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Multilayers quantitative X-ray fluorescence analysis applied to easel paintings

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Abstract X-ray fluorescence spectrometry (XRF) allows a rapid and simple determination of the elemental composition of a material. As a non-destructive tool, it has been extensively used for analysis in art and archaeology since the early 1970s. Whereas it is commonly used for qualitative analysis, recent efforts have been made to develop quantitative treatment even with portable systems. However, the interpretation of the results obtained with this technique can turn out to be problematic in the case of layered structures such as easel paintings. The use of differential X-ray attenuation enables modelling of the various layers: indeed, the absorption of X-rays through different layers will result in modification of intensity ratio between the different characteristic lines. This work focuses on the possibility to use XRF with the fundamental parameters method to reconstruct the composition and thickness of the layers. This method was tested on several multilayers standards and gives a maximum error of 15% for thicknesses and errors of 10% for concentrations. On a painting test sample that was rather inhomogeneous, the XRF analysis provides an average value. This method was applied in situ to estimate the thickness of the layers a painting from Marco d'Oggiono, pupil of Leonardo da Vinci.

Keywords X-Ray fluorescence · Quantitative analysis · Multilayers · Varnish · Thickness estimation

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Introduction

X-ray fluorescence is a mature technique for qualitative and quantitative analysis of materials. It is used in many fields of application because it is rapid, simple and inexpensive and it allows the analysis of a wide range of elements. The growing use of portable systems makes in situ applications possible, particularly in the field of cultural heritage where objects cannot be removed easily from their location [1–3]. With these systems, the analysis is non-destructive and does not require any sample preparation [4–6].

It is recognised as an accurate technique for quantitative analysis. In general, the concentration of an element in the sample can be seen as the combination of three terms: a calibration constant, the measured peak intensity and a correcting term which takes into account the effects of the matrix composition, mainly absorption and enhancement effects [1]. Two methods are essentially used to make this matrix correction: the theoretical influence coefficent method and the fundamental parameter method. The determination of influence coefficents to calculate concentrations from intensities requires a large number of well-analysed standards. In order to overcome this limitation, there has been a growing interest in the provision of an intensity-versus-concentration algorithm; this would allow to calculate the concentration values without using standards [7]. In this fundamental parameter method (FP) the relative ratios between intensity and concentration are calculated from the fundamental equations according to the spectrometer geometry (incident and emergent angles), the measuring conditions (detector–sample distance, X-ray tube target, kV, Be window thickness...). The performances of this method are now well established for bulk materials [8].

In the field of cultural heritage, objects can be inhomogeneous, irregularly shaped and can present a layered structure.

As an example, the painting technique is based on the superposition of several layers of microscopic pigment particles mixed in an organic medium. After the previous paint layer applied and dried, other layers are eventually added as needed. During the Renaissance period, thin transparent layers mainly organic (called 'glazes') were often applied on the painting layers in order to provide depth and volume. A final coating of varnish is added to protect and to improve the finish of the painting. The thickness for the whole structure ranges from 10–20 μm to 1 mm or more [9].

From these kinds of materials arises the problem of appropriate reference and data interpretation. Recent efforts have thus been made to achieve reference-free analysis [10, 11] and to investigate the layered structure of paintings. The recently developed 3D micro X-ray fluorescence spectroscopy enables three-dimensional-resolved investigation of elemental distribution in samples. An analytical model has been developed for quantitative analysis with a synchrotron-based confocal geometry [12, 13]. The depth resolution is about 23–25 μm. With a confocal tabletop setup, the resolution is lower and the quantification is still in progress. Another possibility is to use conventional X-ray fluorescence with the FP method in which the theoretical expression of the XRF intensity is expressed as a function of sample composition, layer thickness, photo-electric cross-sections, and mass absorption coefficients. Equations have been derived for the calculation of X-ray fluorescence intensities from bulk and multilayer samples [14]. The accuracy of this method was demonstrated [15, 16] with quantitative analysis of single and multilayered samples. It was recently applied in the case of a monochromatised radiation (from a Mo anode X-ray tube) for multilayer treatment to estimate painting thicknesses (on reference and historic paintings) [17].

