THE NEW EXTERNAL MICROBEAM FACILITY OF THE OXFORD NUCLEAR MICROPROBE AND ITS APPLICATION TO PROBLEMS IN ARCHAEOLOGICAL SCIENCE

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Abstract

Recent developments of the external beam facility of the Oxford Nuclear Microprobe have led to an enhancement of the capabilities of the instrument for analysing large or sensitive objects in air with a spatial resolution of 50 to 100 μm. Used in conjunction with the 1 μm resolution *in-vacuo* facility this provides a unique elemental analysis facility which is being applied to a number of archaeological problems. This paper describes briefly the capabilities of the facility and outlines the range of applications.

1. INTRODUCTION

Ion Beam Analysis (IBA) has a well-established role in the characterisation of archaeological and historical objects. The combination of trace element sensitivity and quantitative accuracy offered by the techniques of Proton Induced X-ray Emission (PIXE) or Rutherford Backscattering (RBS) presents a solution to many problems involving the study of artefacts and raw materials. Using a suitable micro-focusing system, IBA can be carried out with a spatial resolution of the order of 1 μm [1], but this is often inappropriate for archaeological objects. This is due to the nature of the materials, which are often heterogeneous, containing particulate inclusions with diameters of less than 100 micrometres. The long penetration depth of MeV light ions averages the signal over the range of the ions (tens of micrometres) and so unless thin samples are used, it is not possible to analyse small inclusions separately from the matrix and the advantage of using micron or sub-micron beams is lost. Another practical disadvantage of high resolution microbeam facilities for archaeological applications is the requirement to place the sample in an evacuated chamber, which for most archaeo-

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logical or historical objects requires sampling, which may be highly undesirable for precious, delicate objects.

2. THE OXFORD EXTERNAL MICROBEAM FACILITY

The long range of MeV ions in air presents the possibility of analysing large or fragile objects in air with no sampling required. The beam diameter is degraded by collisions with air molecule (by approximately 10 μm per mm of air path), but as discussed above, this is not a major problem for archaeological samples and by careful design, a spatial resolution of less than 50 μm can be achieved. For the majority of sample ion beam analysis in air is non-destructive; the presence of air or helium around the sample disperses any localised heating cause by the beam, and so prevents any thermal damage. In organic materials, decomposition of large organic molecules can

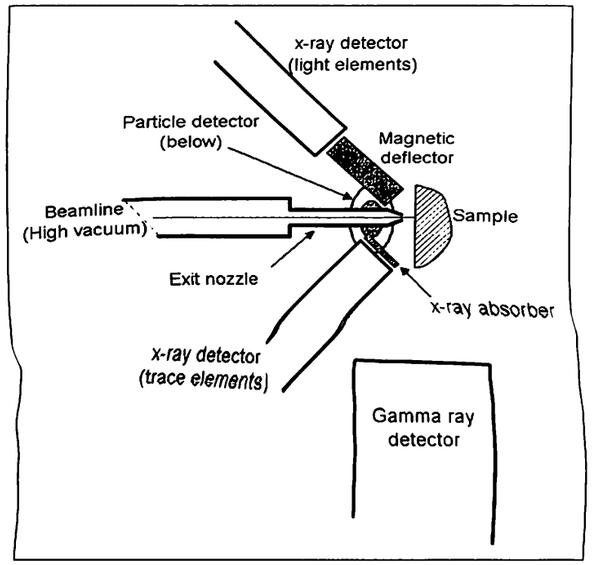

Figure 1. A schematic plan view of the external beam analysis facility at Oxford. The beam emerges from the vacuum of the beamline through a 300 μm diameter hole in a 2mm diameter copper nozzle sealed with a thin (8 μm) plastic foil. X-rays emitted from the sample are detected by two detectors mounted at 45° on either side of the beam. One detector is fitted with an x-ray absorber to kill the intense low energy x-ray lines from Al and Si to ensure good detection limits for the trace elements while the other detector has no absorber and is fitted with a magnetic deflector to ensure that high energy protons do not reach the detector. A detector for gamma rays is mounted at 90° to the beam. Below the beamline, a detector for recoiling protons records the RBS spectrum and allows the total amount of charge falling on the sample to be monitored. Not shown in this diagram are a video microscope which uses a mirror to view the front surface of the sample during analysis and a low power alignment laser to assist in positioning the sample for analysis.

