

European Commission

Ion beam study of art and archaeological objects

A contribution by members of the COST G1 Action

Edited by

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Appendix 6

Essential of PIXE and RBS for archaeological purposes

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Abstract

Proton induced X-ray emission (PIXE) has been proved to be a very rapid and accurate method for the elemental analysis of ancient artefacts. Using protons whose energy is lower than 3 MeV, it is possible to obtain, in a few minutes, the actual composition of narrow parts of artefacts, without any sampling, even at microscopic level. Any element with an atomic weight higher than 20 may be analysed. Rutherford backscattering spectroscopy (RBS) is a complementary technique mainly useful to control the homogeneity in depth and then to study superficial layers containing heavy elements. The present contribution is part of the Seville proceedings book. Its contents have been listed in Appendix 5.

Introduction

Quantitative elemental analyses of archaeological materials are now used to explain the provenance of artefacts and understand the workmanship of ancient craftsmen. When applied to unique archaeological items these analytical methods require to be mainly non-destructive and able to give the chemical composition of different parts of the artefact without any sampling, even at microscopic level. PIXE (proton induced X-ray emission) (2), PIGE (proton induced gamma-ray emission) (3) and nuclear reactions (3) involving the detection of a charged particle (NRA) (three methods sometimes used simultaneously) possess most of these qualities (4). PIXE and PIGE may be applied to artefacts of large dimensions, kept at atmospheric pressure during the irradiation. If necessary, the investigations may be undertaken in a microprobe assembly (beam diameter down to 3 μm) (5-7). RBS may sometimes give complementary information on the distribution of heavy elements. PIXE and RBS are then suitable to study materials containing medium and heavy atoms, PIGE and NRA to study light atoms (3). The energy of the incident particles is low enough (1 to 3 MeV) to avoid any residual activity. They are produced in particle accelerators described by Dran (7).

(1) LARN, Facultés Universitaires Notre-Dame de la Paix, B-5000 Namur.

(2) Deconninck, G., Demortier, G., Bodart, F., *Atomic Energy Review* 13(2), (1975) pp. 367-412.

(3) Kiss, À., 'Elemental analysis based on nuclear reactions' in 'Applications of ion beam analysis techniques to arts and archaeometry' (M. A. Respaliza and J. Gómez-Camacho, eds.). Secretariado de Publicaciones Universidad de Sevilla, Seville, 1996, pp. 41-60.

(4) Lahanier, Ch., Amsel, G., Heitz, Ch., Menu, M., Andersen, M. H. (ed.): 'Ion beam analysis in the arts and archaeology', *Nucl. Instr. and Methods in Physics Research* B14 (1986) pp. 1-167.

(5) Demortier, G. (ed.), proceedings of the Second International Meeting on Chemical Analysis by Charged Particle Bombardment, *Nucl. Instr. and Methods* 197 (1982) pp. 1-258.

(6) Demortier, G., 'Applications of nuclear microprobes in archaeology', in *Principles and applications of high-energy ion microbeams* (F. Watt and G. W. Grime, ed., Adam Hilger, Bristol) (1987) pp. 333-377.

(7) Dran, J. C., 'Electrostatic accelerators. Beam sample interactions' in *Applications of ion beam analysis techniques to arts and archaeometry* (M. A. Respaliza and J. Gómez-Camacho, eds.). Secretariado de Publicaciones Universidad de Sevilla, Seville, 1996, pp. 11-23.

Basic principles of PIXE

The irradiation of all materials with charged particles leads to an ionisation of electronic shells and consequently to emission of X-rays whose energy is characteristic of the atom. The technique using this phenomenon induced by protons is called PIXE. In principle, the analysis of all the elements may be performed but, practically, only elements with an atomic weight greater than 20 may be quantitatively determined. Elements with an atomic weight lower than 20 are more accurately analysed by detection of γ -rays produced by excitation of the internal structure of the atomic nuclei (PIGE) ⁽³⁾ or detection of charged particles arising from the interaction between the incident particle and the nucleus. The characteristic K X-rays of light elements are indeed so highly absorbed in the sample that corrections cannot be made to obtain sufficient accuracy with PIXE.

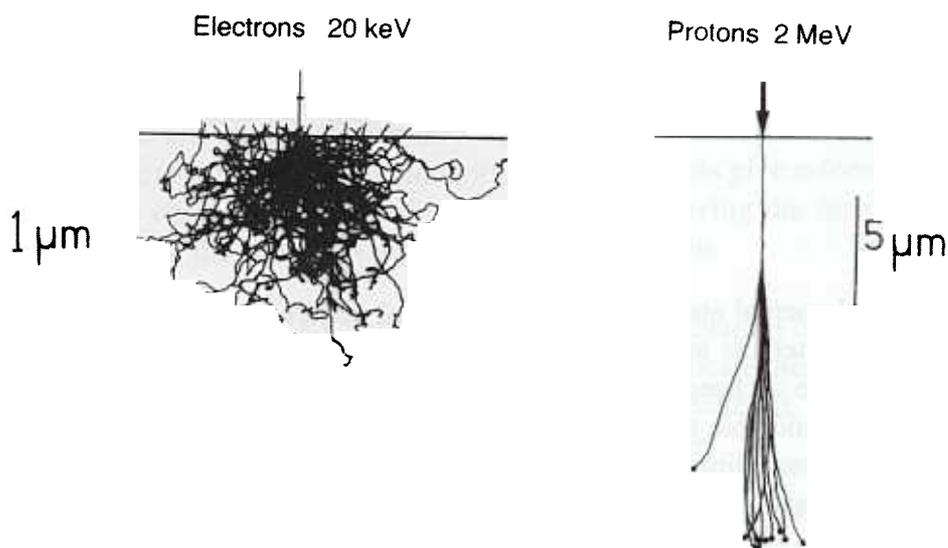
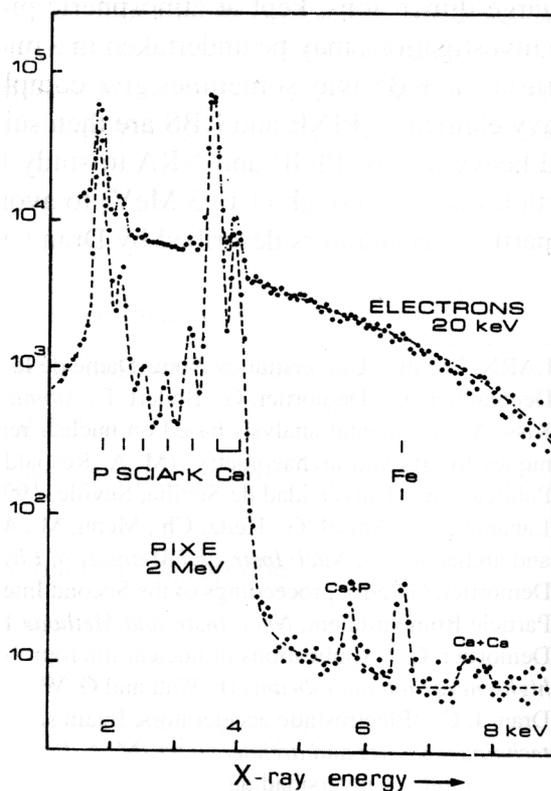


