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Portable EDXRF in a multi-technique approach for the analyses of paintings

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Energy-dispersive X-ray fluorescence (EDXRF) with its portable capability, generally characterised by a small X-ray tube and a Si-PIN or Si-drift detector, is particularly useful to analyse works of art. A variety of works, such as paintings of all types (including frescos and illuminated manuscripts), bronzes and brasses, gold alloys, silver alloys, ceramics, porcelains and faiences, papers, ink, stones of all types (marbles, obsidians, etc), stamps, glass and so on can be studied using portable EDXRF equipment. In some cases, the information gathered is of paramount importance, such as to determine the pigments in a painting or the alloy composition in gold objects. The aspects that mainly characterise the EDXRF technique are its being non-invasive and quasi-bulk. These characteristics that make the technique so powerful and appealing are, on the other hand, the main sources of uncertainty in EDXRF measurements on cultural heritage. In the paper, it will be shown that this uncertainty is intrinsic of every non-invasive technique, especially when dealing with paintings. A Caravaggio canvas painting, Calling of Saint Matthew (1559 AD), and a Signorelli wooden painting, The Altarpiece of Paciano (1517 AD), are shown to address this point.

Introduction

Energy-dispersive X-ray fluorescence (EDXRF) with its portable capability, generally characterised by a small X-ray tube and a Si-PIN or Si-drift detector, is particularly useful to analyse works of art[1]. The most important aspects that characterise the EDXRF technique are it being non-invasive and quasi-bulk.

These characteristics that make the technique so powerful and appealing are, on the other hand, the main sources of uncertainty in XRF measurements on cultural heritage. This problem is even more evident when we analyse paintings because of their intrinsic stratigraphic essence.

As a matter of fact, a painting is made of several layers: the support, which can be made mainly of wood, canvas and paper; the preparation layer, mainly gypsums or white lead or coloured pigment; pigment layers; and, finally, the protective varnish layer. The penetrating power of X-rays makes it so that, most times, the information from all the layers reaches the detector. Studies are being conducted to try to resolve this superimposition, but up to now only simple cases have been resolved[2]. Most of the information that is in the spectrum arrives from deep layers of which we have little or no knowledge. To better understand this concept, let us use the equation of A Markowicz[3]:

$$\sigma^2_{tot} = \sigma^2_{sample\,representation} + \sigma^2_{sample\,collection} + \sigma^2_{sample\,handling} + \sigma^2_{sample\,preparation} + \sigma^2_{analysis} \ldots (1)$$

in which the several uncertainties that influence the analyses with portable EDXRF are reported.

Let us adjust this equation for non-invasive portable EDXRF analyses. The second, the third and the fourth term do not exist, for obvious reasons. Only the first and the last term influence the total uncertainty of an EDXRF analysis. The ways to reduce the influence of the fifth term are known by any scientist: good stability of the system, a long measuring time, correct standard samples, good energy resolution, etc. But what about the first term when we are executing a non-invasive analysis?

An example that shows the influence of the sample representation in the increasing uncertainty of an XRF analysis is a case in which we are asked to determine the original pigments used in a painting. If we have no clue as to where restoration areas are located on the painting, the probability of analysing a 'wrong' pigment is surely high and therefore the probability of having a high uncertainty in our results is also high. Without a good representation of the painting to analyse, the total uncertainty could be very high, even when correctly applying all the analytical procedures for XRF analysis.

The only way to reduce the influence of the sample representation uncertainty in the EDXRF technique is to back-up the EDXRF analysis with different kinds of techniques that help to reduce the total uncertainty. These techniques can be imaging techniques such as UV light, IR reflectography and radiography, which are totally non-invasive as is the EDXRF one.

These techniques already have an independent application in cultural heritage with their own protocols and expected results. For our requirements, we limit their results to the fact that UV light is able to detect surface restorations and IR reflectography intercepts restorations in the deeper layers, while X-rays define even deeper problems. These imaging techniques gain new importance from a scientific point of view when they help in choosing the right spot

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for analysis and therefore reduce the total uncertainty of EDXRF analyses. The sample representation of a specific surface of the painting is greatly increased when, prior to any EDXRF analysis, we are able to fulfil non-invasive imaging techniques.

In a few words, it is possible to state that Equation (1) demonstrates that portable non-invasive EDXRF in cultural heritage needs a multi-technique approach to reduce the total uncertainty of its results.

To show the importance and necessity of a multi-technique approach when using EDXRF on paintings, we describe the cases of:

- Caravaggio, *Calling of Saint Matthew*, in the Contarelli Chapel in Rome, Italy;
- Luca Signorelli, *The Altarpiece of Paciano*, in the National Gallery of Perugia, Italy.

In this paper, only the case in which EDXRF is utilised to determine the original pigments used by the painter and how he used them will be discussed. As it is easy to imagine, there are many more questions that EDXRF can be called on to answer and, for any of them, the method with which the multi-technique approach is applied is different.

