ION BEAM ANALYSIS IN ARCHAEOLOGY: ACCELERATOR BASED TECHNIQUES FOR NON-DESTRUCTIVE ELEMENTAL ANALYSIS

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ABSTRACT

The use of ion beam analysis (IBA) in arts and archaeological sciences has increased significantly during the last decade and several research groups have focused on this application of IBA. The main reason for this development is the non-destructive character of these techniques. In this paper a comprehensive overview of this development is given together with some detailed examples from the author's laboratory and others. The use of traditional IBA is complemented by microanalytical methods.

Introduction

In the sixties the nuclear physicists "abandoned" many small accelerators since their ion energies were too low to produce interesting basic nuclear physics data. This "easy"access to small electrostatic accelerators in nuclear physics laboratories has initiated the development of several methods of ion-beam analysis with applications in many fields of science and technology. The methods employ ions (protons and heavier particles) with energies in the MeV range. Such ions penetrate only a few tens of μm of the irradiated material and hence the analysis will be surface-oriented and essentially non-destructive. The latter is very important in the fields under discussion here, since often precious or irreplaceable objects are to be investigated. The possibility of extracting the ion beam out of vacuum into air makes it possible to irradiate large objects in situ.

The methods which have been most important in materials science and geology are Rutherford backscattering (RBS) (Chu et al 1978) and Particle-induced X-ray Emission (PIXE) (Johansson and Campell 1988). The development of using IBA techniques in these fields has "poured over" into archaeology. The development has also lead to the establishment of at least one ion beam analysis laboratory entirely dedicated to the analysis of art and archaeological objects. In connection with the rebuilding of the Louvre museum in Paris, a laboratory has been financed and built in the basement below the new glass pyramid (Menu et al 1990). This is a substantial investment for no other purpose than in-house ion- beam analyses in arts and archaeology.

Before going into a more detailed discussion on the subject IBA in archaeology, it is essential to stress some factors involved when evaluating these methods as potential archaeological tools. First, it is clear that the need for an accelerator represents a serious limitation in many instances in archaeology. However, it is often quite possible to collect or select material for safe transport to a laboratory for a subsequent analysis. Then, the specific experimental equipment required is of less concern. The rapidity by which the analyses can be performed compensates for the investment costs of the accelerator and hence the cost per analysis is quite competitive. As a consequence several large-scale archaeometric investigations based on IBA methods have been performed (Duerden et al 1984). For a detailed study of the field of IBA in arts and archaeology the proceedings from a special workshop on the subject in France 1985 is recommended (Lahanier et al 1986).

Experimental equipment

The common equipment for all ion beam analysis techniques is an accelerator capable of producing MeV ions, normally an electrostatic accelerator of the traditional Van de Graaff type. Also cyclotrons have been used in some laboratories. The ion beams are normally guided by various means to an experimental vacuum chamber in which the irradiation of the specimens takes place. For some IBA methods, the analysis could also take place under atmospheric pressure (Räisänen 1987). This is often preferable for archaeological artifacts. In connection with the irradiation various radiation components are registered by special detectors and the signals thus produced are collected and processed with nuclear electronics and stored in computers. Evaluation of the raw data in the computers then yields qualitative or quantitative results.

Ion beam analysis methods

Several IBA methods are well applicable to archaeological research. In some investigations it may be of interest to study penetration or diffusion processes in materials and then several non/destructive IBA methods are suitable. Nuclear Reaction Analysis (NRA) employs specific nuclear reactions, often of a resonant type (Cookson 1987). By varying the ion velocity in the accelerator it is thus possible to get a detailed characterization of the depth distribution of elements like hydrogen, nitrogen, fluorine etc. Another possibility is the Rutherford backscattering (RBS) spectrometry in which the energy of the backscattered ions is used to determine the composition and distribution of the lighter elements.