The aim of this work is to show the possibilities of the software PyMca [18] for multilayer quantitative analysis and thickness estimation, in the case of a portable system with a polychromatic X-ray tube. We focus on organic layers (varnish and glazes) thickness estimation. Varnish and binding media consist of organic compounds (such as vegetable oils, egg yolk, egg white and resins) and thereby predominantly contain light elements, and cause only modest absorption for the fluorescent radiation from the heavier elements [6].

Our method was tested on several multilayer references: polymer thin layer standards laid on a thick metallic plate and a test painting prepared by a restorer. As an example of in situ application, we estimated the varnish thickness of a panel painting by Marco d'Oggiono (Milanese pupil of Leonardo da Vinci), the 'Holy Family with St Elisabeth, St Joachim, and the little St John' of the Louvre museum.

Experimental conditions

The XRF spectra were acquired with a portable system designed and constructed in the C2RMF laboratory. This system is equipped with an X-ray tube with a silver anode.

Fig. 1 (C2RMF, Elsa Lambert, 2008) 'Holy Family with St Elisabeth, St Joachim, and the little St John' (around 1515). Panel painting by Marco d'Oggiono, Milanese pupil of Leonardo da Vinci from the Louvre museum (F17301). The lines and the points on **b** indicate respectively profiles and isolated points analysed with XRF
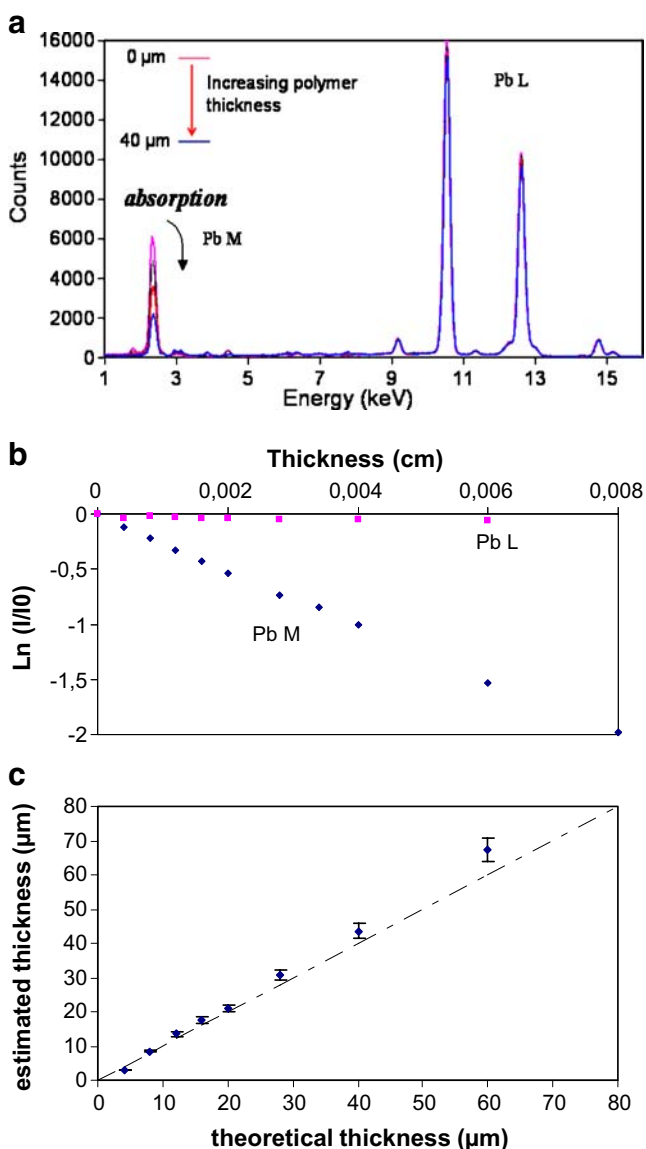
Fig. 2 XRF analysis on polymer layers (8 μm, 20 μm and 40 μm) laid on a thick lead plate. **a** X-ray fluorescence spectra (150 s, He flux 1.5 L.min^{-1}): with increasing number of polymer layers: the absorption increases leading to the decrease of the Pb M lines. **b** Evolution of the transmitted fraction (Ln I/I_0) of the Pb, M and L lines (respectively at 2.35 and 10.55 keV) in function of the polymer thickness. **c** Comparison between the certified (*straight line*) and the estimated thicknesses (*filled circle*) with PyMca treatment

The beam size at the sample surface was limited to approximately 1 mm^2 using a collimator. A Si(Li) AXAS-V detector from Ketek (SDD), cooled by Peltier effect, reaches the energy resolution (FWHM) of about 140 eV at 5.9 keV at the working temperature. The operating conditions of the tube were 35 kV and 95 μA. The distance from the sample to the detector was 2.7 cm, the beam impact angle 45° and the detection angle 90°. Flowing out of the detector, helium allows the detection of elements down to sodium (flux 1.5 L.min^{-1}).

