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Portable X-ray Fluorescence Spectrometry for the Analyses of Cultural Heritage

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Abstract

The x rays are very useful in the characterization of works of arts for several reasons:

- an excellent penetration in many materials constituting the artifacts;
- basically simple interaction mechanisms that facilitate the development of techniques that have good specificity for some diagnostic tasks (such as x ray fluorescence spectroscopy for inorganic pigments);
- sources and detectors that can be miniaturized to set up portable or mobile systems.
- The measurements can be totally non invasive.

The last two reasons produced many new ways of making science on Cultural Heritage and this can be visualized by the number of scientific articles that appear every year on the subject.
In many situations FP-EDXRF (Field Portable X Ray Fluorescence) is the only non invasive technique that can be realistically used to gain some information about the chemical composition of precious and unique objects. FP-EDXRF has though two major drawbacks; the first is connected to the techniques, the information acquired is about chemical elements and not molecular compounds; the second is related to the non invasiveness of the technique, we have very little or sometimes no information about the material under analysis. That is way FP-EDXRF cannot be used as a standalone technique but needs the back-up of other methods of analysis. Even if FP-EDXRF can be applied to most of the materials present in the Cultural Heritage the back-up methods change with the change of the object studied. To use profitably FP-EDXRF it is necessary to carefully plan the session of measurements.

1. Introduction

In the last two decades the use of mobile or Field Portable (FP) spectrometers, mostly for Energy Dispersive X-Ray Fluorescence (EDXRF), in the archaeometric study of ancient artifacts has become a very common practice as testified by the very large number of papers that appeared in the scientific literature and in the presentations of the main archaoemetric conferences ([1], [2], [3]).
The use of a EDXRF mobile system for the characterization of an ancient artifacts is commonly judged as a precious tool in order to formulate initial hypotheses, to be verified through other kinds of analysis, often destructive. Most often, due to the uniqueness of the object no destructive investigations must be fulfilled and so FP-EDXRF remains the only possibility of gaining some

scientific information regarding the elemental composition of the object. As a matter of fact the most attractive thing in this context is the possibility to use the spectrometer in a Non Destructive (ND) manner in order to fulfill the need, often not ineluctable, not to damage the artifact. ND applications of a FP-EDXRF system does open methodological questions about the measure, which sometimes are not being probed into with the necessary attention and criticism, especially now that always more systems are being used by not scientific personnel.

The errors one might make, while performing a measure with a EDXRF spectrometer, can be classified in two large groups: conceptual (or methodological) and experimental.

These last ones are related to (i) the measuring system and (ii) the procedure adopted during the measure [4].

Many additional questions arise when the portable instrumentation is used with diagnostic purposes, which require different approaches to the measurement itself.

A diagnostic procedure is the identification of the nature or the cause of a particular process, which can take place through the detection of one of the components of the examined sample, but which also implies a preliminary knowledge of the process. The discrimination is extremely subtle: a diagnostic test assume a prior knowledge of what one wants to observe and thus makes it necessary to explicit the diagnostic query, not to perform a useless measure. In the case the first hypothesis is not being verified, the obtained results could produce another diagnostic hypothesis. Anyway, this only happens if there is a good knowledge of the process under identification; the practice of “blind” diagnostic tests is nevertheless very common. In other words the diagnostic approach does not increase the knowledge of the process but it helps verifying if it occurs. An important aspect is that the measure should be systematic and reproducible; in this case the difference with a scientific investigation tends to diminish.

A non-destructive measure is almost always repeatable but its reproducibility is limited because the exact repositioning is difficult and the local non homogeneity can change the result of the measure.

The study of an ancient artifact should take into account all of these concepts, since the aim of experimental archeometric investigation is frequently not the same as in pure research and in many different applied fields.

The practice in the use of non destructive spectroscopic systems in the archaeometric field leads to recognize the risk to assign incorrect meanings to the results obtained through ND investigations.

For example, the homogeneity of the sample is often an implicit assumption in most common analytical techniques; this cannot be true for non-destructive analyses because materials, especially ancient ones, frequently show an internal structure due to both production and degradation processes, and this structure is totally unknown to the scientist. This sets a limit for the precision obtainable while performing measures on ancient artifacts, unless it is possible to find zones of the object which are meaningful with respect to the investigation and in which the material is homogeneous.

A good knowledge of the material’s internal structure and of the degradation processes undergoing, allows to improve the methodology and evaluating the degree of precision of the results that can be obtained.

