Ion beam analysis of art works: 14 years of use in the Louvre

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Abstract

For more than 14 years, an IBA facility has been operated in the Louvre for the study of works of art and archaeology. The choice of this equipment derives from the non-destructive character of IBA techniques which has been further strengthened by designing an external beam line permitting the in-air analysis of large or fragile works of art without sampling. Successive improvements have markedly extended the analytical capability of the set-up. The measurements were originally restricted to PIXE–PIGE combination using an external millimetre-sized-beam. By adding a focusing system and an ultra-thin exit window we were able to obtain external beams of protons and alpha particles of respectively 10 and 50 μm in diameter, with low energy straggling. These features have permitted to apply in external beam mode other IBA techniques including RBS, NRA and more recently ERDA. Moreover, elemental maps can be drawn in PIXE and PIGE modes by mechanically scanning the sample under the fixed beam within a lateral range much larger than conventional nuclear microprobes. This facility is used for both short investigations at the request of museum curators and extensive research works in art history and archaeology. Several examples are given to highlight the impact of this tool on cultural heritage.
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1. Introduction

The use of ion beam analysis for the study of art works and archaeological artefacts is linked to the development of the PIXE technique in the early seventies [1]. In this field, information on the elemental composition was previously provided by XRF and SEM-EDX, which at that time were only applicable on small samples taken from the objects. The high sensitivity of PIXE, which strengthens the widely recognised non-destructive character of IBA methods, explains its fast growing popularity. Another important fact is the early implementation of PIXE in air [2] which opened the possibility of in situ analysis of art objects of large size or too fragile to be put under vacuum. These considerations have led at the end of the eighties to the installation of an IBA facility, labelled AGLAE (an acronym for Accélérateur Grand Louvre d'Analyse Elémentaire) at the Centre for Research and Restoration of the Museums of France located in the Louvre palace in Paris [3]. Up to now it is the sole facility of its kind to be entirely dedicated to the study of art

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works and archaeological artefacts. Its use was originally restricted to PIXE–PIGE measurements first in a vacuum chamber, then with an external mm-sized beam [4]. The adjunction of a focusing system and an ultra-thin exit window enabled its transformation into a real external nuclear microprobe [5] and the implementation in air of other IBA techniques such as RBS, ERDA or NRA, not so frequently applied to issues relevant to cultural heritage.

The aim of this article is to briefly recall the successive technical improvements that stand out as milestones in the history of the AGLAE facility, to describe some significant applications and to try predict its future role among the growing number of sophisticated tools which will be likely at the disposal of conservation scientists.

2. Successive technical improvements of the AG-LAE facility

2.1. Construction of an external milli-beam line

During the first period of operation, PIXE analysis was performed in a vacuum chamber, using two proton shots at 1 and 3 MeV for the determination of low Z and high Z elements, respectively, with a single Si(Li) detector, equipped with appropriate filters. Another procedure relied on a single shot at 3 MeV and a so-called ''funny'' filter, i.e. a filter pierced with a tiny hole at the center to collect a small part of the X-rays emitted by the matrix. A major progress coincided with the design of an external beam line based on the use of an 8 μm thick Kapton exit window: the analysis then relied on a single shot at 3 MeV and two Si(Li) X-ray detectors, one dedicated to the detection of low energy X-rays, corresponding to K lines of light elements (Z comprised between 11 and 30) and the other to high energy X-rays (elements of Z above 30). The efficiency of the set-up for the analysis of light elements was further increased by (i) flowing helium on the path of the incident proton beam and that of the detected low energy X-rays and (ii) fitting a deflecting magnet on the low energy X-ray detector to prevent backscattered protons from hitting the detector crystal [6].

2.2. Installation of a nuclear microprobe line

In 1991, a third beam line was built to receive a nuclear microprobe system purchased from Oxford Microbeam [7]. The main components were a triplet of focusing lenses leading to a proton beam size of about 1 μm and a beam scanning system. However, since such a tool had to be operated under vacuum, its use was restricted to small objects or, when allowed, to small fragments sampled from larger ones. Consequently, it quickly turned out that this conventional nuclear microprobe did not provide much more information than the SEM-EDX and thus was not well adapted to the laboratory needs.