Figure 1. Calculated paths of electrons (20 keV) and protons (2 MeV) in a pure copper matrix.

Figure 2. Comparison of X-ray spectra obtained by irradiation of apatite with 20 keV electrons and 2 MeV protons.

PIXE is very similar in its principles to X-ray analyses with an electron microprobe. The main differences lie in: the trajectories of the incident particles (protons penetrate in any material by gradual decrease of their energy along a straight trajectory while electrons zigzag along a complicated path), the depths of the analysed material layers (5 to 10 μm under the surface for PIXE but only 1 μm with conventional electron probes) (Figure 1), the sensitivity (2 orders of magnitude better for PIXE because proton *bremsstrahlung* is nearly absent) (Figure 2).



Furthermore, PIXE analyses may be performed at atmospheric pressure, preventing very large (like parchments, books, paintings, etc.) or fragile objects (like paper, intricate jewellery items, etc.) from being introduced in vacuum (8).

A vast amount of measured cross-section data for X-ray production intensities with protons on numerous chemical elements have been published. They are also very well predicted theoretically by several models. The complete calculation takes into account the energy loss, the depth deflection and the velocity change of the projectile in the coulomb field of the nucleus, the perturbation of the atomic stationary states by these incident projectiles including relativistic effects: ECPSSR model. Accurate data are now available (9) in nearly exhaustive tables.

Selected values of ionisation cross-sections for incident protons up to 3 MeV and corrected for the fluorescent yields to produce $K\alpha$ or $L\alpha$ X-ray lines are given in Figure 3. We can observe that those X-ray emission cross-sections vary by nearly 5 orders of magnitude when the target atomic number varies from 15 to 80. K X-ray emission intensities are then only interesting for quick analyses of elements up to $Z = 50$. L X-rays are more convenient to achieve a sufficient sensitivity for minor and trace elements of high weight.

In Figure 4, we give typical X-ray spectra. Note that the vertical axis is given in a logarithmic scale in order to appreciate the large variation of intensities.

Figure 4a. PIXE spectrum of a black shard (Braive-Belgium).

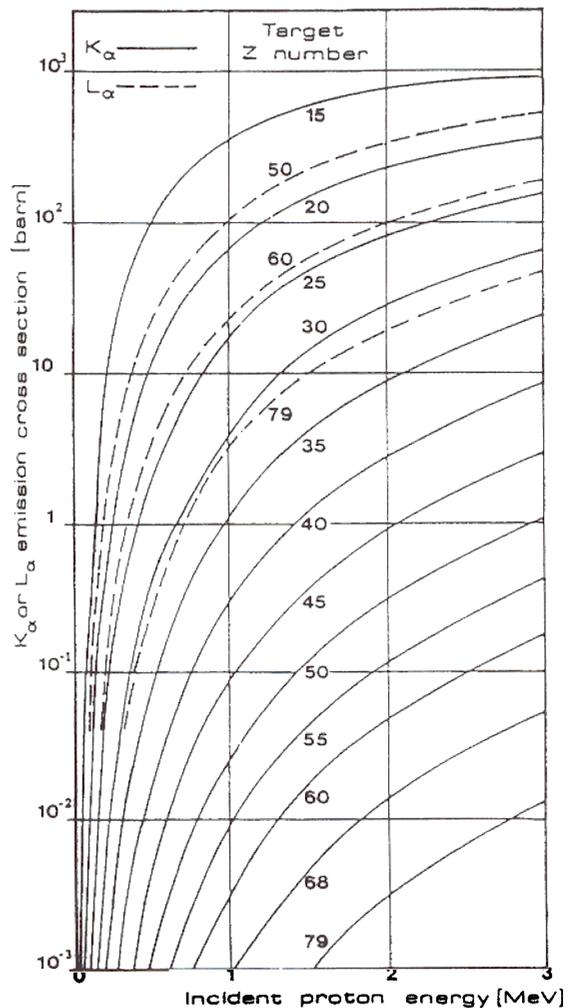
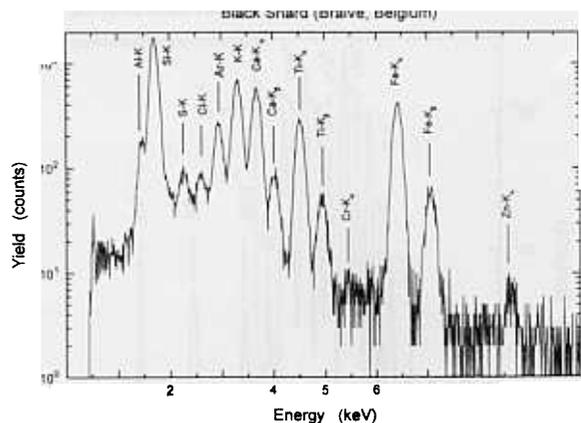


Figure 3. Relative intensities of $K\alpha$ and $L\alpha$ X-rays produced by protons up to 3 MeV on various elements.



