stones were coloured. Since 1400, the natural stone was preferred, without colouring, with slight polishing obtained rubbing with a wet cloth and a mixture of pumice in powder and sulphur, or using oxalic acid.

The practice of painting on stone is in vogue especially in the 1500. The initiator of this technique seems to have been Sebastiano del Piombo (Figure 2.6). Its diffusion is related to the use of oil painting on various supports.

The paintings that have a stone support always are small, because of the softness and fragility of the material. The preparation, which was often realized only in the areas that had to be painted, consists on a single coat of oil. The colours are those of the oil painting (orpiment, lead black, cinnabar, lacquer, blue or green ash, indigo, carbon black, verdigris) mixed with walnut oil, linseed oil and turpentine.



Figure 2.6 – *Pietà* by Sebastiano del Piombo, 1517, Viterbo, Civic Museum: painting on stone. After: [http://it.wikipedia.org/wiki/Pietà_\(Sebastiano_del_Piombo\)](http://it.wikipedia.org/wiki/Pietà_(Sebastiano_del_Piombo)).

Since 1800 the stone is also used as a support for press. The lithographic matrix is a porous limestone, which is cut into slabs of various sizes, often between 5 and 10 cm, and heavy even several tens of kilograms. The slab of stone can be re-utilized: when you have finished printing, you can renew the surface of the slab decreasing its thickness. The

surface is perfectly smoothed if the signs are executed in ink; it is rubbed with sand and water to make it rough if you paint with the brush.

To increase the number of print pages as more as possible, a preparatory process of the stone was added: covering with a light layer of a solution of Arabic gum and nitric acid in water, which makes the surface more porous. This layer is dried for a few hours and then removed with water.

Today, the stone slabs have been replaced by porous metals such as zinc and aluminium, that give the same performance, but are cheaper and easier to handle.

2.2.4 Tarsia or commesso

The term “tarsia”, from Arabic “tarsi”, indicates the technique of combining between them different components and supports. Unlike other techniques that combine different materials between them, such as niello, agemina, cloisonné, champlevé, the tarsia is characterized by the combination of components constituted of the same material, although of different colour.

It is possible to distinguish two forms of tarsia in which precious stones are used. In one case the stone is inserted in the supporting material, while in the other the stones are juxtaposed with each other and put on a common basis. The first case in antiquity was the most common.

The support could be metal, wood or ivory, and the artwork can also be called “incastonatura” (embedding), a technique similar to enamel cloisonné. There were two main methods of this type of tarsia: ihzu and tamlu (Asian words). The first was to fix the stones by means of calcium carbonate in small holes with walls in relief. The second method consists in engraving the support by digging a spot for the insertion of the stone so that this last was at the level of the basic plan.

The term “stone tarsia” indicates the coverings of floors, walls or part of furniture. Thin slabs of stone and coloured marble are used, cut and stuck to each other to form decorations in a compact area. In this tarsia, unlike the mosaic, the components are not regular and not all the slabs have the same shape and size and the mortar does not appear on the surface. In the Roman world, the technique was widely used.

2.3 Artificial stones

2.3.1 Stucco

“Stucco” is a mixture of lime, marble powder, washed sand, and casein, mixed in various proportions according to its function, and the materials available. After being moulded and dried, the amalgam is applied to stable supports, especially wood. The best colours are the mineral colours and the binder usually is glue.

When used with the function of filling or finishing, the mixture should be soft and achieve compactness after moulding; with the function of decoration, the mixture must have plasticity, fineness, malleability. Used for parts in relief is added to the rest through metal tips.

The stucco is used in Mediterranean countries and eastern countries for ornamental architecture, because the material is easy to find and to work; in addition the climate is warm, condition that favours its conservation. In Egypt the masks of mummies were made in stucco, as well as elements such as pilasters, pilaster strips in Greece and Roman Empire. In Islamic countries and in those of their influence (North Africa, southern Italy and Spain) stucco is associated with the technique of engraving (see 8.3.5).

After the twelfth century, stucco became a complementary element to painting and sculpture in wood. In the first case the chalky plaster serves as a preparation to the pictorial layer, while in the sculpture it was used to hide the suture zones of a statue or to moulding the parts in relief, such as leaves, then fixed with iron tips or wooden sticks. In both cases, the stucco should be a fine paste.

In the Renaissance, the stucco became again an architectural complement. The will to imitate the ancient artifacts brings to experiment materials and develop the technique: in the mixture the portion of sand is replaced with marble powder and the stucco becomes more soft. For the exterior - due to rain, ice and wind - a special kind of stucco was prepared, whose paste is made by means of an infusion of elm peelings, Greek hay, and mallow peaks mixed with eight parts of a marble mortar, a part of sulphur and two parts of powdered pumice.

The stucco gains a scenographic role in rococo architecture of the seventeenth and eighteenth centuries. Austria and southern Germany are very famous for their

experimentation, where the stucco imitates the most varied materials. For the most voluminous decorations, the plasterer added chopped straw.

2.3.2 Scagliola

The “scagliola” was invented in the 1600 in Carpi (Modena, northern Italy). The scagliola is obtained from natural gypsum, “selenite”, present in abundance in the Northern Apennines (northern Italy) through cooking (about 300 °C), and fine grinding. The fine powder obtained is then mixed with glue made from pieces of tanned leather, in order to have a workable paste, which is then coloured and polished with pumice, walnut oil or flax. Pastes of scagliola have allowed to imitate all types of marble and these imitations were used for flat surfaces.

Scagliola is also used in the “tarsia”. In this case the base is made by a mixture of plaster and water, placed in a container to solidify, or it is a composition of straws. On this base, a layer of scagliola of a few millimetres is placed; after drying, it is carefully polished; on it, is possible to make the design by dusting. The design is then engraved and the exceeding scagliola is removed, creating ruts. Coloured scagliola is then deposited over the whole surface, but it will remain only in the ruts, when the other parts will have been smoothed. Every time you want a new colour, you can engrave ruts and deposit a layer of new scagliola.

2.3.3 Mortars

DEFINITION

A mortar is a mix of inorganic or organic binder, aggregate mainly fine, water and eventual organic or inorganic additives (or simply a mix of binder and water) in precise ratios in order to give:

- an appropriate workability to the fresh mixture,
- opportune physical properties (porosity, permeability, etc.) and adequate mechanical characteristics (strength, deformability, adherence) after setting, as well as a good durability.

Binders can be aerial or hydraulic. Aerial lime and gypsum are aerial binders; hydraulic lime and cement are hydraulic binders. Aerial binders can harden only in the air, while hydraulic binders can also under water.

The aggregate is the skeleton of the mortar and it reduces its volume change during the setting phase.

The aggregate can be composed of:

- sand (from river, from quarry, from coast)
- crushed rocks
- natural materials with pozzolanic activity (e.g., pozzolan, fossil siliceous sand)
- artificial materials with pozzolan activity, like “cocciopesto”
- Fragments from hardened mortars.

Additives are organic or inorganic substances, often present in small quantities, that modify one or more properties of a mortar.

AERIAL BINDERS: AERIAL LIME

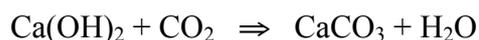
Aerial lime is obtained by the calcination (about 900 °C) of very pure limestone. The calcination produces the formation of quicklime (CaO) according to the reaction:



CaO for being used as binder has to be hydrated in order to transform it in slaked lime (Ca(OH)₂) according the following reaction:



The setting process of slaked lime is due to its reaction with CO₂ present in air and evaporation of water according to this reaction:



Aerial lime can be distinguished in “rich” (fat) and “poor” (thin), depending on the amount of impurities (dolomite, silica, clay minerals, etc.) of the calcined limestone: respectively <2% and between 2% and 8%.

Among the poor limes we can mention the magnesium lime, which is obtained by calcination, and subsequent hydration, of dolomitic limestone, that is calcium carbonate (CaCO₃) with a lower amount of double carbonate of calcium and magnesium (CaMg(CO₃)₂). The calcination, the subsequent hydration, and the setting process of a dolomitic limestone produce the development of magnesium phases: magnesite, hydromagnesite, brucite, nesquehonite. A mortar prepared with a magnesium lime can be easily recognized on the basis of the presence of one or more magnesium phases above mentioned.

AERIAL BINDERS: GYPSUM

Gypsum, the most ancient binder, is obtained through the cooking of rocks containing gypsum at low temperature (130-150 °C). The firing produces a partial loss of water and the formation of calcium sulphate hemihydrate:



Setting process is due to re-hydration of calcium sulphate hemihydrate in air:

**HYDRAULIC BINDERS: HYDRAULIC LIME**

Hydraulic lime is obtained by calcination, at 1000-1100 °C, of marly limestone, where clay concentration is between 8 and 20%, and a subsequent suitable process of hydration. Hydraulic lime is composed of calcium hydroxide ($\text{Ca}(\text{OH})_2$), and several types of calcium silicates or calcium aluminium silicates deriving from the reaction of a fraction of calcium oxide and the amorphous residues of the argillaceous minerals destroyed during the calcinations phase (Figure 2.7). The hydraulic properties of this binder are due to the presence of these silicates.

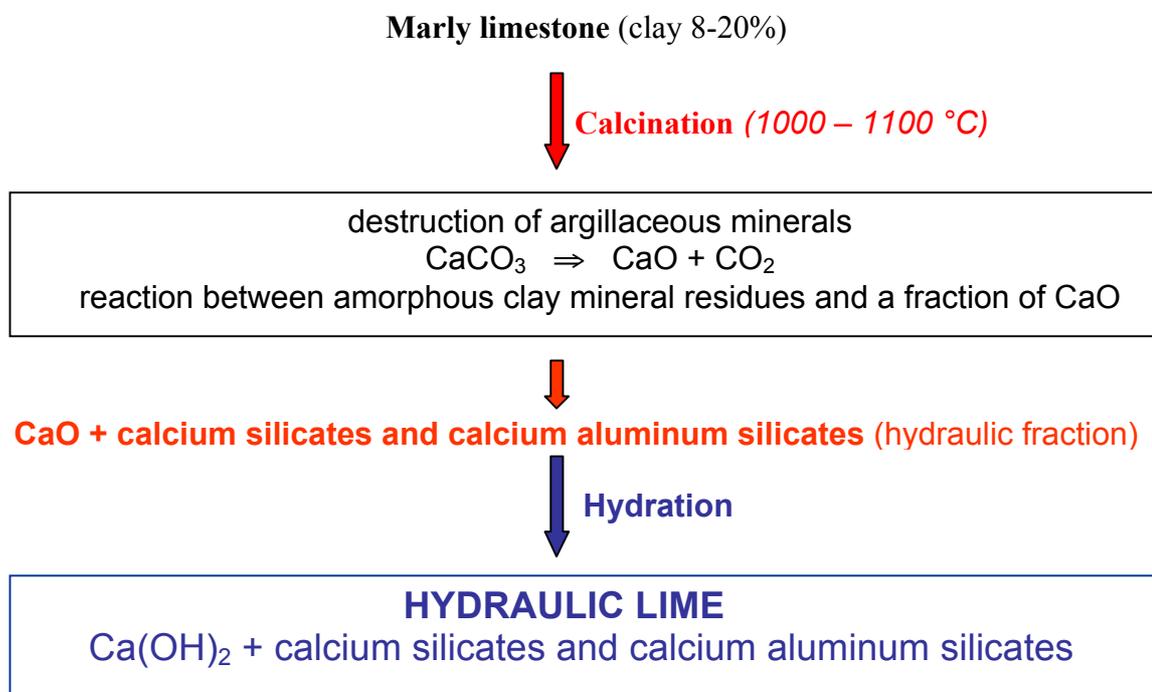


Figure 2.7 – Hydraulic lime: production scheme.

The hydraulic lime has two setting mechanisms:

- aerial, due to the carbonation of the calcium hydroxide,
- hydraulic, due to the hydration of the silicates.

Of course the hydraulic characteristics of these binders are closely linked to the concentration of clay present in the calcinated raw materials. The hydraulic properties can be expressed by the Hydraulic Index (H.I.), which is the ratio between the sum of the percentages of SiO₂, Al₂O₃, and Fe₂O₃ (clayey fraction) and those of CaO, and MgO (carbonate fraction). The hydraulic properties increase with the value of H.I.

$$\text{H.I.} = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \quad (\text{clay fraction})}{\text{CaO} + \text{MgO} \quad (\text{carbonate fraction})}$$

HYDRAULIC BINDERS: CEMENT

Cement is obtained by firing, at high temperatures (1400 °C or more), natural or artificial mixtures composed of limestone, marly limestone and clay, so that the mixture has the following chemical composition: CaO 60-66%, SiO₂ 16-21% and Al₂O₃ 4-12%. The firing process causes the melting of the mixture and, after cooling, a hard material, partially vitrified, called “clinker” is obtained. Then the clinker (calcium silicate, calcium aluminate, calcium iron-aluminate) is pulverized and different additives, natural or artificial, are added to it in order to change some of its properties.

The setting process of the cement is due to a complex system of hydrolysis and hydration reactions. This binder does not contain an aerial fraction.

HYDRAULIC MORTARS

A mortar with hydraulic characteristics can be obtained by means of an hydraulic binder (hydraulic lime and/or cement) or through mixing aerial lime + aggregate with pozzolanic activity (natural or artificial) + water.

In the past, until the middle of the 18th century, the hydraulic binders were not known.

Therefore mortars with hydraulic characteristics were obtained in the following ways:

- aerial lime + “cocciopesto” (fragments and dust of terracotta)
- aerial lime + pozzolana (sand of explosive volcanic origin).

During the setting phase, cocchiopesto and pozzolana react with the aerial lime giving rise to hydrated calcium silicates and hydrated calcium and aluminium silicates, which are the responsible of the hydraulic properties of the mortar.

Rarely hydraulic mortars were obtained with metakaolin and sand instead of cocchiopesto and pozzolana.

Hydraulic mortars based on metakaolin were the result of a sophisticated building technology. They required the production of metakaolin by means of firing (about 600 °C) of kaolin (clayey rock) and a perfect mixture with aerial lime in precise proportions. During setting process, the aerial lime easily reacts with the metakaolin giving rise to the formation of calcium and aluminum silicates in hydrated form.

Before the 18th century, there was the fortuitous and unconscious production of hydraulic limes. In fact the presence of hydraulic mortars based on hydraulic binder was detected in several medieval or late antique age sites.

The production of hydraulic binders, in the past, was due to the presence of marly limestone in the area of the site, to high temperatures of calcination and to a not careful hydration process.

According to the kind of the binder (Italian standard UNI 10924), we can distinguish the mortars based on:

- a) aerial lime;
- b) gypsum;
- c) hydraulic binders;
- d) aerial lime and materials with pozzolanic activity;
- e) organic binders;
- f) clay binders;
- g) Other (e.g. two or more types of binders).

PLASTER

Plaster is a wall coating composed of different mortar layers, applied in a precise sequence.

After hardening, it has protection function and surface finish.

2.4 Deterioration of the stone

2.4.1 Introduction

Each material situated in an environment gets to balance with it. If the environment changes, and the new environment has physical-chemical characteristics very different, the situation appears imbalanced. Then the material will get to balance with the environment through physical-chemical transformations, with worsening of the material properties. The transformation suffered by the material in order to reach a new balance with the environment is called “deterioration”. Therefore, the deterioration is due to the combination of intrinsic characteristics (linked to the material) with extrinsic characteristics (linked to the environment). Intrinsic characteristics are: composition (chemical and mineralogical), structure, type of finishing working (polishing, protection treatments, etc.), positioning during setting up.

The extrinsic characteristics linked to the environment in which is located the artefact can be subdivided in: physical, chemical, biological, anthropic. There is never a deterioration process due to only one of the causes aforesaid. These causes of deterioration generally act together with different intensity. The study of weathering mechanisms is important because understanding the causes of the symptoms leads to understanding the conservation needs and leads us to informed and effective solutions.

Buildings are elements of our environment, and there are multiple causes for their continuous alteration. When the alterations entail physical or structural consequences on the material, they are named decay. The buildings suffer different stresses during their multi-secular existence: physical and chemical, mechanical, human or natural, all provoke continuous alterations to the structures. The issue to be dealt with now for a coherent planning of the conservation activities is what kind of decay do these factors produce. The identification and documentation of the present decay, interpreted in correlation with its genesis, will guide us in searching solutions in order to modify or stop causes and effects.

There are different opinions and approaches in an attempt to classify causes and symptoms of decay. The problematic for creating distinct categories is that a strong interaction exists between natural and anthropogenic factors, as also between causes and symptoms, in stone or brick structures. In addition, natural and artificial stones are porous materials. Therefore the most significant causes of decay derive from the presence of water and from the variations of temperature. Water can penetrate into the walls either by direct contact (e.g.

rainfall) or as rising damp due to the absorption of underground waters. Water and variation of temperature are strictly related to all other causes of decay. Anyway, water can be considered as the main chemical cause of decay.

2.4.2 Physical causes

THERMAL STRESSES

In porous materials, the absorption of water is sometimes followed by a change of its volume. Therefore, the wetting of the walls, in combination with the thermal variations, can create irreversible damages to the buildings. The damages caused by the thermal stresses may be either invisible to the human eye when they occur in the inside parts or manifest themselves on the surface of the material with micro-cracks. The result of such movements is the augmentation of the porosity and permeability of the building's materials.

MECHANICAL STRESSES

The buildings suffer mechanical stresses for two associated reasons. Firstly due to ground movements: the ground should always be considered part of the structure with which it interferes continuously. Secondly due to the fact that the buildings are made of different materials and every material reacts differently to thermal stresses, thus producing at the same time mechanical stresses to the other components.

FROST ATTACK

Another very important factor in the degradation of stones and mortars is the freeze/thaw cycle. The rigid structure of the stones suffers the pressure of ice forming, capable of creating fractures and, in extreme cases, the collapse and complete loss of the material.

The attack by frost affects more materials with very marked weaknesses along the natural bedding plans and those with large porosity (e.g. the limestones are more susceptible than the sandstones). Often, the attack by frost weakens the internal structure leaving the surface apparently undamaged.

SALTS

Also the damages derived from salt crystallization are related to the wetting and drying cycles in stone masonries. Rising damp and rain can affect the whole structure introducing

soluble salts and organic solutions by capillary action. In drying conditions, when water evaporates, we have the crystallization of the salts deposited in the internal parts or the external of the material.

The salts on the surface create an aesthetic disturbance, and are usually easy to remove. More threatening for the material is the growth of salts deposited within the pores as it generates tensions that can overcome the tensile strength of the stone and cause structural failures.

2.4.3 Biological causes

Different organisms and micro-organisms stimulate different decay. Intrusive vegetation, not only obscures the visual perception of the surface but often it transfers acidic moisture on the surface and in depth causing the mineral decay.

Higher plants can create serious damages on the surface and in the internal part due to their roots, that are fed with the mineral components of stone and bricks.

2.4.4 Anthropic causes

POLLUTION

A polluted environment is another decay factor. The problem, already present from antiquity, but accentuated in the last century, relates to the chemical alteration of the minerals constituting the stones, the mortars or the bricks.

Where the pollutant particles present in the atmosphere are deposited on the buildings, depending on whether our surface is protected or not, we have two opposite main phenomena. Constructions and structures not sheltered, which are subjected to many cycles of precipitation, can suffer due to the abrasive power of the water. So, many areas are attacked and run-off channels are created. On the other hand, the protected parts favour the genesis of black crusts, especially in calcareous stones (see 2.4.5).

PREVIOUS INTERVENTIONS

To conclude the observations on the major causes of decay, not of less importance is the human factor and especially the approach of the previous interventions to the historical buildings.

In the past century, during conservation and maintenance treatments, quite often the cements presented above accelerate their action along the time and, very often, the decomposition of the material can be observed.

2.4.5 Anthropogenic deterioration: black crusts

The black crust is a characteristic deterioration layer present on carbonatic surfaces in greatly polluted areas, which is due to the interaction between atmospheric particles (anthropogenic origin) and stone surface. The black crusts can be considered the accumulation areas of atmospheric particles (natural and anthropogenic) and products of the stone degradation reactions. Black crusts are formed in wet areas but sheltered from intensive flow of water (Figure 2.8, left). They are mainly composed of gypsum produced by wet and dry deposition of sulphur which is present in the atmosphere and the subsequent sulphation of the calcium carbonate present in the stone substratum. The sulphation of the carbonate rocks (limestone, marble, etc.) and of the mortars can occur by two mechanisms:

- Direct mechanism

$$\text{CaCO}_3 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \Rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2 \text{ (wet deposition: } \text{SO}_4^- \text{)}$$
- First, in presence of water, there is the formation of semi-hydrated calcium sulphate ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), followed by the oxidation into hydrated calcium sulphate, that is gypsum (*dry deposition: SO₂*).

The responsible components of the black colour of these layers of deterioration are the carbonaceous particles deriving from the incomplete combustion of fossil fuels. These particles, in accordance with their high specific surface (Figure 2.8, right) and small contents of heavy metals (Pb, Zn, V, Cu, etc.), act as catalyst in the sulphur oxidation. Sometimes the carbonaceous particles can produce directly crystals of gypsum. In addition, products of natural deposition (soil dust, biological particles, sea-spray etc.) are usually present in the black crusts. Summarizing the components of the black crusts are:

- ❖ Gypsum (main component, due to the sulphation process)
- ❖ Carbonaceous particles
- ❖ Soil dust (mainly quartz)
- ❖ Sea-spray (in maritime areas)
- ❖ Biological particles
- ❖ Carbonate and silicate granules belonging to the substratum

- ❖ Organic components (biological or anthropic origin).

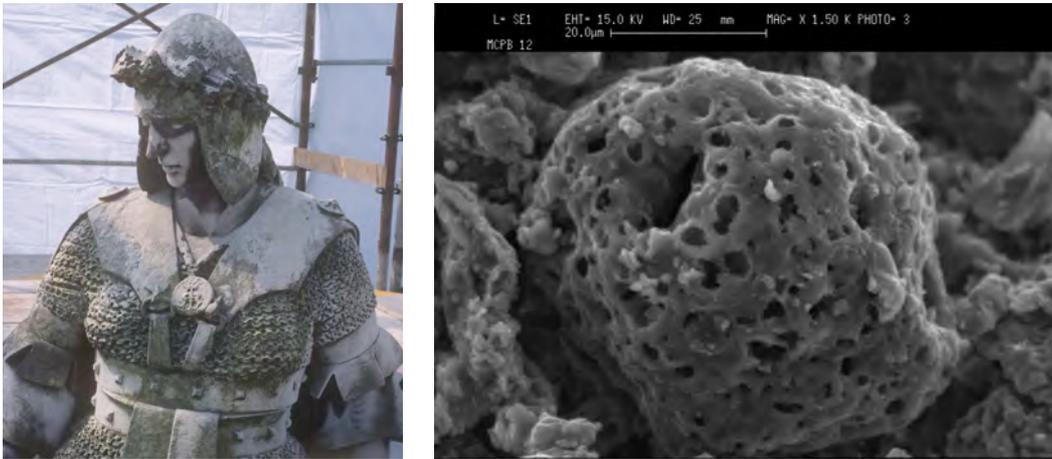


Figure 2.8 – The head and the face of the statue, on the left, show evident black crusts. On the right, a carbonaceous particle observed by scanning electron microscope.

2.5 Cleaning of stone artefacts

2.5.1 General rules to observe during the cleaning

Cleaning must be controllable in every stage, gradual and selective. “Controllable” means that the actual effect of the cleaning must not depend on the operator. The use of the scalpel, for example, is strictly connected to the way the restorer works, while a pack, once the contact time and the concentration of the components are defined, has a final effect which is independent from the operator. “Gradual” means that the operator must be able to stop his action at any time during the cleaning. “Selective”: this word has been used mainly with reference to the preservation of the covering layer; sometimes it is necessary to clean the dirt without even damaging this layer.

Cleaning must avoid production of materials dangerous for conservation (for example: water-soluble salts). This rule has been introduced to handle cleaning with aggressive chemical substances (acids and bases). Cleaning must avoid every kind of alteration of the surface (for example: micro-fractures, abrasions, scratches). This rule has been introduced to regulate the cleaning with mechanical instruments (micro sand-blaster, scalpel, etc.). There are three kinds of cleaning for the stone materials: physical, chemical, mechanical. If needed, they must be applied in the exact order listed above which also refers to the increasing aggressiveness on the surface.

2.5.2 Physical cleaning

In this operation the dirt must be dissolved and the operator must find the solvent for dissolve. In order to choose the correct solvent you need to follow the principle that “the similar dissolves the similar”, which scientifically means that the solvent must have a polarity similar to that of the dirt.

There are 3 ways to find the suitable solvent to clean the dirt, clearly with different costs:

- 1) Make a chemical analysis of the substances to remove and, from their formula, find out the polarity; this is obviously the most scientific method, the most precise, but also the more expensive and not suitable for most of the operators. It is normally used for very important jobs.
- 2) Discover, after a careful observation, the kind of dirt which is on the surface (after a preliminary washing with water, very polar solvent, on the surface there will remain wax, fat and resin). Of course this method implies that the operator is quite experienced. For this method, the Teas diagrams are used which, if correctly applied, can lead to good results. The use of these diagrams is briefly explained below.
- 3) Make tests on the surface in order to evaluate the polarity of the dirt, as explained later.

THE TEAS DIAGRAMS

The Teas triangle is a ternary diagram (Figure 2.9) where in the 3 sides are mentioned the values of F_p (polar), F_h (hydrogen bonding) and F_d (non polar): these are the so-called solubility parameters which define a value of polarity of a specific substance (for example the ethyl alcohol has 19, 45 and 36 respectively). These parameters are useful models to make reasonable forecasts on the efficiency of a solvent towards the substance to be dissolved. In the same diagram you can represent resins, waxes, fats, etc., so that it is simple the comparison between solvent and substance to be dissolved (Figure 2.10).

You can practically operate like this: you can try to melt the dirt which is at the edge of the examined area with a certain solvent; if this does not dissolve the dirt, you try with another one, on the opposite side; if even this doesn't work, you can mix them both at 50% (so having an intermediate polarity) or you can carry on trying with other percentages. Normally, in the most complicated cases, you will use a mixture in equal parts.

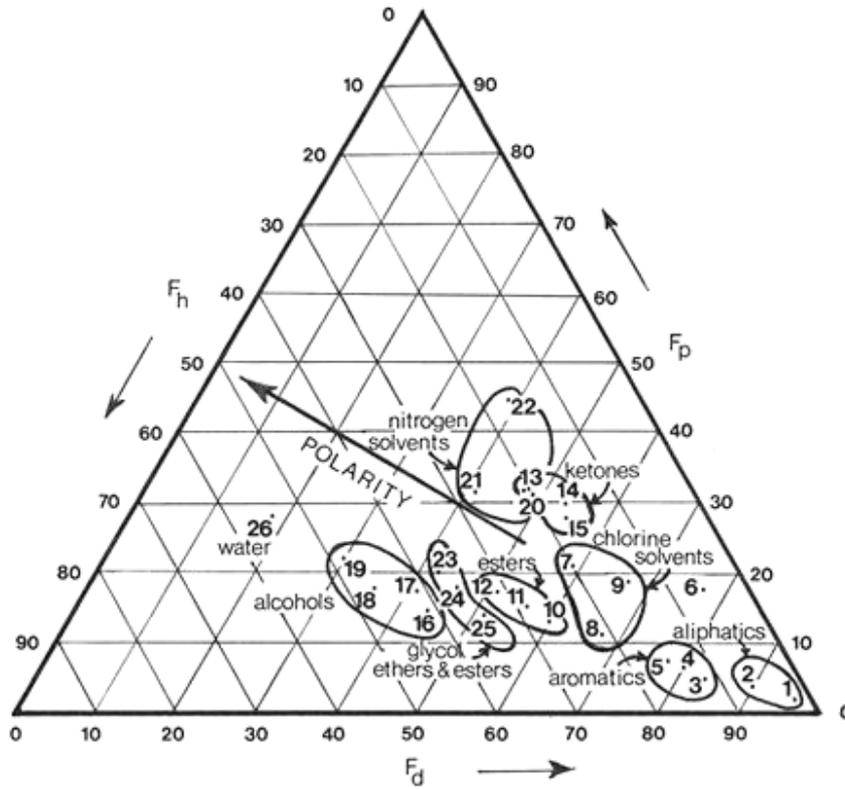


Figure 2.9 – Representation of some solvents in the Teas diagram, where in the 3 sides are mentioned the so-called solubility parameters F_p (polar), F_h (hydrogen bonding) and F_d (non polar).

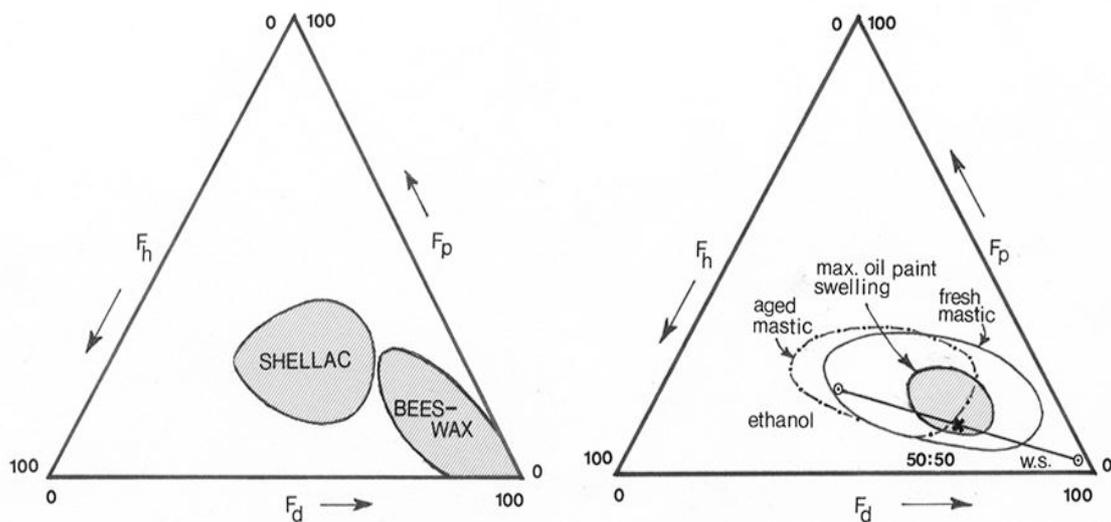


Figure 2.10 – Representation of different substances in the Teas diagram.

TESTS ON THE SURFACE

Various tests can be made on the surface to clean, using mixtures of solvents whose polarity is known (the parameter F_d is considered the more indicative). When the mixture dissolves the dirt, you have a precise indication on the polarity of the substances to remove. One of the most widely used test is to Feller, by using three solvents: acetone, toluene and cyclohexane, and preparing 13 mixtures in the proportions shown in table 2.1. These mixtures contain toluene, a toxic solvent, therefore should be used only to make the solubility tests (where the exposure to fumes is minimum) not for the total cleaning of the work, where there are longer exposure times and fume volumes much bigger. Once that the suitable mixture to dissolve the dirt has been found, a solvent of low toxicity for the cleaning can be selected, which has a similar F_d to that of the mixture found by the test.

Table 2.1 – Composition of the mixtures for the Feller's test.

Mixture		% Volume of		
n.	F_d	Cyclohexane	Toluene	Acetone
1	96	100	0	0
2	92	75	25	0
3	88	50	50	0
4	84	25	75	0
5	80	0	100	0
6	76	0	87.5	12.5
7	72	0	75	25
8	68	0	62.5	37.5
9	64	0	50	50
10	60	0	37.5	62.5
11	56	0	25	75
12	52	0	12.5	87.5
13	47	0	0	100

Even though it is quick and practical, this test reaches the F_d 47 polarity value, leaving unexplored a considerable area of a higher polarity. For this reason, many people use a new test, by utilizing the Ligroin product, a nearly a-polar solvent, and not toxic, which

covers a wider polarity interval ($F_d = 97$ to 36) and is easily found in the Italian market. Test mixtures are prepared using three solvents (Acetone, Ethanol and Ligroin) as shown in table 2.2.

Table 2.2 – Composition of the mixtures by using Ligroin instead of toluene.

Mixture	Volume %			Solubility parameters		
	Ligroin	Acetone	Ethanol	F_d	F_p	F_h
L	100			97	2	1
LA1	90	10		92	5	3
LA2	80	20		87	8	5
LA3	70	30		82	11	7
LA4	60	40		77	14	9
LA5	50	50		72	17	11
LA6	40	60		67	20	13
LA7	30	70		62	23	15
LA8	20	80		57	26	17
LA9	10	90		52	29	19
A		100		47	32	21
LE1	90		10	91	4	5
LE2	80		20	85	5	10
LE3	70		30	79	7	14
LE4	60		40	73	8	19
LE5	50		50	67	10	23
LE6	40		60	60	12	28
LE7	30		70	54	13	33
LE8	20		80	48	15	37
LE9	10		90	42	16	42
E			100	36	18	46
AE1		75	25	44	29	27
AE2		50	50	42	25	33
AE3		25	75	39	21	40

2.5.3 Chemical cleaning

In this phase you have to act on what is left out on the surface, after the physical cleaning, which normally has good success with substances of organic type. The chemical cleaning consists in transforming the dirt, usually salts and salt deposits, into soluble substances with water and so easily removable from the surface with rinses. This kind of cleaning, if not attentively and correctly made, can damage the surface. In effect if strong acids and bases are used, these mixtures can transform the salt deposits but they also attack the surface of the artwork.

USE OF AB57 MIXTURE

To avoid the damages frequently caused by the restorers, in the 70's the Italian Central Institute for Restoration studied a cleaning mixture to use for the chemical cleaning of the stone materials, named AB57, whose composition for a water litre is the following:

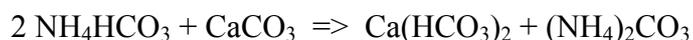
Ammonium bicarbonate	NH_4HCO_3	30 g
Sodium bicarbonate	NaHCO_3	50 g
Disodium or tetrasodium salt	E.D.T.A.	25 g
Desogen		10 cl
Carboxymethylcellulose		60 g

Its preparation is very simple: the various substances are dissolved in water, then mixed with CMC (Carboxymethylcellulose), which makes a high density mixture with very good properties as an excellent water retention. This poultice is applied to stone and frescoes surfaces (Figure 2.11). The various ingredients which constitute the cleaning mixture react with the salt deposits of the surface, especially calcium carbonate.



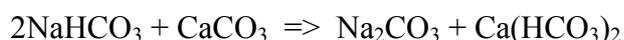
Figure 2.11 – Application of the cleaning mixture AB57 on a stone surface.

The ammonium bicarbonate reacts with calcium carbonate according to the following reaction:



Calcium carbonate is transformed into calcium bicarbonate, which is about 100 times more soluble in water; furthermore the ammonium carbonate ((NH₄)₂CO₃) immediately decomposes into NH₃, CO₂ and H₂O, so that it forms little bubbles which mechanically favour the detachment of the deposits from the surface.

The second component of AB57 (sodium bicarbonate) reacts with calcium carbonate according to the following reaction:



Also in this reaction the calcium carbonate is transformed into bicarbonate, but sodium bicarbonate is more aggressive than calcium bicarbonate. The produced Na₂CO₃ is a very soluble salt, but in this case it does not decompose and remains on the surface: it must be removed with several rinses.

The third component (EDTA) reacts with calcium carbonate tearing out the calcium atom, because it is a strong chelating agent and it tends to form strong bonds with metal atoms, especially with calcium.

The fourth component (Desogen) is a surfactant which improves the wettability of the cleaning mixture. In fact water is a very polar solvent, and the presence of the tensoactive reduces the superficial tension, increasing the contact area with dirt and thus making the penetration easier.

The mixture AB57 is normally suggested for cleaning stone because, as shown in the above-mentioned reactions, it acts attacking the carbonates. To this regard it needs to point out that often artefacts of carbonatic composition have to be cleaned (marble, travertine, marlstone, mortars, etc). In this case deposits of CaCO₃ can be found on a surface of CaCO₃. In this particular situation, in order to avoid the risk to attack also the main surface, it is therefore necessary to modify the composition of the mixture AB57. The main thing is to decrease the quantity of the most aggressive reagents (EDTA and NaHCO₃) and to increase that of NH₄HCO₃, which has a softer action.

To get a correct cleaning in this particular situation it is necessary to find the most suitable mixture by making tests with at least three mixtures of different composition, with low, medium and high aggressive level, respectively. Once the most efficient mixture has been

found, it is very important to determine the correct timing of contact with the poultice. This must be taken away before that a significant attack to the salt deposits occurs. A longer time can bring to a reaction also with the calcareous surface. However you need to consider that the deposits, being of secondary form, are less compact compared to the surface, and normally this last needs a longer time to begin to react. There are no precise rules to formulate the cleaning mixture suitable for calcareous surfaces; three formulas are given in order of increasing chemical aggressiveness:

- 1) NH_4HCO_3 saturated solution
- 2) NH_4HCO_3 , 60 g, plus EDTA, 10 g
- 3) NH_4HCO_3 , 60 g, plus EDTA, 10 g, plus NaHCO_3 , 10 g.

The tests of cleaning should be made following the previous order as follows: for every cleaning mixture prepare a pack on a small area of the surface in a square shape of 20 cm side, which well represents the kind of dirt. Subdivide the pack into four squares and after 6 hours take away the first one and check if the dirt has been attacked. If not, take away the second square after 12 hours and so on, as shown in Figure 2.12. In case you fail with that mixture, you try with the intermediate one and, if necessary, with the most aggressive one. This is the most correct way of operating to find out the best kind of pack and the correct contact time.

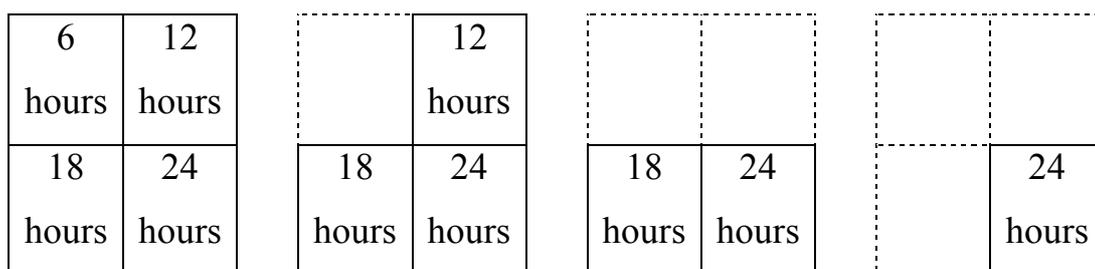
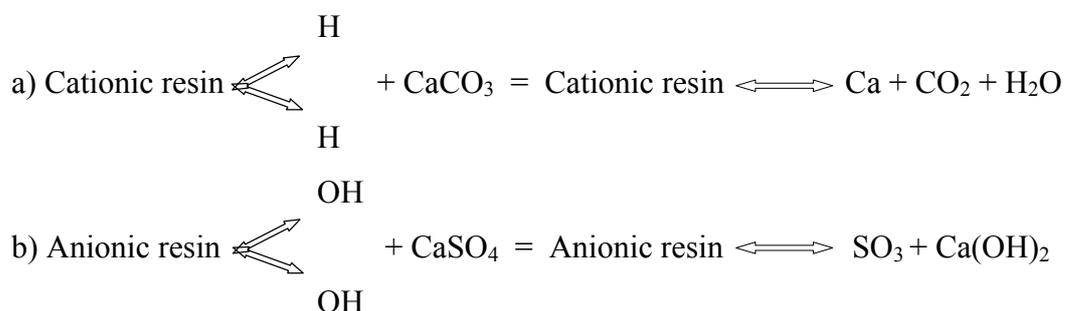


Figure 2.12 – Scheme for the realization of the tests for establishing the most suitable mixture for cleaning surfaces of artefacts made of calcareous rocks.

USE OF IONIC EXCHANGE RESINS

In the chemical cleaning you can also use ionic exchange resins, products widely used in the water treatments. Resins of this type can exchange their acid (H^+) or basic (OH^-) groups with the cations or anions of the salt deposits.

The chemical mechanism of the reactions can be so schematized:



These resins are powders that, mixed with water, give rise to a gelatinous substance that can be applied on the surface with brushes or packs; this substance does not penetrate the pores and is easily removable (Figure 2.13).

The cationic resins bind a metal and free H^+ ions, so creating an acid environment: this you have to consider when operating on a calcareous surface, considering also that the resin can start to bind also calcium of the surface if the contact time is too long.

On the contrary anionic resins bond to the anionic part of the salt and free OH^- ions, so creating a basic environment, which does not create any particular problem. These resins are very suitable for cleaning black crusts (see reaction b); SO_4 is torn from the calcium sulphate, so destroying its structure and even if it deals with calcareous stone, this is not attacked.



Figure 2.13 – Removal of ionic exchange resins from the black crusts on a stone surface.

2.5.4 Mechanical cleaning

MANUAL CLEANING

This type of cleaning is performed by means of simple manual tools, such as spatulas, scalpels, brushes, cutters, and sanders.

MICRO SAND-BLASTER

The use of a micro sand blaster (Figure 2.14) is the mechanical cleaning method, certainly the most popular for cleaning of even big size deposits. If properly used, the micro sand blaster can clean according to the general rules described in 2.5.1.



Figure 2.14 – Micro sand-blaster for mechanical cleaning.

This kind of cleaning is based on the abrasive action of various kinds of particles which are blasted by a compressed air jet on the surface to clean. The parameters that influence this kind of work are:

- 1) hardness of the bullets
- 2) shape and size of the bullets
- 3) jet pressure
- 4) diameter of the exit nozzle
- 5) distance nozzle-surface
- 6) application time of the jet.

The hardness of the bullets is fundamental because, to avoid damaging the surface, you have to remember that the bullet must be harder than the deposit to eliminate but equal or

less than the surface to clean. In the market there is a wide range of products to use as bullets: silica, spheres of marble and glass and various kinds of wood sawdust, as the coat of peach stone, walnuts, and other. These powders can have round or sharp shapes and, of course, different diameters.

The other parameter to control is the pressure of the jet on the surface: to avoid damages, the pressure should never be more than 1.5 Bar. The usual pressure of the machine is 3-6 Bar which, at a distance of 30-40 cm from the surface, produces a pressure of more than 1.5 Bar. To avoid this inconvenient, there are on the market special nozzles (JOS method), which throw the bullets with a helical movement at low pressure (0.1-1 Bar). The traditional and JOS methods are compared in Figure 2.15 and Table 2.3. The JOS system is much better than the traditional, both for low pressure and because the bullets hit the surface with a less dangerous direction.

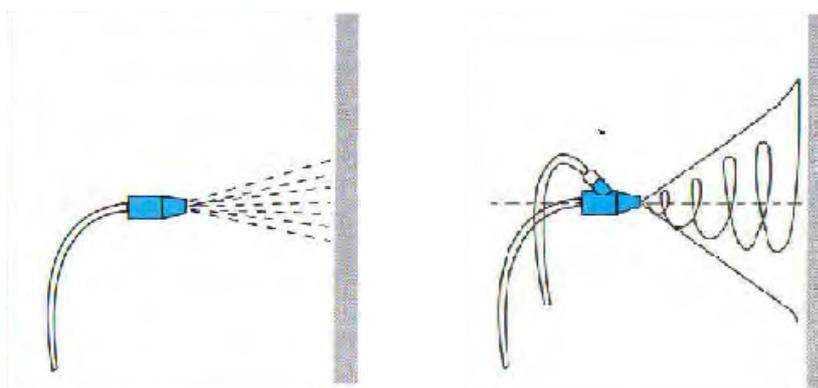


Figure 2.15 – Comparison between the throwing of the traditional (left) and JOS (right) method for micro sand-blaster.

Table 2.3 – Comparison between the properties of traditional and JOS methods for micro-sand blaster

Method	Compressor pressure (Bar)	Distance from the surface (cm)	Pressure on the surface (Bar)	Bullet size (μm)
Traditional	3-6	30-40	> 1.5	400
JOS	2	35-40	0.5	300
	0.5	20	0.2	300

ULTRASONIC DEVICE

This method is used to remove small deposits. It is quite slow, but it absolutely does not damage surfaces. The ultrasounds, generated from a small source (Figure 2.16, left), compress and expand the air that, when reaches the deposit makes it vibrate and after some time manages to detach it from the surface (if it is of small dimensions). The method is recommended to work with a wet surface because the ultrasounds spread more efficiently.

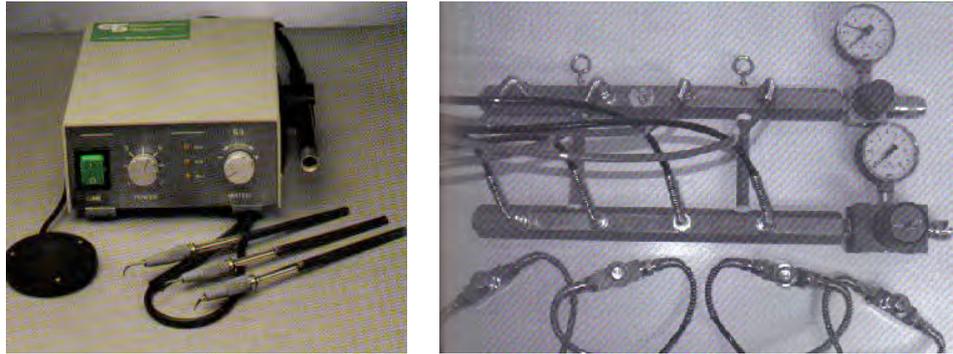


Figure 2.16 – Cleaning apparatus for ultrasounds treatment (left) and device for the atomizing system (right).

ATOMIZING SYSTEM

A very simple and non-destructive way of cleaning stone surfaces is to use atomized water (Figure 2.16, right), which combines a good washing with the removal of soluble salts from the surfaces. Water chemically acts by dissolving gypsum and secondary calcite, the main binder materials of crusts, which can be thus easily removed. The strong pressure of the liquid produces extremely small drops, improving the water penetration into dirt and therefore the cleaning efficiency. Due to their small size, drops are practically not subjected to gravity, thus allowing to reach with their cleaning effect even those areas which are very difficult to reach. Another advantage, though secondary, is the physical cleaning produced by the atomizing of the droplets and by the water steam over the surfaces of the artefact.

LASER TECHNOLOGY

The use of laser technology has given excellent results when applied to the restoration of artwork, and researchers are still at work to further widen the possibilities of laser

applications in the restoration field. Particularly the Nd-Yag laser, used with the Q-switch mode, assures a high cleaning effect, without any kind of thermal or mechanical effect, thus preserving the integrity of the substratum.

So laser cleaning proves to be:

- a) selective: the laser beam is absorbed by dirt without affecting the substratum
- b) graduated: the beam power can be varied according to the operator's needs.

At the moment, laser apparatus, such as the one indicated in Figure 2.17 (left), is mainly used to remove black crusts on light colour stones.

Once certain parameters are fixed, such as length and power of the impulse, the radiations are absorbed by the crust, which is eventually vaporized if brought to very high temperature in a short time (4000-5000 K). When radiations reach the marble or the light colour stone, they are reflected as if they were a normal white light, without causing any damage.



Figure 2.17 – An example of source apparatus for laser beam (left) and conductivity meter (right).

2.5.5 Measurement of soluble salts

The instrument used to calculate amount of water soluble salts in artistic artefacts is a conductivity meter (Figure 2.17, right). To this purpose, the soluble salts are extracted by preparing and applying a carboxymethylcellulose poultice on the stone surface (see 2.5.3, *Use of ionic exchange resins*). The water soluble salts, present inside the stone, go up into the poultice during evaporation.

The carboxymethylcellulose, when is completely dry, is placed in a beaker with distilled water on a magnetic stirrer (Figure 2.17, right). With the conductivity meter it is possible to know the amount of soluble salts in solution.

2.6 Consolidation and Protection

2.6.1 Reasons and aims of treatment

The term “consolidation” indicates a treatment designed to improve the cohesion and adhesion between the constituents of a stone material. The decision to consolidate an artifact is fundamentally related to the cohesion of the constituent material.

The consolidation can be necessary for two main reasons:

- loss or decline of cohesion of the material, with a decrease of mechanical and chemical-physical characteristics that determine the intrinsic properties of a material (Figure 2.18);
- loss or lack of adhesion between layers or parts of the artifact, for example the layers of a fresco.

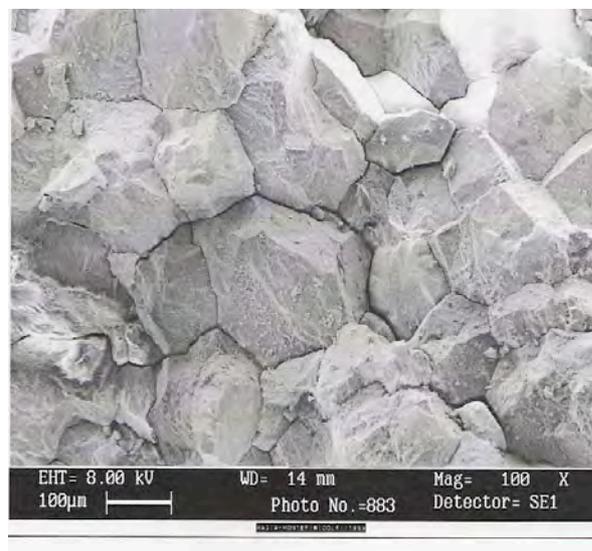


Figure 2.18. – Example of material to be consolidated: deteriorated marble.

In other words, the materials to be used for consolidation should bring structural benefits to the material constituent the artifact, by regenerating the structural continuity of the stone

material, and restoring the primary characteristics of the material, at least near to the initial value. But they must not exaggerate in this, otherwise may generate imbalances and tensions between stone material and consolidated parts, very dangerous for the structures. Practically, they must not have complete continuity nor create blockages of the porosity. In addition the consolidation should comply with the stone materials and everything should be done in the respect of the significance of the artifact, without altering its appearance (increase of reflectance and saturation of the colors) as well as its iconography.

The materials used for the consolidation treatment must have the following characteristics:

- reversibility:

the added material can be removed; this is important especially in case of preconsolidation;

- compatibility:

the added material coexists with the original without causing excessive stress;

- durability:

the added material retains its characteristics for a long time;

- security:

the products used must respect the surrounding environment, during and after the application, and the safety and health of operators.

The consolidating materials may be of organic and inorganic nature. The inorganic consolidants have considerable affinity with the stone, regarding the physical properties, and have a duration exceeding with reference to organic ones. The improvement of mechanical properties induced by inorganic consolidant is lower and it is not possible to weld the cracks if the distances between the walls are more than 50-100 microns. Where the taking of the inorganic compound is too rapid, there may be clogging of the superficial pores. Also for organic consolidants there are difficulties in penetration, since they are polymers with large molecules.

Each stone undergoes processes of transformation which are caused by the imbalance with environment. The aim of protection interventions is to make less likely or slow these changes, and the aim can be achieved by acting either on the environment either on the stone materials.

The aim of protection, made with chemical substances, is to reduce the penetration of water inside the porous structure, so that are reduced all the phenomena that develop in the

presence of water, such as transport and crystallization of salts and the phenomenon of freezing/thawing.

2.6.2. Inorganic consolidants

CALCIUM HYDROXIDE

The consolidation by using calcium hydroxide in aqueous suspension derives from the formation of calcium carbonate by reaction with carbon dioxide of the air:



Treatments with calcium hydroxide have been used in particular in the 20th century with unsatisfactory results. These treatments form a thin layer (“sacrificial layer”), non-transparent, which represents a system of protection for the stone material. So, the principal function of calcium hydroxide is that of protective rather than consolidant.

BARIUM HYDROXIDE

Analogously to calcium hydroxide, barium hydroxide reacts with carbon dioxide to form barium carbonate:



The Ba and Ca ions have a similar ionic radius, so that barium can be substituted by calcium. Barium carbonate has a coefficient of expansion similar to that of calcite (CaCO_3) and a low solubility. The porosity of the stone material is reduced only partially, without any formation of a layer impermeable to water vapor. It cannot weld cracks larger than 50 microns. The bleaching of the surface can be drawback, which can be avoided by removing the excess of hydroxide on the surface.

ETHYL SILICATE AND SILICON RESINS

These two products are intermediate between organic and inorganic consolidants. The ethyl silicate and the silicone resins, in presence of water, will hydrolyze giving rise to the formation of hydrated silica, that precipitates as amorphous material and can bind to the minerals of the stone material or can condense with hydroxyl groups of these materials. Thereafter, the hydrated silica undergoes a slow process of dehydration and polymerization. The ethyl silicate available commercially is dissolved in a solvent (usually ethanol) and contains a catalyst of hydrolysis. The low molecular weight and the low

viscosity of the solutions favor penetration. The complete polymerization occurs after about three weeks after the treatment.

2.6.3. Organic consolidants

GENERALITY

All consolidant organic polymers are synthetic. Their molecules are obtained from basic molecules or “monomers”. If the monomers are equal it is a “homopolymer”, if there are two or three different types you have a “copolymer”.

The structure of molecules can be linear or three-dimensional. The polymers with a linear structure are “thermoplastic”, i.e. they soften and melt by heating. Many have a certain solubility at room temperature in organic solvents, and in theory are removable. In the polymers with reticulated structure, the monomers are able to fasten other chains with cross links; therefore, these resins are known as “thermo-hardening” (they burn at high temperatures). They are irreversible, have high mechanical resistance, less flexibility and high fragility, high adhesive power, strong internal cohesion.

The resins were born in the years 30-40 of the last century and are made from polymer, solvent, stabilizer, plasticizer, charge (inert material), colorant, emulsifier. They can have all these components, or even just the two fundamental: polymer and solvent. All resins are soluble in organic solvents but not in water. The stabilizer delays the degradation of the resin, the emulsifier lets you to mix the resin with water (primal) and the plasticizer makes the resin less fluid; the colors, which are in the mixture, must not react with the resin or the stone.

ACRYLIC, EPOXY AND POLYESTER RESINS

Acrylic resins like Paraloid B-72, Paraloid B-44, Primal B-60, Primal AC33 are thermoplastic materials, soluble in organic solvents, with good resistance to aging, to chemicals and to light. They have good adhesion, but are not structural adhesives.

The depth of penetration is not greater than 0.5-1cm, and it depends on the type of solvent that is used (acetone or thinner neutral).

The epoxy resins are thermosetting materials; for reaction with the hardener is obtained the final product. They have a good chemical resistance, are resistant to water and organic solvents, less well to UV radiation; have good mechanical properties and are excellent as

an adhesives. Unlike other resins, the epoxy can't catalyze if you add an excess of hardener.

The reaction of the polyester resins proceeds rapidly, so that the workability time is 5-15 minutes, and hardening is achieved within 30 minutes. The resin/catalyst ratio is not as stringent as for the epoxy, so that often, to accelerate the reaction at low temperature, just increase the catalyst. The reaction proceeds with a decrease of the volume, which can also get 8 to 9%; this makes these resins unsuitable to be used for structural reinforcement, contrary to the epoxy resins. Polyester resins are sensitive to yellowing and to absorption of water; after cross-linking, they cannot be dissolved in solvents, but their removal can be done by swelling with ethyl acetate or acetone.

SILICONE AND POLYURETHANE RESINS

Silicone resins are called R.T.V. followed by a number, that indicates the plasticity and density of the resin. The formation process is always the same, only changing the plasticizer. They do not enter into the stone, but they have a good adhesion with the material.

Lastly the polyurethane resins (foam) are used in various operation of conservation.

2.6.4 The application methods for the consolidants

For the artifacts of considerable size to be treated in situ, basically there are two methods of application: by brush and by spray.

For small objects processed in the laboratory, it is better to treat them in other ways, for example by capillarity up to complete immersion. The object is placed in a covered container where it is immersed only for a small part in the consolidating solution, that is kept at constant concentration. Then the level of the solution is increased at regular intervals until completely to cover the object.

The treatment by complete immersion, at room temperature and room pressure, is similar to the previous one, except that the level of solution can be increased immediately or gradually to allow the solution to come out from the manufacture.

The treatment under vacuum requires a container with the escape routes for the air and entrance of the solution, and a suction pump capable of achieving a suitable depression. Thus the artifact is dried and de-gassed, in order to facilitate the entrance of the

consolidating solution within the capillary channels. Normally you leave the artifact immersed for 24 hours.

The distribution of the consolidant within the stone depends on many factors, like the concentration of the solution, the type of solvent, the time of contact, pressure and temperature in the work environment, pore size distribution of the stone.

In addition to the choice of the application method, the depth and regularity of penetration of the consolidant depends on the type and size of the artifact to be treated, and its conservation status in various areas.

2.6.5 Protective materials

In the past, the products used as protective materials were beeswax, vegetable oils and natural resins. The protection is much more effective when it will penetrate deep and is not prevented the evaporation of water coming from the inside.

The most important requirements for protective products are: minimal influence on the optical properties of the material, stability to chemicals (in particular pollutants), stability to UV radiation, impermeability to water, permeability to water steam, reversibility when the protection has lost its effectiveness, absence of harmful by-products, and easy applicability.

There are different products for different aims of application: water repellent and waterproofing, against the growth of organisms, antagonist of ultraviolet and visible radiations, ‘sacrifice’ surfaces as those “graffiti resistant”, and products which are against erosion.

Some historical materials for protection of stone artifacts are: surface painting, protein material (milk, white and yolk egg, glue), lime plaster, dried materials, paint (oils and resins) and waxes; while the modern materials are: microcrystalline waxes, synthetic acrylic and acryl-vinilic resins, siloxane, silanes and mixtures thereof with acrylic resins (Dry film 104). These resins are very diverse than those used for the consolidation as it regards polymeric formulation and mechanical characteristics, because they must form consistent and elastic superficial films.

Finally there are some materials which give rise to the formation, on the surface of limestones, of artificial layers which reduce the contact with the harmful materials. One of these materials is the ammonium oxalate, which forms calcium oxalate. Such a film

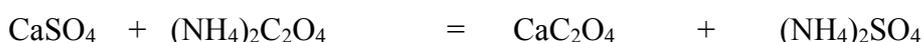
reduces the porosity, rather than to close it. It is not reversible, but highly compatible with the substrates.

The ammonium oxalate, used in saturated solution (5-6%) in de-mineralized water (Table 2.4) is able to react with the superficial calcium carbonate, transforming it into calcium oxalate:



Ca-carbonate + Ammonium oxalate = Ca-oxalate + ammonia + carbon dioxide + water

If gypsum is present, the reagent develops also an effective de-sulphuring action:



Gypsum + Ammonium oxalate = calcium oxalate + ammonium sulphate

Table 2.4 - Physical-chemical characteristics of ammonium oxalate to be used for protection.

Chemical formula	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$
Molecular weight	142.11 g/mol
Purity degree	99%
Content of volatile components	5% (maximum)
pH of a 5% solution	6-7
Content of metals (Na, Fe)	<100 ppm
Content of chlorides	<50 ppm
Solubility in water at room temperature	5%

The protective layer generated by reaction is thin but homogeneous, stable in acid environment, breathable and transparent.

The solution must be applied as poultice with the cellulose pulp, interposing a sheet of Japanese paper between the pack and the stone surface, the duration of applications should be tested from case to case; generally it is 24 hours, but only of the order of 5 hours for frescoes.

2.7 Case studies

2.7.1 Traditional production of lime in Middle East

The construction techniques of ancient furnaces for limestone and the production of lime and slaked lime in the Middle East have remained unchanged over time until the present day. The research here presented was to document the types of kilns and traditional operations for the production of lime in some countries like Yemen, Syria, and Egypt.

The materials for combustion generally vary with time: from wood in antiquity, to coal in the fifteenth century, to fuel oil or manure of animals like in Yemen.

YEMEN

In Arabia Felix “Yemen”, in particular in the valley of Wadi Hadramut, lime (local name “The Nura”) is generally produced by local limestone rocks, very rich in calcium carbonate. The rock pebbles are baked in cylindrical ovens (“Miafi”), about 3 m high, 2 m in diameter, made with raw bricks. They are open from the top and have a small opening for introducing the fuel. Their form recalls the ovens described by Catone in the second century B.C. For combustion, different materials are used: animal manure, old tires for car and matchwood. These ovens are intermittent and must continuously be fed with the fuel to keep the heat inside for two days, until to complete the baking of lime (decarbonation) and the formation of quicklime.

After baking and cooling, the pebbles of quicklime were extracted and carried in another place specially prepared for the slaking. They form a plan (“Al Mahkt”) covering an area of 2.5 x 2 m or more, then sprayed with water, after which it begins to beat with cylindrical sticks of wood until the total hydration of lime. Sometimes a mechanical equipment is used inside the cylindrical cistern to ‘power down’ the calcium oxide pebbles (Figure 2.19).



Figure 2.19 – Steps of the lime production in Yemen: use of dung for burning (left), manual hydration of quicklime (centre), slaked lime for sale (right).

After that, the slaked lime is put on the market, especially for production of plasters (local sand and lime) that are applied in brick made buildings to create a raw surface of sacrifice for architecture of Yemen, which is materially very poor. Only the house of those who have hence greater economic possibilities is adorned with the addition of colored oxides in the mortar.

SIRYA

In Sirya, after a period of research, two old furnaces, abandoned for over one year, were discovered in the area of Al Karma, after the route of Al-Zabaltani, in the outskirts of Damascus (Figure 2.20).



Figure 2.20 – Lime production in Syria: the furnace in Al-Zabaltani.

The furnaces have circular form and are constructed of rough pieces of limestone rocks. They are open from the top and have a small opening at the bottom for feeding the furnace. Their diameter is about four meters, while the height is about eight meters. Both the furnaces inside were plastered with clay. Each of them has a capacity of 75-100 tons of limestone rocks. The stones were brought from the areas of Al-meza (along the road to Lebanon) and Hama, where many rocks rich in calcium carbonate are present. Kernels of apricot, residues of the olive mills and sawdust were used as combustible in the kilns. The product of these furnaces can be sold as pebbles of calcium oxide (quicklime), or as slaked lime. Unfortunately, these kilns were abandoned after the death of the owner.

Always in Damascus, near to Suq Al Hamid, at Bap al-Jabia, a old kiln was demolished some years ago and a deposit for lime from Hama was built in the place of the kiln. The

owner of this kiln made us aware that, in the city of Hama, north of Damascus, there is an entrepreneur of lime, called Ziad Al-Kalas, who is doing this job for many years and also his ancestors were workers of the lime. Very probably for this reason, that family took the surname “Kalas”, which in Arabic means ‘those who work the lime’.

At Hama, Al-Sarihin is the area of production of lime. Here the furnaces are constructed below ground, with local stone and plastered with clay. Their diameter is about four meters while their height is six meters. They are open from the top and have a small opening from the back for feeding the kilns. The raw material is brought from quarries at the south of Hama, it is reduced in blocks of small/medium size (30-50 cm) and put inside the furnace in particular way, in order to obtain a vacuum in the centre of the oven, which will be the combustion chamber. They are continuously fed for seven days, also with the help of air pumps, to enable the flame to reach the top of the furnace. Exhausted or burned fossil fuels are used as combustible. After the baking (calcination of the calcareous stones) and the subsequent cooling, the pebbles of quicklime are removed from the furnace and hydrated in order to obtain lime ready to be used.

The capacity of these furnaces varies between 30-50 tons of stones. In Syria, the lime is used for the preservation of historic monuments, especially for the ancient mosques, and in different sectors of industry.

EGYPT

In Egypt, specifically in the village of Turt Al-Bald, outskirts of Cairo “Shaq Al-Thuban”, there is a large craft area for working marble; at the end of this area, there are several operating quarries of limestone. In vicinity of the quarries of limestone, are located kilns for the production of lime (Figure 2.21).



Figure 2.21 – Lime production in Egypt: openings for feeding ovens (left), preparing oven for cooking (centre), quicklime and hydrated lime for sale (right).

Here the construction of the furnaces is different than Yemenis and Syrians ones. In Egypt, the kilns have a rectangular shape, built with local stone and are open from above and frontally; in the back there are three openings (40 x 70 cm) for the introduction of flames. The ovens are constructed on the surface, with a base of 7 x 6 m and a height of about 3 m. Once transported to the site by means of trucks, the stones are crushed until you get the size required (10-45 cm). Subsequently, you begin a ordered arrangement of the stones inside the ovens, so that the ones of larger size are placed at the bottom, keeping free the openings at the rear; after which you will introduce the small stones until filling the furnace. Each oven has a capacity of 90-100 tons of limestone.

The next step is the ignition of the furnace, with fuel oil that feeds ovens from the back. The cooking cycle, till the complete decarbonation of calcium carbonate has a duration of 24 - 30 hours. After that you let cool the calcium oxide (quicklime), it is then hydrated (lime) and placed on the market.

2.7.2 Development of restoration mortars

The use in restoration interventions of mortars based mainly on Portland cement was very common until few years ago. The spread of cement mortar and reinforced concrete was due to the easiness of application, to the low costs and the rapid hardening. But, because of their chemical-physical incompatibility with the original materials and their scarce durability, the use of these restoration mortars was often one of the main causes of damage for the archaeological and architectural heritage. The main deterioration processes, due to the use of cement or reinforced concrete, are: efflorescence of salts, disintegration, detachments.

Now we are aware of the damages suffered by archaeological and architectonic heritage because of the use of cement mortars in restoration interventions, therefore fortunately a progressive abandonment of cement in restoration works is taking place.

At present in Italy the use of Portland cement in conservation interventions is unusual. Premixed mortars, hydraulic lime mortars, or strange bio-compatible products have taken the place of cement mortars. Unfortunately the composition of the binders, and the physico-mechanical characteristics of the restoration mortars are often ignored by restorers and conservation managers. In addition there isn't a specific European standard for restoration mortars.

In this climate of general confusion there is a proliferation of products (binders and premixed mortars) sometimes worse than the classical cement mortar. Unfortunately the progressive abandonment of the cement in conservation works hasn't been joined by the development of opportune restoration mortars.

The parameters to take into account in order to develop suitable restoration mortars are:

- Compatibility with the materials present in the monument or in the archaeological structure. In order to assure the compatibility we have to characterize the ancient materials and evaluate their conservation conditions. Also the knowledge of the composition and of the mechanical properties of the restoration mortars is indispensable,
- Function: for example mortars for injection, for plastering, etc.,
- Environment in which the artifact is located (internal, external, highly polluted, etc.).

In addition a restoration mortar should have to be removable from the artefact, recognizable from the original materials and obviously non-poisonous for the restorers.

In Italy, at present, the hydraulic lime mortars are the most employed in the restoration interventions. The only European standard on building limes is EN 459-1, that recognises three different limes with hydraulic properties:

- HL (hydraulic lime)
- NHL (natural hydraulic lime)
- FL (formulated lime).

Unfortunately only NHL, according to this standard, is obtained by the calcination of marly limestones, while the other two limes can be a mixture of calcium hydroxide and cement. The previous standard classifies the hydraulic degree according to the compressive strength and the lime (Ca(OH)_2) content (Table 2.5). It doesn't take into account the hydraulic index.

Table 2.5 – Hydraulic degree for NHL according to EN 459-1.

Hydraulic degree	Ca(OH)_2 (%)	Compressive strength (MPa)	
		7 days	28 days
2	≥ 35	-	2 - 7
3.5	≥ 25	-	3.5 - 10
5	≥ 15	≥ 2	5 - 15

In order to develop restoration mortars compatible with original materials, easily removable and at no high costs, several commercial hydraulic limes were examined by CNR-ISTEC in Faenza. The analyses highlighted that all the binders had unexpectedly high concentrations of calcite (aggregate), likely due to low baking temperatures ($\sim 1000^{\circ}\text{C}$), or to a deliberate addition of CaCO_3 in order to obtain values of compressive strength in accordance to European standard EN 459-1. In addition, elemental and mineralogical analyses showed that natural hydraulic limes (for example NHL 3.5) produced by different firms are classified by EN 459-1 in the same manner, even though they have chemical-mineralogical compositions remarkably different, other than different values of hydraulic index.

Subsequently three mortars were prepared by using three commercial binders, and then examined in order to identify their mineralogical composition and evaluate some mechanical properties (in particular adhesive strength and flexural strength).

Considering the high concentrations of calcite detected in the binders, the mortars were prepared in this way: one part of binder, two parts of aggregate (powder of limestone), and water with a percentage of about 20% by weight of the other two components (binder and aggregate).

The mortars were examined two months after their preparation. In order to evaluate the adhesion properties of the mortars, small models of mosaic were made (six for every binder). Tests of adhesive strength were carried out on these mosaics in accordance to a procedure standardized by the CNR laboratories in Faenza (Figure 2.22).

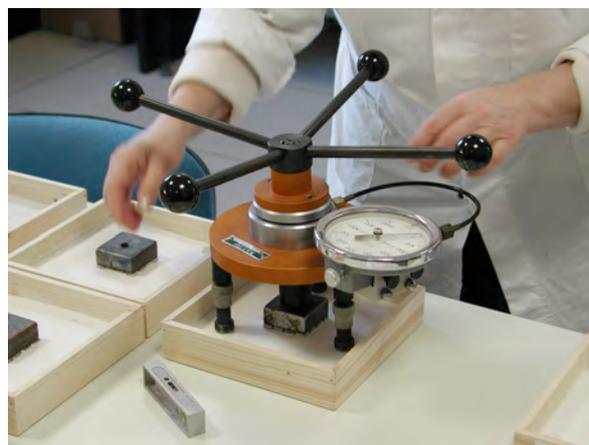


Figure 2.22 – Instrument used in order to determine the adhesive strength of the mortars.

Based on the analytical data (absence of clinker, low hydraulicity degree, negligible concentrations of soluble salts and the best mechanical properties), the ease of use, the quick times of setting and the final colour, a mortar prepared with the best NHL 3.5 was prepared, with the same ratios of the ones investigated. This mortar was tested in a conservation intervention of two floor mosaic fragments coming from the Late Antique Villa in S. Giusto (North Apulia, Italy), from where they had been lifted few years before. The restoration mortar was successfully used for re-laying and connecting the two mosaic fragments on a movable support of aluminium with a honeycomb structure. After this test, different NHL mortars were successfully used for in situ conservation interventions in the Archaeological Park of Classe near Ravenna (Italy). The restoration mortars were applied for plastering, for filling lacunae and for reinforcing wall remains (Figure 2.23).



Figure 2.23 – Archaeological Park of Classe, Ravenna (Italy). In *situ* conservation by NHL mortars: reinforcing of wall remains, filling of lacuna.

More recently mortars based on NHL 5 were used for re-laying about 250 mosaic fragments (about 240 m² of mosaic), coming from the floor of the Church “A” of the Late Antiquity of S. Giusto (Lucera, southern Italy), on movable supports (Aerolam) (Figure 2.24).

2.7.3 Archaeometric case studies of stone materials

Big archaeometric studies of natural and artificial materials coming from three different Italian archaeological sites are shown: San Severo (Classe, Ravenna), Torretta Vecchia (Collesalveti, Livorno), Pietratonda (Civitella-Paganico, Grosseto).



Figure 2.24 – Restoration of the mosaics from the Church “A” of S. Giusto (Lucera, southern Italy) by mortars based on NHL 5.

SAN SEVERO (CLASSE, RAVENNA)

The complex of San Severo is part of the archaeological area of Classe near Ravenna (north-eastern Italy). In the San Severo site, structures of various age are present, from Roman period to Middle Ages. Many mortar samples were collected from remains of wall structures with known age. The samples were analyzed by different analytical techniques according to the analytical sequence specific for mortars showed in the chapter 3, paragraph 3.5.2. The results highlighted that:

- mortars of the Roman period have hydraulic characteristics due to the presence of pozzolana among the aggregate, and the ratio binder/aggregate is 1:3;
- mortars of the Late Antiquity are hydraulic or weakly hydraulic, due to the presence of “cocciopesto” among the aggregate; the ratio binder/aggregate is 1:2;
- mortars of the Middle Ages have aerial characteristics; in addition production techniques of the lime and preparation manner of the mortars were not very accurate; the ratio binder/aggregate is 1:2.

As a consequence, masonries in San Severo can be easily dated on the basis of the characteristics of the aggregate in the mortars: pozzolana for Roman mortars, cocchiopesto for Late Antiquity mortars and sand (without pozzolana and cocchiopesto) for Medieval mortars.

TORRETTA VECCHIA (COLLESALVETTI, LIVORNO)

Torretta Vecchia is a Roman archaeological site located in Tuscany (Central Italy). All mosaics in this site are located in the bath sector: frigidarium, corridor and related rooms. A specific archaeometric-technological study was carried out on all the mosaics in Torretta Vecchia site, and the structures of all mosaic floors were detected. In particular three different stratigraphies were identified:

- mosaic of the Frigidarium (FR1). From the bottom, the following layers can be distinguished: 1) stones + bricks, 2) clay, 3) bricks, 4) lime + coarse aggregate, 5) lime + thin aggregate, 6) bedding mortar, T) mosaic surface (tesserae);
- mosaics F, C, C1 (corridor) and L1 e L5 (rooms adjacent to C1 and F, respectively). From the bottom: 1) terracotta slabs (rarely stone), 2) foundation mortar, 3) bedding mortar, T) mosaic surface (tesserae);
- mosaics D-D1 (north sector of the corridor) and L3 (room next to D). From the bottom: 1) foundation mortar directly on the ground, 2) bedding mortar, T) mosaic surface (tesserae).

The analyses of mosaic materials (stone and glass tesserae, bedding mortars, foundation mortars and brick fragments present in the structure of the same mosaics) were performed according to the sequence shown in chapter 3, paragraph 3.5.2. They highlighted the following results:

- similar lithologies used for obtaining the stone tesserae in the different mosaics (generally local provenance, and a biunique correspondence between colour and lithology)
- foundation mortars with similar composition and characteristics (same raw materials and preparation manner)
- bricks with similar compositional and textural characteristics.

The mosaic floors were built at the same time, while there are three different structures (Frigidarium, foundation with bricks and without) that could be justified by different function of the floors.

PIETRATONDA (CIVITELLA PAGANICO, GROSSETO)

In the archaeological site of Pietratonda three different sectors can be identified: residential sector (AREA 1), productive sector (AREA 2), and baths (AREA 3). Mortars, plasters and bricks coming from the different sectors were analyzed, together with clay samples from Pietratonda's area (XRD, XRF, DTA-TGA). The data obtained showed:

- only in productive sector were found hydraulic mortars (bedding mortars and plaster), whose composition includes metakaolin;
- in the other sectors were found aerial or weakly hydraulic mortars due to the use of cocciopesto;
- all the bricks were obtained by firing (850–900 °C) carbonatic clays, while the local clays analyzed are not carbonatic.

Then the productive sector probably belongs to a different building phase and the bricks of Pietratonda were not produced using local clays. Very probably the choice to apply in the productive sector hydraulic mortars, based on lime and metakaolin, with high hydraulicity degree and high mechanical properties, is due to the specific functions and characteristics of this sector, where mortars and plasters were required, with high mechanical properties and high durability in wet conditions.

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3 – MOSAICS

3.1 Manufacturing techniques

3.1.1 What mosaic is

Mosaic is the art of creating decorative images through the assemblage of small colored pieces of stone, glass or other materials. Mosaic is used for decorating both flat and curved architectonic surfaces, both inside and outside. Usually a distinction is made between wall mosaics and floor mosaics, due to the different realization technique.

The human being since always has demonstrated the pleasure to decorate surfaces by using small pieces of colored stone, and this makes it impossible to establish the origin of mosaic with certainty. Also the origin of the term ‘mosaic’ is not yet established and several hypotheses are suggested. A hypothesis indicates a origin from the Greek *musaikòn*, that means ‘patient work worthy of the Muses’. Somebody suggests a origin from *muzauwaq* that means ‘decoration’ in Arabic language; somebody else sees a connection with the name *Moses*, and mosaic would mean ‘belonging to Moses’.

The decorative pieces of stone or other colored materials can be natural or artificial. In the second case they must be opportunely prepared according to specific processing techniques. In any case, the single pieces must be fixed to the surface to be decorated, so that suitable application techniques have been adopted along the time.

3.1.2 Mosaic implementation

For the realization of the ancient mosaic in the shop of the artist the following facilities were used: hammer, chisel, pliers, tiles (stone, glass, etc.), binder (lime), aggregates of different sizes (sand, marble powder) and water.

Towards the end of the fourth century A.D., the *Codex Theodosius* reveals that in the late-Hellenistic period several specialists cooperated in the execution of a mosaic:

Pictor imaginarius (the cartoonist), which was expected to provide the design and composition “trying out the system, tracing the lines of the composition, and the procedure for the implementation, so that he was the responsible for the realization of the iconographic plan”;

Parietarius, had the task of transferring the idea of the composition on the floor or wall surface;

Musivarius, who inserted the tiles into the bedding mortar;

Lapidarius structor and *Coctor calcis*, laborers for the preparation of backgrounds and materials of stone and glass.

In principle, with some exceptions, according to *Vitruvio*, a floor mosaic was composed of three layers of preparation: after leveling the surface, and if not large enough it was compressed, you begin to prepare the layers.

The first one from the bottom is called *statumen* (river stones and / or brick), the second layer *rudus* (coarse mortar) and the third one *nucleus* (mortar similar to the previous, but with fine aggregate) and finally the decorative tiles. Often mosaic floors did not comply with the rule described by Vitruvio; constant feature is the presence of a layer of mortar (*sovra-nucleus*) that consists almost exclusively of lime, with a thickness less than 5 mm. The thickness of the various layers of preparation is different for each floor mosaic and can change as needed in each ambient.

In general, the mosaics are made in “daily”, namely a piece of the mosaic decoration made within one working day by a ‘musivarius’. The size of this “daily” varies according to: setting time of the binder (bed layer) in which the tiles were inserted, the degree of difficulty of the mosaic and the skill of the mosaicist. As for the history of performance techniques, we have little evidence from the sources. Most of the information therefore derives from direct observation of extant mosaic works.

For the diversity of support structures and composition of the preparatory layers, it is useful to distinguish the mosaics in relation to the architectural structure to which they are applied: floors, walls, ceilings or vaults. Apart from differences in the execution, time to time dictated by the nature of the soil or the variety of available materials, with sufficient accuracy it is possible to outline the phases of a floor mosaic, which remained largely unchanged for centuries. The ground, after being dug, leveled and highly compressed (Figure 3.1), was generally covered with three preparation layers, as was described by Vitruvius in the first chapter of the seventh book. The first layer from the bottom (*statumen*) is usually composed of a thick layer of large stones and / or materials without clay binder; the second one (*rudus*), consisting of lime and sand or gravel, was beaten by teams of workers with the mallet; the third layer (*nucleus*) was composed by the same

mortar above, but with fine-grained aggregates. Obviously, the thickness of each layer varies depending on the type and intended use of the space and the nature of the underlying soil.