2.3. Construction of an external nuclear microprobe

The experience we gained from the daily use of the external beam line and the availability of the focusing system attached to the nuclear microprobe led us to dismount the latter and to fix it to the external beam line in order to obtain an external microbeam. The use as the beam exit window of commercially available special mounts for transmission electron microscopy made of ultra-thin (0.1 μm) Si_3N_4 foil on a Si frame of dimensions 1 mm × 1 mm contributed to reduce the size of the beam spot under the helium atmosphere and to minimise the energy loss, energy straggling and angular straggling. By applying the classical resonance scanning technique, $^{32}S(p,p'\gamma)^{32}S$ for protons (3.094 MeV) and the resonant scattering $^{16}O(\alpha,\alpha')^{16}O$ for alpha particles (3.045 MeV), we were able to assess these quantities to respectively 10 and 5 keV for protons and 80 and 30 keV for alpha particles [5]. The typical beam sizes attainable are 10 μm for protons and 50 μm for alpha particles (see Table 1). The low energy straggling for alpha particles obtained with this set-up then permitted to perform RBS [8] as well as ERDA [9] measurements at atmospheric pressure.

The external microbeam set-up has been regularly improved and is now in a state of versatility which permits the application of all IBA techniques separately or in association, namely PIXE–PIGE–RBS with protons, PIXE–PIGE–NRA with deuterons, PIXE–RBS with He ions. The general

Table 1
Types of experiments and beam features

Analytical technique	Particle	E (MeV)	Straggling (keV)	Beam size (μm)	I (nA)	Dose (μC)
PIXE	p	3	4.5	10–20	0.05–1	1
PIXE–PIGE combination	p	3	4.5	10–20	5	5
PIXE–RBS combination	p	3	4.5	10–20	5	5
RBS He	He^{2+}	3	30	50–100	5	5
ERDA He	He^{2+}	3	30	50–100	5	5
NRA	d	2		10–20	10	10

view of the external beam line and a close-up of the set-up are shown in Figs. 1 and 2. It is worth summarising its main features.

2.3.1. Beam monitoring

This is a difficult issue when operating in external beam mode, as the measurement of the integrated charge deposited on the target is no longer reliable. Several means have been reported in the literature including the use of a chopper, the Ar X-ray signal when operating in air, the RBS signal emitted by the exit window. We have used this last system in the earlier version of our set-up where a millimetre-sized beam was extracted through various windows (Kapton, Al, Ti or Zr). The shift toward the ultra-thin Si_3N_4 window made this means unfeasible because the RBS signal was too low.

Consequently we moved to the Si XK signal of much higher intensity and fixed a compact Si-drift Peltier-cooled detector to record it.

2.3.2. Remote-controlled positioning system

It is based on sample holder with a 3-axis stage moved by stepping motors, a CCD video camera and a laser.

2.3.3. X-ray detection

The emitted X-rays are collected by two Si(Li) detectors cooled at liquid nitrogen temperature and set at 45° with respect to the beam. The first one devoted to low energy X-rays has a very thin BN window, whereas the second of larger size and thickness is aimed at collecting high energy X-rays
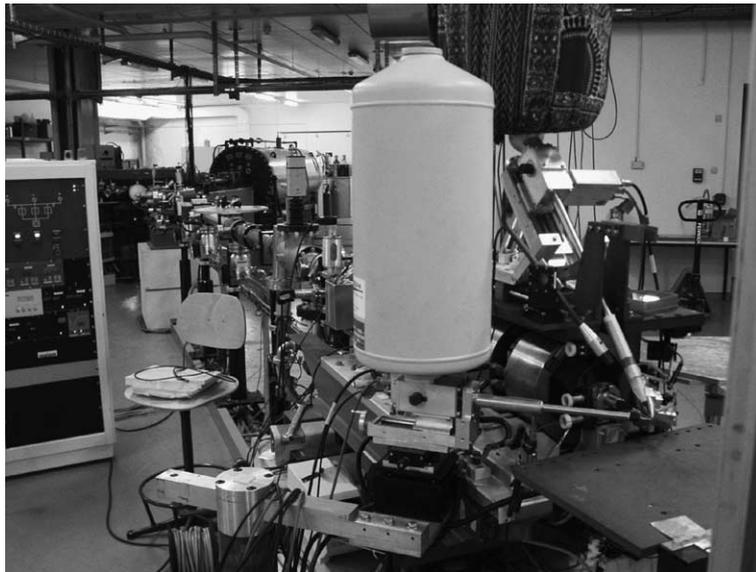

Fig. 1. General view of the AGLAE external beam line. On the foreground is the sample holder stand and the external beam set-up.

