

Lecture Notes in Chemistry 79

Evangelia A. Varella *Editor*

Conservation Science for the Cultural Heritage

Applications of Instrumental Analysis

 Springer

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Editor
 Evangelia A. Varella
 Department of Chemistry
 Aristotle University of Thessaloniki
 Thessaloniki
 Greece

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Equation 4.15 is written for a single level of structure, such as a collection of spherical primary particles, but it can be extended to two levels of structures (i.e. a collection of primary particles that assemble to form clusters), as described by Beaucage [40] for mass fractal-aggregates.

In the field of Cultural Heritage, this approach has been used in order to evaluate both gyration radii and the fractal dimension for some pottery samples. The question was whether the size and surface characteristics of the aggregates of minerals are parameters sensitive to the firing technology used to produce the pottery [41]. In particular, the authors tested the possibility of determining the firing parameters and their correlation with the age of the finds, enhancing the knowledge on some technological choice made in producing the ceramics found in Cuma and Miseno. Moreover, the estimation of firing temperature of this ceramic typology could be useful to identify the production centres [42].

Teixeira method. Teixeira in 1988 modelled the scattering intensity as [43]:

$$I(Q) = AP(Q, r, d_s)S(Q, r, d_m, R) \quad (4.15)$$

$$P(Q, r, d_s) = \left(1 + \frac{\sqrt{2}}{3} Q^2 r^2\right)^{\frac{d_s-6}{2}} \quad (4.16)$$

$$S(Q, r, d_m, R) = 1 + \frac{d_m \Gamma(d_m - 1)}{(QR)^{d_m}} \left(1 + \frac{1}{(QR)^2}\right)^{\frac{1-d_m}{2}} \sin[(d_m - 1) \arctan(QR)] \quad (4.17)$$

where A is a constant dependent on the overall pore concentration and the chemical composition of the sample, $P(Q, r, d_s)$ is the form factor whose value depends on the shape of the individual scatterers and their surface fractal dimension, $S(Q, r, d_m, R)$ is the structure factor that reflects the degree of order in the system and mass fractal behaviour. In these equations, d_s is the surface fractal dimension, $d_m - 1$, R and r are both correlation lengths, $\Gamma(d_m - 1)$ is the gamma function of $d_m - 1$. R and r are both correlation lengths, R gives the size of the fractal aggregates, and r is the size of the individual scatterers.

Teixeira method has been applied to some marbles. The provenance of stone object is of key importance to archaeology in so far as artistic, technological or commercial exchange patterns may be studied and correlated to historical events and social contact between cultures. It was demonstrated that the structural features at a mesoscopic level are strongly correlated to the metamorphic degree. Thus, it is believed that they can offer a fingerprint to trace the stone provenance. With this aim, various marble samples from the Mediterranean basin [24] and from Marble Canyon, Texas [25] were investigated. The scattering intensity analysis by means of Eq. 4.15 allowed to evaluate porosity, pore distributions (characterised by mass fractal dimensions) and grain surface morphology (characterised by surface fractal dimensions).

4.2.5 Conclusions

In this work, a short description of principles, instrumentation, and data analysis methods for SAXS and its application in the field of Cultural Heritage science was presented. The technique is widely used for structure investigation on various kinds of materials. Its application on the field of Cultural Heritage is rather new and, till date, rather exotic. With respect to the more traditional XRD it allows to evaluate size, polydispersity and spatial arrangement of particles in a sample. Moreover, it allows determining interfacial or surface structure. Data acquisition does not require any particular sample manipulation, but, surely data treatment requires a quite strong effort. This, together with the accessibility of high-flux instrumentation, accounts for the few SAXS application in the Cultural Heritage fields. Notwithstanding, the techniques reveal to be unique in order to get accurate and reliable structural details.

4.3 Energy-Dispersive X-Ray Diffraction in Cultural Heritage Science: The Winning Duo of Structural and Elemental Analysis

Lorenzo Gontrani, Ruggero Caminiti, Maria Luisa Saladino, Eugenio Caponetti and Delia Chillura Martino

Abstract The capabilities of Energy-Dispersive X-ray Diffraction (EDXD) in the field of Cultural Heritage are discussed. EDXD diffractometer, equipped with a white source, is particularly suited for the structural and elemental analysis of items having different nature. Given its compact and versatile design, the instrument allows to collect data from samples without tearing down of any portion and with no specific preparation. In the wide energy range sampled during the measurements, both X-ray fluorescence and diffraction features appear. In all cases, data are acquired in air and in a non-destructive way, and their collection is fast.

