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Portable Spectroscopic Techniques for the Non-invasive Identification of two historical yellow pigments: Applications and Practical Challenges

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Abstract. Decades of technological advances in instrumental analysis have transformed many techniques from laboratory in portable analytical tools with increasing their applicability in situ to the study of cultural heritage. It is known that the painting realisation varies from artist to artist, and the identification of the pigments provides a decisive contribution to trace their authenticity and to support an appropriate restoration work. However, in some cases, due to the complexity of painting composition, it is difficult to distinguish between pigments having a similar chemical composition and colour. Here, a systematic study through combined use of portable non-invasive spectroscopic techniques such as Raman, Total Reflectance FT-IR spectroscopy, Fiber Optical Reflectance spectroscopy and X-Ray Fluorescence was carried out on two yellow pigments, the *Naples Yellow* ($Pb_2Sb_2O_7$) and the *Giallorino* (Pb_2SnO_4 or $PbSnO_3$ or $PbSn_{1-x}Si_xO_3$), which sometimes are difficult to distinguish. The results emphasize the techniques' main advantages and drawbacks as well as their limits and the importance of their combination for the discrimination of such pigments.

Keywords: Multi-analytical approach, portable spectroscopic techniques, *Naples Yellow*, *Giallorino*.

1. Introduction

Scientific analysis of artworks can aid in their authentication and attribution, providing information on painters' techniques and restoration strategies [1-3]. In detail, the analysis of pigments is a rich source of information. Pigments represent a class of heterogeneous and complex materials; their composition and recipes are linked with the workshops and the historical period. Over the centuries, lead-based yellows pigments of different composition have been used [4]. The long period of use of lead-based yellow pigments led to many documents in different languages employing various names describing the same compound. For instance, in Europe artists and writers such as Cennini, Lotto, Vasari or Symonds regularly used the term *Giallorino* to indicate a pale yellow material of various compositions. The main manuscripts containing the first examples of recipes for the production of yellow pigments are based on oral sources and on workshop notes [5]. The problem arises from the transcription of these notes that was made by copyists and not by experts. During the transcription many mistakes were made that have been handed down to us creating problems in the identification and their differentiation. In this work, the characterization of two yellow pigments, both by Zecchi store collection [6], the *Giallorino* and



Naples Yellow (NY), through the combined use of spectroscopic analytical techniques that can be employed non-invasively and in situ, is reported. All pigments by Zecchi are produced following the recipes of Cennini (*Il Libro Dell'Arte*), or other artists of the past. So that, in our opinion, the above two pigments can be considered as the original and / or "historical" ones and could be used as a reference. The *Giallorino* is a lead-tin yellow type I (Pb_2SnO_4) or type II (PbSnO_3 or $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$). The *NY* is identified as lead antimonate. It is known that the popularity of each of the Pb-containing yellows changed with time. According to Wainwright et al. and Kühn, both lead-tin yellows type I and II were preferred between 14th and 17th centuries. During 17th century, lead-tin yellows gradually evolved to lead antimonate yellows (Naples) [7]. In detail, *NY* prevailed among Pb-based yellows in the period from 1750 to 1850. Very early studies, e.g. Watin in 1773, placed the origin of *NY* to Naples, Italy, as a manufactured colour or naturally formed mineral found near the sulphur mines on Mount Vesuvius [8]. In addition, it is well-known that the so-called Naples yellow, especially if prepared according to the recipes (such as those of Giovanni Battista Passeri or Valerio Mariani da Pesaro [5,9,10]), is composed of Pb, Sb but also Na or K and that the $\text{Pb}_2\text{Sb}_2\text{O}_7$ compound is not stable [11] or other compounds not well-characterised containing K [9].

With respect to these facts, Pb-containing yellows are considered suitable for dating and for tracing back to a specific geographical location of an art work. However, despite their different chemical composition, their identification is sometimes not easy, because of the limits of the used techniques.

For example, the XRF signals of Sb or Sn may not be easily recognized because rather weak. Furthermore, it must be taken into account that in a real case the determination of tin or antimony could be complicated by the presence of other pigments or by the influence of the preparation. Depending on the concentration of the pigment present, its detectability becomes doubtful in that the counts are very low or not very significant because result at the limit of detection of the instrument [12]. On the other hand, Raman and IR spectra could be affected by the presence of other components. In the case of Raman spectroscopy, fluorescence emission due to some organic components could covering the signals of the pigments.

