

ACCELERATORS IN ART AND ARCHAEOLOGY

Jean-Claude Dran

Centre de recherche et de restauration des musées de France, CNRS-UMR 171
6 rue des Pyramides 75041 Paris Cedex 01

Abstract

For nearly fifteen years, the Centre for Research and Restoration of the Museums of France uses a particle accelerator for the non-destructive analysis of works of cultural heritage. An external beam line has been specially developed for the implementation of the whole set of ion beam analysis techniques under fully harmless conditions for museum objects. Its use extends from the simple materials identification through the analysis of major chemical elements, to the determination of their provenance by means of the composition in trace elements and to the understanding of the fabrication techniques and the ageing mechanisms of art works.

1 INTRODUCTION

A large set of modern analytical techniques is currently applied to get a better insight on art objects as well as to contribute to their conservation and restoration. However these techniques have to meet drastic constraints due to the precious and sometime unique character of works of art. Consequently, non-destructive techniques and even those requiring no (or only minute) sampling, are preferred. Other features should be taken into account, such as the complex shapes and structures, the great variety of constituent materials quite often mixed, their history rarely known, their state of conservation extremely diverse, as well as their degree of alteration susceptible to modify the chemical composition of the outer parts, those directly accessible to analysis. These characteristics generally hinder the simple application of a single analytical technique and require the development of a special experimental approach, combining several techniques of examination and chemical analysis. In this context, ion beam analysis (IBA) constitutes one of the best choices, since it combines quite good analytical performance and non-destructiveness. For nearly 15 years, an IBA facility has been installed in the Centre for Research and Restoration of the Museums of France (Fig. 1). Until now it is the only facility of this kind entirely devoted to the study of cultural heritage [1].



Fig. 1 View of the AGLAE accelerator

This facility, labelled AGLAE (Accélérateur Grand Louvre d'Analyse Élémentaire) is based on a 2 MV electrostatic accelerator of tandem type, equipped with two ion sources, one for the production of protons and deuterons and the other for helium ions. Two experimental lines are presently in use, a classical one leading to a vacuum chamber and the other called the external beam line, specially designed for the direct analysis of art works without any sampling. [2]. This line has been fitted with a focusing system which enables to reduce the beam size to about 10 μm and thus to make a nuclear microprobe at atmospheric pressure.

The analysis is based on the interaction of atomic or nuclear character between the incident ions and the constituent atoms of materials and the detection of interaction products (photons or secondary ions) the energy of which is characteristic of the target-atom. Three main analytical techniques are applied, either individually or in association: Particle-Induced X-ray Emission (PIXE), Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) with a sub-category called PIGE (Particle-Induced Gamma-ray Emission), frequently associated with PIXE.

2 ION BEAM ANALYSIS AND CULTURAL HERITAGE

We should first recall the impact of elemental analysis to the field of cultural heritage.

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 the field of conservation-restoration, the knowledge of the chemical composition and particularly the elemental depth distribution, is essential for checking the state of conservation of the work and in some cases inferring the ageing mechanism by comparison with materials of similar composition submitted to accelerated ageing tests. Furthermore this kind of investigation can yield useful guidelines for choosing the proper restoration procedure.

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. It can also serve as an indirect dating by compositional similitude with well-dated objects.

IBA techniques have most of qualities required for the study of materials of cultural heritage, which can be summarised below. These techniques are:

- (i) non-destructive for most materials with the possible exception of some inorganic materials (paper, parchment) which could be sensitive to heating or radiation damage;
- (ii) quantitative with an accuracy generally better than 5%;
- (iii) multielemental including light elements;
- (iv) very sensitive for at least one of them, PIXE which is well adapted to trace element determination; this high sensitivity permits to limit the irradiation dose necessary for getting a significant signal and thus to reduce the risk of damaging the objects by irradiation;
- (v) complementary and able to be implemented simultaneously;
- (vi) able to yield information on the spatial distribution of elements (depth profile and mapping with a resolution down to the micrometre range).