4.3.1 Introduction: Why Energy-Dispersive X-Ray Diffraction?

The spectroscopic techniques, employed for the investigation of various art works, based on X-ray radiation provide the opportunity to carry out analyses without sample damaging. Different kinds of X-ray analyses may be used such

as XRD [44, 45], XRF [45, 46], PIXE [47] and X-ray photoelectron spectroscopy (XPS) [48]. Among these techniques, XRD represents a powerful non-destructive technique providing information on the structural features of the samples at the atomic level, although for a complete characterisation of the material the elemental composition is often desirable, since, for example, some artists may have used specific paints containing particular compounds. The detection of these components can help in tracing back the sample to a certain artist or time frame. Moreover, it may be essential to understand the elemental composition of the piece to find a means to prevent further decomposition for conservation purposes. XRF provides a valuable tool to obtain the sample bulk composition. This can be assessed since fluoresced X-rays are a fingerprint of the atoms from which they originate [49].

Structural and compositional features may be simultaneously extracted from EDXD experiments. This non-conventional diffractive technique has been generally used for the structural investigation of samples characterised by a short-range order [50]. For this reason, all systems of artistic and historical value with a low degree of crystallinity may potentially be studied by EDXD, though; the technique is not limited to non-crystalline systems only, as witnessed by some recent studies [51]. Therefore, since it provides XRF spectra in addition to XRD patterns, EDXD is a powerful tool that gathers the typical advantages of spectroscopic techniques, being completely non-destructive, with the added value of providing the structural features of the sample. Finally, the acquisition times are sensibly shorter than those typical of any other in-house apparatus being of the order of seconds [52].

4.3.2 Theory

Information about the atomic structure of a sample can be gained by observing the modulation of the intensity spectrum of a probe whose wavelength is comparable with the interatomic distances. If the probe is electromagnetic radiation, the wavelength is in the X-ray range.

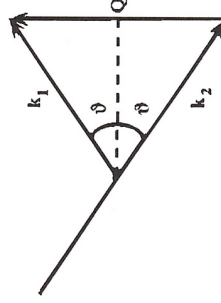
The XRD theory due to Thomson and Debye (a completely classical approach) describes this modulation of the probe intensity spectrum, which arises because of interaction with the sample, as the effect of coherent superposition of waves elastically scattered by atomic core electrons that are regarded as small antennae scattering with a dipolar distribution. Despite the neglect of quantum effects, that can be anyhow added as perturbations by introducing some suitable corrections (e. g. Compton scattering), the theory is able to explain the features and the characteristics of diffraction patterns and to obtain the structural information they carry. The elastic contribution to the scattering is a function of the momentum Δk exchanged (“transferred momentum”) by the radiation with the atomic tightly bound electrons. For a generic system, Δk is a vectorial quantity, having three components, and measurements of the intensity must be carried out by observing

in turn each of them. However, for isotropic systems, the intensity depends only on the modulus of Δk and not on its orientation. In this case, a scalar quantity Q can be defined called the scattering parameter [45], which represents the modulus of Δk expressed in \hbar units.

Diffraction patterns can then be drawn by plotting the scattered intensity as a function of Q .

The relation between q and the experimental quantities is:

$$Q = 2k \sin\theta \quad (4.18)$$



2θ being the total scattering angle and k the modulus of both wave vectors k_1 and k_2 of the incident and scattered radiation [46] respectively. In fact, by assuming that the scattering is elastic, the energy E of the radiation remains unchanged during the scattering process. Moreover, according to the dispersion relation of an electromagnetic radiation, $E = \hbar ck$, where n is the refraction index and c is the speed of light, and k , the modulus of its wave vector (wavenumber) is proportional to its energy. Therefore, in the hypothesis of elastic scattering, the wave vector of radiation interacting with a sample can vary its direction but not its modulus; that is, the X-ray beam can be deflected but it maintains its wavelength unchanged. As E is proportional to k (Eq. 4.18), the following equation holds:

$$Q(E, \theta) = \alpha E \sin\theta \quad (4.19)$$

where α is a constant (equal to $2/\hbar c \approx 1.01354 \text{ \AA}^{-1} \text{ keV}^{-1}$) in the approximation that n at the typical energies of X-rays is always unity, regardless of the material forming the sample (usually $1 - n = 10^{-6}$, as an order of magnitude). The former relation is another way of expressing the well-known relation $Q = (4\pi/\lambda) \sin\theta$, where λ is the radiation wavelength.