(8) Deconninck, G., Proceedings of the Fourth Conference on the Scientific and Industrial Applications of Small Accelerators, J. L. Duggan and I. L. Morgan (ed.), 76CH 1175-9NPS (1976) pp. 533-542.

(9) Cohen, D. D. and Harrigan, M., Atomic Data and Nuclear Data Tables, 33 (1985), 255, and Atomic Data and Nuclear Data Tables, 34 (1986), 393.

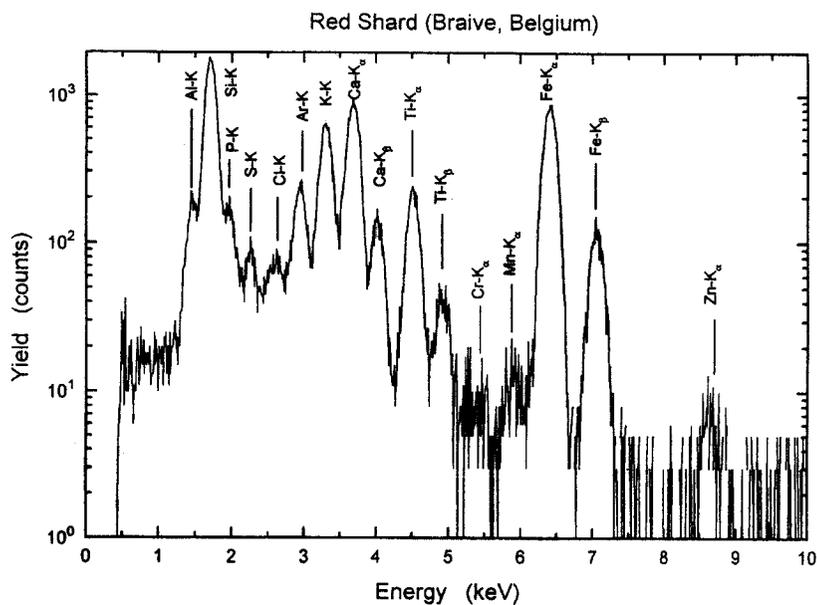


Figure 4b. PIXE spectrum of a red shard (Braive-Belgium).

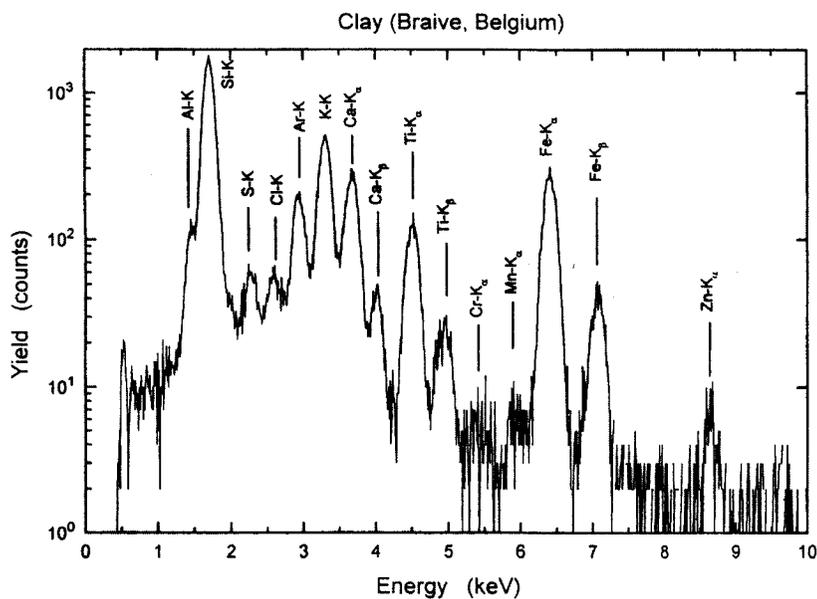


Figure 4c. PIXE spectrum of clay of Braive.

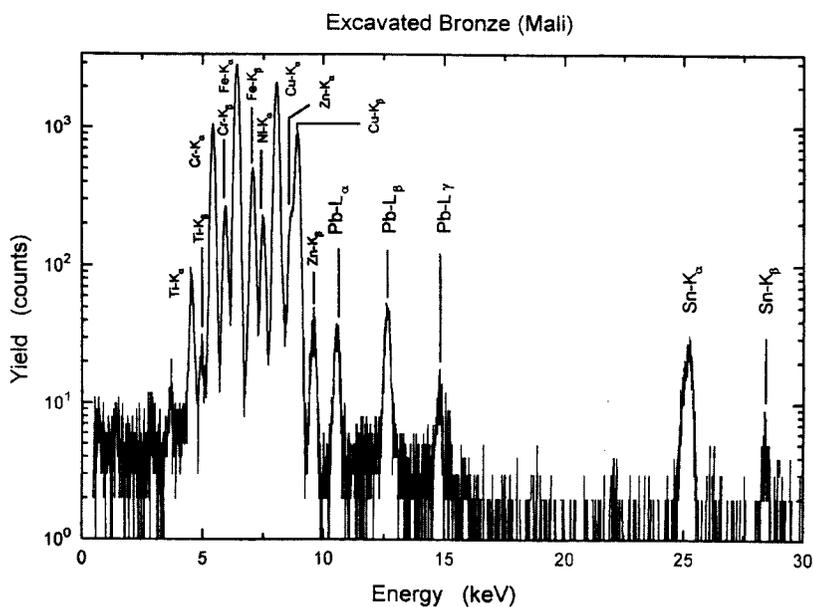


Figure 4d. PIXE spectrum of an African bronze (Mali).