Parameters such as the raw materials used for their preparation or the processes of production, but also the type of binder used or degradation processes affects of some properties of pigments such as the color, making them similar, and consequently difficult to discriminate through FORS spectra and chromaticity coordinates [9]. Here, Total Reflectance FT-IR (TR-FTIR) and Fiber Optical Reflectance Spectroscopy (FORS), X-Ray Fluorescence (XRF) and Raman Spectroscopy are used for the non-invasive characterization of the two yellow pigments in combination with X-Ray Diffractometry (XRD) as micro-invasive technique in order to emphasize the importance of a combined use of several analytical techniques, as well as the main advantages and drawbacks of each technique.

2. Instruments

TR-FTIR spectra were acquired by means of Bruker ALPHA FTIR portable spectrophotometer in the spectral region between 4000 and 600 cm^{-1} with a resolution of 2 cm^{-1} and averaging 30 scans.

FORS spectra were acquired by using Ocean Optics reflectance spectrophotometer equipped with a DH mini light source and a USB 2000 + XR1 detector, operating in the spectral range 350 –1100 nm. The *XRF spectra* were acquired by using the Tracer III SD Bruker AXS portable spectrometer equipped with Rhodium Target X-Ray tube operating at 11 μA and 40 kV and a silicon drift X-Flash SDD with Peltier cooling system and 3-4 mm diameter spot as detector.

Raman spectra were collected in the 300-3200 cm^{-1} range, through a Bruker BRAVO equipment. The instrument uses SSETM (Sequentially Shifted Excitation) a patented fluorescence mitigation that permits to measure a much extensive range of materials with handheld Raman than ever before. Samples were excited by using two lasers centred at 785 and 853 nm and working together to mitigate the fluorescence phenomena and offering highest sensitivity across the entire spectral range.

XRD patterns were acquired by using a Philips PW 1050/39 powder diffractometer in Bragg-Brentano geometry using Cu cathode ($K\alpha = 1.5406 \text{ \AA}$, 40kV, 30mA), in the 2θ range between 5 and 80° , step-size of 0.05° and acquisition time for each step of 30 seconds. Crystalline phases were identified with the X'pert HighScore® software.

3. Results and discussion

TR-FTIR, FORS, XRF and Raman spectra and XRD patterns of *NY* and *Giallorino* pigments are shown in figures 1-4.

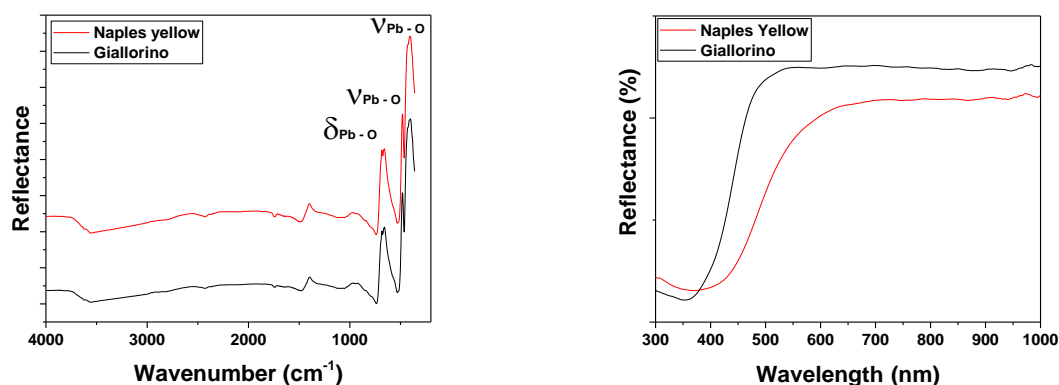


Figure 1. TR-FTIR (left) and FORS (right) spectra of *Naples Yellow* and *Giallorino* pigments. The TR-FTIR spectra of *Naples Yellow* are shifted to better compare the two spectra.