Summarising, two methods are available to perform a scan of q and to draw the scattered intensity profile as a function of it. In the first method, a monochromatic beam is used (the emission spectrum of a laboratory X-ray tube or of a synchrotron is filtered through a monochromator) and q -space is spanned with an angular scan [angle-dispersive X-ray diffraction (ADXRD)], while the second one employs a continuous spectrum radiation, often called white by analogy with the visible light, for example the Bremsstrahlung of the same X-ray tube, the scattering angle being fixed (EDXD). Although it had been known for a long time, the second method became widely available only at the end of the 1960s [50, 53]. In fact, only at that

time solid-state detectors with an acceptable resolution became available allowing the construction of a new kind of diffractometer.

Among the advantages of the use of EDXD to study disordered systems [49, 51], the most important are: (1) the intensity distributed in the entire white spectrum (EDXD) is, approximately, from one to two orders of magnitude higher than the intensity concentrated in the fluorescence line (ADX), this implies a reduction in the acquisition time; (2) The apparatus remains fixed during data collection. This simplifies the experimental procedure, since the beam trajectory is fixed. In fact, unlike ADXD, no movements may compromise the alignment, inducing systematic errors. This is particularly important for the careful treatment of artistic samples. (3) Parallel collection of the spectrum points. While in the ADXD method spectrum points are collected in a sequential way, EDXD permits multiple acquisition—the points are collected simultaneously at each value of Q (or E ; see Eq. 4.19).

Yet, some limitations must be pointed out: (1) Data processing is more complicated, because of the energy dependence of all involved quantities: a separate treatment of each energy component is required. (2) It is necessary to join various X-ray spectra.

In fact, according to Eq. 4.19, at a given angle, using a radiation having a continuous energy spectrum in the interval ($E_{\text{low}}, E_{\text{high}}$), the accessible Q range in the reciprocal space is $\Delta Q(\theta) = Q_{\text{high}} - Q_{\text{low}} = \alpha (E_{\text{high}} - E_{\text{low}}) \sin\theta$. Therefore, to cover the widest possible region of q -space, more than one measurement (i.e. more than one scattering angle, usually up to four-five) is needed. The various spectra must then be joined to reconstruct the whole diffraction pattern. (3) Decrease in the Q resolution. Besides angular resolution (shared by both ADXD and EDXD), in EDXD an additional electronic resolution term originated by the detector and by the electronic chain has to be taken into account. This is the most important reason why EDXD is preferred for non-crystalline systems: its broad peaks are less affected by the energy uncertainty than the sharp Bragg peaks of crystals. However, the versatility and rapidity of the technique makes a lot of non-conventional measurements otherwise not possible (e. g. time-resolved experiments, to follow phase transitions, etc.), so that the drawbacks are completely overcome.

As already mentioned, in addition to scattering, samples irradiated by X-rays can absorb and eventually re-emit a radiation (fluorescence). The fluorescence lines are detected and superimposed on the pure diffraction spectrum; thus, additive contributions represented by extra intensities at characteristic energies appear. Such lines that are generally removed in a diffraction experiment can be conversely very useful in the analysis of cultural heritage samples, since they yield the elemental composition (both qualitative and quantitative, if a suitable calibration is performed). It is worth noticing that the energy of a fluorescence emission is independent of the diffraction geometry (θ): this implies that the fluorescence lines do not vary with the angle. On the contrary, the diffraction peaks positions depend on both the energy and θ . This also implies that changing θ will result in the shift of diffraction peaks (ascribed to a given q value) to lower or higher energies.