The spectra were processed by PyMca software (version 4.3.0) [15].

First experiments were performed with very thin metallic and polymer layers of known composition and thickness in order to confirm the efficiency of the setup and the analytical procedure for our applications. Various 4-μm layers of polymer (ultralene, from SPEX CertiPrep, $d=$ 0.73 g cm^{-3}) were laid on a thick lead plate to model a varnish layer applied on a white lead-based painting layer.

Then, a test painting, prepared by a restorer according to the fifteenth to sixteenth century recipes [19], was also analysed. This test painting is composed of a *gesso* layer, a mixture of gypsum and animal glue, laid on a wood support as a preparation layer. Various layers of lead white mixed with linseed oil were applied on the *gesso* substrate. In some parts of the painting, vermilion (HgS) was added. Then, glazes, containing linseed oil and a few content of manganese oxide as a pigment, were applied. No final varnish was added. Thus, polymer layers were also laid on some part of the surface painting to replace the varnish and obtain a more complete model for Renaissance paintings. Finally, a panel painting by Marco d'Oggiono, a Milanese pupil of Leonardo da Vinci, '*The Holy Family with St Elisabeth, St Joachim, and the little St John*' (around 1515) of the Louvre museum, was studied (Fig. 1a). Several points on the carnations and two profiles, with steps of 3 mm, on the Virgin and St Joseph faces, were analysed by XRF and are indicated on Fig. 1b.

In order to measure the thicknesses of the test painting layers and thus confirm the results obtained with our method, SEM observations were carried out on a Phillips XL 30 CP, using cross-sections of tiny samples embedded in resin (operating at a current intensity of about 100 mA and an excitation potential of 20 kV).

Data treatment

Principle: differential X-ray attenuation

As described in [6, 9], the main difficulty in quantitative analysis of painting is to discriminate a layer from the upper one. A possibility is to use the differential X-ray attenuation. When an X-ray beam goes though a specimen, it is absorbed along its path depending on its energy. The transmitted fraction is given by the expression:

$$\frac{I(\lambda)}{I_0(\lambda)} = \exp(-\mu(\lambda)\rho x)$$

where μ is the mass attenuation coefficient of absorber for the wavelength, ρ the density of the specimen and x the distance travelled through the specimen. As an

illustration, Fig. 2a and b presents the XRF analysis performed on various thicknesses of polymer laid on a lead plate. One can notice on the XRF spectra (Fig. 2a) the decrease of the Pb M lines (around 2.35 keV) with increasing polymer thickness due to the absorption. The evolution of the transmitted fractions of the L and M lines were reported Fig. 2b 60 μm of polymer (with d=0.73 g cm^{-3}) laid on a lead layer induces the absorption of 73% of the X-ray beam at 2.3 keV (Pb M line) whereas only 1% is absorbed at 10.5 keV (Pb L line) [20]. The polymer absorption leads to a modification of intensity ratio of L and M lines. Measuring this ratio, it is thus possible to estimate the polymer layer thickness.

For more complex cases, one has to consider the complete equation of the characteristic line intensity. The number of characteristic photons leaving a specimen is dependent upon the attenuation due to the different absorbers on its path, and the relative absorption effects of the different atoms forming the specimen. Thus, the number of observed photons is a function of the composition of the specimen and its thickness. L. Bonnizzonni et al [21] develops the intensity expression for multilayer samples excited by monochromatic radiation. In the case of layered samples such as easel paintings excited by a polychromatic beam the use of the PyMca software is particularly useful.

PyMca data treatment

X-ray spectra were analysed by the dedicated software PyMca, using the fundamental parameter method. The performances obtained for a bulk sample are extensively presented in [8]. This programme models polychromatic sources as a set of discrete energies and weights and takes into account incident beam hardening. A detailed description of the algorithms used is presented in [12]. The software takes into account the X-ray attenuation in all layers and windows between the sample surface and the active area of the detector. The user has thus to define the density, composition and thickness of these absorbers. To estimate layer concentrations and/or thicknesses, users can compare the theoretical concentrations against the calculated ones or the modelled theoretical spectra under different conditions against the experimental data.