The use of micro-analytical techniques is most of the times advantageous, even though an average (macroscopic) composition is a parameter both more significant and more easily usable for an analysis on the single components of the sample.

2. Experimental set up

A FP-EDXRF equipment is composed of an X-ray source, an X-ray detector and a pulse height analyzer and naturally a computer. A portable EDXRF equipment must be of small size and light-weight [5].

For this reason a small size X-ray tube may be employed, coupled with a Si-PIN or a Si-drift X-ray detector. Considering the elements to be analyzed and their concentration in typical works of art, the following equipments are currently suggested:

- a small size and low power X-ray tube, working at about 50 kV maximum voltage, and about 100 μA of maximum current; the X-ray tube anode should be selected according to the specific problem;
- a Si-drift detector, with a thickness of about 400–500 μm, and an energy resolution of about 130–150 eV at 5.9 keV or less (the less the better);
- a small size pulse height analyzer.

Filtering the X-ray tube output should be done according to the elements to be analyzed, this operation is very important, with the right filtering it is possible to enhance the needed chemical elements.

When elements emitting low-energy photons (typically from 2 keV to about 5 keV) are analyzed, filtering should be avoided. On the contrary, when elements emitting X-rays from about 5 keV to about 35 keV are analyzed, filtering is needed, and sometimes mandatory, to eliminate the low-energy tail of the incident X-ray spectrum, which only contributes to the background and slows down the system.

Collimation of both X-ray tube and detector is in any case useful; the X-ray tube collimation should be carried out according to the area and concentration of the element to be analyzed. The detector should be weakly collimated, only to avoid scattered photons in the detector.

3. Results

We now show three applications of FP-EDXRF to illustrate the possibilities of the method all carried out with non destructive procedure and *in situ*. The cases are related to paintings, bronzes and stone like materials.

In most of the cases it is evident the fact that FP-EDXRF needs as a backup other non invasive techniques in order to optimize and enhance its results.

“Peter Paul Rubens's painting "Saint Gregory the Great surrounded by the Saints Papianus, Maurus, Flavia Domitilla, Nereus, and Achilleus" in the Musée de Grenoble”

Non-invasive analyses on the huge canvas of Peter-Paul Rubens "Saint Gregory the Great surrounded by the Saints Papianus, Maurus, Flavia Domitilla, Nereus, and Achilleus" (2.88 m x 4.77 m), which is today in the Musée de Grenoble, France were conducted. The painting was studied for the first time by art historians and scientists together.

In September 1606 Rubens has received from the Oratorian Fathers the commission to paint the high altarpiece for Santa Maria in Vallicella (known also as Chiesa Nuova), their main church in Rome. The commission was linked on a decision to move the Madonna della Vallicella, a venerated, miracle-working fresco dating from the fourteenth century, from a side chapel to the high altar where both

images should have appeared together. On 30 January 1608, the painting was refused and Rubens was given the opportunity to complete a new, three-parted ensemble for the altar, finished in October 1608 and still *in situ* (see Figure 1).
Rubens's high altar paintings have received ample attention from art historians for the abundance of surviving archival and pictorial material but no global scientific investigations of Rubens's Grenoble painting were carried out up to now. On the huge painting imaging techniques and spectrometric techniques have been applied: grazing light, ultraviolet photography, IR reflectography, digital X ray Radiography, EDXRF, SEM/EDS and micro FTIR.

Figure 1: Rubens canvas in Grenoble

The work found severe problems due to the dimensions of the painting and due to the fact that the museum room could not be closed for too many days. The canvas was therefore dismantled from the frame and set vertically on the floor along the widest dimension. The first half of the painting was at this point easily analyzed. The painting was rotated and the second half was finally analyzed. The work was done mainly during night because it was impossible during day time to cut the parasite lights. The work in its all took three full nights. To cover the full painting more than 400 UV and infrared photo were made and 166 X-ray radiography were shot (see Figure 2). 32 EDXRF were fulfilled to determine the palette used by Rubens. Availing of the IR and the X ray radiographic results it was possible to sketch the different versions that the painting undergone in the course of its life. It was possible to connect all the versions found in the underlying levels to drawings of Rubens itself or to copies that were made in time.