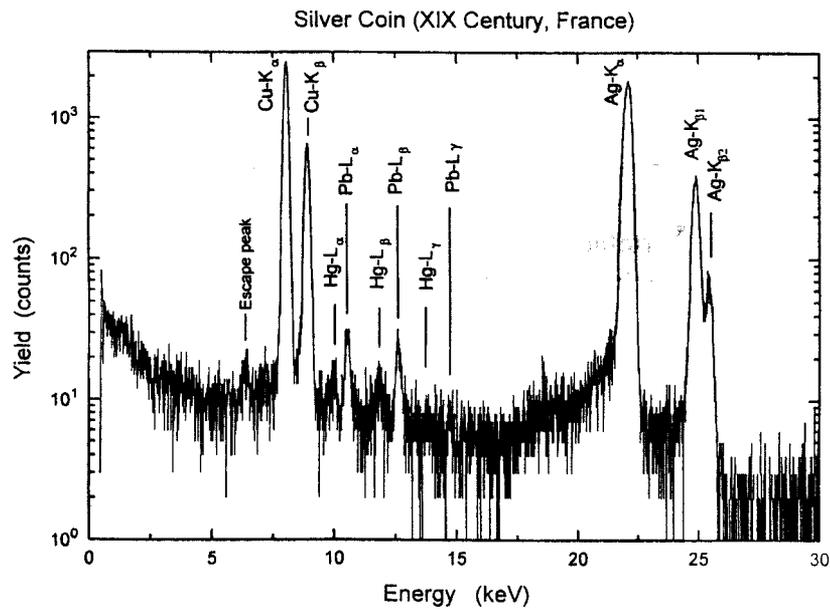


Figure 4e. PIXE spectrum of a silver coin (France, 1805).

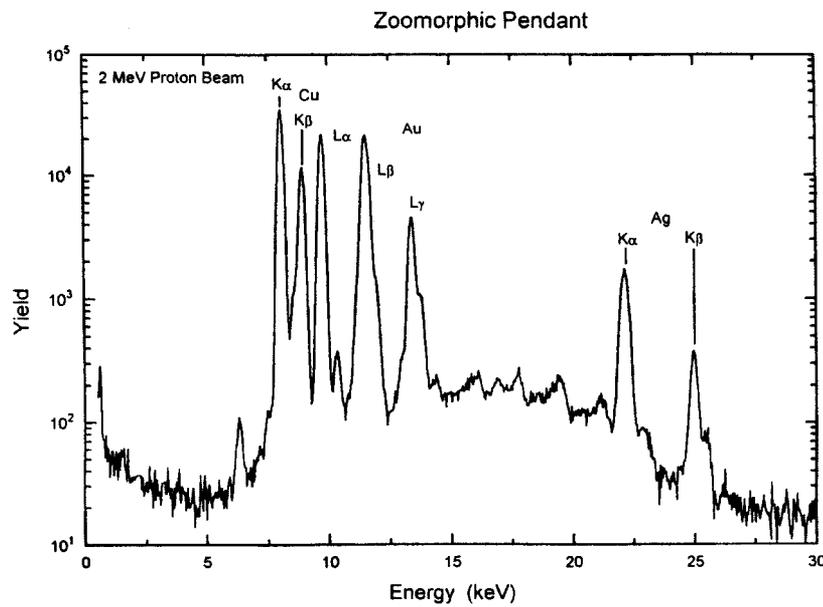


Figure 4f. PIXE spectrum of a gold jewellery item (Mesoamerican).

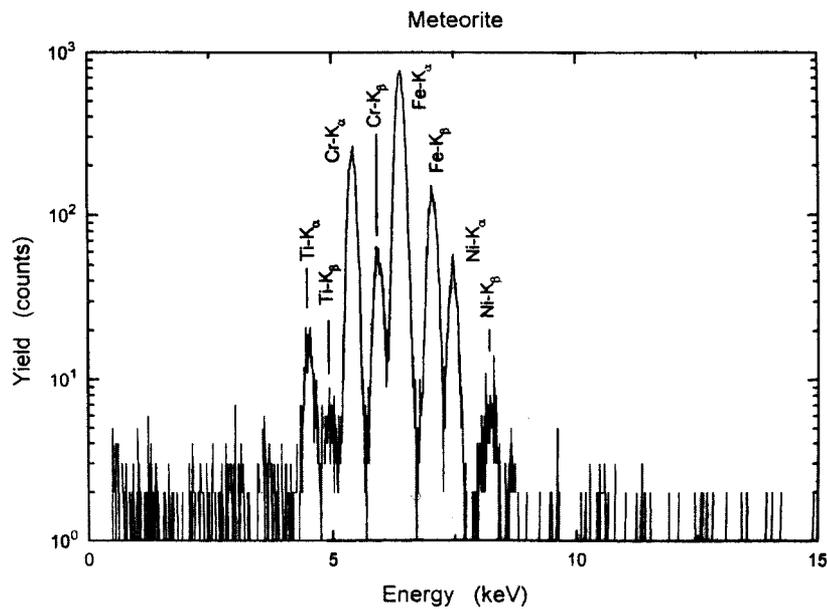


Figure 4g. PIXE spectrum of a meteorite sample.

Each element ionised with the incident protons gives several X-ray signals. When K lines are selected for the analysis we may choose two different signals $K\alpha$ and $K\beta$ with known intensity ratios. If L lines are selected (for heavy elements) one may select $L\alpha$, $L\beta$ or $L\gamma$, depending on the eventuality of coinciding energies from various elements; see below for Zn and Au interferences.

The analysed depth of the irradiated artefact is less than 10 μm , even for particles crossing 25 to 30 μm in the material due to the decrease of X-ray production with decreasing energy of the projectiles. Archaeological applications are then restricted to non-corroded materials or to drillings involving partial destruction of the sample. PIXE is very fast and accurate for the non-destructive characterisation of the main components of narrow regions on gold jewellery artefacts in a non-vacuum 'milliprobe' arrangement: gold jewellery items are indeed well preserved and not affected by a surface corrosion in a depth comparable with the thickness of the analysed layer.