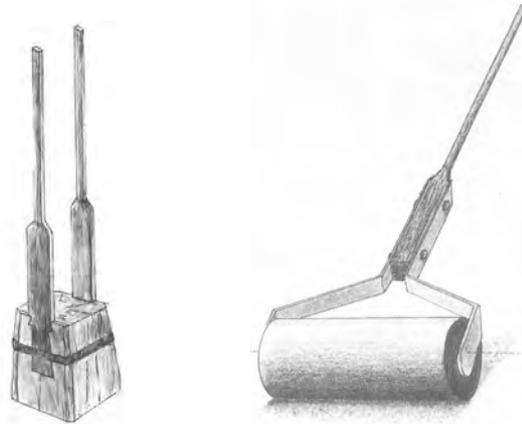


Figure 3.1 – The mallet to beat the ground and the roller for levelling the layers of mortar.

After that the preparation of the substrate has been completed, to better realize the composition, the mosaicist draws the sketch of the figure (sinopia) with mortar applied with a brush. Then a bedding layer (sovra-nucleus) is spread, less than 5mm thick, only consisting of lime (sometimes with a small fraction of fine aggregate) in which the tesserae are inserted (Figure 3.2).

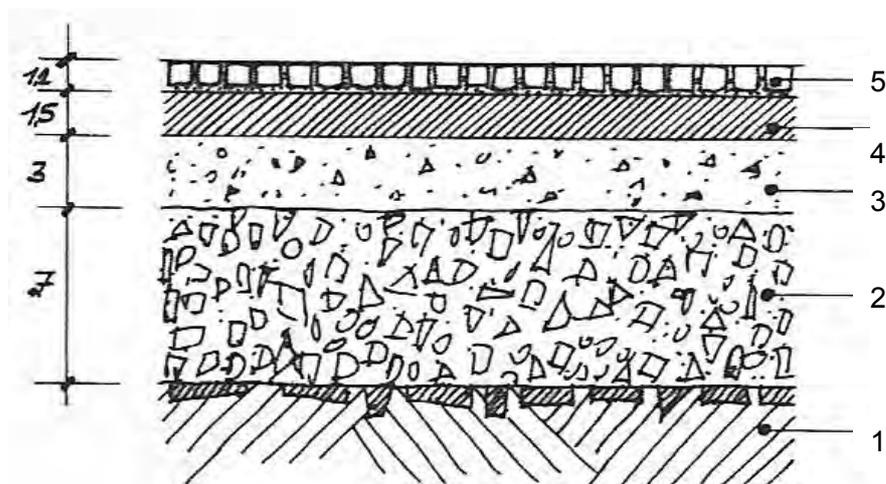


Figure 3.2 – Vertical section of a Roman floor mosaic: 1-clay; 2-cobblestone and brick chips; 3-lime mortar with aggregate of average size; 4-mortar with fine aggregate; 5-tesserae. **The thickness of the layers is indicated on the left in cm.**

The preparation of the base bed was made “daily”, i.e. only the necessary during a working day; the measure of the “daily” was variable in accordance with the drawing to be carried out, the skill of the mosaicist and the setting time of the mortar bedding. After the completion of the mosaic, the floor was plastered with mortar of marble dust, sand and lime to obtain a compact surface. It was then carefully polished, before with a pumice stone, and then with beeswax or with other things. Instead, regards the technical implementation of wall mosaics, the architectural and aesthetic necessities require that it runs differently than the floor mosaic, especially as it regards the layers of preparation and the processing accuracy of the surface. In general, the technique foresees the creation of a first layer of mortar, called “ariccio”, composed by lime and coarse inert material, directly applied on the wall to eliminate its lacunas and asperities. The thickness of this layer is variable and depends on the imperfections it has to hide. After the application of this layer, the surface appears uniform. Then a second layer of mortar was applied, a bit thinner than the previous one: it is composed by lime containing inert material with variable grain size. This layer, about 2 cm thick, has the function to sustain the following layer, whose direct application to the wall is impossible because of its characteristics.

A characteristic of the second layer is the property to give elasticity and thickness to the support of the mosaic, guaranteeing the physical stability to the decorations and the transpiration of humidity. Usually in the first or in the second layer we can find straw in the side of the mortar. The third and last applied layer is called layer of “allurement” and there the tesserae are inserted when the mortar is still fresh (Figure 3.3). Its composition is made of lime with very small fragments of inert materials. Its thickness varies from 3 to 5 mm, a thickness sufficient to ensure proper anchoring of the tiles.

3.1.3 Materials for mosaics

STONE MATERIALS

Due to the proximity of the Greek provinces, the customs and arts of the Greeks arrived in Rome. This began when in 146 BC Lucio Mummio, Roman consul, took and sacked Corinth and brought to Rome many works of art.

From 59 BC foreign marbles were imported and mosaic floors were spreading. Giulio Cesare ordered that the camps had floors of this type, so in a few years, the spread of multi-colored stones in Rome was very rapid.

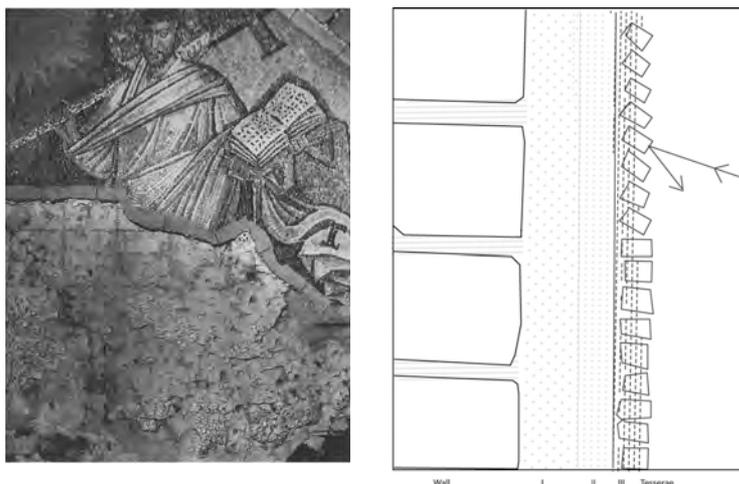


Figure 3.3 – Mausoleum of Galla Placidia (Ravenna, Italy) where you see lines of composition, pattern of implementation and the notches of the trowel (on the left); section of a mosaic wall (on the right).

In Rome, marble¹ from around the world was used for statues, columns and bas-reliefs, to enrich not only the public buildings, but every single private house. The walls and floors of the most beautiful temples and palaces were lined with imported marble, cut into different shapes or tiles of various colors. For luxurious floors decorated with slabs of marble or with compositions in *opus sectile* or *tesselatum*, the artists utilized colored marble of exceptional beauty. The marbles were sent from each province: Spain, Mauritania, Numidia, Tripolitania, Egypt, Asia Minor, Greece, etc.

In the big public buildings, *thermae*, and villas in the provinces far from Rome, where all these rocks could not arrive, mosaic artist employed local stones.

THE GLASS

The amorphous solid material, commonly called glass, is characterized by the fact that it has a long-range structural order, contrary to the typical crystalline solid substance (see Chapter 6). The principal component of the glass is silica, which is defined component for vitrification. Silica is found in nature in form of quartz in quartzite and quartz sand, that are the main sources of silica.

The high fusion point of silica (about 1700 °C) limits its use in pure form; in fact, in ancient times it was not possible to reach temperatures above 1000 °C. It was therefore

¹ The term marble is used here as historical and commercial sense. From a petrographic point of view, marble is a carbonatic metamorphic rock derived from a structural change of sedimentary carbonate rocks.

necessary to introduce certain substances that are able to change some physical and chemical characteristics, such as the “melting”. Alkaline compounds are added to lower the fusion point of the mixture; those most commonly used were sodium compounds, while in more recent times were also used potassium compounds.

These compounds facilitate the production of a melted phase at relatively low temperatures, but produce easily alterable glass. In the glassy mixture it is necessary to introduce “stabilizer” substances in order to increase the hardness and decrease the perishability of the glass. Calcium oxide (CaO) or magnesium oxide (MgO), but also lead oxide (PbO), are among the most common stabilizers in ancient glass.

The glass, with its various shades of color and its sheen, is the most fascinating aspect of the ancient mosaics. The glass is used almost exclusively for the construction of wall mosaics, with some exceptions for floor mosaics.

Works in mosaic made with glass honored marble temples and public buildings, the floors and walls of the villas in Rome and in the most distant provinces as well.

The nature of glass mosaic tessera is very complex; in reality, this category includes various types of glass-based materials, with very different physical and chemical properties. This diversity is demonstrated by the use of terminology sometimes confusing and not universally recognized.

The metallic-leaf tessera is a tile in which a thin sheet of beaten metal (gold and silver) is heated, placed on a glass substrate (a few millimeters thick) and another glass layer, called folder (less than one millimeter thick), covers the metallic leaf to protect it from oxidation and to increase the brightness.

OTHER MATERIALS

Besides the use of stone materials and glass for the creation of wall or floor mosaics, in some cases it has been observed the use of different materials, such as terracotta, ceramics, precious stones, shells, nacre, etc.

THE BINDERS (MORTAR FOR SUBSTRATES)

In ancient mosaics, they used mortar-based binders, that are inorganic materials capable, when mixed with water, to join together the different components (see Chapter 2).

The mortar is a mixture of organic or inorganic binders with predominantly fine aggregates, water and any addition of organic and/or inorganic additives (or only a mixture

of binder and water) in such proportions as to give a workable dough, at the fresh state, with suitable physical characteristics (porosity, permeability, etc.), mechanical properties (strength, deformability and adherence), and opportune appearance and long durability when hardened.

The complex of chemical and physical reactions that lead to the consolidation of the binder takes the name of “setting reaction and hardening”. The first reaction is the transformation of the material from ‘liquid’ to ‘solid’ that confers adhesion in a quite short time. The complete process, however, occurs in many hours and sometimes several days, and leads to the transformation of the binder in a very hard substance.

The binders, according to their characteristics, are divided into aerial binders and hydraulic binders. The aerial binders (lime and gypsum) are mixed with water, but they harden in presence of air. The hydraulic binders, on the contrary, require water, but they also harden in water.

3.1.4 Definition of mosaic typologies

FLOOR MOSAIC

In the ancient world the floor mosaic was common in public and private buildings of every social class, sometimes using recycled materials. In this chapter reserved for the mosaics, it seems appropriate to list and describe in summary the main and most famous types of ancient mosaic.

- *Pebble mosaic*: is a floor mosaic made of small and coloured pebbles laid on a layer of lime or clay. In the most refined examples the details of the figures are rendered with thin strips of lead or terracotta (Figure 3.4).
- *Cocciopesto*: floor mosaic made of mortar and cocciopesto (pieces of terracotta and lime), red colored, sometimes with tesserae, irregular in shape and size, distributed randomly. It was used to cover both pavements and cisterns (Figure 3.4).
- *Opus Signinum*: cocciopesto floor with lime cement, decorated with tesserae of limestone to produce simple geometric designs (Figure 3.4).
- *Opus Sectile*: floor or wall decoration made of polychrome marble slabs with different thickness, cut in geometric shape, and laid in lime mortar to produce simple or complex designs (Figure 3.5).



Figure 3.4 – Typologies of floor mosaic: pebble mosaic (on the left), cocciopesto (in the centre) and opus signinum (below).



Figure 3.5 – Typologies of floor mosaic: opus sectile.

- *Opus Scutulatum*: floor characterized by the insertion of irregular fragments of polychrome marbles and stones (scutulae) on a background of white limestone tesserae (Figure 3.6).
- *Opus Mixtum*: floor decoration characterized by the interaction of different mosaic typologies (scutulatum, sectile and segmentatum) enclosed by a black background of opus tessellatum in white limestone (Figure 3.6).
- *Opus Tessellatum*: all types of floor mosaic, monochrome and polychrome, geometric or figurative, realized with marble or stone tesserae quite large in size (Figure 3.7).
- *Opus Incertum*: floor mosaic made with tesserae irregular in form and size, placed in lime mortar in disconnected way to form geometric or figurative design (Figure 3.7).

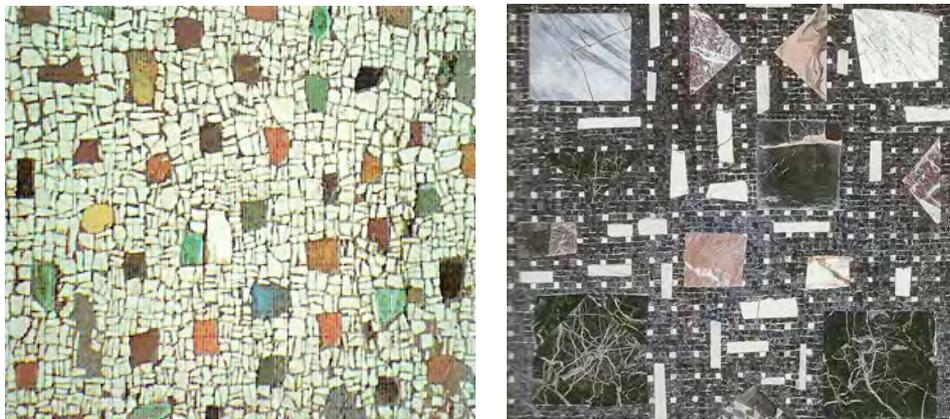


Figure 3.6 – Typologies of floor mosaic: opus scutulatum (on the left) and opus mixtum (on the right).



Figure 3.7 – Typologies of floor mosaic: opus tessellatum (on the left) and opus incertum (on the right).

- *Emblema*: polychrome mosaic of small dimension produced in the workshop with small tesserae, on its own base to facilitate its successive placement in another place (Figure 3.8).
- *Asaroton*: floor mosaic used in the decoration of triclinia; produced using small tesserae, it represents the floor of a dining room on which there are the remains of a banquet such as: fishbone, fruit peelings and bones. The Greek term means an upswept floor. Plinio attributes the invention of this subject to Soso of Pergamo, a Hellenistic mosaicist lived in the second century AD (Figure 3.9).

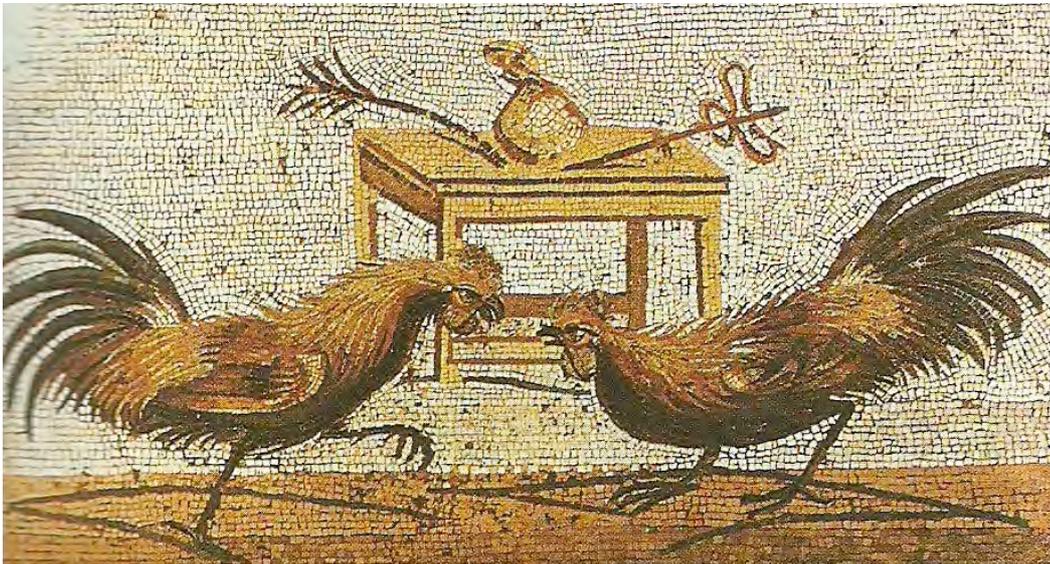


Figure 3.8 – Typologies of floor mosaic: emblema.



Figure 3.9 – Asaroton, a typology of floor mosaic (on the left), and opus musivum, the only wall mosaic typology (on the right).

WALL MOSAIC

- *Opus musivum*: a wall or vault mosaic, realized with glass and stone tesserae and nacre, which has a very rough surface in comparison with the floor mosaic (Figure 3.9); ‘musivum’ refers to the art of decorating *nymphaea* with shells, pumice and stone.

3.2 History of the mosaic

3.2.1 The origins of the mosaic

In the Old Orient was very widespread and developed the inlay technique, but it is not real mosaic. Very unusually shaped mosaic tesserae were used in the Sumerian city of Uruk (third millennium B.C.). They were made up of cones of clay with their base left at its natural state or decorated with red or black painting. Inserted in the walls still fresh with the base outwards, they formed interesting decorative figures. Because of its complexity, the mosaic of clay cones did not widespread and it lasted for a short time.

3.2.2 Mosaics in the Greek world

In the Greek world, the oldest forms of mosaic are those obtained with small colored pebbles on a dark background to form floral decorations or meandering tendrils around mythological figures or animals, like those in Olinto, dated back to 348 B.C. (Figure 3.10). Mosaics with pebbles and shells appeared in primitive form since the eighth century B.C. at Gordion, Crete and Asia Minor, but they developed thanks to more sophisticated techniques in the fifth century in Athens, Sparta and Corinth. Later, in the mosaics in Olympia, Alexandria, and Sicily, appeared tesserae cut in the shape of a cube (*tessellatum*).



Figure 3.10 – Greek mosaics: “Lion Hunt” (4th century B.C., Pella, Macedonia) on the left; mosaic in Olinto on the right.

3.2.3 The mosaic in the Hellenistic period

In the Hellenistic period (2nd half of the 4th century to 2nd half of the 1st century), an important school of mosaic artists developed, which was located in Pergamon. The most beautiful works were described by Plinio who defined admirable the “*Asarotos*” performed between 197 and 159 B.C. by Sosos, master of Pergamo. In the *Asarotos*, which literally means “unswept floor”, the remains of a meal on a homogeneous background are depicted, and the work is considered as a *trompe l’oeil* ante litteram. This theme was later taken over by the Romans. The contact with the Italian school in this period (1st and 2nd century B.C.) and the frequent trips of the same masters in various areas make the classification of Hellenistic works difficult.

3.2.4 Roman mosaics

The use of mosaics in Rome, according to Plinio, was introduced in the Silla age. The first wonderful examples are certainly those of Pompeii. The mosaics of the House of the Faun date back to the 2nd century B.C., and represent very different issues: the battle of Alexander, a cat eats a bird, fish (Figure 3.11). The style of these works could be called Baroque; it preferentially deals with complex themes and the sophisticated technique indicates a virtuosity of execution.

This style is adopted in all schools with Hellenistic influence and is so marked as to suggest non-Italic performers, almost a “Koine” of Alexandrian master in the service of the Romans. To this style one must also refer the mosaics of Palestrina, S. Lorenzo in Penisperna in Rome, the “Lion of Teramo” and many others.



Figure 3.11 – Examples of Roman mosaics in Pompeii: the battle of Alexander, a cat who is eating a bird, and fish (2nd century B.C.)

During the transition period from late antiquity to the early Christian age, the mosaic spreads much. It is commonly used on the floor before moving, especially in Christian buildings, to wonderful wall decorations. Polychrome mosaic still prevails, though the technique differs somewhat from that of *opus vermiculatum*.

At the beginning of the century, mythological scenes still prevail, which then leave the place to more static representations, often of people in front attitude. Stylized depictions of landscapes and trees also appear, but the prevailing tendency is the realization of geometric figures. Some passages of the famous mosaics of Piazza Armerina (Sicily, Italy) are to be attributed to this period between third and fourth century, while the wall and vault mosaics go back to the early Christian age. The techniques used here were needed for different reasons both practical and expressive. The bottom of the mortar was not smooth like a floor, but more rough and uneven, and due to the rough surface of the tesserae the mosaic also takes a different appearance determined by the refraction of light on the irregularities of the stones.

There are no texts that describe the technology used for early Christian, Byzantine and medieval wall mosaics, but there are many studies on the monuments. The wall was covered with three layers of lime mixed with marble powder, or at a lesser extent brick powder. To allow a easy adhesion between successive layers, cavities were made on the rough surfaces (in form of diamond or ladder) or hooks and even nails were inserted. The third layer, the finest one, was the bed destined to host the tesserae; it was realized in small portions at a time, so that the mosaic master could arrange the tesserae before the mortar hardens.

On this bed the preliminary sketch (*sinopia*) was made. Traces of *sinopia* sometimes found on the first or the second layer can not be considered other than the evidence of the tests performed by the artist. The color given to the *sinopia* had perhaps intended to attenuate the impact of the fund, which appeared, the work done, in the interstices between the tesserae.

The technical realization was no longer differentiable as in the Roman period; the distinction between *vermiculatum* and *tessellatum* mosaics disappears, because in the same mosaic the tesserae have different sizes and shapes depending on the extent of the mosaic area.

The use of glass tesserae made it possible to produce an infinite number of color tones and allowed to refine the techniques. In addition, one continued the use of tesserae of marble and other stones, especially to simulate the color of the meat. It also employed mother of pearl and terracotta tiles.

The golden or silver color was obtained by applying a sheet of precious metal on pieces of glass, then covering the surface with a transparent glass paste and finally baking the whole. A widespread technique was to intersperse tiles upside down, eventually monochrome tiles with different colors in order to achieve particular effects of reflection, or punctuation. In the Christian buildings clearly changed the theme of the mosaics: the apses are usually adorned with the figure of Christ and the Apostles (only with Pope Damasus, in the 4th century AD, passed to honor the cult of figures of the Saints became usual).

In the fifth century techniques, themes, and styles seem canonized, for which large holy figures are static, stylized, in a rigidly frontal and hieratic attitude, and almost always on dark and nebulous backgrounds. We remember the apses of S. Maria Maggiore, S.S. Cosma and Damiano, and S. Theodore in Rome, and also the 'triumphal arch of S. Paul outside the walls and the Oratory of S. Giovanni Evangelista still in Rome.

3.2.5 Mosaics in Ravenna

A separate chapter is the copious production of mosaics in Ravenna. They developed between the fifth and sixth century by bringing together the Byzantine art and the early Christian one. The pictures that we found in older works (mausoleum of Galla Placidia, Neonian Baptistery) of the monuments of this area still appear realistic, while the later representations (Baptistry of the Arians, S. Apollinaris New) lose depth and shine with bright colors on contrasting backgrounds usually monochromatic (mostly gold).

The particular expression of the figures and the use of chromatic techniques with sharp contrasts, based primarily on the edges, suggest the influence of the new masters clearly inspired by Byzantine art. Byzantine is that sense of serenity and contemplation that spreads over all the figures of S. Vitale, and that is also reflected, although certainly by other hand, in the mosaics of S. Apollinaris in Classe.

3.2.6 Byzantine mosaic

The optimum effect was undoubtedly achieved by the pictorial expression in Byzantine wall mosaics from the sixth century onwards. The decoration of churches was canonized

by location and choice of icons. The mosaics were destined to the upper part of the church and were interspersed with architectural structures that marked the areas decorated as backgrounds. This scheme was in response to a basic concept that wanted to separate in the Church a spiritual area (the dome and the presbytery, compared to the heavenly vault), earmarked for the Christ Pantocrator (Figure 3.12) and the Virgin Mary, and a terrestrial area (the naos and the narthex) destined to images of the life of Christ and the Virgin. Secondary apses were destined to saints, martyrs and so on.

Beautiful is the harmony achieved from the walls and structures (scale) covered by multi-colored marbles with the mosaics of the vaults and domes. The Byzantine art reached such refinement by delegating to the reflection of the mosaics, especially gold and silver ones, the special function of expanding space and light. Due to these characteristics, enhanced by the technique of embedding the tesserae according to certain angulations, mosaic art came to play a crucial expressive role. There is no doubt that even the best paintings could not achieve the same effect as in the wonderful movement of Byzantine polychromy, hence the belief that the mosaic has not to be considered a minor art.

In the Byzantine era we distinguish a first period (565-726), during which the iconographic and thematic scheme, first synthetic, is refined and matured; at the height of that era, the function of the Saints' images was enhanced till to reach central roles.

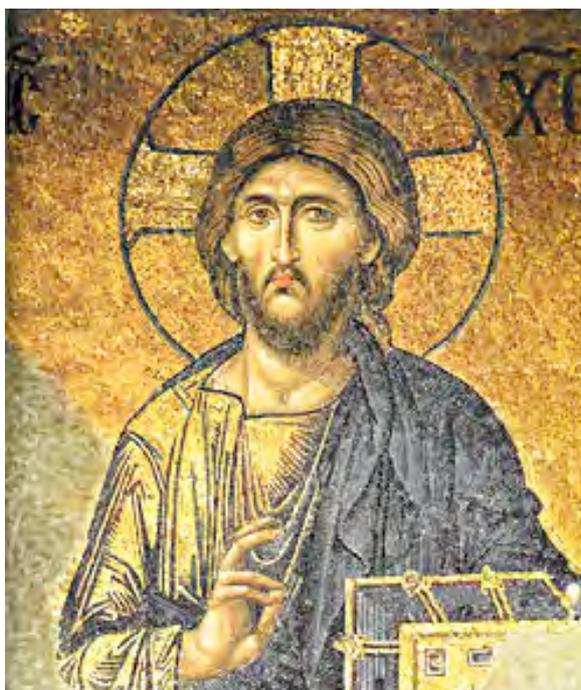


Figure 3.12 – Christ Pantocrator in St. Sophia, Istanbul.

In the Iconoclastic periods (726-787 and 814-843) clearly images disappear, replaced by simple symbols (mostly the Cross), animals, plants, birds and so on. The first images that reappear in the post iconoclastic era are isolated figures that revive the classic scheme and then produce complex scenes, ordered by complete cycles. It is at this stage (ninth century) that they expressed the greatest mastery of the “sloping tesserae”, which usually characterize two-dimensional backgrounds and make vibrant the surfaces, surrounded by tesserae with a more pronounced color (for example St. Sophia in Istanbul).

From the tenth century the figures tend to assume strong plastic characteristics, with emphasis on the nuances of the images, so that they seem to come alive and take shape. The lines reach more grace in the boundaries to the “painting”, so that the results are of particular effectiveness and realism of the twelfth century. We remember the mosaics of the Dafne Villas in Turkey (Figure 3.13), and the Dome of the Cathedral of Monreale and Cefalù in Italy. At this time we reach the full capacity of the mosaic expression in Byzantium.



Figure 3.13 – Some of the mosaics of Daphne Villas in Turkey.

3.2.7 The Roman and Gothic mosaics

The influence of Byzantium and the reflections of this art outside were numerous. In Kiev, Georgia, Syria and Palestine there are examples of great significance.

In Italy, works and schools (perhaps for the presence of masters of Byzantium) focused in Sicily (Palermo, Cefalù, Monreale) (Figure 3.14), Campania (Naples, Salerno, Capua), Lazio (Montecassino, Rome), and Veneto (S. Marco in Venice and Torcello island). Unlimited design themes from local cultures merged to take unique characteristics. The

same iconography, to express these issues outside the orthodox domain tends to overcome the classical scheme, as if to be in competition with the glories of Byzantium. With sure originality, is part of this period the extensive activity of the Roman masters Cosmati, very skilled in inlay technique, *opus sectile* and also in the mosaic in general.



Figure 3.14 – Mosaics in the Cathedral of Monreale (left) and Cefalù (right) (Sicily, Italy).

From the “thirteenth century” we can see the beginning of the decline of the Byzantine mosaic. The mosaic begins to be replaced by the painting, aimed at the discovery of new effects of depth and luminosity performances. The painting became the guide for mosaic art, which in particular tries to imitate its virtuosity, producing tiny pieces of mosaic and placing them in a secondary level.

Only in Venice mosaic had longer life than anywhere till the advent of the new aesthetic principles of the Renaissance. Due to continuous operations and the subsequent restoration one can now say that the basilica of S. Marco represents a real “store of the Medieval and Renaissance mosaic”, as well as Pompeii for the Roman period.

Some mosaics in the Basilica of S. Marco in Venice and St. Maria on the island of Torcello (Figure 3.15), where great works were realized throughout the twelfth and thirteenth century, demonstrate that there was born without a doubt the most important school of mosaic at the time.



Figure 3.15 – Venetian mosaics in S. Marco basilica (left) and Torcello island (right).

The school in Florence, which operated in the Baptistery of S. John since 1225, originated from its teaching and certainly its influence was decisive for the Roman school.

Notwithstanding the relation of subordination to painting, the mosaic is still widely used throughout the fourteenth century especially for the facades of churches, and this occurs almost exclusively in Italy (Rome, Pisa, Siena, Orvieto and again S. Marco in Venice). The few episodes abroad in this century and in the previous one (Westminster, Saint Denis, Prague, etc.) are the testimony of the rare cases of “export” of Italian art.

The diffusion of the principles of the Romanesque and Gothic style effectively excludes the use of wall mosaic. There’s still some spread of the floor mosaics in which the composition is based mostly in *opus sectile* with mosaic textures. But, especially from northern Italy and Nordic regions, the development of the manufacture of colored floor ceramic tiles is soon an alternative to the expensive mosaic decorations.

3.2.8 Mosaics during the Renaissance and subsequently

During the Renaissance, the mosaic art is increasingly seen as subordinate to painting. There is no longer any originality; tracing the strokes of frescoes with tiny tesserae, mosaic tries to compete in virtuosity but eventually decays to imitative and secondary roles. In the fifteenth century and in the sixteenth century, the masters of mosaic are usually artists who entrust with their designs in craftsmen, who then realize the works.

There are many examples of mosaic reproducing famous paintings, such as the *Dormitio Virginis* by Mantegna, paintings of Tiziano, Tintoretto, Veronese and so on.

In 1516 Raffaello, with the Venetian master Luigi da Pace, realizes one of his works for the cupola of the Chigi chapel in S. Maria del Popolo in Rome. In Venice the most important work is done in the fifteenth century with the decoration of the vault of the chapel of Males in S. Marco by Paolo Uccello. Referring to the activity of this era, Filarete cites the proliferation of furnaces in Venice, specialized in the production of glass tesserae. But equally important event of the Renaissance is considered the beginning of the decorations of S. Peter in Rome by Muziano of Brescia, who opened a shipyard very active until the nineteenth century.

Pope Urban VIII decided to reproduce some paintings in Rome with mosaic to preserve them from decay; all the techniques and the research were then refined for the sole purpose of imitating the best performances of the artists and thus perpetuate the misunderstanding of mosaic as “eternal painting”.

In the seventeenth century, in the S. Peter Basilica, Paolo Cristofori created the copy of the “Burial of Petronilla” by Guercino and the “Communion of S. Jerome” by Domenichino; in Naples G.B. Calandra in 1624 reproduced paintings by Guido Reni. But the seventeenth century should be credited with having initiated the search for new results in the production of glass paste. The completion of these productions in the eighteenth century reached such a level of refinement to lead to amazing results. In 1731 Alessandro Mattioli invented a manufacturing process that will provide at least 15,000 colors for the Vatican mosaic tesserae. Also in the eighteenth century, you will get the “flowing glaze”, which allow you to produce tesserae with a thickness also less than a millimeter. Were these new techniques to achieve “perfection” in the reproduction of paintings and to facilitate the dissemination of the fine mosaics (Figure 3.16). The results fueled the spread of the mosaic, which returned to life and regained interest. In 1752, a mosaic school was imported to St. Petersburg from Rome, and a workshop was implanted in Palermo, at the court of Charles Bourbon. In 1803 the opening of a laboratory was inaugurated in Milan under the guidance of Giacomo Raffaelli, who is considered the inventor of the flowing tesserae. In 1811, in Naples there is a mosaic workshop, as well as in England, where the workshop of South Kensington Museum was opened.



Figure 3.16 – Some mosaics of the 17th century in the Basilica of San Clemente in Rome.

In 1848 Czar Nicola I created a laboratory in Rome for Russian students, that then moved to St. Petersburg in 1850. The activity of this laboratory was remarkable, especially in terms of quantity, and it is responsible for the reproduction of many paintings. In 1876 was inaugurated in Paris the National School of Mosaic; at the end of the century and the beginning of the next, several families of mosaic craftsmen from north-eastern Italy open mosaic laboratories in Paris, Berlin, Vienna, Copenhagen, London, New York, Nimes, Nice, Lille, and other localities.

3.2.9 The Oriental mosaic

In Orient, apart from rare examples found in the Sasanian art (Iran), one can follow the development of mosaic observing the many decorations of Islamic art. Among these, of great value is the Dome of the Rock in Jerusalem (Figure 3.17), with floral ornaments of the Syriac-Hellenistic style, but also with original themes of Islam (candelabra, trees of life, palm trees dotted with jewels, etc.).

Another important work of Islam is the Great Mosque of Damascus (700-715 AD) (Figure 3.17) with an amazing panel depicting a fictional town in many meticulous details.

Well developed in the Mamluk period (1200-1300) and until the peak of the sixteenth century was a mosaic of glazed ceramic, which reached its zenith under the Safavid rule (tomb mosque of Saih Safi at Ardabil, Iran, Figure 3.17).

India was very strong influenced in the Islamic period and the best examples of mosaic were produced mostly in the Daccan and in the central regions in general. Here mosaic of glazed ceramic found employment on a large-scale, preferring in the seventeenth century the use of square tiles.



Figure 3.17 – The Rock in Jerusalem, the Mosque of Damascus (700-715 A. D.) and the Tomb mosque of Saih Safi at Ardabil, Iran.

3.3 Degradation of mosaic

The mosaic is made up of several layered components including two/three or more preparation layers and the surface layer of tesserae:

- the first preparatory layer from the bottom is made of large stones laid on the ground, previously leveled and rammed. This layer only exists if the mosaic has been constructed on a natural soil;
- the second preparatory layer, which is spread over the first one, this layer is made of a lime mortar with large aggregate;
- the third preparatory layer is spread over the second one in a thin thickness, and it is made of a mortar with fine aggregate;
- the fourth preparatory layer is called “bedding layer”; it is a thin layer of very lime-rich mortar, and is applied in stages over the third preparation layer;

- tesserae of different materials (stone, brick, glass, etc.) are inserted in the previous layer before the mortar sets and hardens, so that the mosaic surface is composed of tesserae with mortar that fills the interstices between the tesserae.

Obviously, these materials in contact with the micro- and the macro-environment, or because of human intervention, are subjected to numerous types of alteration and degradation phenomena, sometimes irreversible. When stone materials are the principal constituents of the mosaic, the various morphologies of alteration and degradation affecting it are very similar to those treated in the section devoted to degradation of natural and artificial stone materials in the Chapter 2. One can easily find lacuna, alveolization, fracture, pitting, superficial deposit, deformation, microbiological organism, and so on. But there are some degradation morphologies which are specifically related to the particular structure of the mosaic or have an original appearance linked to it. These degradation morphologies will be illustrated below.

Mobile tesserae (Figure 3.18, left): degradation that occurs when there is a loss of adhesion between the tesserae and the mortar; it is usually caused by disintegration of the mortar with the consequent possibility of detachment and loss of some tesserae.



Figure 3.18 – Mobile tesserae (left) and scaling (right).

Scaling (Figure 3.18, right): degradation that occurs with total or partial separation of parts of the work (scales), often connected with discontinuities in the original material; generally the scales are made of apparently unaltered material, and have an irregular thickness.

Encrustation (Figure 3.19, left): compact degradation layer, generally adherent to the substrate, consisting of inorganic or organic material. When preferentially connected to the mortar, this degradation phenomenon follows the borders of the tesserae.

Efflorescence (Figure 3.19, right): surface formation of generally whitish salts, that have crystalline or powdery or filamentous appearance. The salts generally come from the mortars, because these are very porous, so that the borders of the tesserae are well evidenced.



Figure 3.19 – Encrustation (left) and efflorescence (right).

Disintegration (Figure 3.20, left): it deals with a degradation characterized by detachment of granules or crystals.

Differential Degradation (Figure 3.20, right): type of degradation to be put in relation with the compositional or structural heterogeneity of the materials, mainly the tesserae; often the result is the formation of two different levels, one for the more resistant material, that is practically correspondent to the original level, and a lower level corresponding to the less resistant tesserae.



Figure 3.20 – Disintegration (left) and differential degradation (right).

Stain (Figure 3.21, left): alteration that occurs with formation of accidental pigmentation localized on the surface; it is related to the presence of foreign material (rust, copper salts, organic substances, paint, etc.) mainly on the surface of the tesserae.

Chromatic alteration (Figure 3.21, right): type of deterioration that occurs as a consequence of the variation of one or more parameters of the color; it can occur with different patterns depending on Figure 3.21 is connected to the transformation of the red glass into green compounds which cover the surface of the tesserae in mosaics of Pompeii.

Detachment (Figure 3.22): interruption of continuity between the different layers of the mosaic, both among themselves and respect to the base.

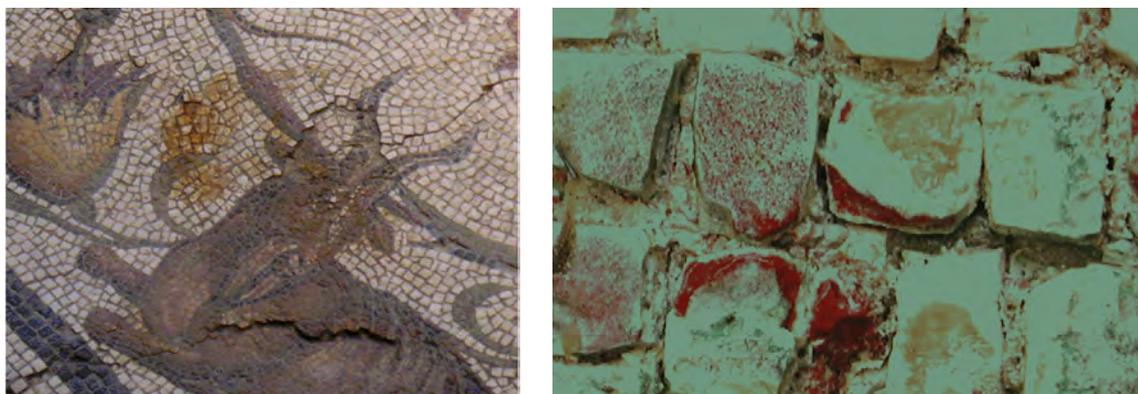


Figure 3.21 – Stain (left) and chromatic alteration (right).



Figure 3.22 – Two different manifestation of the degradation type called “detachment”.

Metallic elements (Figure 3.23, left): presence of structural reinforcements belonging to the new support of a re-laid mosaic.

Presence of vegetation (Figure 3.23, right): the presence of herbaceous shrubs or trees in mosaic works assumes a characteristic appearance, due to the fact that the vegetation preferentially takes root in the mortar layer and comes out through the layer of the tesserae.



Figure 3.23 – Metallic elements (left) and presence of vegetation (right).

3.4 Restoration of mosaics

3.4.1 The restoration of floor mosaics in situ

The conservation work is influenced by environmental factors such as humidity, temperature, pollution, light, contact materials, and other.

In the case of mosaics buried for a long time a relatively stable balance was maintained, which is suddenly broken with the discovery and the mosaic is subjected to new conditions, generally much more dangerous for its preservation compared to previous ones. A very important operation for a re-discovered floor mosaic is the cleaning of the surface, which leads to the first revelation of the artwork and makes it known from various points of view: conservation status, nature of material, artistic and aesthetical value. Cleaning is normally done manually, with broom, brushes, sponges and water; then we proceed with the other types of necessary interventions, as the application of mortar to hold the peripheral edges and those of gaps, and the pre-consolidation of the substrate through injections. These operations are designed to prevent loss of materials of the artwork.

In the case of the mosaics preserved in situ is of fundamental importance the development of a good conservation plan. When you can not proceed immediately with the safeguard operations, waiting for a permanent protection, it is opportune to cover the mosaics. This intermediate operation may provide the implementation of a temporary coverage, or permanent when an intervention can not be planned in a defined time. The materials placed in contact with the surface of the mosaic should be inert with respect to the materials of the mosaic, ensuring reversibility, durability, good drainage, resistance to mechanical, chemical and biological stresses.

The operation of restoration in situ may include the following phases:

- photographic and graphic documentation
- preliminary investigation with analytical methodologies: optical microscopy in reflected light, to observe the structure of the samples and define their state of conservation; use of Munsell tables, for the definition of color; optical microscopy in transmitted and polarized light, to define the mineralogical and petrographic characteristics of the materials constituting the mosaic, the volumetric ratio binder/aggregate of the mortars and to determine form, size and nature of the granules constituting the aggregate; diffractometric analysis (XRD) for the identification of the mineral phases; thermal analysis (DTA-TGA), for the quantification of calcite, an estimate of the organic matter and of the nature of the binder in the mortars; chemical analysis (ICP or XRF), for the definition of the elemental composition of the glass.
- study of alterations (UNI 11182/2006, Cultural heritage - natural and artificial stone materials-Description of the type of alteration, Terms and definitions).
- intervention stages: cleaning (physical, chemical and mechanical); consolidation of the preparatory layers and the mosaic tissue; integration of the lacunas, and surface protection.

3.4.2 The restoration of a wall mosaic in situ

Normally, the wall mosaic is kept indoors. Rarely you remove a wall mosaic and therefore you proceed with in situ conservation work.

The structure of a wall mosaic is generally easier than that of the floor mosaic. Normally on the wall was applied a first layer of mortar made of lime and aggregate (sand, marble dust, pozzolana, fragments of straw, etc.), and on this layer was placed the bedding mortar

of lime with or without inert. This last layer was wetted in order to define the “preliminary sketch” with colored areas to guide the laying of mosaic tesserae.

The tesserae in the wall mosaics are basically of four types: stone, glass, nacre and ceramics. The more specific problems are those affecting the glassy tesserae, which are very sensitive to various types of degradation.

The cleaning of the wall mosaics is generally performed through a chemical action, that is mostly removal of soluble salts; for more resistant encrustations, cleaning is done through mechanical operations. In the consolidation of degraded tesserae you can use acrylic or silicone resins.

Regarding the preparation layers, which generally suffer problems of adhesion loss of the tesserae, the detachments and cavities in the support layers are usually filled by injecting mortar.

In the past and even today, to consolidate the preparation layers, is also used to anchor the implementation in the areas of mosaic decoration with big detachments, because the simple injection of filling the cavity may cause a danger of collapse, due to the heaviness of the detached layers.

While in the past the use of metal was encouraged, now special ceramics or plastic materials suitable for this use are preferred.

3.4.3 The restoration of the mosaics on cement support

The industrial manufacture of cement has been started in the second half of the nineteenth century. The application of this binder in the field of restoration lasted until a few years ago, supported from the mistaken idea that saw it as the material for a definitive restoration.

In particular the high mechanical resistance of this material has suggested the lifting of the mosaics and their re-laying in situ on a cement support. As a result, more and more often you has had to intervene on these restorations because of the occurrence of damages, sometimes so severe to cause partial or total loss of the mosaic. This was due to the deterioration (oxidation and swelling) of the cement that is characterized by high coefficient of thermal expansion, and presence of a high concentration of soluble salts.

The numerous interventions on mosaics lifted and re-layed on concrete supports allowed to observe the various techniques for implementing them.

In the twenties and thirties of the twentieth century, metallic grids with welded joints were specially prepared for each slab. In more recent interventions, generally there is a greater carelessness, with the iron rods irregularly placed, often bound and almost in contact with the base of the tesserae, making it even more damaging.

In addition, over time there has been a tendency to completely eliminate the spaces between the tesserae, and to replace the original mortar. This was done to make the artifact thinner and therefore lighter and easier to handle. In this way, the state of conservation of mosaics which have just been re-layed few decades ago is often worse than that of mosaics restored using the same technique in the first half of the twentieth century.

The process of intervention on the mosaics re-layed onto concrete must be tailored to each case; it is important to accurately identify the level of the iron grid and implement its removal all at once. Of course it is a risky action for the layer of tesserae, which sometimes can cause great damage and possible loss of tesserae.

The technical intervention is started pasting several layers of cotton canvas onto the mosaic surface, utilizing animal or vinyl glue.

The mosaic is turned over and placed on a table. By the use of diamond wheels, parallel incisions are made up to a depth of just a few centimeters (or a few millimeters) from the base of the tesserae in two perpendicular directions.

The different squares of the support so obtained are removed using hammer and chisel, then proceeding in a mechanical way to remove residual cement in contact with the base of the tesserae.

The mortar which is present in the interstices between the tesserae, whether original or cement, must be maintained: the original must be kept for obvious reasons, and cement is so tenacious that its elimination would lead to severe damage for the tesserae.

3.5 Case study

3.5.1 Restoration of mosaics in the Basilica of St. Leucio (Italy)

PRELIMINARY OBSERVATION

The Basilica of S. Leucio in Canosa di Puglia (Italy), built in the sixth century A.D. on a Hellenistic temple, has a double tetra-conical plant inspired by the Syrian style, which is

present in Italy only here and in the basilica of S. Lorenzo Maggiore in Milan. The basilica underwent a number of restoration works already starting since shortly after its construction, due to static instability that damaged the structure.

The current restoration has involved the floor mosaic panels which were already considered in the years 1962-'63 and in 1985; in that occasion they were lifted, restored and then re-layed in the apse, in the inner western area of the canopy, in elevated places compared to the original floor of the basilica.

The fragments involved in the operation of restoration and conservation were positioned in space in front of the west apse more elevated of the original floor in the basilica and surrounding the tabernacle (Figure 3.24). They have undergone a significant degradation, due to the exposure to the direct action of weathering, which has produced an advanced state of oxidation of the reinforcing bars, loss of cohesion between mortar and tesserae, as well as cracking of the mosaic decorations.



Figure 3.24 – Design of the basilica of S. Leucio (left), remaining of the basilica (centre) and detail of the floor mosaic (right).

Widespread on the surface of all the mosaics is the presence of lichens, moss and algae (Figure 3.25); these species of microorganisms are the cause of chemical and physical as well as aesthetical degradation. The chemical degradation is due to the production of acids by lichens, leading to a chemical attack of the raw materials which constitute the mosaic tiles, while the physical action is exerted by the thallus that link the lichens to the substrate, that is the tesserae.

The tesserae mainly consist of brick fragments, which were produced with raw materials coming from clay sediments near river Ofanto; some are made of imported marble (or

materials for reuse), given the lack of outcrops of marble in central-southern Italy, and many tesserae consist of limestone from local quarries.

The biological alteration was present on the surface of tiles with calcareous gray and white colored *Aspicilia* species, with some orange thallus of *Caloplaca* and other black kind of the genus *Verrucaria*; the thallus is rather thin and does not penetrate much in depth.



Figure 3.25 – Lichens, moss and algae on the surface of the mosaic.

CONSERVATIVE INTERVENTION

The first phase of work included the photographic documentation of the general archaeological context and the conservation state of the mosaics with attention to the different degradation morphologies. The preliminary cleaning with biocide allowed to make clear the geometric pattern and colors of the tesserae, and thus making possible most of the graphic documentation of the mosaics.

Then a linear plot was realized by contact (Figure 3.26, left). It is important because it will serve as support for the drafting of thematic tables documenting the state of conservation of the mosaics before the conservative intervention both in the original parts and those reconstructed in previous restorations. The consolidation of the mosaic decorations, with application of double cotton gauze and glue diluted in water, ensured stability to the tesserae. Then the transportable fragments were moved to the restoration laboratory for the total removal of cement and iron reinforcement on the back (Figure 3.26, right, and 3.27). With regard to large mosaic fragments, we proceeded by cutting them into smaller and movable fragments with two rows of tesserae in order to facilitate cutting and splitting between a section and the adjacent ones.



Figure 3.26 – Realization of a linear plot (left) and removal of cement from the back of the mosaic (right).



Figure 3.27 – Back of the section after the removal of concrete.

Then we applied a layer of hydraulic mortar, consisting of:

- sand as inert in two different particle sizes,
- pozzolana to provide greater physical-mechanical resistance,
- natural hydraulic lime, with a small percentage of acrylic emulsion mixed with water to ensure greater workability; this mixture is consistent with the mosaic materials in terms of physical-chemical properties and at the same time reversible.

After throwing a first layer, which was not pulled, a network of synthetic fibers with apertures of 0.5 cm per side was laid. A second layer of mortar was then applied with a wooden straight bar sliding along the wooden rails, providing the final thickness of the mosaic of 2.5-3 cm at all points for each mosaic fragment (Figure 3.28).

After the carbonation of the mortar, about seven days, we passed to gluing of strips of mosaic on mobile devices, the choice of them focused on a media type of alveolar aluminum and fiberglass. It deals with a sandwich of two sheets of glass fiber woven (thickness of 0.5 mm) embedded in a epoxy resin and made to adhere to an internal structure made of honeycomb aluminum with cells of 6.35 mm side and a thickness of 2.5 cm.



Figure 3.28 – Application of new hydraulic lime-based mortar on the back of the mosaic.

Of course the cellular supports were reinforced from the rear with aluminum tubes (size 6 x 3 cm), to ensure greater stability to the mosaics, allowing you to move them in future without problems. Turned the fragments in the direction of the tesserae, the cotton gauze was removed (Figure 3.29), and the cleaning of the mosaic surface was made with sorghum brushes, scalpels, and jets of water vapor to remove any residue of the acrylic resin.

Tesserae were reinforced with local treatments and the ultimate use of a consolidant. We suggested the method of integration of the gaps with the same color of the mosaics (Figure 3.30).



Figure 3.29 – Removal of the cotton gauze from the mosaic surface.

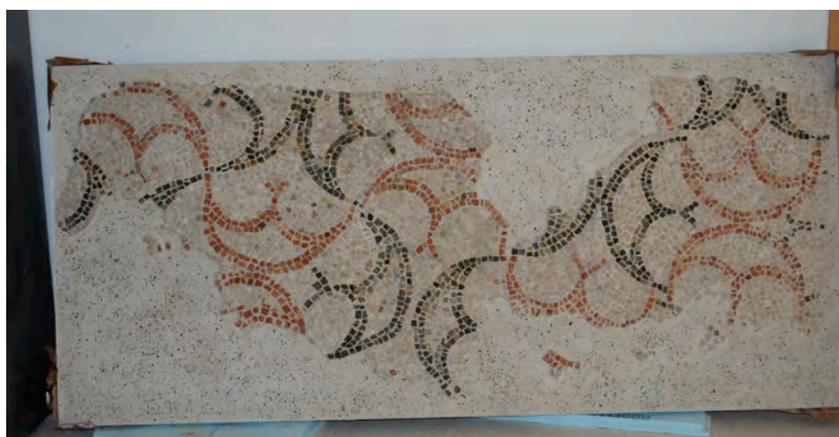


Figure 3.30 – The mosaic fragment after restoration.

3.5.2 Analytical sequence for studying mosaics

INTRODUCTION

A mosaic is composed of a sequence of preparation layers, of a bedding mortar layer, and surface layer made of tesserae (or slabs). In the study of a floor or wall mosaic it is very important to distinguish the different layers. A floor mosaic can have a complex structure; sometimes we can find a mosaic set up on another older. The structure of the wall mosaics is certainly more simple than the one of the floor mosaics. In fact it is generally composed of two preparation layers, the bedding mortar and then the tesserae.

The various mortars have different functions: foundation, stucco.

Mosaic tesserae can be made of stone, glass, ceramics and other (shells, Egyptian blue, etc.). Glass tesserae prevail in the wall mosaics, even though they can be often identified

also in floor mosaics. Stone tesserae are generally obtained by cutting carbonate rocks, especially sedimentary (limestone and dolomite), subordinately metamorphic rocks (marble). Marl, sandstone, volcanic rocks and flint are definitely less frequent. Sedimentary carbonate rocks are frequently encountered because they are easily workable; in addition they show a large number of colors.

ANALYTICAL SEQUENCE FOR TESSERAE

The tesserae are studied by means of different analytical methodologies that allow their documentation, colour identification and petrographic classification; in particular:

- Munsell Rock Colour Chart: classification of the color,
- XRD: identification of the crystalline phases,
- reflected light microscopy: documentation, sample appearance, deterioration forms,
- transmitted polarized light microscopy on thin section: mineralogical-petrographic analysis, classification,
- DTA-TGA: quantification of the calcite,
- SEM-EDS: micro-structural observations, chemical analyses of small surface areas,
- ICP-AES or XRF: whole chemical composition.

In order to obtain an accurate documentation of the sample, the description of the structure and deterioration forms, and the determination of the chemical composition of the whole sample (useful for the classification) or small surface areas of the glass tesserae, the analytical sequence for studying stone tesserae is:

- polishing of the tessera surface by ultrasound bath,
- classification of the color by comparing the tesserae with Munsell Colour Chart,
- observation at the stereo microscope, for documenting the sample, describing the structure, and identifying the deterioration forms,
- cut of a tessera into two pieces,
- grinding of one piece into powder suitable for performing XRD and DTA-TGA,
- preparation of a thin section by using the other half; the material remaining after preparation of the thin section is kept as a testimony,
- observation of the thin section (mineralogical microscope),
- micro-morphological and micro-structural observations, chemical analyses of small surface areas (SEM-EDS),
- chemical composition of the whole sample (ICP-AES or XRF)

The analytical sequence for studying glass tesserae is slightly different, because XRD analysis is useless. So, first the tessera is observed by reflected light microscopy, and then cut into two pieces. One piece is cleaned by ultrasound bath in order to classify the color by Munsell Chart and to perform new observations by stereo microscope, before grinding this piece for the chemical analyses (ICP-AES). The other half piece is cut again into two parts, so that one of them is used for performing SEM-EDS analyses and the other one is preserved as a testimony.

Ceramic tesserae or fragments, which are present in different layers of the mosaics, are generally made of simple terracotta. They can be studied following the analytical sequence typically used to analyze ceramic materials. Practically it coincides with that illustrated for the stone tesserae. In fact, these analytical techniques allow the documentation of the sample, the attribution of the color, the determination of the chemical composition (important for the identification of the raw materials), and the mineralogical-petrographic characteristics (useful for reconstructing the paste composition and the firing degree).

ANALYTICAL SEQUENCE FOR MORTARS

Mortars (bedding and foundation layers) are studied by means of several analytical methodologies that allow the documentation of the sample, to identify the composition of the binder and of the aggregate, the determination of the shape and of the dimensions of the aggregate, the recognition of the characteristics of the mortar (hydraulic or aerial), the evaluation of the ratio binder/aggregate, and finally the description of the micro structural characteristics, and the determination of the chemical composition of different surface details or of single crystals.

In particular the analytical techniques used are:

- reflected light optical microscopy (documentation, sample structure, evaluation of the ratio binder/aggregate)
- mineralogical microscope (binder/aggregate ratio, mineralogical-petrographic characteristics)
- XRD (identification of the crystalline phases)
- DTA-TGA (quantification of calcite, portlandite and gypsum; evaluation of the organic matter; characteristics of the mortar (hydraulic or aerial).
- SEM-EDS (micro morphological and micro structural observations, chemical analyses of surface single points).

The analytical sequence for studying mortars is:

- cleaning and polishing of the mortar
- observation of the sample (stereo microscope)
- cut of the mortar in different pieces
- grinding of one piece (XRD, DTA-TGA)
- cutting of an other piece in thin section (mineralogical microscope)
- observation of a small piece (SEM-EDS).

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4 – CERAMICS

4.1 Ceramic technology

4.1.1 Clay materials

The manufacturing cycle of the ceramic products, starting from suitable raw materials, which are some specific types of clays, includes three main necessary steps. After preparing a suitable mix of clay and water, they are: shaping, after that we obtain an object usually indicated as “green”; drying, after which we have the “dry” piece; firing, that gives rise to the final object.

The clay minerals are the principal mineralogical phases of the clays. They have a crystalline structure that is constituted by two basic structural units, whose repetition in the space gives rise to the various clay minerals. The two structural units are:

- tetrahedron SiO_4
- octahedron $\text{Al}(\text{OH})_6$ or $\text{Mg}(\text{OH})_6$

Both them are electrostatically not saturated, being the first with four negative free charges and the second with three (with Al) or four (with Mg) free charges. The free charges of the tetrahedrons are progressively diminished by joining together six of them, so that they make an hexagonal form. The tetrahedrons are joined putting in common two of their oxygen atoms, so decreasing their free electric charge. Then, several hexagons are joined together in the same way, so forming a planar structure, which is called tetrahedral sheet.

In the same way, three octahedral units originate an hexagon, and the joining of several hexagons gives rise to the formation of the octahedral sheet.

The clays can be characterized from three points of view: grain size distribution, mineralogical composition, chemical composition.

The particle size is mainly concentrated in the field of the clay fraction (less than 2 micron) and of silt fraction (between 2 and 64 micron), while the sand fraction (>64 micron) is usually less than 5%. The clay minerals are always very fine, so that they are mostly included in the fraction less than 2 micron.

The principal minerals which can be present in the ceramic clays are usually subdivided

into four groups, according to Table 4.1.

Table 4.1 – Principal minerals which constitute the ceramic clays

CLAYEY MINERALS		OXIDES/HYDROXIDES	
Illite	$K_{2-x}Al_4(Si_{6+x}Al_{2-x}O_{20})(OH)_4$	Quartz	SiO_2
Chlorite	$(Mg_{1-y}Fe_y)_{6-x}Al_{2x}Si_{4-x}O_{10}(OH)_8$	Hematite	Fe_2O_3
Smectite (Montmorillonite)		Goethite	$FeOOH$
	$4SiO_2 \cdot 0.85Al_2O_3 \cdot 0.33MgO \cdot 0.15Na_2O \cdot 0.5H_2O$	Limonite	$\sim 2Fe_2O_3 \cdot 3H_2O$
Kaolinite	$Al_4(Si_4O_{10})(OH)_8$		
FELDSPARS		CARBONATES	
Albite (sodic feldspar)	$NaAlSi_3O_8$	Calcite	$CaCO_3$
Orthoclase (potassic feldspar)	$KAlSi_3O_8$	Dolomite	$CaMg(CO_3)_2$

There are two groups of ceramic clays, which are distinguished by the presence/absence of carbonate minerals.

The *carbonate-rich clays* have an average composition given by about:

- 45% clay minerals, of which illite ~30%, chlorite ~8%, smectite ~7%, and kaolinite in traces,
- 30% of quartz and feldspars, subdivided into quartz ~25%, feldspars ~5%; no difference can be individuated in the frequency of sodic and potassic feldspar,
- 5% of iron oxide or hydroxide,
- 20% carbonates, which can be subdivided into calcite ~15% and dolomite ~5%.

In the case of *non-carbonatic clays*, we have about:

- 55% clay minerals, subdivided into illite ~35%, chlorite ~10%, smectite ~10% and kaolinite in traces,
- 40% quartz and feldspars, subdivided into quartz ~30%, feldspars ~10%; no difference can be individuated in the frequency of sodic and potassic feldspar,
- 5% of iron oxide or hydroxide.

Among the many other minerals which can be present in the raw clays, mica is the most diffuse, being represented mainly by muscovite (white mica), while biotite (dark mica) is

less frequent.

As it regards the chemical composition of the ceramic clays, it depends on the chemical composition and abundance of their minerals. As it can be seen in the table 4.1, the most important minerals are made of less than ten chemical elements and the most frequent and abundant are silicon and aluminum, and calcium when it deals with carbonatic clays. The presence of mica does not change this general rule, because muscovite is constituted by the same elements of illite. As a consequence, the chemical composition of the ceramic clays can be expected similar to those reported in Table 4.2, where each element is evaluated as percentage of its oxide.

In addition to the elements that appear in the mineral formula, titanium, manganese and phosphorus are generally taken into consideration, because they are present in the clays as impurities. Finally, we have to explain the parameter I.L. in table 4.2. It represents the volatile elements, which leave the clay during firing up to 1000 °C, in particular water from the clay minerals and carbon dioxide from the carbonates.

Table 4.2 – Average chemical composition of Italian clays for brick and tile production.

Clay type	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	I.L.
Carbonatic	45.2	11.9	0.7	5.1	0.1	2.9	14.9	0.8	2.3	0.1	16.3
Non carbonatic	71.5	12.9	0.6	4.7	0.1	1.5	0.9	1.0	2.0	0.1	5.1

4.1.2 Shaping techniques

Shaping is the processing methodology which permits to give a shape to a suitable ceramic clay mixture. The addition of water to the clay raw material is necessary in order to obtain a suitable physical state for the shaping operation. The water content depends on the shaping technology to be used. It is possible to operate with three different physical states of the clay/water mixture: plastic, fluid, dry.

A ceramic body at plastic state contains an amount of water sufficient to give cohesion between the particles of the ceramic powder: the obtained paste can be deformed without rupture. The water amount is comprised between 20 and 30%. The ceramic bodies at plastic state are the most frequently used since the beginning of the ceramic production in the Neolithic time.

The cohesion capacity is called ‘plasticity’; it is due to the presence of clayey minerals, in particular to their capacity of absorbing water molecules on their surface. The presence of water guarantees the cohesion between the particles and a lubricant action between them. Smectite is the most plastic mineral, followed by illite, kaolinite and chlorite. Quartz, carbonates and feldspars have no plasticity. The aplastic component of the paste is called ‘temper’. All the non-clayey minerals of the ceramic pastes can be used as temper, for example in form of natural or artificial sand. A very particular temper material is given by “chamotte”, that is ceramic material ground till the dimension of a sand.

A ceramic body with an amount of water insufficient to guarantee cohesion between all the particles of the ceramic powder is at ‘dry state’. The water amount is less than 10%; this water gives rise to the formation of aggregates, so avoiding the volatilization of the powder. These ceramic bodies can be shaped only by using the modern pressing technique. When the amount of water is more than 40% approximately, they say that the ceramic body is at ‘liquid state’. This type of mixture is used only with the slip casting technique since the middle of the XVIII century.

COLOMBINO AND SLAB TECHNIQUE

As it can be seen in the Figure 4.1, the ‘colombino’ technique operates by hand assembling thin sticks of paste in a suitable way and then eliminating the discontinuities between them. Instead of sticks, the slab technique foresees the assembling of thin slabs of plastic clay.



Figure 4.1 – Illustration of the ceramic shaping with the ‘colombino’ technique.

WHEEL SHAPING

As it can be seen in the Figure 4.2, this technique utilizes an instrumentation constituted by two rotating discs, one for placing the ceramic paste to be shaped and the other for giving a rotation to the system. This technique is known from the third millennium B.C. and represented the most important shaping technique till today.

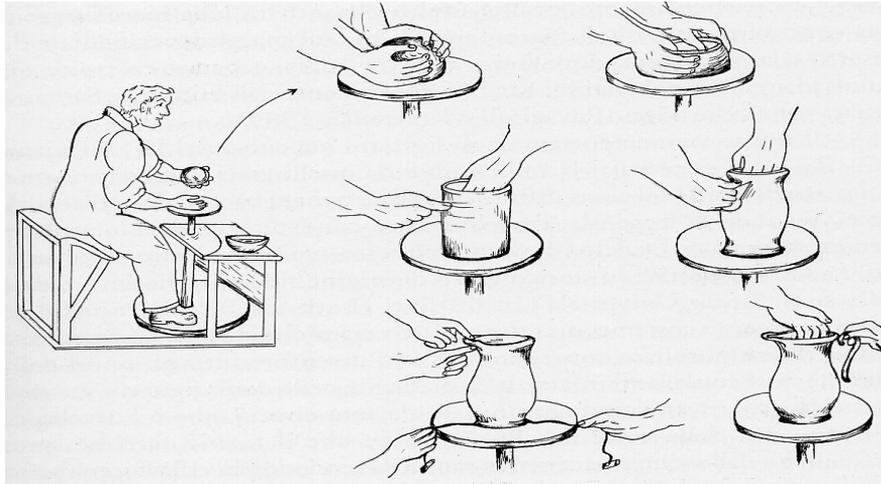


Figure 4.2 – Scheme of operation of the wheel shaping technique in a modern version.

SLIP CASTING

Slip casting is the only shaping technique which utilizes the ceramic body at liquid state (barbotine). This technique is very useful for manufacturing complex forms which have not circular sections. Barbotine is introduced into a porous mould, which absorbs part of the water forming a thin layer of solid material adherent to the internal surface of the mould. When the right thickness of the solid layer has been achieved, the mould is emptied, and the object is extracted after a short solidification phase.

4.1.3 Drying

The drying is the technological phase during which the processing water is eliminated from the shaped object through evaporation, without provoking any damage. At the beginning, the grains are separated by inter-granular water; evaporation occurs on the surface of the object and the water moves from inside to the surface. The total volume decreases till the grains come in contact between them; this first phase is called ‘phase of shrinkage’: it needs attention and is time consuming. In the second phase, the evaporation continues, but the total volume does not decrease; this phase is called ‘phase of porosity’ and is less

dangerous than the previous one. In general the two phases are connected by an intermediate phase.

The drying evolution is well illustrated by the Bourry diagram (Figure 4.3).

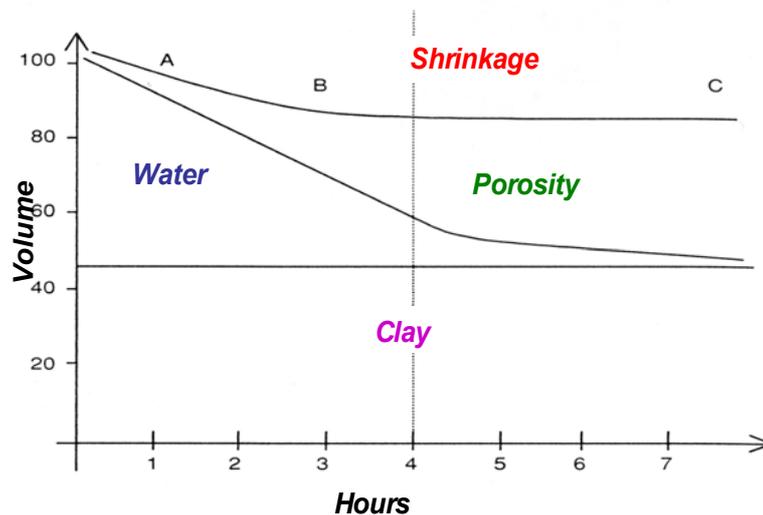


Figure 4.3 – Illustration of the drying evolution through the Bourry diagram:

A= phase of shrinkage; B= intermediate phase; C= phase of porosity.

LEATHER HARDNESS

Physical state of a partially dried object, when the piece is sufficiently hard to resist to mechanical stresses, due to particular operations of the ceramic processing cycle (e.g. application of slip or decoration), but still sufficiently humid to permit such operations and to join together independently shaped pieces.

4.1.4 Firing

Firing is the thermal treatment which promotes irreversible physical-chemical transformations, in order to obtain a product with suitable aesthetical, mechanical, and chemical properties. The firing cycle includes both the heating and cooling phase.

The main characteristics of the firing process are:

- maximum temperature,
- heating and cooling rate,
- firing atmosphere (oxidant or reductive),
- soaking time at the maximum temperature.

The heating and cooling rates, and the firing atmosphere can be varied several times,

according to the reactions, which occur in the ceramic paste, and to the aesthetical effects to be obtained. But the possibility of controlling the firing parameters (temperature and atmosphere) depends on the type of firing system at disposal. In the most ancient firing systems they could not be controlled, mainly because:

- the thermal insulation is very poor, so that very different temperatures can be measured for different vases, and also in various points of the same artefact, depending on their position and orientation with regard to the heat source;
- there is no separation between combustion area and firing area, so that the firing atmosphere is greatly influenced by the combustion of the wood and the atmosphere will tend to be reductive during the heating, but oxidant during cooling, when the combustion has been stopped.

The gradual evolution of the firing systems led to a better control of both temperature (insulation of the firing system) and firing atmosphere (separation of the firing zone from the combustion area).

DESTRUCTIVE CHEMICAL REACTIONS

The first reactions which occur during the heating phase are destructive reactions, which destroy the primary minerals; among these reactions the most important are:

- 1) at 100-200 °C, illite and smectite loss some of their water content,
- 2) at 300-350 °C, iron hydroxides loss their water content,
- 3) at 400-500 °C, in presence of oxidant atmosphere, the organic substances oxidize producing carbon dioxide and steam,
- 4) in the interval 500-700 °C approximately, all the clayey minerals completely loss their water content,
- 5) at 573 °C, the SiO₂ phase stable a low temperature (α -Quartz) transforms into the phase stable at higher temperature (β -Quartz), with an increase of volume more than 10%; this reaction is reversible, so that during cooling β -Quartz transforms into α -Quartz with a decrease of volume,
- 6) at 700-850 °C, the carbonates decompose with the liberation of carbon dioxide,
- 7) at about 950 °C melting of eutectic compositions with feldspars begin, while the theoretical melting temperatures for feldspars are: sodic feldspar = 1120 °C,

potassic feldspar = 1200 °C, plagioclases >1200 °C.

RECONSTRUCTIVE CHEMICAL REACTIONS

The residues of the destructive reactions give rise to the formation of new crystalline phases. The principal reactions involve the residues of the decomposed carbonates, together with silica and alumina from the clayey minerals. As the firing temperature increases, the following new compounds form:

- 1) $\text{CaO} + \text{SiO}_2 = \text{CaSiO}_3$ (wollastonite),
- 2) $2\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 = \text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite),
- 3) $\text{CaO} + \text{MgO} + 2\text{SiO}_2 = \text{CaMgSi}_2\text{O}_6$ (diopside, mineral of the pyroxene group),
- 4) $\text{CaO} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 = \text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite, calcic plagioclase); the same reaction can be written as: $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite) + $\text{Al}_2\text{O}_3 + 3\text{SiO}_2 = 2\text{CaAl}_2\text{Si}_2\text{O}_8$, that means that anorthite can also form at expenses of gehlenite,
- 5) at 750-800 °C, in oxidant environment, Fe_2O_3 starts to crystallize.

RAKU TECHNIQUE

This firing technique is characterized by a very rapid cooling phase, which is obtained by extracting the shaped artefact from the kiln when it is still at high temperature, and putting it into water at room temperature. In addition, before immersion into water, the object is put in contact with organic material, in order to lead the chemical elements of the glaze to their reduced state.

4.1.5 Characteristics of the fired paste

CHEMICAL AND MINERALOGICAL COMPOSITION

A part from the elimination of the volatile elements, the chemical composition of the fired paste is the same of the unfired paste; on the contrary, the mineralogical composition has changed. The mineralogical composition is very simple when non-carbonatic clays are used: very abundant quartz, remarkable amounts of feldspars and small amount of hematite, together with a large amount of amorphous phase, may be some 20-30%. On the contrary, when carbonatic clays are used, the fired paste shows several new compounds (gehlenite, diopside, anortite), other than primary quartz and feldspars, and practically no

amorphous phase.

DIMENSIONS OF THE ARTEFACTS

The chemical reactions which occur during firing give rise to a significant shrinkage, mainly due to the elimination of water and other volatile compounds. The shrinkage due to firing can be some units percent, and it is much lower than the shrinkage during drying.

The thermal expansion of the ceramic artefacts does not influence their final dimensions, because the expansion during heating is compensated by the contraction during cooling.

COLOUR

The colour of the fired products depends on:

- the presence of iron, which is usually between 4 and 8% Fe_2O_3 in the ceramic clays; it is the main responsible of the colour, because its oxides are intensely red or black coloured;
- the presence of calcium, because the calcium silicates formed during firing, particularly gehlenite and diopside, can include some iron, so that the amount of free iron forming iron oxides decreases; therefore the red or black colour is intense when calcium is low and vice-versa;
- the firing atmosphere, that can be oxygen-rich (oxidant) or oxygen-poor (reductive) depending on the firing system; oxidant atmosphere favours the formation of red coloured hematite (Fe_2O_3); in reductive atmosphere there is the formation of magnetite ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$), which is black; if the atmosphere varies during firing, for example during heating and cooling, layers of different colours (red and black) with different tonalities can form;
- the presence of NaCl, which favours the formation of new alkaline silicates during firing, which can inglobate iron; the whitening effect is particularly developed near the surface, and gives rise to the formation of the so called 'ghost coating' (see 4.1.6).

MECHANICAL RESISTANCE

The mechanical resistance is generally measured as resistance to compression and/or bending strength; this last is about 20% of the resistance to compression (Figure 4.4). The mechanical resistance is inversely proportional to porosity.

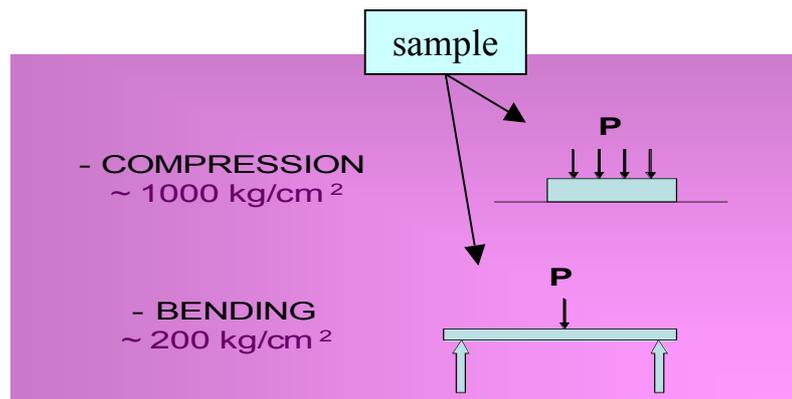


Figure 4.4 – Schemes of determining the mechanical resistance.

POROSITY AND PORE SIZE DISTRIBUTION

With the exception of stoneware and porcelain, all the ceramics are porous. Measured with the mercury intrusion porosimeter, open porosity is of the order of 30-40%, while is less if measured as water absorption, because water molecules do not enter the smallest pores. The dimensions of the pores vary in a large interval, as it can be seen in Figure 4.5. Stoneware and porcelain have less than 1% open porosity, but they can have very high levels of closed porosity, up to 25-30% by volume.

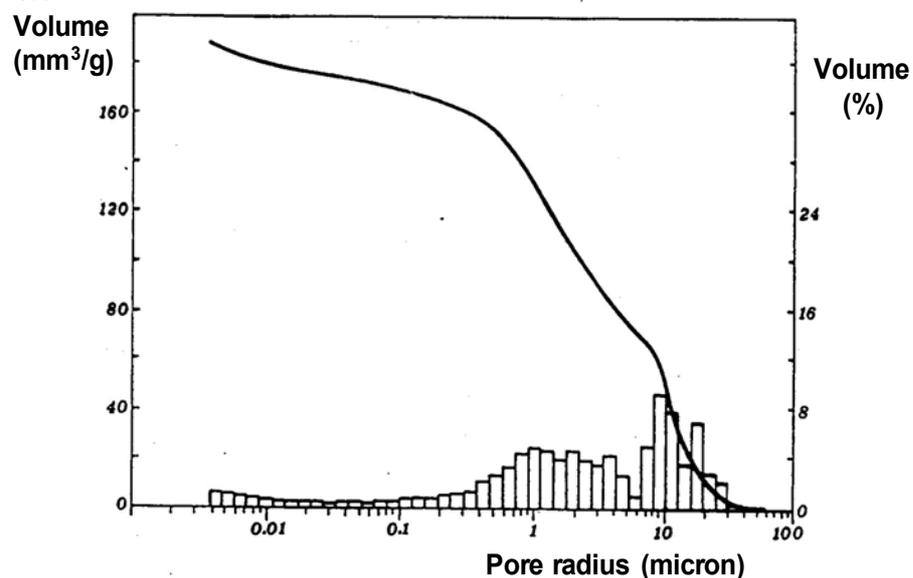


Figure 4.5 – Frequency histogram and cumulative frequency curve of the pore size distribution of a ceramic material analyzed by mercury intrusion porosimeter.

4.1.6 Ceramic coatings

TYPES OF COATINGS

The development of ceramics by the man pursued two different objectives that are the improvement of both aesthetical and technical characteristics.

The most important way was the application of more and more sophisticated coatings, with the main goal of impermeabilizing the ceramic surface, because all the fired pastes were very porous. There are four different types of ceramic coatings:

- A) Clay-type, obtained with suitable clays
 - 1) Engobe, porous
 - 2) Slip, non porous
- B) Glassy-type, characterized by a complete impermeability
 - 3) Transparent glaze
 - 4) Opaque glaze

APPLICATION OF THE COATING

The raw powder of the coating can be applied on the surface of the artefact, after dispersion in water, with three different application techniques: immersion, pouring or brushing. Depending mainly on the type of coating, the application can be made when the ceramic paste is at leather hardness, or dried or fired; in the first two cases, paste and coating will be fired with a unique process (single firing), while in the last case, there will be two firings, one for the paste and the second for the coating (double firing). When decorations are applied on the surface of the coating, in most cases they are fired together with the coating, but certain decorations need a subsequent specific firing at lower temperature.

Independently on the application technique used, a layer of powder coating is formed on the surface of the object due to water sucking by the porous paste, that is the same mechanism that has been seen speaking about the shaping technique called “slip casting”. The thickness of the layer is very uniform when the immersion technique is used, much more uniform than in the case of the other two techniques. In any case, the thickness is of the order of some ten microns in case of clay-type coatings, and some hundred microns for glassy ones.

COMPOSITION OF THE COATINGS

Due to their nature, the clay-type coatings have a mineralogical and chemical composition very similar to those of the ceramic pastes. The phase composition is mainly constituted by quartz, feldspars and iron compounds in case of coloured coatings. On the contrary, the chemical composition of the glassy coatings is very different from that of the ceramic pastes. In addition, they are completely or almost completely transformed into glass, with no or very small amounts of crystalline phases (transparent and opaque glaze respectively). The chemical elements that compose the glazes can be subdivided at least into five groups, each with a specific task (Figure 4.6). The basic component (SiO_2), the modifier or melting elements, and the stabilizer element (Al_2O_3) are always present. There are several colouring elements, each one with a particular colour, also depending on the chemical composition of the glassy matrix. For example:

- Iron (Fe): red, brown, green, blue;
- Manganese (Mn): brown, violet, light red, black;
- Copper (Cu): green, blue, turquoise, red;
- Cobalt (Co): blue;
- Chromium (Cr): green, yellow, red, brown;
- Antimony (Sb): yellow, orange.

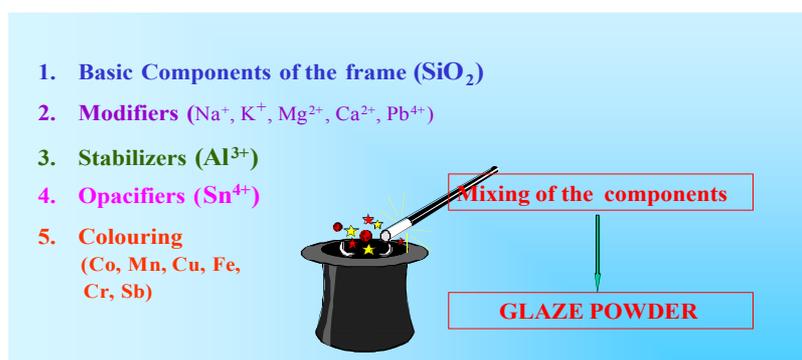


Figure 4.6 – Task of different chemical elements which can be contained in a glaze.

LEAD GLAZES AND ALKALINE GLAZES

Most of the ancient glazes contain lead and/or alkaline elements (sodium and/or potassium) as modifier elements. Lead glazes have a lower melting temperature (600-750 °C) compared with alkaline glazes (750-1050 °C). Lead glazes are very brilliant, very

transparent and deeply penetrate the ceramic paste. Alkaline glazes are more suitable when colouring elements are present. In addition, the presence of alkalis can change the final colour for a same colouring element, for example copper (green or turquoise) and manganese (violet or black).