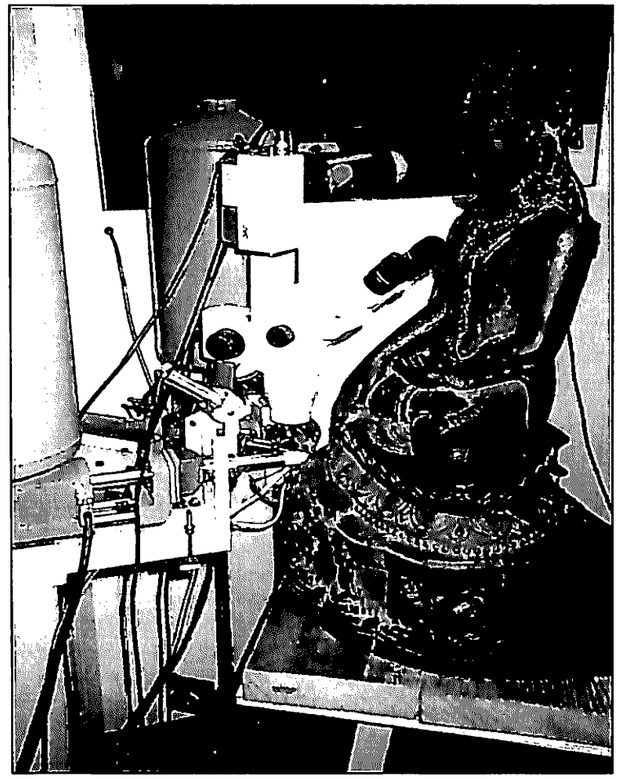

Figure 2. A general view of the new external beam facility being used for the characterisation of surface layers on an 18th century bronze statue of Buddha.

cause discoloration, but in many cases (e.g. papers) this fades over a period of days and in any case is confined to the small area of the beam.

An external beam system has been developed for the Oxford Scanning Proton Microprobe facility using design concepts described first by the AGLAE group in Paris [2] (see figures 1 and 2). The key to high performance of this type of system is to minimise the distance between the exit of the beam from the vacuum and the sample. This reduces beam scattering and also reduces the absorption of the emitted signals, but in order to allow a free path from the sampling point to the detector. In this design the exit nozzle consists of a hollow copper cylinder with the diameter reducing in steps from 12 mm to approximately 2 mm. Copper was chosen for the nozzle material in order to reduce the gamma ray background which might result if light elements such as Al were used and the beam strikes the inner surface. The only signals induced from copper are the Cu x-rays, which do not escape from the walls of the nozzle. The beam emerges into air through a 300 μm diameter aperture covered with an 8 μm Kapton

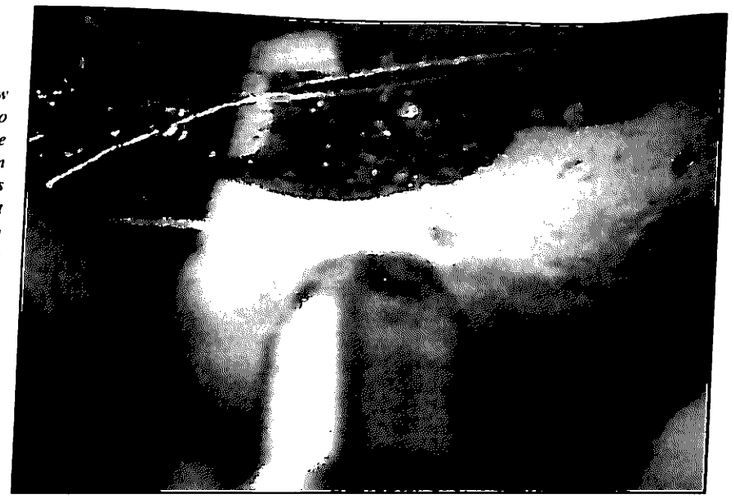

Figure 3. View through the video microscope of the external beam facility. This shows the copper exit nozzle projecting from the bottom of the image and the surface of a sample of 18th century Islamic lustreware. The outline of the lustre glazed decoration can be seen as the dark regions of the sample.