Experimental procedure for PIXE

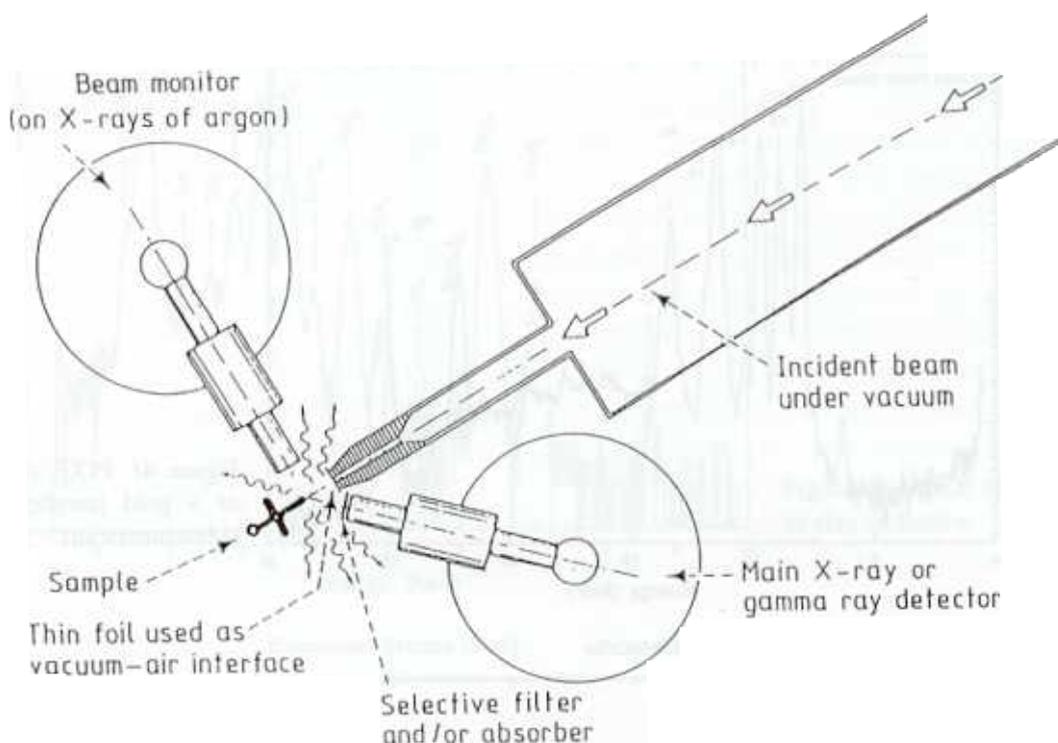


Figure 5. Typical arrangement installed at LARN (Namur) for non-vacuum PIXE. The incident proton beam crosses a thin foil of Al before reaching the target sample situated at 1 cm in the air. The X-rays of the sample are collected in the main detector. A lateral monitor collects X-rays of argon (in air) which gives relative intensities of the incident proton beam.

Figure 5 illustrates the experimental set up for non-vacuum PIXE at LARN (Namur, Belgium). The proton current from the accelerator is maintained at a low level (0.1 to 10 nA) in order to keep the total counting rate of X-rays compatible with the best energy resolution of the solid state Si(Li) detector (500 to 700 counts per second). The problem of different counting rates in characteristic X-ray peaks of main and minor elements can be solved here by using appropriate filters. Foils of selected materials are used to reduce selectively the X-rays of the main component, and therefore enhance the relative intensities of all other useful X-ray lines.

The presence of the filter between the irradiated target and the detector may give rise to an additional X-ray fluorescence. As the characteristic X-rays of the element(s) of the filter(s) appear in the spectrum, the determination of such element(s) in the target is then impossible. Figure 6 illustrates typical spectra obtained during proton irradiation ($E_p=2.8$ MeV) of an artefact containing Cu, Au, Ag, in the presence of Zn lines produced in the selective filter.

With the help of a small computer, each X-ray spectrum is examined in order to subtract the actual background (mainly from secondary electron *bremsstrahlung* origin) giving rise to a continuum up to 6 keV, to identify all peak regions, and to calculate peak areas. The computation of actual X-ray intensities takes several parameters into account such as: X-ray cross-sections, X-ray absorption, sum and escape peaks.

All the useful physical data are available to allow quantitative analysis by calculation. In order to avoid having to calculate all the geometrical corrections (proton beam intensity, solid angle of the detector, its efficiency for different X-ray energies and mainly absorption of X-rays in the materials between the target and the detector), comparison with known reference materials is more straightforward.

Modern reference samples containing most of the elements of interest in archaeological artefacts are commercially available, and may be irradiated in the geometrical conditions used for the studied artefacts. Consequently, each measurement is reduced to the determination of relative peak areas. The actual concentrations have to be calculated from the peak area ratios taking all the target internal parameters into account: projectile range, cross-section for X-ray production, differential X-ray absorption, secondary X-ray fluorescence yields. Any variation in the relative concentrations of only two components in an alloy containing more than these two elements modifies the X-ray intensities of all other elements. Several steps in achieving the precision in the actual composition have then to be followed. A known commercial compound is taken as a reference. All the X-ray intensities collected during the analysis of the samples are then determined using several steps of sophistication in the calculation: (1) concentrations are first calculated