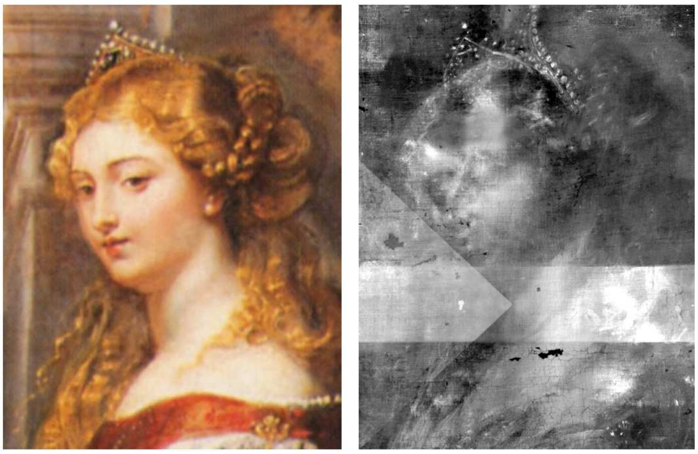

Figure 2: details of Saint Domitilla in visible light and X ray

For non invasive chemical analyses FP-EDXRF was the only technique available: non invasive, fast, reliable and with immediate results. The UV, IR and RX results were used to successively choose the points to analyze. Along the centuries the painting had received damages that were restored in time. The imaging techniques previously fulfilled in respect to the XRF were necessary to identify points that belonged to the restored sections and points that were a stratification of different versions of the painting. Without this information, the interpretation of the XRF spectra would have lead to wrong results.
In Figure 3 a spectrum of a violet pigment is presented, the complexity of the mixture is evident, a part the white lead present in the preparation, the tone in composed of white lead, red cinnabar, ochre and copper blue while zirconium is a component of the X ray tube collimator.

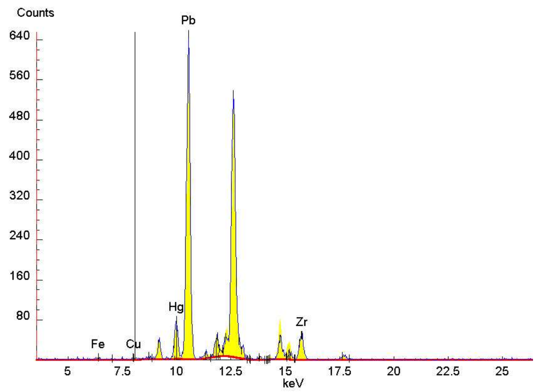

Figure 3: XRF spectrum of a violet pigment in Rubens painting.

The use of XRF technique to define the components of the alloy and patina in a Chinese bronze finishing, in the form of a Taotie Mask (X-VIII Century B.C.E.)

A bronze finishing in the form of a Taotie mask was examined within the ambit of a campaign for the diagnostic investigation and conservation of East Asian works of art.

The radiographic and subsequent conservation work revealed that the artifact consists in a number of tin/lead-soldered fragments; to clarify possible pertinence and homogeneousness, quality-quantity fluorescent energy dispersion X-ray analyses were carried out.

The analyses revealed that the object is composed of 13 fragments of various compositions; this implies that some parts of the object are the result of restoration integrations. The EDXRF and PCA multivariate examinations permitted the recognition of fragments in ternary alloy, homogeneous among themselves and, probably, the originals. These are different from the other fragments that present heterogeneous compositions and may, therefore, be considered extraneous. In Figure 4 the thirteen fragments are sketched.

Figure 4: in red EDXRF analyses, in false colors, the subsequent sub-division based on the multivariate data interpretation of the results.

In table 1 the semiquantitative results (ROI area) are presented and in Figure 5 the PCA multivariate results are shown.

Table 1: Semi-quantitative results (peak areas) of the analyzed points.

Measure	Fe	Cu	Zn	Ag	Sn	Sb	Pb
1	607	274240	4840	185	417	566	3971
2	525	182703	3044	128	886	469	1771
3	235	6711	1002	-	12198	78	27298
4	468	191024	2843	131	302	470	1216
5	47	20904	-	-	1912	-	4351
6	268	115217	1794	61	139	216	668
7	352	36754	-	41	3287	-	1453
8	50	43230	-	50	5637	-	1466
10	135	82290	-	-	218	-	477
11	190	140551	-	178	12112	-	4455
12	138	108492	-	118	9475	-	3786
13	113	19370	-	-	1447	-	3310
14	-	6400	-	-	3455	97	9502
15	701	252342	4184	174	172	497	1964
16	267	73870	-	93	7487	-	2622
17	825	210186	3535	167	286	471	3698
18	213	107609	1680	84	461	232	981