COMBINATION OF COATINGS

Different types of coatings can be applied in the same artefact, where each one develops a different task, depending on its characteristics. So, four combinations are possible:

- porous clay type coating before, and transparent glaze as external surface,
- porous clay type coating before, and opaque glaze as external surface,
- opaque glaze before, and transparent glaze as external surface,
- porous clay type coating before, then opaque and transparent glazes in the order.

GHOST COATING

Sometimes the external surface of the artefacts is light coloured, while the ceramic mass shows a red or orange/yellow colour. As a general rule, the observer deduces the presence of a light-coloured clay-type coating, but sometimes it is not true. The light colour may be due to the action of sodium chloride during firing. Sodium chloride had been introduced into the ceramic mass dissolved in the processing water (for example by using sea water).

4.2 Technological classification of ceramics

4.2.1 Classification criteria

Three are the main classification criteria for ceramics:

- formal, based on the shape of the artefact
- functional, based on the use of the artefact
- technological, based on the manufacturing technique of the artefact.

While formal and functional criteria are well established since a long time, technological classification is still in discussion. For this kind of classification, the following parameters are usually considered: colour and porosity of the clay-based ceramic paste, presence and type of coating, firing atmosphere. These parameters can be applied with relative facility

even with simple macroscopic observations, eventually with the help of a small magnifying lens, provided that the observations are performed on fresh fracture surfaces. The colour is used to distinguish the coloured (red or grey) bodies from the “white” ones. The distinction between porous and non porous bodies is very easy. The best system is to evaluate the water suction by the body. To this purpose a drop of water can be put on the ceramic surface for observing whether the water is sucked by the ceramic paste or not. Instead of water, saliva can also be used. If the surface is clean, the observer can also put his tongue into contact with the artefact: he will feel the sensation of strong adhesion of the tongue to the ceramic mass in case of porous material. In addition, non porous bodies show the typical fracture of a glass. The presence or absence of any coating is not always easy to be recognized. A useful help can derive from the comparison of the colour on the natural surface and on the fracture surface. In addition, the brilliance of the coating can be used to distinguish between “clayey coatings” and “glassy coatings”. The definition of the firing atmosphere can be made specifying if the colour has a red or grey tonality, corresponding to oxidant or reducing atmosphere respectively. Starting from the above observations, many different ceramic typologies can be recognized according to Table 4.3.

Table 4.3 – Technological classification of the ceramic materials.

CERAMIC PASTE		COATING	FIRING ATMOSPHERE	CERAMIC TYPOLOGY
Coloured	Porous	Absent	Oxidant	1) Terracotta 2) Polichrome terracotta 3) Coarse ceramics 4) Thin walled ceramics
			Reducing	1) Reduced ceramics 2) Bucchero
		Porous slip	Oxidant	Porous slipped ceramics
		Non porous slip	Oxidant	1) Non porous red slipped ceramics 2) Sigillata
			Reducing	Non porous black slipped ceramics
		Discontinuos, non porous slip	Ox/Red/Ox	Red or black figures ceramics

		Transparent glaze	Oxidant	Transparent glazed ceramics
		Porous slip + Transparent glaze		1) Porous slipped, transparent glazed ceramics 2) Sgraffito ceramics
		Opaque glaze		Majolica and lustre majolica
	Compact or less porous	Absent or transparent glaze		Stoneware, glazed stoneware, salt stoneware
White	Porous	Transparent glaze	Ox/Red/Ox	Hard earthenware, Soft earthenware
	Compact	Transparent glaze or absent		Hard porcelain, soft porcelain
Very quartz rich, more or less coloured paste	Porous	Opaque or transparent glaze	Oxidant	1) Stonepaste 2) Siliceous Faenza (or Egyptian fajence)

4.2.2 Typologies with coloured porous body without coating

TERRACOTTA AND POLYCHROME TERRACOTTA

Terracotta is the simplest type of ceramics. Practically it is a ceramic typology made with the clay as it is found in nature, with coloured and porous body, without coating, usually fired in an oxidant atmosphere. The ceramic paste is made of not treated clay, so that the surface is quite irregular. The firing temperature generally is below or around 900 °C. The statues of the famous Terracotta Army in China, (221-206 B.C.) are a great example of this typology (Figure 4.7).

Terracotta decorated with unfired colours (Figure 4.7) is called polychrome terracotta. The pigments are generally organic and the artefacts are not re-fired after painting.

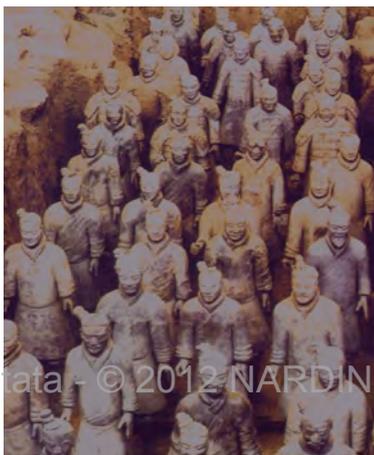


Figure 4.7 – The Chinese Terracotta Army (on the left); a religious scene with statues made of polychrome terracotta (on the right).

COARSE CERAMICS

Terracotta characterized by the presence of large inclusions (up to some millimetres) inside the paste, which were voluntary added by the potter to reduce the shrinkage of the paste during the ceramic processing, and to improve the thermal shock resistance of the artefact during its use as cooking ware. The commonest inclusions are made of calcite, silicates and chamotte (Figure 4.8). When calcite is used, the firing temperature cannot exceed 800 °C.

THIN WALLED CERAMICS

Terracotta characterized by very thin walls, up to about 2 mm. These small thicknesses put into evidence the great ability of the potter in the shaping technique, mainly through moulding. Artefacts of this type (vases, cups and glasses) are very common in northern Italy in the Roman period, between II century BC and II century AD.

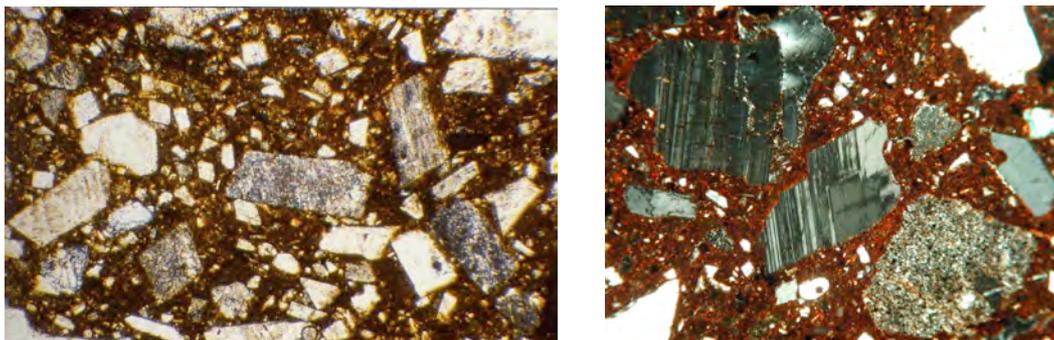


Figure 4.8 – Thin sections of coarse ceramics with calcite (left) or silicate (right) inclusions.

REDUCED CERAMICS AND BUCCHERO

Reduced ceramics are typologies with porous paste, without coating, and characterized by a grey colour obtained by firing in reducing atmosphere at least around the maximum temperature and in the first phase of cooling. Bucchero is a particular type of this typology;

it is completely black coloured and shows a brilliant surface. These characteristics are obtained in a strongly reductive atmosphere, due to the presence of volatile carbonaceous particles in the combustion fumes. *Bucchero* is a typical production of the Etruscan people in Italy before the beginning of Rome's power.

4.2.3 Coloured porous body and clay-type coating

BLACK SLIPPED CERAMICS

Ceramic typology with fine porous and coloured paste, with a coating made of a very thin 'argillaceous' layer (Figure 4.9), which is compact and typically black coloured due to firing in oxidant atmosphere and then in reducing atmosphere, around the maximum firing temperature, so that the body is red coloured, while the slip is black coloured. Its production started in the central southern part of Italy (Figure 4.9, left).

CERAMICS WITH RED OR BLACK FIGURES

Ceramic typology with fine porous and coloured paste, with a coating made of a very thin 'argillaceous' layer, which is applied in a discontinuous way, in order to draw the figures you want (black figures) or cover the area that contains the figures (red figures) (Figure 4.9, right). The result is obtained through a oxidant atmosphere followed by reducing atmosphere around the maximum temperature, and then oxidant atmosphere during cooling. The reducing atmosphere induces a black colour in the paste and in the coating as well; on the contrary, during cooling in oxidant atmosphere only the ceramic paste turns to red because the black coating is impermeable and cannot be oxidized.

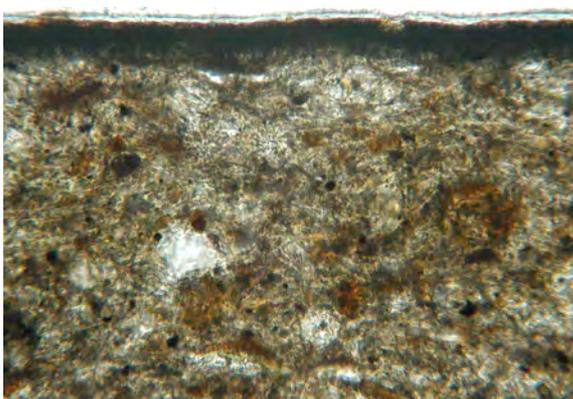


Figure 4.9 – Thin section of black slipped ceramics (on the left),

and ceramics with red figures (on the right).

SIGILLATA

Ceramic typology with fine porous coloured paste, with a coating made of a very thin and compact 'argillaceous' layer. Both paste and coating are usually red-orange coloured; decorations are present, which are obtained by moulding (Figure 4.10). Sigillata is a typical valuable Roman production, obtained through very oxidant firing at a temperature as high as 900-1100 °C.



4.10 – Examples of sigillata ceramics.

4.2.4 Typologies with coloured porous body and glassy coating

TRANSPARENT GLAZED CERAMICS

Ceramic typology with fine porous and red coloured paste, with a coating constituted by a coloured or not coloured transparent glaze.

POROUS SLIPPED, TRANSPARENT GLAZED CERAMICS, AND SGRAFFITO CERAMICS

Ceramics with a colourless or coloured transparent glaze applied on another coating, which generally is a white porous engobe layer (Figure 4.11). The white surface of the engobe can be used as a basis for decoration, which is then protected by a colourless transparent glaze, that also increases the aesthetical value of the decoration. When the decorations or part of them are obtained by incising the engobe up to uncover the red support, the product is called sgraffito ceramics (Figure 4.11). These products are manufactured through double firing:

1st firing = paste + engobe: the engobe had been applied when the support was at leather

hardness,

2nd firing = painted decorations + transparent glaze.

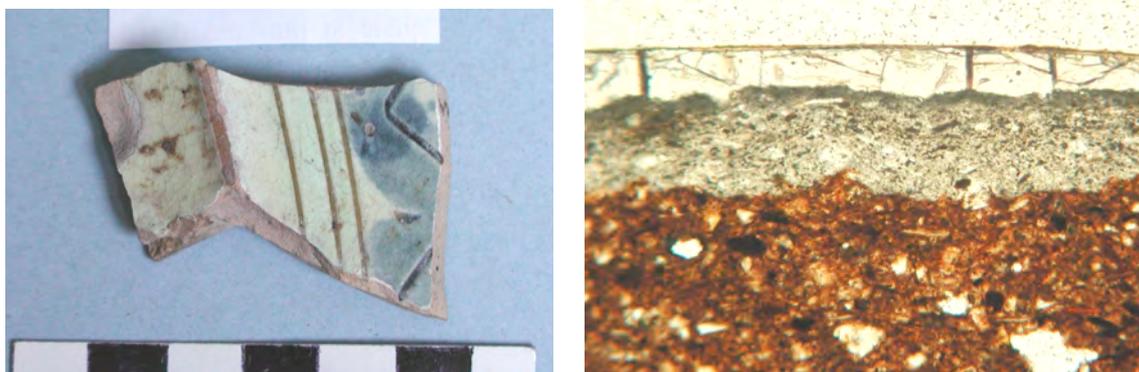


Figure 4.11 – A fragment of ‘Sgraffito’ ceramics and its photo in thin section.

MAJOLICA AND LUSTER MAJOLICA

Typology with fine, yellow-orange and porous ceramic paste, with a layer of opaque glaze (Figure 4.12). Sometimes there is a white porous engobe under the glaze, and/or a transparent glaze layer on the opaque glaze, in order to protect the decorations painted on the opaque glaze surface. Majolica is usually processed through double firing: at about 950 °C the first one, and some 30-40 °C less, the second.

Luster majolica is a kind of majolica with a metallic effect on the surface of the glaze (Figure 4.12), which is obtained by treating the surface with metals (copper, silver or gold) and re-firing the object at a temperature as low as 500-600 °C (low-fire firing).





Figure 4.12 – Examples of majolica and lustre majolica artefacts, and a photo under the mineralogical microscope in thin section.

4.2.5 Stoneware (Gres)

Ceramic typology with a more or less coloured paste, which is compact or less porous because it contains a glassy phase (20-40%), more frequently without coating (Figure 4.13). A special impermeabilization treatment, which was common in the past centuries, was realized by introducing sodium chloride into the kiln at the maximum temperature (around 1100 °C), so promoting the formation of a surface layer of completely melted material (salted stoneware).



Figure 4.13 – Stoneware artefacts.

4.2.6 EARTHENWARE

Ceramic typology with a white porous body, with non-coloured or coloured transparent glaze. The paste can be obtained by two different types of mixture, which are always constituted of iron-poor raw materials:

- clay, sand and feldspar (about 55:30:15 respectively). The artefacts are produced in double firing: the paste is fired at about 1250 °C, then the transparent glaze is fired at 1100-1150 °C (*hard earthenware*) (Figure 4.14 on the left);
- clay, sand and limestone (rock mainly made of calcite) (about 50:30:20 respectively). It needs two firings: the first is for the paste (about 1000 °C) and the second for the glaze at 900-950 °C (*soft earthenware*) (Figure 4.14 on the right).



Figure 4.14 – Hard earthenware (on the left)
and soft earthenware (on the right).

4.2.7 PORCELAIN

Ceramic typology with a very fine, white and compact body, often translucent because it is prevalently constituted by a glassy phase which surrounds the crystalline phases. Depending on the nature of the glassy and crystalline phases, there are different types of porcelain, obtained with different formulations of the paste.

The type of porcelain obtained with a mixture of kaolin, feldspar and quartz (50:25:25 approximately), fired at 1300-1400 °C in an oxygen-poor atmosphere, is the most valuable and it is called *hard porcelain* (Figure 4.15); mullite is its typical crystalline phase, which



Figure 4.15 – Artefacts of hard porcelain (on the left)
and soft porcelain (on the right).

forms during firing. Generally, a transparent glaze is applied, which has the same components of the paste, but with less kaolin and/or quartz and more feldspar, so that it results more fusible. The glaze is applied on the surface of the porous product obtained by a pre-firing at 800-900 °C.

Soft porcelain is fired at lower temperature, about 1200 °C, and its composition is very variable. There are at least two types of soft porcelain: one of them is manufactured with a paste containing alkaline and/or earth-alkaline compounds (some lead can also be present), which melt during firing and link the grains of the body (Figure 4.15); the second one, typical of the English production, is obtained by using bone ashes, which are mainly made of calcium phosphate, with the task of producing the melted phase (*bone china* or *phosphatic porcelain*).

4.2.8 SILICEOUS CERAMICS

Ceramic typologies with a light coloured porous body, whose chemical composition is represented by about 80% of silica, with a generally coloured transparent glaze. Two types of artefacts are known with this characteristics: small Egyptian statues or other (*Egyptian fajence*), and Islamic architectonic ceramics (*stonepaste*).

4.3 Alteration and degradation processes

4.3.1 CAUSES OF ALTERATION

An ancient object is subjected to different factors that can modify its original characteristics, starting from the moment of its realisation up to its recovering. The interaction with the surrounding environment, in fact, can promote physical and chemical modifications of the archaeological objects. This issue is treated in particular in the Chapter 2, so that here the more general questions will be just mentioned, while some processes specific for ceramics will be treated more deeply.

The modifications can be distinguished into alteration and degradation. Alteration provokes transformation in the chemical and mineralogical compositions, but does not apparently compromise the integrity of the artefacts. It depends on the artefacts characteristics:

- porosity, the most important element because favours the interaction with all the elements that “live” in the environment,
- the crystalline/glassy phase ratio,
- the composition, shape and size of the crystalline grains,
- the presence of coating, because the behaviour of paste and coating is quite different, and the interface between paste and coating represents a point of weakness.

Opposite to alteration, degradation compromises the integrity and the original characteristics of the artefacts, causing mainly a mechanical disintegration.

The soil solutions are the main spreading vehicle of the alteration agents by considering that the majority of ancient finds are in archaeological sites, that means buried underground.

By considering all the environmental situations, four are the main causes of the degradation phenomena, usually linked to each other:

- *Humid pathology*: The contribution of water is fundamental. Water solutions containing salts, ions and other particles can come from the environment by means of percolating water, rain, etc. or, as well as arising for capillarity in case of architectural ruins. The situation is harmful for both glazed and not glazed ceramics.

- *Structural movements*: These movements can originate inside the artefacts (Figure 4.16), but in the majority of the cases are determined by external causes, for example earthquakes.



Figure 4.16 – Ceramic sculpture with cracks provoked by structural movements originated inside the artefact.

- *Anthropic interventions*: Old and not well executed restoration works fall in this category. Anthropic interventions also include the mass tourism that provokes changes of the micro-climatic conditions.

- *Other causes*: These can include the interactions between different materials that constitute the cultural assets (for example mortars and bricks), and the manufacturing defects (such as the so-called “calcinello”).

4.3.2 PHYSICAL DEGRADATION

Physical degradation is the result of mechanical stresses acting on the artefacts. The factors causing physical degradation can be schematized as in Table 4.4, where their importance is related with the type of environment where ceramics rest before their recovery.

Table 4.4 – Importance of the causes of physical degradation in different environments.

Factor	Environment of permanence		
	Underground	Air	Underwater

		<i>Indoor</i>	<i>Outdoor</i>	
Frost/thaw			+++	
Soluble salts	+	+	+++	+
Humidity	+	+	+	
Thermal shock		+	+++	
Fluent water			+	+++
Wind			+++	
Weight	+++	+	+	+
Vibrations	+++	+	+	+
IR radiation		+	+	

Frost/Thaw is to be considered practically only for outdoor exposed artworks, because the water present inside porous structure of ceramic object varies its physical state in relation with the climate. In particular, the increment of the water volume during the passage to the solid state provokes internal forces of compression and traction.

The same could be said for the *soluble salts*, whose migration through the pores or fractures of a ceramic paste favours the crystallization of deposits over or under the external surface, or immediately under the glaze in the cases of glazed ceramics. In extreme situations, you can arrive to the complete detachment of surface portion of the artefacts, or glaze layer in the case of glazed materials. The problem of the soluble salts also exists for objects buried underground or underwater, even though it appears only after their recovery.

The variations of relative *humidity* and the consequent phenomena of condensation and evaporation favour a gradual and constant infiltration of the water under the surface of the ceramic object causing development of mechanical stresses that can diffuse in the whole artwork.

Ceramics are subjected to *thermal shocks*, such as the majority of the materials, due to rapid and noticeable variations of temperature, for example from day to night or from summer to winter. Of course, these variations are practically possible only outside.

Fluent water has an abrasive action on the surface of the artefacts, which occurs particularly underwater. The mechanical action of *wind* is similar to fluent water, but it acts in air (outside) instead of underwater. In addition to corrosion, it is possible that deposits of pollutants are formed on the artistic surfaces.

Most archaeological finds come from underground where the *weight* of the soil over the

objects exerts a significant pressure, so that cracks and deformations are possible even though the resistance of the ceramic materials to compressive forces is good.

The *vibrations* deriving from human actions, such as traffic, drillings, etc., can cause instability; they can act on historical buildings as well as on archaeological sites.

IR radiation is a possible cause of degradation: its focusing on the object can cause a localised increase of temperature and consequently the formation of stresses.

4.3.3 CHEMICAL MODIFICATIONS OF THE PASTE

The chemical alteration is the result of several modifications that change the original composition of an artefact. They can be caused by human or environmental interferences during the “life” of an object. It is well known, for example, the presence of carbon in vessels used as cooking pots, whose visible consequence is a surface blackening, with variable intensity depending on the position referred to the heat source.

In the ceramics, the chemical transformations can affect both paste and coating, even though the paste modifications are more frequent. Apparently these modifications do not give serious problems, because the transformations are often not visible at naked eyes, and the physical integrity of the object is preserved. Anyway, it is important to know these types of alterations, because the archaeological objects are sources of a lot of information that permits to reconstruct several points of their working processes. The chemical composition is particularly important for provenance studies, while the mineralogical patterns permit to define the range of the firing temperatures.

Among the many possibilities of chemical changes, the most sensible seem to be the alkaline elements (Na, K and Rb) and the earth-alkaline ones (Ca, Sr and Ba), with an increase or decrease of concentration depending on the type of alteration process.

Several examples of pollution of manganese have been also found, but the pollution of phosphorus certainly is the most common especially in the oldest ceramics, where it can attain very high concentrations. This last type of chemical pollution is here commented in detail.

Phosphorus contents in the clayey raw materials are usually much less than 0.5% P₂O₅, due to the presence of phosphate minerals. Therefore, if a chemical composition of an archaeological ceramic find shows higher phosphorus contents (up to 10% P₂O₅), doubts

about the chemical integrity of the artefact have to arise. The macro-pores in the ceramic fragments accept the solutions containing phosphorus and some chemical elements of the ceramic paste, such as calcium, iron and aluminum interact with it to form new phosphate compounds.

But what is the provenance of the phosphorus?

Taking into account that phosphorus pollution only occurs in buried ceramics, the most likely hypothesis is that the phosphorus comes from bones, which are often found in underground archaeological deposits. The bones are constituted by calcium phosphate and they can be attacked by soil solutions and release phosphorus. For this reason the more polluted finds are the oldest ones, in particular Neolithic ceramics. It is also possible that the vessels can have been used as container for food or for funeral purposes such as cinerary urns. Another source of this pollutant element can be the fertilizers used in the agriculture.

Apart from the source of phosphorus, it is also interesting to know how it is fixed into the ceramic paste. Phosphorus precipitation from soil solutions is related to environmental conditions, particularly to pH and Eh, which are controlled by changes in the water content, movement of water-level in the ground, the presence of organic matter, and bacterial activity.

Summarizing, first it is necessary to have acid soil solution able to attack bones and then the solutions change their characteristics in order to favour the deposition of phosphorus. The ceramic fragments provide the cations necessary to fix the phosphorus.

In some cases, such as the Neolithic ceramics from Sammardenchia (Italy), the macroscopic aspect changes. The finds show big vacuoles, which could be erroneously interpreted as result of the technological process, but in reality due to the dissolution of calcite grains by acid solutions, which facilitate the mobilization of phosphorus and its precipitation within these secondary cavities. SEM investigations have revealed local chemical composition with about 50% of iron oxide, 20-25% of P_2O_5 and 10-15% of aluminum oxide, other than minor amounts of silica and calcium oxide. These data suggest a significant presence of vivianite, a hydrate iron phosphate ($Fe_3(PO_4)_2 \cdot 8H_2O$), crystallized to form a honeycomb structure (Figure 4.17).

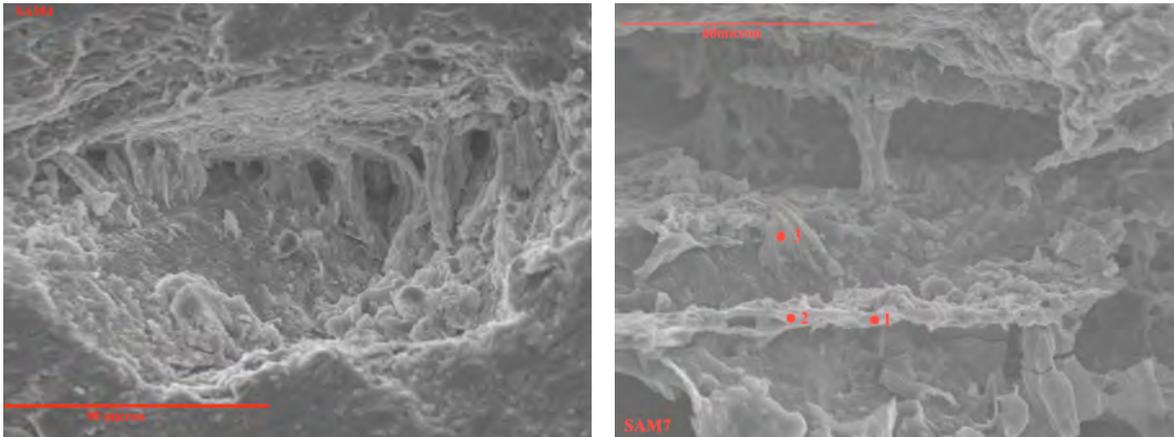


Figure 4.17 – SEM micrograph of phosphorus-polluted ceramics: the three points indicate some of the analyzed positions, where the results suggest the presence of vivianite.

4.3.4 MINERALOGICAL MODIFICATIONS OF THE PASTE

The ancient ceramic objects recovered from archaeological excavations were for a long time in contact with soil solutions and pollutants. This interaction can provoke transformations in the mineralogical composition of the artefacts, other than in the chemical composition. The mineralogical transformations mainly occur in the ceramic paste. In any case water has a basic role; in form of rain, as well as percolating water and humidity, it is the trigger for the transformation processes. In addition, water is a vehicle for acids, carbon dioxide, soluble salts and other types of pollutants.

The main mineralogical modifications occurring in a ceramic paste are explained below:

- rehydration,
- transformation of gehlenite,
- secondary calcite from carbonation,
- calcite from external contribution.

Rehydration. In the ceramic paste can be present relicts of argillaceous minerals, probably because the firing process did not favour their complete utilization for reconstructive chemical reactions. This phenomenon mostly occurs in terracotta and raw ceramics.

The argillaceous relicts are very reactive and when they meet water they interact with it and re-hydrate. The water molecules are captured by the argillaceous relicts that partially reconstruct their micro-structure. It is a sort of re-argillification, with a partial reconstruction of the starting mineral phases. At the end there is a very little crystalline

phase with a structure similar to smectite.

How is it possible to recognize this situation?

Sometimes in XRD spectra a broadened peak is present in correspondence of the smectite angles. In addition, TG-DTA curves show dehydration process with a loss of weight that occurs gradually in a large temperature range, from 200 to 400 °C approximately.

The broadened peak in the XRD and the large temperature range in thermal analysis are attributable to the weak bonds in the new crystalline structure. The weakness is confirmed by the disappearing of this peak after re-firing at very low temperature (<400 °C).

Transformation of gehlenite. This reaction is typical of calcareous ceramics and occurs in presence of humidity or water, not in arid environments.

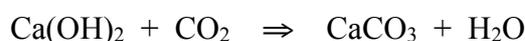
During firing the carbonate minerals present in the original raw mixture are destroyed and participate to the formation of new calcium silicate phases such as gehlenite, pyroxene, anorthite. Among them, gehlenite is the less stable phase, so that it can be attacked by soil solutions and it undergoes the following main transformation:



At a first stage, the hydration of gehlenite gives rise to the formation of wairakite, which is a hydrate alumino-silicate of calcium, together with calcium hydroxide and aluminum hydroxide:



Through reaction with the carbon dioxide present in the air, the calcium hydroxide transforms into calcite:



The interpretation of XRD spectra permits to recognize this type of alteration.

Usually a diffractogram of well-fired and preserved ceramic body made with calcareous clays shows a mineralogical pattern with a combination of new calcium silicates like pyroxene, gehlenite, anorthite and wollastonite. On the contrary, when a diffractogram of an altered paste is interpreted, it is possible to observe wairakite and/or calcite together them. It is also possible that gehlenite is even absent. This is an anomalous situation, because calcite and wairakite cannot exist at the temperatures necessary for the formation

of calcium silicates such as pyroxene and anorthite ($>850\text{ }^{\circ}\text{C}$). Therefore, the situation has to be interpreted as a consequence of alteration processes mainly due to the action of water. In these cases, next to a rather noticeable mineralogical transformation, there is no change of chemical composition, apart from the acquisition of water and carbon dioxide which are included in the ‘loss on ignition’ (LOI) or ‘ignition loss’ (IL).

Secondary calcite from carbonation. As mentioned above, during firing the carbonates, mainly calcite, present in the clayey raw materials, are destroyed in order to permit the formation of calcium silicates. So, if calcite is recognised into the ceramic paste, it is possible that it is secondary calcite. In other words, the observed calcite is not the same mineral that was present in the raw material. It is likely the result of an interaction with the environment after firing, as in the case of transformation of gehlenite.

A type of secondary calcite is formed by carbonation of CaO, which remains free in the ceramic paste, as residue of the destruction of primary calcite.

During firing, the destruction of carbonates provides calcium oxide (CaO) that combines with silica (SiO_2) and aluminium oxide (Al_2O_3) of the argillaceous minerals. If the CaO amount is slightly in excess respect to the other oxides, or the firing time and/or the firing temperature are not sufficient, there will be any residual CaO. This “free CaO” in the paste can react with carbon dioxide (CO_2) present in the environment, just after firing or during the use of the artefact, so that new crystals of calcite are formed. First CaO interacts with H_2O in order to form $\text{Ca}(\text{OH})_2$; then $\text{Ca}(\text{OH})_2$ reacts with CO_2 and transforms into calcite. This type of calcite can be recognized by crossing the results of different investigation methods, in particular the results of XRD and thin section observations at the optical microscope. The small sizes of the new grains homogeneously distributed into the paste, in fact, do not permit to recognize calcite. You can be sure that there are grains of new crystalline phases, but you cannot identify their composition. So it is necessary to confirm or not the attribution by using XRD technique.

The formation of secondary calcite through carbonation of ‘primary calcium oxide’ does not alter the original chemical composition of the paste, so that it is possible to use the chemical data for provenance studies.

Calcite from external contribution. Water solutions rich in calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$ transport it into the soil and inside the vacuoles of porous ceramics. In suitable

environmental conditions, the instability of the bicarbonate favours the precipitation of calcite inside the pores of the ceramic body. The precipitation of calcium carbonate occurs according to the following reaction:



Sometimes the new grains are in form of acicular crystals that start from the rim toward the centre of the pore, sometimes completely filling it.

In order to recognise this type of secondary calcite, it is useful to combine different analytical techniques: optical microscopy in thin section, XRD and XRF for example.

The observation in thin section is very useful because the calcite from external contribution re-crystallizes inside macro-pores and fractures of the ceramic body (Figure 4.18).

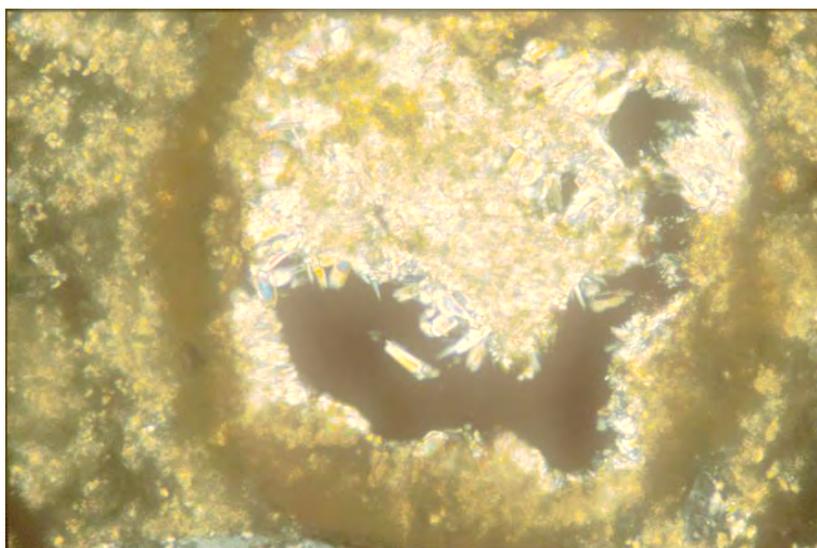


Figure 4.18 – An example of secondary calcite from external contribution, observed in thin section at the mineralogical microscope.

Secondly, the XRD technique is useful to confirm the presence of calcite. Finally, the chemical analysis can also give an indirect but decisive contribute. In fact, a group of ceramics, recovered from one archaeological excavation and belonging to the same typology, usually should have the same or quite similar chemical compositions. Conversely, in case of ceramics containing post-depositional calcite, the chemical composition randomly varies from a sample to another. In fact, the precipitation of calcite is not uniform, depending on the position of the finds in the ground.

The presence of calcite from external contribution significantly modifies the whole chemical composition of the ceramic pastes, also because other elements can be present in the soil solutions and trapped into the ceramic paste, even though in less amounts.

This makes it is very difficult to know the original chemical composition of the shards, so that the possibility of using these chemical data for provenance study is strongly compromised.

The calcite from external contribution and from carbonation are easily distinguishable between them, because the first is concentrated inside the macro-pores while the calcite from carbonation is in micro-crystals widely dispersed in all the ceramic body.

4.3.5 CHEMICAL ALTERATION OF THE COATINGS

The ceramic coatings are subjected to alteration/degradation phenomena as the ceramic pastes, but they have a different structure and/or composition, so that the effects also are different. Usually, during burial, the glassy coatings can change their chemical composition more easily than the argillaceous coatings. Sulphuration and phosphatation are the main chemical alteration processes involving the coating layer of buried glazed ceramics.

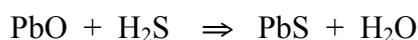
Sulphuration. This phenomenon affects lead glazes, both opaque and transparent. The sulphuration appears as a blackening of the object surface, that quite completely hides every decorative elements (Figure 4.19).

From the chemical point of view, it is a patina characterized by a high sulphur content. Usually, no crystalline compound have been found, but sometimes the XRD investigations revealed the presence of lead sulphide (galena).



Figure 4.19 – Appearance of sulphurated lead glazes.

In order that the sulphuration occurs, it is necessary to have reducing conditions in the burial environment. This is possible when the ceramic objects and rubbish of organic materials are in the same place. The presence of organic materials permits the growth of bacteria that metabolize sulphur ions for producing hydrogen sulphide (H₂S). This last then interacts with the elements present in the glaze layer, specifically lead, and amorphous lead sulphide (PbS) forms, which is black in colour:



Depending on the available time, the lead sulphide could partially crystallize as galena. The thickness of the blackened layer and its consistence depends on the closeness to the pollutant source and on the duration of reducing conditions in the surrounding environment. It is possible, in fact, that different fragments of a unique artefact can have been subjected to different levels of sulphuration and blackening, which will appear very evident after reassembling several fragments of the same object.

Several laboratory tests evidenced that it is possible to annul this blackening effect, through a chemical treatment consisting in the use of hydrogen peroxide (oxygenated water, H₂O₂), or by means of a thermal treatment at relatively low temperature (<350 °C). The final result is apparently the same, that is the lightening of the surface. But by using hydrogen peroxide, the cleaning is limited to the top part of the glaze layer, while the heating treatment acts on all the thickness of the blackened parts.

Phosphatation. This type of alteration consists in the formation of thin patinas on the glaze surface and provokes an iridescence of the glaze, with a subsequent loss of its brightness. These crystalline or amorphous patinas are mainly characterised by hydrate phosphate of calcium and lead and are the results of leaching processes by soil solutions. These remove the more unstable elements releasing the transported cations, for example phosphorus, which combine with some components of the glaze (calcium and lead), so fixating on the surface. The Table 4.5 shows that it deals with is a very deep alteration of the original chemical composition of the ceramic glazes, because phosphorus is practically absent in the original glazes, and the content of silica is generally lowered.

4.4 Ceramic conservation and restoration

4.4.1 EXAMINATION OF THE ARTEFACT AND RECORDING

The first examination of the object is done with the naked eye. If the object allows, handle it carefully and look at it. All observations are to be recorded in new record or checked with an existing written and photographic record.

Table 4.5 – Chemical composition of phosphorus polluted ceramic glazes.

COMPOUND	SAMPLE		
	PO3	PO7	PO14
PbO	30.75	44.26	54.66
SiO ₂	41.38	9.07	3.78
Al ₂ O ₃	2.34	3.49	6.43
TiO ₂	0.03	0.06	0.10
Fe ₂ O ₃	0.36	0.52	0.74
MgO	0.39	2.09	0.79
CaO	10.33	27.01	19.83
Na ₂ O	0.40	0.47	0.59
K ₂ O	0.41	0.57	0.22
P ₂ O ₅	13.61	12.42	11.64
SO ₃	0.00	0.00	1.21
Ca _{5.5} Pb _{4.5} (PO ₄) ₆ (OH) ₂	+++	+++	+++
Pb(CO ₃) ₂ ·2H ₂ O			+
Pb ₃ O ₂ CO ₃		+	
Quartz	+++	+	++

The written and photographic record is something that must always accompany the object. The better and more precise the record is, the easier it is for the next conservator, scientist or researcher to benefit from it.

If further investigation is necessary, this will be done with ultraviolet, infrared, x-ray aided

examination as well as scientific analysis.

It is essential to keep clear records and documentation relating to the condition and treatment of objects. In many collections, pro forma lists that just need to be checked are useful; drawings are helpful as well as photographic recordings.

In an archaeological context, where objects have been excavated and may have required some emergency on-site treatment, good written and photographic records are extremely valuable for later work in the conservation studio.

Numbering is often important for archaeological objects as soon as they are excavated. A temporary number may be temporarily placed on the object itself, or on the packaging, or even as a label attached to the object. It may be necessary to put a number directly on to the object either on the excavation site or in the conservation studio. The numbering needs to be done in a way that is easily located but not obtrusive. A small rectangular area can be painted with a primer such as Paraloid B-72 and on it the number can be written with a stable marker or with drawing ink. This prevents the marker ink being absorbed into the body of the object.

For a long time ancient repairs have been neglected by archaeologists and conservators. This is also something that should be carefully documented as belonging to the history of the object.

To the pottery repairs belong the use of metal staples that keep together the fragments or cracks, through holes drilled into the ceramic and joined together by metal thread, and also sometimes the use of alien fragments.

4.4.2 PLANNING A RESTORATION INTERVENTION

It is important to establish what sort of ceramic material the object is made of, for example, unfired, low fired or high fired. If it is glazed, how stable is the decoration? Is it unfired?

The characteristics of the ceramic will influence the choice of the treatment.

The surface of ceramic is often contaminated by concretions of lime, gypsum or siliceous materials which may obscure any decoration.

A principal cause of damage to ceramic objects that have been excavated is due to the presence of soluble salts which are absorbed by the pottery whilst in the ground. The salts can physically break the ceramic apart, so that the surface will exfoliate away and if this

process is allowed to continue the whole object may be destroyed.

4.4.3 CLEANING

Before attempting to remove any surface deposit, the chemical nature of the concretions should be established.

Incrustations can be removed mechanically as well as chemically. It is important to make tests first, to make sure the object is not harmed and to choose the appropriate method.

If the excavated object is still wet or damp, the surface dirt should be removed as soon as possible before it dries and it is drawn into the body.

Surface dirt can be cleaned first using a soft brush. The surgery scalpel and dental drill are often a valid instrument to take away some surface deposit. Particularly for unglazed pottery, several kinds of rubber powders and sponges have been developed for removing surface dirt.

Some deposits can be removed with ultrasonic tools.

For carbohydrates, proteins and fats in the ceramic, enzymes can be used to enable to be washed away.

Soluble salts which are a potential cause of deterioration may be removed by prolonged soaking in distilled or deionized water. At regular intervals the water should be measured to see if the treatment has been completed and is without salts.

Incrustations of calcium carbonate or calcium sulphate formed on the surface can be removed using acids.

Care must be taken using acids. The ceramic should be thoroughly soaked in water first, and the acids applied with a dropper, pipette or paper pulp in sufficient quantity to remove only the concretion. It must be remembered that in using an acid to remove deposits we are creating at the same time soluble salts: to objects treated in this way therefore must be given a prolonged washing.

There are also lead sulphite blackening that can be removed if necessary, the eventual cleaning should be carefully evaluated because it might not always be necessary.

4.4.4 CONSOLIDATION

If an object has been excavated it may require temporary reinforcement.

Cyclododecane ($C_{12}H_{24}$), a solid hydrocarbon that sublimates at room temperature, can be

used as a temporary consolidant for weak or brittle material also straight after excavation. Cyclododecane can be heated and applied as a melt, using a brush or heated spatula, or dissolved in non-polar or aromatic solvents and used by spray, brush or injection.

If the object requires consolidation, then the consolidants may be applied by brush, airbrush, pipette, injection, with compresses or by immersion. The choice of consolidants and the method of application will depend on the condition of the object. The correct choice of the method is extremely important as the consolidant is going to remain in the object forever.

Experience showed that solvent based consolidants such as Paraloid B-72, acrylic resin or polyvinylacetate in acetone or toluene are better than emulsions.

4.4.5 BONDING

The chosen adhesive needs to be reversible, non yellowing, stable, and easy to apply. It must not affect the ceramic body in any way. Equally, it must have enough strength to hold the fragments together without shrinkage.

The viscosity of the adhesive chosen is also important.

The correct density will depend on the porosity of the ceramic.

It should remain stable within the parameters of the Class A resin (which is for 100 years).

The best results are given by a solvent-based adhesive, which is the acrylic adhesive such as Paraloid B-72 (known as Acryloid B-72 outside Europe). Paraloid B-72 has been found very stable and reversible in its wide range of use in conservation.

On the other hand, in the last 2 decades there are publications in international conservation journals about the instability of the cellulose nitrate, which is unfortunately still widely used for bonding archaeological ceramics.

4.4.6 INTEGRATION OR FORMAL RESTORATION

There are various arguments for and against the use of fillings.

The decision to use fillings, and to what extent, will depend on the importance of the piece, the historical context of the object, the extent of the collection, the money and time available, the future handling, storage and display. If the object requires reconstruction, the general rule is that the material chosen needs to be reversible and have good aging properties. The best material used is based on a particular industrial plaster. The best filler

is Polyfilla powder for indoor (also called Moltotill innen) based on calcium sulphate. It does not shrink, it is easy to shape and remains workable for longer; is easy to mix with pigments and can be easily painted. It also allows further filler to be added once the first application has set. In some cases only large gaps should be filled but not missing chips.

The best solution is to fill the area to the same level as the original surface and not a few millimeter below it. In the archaeological world, the decision was often taken to fill lower in order to highlight the difference between old and new. This gap often attracted dirt and by making the filling lower, the original border got damaged or weakened.

It is worth mentioning that in some cases detachable fills can also be made.

4.4.7 CHROMATIC RESTORATION

In some cases, pigments are already put into the powder of the filling material, in order to obtain a suitable homogenous colour. In this case no painting is necessary, sometimes the surface only needs a protection coat depending on the surface to be obtained.

In most cases it is right to choose a background colour to paint on the fill. This makes the fills distinguishable from the original whilst at the same time being discreet. In other cases the retouching of the decoration might close break lines or even go further and complete iconographic motifs if they are known.

There is no general rule; it really depends on the demands of the collection.

If it is necessary to retain the reconstruction of the decoration, it needs to be closely matched to the original but easily distinguishable on closer examination.

From an aesthetic point of view, it is important that the gaze of someone looking at the objects slips away and does not hang anywhere.

4.4.8 CATALOGUING AND PHOTOGRAPHIC DOCUMENTATION

Examination should be done when the object arrives in the museum, studio or collection. It is important to record all observations before any treatment begins: how it was transported, packed, its general condition, the size and number of fragments and anything else of relevance.

The photographic and graphic record plays an important part.

Digital photographic recording makes everything easier nowadays, the recording is easy and data can be immediately entered in a data base.

If possible black and white photos and colour slides should also be made because, if properly stored, they last a long time. A scale of millimetres should appear in each photographic record and possibly with the reference numbers of the object.

4.4.9 HANDLING AND PACKAGING

The package, already done at the site, is very important because sometimes it is the definitive one for the object. Also important is to place the object in the container and pay attention to possible wrong climate that could be created within it. It is therefore important to choose the right material for storing items, depending on what kind of storage room is available, which also takes into account whether the object is dirty, heavy, etc.. The best material for containers are boxes made of polypropylene. It is important that the boxes are easy to handle and therefore not too large, rigid, impact resistant, that do not chemically interact with the exhibits, resistant to weathering, moisture and biodeterioration. It is very important that the object is always accompanied by a fact sheet with information about the origin, the excavation data, with the dates of discovery and storage, conservation status and everything is useful to know it immediately.

For excavated ceramic objects it is important that the relative humidity remains below 55%, in order to prevent mold.

If inventorying data is to be written on the surface of the find, in this case a small rectangular area should be painted by brush with a primer such as Paraloid B-72 diluted in solvent. Once dry, the inventory number or data can be written on it with a stable marker or drawing ink.

4.5 Case studies

4.5.1 SYRIAN PAINTED POTTERY

DESCRIPTION OF THE PROBLEM

The material is represented by fourteen large fragments coming from a Ugarit archaeological site and dates back to the XII century B.C. (medium Bronze Age). Two main questions were individuated with reference to these samples:

- a) Is there a slip applied on the surface of ceramics with the aim of giving a light colour to the surface and therefore a good evidence to the decorations?
- b) Is the composition of the red and brown decorations always the same or there is a difference between red and brown?

Depending on the colour of the surface and of the decorations, two homogeneous groups were observed, for a total of 11 fragments (Figure 4.20), while three are different, also between them, and were neglected. The characteristics of the two groups are as follows:

- 1) very light coloured surface (beige) with brown decorations: fragments SAMA1, SAMA2, SAMA3, SAMA4, SAMA5 and SAMA11;
- 2) light coloured surface with red decorations: fragments SAMA1, SAMA7, SAMA8, SAMA9 and SAMA10.

SAMPLING

To answer the previous questions, four pieces (two for each group) were selected for observing them in thin section:

- Group 1: SAMA3 and SAMA4
- Group 2: SAMA7 and SAMA8

After breaking of the specimens for the thin sections, new observations were made on the fresh surface, also with the help of a stereomicroscope, in order to confirm or modify the observations already made on the old rupture surfaces. As it regards the coloured decorations, it was decided to analyze them through portable EDS-XRF, because this technique is non destructive.



Figure 4.20 – The two groups of painted pottery selected for sampling.

OBSERVATIONS AT THE OPTICAL MICROSCOPE

Observations at the stereomicroscope were made on the fresh fracture surface of the ceramic samples SAMA3, SAMA4, SAMA7 and SAMA8. In particular it was confirmed that there is not a clear border between the superficial light-colored paste and the internal red-colored ceramic paste. This would mean that there is a superficial whitening phenomenon, but not the application of a white slip layer.

At the mineralogical microscope, in thin section, all the samples observed look similar to each other. The paste is red in color, grain-size distribution is serial, the maximum dimension is around 250 micron, that is fine sand; the non plastic grains (around 15%) are made of rounded mono-crystalline quartz, mica (muscovite more than biotite) and feldspar. The matrix is isotropic; iron nodules and argillaceous rock fragments are also present. Towards the outer surface, there is a layer, with a thickness around 500-700 microns, which presents a great amount of mica lamellae and it is clearly distinguishable from the paste due to the lighter color and the scarcity of non plastic grains. Nothing similar is present towards the inner surface.

X-RAY FLUORESCENCE ANALYSIS

Through the X-ray fluorescence analysis (Figure 4.21), it was possible to realize that all the decorations are made with a iron-rich pigment, for both the two series of samples. In

particular, no manganese was observed apart from the usual traces that are in clays. In addition, it was possible to ensure that the calcium concentration is very high and similar inside and outwards.

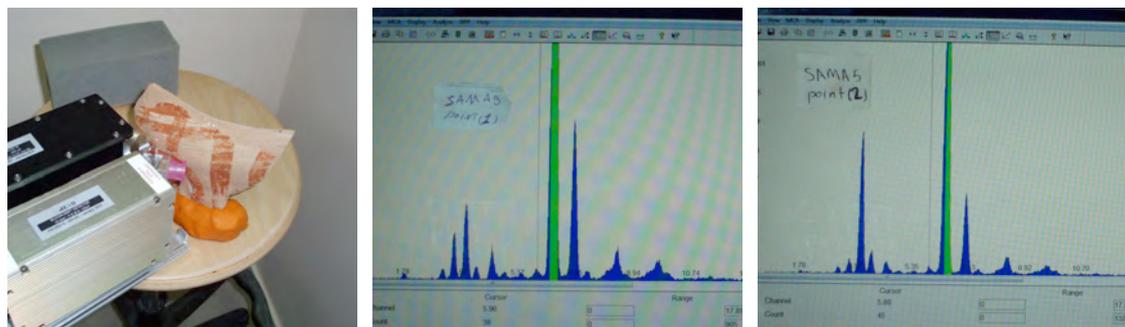


Figure 4.21 – Analysis of the red colored decoration and two of the obtained spectra.

CONCLUSIONS

The presence of the lighter colored layer could be interpreted as a coating maybe made with the same clayey raw material used for the paste, after separation of the coarse fraction, with concentration of the finer clay fraction. This assumption derives from the greater abundance of mica in the lights layer than the internal parts. The light color of the layer could be due to the use of sea-water that during firing allows to obtain a lighter color. The sodium chloride, present in the sea-water, during the drying step migrates toward the surface and so its presence during firing provokes the whitening.

Because a light surface layer is clearly present only on the outer surface of the artefact, it is possible that the sea-water was used only for the external surface treatment (realization and/or application of slip by brush or by hand) and not as water for mixing the clay for the ceramic paste. It is worth mentioning that the archaeological site is near the sea and thus the supply of sea water was very easy.

All the decorations contain only iron as coloring element. As a consequence, the different tonalities of color should be interpreted as the result of a different firing atmosphere: more oxidant in case of red colored decorations and vice-versa. The reddish color of the paste under the decorations is in agreement with this hypothesis.

4.5.2 INLAID ISLAMIC CERAMICS

In the Timurid period most of the wall ceramic coverings were made by the technique of the inlay work. One of the oldest example is given by the funerary monuments in the cemetery of Sahi Zinde in Samarkand (Uzbekistan), which date from the second half of the 14th century to the beginning of the 15th century (Figure 4.22). Then the technique quickly spread throughout the Islamic world, from neighboring countries like Iran today, where the Imam Mosque in Isfahan is one of the best known examples.

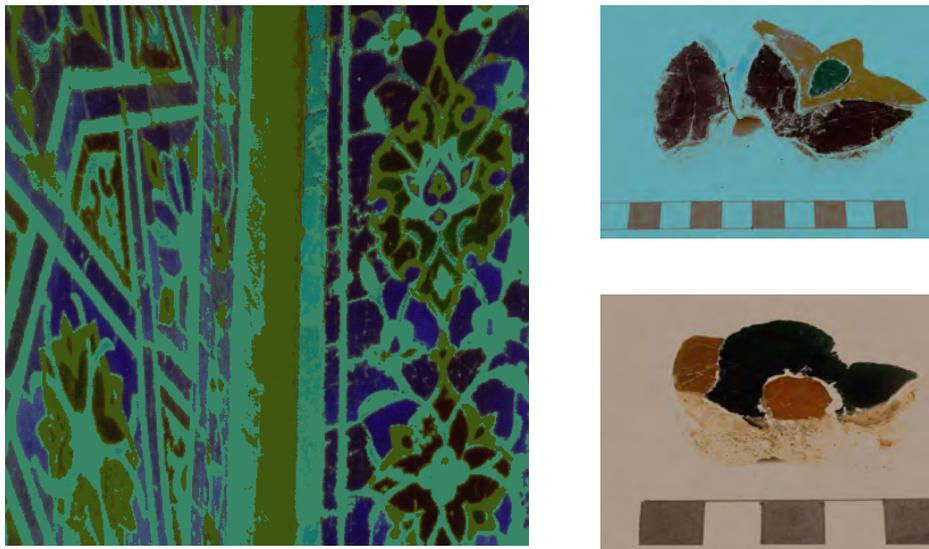


Figure 4.22 – Inlaid ceramic coverings in the Sahi Zinde monumental cemetery in Samarkand, Uzbekistan (half 14th century – beginning 15th century).

This architectonic product needs a suitable ceramic paste which could be easily cut into very different and often very complicated shapes. Its chemical composition, compared with that of a brick and local clay (Table 4.6) shows that it is characterized by a large amount of silica, while the brick paste is very similar to the local clay.

Of course, the high content of silica is due to a high content of quartz (around 70%). This means that the paste has not strong ceramic linkages, which ensure the possibility to cut the fired paste without particular difficulty. This special composition of the ceramic paste, suitable for inlay works, is named ‘stonepaste’.

The large amount of quartz also gives a light color to the ceramic paste, thereby allowing variously colored glazes have better efficacy. Both transparent and opaque glazes could be applied on the unfired support, because very small amount of gases developed from the

paste.

Table 4.6 – Chemical composition of ceramic pastes and clays from Samarkand.

Oxide	Stonepaste		Brick SZ10	Local clay
	SZ7	SZ8		
SiO ₂	82.53	80.70	60.42	63.30
Al ₂ O ₃	4.30	4.89	12.00	12.02
TiO ₂	0.12	0.14	0.71	0.69
Fe ₂ O ₃	0.84	1.00	4.89	4.38
MnO	0.06	0.05	0.10	0.09
MgO	3.52	3.65	4.09	3.25
CaO	5.87	6.07	13.10	11.56
Na ₂ O	1.30	1.84	1.56	1.53
K ₂ O	1.28	1.42	2.87	2.95
P ₂ O ₅	0.18	0.24	0.26	0.23
Total	100.00	100.00	100.00	100.00
I.L.	1.44	0.90	10.04	11.87

As it regards the chemical composition of the glazes in Samarkand (Table 4.7), it can be seen that the transparent glazes are very different from the opaque glazes. These last are lead-alkaline glazes (12-13% PbO, 10-12% Na₂O+K₂O) and contain tin oxide (6-7% SnO₂), while transparent glazes are lead-free as well as of tin. Tin oxide develops the function of opacifier and lead is added together with tin oxide in order to favour its opacifying power.

Table 4.7 – Chemical composition of transparent and opaque glazes from Samarkand.

Element	Transparent glazes				Opaque glazes	
	IK2 blue	IK8 white	IK8 blue	IK10 blue	IK4 turquoise	IK1 turquoise

SiO ₂	77.54	79.13	77.74	70.37	59.00	58.87
Al ₂ O ₃	2.82	2.54	2.49	3.22	2.36	2.68
TiO ₂	0.10	0.10	0.10	0.12	0.09	0.10
Fe ₂ O ₃	2.07	0.95	2.34	2.79	0.76	0.87
MgO	2.12	2.68	2.37	2.52	2.14	2.00
CaO	3.65	4.34	3.91	5.02	3.50	3.57
Na ₂ O	8.16	6.69	6.27	10.33	7.90	10.03
K ₂ O	2.15	1.89	1.97	3.09	2.10	2.28
PbO	0.07	0.86	0.82	0.91	12.96	11.63
SnO ₂	0.01	0.35	0.33	0.01	7.04	5.76
CuO	0.01	0.01	0.03	0.06	1.75	1.70
CoO	0.34	0.05	0.67	0.32	0.01	0.01
As ₂ O ₃	0.34	0.05	0.54	0.34	0.00	0.00
MnO	0.05	0.03	0.03	0.04	0.04	0.04
P ₂ O ₅	0.27	0.26	0.25	0.39	0.25	0.30
SO ₃	0.30	0.07	0.14	0.47	0.10	0.14

4.6 Examples of restoration

4.6.1 RESTORATION AND PRESENTATION OF AN ETRUSCAN BUCCHERO

The intervention illustrated herein involves a one-handled jug, or *oinochoe*, in Etruscan bucchero, dated at the second half of the VI century B.C., produced in the city of Chiusi (a city of Etruscan origin in the province of Siena, Italy). This artefact, which came from a private collection, was seriously damaged after falling from a height of over 2 metres (Figure 4.23). As a result, this archaeological find, when delivered to the restorer, was in such a fragmentary state (about 125 pieces) as to make it difficult to correctly identify its original form, which had been substantially compromised.



Figure 4.23 – View of the fragments of the *oinochoe* on the external (left) and internal (right) surfaces.

Furthermore, an initial ‘inspection’, aimed at evaluating the state of conservation, indicated that the artefact had already undergone two previous restorations, as demonstrated more specifically by:

- the presence of at least two kinds of glue, one of which, likely the older one, was resinous and found only along the crack between globular body and foot of the *oinochoe*;
- the inner surface of numerous shards totally coated in grey plaster with shreds of paper;
- the several fracture lines, which showed traces of colophony and several signs of filling;
- the missing parts previously reconstructed; in fact, some limited zones were not made of earthenware, but rather of plaster mixed with animal glue and black ink.

First of all, the various fragments of these plaster-animal glue-ink “fillings” came loose after being soaked in warm water (45°-50° C). Once dried, the surfaces were carefully dabbed clean with pads dampened in a solution called 3A, containing water (30%), alcohol (35%), and acetone (35%), and then further cleaned with benzene, trichloroethylene, and petroleum ether. In fact, the water-alcohol-ketone solution is capable of removing the plaster, ink, and animal glue residue, and colophony (the latter of which was used locally as an adhesive), while the aliphatic hydrocarbon and aromatic solvents remove wax and other fatty substances (including, probably, even shoe polish) used in the past to give the surface of the *bucchero* greater sheen and a more intense black hue.

At this point, following standard consolidation by applying acrylic resin (Paraloid B72) dissolved in 2-3% acetone, the assembly phase and gluing the numerous fragments together began. This operation was the most complex of the entire intervention, mostly due to the extensive filing, carried out during a previous restoration, presumably during the

XIX century, found on several edges of the shards (to the point that some of these shards no longer made precise contact with the adjacent pieces).

Therefore, first the parts resulting from the most recent and devastating fall (thereby with “freshly” broken edges that fit perfectly together) were glued with a polyvinyl butyral resin (Mowital B60H in pure alcohol) spread repeatedly over the abovementioned cracks. Successively, the gluing of fragments presenting abrasions and/or filing of the joints was organised as follows. The various shards were arranged, taking into account a series of elements like: the existing potential points of contact; the decoration; the thickness; the curvature; the potter’s turning lines visible on the back. Then, the pieces were temporarily glued together with sporadic drops of cyanoacrylate resins (Figure 4.24, left) and (once the correct position had been verified) were definitively glued with two-part epoxy resin being allowed to run into the spaces between the pieces: before, a coat of acrylic primer had been applied to the fracture lines to facilitate a potential reversal of the gluing process.

Upon conclusion of the reassembly and gluing of the fragments, the problem of the reconstruction of the missing pieces (that had been previously and ineptly reconstructed with plaster, glue, and ink) was dealt with, as well as restoration of the areas where vigorous filing had abraded the ceramic material. This procedure was necessary not only for aesthetic reasons, but mainly to guarantee the overall static and structural stability of the artefact. Therefore, all these ‘spaces’ were filled with a mixture of dental plaster (70%) and fine *scagliola* (30%) suitable moulded and finished (Figure 4.24, right). Successively, the surface was coloured to minimise the differences between the reconstructed and original parts of the artefact, always guaranteeing easy distinction between reconstructed and authentic zones. More specifically, the following procedure was used in applying the ‘*a puntinato*’ chromatic treatment. The missing parts were duly integrated and shaped before being tinted uniformly with an acrylic base color, fundamentally ‘black anthracite’, to emulate the color of the bucchero (even if of a slightly lighter tone). The second step was to ‘spray’ multiple fine ‘pinpoints’, done with the use of hard-bristled tooth brush. The shades of the pinpoints vary from intense black to dark grey, with sporadic pinpoints of dark blue, dark red, and ochre yellow, depending on the shades of color perceptible on the original earthenware. This method of spraying ‘pinpoints’ takes into account the ‘suggestions’ indicated by the artefact itself. In fact, the *oinochoe* in bucchero, following

close observation, has not a uniformly black surface, but rather various shadings, even if extremely subtle.



Figure 4.24 – Assembling and gluing stages (left); reconstruction and filling phases (right).

Therefore, the application of colors with this method of using small and variegated pinpoints (overlapping and/or combined) served both to better blend the colors of the original earthenware with those applied to the reconstructed areas, while also facilitating the identification of the reconstructed areas and distinguishing them from the authentic ones thanks to this colored “dusting”. Furthermore, the “*a puntinato*” method resulted in the replication of the characteristic sheen of the bucchero, always by means of spraying minuscule pinpoints of pearl white color (Figure 4.25).



Figure 4.25 – Details on the pictorial restoration on the reconstructed zones with the “puntinato” method.

Thanks to this restoration, it was once again possible to comprehend, and therefore appreciate, the artefact that would have otherwise been compromised by such a devastating event; consequentially, the recovery of the *‘form’* also allowed the recovery of the *‘essence’* of this work (Figure 4.26).



Figure 4.26 – The *oinochoe* upon conclusion of the restoration.

4.6.2 RESTORATION OF THREE MAJOLICA PLATES OF THE 15TH CENTURY

The conservation work illustrated here is about three majolica plates, tin glazed terracotta, dated 15th century. These three artefacts, which are from a private collection, were broken and dirty. Plate number 1 was broken into five fragments, number 2 in three fragments, number 3 in two fragments (Figure 4.27, at the top). All three plates had encrustations along the fractures and had missing areas.

The owner has kindly made available the three plates as case studies, in order to show three different ways of decoration of the missing areas. The reconstruction of the missing pieces in this case was necessary for aesthetic reasons, but at the same time to guarantee the overall static and structural stability of the artefact (for plate 1 and 2). The task was that no original glaze should be covered by the retouching.

The first cleaning was done by washing with distilled water using a soft sponge and brushes. The glaze was then cleaned with cotton swabs wetted with a solution of 5% ammonium hydroxide in distilled water.

The incrustations along the breaks were removed mechanically with hand tools because otherwise a perfect alignment of the fragments was not possible. The assembly of the fragments was done with the reversible adhesive acrylic resin (Paraloid B72) diluted in acetone (Figure 4.27, in the middle).





Figure 1 – The three majolica plates dated 15th century: before, during and after restoration (over, in the middle and below respectively).

There is no general rule about how far one should go with the retouching of the missing areas; it really depends on the demand of the collection. The three plates were a good example to show three options (Figure 4.27, at the bottom):

- for one plate it was chosen a ground color to be painted on the fill, to make the fill distinguishable from the original but at the same time discreet;
- in the second case, above the ground color, the inpainting of the decoration was applied; in any case the retouching of the decoration ends near the fracture lines;
- in the third case it was decided to go further and complete the iconographic motifs because the chromatic integrations are easily reversible; in this case the decoration was closely matched to the original, but is easily distinguishable by close examination. No original glaze was covered by retouching.

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5 – CLAY TABLETS

5.1 Definition

The clay tablets are slabs of unfired or fired clay used in the past as a writing medium for documents on various subjects in order to conserve them for a more or less long time. They can be of various size and shape, starting from few centimetres to half a meter or more. The largest tablets are approximately rectangular with a plane shape, while the smallest ones are biconvex in shape and can be held in the palm of the hand. In fact, they were shaped by mixing the clay in the palm of a hand.

Only a minority is constituted by a clay envelope enclosing the true tablet. The clay tablets were used by the Mesopotamian civilizations (Sumerian, Babylonian, Assyrian and Hittite) since the second half of the fourth millennium B.C., and most of them are written in cuneiform characters, which were generally imprinted with a blunt reed stylus (Figure 5.1). Cuneiform script is one of the earliest forms of writing, which emerged around the 33th century B.C. It included about one thousand characters in the Early Bronze Age, but only about four hundreds in the Late Bronze Age. The latest known tablet in cuneiform characters dates back to 75 A.D.

The tablets were imprinted when the clay paste was at plastic state, that is sufficiently soft to impress the characters of the writing, and with a sufficient mechanical resistance that allowed to resist to the stresses of writing.



Figure 5.1 – A Babylonian tablet (87 B.C.), which describes the arrival of the comet of Halley.

After impressing the text, the tablets were dried by exposition to the sun, and sometime fired in order to make them much harder and durable, in particular the largest ones and destined to be kept for a very long time.

The compositional characteristics of the clays used for the tablets are the same of the clays for ceramics and one can find everything in the correspondent Chapter 4. There, information can be found also with reference to the significance of 'plastic state' of a clay and the behaviour of the clay during drying as well.

The tablets may be personal or business letters, can represent legal documents or parts of books as well. The clay tablets that function as checks, provided by the famous Code of Hammurabi, the Babylonian king who reigned from 1792 to 1750 B.C., are a fine example of use of this type of artefact in commercial field.

After a certain time, most unfired tablets became useless, so that they were destroyed and the clay reused for new tablets. Therefore, it is clear that the tablets produced in the past are much more numerous than those recovered. Notwithstanding this, at least five hundred thousand tablets are today kept in museums, and others are continuously retrieved from the archaeological excavations in the regions where they were used.

Cuneiform writing lasted several centuries; then, during the Iron Age, it was completely replaced by alphabetic writing.

5.2 Deterioration

The clay tablets are found in regions where the climate is generally dry, so they are often in good condition. In fact, the main deteriorating consequences of unfired clay tablets are due to the interaction with water. This occurs when the burial environment is humid, because the clay minerals are highly sensitive to the action of water and can absorb it in large quantity. As a consequence, they will get plastic or even muddy, so suffering different kinds of damage. If it deals with many tablets, all coming from the same store, they will be piled randomly and will join together to become practically non-detachable from one another. Of course, in this case you may lose the opportunity to read the entire text imprinted on the clay surface. In addition, the tablets undergo significant deformations, and the cuneiform characters with them, so that even the characters that are in sight could

become readable with high difficulty.

The alternation of wet and dry phases also leads to swelling and contraction phenomena, which can give rise to deformations, formation of fissures, fragmentation of a tablet in two or more pieces, and even to structural weakening and subsequent pulverization.

When tablets are humid, particles of the burial soil can adhere to them, and after recovery many of these particles remain adherent to the surface. The elimination of these particles surely is one of the most difficult cleaning operations. Obviously, the removal of soil particles is necessary in order to highlight the angular form of the characters of the cuneiform writing.

The problem of soluble salts also applies to raw clay tablets, because they are very porous even though they rapidly become little permeable in contact with water solutions. But the duration of burial and then the contact with water is so long that all the clayey mass can be infiltrated by the solutions which circulate in the soil.

The problem of soluble salts likely is more hard for cooked clay tablets, because they are less sensitive to water and their permeability virtually does not change. In such a way, all the mass of the tablets can be rapidly soaked with water and its evaporation concentrates the soluble salts near and on the surface. The crystallization of these salts, mainly chlorides and sulphates, generates internal tensions in the tablets and little by little they undergo a gradual detachment of material starting from the surface. This effect adds to that of the hydration / dehydration of clay minerals, thus increasing the speed of the degradation process.

5.3 Conservative intervention

5.3.1 Intervention during the excavation

During an archaeological excavation it is possible to find only one or few clay tablets, but more frequently small or big archives are encountered. Three different types of clay tablets can be present:

- unfired clay tablets,
- fired tablets,
- originally poorly fired clay tablets, or badly cooked clay tablets as a consequence of accidental conditions such as the fire of the rooms where they were stored.

Most of the recovered tablets are unfired, because only a minority of tablets was destined

to be fired, and the majority was stored in form of dried clay. During the recovery, however, it is difficult to determine with certainty whether they had been baked or not.

The unfired cuneiform tablets can be distinguished from the archaeological ground with difficulty, because this last often formed through the collapse of the walls where the tablets were kept. In fact, in most cases the walls were built by using clayey material. The main difference comes from the fact that the tablets were usually manufactured with depurated very fine clay.

It is very important to recognize the single artefacts inside the ground, so that it is possible to separate them from each other. Of course, you have to avoid the forced separation of the tablets which adhere between them due to the humidity in the ground. In these cases it can be sufficient to carry out a natural drying for obtaining an 'automatic' detachment. But the drying should be gradual in order to avoid further cracking and fragmentation of the tablets. To this purpose, it is opportune to protect the objects from the sun during the excavation. It can not be excluded that at the beginning of the twentieth century it was just the recovery of fired or partially fired tablets to suggest to cook the unfired clay tablets for their better conservation. Both in past and in recent times, somebody has realized the firing of the clay tablets on-site just at the time of excavation.

The procedure of the preservation work can be a little different in the case of raw and cooked clay tablets. In addition, there are two different approaches regarding intervention on the uncooked tablets: on one side the supporters of the opportunity to cook the tablets to give them a high mechanical strength, on the other side the supporters of the opportunity to keep the tablets as they are, that is uncooked.

The different procedures are summarized in Figure 5.2, where documentation is not considered, because it is very important and should be realized in every step of the intervention.

5.3.2 Preliminary cleaning

Preliminary cleaning of the recovered tablets should be executed after drying the objects, when most part of the soil particles spontaneously detach due to the shrinkage occurring during drying. In addition, the drying favours an increase of the mechanical resistance of the tablets, so that they can better support the mechanical stresses caused by the tools used for cleaning them.

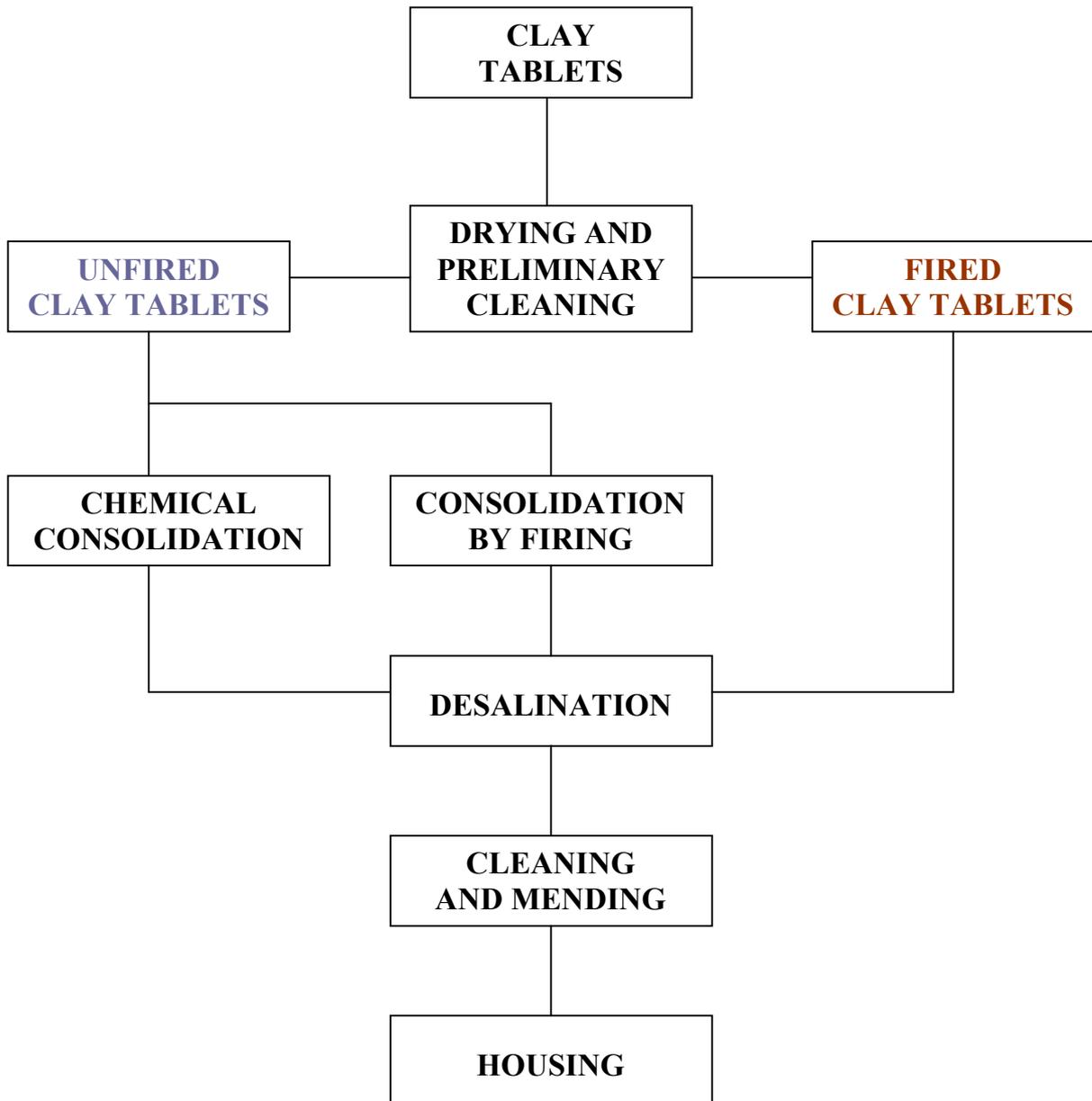


Figure 5.2 – Schematization of the different procedures proposed for the conservation of fired and unfired clay tablets.

Another positive effect of drying before cleaning refers to the soluble salts which are usually present in the clay tablets. These salts come out and crystallize on the surface of the residual burial soil that covers the artefacts, so that they are at least partially eliminated during the preliminary cleaning together with the same soil particles. From this point of view, this procedure constitutes a good way for realizing a first phase of desalination. On the other hand, the salt crystallization can weaken the structure of the tablet; therefore the preliminary cleaning should be performed with caution, avoiding the occurrence of too strong stresses. Of course, fired or partially fired tablets need less caution than the unfired ones.

Preliminary cleaning should be always carried out at the stereomicroscope by means of scalpel and acuminated wooden instruments, paying attention to fix all the areas at risk with acrylic adhesive.

Finally, in order to avoid greater damages, carbonate deposits and thick deposits of salt crystals should not be removed, even though they partially or completely impede the readability of the text. Analogously, eventual roots should be cut near the surface and not extirpated from the artefact.

In case of tablets originally baked or today cooked, when the cuneiform images are almost illegible, the use of some soft form of sand blasting can be taken into account in order to remove debris and minute particles from the surface without causing any damage.

5.3.3 Consolidation of unfired tablets

It is very difficult to successfully treat the unfired tablets, and the use of an adhesive/consolidating should be done after a careful evaluation by an expert conservator of clay tablets and ceramics, with the aim of evaluating the general characteristics and particularly the conservation state of the tablets.

In addition, it would be very useful to be sure that the tablets are really unfired. This information can be quite easily achieved by analyzing them by means of X-ray diffractometry.

Unfortunately it deals with a destructive technique, but this should not be a big problem when a lot of homogeneous archaeological material was recovered. Alternatively, an expert researcher can obtain good indications by analyzing the tablets by means of UV/Vis spectroscopy, which needs only few milligrams of specimen.

CHEMICAL CONSOLIDATION

Since a lot of time, firing is a very usual practice for the consolidation of unfired clay tablets. When this practice was introduced, the studies on the conservation treatments were at an initial stage, while today it is sometime possible to realize conservation procedures that can allow the unfired clay artefacts be well conserved without applying thermal treatments. In addition, it needs to consider that the number of recovered tablets is very high and it would not be possible to cook all them in a relatively short time.

Environments with controlled temperature and relative humidity can be sufficient for the conservation of the tablets without any other intervention, because these conditions prevent the leakage of the soluble salts. On the other hand, it is evident that a perfect control of these environmental parameters is practically impossible, so that some conservation intervention is advisable.

After the preliminary cleaning, the restorer will proceed to reassemble the fragmented objects, if they are. It is suggested to pre-consolidate the fracture surfaces by applying a diluted solution of paraloid B70 in acetone or ethyl silicate. Then, the joining of fragmented portions can be executed by using acrylic glues, which are preferable in comparison with the vinylic ones, because they are more resistant to humidity action. If there are points with more or less deep fractures, they will be treated with infiltrations of medium concentrated paraloid B70. Alternatively, you can try to consolidate the tablet by using ethyl silicate, which is generally utilized for consolidating unfired clay bricks.

In general, the consolidating treatments of unfired clay tablets are possible accordingly to the high open porosity of the unfired clay, even though the penetration will be not very high because the treatment rapidly makes the surface impermeable. Of course, it needs that the clay is not humid, because the water would make the surface of the clay artefact impermeable and would preclude any penetration of the consolidating solution. The consolidation treatment can be carried out by immersion for some hours, or for less than one hour when it is realized under partial vacuum.

The research about the conservation treatments of the unfired tablets is quite scarce, and it would be hoped for an increase of activity in this field. Some research groups are evaluating how to use the nanotechnologies and the nano-materials to this purpose. In particular, they are planning to experiment nano-limes and nano-silica as consolidating materials, because they are inorganic compounds and would not change the composition of the clay tablets in a significant way. This would be particularly true when it deals with

tablets made of carbonate-rich clays, as frequently happens.

On the other hand, nano-limes have been already successfully used for the consolidation of stone, mortar, plaster, fresco, and wall painting. The particles of nano-lime have an average size of the order of one hundred nano-meters and are sold in form of suspension in different solvents. Treatment with these products will result in the evaporation of the solvent and formation of calcium hydroxide. In presence of humidity, the calcium hydroxide converts into calcium carbonate, through reaction with atmospheric carbon dioxide, as occurs in the traditional mortars. This means that the treatment should be carried out before the complete drying of the clay tablet, unfortunately when the object has not its maximum mechanical resistance. The drying will be completed after consolidation of the treated tablets.

Notwithstanding the fineness of the particles, it seems that the penetration of the nano-lime suspensions is not very high. The result will be a good consolidation of the superficial parts of the clay tablets, which, however, are the ones more likely subjected to wear.

CONSOLIDATION THROUGH FIRING

Unfired clay is little resistant against the action of water, because it is easily disaggregated and many clay minerals are easily attacked and altered. In addition, clay artefacts have a low mechanical resistance. On the contrary, fired clay (terracotta) is mechanically resistant and less attacked by water than unfired clay. Having this in mind, since the beginning of the twentieth century is common practice to cook the raw clay tablets, in order to consolidate them. Tablets were sometimes baked at the time of excavation by using metal boxes filled with sand, even though more recently the on-site cooking was more controlled. But such a type of practice should not be considered a normal conservative intervention, because it completely modifies the composition of the objects and the nature of what is conserved is very different from that of the unfired items. This is not in line with the principles of conservation; in fact, this type of treatment is not practiced in any other kind of artefacts.

The firing of clay tablets should be considered an exceptional type of intervention to be implemented when you cannot do otherwise in order to retain the ability to read what is written on the tablets. Fortunately, usually a large number of tablets are found together, so you can keep many of them raw, as evidence of the initial condition of those cooked. On the other hand, the work of cooking is very long and in the case of a large collection of

clay tablets could take years. Preferably, will be fired those tablets or fragments that show the presence of deposits of calcium carbonate or other salts which cannot be mechanically removed, unless some parts are held together just by the salts. After cooking, if still present, probably the deposits will be more easily removed, mechanically or chemically.