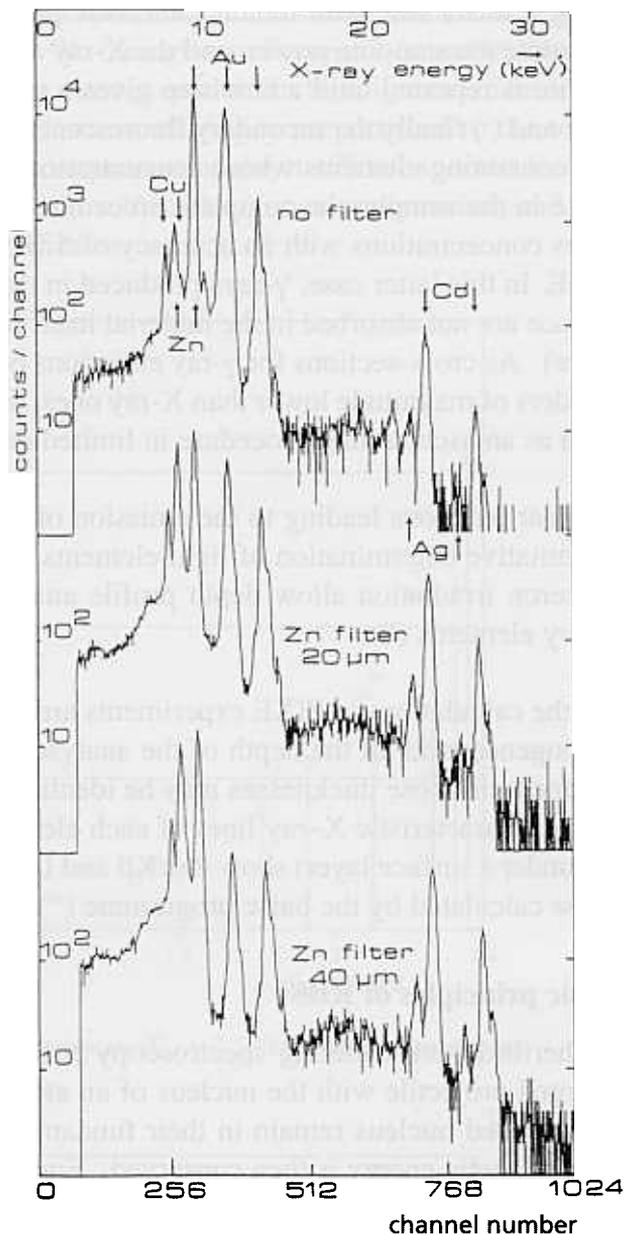


Figure 6. PIXE spectrum of a gold artefact collected in the presence of a zinc filter.

using a linear rule with the characteristic peak areas, (2) these results are then used to calculate the stopping power, and the X-ray absorption in this new material, (3) this procedure is repeated until a new step gives a modification lower than the statistical accuracy and (5) finally the secondary fluorescence is calculated. Even with a reference material containing elements whose concentrations may vary from a factor 3 compared with those in the sample, the complete procedure of calculation on the X-ray spectra finally gives concentrations with an accuracy of 5 % or better. A control has been made using PIGE. In this latter case, γ -rays produced in the 20–30 first microns under the irradiated surface are not absorbed in the material itself because of their high energy (100 keV and more). As cross-sections for γ -ray emissions on medium and heavy elements are around 3 orders of magnitude lower than X-ray ones, this procedure takes a long time and is only used as an ascertaining procedure in limited cases.

Nuclear reactions leading to the emission of charged particles may also be used for the quantitative determination of light elements. Characteristic protons spectra induced by deuteron irradiation allow depth profile analysis of Si, S, Al... in matrices containing heavy elements (3).

All the calculations in PIXE experiments are based on the hypothesis that the material is homogeneous in all the depth of the analysed material (5–10 μm). Nevertheless, heterogeneity in those thicknesses may be identified by comparing the relative intensities of all the characteristic X-ray lines of each element. Elements concentrated at the surface (or under a surface layer) show $K\alpha/K\beta$ and $L\alpha/L\beta$ intensity ratios greater (or lower) than those calculated by the basic programme (10).

Basic principles of RBS

Rutherford backscattering spectroscopy is based on the elastic collision of an incident charged projectile with the nucleus of an atom. In this elastic process the incident and the collided nucleus remain in their fundamental energy level after the interaction: the whole kinetic energy is then conserved. Equations of conservation lead to a single relation between the energy of the backscattered particle (emitted angle close to 180°) and the incident energy:

$$E_{\text{sc}} = E_0 \left(\frac{M - m}{M + m} \right)^2$$

where m and M are the masses of the projectile and of the nucleus respectively (in this procedure $m < M$). One observes that E_{sc} is proportional to E_0 and is closer to E_0 when m is very light by comparison with M . If this parameter is to be chosen to distinguish scattered particles of mass m from various nuclei of mass M , m must be the highest as possible but always smaller than M .

(10) Demortier, G., 'Differential PIXE analysis of Mesoamerican jewellery items', proceedings of the IBA-12 International Conference, (Phoenix, Arizona, 1995), accepted for publication in *Nucl. Instr. and Methods*.

Practically, for both acceleration and detection purposes, the incident particle is of a proton (mass 1) or an alpha particle (mass 4). We then give in Figures 7 (a and b) the scattered energies of protons and α -particles on various nuclei. In this figures we have also taken into account that the probability of elastic scattering is proportional to the square of the atomic number of the target. This true proportionality to Z^2 is expected for high Z values but large variations would arise for low Z nuclei (for example carbon and oxygen). Note the logarithmic scale in the ordinates.

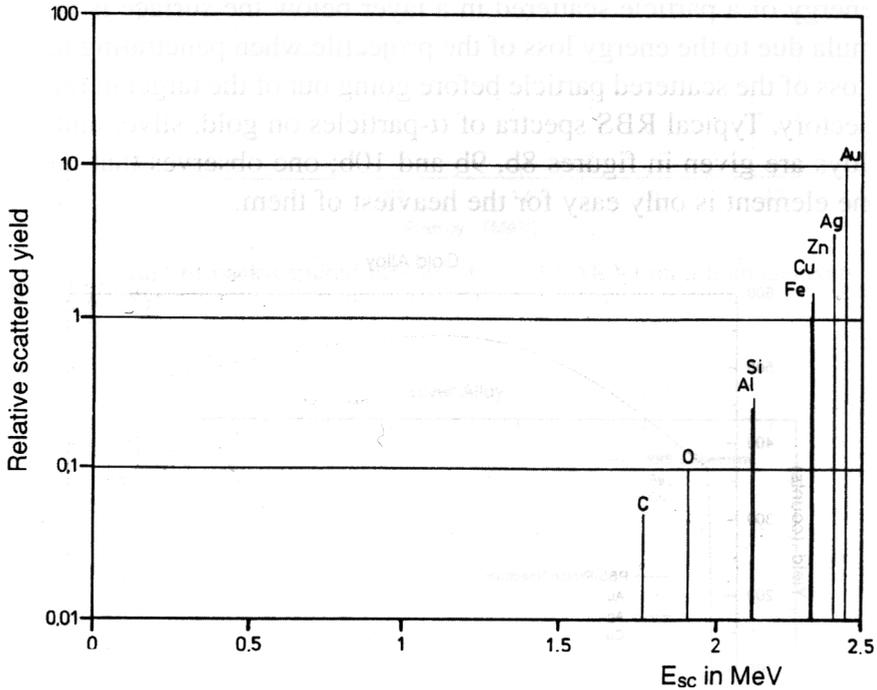


Figure 7a. Calculated energies E_{sc} of backscattered protons ($E_i = 2.5$ MeV) on various masses.