Fig. 2. Close-up view of the external beam set-up. The numbered main components are: 1. low energy X-ray Si(Li) detector equipped with a deflecting magnet; 2. high energy X-ray Si(Li) detector; 3. surface barrier detector; 4. Si-drift detector cooled by Peltier effect for dose monitoring; 5. pointing laser.

with high efficiency. It is covered with a filter of composition and thickness chosen in view to selectively reduce the matrix signal.

2.3.4. Charge particle detection

For both RBS and NRA measurements at atmospheric pressure, we use a surface barrier detector set at 150° with respect to the incident beam; this is the maximum angle allowed by the geometry of the exit nozzle. This certainly presents some inconvenience because of a lack of data for this angle on cross sections of nuclear reactions or non-Rutherford scattering on light nuclei. We envisage in the future to modify the design of the nozzle and fix an annular detector to use a more conventional diffusion angle in the range 160–170°. The detector is placed in a housing put under vacuum and terminated by a Si_3N_4 window of the same type as that of the nozzle, which insures the interface with the atmosphere. The detector can be moved along the housing axis in order to optimise the count rate.

2.3.5. Scanning capability

Two separate scanning modes are available. The first one, based on the use of the scanning coils

provided with the original nuclear microprobe, permits to draw elemental micromaps over an area of 0.5×0.5 mm^2 at maximum, limited by the dimensions of the beam exit window. The second mode is a mechanical scanning using high precision stepping motors fixed on our remote-controlled sample holder. With such a system, quite large areas (up to several tens of centimetres in width and height) can be scanned, a feature which obviously cannot be attained by conventional microprobes and could be a good argument for the in-air microprobe.

2.3.6. Data acquisition

It is based on the MpaWin system (FastComTec) coupled with a home-made Labview interface. For most experiments, three detection channels are used, corresponding to the two X-ray detectors and either the surface barrier detector or gamma-ray detector for accordingly simultaneous RBS or PIGE measurements.

2.3.7. Performance in RBS mode

Due to its lack of depth information, the PIXE technique sometimes leads to ambiguous data and

for instance is unable to yield the layer arrangement in multilayered materials like paint layers. The adjunction of simultaneous RBS measurement helps deciphering this problem. Previous reports of RBS analysis with external beams of helium ions are very scarce, due to the large energy spread generally produced by conventional exit windows, which made them inappropriate to conduct accurate RBS measurements. Using the above-mentioned ultra-thin window and a helium flow to fill the inward and backward ion paths, it is now possible to perform experiments with a quite good energy resolution as illustrated by Fig. 3.

2.4. Set-up for real time RBS measurements with the external beam

The set-up used for dynamic RBS [10] includes an oven based on a halogen lamp and a gold reflector, a sample holder made of nickel mounted on a ceramic body and a thermal shield made of a water-cooled copper plate for protecting the beam line from the heat. The millimetre-sized sample under study is fixed inside a small pit drilled in the holder by means of an adhesive made of a thermal conductive ceramic. The sample can be heated up to 600 °C, the temperature being regulated by means of a home-made circuit and a chromel–alumel thermocouple inserted in the sample holder. While heated the sample is set at about 3 mm from the beam exit window. During heating in air, RBS measurements are performed at regular time intervals with a 3-MeV ^{4}He^{2+} external beam. The average beam characteristics are the following: size 0.1 mm, intensity 5 nA, integrated charge for each RBS run of the order of 1 μC.

2.5. Construction of a beam line dedicated to XRF induced by PIXE

The PIXE technique has two noticeable limitations:

(i) The proton beam can deteriorate sensitive materials, in particular those containing organic constituents. In the context of art and archaeology, it is the case of painted works, textiles,
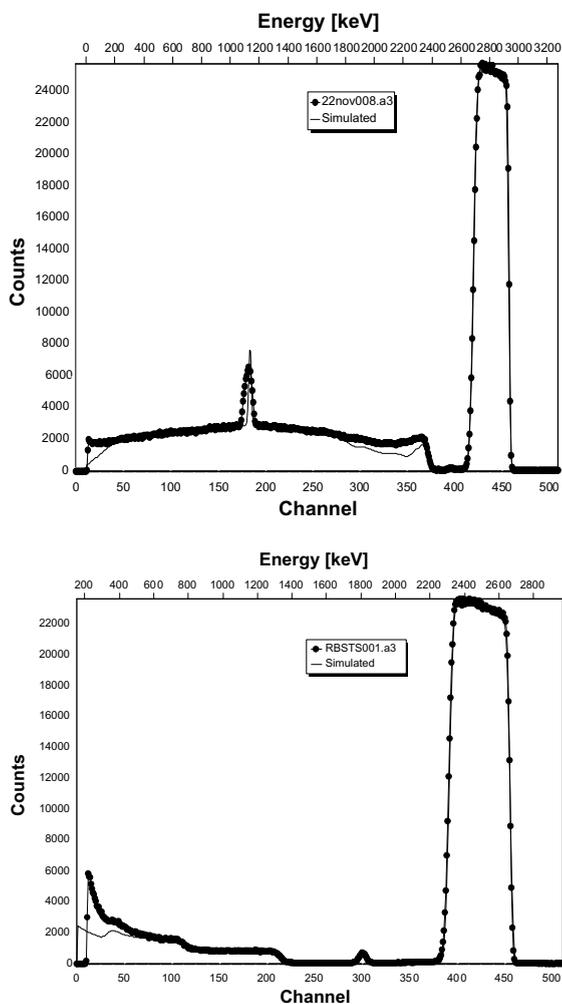

Fig. 3. RBS spectra of thin gold standards obtained with external beams of 3 MeV protons or He^{2+} ions. Top spectrum: 2 μm thick Au layer on Si substrate; 3 MeV protons, 2 mm path in helium, diffusion angle 150°, integrated dose 2 μC, energy resolution at the gold edge about 30 keV. Bottom spectrum: 280 nm Au over 10 nm Cr on SiO$_2$ substrate; 3 MeV He^{2+} ion beam, same 2 mm path in helium, diffusion angle 150°, integrated dose 1.5 μC, resolution 30 keV. Spectrum simulation uses the SIM-NRA software.

woods or biological samples such as skin or hairs.
(ii) The proton beam induces the X-ray emission of all elemental components of the target. In the case of high Z materials like metallic alloys, the intense emission of the characteristic lines of the matrix considerably limits the

sensitivity for lighter impurities. A way to circumvent such a drawback is to selectively induce the X-ray emission from these impurities without that from the matrix, in using as the excitation source X-ray photons of energy below the absorption threshold of the matrix heavy elements. This can be obtained by placing under the proton beam an intermediate target adequately chosen.

The conversion of the proton beam into an X-ray beam thus permits to meets the two abovementioned difficulties. In the first case the choice of the intermediate target is very large, the only condition is that the produced X-rays can induce the X-ray emission from the constituent elements of the material under analysis. The choice is more restricted in the second case, since the intermediate target must produce X-rays of energy above the absorption threshold of the element to be analysed but below that of the matrix. The technique which derives from this approach is a variant of XRF and is sometimes labelled PIXE induced XRF [11]. The first application of our set-up was the measurement of the platinum content in archaeological gold to infer its provenance. The intermediate target is made of arsenic which emits XK lines capable of exciting the L lines of platinum ($Z = 78$) but not those of gold ($Z = 79$). The detection limit lowered by an order of magnitude with respect to PIXE, is about 100 ppm.

3. Examples of applications

The AGLAE facility has two distinct roles. It is used for diagnosis tasks at the request of curators of public museums on various occasions, for instance for authentication prior to purchase on the art market, or for knowing the state of conservation before restoration work. It also serves as a research tools in art history, archaeology, conservation science and preventive conservation. Concerning art history, the main objective of applying methods originating from the physical sciences is to complement conventional typological approach and contribute to a better understanding of the

technique of the artist through the identification of the raw materials used, the way they have been mixed, the treatments applied. The data obtained constitute solid grounds for the authentication of a work or its attribution to an artist, a workshop, etc. In archaeology, the main purpose of analysis of artefacts is to contribute to a better understanding of the technical development in the remote past and to identify the sources of raw materials and the trade routes. The main objective of conservation science is to define the state of conservation of the art object and the best restoration procedure. The studies involve the analysis of both art works and experimental samples subjected to accelerated aging tests in view to infer alteration mechanisms. Preventive conservation is aimed at controlling the environment of the work during transportation, storage or exhibition. The task of our IBA facility for this purpose has been limited to the characterization of corrosion monitors. Table 2 contains a non-exhaustive list of applications in all these fields, classified according to significant issues.