One should however keep in mind the following limitations:

- (i) the analysis concerns the outer layers of the material (up to several tens of micrometres) and thus can be

irrelevant to the bulk composition in case of surface alteration (corroded metals, hydrated glasses, for example);

- (ii) no information is provided on the chemical state of elements;

- (iii) the analysis of insulators can be problematic due to accumulation of electric charges.

The features mentioned above show that IBA techniques and particularly PIXE, because of its high sensitivity, constitute an extremely useful tool for the knowledge and the preservation of cultural heritage [3]. Indeed they have the essential quality for such a research field, the non-destructiveness. A decisive improvement has been done in developing an experimental set-up permitting the direct analysis of objects without sampling. This is carried out by means of a beam extracted to air through an ultra-thin exit window. This set-up is briefly described in the following section (Fig. 2).

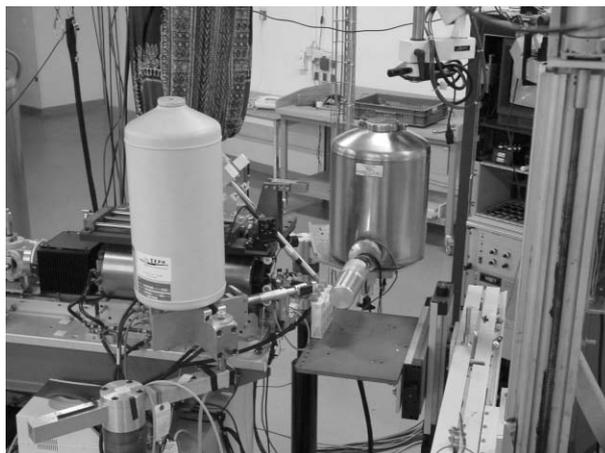


Fig. 2 View of the external beam set-up

3 EXTERNAL BEAM SET-UP

This type of set-up is at present increasingly used by scientists involved in applications of ion beam analysis to cultural heritage issues, due to the easy implementation of IBA techniques in air. Its principle consists in extracting the ion beam through a window sufficiently resistant to stand atmospheric pressure and beam induced damage, but thin enough to minimise the energy loss and energy straggling of the incident beam. The art work is then freely placed in front of this window at a distance of a few mm, in air or helium atmosphere.

The exit window must meet the following conditions:

- (i) minimum of energy loss and energy straggling;
- (ii) minimum of interfering signal;
- (iii) good resistance to pressure and irradiation. Three types of window have been used: for macro-beam, 0.75

μm of aluminium (PIXE) and 2 μm of zirconium (NRA deuterons) and for micro-beam, 0.1 μm of silicon nitride Si_3N_4 (all techniques).

In addition to the obviously easy operation in air, the main advantages provided by an external beam are:

- (i) the possibility of handling items of any size and shape;
- (ii) the possible analysis of fragile objects which could suffer from being put under vacuum;
- (iii) a marked reduction of beam induced heating;
- (iv) the suppression of accumulated electric charges in insulators with no longer the need of conductive coating necessary when operating under vacuum.

Some details of the set-up are given hereafter.

3.1 Beam monitoring

Quantitative analysis implies the accurate measurement of the integrated dose of incident ions. For conventional in-vacuum measurements, this is done by collecting the electric charge deposited on the sample (coated with a thin conductive layer if needed) connected to a charge integrator. This method can no longer be used when operating in air or helium and some scientists rely on a signal emitted by the air (luminescence or Ar X-rays). We prefer to use a signal emitted by the exit window under the impact of the beam (backscattered ions or X-rays). The first mode is used for a macro-beam (Al or Zr window) and the second one for a micro-beam (Si_3N_4 window) since the backscattered signal is too small. Beam monitoring is then done by detecting the Si X-rays of the window with a detector cooled by Peltier effect.