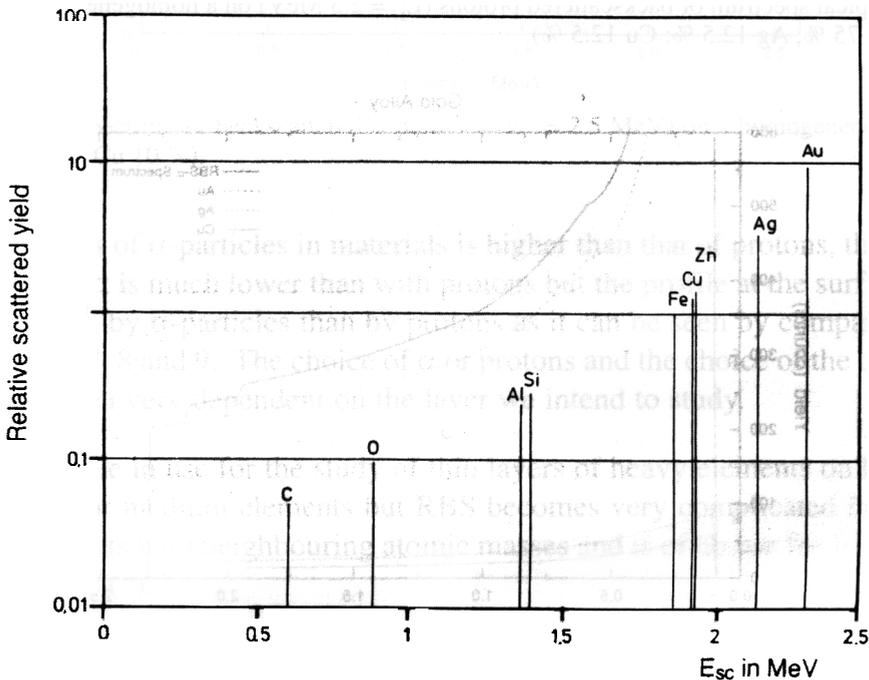


Figure 7b. Calculated energies E_{sc} of backscattered α -particles ($E_i = 2.5$ MeV) on various masses.

The relative intensities of scattered particles on Au and O are then in a ratio of 97.5. RBS is then 2 orders of magnitude more sensitive for gold than for oxygen. Comparing Figure 6a with 6b, one clearly observes that the mass separation is better for α -particles than for protons but this separation becomes often insufficient to distinguish neighbouring elements like Cu and Zn, and even Ag and Au.

The study of materials using RBS is not straightforward for bulk material, due to the decrease in energy of the incident projectiles when they penetrate in the material. The measured energy of a particle scattered in a layer below the surface is not given by the simple formula due to the energy loss of the projectile when penetrating the material and the energy loss of the scattered particle before going out of the target in the backscattered straight trajectory. Typical RBS spectra of α -particles on gold, silver and bronze homogeneous alloys are given in figures 8b, 9b and 10b; one observes that the safe identification of one element is only easy for the heaviest of them.

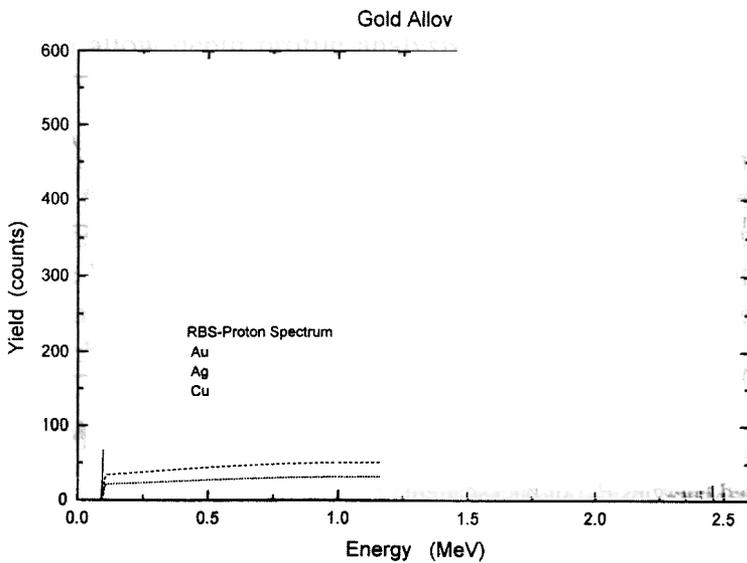


Figure 8a. Typical spectrum of backscattered protons ($E_i = 2.5$ MeV) on a homogeneous gold-silver-copper alloy (Au 75 %; Ag 12.5 %; Cu 12.5 %).

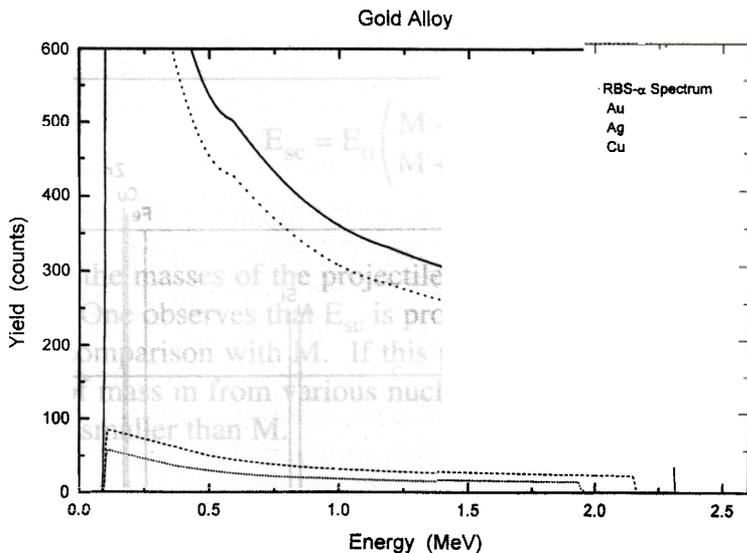


Figure 8b. Typical spectrum of backscattered α -particles ($E_i = 2.5$ MeV) on a homogeneous gold-silver-copper alloy (Au 75 %; Ag 12.5 %; Cu 12.5 %). A indicates the E_{sc} on Au at surface, B and C for Ag and Cu at surface. In the region D, signals of all the elements (present in the bulk) are superposed.