Applications of IBA techniques to cultural heritage date nearly from the very beginning of the development of PIXE, with the study of ceramic potsherds and obsidian tools. The use of PIXE then rapidly expanded to other materials of cultural significance. However, this technique is clearly more suitable for some types of materials than for others, as for example those constituted of thin layers of high Z elements over a substrate of low Z elements, a situation found in drawings or illuminated manuscripts. In contrast the in situ analysis of easel paintings without sampling is generally quite difficult, due to the frequent presence of a thick varnish layer which can mask the paint layer and the complex structure of the latter. Moreover one cannot discard the risk of leaving a visible mark of the beam spot on the varnish surface or on some white pigments like lead white. These facts explain the limited use of our facility for the study of paintings which still today relies preferably on the more conventional SEM analysis of cross sections of minute samples taken from the paint layer. However in some favourable cases, PIXE can be used to decrypt the layer arrangement in the painting by using increasing energies

Table 2
Applications listed according to fields and issues

Research field and issue	Type of object	Component of interest	IBA technique	Reference
Art history and archaeology				
Material identification	Manuscripts and drawings	Ink, metal point, pigments	PIXE	[14,15]
	Stones, gemstones		PIXE	[16,17,19–21]
	Painted works	Pigments	PIXE	[22,23]
	Ceramics	Clay and glaze	PIXE	[24,28]
Material provenance	Stones, gemstones		PIXE, PIGE	[16,17,19,25]
	Ceramics	Clay and glaze	PIXE	[24]
Fabrication technique	Bronzes	Patina, guilt	PIXE, RBS, NRA	[8,26,27]
	Glazed stones	Glaze	PIXE, PIGE	[29]
	Ceramics	Glaze, lustre	PIXE, RBS	[30]
Conservation science	Glasses enamels		PIXE, PIGE, RBS	[31]
	Bronzes	Patina	PIXE, RBS, NRA	[26,27]
	Papal bullae	Lead seals	PIXE, RBS	[18]
Preventive conservation	Corrosion monitors	Diverse pure metals	RBS	[18]

of the incident beam (or at a fixed energy diverse incident angles) in order to imply the X-ray emission of layers of increasing depths [12,13].

We will briefly describe below a few examples according to the current issues of cultural heritage.

3.1. Materials identification

The identification of constituent materials of art works is the basic objective of any scientific study. It yields important indices for the knowledge of the artistic technique and the authentication of works. It can be also sometimes the clue for an indirect dating of the work. For example the finding of a XIX century pigment in a painting supposedly representing Bernard Palissy, a Renaissance French ceramist, excludes the possibility of a live portrait. External beam PIXE is perfectly adequate to materials identification through the measurement of their major constituent elements. This is illustrated by numerous studies on papyri, manuscripts, miniatures and drawings, the aim of which is to determine the nature of inks, pigments or metal points.

This technique was applied to a set of drawings by several Renaissance artists, such as Pisanello or Dürer. It was shown that the artists used several types of metal points: lead on parchment or paper without preparation and pure silver on a preparation based on bone white or calcium carbonate [14].

Concerning Egyptian papyri, the palette of a Book of the Dead from the Middle Empire has been investigated. Macroscopic distribution maps of elements have permitted to identify the different pigments: red (hematite, ochre), black (carbon), yellow (orpiment) and white (huntite). A light blue pigment containing strontium (celestite) has been revealed for the first time [15].

Another example of mineral identification stems from the study of a Parthian statuette kept in the Louvre and representing the goddess Ishtar. The red inlays representing the eyes and navel turned out to be rubies and not coloured glass as previously thought. In effect, the PIXE spectrum of major elements indicates the presence of aluminium and chromium, characteristic of ruby [16].

3.2. Materials provenance

This issue is of great interest in archaeology and to a lesser extent in art history, since it provides clues for inferring trade routes and relationship between past populations. For many years it was almost the monopoly of neutron activation analysis (NAA) due to its high sensitivity for trace elements which act as the fingerprint of materials source. At present PIXE and X-ray fluorescence (XRF) have replaced NAA in most studies where sampling is forbidden. The current protocol consists, first in measuring trace elements in the object

and in geological samples of well known provenance. Then using multivariate statistical methods (principal component analysis, clustering), one identifies discriminating elements and determines the object provenance. Such an approach has been applied to a large number of materials, including stones (obsidian, flint), gemstones (ruby, emerald, garnet) and ceramics.