The most commonly used technique, which will also be emphasized in this paper, is the Particle Induced X-ray Emission (PIXE) analysis (Johanson and Campell 1988). It was originally invented at our department in the early seventies and is now in use in hundreds of laboratories all over the world. It is by now an established standard method and has been used frequently also in archaeological studies. The technique is similar to the more well known X-ray fluorescence and electron microprobe techniques. The X-rays are registered by an energy-dispersive X-ray detector and the resulting X-ray spectra contain many peaks of characteristic X-rays superimposed on a continuous background (fig 1). The probability of detecting the characteristic X-rays and the intensity of the background determine the analytical sensitivity. The background in PIXE spectra is much lower than for the electron microprobe and the detection limits are at least two orders of magnitude lower, allowing quantification of trace elements down to the parts per million level. The best sensitivity is reached for the medium-heavy elements, eg copper and zinc, but the elemental variation is slow.

The use of ion beams in air is suitable to combine with PIXE analysis since the X-rays penetrate the air fairly well. Consequently, it is straightforward to irradiate an archaeological specimen in air, thus reducing heating and avoiding the stress induced

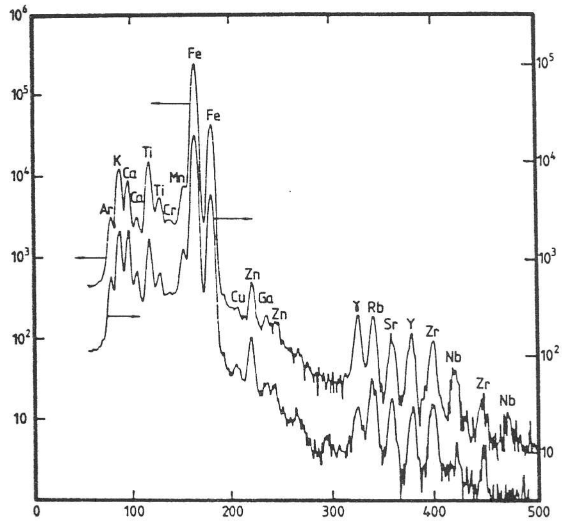

Fig 1. X-ray spectra from PIXE analysis of clay (top) and pottery (bottom)(from Peisach et al, J. Radioanal. Chem. 69 1982;349)

when pumping on the objects. As will be elaborated on later, this approach has been used, especially when analysing very fragile and sensitive objects, eg paper, papyrus, paintings etc. This approach gives a unique method of a very localized trace element analysis of large objects in air essentially without any sample preparation.

Since the X-ray methods are always limited by the strong attenuation of the low energy X-rays produced by the lighter elements, it is important to find complementary and preferably simultaneous methods to determine light elements. In IBA applied to arts and archaeology several studies have included the use of particle-induced gamma-ray emission (PIGE) (Tuurnala et al 1986) which is favourable for the lightest elements, eg, nitrogen. In this way, for instance, organic material may be analysed for the bulk composition.

Applications

In order to fully understand and appreciate the IBA techniques in the field of arts and archaeology it is necessary to present a number "typical"applications which will hopefully shed some light over the analytical properties involved. I will divide the presentation in two major sections: *macro and microanalysis*. The first name denoting that the analysing probe has a size of about 1-10 mm. Consequently, microanalysis denotes probes, normally well below one mm and sometimes only a few thousands of a mm. A clear difference exists between these two main groups since the macroanalytical approach normally attempts to analyse a representative part of an object. Microanalysis, however, normally aims to find highly localized information or characterize very heterogeneous structures.

Macroanalysis

Measurements in vacuum

Although the insertion of precious objects in vacuum should be avoided it is sometimes necessary in order to obtain proper analytical conditions. In archaeometric investigations, in particular, large numbers of samples have been processed by in-vacuo PIXE-/PIGE analysis. At the Lucas Heights laboratory in Sidney, Australia, several large-scale investigations have been performed mainly for provenance studies (Duerden et al 1984). The trade routes for volcanic obsidians in the general south-west Pacific region have been studied by a combination of IBA and multivariate statistical methods. Both major elements, eg, silicon, potassium and calcium, and trace elements, eg, copper, zinc, rubidium, strontium and yttrium, were determined and used for the evaluation. Both the multi-elemental character of the IBA techniques and the large analytical capacity, which has made it possible to analyse close to 10000 samples altogether, play important roles in these projects.

