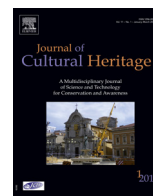




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Original article

## X-ray fluorescence investigation on yellow pigments based on lead, tin and antimony through the comparison between laboratory and portable instruments

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### ABSTRACT

This paper presents an investigation of yellow pigments based on lead, tin and antimony through X-ray fluorescence spectroscopy with the aim of comparing portable and laboratory instruments and discussing the potential application on artworks. Artificial yellow pigments, based on Pb-Sb-Sn, and produced in our laboratory, were chosen in order to have a well-known and already characterized sample set. The differentiation in artworks of these pigments is still a challenge if non-invasive portable X-ray spectrometers are used, as commonly occurs in practice. The analysis was performed by using the Bruker M4 Tornado laboratory equipment and the Assing Surface Monitor II portable apparatus. Scanning electron microscopy with energy dispersive spectroscopy was also applied for a semi-quantitative analysis of the chosen pigments. In order to perform a significant statistical comparison of acquired and processed data, all the analyses have been carried out by using the same sample, the same acquisition set-up and, at the same time, operative conditions for both instruments. A chemometric approach, based on the principal component analysis and multivariate analytical tools, was applied in order to verify the spectral differences, and related informative content, between the different produced yellow pigments. The multivariate approach revealed instrumental differences between the two systems and allowed the comparison of the common characteristics of the analyzed pigments set. The potential of this new approach is also linked to the possibility of differentiating artificial yellow pigments, both in terms of composition and, above all, in terms of recipes for their production.

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### 1. Introduction

X-ray fluorescence (XRF) is a diagnostic approach particularly suited to use in cultural heritage since it falls under the class of non-destructive and non-invasive analytical tools [1–8]. Indeed, among the variety of non-invasive in situ techniques, XRF spectroscopy is one of the most widely utilized techniques in cultural heritage applications despite some intrinsic limitations [3–9]. Moreover, 2D scanning is possible with more recently developed instruments allowing the element distribution in a selected area of interest to be obtained [10–13].

Portable X-ray fluorescence (p-XRF) instruments and their applications have gained considerable attention within the archaeological community in recent years [14], but the skepticism

regarding performance dominates debate today [15]. On the other hand, laboratory XRF based techniques have been a staple of archaeological science since the 1960s [16–19]. An appreciable number of these instruments in the past used radioactive isotopes rather than miniaturized X-ray tubes, making them difficult to transport across borders. So the term “portable” in XRF instruments has varied definitions, ranging from “being able to be carried by porters” [20] to “handheld” [21]. Portable XRF analyzers have approximately the size, shape, and weight of cordless drills and have a similar trigger. Weight and power consumption are also concerns for field use, however, the device sacrifices performance to gain portability [14]. The determination of the relationship between the intensity of the characteristic X-ray emission of an element and its concentration within a material is not simple and today it is possible only with benchtop XRF devices. In general, various effects, including the excitation of lighter elements by X-rays emitted from heavier elements and matrix effects, occur within a material, changing the measured intensities. Calibration standards

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(“matrix matched”) can be used to correct X-ray measurements. This analytical approach permits the quantification of the element in the analyzed matrix but it necessitates a priori knowledge of the “unknown material’s” approximate composition. Therefore, the analyst’s knowledge and experience are critical, in part, to recognize when data may be compromised by inappropriate calibrations [14–22]. The p-XRF measurement can be considered only for qualitative investigation, but recently, the analytical power of portable instruments has increased dramatically, and they are now frequently applied in mining, soil exploration and in the analysis of consumer goods [23]. The evolution of XRF devices has enabled the comparison of benchtop and portable instruments in different fields of research [24–26]. Modern benchtop XRFs are equipped with polycapillary optics that allow for generating high fluorescence intensities on even very small sample areas. The X-ray optics can focus tube radiation from a large solid angle to spots of less than 30  $\mu\text{m}$ . Moreover, the vacuum chamber permits better detection of light elements [27]. In order to compare benchtop and portable XRF spectrometers efficiently, a multivariate approach is necessary, as widely discussed in the literature [3,12,28–31]. This approach makes possible the extraction of information on variance and dispersion of many acquisitions and it enables the spectral results from techniques based on the same physical principles to be understood [32–35]. In addition, a comparison of the signals obtained by portable and benchtop X-ray spectrometers allows the best set-up for p-XRF to be chosen in order to obtain signal quality similar to that of benchtop apparatus.