A typical example stems from the determination of the origin of the rubies inlaid in the Parthian statuette found in Mesopotamia, which has been mentioned above. For this study a data base of the composition of about 500 rubies from different mines has been obtained by PIXE. The trace element fingerprint of the rubies of this statuette indicates that they come from Burma and that they are a precious witness of a gemstone trade.

3.3. Fabrication technique

Important clues about the fabrication technique of works of cultural heritage can be already derived from the simple identification of materials used for making the object, but most of time the spatial distribution of elements, either lateral or in depth, constitutes a decisive criterion. In the first case, micro-PIXE appears extremely useful and has been used for example for determining the soldering technique of antique and medieval goldsmith's work. Elastic scattering of protons and more recently of helium ions has been applied to the study of gilded objects in order to determine the composition and the thickness of the guilt.

For example, the study of the gold employed in the different parts of the crowns and crosses of the Guarrazar treasure quoted earlier has provided information on the goldsmith's technology. On one hand, the original parts have been clearly distinguished from modern ones added during the restoration of the treasure shortly after it was found (XIX century) and on the other hand, it is demonstrated that in today presentation the crosses and crowns are not correctly associated. Moreover the gold used in these jewels has a content higher than the Visigothic coinage of that period, which excludes the assumption that the latter has been reused in royal jewellery [17].

3.4. Alteration phenomena

The possibility to carry out RBS experiments with external beams of helium ions opens a new field of research centered on the alteration of art works in the museum environment. One of the first applications concerns the study of lead seals attached to papal bullae kept in the National Archives. Some of these seals are highly altered, most likely as a result of attack by organic acids emanating either from cardboard boxes in which the documents were formerly kept, or from the nearby storage environment, in particular the wooden structures (various furniture, shelves, etc.). The extent of alteration has been investigated by RBS together with the kinetics of alteration of lead monitors placed in diverse locations of the Archives in order to assess the level of harmfulness of the environment.

4. Conclusions and prospects

After over fourteen years of continuous use, the AGLAE facility constitutes the best tool for the non-destructive analysis of works of cultural heritage on which rely almost systematically the studies performed at the Centre for Research and Restoration of the Museums of France. The successive improvements made on the external beam line permit the application of the whole set of IBA techniques, under totally harmless conditions for museum objects, although PIXE is by far the most used technique. Further progress can be made to render this facility even more efficient. In particular RBS measurements should be systematically coupled with PIXE. Because of the poor mass resolution of RBS with protons, combined PIXE–RBS with high energy helium ions (up to 6.5 MeV) should be conducted. The choice of this energy range is conditioned by the need of sufficient depth penetration for RBS and X-ray emission cross section for PIXE. This non-conventional approach is under study at present.

However we cannot mask the fact that the place of ion beam analysis for the study of art objects is susceptible to shrink in the future. Indeed on one hand, two concurrent techniques, namely XRF

and Raman spectrometry have recently made significant progress in terms of miniaturisation and portability which explains their increasing use for the characterization of art objects. On the other hand analytical techniques based on synchrotron radiation start also to be employed, although not yet routinely. These last techniques can provide a wealth of information far beyond the capability of PIXE. Between these two groups of competing techniques, there is a gap which only ion beam analysis can fill, that is the depth information provided by RBS and NRA. Therefore to our opinion much effort should be now done to demonstrate the usefulness of these techniques in external beam mode for in situ elemental depth profiling on materials relevant to cultural heritage.

Acknowledgements

References

[1] G.M. Gordon, H.W. Kraner, J. Radioanal. Chem. 12 (1972) 181.

[2] G. Deconninck, J. Radioanal. Chem. 12 (1972) 157.

[3] G. Amsel, M. Menu, J. Moulin, J. Salomon, Nucl. Instr. and Meth. B 45 (1990) 610.

[4] T. Calligaro, J.-C. Dran, H. Hamon, B. Moignard, J. Salomon, Nucl. Instr. and Meth. B 136–138 (1998) 339.

[5] T. Calligaro, J.-C. Dran, E. Ioannidou, B. Moignard, L. Pichon, J. Salomon, Nucl. Instr. and Meth. B 161–163 (2000) 328.

[6] T. Calligaro, J.D. MacArthur, J. Salomon, Nucl. Instr. and Meth. B 109–110 (1996) 125.

[7] N.E.G. Lovestam, T. Calligaro, A. Duval, J. Salomon, Nucl. Instr. and Meth. B 77 (1993) 66.