The weathering processes taking place at the surface of obsidians have been studied using ion beam analysis capable of depth profiling of, eg, hydrogen (Ambrose 1984). The hydrogen profile as determined by resonant NRA yields information on the water uptake in flint (Andersen and Whitlow 1983) and could be used to understand the mechanisms behind the brown patination of flints. Another interesting use of a depth-profiling method is the use of RBS to study the composition of desert varnish. This coating of rocks in Australia and in other arid climates forms a thin layer of varying colour. It has been proposed that it would be possible to date engravings in such rock varnishes (Dorn et al 1990), by using PIXE to determine the ratio between the sum of calcium + potassium and titanium. However, to implement such a method it is essential to fully understand the varnish formation processes and then the depth profiling IBA methods are very useful.

The trace elemental composition of metallic objects may reveal information on, for instance, the manufacturing processes (casting technique etc) and on trade routes. In many cases the corrosion of old objects may be severe and since the effective analytical depth of IBA is shallow it may be difficult to obtain relevant elemental information. The PIXE method is particularly useful when the sample masses available are limited (μg-mg). By drilling small holes, to reach the bulk material without leaving any visible damage on the object, a sample suitable for PIXE analysis is obtained. In a study of Etruscan bronze mirrors this method has been successfully employed (Wiman 1990). In other materials, eg, noble metals, it may be adequate to directly irradiate the fresh surface and use the IBA methods to analyse trace constituents. A chinese arrow head from around 200 BC demonstrated a surprisingly fresh and uncorroded exterior and an unusually well preserved sharpness of the edges. In order to understand this phenomenon a combination of RBS, NRA and PIXE was used to analyse the surface. The results show a complicated composition which varies in different parts of the arrow head. The anticorrosive treatment seems to be a layer of a mixture of calcium, tin, lead and chromium oxides (Chen et al 1981). Similar treatment has been patented in the 20th century both in Germany and US. Ion beam techniques have also been used to reveal forgeries in jewelry (Demortier 1984). The composition of the gold alloy (cadmium concentration) proved that the actual date of the objects was much later than was originally assumed.

In some instances surface contamination on objects may be interesting in order to understand the actual purpose for which they have been fabricated. An example at our laboratory was a wedge-shaped pendant, assumingly used as a gold quality test probe 800 years ago. The problem was to confirm the hypothesis and exclude that the traces of gold visible on the surface was of modern origin, eg, by intentionally rubbing the pendant with a wedding ring. By a simple in-vacuo PIXE analysis with a 1 mm ion beam (fig 2) the composition could be shown to be proper for the time assumed, without any copper which is always present in modern gold (Ahlberg et al 1976).

In characterization of gem stones, the experience of IBA from geology has been useful. The combination of analytical methods such as PIXE, RBS and NRA can produce detailed information on the quality and origin of the gem stone (Bird 1986). One important factor is the elemental analysis of inclusions which could reveal information on the origin and genuinity of the gem stones.

Non-vacuum analysis

The possibility to reduce heating by convective cooling, makes in-air IBA analysis of archaeological objects particularly useful. In addition, many objects within archaeology are non-conductive and during

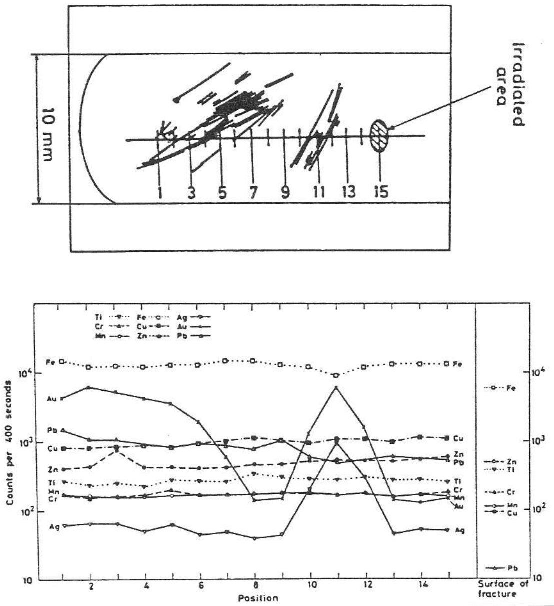

Fig 2. Analysed spots and "gold streaks" on pendant (top) and corresponding X-ray intensities for the elements Ti, Cr, Mn, Cu, Zn, Ag, Au and Pb (Ahlberg et al 1976).