In the simple case of polymer applied on a lead layer, the thicknesses are thus easily obtained by this method. On one hand, the intensity of the L line (slightly affected by absorption) provides the thickness of the layer containing lead and on the other hand, the intensity ratio between the different characteristic lead lines provides the thickness of the absorbing layer:

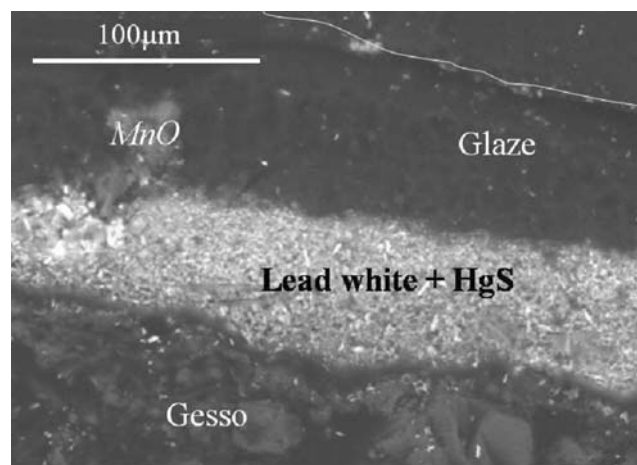- The L/M ratio permits to access the polymer layer thickness. The user will adjust the polymer thickness

Fig. 3 SEM picture of a cross section taken from the test painting ('zone 4' with four glaze layers superimposed). Three layers are visible: the *gesso* layer, the lead white layer and the glaze layer, more organic, containing one grain of manganese oxide

(in the matrix definition) so that the calculated lead concentration obtained from the L lines is equal to the one obtained from the M lines.

- The intensity of the L line will permit to access to the lead layer thickness if it is thin enough. Typically, we consider the 'infinite thickness' of a sample as that thickness from which 99% of the intensity of the given element (analyte) is collected. The thicknesses can only be estimated for values lower than this limit. One has to notice that this infinite thickness depends on the X-ray penetration and absorption: it is thus much more important if we consider the Pb L line than the Pb M line.

Users often proceed by iteration: making hypothesis on the sequence and composition of layers and adjusting them depending on the calculated results. If an element is present in several layers, the programme gives the concentration as if the entire signal would come from each layer. In such cases, the composition and thickness estimation will rely only on the simulation of the matrix spectrum.

Results

Metallic standards

Figure 2c presents the results obtained for various thicknesses of organic layers laid on a lead plate, compared to the certified values. Results obtained on the standards confirmed the accuracy of the method. A maximum error of 13% on the calculated thickness was obtained for thicknesses above 5 μm. Under 5 μm thickness, the error is not higher than 1 μm.

Table 1 Thickness estimation by quantitative XRF analysis (with PyMca treatment) on a test painting, compared to observed thickness on the SEM images. For these estimated thicknesses, the massic concentration of mercury and manganese were also calculated by PyMca

	Lead white layer			Glazes		
	Observed thickness SEM (µm)	Estimated thickness XRF (µm)	Hg Wt%	Observed thickness SEM (µm)	Estimated thickness XRF (µm)	Mn Wt%
Zone 1	20–40	30	1.5	?	4	5
Zone 2	35–50	50	1.4	11	11	4.2
Zone 3	35–60	45	1.5	9–37	16	4.2
Zone 4	40–60	42	1.4	25–60	40	2.8

Application on paintings

Model samples

Various thicknesses of polymer, modelling a varnish layer, were applied on a thick lead white painting layer on the panel prepared by the restorer according to Renaissance recipes. The thicknesses were estimated by the same method. The error obtained is still lower than 10%.