[8] E. Ioannidou, D. Bourgarit, T. Calligaro, J.-C. Dran, M. Dubus, J. Salomon, P. Walter, Nucl. Instr. and Meth. B 161–163 (2000) 737.

[9] T. Calligaro, J. Castaing, J.-C. Dran, B. Moignard, J.-C. Pivin, G.V.R. Prasad, J. Salomon, P. Walter, Nucl. Instr. and Meth. B 181 (2001) 180.

[10] P. Martinetto, J.-C. Dran, B. Moignard, J. Salomon, P. Walter, Nucl. Instr. and Meth. B 181 (2001) 703.

[11] G. Demortier, in: G. Furlan, P. Cassola Guida, C. Tuniz (Eds.), Proc. Symp. ''New paths in the use of nuclear techniques for art and archaeology'', Trieste, Italy, 30 September–3 October 1985, World Scientific, Singapore, p. 48.

[12] C. Neelmeijer, W. Wagner, H.P. Schramm, Nucl. Instr. and Meth. B 118 (1996) 338.

[13] G. Weber, J.M. Delbrouck, D. Strivay, F. Kerff, L. Martinot, Nucl. Instr. and Meth. B 139 (1998) 196.

[14] A. Duval, in: Proc. 6th International Conference on Non Destructive Testing and Microanalysis for the Diagnostics and Conservation of Cultural Heritage, Rome, 17–20 May 1999, p. 1007.

[15] A.-M.B. Olsson, T. Calligaro, S. Colinart, J.C. Dran, N.E.G. Lövestam, B. Moignard, J. Salomon, Nucl. Instr. and Meth. B 181 (2001) 707.

[16] T. Calligaro, A. Mosmann, J.-P. Poirot, G. Querré, Nucl. Instr. and Meth. B 136–138 (1998) 846.

[17] T. Calligaro, J.-C. Dran, J. Salomon, J.-P. Poirot, Nucl. Instr. and Meth. B 161–163 (2000) 769.

[18] M. Dubus, I. Colson, E. Ioannidou, B. Moignard, J. Salomon, P. Walter, J.-C. Dran, in: Proc. 6th International Conference on Non Destructive Testing and Microanalysis for the Diagnostics and Conservation of Cultural Heritage, Rome, 17–20 May 1999, p. 1739.

[19] G. Querre, A. Bouquillon, T. Calligaro, M. Dubus, J. Salomon, Nucl. Instr. and Meth. B 109–110 (1996) 686.

[20] T. Calligaro, S. Colinart, J.-P. Poirot, C. Sudres, Nucl. Instr. and Meth. B 189 (2002) 320.

[21] I. Reiche, C. Vignaud, T. Calligaro, J. Salomon, M. Menu, Nucl. Instr. and Meth. B 161–163 (2000) 737.

[22] M. Menu, Ph. Walter, Nucl. Instr. and Meth. B 64 (1992) 547.

[23] M. Menu, Nucl. Instr. and Meth. B 75 (1993) 469.

[24] A. Zucchiatti, A. Bouquillon, G. Lanterna, F. Lucarelli, P.A. Mando, P. Prati, J. Salomon, M.G. Vaccari, Nucl. Instr. and Meth. B 189 (2002) 358.

[25] L. Bellot-Gurlet, T. Calligaro, O. Dorighel, J.-C. Dran, G. Poupeau, J. Salomon, Nucl. Instr. and Meth. B 150 (1999) 616.

[26] L. Espié, M. Aucouturier, Rev. Métall. 9 (2001) 751.

[27] M. Aucouturier, A. Zymla, B. Mille, A. Texier, D. Bourgarit, in: Proc. 7th International Conference on Non Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Antwerpen, Belgium, 2–6 June 2002, CDROM art 2002.

[28] A. Zucchiatti, A. Bouquillon, J. Castaing, J.R. Gaborit, Archaeometry 116 (2003) 391.

[29] A. Bouquillon, B. Barthélémy de Saizieu, A. Duval, in: Materials Research Society Symp. Proc., Vol. 352, 1995, p. 527.

[30] E. Darque-Ceretti, D. Hélary, M. Aucouturier, Gold Bull. 35 (2002) 118.

[31] C. Bonnet, A. Bouquillon, S. Turrell, V. Deram, B. Mille, J. Salomon, J.H. Thomassin, J. Non-Cryst. Solids 323 (2003) 214.