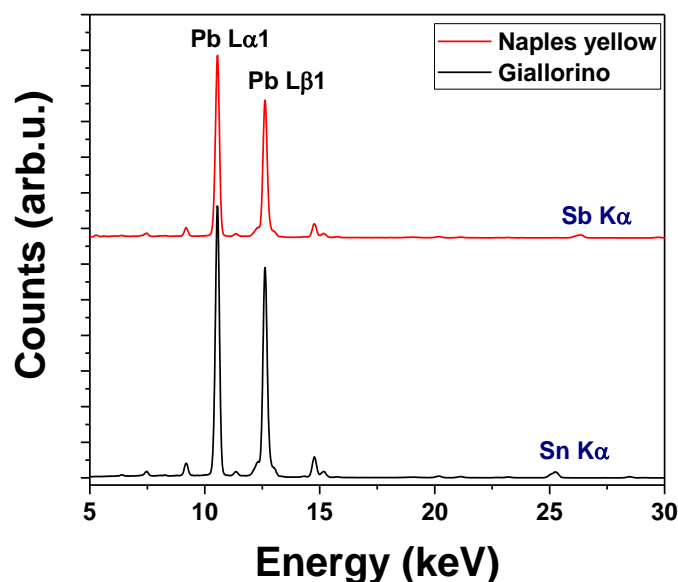


Figure 2. XRF spectra of *Naples Yellow* and *Giallorino* pigments.

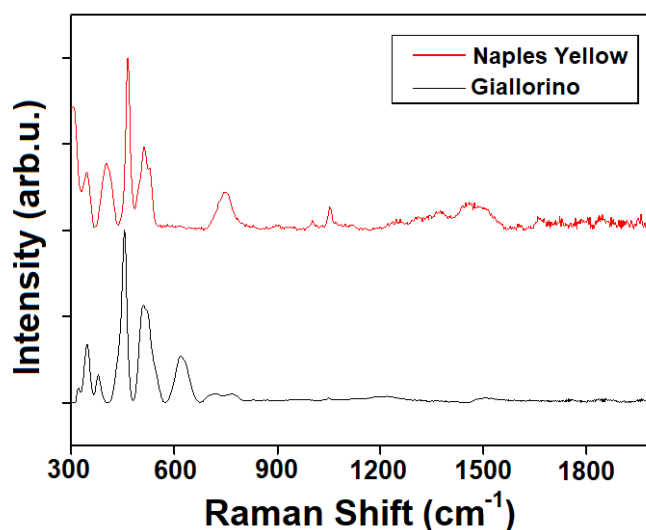


Figure 3. Raman spectra of *Naples Yellow* and *Giallorino* pigments.

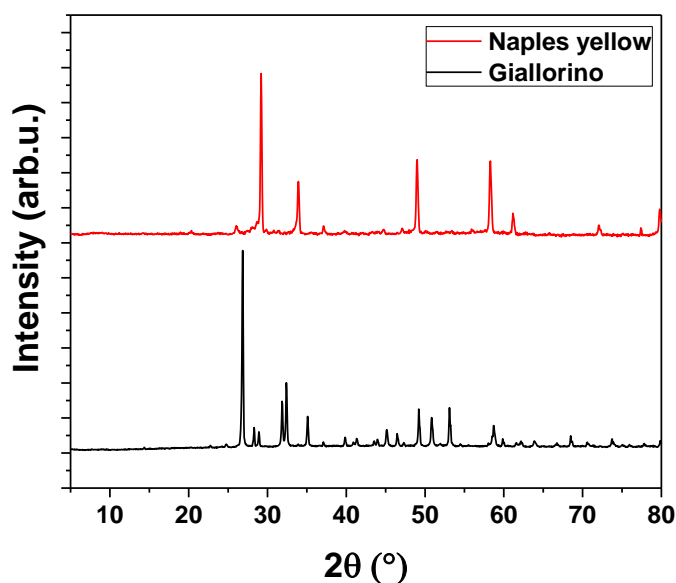


Figure 4. XRD patterns of *Naples Yellow* and *Giallorino* pigments. XRD references are: Pb_2SnO_4 , Ref. code 00-024-0589, tetragonal crystal structure. $\text{Pb}_2\text{Sb}_2\text{O}_7$, Ref. Code 01-077-0543, pyrochlorine crystal structure. $\text{Pb}_{3+x}\text{Sb}_2\text{O}_{8+x}$ Ref. Code 00-034-1196, hexagonal crystal structure.