3.2 Production of a micro-beam

By adding to the external beam line a focusing system constituted of three quadrupole lenses, the performances of the set-up have been significantly improved. Indeed a real external micro-beam has been produced, permitting the direct analysis of museum objects at atmospheric pressure with a markedly increased spatial resolution. When using an exit window made of 0.1 μm Si_3N_4 , a beam diameter of about 10 μm is attainable in placing the object at 3 mm from the window in a helium atmosphere. Such a beam size enables the analysis of small details like inclusions in gemstones or illuminated manuscripts. Moreover, the capability of a real nuclear microprobe is reached using a multiparametric acquisition system and moving the sample under the fixed micro-beam with accurate stepping motors. It is then possible to draw elemental micro-maps with a lateral resolution of a few tens of μm .

3.3 Implementation of IBA techniques

PIXE is by far the most frequently applied IBA technique to issues relevant to art. This fact stems from its higher sensitivity, its easy implementation and its low demand in beam quality (low sensitivity to energy straggling or to variation of incidence angle). This is even more marked when operating with an external beam. However recent improvements of the set-up permit to apply other IBA techniques: RBS with helium ions, NRA with deuterons.

RBS, currently used in materials science, is generally performed under vacuum with a beam of helium ions of a few MeV. Consequently, it has been relatively little applied to museum objects, as the extraction of a helium beam to air faces a serious difficulty, namely the high energy straggling. The few previous attempts to apply this technique in external beam mode relied on proton beams, poorly efficient in terms of mass and depth resolution. The availability of ultra-thin exit windows enables now to perform RBS runs at atmospheric pressure with a beam of helium ions of energy in the range 2-4 MeV, with a good energy resolution (a few tens of keV with a conventional surface barrier detector, as compared to about 15 keV under vacuum). The first applications concern the characterisation of patinas formed on copper alloys, the alteration of lead seals kept in the National Archives of France and the control of conservation conditions in this institution, using lead monitors [4].

Light element analysis can be performed with deuteron induced nuclear reactions. In the framework of a study of the black patinas formed on archaeological bronzes, we have developed an analytical protocol combining proton elastic scattering and (d,p) nuclear reactions with proton detection, for the determination of the concentration profile of both constituent metals and light elements C, N et O.

4 EXAMPLES OF APPLICATIONS

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. They have been then quickly extended to all other kinds of materials of cultural significance. However, they are 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. Some materials, such as for example metallic alloys, face another difficulty which hinders their direct analysis, namely the high detection limit for elements lighter than major constituents.

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

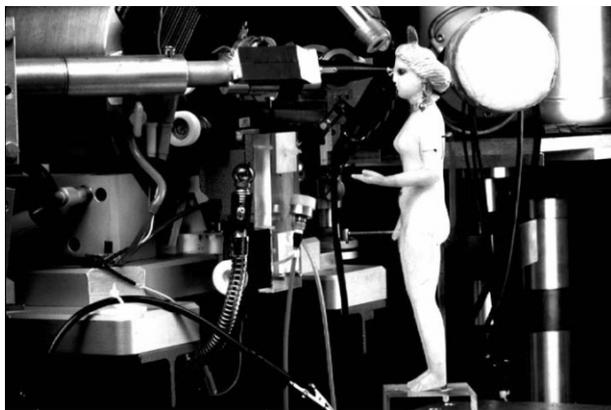


Fig. 3 Parthian statuette facing the external beam

4.1 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. This task can be easily carried out by external beam PIXE. Such an approach 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 Pisanello, a famous Italian Renaissance artist. It was shown that the artist used several types of metal points: lead or silver-mercury alloy on parchment or paper without preparation and pure silver on a preparation based on bone white or calcium carbonate [5]. Another study has been devoted to the identification of pigments used in medieval illuminated manuscripts, kept in the National Library of France.

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 [6].

Another example of mineral identification stems from the study of a Parthian statuette kept in the Louvre and representing the goddess Ishtar (Fig. 3). 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 (Fig. 4) indicates the presence of aluminium and chromium, characteristic of ruby [2].