ion bombardment in vacuum a charge build-up will lead to reduced sensitivity (Ahlberg et al 1975). This is avoided in air. In studies of, eg oil paintings, the possibility of keeping the object in air during analysis is mandatory due to the dimensions as well as to the sensitivity of the paintings. In a study to reveal possible forgeries oil paintings were analysed using both PIXE and PIGE analysis and from the composition thus obtained the origin of the objects could be determined (Tuurnala et al 1986). In a large-scale project at Davis, California, several studies have been made on documents in order to understand printing techniques and verify genuinity. The famous Gutenberg bible was investigated with an 1 mm in-air ion beam in order to characterize the ink used (Kusko et al 1984). In another study the Vinland map (fig 3) was analysed in order to sort out the controversy around its age and origin (Cahill et al 1987). An attempt to analyse this map in 1974 showed that the pigment was of modern origin due to its high titanium concentration. However, when analysed for titanium with IBA at Davis the concentration was found to be much too low to be interpreted as a recent recipe.

Microanalysis

The ultimate use of ion beam analysis is realized in a Nuclear Microprobe. In such a system an ion beam of sub-mm dimension is used and allowing analysis of fine structures of archaeological objects. Also in this case, both vacuum and non-vacuum analysis can been carried out. At some laboratories, dedicated nuclear microprobes will or already have been set up for arts and archaeology (Menu et al 1990, Swann 1983).

The experimental equipment used for a nuclear microprobe is normally significantly more complex than for normal IBA. The data acquisition is based on advanced computers with large data collection capacity. This means that the "customer" (in this case the archaeologist) will have less possibilities to take active part in the details of the analytical procedures. However, this does not have to be a serious limitation since the other stages in the analytical procedure -- selection and sample preparation, sample mounting and choice of analysed area -- are the most critical and time-consuming parts of the analytical procedure.

In the external nuclear microprobe the ion beam is extracted into air which will scatter the ions and thus limit the lateral resolution. However, it is still possible to obtain useful resolutions (0.05-0.3mm) for most applications within art and archaeology. Since the non-destructiveness is essential in this field it is often worthwhile to trade off in lateral resolution. In some experimental facilities the region between the sample and the detector is flooded with helium gas to reduce the absorption of X-rays and to enhance the cooling rate of the sample (Swann and Flemming 1987).

Special aspects on microanalysis with ion beams

The heterogeneous structure of many archaeological artifacts makes the use of a highly collimated ion beam difficult since the interpretation of the obtained elemental data depends very much on the positioning of the beam. Many objects may contain inclusions and grains which may be not representative for the bulk. Such data, therefore, has to be very carefully evaluated and one should be careful to draw conclusions from a few single spot analyses.

Another problem is the risk of damaging the specimen. Even if the technique, in principle, is non-destructive it is still possible to damage the analysed specimens by using too high beam intensities or too large accumulated dose (Themner 1991). Discoloration of glass, ceramics and even bronzes have been observed after irradiation with too intense ion microbeams or with too high total dose (Swann and Flemming 1987). This risk is, of course, more serious for very sensitive materials, eg paper, parchments etc. Special precautions have then to be taken by using very low intensity beams and in-air analysis and, since this is mainly a dose-dependant effect, to restrict the accumulated dose of ions.

For elemental analysis with a very high lateral resolution, it is important to emphasize that the depth resolution, when using a nuclear microprobe with X-ray detection, is low. The beam will penetrate several tens of micrometers into the material and may very well analyse an underlying structure which is not relevant for the particular investigation. It is then better to use resonant nuclear reaction analysis, which allow high depth-resolution by detection of gamma rays or charged particles.

Microprobe applications

The selection of applications presented here is only intended to give hints to which possibilities the nuclear microprobe is offering to the field of archaeological research.

Osteology

The nuclear microprobe has been used to date excavated bones by determining the progressive substitution of the hydroxyl ions by fluorine ions in the bones. By using the microbeam and particle-induced gamma-ray emission (PIGE) a radial distribution of fluorine could be determined in sections of bones (Coote and Dennison 1988) The shape of this profile depends on the age of the specimen and is caused by diffusion mechanisms in which water plays an important role.