TR-FTIR spectra show well-resolved bands at 423, 473 cm^{-1} (Pb – O stretching) and 650 – 654 cm^{-1} (Pb – O bending), but not exhibit a significant difference that could provide information on the molecular composition of the two pigments, useful for their identification.

The FORS spectra show an S-curve typical of yellow pigments; the reflectance curve of *NY* shows a spectral trend characterized by an inflected around 500-520 nm, while the spectral trend of *Giallorino* is characterized by a very accentuated inflection around 420-430 nm. However, it is well known that the spectral trend of reflectance curves depends on the chemical composition of material, therefore FORS spectra are useful references for the identification of these two pigments, though the interpretation of

spectra relating to the colour fields in works of art is often not immediate for example due to the mixture of the pigments itself with others, such as black or white ones, or due to degradation processes. All these factors can cause a variation of the spectral trend, a shift of the curve or a variation of its intensity [9]. XRF spectra give the immediate information on the nature of the pigments. In fact, they show the strong Pb peaks as expected for lead-based pigments. In addition to Pb, the signal of Sb in the spectrum of the *NY* and of Sn in the spectrum of *Giallorino* were detected, respectively. Since the Si signal was not detected, the elemental analysis could indicate the identification of lead stannate type I (Pb_2SnO_4). However, this analysis cannot permit the determination of the Pb oxidation state, thus the Raman Spectroscopy or the X-ray Diffraction techniques could be necessary.

Raman spectroscopy is able to discriminate between *NY* and *Giallorino* pigments. In detail, concerning *NY*, the spectrum shows typical bands at 346, 465 and 513 cm^{-1} in accordance with the literature [13], while others bands at 400 and 540 cm^{-1} indicates the presence of Pb II oxides impurities. Instead, Raman spectrum of *Giallorino* pigment shows the typical bands of lead stannate type I (Pb_2SnO_4) characterized, in addition to the others, of the Raman band at 614 cm^{-1} and a shift from 465 to 454 cm^{-1} compared to *NY* pigment. On the other hand, XRD analysis is useful because the pattern of *NY* indicates the presence of $\text{Pb}_2\text{Sb}_2\text{O}_7$ (Ref. Code 01-077-0543, pyrochlorine crystal structure), but also of other types of lead antimonate with a different stoichiometry, in agreement with Raman spectrum. In detail, the XRD analysis showed the presence of compounds like $\text{Pb}_{3+x}\text{Sb}_2\text{O}_{8+x}$ (Ref. Code 00-034-1196, hexagonal crystal structure), also found by other authors, proving that it is not pure [7]. The XRD pattern of *Giallorino* gives the typical reflections of lead stannate type I (Pb_2SnO_4) corresponding to the file with reference code 00-024-0589 (tetragonal crystal structure), in agreement with Raman results.

4. Considerations

The knowledge of constituent materials contributes to the correct placement and “reading” of an ancient artefact. TR-FTIR, Raman and XRF spectroscopies are usually very useful and powerful techniques for the pigment characterization as both can be used in situ, are non-destructive and non-invasive. Concerning the identification of *NY* and *Giallorino*, while TR-FTIR spectroscopy does not provide a molecular imprint, FORS, XRF and Raman spectroscopy are able to discriminate between them.

FORS spectra are distinguished thanks to the molecular compositions of the two pigments. However, it must be remembered that the pigments are hardly applied pure and that a different hue changes the trend of the reflectance curve.

XRF spectroscopy showed the discriminating chemical elements for pigment recognition. In fact, the Sn and Sb counts are determinable with the portable instrument used. Further specific and in-depth information on composition of two pigments can be achieved by Raman Spectroscopy as confirmed by XRD analysis.

In this paper we wanted to test non-invasive investigation techniques for the characterization of pigments. The work has highlighted the limits and potential of each technique in the ability to discriminate the two pigments. Similar considerations could be done for other kind of pigments having similar chemical composition and colours such as *Orpiment* and *Realgar* where their identification is not easily unique.

In any case, even if the gold standard in the scientific examination of cultural heritage are the non-invasive methods, sometimes the microinvasive investigation could help to answer properly to the questions of the restorers and conservators.

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