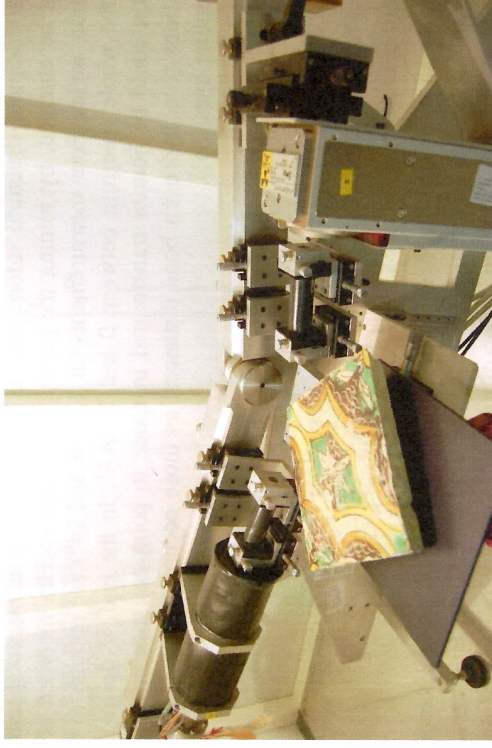


Fig. 4.16 EDXD Diffractometer “at work” with a decorated eighteenth century Sicilian floor

4.3.3 Instrumentation and Data Treatment

The EDXD diffractometer shown in Fig. 4.16 operates in vertical θ/θ geometry and is equipped with an X-ray generator, a collimating system, two-step motors, and a solid-state detector connected via an electronic chain to a multichannel analyzer. The X-ray source is a Seifert tube (W target) operating at 55 kV and 45 mA whose Bremsstrahlung radiation is used whereas the detecting system is composed of a solid-state photon (HPGe) detector (Ortec) cooled by an X-cooler system and connected to a PC through ADCAM hardware.

Both the X-ray source and the detector can rotate, by an angle θ , around the focus where the volume of the sample to be investigated is placed. Alternative instrumental geometries are possible: in the $\theta/2\theta$ vertical geometry, the X-Ray tube remains fixed (X-axis), while the detector is moved vertically (Y-axis); the same configuration can be reproduced in the horizontal plane by replacing the step motors with a ring-nut system.

The measuring time for a given scattering angle, necessary to obtain data with a high signal-to-noise ratio, depends on the absorbance of the sample under investigation and ranges from thousands of seconds for the smallest angles (up to 8°) to hundreds of thousands of seconds for the largest ones (10 – 30°). Besides the scattering measurements, the “transmission” of the full and of the empty cell (i. e. at zero scattering angle) is recorded, and used to perform the necessary corrections for the sample absorbance. A couple of single angle measurements (that corresponds to diffraction spectra with Q range given by Eq. 4.18) may be sufficient to identify the fluorescence lines, and consequently to obtain the qualitative elemental composition of the sample, or to confront the diffraction peaks with those of known samples, to point out the presence of structural features in the specimen.

If more complete structural information is needed, the continuous spectrum in Q must be obtained, by joining the partial diffraction spectra recorded at more diffraction angles. Four measurements (at 1, 3, 8 and 24°) are enough to reconstruct the whole spectrum between 0 and 20 \AA^{-1} . In the end, if desired, such spectrum could be Fourier transformed in space to point out specific structural correlations (i. e. hydrogen bond distances, as those occurring between proteins and painting dyes [54]).

4.3.4 Examples of Simultaneous Detection of Diffraction and Fluorescence

The presented technique has been successfully employed on several samples of interest in the field of Material Science. In the field of Cultural Heritage, information have been obtained on: composition and structure of layered samples (surface and cardboard of old photos), characterisation of buried samples, elemental composition of alloys of jewels, structural analysis of books, with particular regard to the ageing processes; [55] comparison of cellulose polymorphs in old and modern papers; [44] analysis of polychromies in ancient potteries from Pesaro and Faenza [56]

In the present paper, a study of an eighteenth century Sicilian finely decorated floor tile (see Fig. 4.16) from an ancient villa in Ribera (Agrigento, Sicily) is reported. The floor tile, in good overall conservation state, shows glossy front side stylized and coloured, reddish-white rear side. The aim of the investigation was to shed some light on the elemental composition of pigment used in the various decorated zones.

It is important to underline that all the experiments were performed with no removal of parts of the ancient tile, and with no modification of its properties.