The cooking of well dried clay tablets is usually carried out in programmable kilns with a very low thermal gradient and several steps before reaching the maximum temperature, so that cooking can last up to one week. Depending on the authors, the maximum firing temperature may vary greatly, from 675 to 800 °C.

In this way they try to reduce to the minimum the breaking of tablets, due to the chemical reactions which occur during heating and cooling (see chapter 4, and in particular 4.1.4 and 4.1.5). The main result of these reactions will be a significant reduction of the dimensions of the tablets, with the possibility of breaking if the contraction does not occur contemporarily in all the positions of a tablet.

Another factor that may affect the outcome of cooking is the technique of manufacturing the tablets. Where they were processed using a homogeneous clay paste, there is a good guarantee of success. On the contrary, when the tablets were manufactured by superimposing several layers of clay, likely these layers can separate during cooking.

Anyway, you can never completely avoid the occurrence of fractures due to their presence at a latent state. In fact, the proportion of broken tablets after firing is always very high and often beyond repair. For this reason someone cooks the tablets immersed in sand contained in suitable container. This safety measure should avoid, in case of detachment, the fragments move away from each other and thus can easily be relocated successfully. In any case, also the tiniest fragments must be recovered and reattached, especially when they have characters engraved on the surface, and their loss would make the reading very difficult. In this case it is opportune to cook the fragments separately and attach them together after cooking, because the thermal treatment would burn the adhesives used. These adhesives are the same used for pottery (see 5.3.4 and also Chapter 4).

Because the clay tablets often break further during the cooking process, it is advisable to take pictures of the tablets before cooking them. Then the pictures will be used as guides for understanding the precise position of the fragments, as they were pieces of a puzzle. An acrylic adhesive is suitable to join the fragments.

The practice of firing the tablets has become very common, but there are not enough

studies available to determine which are the best conditions especially with regard to the maximum firing temperature. In fact, the above mentioned temperature of 675-800 °C does not take into account the composition of the clay, namely the presence or not of carbonates. In their absence, 675-800 °C can be retained a valid temperature, because it ensures the complete destruction of clay minerals and the achievement of a sufficiently stable physical state.

On the opposite case, that is in presence of carbonates (for example calcite), cooking at 750-800 °C could result in the partial or complete decomposition of calcite, with a more or less abundant residue of calcium oxide. In fact this temperature could be non sufficiently high to ensure the formation of stable compounds and the residual calcium oxide will then be transformed into calcite again (see Chapter 4, namely 4.1.4 and 4.3.2). This reaction implies an increase in volume which can lead to the fragmentation or even the pulverization of the tablets.

In conclusion, it would be opportune to know the mineralogical composition of the tablets, and to establish the treatment temperature taking it into consideration. It would be even better to look for the clay used for manufacturing the tablets and to use it to test the best firing temperature for the tablets.

5.3.4 Conservation of fired tablets

The restoration of clay tablets usually is simple when they were well cooked and today they are nothing else than a terracotta.

A viscous solution of Paraloid B70 is relatively not toxic and easy to use for reattaching the detached fragments; a more diluted solution of the same product can act as consolidating for the weak parts close to the junction. The two solutions (viscous and diluted) can be contained in small polythene bottles with a spout, from which their application on the clay tablets is easy.

All the conservative interventions must be done after having well-dried the items, because they acquired a high level of moisture during the burial. Somebody uses to re-fire the tablets, but this would definitively compromise the possibility of dating them through thermo-luminescence analysis. Therefore this practice is not advisable.

Perhaps to facilitate handling of the tablets is opportune to apply a film of Paraloid B70 in solution; other than to consolidate the item, it would have the function of protecting the

surface during the study.

In conclusion, the fired clay tablets can be treated as you act in case of ceramics, and you can refer to Chapter 4.

Sometime the clay tablets are partially cooked as a consequence of accidental events (for examples fire) after their use. In this case the tablets coming from the same excavation would present very heterogeneous cooking level, with large differences among objects and part of a single object. Such a situation does not allow to treat the tablets as if they were cooked; on the contrary, it is advisable to consider them as if they were raw.

5.3.5 Extraction of the soluble salts

Both uncooked and cooked clay tablets very frequently contain soluble salts, which accumulated during the burial period into the porous structure of this type of artefact. In case of uncooked tablets it is better not to perform any desalination treatment before consolidation, because the material is soft and the artefact could be easily damaged, so making the readability of the inscriptions more difficult or even impossible. As a general rule the desalination treatment should be done after consolidation, avoiding the firing of the clay tablets, even though the desalination treatment is easier for the cooked ones.

The extraction of the soluble salts from the smallest tablets can be carried out in distilled or de-ionized water kept in slow motion, changing the water several times and measuring the content of salt in the used solution by means of silver nitrate or a conductivity meter till the disappearance of the salts.

Alternatively they can be soaked in custom designed desalination systems where water is constantly circulating. Generally a long time, of the order of a month, is necessary for completing the treatment. At the end many clay tablets may have broken into two or more pieces, so you need to mend them with the help of photographs taken before the desalination treatment. For the largest tablets, the desalination can also be achieved by using ion exchangeable resins, as it has been illustrated for stone (see Chapter 2).

In any case, it is advisable to think of the possibility not to desalinate the tablets and to keep them in suitable environment, impeding the formation of efflorescence and associated cracks. This is certainly difficult to realize, but today there are the means to do it, without recourse to firing, by controlling temperature and relative humidity in the deposits or in the exhibition rooms.

5.3.6 Housing and digitizing

The problems of the reaction between clay minerals of the unfired clay tablets and atmospheric water are greatly related to their conservation. In many cases also the presence of carbon dioxide in the environment can become very important because it could start carbonation reactions of the calcium contained in the tablets.

This is especially true in the case of tablets cooked in order to consolidate them, when you get highly reactive calcium oxide, ready to form calcium carbonate again. Carbonation occurs with a great increase in volume of the particles and the birth of internal tensions. Therefore, housing projects for clay tablets are very important and requested, according to what has been illustrated in Chapter 1 (Preventive conservation).

Sometimes, clay tablets are housed in small plastic or metallic boxes, stuffed with cotton batting in order to give protection to the tablets. But cotton batting is rather abrasive with reference to unfired clay tablets and, in addition, this type of housing appears rather unprofessional and un-presentable.

In order to manipulate the clay tablets as little as possible, several institutions started to register their collections decades ago using conventional photography. But these registration methods are insufficient because the clay tablets are objects in three dimensions. This is why in recent times several three-dimensional projects of digitization of the clay tablets have been proposed.

Of course these methods are still expensive and not available for all researchers involved in the study of cuneiform texts. However, they are rapidly developing systems cheap enough and also easy to use in the field.

5.4 Case study: Syrian tablets

5.4.1 The archaeological material

The material comes from Tell Mari, Hariry, Derelzoor (Syria), and dates back to the beginning of the II millennium B.C. (Figure 5.3). It deals with thousands of small tablets, about 5 cm long and large, and about 2 cm thick.

The main conservation problems of these tablets come from the apparent formation of grey coloured soluble salts, also during the conservation in the museum, which produce the break-up of the clay; the sample MA-1 (=Th07-05) well represents this problem (Figure

5.3 and 5.4). In order to try to solve the problem, it would be necessary to know the nature of the soluble salts, to understand the mechanism of their formation, and how to eliminate them for stabilizing the artefacts.



Figure 5.3 – The two sides of some clay tablets from Tell Mari (Syria).

5.4.2 Laboratory investigations

The first investigation was made by observing the tablet MA-1 at the stereomicroscope. It was observed that this tablet shows a radial cracking, which concerns a superficial layer of clay, apparently due to the internal growth of a white transparent crystal or aggregate of

crystals.

Semi-quantitative chemical analyses were performed by EDS-XRF through measures in the area of the defect and in a well preserved area of the same side of the sample MA-1 (Figure 5.4).

It was expected that the comparison between the results of the two areas would have given the possibility to deduce the qualitative composition of the whitish material present under the clay at the convergence point of the cracking lines.

The analyses were carried out with 30 KV and 20 μ A and the signal was recorded for 60 seconds. The results, reported in Table 5.1, show only two intense peaks, referable to iron (Fe) and calcium (Ca) respectively.

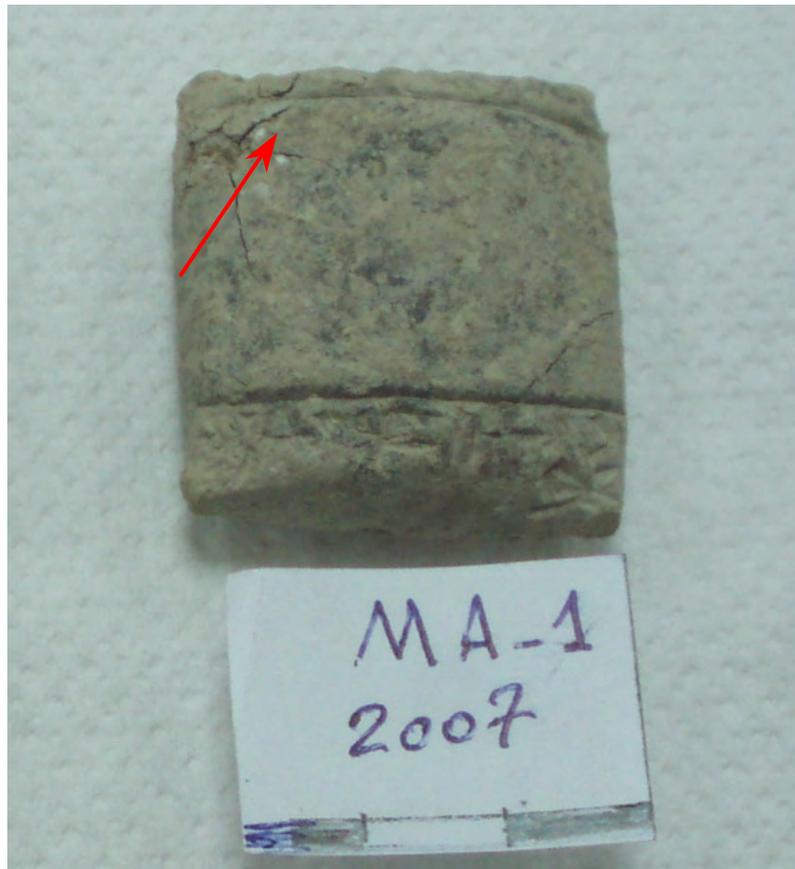


Figure 5.4 – The red arrow indicates the defect where an EDS-XRF analysis was carried out; another analysis was made on the same side at the centre of the tablet.

Table 5.1 – Results of the XRF analyses of the clay tablet MA-1.

Sample	Fe	Ca	K	Mn	Ti	S	Ni	Si	P	Cr	Cl	Sr	V	Zr
Clay paste	4,000	2,200	180	200	120	15	65	35	35	35	20	35	30	35
Defect area	2,400	2,100	110	90	80	75	35	20	30	20	15	40	25	20

All the other peaks are low or very low, taking also into account the background intensity, and they can be attributed to: potassium (K), manganese (Mn), titanium (Ti), sulphur (S), nickel (Ni), silicon (Si), phosphorus (P), chromium (Cr), chlorine (Cl), strontium (Sr) and zirconium (Zr). All these elements are present in low or very low percentages, excluding silicon. Due to its low sensitivity, the detection of silicon means that its concentration is very high, of the order of 50-60% SiO₂.

In the defect area, the main part of the elements (Fe, K, Mn, Ti, Ni, Si, P, Cr, Cl, Zr) shows a drastic decrease of their peak intensity; calcium remains at the same level, while sulphur and strontium show an evident increase of intensity.

These results indicate that only calcium, sulphur and strontium are contained in the material under the cracking, while all the other elements detected by the analysis in this point are attributable to the contribution of the surrounding clay. In addition, because the intensity of calcium is the same in the two analyzed points, it is possible to affirm that calcium is a big component of the internal “crystal”. In fact the contribution to the intensity of calcium by the internal crystal compensates to the lack of intensity due to the smaller exposed portion of clay, which contains a large amount of calcium.

In spite of the low intensity of the sulphur line, it can be stated that also sulphur is a main component of the material under the cracking, because sulphur has a low sensitivity with this type of analysis. On the contrary, the low intensity of strontium indicates that it is present only in minor amount.

In conclusion, the internal crystal would appear to be constituted by calcium and sulphur with minor amounts of strontium. Therefore, it can be hypothesized that it deals with gypsum (CaSO₄·2H₂O).

With the aim of confirming this hypothesis, a small amount of whitish material was taken from another tablet, which was already damaged and broken, and submitted to mineralogical analysis by X-ray diffractometry (XRD). This analysis fully confirmed the hypothesis, showing a lot of gypsum accompanied by traces of quartz, calcite and

plagioclase. Of course, these last are present due to impurities of the clay paste in the analyzed sample.

5.4.3 Conclusions

After attaining the above conclusion on the nature of the whitish material which is present under the clay at the convergence of the cracking lines, it would be very interesting to continue the research, in order to individuate the growth mechanism of gypsum inside the tablet even during its conservation in the museum. Three hypotheses can be suggested:

- gypsum is present in the raw clay used for the preparation of the clay tablets, and it accumulates due to the humidity action,
- gypsum forms due to a reaction between calcium and sulphur already present in the raw clay in separated compounds,
- gypsum forms due to a reaction between calcium present in abundance in the raw clay, in form of calcium carbonate, and sulphur coming from the surrounding environment (pollution?).

According to these hypotheses, a research project could be planned for analysing the raw clay materials outcropping in the area of the archaeological site from where the tablets come, and to evaluate the air quality inside the museum. In addition, it would be opportune to know whether the tablets are fired or simply dried in the sun.

In conclusion, it can be discussed about interventions of consolidation, necessary to restore the compactness of material, but clay tablets show many unsolved problems. Therefore we have reached the awareness that such a particular material still requires deeper and more accurate studies.

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6 – GLASS

6.1 General information

6.1.1 Origin

Glass is a rigid, non-crystalline and transparent material resulting from a treatment at high melting temperature (melting point 1300-1500 °C; partial melting at 1000 °C was achieved in antiquity) of a mixture of silica (vitrifying element, extracted from sand, river pebbles, quartz), calcium carbonate and sodium or potassium (flux elements). From the casting of this mixture a product is obtained called the frites. The frites can be added to accessory elements and then placed on a second fusion.

Plinio tells the story of how some Phoenician traders used sodium carbonate (nitrun) to light a fire on the sandy shore of a river. They saw how the present nitrun fed the flames and melted with siliceous sand, producing an unknown material that became brilliant after cooling. It is likely that the production of glass was born in the Mesopotamian area and in Egypt (the oldest artefacts come from Syria from the fifth millennium BC), and from there it spread to China and the Far East. From the beginning, the working technique was difficult and so the glass was considered a semiprecious material, used in jewellery along side gems. Glass making then spreads to imperial Rome, with the technique of blowing. Later, in the Middle Ages comes the separation of the sodium glass in the Mediterranean, and potassic glass appears within the French-German Countries. At the end of the tenth century the glassworks of Venice started, transferring to Murano from 1291.

6.1.2 Structure and composition

Glass is an amorphous solid obtained by the melting of mixtures with siliceous compositions and by a subsequent fast and controlled cooling. The fundamental structural unit of glass is the SiO₂ tetrahedron. In glass the tetrahedrons are arranged in a disordered manner and the bonds amongst them are variable; also in quartz the SiO₂ tetrahedron is the fundamental structural unit, but here the tetrahedrons are arranged in a regular manner and

bounded among them by precise bounds (Figure 6.1)

Silica (SiO_2), a fundamental component of glass, is called “network former”. The main sources of silica in nature are silicate rocks such as quartz sands and quartz sandstones. Quartz has a high melting point (about $1700\text{ }^\circ\text{C}$) and the kilns in the past were not able to reach these temperatures. At that time, it was necessary to add a flux that lowered the melting point of the glass batch. Fluxes were alkali compounds (Na or K). Historically, the main sources of flux were:

- *Natron* (Na flux)
- Ash of maritime plants (Na flux)
- Ash of continental plants (K flux)

Natron = evaporitic deposit mainly composed of hydrated sodium carbonate.

Ash of maritime plants (called “allume catino”) is mainly composed of sodium and calcium carbonate, with reasonable quantities of Mg and K, and perceptible concentrations of phosphorus.

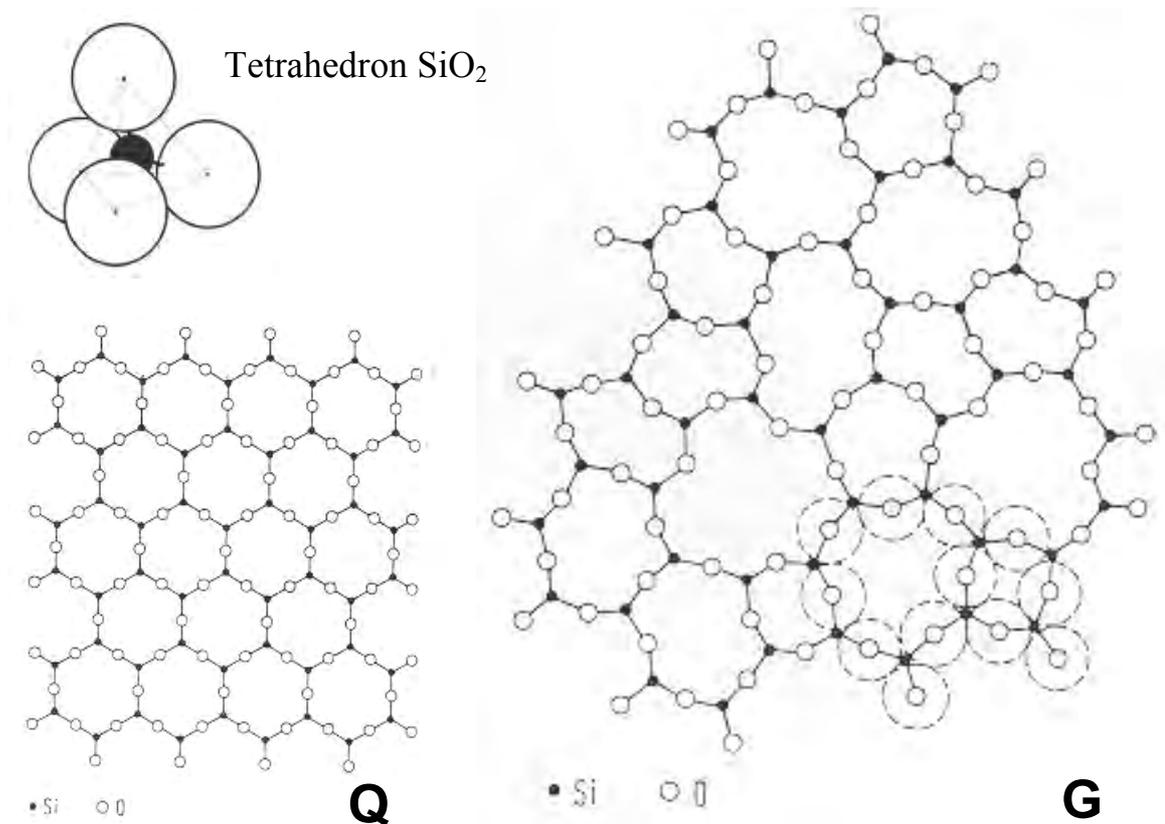


Figure 6.1 – Glass disordered network (G) and regular reticular structure of quartz (Q).

Ash of continental plants is particularly rich in potassium (K).

Their use changes according to the historical period and geographic area.

Flux lowers the melting point but weakens the bonds inside the glass network, making the glass more alterable. It becomes indispensable to add a new component (stabilizer) to the glass batch in order to strengthen the bonds inside the glass network. The stabilizers used in ancient glass were calcium oxide and magnesium oxide. The role of the stabilizer is to strengthen the internal bonds so that the glass becomes less alterable. Flux and stabilizer are called “network modifiers” according to the role they play.

In summary, the principal components of a glass are: network former, flux and stabilizer. A glass (like mosaic glass) can be coloured and opaque. Then in a glass colouring and opacifiers, the so called “accessory components”, can be present.

Furthermore, in ancient glass obtained by natural materials it is possible to detect a lot of elements linked to the impurities of the raw materials (Al, Ba, Mg, K, Fe, etc.). These elements can be called “fortuitous components”. Another important element is the lead. This has different functions in glass technology (flux, colouring and opacifier).

Colouring elements in ancient glass are simply copper, iron, manganese and cobalt. An enormous quantity of colours could be obtained according to the presence of these elements, their firing atmosphere, firing temperature and the presence or absence of lead. Opacifier elements were antimony and tin.

Opacity in a glass could be obtained by means of primary opacifiers or of secondary opacifiers. Primary opacifier is an opaque material in granules (often quartz) added to the melt during its cooling. Secondary opacifiers are minute crystals that are formed from the melt during its cooling (opacifier elements).

The presence of bubbles also contributes to increase the glass opacity.

Until the 8th century A.D., Hellenistic, Roman and Byzantine glasses were produced by siliceous-calcareous sand coming from the mouth of river Belus or Volturno plus *natron* as flux. In Mediterranean Europe during the 9th century the substitution of *natron* with *allume catino* (ash of maritime plants) begins for glass production. Between the 9th century and the middle of the 12th century two fluxes (*natron* and *allume catino*) coexist.

From the end of the 12th century there is exclusive use of *allume catino* as flux in the glass production. The success of the *allume catino* was sometimes followed by the use of new network formers (quartz pebbles, new sands). Of course there are some exceptions in the

general evolution of the glass technology over its long history. In fact glass that is particularly difficult to produce such as red, yellow or white opaque is often the result of precise recipes and production techniques that are not in agreement with the compositional and technological characteristics of the other coeval glass. For example red opaque glass can be detected, which was produced with a Na flux obtained by ash or marine plants in Roman period.

The identification of the chemical composition is fundamental for characterizing ancient glass. In fact chemical composition gives precise information on raw materials and on production technologies. In order to easily show the results of chemical analyses, ternary (for example, the ternary diagram of the principal components Si, Na and Ca, or of the fortuitous components Al, Mg and K) or binary diagrams (e.g. K/Mg) are generally used. It is possible to distinguish a glass produced by a sodic flux obtained by *natron* from a glass with a sodic flux obtained by maritime plant ash, taking into account the percentage of K_2O and MgO. In particular, in *natron* glass K_2O and MgO are $\leq 1\%$; while the concentrations of K_2O and MgO are $>2.2-2.5\%$ until 6-7% in glass made with ash of maritime plants.

6.1.3 Classification referred to composition

SODIC AND POTASSIC GLASS

Glass obtained with soda or potassa as flux. Soda ash is obtained from the calcination of algae and marine plants, while potassa is extracted from the ashes of the forest trees, usually beech and flint. Sodic glass is also called “long glass” because it remains plastic for a long time, it is lighter than potassium glass, has no resonance and has a yellowish or brownish tone.

CRYSTALLINE AND CRYSTAL GLASS

Crystalline glass is a very transparent, very light and thin sodium glass. It is obtained using vitrification of the pebbles of Ticino that are rich in quartz and with few impurities. The stones are first crushed and subjected to thermal shock and numerous cleanings. The resulting powder is mixed with high amount of flux, which is also cleaned several times in the water. Crystal glass, more commonly called just “crystal”, is the glass of superior quality and represents an evolution of potassium glass, purified from impurities that made

the green. Made of silica, potassium and lead oxide, it is a transparent, lightweight, thin, shiny and bright, with high refraction index of light, hard and heavy glass. Because of its hardness it is characterized by incised decorations and facets.

GLASSES THAT IMITATE OTHER MATERIALS

- 1) chalcedony glass (tin oxide is added to the mixture as opacifier, while various metal compounds are added in order to create multi-coloured streaks).
- 2) strass glass (potassium glass in which the lead component is greater, and in which coloured substances are added to imitate precious stones).
- 3) milky-glass (opaque white and glossy glass, imitating the porcelain. It is obtained by combining the mixture with the sodium manganese dioxide as a whitener and the tin oxide as opacifier).

6.2 Processing techniques

6.2.1 Forming

Each forming technique starts from the “bolo” which is the melted glass.

Casting. Casting the bolus within closed clay mould, which give both the form and the decoration. This technique only allows the production of objects with a full shape, that is without cavities inside them.

Moulding. Casting the bolus in the interspaces between two identical twin moulds, or casting it into one mould and modelling it in the same mould, still hot.

Cold cutting. After solidification, the glass can be worked on using grinding, cutting and engraving.

Blowing. The glass is removed from the crucible and rolled on a slab of metal, to give it a cylindrical shape. The bolus is then attached to a glassy long hollow metal tube, named “rod breath”, through which the glazier inflates the air to create the bubble. Often the piece is heated and blown several times. The blowing may be carried out without tools or with a metal mould. To shape the blown glass according to the desired shape forceps and scissors are used.

Ice glass. It recalls broken ice. It is obtained by immersing the semi-finished piece in cold water and then again in the furnace: the temperature changes cause the cracks. The piece is

then further blown and polished.

Murrine. The first step is to prepare murrine sticks, each with different colours, and weld them together to obtain one stick in several colours. This large cylinder is then heated and stretched in order to obtain a much longer and thinner one, that has the same colours and composition of the beginning. Once cooled, the cylinder is cut into round pieces, that are enclosed by a glass ring then arranged in a plane surface and heated till they are welded. Such a disk is cooled and then reheated and worked as one piece, in order to reach the desired shape.

Filigrana. This technique employs strings of glass used for the entire length. Often the *filigrana* technique regards the insertions of strings of opaque glass into transparent glass.

6.2.2 Decoration

Enamel painting. Cold-drawing of the enamel (powdered glass obtained from enamel ingots powdered and then mixed with metal oxides and a fat binder), cooked in the oven at a moderate temperature (500 °C) to melt and fuse the glass with enamels.

Cold paintings, grisaille. They use powdered glass combined with metal oxides diluted in wine or liquid resin. Then the mixture is warmed in order to obtain coloured glass.

Incision. Working with special tools directly on the body of the objects. It removes material, so it is possible on hard, thick glasses, such as lead crystal. It can be done using:

- grinding wheel, producing furrows on the wall of the object.
- diamond tip, producing scratches or tiny dots under the action of the diamond. It is applied to glass with thin walls.
- sand blasting, recent system (last quarter '700), which is to scratch the wall with a continuous stream of sand at high speed.

Applied decoration. Glazed decorative elements are applied to the object in relief. This happens when the parts are not completely solidified.

Golden glass. The gold leaf is applied to a glass surface and then engraved. It is then covered with a thin layer of glass that protects the gold. The whole complex is slightly heated in order to close the glassy layers and enclose the gold leaf.

6.2.3 Glass windows

The glass window is a mosaic of glass pieces of different colours. Sometimes a preparatory drawing on paper of the same dimension of the glass window is prepared. It is cut and used as a guide in the process of cutting the glass. The slabs can be achieved in two ways:

- 1) the bolus can be blown as a bottle, obtaining cylinders cut in their length and then flattened on a surface of stone;
- 2) The second system consists on a fast rotation performed by two glass makers that use two tolls at the same time in order to obtain a big glass disk.

The pieces of glass are cut by means of hot tips or diamond tips. At the end these pieces are inserted into a lead frame, strengthen by means of a large iron frame.

6.2.4 Egyptian blue

While not a glass in the strict sense, the Egyptian blue is treated in this chapter as it seems to be the most suitable part of the book. In fact, the name “Egyptian blue” is given to a blue glass paste, whose color is due to the presence of crystals of cuprorivaite as well as other crystalline compounds. It is used as pigment in painting (in powder form) and to obtain blue mosaic tesserae, that were utilized, especially in the 1st century A.D., for covering fountains.

Egyptian blue is obtained by the calcination of a mixture composed of quartz, calcium carbonate, copper carbonate and small quantities of *natron* (900-950 °C). During the baking in oxidizing atmosphere the calcination of CaCO₃ and copper carbonate is followed by the reaction amongst calcium oxide, copper oxide and quartz (SiO₂). This reaction produces the formation of Cuprorivaite (blue in colour, CaCuSi₄O₁₀). The presence of *natron* in the mixture favours the synthesis process. Egyptian Blue is composed of Cuprorivaite (responsible for the blue colour), quartz and sometimes small quantities of silica phases of high temperature in a sodium rich glass paste (Figure 6.2).

6.3 Glass deterioration

The main deterioration process of the glass is the leaching (removal) of the alkaline flux (Na and K) due to hydrolysis by water. In this way the H⁺ ion enters in the glass structure in the place of Na⁺ or K⁺.



Figure 6.2 – Egyptian blue tessera.

The ionic radius of H^+ is smaller than Na^+ and K^+ ones; for this reason a reduction phenomenon takes place in the external part of the glass structure. With the passing of the time exfoliation process can develop due to this phenomenon. In addition the complex mechanism of reflections and refractions of the light that goes across the thin sheets constituting the exfoliation gives rise to iridescence. Then exfoliation and iridescence are deterioration forms closely connected to a chemical process which is the leaching of the alkaline flux (Figure 6.3).

Other deterioration phenomena are the precipitation of soluble salts (in fractures and bubbles inside the glass), that can lead to the disintegration of the glass, and sulphation phenomena (formation of sodium sulphate on the glass surface).

6.4 Glass conservation and restoration

6.4.1 Examination of the artefact and its documentation

It is important to record all the data belonging to the object. The box container should carry the following:

A) Labelling

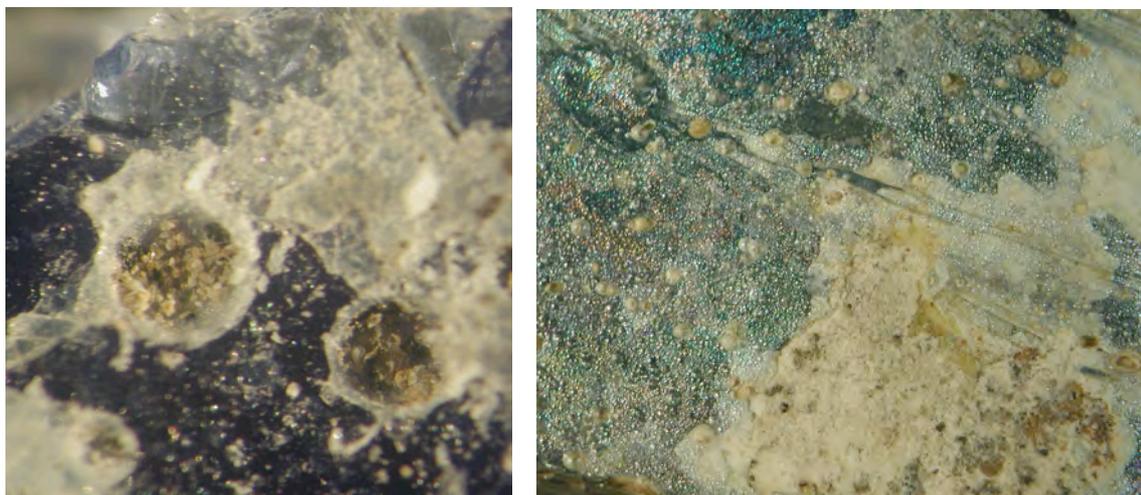


Figure 6.3 – Glass deterioration: exfoliation (left) and iridescence (right).

B) All the excavation data

For the object itself a catalogue should be prepared with information about the site including:

- C) Where the object comes from: county, city, road
- D) The name of the archaeological site
- E) The date when the excavation took place, under whose scientific direction, from which company
- F) Coordinates of the site, data, drawings, photographic record

The first visual examination is very important. The use of good light and microscope magnification makes the examination easier.

The result of the observations should be written in the report at the time they are done. Drawings and a photographic record are very important, as well as the list of any treatment done, and a scale check list giving priority to the conservation treatment and fragility of the object.

It is useful to prepare a check list containing data fields, for example, whether the surface is iridescence, has a brittle surface, has a craquelè, is sweating or weeping; all this to determine the kind of body, the transparency or opacity, the colour, the thickness, as well as indications of fabrication techniques and other useful information.

6.4.2 Planning a restoration intervention

First, it is important to ask and answer the following questions.

Is a conservation treatment necessary? How fragile is the object to get the treatment? Which kind of effects can be expected from the treatment? How often should the treatment be repeated? Instead of a treatment is there a way to use any prevention? What is the final destination of an object, the storage room or an exhibition or should it be just made presentable for a publication?

6.4.3 Cleaning

It is crucial to examine the object or the fragments with complete attention. The fragility of the body and the surface of the object must be clear. The materials chosen will depend on the substances to be removed.

A standard procedure for “healthy” glass – that is, not having any glass disease and any kind of cold painted decoration or gold – would involve cleaning the glass with distilled water – if necessary, with an added non-ionic detergent.

The weathering on archaeological glass should not be removed under any circumstances because this would also remove what is left from the original surface of the glass.

All glass or glass fragments that can be safely washed should be washed, including some glass with glass crizzling, unless it is too fragile or has dangerous and/or unstable cracks and repairs. Here the experienced conservator should judge what is best.

The fragments edges should be cleaned before gluing - if possible using acetone or ethanol.

6.4.4 Consolidation

Also for glass as well as for ceramics Cyclododecane can be used as a temporary consolidant for weak or friable material on excavation as well as in the conservation study.

Following the excavation of glass pieces or fragments, it is important that they are taken out of any plastic bags and stored in an atmosphere neither too humid nor too dry.

Any attempt done by researchers and conservators to consolidate the exfoliating surface of the glass did not give good results. Archaeological glass with lifting weathering layers may require a little fixing and/or consolidation with a dilute solution of Paraloid B-72 in about 10%-15% weight/volume in acetone.

When attempts at impregnation of the glass with various materials were also made in the previous decades, it was found that the sealing of the surface of finely fissured glass gave

various problems. The only method of preserving the glass as far as possible is to store it at all times in a controlled climate (see 6.4.8).

6.4.5 Assembling and bonding

The best adhesive for glass may not yet exist! However, a solvent based adhesive like the acrylic polymer Paraloid B-72, as well as some epoxy adhesives can give the best results in restoring glass. (This fact follows several decades of experience by conservators and draws on scientific publications from all over the world).

Glass divides into two categories as far as bonding is concerned: healthy glass and weathered glass (also called with glass disease). For healthy glass the best adhesives are epoxy adhesives, for glass that has a strong or less strong weathering must be decided individually which material to choose. It is important to add that modern glass can also suddenly suffer from glass disease, which can be caused by the environment in the storage or by the wrong materials used for the exhibit cases.

The best epoxy adhesives for glass are adhesives with the same refractive index of the glass, transparent, non yellowing, chemically inert, with an expansion coefficient as close as possible to that of the artefact, with mechanical resistance to tensile stress and tear, with resistance to microbiological attack, reversible, or at least removable through swelling with solvents without damaging the original.

The experience of the last decades demonstrates that the best non-yellowing epoxy resins on the market are: Hxtal Nyl-1 and Epo-Tek 301-2. These have proven to be stable over a long period of time and have the parameters of class A resin; this means that they should remain stable for 100 years.

The technique used for the gluing is very important. The fragments must first be taped or fixed together in order to support firmly the fragments while the adhesive is setting and this can take several days.

The best method is to use tape. The choice of tape used depends on the surface of the glass, whether it is weathered or not. In some cases transparent tape, which is elastic and has a good sticking capacity on the surface, might be the best; in other cases, medical tape used for the human skin might be better.

Strips of tape should be used, made with scissors, cut lengthwise and then crosswise. The length or thickness of the strips will depend on the size of the fragments and the thickness

of the glass. The strips can be also very small, depending on the size of the fragments and should be held and fixed with tweezers. The strips might be also of 1 or 2 millimetres, if possible not thicker than the glass thickness to allow the epoxy adhesive to flow underneath. The tape strip should be attached on the surface of one fragment and pulled onto the other fragment placed across the break. All the strips should be put at right angles to the line of the break. It is not always necessary to put the strips on the front and the back of the object. If the object is round then the strips can only be put on one side, in this case on the outside.

This method enables the object to be stuck completely together in a perfect alignment, only held by the strips. At this point the adhesive can then be applied by capillary action along the breaks.

The filling of the adhesives in the break is done by capillary action. The resin is applied carefully along the upper half of the crack and is drawn in by capillary action. As soon as the resin penetrates, the crack immediately becomes invisible.

Any excess of the epoxy resin on the surface must be cleaned away before the adhesive has set by using a cotton swab dipped in acetone.

It is important to mention an alternative to the tape. For fragments that are difficult to fix, or may be damaged on the surface by applying the tape because they suffer with the glass disease, there are small metal pieces, which can be made individually to make a bridge across the join.

The best metals to us are stainless steel or brass. These can be bent like a rounded “W” and can be glued on with a small drop of cyanoacrylates adhesives. Also small clamps as well as other self constructed aids can be used.

The broken object itself will determine the most appropriate method. Sometimes the surface allows the use of both tape and clamps.

Under no circumstances should heat be used to speed up the process of setting of the epoxy or on the glass.

For archaeological glass that has weathering it may be good to use an acrylic polymer solvent-based adhesive such as Paraloid B-72 for the bonding. Archaeological glass that suffers with glass disease should not be taped.

The tape would remove parts of the surface weathering or leave an imprint on the surface. Therefore a different method must be used. Paraloid B-72 is the correct adhesive as long as

an absolutely transparent result is not required.

A small amount of adhesive B-72 should be applied to one of the broken edges and joined with the edge of the matching piece. All the pieces will then be joined by piece-by-piece assemblage. In case it is difficult to hold the fragments, small metal clamps, as mentioned above, might be used. Deciding when to remove the excess adhesive will depend on the fragility of the glass.

It may be wise to remove it only once it has set. The prerequisite for good results in glass restoration are a mixture of experience, skill and intuition.

6.4.6 Filling in missing areas

Filling in gaps in glass is generally a very difficult task.

The matching of the colour of the glass and the actual filling of the missing area requires great precision, technique and a lot of time. In the case of modern glass, filling in missing areas might be considered in some cases if the piece is very important aesthetically.

The best materials for replacing missing areas on glass are resin-based fillers: the above two epoxy's mentioned above: Hxtal Nyl-1 and Epo-Tek 301-2.

In most cases is possible to achieve a close or identical match between the glass and resin by using dyes, or finely ground pigments.

There are various types of materials for making a simple backing or a double-sided mold for the resin, are such as plasticine, tape, dental waxes, silicone rubbers and various other supports.

A successful cast, with the right colour, shape and free of bubbles is very difficult to make. In many cases the cast has to be worked with drills and sand paper and then polished which places stress on the object.

Where archaeological glass is concerned, it may be desirable for long term aesthetic reasons to leave the object with the missing areas not filled with resins. If a support is necessary to give structural stability, it can be made out of glass, Plexiglas, metal or other materials, instead of resin.

In many museums collections of archaeological glass, we see how the reconstructed or restored areas have badly aged. This has frequently led to heavy yellowing, shrinking and breaking not only of the resin but also the glass attached to it.

Most of the epoxy resins that have been used in the past 30-40 years have already changed

colour and transparency and are more visible and disturbing than if the glass had been left without reconstruction of the missing area.

Add to this the stress placed on the object that has to be treated with a releasing agent, various modelling materials like Silicon and is then often scratched by modelling and shaping the epoxy resin fill.

As an alternative for very damaged objects, a digital reconstruction can be made and placed alongside the original object or a modern copy can also be created.

6.4.7 Recording and photographic documentation

As soon as the objects arrives in the museum, studio ort collection, should be examined. It is important to record all observations before any treatments begins: how it was transported, packed, its general condition, the size and number of fragments and anything else of relevance.

The photographic record plays an important part.

Traditionally, black and white still photos have been the preferred record for objects in museum collections because if properly stored would last a long time. However, it must be pointed out that digital photographic recording is now become more widespread and can be easily incorporated in the record. If possible also colour slides should be made because if properly stored these can last a long time. A scale of millimetres should appear in each photographic record and with the reference data of the object.

6.4.8 Packaging and storing

Fragile objects should be packed in acid-free tissue and put in an inert cardboard box.

The most effective storage for glass conservation, especially from an excavation site, is in a stabile environment at a moderate temperature (18°-30°) with the humidity kept between 40-55%, protected from pollution and strong lighting, not only from the sun but also from the artificial light.

The materials used to make storage cupboards and exhibition display cases need to be free of solvents and adhesives. These could give off negative exhalations over many years and infect previously healthy glass. This is also valid for modern glass, whereby glass disease caused by airborne chemicals were found in some collections.

We know that paper labels attached to the glass surface, which were widely used in the past, do affect the glass. Therefore it is wise to use, as for the ceramics, a safe system to

write on the surface. A small rectangular area should it painted by brush with a primer such as Paraloid B-72 diluted in solvent. Once dry, the inventory number can be written on it with a stable marker or drawing ink.

6.5 Case studies

6.5.1 Restoration of archaeological glass from Forlì (Italy)

The *ex Monte di Pietà* building is owned by and headquarters of the Fondazione della Cassa dei Risparmi in Forlì (Italy). The restoration and renovation of this building and the excavation of the 800 square meter site brings to light the story of a historically important 15th Century urban settlement in the city of Forlì. Between 2004 and 2005, ceramic, metal and quite a lot of vitreous material were excavated at the *ex Monte di Pietà*.

The excavated glass included many fragmented vessels, for example, drinking glasses and bottles of various sizes. The fragments of a cup on a high foot (Figure 6.4) constituted quite a rare find as did some receptacles like urinals which were also used for scientific observation of urine. Following their excavation:

- all the fragments were placed in plastic bags and given an excavation location number;
- all the fragments were very dirty with the excavation earth (Figure 6.5);



Figure 6.4 - Cup with high foot upon conclusion of restoration.



Figure 6.5 - State of conservation (left)
and group of fragments (right) prior to conservation.

- all the fragments were of various dimensions, colour and thickness;
- in the conservation laboratory the glass fragments were placed in flat dishes and each fragment was washed with water and a soft brush;
- most of the fragments showed to some extent the symptoms of the glass disease, iridescence, craquelè and flaking of the surface;
- the hardest task was sorting out all the fragments (Figure 6.6).

This labour intensive work required much patience and a good eye to recognise the fragments belonging to each other. The skill lay in separating out the glass rim fragments from pieces of the body and base and laying them all out on trays in as near as possible their correct position.

At the same time the fragments with an identical or a similar colour were also kept in groups. In order to do this was important to look at the glass colour not only placing the fragment on a white sheet of paper but also by looking at the cut of the glass.

The thickness of most of the glass fragments, especially belonging to drinking glasses was about 1mm to 1.5 mm thick. The colour of the glass ranged from greens to almost transparent whites. Some surfaces had typical finishes of drinking glasses.

To glue the fragments, epoxy resin Epo-Tek 301-2 was chosen because it enabled very thin fragments to be held together. Attempts were undertaken with Paraloid B-72, but with poor results. Filling the break with the adhesive was done by capillary action. The resin was applied carefully along the upper half of the crack. As soon as the resin penetrated, the crack immediately became invisible.



Figure 6.6 - Group of fragments after cleaning.

The missing lacunae were not filled up. This is because many of such museum restorations show widespread discoloration of the resin fills. We must remember the physical stress placed on the glass by moulding, casting, sanding and polishing of the resin.

Some representative objects were chosen for public exhibition, for example, two urinal (Figure 6.7), some drinking glasses, necks of bottles. Special Perspex supports were made to hold the glass objects that were shown in the exhibition in May 2009 in Forlì.



Figure 6.7 - Urinals upon conclusion of restoration.

6.5.2 Analysis of a glass ball

This is just a very simple example on how non destructive analytical techniques can be usefully utilized in an archaeological museum, in particular ED-X-ray fluorescence.

A glass ball was discovered by the restorers of the Archaeological Museum in Damascus during the examination of metal artefacts, which were there stored since a long time. It

deals with a ball of approximately 1.5 cm in diameter with a hole of about 4 mm in diameter.

The surface is blue coloured for the main part, and the internal surface of the hole as well, but there is a large surface area which is white both outside and inside the hole (Figure 6.8). The restorers made the hypothesis that it deals with the clapper of a bell (about 10 cm high and 6 cm in diameter), which was found together the drilled glass ball.



Figure 6.8 – Archaeological glass ball.

Analyses were performed by energy dispersive XRF (30 KV, 20 μ A, 60 seconds) in the white and blue zones, in order to explain their different colour; the results are reported in Table 6.1.

The elements detected are always the same, with silicon, copper, calcium and potassium prevailing on the others, which are represented by iron, chlorine, titanium and phosphorus. Of course, the intensity of the silicon peak is low, but its content is high, due to its very low sensitivity to the adopted analytical technique.

Therefore, the sample under examination seems to be a calcium-alkaline glass, which was produced by a not well homogeneous mixture of the raw materials. In fact, the white zone shows a particularly low content of calcium, which is not compensated by the higher amount of potassium. Possibly, the scarcity of calcium does not guarantee the complete fusion of the mixture and copper cannot develop its typical blue colour.

Table 6.1 – Semi-quantitative chemical composition of the glass ball by EDS-XRF.

Area	Ca	Cl	Cu	Fe	K	P	Si	Ti
Blue	1512	29	1685	115	315	20	43	38
White	802	52	1360	142	414	15	43	39

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7 – METALS

7.1 Origin of metals

7.1.1 Natural and artificial metals

Metals exist in nature in form of minerals (oxides or other substances), so that they must be extracted. Only a few exist in the native state, like gold, silver and copper.

In Latin, *gold* was called “aurum”, that means “shiny sunrise”; in nordic languages “gold” means “yellow”; it is the metal of the Sun. Its chemical symbol is Au.

In nature, gold is wild or native, in form of flakes (Figure 7.1) or nuggets or within quartz rocks. In the latter case is alloyed with silver (gold-silver alloy = electro) or copper, which is extracted with the method of “salgamma”. Characteristics: High density, melting point at 1063 °C, ductile, malleable, low hardness, unalterable.

In Greek language, *silver* (symbol Ag) was called “argos”, that means “light, brilliant”; or from other terms “plata”, “silver” that have reference to its brightness; it is the metal of Diana or of the Moon. It occurs naturally in its native state or free, or is inside minerals of lead or copper, from which is extracted by the method of ‘cupellation’. Characteristics: ductile, malleable, low hardness, durable, low resistance to corrosion.

In Latin, *copper* (Cu) was named “aes” or “cuper” from Cyprum, that had the most conspicuous mines of the world; it is the metal of Venus. In nature, copper is in its native state or free (Figure 7.1) or as an impurity in minerals containing sulphur. Characteristics: ductile, malleable, low hardness, low resistance to corrosion.

In Latin the name of *lead* is “plumbum”, that means “heavy”. It is the metal of Saturn. Lead (Pb) occurs in nature in the form of mineral and is extracted through ‘cupellation’. Characteristics: ductile, malleable, low hardness, low resistance to corrosion.

Tin (Sn) is the metal of Jupiter; its Latin name is “stannum”. In nature it exists as tin oxide and is extracted through ‘cupellation’. Characteristics: ductile, malleable, low hardness, low resistance to corrosion.



Figure 7.1 – Native gold (on the left) and copper (on the right).

Iron (Fe) can be found in nature in the form of iron oxide and is extracted through ‘cupellation’. Characteristics: ductile, malleable, low hardness, low resistance to corrosion.

In addition to natural alloys, there are the artificial ones, made for their chances of workability. One of these is *pewter*, made of tin (73 to 90%) and copper, with additional antimony (Sb) and bismuth (Bi), or antimony and lead, or antimony and zinc (Zn). Tin has bright colour and is also durable; therefore, this alloy was used for the production of artefacts instead of silver. To increase the fusibility, an amount of lead was often added.

Bronze (from Germanic “brun”, that means dark) and *brass* (from Latin “luteum”, flat, for the flat shape on which it is worked), are two alloys made of Cu with minor amounts of white metals, like tin and zinc, which lower the melting point and increase the fluidity of the more abundant metal. The colour varies depending on the proportion between the component metals. Both in the bronze and in the brass, you may find the addition of lead, which increases the malleability of the alloy.

7.1.2 Copper and copper alloy

Copper, a reddish-yellow metal that is malleable, ductile, and has a brilliant lustre when polished, was first used in antiquity in its native, or un-combined form. The greatest proportion of copper used in antiquity, however, was obtained from smelting the many minerals containing this element. Although easily worked, it is too tender to be suitable for tools, weapons, or implements. But it is possible to harden copper by hammering it while it is cold. As copper takes the desired shape, it hardens and becomes more brittle. In this way,

usable cutting and working edges can be fashioned. Cold-working of copper was known and practiced in antiquity. Copper can also be hardened by alloying it with various other metals, a procedure that was practiced in antiquity as well.

Addition of 1% to 10% of tin to copper produces an alloy known as *bronze*. If the tin content is raised to approximately 30%, the alloy becomes whiter and is called *speculum*. Speculum is a hard, tough metal, which needs a high polish; it was used primarily for making mirrors and coins. The addition of up to 40% of zinc to copper produces *brass*, which becomes more yellow, the higher the proportion of zinc is.

The properties of these alloys vary with the percentages of copper to tin and zinc.

7.2 Manufacturing technique

7.2.1 Direct manufacturing techniques

These techniques were used to make and to decorate simple objects (plates, cups, pots, etc.), but also for the monumental statuary before the improvement of the fusion techniques.

Spinning: getting twisted strands, or hammering a sheet, or passing a sheet through a perforated plate.

Lamina: getting laminas through hammering on a flat or curve surface. In order to compose a large statue, it was necessary to model several sheets and then mount them on a core of wood with pivots of copper or bronze. The wooden support was coated with bitumen, so that the sheets will adhere perfectly. The processing of the lamina implies the technique of “re-firing”. As a result of beating, the metal becomes harder and to continue the work it is necessary to heat the sheet and then let it cool down slowly, so it regains its original elasticity without changing shape.

7.2.2. Fusion

This technique requires the preparation of the model, which is the most important phase of the process of fusion.

FUSION IN SIMPLE OR MULTIPLE FORMS

The fusion is done in forms made of stone or ceramic. The forms could be open, for the realization of flat items such as weapons and tools; the three-dimensional objects can be made of two or more shells. To save the metal, especially the precious one, a core of earth is placed inside the form.

LOST-WAX FUSION

- 1) Indirect: it creates a clay model from which to make a plaster mould and then to create any number of models in wax.
- 2) Direct: creating a full wax model or wax coated on clay. In both cases the pattern is lost. It can be full or empty. The wax is then eliminated through holes.

STAFF FUSION

A technique used since the Renaissance to melt reliefs, medals, and generally small objects. “Staff” is called the box or metal frame in which is placed the foundry sand used for forming.

ELECTROPLATING

Technique that uses electrolysis in the mass production of metal objects. Its discovery dates back to 1836-38. The method consists of depositing by electroplating a metal on the inner surface of a form. The form is used as the cathode, while the anode is made by a slash of the same metal.

7.2.3 Joining techniques

FOLDING AND RIVETING

The edges of the metallic sheets are folded and hammered (folding) or the edges of the overlapped laminas are drilled and joined with hammered rivets and pivots (riveting).

WELDING

With addition of materials (brazing) or without addition of materials, just warming the metals to join (autogen).

7.2.4 Decorative techniques

Chipping: tracing furrows through chisels (chisels with round cut), without removing material.

The chisel is beaten by a hammer, it lowers the surface without removing material.

Bulinatura or engraving: track furrows by removing material, engraving with chisels with rectangular or triangular cut.

Punching or stamping: technique based on the action of a bar of iron or lead, on whose tip is carved the design to impress. Techniques typical of coinage.

On relief: direct decorative techniques on a metal lamina. It consists in hammering the back of the lamina fixed to a support of wood or clay. The technique is called “Toreutics”, although the term generally indicates the techniques associated with the processing of metals (from the greek “toreus”, chisel).

Granulation: Typical technique for decorating the surface of metal objects with small spheres, obtained by melting scrap metal in crucibles with charcoal or by dripping molten metal in water or oil. These spheres were then welded on a base with glue, animal bones, or resins, or welded with low-melting alloys.

Filigree: typical jewellery technique for decorating the surface of metallic objects with gold wires attached to the lamina with adhesives or by welding with low-melting alloys.

Agemina: technique that involves inserting metal wires through hammering them in furrows. This wires can be of the same metal or another metal.

Damaschinatura: consists of inserting metal laminas in furrows or delimited areas.

Niello: making a layer of hot dark coloured sulphides of Ag, Cu or Pb, pulverized and dispersed in a matrix of wax, and then insert it in incisions on the surface of the object.

Combination of metals and other materials:

1) Cloisonné: put strips in the metal surface so as to surround the alveoli intended to receive precious stones or glass or enamel; 2) Champlève: the alveoli are arranged inside the lamina with chisels or moulds; 3) Inlay; 4) Crisoelephantine technique: use of ivory and gold.

7.2.5 Finishing

Rasping: rubbing with scraper or rasp the object just after casting, to perfect it. The presence of fusion defects can have several causes.

Burnishing or polishing: rubbing the surface with a hard tool in order to smooth the roughness, to darken the colour and polish the surface.

Gilding:

- 1) a gold leaf covers the surface. It is applied warm or with stucco or plaster;
- 2) fire gilding or amalgam: a mixture of gold and mercury was brushed onto the surface and heated; at about 400°C the mercury evaporate, leaving the gold layer;
- 3) galvanic gilding: electrochemical procedure, whereby the metal is covered with gold;
- 4) “Mecca”: a sheet of tin is applied to the metallic support; it is then painted with a special varnish (Mecca), so as to appear gold. For the gilding both the leaf and the support must be prepared.

Plaque: precious metal laminas are welded on sheets of less precious metal; “simple” if conducted on a single side, “dual” on both.

Coating: black cuprite was laid on bronze surfaces to give them dark colour and compact aspect.

7.2.6 Sculpture

For a long period, the monumental metal sculpture was made with the primitive technique of hammering metal laminas, while the use of moulds and fusion was only applied to small statues. Only toward the end of the sixth century in Greece, with the fusion technique are produced even monumental statues. After that, this technique becomes the only used for the production of metal sculptures.

The most important metal used in sculpture is copper, because it is abundant in nature, and also for its characteristics. Because copper has a melting point high enough (1085°C) and a low degree of fluidity in the molten state, it is not particularly suited to casting in forms. But the addition of white metal to copper, such as tin and zinc, gives alloys, bronze and brass, respectively, with lower melting point and increased fluidity.

Bronze with 5% tin retains the red colour typical of copper, with 10% the colour is dark yellow, between 10 and 25% is pale yellow, more than 25% is silvery.

To make the alloy more economical, tin is partially replaced with lead, which makes the alloy more suitable for the working technique in cold state, as well as heavier and darker.

7.2.7 Decoration on copper laminas

OIL PAINTING

The copper lamina was used as pictorial support from the second half of the sixteenth century.

Reasons for its spread:

- 1) conviction of durability,
- 2) invention of the places where to produce mechanically thin metal laminas,
- 3) introduction of relief printing, obtained by an engraved matrix,
- 4) diffusion of the oil painting,
- 5) easy preparation.

Disadvantages:

- a) flexibility of the lamina;
- b) small dimension;
- c) poor adhesion of colours;
- d) bubbles, cracks and detachment if you use a binder;
- e) corrosion of the slab.

ENGRAVING (CHALCOGRAPHY)

In chalcography the ink goes into the furrows, corresponding to the blacks on the sheet, and is removed from the parties that don't affect the surface, corresponding to the whites. That's why it is called "engraving print".

The diffusion of this technique was a few decades later than the xylography; it was born between 1430-50 in Germany and in Italy. It remains popular until the nineteenth century when it is supplanted by the lithographic technique. Chalcography replaces xylography for the fact that the signs of engraving on copper can be thin, very close to each other and crossed in all directions. The thickness of the layer of copper, obtained from a perfectly flat and clean surface, ranges from 1 to 2 millimeters.

The signs can be traced by means of various tools:

- 1) "bulino", with a characteristic triangular-shaped tip, which causes rigid-edged furrows; it is used almost parallel to the surface;
- 2) "dry-point", a steel tool in the form of a robust needle with a circular section, used in a

vertical position determining very deep but not very wide furrows, with edges characterized by the presence of curled pieces of metal.

Both these techniques are of direct engraving on metal and therefore with limited possibilities of making curvatures. Otherwise there are indirect techniques, which employs a chemical attack:

3) etching, in which the incision is carried out on a layer of varnish on the metal lamina, while the incision of the metal is done by the chemical action of a dilute acid (usually nitric acid);

4) aquatint, which gives an effect of granulation of the slab in order to get the impression of perspective. The granulation is done with acid.

The paper used for the incision on copper has to be soft and elastic, so that it can enter into the furrows and catch the ink. To make it softer, the paper is wetted before passing under the press, which means a shrinkage of about 1-2%.

7.3 Conservation state of metals

7.3.1 Metals from excavation

Every material has a stable form in relation to the environment in which it exists. When it is buried, an object is situated in a new microclimate, possibly one vastly different from its previous state. The material of which the object is made will adapt to these new conditions, so that it will undergo a process of modification to approach a stable relationship, or equilibrium, with the new environment. As the material approaches equilibrium, the rate of change will decrease and eventually stop when equilibrium is actually reached. This stability will remain constant as long as the object remains buried in the ground.

Iron, copper and copper alloys undergo to big corrosion in acid environment and in presence of saline solutions, while they have a good preservation in alkaline environment. On the contrary, lead shows a reasonable preservation in saline environment, while it has a poor preservation in both acid and alkaline environment.

When it is absolutely necessary to undertake a treatment, keep in mind that whatever is done in the field by a non conservator almost certainly must be undone in the laboratory. This

underscores the importance of the principle of reversibility, an importance concept in any conservation treatment. This means that any treatment applied to an object must be reversible, that is it must be capable of being reversed or removed at a later date with no resulting damage or change to the object. It should make no difference whether the reversal process takes place several hours later, several days later, or as long as a year or more.

Reversibility is especially important for field conservation because one is often forced to carry out procedures under less than ideal conditions.

It must always be kept in mind that any treatment applied to an object, including mere cleaning, can contaminate it and invalidate any subsequent analysis, whether it is for dating purposes or elemental analysis. If any kind of analysis will be required at a later date, representative samples of the material should be taken carefully and set aside. Even if analysis is not immediately envisaged, it is wise to set aside samples automatically so that testing can be done later. Moreover, to the experts who make the analysis should be given a copy of the complete conservation record of the object.

7.3.2 Bronze conservation state

Excavated objects of copper alloy can exhibit a variety of colours of corrosion products. Green is by far the most common one, but blue, black, red and reddish brown are found, as well as mottled combinations of all of them. Copper alloys frequently are found well preserved but suffer drastically if buried in saline soil. Chlorides will form an unstable corrosion product which, in presence of moisture and oxygen, will set into motion a self perpetuating system of corrosion. Within only a few hours of excavation, this corrosion can lead to what is called *bronze disease*, a form of corrosion producing a fluffy, powdery material varying in colour from emerald to pale green. Bronze disease can cause considerable damage to copper alloys, resulting in deep pitting and disintegration of the metal.

Preservation of copper alloy objects is further complicated by the presence of decoration composed of other metals or other materials. On freshly excavated objects, it may be difficult, if not impossible, to distinguish such coatings, especially if the object is heavily corroded. When the copper underneath corrodes, corrosion products form on top of the gilded, silvered, or thinned surface. Because the object is covered with these products, it is easily assumed to

be made exclusively of copper. The layer of gold, silver or other materials may have been disrupted if the corrosion of the copper alloy substrate is particularly extensive; as a result, it may be lost within the corrosion.

7.3.3 Cupreous metal corrosion

The cupreous metals are relatively noble metals that normally survive in very hostile conditions, including for burial underground or submersion in salt water, where they often completely oxidize.

Cupreous metals react to the environment and form similar alteration products, such as cuprous chloride (CuCl), cupric chloride (CuCl₂), cuprous oxide (Cu₂O), and the green- and blue-coloured cupric carbonates, malachite [Cu₂(OH)₂CO₃] and azurite [Cu₃(OH)₂(CO₃)₂]. In a marine environment, the two most commonly encountered copper corrosion products are cuprous chloride and cuprous sulphide. The alteration compounds of copper alloys, however, can be more complex than those of pure copper. The chlorides can be found in the soil, in the sea, in the air (in the acid rain), in every state of water (even in the form of moisture) and gases which are normally found in an unpolluted atmosphere. The first step of this corrosion by the hydrochloric acid is the formation of the cuprous ion:



Cuprous chloride (nantokite) is a very unstable mineral compound. When cupreous objects that contain cuprous chlorides are exposed to the air, they inevitably continue to corrode chemically by a process in which cuprous chloride is hydrolyzed in the presence of moisture and oxygen and forms hydrochloric acid and basic cupric chloride. The hydrochloric acid in turn attacks the un-corroded metal and form more cuprous chloride:



The reactions continue until no metal remains. This chemical corrosion process is commonly called 'bronze disease'. Any conservation of chloride-contaminated cupreous objects requires the chemical action of the chlorides to be inhibited either by removing the cuprous chlorides

or converting them into harmless and very stable cuprous monoxide (C_2O , cuprite). If the chemical action of the chlorides is not inhibited, cupreous objects will self-destruct over time. The bronze disease manifests itself either as a powdery green substance on the surface of the metal or as a warty or waxy film over the surface of the artifact. It may simply resemble a natural patina to the untrained eye. However, while a patina is not destructive, bronze disease certainly is.

Copper objects in sea water are also converted to cuprous and cupric sulphide (Cu_2S and CuS respectively) by the action of sulphate-reducing bacteria. In anaerobic environments, the products of copper sulphide are usually of lower oxidation state, as well as the iron sulphide and the silver sulphide. After recovery and exposure to oxygen, the cuprous sulphide undergoes subsequent oxidation to a higher oxidation state, i.e., cupric sulphide.

After removal of a marine incrustation, articles made of copper are inevitably covered by a black layer, of variable thickness, of powder of copper sulphide which confers an unsightly appearance. Occasionally, the process of corrosion pits the surface of the artefact, but this is more common in copper alloys where tin or zinc are corroded preferentially. The stable layer of copper sulphide does not affect the object after his recovery from the sea as do the chlorides of copper.

7.3.4 Record of the conservation state

When any conservation treatment is undertaken, whether in the field or in the laboratory, it is imperative to make detailed and accurate records of everything done to the object. To the archaeologist, the treatment applied may seem obvious, but it may not be so to the conservator in the laboratory who will eventually work on the object. Considerable time and effort of the conservator, not to mention possible damage to the object, can be avoided if you do a proper documentation in the field.

A treatment report should include a brief but clear description of the object, the materials of which it is made, and the condition in which was found. Any weak areas, cracks, and the like that might not be readily visible should be indicated. It is always helpful to include sketches and photographs to indicate these weak areas and the position of cracks.

Clearly you must record what was done to the object, how it was done, and under what

conditions.

Be sure to state what specific materials were used, including the full trade name and grade, the solvents used and in which concentrations.

7.3.5 Principal diagnostic techniques

Historical artefacts and works of art deteriorate over time because of exchange of energy and matter interactions with the surrounding environment. These processes are complex from a chemical-physical point of view and can lead to changes in the original appearance of an object, as well as to weakened structures, corruptions and other alterations. Without any intervention to stop or slow down the degradation, you could completely lose the artefact. The implementation of conservation and restoration first of all involves recognising a work of art as a physical object possessing both aesthetic and historical value. This is followed by work (such as cleaning, consolidation and protection) that is based on full respect for the original work of art in its historical context, on the principle of the reversibility of any intervention, and on the stability and safety of the used materials.

Scientific research gives a significant contribution to the conservation of our heritage.

Several methods are used to explore the bulk, microscopic and surface properties of the artefacts, including both traditional and advanced analytical techniques. Before a piece is restored, conservators use scientific investigations to learn about the materials and techniques used to create it. This allows them to make sure that they use materials that are compatible with the originals and that the intervention is effective and durable. Other investigations include the study of alterations and their origin, the identification of previous restorations, assignment of provenance and dating.

Science is also used to develop and test new conservation methods and to create innovative diagnostic tools. All these studies are by their nature multidisciplinary, bringing together specialists from the arts and the sciences to exchange ideas and develop creative and sustainable solutions.

The importance of scientific support for conservation of cultural property has long been recognized. Since then the analysis of constituent materials remains one of the main concerns not only to improve the knowledge of the object and its context, but also to understand the

deterioration processes and identify proper conservation treatments.

The fact that archaeological and historical objects are often unique, artistically relevant and not easily movable clearly encourages the use of non-destructive techniques and portable instruments.

On this ground X-ray fluorescence (XRF), which is an elemental analytical technique, is one of the most widely explored. Though early applications date back to the 50's and 60's, portable or, at least transportable, XRF spectrometers started being effectively used in early 70's, when semiconductor detectors became available. Carrying the object to the laboratory was no more necessary: thanks to the feasibility of *in situ* investigations the application of XRF was virtually extended to any type of object. In recent times a significant improvement in portability of spectrometers has been produced by both thermoelectrically-cooled detectors and miniaturized X-ray tubes.

Opposite to ceramics, metals do not keep a close chemical connection between the raw materials and the alloy, moreover they can be re-melted; this precludes in general the possibility of giving a compositionally-based provenance. Nevertheless differences in elemental composition can be significant of different fabrication contexts; for instance not original parts can be identified in statues, doors and other complex objects. Used in combination with microstructural techniques, elemental analysis can provide information on the fabrication technology, with special regard to casting, soldering and repairing.

7.4 Conservative intervention for metals

7.4.1 Prevention measures

Corrosion products of copper alloy can be extremely tricky and difficult to remove. Their removal, therefore, should be undertaken only by a trained conservator. If little or no metal remains, the entire object can disintegrate if cleaning is attempted by an inexperienced person. Injudicious cleaning can irreparably damage an object; it can destroy not only surfaces and decorative details, but also organic and environmental evidence preserved by the corrosion. Small textile fragments can be found adhering to object of copper alloy; in which case you

must stop the process of biological deterioration of the fibres by the toxic ions of copper.

7.4.2 Mechanical cleaning

Do not pull object of copper alloy out of the ground because they snap and break easily. The object can be removed from the ground following general procedures. First, carefully remove all dirt surrounding the object, being sure not to scratch the surface, gently undercut the object and, when it is completely free, carefully pick it up in the palm of the hand. Place it in a paper envelope until it can be properly packed in the dig house.

The paper envelope is only a temporary measure, but it will allow the object to dry out. A object of copper alloy should not be placed directly into a polyethylene bag when it is still damp. Moisture will collect on the inside of the bag and keep the object wet, which can easily initiate or exacerbate the corrosion process.

Always handle objects of copper alloy carefully. There may be little metal left, and dirt and corrosion can easily hide cracks and splits. Unnecessary handling causes considerable damage; so, handle the object as little as possible. All the objects of copper alloy, especially the long and thin ones, should be carefully supported at all times.

If the metal is shattered or badly corroded with deep cracks, we must consolidate it using a solution of acrylic resin. Do not use an emulsion because the water in it could initiate or exacerbate the corrosion process. Any method of lifting blocks can be used to lift fragile objects in copper alloy.

Principal mechanical instrument for cleaning: scalpel, micro sand-blasting machine, ultrasonic device, precision rotary micromotor.

7.4.3 Chemical cleaning

The chemical cleaning aims to eliminate fouling, stains and thickenings caused by the corrosion products and also to reclaim and stabilize zone with high presence of chlorine.

Cleaning is completed by several dips in deionised water in order to extract and neutralize harmful presence of salts. This method inhibits the electrochemical corrosion, turning them into unstable corrosion products and stopping the cathodic and anodic processes.

Most of the archaeology's masterpieces found under ground, near water, oxygen and chlorine

anion, are really damaged by those elements as they lead up to a total oxidation of the original metal with a stratified unstable and separated structure.

The first action to do is to dry the surface, possibly with treatment by means of infrared rays.

The better way to conserve pieces, in this case, is to dip them into a reducing solution of sodium sulphite which preserves them by the akagenit (β -FeOOH) fallen into the holes and difficult to be removed. After the removal of soil and the weaker fouling, you can stabilize the surface through deionised water or chemical products.

Chemical agents usually used for this kind of cleaning are:

- Descaler (ammonium acetate),
- complexing (E.D.T.A.),
- organic acids and their salts (citric acid, ossalic acid, ammonium citrate, etc.),
- inorganic acids (orthophosphoric acid).

An alternative to the above mentioned products can be considered the use of tannic acid solution, all over again after the chlorine extraction.

Treatments realized by rust converters have the double aim to stabilize and protect.

It is quite always preferable to utilize mechanical cleaning after water dives because in such way it is better controllable, even if worked surfaces could be damaged by the operator.

7.4.4 Final protection

To limit the damages produced by corrosive agents, mainly of atmospheric type, some evaluations have to be carried out:

- how aggressive is the atmosphere in the place;
- how much is damaged the masterpiece and what is necessary for the future conservation;
- which products are better to protect them.

For what concern the first step is necessary to check the daily and yearly relative humidity reports. Then analyze the atmosphere, check predominant winds, the temperature and the rain trends during the year. Once achieved all these controls, it is possible to decide whether to apply a protective layer of varnish or not, in order to isolate the surface from environmental attack.

Varnish could be passive, if it is used only to protect the surface, otherwise active if it

develops a cathodic effect, when made with zinc or aluminium pigments.

The commonly used varnish is composed by binder, which could be done with resins or oils to be film-forming, or made by solvents or thinners, to melt the resins and let it be more viscous for the application, or plasticizer, to let it be more elastic and at least with pigments, to have a covering effect or protective with zinc or aluminium.

If using inhibitor protections, commonly polar organic substances, in order to create thin oriented layers over the surface, it is possible to prevent the attack of aggressive agents changing the potential of corrosion or increasing the surge. The most used inhibitors are the organic amines (zinc naphthenat), alkaline salts of sulphanat oils.

It's better not to use inhibitors for outdoor iron masterpieces, but you can use them in indoor places, mixing them with oils, waxes or acrylic products.

Different method can be used for copper or copper alloys, where you can use inhibit both for outdoor and indoor pieces. The most used one is BTA (Benzotriazole) and its derivatives. This product together with copper ions creates a stable link.

From the point of view of the reversibility of the varnish, it must be deemed that it is easier to clear away the nitrocellulose one, while the inhibitors are quite impossible to be removed.

7.5 Case study: Recovery of metallic artefacts from terracotta containers

In the archaeological museum in Damascus (Syria) there were two terracotta vases which contained a lot of metallic artefacts (Figure 7.2); they date back to the half of the third millennium B.C., and come from Tell Mabtoh (Hasaké, Syria). The archaeologists would want to examine the metallic artefacts, so that the question is “How to conserve these two artefacts and at the same time to study their content?”. First of all it was decided to increase the knowledge of the content performing preliminary analyses by means of non destructive techniques, such as radiography and X-ray fluorescence.

The radiographic investigations with increasing power permitted to observe that the vases are full of metallic tools, in a number much higher than that visible from outside, but it is not

possible to say how many they are and which is their dimensions and shapes. The chemical analysis by means of portable XRF (30 KV, 20 μ A, acquisition time 60 seconds) confirmed the impression that it dealt with copper tools, with impurities represented for the most part by iron. Anyway, the presence of small amounts of tin cannot be excluded, but not more than 2-3%.



Figure 7.2 – Terracotta container with metal artefacts inside.

As a consequence of these results, it was decided that it was opportune to recover the metallic tools for their specific characterization. The following plan of what to do was defined:

- Conservation of one terracotta vase as it is, a part from moderate external cleaning,
- Opening of the second terracotta vase by breaking it into two parts,
- Progressive recovery of the metallic tools,
- Restoration of the broken terracotta vase,
- Cleaning of the recovered metallic tools,
- Adequate documentation of all the operations,
- Study and conservation of the cleaned metallic tools.

All the operations for opening the container into two parts were executed very slowly and with some worry; anyway the objective was attained without any inconvenient (Figure 7.3). When the content appeared to the observers, the surprise was great and any doubt about the opportunity of the operation disappeared. The surprise was also greater while the recovery of

the metallic tools proceeded, due to their large number and the variety of forms (Figure 7.4). When all the content was extracted, it was possible to classify 189 metallic objects of various dimensions and shape, even though most of them were arrows.



Figure 7.3 – Opening of the terracotta vase into two parts.

The metallic objects were completely covered by layers of alteration compounds (Figure 7.5), typical of archaeological copper artefacts, so that it was impossible to observe the original surface. Therefore, all the metallic objects were mechanically cleaned and then chemically treated accordingly to the usual procedure for this type of metal.

It was at the end of this step of the intervention plan that the satisfaction of archaeologists and restorers for their decision to open one of the terracotta containers reached the maximum level.



Figure 7.4 – Recovery of the metallic tools from inside the terracotta vase.



Figure 7.5 – Alteration products of the metallic objects observed at the optical microscopy.

After cleaning, in fact, several artefacts showed very interesting incised symbols, as it is shown in Figure 7.6.

Likely the interpretation of these inscriptions will be useful in order to answer the question about the significance of the two terracotta vases full of metallic tools.



Figure 7.6 – Some cleaned metallic tools with incised symbols.

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8 – GOLDSMITH ARTEFACTS

8.1 Goldsmith's metals

Goldsmith's artifacts are created in part for devotional purposes, a desire to manifest power and cultural enrichment; each one of these motivations induces the client to request long-lasting and possibly precious materials from the artist.

These banal motivations may in fact be the luck of these hand-manufactured objects leading to their realization, maintenance, and often their survival. This is due to what these objects had represented, for whom they had been created, and even for the materials they had been made of.

The main characteristic differentiating the Goldsmith's artifacts from those simply made of metal is not only the fact that they are made of precious metals, but also the fact that they are composed of many other precious elements: enamels, stones, coral, wood and amber.

Gold and silver are the principal metals for goldsmith artefacts, but copper and bronze also are often used. The principal characteristics of these metals can be seen at chapter 7, together with their manufacturing techniques.

8.2 Enamels

8.2.1 Material

Developed independently from the glass, enamel was born later than the glass in the fifth century B.C. in the Celtic area. It became widespread coming from Byzantium throughout medieval Europe between the eleventh and sixteenth century, when real schools of enamels were created (the Rhine, the Meuse, and the most significant for the industrial production and the distribution of manufactured goods, the Limoges). In the sixteenth century it loses the characteristics of an independent technique and becomes a variant of painting.

This is a technique that takes inspiration from jewellery and glass manufacture. A glass mixture is prepared, mostly coloured: 50% silica, 35% red lead (minium), 15% sodium or potassium + metal oxides which are the colouring matter. The mixture is completed with

additives such as borax, soda, magnesium to give to the product greater hardness, stability and elasticity. The glass paste, prepared in small loaves, is cut and pulverized.

The glass powder is wetted with water and applied to a metal lamina (gold, silver, bronze, copper and recently iron). The adhesion of the enamel occurs through recasting in muffle (without contact with the fire), or through cold process, using resins and mastics in which the powder is dispersed. To adhere better to the enamel, the metal supports were sometimes made wrinkled.

The next step is cooling, to make a fixed texture of the glass. If necessary, a levelling stage and a polishing stage are performed.

8.2.2 Technological typologies

- *cloisonnè*, it consists in the insertion of wet pastes of coloured glass on the metallic lamina inside small strips in relief, which are obtained by welding little metallic strips (*cloison*) curved in the shapes of little pools. In order to fix the strips to the laminas, a provisory resin is used. With the firing, the pressure of the enamels and the warm temperature definitely attach the strips, burning the resin.
- *plique a jour*, similar to *cloisonnè*, with the difference that after the firing the little strips are removed, leaving only the semitransparent enamels.
- *champlevè*, here the pools are produced engraving the metallic lamina, without adding any material.
- *bassetaille*, a drawing was made directly on the metallic lamina and then the vitreous paste is applied on it, without hiding the drawing due to the transparency of the enamel.
- *email de ronde bosse*, the enamel is applied on the lamina worked in relief.

8.3 Precious stones

8.3.1 The materials

Some natural minerals are used to make jewellery and art objects by virtue of structural features such as colour, transparency, brightness, hardness and rarity. Typically, these minerals are divided into three groups:

- 1) precious: rare and characterized by great hardness and brightness (diamond, corundum, ruby, sapphire, emerald);

- 2) semi-precious: moderately rare, generally transparent and coloured (amethyst and topaz);
- 3) gems: mainly non-transparent, compact, with a micro-crystalline structure (onyx, agate, turquoise, lapis-lazuli).

One of the characteristics of these minerals is the hardness, so that they occupy the highest steps of the Mohs scale. The Mohs Scale, which takes its name from the Austrian mineralogist Friedrich Mohs, is an empirical criterion for assessing the hardness of materials. It takes as reference the hardness of ten numbered minerals and such that each is able to scratch that which precedes it, and is scratched from the one that follows it (Figure 8.1).

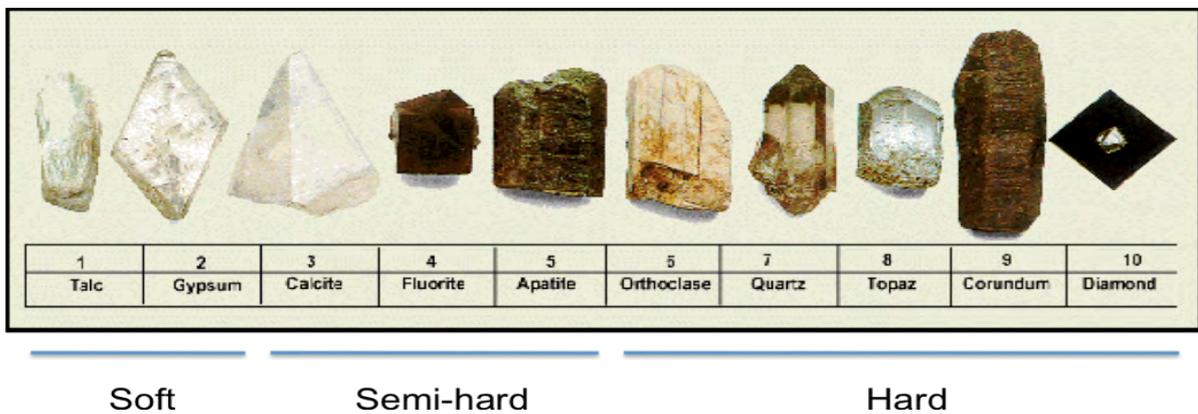


Figure 8.1 – The minerals of the Mohs scale.

The crystalline form of a gem is a feature undoubtedly related to its chemical composition, but not always determined only by this, because it is known that the same substance can occur in one or more different crystalline phases (polymorphism). Similarly, it is not the chemical composition to determine the physical characteristics of a material, but its crystalline form. There are minerals with the same chemical composition, but different colour, density, hardness, transparency, refractive index, scattering coefficient.

The use of these stones date back to ancient times, in prehistory, when they were used in their natural state, without processes, if not rudimentary. To go back to embryonic forms of processing, such as cutting and polishing, we must go back to the times of the historic civilizations of the rivers of Mesopotamia, to which is attributed the invention of the carving and engraving of stones.