Pottery, glasses and related materials

The use of microprobes for the analysis of sherd material is limited due to the large heterogeneity of the material. However, in studying well-defined regions of glazes with interesting colouring etc the technique may be quite useful. The same is true for glasses with external decorations which could be analysed with IBA. The nuclear microprobe was used to characterize pigments used in faience beads and pendants excavated in Jordan and dated about 1400 BC (Swann 1983). The compositions of the pigment varied significantly and could be used to trace the origin and to understand the manufacturing processes. When dating chipped flints the hydrogen distribution has been studied using both microprobes and broad-beam irradiation (Andersen and Whitlow 1983). In the earlier discussed method for dating by analysis of rock varnish (Dornn et al 1990) the nuclear microprobe could be important when following the details of the varnish formation process.

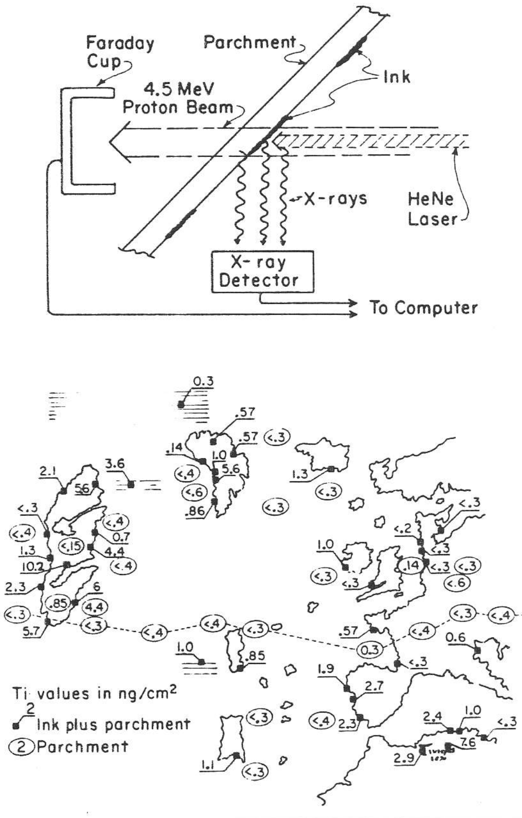

Fig 3. Experimental arrangement for external PIXE analyses of the Vinland map (top) and analytical results for titanium on various positions on the map (bottom)(Cahill et al 1987;829-833).

Metals

Several large scale studies have been performed on copper based alloys. In such studies great care has to be taken to avoid erroneous analytical data due to surface effects caused by corrosion. In figure 4 this effect is shown by analysing various parts of a Roman bronze coin (Doin et al 1978). The analysis of the patina and the core part shows large deviations. The interpretation of the data obtained from such analyses has to take such effects into account. On the other hand, the nuclear microprobe offers possibilities to non-destructively characterize objects in much greater details than has previously been possible.

In some applications these problems are less important since noble metals are essentially unaffected by corrosion also over longer time spans. Demortier et al (Demortier 1984) used the external nuclear microprobe at Namur in Belgium to perform extensive systematic investigations of gold jewelry in order to determine the age and manufacturing processes. Since the 19th century cadmium has been used as an additive to lower the melting point when soldering gold and the presence of cadmium has been regarded as a sign of a modern object. By detailed studies