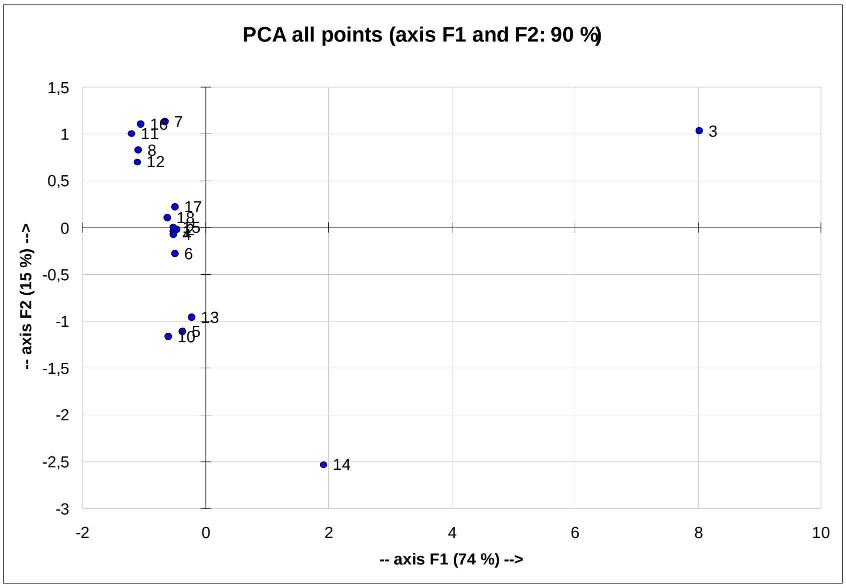

Figure 5: PCA multivariate results on data in Table 1 with outliers.

FP-EDXRF Sulfur-concentration analyses carried out on the facade of the Scrovegni Chapel in Padua.

Within the planned works of preservation, which are previous to a restoration stage, sulfur-concentration analyses have been carried out on the facade of the Scrovegni Chapel in Padua with classical methods and availing of portable non invasive EDXRF system (see Figure 6). The aim of the measures was to quantify the level of sulfation of the mortars and bricks belonging to the facade.
A very dangerous weathering process which deteriorates stone monuments, and is caused by human activity, is air pollution. One of the worst pollutants for carbonated monuments is associated with sulfur compounds and, when all is said and done, with gypsum. Gypsum is a rather soluble compound that may be washed away by rain. It leaves the surface clean but eroded and open to new corrosive processes. In 1993 the mortars between the bricks that were presenting high sulfur levels were eliminated and at the same time a waterproof protective coating was laid on the facade.
Forty EDXRF measurements were fulfilled, the first 25 in relation to a grid that the restorers had prepared for the monitoring processes among the years. The last 15 spots were chosen *in situ*, during the last measuring campaign. The analyzed spot is 1 square mm and the deepness reached is of few microns, in relation to the low excitation energy of the sulfur atoms. The measurements, totally non invasive, were fulfilled in a quantitative manner availing of portable EDXRF system optimized for the sulfur analyses and a set of sulfur standards. The measurements were fulfilled, furthermore, with the classical methods.
The EDXRF results showed the presence of a gradient with the sulfur concentration over all the facade. The gradient had is maximum at the ground level of the facade and diminished with the height (see Figure 7). Two possible reasons of such a behavior could be connected to the high molecular weight of the sulfur based molecules in respect to the air and to the vertical air streams gradient.

Figure 6: EDXRF sulfur analyses on the Scrovegni facade

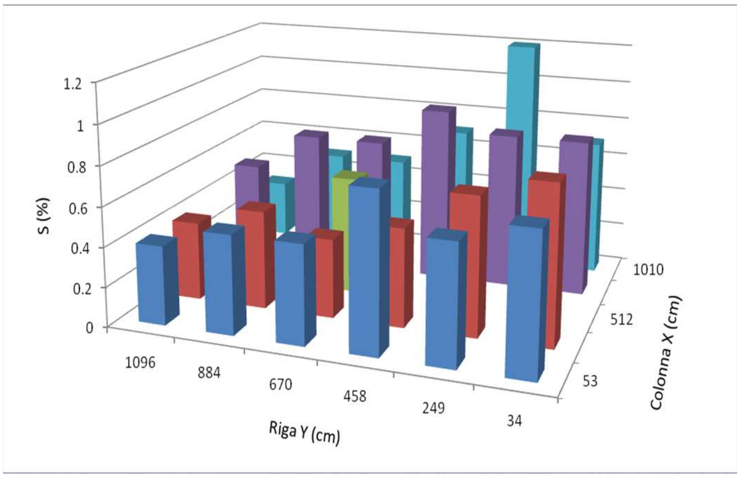

Figure 7: 2D representation of the sulfur results

4. References

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