“Glyptic” indicates the art of carving and working gems to obtain items for use and decoration (from the Greek γλύφειν = carving). This technique differs from others that use precious minerals, for example jewellery and certain kind of mosaic, as a consequence of direct processing on the stone, while other techniques use stones placed in a more complex system.

Artistic techniques on gems are fairly simple and are transmitted almost unchanged to this day, if we exclude the processes of mechanization. The techniques are characterized by different procedures depending on the structural characteristics of the stones and on the ornamental use. The glyptic includes essentially two groups of products: the carved gems in negative and the carved ones in relief. But there are stones that require only the cut.

8.3.2 Synthetic and false stones

The synthetic stones are those produced chemically imitating the composition and the structure of natural gems, and therefore the physical aspect. The false stones have nothing in common physically and chemically with the natural products, imitating the only colour. They are obtained with glass pigmented with metal oxides, or with other natural stones of poor quality.

8.3.3 The cutting

The cutting is practiced by means of circular saws, or rotating grinding wheels, usually in a metal material, whose hardness varies in relation to that of gems (in descending order of hardness: steel, copper, tin, lead). An oily mixture of abrasive corundum or diamond facilitates the work of cutting. The process is very simple and consists in setting the stone to be cut to a mobile support, then submit it to the rotating grinding wheel (the rotation varies from a minimum of 2000 to 3000 rounds per minute and increases depending on the hardness of the stone). The cut can be applied at random on the stones, for example to highlight certain structural characters (“cabochon” cut). Or it can be planned in order to obtain regular faces (“geometrical cut”). Increasing the number of faces, it is possible to multiply the effect of brightness, amplifying the angles of incidence and the refraction of light.

The cut must be made with precision, faces and angles must be chosen carefully. Sometimes the ancient cutting was less precise, almost always obtained empirically, not always reaching the effect of maximum brightness. The results were improved with the

progress of scientific knowledge concerning the physical structure and the optical properties of the minerals. For example, the modern cutting takes into account another characteristic of the mineral, discovered by physics: not all the points inside the crystals are equal, but some parts can present weakest links (“cleavage”). These parts are the ones that the cutter preferably follows, reducing the possibility of waste or breakage.

The cutting technique is mostly applied to gems with high refractive index, such as diamond. Diamond occupies a unique position in human history. It is pure and bright, and its hardness, the highest ever in the Mohs scale, makes it a symbol of eternity and strength. These concepts are inherent in the word diamond, that comes from the greek *Adamas*, “unchangeable, indestructible, wild”. Diamonds are formed deep in the earth’s crust and then transported to the surface along with other minerals, under the pressure of magma movement. The diamond is composed of pure carbon atoms arranged in a tetrahedron, and in the raw state appears predominantly dull and unattractive. It should be appropriately cut to highlight the high refraction coefficient and consequently the great dispersion of light (Figure 8.2).

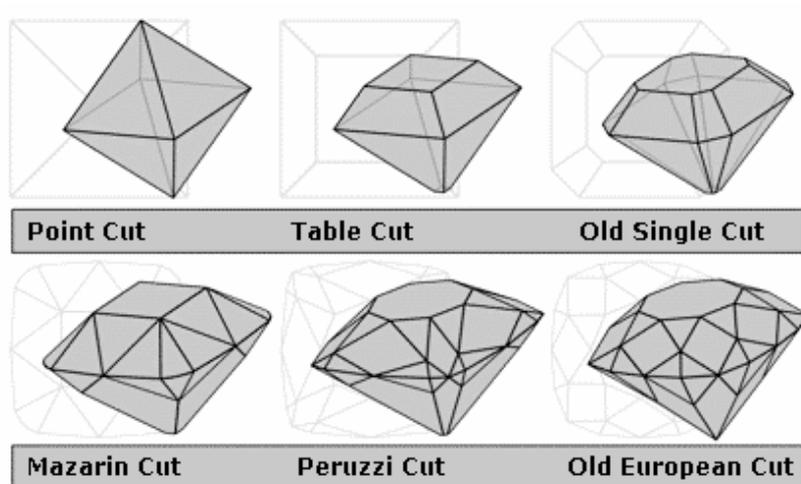


Figure 8.2 – Different cuts of the diamond.

The ancients did not know how to work the diamonds and were limited to basic operations of cleaning or smoothing. Later, in the fifteenth century, was made the first attempt to cut: it seems that in 1475 a French was able to produce a diamond with 33 facets and was an Italian to realize 58 facets. Today it is possible to see multi-faceted cuts. The most famous diamond is colourless or with light colours, which is the most valuable and most rare, but

there are also a variety of diamond yellow, green, blue, pink, red and black.

The diamond powder used as an abrasive comes from diamonds not used for cutting, due to the presence of defects in the natural stone.

8.3.4. Carving and engraving in negative

Until the Hellenistic age only the carving and engraving of gems in negative was practiced.

The engraved gems in the past were usually used as seals (Figure 8.3).

The technique consists on practicing incisions on the surface of the minerals by means of peaks of various shapes, depending on the design to be carried out. Tips may be of metal or rocks harder than the gems to be worked, usually diamond or corundum. Other instruments used: grinding wheels, drill, chisels, hammers, blades, abrasive quartz and garnet mixed with oil or water, clamps and forceps. The action leaves opaque tracks of the tips, so that the stones need to be polished with powdered pumice or tin oxide.



Figure 8.3 – Examples of carving and engraving in negative.

Carving by means of acid attack is practiced for example in quartz, taking advantage of its siliceous composition. The stone is covered with a thin layer of wax; the decoration is made engraving the wax with a tip; the hydrofluoric acid attacks the quartz in the parts where the wax was removed from the tip, remaining intact the parts still protected by the wax. The longer you leave the acid, the deeper is the incision. Using the acid in aqueous solution, the incision is glossy, while it remains opaque when acid is used in gaseous form.

8.3.5 Carving and engraving in relief

From the Arabic word *gama'il* (flower bud), the cameo is an artistic object made by

carving and engraving a stone in relief, using a two tone layered gem (typically onyx, sardonic, agate), or producing the bichrome effect overlapping the precious stones with coral or shell (Figure 8.4).

The stones at the base are usually dark, to create contrast. The procedure for the realization of a cameo is all manual and still now processed by craftsmen. The first phase consists in the choice of the shell suitable for the engraving and carving action. Later, is practiced the cutting of the convex part of the shell and then its shaping, eliminating the unnecessary parts (“scoppatura”). Finally, the “aggarbatura”, which consists in giving to the piece the desired shape (usually round or oval) using a special grinding wheel. After that the piece can be mounted on a spindle of wood with hot mastic composed of Greek pitch, wax and scagliola.



Figure 8.4 – Examples of carving and engraving in relief.

After this operation, the “scrostatura” consists in abrading the external part of the shell in order to leave the light-coloured part as surface. Finally the artist draws on the surface the wanted subject.

Only at the end, the shell is attached to the cut gemstone with glue. Working cameo has experienced its greatest peak in the Renaissance.

8.4 Alteration and degradation

Goldsmith's artifacts, even if composed of noble metals, suffer changes and deterioration as all other objects do.

In order to manipulate the metal, it must never be pure, but instead be an alloy with less noble metals able to fluidify according to the specific work needing to be done. The less noble elements experience a natural oxidation and the most sensitive of these objects made with different materials are altered by incorrect thermal-hygrometric regulation in the environments where they are housed.

Beyond the metal alterations in alloy we cited in chapter 7, we can add silver oxidation, a light and superficial oxidation (Figure 8.5), and silver sulphide, a more tenacious and thicker encrustation due in great part to the atmospheric pollution (Figure 8.6).



Figure 8.5 – Small silver jar (MV12131), Vatican Museums: silver oxidation.

Silver oxide (Ag_2O) has typically aesthetic consequences; indeed the black-yellowish tarnish is caused by contact with the air, and it is easily removed with a light mechanical cleaning. Instead, the most damaging sulphur effects come from atmospheric pollution although they are also a result of objects being found in sulphur rich earth at various archaeological sites ($2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + \text{H}_2$). This alteration causes a strong metal corrosion, which causes also the mineralization with subsequent weakening of the material.



Figure 8.6 – Silver strainer (MV65426), Vatican Museums: silver sulfide.

Fortunately, as far as it concerns gold, there are no evident alterations with the exception of those coming from the deterioration of the other metals surrounding the gold. In gilded works, the formation of alterations underneath the level of gold causes a lifting off of it even though there is the risk of losing the golden finish, which was intended at the moment of its creation as a protective function of the underlying metal against the atmosphere and other altering agents.

Further degrading can be caused by mechanical actions since frequent damage is experienced following bumps or structural changes not consistent with the original construction of the works.

8.5 Conservative intervention

8.5.1 Introduction

The nature itself of the artifacts requires a delicate and refined composition that will need to be applied even at the moment of the maintenance work.

This type of maintenance was often entrusted to people who sought to bring back the original form of the piece as if it had just left the hands of the goldsmith who created it; however, this is also the case today as a result of a lack of culture. This type of work requires the use of strong natural and artificial cleaners being difficult to remove and favouring the reformation of oxidation if not sulphuration.

This use had often caused structural damage that required new reinforcing soldering; this soldering unfortunately would immobilize some of the original elements that were supposed to be taken apart for maintenance work.

Conservative restoration of goldsmith artifacts today is still considered a niche sector, even if it is a opinion not always shared. This art dates back to the 1800, and belongs to the category called “minor art”, which today has been substituted by the expression “applied art”. As such, it was not a subject of conservative study like the most fortunate “major arts” around which a thick historical artistic fabric was constructed; at the same time technical and conservative knowledge was developed that today are within reach of everybody.

“Decorative art” has been handled as an object of daily life, appreciated by a small circle of scholars and experts. This has impeded the debate even on their conservative method often leaving to the “sensitivity” of the owner the choice of the result to be achieved.

Only in the last 20 years, we have tried to apply the theory of art restoration in this aforementioned sector by developing guidelines and common methodologies based, as other art, on Brandi’s theory, thereby making uniform the interventions from archaeological artifacts to modern ones.

8.5.2 Dismounting

When the work of art allows for it, its disassembly is the principle operation that permits an in-depth study of its executive method and a differentiating restoration among the various elements the piece is composed of (Figure 8.7).



Figure 8.7 – Lateran Cross (SGL288), San Giovanni in Laterano, Rome: disassembly.

It was exactly the conservation of the piece itself at the base of the choices surrounding its construction, making it possible to intervene on every singular element of the work of art needing help without damaging the rest of the piece. This is a reason why these pieces were almost always able to be taken apart completely, as Valadier said, because they were “the architectonic constructions in miniature”.

The reassembly requires the arrangement of the elements (or pieces) as they were at the time of the disassembly since they were hand-made by artisans, and each one was different from the other. What is required is a constant graphic and photographic mapping during the work phase and an attentive highlighting of the inscribed numbers on every element by the goldsmith in the construction phase.

The disassembly must not create any damage to the individual elements which would cause difficulty in repositioning them (e.g., the opening of riveted hinges or fracture of a metallic flap). The intervention of the art restorer, therefore, stops at the point in which his or her work becomes more damaging than beneficial.

8.5.3 Cleaning

Having all the pieces taken apart, the restorer can step in and begin in a balanced and separate way, according to the composition of the materials and the type of alteration present.

At first, a degreasing bath in ketone solvents is made in order to remove possible protective products that were used in previous maintenance interventions. If a full immersion is not possible, attempts to obtain similar results can be undertaken by padding the elements with the solvents. Both silver oxide and copper salts are sensitive to immersion actions in Rochelle salts; this solution may be milder or stronger according to the percentage of dissolved salts in the de-ionized water and the time the salts are left in such solutions.

If the encrustation of the excavated objects is very strong and tenacious, one can add a percentage of E.D.T.A. to the solvents. Without the possibility of immersing the work, one can intervene with a piezoablator. Once the encrustation is removed, the work needs to be finished off with sodium bicarbonate which will be explained below.

Excellent results have been obtained by using laser cleaning. Indeed, the ray has a very good mechanical action on dark encrustations often found on metals, and it makes a detachment of the entire patina without scratching the original metallic layer underneath.

The structuring or layout of the laser depends on the type of patina having formed, which can be different according to the composition of the alloy and the environmental agents with which it came into contact. Therefore, in order to reach the optimal result, several samplings need to be taken in order to get to the desired results.

Before proceeding with the mechanical cleaning with wooden chisels, a bath with surface active agents will help the next step. At this point, if the patina is very thin, the chemical cleaning can be balanced with the mechanical one through the use of dissolved sodium bicarbonate in water with the aid of wooden chisels or soft sponges. This paste of sodium bicarbonate will have a light chemical reaction but a fundamentally abrasive one, so it should be used delicately. At the end of this process, one should proceed with long rinses in de-ionized water and finally with a drying with infrared rays.

Nowadays, a laser cleaning of the surface is more common and favours a dry cleaning or possibly with little water with careful attention paid not to use too much force on the surfaces which are often weakened by the alterations. The intensity of the ray is easily regulated depending on the stubbornness of the surface encrusting that needs to be removed. After the removal of the encrustation, this process subsequently requires a homogenization of the sodium bicarbonate cleaning since the ray may leave a light oxidation on the non-noble elements of the silver alloy.

Unfortunately, the aid of such machinery is not widespread since the equipment is costly, but also due to the environments where such operations are carried out.

8.5.4 Consolidating

After the cleaning, a consolidation or even integration will occur in order to finish with the protection of each and every single element. Some elements require a consolidation especially if they are a structural part of the piece.

The most used methods so far are mechanical with hinged metal rivets, but the reversibility in these cases is difficult given the invasiveness of the operation; subsequently, epoxy bi-component resins are utilized. However, the durability of these materials is always conditioned on the methods and places where the pieces are housed since they are sensitive to the thermo-hygrometric variations. The use of the micro-welding laser has been introduced in the last few years in order to obtain micro-consolidation with a strong seal without any noticeable alteration of welded materials except for under a microscope.

8.5.5 Integrating

Some of these consolidations require, however, even the necessity to reconstruct some of the missing parts, and in a particular way for structural needs when the missing of one element may call into question the very nature of the work itself by limiting its use as well as its exposition. The integration of the metals is carried out mostly with bi-component pigmented epoxy resins; sometimes even with metallic dust should the weight of it not be dangerous for the piece's intactness. Otherwise, you can use compatible metals, if not the same of the work itself, attached in a mechanical way or with resins if not exposed to excessive force. This integration will be recreated similarly to the model with such a finish so as to distinguish it from the original without rendering it aesthetically invasive.

8.5.6 Conclusive operations

Because of the very nature of metals, contact with oxygen causes a surface alteration.

This natural occurrence can never be totally avoided, however, it can be at least slowed down by housing the works of art in thermal-hygrometrically controlled environments and protecting the surfaces with synthetic wax, silicon or nitrocellulose gloss.

These types of products create a film that limits the direct contact with oxygen and consequently the oxidation of the metals itself. However, even these materials are exposed to alterations, and from time to time need to be substituted with new products. This necessity requires the consideration of which protective products to use, because they need to be able to be removed without causing any damage to the work underneath.

8.6 Case studies

8.6.1 Disassembly

THE LATERAN CROSS

The cross (SGL288, Treasure Museum of the Basilica of San Giovanni in Lateran, Rome, Figure 8.7) was completely taken apart because its wooden interior was damaged and its ability to stand was compromised. The nails that kept in place the gold-plated silver layers had been mostly substituted during the maintenance work with iron and some brass nails.

Thanks to this operation, many of the stamps inscribed by the 18th century goldsmith were found on many layers on the backside of the piece.

The piece's structure in walnut was assisted with walnut plugs and the original nails in silver still found inserted in the wood were substituted with brass ones (Figure 8.8) in order to differentiate between the modern ones and the antique ones.



Figure 8.8 – The Lateran Cross: original silver nail and the brass one substituting it.

AMBER SALT SERVICE

Even these salt services (MV61841-61845, Vatican Museums, Figure 8.9) were disassembled in order to effectuate a cleaning on the metals without damaging the amber otherwise sensitive to solvents for metallic elements.



Figure 8.9 – An example of amber-made salt shaker of the Vatican Museums.

GOBLET/GLASS

This goblet (MV61858, Vatican Museums, Figure 8.10) could no longer guarantee its integrity to stand erect since its stem was fractured and, therefore, could no longer be upright. It was disassembled in order to give space to a silver tube which went to connect the two parts internally, thereby ‘reinforcing’ the original stem.



Figure 8.10 – Goblet of Vatican Museums (MV61858).

VARA OF SAN SILVESTRO OF TROINA

Even the Vara of San Silvestro of Troina (Figure 8.11) needed a complete disassembly since every element was in need of cleaning in ketonic solvents in order to remove the altered gloss from a prior restoration; in that restoration the correct disassembly had not been made since the original numeration of the goldsmith was evidently neglected.



Figure 8.11 – Vara of San Silvestro of Troina.

THE IMMACOLATA

This statue (San Biagio Church, Acireale, CT, Figure 8.12) was taken apart in order to homogeneously clean the thin layers of silver, and they were replaced in a way to plug the gaps that were created by a previous incorrect reassembly and placing new ones where the original ones were not sufficient.



Figure 8.12 – The Immacolata in the San Biagio Church in Acireale, Italy.

8.6.2 Cleaning

BOWL

This archeological bowl, kept in the National Archaeological Museum of Damascus, Syria, presented a strong sulphuration, and above all a thick encrustation (Figure 8.13).

In this case, a cleaning with a piezoablator had good results, and it was followed by a sodium bicarbonate rinse in water.

STRAINER

This strainer (MV65426, Vatican Museums, Figure 8.6) was not able to withstand damaging mechanical actions due to its fragility and its diffused fractures. In order to remove the thick crust of silver sulphide, it was decided to use a laser and subsequently to uniform the cleaning with sodium bicarbonate in water by padding (Figure 8.14).



Figure 8.13 – Encrustation and sulphuration of the goblet of the National Archaeological Museum of Damascus.



Figure 8.14 – Strainer (MV65426) after cleaning (the strainer before cleaning is in Figure 8.6).

8.6.3 Consolidation

CHALICE (MV61790, VATICAN MUSEUMS)

This chalice was taken apart with its pieces cleaned according to their specific nature. The enamels of the crux were heavily fractured with many parts missing, and therefore, needed an adequate consolidation using the same nitrocellulose gloss that was used to protect the silver layer on which they were created (Figure 8.15).



Figure 8.15 – Chalice of the Vatican Museums (MV61790).

PYX WITH LEAD NAILS

The pyx (MV61794, Vatican Museums) presents a strong deterioration in one of its lead elements and the beginnings in another (Figure 8.16). It seems to have been caused by the internal wood that was placed on the inside of the copper stem. From an analysis carried out in the diagnostic laboratories of the Vatican Museums, it was determined that the wood put in contact with lead can cause “cancer” in the latter manifesting itself with the pulverization of the material. The nails were taken out, cleaned with pure alcohol and consolidated with paraloid B72 (3%) and at the end reset after the cleaning of the pyx and the removal of the internal wood.

BOWL

The archaeological bowl, kept at the National Archaeological Museum of Damascus had a fracture along its edge. The encrustation strengthened the underlying very weak surface which at the moment of its removal during the cleaning had a fragment detachment (Figure 8.17). In order to reposition the fragment in its place, the cleaning was terminated and consequently consolidated with a bicomponent epoxy resin.



Figure 8.16 – Pyx of the Vatican Museums (MV61794).



Figure 8.17 – Bowl of the National Archaeological Museum of Damascus.

8.6.4 Integration

MANDYLION OF EDESSA

The silver frame of the Mandylion of Edessa (VAT1000, Papal Sacristy, Vatican City) was disassembled and restored. Each element was taken apart in order to distance them from the ancient Christ image so as not to damage it.

During this phase, it was noted that the enamel of the collet petals of the frame were not originally heated, and therefore they are modern, and the gold plate that covered the hidden face of the original riza is therefore also modern. The silver plated copper strings that fixated the pearls to the crown were as well modern (Figure 8.18).

These were in fact strung with modern iron strings whose alteration stained the pearls and

the ancient fasteners that originally guaranteed the attachment were shattered during the maintenance work. To make up for this damage, the aforementioned strings were used. It was considered to eliminate them, and using the openings of the ancient fasteners, some silver screws were welded with a laser blocking the bolts, making it possible to continue with the maintenance without causing any damage.



Figure 8.18 – Silver frame of the Mandyion of Edessa.

THE PALIOTTO OF PIETRO PIFFETTI

The Paliotto of Pietro Piffetti (Papal Sacristy, Vatican City) is composed of a wooden structure on which a multitude of sheets of mother of pearl, ivory, decorated in turtle shell and various woods are attached. The trimmings created by these polymetric elements are highlighted and enriched by brass lines that have at the same time the function of absorbing the shocks of movements that such hard elements must endure being layed on the “live” surface of wood (Figure 8.19).

Therefore, in addition to integrating the sheets of mother of pearl, ivory and turtle, and having consolidated almost all the sheets whose Cervione glue had lost elasticity and

adhesion, it was decided to integrate even the brass line in a circular shape instead of a square one for an aesthetic and mechanical end.

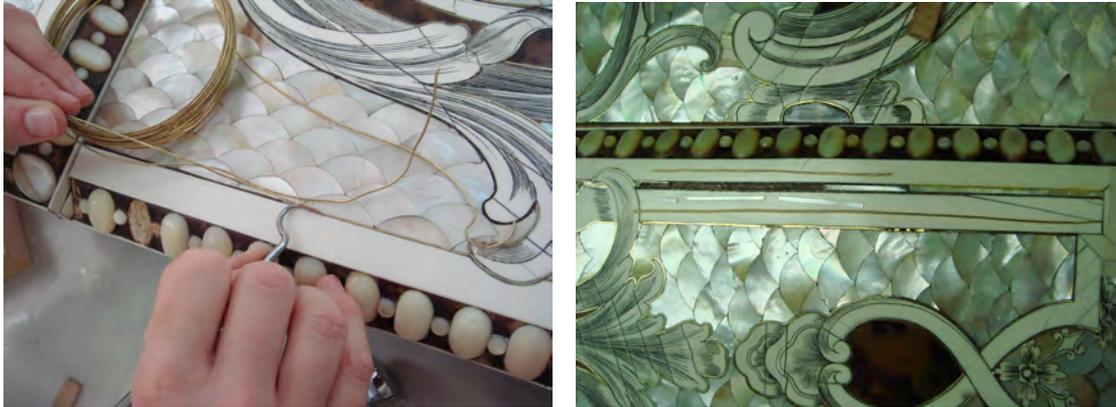


Figure 8.19 – A Paliotto of Pietro Piffetti (Vatican City).

8.6.5 Protection and reassembly

The end result of any restorative operation of Goldsmith artifacts is the protection of the metallic surfaces with a gloss that slows down the natural oxidation, and the object's total reassembly. The protection may be done with microcrystalline wax or with nitrocellulose gloss, which are both removable. According to the nature of the artifact, it is preferable to choose one way or another.

The fundamental rule of the reassembly is to follow painstakingly the mapping followed at the moment of the disassembly, and even sometimes this needs to be called into discussion if one realizes that the original structure may have been modified in a previous intervention. That which can happen in the case where we observe the goldsmith's mark or engraved numbers at the moment of construction or should some element not coincide with its adjacent part. We, therefore, try to reassemble following the hypotheses of original construction in the hopes that the piece did not suffer any large variations so that it will easily coincide together.

The *Immacolata* (Church of San Biagio, Acireale, CT) was therefore reassembled following the mapping of the disassembly, but making small changes or allowances for some of the lamina that were placed badly in a prior restoration (Figure 8.12 and 8.20).



Figure 8.20 – The Immacolata in the Church of San Biagio in Acireale, Catania (Italy).

The *Crucifix* (MV61794, *Vatican Museums*) had been reassembled by inverting the order of the composed parts and therefore, it was reset in the correct positioning (Figure 8.21).



Figure 8.21 – Crucifix of the Vatican Museums (MV61794).

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9 – WOOD ARTEFACTS

9.1 Characteristics of the wood

Wood is one of the oldest materials used by humans, because it is easy to find and it is relatively easy to be manufactured. The man used it to build houses and furniture, as well as to create everyday objects and ornaments.

The chemical composition of wood is made up of approximately 50% carbon, 44% oxygen, 6% hydrogen; minor amounts of other chemical elements can be present, in particular nitrogen (not more than 1%), Ca, K, and Mg compounds (the sum of which is generally less than 1%) and traces of pigments. The main elements are combined together to form mainly cellulose, hemicellulose and lignin in different proportions depending on the type of tree. Coniferous plants show 40-50% cellulose, 20% hemicellulose and 25-35% lignin, while broadleaf plants have approximately the same percentage of cellulose, but less lignin (17-25%) and a variable percentage of hemicellulose (15-35%).

The compactness of the wood depends on the speed of growth and deterioration of the cells, so that the wood can be divided into “hard” and “tender”; oak, walnut, boxwood, pear, and cherry are hard woods, while pine, poplar, linden, and fir are tender. The types of wood used for artistic purposes are the medium-hard ones, resistant to animals and less sensitive to temperature changes.

The wood is characterized by a strong anisotropy, that means that the behaviour differs depending on the direction, due to its fibrous structure. If we look at the cross section of a trunk, we can distinguish clearly a number of tissues arranged in concentric bands (Figure 9.1). This implies a different behaviour to variations in temperature and humidity and determines different rheological properties (elasticity and plasticity). The wood is affected by the climate changes, so that it swells with moisture and heat, and it tends to form cracks when it dries. This last phenomenon also occurs when the wood dies, after killing the tree, because its cells lose water.

The wood can show further heterogeneity due to the presence of natural defects:

- *nodes*, that are branches incorporated into the wood during the growth of the circumference of the trunk; they have a mass volume different from that of the

- surrounding wood, and then retire differently during aging (Figure 9.2),
- *onion structure*, that is a gap between two consecutive growth rings, caused by frost or by a high temperature; this defect may emerge during aging,
 - *star cracks*, which consist in radial cracks caused by the tensions of plant growth or by the different behaviour of the central part of the trunk and the rest (Figure 9.2),
 - *eccentric heart*, that is a conspicuous irregular growth rings which are eccentric due to the fact that the plant is grown in steep slopes or in very windy areas,
 - *bags of resin*, which constitute tree's natural defences when it suffers an injury.

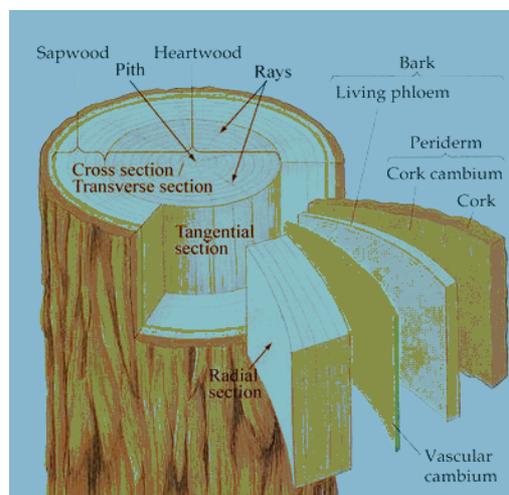


Figure 9.1 – Section of a trunk of wood.



Figure 9.2 – Some natural defects of wood: nodes and star cracks.

9.2 Working techniques

9.2.1 Cut and seasoning

The trunk can be reduced to axes according to different patterns of cut, parallel to the length of the trunk (Figure 9.3). Each cut, according to the point where it takes place, has a different name. After cutting, the wood loses quickly the water present in the cell cavity. All axes tend to embark, but the central axis is more stable.

The natural seasoning ensures the greatest stability; it is achieved by piling the boards and interposing strips to allow air circulation. Since it would take a long time, the artificial drying is used, which occurs in special environments, real furnaces with controlled humidity and temperature. At this stage the wood continues, but more slowly, to lose water until it reaches equilibrium with the environment around 17-23% humidity. At this stage the wood is deprived of substances carried by the resin flowing into the wood.



Figure 9.3 – Scheme of different positions where a trunk can be cut for achieving axes.

9.2.2 Paintings

When necessary, the first stage is the assembly of several well seasoned axes, with casein and mortar, reinforced with wood and pivot: pivot's head is planted on the side of the surface to be painted and then covered with a layer of wax. Rigid wood axes fixed on the back must be avoided because they prevent the natural movement of wood; flexible wooden armatures should be used. The connected axes are covered with strips of canvas. The preparation of the surface to be painted begins with the application of a first coat of glue on the canvas and then a layer of plaster and glue, smoothed after drying. The process was then repeated several times until you have a preparation chalk/glue of 1-2 mm, on

which lies the film of painting. The most important types of painting are:

Encausto: the wax is used as a binder for colour. The pigments are moistened in hot beeswax lying on the wood. The colours are kept liquid through braziers and applied by brush, with a hot spatula. Solidifying, the pigments are captured. Encaustic painting is very opaque, thick and creamy.

Tempera: a mixture of glue with mineral filler (usually chalk) is used to build cohesion between painting and wooden support. The glue is diluted in water, causing a temporary swelling of the surface. Therefore, there should be a period of drying, after which the mixture comes into contact with the wood. Then the colours are applied. The tempera can be meagre or fat. Meagre if the binder is egg yolk, milk, animal tissues, fig latex, animal glues. Fat if the binder is composed of oils and varnishes.

9.2.3 Sculpture and intaglio

As for stone, sculpture of wood consists in definitively removing portions of material. The wooden sculpture was often painted or covered by other materials (metal, leather, etc.).

An artefact is preferably derived from a single block of wood, but some parts are made from other blocks and then joined.

After carving, the obtained object may be left “raw” or covered with a thin layer of colour diluted in water, and then polished or painted.

Also the ‘intaglio’ technique for wood is similar to that of the stone. The tools used are chisels, gouges, mallet (Figure 9.4).

After an accurate design and sometimes three-dimensional model in clay, the block is moulded with a saw, then finished with a great gouge and the artefact completed with the help of other tools. The polishing is performed with walnut oil or flax, or with lacquer, rubbing with linen cloths.



Figure 9.4 – Tools used for the ‘intaglio’ technique for wood.

9.2.4 Inlay

Marquetry is an ancient technique that can also be called inlay (“rimesso” is the Italian word) when it concerns wood. It consists in inserting and pasting elements of the same or different material, with mastics or organic glues, on a purposely prepared surface, to create geometrical drawings (like “*certosino*”) or figurative drawings, both on complete surfaces and on panels. This is the art of painting with wood.

This art develops a lot in Italy in the 14th century just with a painstaking form of inlay work, known in Italy as “*certosino*”. This is a composition of geometrical drawings, realized through small sections of wood, detailed with light and dark pieces, which were fitted together into a corresponding opening. At first, inlayers shaded the pieces blackening them, besides alternating them; initially they made use of a red-hot iron, afterwards they dipped the small sections of wood into scorching sand, and subsequently they began to boil the same small inlaid sections with vegetable oils or herbal essences.

At the beginning of the 17th century the wood inlay regained favour thanks to the great Dutch cabinet-makers, who introduced the new technique of ‘marquetry’ (marquetterie in French) into France; unlike inlay, marquetry lies on the plane.

This is a technique decoration based on the colour contrast of different woods, but also metallic plates, silver flakes of mother of pearl, ivory, tortoiseshell, and other. The inlay is made with very fine views. Ultimately, there are two types of inlay (Figure 9.5):

Certosino: you use small pieces of solid woods, light- and dark-colored fixed to the basic structure with mastic.

Marquetterie: overlapping sheets of various woods with equal thickness and size; with a single cutting operation is obtained the desired design.



Figure 9.5 – Wooden artefacts with ‘certosino’ (left) and ‘marquetterie’ (right) technique.

9.2.5 Gilding

The gilding techniques concerning wood are two:

leaf gilding, which involves the application of gold leaf on a surface properly treated;

dust gilding, which is technically identical, but it uses gold dust instead of gold leaf.

Gilding is a difficult technique: we think that an inexperienced person can not possibly realize this technique only reading these pages, or even a more exhaustive book than this. Only the experience gained working alongside a good artisan allows people to get satisfactory results.

This technique, certainly difficult to realize because of the awkwardness of the extremely fascinating process, requires different stages and it takes several days to complete the inlaid work. However the outcome surely rewards patience of the restorer trying one's hand at this ancient art that lasts from more than a century.

The process have remained the same for a very remote time. Modern technology adds a change in terms of rolling gold, that is not hand-wrought by the “gold beaters” anymore, on the contrary it is processed in a factory.

The following necessary materials and tools can be found in a well-stocked paint shop, or in a Fine Arts shop, or in a shop specialized in the field of restoration:

materials: plaster of Bologna, rabbit-skin glue (known as “colla Lapin”), fish-glue sheets, Armenian bole (also known as “bolus armenus” or “bole armoniac”), pure gold foils.

tools: gilder's pad, gilder's knife, gilder's brush, burnisher, bain-marie pan, various brushes, fine-grained sandpaper (120, 180, 240).

In any case, gilding requires that the support is made perfectly smooth, with the surface pores closed; of course this operation must be carried out on a cleaned surface, free of dust.

9.2.6 Ebanisteria (cabinet making)

Woodworking technique fairly recently (since the seventeenth century), especially for furniture, initiated by the introduction of the use of ebony, a solid wood with fine grain. Actually ‘ebanisteria’ can include all the highly specialized works, using precious woods. Typically, this work provides a structure or a veneer, the first made from hardwoods such as walnut, oak or pear tree, and the second by precious sheets of woods such as ebony or mahogany and other exotic woods.

9.2.7 Xilography

Xilography comes from the greek words ‘xulon’ = wood and ‘grafein’ = to write.

In a matrix of wood the surface of the not engraved parts receives the ink and makes the sheet black, while the carved parts remain white. That’s why this technique is called “print on relief”.

For the xylography, blocks of hard woods are used, cut along the wood fibers. The instruments used to engrave are various types of knives and gouges. On the well seasoned and polished tablet of wood, the drawing with pencil and then ink is made.

This design will be the reverse of the image that is wanted. With a short cutter you start to carve the wood, keeping close to the design.

When the whole design is surrounded by the groove, you proceed to remove the wood in the parts that should be white, using gouges of various sizes. And then a pad or a roller passes over leaving the ink. The print is then made by hand or with a flat press. The earliest prints were almost always completed by adding a coat of colour. But then the colours were added in the same printing process.

Initially, many pieces of wood with different inks were printed simultaneously, as many as were the desired colours. But the colours were flat. At the beginning of ‘500 a procedure based on the use of different matrices was introduced, which produces effects similar to drawings in ink and watercolour on coloured paper.

9.3 Degradation of wood

9.3.1 General information

Wood, contrary to the common convictions, shows a remarkable intrinsic degradation resistance. Or rather, the only element ‘time’ doesn’t play a leading role in bringing about a change in the features of the materials.

The outside agents alone, in particular among them the biotic agents (bacteria, fungus, insects), can be cause of degradation, provoking serious aesthetic/artistic/functional problems and grave difficulties in terms of preservation, especially in the area of expertise of cultural goods.

The settlement and the development of the biotic agents is strongly influenced by the environmental conditions; bacteria and fungus generally need a very moist environment to

succeed in destroying wood, while insects are more harmful than them, because they do not need particular environmental conditions.

There are a lot of insects interested in works of art, but the most common xylophagous insects belong to the orders of Coleoptera (commonly called beetles), Isoptera (also known as termites), Lepidoptera, and Hymenoptera. The first three are really involved in the restoration field.

Each species has distinctive biological and ethological features. It is essential that the restorer has a good knowledge of these orders of insects to protect and preserve works of art from them.

9.3.2 Coleoptera

“Woodworm” (“tarlo” is the Italian noun) is the common noun to identify various types of Coleoptera (beetles), which feed on wood (Figure 9.6). Some beetles can be found more easily today than in the past, because the temperature within our houses, thanks to the heating system in wintertime, is in favour of their production cycle; in fact in these favourable conditions they are able to reproduce themselves three times a year.



Figure 9.6 – The common woodworm: insect of Coleoptera family (beetles).

The female of the common woodworm (*Anobium punctatum*, “woodworm of furniture”) lays eggs into cracks, holes, erosions of the wood and into all the points of the furniture, where the newborn grub will have the opportunity to feed itself, beginning to dig its tunnel. It follows that the well-polished and preserved parts of our furniture aren’t a favourable environment for woodworms, therefore it is very important to devote some time to take care of the furniture so as to protect them against these undesired insects.

Grubs, once they have entered the wood, live into it, wood-feeding themselves and digging

long tunnels, which naturally follow the grains of the wood. The life cycle of these insects also lasts several years, and at the end of that (generally in the spring and in the autumn seasons), the fully grown insect go towards the outside. It follows that, contrary to what people think, the hole we normally see and which inform us of the presence of woodworms in our furniture, isn't the entrance hole, but it is the exit hole.

Therefore when we see the small opening, the damage has already committed.

Among the most common species, which infest furniture, there are the woodworms of the family of Anobium. These come out when they are fully grown, in particular in the months of May or July. During these periods people can listen peculiar and regular tapping against the surface, that the male of the woodworm provokes hitting the wooden surface with its head.

In this case we have to do with loving calls. For this reason, the woodworm of this species is also called "death watch beetle" (it belongs to the *Xestobium refovillusom* species).

Another insect of the family of the Cerambycidae, also known as "capricorn beetle", become very acclimatized in our houses. The woodworm of this family is very voracious and it doesn't despise resinous or hard woods. These insects are hardly identified, because they spend all their life into the wood, where they mate and reproduce themselves. The only clue is the typical sound, which people can listen when this insect feeds itself.

Another type of Xylophagous insect belongs to the Lyctus kind. It is recognizable for the distinctive form of the exit holes (round holes, which are 2-3mm wide) where the female of this species lays eggs. This happens between April and May months.

9.3.3 Isoptera

Termites belong to the order of the Isoptera. They are social insects, in fact they live in colonies, composed of until two million of members; they are afraid of light, so they work within, provoking a complete emptying of the artifact at the expense of cellulose. There is no exterior signal of their corrosive action and very often people notice their presence when the damage is irreparable.

There is a partition into castes: fecund male and female on the one hand, worker and soldier on the other; the development of the different castes is organized through a differed feeding. The final development of a colony, complete of all castes, takes three or four years.

The queen lays eggs as much as thirteen million a year; only in certain periods some sexed species appear, swarming outside in springtime; they mate, they lose their wings, then they come back into wood and they create a new colony.

The relation between the members of the colony are regulated by secreted chemical factors called pheromones: there are pheromones of alarm, of trace, and of mating.

9.3.4 Damage analysis of woodworm

Woodworms don't attack by chance, but they look for the thicker parts, which provide them with a larger quantity of food. They search the soft sections of the rings marking the age of the wood, or the signs of these circles in wood having large grains. Woodworms dig perpendicular to the surfaces, with curvilinear and branched development.

Woodworm presence is revealed by small dust drifts, which suddenly appear on the floor, under the furniture or inside it. If we take a look at the supposable point, where we think the hole is, we will soon find it. The exit holes of the Xylophagous insects are very evident: the recent holes have a clear outline, because they have done not long before (Figure 9.7, left). When we see holes having a dark outline, or partially closed with wax, we can easily consider that they are holes caused by the passage of some woodworm long time ago, but also in this case we can not overlook them (Figure 9.7, right).

Damages, which the woodworm can do, include both small holes, scattered everywhere without compromising the quality of the furniture, while sometimes the excavation can cause the crumbling of entire parts. At times the insect digs its tunnel beneath the surface, making the outer layer thin and breakable: this type of damages is provoked by the *Anobium Punctatum* ('or furniture beetle') and Capricorn beetle.

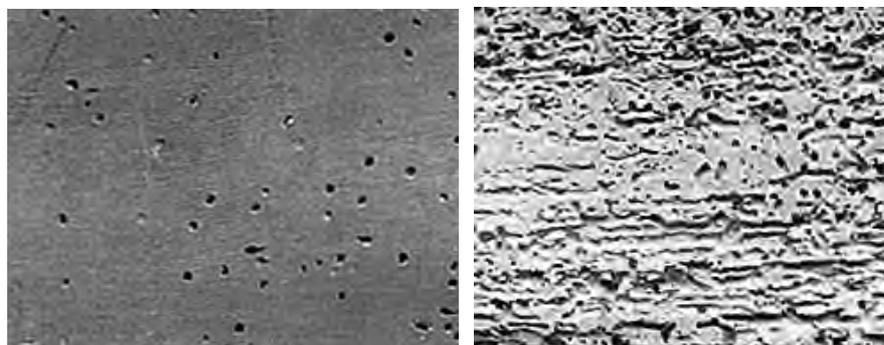


Figure 9.7 – Recent (left) and old (right) exit holes of the Xylophagous insects.

In this case we must pay attention to use abrasive paper, because we run the risk of removing this light wrap, leaving into the open an irrecoverable unaesthetic tunnel. The latter just called “long woodworm” becomes an alarming sign for not declared falsifications. In fact, in the world of the falsification, the furniture is made with salvaged materials and they are passed off as original. The adaptability of wood for new furniture makes often possible to find more or less deep woodworm’s tunnels.

For this reason, we must be suspicious in relation to a presumed authentic furniture. We must show the doubt to the dealer and we must demand explanations about the presence of the “long woodworm”. Certainly, if it is not the case of a falsification, it is a case of misguided attempt of restoration.

Generally, the main woodworms which infest beams and wooden artifacts are the so-called Capricorn of the conifers and broadleaved Capricorn.

9.3.5 Corrosive wear

It is quite easy to find old or even ancient wooden material (beams of old houses, some period furniture that can not be restored) and to assemble or rebuild or alter a piece, placing it in a previous age to its origin. A system which can help us to bring into the open the fraud, will be the corrosion.

The latter should appear on all the parts of the object or of the furniture, obviously appearing more marked in the lowest parts, because these are more subjected to use: in the case of furniture placed on the floor, there will be a lot of damages in the low parts, because of bumps, rodents, or floor washing. In the external parts, which are exposed to severe weather conditions (light, water, sun) some deep cracks will develop; if these are authentic, they will follow the direction of the fiber of the wood.

The drawer runners will be corroded by the continuous running.

9.3.6 Warping

If a wooden surface is exposed to the environmental changes (heat, dampness, etc), it will warp, so that the surface of the furniture will take a concave or convex form.

9.3.7 Patina

Patina on wood is the element that reveals the age, the history and the authenticity of an object, and it is the result of different components, which form it in the course of the time.

Wooden fibers, having different structure visible with magnifying lens, have a shiny and transparent look, almost a crystalline aspect, but they change their physical features through the action of the atmospheric agents. The several operative phases for the manufacture of a furniture also affect the appearance of the wood; in fact in this last case the wooden fibers are deprived of some pigment and resin.

Besides the natural ageing process, we have to consider the dust settled in the small crevices of the varnish (oils, wax, etc), used for the polishing phase. Then the deterioration of these organic materials will occur due to the attack by bacteria living in the air. Finally we have to take into account the life of the object that brings about the formation of the precious patina (coating). It is possible to fake the patina; in this case it gives the furniture a velvety look, which appears smooth and dry to the touch. This false look can not be confused with the greasy coating, made up by wax or old-fashioned varnishes, which is very often used by the forgers to cover the surfaces.

9.4 How to start restoring

9.4.1 Leading scheme and operation plan

In this paragraph we take the matter of how to start restoring of an object or a furniture into consideration. In particular, we examine the various basic operations or procedures enforceable for each artifact having different style and age, distinguishing the interventions that, after a choice, can be more appropriate for the piece subjected to our cares.

Since each restoration needs a defined procedure, a general leading scheme makes easy to choose the technical, practical, and operative phases, which will be applied to the object being restored. The artifact must be observed with great attention, so that we can understand:

- the age, and the compositional style,
- the thought of the artist, or the artisan, who is the maker of the artifact; this is an important element because the deepening of this knowledge can make it possible to perform an intervention in harmony with the artifact,
- if the artifact is authentic, fake or compromised by previous interventions, or even, if it is in so bad conditions that any restoration could be excessive, due to working time and/or materials cost,

- the extent of the damages, which can be defined as:
 - considerable; if the damages concern artistic objects, they are resolvable only with experience and ability,
 - considerable, but concerning less noble or rural artifacts; the patient collector can act alone if he has an adequate preparation,
 - of limited extent, therefore quite easily solvable. Then follows a valuation of the artifact, estimating the damage on which the restorer has to professionally act.

At this watchful analysis follows the typological choice of the restoration and of the materials suitable for the achievement of the work.

The plan of operation includes the following phases:

- a) reinforcing (replacing pieces),
- b) cleaning,
- c) pest control (disinfestation),
- d) integration of stucco-works or holes,
- e) painting or coloring,
- f) polishing and finishing,
- g) final phase of protection.

Not always the restoration requires all the above working phases; for this reason it is important to choose according to the criteria related to the different restoration techniques. In fact the restoration of wood shows several aspects, and the attitude towards this artistic and handicraft area changes over the time. The causes of this change are different, for example the taste, the coming of new technologies and new materials, the more or less idealist thought of the restorer, and the social, economic, and commercial aim of the intervention.

9.4.2 Restoration typologies

Scientific restoration: it is employed for the renovation of the work of art; this type of restoration includes the interventions that ensure the observer about the authenticity of each section of the archeological find, excluding any intrusion on an artistic or formal level. For example, the archeological find acquires the original stylistic form, but the integrations are not hidden through and through, so that the restoration is clearly visible.

Aesthetic restoration: this technique is used in full obedience of the compositional and

structural elements but also artistic and decorative features of the work of art. Following specific and well defined criteria, the restorer intends to return the work of art its original aspect: obviously after a meticulous study of the compositional elements and after considering an accurate video-graphic and graphic documentation.

Commercial or supplementary restoration: it is used to reach the prearranged purpose in the shortest possible time. Nowadays this type of restoration is more than ever applied, giving rise to fakes and, above all, negatively acting on the work of art. Taking this type of restoration into consideration in a completely negative way, it is important to remember the supreme thoughts of some ancient masters: Vasari, Suardo, Melani, who give us strict judgments about the restorer's work.

Deviant restoration: this type of restoration changes the aspect of the object in a significant way, only and exclusively for profit. In this case, the restoration mainly aims at a rapid profit, without scruples and without worrying about the state of the furniture.

Primitive restoration: it is a restoration work for objects which are currently used by the possessor; therefore they are restored so that they can still be used, without worrying for the aesthetic aspect of the restored artifact.

Destructive restoration: it is used to make the artifact, or a section, credibly authentic, especially if the object has a certain value; therefore it is used for profit.

9.4.3 Curative treatments for wood

Among all the building materials, wood is the one that suffers more for degradation problems, due to the action of woodworms, fungi, and bacteria. Like other materials of organic origin, wood also needs proper curative interventions.

All kinds of artifacts (beams, wooden ceilings, truss, furniture, painted tables, parquet, stairs, frames) can be and have to be treated by choosing the most appropriate of the following treatments:

Microwave treatment: ecological system for wood treatment, which does not use any chemicals, it has no residual effect, and it does not need to leave home.

HP technique: an odorless curative product is injected into the wood, which ensures the elimination of any woodworms infestation. This product makes the wood water-repellent, and protects wood against the dampness. Furthermore it forbids the so-called “shrinkage” in a dry climate, and protects wood from fungi, algae or bacteria. Finally, it

does not remove gildings and does not corrode tempera paintings.

Micronization: a special product is micronized on the surface of the wooden artifact through a particular pump.

Toxic fumigation gases: The fumigation using toxic gases penetrates into the structures of the wood to reach the crevices, where termites build their nests; because of the inherent risks, this treatment is subjected to particular regulations.

9.5. Restoration of a small inlaid table

9.5.1 Description of the work of art

Object: small table completely inlaid with ‘intarsio’ technique, 85x60 cm (Figure 9.8).

Age: beginning of the 20th century.

Artist: unknown artist (masters in the art of “ebanisteria” of Palermo).

Compositional stylistics: geometrical/Empire/restoration/floral.

Architectural composition: foot central column supporting the square top and three legs in the form of lyre at the base of the column.

Property: private.

Year of restoration: 2010.

Description of the inlay: the small table has in the lower part three small feet double-s-shaped, which are inlaid in the crest part; in the central part there is the column foot completely inlaid; in the upper part the square top shows a geometrical inlay, which represents Saint George killing the dragon.



Figure 9.8 - Small inlaid table before (left) and after (right) restoration.

Executive technique: the small table shows various inlay techniques; the lower part is an example of the “certosino” technique, while the upper part shows geometrical and figurative techniques with different wooden typologies.

Wooden typologies present on the small table (Figure 9.9):

Ebony: very dense black wood, coming from Africa.

Walnut: this wood tends towards a dull brown color with dark grains. It is a native Sicilian tree and its wood is widely used.

Mahogany: sturdy and hard wood, having a reddish brown coloring.

Acer: heavy wood having light color; it is a native Sicilian tree.

Beech: it is a semi-hard wood, having light color.

Chestnut: strong wood, light brown in color, almost tawny yellow; it is a native Sicilian tree.

Ashwood: strong wood having light color; it is a native Sicilian tree.

Olive tree: hard yellowish wood with back grains, suitable for inlay works. It is a native Sicilian tree.

Rosewood: very fine wood, widely used in France and England.



Figure 9.9 – Some wooden qualities in the small table.

Retaining and supporting structure (Figure 9.10): the retaining structure of the top of the small table is made up of three walnut sections: chestnut planks surround the perimeter; in the central part there are two walnut planks, and, in the middle of them, the screw lodging for the central leg. The median part consists of walnut wood, which is decorated with small inlaid works in the “certosino” style, characterized by various

wooden typologies that create a geometric pattern. The wood of the three lyre-shaped legs is dark walnut; in this lower part walnut wood is inlaid with geometrical “certosino”, creating a fishbone structure.



Figure 9.10 – Retaining and supporting structure of the table.

9.5.2 State of preservation

At a first general glance of the artifact, we can notice a disparate preservative condition. The wooden structure appears in a decent state of preservation, and the same thing for the surface inlays. There are clear signs of chromatic changes and abrasions on the surface of the small table, caused by the wearing effect of time and by its use. However the small table on the whole keeps very well the stylistic features and the good readability.

The anthropological elements strongly influenced the state of preservation of the artifact and its continuous use created many structural/static problems. The wood of the support presents an extended attack of active Xylophagous insects; the flickering holes are clearly visible to the naked eye, both on the support and on the inlaid sections. It can be possible to see some previous restoration works on the three legs supporting the small top.

9.5.3 Restoration work

The restoration activity follows the watchful observation of the artifact, to point out and elaborate all the information useful for a further knowledge of the work of art and in support of the most appropriate planning of the restoration work.

The cognitive researches constitute the base for the execution of a restoration work, conducted according to scientific criteria and in respect of the work of art, its materials and its history. All the information gathered in this cognitive stage is added into a register,

well-supported by a complete photographic documentation of the whole restoration activity. This documentation consists of four main stages of study: executive techniques, constituent materials, preservation state, previous actions and restorations.

The restoration work foresees a preliminary removal of the dust and additional deposits with the brush, on the whole surface of the top and of the legs of the small table (Figure 9.11, left). For the removal of the fatty dusts, it was necessary the use of a padding with a non polar neutral solvent (white spirit), used on the complete surface.

Then, given the presence of several flickering holes of woodworms, as a preventive measure, the wooden support was disinfected with biocide products (Figure 9.11, right). This was done covering the surface by brushing and through injections on the direction of the artifact, to forbid a possible infestation of biodeteriogen organisms (mycological organisms).



Figure 9.11 - Removal of the dust and additional deposits with the brush (left) and disinfection with biocide products (right).

After this preventive treatment, a 'pvc' hermetic chamber was built for the small table; in particular, the artifact was placed in the chamber and it was treated with an anti-woodworm permethrin-based product for a month (Figure 9.12, left).

Subsequently, was made to the manufacture a injection of Paraloid B72, a 7% melted in a mixture of thinner nitric paint and acetone, having the same quantities.

Then the small wooden sections, lifted from the table top, were pasted with an organic glue, consistent with the original one (rabbit-skin glue).

It was necessary to close all the present holes on the surface of the small table, provoked by the attack of the woodworms, to avoid the inclusion of dangerous dusts for the

preservation of the artifact. This was done through some beeswax (Figure 9.12, right), making uniform the whole surface. At the end of the restoration work, a layer of neutral protective beeswax was applied on the whole surface, in order to protect it and make it smooth and shiny.



Figure 9.12 - Treatment with an anti-woodworm permethrin-based product (over) and closure of surface pores with beeswax (below).

9.6 Restoration of a commemorating wooden tablet

9.6.1 The artifact and its conservation state

The artefact is a polychrome commemorating wooden tablet, containing tri-dimensional inscriptions and composed by three planks with a frame, kept in the Archaeological Museum in Damascus (Syria).

Thanks to a document found in the archives, it was possible to date the piece of art to the XIV century AD (Figure 9.13). The results of the analysis of the conservation state of the artwork are reported in table 9.1.



Figure 9.13 - Polychrome commemorating wooden tablet (XIV century AD).

Table 9.1 – Results of the analysis of the conservation state of the wooden tablet.

Type of damage	Front	Back
Remarkable surface dust layers	+	+
Cleavages, holes and breakages	+	
Detachments of colour layers from the wooden surface	+	
Lack of colour and blanks on all the surface	+	
Colour cracks on all the surface	+	
Many whitewashing traces on the frame	+	+
Traces of different colour layers on all the surface due to previous restorations, and a glossy protective film that fixes dust and dirt and provokes many detachments and losses	+	

9.6.2 Description of the intervention

Due to the high documental value of the tablet, the bad conditions of the colour film and the important paint losses (around 50%), we proposed a highly reversible conservative intervention. Then, because of the complexity of the case, we decided for a diagnostic campaign to identify and confirm the original layers and to distinguish them from later paintings. Furthermore we had to understand the composition of the glossy film, which at a first glance at the microscope, looked like an alkyl varnish utilised for planking.

The intervention on the front surface included:

- First consolidation test.
- First consolidation and emergency fixings of the detached parts using sturgeon glue injections of all the surface, according to the test results.
- Emergency plastering of all the surface using French plaster and local plaster, whose recipe was modified due to the conservative needs of the highly unstable colour flakes.
- Cleaning test to remove the attached dust.
- Cleaning of all the surface by using solution of Contrad 2000, 20% concentration; it was strongly recommended to move slowly and precisely.
- Final consolidation of all the detachments.
- Plastering with local plaster only in those gaps that can improve the reading of the artifact and of the inscriptions.
- All the plastering and the white traces were retouched with small slightly opaque water-colour lines.
- Before removing the glossy varnish, we thought it is mandatory to delay any decision after the execution of the scientific analysis to identify its nature and precisely choose the best solvent to remove it.

On the back surface the following interventions were made:

- Dry cleaning test;
- Cleaning of the entire surface from dust, using soft brushes and Wishab sponges.
- Cleaning tests made with surface-acting agent and de-mineralized water. That was made in order to identify timings, methods and right concentrations.
- Whole surface cleaning, according to the tests.
- Mechanical removing of the whitewashing traces using lancets.

9.7 The restoration of a seventeenth-century crucifix

9.7.1 The artwork and its conservation state

The artwork is a seventeenth-century wooden polychrome crucifix, by unknown author, located in the last bay of the right aisle in the Church of Santa Maria in Bethlem in Pavia (Italy). The crucifix has a total height of 495 cm, and underwent restoration in the years 2003 to 2004 with the collaboration of the Superintendence for the Historical and Artistic Demo-ethno-anthropological Heritage of Milan (Figure 9.14).

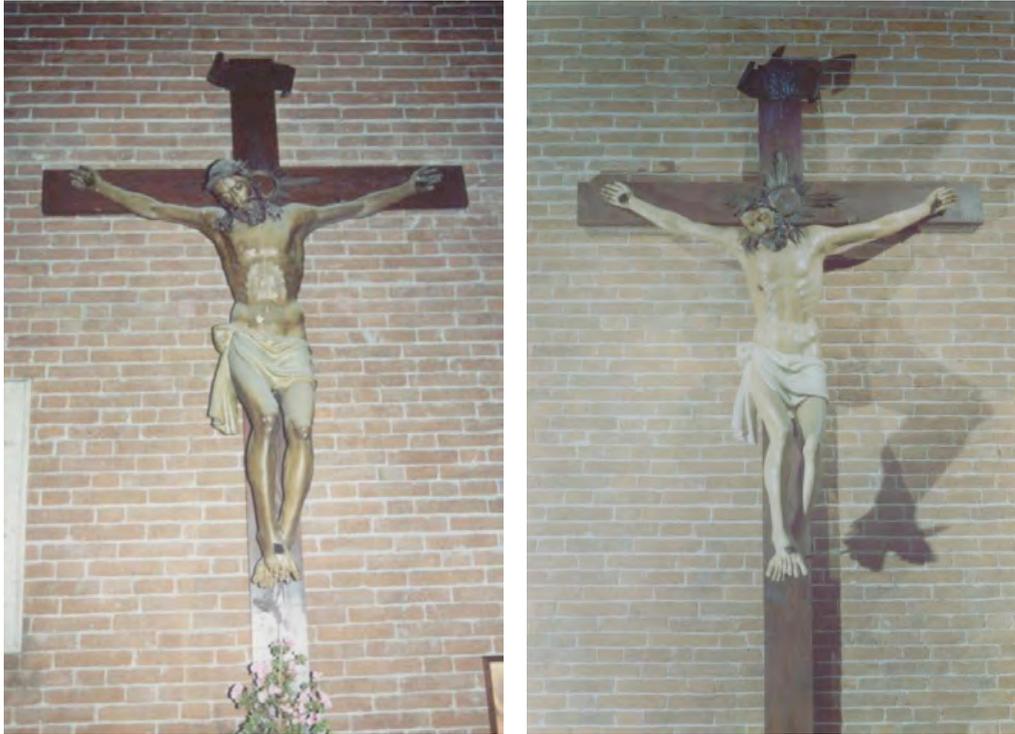


Figure 9.14 – The wooden polychrome crucifix in the Church of Santa Maria in Bethlem (Pavia, Italy) before (left) and after (right) restoration.

The sculptural work in question has a great expressive power and a side profile of a particular beauty. The sculpture of the Christ might have realized shortly before 1600. The cross does not seem coeval with the figure of Christ, but it could have been replaced later. The radial pattern at the intersection of the arms of the cross, as well as the cartouche with the inscription INRI, is made of copper, now very oxidized and difficult to date.

The work was impaired by the following pathologies:

- infestation of Xylophagous insects;
- significant deposits of particulate matter, and fat fumes;
- repainting scattered everywhere;
- relevant fissures between the torso and arms;
- lack of three phalanges of the right hand, and one finger of the left hand;
- loss of color, and subsequent application of gypsum, on the stomach, on the loincloth, and on the knees (in the vicinity of such failures, there are many small unstable parts of matter);
- presence of a thick layer of paint on the loincloth;
- layer of transparent varnish, such as for boats, given on the entire cross.

9.7.2 Diagnostics and methodology of intervention

During the intervention of restoration it was established that the cross is not contemporary with the figure of Christ, as well as the radial pattern and the cartouche; the latter are not made of brass, as had been supposed, but in copper, and their execution is certainly of recent times.

The first observations, carried out at a small distance, have also allowed us to discover that the back of the sculpture is completely hollow from the head until the pelvis (for reasons of manufacture). The cavity was then occluded and modeled with felt impregnated with gypsum and then painted. In the marginal areas of this filling, many gaps were found, as

well as unstable fragments of fill material due to movements of the wooden support. The

chemical and physical analyses have also found that the Christ has been subjected to interventions three times, and each intervention was carried out with a new plastering and subsequent application of renewed colors.

They found a total of 18 different layers of paint and plaster, often uneven and incomplete; the concave shape of the flakes of color, in section, leads one to suppose that the problem lies in the wooden support. This support is a piece of linden wood, and in particular the piece in question fails to reach the full stability of the fibers and therefore you have constant movement of matter and detachment of what has been put on.

With these assumptions, even taking into account that the traces of original color are scarce and that the color is very delicate because the binder is protein, it was decided to keep all the repainting, removing only the last two layers, which are very dark and have a oleo-resinous composition.

9.7.3 Restoration intervention

After excluding the removal of Christ from the cross to avoid the risk of losing the stability of the arms, the restoration was conducted by implementing the following phases:

- photographic campaign before the intervention;
- stratigraphic investigations combined with physical-chemical analyses for the identification of the original colors;
- execution of thematic tables on the conservation state;
- disinfestation by woodworms with Permethar, in a specially built room;
- application of veils in all the unstable colored parts (Figure 9.15);

- injecting a rabbit skin glue, diluted to 5-7%, below the unstable flakes and at the perimeter of the gaps, all already covered with veils;
- dry cleaning with very soft brushes and a small aspirator;
- re-adhesion of the flakes of color and soldering with thermo-cautery;
- removal of veils with luke warm water and cotton wool;



Figure 9.15 – Application of veils in all the unstable colored parts.

- testing to evaluate the consistency of the oleo-resinous layer to be removed and the materials to be taken;
- repair of the damaged parts between torso and arms, and of the fingers, with a mixture of gypsum (90%) and glue (10%);
- cleaning the entire surface with a swab and synthetic saliva to soften the layer of oily varnish, then removed with a mixture of lavender and alcohol (Figure 9.16);
- execution of the necessary fillings with gypsum of Bologna admixed with rabbit glue

(5%);

- integration of the painted parts, with the use of water colors, according to the striped technique ('rigatino' technique);
- application of a thin protective layer of microcrystalline wax over the entire work;
- cleaning of the metal components to remove the oxidized material, straightening, final protection with microcrystalline wax, and reassembling of the metal components;
- complete photographic documentation after the restoration.



Figure 9.16 – Cleaning with a swab and synthetic saliva to soften the layer of oily varnish, then removed with a mixture of lavender and alcohol.

Throughout the time of restoration intervention, thirteen thematic tables were prepared to document all information and the intervention phases:

- materials constituting the artwork,
- collection points of the samples analyzed,
- lifting positions of the surface finishing layers,
- application of emergency veils,
- application of veils and consolidation,
- fillings and plastic reconstructions,
- pictorial integrations.

Two thematic tables are shown as an example in Figure 9.17: they refer to the phase of application of veils and consolidation.



Figure 9.17 – Two examples of the thematic tables prepared during the intervention: application of veils and consolidation on the right (over) and left (below) side.

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10 – ICONS

10.1 The construction of icons

10.1.1 Introduction

In this context the “icon” is considered as an image on a wooden basis. Cases such as painting on metal, on stone, on canvas, etc, are not considered here.

Methods and principles of conservation of traditional icon painting, that is Russian icons, originating from Byzantine, are assumed as a basis. However, besides Russia and Greece which are first of all associated with icon painting, this art exists in other countries such as Serbia, Bulgaria, Rumania, Poland, Ukraine, Belarus, as well as Egypt (Coptic icons), Ethiopia, Near East (Melchites icons).

Despite the similarity of processes of manufacturing icons, in each of these regions there were local features of painting techniques and the applied materials, changing throughout centuries. This should be considered when choosing methods of restoration, preliminary having studied sources describing their peculiarities and data of technical examination. For example, for the Greek icons characteristic are mixed techniques with application in multilayered structures of various materials, including wax.

East icon painting was not always made using egg tempera, but also glutinous binding media. Moreover, it was not always varnished with protective layer, what made it very sensitive to the influence by water solutions, including the process of consolidation. In icons originating from Eastern Europe countries we find gypsum grounds, which react differently to consolidation.

10.1.2. Technique and materials

Icon supports are made of well dried seasoned wood, mainly soft, low resin kinds with homogeneous structure. There was enough width of one board for small icons; for large icon panels the boards were stuck together. On the reverse side (and later on both plank ends) of the panel slats were inserted, made, as a rule, from harder wood, for preventing the deformation of the wood panel (Figure 10.1, left). On the front side, the central part of a board was carved

out, dividing the surface into a hollow area (*kovcheg*) and borders; the sloped edge between hollow area and borders is called *luzga* (Figure 10.1, right).

Before application of the ground on the glued board a piece of cloth, the so-called *pavoloka*, was often pasted. Sometimes pieces of this cloth were pasted to cover the joints of the boards, knots and other defects of the wood. Since the end of 18th century on cheap icons a cloth could be replaced in paper.



Figure 10.1 - Reverse side of the panel with slats (left);
grounded panel with *kovcheg*, *luzga* and borders (right).

The icons ground, known as *levkas*, was prepared from collagen glue (animal or fish glue) and “gesso” (gypsum, chalk, or their mixture). It was applied in thin layers one over the other in several stages, after which it was dried and polished.

Then a preparatory sketch on the *levkas*, with a brush by hand, or mechanically copied from model manuals, was drawn. To make the sketch contours visible through the painting and gilding layers, they were often incised in the ground; this was called *graffa*.

A traditional technique of icon painting is egg tempera in which as binding media the emulsion on the base of an egg yolk is used. There are other but rare binding media, like gum, animal glue, and vegetable glue. The basic pigments used in icon painting were of mineral

origin; organic pigments, as a rule, are less resistant to external action, but due to their transparency and colour intensity they considerably enriched the palette of icon painters.

A protective layer was put on the ready image, for this purpose oil-resin varnishes of various composition were applied. *Olifa* (drying oil), prepared on the base of linseed oil boiled with siccatives, was the most widespread protective coating in the Russian icon painting.

10.2 Degradation and damages of icons

All materials constituting the multilayered structure of an icon are subject to climatic influences, and cycles of temperature-humidity that lead to degradation. As on the whole the icons manufacturing processes are similar to early Italian works of art, we will not consider a problem of conservation of a wooden support and of influence of insects and microbiological factors, since they are considered in the corresponding chapter “Wood artefacts”.

One of the main consequences of changes in temperature-humidity cycles are layer decohesion and detachments on different levels: *pavoloka* can separate from the board, *levkas* from the board or from *pavoloka* (blisters or longitudinal deformations are formed, Figure 10.2 left and right), paint film from *levkas* (Figure 10.3); besides we can observe internal layer detachments within the ground. These damages which have been not corrected in due time, lead to losses of *levkas* and paint layer.



Figure 10.2 - Detachments of levkas with pavoloka (left), and detachments of levkas (right).



Figure 10.3 - Flaking of the paint layer.

The most widespread degradation of *levkas* and paint layer is the formation of cracks-craquelure in the course of drying and ageing of constituting materials (Figure 10.4, left and centre). Excess of glue in *levkas* provokes rigid craquelure with the raised edges (Figure 10.4 right).



Figure 10.4 - “The Mother of God of Kikkos” (Greece, XVIII century, private collection):
 deep craquelure (left), superficial craquelure (center),
 and craquelure with the raised edges (right).

Other serious problem is darkening of a protective film of *olifa* or varnish (Figure 10.5). This, as we already mentioned, because of poor legibility of the image often led, on the one hand, to periodic “washings” of painting with strong alkalis, which damaged it; on the other hand to partial or full renovation of painting and formation in due course of multilayered structures with application at different times of inserts of *levkas*, where it has lost, and overpainting (Figure 10.6).



Figure 10.5 (on the left) - Quadripartite icon (Russia, XIX century, private collection):
darkened protective coating.

Figure 10.6 (on the right) - “Selected saints with the Scenes from the Life of St. Nicholas”
(Russia, middle of XVI century, State Russian Museum, Saint Petersburg).

When a new protective layer is put on the old one or when there is excessive thickness of *olifa*, its deformation and formation of roughness on the surface are observed (Figure 10.7, left).

In some case the surface coating does not darken, but loses the transparency and dims, for example due to films of the egg white (applied in Ukrainian and Belarus icon painting), or shellac coating under the influence of moisture (Figure 10.7, right).



Figure 10.7 - Roughness of the surface film (left); destruction of the surface film under the influence of moisture (right).

10.3 Methods of conservation and restoration of icons

10.3.1 Consolidation of layer detachments of pavaloka, levkas and paint film

According to traditions of Russian school of conservation, for the consolidation of icons, materials similar to those employed for their manufacturing are used, that is sturgeon and rabbit skin glues. These glues are water soluble, therefore they may be reused after softening; they provide reliability of fixing, are elastic enough and do not introduce alien elements into the icons. Before the use it is necessary to warm them up in bain-marie at temperature not above 60-70 °C, since at higher temperature and longer warming the glue loses its properties. If the object is intended to be stored not in a museum with constant climatic conditions, but in damp places, a preservative should be added into the water solution of glue.

If detachments of the *pavaloka* or *levkas* from the board are observed, but the ground is stable

and homogeneous, on the places requiring consolidation we put a preventive piece of tissue-paper on 5% glue. In case of the closed blisters of the ground we make two holes with a needle on opposite edges of the blister and introduce 7-10% warm glue using a syringe. If there are losses of *levkas*, the glue can be introduced directly through them. After absorbing of the glue, while the ground is still damp and elastic, the blister should be thoroughly put down with Teflon spatula. If it is necessary, after drying of the ground the glue can be introduced again. A little bit dried up, but still elastic, ground is finally leveled with Teflon spatula and dried up through an absorbent paper with a warm small iron (at temperature not above 45-50 °C). At a considerable thickness of the ground or in case of detachment of *pavoloka* on the fixed place it is recommended to put some weight.

If the painting surface is dust covered or the ground is powdered, for the best wettability and deep penetration of the glue, the surface is preliminarily impregnated with ethyl alcohol in water (approximately 1:1) by means of a brush, and then is kept until full evaporation of the alcohol.

Superficial thin flaking of the *levkas* as well as paint film (Figure 10.8) is consolidated by means of impregnations with warm glue. Glue of low concentration (from 1.5 to 3% depending on density and degree of degradation of the *levkas*) is used to provide its best penetration and uniform distribution through the whole thickness of the ground. As plasticizer for increasing elasticity of the glue, some honey is added to the solution (in the ratio 1:1 by weight of dry glue). After each impregnation it is necessary to wait as long as absorbing of the glue is completed, and to repeat the procedure until formation, on the dried surface, of a thin glue film, that means sufficient saturation of the ground with the glue.

Each subsequent impregnation is made after complete drying of the previous portion of the glue. After the last impregnation, while the ground and the paint layer are not completely dried out and keep elasticity, the surface is stuck with pieces of tissue-paper (their size about 10-15 x 20-25 cm) and dried with warm small iron, pressing thoroughly every flake (Figure 10.9). Before putting it on the surface, the tissue-paper is moistened with the brush to avoid formation of folds which during drying with the iron can be printed on the surface. If it is necessary to consolidate a large area, the work is carried out on separate areas of the surface that allows to dry the surface uniformly with the iron and to prevent its premature drying.



Figure 10.8 - “Saint Trifon” (XX century, private collection): flaking of the paint layer, before (left) and after consolidation (right).

A special kind of consolidation is the one through steaming. This method is applied in case of rigid detachments of *levkas*, resisting to softening with impregnation of glue, or with bad penetration of the glue through the surface. Its peculiarity involves the application of abundant warm glue (usually 3% since it is put once) on the treated position, then a piece of tissue-paper is put on it, and the surface is gradually warmed through a Teflon film with a small iron till complete absorbing of the glue. Lastly the surface is dried through absorbing paper as after common consolidation.

When paint film and all the thickness of the *levkas* are dried completely (not less than 24 hours) the protective tissue-paper is removed with a wad of cotton wool, which was moistened in hot water and hardly wrung out. The rest of the glue is carefully removed with a similar wad and then the surface is dry-cleaned.

During the consolidation of the icons with water sensitive surfaces, synthetic materials can be used.

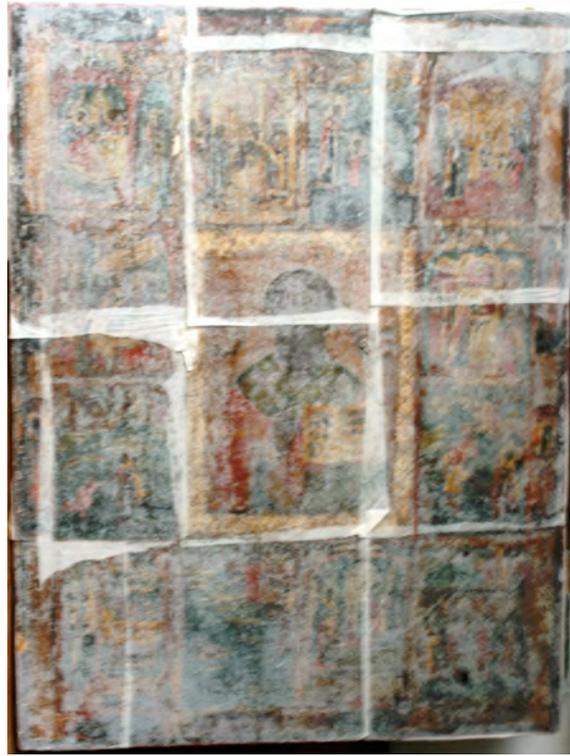


Figure 10.9 - Icon surface covered with tissue-paper in course of consolidation.

10.3.2 Removing of surface grime

Surface grime includes deposits of dust, soot from candles, mould, remains of insects and their excrements (especially when accumulated under metal covers of icons), splashes of paint, wax drops etc.

They can be removed from the surface only when you are certain that *levkas* and a paint layer have no flaking. If the icon was already consolidated, considerable part of surface grime was removed when the protective tissue-paper was detached.

From the surfaces well protected with oil-varnish or *olifa* covering, the surface grime can be removed with a damp wad.

If the protective varnish coating is transparent and uniform, the removal of surface grime can be the conclusive process of the object restoration (Figure 10.10). Resistant deposits of surface grime can be easily removed with ox gall, whose residue is cleaned off with a damp wad.

Wax drops at first are thinned with a scalpel, and then removed with a cotton wool wad moistened in turpentine.



Figure 10.10 - Removal of surface grime.

10.3.3 Cleaning

Cleaning of a paint surface depends on the nature of the protective film (its thickness, uniformity, and dimness degree), and presence of over-painting.

Prior to the beginning of works it is necessary to carefully examine the icon under the microscope to have a clear idea of the sequence of layers and the applied materials.

For cleaning, the following solvents are applied: ethyl alcohol (often mixed with turpentine in different proportions or with addition of spike oil), ethylene glycol, monomethyl ether, dimethyl sulphoxide, etc.

Nowadays gels are being introduced into practice, which bind molecules of solvent and prevent its deep penetration into the layers.

The chemical analysis of a surface film helps to define its components and correctly to choose the solvent. All cleaning works are carried out under a microscope that provides the control of the condition of the surface and allows to avoid damages.

THINNING OF THE SURFACE FILM

Cleaning does not produce the full removal of the protective film, but only its thinning; the thin layer of the original film which remains on the surface attests the work done was correct and the author's painting was not damaged during the cleaning (Figure 10.11).

Cleaning always begins on a test segment on the least important area of the image (as a rule, on the background or borders) for choosing the methodology.

Solvent selection begins with the less effective ones, and, in case of their inefficiency, gradually raising the treatment degree. The sign of effectiveness of a solvent is the colouring of the wad, which was moistened in solvent, in yellowish colour of the darkened varnish during cleaning of the segment chosen for test.



Figure 10.11 - Quadripartite icon (Russia, XIX century, private collection):
thinning of the surface film.

Thin layers of soft varnish can be thinned by means of a cotton wool wad moistened in solvent. Extra care should be taken of the late icons of the 19th - early 20th centuries as their paint layer has not yet polymerized completely and is very sensitive to the solvents.

Considerably thick and strong protective coating should first be softened by solvent. It is an

expedient to use a compress of flannel, moistened in solvent and well wrung out. The compress of flannel is put on a test segment and, based on the degree of its action, the optimum time of application is chosen. It is important to watch the protective film not dissolving the whole layer. The softened layer of varnish or *olifa* coating is removed with a cotton wool wad and then, by means of a microscalpel under a microscope, varnish layer left is leveled. If necessary, during the work the surface is humidified with turpentine which is neutral to old painting (CESMAR recommends to replace turpentine with ligroin).

Various pigments have different degrees of adhesion with the protective film, therefore on different segments it is necessary to vary the time of treatment and sometimes the choice of the solvent.

When the protective coating is not uniform, with the presence of clots and roughness, it is forbidden to apply solvents, in order not to damage a paint layer under a thin varnish film. It is necessary to preliminarily level the surface film mechanically with a scalpel, or abrade it with pumice or emery paper.

REMOVAL OF OVERPAINTING

When there are overpaintings or partial re-paints, before starting their removal it is necessary to carry out complete diagnostics of the icon (using a microscope and methods of technical examination) for defining the safety level of the layer of author and the expediency of the cleaning.

Over-painting can be:

- continuous, covering all painting surface;
- partial, laying on the most damaged segments (including the re-painting on inserts of the restoration ground in lacunas of the original material) or on the parts where for renovation high qualification was not required, especially on the background and on the borders of icons (Figure 10.12).

Irregularities of the surface before re-painting can be covered by a new priming. Sometimes the older image is completely covered by a thick layer of *levkas* and then over-painted; in such cases also the composition of the image changes (Figure 10.13).



Figure 10.12 - “Sinaxis of Archangels” (Romania, XIX century, private collection): icon with overpainting on the background (left), and after the cleaning (right).



Figure 10.13 - “The Mother of God of Tolga” (Russia, XIX century, private collection): test of cleaning, original painting (fragment of the composition “Entrance to Jerusalem”) under the layers of the new ground and overpainting.

On a test segment, you should make a cleaning layer-by-layer for discovering type and sequence of overpainting layers, intermediate layers of *olifa* or varnish, features of authentic painting (Figure 10.14). It is expedient to carry out this cleaning mechanically, without application of solvents before defining materials and methods of original painting, not to damage layers which can be especially sensitive to treatment with solvent.



Figure 10.14 - “ The Mother of God of the Sign” (Russia, XVIII century, Icons Museum of Peccioli, Italy, collection of Francesco Bigazzi): the segment of stratification on the border; original painting is covered with blackened *olifa*, then repainted and covered with a protective layer also darkened.

Then studying the method to remove the superimposed layers and to thin the original surface film is done. The oil overpainting is easily removed with alcohol-turpentine solution. Selection of solvents for the removal of egg tempera overpainting is defined by its thickness and pigmentary composition. In general the work is being done as described in the previous section “*Thinning of the surface film*”. Especially solid layers, for example ochre, if they lay

on intermediate layer of *olifa*, is recommended to abrade mechanically with pumice or emery paper to reduce time of solvent action. Approaching the original surface it is necessary to use solvents with special cautious so that not to damage the finishing coating impregnated with *olifa* and hence particularly vulnerable.

CASES OF LIMITED APPLICATION OF SOLVENTS OR THEIR COMPLETE EXCLUSION

Works on cleaning icons under a microscope, which have been conducted since the 70s, have enabled to make a number of observations, which have led to restrict the application of solvents or, in some cases, to their complete elimination.

The application of coloured lacquers (mainly green and various shades of red) for more decorative effect in icons painted in the 17-18th centuries is well known. In these cases restorers as a rule show due care, being aware of their sensitivity to solvents. But researches have also revealed the application of yellow organic lacquers in icons of the 13th century (for example, in the flesh paint of the “Mother of God on a throne with Sts. Nicholas and Clement”, collection of the State Russian Museum, Saint Petersburg), and of yellowy-brown lacquer in the icon painting of the 16th century. These lacquers are not easily distinguishable under a layer of darkened *olifa*, and the restorer should be especially attentive at the initial stage of research to reveal them, as short-term action of solvent results in their complete disappearance.