Using this general overview as a starting point, in the present paper, we chose to investigate the application of portable X-ray fluorescence (p-XRF) and benchtop XRF instruments in order to differentiate lead-tin-antimony based yellow pigments, whose preparation and composition is well-known, with the aim of making a comparison in terms of quality and reliability of the results on the same analytical sample set. To reach this goal, a comparison was carried out between portable and benchtop X-ray fluorescence devices applied on different types of yellow pigments based on lead, tin and antimony produced in our laboratory and characterized by different analytical techniques [36]. The yellow investigated were prepared according to the stoichiometry ratio of the chemical elements in the final compounds and according to the instructions described in “old” recipes [36–40]. Scanning electron microscopy (SEM) was also applied to the powder samples for a semi-quantitative analysis. The data obtained by XRF acquisitions were elaborated by principal component analysis (PCA) and multivariate analytical techniques in order to verify the spectral differences and the related informative content among the different yellow pigments produced [12,41–43]. Principal component analysis was chosen as a preliminary and explorative technique, which is particularly useful for comparing the results, obtained with the two spectrometers (benchtop and portable) tested in the research. The main advantage of PCA is the possibility of evaluating data variance and, through loadings, of understanding which kind of signal has been obtained (not only the peaks but also the noise). By using PCA, it is possible to choose the best pre-processing methods in order to make the data comparable between the two different instruments.

## 2. Research aim

The main aim of this work is to evaluate the potential of two X-ray fluorescence instruments, laboratory and portable, in order to propose operative procedures in the context of cultural heritage.

In order to evaluate the results from the two different instruments, well-known and characterized yellow pigments based on lead, tin and antimony were chosen. These pigments, as already mentioned, were prepared in our laboratory according to ancient

recipes and also according to the stoichiometric ratio of the chemical elements in the final products. Following this strategy, an XRF based comparison, not affected by uncertain compositions often associated with commercial pigments, was carried out handling the resulting spectra by a chemometric approach (i.e. principal component and multivariate analysis) with the specific aim of verifying the spectral differences, and related informative content, between the different produced yellow pigments. XRF spectroscopy, as previously outlined, is a technique widely used in painting analysis due to its non-invasive and non-destructive characteristics. It has also been used for identifying and differentiating yellow pigments based on lead, tin and antimony, but some uncertainty remained due to the similar composition of these yellows and also due to the presence of other pigments often mixed with yellows, such as lead white or copper based compounds, which could alter element ratios and colour characteristics [44–46]. The possibility of differentiating yellow pigments, especially that based on lead and antimony, produced according to different recipes, is particularly relevant in artwork examination through the XRF technique. Indeed, this makes it possible to gather information on the period of production, the workshop and the geographical area [44,47–49].

## 3. Experimental

### 3.1. Investigated pigments

Eleven pigments samples were selected for the X-ray fluorescence spectroscopic investigation (Table 1). The chosen pigments were prepared according to both the stoichiometric ratios of the final compounds and the indications supplied by the recipes [36,38]. The quantities of reagents in the recipes are reported in Libras (ancient Roman measure equal to 327 g). Some pigments, one for each typology, were then selected for preparing paintings on commercial canvas and wood support. Both kinds of support were prepared by applying a traditional setting made of gypsum and glue. The commercial canvas may contain additives used to prepare the support, such as titanium white. The chosen pigments are: PSA2 (lead/tin yellow type I, prepared according to the Pb:Sn = 2:1 molar ratio), PSB3 (lead/tin yellow type II, prepared according to the stoichiometric ratio of Pb and Sn, starting from PSA2 with the addition of silica), APA3 (lead/antimony yellow, prepared according to the stoichiometric ratio of Pb and Sn) and APSA (lead/tin/antimony yellow, prepared according to the stoichiometric ratio of Pb, Sn and Sb). They were applied by linseed oil and rabbit skin glue binders.

### 3.2. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)

Yellow pigments were examined by SEM-EDS by using a JSM 5400 system with SIRIUS-SD 10128 LE electron probe micro analysis supplied by iXRF Systems. The crystal area is 10 mm<sup>2</sup> and the work distance 20 mm. The probe operated at 25 kV and 80 mA.

### 3.3. X-ray fluorescence spectroscopy set-up

X-ray fluorescence analysis was performed with the following instruments:

- Bruker Tornado M4 equipped with a Rh tube, operating at 50 kV, 500  $\mu\text{A}$ , spot 25  $\mu\text{m}$  obtained with polycapillary optics [50];
- Assing Surface Monitor II equipped with Au tube, operating at 50 kV, 300  $\mu\text{A}$ , spot 2 mm.

For each sample powder, 20 points of measurements were executed at three different acquisitions times: 30 s, 60 s and 240 s. In

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