Spectra at two angles were acquired to discriminate fluorescence from diffraction contribution. As an example, the spectrum of an orange coloured area is reported in Fig. 4.17. From the lower spectrum registered at $6.7^\circ \theta$, several peaks were revealed. The correct attribution to emission fluorescence or diffraction is prevented unless, as previously said, the measure is repeated at a different angle. In fact, the upper spectrum acquired at $14.9^\circ \theta$, shows a number of peaks falling at the same energy of some of the previous peaks. These peaks were thus attributed to the fluorescence emission of Pb, Sn, Ca, Fe and Sb. The unmatched peaks are diffraction ones. Measurements were repeated in various areas of the same colour and the spectra were superimposable.

Spectra acquired, by means of the same procedure, from the different coloured areas allowed to detect the emission lines of the elements listed in Table 4.5.

Pb and Sn are referred to the enamelled glassy surface, while Fe and Ca derive from minerals constituting the original argillaceous matrix. Fe engendered the reddish colour in the rear side of the tile. The simultaneous presence of Ca, Fe, Pb

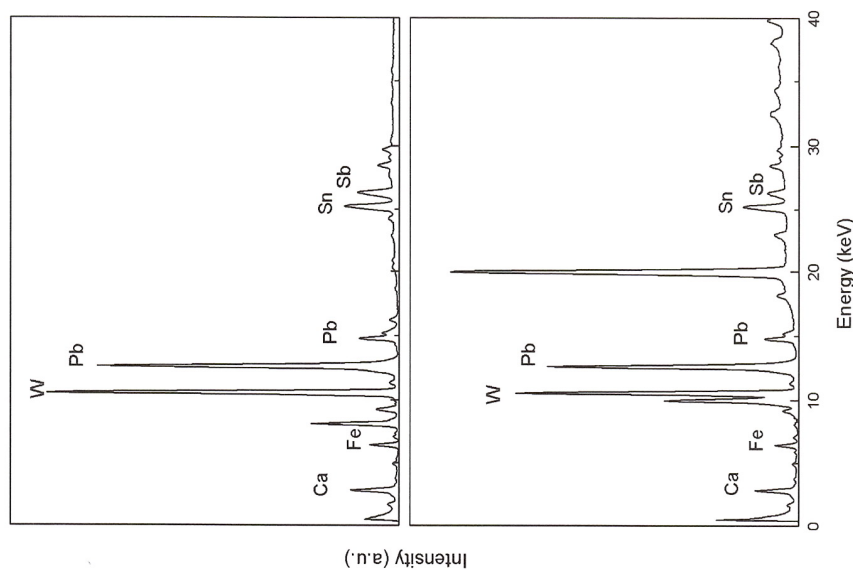


Fig. 4.17 EDXD spectra from *orange* coloured area: lower spectrum registered at $6.7^\circ \theta$; upper spectrum registered at $14.9^\circ \theta$. The fluorescence lines are indexed by the element symbols

and Sn, therefore, indicates that the analysed volume extends to a layer deeper than the thickness of the coloured layer.

The orange and yellow pigments are characterised by the Sb presence. It, as antimonates and mixed with Pb oxides in different ratios, accounts for the different shades.

The green pigment contains Cu, as the typical rameic compounds do.

The brownish/black colour evidences the Mn presence. It, as MnO_2 , causes different brown shades [57–60].

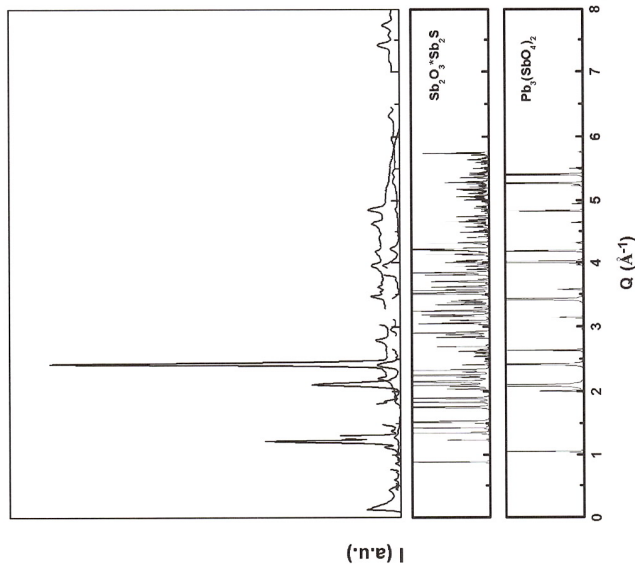
In order to compare the diffraction spectra with those of the mineral compounds present either in the pigments and the ceramic body, the energy scale in the EDXD spectra was converted on a Q -scale by means of Eq. 4.19. As an example, data acquired at 6.7 and $14.9^\circ \theta$ for the orange pigment are reported in Fig. 4.18. The fluorescence lines have been manually removed in order to improve the readability of the graph.