4.2 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 gemstones (rubies, emeralds) 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 route

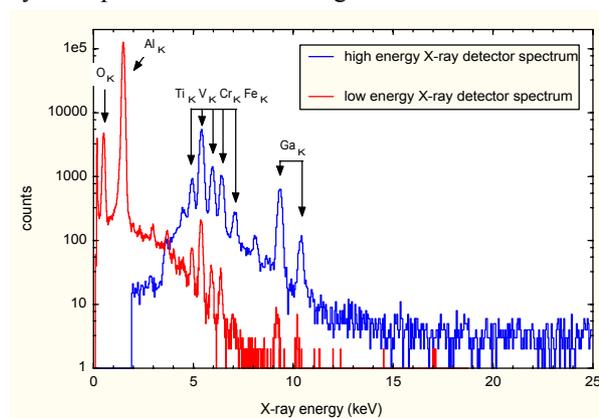


Figure 4 : PIXE spectra of the statuette rubies

between Mesopotamia and Far East. More recently this method has been applied to determine the origin of emeralds set on Visigothic votive crowns originating from the royal treasure of Guarrazar Spain (VIIIth century), part of which is kept in the Middle-Age National Museum in Paris. From trace element measurement by PIXE and PIGE, it is concluded that these emeralds have been most likely extracted from the Habachtal mines in Austria. This result is quite interesting, as the exploitation of these mines is only certified after the XVth century [7].

In the case of ceramics, in-situ analysis is seldom performed because of risk of error induced by their

heterogeneous structure. Consequently, most studies rely on small samples of matter crushed and then compacted into flat pellets. Sometimes elemental composition is not sufficient to discriminate between several potential sources and additional parameters have to be used.

4.3 Fabrication techniques

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 [8]. 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 gilt.

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 (XIXth 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 [9].

4.4 Alteration phenomena

The possibility to carry out RBS experiments with external beams of helium ions opens a new field of research centred on the alteration of art works in the museum environment. One of the first applications concerns the already mentioned 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.

5 CONCLUSION

After fifteen 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. We can mention for example the current development of a line dedicated to PIXE-induced X-ray fluorescence which will hopefully decrease the detection limit (several tens of ppm at present) for trace elements lighter than the major constituents of metallic materials (gold or lead alloys). By using the X-rays emitted by an intermediate target placed under the impact of the proton beam, one prevents the emission of X-rays by matrix elements and only produces the emission of X-rays by trace elements. An alternative to gain in sensitivity would be to use in conventional PIXE mode, a high resolution X-ray spectrometer, based on the wavelength dispersion of the spectrum (WDS system).

REFERENCES

- [1] M. Menu et al., Nucl. Instr. and Meth. B 45 (1990) 296.
- [2] T. Calligaro et al., Nucl. Instr. and Meth. B 136-138 (1998) 339.
- [3] J.-C. Dran et al., In "Modern Analytical Methods in Art and Archaeology", edit. E. Ciliberto and G. Spoto (John Wiley and Sons, New York 2000).
- [4] M. Dubus et al., Proc. 6th international conference on non destructive testing and microanalysis for the diagnostics and conservation of cultural heritage, Rome, 17-20 May 1999, pp. 1739-1749.
- [5] A. Duval, Proc. 6th international conference on non destructive testing and microanalysis for the diagnostics and conservation of cultural heritage, Rome, 17-20 May 1999, pp. 1007-1021.
- [6] A.-M. B. Olsson et al., Nucl. Instr. and Meth. B 181 (2001) 707-714.
- [7] T. Calligaro et al., J. Nucl. Instr. and Meth. B 161-163 (2000) 328.
- [8] G. Demortier Nucl. Instr. and Meth. B 113 (1996) 347.
- [9] A. Perea et al., Proc. 32d Intern. Symp. on Archaeometry, Mexico May 15-19 2000.