As a rule, cleaning of icons is sophisticated when the background gilding is simulated by means of yellow lacquer on leaves of white metal (tin, aluminum, silver; Figure 10.15).

Besides coloured lacquers, special sensitivity to solvents is inherent to oil painting. Along with pure oil technique applied in late icon painting, researches confirmed the application (since the 17th century) of a mixed technique in which egg tempera and oil layers alternate.

A special case of cleaning the icons executed in oil technique is the removal of the pebbled *olifa* film from their surface. In similar situations, in order to avoid damage of the thinnest paint layer, it is recommended to use a mechanical thinning of the surface coating working with microscalpel under a microscope (Figure 10.16).

Another contraindication to application of solvents for cleaning icons is a great *olifa* content in the ground (the recipes are known, recommending to add a little *olifa* during preparation of

levkas for its better plasticity). Visually such grounds may be recognized based on their yellow-brownish tint. During the application of solvent, it penetrates into the ground through cracks of craquelure and causes ground softening resulting in weakening of cohesion with the paint layer. This leads to losses of paint.



Figure 10.15 (on the left) - “The Mother of God of Kazan” (Russia, XIX century, private collection): cleaning of the background gilding simulated by means of the yellow lacquer on leaves of tin.

Figure 10.16 (on the right) - Test of cleaning of the oil painting covered with pebbled olifa film.

10.3.4 Filling of lacunas in the ground and in the paint layer

To prevent absorption of moisture by groundless wooden support and to prepare the object for the following retouching, the lacunas of the *levkas* (and of the paint film if it is thick enough) are filled with a restoration ground. It is prepared from the same materials, as were used at icon manufacturing, that is chalk and sturgeon or rabbit glue.

Before application of a new ground the lacunas are saturated with warm 2-3% glue and, after drying, with the glue of higher concentration to form a thin film of glue on the surface. Doing this it is necessary to avoid accumulation and overflow of glue, as well as soaking of edges of the old *levkas*. Then warm 8-10% glue is mixed up with chalk to obtain homogeneous dense paste, which is put with a palette knife. When the *levkas* is thick, the restoration ground is put layer on layer to provide uniform drying and to avoid its cracking. The level of the new ground should be above the original one because during drying it shrinks, and then it will be thinned when polished. Dry inserts of the ground are polished with a flat surface of natural cork slightly moistened with water, or with a fine-grained emery paper without water. During polishing it is necessary to be careful not to damage the surrounding surface of the painting. The finished inserts of the restoration ground are covered with a thin layer of mastic or dammar varnish mixed with turpentine in the approximate ratio 1:4, for protection against washing out during retouching and prevention of the absorption of paint in the ground (Figure 10.17).

10.3.5 Retouchings

To achieve integrate perception of a work of art retouchings of losses of the painting are carried out. Some main principles are observed:

- retouchings are carried out strictly within the borders of losses of the original painting;
- retouchings are carried out with reversible materials (as a rule, with water colour) which are easily deleted without risk of damaging the original paint layer;
- retouching should be easily distinguishable and should not create the impression of resemblance with the original texture. Therefore different restoration schools use various methods: retouchings with points, strokes etc. (Figure 10.18).
- the lost details of the image are not reconstructed.

10.3.6 Application of protective varnish

After restoration a thin protective film of a suitable varnish is applied on the icon surface. For this purpose mastic varnish is used. It is mixed with turpentine in the ratio from 1:5 to 1:2, depending on nature of the surface and absorption capacity of the varnish. A thin layer of the

varnish is applied with a gauze-cotton wad, and after drying in case of necessity the procedure is repeated to obtain a uniform film.

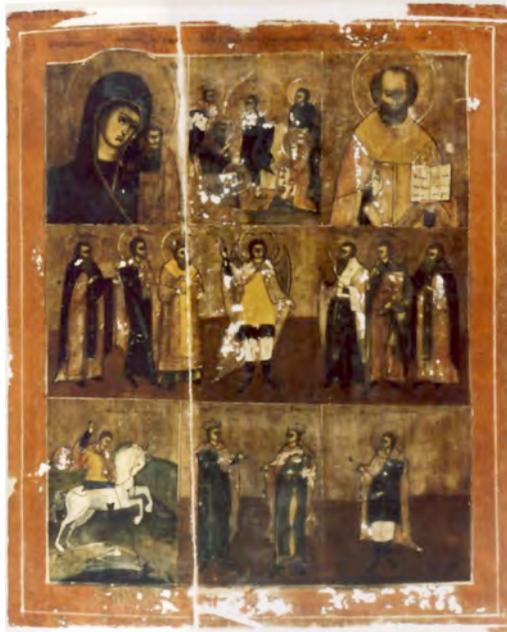


Figure 10.17 (on the left) - “The Mother of God of Kazan, Resurrection, St. Nicholas and selected saints” (Russia, XIX century, private collection): inserts of the restoration ground.

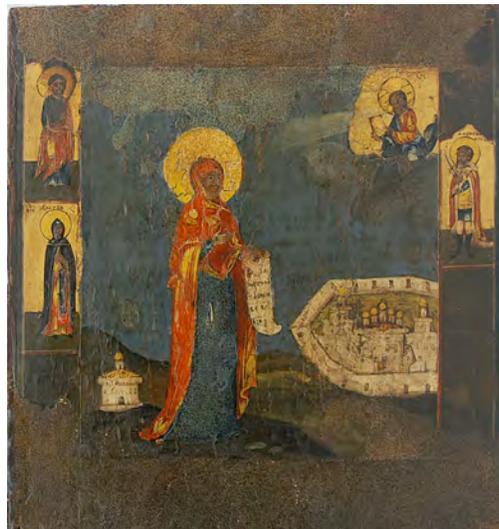


Figure 10.18 (on the right) - “The Mother of God of Bogolyubovo” (Russia, XIX century, private collection): retouching with points.

10.4 Examples of conservative interventions

10.4.1 Icon “The Mother of God of Korsun”

(Russia, 17th century, private collection)

The icon has arrived for restoration with extensive detachments of the ground and of the paint layer, while considerable parts of the *levkas* with painting were lost (Figure 10.19, left). A part of fallen off fragments was kept in a small bag (at the top of the photo in the above figure), and some pieces of the ground were randomly glued with synthetic glue. The borders and the background of the icon were covered with a silver *oklad* (cover of the icon) with traces of gilding. Because of its poor condition it was not expedient to dismantle the *oklad* (also because its restoration was not stipulated in the present work), so only the grime was removed from its surface.

Before consolidation, the painted part of the icon was impregnated with ethyl alcohol mixed with water (1:1) to remove the dust from the surface and to improve the penetration of the glue. Consolidation was done by repeated impregnations with 1,5% warm sturgeon glue. Places for fallen fragments of the *levkas* were chosen in accordance with their colour, thickness, features of craquelure, etc., then the fragments were glued with 7% glue. After protecting the large blister (on the left of the face of the Virgin) with tissue-paper, 5% glue was injected with a syringe.

When all surface was protected with a tissue paper and dried with a small iron, the silver *nimbus* of the Virgin with Christ was dismantled (Figure 10.19, right).

The grime and the dust which were accumulated under it were removed with a soft damp brush, and then consolidation of the damaged *levkas* was done on this part too. After removal of tissue-paper, the fragments of *levkas* previously pasted with synthetic glue were moistened with acetone. Then the softened glue was removed, and fragments were fixed with 7% sturgeon glue. Finally a covering with tissue paper and drying with a small iron were done.

The painting examination with a microscope and test cleanings showed the presence of two layers of overpainting on clothes; in addition, on the flesh painting some other layers applied in different times were revealed. Removal of overpainting on clothes and on the background was done by means of compresses with ethylene glycol monomethyl ether.



Figure 10.19 - “The Mother of God of Korsun” (Russia, XVII century, private collection): before conservation (left) and after consolidation with nimbus dismantled.

On the flesh painting, owing to non-uniformity of distribution and fragmentary preservation of the original paint layer, the cleaning was carried out mechanically with a microscalpel under the microscope. On old inserts of the ground, in lacunas of the author’s painting, the overpainting was preserved, which are not too much differing in colour from the original. Such preservation of the intermediate re-paintings enables to reduce the area of restoration retouchings and gives the idea of the history of the icon’s life.

Examination through a microscope showed, that the olive-color background belongs to the first renovation of the icon, under which a gilding is visible. Probably, originally the icon had no metal cover. However, because now all the background is covered with the silver *oklad*, and the authentic gilding poorly remained, this over-painting was preserved.

Lacunas of the *levkas* were filled with the ground with small addition of a dry ochre pigment, that neared the tone of the inserts to the coloring of the original painting and facilitated the retouchings process (Figure 10.20, left).

Retouchings were done with water colours. According to the task set by the owner of the icon, some details of the image were re-constructed during retouching on the basis of the remained contours and of fragments of the authentic painting (Figure 10.20, right).



Figure 10.20 - “The Mother of God of Korsun” (Russia, XVII century, private collection): after cleaning, with inserts of restoration ground (left), and after complete conservation treatment (right).

10.4.2 Icon “Last Judgement” (North Russia, middle of the 16th century, private collection)

The icon represents a fragment of the composition “Last Judgement” (Figure 10.21, left), lateral parts of a board are lost. Through examination, two continuous layers of over-painting and numerous inserts of different times were revealed (Figure 10.21, right). A feature of this icon is the wide application of mixed techniques: the background is covered with a thin transparent layer of light-yellowish lacquer, but at the bottom in the scenes of infernal tortures the backgrounds are executed in a brown lacquer over a pale-green layer of copper-green colour; mountains are painted in light ochre with shades of brown mineral pigment; undertints are softened and enriched with a layer of brown lacquer (Figure 10.22, left). Some other details of the image are also painted with yellow lacquer. Such abundance of coloured lacquers, sensitive to the application of solvents for cleaning, led to the choice of a mechanical way of cleaning under a microscope on the above-stated parts.



Figure 10.21 - “Last Judgement” (North Russia, middle of the XVI century, private collection): before conservation (left), and in course of cleaning (right).

Cleaning was done layer by layer. The surface over-painting was removed with ethylene glycol monomethyl ether with a wad; intermediate (second) over-painting was first softened with compresses impregnated with ethylene glycol monomethyl ether and then removed with microscalpel under a microscope, and after that the underlying protective film was thinned. The work was carried out with great (16-fold) magnification, as the original surface has a visibly pronounced relief, caused by craquelure with rigid raised edges; there was risk of damaging their top in the course of work. This relief and the abundance of minor losses of the fragile coloured lacquer led to the need to level the surface up to the previous renovation; this was done by covering with a layer of a liquid ground. The presence of strong animal glue over the old protective coating had made it very hard and fragile; therefore, in order to avoid chips and tiny losses during the cleaning, the surface was slightly moistened with ox gall or water with alcohol (1:1). The same solution was used for softening layers of the re-priming before their removal, since this ground had been impregnated with *olifa* and could not be softened with water only.

In the course of the work, another feature of the techniques of execution of the icon was revealed: details painted with cinnabar appeared to be very unstable not only to solvents, but

also to water solutions. According to ancient sources, cinnabar was sometimes prepared with vegetable glue binding. Therefore, before the filling of the lacunas in *levkas* with the inserts of the ground, the areas with cinnabar details were protected by a thick layer of mastic varnish, which was removed upon termination of the process.

Minimal retouching was done with water colours, some losses of the *levkas* were preserved without filling them with restoration ground (Figure 10.22, right).

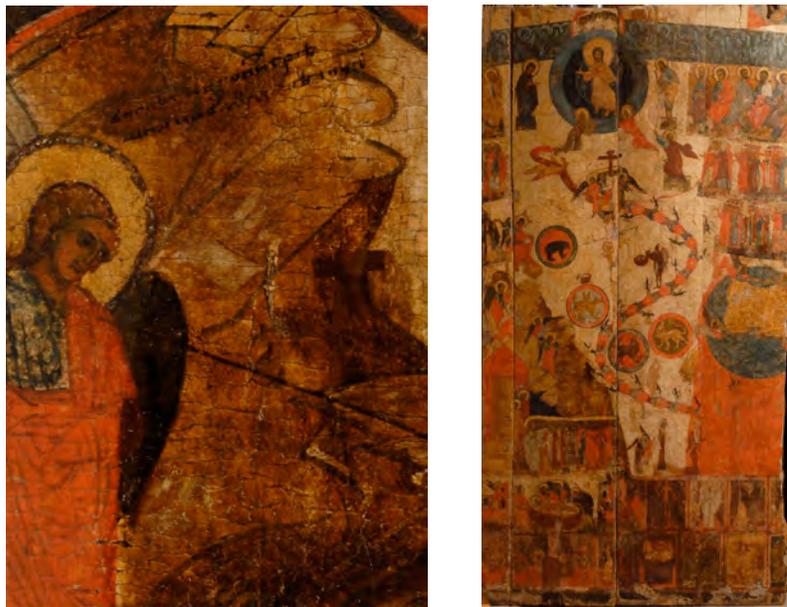


Figure 10.22 - “Last Judgement” (North Russia, middle of the XVI century, private collection): brown lacquer for modeling the shades of under-tint layer on the mountains (left), and after conservation (right).

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11 - TEXTILE FINDS

11.1 Morphology, characteristics and properties of textiles

11.1.1 Fibres

Textile objects of historical interest are made by fabric, frequently combined with other materials (for instance garments or upholstery). Fabrics in their turn are obtained interlacing yarns of four natural fibres: cotton and linen (cellulosic), wool and silk (proteinous).

Fundamentally fibres are built up by polymerisation (also called condensation), that is the combination of molecules until long chains are formed. The morphology of the fibre corresponds to the nature of these fibrous structures: one or more molecular chains, arranged parallel to each other (or else spiralling around the axis of the fibre) and relatively stable.

CELLULOSIC FIBRES (COTTON AND LINEN)

They are obtained by polymerisation of molecules of β -glucose, the structural formula of which can be simplified according to Figure 11.1.

Linen or very strong cotton fibres are made up by straight chains of at least 2,200 molecules.

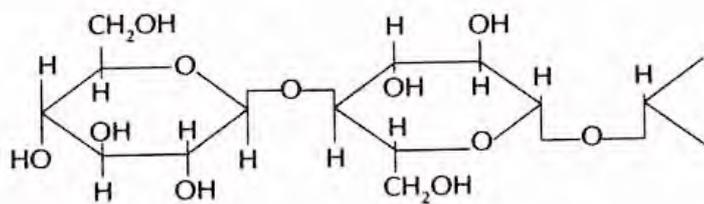


Figure 11.1 – Simplified structural formula of molecules of β -glucose.

PROTEINOUS FIBRES (WOOL AND SILK)

Wool fibres are made up by polymers of 18 different amino acids. Being amphoteric, these have a terminal acid group (-COOH) and a basic one (-NH₂): the acid group of a molecule can combine with the basic group of another and, through the elimination of a molecule of

water, constitutes a bond called peptidic that is at the base of the process of polymerisation. The general structural formula of an amino-acid is reported in Figure 11.2.

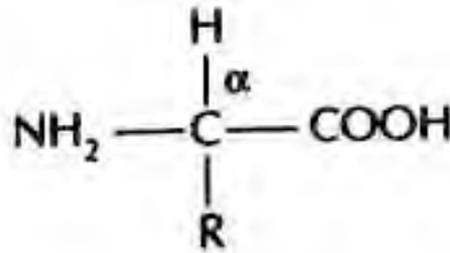


Figure 11.2 – Structural formula of amino-acid.

In the case of cystine, the amino-acid from which wool is mostly formed, the radical R forms a further bond, beyond the peptidic, that links two adjacent molecular chains. The keratin formula presents, instead, two chains of amino-acid, going helicoidally, joining across a transverse bond made up of two atoms of sulphur. The presence of this second bond determines a three dimensional structure due to the forces of lateral attraction, which confers to the wool a resistance to the solvents capable of splitting the only peptidic bond that characterises its behaviour, giving stability and durability. Its extensibility must, at least be partially, owed to the helicoidal form of the molecule.

Silk is a continuous filament, each one composed of two filaments of fibroin surrounded by a coating of sericin. Fibroin and sericin are also produced by the polymerisation of about 15 amino-acids, the formula differing according to the area of provenance of the fibre. Silk differs from wool because it does not contain keratin and therefore has no transverse bonds with double atoms of sulphur. Its great mechanical resistance depends on the high crystallinity of the fibre.

The performance and look of textile fibres and, therefore, of the yarns made from them, depends on their characteristics such as length, shape, density, surface structure and crystallinity.

The length of the fibre is correlated with mechanical resistance to many stresses, in particular to tension.

The surface conformation of the fibres substantially determines the reaction to light: fibres with smooth surface reflect the greater part of light with which they are invested, while those with rough surface absorb it.

The degree of crystallinity of the fibre influences its response to changes of humidity with the environment (moisture regain figure) and its mechanical resistance. A fibre with a low level of crystallinity tends to absorb humidity with great ease because this change mostly affects the surfaces and amorphous parts of the fibre; at the same time each fibre has less resistance to mechanical stress.

The density of the fibres (weight per unit of volume) determines the way in which the threads and textiles drape.

11.1.2 Yarns (or threads)

Reactions of textiles to mechanical stress are closely related to their structure, obtained through two fundamental stages: the assembly of the fibres into yarns and the creation of the textile by interweaving.

In the yarn numerous fibres lie parallel to each other, to a certain degree with the help of twisting. In this new situation the fibres are submitted to a forced cohesion and the thread reacts as a system to the application of tension, twist, bending and their combination. The character of this system is the basis of the strength of the thread: its resistance is founded on the combination of the individual elements of which it is comprised.

By contrast the weakness of one or more elements is automatically transferred to the whole system.

From the mechanical point of view the peculiar function of the twist, in contrast with the technical construction of many other materials, is that of producing its effects without substantially compromising the flexibility of the yarns. It is true also that a thread with high twist, in comparison with other conditions, is stronger but less flexible than the one with less twist.

METAL THREADS

So called silver and gold threads are obtained by twisting a soft laminate of metal in a spiral around a core thread, usually of silk. Sometimes the laminate is applied to a support of a membrane of parchment or paper. The metal laminate is usually made from an alloy, such as copper and silver for example, covered by a layer of a richer alloy, such as copper with silver and gold. In this way the brilliance of silver and gold is obtained with less cost of noble metal, but the characteristics of the metal corrosion tend to get worse more rapidly.

11.1.3 Textiles

A textile, in the narrowest sense, is the result of interweaving between one group of threads (the warp), disposed parallel to each other and a yarn (weft) which runs at right angles to these from one side (the selvage) to the other.

Like other techniques of interlacing threads, weaving gives rise to a coherent system, the strength of which is founded on the evenness of the distribution of stress on the threads that take part in its formation.

As for the yarn, then, the weakening of each of the components and the eventual breakdown puts a load on the entire textile and can rapidly result in a tear.

MECHANICAL PROPERTIES

Altogether, mechanical properties determine the reaction of threads and textiles to mechanical stress.

The most significant to emerge from this examination are resistance to tension, extensibility, flexibility, elasticity and plasticity.

- The resistance to tension of a fibre is conventionally measured by the weight necessary to break it, being directly proportionate to the length of the molecule, to the level of crystallinity and to the compactness of the bundle of molecules.
- Extensibility is the lengthening of a fibre under tension that it can suffer without breaking. Wool can elongate easily by 10%; silk, cotton and linen much less. Normally fibres extend more easily when they are wet.
- Flexibility is the most proper characteristic of textiles; it is tied to the shape, weight and density of the fibres. The decrease of flexibility is the source of much damage suffered by textiles.
- Elasticity is the measurement of the stretch of which a fibre is capable under tension that vanishes when the tension is removed. It is a property that tends to diminish with age and use.
- Plasticity of a fibre under tension measures the amount of stretch that remains when the stress is removed. Normally it is correlated with fineness of the fibre. Wool is the most plastic among the natural fibres, and its plasticity becomes greater under the action of heat and humidity.

11.1.4 Fibres identification

OPTICAL MICROSCOPE OBSERVATION

The analysis of fibres constituting historical artefacts (textile and paper) plays an important role in order to reconstruct their history and for a correct conservation strategy.

According to their origin fibres are generally divided in natural fibres and techno-fibres; usually, the analytical interest is towards to natural animal and vegetal fibres, that represent the main support of a wide range of artefacts. Animal fibres are wool (from sheep, goat, camel) and silk produced by some insects. Vegetable fibres are cellulose based and are distinguished in fibres from seeds (cotton), from stems (hemp, flax), from leaves and fruits. Optical microscopy is one of the most common scientific method for examination of material structures otherwise invisible to the naked eye, by using reflected or transmitted light through a magnification from 10 to 500 times. Moreover, fibres analysis can be performed by Scanning Electron Microscope (SEM), usually after coating the sample by thin layer of electrically conductive materials (gold).

Microscope analysis makes possible fibres identification through their structural profiles, and shed some light on state of its conservation (e.g. detection of presence of microbial and insect activities).

First of all it is necessary to prepare the sample by removing the extraneous substances from the fibres surface by means of organic solvents (trichloroethylene, ether). If the fibres are heavily sized with starch or coloured, it is necessary to treat them in a test-tube with a boiling solution (1% sodium carbonate, 3% hydrochloric acid). After this treatment, the fibre loses the colour but for a better microscopic resolution, it is recommended to dye the fibres by a iodine-sulphuric reagent.

For paper samples it is necessary to manually tear the sample in small pieces, then boil them to obtain homogeneous fibre suspension. Then a small amount is stratified on a slide, let dry on warmed surface and proceed through the chemical treatments.

The fibre structural morphology can be described as follows:

Wool. Wool fibre has irregular, roughly cylindrical, multi-cellular structure with tapered ends. Through microscope observation, three basic layers are distinguished: epidermis (outer layer), cortex (middle layer) and medulla (inner layer). Medulla is seen only in coarse and medium wool fibres and by a highly powerful microscope.

Silk. In raw silk fibre, two filaments can be distinguished with an elliptical shape under microscope observation. Wild silk, or tussah fibre, has different morphology than the cultured silk. It is flattened, coarse, thick and broader fibres have fine, wavy lines all across its surface, whereas cultured silk is composed by narrowed fibres with no marks.

Cotton. The cotton fibre is a single elongated cell. Under microscope it looks like flat, spirally twisted ribbon like tube with rough granular surface. Its colour can change from white to reddish. Fibre length is between 10 and 60 mm.

Hemp. Hemp fibre looks like having multiple sided cylindrical filaments with between 30 and 70 mm in length. Fibres are slightly flattened with longitudinal stripes and rare transverse irregular stripes. Their colour is between ivory and beige. In the raw hemp the fibres are covered by encrusting substances like lignin.

Flax. Flax fibre shows multiple sided cylindrical filaments with fine pointed edges. The filaments are spaced by nodes, looking like a bamboo stick. Hemp fibres are between 6 and 50 mm in length. Distinguishing between flax and hemp is not easy: hemp has a more irregular and flattened shape, and with multiple nodes. Moreover the outside layer is less transparent than the flax and the ends are rounded instead of pointed.

CHEMICAL TESTS

Fibres analysis through chemical tests is based on the assumption that they react with chemical reagents in different ways according to their chemical composition and structure. Chemical spot tests are destructive but they are widely used because they allow the identification of specific elements of the sample with a minimal amount of material. Some of the tests are listed below.

Burn test. Animal fibres burn slowly with a smell similar to burnt hair or feather, leaving abundant black brittle residue; natural vegetal fibres burn quickly, smelling like burnt paper, and leave soft and fine ashes that turn to dust if touched.

Sodium hydroxide test. Let the sample boiling for 30 minutes in 10% NaOH: the animal fibres (wool and silk) dissolve; cotton forms soda-cellulose; flax remains practically unaltered; hemp and vegetal fibres containing lignin become yellow.

Treatment with acids. Concentrated sulphuric acid (H_2SO_4) induces the decomposition of all the fibres except wool, which dissolves only if the acid solution used is hot. With concentrated nitric acid (HNO_3), wool becomes yellow-orange and then dissolves; silk becomes yellow; vegetal fibres do not change colour and do not dissolve.

Schweitzer test. Wool dissolves in a different way than silk; cotton swells before dissolving; hemp dissolves slowly in relation to its contaminator.

Iodine-sulphuric test. Two solutions are needed for this test. The first contains 1 g of potassium iodide (KI) and 0.5 g of iodine-powder, dissolved in 100 ml of water. The second solution is obtained mixing 40 ml of bi-distilled water with 20 ml of glycerine, then adding 60 ml of concentrated sulphuric acid, drop by drop and under cooling and stirring. Fibres or part of them containing lignin turn their colour into yellow, while cellulose based fibres turn their colour in blue.

Cotton fibres turn into blue as well, while in flax fibres the outside layer turns into blue, transverse stripes turn into dark blue and the inside layer turns into yellow. Raw hemp turns into green-blue in the middle and yellow on the outside because the presence of lignin. Treated hemp, without lignin, turns into green.

Fluoroglucinol test. The reagent is prepared adding concentrated hydrochloric acid (HCl) to a 1% fluoroglucine in alcohol solution. Fibres stain in red, but the colour is strongly related to the lignin content:

cotton = no stain (no-lignin); flax = slightly pink; hemp = dark red.

Lugol's iodine test. Dissolve 2 g of zinc chloride ($ZnCl_2$) into 10 ml of distilled water and 2 g of potassium iodide (KI) in 5 ml of distilled water; mix the two solutions together (it is important to add some iodine grain). This reagent is able to stain the fibres as follows:
cotton = red/purple; flax = dark purple; fibres with lignin = dark yellow; silk = yellow.

11.2 Decay of textile fibres

Textile fibres suffer, equally with all organic materials, an unstoppable process of molecular decay, by reason of their intrinsic nature.

The process of polymerisation or condensation is reversible: the presence of certain external conditions can determine the inverse reaction, called hydrolysis (or depolymerisation), that happens through the absorption of molecules of water: the internal bonds of the chains weaken and these break into shorter chains. Different methods of chemical testing confirm that the more the chains shorten the more, proportionately, the fibres weaken.

11.2.1 Decay in archaeological microclimate

In the microclimate of archaeological contexts some of the main phenomena of fibres decay, such as photochemical degradation and damage produced by pollution, became negligible; on the contrary they suffer irreparable damage, sometimes till complete destructions, due to thermal and hygro-chemical factors.

In conditions of high humidity, fading of colour and weakening of the fibres is accentuated; while too dry an atmosphere causes loss of flexibility, elasticity and resistance to tension. Experience shows that in very humid environment, the possibility of biodegradation from attack by micro-organisms and insects is increased while the risk of damage of a physical nature is lessened. Insect attack is a great danger for proteinous fibres; when they prosper in a textile they weaken it on the one hand by eating it and on the other by depositing excrement. This is often acid in nature, which can cause further deterioration.

Also important is the acid/basic balance in archaeological sites, mainly because they are frequently wet or damp. Wool and silk react better than cotton and linen in an acidic situation and/or a damp or waterlogged one. In a similar condition the laminates of metal threads, in particular those of copper and of its alloys, are attacked through electrolytic phenomena favoured by high humidity; on the other hand any membrane (the underlying proteinous layer of some gold threads) is attacked by water and alkaline conditions.

The influence of temperature on the conservation of textiles is almost negligible if they are kept within the middle range; proteinous fibres are more sensitive than cellulosic ones at high temperatures and silk more than wool.

11.2.2 Typology and chronology of textile finds

Textiles are, among all organic materials, the most rare archaeological finds because of their extreme perishability. By side their saving and first aid operations are frequently very problematic and risky.

As far as their age is involved, archaeological textile can be classified as: pre-historic, antique and late-antique, medieval.

Generally speaking, they are mainly the remains of garments worn by the dead body, or items of the outfit for the deceased. Inside the grave their surviving becomes extremely difficult. Frequently a high level of humidity, if not the presence of water, promotes fibre's de-polymerisation by hydrolysis and microbiological and insects attack. For these reasons

the most plentiful findings of ancient textiles came from geographical areas with a dry climate, as in Egypt; or where inserting textiles in the graves is very set in the social habits, as in different countries of Latin America. More recently large quantities of archaeological textiles came out from excavations in China and Central Asia. Sometimes a very cold climate created good condition for survival, as it happened in the site of Moščevaja Balka (Northern Caucase).

In Europe too little fragments have been found in burials, frequently including gold or gilt threads. They are mainly taken from tombs of personalities of high rank, both secular or religious.

Sometimes tiny portions of natural fibres interlacing survive from the pre-history, incorporated in salty incrustations of metal objects, or completely mineralized (carbonized), or simply as traces left on plastic materials, like clay or mud.

Since till the dawn of civilization weaving has been the most complex technology practised by human beings, and frequently the same interlacing gives rise both to the fabric and to its decoration, no matter how little a find is: it brings up this production proceeding, as much important as its age. Once again, since textiles have always been longed for wealth and status symbols, and very easily transportable, they have to be considered privileged means to investigate the traffic of goods in relation to power and economy centres.

In Europe the most ancient textile finds come frequently out in the course of circumstances different from normal archaeological excavations, such as the opening of tombs of dynastic or church characters or saints. These are often buried inside sarcophagus, where the environmental conditions are not the same as in a grave, even if comparable to that. During the three last decades an intense activity of studying and conserving of this kind of objects has been undertaken. Among them the following ones are worthy to be mentioned:

- the liturgical vestments found in some of the sarcophagus in S. Apollinare in Classe at Ravenna (7th century);
- the costumes of noble men and women from the site of Moščevaja Balka (Northern Caucase; 8th-9th century);
- the burial vestments of Saint Ulrich († 973) discovered in the Augsburg cathedral;
- those of Pope Clemens the 2nd († 1047) from his tomb in the Bamberg cathedral;
- the burial garments worn by St Antoine († 1231) in the Basilica del Santo in Padua;
- the large collection of vestments found inside the dynastic sepulchres in the

- Panteón Real of Burgos (13th century);
- the garments of Cangrande della Scala († 1329) taken from the sarcophagus of the Scala family in Verona;
 - the mantle of Sigismondo Pandolfo Malatesta († 1468) removed from his tomb in the St. Francis church at Rimini;
 - the textiles found in the sarcophagus of the bishop Moricotti (15th century) in the Cimitero Monumentale of Pisa;
 - the female dress found in a tomb of the Calvinist church of Boldva (Hungaria; 1560 ca.);
 - the grave garments of Cosimo de' Medici, of his wife Eleonora of Toledo and of their very young son Garcia, taken from the family tombs in Florence (16th century);
 - the overdress associated to the mummified body of Sainte Eustochia Calafato in the Montervergine's Monastery at Messina (second half of 16th century).

11.3 Conservation treatments of archaeological textiles

Methodology and practice of conservation do not depend on the context of provenance of the find, but just on its condition. That is from one hand the decay's degree of the fibres and, from the other, the level of integrity of the object as such. Anyway be aware that, generally speaking, as old a piece is, as rare it is supposed to be. From another point of view, it does not matter how deteriorate a piece is: it always brings up information if it met somebody able to single out and interpret the historic and technical evidence and the traces of structure. Gathering and studying these information is the first aim of the conservation of archaeological items; sometimes the only one, aside is the preservation of the material as much undisturbed as possible. When its reconstruction even partial is not possible, the graphical one is a recommended complement.

The importance of this side of the question is such to come first of the recovery of the aspect of a item. This too have to be considered non purely from the aesthetic point of view, but more properly as the possibility to appreciate its shape, to recognise its structure and guess its function.

The practice of conservation has to follow the general rule of doing everything that is truly and strictly necessary, but nothing more than that.

The first decision to be made is: does the survival of the piece require to dismantle or remove something and, in that case, what? Facing the conservation of garments and clothes, with no sufficient knowledge of their structure and dressmaking it is easy to lose some of this aspect, which are particularly important not only for the garment under treatment but for the entire class of these objects. It will never be sufficiently stressed to avoid undoing any seam and part of their structure. Most of all must be blamed their disassembling to the purpose to recover easily any separate flat component (unfortunately this also has been frequently made).

The final result of such a practice would be an object which has lost its specific authenticity, that is a *replica* built with original components. The same is true for any three-dimensional piece.

In general terms one can describe the conservation proceeding of an archaeological textile through the following steps: excavation, disinfestation, documentation, cleaning and consolidation.

11.3.1 Excavation

All objects which have survived into the ground, or in a similar situation, for any length of time became accustomed to their surrounding environment; so when they are brought to the open air the processes of decay undergo a drastic acceleration; this has to be limited as much as possible.

Remember that textiles are less clear in the ground and more brittle than many other objects. Do not try to clean them immediately. In the handling never consider them self-sufficient but prearrange a proper support. If the textile is dry maintain it dry and pack in acid-free tissue paper or perforated polyethylene bag and store flat. If it is waterlogged keep it in the same condition, with its surrounding mud, pack it in a sealed polyethylene bag and store in a cool place. If it will require time to bring it to a stable store check frequently that it does not dry out; if necessary use a humidity-chamber. Don't forget that textiles sometimes survive simply as a track on another material; it is always worthwhile to preserve this track.

11.3.2 Disinfestation

In a heavy humid atmosphere moulds and other micro-organisms proliferate. In order to neutralise those still alive and contrast future developments, products already tested to this purpose can be found in every country.

They do not have to be used to impregnate the textiles but to saturate a sealed chamber in which they have previously been introduced. With light attacks, a current of air can sometimes be enough; but be careful because when the level of humidity becomes too low the brittleness of the piece grows up. Among the disinfestants, ethyl alcohol can frequently be used: it is efficient against many micro-organisms, it does not interfere chemically with the fibres molecules and very little with their humidity content.

11.3.3 Documentation

One of the first steps is the gathering of information. The result of a conservation project is frequently as good as thorough preliminary studies and documentation are. This cannot obviously be considered settled once forever; important pieces of information are normally singled out only when a certain familiarity with the object has been reached.

The activity related to the documentation frequently needs the piece to be handled and everybody can realize, in a while, how much dangerous this can be to the aim of its preservation without an adequate temporary support and a sufficient experience.

Facing three-dimensional objects information can be collected following a general scheme as this:

a) shape of the object; b) its use and function; c) its structure; d) material or materials of which it is made of; e) decorations, if present.

A suitable knowledge of the main interlacing techniques and kind of textile objects can be very helpful.

In the course of excavations photos cannot be considered enough in themselves; drawings help to collect what an expert eye appreciates but slips out of the object glass.

11.3.4 Cleaning

Three are the main methods for the cleaning of historical textiles:

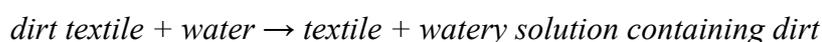
- vacuuming;
- washing;
- treatment with organic solvents (non polar).

VACUUMING

The first cleaning means to eliminate mechanically as many foreign substances as possible, particularly soil. A careful vacuuming for many finds is the only opportunity and not always advisable. The degree of chemical degradation must be previously assessed and, in case of brittle fabrics, a low power vacuum cleaner has to be used, meanwhile the piece has to be saved from any mechanical stress that can injure it. For pieces which are particularly fragile and/or very important it is advisable to work under magnification.

WASHING

It is a dynamic physical-chemical process, represented by the equilibrium:



A part from being irreversible, washing exposes the piece to an inevitable risk, since a textile handled when wet is more damageable. So it must be avoided if there is lack of adequate equipment and proper experience. Archaeological textiles which can be safely washed, in water or aqueous detergent solution, are rare; for deeply mineralised fibres it can be a disastrous shock. On the contrary many textile finds from Egypt and Pre-Columbian America, thanks to a correct washing, can get to a relaxation of the fibres, a correct value of pH and content of humidity. But remind: dyes are almost certainly stable in textiles from Egypt but check carefully those of the Pre-Columbian ones.

The first property of water is the capability to penetrate by capillarity into the fabric: its molecules enter among the fibres, spacing them out, in this way they reach the hidden dirt. That makes possible the action of intermolecular forces between the solid dirt and liquid. If the solid combines with water to make a hydrogen bond it is called hydrophilic. Thanks to this property water can solubilize, swell and soften organic substances of which the molecules contain a sufficient number of polar groups (normally a hydroxyl group): sugars, salts, starches, gelatine, many of the dyes. Beyond this, water has the ability to separate many inorganic substances into ions, thus favouring their chemical combination with other substances. That assumes great importance in the aim of separating a second category of foreign substances in textiles.

But water alone is not effective against a large range of substances like grease and oily compounds, so an effective washing solution makes necessary the join of some additives. To this purpose a recipe has been prepared ready and tested by Judith H. Hofenk-de Graff at the Central Laboratory for Objects of Art and Science in Amsterdam, widely used in

textile conservation. The general formula advisable for non particularly degraded pieces, contains:

- a detergent or surfactant (amphoteric compound), non-ionic or anionic;
- a sequestrant that is an organic or inorganic compound which helps the detergent to make soluble complexes with polyvalent metallic ions;
- sodium carboxymethyl cellulose, a compound that absorbs the dispersed particles and acts as a porter to carry away the dirt, preventing it from re-depositing on the textile.

The formula mostly used contains: 1 g/l of a non ionic detergent, 0.5 to 1 g/l of a sequestrant, and 0.25 g/l of sodium-carboxymethyl cellulose, in distilled water. Many variations have been suggested by the Dutch scientist since its first formulation (1968), in relation to the kind of fibres, the severity of the decay, the dyes stability, the availability or not of deionised water. Someone suggests a final rinsing containing an emollient substance, frequently a 5 to 10% solution of glycerol.

But water, being partially polar (split in H^+ and OH^-), can react directly with fibres and dyes too: some of the molecules of the chain can hydrolyse damaging the textile. For this reason washing can have drastically negative effects, especially when, to improve its efficacy, the detergent aqueous solution contains additives that make the pH go up, a condition that can weaken the proteinous fibres, such as wool and silk.

A second phenomenon is caused by the washing: the swelling of fibres that can be responsible of loss of colours (fairly easily on cotton and silk) and wool's felting. On the other hand it could cause fibres realignment giving rise, in the course of drying, to a natural flattening. It can bring the pH up to the centre of the scale (6 to 7) and recover a correct level of humidity inside the fibres.

Lastly, since water is such an effective solvent, it often contains relevant quantities of free ions (above all calcium, magnesium and chlorine). This water, called hard, forms a insoluble scum with soap following a reaction of exchange between the ions of calcium present in the water and the potassium ions from the soap. That is why the water to be used for washing historic textiles must be purified: distilled or de-ionised.

The practice of washing mostly adopted follows a sequence of operations, such as: preliminary tests; proper washing; rinsing; drying.

- To verify if the piece can safely stand the watery treatment you have to observe its reactions to different mixtures of ethyl alcohol and water, with an increasing

percentage of this one, using a sprayer in a little portion of it.

- To test the stability of dyes: take little specimens of dyed yarns from the object, put them on a sheet of blotting paper, imbibe them with the washing solution, cover with a polyethylene sheet and leave over-night; if all the colours are with no doubt stable it is possible to go on.

The pH has to be previously monitored too, because the final neutral position has to be reached gradually and, even worse, because a too low starting value can bring the textile after washing to a fibres pulp.

- To be safely washed a textile has to be flattened on a smooth, slightly inclined, plane; with archaeological finds this operation requires frequently a long time, first spraying a mixture (1:1) of ethyl alcohol and deionised water and trying to unfold step by step the creases. When flat, cover the piece with a layer of nylon net, start the proper washing with just deionised water and, if truly necessary, with detergent solution. Remember that any chemical introduced has to be extracted by rinsing and this will always means a risky handling.
- The aim of rinsing is to extract and carry out both the solubilized dirt and the chemical components of the washing solution. Spraying the water on the top of the textile and leave it drain along the inclined surface is more safe and effective than submerging it in a basin.

Since the washing produces a lowering of the pH, the rinsing can be considered finished when its value is stable between 6 and 7. For the reason seen above deionised water has to be used.

- To improve the drying the textile can first be padded with a sheet of blotting paper or absorbent textile, put on top of the nylon net. After having taken away carefully this latter, the piece will dry naturally on the plane at room temperature; evaporation of the water can then be facilitated by a current of cold air. Till it is wet the piece can be gently put in a more correct shape and threads orientation.

TREATMENT WITH ORGANIC SOLVENTS

Cleaning with organic non polar solvents is based, substantially, on the same phenomena of washing, that is to solubilize, emulsify and carry away the foreign substances from the textile, but without triggering chemical reactions with the fibres and swelling them. It is rarely practised with archaeological textiles, unless they are deeply contaminated with

grease dirt. Treatment with organic solvent can be realized in a basin on which the textile is submerged by the solvent, better if crossed by a current of air which maintains it in a slight movement. It remains less effective than washing, it is not able to neutralize the pH and can impoverish the natural fat content of wool. Keep in mind that the use of organic solvents is strictly under provisions of the law.

11.3.5 Consolidation

The aim of consolidation is to give back to an object enough strength to stand the stress of being safely handled, studied, exhibited in a Museum window or kept in storage. To do this one has to adapt to the remaining flexibility of each object, due to its degree of fibre's decay, the few basic techniques of textile conservation, each one with advantages and disadvantages: storage; support by means of one or more stitching techniques; sandwich between two layers of fabric; support by adhesion; coating.

STORAGE

Obviously it is the less risky solution but with contraindications; first of all it does not make possible to appreciate the objects. Therefore it has to be taken into consideration if a more invasive technique is worth to be applied if it can recover at least partially the shape of an object; especially when complex and/or three-dimensional objects are split a part in fragments. On the other hand the pre-historic fragment can rarely survive without being coated.

In spite of being a minimal intervention it requires at least: a good familiarity with archaeological finds, the availability of materials chemically inert, storage space and equipment.

Every piece must be adequately hold; flat textile of large dimensions can be rolled on cylinders (6 to 20 cm in diameter), according to their thickness and residual flexibility. Rolling very degraded textiles can aggravate the situation; these need to be preserved flat or folded as less time as possible, avoiding squashed creases.

SUPPORT BY STITCHING

When a textile has not been involved in a deep alteration of the fibre morphology but, even if still maintaining a fairly good flexibility and strength, it is damaged by a loss of integrity, its consolidation normally means to lay it on a new fabric, which acts as a

support, and stitch it down. The support can be localized in the damaged sections, or complete under the entire object. To make the holes become as less disturbing as possible the support fabric would have to have thickness, texture and shining similar to those of the old one, and be subsequently dyed in a colour which matches that or those of the piece to be consolidated.

Using support fabrics of natural fibres is, in general terms, preferable; but fabrics of man made fibres (techno-fibres), particularly polyester, polypropylene and their mixture with cotton, have, under the same performance, a much lighter weight and a much greater lastingness.

Stitching operation can be made in two ways: over a rigid plane using a curved needle; by means of frame built on the principle of the traditional one to embroider, on which one works with one hand on top and the other underneath, using a straight needle. In both cases the support fabric has to be put with warp and wefts aligned with those of the object, and adapted to its possible deformations and not *vice versa*. The stitch mainly used is couching, drawn from the gold embroidery technique; but many other stitches are used.

SANDWICH

If the molecular decay got forward to the point that cannot stand, without further damaging, the actions of a needle crossing the old textile, this can be placed between a support layer, with the characteristics seen in the previous treatment, and a protective layer, as transparent as possible (nylon net, silk organza, polyester gauze). Stitching normally runs outside the external perimeter, along the splits and the internal perimeter of holes. Dyeing both layers in appropriate makes the colours losses less visible and the upper layer more transparent.

The treatment cannot be applied on three-dimensional objects.

Strictly speaking it does not give rise to a true consolidation: if the piece is not maintained flat on a plane its effectiveness is truly poor. For very brittle fragments, as the pre-historic ones, a sandwich between a padded wood ground and a glass is sometimes effective.

SUPPORT BY ADHESION

In the case of a textile chemically degraded at such a point that it could not stand a mechanical treatment, a different approach is to support it by using an adhesive instead of the stitching. In spite of contrary opinion the application of this technique needs as much

experience and ability as the one based on stitching; and one must admit that many of the past criticisms have been largely motivated by wrong or too scarcely experienced applications. Last but not least since the first apparition of the method, products used are substantially upgraded and many objects have received a specific treatment. The result is a general improvement and a more proper use of the technique.

The adhesive used to this purpose can be a natural substance, like starch, hydrolyzed; more practical and widespread are thermoplastic resins.

These can be applied in different ways: as a film on a fabric like polyester gauze or silk organza, or coating a nylon net, or producing a film on a sheet of siliconized paper, later transferred on the preset support fabric. The coupling of the piece to consolidate and the adhesive interface is usually obtained following a process called “heat-sealing”, which acts heating the resin till it is plasticized and exerting a pressure suited to the residual strength of the textile.

Experience makes possible to treat in this way also three-dimensional objects, without taking them to pieces, working on subsequent portions of the textile kept flat, till all the surface has been supported.

For large scale objects a hot vacuum table of appropriate dimensions can make the operation quicker, safer and more homogeneously effective. Once supported by adhesion the treatment can be completed with a further support, to fit the loss, using moderately the stitching technique made possible by the first consolidation.

COATING

Coating is used when it is necessary to give back a certain strength to a textile which has suffered such an extreme decay process that is no more able to stand its own weight and maintain its shape. Archaeological finds are frequently in this condition.

Consolidation is obtained using impregnating substances; these create inside the molecules of the fibres new links to substitute the broken ones, without which they run into the risk of disintegration.

Polyvinyl alcohols and Paraloid B72 have been mainly used in the past; at present they have been replaced by emulsions of polyvinyl acetate or by an acrylic resin (Plexisol). As far as little objects are involved, the application of aeriform resins shows a great consolidation efficacy and almost negligible effects on their aspect (see 11.4.2).

11.4 Conservation practice: two case histories

The two following case histories represent the extreme situations that a conservator has to face. The first one is a large dimension's garment, the fabric of which was severely degraded in the sections that were under the buried and almost in good condition somewhere else.

On the other hand its level of integrity made possible not only to single out its shape, dressmaker structure and dimensions, but also to recover it physically as a garment, even if with some uncertainties. On the contrary the second case is a very small fragment, relatively recent (13th-14th century) which was truly in danger of disintegration in a middle term time.

These differences have obviously brought to different treatments; and not because of the dimensions but because of their different states of conservation. In the first case the traditional techniques based on the stitching was still a possible practice, even if with many cautions, and followed by a protective sandwich. For the second object an experimental process has been adopted, already used in medical and aeronautical fields to make chemical proof metal prosthesis and pieces of equipment, and successfully tested on archaeological clay object.

Five years after the treatment had been applied and published, a research carried out on a similar polymer looks as if its durability - that means the efficacy of the treatment in time - once considered extremely long, was substantially reduced.

Nevertheless the case is introduced because this fragment is one of many objects exposed to a risk of rapid destruction. In such situations the only possible option to store them practically undisturbed is the application of the best techniques known at the moment. This attitude is based on the belief that conservation, as any other human activity, is not free from the necessity of making decisions; and that, in spite of any dutiful effort, our scientific knowledge of the phenomena which cause the behaviour of the objects is rarely exhaustive and indisputable to such a level to let us operate choices in a total certainty.

11.4.1 An Egyptian shawl/mantle (11th-12th century)

HISTORICAL SETTING

Dimensions: 294 cm wide and 132 cm in height (plus 16 cm of the superior appendix,

which, however, has lost its outer edge). Fabric: wool tapestry weave, originally white, with hairs on the right face. Decorations: crosses in red and blue, with tresses on the wrong face.

Found in the region of Fayoum, it is a late version of the shawl, since ancient times a garment quite common in the Mediterranean area. Generally woven to shape in a piece, with fine wool threads, it has a rectangular shape and, according to paintings of dynastic Egypt, it can be worn in many different ways, wrapping it around the body; it was also used as a bed cover or as a shroud. The shawl is characterized by three narrow decorative bands in the weft direction, one in the centre and the other two close to the side hems. At least since 7th century, these bands were sometimes decorated with inscriptions, both in Coptic or Arabic, often invoking protection by God.

Because of the dimensions of these garments, frequently very large, they survived always in state of fragment; this fact has been made worse by the antiquarian market that preferably preserved the decorated sections, discarding the rest. The piece is exceptional first of all because it is whole. In fact, even if large areas are missing it has been possible, placing the fragments in their right positions, to recover its completeness, the correct shape and dimensions.

Judging from the present knowledge there is also a peculiarity that makes this piece unique. Since the fabric is heavy and relatively little flexible, it was not draped around the body but worn on the shoulders with the centre of one of the larger sides on the back of the neck. Because of the weight of the fabric it tended to slip down from the shoulders, producing a lightly triangular opening to the front. The problem has been solved with a solution that represents a little but meaningful evolution from the traditional garment woven to shape, toward a more elaborate tailoring technique. Four little sections of textiles - two long rectangular strips and two trapezoidal - have been joined to the front edge, which possibly overlapped partially to guarantee a good closure. For this reason the garment has a very special importance as a source of information about the costume's history, not only because of its structure, but also for its stitching largely untouched.

STATE OF CONSERVATION

Like many other textiles coming from graves, the fabric that has been in contact with the body deeply degraded by effect of the biological fluids. The result is the loss of large portions of it, meanwhile others are at present completely mineralised and, as a

consequence, very brittle. On the contrary other areas are in relatively good conditions. Between the two extremes all the possible levels of degradation, revealed by differences in colour, can be recognized.

TREATMENT

As a result of a previous treatment the fragments were mounted on a *replica* of the three-dimensional cope used at present, made with a strong plain-weave linen fabric (Figure 11.3). Being the garment substantially misinterpreted, most of them were obviously out of place and shape and dimensions of the piece totally obscured.

As a first operations the linen fabric has been cut in correspondence of the missing areas, in order to be able to move at least the largest fragments, and accommodate them more correctly on the basis of: orientation of warp and weft, positions of the decorations, hems, and other technical details. The shape of the shawl was in this way first recognized, together with the system of the front closing (Figure 11.4), thanks also to a further fragment found almost by chance among others stored textiles. After an exhaustive photographic documentation the object was then put back to storage, to have time to study similar pieces in other museums' collections.



Figure 11.3 (on the left) – The fragments of the shawl/mantle as mounted in the previous treatment.

Figure 11.4 (on the right) – A detail showing part of the neckline, before conservation.

Coming back to the problem three years later, the new examination of the piece has confirmed the first hypothesis and suggested simply a few little adjustments. The fragments for which it was possible to locate with no doubts the right positions were

removed from the previous linen support and placed on the new one, a cotton rep fabric, which has a grain similar to that of the original fabric, dyed in a colour which matches those of the object (a range between a light yellow-beige and a dark reddish brown). The other fragments, pulled off from the linen fabric, were placed on polyethylene sheets and moved on top of the support to find the correct location. Only for very few of them there is still a certain dubiousness. All the fragments have then been stitched down (with the couching technique) and covered with a dyed nylon net, to maintain in position those that are in danger to break and disintegrate and to avoid abrasions when the piece will be handled (Figure 11.5). The supplementary section corresponding to the front opening have been reconstructed in shape but not in dimensions (Figure 11.6) because of the lack of information in the remaining bits. Eventually the shawl/mantle has been rolled on a polyethylene cylinder, with the right face outside, and protected by means of sheets of white paper and a layer of strong cotton/polyester fabric.



Figure 11.5 – The mantle after conservation.

11.4.2 Treatment of an Italian fragment (13th-14th century)

The fragment, a few centimetres square of a silk ribbon (Figure 11.7), brocaded with a gold thread (Figure 11.8), has been discovered in 1988 in one of the tombs inside the church of the Benedictine Abbey of S. Fruttuoso (Camogli, Italy). It was probably part of the decoration of a liturgical garment, made in the course of a period of particular splendour in the history of the Abbey, such between thirteenth and fourteenth century.

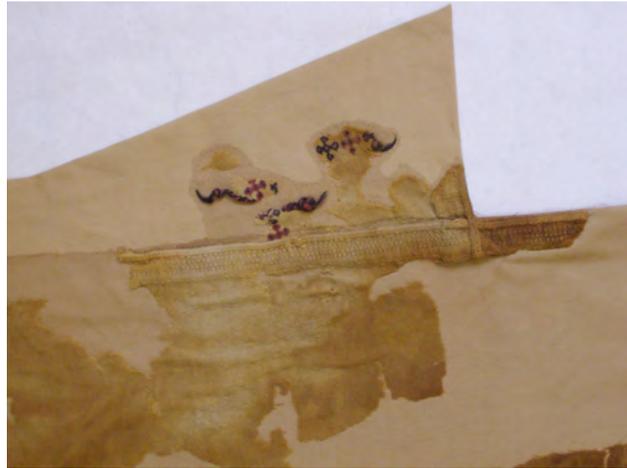


Figure 11.6 – Detail of the neckline of the mantle, partially restored.



Figure 11.7 – The fragment of gold brocaded ribbon, tablet woven, after cleaning.

STATE OF CONSERVATION

In spite of its apparent solidity the textile showed at the microscope a propensity of disintegration at the edges (Figure 11.9), a symptom of a very advanced molecular decay of the fibres. The prolonged permanence in relatively stable thermohygrometric conditions, which have favoured its survival, has however provoked a mineralization process, in the course of which salts, mould particles, dust and insects hides have been incorporated (Figure 11.10).



Figure 11.8 (on the left) – SEM micrograph of the gold laminate wound around a silk core.



Figure 11.9 (on the right) – Detail showing the extreme brittleness of the silk core (photo SEM).



Figure 11.10 – The dusty surface of the gold laminate (photo SEM).

TREATMENT

Once taken away from the confined environment of the tomb, the danger of disintegration of the specimen, due to the almost complete loss of mechanical resistance, was such that normal cleaning procedures could not be taken into consideration. The solvents or detergents solutions (even water itself), used as a rule either in the removal of the soluble encrustations or of the solid particles harboured in the weave, would have made soluble or carried away the degraded products of the fibres too, thus definitively compromising the solidity of the material.

Only a prudent mechanical cleaning was possible. In order to realize the operation with no risks, it was necessary to fix the fragment on a rigid seat which allowed it to be safely moved; the cleaning was then carried out with a sharp wooden tool and the help of a binocular microscope (20x) and of a micro-aspirator. It got back, at least partially, to the shining of the metallic threads that give rise to the typical lozenges pattern of the tablet weaving.

Once cleaned it was evident that any intervention of support, either mechanical or by adhesion, would not have had any possibility of success.

An accentuate bending, in fact, would have made the extreme resource which is the imprisonment between a padded ground and a rigid transparent surface, too risky. Moreover one wished to avoid solutions which would have substantially altered the aspect of the material: for this reason, propositions like the incorporation of synthetic resins were discarded.

Previous experiences whose results were revealed positive and are confirmed by similar research published by the specialized literature, have led us to choose a particular treatment which requires the use of a paraxililenic product (Galxyl C). The technique consists in coating the object with a very thin layer obtained through polymerisation of monomer vapours of paraxililene, which closely follows the object's surface. The film obtained in this way is extremely resistant, of high chemical inertness, completely transparent and colourless. The option of a treatment which, because of its stability has a very difficult reversibility was based on the consideration that, in the absence of any consolidation, the life expectation of a so brittle textile is limited to a few decades, if not a few years.

Since the paraxililenic based polymers are insoluble in the common organic solvents and thus cannot be applied as solutions, the application requires a longer process and a special piece of equipment (Figure 11.11). One starts from the dimer of paraxililene, which is a

solid crystal at room temperature, manageable with no special precautions.

The object to be treated is placed in the coating chamber where vacuum is applied up to the achievement of about 0.1 mm Hg; the dimer is heated up to 150 °C in the sublimator making it pass to the vapour phase; the dimer is then introduced in the pyrolytic area at about 680 °C, where it changes in paraxililenic monomer; the reactive monomer enters successively in the coating chamber, maintained at room temperature, where it is deposited on all the cold surfaces, it condenses and meanwhile polymerizes producing a thin continuous coating, free of irregularities, of the same thickness (4 µm) in every point of the surface of every thread. After the treatment the visual aspect of the specimen is practically unaltered and the reached consolidation can be appreciated acting a bland surface rubbing. Thus it can handled with sufficient safety and preserved without special precautions.

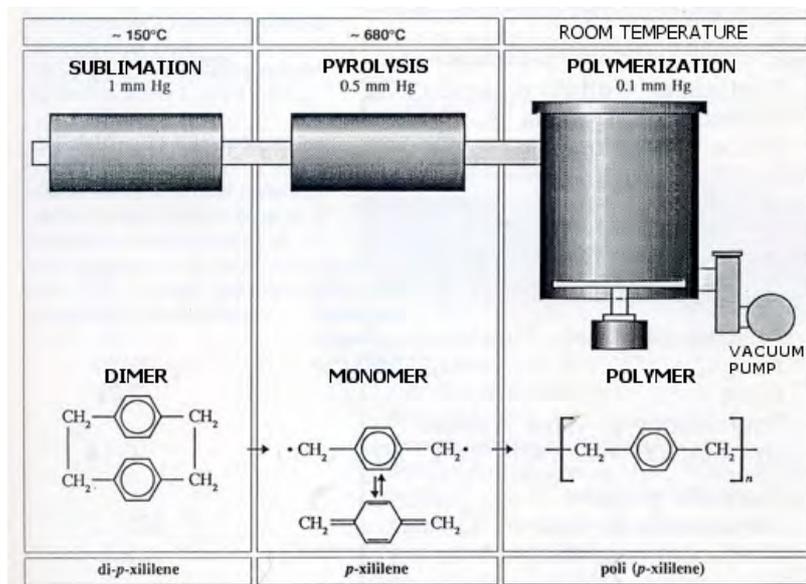


Figure 11.11 – Graphic scheme of the coating process.

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12 – LEATHER AND ANIMAL SKIN OBJECTS

12.1 Introduction

Leather is a product derived from animal skin. It has been utilized by human beings since prehistory, as is documented in cave paintings and by the finding of flint and ivory tools likely used for skin processing. The original use was for clothes: the skins removed from the animals were used for protection against low temperatures or as ornament. Recent evidence of this was found with the Similaun man discovered in the ice in Alto Adige, northern Italy. Along with the body, the ice preserved his clothes made of skins all dated back to five thousand years ago, though the use of animal skins, as documented in cave paintings is much older. At that time animal skin was probably utilized in its natural state after flaying the animal and drying the skin.

Unfortunately, dried skins could only be used for a short time, because they rapidly decompose in hot and humid climates or become rigid in cold climates. The rotten smell of the decomposing skins did not likely offend the nostrils of our ancient ancestors. The skin was probably discarded when fungi and bacteria made the material fragile and possibly because it could then spread to human skin. In addition rigid skins were not suitable as clothing, so they could no longer be worn. As a consequence, people learned that the skin must be treated in order to maintain its elasticity and impermeability, that means that it must be tanned.

12.2 Skin

Skin is a biological tissue, which can be defined as a specific community of cells and substances derived from similar cells, with common morphological characteristics and having the same function.

The category of epithelial animal tissue can be subdivided into glandular and covering tissues. The latter are tissues comprising tightly connected cells, in geometric forms and

are well defined. The covering epithelium tissue can line internal cavities without any connection with the outside, for example the blood vessels or cavities connected with the exterior, like the digestive and respiratory tract, and can even cover external surfaces where it is called the epidermis. The tissue is formed differently depending on its specific functions:

- a simple single, plate-like layer in the airways and blood vessels
- a simple, single cube-like layer (polyhedral shaped cells), in the digestive system and excretion ducts in glands
- a multi-layered plate composed of three layers (deep, intermediate and external) in areas that have contact with air.

Surface cells can be alive and continuously moistened (saliva for the mouth, mucous secretions in the pharynx, oesophagus and vagina, and lachrymal fluid for the cornea) or dead if transformed into corneum. The cells directly in contact with the air and those in the intermediate layer are subjected to a corneum transformation, which forms a continuous, sometime very thick, keratin sheath, or forms specific organs such as reptile scales, antlers, nails, or bird beaks.

The skin is the external covering of an animal's body and is composed of three very distinct layers (Figure 12.1):

- *epidermis* - the outermost layer is composed of the various layers of epithelium cells, including the dead cells and those active in the deeper layer, or stratum germinativum. This layer equals 1% of the total thickness of the skin;
- *dermis* - with a thickness that varies from animal to animal, it can equal 85% of the total skin, contains blood vessels and nerve endings. It is composed of two layers, the papillary and reticular dermis.
- *hypodermis* - or subcutaneous fatty tissue, connects the skin with the organs underneath. It represents 14% of the total thickness of the skin.

The connective tissue of the dermis is a dense connective tissue, rich with fibres. There are three types of connective fibres:

- collagen fibres - are made up of small bundles of fibres 0.2-0.5 µm thick which are cemented together by a substance, called mucin, which dissolves in acids or boiling water. Each fibre comprises proto-fibres, which are created by long polypeptide chains. Each chain is composed of amino-acids: proline, hydroxyproline, and

glycine. Three chains united together in spiral form, create the basic unit of collagen which is called tropocollagen;

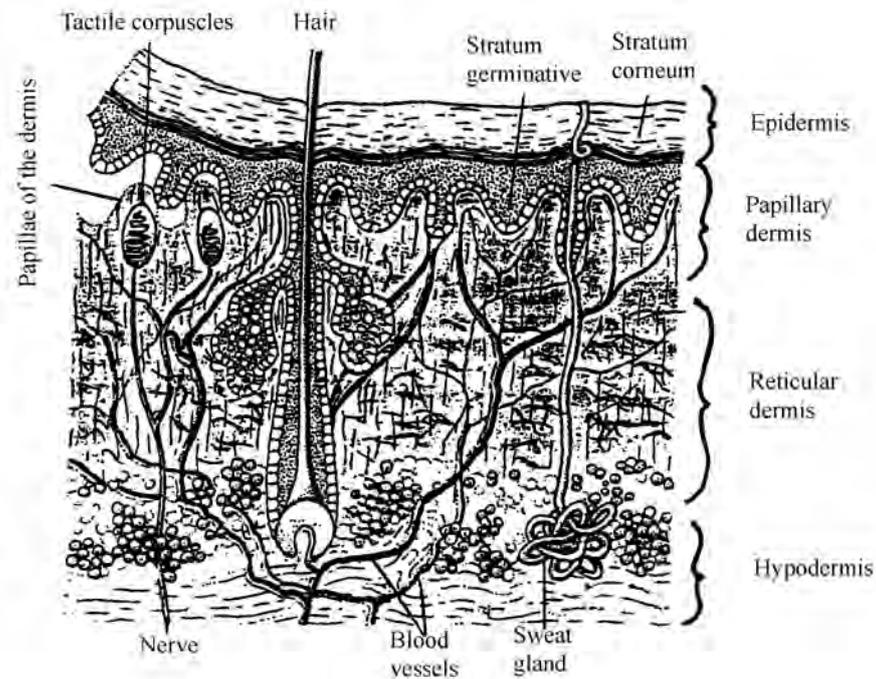


Figure 12.1 – Cross-section of skin.

- reticular fibrils - these differ from the previous in their ability to divide or join to other fibres during the anastomosis process; they are made of a different scleroprotein, reticulin; like collagen, it can be dissolved in boiling water, or other alkaline solutions;
- elastic fibres - are found in lower quantities than the previous fibres, have a totally different chemical composition and physical properties; they are formed by the protein elastin, which is insoluble in boiling water and acid solutions. It can be dissolved only in a highly alkaline environment.

Connective tissues can undergo two types of transformations: swelling and shortening. Swelling can be caused by increased water content (acid or alkaline solutions) in the space between the fibrils; this is known as osmotic swelling and is substantially reversible. On the contrary, a swelling due to neutral salts or non-ionic reagents, called lyotropic swelling, is irreversible because it disturbs the organization of the proto-fibrils. Shortening is caused by heat, which shortens the collagen fibrils and makes the process irreversible.

The combination of water and heat destroys the skin and forms gelatin (animal glue).

12.3 The tanning process

12.3.1 Tanning in ancient times

Prehistoric human beings became aware that the skin of the killed animals could be suitable for many applications. They also understood that it had to undergo a process to avoid decay, so that it could be used for a long time maintaining its elasticity, resistance and impermeability. This process is called tanning. It is only possible to speculate about the primitive tanning process, such as the discovery of the effect smoke from fires inside a cave had on a flayed skin. Tanning through smoke exposure is still used today in some regions of the Orient. Another assumption is the use of fats by rubbing them directly on the skin; this type of tanning is still utilized by the Eskimos.

These primitive treatments cannot actually be called tanning, but a type of pseudo-tanning. During the actual process of tanning all the parts which tend to rapidly putrefy, the epidermis and hypodermis, have to be eliminated. The epidermis can be left only when the skin belongs to an animal with thick fur which needs to be conserved. Therefore, only the derma is tanned, in other words, transformed into leather. We can define tanning as the process which fixes the collagen fibrils and impedes their decomposition, maintaining its characteristic resistance to water and heat.

Early attempts at tanning utilized the degenerative action of bacteria, trying to control their effect. Historical documentation shows us that there were tanneries in ancient Mesopotamia where the skins were dipped into solutions containing fermenting substances, such as flour, grape juice, milk and salt. The enzymatic action of the bacteria was very difficult to control, so it was necessary to check the state of the skins and repeat the process, washing it in clean water before each enzyme bath. Baths of fermented urine were also used, but it was even more difficult to control the bacterial growth. Immersion into fermented solutions was also practiced by the Egyptians, and this procedure was still occasionally utilized until the 17th century.

12.3.2 Operations prior to proper tanning

DRYING

After the animal has been killed and flayed, the integument is laid to dry in aerated environment, far from the sun rays in order to avoid an excessive drying of some parts of

the object. Speed drying, in fact, can leave humid parts inside with subsequent bacterial formation and severe damage. In the past, the tanning occurred just a short time after drying, but after the spread of the process it was necessary to learn storing and conserving methods for the dried product. Like today, the conservation of the dried skins was carried out by salting. The skins are sprinkled with solid salt on the hypodermis side (flesh side) and stacked up. The salt dissolution determines the loss of about 30% out of the total water.

The conserved hides are ready to undergo the various tanning steps. All kinds of animal skins can be tanned, but ovine, caprine and bovine are the most utilized, today like in the past. The skin of other mammals can more rarely be used depending on the geographic area.

SOAKING

Reviving a dried skin means restoring its characteristics which it had just after flaying. So that the tanning is effective, and that all the tanning materials are fixed to the collagen fibrils, it is necessary that the fibrils are very rich with water. The soaking phase is simply leaving the dried skins immersed in clean water. In antiquity, this operation was done directly in the water flow from rivers or streams. Then basins were used making it necessary to change the water and the skins must be beaten. Apart from absorbing water, during this phase, the animal skins were cleaned, eliminating the salt and the dirt.

Only in the 19th century were basins substituted by big wooden barrels, which rotated on their axis by hydraulic power. Inside the barrels, the skins were delicately beaten by the rotating action (Figure 12.2).

LIMING

The liming is the impregnation of the skins with lime. Such a treatment has the aim to free the integument from those parts that are not transformed into leather, the epidermis and hypodermis. The lime is an earth-alkaline compound which has the property to attack the keratin; in addition, the fibrous structure of the derma reacts more easily with the tanning substances. Therefore, through liming it is possible to achieve the separation of the epidermis with the hair side, the loss of the hypodermis through saponification of the fats, and the swelling of the dermis.



Figure 12.2 – Internal view of a barrel with some skins during the reviving.

HAIR REMOVAL

The liming has produced a chemical relaxation between epidermis and derma. As mentioned earlier, this detachment can also be obtained through a biological route, meaning a controlled decay of the skin using fermented baths. In both cases, one must then proceed to the physical separation of the two parts. In antiquity, the separation was done by hand; the skin was placed on an inclined plane and the leather worker completely removed the hair and the epidermis using a convex half-moon knife held with two handles. Today the same operation is performed by machines. At the end of this phase, the skin looks like Figure 12.3.

THE FLESHING

After the hair removal, the skin is washed and the treatment continues with the fleshing. This operation is very similar to the hair removal, but it is made on the opposite side, that is on the flesh side. Then, when the skin is very thick, it is possible to make the split and separate the derma into two or more thin leather pieces from the single skin.

Ovine, caprine and bovine skins, the most used, are split into two parts to increase yields and to obtain more elegant and easy to handle leather objects. In modern times, with the use of appropriate machines, more layers are obtained from the skins of big animals. For example, before the elephant became a protected animal, up to ten layers could be obtained from its skin. After fleshing, the skin is reduced to only the derma.

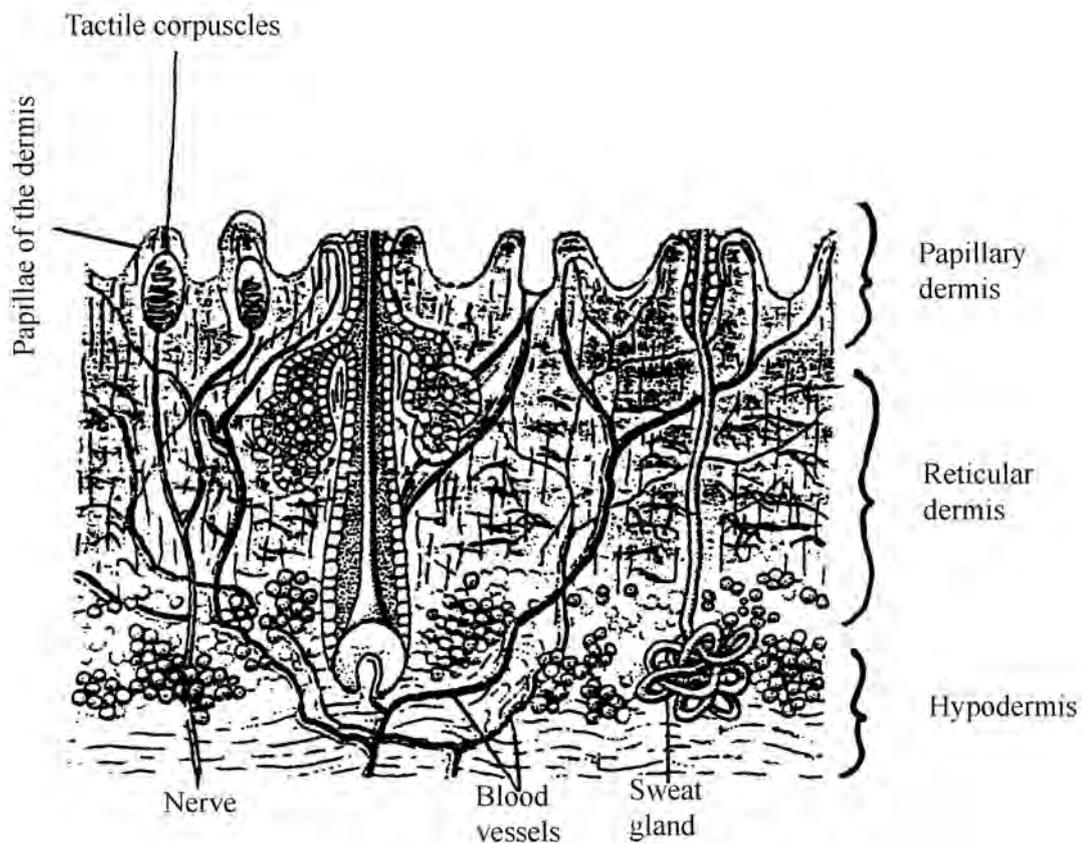


Figure 12.3 - Section of skin after hair removal.

THE MACERATION

Fleshing is followed by maceration, which eliminates all the keratin and epidermis residue. This type of processing is limited to the ‘light’ skins from sheep and goats, and is preceded by a lime elimination phase to remove all the traces of lime if liming was used. This work was done on an inclined plane using the knife and by compressing the skin to bring out all traces of lime.

In the Medieval Ages, maceration was performed with animal dung (birds and dogs), thanks to the action of the organic acids and bacteria which produces enzymes. Since the 17th century maceration with dung was replaced by bran and oat chaff to obtain fermentation with formation of lactic acid, acetic acid and other acids. Today maceration is executed by means of enzymes, of which the most used ones comes from the pancreas.

12.3.3 Proper tanning

After the above operations have been completed, the skin is limited to the only derma, and it looks white, flaccid and slippery, even though the flesh side (internal part that was in

contact with hypodermis and muscles) and the flower side (external part that was immediately under the epidermis) can be recognized. Proper tanning is carried out on this material, so leather consists only of an appropriately treated derma.

Different methods of tanning exist, depending on the substances used. In each case the purpose of tanning is to fix the collagen in order to avoid its degradation, mainly because of water and heat. The resistance to these factors is measured as temperature of gelatinization, which may vary from case to case.

VEGETAL TANNING

Vegetal tanning is one of the most ancient procedures and it is still employed today to obtain leather suitable for soles, saddles, horse harness, linings, and book-binding.

This system involves the use of materials of vegetal origin, that contain tannin in variable percentages depending on the vegetal species and the part of the plant which is utilized. Favoured by the acidity of the bath, the tannin is fixed irreversibly to the collagen.

Tannins are phenolic compounds, which are classified into two groups:

- hydrolysable tannins, or pirogallico tannins
- condensed tannins, or catechin tannins.

Sometimes the same plant can contain both types of tannin, for example the oak tree. Bark, wood, leaves and fruits are the parts of a plant which contain different tannins and in variable percentage. In particular, the vegetable growths (gall nuts) which are formed due to insect bites have a high tannin content.

The oldest form of vegetal tanning was done in pits which were prepared lining them with sturdy wood. A first layer of humidified bark was placed on the bottom, and the skins were posed on it with the flesh side facing down. Then a new bark layer was placed on the flower side of the skin and on the bark a new layer of skins with the flower side facing down. They proceeded by alternating the directions of the skins, always separated by bark layers until the pit was full. The last layer was a bark layer which was covered with wood boards to the purpose of closing the pit and keeping the skins stopped. Finally, water was poured until the pile of skins and bark was completely covered.

In this first stage the material was left for a minimum of two months, then the skins were recovered, cleaned and placed in another pit with the same above described system. Here the skins stayed another few months. They repeated the procedure of changing the pits six or more times, so that the entire process lasted 2-5 years in order to obtain high quality

tanning. After extraction from the last pit, the skins were washed with fresh water and then left to dry. After some time, they noticed that it was possible to save material if they didn't use new bark every time. In addition, the reuse of old tannin-poor bark led to a slower tanning with best results.

The skins extracted from the last pit were washed and hung out to dry.

The selection of the vegetal substances to be used for tanning was made not only depending on the type of tannin present, but also in consideration of the final quality of the leather: the leather obtained by using oak was more compact and harder, while the one obtained with valonia was more spongy. Also the colour varies from pink to light green depending on the vegetables used.

Today, by using extracts of tannin and utilizing the rotating barrel, tanning has become much faster, from 8 to 20 days. The yield of a tanning process is the following: 100 kg of dried skins yield 115 kg of leather, while 100 kg of soaked skins produce 50 kg of leather.

MINERAL TANNING

Mineral tanning is realized by using mineral compounds of aluminium, iron, chromium, and zirconium. Before tanning, the macerated skin has to undergo a treatment with strong acid solutions, e.g. sulphuric acid, to which salts are added to avoid swelling. This treatment has the function of eliminating the last lime residues and to permit a rapid and deeply effective tanning action. When the tanning is not carried out immediately, the acid treatment allows the skin to be conserved for a certain time.

The most ancient tanning was realized with aluminium, usually in form of rock alum, which is a sulphate of aluminium and potassium. Rock alum has been known since ancient times and was mainly used in the tincture process. In contrast to vegetal tanning, tanning with alum does not always lead to a complete fixation of collagen, because it is based on the stability of the protein-metal salt in the collagen-aluminium complex. The leather obtained is soft, elastic and ivory-white coloured, but not very resistant to water, which can restore the skin to a state prior to tanning. This could be called pseudo-tanning, but the above mentioned characteristics of the leather treated with alum made it desirable for producing gloves and book covers. The most utilized are lamb and kidskin, pigskin was also used in ancient times.

More recently, tanning with alum was performed in two steps. The first step is as above, but with the addition of sodium chloride, which has two objectives:

- to avoid the swelling of the skin due to the action of sulphuric acid formed through hydrolysis,
- to favour the absorption of aluminium oxide, that plays the role of tanning

The second treatment was carried out in the barrel by means of a mixture of albumen, egg yolk, sodium chloride and flour; it lasted about 45 minutes.

Tanning with iron can be ignored because it was used rarely and only as a substitute of chromium due to its lower cost. Tanning with zirconium can be skipped as well, because it is now in development. On the contrary, it is worth saying something about tanning with chromium.

Chromium salts have been recently introduced, in fact the first attempts were made by Americans in the year 1855. Schultz (1883) and Dennis (1893) patented the successful system that most skins are still treated with.

Tanning with chromium, primarily utilized for bovine skins, is done through one or two baths inside the tank; then a maturation period follows on the inclined plane. After that the skins are pressed in order to squeeze most of the liquids retained, and shaved on the flesh side to make the thickness uniform. Finally the skin will be neutralized by weak alkaline compounds (bicarbonate) to prepare it for the tincture process.

Leather tanned with chromium shows a fine flower side and a compact fibrous tissue; it is water, wear and tear resistant; and it has a tensile resistance higher than that of the leather obtained with vegetal tanning.

TANNING WITH OIL

Like smoking, tanning with oil was among the first techniques used, but then it practically disappeared. Therefore, it is not worth describing in detail. It was executed using fish oil or animal fats, and it served to obtain suede leather.

12.3.4 Dyeing

Speaking of tanning and its various systems and materials it was said that vegetal tanning does not always produce leathers of uniform colour, and that different shades are obtained depending on the vegetable substances employed. Leathers tanned with alum are white and generally these were left unaltered, while those treated with chromium are yellowish. Therefore, sometimes you must run the dye after tanning, in order to obtain a uniform product. Today dye is indispensable to make the leather look appropriate depending on its

subsequent use. To dye the leather you can use natural or synthetic dyes.

Natural dyes are obtained from some kinds of wood:

- ‘campeggio’; through the so-called haematin, it produces blue and black shades,
- red (or Brazilian) wood; it gives ‘brasilina’, that produces pink and red shades,
- ‘fustello’ (or yellow) wood; that contains ‘fustina’ and produces yellow to brown shades.

Synthetic dyes can be subdivided into:

- basic dyes, used for the leathers that underwent vegetal tanning,
- acid dyes, used for all leathers, but mainly for those undergoing chrome tanning.

Tinting can be done by brushing on only one side, or by immersion with the use of a tank.

12.4 Parchment

12.4.1 Definition

Another important product derived from skin is the parchment which has had several uses even though the most important use is as writing support.

Parchment is a skin that was made stable through almost exclusively mechanical operations instead of proper tanning. Parchment is obtained, for the most part, from all types of sheep skins, goat and more rarely calf which is common in German parchments.

The flesh side of a dried skin is very similar to parchment, therefore, the first parchment was likely created as a dried skin with the hair removed, even though it wouldn't have lasted long before decomposing. It was probably created by chance after drying an untanned skin, that had undergone all the preliminary operations of hair removal and fleshing. Certainly, at the beginning it was not produced as a writing support, but to satisfy other needs related to rural life, such as sieves, musical instruments, etc. The legend says that parchment was borne in Pergamon, a city of Asia Minor, in the 2nd century B.C., but its origin is much more ancient. In Pergamon it definitely spread as writing support, when its manufacturing quality improved.