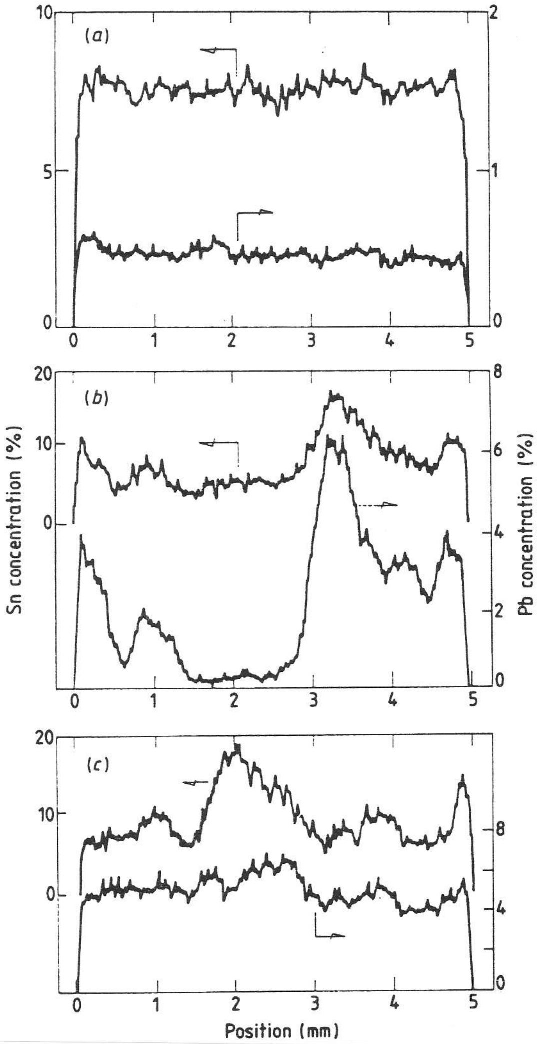

Fig 4. Lateral concentrations of Sn and Pb in (a) the core, (b) the patina and (c) the patina on the other side of a Roman bronze coin (Doin et al 1978).

using the nuclear microprobe the Belgian group has shown that cadmium can be found also in ancient gold objects. However, the correlation between copper and cadmium is reversed in the newly manufactured material and by the multi-elemental character of the PIXE method forgeries of "ancient" gold items could be revealed.

Printed and written material

The use of ion beam analysis to investigate old documents has already been discussed. By using the high lateral resolution of the nuclear microprobe it is possible to extend such studies for even more details. One example of using a scanning nuclear microprobe combined with sophisticated multi-variate statistical methods is the identification of fainted letters in ancient Greek handwriting on papyrus (Lövestam and Swietlicki 1989). The irradiation was performed in an external microprobe where the sheet of papyrus was mounted on a x-y scanning table. By moving the specimen during analysis, two-dimensional elemental maps were produced and the idea was to use these maps to identify the letters by their "elemental images". It turned out, however, that this simple approach was not enough to obtain a good image contrast. After compilation of maps from several elements by multi-variate statistical methods the contrast was enhanced and the letters revealed (fig 5).

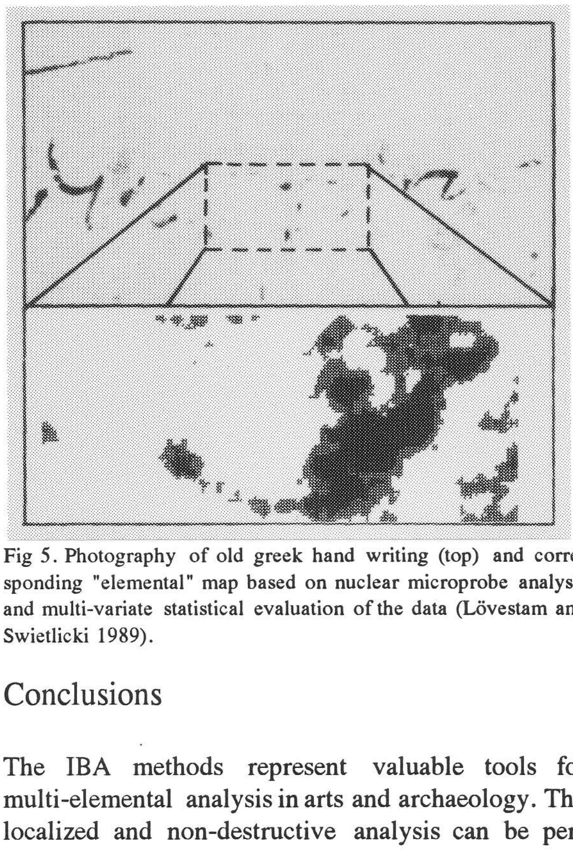
Fig 5. Photography of old greek hand writing (top) and corresponding "elemental" map based on nuclear microprobe analysis and multi-variate statistical evaluation of the data (Lövestam and Swietlicki 1989).

Conclusions

The IBA methods represent valuable tools for multi-elemental analysis in arts and archaeology. The localized and non-destructive analysis can be performed in air, thus offering unique possibilities to study sensitive and bulky archaeological artifacts in situ. The surface oriented analysis can be utilized favourably, but care should be taken in analysis of ancient objects with a significant corrosion. The IBA-methods can play an important role in very detailed investigations (nuclear microprobe) and as well as in large-scale studies comprising many archaeological objects.

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