window. Two quadrupole lenses focus the beam through the nozzle, so that the amount of beam striking the aperture is minimised. Note that this also means that the spatial resolution is not determined by the size of the aperture hole. The sample is mounted at approximately 4 mm from the window, allowing a resolution of 40-50 μm to be achieved on the sample. Detectors for x-rays, recoiling protons and gamma rays allow analysis using PIXE, RBS and also Proton Induced Gamma-ray Emission (PIGE) analysis for the detection of light elements such as Li and F. This allows virtually the entire periodic table to be covered in a single measurement. A video microscope and a low power laser are used to align the desired region of the sample in the beam (see figure 3). Full technical details of the new external beamline will be presented elsewhere [3].

In a separate development, the external beam facility has been fitted with a high power focused pulsed laser to enable the surface of the sample to be ablated at exactly the same spot as the analysis is taking place [4]. This exciting development is aimed specifically at the study of thick corrosion layers on ancient metals, but the ability to remove surface films in a well controlled manner over an area of less than 100 μm diameter will have implications for many aspect of the analysis of ancient materials, where it is desirable to characterise separately both the corrosion film or patina and the underlying bulk material.

3. APPLICATIONS OF THE OXFORD EXTERNAL BEAM FACILITY

The wide range of applications of the Oxford external beam to archaeological materials is summarised below:

Panel	*t (μm)*	*Hg%*
Top	5,08	11,30
Top	5,08	11,60
Centre	5,06	15,00
Bottom	6,16	14,50
Mean	*5,35*	*13,10*
s.d.	*0,54*	*1,92*

3.1. CORROSION FILMS, SURFACE LAYERS AND BULK COMPOSITION OF METALS

In addition to using PIXE to characterise the composition of bulk metals, thin (< 10 μm) surface layers can be characterised accurately and non-destructively using RBS. This provides information complementary to that which can be obtained for thick layers using the laser ablation facility. The Oxford external beam has been used to investigate a wide range of metal types, and alloys based on copper, silver, gold and iron have been investigated. In a study of a medieval altar cross [3], the thickness and composition of the gilding layers was determined from the relative intensities of the gold, mercury and copper x-rays induced by the beam. The ratio of the gold and mercury L-lines provided the Au:Hg ratio in the amalgam gilded film, and since the copper x-rays from the substrate are absorbed by the overlying gilding layer, the ratio of the copper K-line to the gold L-line provides a very accurate measurement of the thickness of the film, as shown in table 1, in which presents the thickness and percentage of mercury recorded on the three back panels.

Another example, shown in figure 2, involved the investigation of a 17th century Buddha from Thailand. Although this object was bronze, the black surface had an unusual appearance. Using RBS, it was possible to determine that the surface was coated with a thin layer of organic material rich in carbon and oxygen which was diffusing into the copper. One explanation for this could be the interaction of the metal with the smoke of devotional lamps and candles over a long period.

3.2. POTTERY AND GLAZES

A major advantage of the external beam facility in the study of pottery is the ability to analyse the whole object without sampling, which can be difficult and undesired on rare fragile objects. A range of analyses have been carried out both on whole objects (e.g. the characterisation of blue and white glazes on Chinese porcelain) and on fragments (e.g. the analysis of 18th century Islamic lustre glazes). In the case of the lustre glazes, the composition of the metal surface layer can be determined using PIXE and the thickness of the metal layer can also be determined using RBS. Figure 3 shows the surface of a lustre glazed sherd viewed through the video microscope of the external beam facility. The copper beam exit nozzle can be seen at the bottom of the picture and the decoration of the sample can be seen. The dark regions are lustre glazed. Figure 4(a) shows the RBS spectrum acquired from the lustre glazed region using a primary beam energy of 3 MeV. The small high energy peak in the spectrum indicates the metallic copper layer resulting from the lustre glaze. The total area of this peak is a measure of the amount of copper present in the film, while the shape gives an indication of the depth distribution. In this case, although the statistics were not con-