The diffraction patterns of the $\text{Sb}_2\text{O}_3 \cdot \text{Sb}_2\text{S}_3$ (orange) and $\text{Pb}_3(\text{SbO}_4)_2$ (yellow) are reported on the same Q -scale at the bottom of Fig. 4.18. The comparison

Table 4.5 Elements revealed in the colour of the floor tile

Orange	Pb	Sn	Ca	Fe	Sb
Yellow	Pb	Sn	Ca	Fe	Sb
Green	Pb	Sn	Ca	Fe	Cu
Brownish/black	Pb	Sn	Ca	Fe	Mn
White	Pb	Sn	Ca	Fe	—

Fig. 4.18 EDXD spectra, intensity versus Q ($Q = \alpha E \sin\theta$), from orange coloured area. In the two graphs on the bottom, the diffraction patterns, on the same Q -scale, for $Sb_2O_3 \cdot Sb_2S$ (orange) and $Pb_3(SbO_4)_2$ (yellow) are shown



between reference patterns and experimental spectra allows identifying some of the diffraction peaks thus further confirming the fluorescence findings.

Even if the study here discussed is purely qualitative, the presented approach is particular useful for the non-destructive investigation of decorated samples. It is worth noticing that the composition and the structure of pigments are strongly dependent from the raw material used and from the production methodologies.

4.3.5 Conclusions

In this work, the description of an Energy-Dispersive X-ray Diffractometer and its capabilities in the field of Cultural Heritage science is presented. The instrument proves to be well suited to get both compositional and structural information from

a unique measurement. Its design turns to be particularly advantageous in the field of Cultural Heritage because it allows obtaining data from a very large variety of samples without any particular preparation and without sampling of any portion.

A study of a decorated floor tile has been presented. The analysis of the fluorescence emission from the decorated layers allowed identifying the elemental composition. In addition, the qualitative comparison of the diffraction peaks with those of reference patterns confirms the composition of the pigments, in terms of relative amounts of different minerals. The main advantage of this approach lies in the availability of both compositional and structural information by a unique measurement on the same area of the sample, thus avoiding variability of results deriving from a non-uniform distribution of components. Obviously, the method here presented can be developed in order to gain quantitative results.

4.4 Particle Induced X-Ray Emission Spectroscopy in Conservation Science

Nick Schiavon

4.4.1 PIXE: Introduction

In the often-interconnected archaeometry and conservation science research fields, acquiring data on the bulk and surface elemental composition of objects of art and archaeological artefacts constitutes an essential step in any methodological research approach. Geological provenance of raw materials, identification of ancient production techniques and reconstruction of commercial trade routes are just some of the topics in archaeology where advanced chemical analyses of materials play a crucial role in confirming (or refuting) hypotheses by historians and archaeologists. Similarly, identification of pigments in paintings, pottery and ancient manuscripts and/or characterisation of corrosion products and mechanisms affecting various cultural heritage materials (stone, glass, metal amongst others) are some of the topics in conservation where chemical data provides a much needed helping hand. In fact, it is fair to affirm that only by knowing the bulk and surface chemistry of materials a conservator may be in the position of selecting the most appropriate restoration products and methods to be applied to any given case study.

The range of analytical techniques available to scientists for the chemical characterisation of heritage materials is extremely vast. In this respect, spectroscopic analytical techniques, i.e. techniques that analyse the electromagnetic radiation absorbed, emitted or scattered by molecules or atoms in irradiated samples, now play a pivotal role in any analytical protocol in cultural heritage