The manufacture of parchment achieved its maximum development in the Middle Ages and it has remained unaltered till today.

12.4.2 Manufacturing

According to the most ancient method for manufacturing parchment (8th century), the skins were immersed into lime water for three days, so that the hairs were removed from the epidermis and the fat layer of the hypodermis dissolved. After air-drying, stretched on a frame, the skin was scraped with a convex crescent knife and then rubbed with powdered chalk.

Parchment manufacturing reached its height during Medieval times and has remained virtually unchanged even today.

Dried skins undergo a series of preliminary operations identical to those mentioned in tanning: soaking, liming, hair removal and fleshing. In antiquity, liming was performed by putting the skins in stone pits with the lime solution and turning them from time to time for 5-10 days. Today, by using the rotating cylinder, the liming stage lasts 2-3 days only.

After hair removal, the skin is washed and dried keeping it stretched on a wood frame by means of nails (for the thick skins) or ropes for small and thin skins in order to avoid lacerations. While the skin is under tension, the residues of fat substances and hairs are eliminated by scraping with a convex crescent knife; scraping is executed on the hair side or flower side, while fleshing on the other side. Drying under stress makes the collagen fibres arranged in aligned layers, and the plane sheet maintained even after the skin is removed from the frame.

The manufacture is completed by treating the flower side of the parchment with a piece of pumice stone. In Italy, probably during the 8th century, the pumice stone was substituted by chalk, while they continue to use pumice stone in Germany; pumice stone will be used again in Italy in the 18th century. The scraping also has the function of reducing the thickness of the parchment. But the request of thin parchment was better satisfied by using a skin from a newborn or stillborn lamb; *vellum* was probably parchment obtained from a calf foetus. Today machines can split skins to obtain thin parchment from any animal, though goat is usually used.

12.5 Leather deterioration

Leather degradation can occur due to intrinsic and external causes. Intrinsic causes are connected to tanning and the links formed between the tanning substances and the collagen

fibres. The block of collagen plaits is stable between pH 3 and 6; outside this parameter the links loosen and the fibres are more easily degraded. Water is the most important deteriorating agent, which causes swelling of the fibre tissue and removes the tanning substances. Alum tanned leather is particularly sensitive, because water alone is able to break the links between the aluminium compounds and the collagen fibres.

If any acid accumulated inside the derma due to erroneous tanning processes, it causes a softening of the leather, and if pH goes down to 3, the tanning loses its efficacy. Contemporaneously, the acid corrodes the fibres making the leather brittle till its destruction. Alkaline substances also lead to the same damage, because they increase the pH value over 6.

Intrinsic causes of damage are completed by defects of the starting skin, due to the presence of injuries or diseases present in the skin before tanning, if the affected piece was discarded.

Among the external degrading substances, other than water and heat, atmospheric pollution must be taken into account. In particular, sulphur dioxide is absorbed by leather and starts a series of oxidant reactions which leads to the formation of ammonium sulphate. When these substances are above 10% inside an antique leather, this compound surely indicates an advanced state of decay.

Also the reaction between collagen and atmospheric water is favoured by the presence of acid, so that a very acid leather, kept in a very humid environment, is a high risk for conservation.

Among the external degradation factors there are the biological ones of micro-organisms and insects.

Micro-fungi mainly develop when humidity is more than 65%; they cause the formation of stains and leather degradation particularly in dyed leather. Chromium tanned leather is the most resistant; unfortunately ancient leather was almost exclusively prepared through vegetal tanning.

Some species of insects prefer leather for their diet, the most common and frequent are Beetles such as the Dermestidae: their larvae eat the leather and dig deep channels (Figure 12.4).

Some woodworms, for example Anobidae, prefer wood and paper, but can also eat leather: the holes produced in leather covered books by the larvae during their transformation into

adult insect are well noted. Finally one must mention termites, which eat any organic product, Blattodea, which erode the leather surface, and ravenous mammals such as *mus musculus* and the like.

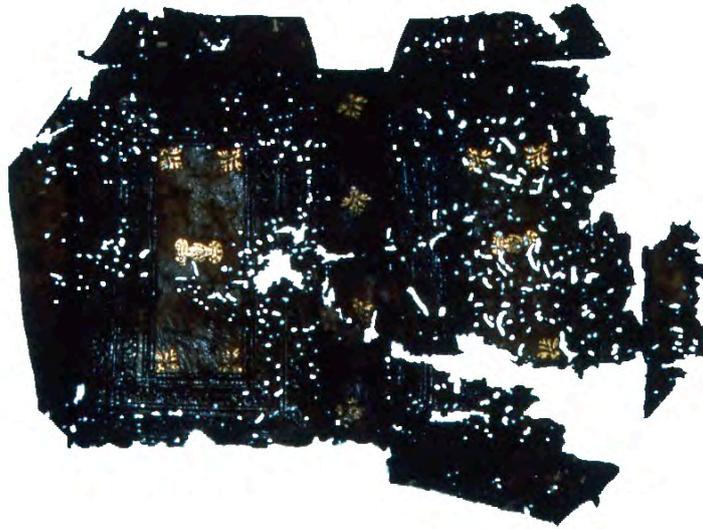


Figure 12.4 – Example of a book cover eroded by Dermestidae grubs.

12.6 Conservative intervention

12.6.1 Prevention

The general principles for the lasting conservation of leather objects, or partial leather objects, derive from the previous analysis of the degradation factors. First of all it is necessary to keep the objects in stable climatic conditions. Sudden changes in temperature or the presence of high humidity can produce the dangerous phenomenon of condensation, so that the small water drops are adequate for the development of fungi and microbes from the spores present in the dust deposited on the surface of the objects. Therefore, the objects must be protected from dust, which also contains insect eggs and polluting substances. The best conditions are less than 65% relative humidity and a temperature around 18 °C.

12.6.2 Leather analysis

Before the final placement of the objects, the leather should be investigated by analyzing it in order to establish whether it needs to be restored and how. Therefore, the objects should

be well cleaned to eliminate the dust, that could alter the analytical data.

NON DESTRUCTIVE AND MICRO-DESTRUCTIVE ANALYSES

There are only three types of analysis which do not need to take a sample:

- to recognize the type of animal of which the skin was part,
- to measure the water content,
- to measure the pH value.

Direct observation with a stereo-microscope on the hair side, is used to determine the unique characteristic hair pattern of each mammal.

The measurement of the water content is executed by means of an instrument equipped with micro-electrodes which are inserted in the leather and, through the voltage difference, indicate the percent of water contained. The pH measurement is realized by means of an electrode in contact with the leather. Its measurement in a distilled water solution obtained by introducing some powdered leather would be more precise, but this is a micro-destructive method.

The search for ammonium sulphate is a micro-destructive investigation too, but there is no alternative. One can utilize the same solution obtained for measuring the pH value, by adding some drops of distilled water solution containing 0.1% of nitric acid and 1% of barium chloride. The presence of ammonium sulphate is demonstrated if the leather solution becomes milky white.

DESTRUCTIVE ANALYSES

This chapter should be excluded *a priori*, because it is almost never possible to destroy significant parts of any cultural object. Only in the case of leather covers can you sometimes sacrifice a sample taken from non visible parts, in order to determine the type of tanning, the temperature of denaturing, and the content of fats.

12.6.3 Restoration

After photographic documentation of the current state of an artefact, the elimination of dust is the first operation that must be done. The results of the analyses will indicate the most appropriate methods for the conservative intervention, which begins with adjusting the water content in the range 12-20% at 21 °C and 50% RH conditions.

Then, the first operation is cleaning. Droppings of insects and other encrusting substances

can be mechanically removed under the stereo-microscope; a wet surface cleaning with methyl-cellulose or neutral detergent is done depending on the level of dirtiness and decay. The next step is the suturing of tears or the integration of lacunae; it must be always done with leather of the same type of animal and tanning, by using the part of the skin identical to the missing one. For example, if the lacuna is on a skin from the animal's back, you will use a new leather part coming from the back, and not from other parts of the animal. This solution will prevent tensile differences between original and added parts. In addition, you will have the best aesthetical result, because the leather texture changes in the different parts of the body.

If a leather object is very damaged, due to microbe or insect attack, it needs a reinforcement, that can be done with pure cotton or with very thin leather. There is not a general rule: the use of cotton or leather should be decided on, case by case depending on the type of artefact and degradation problems.

Lubrication is the last phase of the intervention: there are several industrial products, but one can also prepare a solution according to known recipes.

12.7 Examples of conservative interventions

12.7.1 Seal container

It deals with a seal container made of painted leather (8 x 7.5 cm, XV century), kept at the Medieval Museum in Bologna (Italy). One can see (Figure 12.5) the extreme dryness of the leather, with losses of colour and fragmentations on the lower part on the right. The two valves were probably initially joined by two wood or ivory small cylinders.

After an accurate cleaning, the object was left in climatic cell for 30 days at a temperature of 16 °C with 50% relative humidity. In this way the leather has slowly absorbed the lost water and has become more malleable. So, it has been possible to restore the fractures and to fix the colours by introducing Paraloid B72 under the pictorial film and joining it to the leather surface. In order to maintain fixed the two parts, a modern material like two Plexiglas bars was selected (Figure 12.6).



Figure 12.5 – View of the seal container before restoration:
two halves interior and exterior details.

12.7.2 Book covers

The second example presented here refers to three leather covers from books kept at the Manfrediana Library in Faenza, including a cinquecentina. The first case is a book from the year 1552 (Z.N. 006 004 017), the cover of which has been already shown in Figure 12.4. It is evident that the leather was so eroded as to be the limit of its resistance, but the cover, that depicts two hands crossed, is very important due to its impressed golden figures. Therefore it was decided to proceed with its reapplication after lining it with split leather, vegetal tanned and dyed as the original; the result is shown in Figure 12.7.



Figure 12.6 – Recto and verso of the seal container after restoration.



Figure 12.7 – Leather cover eroded by *Dermestiae*, reapplied to the book after restoration.

The second example of leather cover refers to a incunabulum of the year 1483 (inv. 1158, BCF, inc. 84). In this case the leather cover lined wood planes which had been attacked by xylophagous insects of the species Anobidae. Then erosion was transferred from the wood into the leather, which had been weakened due to repetitive mechanical use and it had lacunas in various areas (Figure 12.8, left).

Before leather restoration, the volume underwent disinfestations with ethylene oxide in autoclave, to neutralize possible eggs still present. Then the leather was separated from the



Figure 12.8 – Leather cover on wood axis, before (left) and after restoration (right).

wood. The analytical results demonstrated that it was vegetal tanned goat leather; therefore, the leather was cleaned with methyl-cellulose and a neutral detergent, and integrated with new leather of the same type (Figure 12.8, right).

The last example of restoration of a leather cover is presented due to its particular damage connected to a tanning defect and its conservation in very humid environment. It deals with a manuscript volume (*Index Zauli Naldi*, 18th century, Manfrediana Library in Faenza), whose front cover was broken and detached from the wood, while the back cover was almost completely missing (Figure 12.9). The analyses revealed that it had been vegetal tanned and its pH was 2.8.

In this case the cover was cleaned and humidified on the flesh side with calcium bicarbonate to increase the pH. The usual integration with new non dyed vegetal tanned leather completed the work (Figure 12.9).



Figure 12.9 – Volume *Index Zauli Naldi* before any intervention (left) and after restoration (right).

12.7.3 Upholstery of a telescope

This ancient Campani telescope, dated back to 1700 ca., is kept at the Specola Museum in the University of Bologna. It is composed of six tubes inserted into one another; the closed telescope is 134 cm long, and 9.5 cm in diameter; when open, the length reaches 474 cm. The tubes are paper made with wooden slats; the five smaller tubes are coated with leather

in their initial section, and with marbled paper in all the remaining length. The external tube is completely covered with leather, and the analyses demonstrated that it was made from two vegetal tanned skins of goat. The leather surface is decorated with golden stamping.

The telescope has come to us in bad conditions, with tears and lacunae on the external tube, as well as the initial coating of the other tubes (Figure 12.10).



Figure 12.10 – External tube (over) and detail of the head of a minor tube (under) of the Campani telescope.

The conservative intervention has consisted of thorough cleaning with methylcellulose and neutral detergent, followed by the arrangements of lacunae and tears. The last operation was lubrication with a mixture of oil of ox foot and anhydrous lanolin (Figure 12.11).

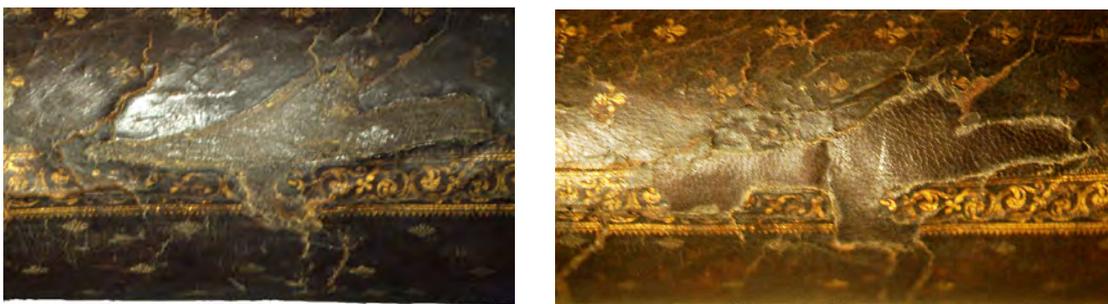


Figure 12.11 - Details of the leather coating of the Campani telescope, before (left) and after (right) restoration.

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13 – INORGANIC MATERIALS OF ORGANIC ORIGIN

13.1 The materials

13.1.1 General information

This section is about a range of little-known raw materials, but always employed for making artefacts using specific and very particular production technologies. All these materials are usually defined as inorganic, but they have an organic origin. They are bone, ivory, coral, and mother of pearl. These materials have been dealt together because are formed by inorganic matter intimately combined with a small fraction of organic matter and because their conservation and restoration operations are similar.

As far as conservation concerns it is important to respect the chemical, physical and structural differences that distinguish everyone of these materials. Bone and ivory have a proteic nature and are part of the load-bearing frame of vertebrates of the Cordata phylum and in particular of Mammalia class. Coral and mother of pearl are calcareous formations, which support and protect the invertebrates of the Cnidaria phylum and the Mollusca phylum.

Artefacts of bone and ivory, coming from an archaeological site, suffer a loss of their original appearance because of a regression of the organic substance in their chemical composition. Similar artefacts, not coming from soil but placed in a museum without suffering any aggressive treatment, preserve a good look and can regain their vitality if subjected to adequate operations.

Coral and mother of pearl have a very low percentage of organic substance in their chemical composition. For this reason, in archaeological sites with not acid soil they maintain their original appearance, while in museum collections, without regular maintenance, can lose their good original look.

13.1.2 Bone

Bones are the components of the skeleton, which is the support apparatus of all the vertebrates. In the great class of Mammalia, the most frequently used bones for getting

manufactured articles are those belonging to the Ungulate order.

Moreover it is correct to associate to the bones also the antlers of the Mammalia of the Cervidae family, as material for this type of use. In fact, the antlers are an external development of the skeleton of these animals and, in particular way, of the bone of the skull in some kinds of Cervidae. For a long time, bones and antlers have been used for the predisposition of utensils and elegantly you can work them for the realization of artistic articles and coverings of value for other types of material: wood and metal. Their use is linked to the availability in the geographical zone of production.

The hard tissues of the vertebrates of the Equidae and Bovidae families, because of their good characteristics, were the most commonly used; both the longest and the largest bones were exploited. To obtain artefacts, even bones of animals of smaller size were not disdained, as well as larger and light ones of the order Cetacea, although they are very spongy. The matter that constitutes the hard tissues of vertebrate is formed by the mineralization of connective tissues. That is why we can find, in bones, an inorganic component that varies from 57 to 60% and 43 to 40% of an organic component. The percentages, however, can be very different depending on many factors.

The chemical composition of bone is defined by a predominantly inorganic fraction, consisting mainly of calcium phosphate and calcium carbonate associated with minor amounts of other salts. This mineral component comes in the form of microscopic crystals known as hydroxyapatite, with chemical formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. This calcium phosphate hydrate is intimately combined with the organic portion, which consists of collagen fibers contained in an amorphous substance of protein complexes.

The material that makes up the bones shows a structure with lamellar systems, organized in different levels of growth (Figure 13.1). The typical conformation highlights areas of compact tissue where are more or less visible nutritional channels, and less compact areas that have the characteristic sponginess. The bones have a low hardness (2-3 on Mohs scale, see chapter 8, paragraph 8.3.1) and can be easy to work with specific technical solutions.

The material to be processed is selected and drawn from strategic parts of the skeleton. Usually the parts used are the ones where you can make the most of the original size of the bone in comparison to the model of the artefact to be realized and, in particular, where are less frequent those elements characterizing the bone, as the cavities, the alimentary canals, the most porous and spongy parts (Figure 13.2).



Figure 13.1 – Crossing section of bone.



Figure 13.2 – Longitudinal sections of cow bones with the alimentary canals.

The antlers of Cervidae family, as it has already been specified, are a modification with external development of bones of the animal's skull. The chemical composition of antler is comparable with that of the bones of the skeleton, but some differences are given due to a different internal structure as a result of specific development needs. This therefore results in a lower hardness than the bones. Each year the antlers grow on small permanent protuberances of the frontal bones named pedicles. For this reason, the morphology of this material is coarser and may vary depending on the physical development of the animal (Figure 13.3). Although seemingly the material of the antler is compact as that of the bone, it is immediately distinguishable by the more heterogeneous and shapeless outside, and mainly for a higher internal porosity.

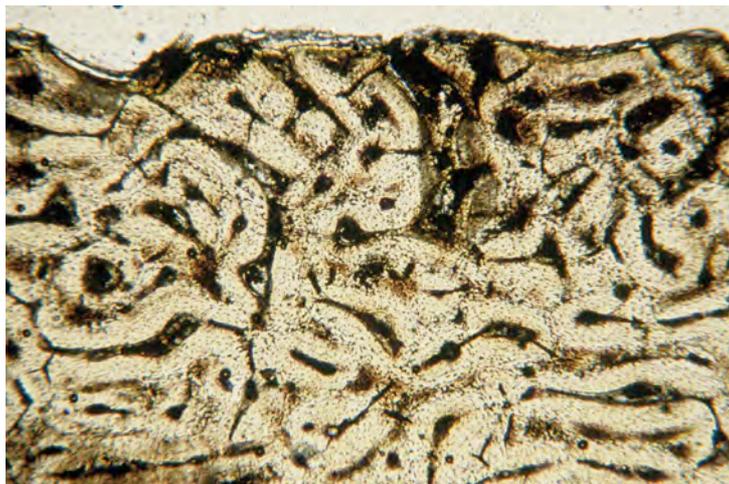


Figure 13.3 – Crossing section of antler.

13.1.3 Ivory

The ivory is a differentiated form of dentine, the material that makes up the teeth of most vertebrates belonging to the mammalian class. The teeth are a specialized form of bone tissue and are composed mostly of dentine. The dentine, arranged around a cavity of the pulp, is provided with a protective layer. In the upper part, i.e. the area more exposed to use, is covered by the enamel, while in the lower zone, in correspondence of the root, is covered with cement.

Ivory, for its warm appearance, its excellent strength, ductility, and ease of processing, was considered a very sought material, already very rare in Roman times.

The animals from which the ivory was mainly obtained were the great pachyderms, among which we should remember the mastodon and the mammoth, whence comes the so-called “fossil ivory”, and the most recent examples of African and Asiatic elephants. It was also used the material obtainable by the big canine teeth of the Mammals belonging to the Hippopotamidae family, and most of the ungulate Suidae family like pig, wild-boar, warthog, babirusa and peccary (Figure 13.4). Among the marine Mammals they used to use the tusks of the walrus, the canine tooth of narwhal, and various types of teeth and whalebone of the Cetacea order.

However, the term “ivory” has often wanted to state only the most valuable dentine obtained from the tusks of elephant, from which we obtained a dense and compact material, with a silky look, which has a radial reticular structure (Figure 13.5, left), consisting by a tubular system (canalization) (Figure 13.5, right).

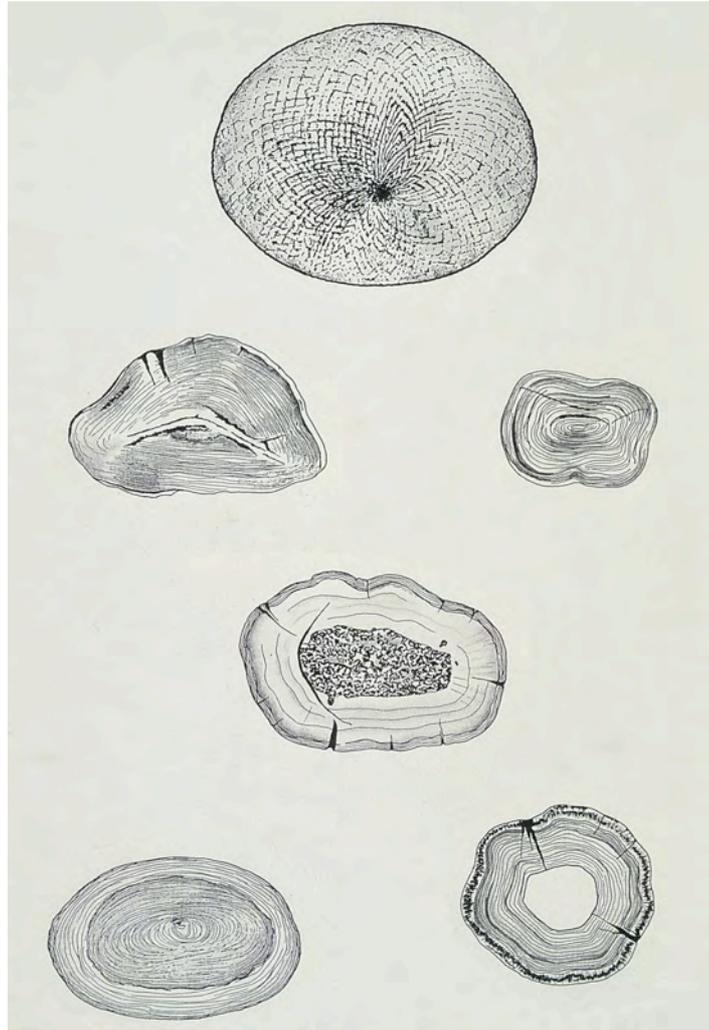


Figure 13.4 – Transversal section of terrestrial and marine Mammals: elephant, hippopotamus, wart-hog, walrus, narwhal, and sperm whale.

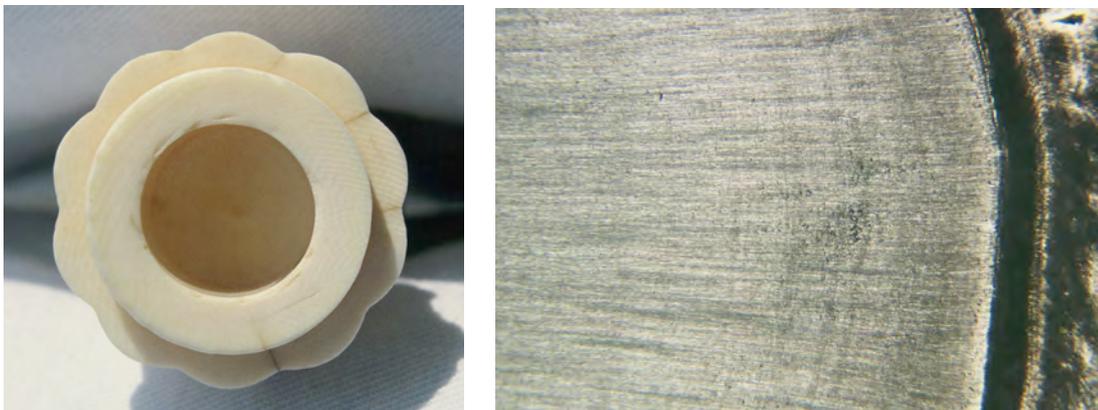


Figure 13.5 – Ivory artefact whit radial lines (left) and crossing section of ivory (right).

Each type of ivory has a different aspect, structural characteristics that vary, and a transverse section which is very characteristic. All types of ivory, as well the bone, have a chemical composition, where the most important part of mineral salts is combined with an organic substance, in varying percentages depending on many factors. The inorganic part is mainly composed of calcium and magnesium phosphates, and is however attributable to the formula of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, since the unit cell consists of two molecules. The organic matrix consists of collagen fibers and protein complexes.

Ivory is easy to work for its limited hardness. In fact, the dentine is softer than bone, because what makes the teeth resistant are enamel and cement, which in the processing of artifacts are usually removed. For its protein nature, ivory is anisotropic, has a medium degree of porosity, and a degree of hygroscopicity which can vary depending on the animal it comes from and the processing method used for the production of the artefact.

13.1.4 Coral

Corals are marine animals included in the Cnidaria group. Considered for a long time a marine plant, instead coral is a colony of tiny polyps that build a protection of limestone composition that takes complex forms. The coral is, therefore, hard exoskeleton due to a calcareous secretion of several species of tiny polyps. Depending on the species, these marine animals are able to build reef formations of different shape and color (Figure 13.6).

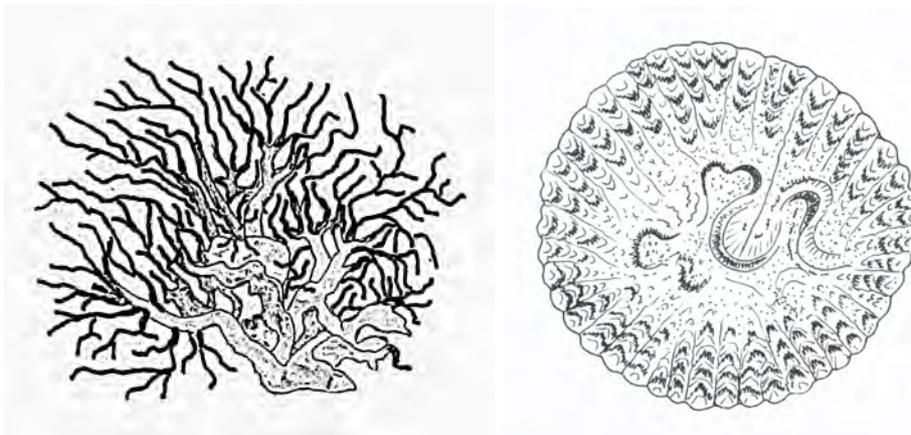


Figure 13.6 – Form and transversal section of coral.

Corals have form of a tree, varying in color from dark red to pink to white. They consist of two distinct parts: an inner harder and compact that acts as a support, and an external, more tender (leather hardness), where the polyps are. This sort of outer shell, called ‘cenosarco’,

through a system of small channels, connects together all the individuals composing the colony. The inside of the branches, used for the production of manufactured goods, is called ‘ceppo’ and is made mostly of calcium carbonate (CaCO_3) in the form of calcite produced by the secretion of polyps.

The chemical composition of the ‘ceppo’ also includes minor amounts of magnesium carbonate, and variable amounts of calcium sulphate, iron oxide, and phosphates. All the differences found by the analyses published in the literature are due to different species of corals examined. Part of the organic component (around 1.35%) is not yet well determined, but it was associated with the presence of pigments. The structure consists of needle-like particles, radially arranged in layers perpendicularly to the axis of growth. This particular structure defines the radial transverse section of the coral.

The hardness of the material is variable depending on the species of coral and can be evaluated between the 3rd and 4th degree in the Mohs scale (see paragraph 8.3.1).

The material used for the production or for the coating of artifacts is carefully selected and taken so as to maximize the form of branches and branch points of the coral formations. The coral, regardless of its color, has a mat appearance, but, with a good manufacturing process, it can acquire a considerable luster.

13.1.5 Mother of pearl

The mother of pearl is a material produced by animals that live in the water and that belong to the Mollusca group.

In particular, the mother of pearl is present and is easily visible in some Bivalve Mollusca and some Gasteropoda Mollusca living in freshwater and saltwater. This material is part of a protective structure that we all know as shell, and which shows itself in many shapes and colors (Figure 13.7).

More exactly the shells are formed by the secretion capacity of the epithelium of the mollusk and by the overlapping of the layers of growth. This process is able to form a hard and rigid structure that the mollusk uses for protection. The layers that make up the thickness of a shell show different characteristics. The outer layer, called ‘periostraco’, is the oldest layer of the shell, where the typical colors are located. The innermost layer, in contact with the shellfish, called mother of pearl, is the newest layer of the shell and has a light color with iridescent shine.



Figure 13.7 – Two kinds of mother of pearl with two different colours.

The chemical composition of a shell is given by a high percentage of calcium carbonate (calcite, CaCO_3), which in the inner part is in the form of lamellar crystals of aragonite. Calcium carbonate is connected to a small organic part, formed mostly by ‘conchiolina’ ($\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_{11}$), which is a scleroprotein with a high water content.

The percentages of the three components vary depending on the area of the shell, the type of mollusk and the geographical area of origin. Depending on the characters just mentioned also the hardness varies.

In the past, the mother of pearl was obtained only from the shells of some species of mollusks. Its value is due to a good workability, but especially to a shiny and iridescent appearance, due to the stratified structure (Figure 13.8).

The mother of pearl is also the matter that constitutes the pearls. Also the pearls are of various shape, size and color.

The pearls are formed by the same secretion that forms the mother of pearl, which incorporates any foreign particle that is accidentally introduced into the valves of the shell. In this way the mollusk isolates and makes ineffective the foreign body. Over time, the deposit of secretion becomes increasingly large, with the same characteristics of the mother of pearl. Therefore, the pearls are the product of a reaction implemented by the mollusk as a defense. Of course, the cultivation of pearls involves the introduction of artificial particles within a particular species of mollusks.

The defense mechanism will immediately coat the foreign body, which is extracted from the mollusk when it has reached the desired thickness and then the desired size of the pearl to be produced.



Figure 13.8 – Mosaic tesserae made of shiny and iridescent mother of pearl, and detail of their surface.

13.2 The restoration operations

The principles required to operate on an artifact with cultural value are common to all types of matter, but it should be stated that for this particular type of products made from inorganic materials of organic origin is even more necessary to have an excellent knowledge and use much caution, because of their delicacy. It is well known that if you restore the matter of a work and not working properly, you may worsen the conservation state and even lose information that an ancient artifact may give us. Before developing the restoration project is necessary, therefore, to acquire a set of data that should lead to the complete knowledge of the artifact in question (Table 13.1).

The conservation state, defined by alteration and degradation that affect the appearance of the artifact, can be defined based on previously published specific denominations.

For products made with the above mentioned materials is certainly more difficult to find evidences on the technology of production, which, however, would open a vast and interesting chapter. It should be borne in mind that the production techniques over the centuries have changed, and their study is only now becoming predominant over the restoration project.

A wrong restoration could remove a high percentage of data that can be transmitted from the cultural object. The restoration intervention will be oriented to avoid excessive changes of the properties that characterize the work (Table 13.2).

Table 13.1 – Plan of the preliminary phase of study.

Cognitive investigation	Historical context Material characterization Production technique
Anamnesis of the conservation state	Transformation related to the matter and production technique Transformation related to the life of the work
Diagnostic investigations	Determination of the nature of matter Determination of alteration and degradation
Photographic and graphic documentation, and mapping	
Testing and verification of the tools and products that you intend to use	

Table 13.2 – Plan of the operative phase.

Preservation	Microclimatic characters Thermohygrometric conditions Light radiations Air quality Biodeteriogens
Restoration	Pre-consolidation, consolidation Cleaning Bonding Grouting, integration Protection
Written, graphic and photographic documentation	
Maintenance	

Due to the material of which is made this kind of artifacts, it is important to detect even the slightest trace present on the surface. For this reason, most operations are performed with the aid of the microscope. Tools and products must be used with infinite caution.

As for the products to be used for cleaning, to avoid introducing substances that may alter the original chemical composition, it is preferable to intervene with mechanical methods because the blade of the knife, if used with extreme lightness, is harmless in respect of these delicate materials. It may be possible to act with volatile solutions prepared with different percentages of water, alcohol, and acetone depending on the case to be addressed. The previously tested aliphatic solution, called “3 A”, can not be purchased already made, but it should be prepared with the individual components in different percentages depending on the needs to which to cope.

The same caution is required in the pre-consolidation, the consolidation and bonding

necessary in situations of disruption and breakage of the material. The resins used must be very tough and indispensably reversible with water, alcohol or acetone.

Fillings and integrations are to be avoided. If they are really necessary to give firmness and support for the piece, they must be obtained with the help of a material that is softer than the material forming the article and with a proper tonal gradation to the case. To do this you can prepare the pastes to color, or pre-colored, that are placed in contact with the original matter of the work by means of a primer. In addition, the color must have a tone that is not invasive, and does not quickly darken.

Very important is also the storage environment of the work that must meet certain parameters related to temperature, humidity and light. The literature provides many details about it, but it is better to specify that, in relation to humidity, sometimes even inadequate values can be considered suitable if they maintain the continuity already gained from the material of the artifact.

13.3 Cases of study

13.3.1 Recovery and restoration of an archaeological artifact

In an archaeological site is not usual to find ancient artifacts made with the materials discussed in this chapter. As already specified in the preceding paragraph, the state of conservation of artifacts made of bone and ivory, found in soil, is different from that of objects made of coral and mother of pearl. Surely the discovery of artifacts in coral and mother of pearl is rarer and in any case limited to the decorated surfaces of artifacts made with other materials. In addition to the small size, the difficulty of the discovery is related to the difficult recognition of these materials. As for the artifacts of bone and ivory, the identification is definitely easier, but the material aspect is very different and dependent on the type of soil in which the artifact remained.

THE IVORY FROM PHOINIKE

The ivory artifact was found September 24, 2003, in the grave 41 (S5 Lower Town, US192) at the necropolis of the Hellenistic-Roman town of Phoinike in southern Albania.

The Italian Archaeological Mission directed by prof. Sandro De Maria (University of Bologna) was working in this archaeological site since 2000. After the first surveys made

by Luigi Maria Ugolini between 1926-1927, the research has been resumed, either in the urban area, either in the territory belonging to the town.

The necropolis, excavated and studied by prof. Giuseppe Lepore, is at the base of the southern slope of the hill on which stands the ancient town of Phoinike. In this area there is a succession of burials ranging from the Hellenistic period (second half of the fourth century BC.) to the imperial Roman age (the most recent attestations concern the beginning of the third century AD).

The tomb 41, or 'burial of the surgeon', was obtained into the space between two tombs of the Hellenistic period and it contained two separate depositions: a double inhumation, attributable to a 40 year old man and a woman of 30, and a incineration attributable to a man of about 35 years. The dating of the finding seems to lie in the Flavian-Trajanic age (late first century to early II century AD) and states an interesting case of coexistence of different rituals in the middle imperial age (Figure 13.9).

The two individuals in the inhumation burial had been deposited in a unique wooden box and with the head northward. Abundant and of great interest was the outfit that had been laid at the feet of the burial: at south-west there were toilet items relevant to the woman, and in any case referring to the female world, among which a gilded bronze pin with a decorative element made of mother of pearl, while to the south-west there were items related to the man, that included an interesting set of surgical instruments from which it derived the name of the burial.

It is precisely in the context of the surgeon burial, that the ivory under study was found. In a predominantly calcareous soil, light in color but with variable appearance due to the presence of residues of the burial, iron tools were identified along with a stone 'tabula scriptoria' with its stylus in bone, and in particular a iron pincer and two bronze scalpels which had to be placed within a container. Of the container, with cylindrical shape, has been found only the precious cover made of ivory material. It was presumably obtained from a section of African elephant tusk. Due to the size of the diameter (about 8 cm) and given the evident cleavage of the material (the reticular structure and radial typical of the elephant tooth is more resistant to cleavage), it is also possible to envisage the use of ivory from the canines of hippopotamus, very much in use at that time because of the already difficult availability of elephant ivory, in any case wanted for his more evident whiteness.



Figure 13.9 – Tomb n. 41 with multiple burial and detail of where the ivory was found.

The ivory of Phoinike, definable as a lid for pyx, has been restored on the occasion of classes during the 2005-2006 edition of the Master Degree course on “Science for the conservation-restoration of cultural heritage” organized by Dr. Rocco Mazzeo, Professor of Chemistry for Cultural Heritage at TE.CO.RE., University of Bologna, Ravenna Campus. The restoration was carried out as a practical example from 19 to 23 June 2006.

The finding, with shape of a lid, was received still incorporated into the soil of excavation (Figure 13.10, left). By a first visual analysis of the find, one could see that the material had a color that was altered by staying in a soil rich in elements relevant to a inhumation burial and it appeared significantly flaked.

The first intervention was to perform a cleaning of the surface of ivory, to remove the excavation soil and to allow an adequate pre-consolidation with acrylic resin, in order to avoid the loss of the flaking parts. Despite this and because of disconnections, many flaking parts did not reach a sufficient adhesion, so it was necessary to apply, with glue, gauze perfectly adherent to the entire surface (Figure 13.10, right).

Applied on the visible side of the artifact, it has ensured the complete fixation of all flaking parts and allowed to operate in the lower side of the artifact without any problems. The removal of the soil was performed with a scalpel. Then, punctual micro-washes were carried out with the solution “3A” (acetone, alcohol and water in equal parts), immediately followed by a fast drying.



Figure 13.10 – The ivory artefact in the archaeological soil (left), and gauze adherent to the surface of the ivory artifact (right).

Consolidations and adhesions were made with acrylic resin to ensure good reversibility. The subsequent application of gauze, on the cured side of the artefact, has allowed the removal of the previously applied gauze and the execution of the same cleaning operations: micro-washing, drying, consolidation and adhesion even on that side of the artefact.

Each operation was carried out with extreme precision and speed in particular, in order not to lose sight of the integrity of the artefact. The small flaked pieces looked all equal, but at the end of the work a decoration formed by ovals appeared on the surface of the ivory, which had been realized as bas-relief (Figure 13.11, left). A graphic representation could evidence the important ornament, which was dug on an abundant portion of material (Figure 13.11, right).

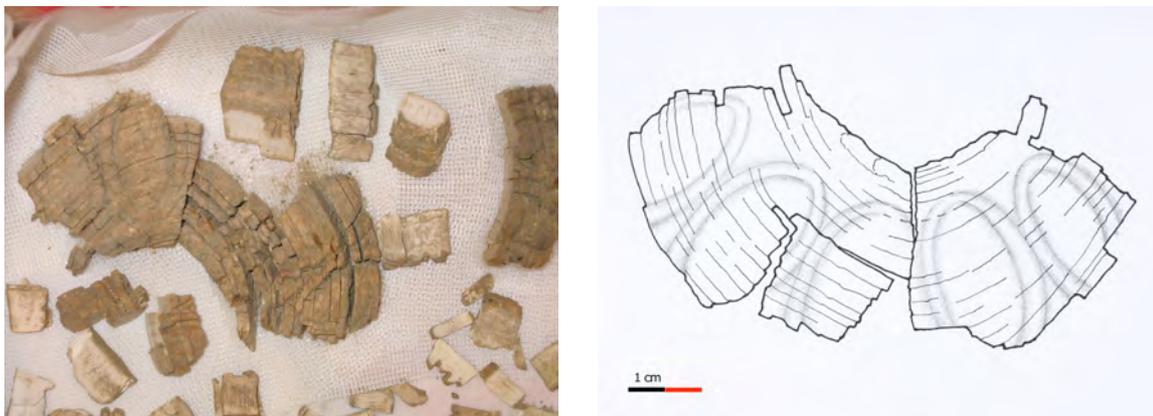


Figure 13.11 – Ivory fragments before gluing (left) and drawing of the ivory artefact (right).

13.3.2 Interventions of structural reconstruction

The artefacts coming from collections, if well preserved, have a more realistic and recognizable appearance. In the exhibition ambit, it can happen that you must intervene on the shape of an artefact to ensure a linkage between the detached parts, to compensate the loss of supports, or to reconstruct missing parts in order to deliver its correct reading to the artwork.

THE 'DITTICO DI MURANO'

In the hall of the ivory material of the National Museum of Ravenna, is exposed the so-called 'Dittico di Murano' (inv. 1002), which is actually a cover of gospels, dating to the sixth century. It was restored in the Restoration Laboratories of the Soprintendenza per i Beni Architettonici e Paesaggistici of Ravenna in November 1989 (Figure 13.12).

The artifact, executed in African elephant ivory, is composed of five panels of considerable thickness, which were originally held together through a series of tenon and mortise joints. During its lifetime it suffered damage and structural changes until it has lost its original unit. Due to the loss of the functions of connecting of the various panels, it had been placed, in an unknown time, on a wooden board to which it was glued through a thick sheet of paper that should probably serve as a cushion or protection against the wood.



Figure 13.12 – 'Dittico di Murano' before and after restoration, which includes its structural reconstruction.

After analysis of the conservation state, a restoration work was planned, which is extremely respectful of the characteristics of the different parts to be joined and tolerant of the physical characteristics of flexibility caused by climatic changes. After the total reclamation of carved surfaces, it was decided to free the artwork from foreign materials, and in particular to study a system of rejoining that made possible all movements to which the ivory could be subjected.

The disassembly of the different parts of the 'dittico' has allowed us to observe and identify the original conjunctions of the structure, discriminating the holes made during repairs to which the artefact had been subjected over time. The original system foresaw that the central plate, provided with tenons on all four sides, get stuck between the four external plates. In addition, the original method of joining was concealing the mechanisms linking the ivory sheets, leaving undisturbed the iconographic program represented.

All holes drilled for the subsequent rejoinings, however, were remarkably clear, because they interrupted the serial design of the frames, and interfered with the background of the representations.

After careful study of the ancient functionalities of the covering, it has been put in place a system of assembly that even satisfied the exhibition requirements. The reconstitution of the unit of the artefact was obtained by respecting the joints of 'tongue' type, characteristic of the original mounting system, without introducing any attachment point between the different panels. It was therefore necessary to introduce an element that can create a support without interfering with the artifact in order to ensure a clear 'reading' of the artwork (Figure 13.13). For this reason we have chosen a Plexiglas support. The favorable conditions, offered by this synthetic material, are transparency and a low coefficient of expansion.

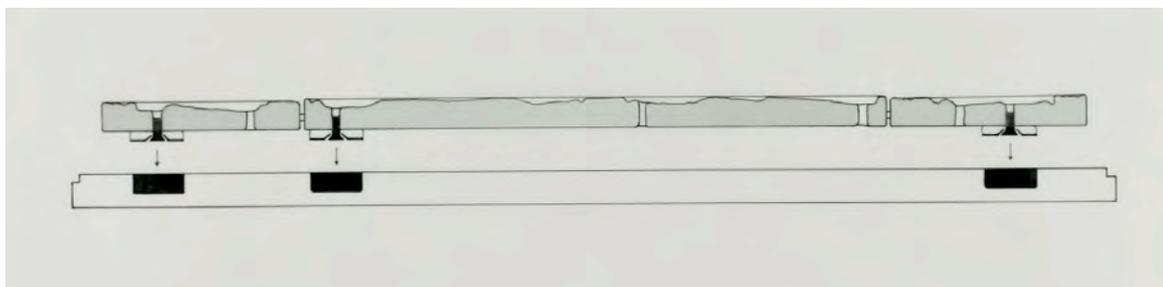


Figure 13.13 – Drawing of the complete longitudinal section of the 'Dittico di Murano' and its support.

The joining of artifact and support was given to the action of magnets that have the advantage of providing a good bond without creating constraints (Figure 13.14). The magnets inserted into the holder are six. They exert attraction on correspondent washers, which are isolated from ivory through felt pads, and are fixed by flat-head screws carefully coated with Teflon. This system has enabled reassembly of the artefact with movable joints, properly insulated and fully reversible (Figure 13.15).



Figure 13.14 – Fixing system for the ‘Dittico di Murano’.

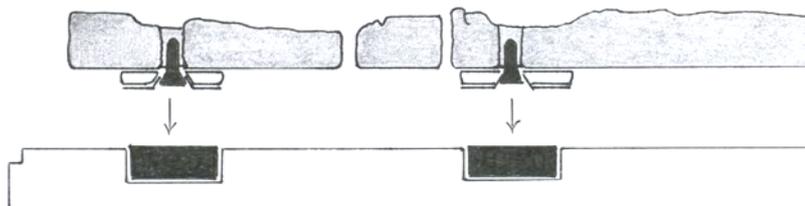


Figura 13.15 – Detail (over) and drawing (below) of the working system of the magnet.

THE PASTORAL OF THE NATIONAL MUSEUM OF RAVENNA

Exhibited in the hall of the ivory material of the National Museum of Ravenna, the pastoral concerned (inv. 1115) is an artifact that consists of a crook in ivory, of the thirteenth century, and a polychrome stick of the fifteenth century, divided into independent sections according to a typology suitable for traveling (Figure 13.16).

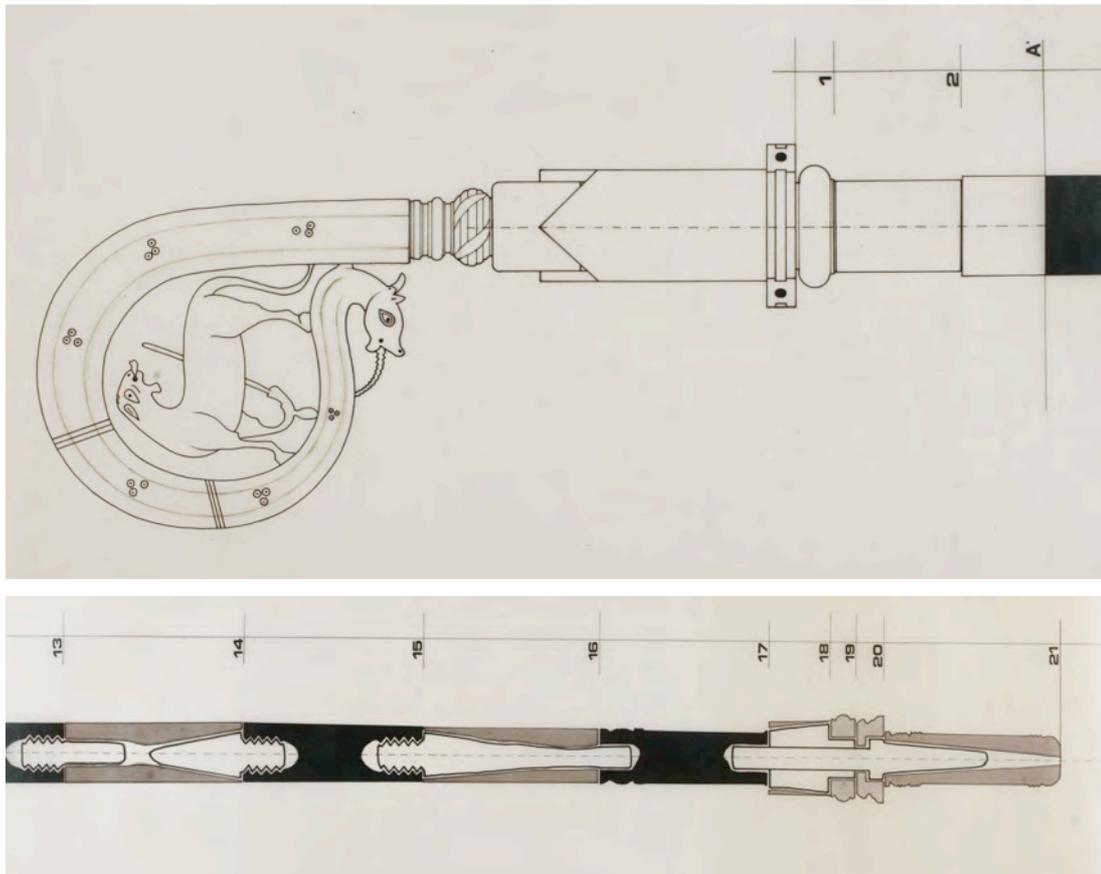


Figure 13.16 – Drawing of the pastoral in the top (crook) and low part with joint system.

The artifact was restored in April 1990 in the Restoration Laboratories of the Soprintendenza of Ravenna. Before the conservative intervention, the pastoral showed significant structural damage due to loss of material and especially the loss of his duties as disassembly and reassembly.

The stick, 165 cm long, is composed of 21 elements of different length and sloping downward. The strong chromatic effect of the artefact is caused by the different materials used for the realization. The bi-chromatic alternation of ebony wood and bone is made precious with a floral decoration painted in red, black and gold (Figure 13.17).



Figure 13.17 – Detail of the pastoral with decorated bone and ebony,
and microscopic image of pigments on bone.

The possibility of disassembly was provided by fixed conjunctions, and by eight screw-junctions that were obtained between the ebony and the beech, which constitutes the inner core of the elements in bone.

In addition to degradation due to wear relating to its use, the object showed remarkable tampering due to several repairs over time. The materials inserted to recreate the union of different parts were nails and metallic wires, bonds with irreversible polyester resin, and the insertion of wedges of light wood. All these insertions, in addition to providing a fixed but shaky union, were the major cause of the significant structural damages present (Figure 13.18).

A careful graphic documentation was then necessary for a thorough study and for the elaboration of the executive project. The resolute project had to return the pastoral to its original function, with the possibility of disassembly and reassembly.

So, it was decided the complete disassembly of the pastoral in all its parts and especially to eliminate all foreign materials (Figure 13.19). After having predisposed an accurate protection, that would have allowed handling the original parts, the work of disassembly began.



Figure 13.18 – Detail of old fixing connections among the elements.

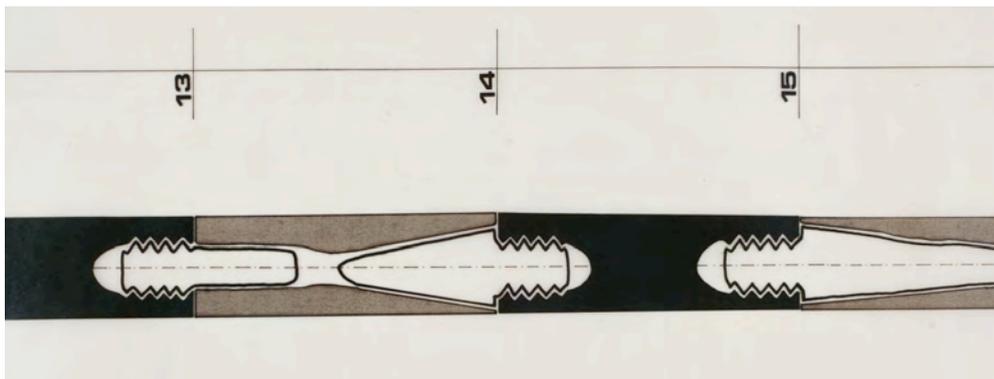


Figure 13.19 – Drawing of the original joining system among the elements.

The bold intervention of structural reconstruction has provided the remake of the original assemblage by means of screw-type mortises and tenons. In the parts in ebony, the thread of the mortises was reset, and was rebuilt the internal structure of bone parts with beech wood. Each interior remake in beech was provided with a screw-threaded tenon that is adapted to the threaded mortise of the ebony parts. All work was carried out with the help of a skilled turner who reconstructed the screwing originally planned, so that each side could match perfectly (Figure 13.20). The return of a solid structure made it possible to proceed with the normal stages of restoration, which has returned to the artifact its original identity.

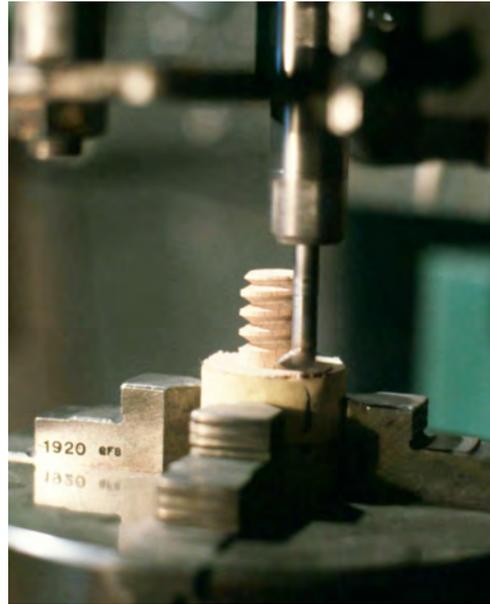


Figure 13.20 – Turning of the wood elements for joining system.

13.3.3 Analysis of a stain on ivory artefact

Among the most important pieces kept in the National Archaeological Museum in Damascus, there is a ivory head, dated 13th century B.C., from Ugarit (Syria), with a metal crown on the forehead. Since some time, a light blue coloured stain is growing above the right eye, just few millimetres under the crown. So, the light blue stain was analyzed by energy dispersive XRF (30 KV, 20 μ A, 60 seconds), as it is shown in Figure 13.21.

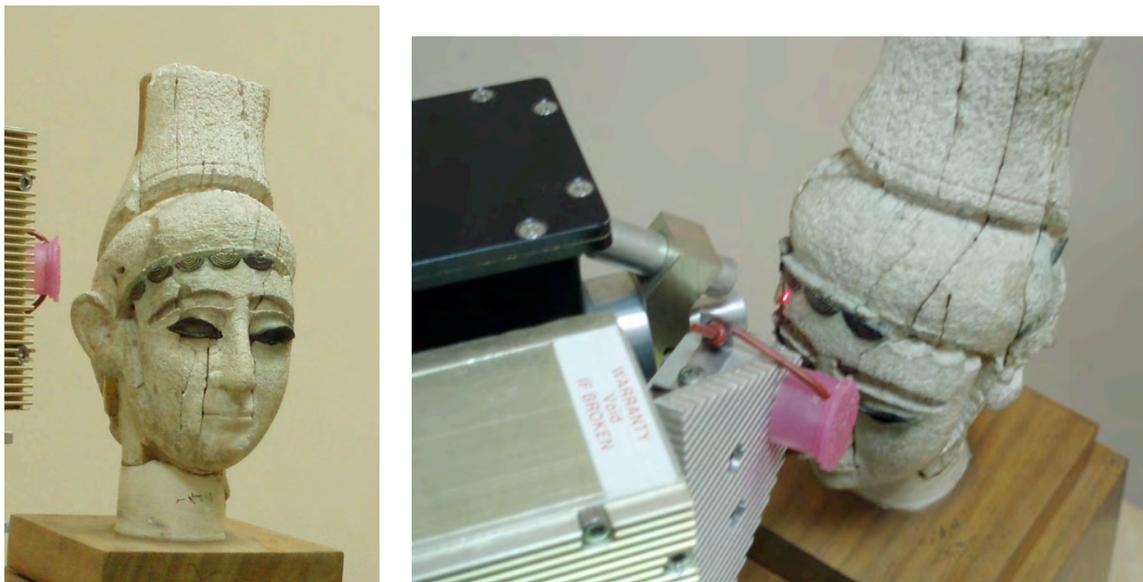


Figure 13.21 – XRF analysis of a light blue stain on the forehead of a ivory head.

Three different measurements were done: two in light blue area and one on the crown metal. Results are shown in Table 13.3. As expected, the ivory is constituted by calcium, with unusual concentrations of iron and copper, while the other detected elements are negligible.

The metallic crown is mainly made of copper, with minor amounts of gold and iron, and traces of calcium, arsenic, sulphur and silver. This metal can be recognized as ‘shakudo’, a Japanese term which indicates an alloy of copper with gold (around 4-5%).

Table 13.3 – Chemical composition of the ivory head (relative intensities).

Element	Light blue stain		Metallic crown
	Position 1	Position 2	
Ca	5458	5056	252
Fe	694	467	1425
Cu	419	659	16106
P	43	78	---
K	75	67	---
Ti	59	55	---
S	36	51	70
Mn	39	41	---
Au (L_{α})	---	---	1120
As	---	---	108
Ag	---	---	19

According to these results, the anomalous contents of iron and copper in the ivory are evidently due to diffusion of iron and copper coming from the crown. In addition, if the composition of the crown is taken into account, it can be noted that the diffusion of iron is proportionally greater than that of copper.

In conclusion, the growth of the light blue stain on the ivory head is due to the diffusion of iron and copper from the crown, favoured by the fibrous microstructure of the ivory. The stain appeared and grew after a cleaning treatment, carried out just one or two years ago. So, probably it is the consequence of the use of not suitable chemical reagents and/or a not well washing at the end of the treatment.

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14 – ANALYTICAL TECHNIQUES

14.1 General information

14.1.1 What analytical techniques are

An analytical technique is a method that is used to determine the value of a certain characteristic of the material, for example the amount of a chemical compound or the concentration of chemical elements. There is a wide variety of techniques used for analysis, from a simple analytical balance to very advanced techniques using highly specialized instrumentations. As an example, the most common techniques used in analytical chemistry are listed in Figure 14.1.

The analytical techniques are characterized by their invasiveness, type of information supplied, physical state of the sample, being portable or not, resolution, how much sample it needs, expression of the result, what materials can be analyzed, costs of instrumentation and analysis.

The contribution given by analytical investigation to the knowledge of the cultural heritage can be related to:

- technological information,
- provenance studies,
- conservation and restoration,
- dating or authentication of a finding.

Some examples have been shown in the previous chapters.

14.1.2 Invasive and not invasive techniques

For conservation and restoration activities, it is very important to know when it is necessary to take a sample and to bring it into the analytical laboratory or not. In addition, when a sample is needed, it is important to know if it will be destroyed or not, and in which amount.

As a consequence, the analytical techniques can be classified into:

- *destructive*, when the sample or most part of it is destroyed during the analysis: optical microscopy with transmitted light (for the observation of thin sections),

wavelength dispersion X-ray fluorescence (WDS-XRF), X-ray diffractometry (XRD), ionic chromatography;

- *micro destructive*, when only few milligrams of sample are destroyed: thermo-differential and thermo-gravimetric analyses (TGA-DTA);

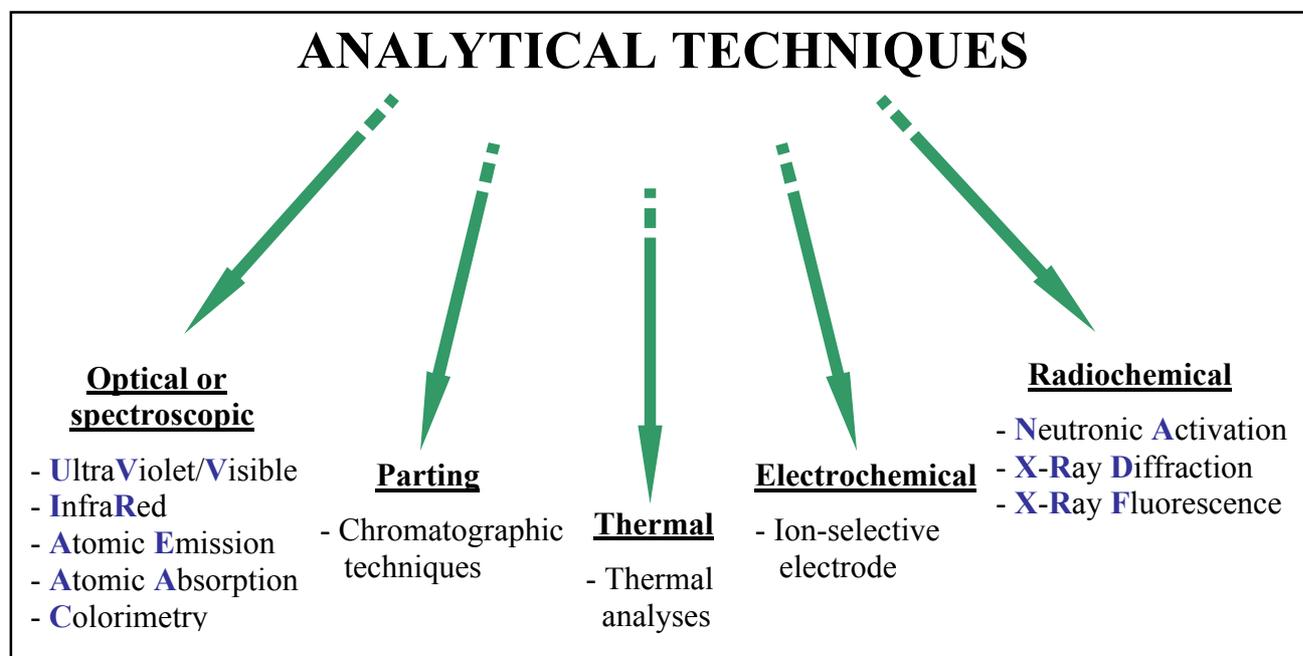


Figure 14.1 – List of the most common techniques for analytical chemistry.

- *invasive but not destructive*, when they need a sample that will not be destroyed: scanning electronic microscopy with energy dispersion microprobe (SEM-EDS), infrared spectroscopy (IR), ultraviolet/visible spectroscopy (UV/Vis), optical microscopy in reflected light (stereomicroscopy);
- *not invasive*, when there is not the need of a sample and the analyses can be done directly on the artwork: colorimetry, energy dispersion X-ray fluorescence (EDS-XRF), Raman spectroscopy.

In addition we can distinguish:

- ♦ qualitative analyses = only identification of chemical elements or minerals or other,
- ♦ quantitative analyses = quantification (% , mg/l, etc.) of the detected chemical elements, minerals, and so on,
- ♦ semi-quantitative analyses = only an approximate evaluation of the detected chemical elements, minerals, etcetera.

The needs of each technique with reference to the preparation and amount of sample to be

analyzed will be outlined in the subsequent specific paragraphs.

Most of the analyses are performed in scientific laboratories where a precise and/or heavy analytical apparatus can be appropriately located and set up. These equipments usually need a very stable support, because they include very delicate parts. In addition, sometimes it is necessary to cool them by water circulation, or they need to work under vacuum, and so on. Therefore, in most cases it is necessary to take samples from the artwork, or from the monument, and to analyze them in laboratory. Of course, it deals with invasive and often destructive analytical techniques.

When it is not possible to take samples, the analyses cannot be performed, unless it is a ‘transportable’ instrumentation, and it is possible to bring it in the place where the object to be analysed is. This is possible when the analytical instrument is not too much heavy and/or bulky, and it does not need any special plant, other than a source of electricity. Usually it deals with non invasive analytical techniques.

Among the transportable instrumentations, a special category deserves to be highlighted, i.e. the ‘portable’ instruments. These are very interesting and useful, because they are light enough to be held in hand and easily approached to the object to be investigated. The energy source of these instruments generally is a battery, so that their time of operation is conditioned by the duration of the battery. Therefore, it is opportune to have a reserve battery to be used while charging the other.

Not many analytical techniques permit to perform ‘in situ’ analyses, but in recent years their number is growing steadily, even though some of them are not so precise as the correspondent laboratory instrumentations.

14.1.3 Definition of chemical analysis

Chemical analysis is the identification, in case determination, of the chemical elements present in a material, without considering how they are combined (crystalline phases, organic substance, etc.). As said before, also chemical analysis can be:

- ◆ qualitative = only identification of chemical elements,
- ◆ quantitative = quantification of the detected chemical elements,
- ◆ semi-quantitative = only a very approximate quantitative evaluation of the detected chemical elements.

In a chemical quantitative analysis, the detected elements can be grouped on the basis of

their concentration:

- main elements >1%,
- minor elements 0.1 - 1%,
- trace elements < 0.1 %.

The results of a chemical quantitative analysis are generally expressed in form of percentage of the oxides of the different elements, with the addition of the 'loss on ignition' (LOI), which includes all the volatile component under 1000 °C, mainly water and CO₂.

The preparation of a sample for chemical analysis must be particularly careful. In particular we have to pay great attention to the grinding level and the precision of the weighing. Of course no pollution of the specimen must always be assured.

Some techniques for chemical analyses require the specimen in solution, so that it is necessary to know how to dissolve the sample.

14.1.4 Planning the sampling

The sampling (number of samples, collecting points, characteristics of the samples, etc.) have to be carried out according to the aim of the analytical study.

The sampling must be representative, so that the number of samples to collect is closely influenced by the different situations, for example:

- types of materials constituent the artifact or the archaeological or architectonic structure,
- visible deterioration phenomena to investigate,
- extension of the archaeological-architectonic structure to study.

The sampling must take into account the conservation requirements of the artifact/monument or of the archaeological structure.

The sampling must be carried out taking care to avoid being too invasive and producing aesthetic damages. Only the minimal amount of material should be taken, according to the kind of analytical program of investigation.

Sometimes scarce availability of money and/or time can reduce the number of samples and then the sampling can be little representative.

The documentation of the sampling is fundamental. For this purpose is indispensable to give a code to each sample and to describe its characteristics and the collecting point. Wide photographic documentation illustrating the collecting area of each sample is very useful.

In addition the collecting points have to be indicated on a map or a photo. Sometimes the location of the sample can be simply indicated by a free-hand sketch.

According to the consistence and the structure of the material, the samples can be fragments or powders, and different appropriate tools and sampling techniques can be required: chisels of different dimensions, scalpels, drill for coring, brushes (for powdering material). Of course a fragment can be composed of different parts (as in case of plasters, glazed ceramics, mosaics) and each part will be analyzed separately.

The sampling should be carried out by, or in presence of, the professional who will analyze the samples. Anyway, only a perfect understanding with the scientist conservator and/or the restorer can bring to good solutions for all the situations.

The samples will be kept in plastic containers (transparent or opaque) of appropriate size. On each container the identification code of the sample should be written by indelible marking pen.

Analytical methodologies, typical of the exact sciences (physics, chemistry, etc.), applied to the study of ancient materials can provide precise information about the provenance of the raw materials, the production technologies, dating, the identification of the deterioration products and of the deterioration mechanisms (diagnostic). Of course the knowledge of the ancient materials and of their deterioration processes are fundamental support for a correct conservation intervention.

Before starting the sampling, it is necessary to know and/or to do several things, according to the following list:

- to define as well as possible the problem linked to the conservation intervention,
- to have an idea of the composition of the artefact,
- to define the state of conservation: alteration and degradation types,
- to individuate the analyses to perform at a first stage of the study,
- to decide if only non invasive analyses can be made or not,
- to define the type and the number of samples which seem necessary,
- to define the exact points for non invasive analyses,
- to prepare all is necessary to collect samples for destructive analyses; the sampling must be carried out with the more suitable instruments in order to have the necessary amount of sample with the minimum invasiveness,
- to give a code to each sample; the code should individuate both the single sample

and the group to which it pertains,

- to prepare the instruments for documenting the sampling operations,
- to prepare the containers for the samples collected.

Of course, the practical realization of these points depends on the type of artefact under observation and the type of material of which is made.

14.2 Optical microscopy

Optical microscopes can be subdivided in reflected light microscopes and transmitted light microscopes. In the reflected light microscope (stereo-microscope) the image is obtained through the light reflected by the surface of the specimen and enlarged by means of lens (objectives and oculars). In the transmitted light microscope (mineralogical microscope) the light passes through the sample, which was made transparent through an opportune reduction of its thickness.

14.2.1 Stereomicroscopy

Reflected optical microscopy is useful for detecting the structure of the sample (Figure 14.2) and for identifying the deterioration forms. In addition, by means of a stereo microscope it is possible a photographic documentation of the sample. This last operation is very important because the other analytical methodologies performed for characterizing the samples are generally micro-destructive. A complete photographic documentation allows us to preserve the memory of the sample.

Reflected optical microscopy is the first analytical technique that we have to carry out for the characterization of materials (stone, mortars, ceramics, glass, etc.). The stereo microscope suitably equipped (support, jointed arm, lighting system, etc.) is very useful for observing details of big and composite samples (wall painting fragments, mosaic fragments, pieces of wood artefacts) or whole artefacts (icons, coins, ceramic vases, glass objects etc.). Of course the use of this microscope can be also useful for carrying out in better manner several restoration operations (cleaning, plastering, repainting) on small objects or on details of bigger ones.



Figure 14.2 – Stereo microscope (mod. Olympus SZX9) on the left, and smoothed bedding mortar and foundation mortar observed by stereo microscope (on the right).

To better observe the structure and the components of a sample, it can be useful to prepare a polished section, because in this way all the surface of the sample is simultaneously in focus. Polished sections can be prepared by using increasingly fine abrasives in presence of water, unless there is a risk of loss of soluble compounds; in this case it is necessary to work dry.

14.2.2 Mineralogical microscope

Mineralogical microscope is a transmitted light microscope that uses polarized light and is equipped by accessories useful for observing phenomena due to the birefringence (or double refraction) of minerals (Figure 14.3).

In a mineralogical microscope, from the bottom, can be recognized these main parts:

- lamp,
- first polarizer,
- revolving plate with a central opening in the middle, on which the sample (thin section) is put,
- lenses (objectives) with different magnifications,



Figure 14.3 – Mineralogical microscope with a thin section inserted under the objective.

- second polarizer (analyzer). The vibration direction of the light obtained by the analyzer is rotated of 90° in comparison with the vibration direction of the first polarizer. The second polarizer can be put in the optical system of the microscope or can be taken off, while the first is fixed,
- Amici's lens,
- two ocular lenses,
- connection for camera.

Mineralogical microscope allows the identification of the minerals according to optical characteristics that it is possible to observe in 'thin section' (25-30 micron) under different polarized light conditions.

In order to identify these optical characteristics three different conditions of observation are possible in this particular optical microscope:

- with parallel nicols
- with crossed nicols
- with crossed Nicols in converging light, Amici's lens inserted, maximum brightness and magnification (used only for very specific mineralogical studies).

Each observation condition gives us optical information useful for identifying the minerals present in the thin section of the sample.

In particular by parallel nicols (nicols //):

- **shape** and **size** of the crystals,
- **colour**: the crystals can appear coloured or colourless,
- **pleo-chromatism**: during the rotation of the plate of the microscope some crystals change their colour (pleo-chromatism),
- **cleavage traces**: one or two systems of parallel lines that can be observed in a crystal,
- **relief**: some crystals appear in relief in comparison with others or the matrix.

While by crossed nicols (nicols X):

- **interference colours**: not real colours that appear when we insert in the optical system the second polarizer (analyzer). Each crystal of every mineralogical species present in the thin section shows a new colour (interference colour),
- **extinction**: rotating the plate, the interference colours change from the highest brightness to dark (extinction); direction and type of extinction can be measured,
- **gemination**: presence of set of crystals with the same composition and structure (same mineral) grown according to specific crystallographic rules; you can easily measure the extinction angle, which is typical for a given mineral,
- **pores**: they can be identified because they appear white with parallel nicols, and dark with crossed nicols (even rotating the plate).

By the use of handbooks, in which are reported the optical properties of the minerals, it is possible to recognize those present in the thin section of the sample. In addition several photographic atlas, in which are shown photos of different rocks taken by mineralogical microscope, can be consulted.

By the use of the mineralogical microscope it is also possible to observe the texture of the thin section: if the crystals or granules are in contact with each other, or if they are submerged in a matrix, or bounded by a cement; if the crystals/granules are orientated, if there are microfossils (sedimentary rocks), and so long. On the basis of the mineralogical composition and the texture is possible to classify the rock fragments.

Mortars can be considered artificial sandstones with a framework (aggregate) composed of granules from natural and/or artificial stones bound by a carbonate and/or gypsum cement (ancient and traditional mortars). In modern and contemporary mortars (mortars based on cement) an amorphous-micro crystalline cement composed of different calcium silicate

hydrated and calcium aluminum silicate hydrated can be present in the place of the traditional carbonate/gypsum binder.

By means of the mineralogical microscope it is possible to recognize the shape, the dimension and above all the petrographic characteristics of the aggregate, the composition of the binder, the evaluation of the porosity, the probable presence of reaction borders between the binder and some granules of the aggregate (“cocciopesto”, volcanic granules, etc.) and finally the reconstruction of the ratio binder/aggregate (by volume).

As said before, the observations at the mineralogical microscope need the preparation of the sample in form of ‘thin section’, i.e. a slice of sample with a thickness of 30 microns approximately. A thin section is prepared from a fragment of material through a gradual reduction in thickness to the desired value. The thickness should be uniform, and the two opposite surfaces of the slice perfectly flat and parallel. This is a difficult task, and it is usually carried out in specialized laboratories by means of appropriate machines.

Of course, a so thin slice of sample is not auto-sustaining, so that it is placed on a suitable support and covered with an extremely thin protective glass. Therefore, the preparation of a thin section includes the following steps:

- cut a suitable piece of sample, with the cutting surface oriented in the most suitable direction for the observations to do,
- polishing of the cutting surface as smooth as possible,
- gluing of the polished surface on a sample-holder, which can be constituted of a small rectangular glass plate, about 1 mm thick, 5 cm long and 3 cm wide; the glue is a resin,
- abrasion of the sample parallel to the surface of the glass slice, up to a thickness of about 30 microns,
- coverage of the sample with an extremely thin glass plate.

14.2.3 Observation and interpretation of ceramic thin sections

The examination of thin-sections under polarising microscope allows to observe textural features of the argillaceous matrix (colour, fineness, homogeneity, isotropy, etc.), of the grains and macro-pores larger than 50 microns approximately (shape, size, roundness, preferential orientation, etc.), as well as the identification of the minerals and their abundance, the grain packing and size distribution of crystalline plastic inclusions (temper) contained in the ceramic paste.

All this information can be used to reconstruct the life of the artefact, from the origin to the recovery. In fact, the abundance and mineralogical composition of the a-plastic inclusions can provide information on the technological process used in the artefact production: the paste preparation, the nature of the temper and its possible origin, the surface treatments (smoothing, polishing, application of slip, painting, etc.) and the firing conditions.

The quality of mineral and/or rock fragments (for example magmatic rock fragments), their distribution and amount and other physical properties of the a-plastic inclusions can provide information on the provenance of the artefact, also taking into account the geological data from the presumed area of origin.

At the beginning of the observation, it is important to distinguish the three main components that compose the microstructure of a ceramic paste:

- *Matrix or groundmass*: the fine component of the paste, that derives from the clayey materials (much less than 50 μm in size);
- *Skeleton or framework or temper*: usually it derives from sandy grains originally present in the clay or intentionally added by the potter (>50 μm in size);
- *Voids*: the macro-pores (>50 μm) present in the ceramic paste.

To this purpose, visual comparators are used, which also take into account the dimensions of the grains, so that it is possible to immediately note the fineness of the ceramic paste.

The second step is to observe the features of the *matrix*; you should look at its colour and homogeneity, the presence of argillaceous rock fragments (ARF) and/or iron nodules, an eventual changing distribution of micro-crystalline grains in the matrix.

An important parameter is the isotropic behaviour, because it is indicative of the *firing level*: more isotropic is the matrix, more fired is the ceramic. In fact, during firing the clayey minerals become amorphous and change their appearance. So, an anisotropic matrix indicates a low firing temperature, and vice-versa. The colour of the matrix can be useful to define the *firing atmosphere*: red colour indicates an oxidant atmosphere, while grey or black colour an oxygen-poor atmosphere (reductive). In the first case, the oxygen inside the kiln favours the oxidation of the iron present in the clay; in the second this oxidation does not occur or is incomplete.

Subsequently, the attention has to be devoted to the grain-size of the temper that composes the framework. The conventional size range starts from <63 μm (silt) up to >500 μm (coarse sand). By considering the *distribution of the temper* in this range, two types of

distribution can be distinguished: *serial*, that means all the sizes are represented, or *hiatal*, when there is a gap in the distribution range of the temper.

What does it mean? Usually a serial distribution of the temper is indicative of the use of “natural” raw material. On the contrary, hiatal distribution could indicate a human intervention in the preparation of the clay paste, because the coarse fraction may have been intentionally added by the potter for realising a special product for a specific use. In the last case, it is also important to observe the shape of the grains, more precisely the level of *roundness* of their borders: sharp border usually indicates sand obtained by breaking rocks, while rounded grains are typical of sands resulting from natural processes, for example due to wind or water transportation.

Another important step is to recognize the *mineralogical composition* of the temper. In general, the attention has to be devoted to: quartz (single grain and in crystalline aggregates), K-feldspar, plagioclase, calcite (*micrite* and *sparite*), biotite, muscovite, pyroxene, amphibole, volcanic rock fragments, flint fragments and fossils relicts.

The *macro-pores* are the result of the different steps of the ceramic working process. They can form during shaping due to residual air bubbles, or can be leaved by the burning of organic matter present in the clay or by the decomposition of carbonate grains (such as calcite). By the way, sometimes macro-pores produced by air bubbles can be oriented parallel to the surface, such as argillaceous lamellar particles; it is possible to interpret this information as the use of wheel during the shaping process.

On the surface of some ceramics it is possible to highlight *surface treatments*, when the surface layer shows a different appearance in comparison with the ceramic body (see paragraph 4.5.1).

As regard the coated ceramics, after distinguishing the type of *coating* (clay-type or glassy type), the observer has to describe the presence of one or more coating layers, the microstructure (presence of bubbles, cracks, pigments, not-dissolved crystals, new crystalline phases), the thickness (an average value has to be measured), and finally the extension of the *interface*, that is the interaction zone between paste and glaze.

All this information has importance from a technological point of view. Similar thickness on the two sides of the fragment indicates that the *application* was likely made simultaneously, dipping the artefact into the glaze suspension; on the other hand, different thickness values indicate application in two times, likely by sprinkling or by brush.

The thickness of the interface zone may be related to the number of firings. In fact, glazed ceramics can be single or double fired. The interface zone is very thick (more than 40 μm) in case of single firing, because body and coating interact much with each other. In case of double firing, the interface can be practically invisible, because the paste has reached its stability during the first firing and it interacts little with the glaze during the second firing.

14.3 Spectroscopic techniques

Spectroscopy was originally the study of the interaction between radiation and matter as a function of wavelength (Figure 14.4). Later the concept was greatly expanded to comprise any measurement of a quantity as function of either wavelength or frequency.

Spectrometry is the spectroscopic technique used to assess the concentration or amount of a given species. Spectroscopy/spectrometry is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them.

14.3.1 Measurement of colour

The color of an object depends on the frequencies absorbed by the object itself in the field of radiation perceived by the human eye. The range of frequencies to which our eye is sensitive is from about 400 to about 700 nm, so that this range is called the ‘visible’.

The object that reflects light energy evenly throughout the visible range has a white color. If some energy is absorbed uniformly throughout the range, the color is a shade of gray, becoming black when all the energy is absorbed.

When the reflection (or absorption) of energy is not uniform, the object has a different color depending on the frequencies absorbed more. The graph of variation of the energy absorbed from the surface of an object in the visible range is the ‘color spectrum’ of that object (Figure 14.5, left). The spectrophotometer is the measurement instrument able to record a spectrum.