Case studies and results

Calling of Saint Matthew by Caravaggio, in the Contarelli Chapel in Rome, Italy[4]

In 1559, Caravaggio was asked to decorate the Contarelli Chapel in the Church of San Luigi dei Francesi in Rome. A year later the *Calling of Saint Matthew* was delivered. The painting is 322 cm × 340 cm. The wonder of the painting, which was an immediate sensation, is the beam of light that enters the picture from a window following the arm of Jesus and depicting the change of the destiny of Saint Matthew. On the painting, 38 EDXRF analyses were fulfilled. The work on the EDXRF results had three directions of research. For the first, it was necessary to study the pigments used by Caravaggio; for the second, retouches and restoration pigments were looked for; and for the third, clues were sought as to how Caravaggio was able to reach his aesthetic goals availing of a simple palette of colours, as it was pointed out from the first research. It was therefore necessary to understand how the painter was using the different colours in different situations, such as, for example, the dark shades near a bright light in comparison to the use of dark pigments in dark environments. This is the case presented in the next Figures. In Figure 1, the point of EDXRF analysis (red dot) can be seen. It was necessary to understand if Caravaggio was building the dark area close to an illuminated area of the painting in a different way, for example, as in the completely dark high left side of the canvas.

In Figure 2, the EDXRF spectrum of the analysed point is shown. The high quantity of lead (related to white lead pigment) and a high quantity of iron (related to an ochre pigment) and manganese (related to a burned ochre pigment) is evident. The zirconium peaks are part of the instrumental background.

The presence of white lead could be related to a white preparation and this is easily detected by the presence of a uniform occurrence of the pigment in every EDXRF measurement. But, in this specific point of analysis, the presence of lead was explicitly high. A thoughtful conclusion could be that Caravaggio was passing from light to dark with the superimposition of a dark pigment over a brighter one. This idea could have been very important in the study of Caravaggio's painting technique, but this was wrong. In Figure 3, an infrared reflectography image of the section of Caravaggio's studied painting is shown and it is possible to realise that, exactly under the EDXRF

Figure 1. Caravaggio, *Calling of Saint Matthew*, EDXRF spot of analysis (marked in red)

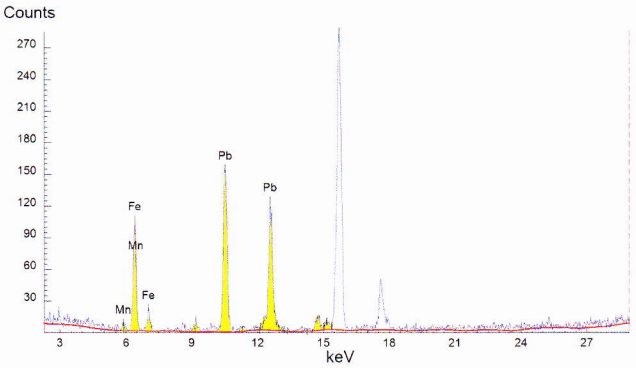

Figure 2. EDXRF spectrum of the spot on the Caravaggio's painting

point of analysis, an important pentimento was present. Caravaggio had painted Jesus's arm higher in respect to the final representation and, rather than erasing the first thought, he simply covered it with a dark pigment (as is usually done). EDXRF is a penetrating technique due to the penetrating capabilities of X-rays and therefore, in a single spectrum, the first version and the second were recorded. This explains the abnormal presence of white lead.

It is evident that the interpretation of the EDXRF spectrum with or without the correct awareness of an under painting would be very different. In the second case, it would be difficult to understand why Caravaggio used white lead and dark ochre to build a dark shade and the uncertainty of the result would be very high.

The Altarpiece of Paciano by Luca Signorelli, in the National Gallery of Perugia, Italy[5]

The Altarpiece of Paciano is a large wooden painting (215 cm × 310 cm) now located at the National Gallery of Perugia in Italy. The painting has the signature of the painter and is dated 1517; at the bottom of the painting it is possible to see the old city of Paciano that commissioned the work.

An intensive scientific campaign was fulfilled during the restoration of the painting. The painter Luca Signorelli is not well studied, or at least, is studied less than more famous painters. It was therefore important to characterise as much as possible the palette of the pigments usually