Then, we analysed another part of the test painting, consisting in glazes (a few content of manganese oxide in oil) applied on thinner lead white layers containing vermilion. Four zones were considered corresponding to four glazes thicknesses: in 'zone 4', four glaze layers were applied, whereas in 'zone 1', only one glaze layer is present. Samples were taken in each analysed zone and the cross-sections, embedded in resin, were analysed by electronic microscopy in order to compare the local thicknesses observed by SEM to the calculated ones by XRF (Fig. 3). The estimated thicknesses for the lead white and the glaze layers are reported Table 1 and can be compared to the observed ones. The calculated concentrations of mercury (from HgS in the lead white layer) and manganese (from MnO in the glazes) were also calculated for these estimated thicknesses, and are indicated Table 1. The results obtained are coherent with the SEM observations. The modelled thicknesses are all within the observed intervals. The observed thicknesses are not constant on the SEM images which give access to the local thicknesses. On the contrary, X-ray fluorescence data provide average thickness on the analysed zones as the X-ray beam diameter is about 1 mm. Moreover, the mercury concentration is rather constant as it could be supposed for a common painting. This is not the case for manganese oxide which was not easy to mix with the binder according to the restorer. A grain is visible on the SEM image (Fig. 3) and the calculated manganese concentration is not constant on the four analysed zones.

Layers thickness estimation on a Renaissance painting

X-ray fluorescence was then performed on the panel painting "*The Holy Family with St Elisabeth, St Joachim, and the little St John*" by Marco d'Oggiono, Italian Renaissance painter. The varnish thickness could be easily estimated and values between 23 and 34 µm are obtained depending on the analysed zones (Table 2).

To go further in the interpretation, we defined a simple model as matrix composition consisting in two layers: a varnish ($d=1$ g cm^{-3}) and a lead white-based painting layer (PbCO$_3$ 80 wt.% and oil 20 wt.%, $d=3$ g cm^{-3}). We could then estimate the thickness of lead white and obtain the concentration of other elements present in this layer (Table 2). As an example, iron increases regularly from 0.5 to 1.7 wt.% depending on the analysed zone: in the lightest part, the iron concentration is small and increases in the darker zones. On the contrary to the thickness variations, these concentration variations are not due to painting inhomogeneities and are indicated by arrows in Table 2. Thus, this simple model provides interesting clues about the technique used by the artist. The model proposed could be precised by adding several painting layers, the upper one containing an iron pigment.

However, it is important to underline here inherent limitation of the (conventional, not confocal) XRF technique for quantitative multilayer analysis. The measured fluorescence intensity leads to the determination of the density multiplied by the thickness; a hypothesis has to be made on the layer density and thus on its composition to be able to estimate the layer thickness. In the case of Renaissance lead

Table 2 Thickness and concentration estimation by quantitative XRF analysis on the panel painting from Marco d'Oggiono

	Virgin	St Joseph	Jesus	St Jean
Number of analysed points	9	8	2	2
Varnish thickness (µm)	28–34	25–32	25–34	23–29
Lead white thickness (µm)	16–25	20–25	24–35	20–42
Fe Wt% (in the lead white layer)	0.6→1.7	0.5→1.1	0.5→1	0.4→1.2

white-based layers, efforts have been made to precise the possible binder pigment/ratio and thus provide an accurate density [22]. A pigment proportion of 80 wt.% can be considered as an average value; however, one can find on all the lead white-based layers a pigment content from 70 to 90 wt.%. As an example, a 25-μm lead white layer, with a pigment content of 80%, is 19 μm thick with 70 wt.% of pigment (density=2.3 g.cm^{-3}) and 34 μm thick with 90 wt.% of pigment (density=4.1 g.cm^{-3}).

Another limitation is the discrimation of two layers of global similar composition: as an example, a lead white-based paint layer and the printing layer in Renaissance paintings cannot be discriminated. The same is true for the superposition varnish–glazes layers: the Pb L/M ratio provides the estimation of a global organic thickness. To overcome this problem, one can estimate the varnish thickness in zones without glazes and then deduce the glaze thickness in the shadows.

The accurate stratigraphy reconstruction (including paint layer) has to be based on a deep knowledge of the technique used by the artist and of the layers composition, on the contrary to the varnish thickness estimation which does not require a complete stratigraphy modelisation.

Conclusion

We thus demonstrate the possibility to do XRF analysis in multilayer structures by the use of PyMca software. This method provides valuable results for the thickness and/or the composition of the different layers.

For painting analyses, a very fast and accurate varnish and glazes thickness measurement can be obtained. A more complete study of the paint layers stratigraphy implies a great knowledge of the technique used as it necessitates making hypotheses on the layer sequence.

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