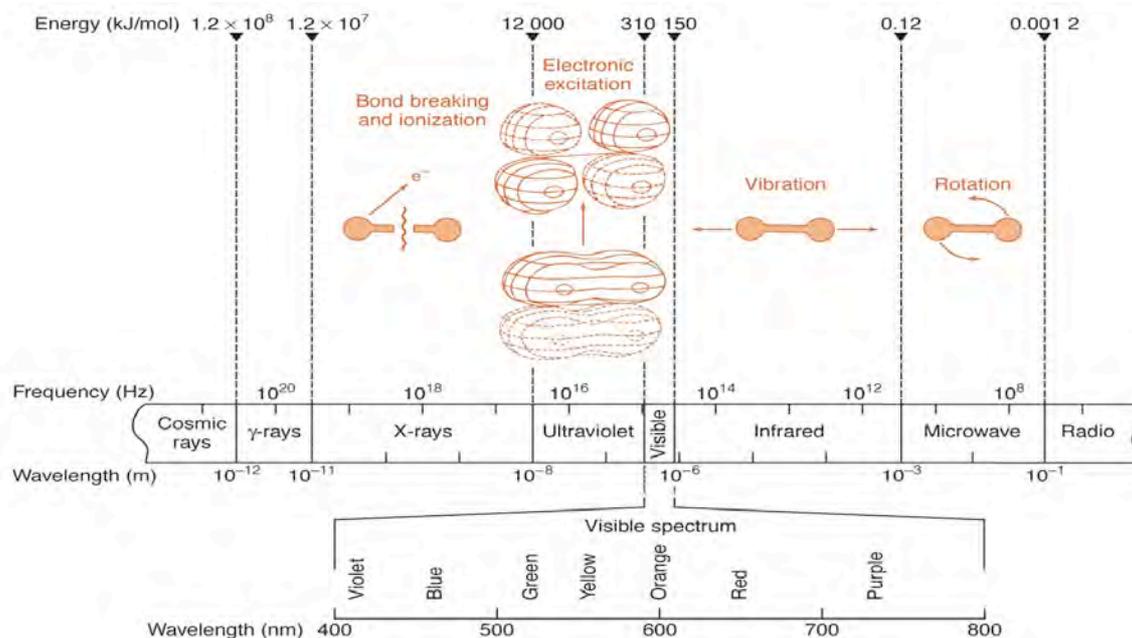


Figure 14.4 – Different interactions between radiation and matter depending on the radiation wavelength.

In 1931, an international commission (CIE = Commission Internationale de l'Éclairage) established that a color could be defined as the sensitivity of the human eye to spectra of three colors: red, green and blue. So, they introduced the possibility to define a color with numbers, rather than adjectives. In this way, each color became defined in the same way by anyone, without subjective margins. In the same year, in fact, it was introduced the so-called 'chromaticity diagram' (Figure 14.5 right), where each color could be detected by two chromaticity values (x, y), while a third value indicated the 'clarity' of the color.

Subsequently, the definition of the color underwent further development, first with the introduction of the Hunter L, a, b system, then elaborated by the already mentioned Committee CIE in 1976. The new color space CIE L, a*, b* (or simply CIELab) differs from the previous system for the method of calculating the three parameters.

CIELab space is defined by three coordinates (Figure 14.6), two on the horizontal axis (a^* , b^*) and the third on the vertical axis (L). The three variables are:

a^* = axis of contrasting colors green ($-a$) and red ($+a$);

b^* = axis of contrasting colors blue ($-b$) and yellow ($+b$);

L = clarity of color, ranging from 0 (black) to 100 (white).

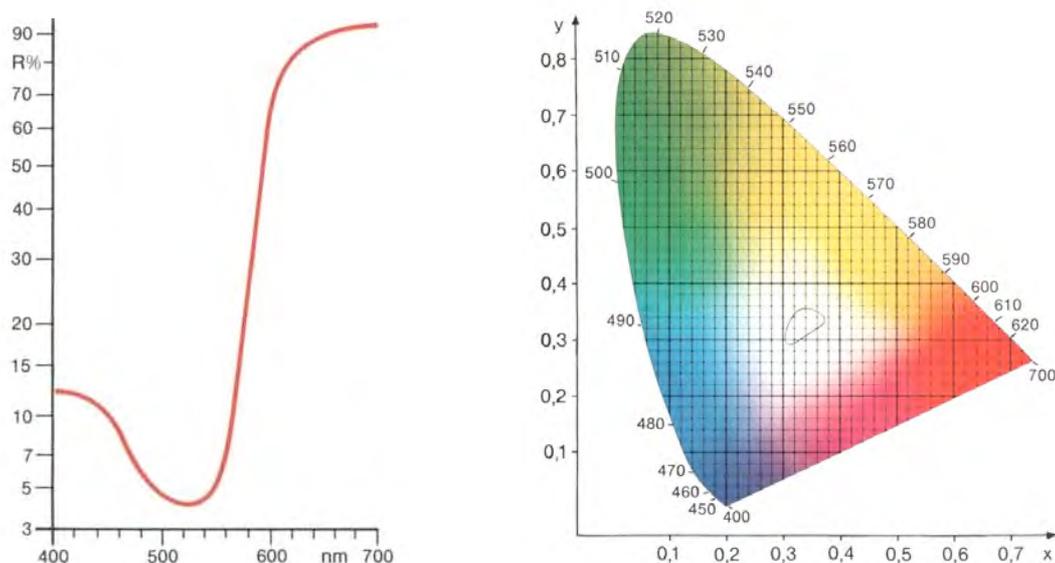


Figure 14.5 – Example of colour spectrum (left) and chromaticity diagram (right).

After 1976, some new parameters have been introduced, for example to define differences in ‘tone’ and ‘saturation’, but the CIELab method is currently the most used, and the colorimeter is the instrument for measuring color according to this system. The instrument illuminates the sample at an angle of 45° , while a detector records, through the interposition of filters, how much red, green, blue and yellow is absorbed by the sample, so as to provide the parameters L, a, b. These data can then be plotted to show the differences between different samples.

The two types of instrumentation (spectrophotometer and colorimeter) on the market for color analysis, therefore, have very different performances. The colorimeter has the advantage of providing numerical data, but the spectrophotometer has the advantage of providing the full spectrum and to allow a better identification of the differences. The choice of an instrument rather than the other depends on the purpose for which it is used. In the field of restoration, the colorimeter can provide sufficient information to assess how an intervention might have altered the characteristics of the material. In addition, the colorimeter is a portable instrument that is well suited to the needs of this sector, and the technique of measurement of color using colorimeter is neither destructive nor invasive.

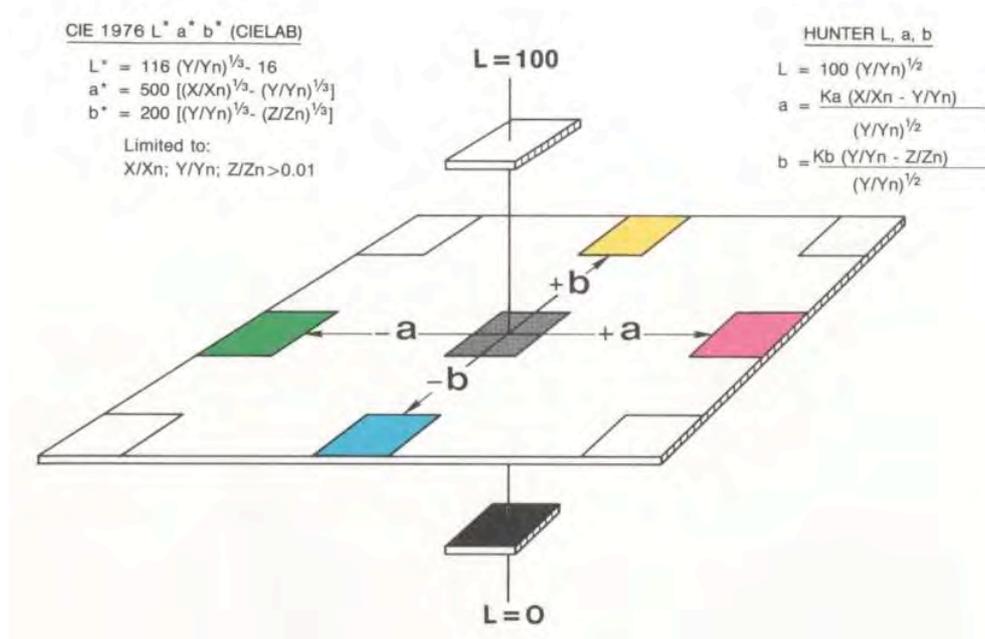


Figure 14.6 – The HunterLab and CIELab space; the different way of calculating the three parameters are indicated.

14.3.2 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary information.

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is the separation of the weak inelastically scattered light from the intense Rayleigh scattered laser light.

Raman spectroscopy is a non destructive analytical technique. Portable instruments also exist, but they are less sensitive than the laboratory instruments. When fitted with a

microscope, the laboratory instrumentation becomes able to perform micro-analyses (micro-Raman spectroscopy).

An example of Raman spectra is shown in Figure 14.7, for organic and inorganic compounds.

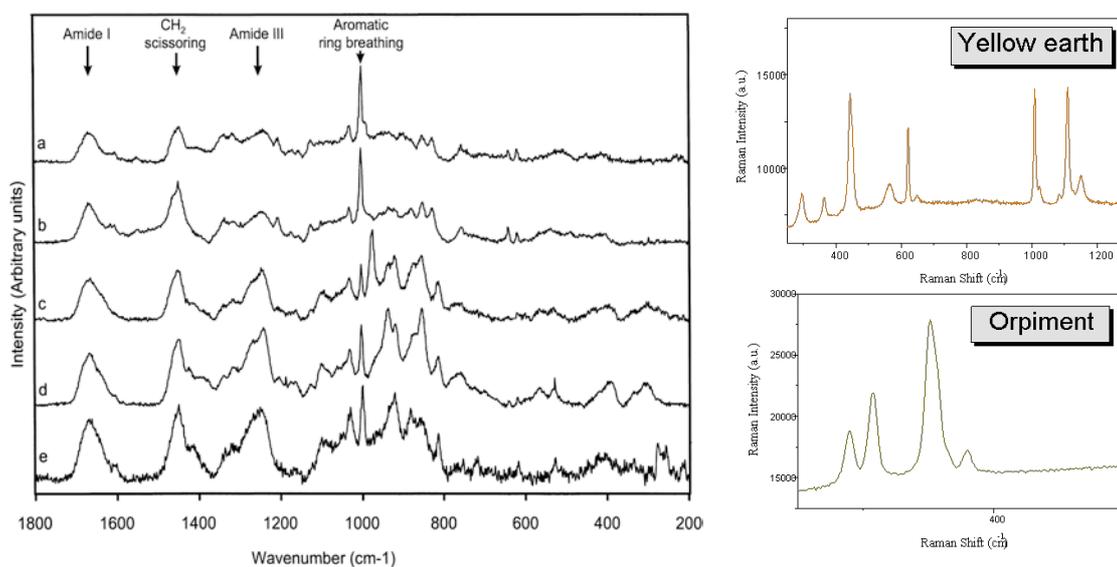


Figure 14.7 - Example of Raman spectra: a) albumine, b) casein, c) gelatine, d) sturgeon glue, e) fish glue (on the left) and some inorganic materials (on the right).

14.3.3 Infrared spectroscopy

Infrared spectroscopy (IR spectroscopy) is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes). As all spectroscopic techniques, it can be used to identify compounds or investigate sample composition. Correlation tables for infrared spectroscopy are tabulated in the literature.

The infrared portion of the electromagnetic spectrum is divided into three regions: the near-, mid-, and far-infrared, so named for their distance from the visible spectrum. The far-infrared, approximately 1000–30 μm , lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately 30–2.5 μm , may be used to study the fundamental vibrations and the associated rotational-vibrational structures. The higher energy near-IR, approximately 2.5–0.8 μm , can excite

overtone or harmonic vibrations. The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. The examination of the transmitted light reveals how much energy was absorbed by the sample at each wavelength. This can be performed by means of a monochromatic beam, which changes in wavelength over time. In such a way, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these characteristics of absorption reveals details about the molecular structure of the sample.

The same spectrum can be obtained by using an instrument based on Fourier transform to measure all wavelengths at once. Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied by means of a monochromator, the IR light is guided towards an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal you may obtain a spectrum identical to that from conventional dispersive infrared spectroscopy.

14.3.4 UV-Vis spectroscopy

Many atoms emit or absorb visible light. Visible absorption spectroscopy is often combined with UV absorption spectroscopy in UV/Vis spectroscopy. Ultraviolet-visible spectroscopy involves the spectroscopy of photons in the UV-visible region. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

UV/Vis spectroscopy is routinely used in the quantitative analysis of solutions of transition metal ions and highly bonded organic compounds.

Solutions of transition metal ions can be coloured (i.e., absorb visible light) because electrons can be excited from one electronic state to another. The colour of these solutions is strongly affected by the presence of other substances. For instance, the colour of a dilute solution of copper sulphate is very light blue, but adding ammonia intensifies the colour and changes the wavelength of maximum absorption.

Organic compounds, especially those with strong bonds, also absorb light in the UV or visible regions of the electromagnetic spectrum. In order to analyze them, they are

dissolved into water (water soluble compounds). For non water soluble compounds, you can use ethanol, because this solvent has very weakly absorption at most wavelengths. Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases its absorption when pH increases from 6 to 13 or when solvent polarity decreases.

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution:

$$A = -\log_{10}(I/I_0) = \epsilon \cdot C \cdot L$$

where:

A = measured absorbance,

I_0 = intensity of the incident light at a given wavelength,

I = transmitted intensity,

L = path length through the solution,

C = concentration of the absorbing species,

ϵ = constant value, known as molar absorption or extinction coefficient, for each species and wavelength, at a particular temperature and pressure; sometimes is defined in terms of natural logarithm instead of the base-10 logarithm.

Thus, for a fixed path length, UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution:

$$C = A/\epsilon \cdot L$$

The instrument used for the analysis is called UV/vis spectrophotometer, whose basic parts are: a light source (often a tungsten filament, 300-2500 nm), a monochromator, a sample holder, and a detector (Figure 14.8).

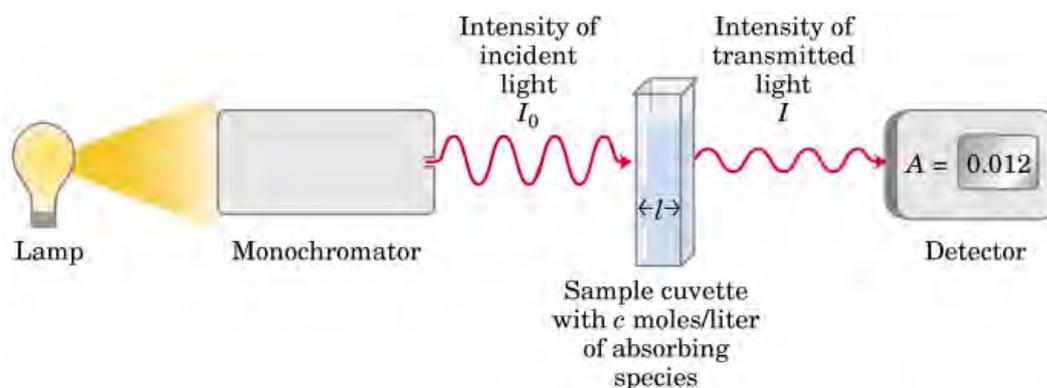


Figure 14.8 – Scheme of the working principle of a UV/Vis spectrophotometer.

The spectrophotometer measures the intensity of light passing through a solution (I), and compares it to the intensity of the incident light (I_0). The ratio I/I_0 is called transmittance (T), and is usually expressed as a percentage; the absorbance (A) is calculated based on the transmittance: $A = -\log(T/100)$.

14.3.5 Emission spectroscopy

Emission spectroscopy is a spectroscopic technique which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state. Each element emits a characteristic set of discrete wavelengths according to its electronic structure, so that the elemental composition of the sample can be determined by recognizing these wavelengths. Emission is the process by which the energy of a photon is released for example by an atom whose electrons make a transition between two electronic energy levels (Figure 14.9). The emitted energy is in the form of a photon.

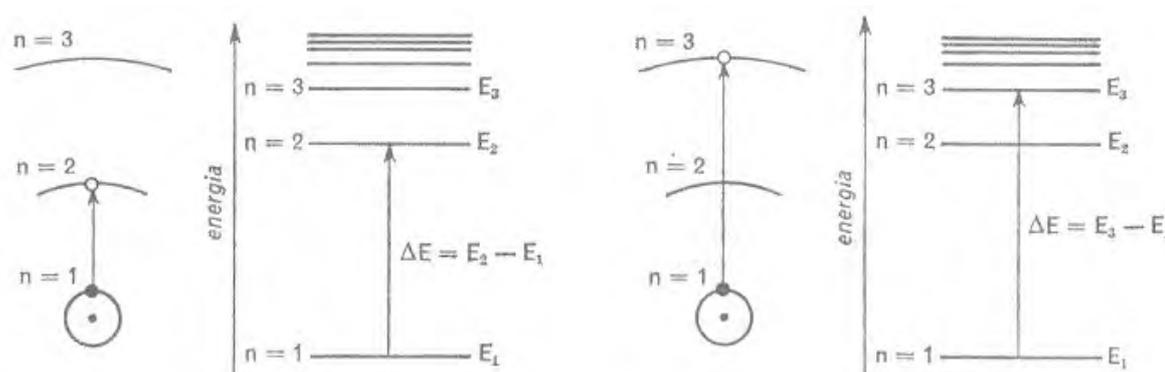


Figure 14.9 – Absorption and emission of radiations.

There are many ways in which atoms can be brought to an excited state, each one of them characterizes a different analytical technique. Interaction with electromagnetic radiation is used in fluorescence spectroscopy, protons or other heavier particles in particle-induced X-ray emission (PIXE) and electrons or X-ray photons in energy-dispersive X-ray spectroscopy (EDS) or X-ray fluorescence (XRF). The simplest method is to heat the sample to a high temperature, after which the excitations are produced by collisions between the sample atoms.

Emission spectroscopy, which developed in the late 19th century, is often referred to as optical emission spectroscopy (OES), due to the nature of the emitted light.

14.3.6 ICP-AES

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is a spectral method used to determine very precisely the elemental composition of samples, and to quantify the concentration of each element.

The inductively coupled plasma (ICP) is a type of plasma in which the energy is supplied by electrical currents which are produced by electromagnetic induction. Plasma temperatures can range between 6,000 K and 10,000 K, and are comparable to those of the surface of the sun.

ICP-AES uses high-energy plasma from an inert gas, like argon, to burn very quickly the analytes. ICP-AES works through the emission of photons from analytes that are brought to an excited state by the use of high-energy plasma. The colour that is emitted is indicative of the elements present, and the intensity of the spectral signal is indicative of their concentration.

The plasma source is induced when passing argon gas through an alternating electric field that is created by an inductively coupled coil. When the analyte is excited the electrons try to dissipate the induced energy moving to a ground state of lower energy. Doing so, they emit the excess energy in form of light, whose wavelength depends on the energy gap between the excited energy level and the ground state. This is specific to each element according to the number of electrons that the element has, and the orbital that is filled by the electrons.

By detecting the light at specific wavelengths, it is possible to determine what elements are present. In addition, one can create a calibration curve (intensity vs. concentration) by using solutions of known concentration, compare the intensity in a sample of unknown concentration with the calibration curve, and determine the concentration of the analyte.

An ICP-atomic emission spectrometer is composed of two parts: the ICP and the optical apparatus. The ICP is generated in a torch that consists of 3 concentric tubes of silica glass and a coil of the radio frequency (RF) generator which surrounds part of this torch (Figure 14.10, left). Argon gas is typically used to create the plasma.

When the torch is turned on, an intense magnetic field from the RF generator is activated. The argon gas flowing through is ignited with a Tesla unit, which typically is a copper strip on the outside of the tube. The argon gas is ionized in this field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the RF coil. A stable, high

temperature plasma of about 7000 K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles (Figure 14.10, right).

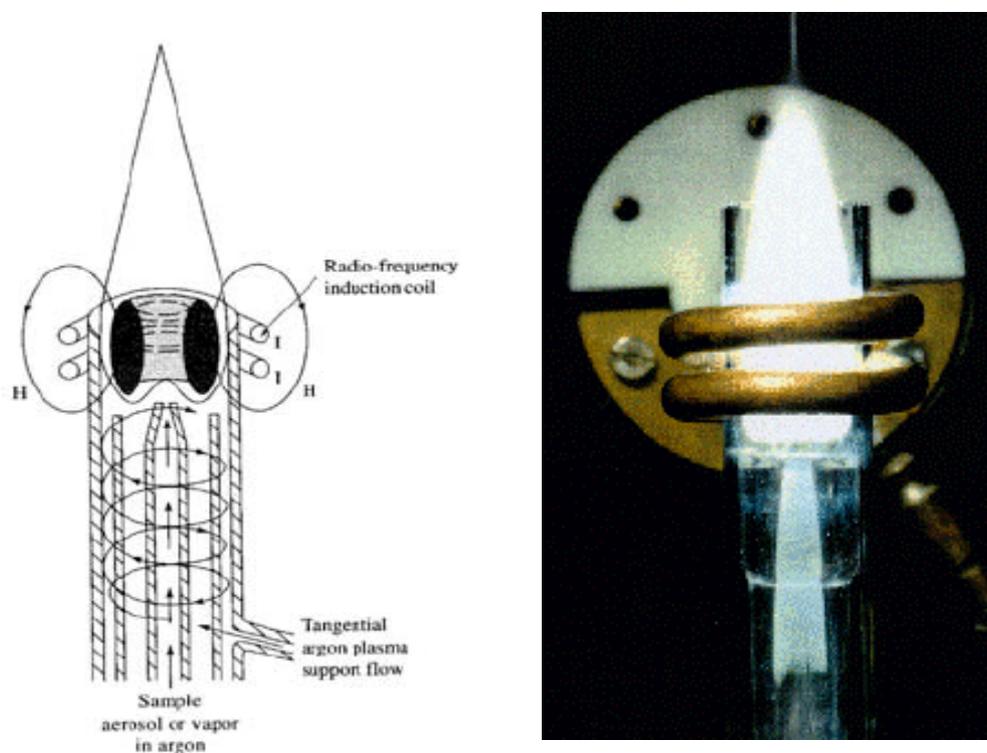


Figure 14.10 – Structure of a torch for the generation of a plasma source (left) and a lighted torch (right).

A peristaltic pump delivers the sample solution into a nebulizer where it is atomized and introduced directly inside the plasma flame. The sample immediately collides with the electrons and other charged ions in the plasma and is broken down into charged ions. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off the characteristic wavelengths of the elements involved. One or two transfer lenses are then used to focus the emitted light on a diffraction grating where the radiations that compose it are separated.

The light intensity is then measured with a photomultiplier tube at the specific wavelength for each element involved. The intensity of each line is then compared to previous measured intensities of known concentrations of the element and its concentration is then computed by extrapolation along the calibration line.

The analysis by ICP-AES requires a sample in form of solution. Therefore, when solid

samples (like stone, ceramics, glass, clay) are to be analyzed, it is necessary to dissolve them in order to obtain a diluted solution. There are two principal ways for the dissolution of solid samples: acid attack or alkaline fusion. The samples to be analyzed contain a significant amount of silica, so that you cannot dissolve them by using hydrofluoric acid, which would cause the loss of silica in form of silicon fluoride. Therefore, alkaline fusion is recommended. The melting can be obtained by heating at about 1,000 °C a mixture of sample (for example 0.1 g) and flux in proportion 1:10 approximately; the flux can be a mixture of lithium tetra-borate and lithium borate. Then, the melt can be dissolved with aqueous solution of nitric acid.

The ICP-AES is a destructive analytical technique, but the amount of sample needed is very low, so that this technique is very useful in order to analyze many different materials.

14.3.7 Laser induced plasma spectroscopy

Laser induced plasma spectroscopy (LIPS), also named laser induced breakdown spectroscopy (LIBS), is a micro-analytical elemental technique based on the spectral characterisation of the plasma plume produced by focusing a pulsed laser beam on the material to be analysed. The technique does not require any preparation of the artefact under study. It is micro-destructive but often non-invasive, since the analysis is carried out on a very small quantity of laser ablated material, which does not imply any relevant invasiveness issue in most cases. As schematised in Figure 14.11, the basic set up of LIPS includes a pulsed laser, focusing (L_1) and gathering (L_2) optics, spectrometer, and personal computer.

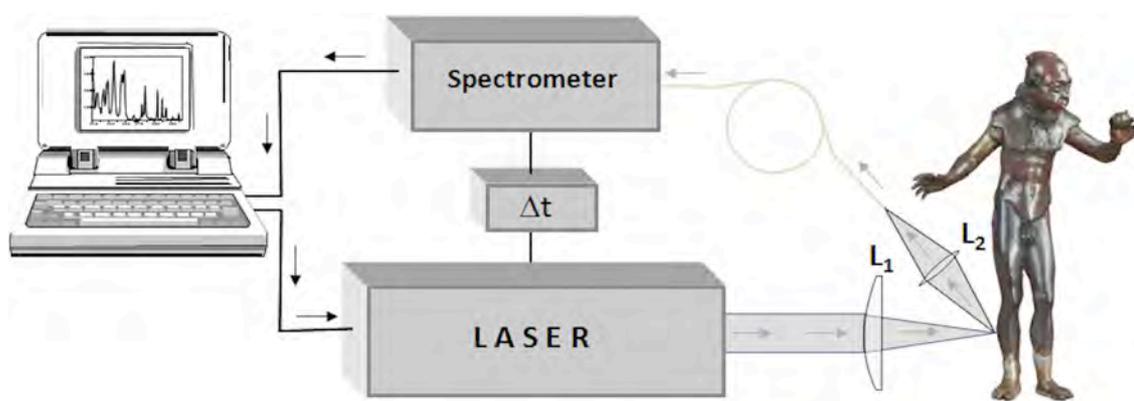


Fig. 14.11 - Schematic set up of the LIPS technique.

A low energy (10-100 mJ/pulse) Q-switched Nd:YAG laser is typically used to excite the plasma emission. The very high peak intensity associated with its short pulse duration (5-10 ns) and tight focusing (10-100 μm spot diameter) produces material ablation, ionisation and then a rapidly expanding luminescent plasma plume. The spectral lines of the latter are characteristic of the atomic species composing the material under analysis.

The lifetime of the plasma ranges from a few to several microseconds according to the irradiation parameters and material composition.

During the early hundreds of nanoseconds the optical emission is characterised by a continuum spectrum, then atomic lines become visible with an increasing signal/noise ratio and finally the noise gradually disappears. One of the main concerns of LIPS is the selection of the optimum time delay between laser irradiation and spectral acquisition. In order to maximise the signal/noise ratio also double pulse lasers and gated spectrometers including intensified CCD sensors (iCCD) are used in complex laboratory setups. However, simplified portable devices using single pulse compact Q-switching Nd:YAG lasers and low-cost spectrometers appear to be more promising as a powerful and easily accessible archaeometric tool.

In principle, LIPS can allow detecting and recognising all the elements whether using a multichannel optical spectrometer with sufficiently wide range, high resolution, and high sensitivity.

Besides qualitative analysis, preliminary calibrations using suitable reference samples also allow relative quantifications based on the measurements of line intensity ratios. In this respect, apparatuses including double pulse lasers and iCCD detectors are up two orders of magnitude more sensitive than low-cost portable devices, which are usually employed to measure the main atomic components with a sensitivity of some thousands of ppm.

The micro-scale material volume analysed for each laser shot is determined by the spot diameter (10-100 μm) and ablation rate (0.1-10 $\mu\text{m}/\text{pulse}$). Usually, several spectra are collected in each measurement spot, whose elaboration allows achieving quantitative elemental depth profiles along penetration depths up to the order of millimetre with a high spatial resolution.

Depth profile analysis can be considered the main feature of LIPS since it provides the main advantage with respect to other surface elemental techniques, such as X-ray fluorescence (XRF), electron microprobe (SEM-EDX/WDX), and particle induced X-ray

emission spectroscopy (PIXE). Depth profiling has a fundamental importance whenever material stratifications and substantial compositional differences between surface material layers and the bulk underneath are encountered.

The introduction of LIPS dates back to the origin of the laser technologies while its significant potential application in archaeometrical investigations was thoroughly proven along the last fifteen years.

The studies reported concern pigments, metal alloys, glasses and ceramics. However, today copper, silver, and gold alloy artefacts represent the more successful and promising applications. Museum collections and large bronzes such as the Etruscan masterpieces named the Arringatore and the Chimera from Arezzo from Florence's National Museum of Archaeology, as well as a number of Renaissance masterpieces were thoroughly characterised along the last years using portable LIPS.

As an example, Figure 14.12 shows a detail of the spectrum and the tin depth profile of a Roman bronze figurine. As it can be seen, a surface enrichment of tin content of a factor 2.5 was observed in this case, which decreased to the bulk value after about 400 laser pulses. Such a strong compositional modulation, which was determined by long-term corrosion, represents a peculiar feature of archaeological bronzes, which can be revealed in a non invasive way using LIPS.

It is also worth noting that surface enrichment/depletion phenomena of the metal alloys have been recently recognized as a key feature for distinguishing between genuine ancient copper alloy artefacts and modern counterfeits.

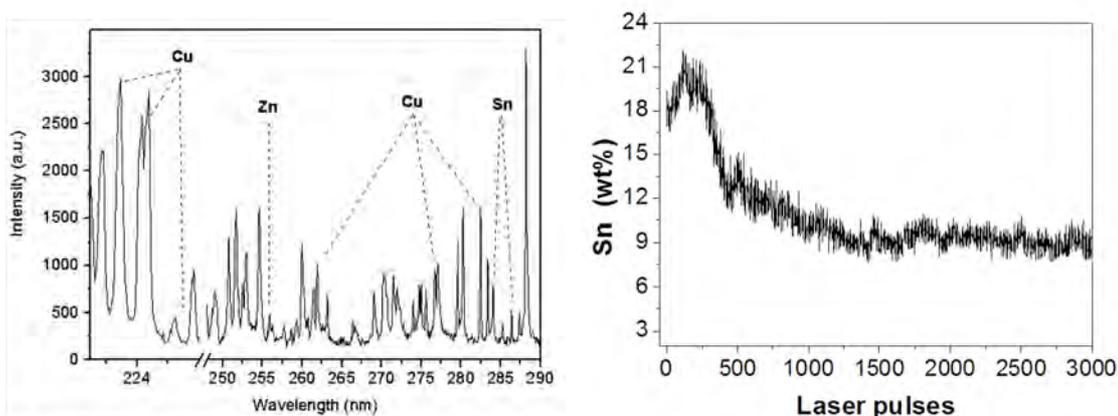


Figure 14.12 - Examples of plasma emission spectrum (left) and tin depth profile (right) of a Roman bronze figurine.

14.4 Radiochemical techniques

14.4.1 X-ray diffractometry

The identification code of X-ray diffractometry is XRD. This analytical methodology enables the identification of crystalline phases (minerals) present in the specimen. Generally it is a micro-destructive and semi-quantitative analysis, but sometimes it can be not destructive, when the specimen has a perfectly flat surface.

The instrument used for carrying out this analysis is the diffractometer, which gives the results in graphic form (diagram), which is called diffractogram.

The physical principle on which this analytical methodology is founded is the Bragg equation, which says: a sheaf of parallel planes of a crystalline structure causes the reflection of a monochromatic X-ray beam only for some angles of incidence, according to the equation: $2d \sin\theta = \lambda$, where:

λ = wavelength of the incident x-ray beam

d = distance between two adjacent parallel planes

θ = angle of incidence.

The Bragg equation can be easily obtained by observing the geometric scheme reported in Figure 14.13. Two X-ray beams will be in phase between them when the difference between their paths ($AB + BC$) corresponds to the wavelength (λ), or multiple of it:

$$\lambda = AB + BC = 2d \sin\theta$$

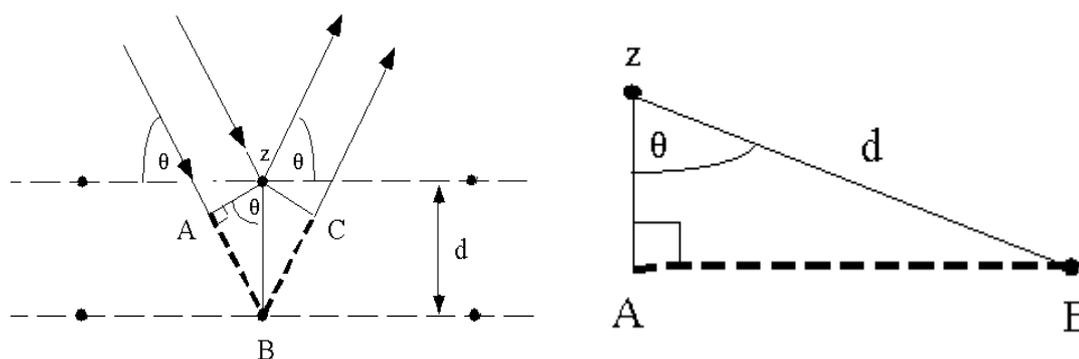


Figure 14.13 – Geometric scheme for obtaining the Bragg equation.

From this equation it is possible to calculate the 'd' value, after measuring the reflection angle (θ) for a prefixed wavelength (λ): $d = \lambda / 2\sin\theta$.

Each mineral has a crystalline reticulum with a precise composition and structure, so that

each crystalline phase is characterized by a precise set of “d” values. In this way it is possible a mineralogical analysis on the basis of the attribution of a set of calculated “d” values.

A scheme of diffractometer is shown in Figure 14.14. The powdered specimen rotates, while the X-ray source is fixed. When, for a sheaf of reticular planes in a mineral the equation of Bragg is satisfied, a reflection occurs; than the reflected ray is captured by the detector, which measures its intensity.

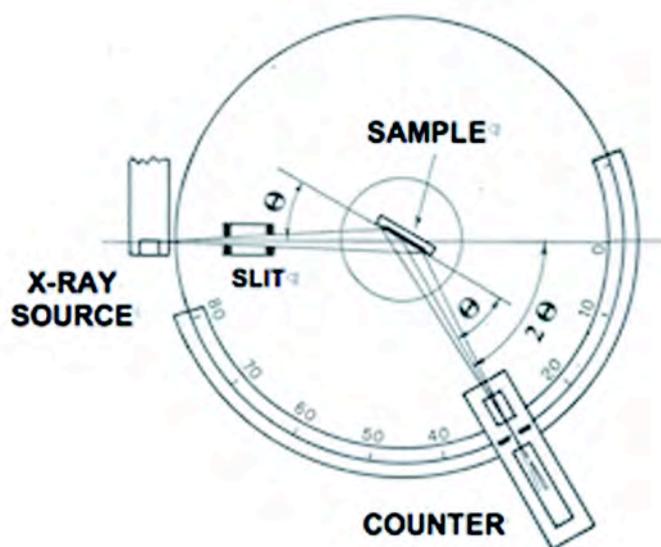


Figure 14.14 – Working scheme of a diffractometer.

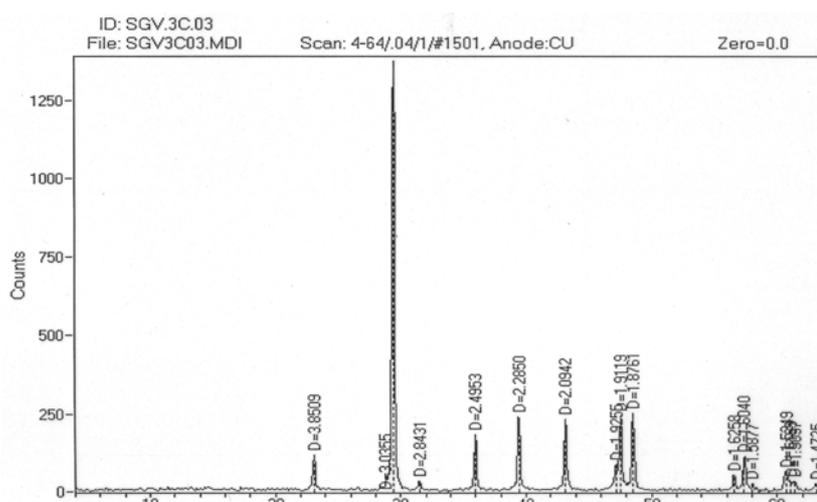


Fig. 14.15 – Diffractogram with “d” values calculated by computer according to the Bragg equation.

At the end of the analysis, the instrument gives a diagram (diffractogram) which is composed by an irregular base line from which more or less intense peaks can be identified (Figure 14.15). Each peak corresponds to a reflection by a sheaf of parallel planes of a crystalline phase in the sample. The value of “d” in correspondence with each peak can be easily calculated by the Bragg equation.

The interpretation of a diffractogram means to identify the different “d” values and to attribute them to the several minerals present in the analysed sample. The attribution of the peaks to different minerals is possible by means of manuals and cards (now in digital format) that show all the “d” values and the intensity of the peaks of each mineral.

XRD analysis is generally semi-quantitative. The relative amounts of the identified minerals can be shown by a different number of crosses. For example:

+++++ = very abundant, ++++ = abundant, +++ = not very abundant, ++ = reasonable, + = scarce.

X-ray diffractometry is a typical laboratory instrumentation, so that it is invasive because it needs a powdered sample, even though of small size. In very recent times, portable instrumentation has been developed that allows a non destructive mineralogical characterization of materials in the cultural heritage field.

14.4.2 X-ray fluorescence spectrometry

The X-ray fluorescence spectrometry (XRF) is a technique of qualitative and quantitative chemical analysis. It exploits the emission of X-rays by the sample when hit with an adequate energy. This energy is supplied by a source of X-rays with a broad spectrum of wavelengths, mostly continuous, so as to be able to excite most of the chemical elements.

The X-ray radiation emitted from the sample, however, is discontinuous and is characteristic of the elements present in the sample. The recognition of the different wavelengths (λ) and their attribution to a specific chemical element is obtained by means of an analyzer crystal that rotates during the running and on which the total X-ray fluorescence emitted by the sample is collimated. The identification of the different wavelengths allows for the qualitative analysis of the sample, while the intensity of the radiation allows the quantitative analysis.

The measurement of λ is done according to the equation of Bragg ($2d \sin\theta = \lambda$), the same shown for the x-ray diffractometry. In XRD the wavelength (λ) is constant and known, so that it is possible to determine the values of ‘d’ and recognize the correspondent minerals. In XRF, on the contrary, there is a crystal with well known ‘d’ value, so that it is possible

to calculate the wavelengths of the x-ray radiation emitted by the sample (wavelength dispersion system = WDS). A scheme of a WDS-XRF spectrometer is shown in Fig. 14.16.

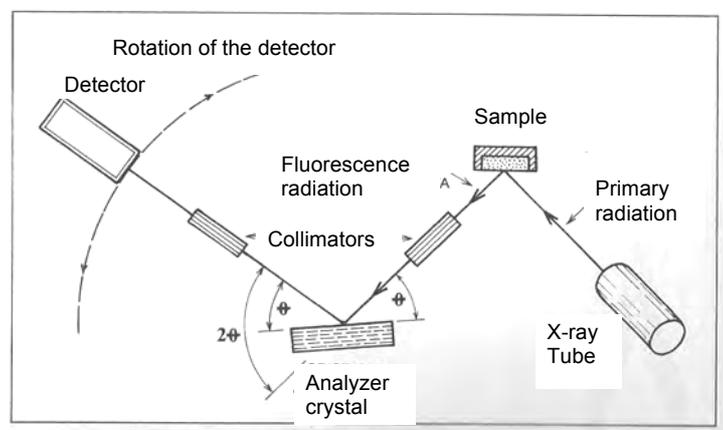


Figure 14.16 – Scheme of X-ray fluorescence spectrometer.

WDS-XRF is a non-destructive analytical technique, if the sample is analyzed in the form of pressed powder (tablet). However, the results are better when the analysis is performed on the sample mixed with a flux (lithium tetra- and meta-borate), melted and cooled to give rise to a glass disk, commonly called ‘pearl’. In this way, the technique becomes destructive, other than invasive. In addition, the amount of sample analysis must not be ignored, because it is about 1 gram. However, the WDS-XRF technique remains the most interesting for the precise chemical analysis of solid samples (stone, ceramics, glass, metals), taking into account the speed of analysis and the ability to analyze virtually all elements, from traces to the highest percentages.

14.4.3 Transportable and portable XRF spectrometry

Energy dispersion system-XRF is a very useful analytical technique in the field of the cultural heritage, because it allows to analyze the artifacts in situ without destroying material. The general principal is the same of WDS-XRF, that is to recognize the elements which have emitted X-ray radiations when the sample is hit by a X-ray beam, and to transform their intensity into concentration values. This is made possible by changing the recognition system of each emitted radiation: energy dispersion instead of wavelength dispersion.

Only the energy dispersion system permits to realize transportable or portable

instrumentations, which can perform in situ analyses. The transportable instruments have to be mounted near the artifact to be analyzed, while the portable instruments have a battery as energy source, can be kept by hands and placed in contact with the object. Anyway, EDS-XRF is particularly useful for the analysis of metals, because the metallic elements are the most sensitive (Figure 14.17). But all the elements become sensitive enough if the instrumentation can be used in contact with the object to be analyzed, or argon is continuously insufflated into the space between instrument and object.



Figure 14.17 – Analysis of an ancient bronze coin by means of transportable XRF.

Of course, EDS-XRF has also some disadvantages, which mainly derive from the fact that it analyzes just the surface layer of the sample, so that the result does not represent the real composition of the artifact, unless it is very homogeneous from the core to the surface. As a consequence, this type of instrumentation is very useful in order to analyze the alteration layers, as well as for a speedy campaign of qualitative analyses.

14.5 Chromatography

14.5.1 General information and terminology

Chromatography is the collective term for a set of laboratory techniques for the separation of mixtures. It involves passing a mixture dissolved in a “mobile phase” through a stationary phase, which separates the analyte to be measured from other molecules in the mixture based on differential partitioning between the mobile and stationary phases. Subtle differences in partition coefficient of the compounds will result in differential retention on the stationary phase and thus separation.

Chromatography may be preparative or analytical. The purpose of preparative

chromatography is to separate the components of a mixture for further use (and is thus a form of purification). Analytical chromatography is done normally with smaller amounts of material and serves for determining the existence and possibly also the concentration of analyte(s) in a sample. The *analyte* is the substance to be separated.

A *bonded phase* becomes a stationary phase when it is covalently bonded to the support particles or to the inside wall of the column tubing.

A *chromatogram* is the visual output of the chromatograph. In the case of an optimal separation, different peaks or patterns on the chromatogram correspond to different components of the separated mixture. Plotted on the x-axis is the retention time and plotted on the y-axis a signal (for example obtained by a spectrophotometer, mass spectrometer or a variety of other detectors) corresponding to the response created by the analytes which exit the system. In the case of an optimal system the signal is proportional to the concentration of the specific analyte separated.

A chromatograph is an equipment that enables a sophisticated separation, e.g. gas-chromatographic or liquid-chromatographic.

Chromatography is a physical method of separation, in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction. The *effluent* is the mobile phase, which leaves the column. A immobilized phase is a *stationary phase*, which is immobilized on the support particles, or on the inner wall of the column tubing.

The *mobile phase* may be a liquid (LC = liquid chromatography), a gas (GC = gas chromatography), or a supercritical fluid (SFC = supercritical-fluid chromatography). The mobile phase includes the sample to be analyzed and the solvent that transports the sample towards the chromatographic column (the stationary phase), which interacts with the sample. The *retention time* is the characteristic time it takes for a particular analyte to pass through the system under set conditions.

The sample may consist of a single component (*solute*) or it may be a mixture of different components. In the course of an analysis, the phase containing the analytes of interest is referred as the sample, whereas everything which is separated from the sample, before or in the course of the analysis, is referred as waste.

14.5.2 Liquid chromatography

Liquid chromatography (LC) is a separation technique in which the mobile phase is a liquid, and can be carried out either in a column or a plan. At present day, liquid chromatography generally utilizes very small filling particles and a relatively high pressure. It is referred as high performance liquid chromatography (HPLC).

The sample is forced through a column by a liquid (mobile phase) at high pressure. The column is filled with particles, irregularly or spherically shaped, or with a porous monolithic layer (stationary phase).

HPLC is historically divided into two different sub-classes based on the polarity of the mobile and stationary phases. When the stationary phase is more polar than the mobile phase (e.g. toluene as the mobile phase, silica as the stationary phase), the technique is called normal phase liquid chromatography (NPLC).

In the opposite case (e.g. water-methanol mixture as the mobile phase and C18 = octadecylsilyl as the stationary phase), it is called reversed phase liquid chromatography (RPLC). Ironically the “normal phase” has fewer applications and RPLC is therefore used considerably more.

14.5.3 Ion exchange chromatography

The ion exchange chromatography uses a ion exchange mechanism in order to separate the analytes. It is usually performed in columns, but can also be used in planar mode.

The ion exchange chromatography uses a stationary phase, which is electrically charged, with the aim to separate compounds including amino acids, peptides, and proteins. In conventional methods, the stationary phase is a ion exchange resin, characterized by functional groups which have a charge such that they can interact with oppositely charged groups of the compound to retain.

Ion exchange chromatography is commonly used to purify proteins.

In the field of the cultural heritage, it is very useful and currently used for analyzing the quantitative chemical composition of soluble salts previously extracted from solid samples like natural stones, mortars, clay bricks, ceramics.

This technique can analyze the various cations (Na^+ , K^+ , NH_4^+ , Ca^{++} , Mg^{++} , etc.), as well as the anions (Cl^- , F^- , NO_3^- , SO_4^{--} , etc.).

14.6 Electron microscopy

Particles or specimen details under 1 micron can be observed only by electron microscopy, which has a higher resolution power than optical microscopy.

Electron microscopy uses an electron beam and lenses that are adjustable magnetic fields.

14.6.1 Scanning electron microscopy (SEM)

In SEM observations the magnified images of specimen details are obtained by electrons emitted by the surface of the sample (secondary electrons).

An incandescent filament gives out electrons. By means of a system of electro-magnetic lenses these electrons (primary electrons), transformed in a thin sheaf, are addressed on the specimen. The area of the surface hit by the primary electrons gives out electrons (secondary electrons) that are used for obtaining the enlarged image of a detail of the surface of the sample.

SEM analyses give us three-dimensional images, in addition the preparation of the sample is very simple and doesn't modify the morphology of the sample. In this way micro-morphological and micro-structural studies are possible. A scanning electron microscope can reach magnifications about 20,000 times.

Scanning electron microscopy can be equipped with an instrument (energy dispersive X-ray spectrometer, code: EDS) that enables to detect the chemical elements present on the superficial layer of the sample.

When the primary electrons hit an area of the sample the atoms present in this area give out secondary electrons (used for obtaining the image of the sample) and x-ray radiations (fluorescence x-rays) which wavelengths and associated energies are typical of the chemical elements that emitted them. If we have an instruments enable to detect the energy of these X-rays, we can easily recognize the elements present on a surface layer of the sample. By EDS microanalyses is possible to carry out chemical analysis of surface details of the sample, and to know the distribution of chemical elements on the surface of the sample.

In Figure 14.18 a SEM-EDS instrument is shown.



Fig. 14.18 – SEM-EDS instrument, mod. Cambridge Stereoscan 360.

14.6.2 Transmitted electron microscopy (TEM)

In TEM analyses the electron beam goes across the specimen. If the sample is not transparent to electrons a cast of the specimen surface, obtained depositing a thin film made of a suitable material, is observed.

TEM observations give us bi-dimensional images that can reach maximum magnification about 100,000 times.

An incandescent filament gives out electrons. These electrons are captured, transformed in a thin beam and sent on the specimen by a system of electro-magnetic lenses. The electron beam after crossing through the specimen is captured and elaborated by an other system of electro-magnetic lenses that gives us the enlarged image of a detail of the sample.

TEM analyses are not frequently used in cultural heritage sector.

14.7 Thermal analyses

The thermal analyses are analytical techniques that study the physical-chemical transformations of the material due to variations in temperature (heating and/or cooling) of the specimen.

Inside this big family of analytical techniques only differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) will be taken into account, because these two

analytical methodologies are used very much from several years in the cultural heritage sector, especially in the study of mortars.

DTA and TGA request the heating of the sample with a constant rise in temperature.

All the physical and/or chemical transformations of the materials are always associated with variations in energy, that is heat exchange between sample and environment.

In particular heat absorption by the environment corresponds to a endothermic reaction, while heat cession to the environment to a exothermic reaction. In addition, often the transformations of the material produce variations in weight, generally loss of weight.

DTA-TGA analyses allow the identification and often the quantification of the thermo-unstable compounds. In addition, in mortar study these analyses also identify the hydraulic or aerial characteristics.

Differential thermal analyses indicate variations in temperature during the test between the specimen and an inert material (generally alumina) present in the same oven and warmed in the same manner.

Thermal gravimetric analyses indicate variations in weight of the specimen during the test, expressed in percentage with reference to the initial weight of the sample.

The apparatus for differential and gravimetric analyses is shown in Figure 14.19. It is composed of a oven and a precision balance connected to a small staff on the base of which there is the housing for two small crucible. In one of these crucibles (made of alumina or platinum) few milligrams of powdered specimen are put, while in the other crucible few milligrams of powder of alumina are put. During the test, the inert material (alumina) always has the same temperature of the oven. When the sample doesn't change it has the same temperature of the alumina, but when during the test the specimen undergoes a transformation, its temperature is different from that of the alumina. In particular in correspondence of endothermic transformations the temperature of the specimen is lower than the temperature of the inert material; while in correspondence of exothermic reactions the temperature of the specimen in the oven is greater than the temperature of alumina. The differences of temperature between sample and alumina are measured by two thermocouples.

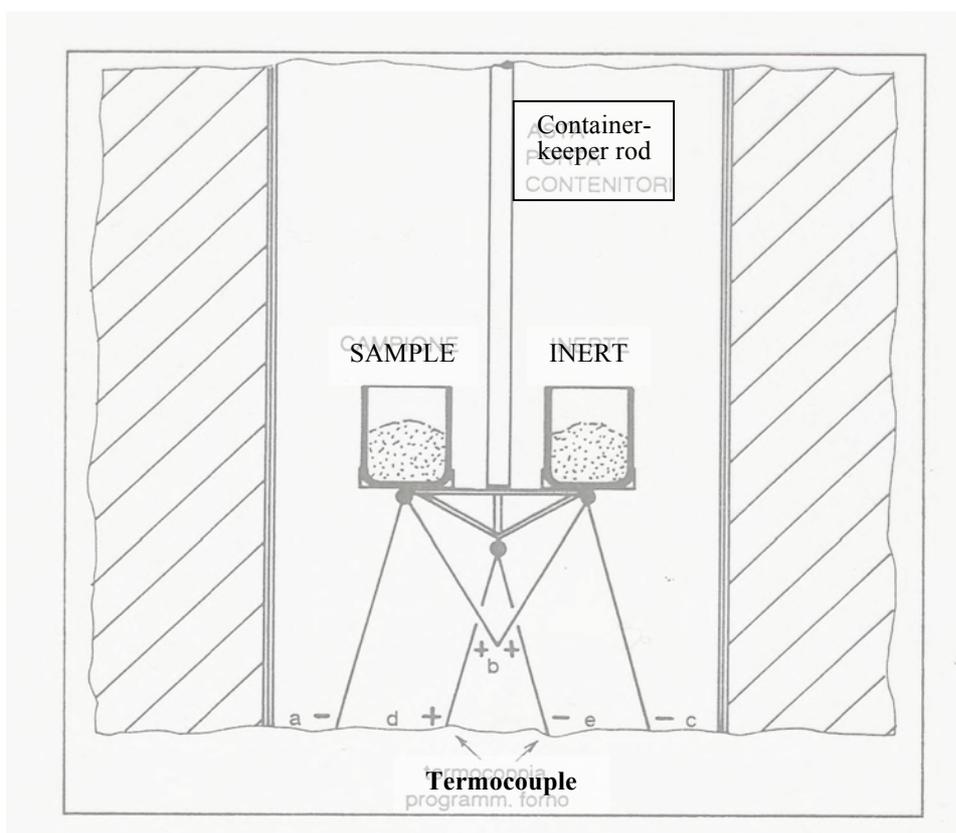


Figure 14.19 - Scheme of DTA-TGA apparatus.

In differential thermal curve an endothermic reaction is generally shown by a peak in down direction, while an exothermic reaction is shown by a peak in high direction. Each substance changes at precise temperature; then comparing the DTA curve of the sample with the DTA curves of known substances, the identification of the different compounds present in the samples is easily possible.

When the sample doesn't lose weight during the test the TGA curve is quite horizontal. While in correspondence of a weight loss the curve is inclined.

In a DTA-TGA analysis performed at the same time, by means of the weight loss in correspondence of the reactions and simple stoichiometric calculations it is possible to obtain the quantification of the substances identified in the samples. Therefore the combination of DTA and TGA is a quantitative analysis.

In Figure 14.20 is shown a thermogram DTA-TGA of a marble covered by a black crust.

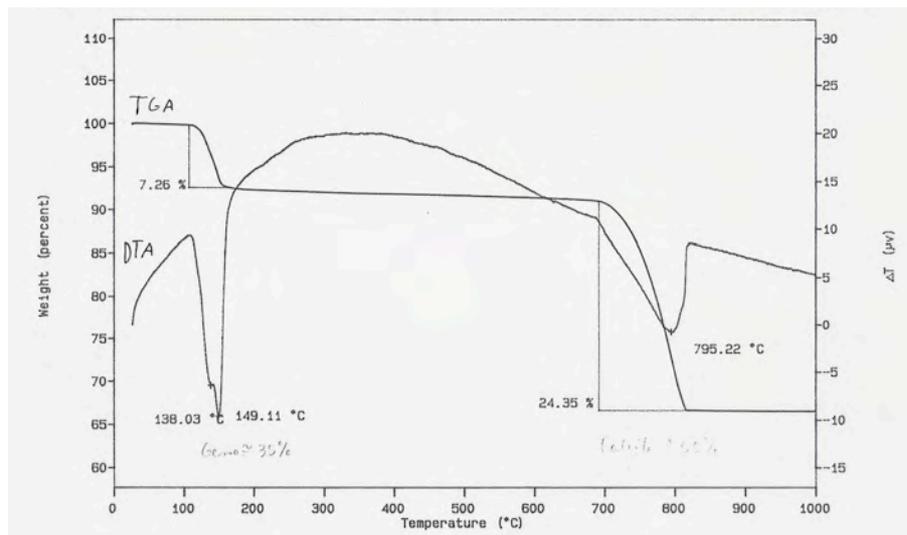


Figure 14.20 – DTA-TGA thermogram of a marble covered by a black crust. Gypsum and calcite are the substances identified and quantified.

14.8 Open porosity measurements

The open porosity is an important parameter for diagnostic purposes for several materials, stones and ceramics in particular. The porosity of an artefact is the sum of the pores, fractures and cracks, and it can be determined by visual or physical methods. Visual methods (optical and electronic microscopy) permit to describe dimension and shape of the pores and it is possible to count the number of pores and define a percentage of them. Physical methods (dipping the material in a liquid, water or mercury) permit to determine the percentage or the volume of the liquid absorbed.

14.8.1 Water absorption

Dried samples, previously weighted (W_d), are put into a container filled with demineralised water. After 2 hours boiling, when the water is not so warm, the samples are slightly dried with a rag and then weighted again (W_w). The difference of the two weights is the amount of absorbed water. In this way, it is possible to determine the total open porosity of the artefact, given by the pores larger than $0.01\mu\text{m}$ approximately, that is the percentage of water that a material is able to absorb:

$$W.A. (wt\%) = 100 (W_w - W_d) / W_d$$

with: W.A. = water absorption; W_w = wet weight; W_d = dry weight.

14.8.2 Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry allows the determination of the open porosity and dimensional distribution of the pores.

The specimen (a small piece of about 1 g) is put in a bulb, in which vacuum is made. Then mercury is put in the bulb. Step by step an increasing pressure is applied to the mercury that in this way can enter in pores gradually finer. The instruments can measure the volume reduction of mercury after every increase of pressure.

There is an equation (equation of Washburn) that, supposing pores in the shape of cylinders, binds the radius (r) of the transversal section of the pore to the pressure (P) which mercury needs for entering the pore. Equation of Washburn in simplified form:

$$r = 7.36/P$$

where “ r ” is expressed in micron and “ P ” in atmospheres.

According to this equation by means of a mercury intrusion porosimeter it is possible to determinate the total open porosity (total decrease of the mercury during the test) and the dimensional range of the pores (radius) between 18 Å (4,200 atmospheres) and 100 micron (<1/10 of atmosphere). The results can be shown in graphic form of histogram or cumulative curve (Figure 14.21).

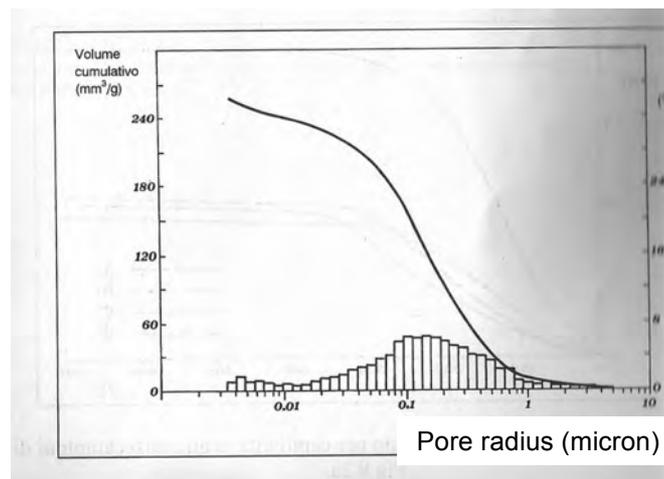


Figure 14.21 - Result (histogram and cumulative curve) of a mercury intrusion porosimetry analysis for the external layer of a plaster.

14.9 Analysis of microbial colonization

Biodeterioration of works of art is a complex process involving a high number of microbial species in both inorganic and organic materials. Particularly, fungi and bacteria (frequently associated with green algae, cyanobacteria, lichens), wide-spread in biosphere environments, are the main microorganisms related to the deterioration of cultural assets. Moreover, complex microbial communities may emit mixed aerosol into indoor environments with human (visitors, professionals) health damaging proprieties, that may persist in the environment.

In order to identify the components of microbial populations colonizing the surfaces of works of art and dispersed in the aerosol, it is possible to perform the investigation by different methodologies, such as microscopy, *in vitro* culture and molecular biology (Figure 14.22).

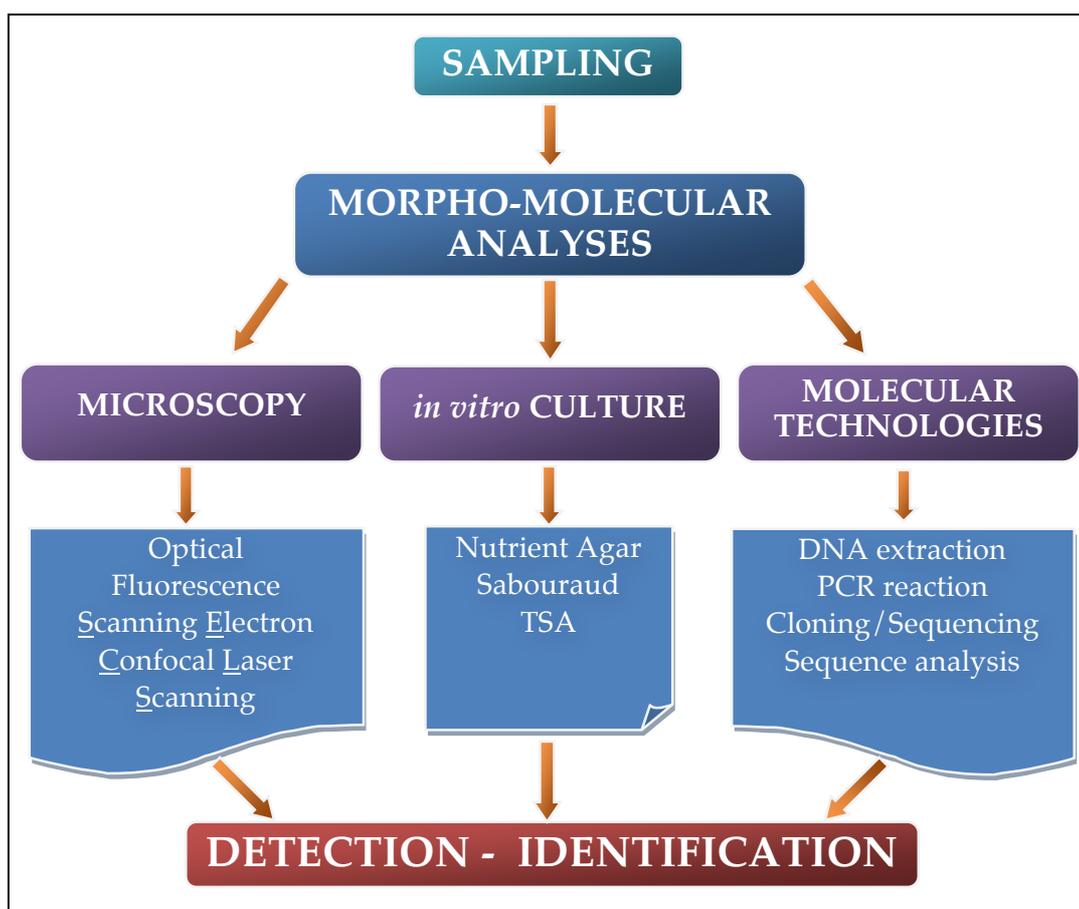


Figure 14.22 - Methodologies that can be used in order to analyze microbial populations.

14.9.1 Sampling

Non invasive sampling on surfaces of work of art can be done by using biological tools such as sterile swabs, adhesive tape and Nylon H⁺ membrane (Amersham). This methods is mainly utilized to collect the *particles* and the microbial colonies present on the surfaces (Figure 14.23).



Figure 14.23 - Sampling on paper and leather specimens by Sterile swab (A), Nylon membrane fragment (B), Aluminium stab for SEM analysis (C).

Specifically, for indoor environments, the aerosol sampling can be performed by portable (or fixed) instrumentation, such as AirPort MD8 sampler, equipped with disposable gelatine filter (Figure 14.24); flow rate and sampling time are selected in relation to the volume of the environment analysed.

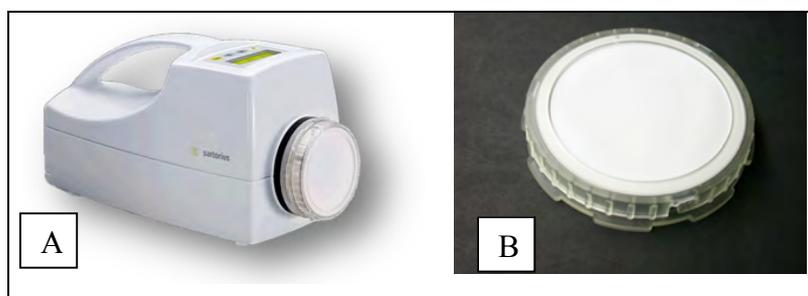


Figure 14.24 - Portable equipment from Sartorius: AirPort MD8 (A); sterilized disposable gelatine filter (B).

Gelatine filter represents a very good method for sampling and for the following identification procedure, because it maintains the viability of the collected microorganisms and the filters are completely water-soluble. Therefore microbes can be cultivated in/on different nutrient media (*in vitro* culture) or microbial genomic DNA can be directly extracted (molecular technologies).

14.9.2 Characterization of fungi by Optical Microscopy

In order to recognize fungal contamination, agar medium plate (Sabouraud) can be inoculated by swab, nylon membrane or gelatine filter fragments (Figure 14.25). The agar Sabouraud, is a selective medium for fungi; it contains 1.5% agar, 4% dextrose, 1% peptomycol and cloramphenicol (16 µg/ml). Both pH value and antibiotic presence inhibit the growth of most bacteria. Agar plates are incubated at 30 °C at least for 3 days and the colonies are analyzed through their macroscopic and microscopic morphology. A simple method to examine fungi morphology is the “adhesive tape method” (Figure 14.25):

- put few drops of Lugol’s solution onto a slide (Lugol’s solution consists of 5 g iodine (I₂) and 10 g potassium iodide (KI) mixed with 85 ml distilled water, to make a brown solution with a total iodine content of 150 mg/ml);
- delicately push the adhesive side of the tape on the mould surface;

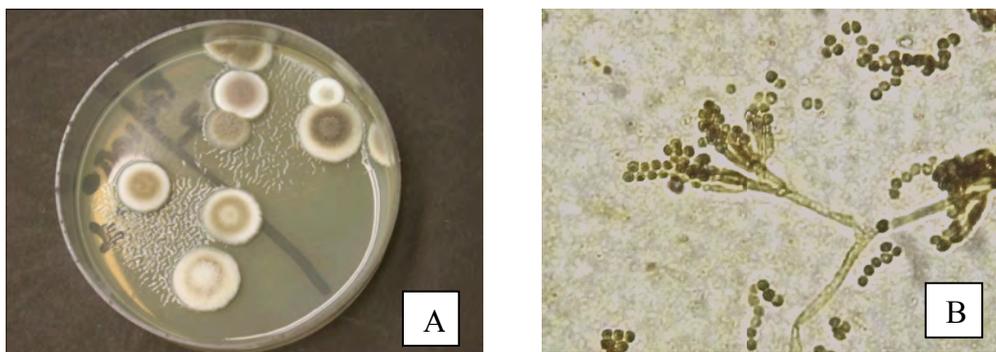


Figure 14.25 - A) Fungal colonies growth on agar medium, inoculated by gelatine membrane fragment. B) *Penicillium* sp. structure stained by Lugol’s solution, observed by optical microscope (40X magnitude).

- wet this side with Lugol’s solution to achieve the coloration of fungal hyphae;
- observe by optical microscope.

14.9.3 Electron microscopy (SEM, CLSM) observations

In order to establish the presence of microorganisms by electron microscopy, both scanning (SEM) and confocal laser scanning (CLSM) provide a valuable contribution to the characterization of microbial consortia, highlighting the possible deteriorogen action (Figures 14.26, 14.27 and 14.28).

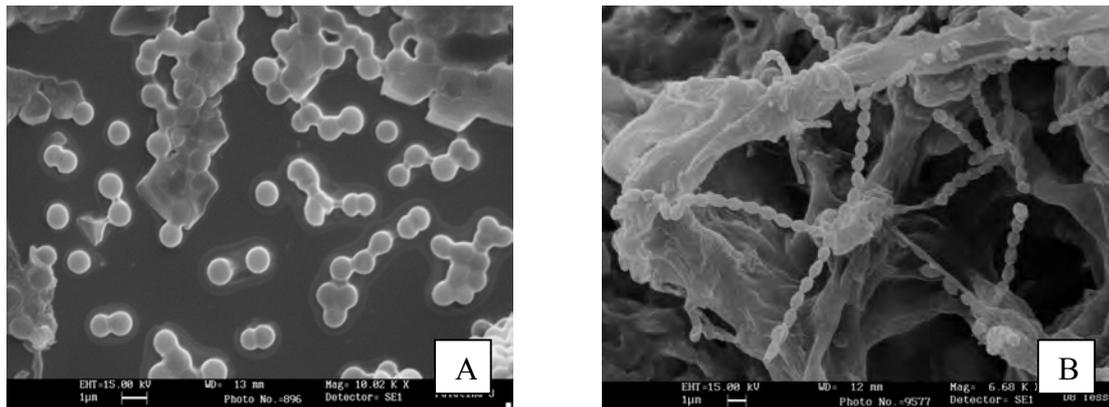


Figure 14.26 - SEM micrographs of microbial structure:

A) bacteria from liquid culture;

B) chains of *Actinomyces* spores from mosaic mortar.

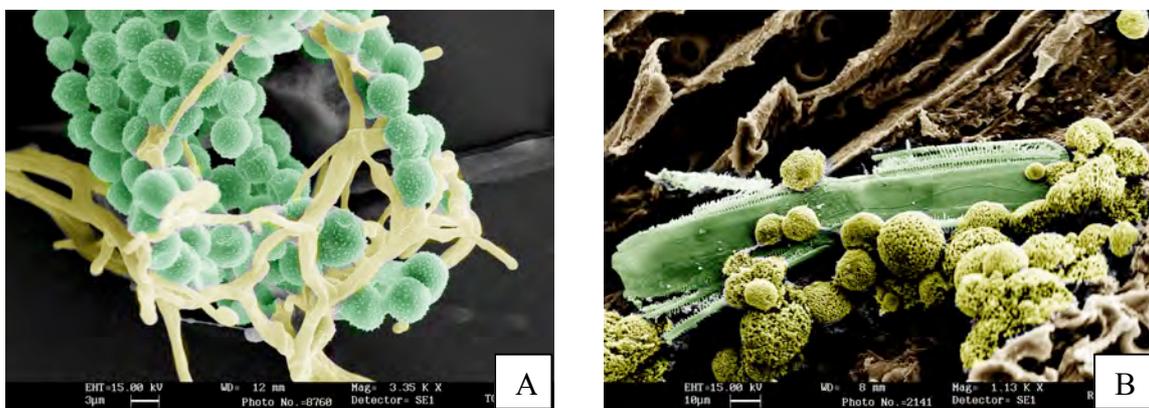


Figure 14.27 - SEM micrographs of micro-structures, from waterlogged wood specimen, artificially coloured in laboratory by Photoshop:

A) Fungal spores (green) and mycelium (yellow);

B) Pyrite framboids (yellow) and Diatomeae (green).

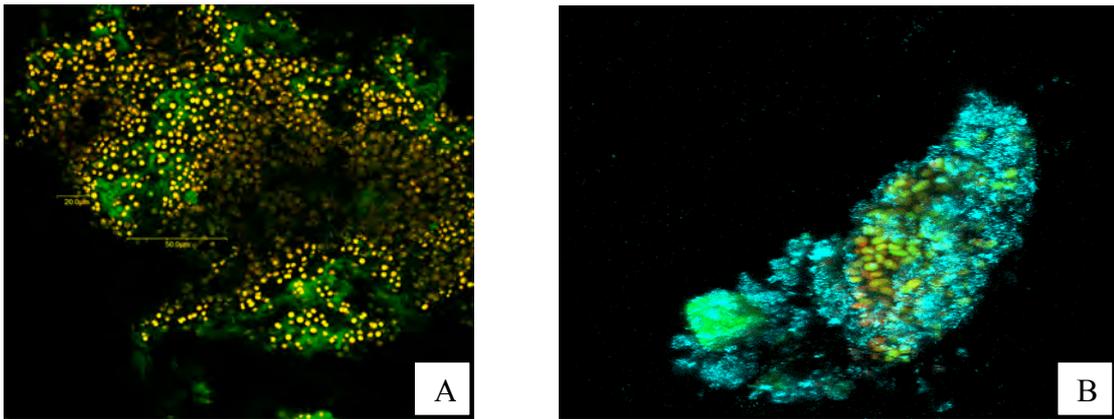


Figure 14.28 - CLSM micrographs of biofilms from hypogean environment (A) and mosaic mortar (B); cyanobacteria and green algae are recognizable.

14.9.4 In vitro culture

Sterile swab and nylon membrane fragments (surfaces) or gelatine filter fragments (aerosol) can be used to inoculate agar plate, performing the *in vitro* culture analysis on Nutrient-agar (general medium) (Figure 14.29) or Sabouraud (fungal growth medium) (Figure 14.30).

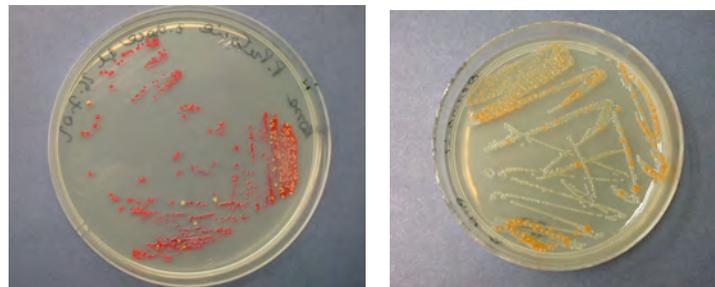


Fig 14.29 – Bacteria colonies growth on Nutrient agar plate inoculated by swab (surface sampling).

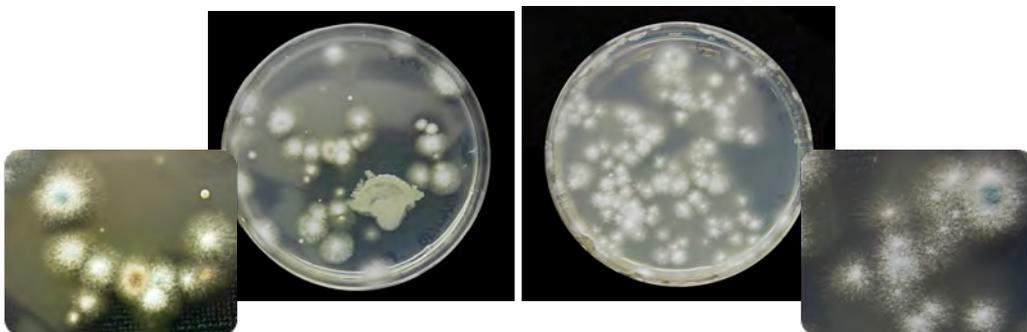


Fig 14.30 – Fungi colonies growth on Sabouraud agar plate inoculated by gelatine filter fragments (aerosol sampling).

14.9.5 Molecular biology technologies

The study of microbial communities in a work of art, performed by microscopy observation and/or *in vitro* culture does not provide comprehensive information on the composition. That is due to the fact that only the morphological profiles can be detected by microscopy and that less than 1% of environmental organisms can be cultured in laboratory by standard techniques. Therefore, straightforward and precise methodologies are needed for studying microbial colonization of cultural heritage. In recent years molecular biology and the new biotechnologies, have been used in the field of cultural heritage diagnosis, at the aim to identify biological damages and to establish the consequential conservation/restoration strategies. Moreover, this approach minimizes the sample amount, and optimizes the diagnostic studies on microbial colonization because it allows the specific identification of microbial species.

Molecular biology provides a sensitive study on microbial contamination of works of art, based on the analysis of specific DNA genomic sequence. It is performed by the technique of *in vitro* amplification (able to increase specific target sequence of microbial genomic DNA), named Polymerase Chain Reaction (PCR).

MICROBIAL DNA SOURCES

Microbial particles (MP) can be sampled by swab, nylon membrane or gelatine filters fragments. In order to recover the MP, swabs or nylon membrane fragments were re-suspended in 500µl of 1X TE solution (10 mM Tris-HCl pH 7.5 / 1 mM EDTA) incubating at 4 °C for four hours; subsequently MP are collected by microfuge centrifugation at 14,000 rpm for 10 min.

MOLECULAR IDENTIFICATION

Reliable detection and characterization of microbial taxa by molecular analysis is based on: *i*) microbial genomic DNA extraction; *ii*) set up amplification profiles of specific target sequences (molecular markers) by polymerase chain reaction (PCR); *iii*) determination of base composition of PCR products (sequencing); *iv*) sequences analysis by using dedicated software (bio-informatics) and design of relative dendrograms.

Microbial particles represent one of the source of microbial genomic DNA, that can be extracted by using specific laboratory protocols or commercial kits. Routinely, we utilize QIAamp DNA Stool mini kit (*QIAGEN*) or Genomic DNA Purification kit (*Fermentas*),

properly modified in relation to the samples characteristics (Figure 14.31).

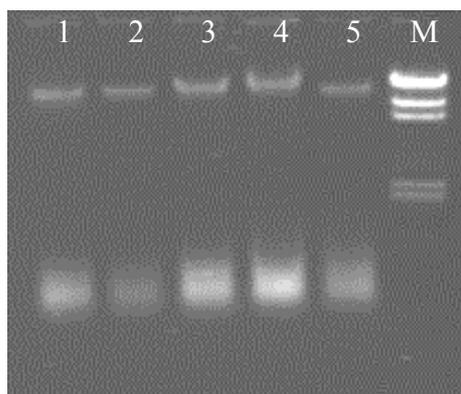


Fig 14.31 – Agarose (0.8%) gel electrophoresis. Genomic microbial DNA extracted from isolated bacteria and fungi colonies (lines 1-2), directly from MP sampled by gelatine filter (line 3), nylon membrane (line 4), sterile swab (line 5).

M = molecular marker λ -Hind III.

Standard PCR amplification profile provides 30-40 cycles of amplification, in thermocycler, with the following steps:

- 1) denaturing at 95 °C for 30 seconds;
- 2) primer annealing at 50-60 °C for 1 minute;
- 3) polymerization at 72 °C for 1 minute.

These steps are preceded by a denaturing step at 95 °C for 4-8 minute, and followed by a final polymerization step at 72 °C for 7 minutes, to ensure that all PCR products were full-length and 3'-adenylated.

Primers for target sequence amplification can be designed on the basis of the rRNA genes/ rDNA intergenic sequences, called Internal Transcribed Spacer (ITS).

The identification of taxa is performed by sequencing of the PCR fragments, in order to determine the DNA nucleotide composition, followed by the homology research by the algorithm BLASTN in nucleotide data bank (NCBI-NIH – USA, EMBL-Germany), which allows to draw the corresponding dendrograms (Figure 14.32).

In conclusion, molecular technologies provide a non invasive sampling and a direct analysis of microbial DNA target sequences. It provides a repertoire of techniques with high specificity and speed of execution that implements significantly the microbiological analysis. Combining the results from microscopy, *in vitro* culture and molecular analyses we are able to describe the almost complete composition of microbial consortium. This is

essential for understanding the microbial deterioration in indoor environments, in order to control the microbial development and the related potential illness for visitor and/or professionals.

So, the precise identification of fungal and/or bacterial species, related to the environment and to the constitutive materials of the artefacts, leads to the definition of the indices of “Attention” and “Risk” for both deterioration of cultural assets and health of the users/operators.

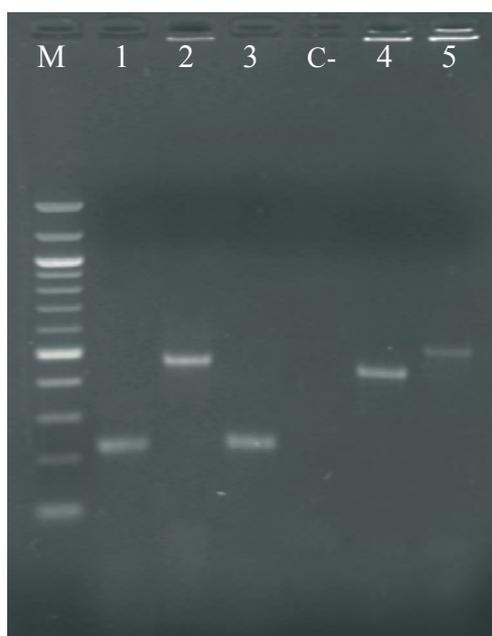


Fig 14.32 – Agarose (2%) gel showing the PCR-products obtained by amplification of ITS regions. DNA fragments between 220 bp and 500 bp in length (lines 1-3, 4-5) are shown.

Negative control = C-; molecular marker 100bp DNA ladder = M.

Sequencing and sequences homology analysis identified four different microbial taxa.

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