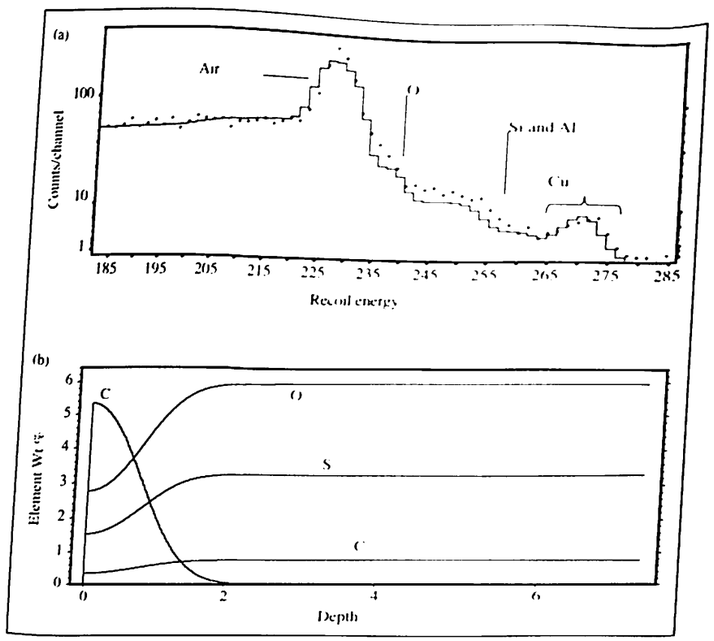

Figure 4. (a): RBS spectrum of lustreware glaze recorded in air using protons with an initial energy of 3 MeV. The measured data is shown as dots and the thin line is a theoretical simulation using the sample profile shown in (b). The metal layer appears as the small peak in the high energy region of the spectrum, and the Si and O from the glaze appear as steps at lower energy. The large peak in the centre of the spectrum is due to recoils from nitrogen and oxygen nuclei in the air. The data was recorded in 90 minutes at a beam current of 300 pA. (b): The theoretical sample depth distribution used to calculate the simulated spectrum in figure 4 (a).

clusive in this feasibility study, there is a strong indication of a diffusion profile of the copper into the glaze, as shown by the simulated curves, resulting in the profile shown in figure 4(b).

3.3. GLASS AND ENAMEL

The same considerations of sampling also apply to glass objects and the external beam facility has also been applied to the characterisation not only of ancient glass objects and large fragments but also miniature mediaeval enamelled panels. The objective in these analyses has largely been to determine the nature of added constituents such as colorants.

3.4. JEWELLERY AND GEMSTONES

There is an increasing interest in the analysis of ancient gemstones as an aid to provenance studies [5 and 6]. Many gemstone minerals do not have a fixed composition, and may comprise a mixture of end-members in varying concentrations. Examples of these include garnets which have three end members and tourmalines with as many as twelve. Determining the end-member fraction allows the comparison of stones (e.g. to determine whether all stones in an object were from the same source), while the trace element content may be characteristic of the mineral deposit, although there is still a only a limited amount of comparison data available for this type of application. The external beam facility is ideal for the characterisation of mounted gemstones, since they do not have to be removed from the object in which they are mounted and the technique is non-destructive. The Oxford facility has been used in a number of feasibility studies, including the characterisation for the first time of the tourmaline intaglio of Alexander the Great from the Ashmolean Museum [7].

4. CONCLUSION AND ACKNOWLEDGEMENTS

This brief description of the Oxford external beam facility has demonstrated the capabilities of in-air micro-analysis using focused beams of MeV ions. This technique offers unique advantages to the archaeological scientist for the characterisation of ancient materials and artefacts, and a brief summary of applications has been presented. This work has naturally involved the collaboration of co-workers from many different institutions, and the author especially wishes to acknowledge the contributions of the following people: Ms M.H. Abraham and Dr J.P Northover of the University of Oxford Department of Materials, Dr R. Camber of Sotheby's, London, Dr M. Vickers of the Ashmolean Museum, Oxford, Prof. M. Tite of the Research Laboratory for Archaeology and the History of Art, Oxford and Dr L. Thoreson of the Getty Museum, Los Angeles.

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