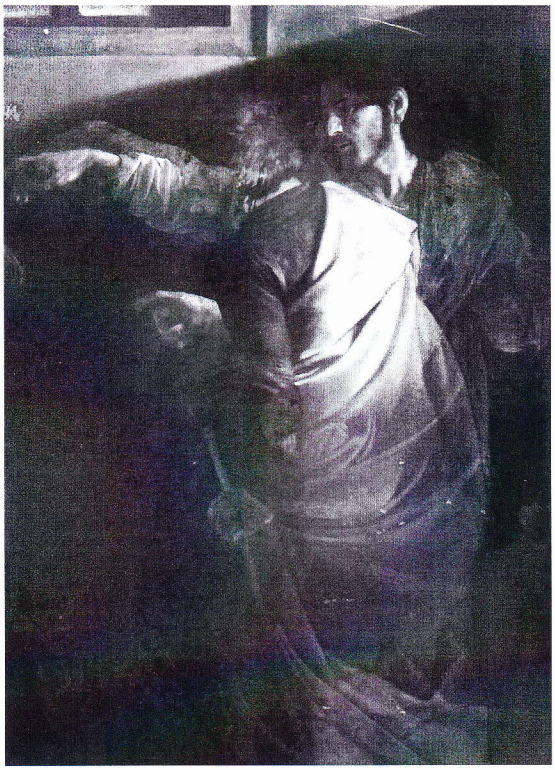

Figure 3. Caravaggio, *Calling of Saint Matthew*, infrared reflectography

used by him. It is reported that the painting showed conservation problems a few years after the Signorelli conclusion and other painters' restoration portions were expected to be found.

The multi-technique approach was applied to try to differentiate the original sections from the restored ones.

In Figure 4 it is possible to see a full view of the altarpiece with the points indicated where EDXRF analysis was fulfilled. 51 EDXRF analyses were conducted on the altarpiece.

One of the questions posed was how the painter was able to show such a bright incarnate for which he was famous. The face of the Holy Mother was chosen to solve this puzzle. In Figure 5, the results of the head of the Holy Mother analysed in different imaging techniques are shown. It is easy to see areas with pentimento, such as the crown of the Holy Mother that was made in antiquity and areas with restorations such as the one on her right eyebrow.

The different diagnostic techniques applied to characterise the area of the painting are able to show a stratigraphic non-invasive analysis of the chosen area. From UV reflectography to visible light to infrared reflectography to radiography, the depth of the information increases, showing restorations that go from the newer to the older correspondingly.

Only after a deep study of the above results is it possible to choose the right spots to fulfil EDXRF analyses. The project is still ongoing. The results of the study will be published soon.

Conclusions

The aspect that mainly characterises EDXRF when applied to cultural heritage is its being non-invasive. This characteristic, together with the capability of reading information from deep layers, is the main source of uncertainty in XRF measurements on cultural heritage. The only way to reduce the influence of this uncertainty is to apply a multi-technique approach. In painting analyses, it is necessary to back-up EDXRF results with multi-spectral imaging.

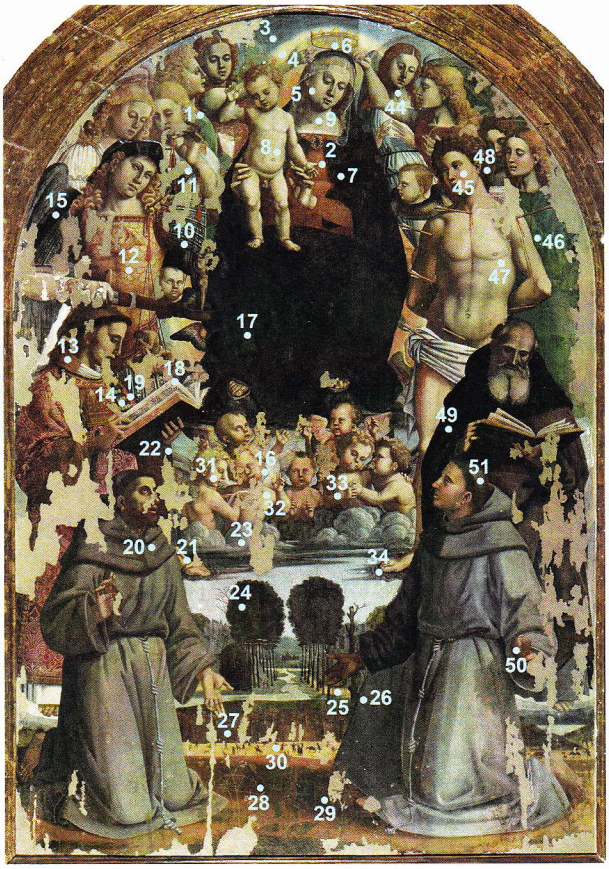

Figure 4. Signorelli, *The Altarpiece of Paciano*, EDXRF spots of analyses

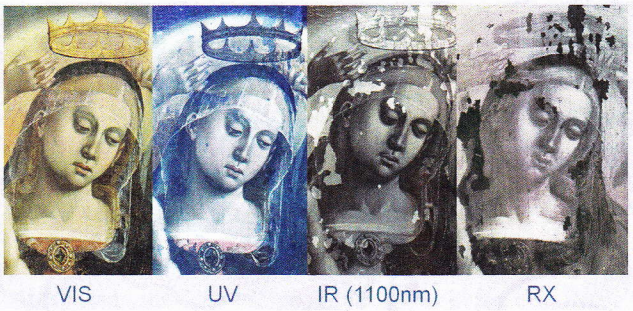

Figure 5. Signorelli, *The Altarpiece of Paciano*, multi-spectral imaging of the Holy Mother's head

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