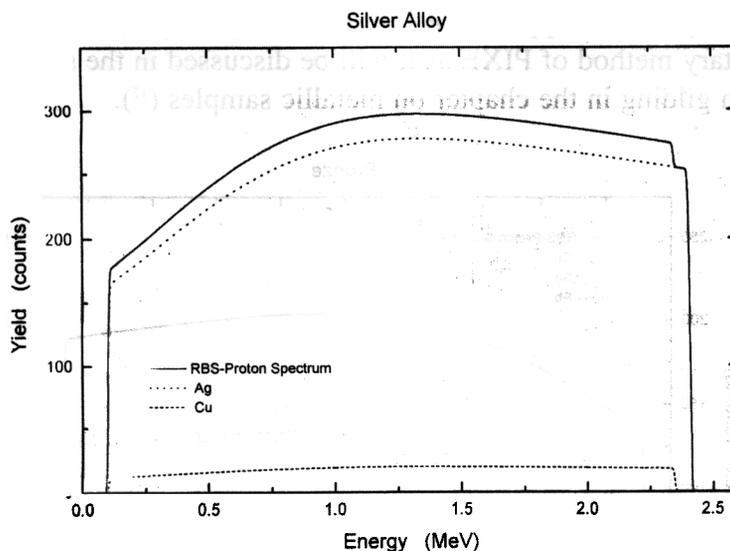


Figure 9a. Typical spectrum of backscattered protons ($E_i = 2.5$ MeV) on a homogeneous silver-copper alloy (Ag 90 %; Cu 10 %).

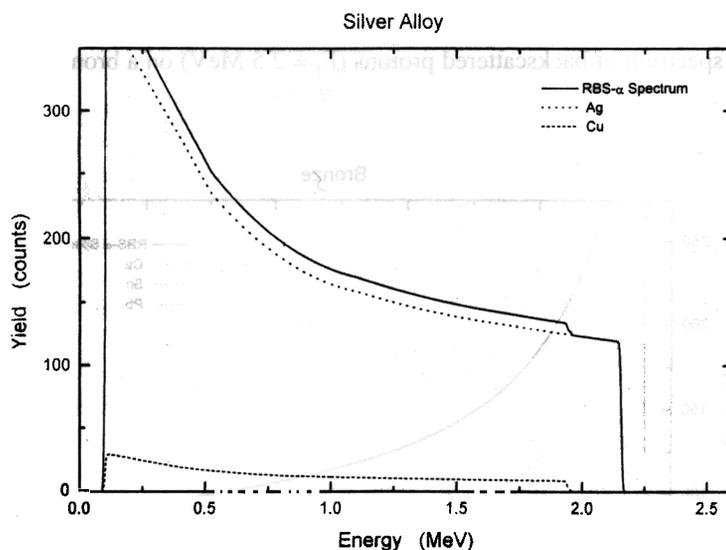


Figure 9b. Typical spectrum of backscattered α -particles ($E_i = 2.5$ MeV) on a homogeneous silver-copper alloy (Ag 90 %; Cu 10 %).

As the energy loss of α -particles in materials is higher than that of protons, the total analysed depth with α is much lower than with protons but the profile at the surface is more easy to determine by α -particles than by protons as it can be seen by comparing parts a and b of Figures 7, 8 and 9. The choice of α or protons and the choice of the typical incident energy is then very dependent on the layer we intend to study.

RBS is very simple in use for the study of thin layers of heavy elements on bulk matrix containing light or medium elements but RBS becomes very complicated for materials containing elements with neighbouring atomic masses and is of no use for light elements in heavy matrices ⁽¹¹⁾.

⁽¹¹⁾ Ruvalcaba-Sil, J. L., Demortier, G., Misaledis, P. ed., Application of particle and laser beams in materials technology (1995), pp. 463–470, *Kluwer Academic Publ.*, and J. L. Ruvalcaba-Sil, G. Demortier, Ecart Conference, Zurich 1995 (to be published).

RBS is then of very limited application for archaeological purposes but is ideally used as a complementary method of PIXE as it will be discussed in the study of gold plating or gold depletion gilding in the chapter on metallic samples ⁽¹²⁾.

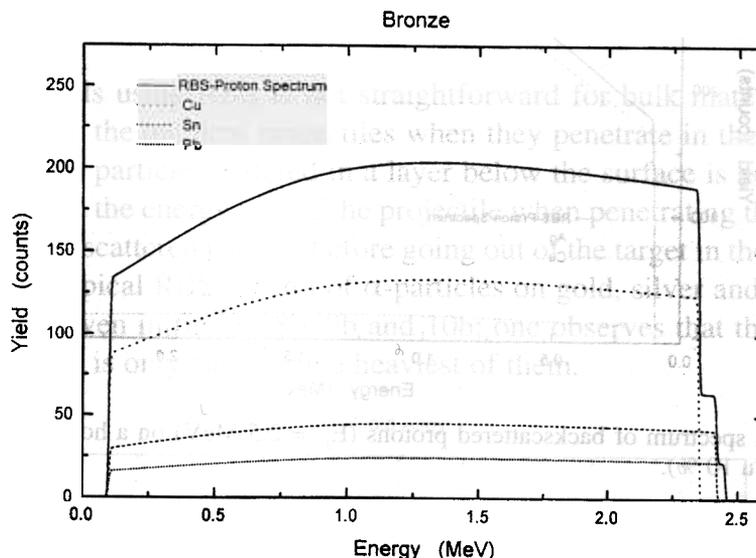


Figure 10a. Typical spectrum of backscattered protons ($E_i = 2.5$ MeV) on a bronze artefact (Cu 78 %; Sn 18 %; Pb 4 %).

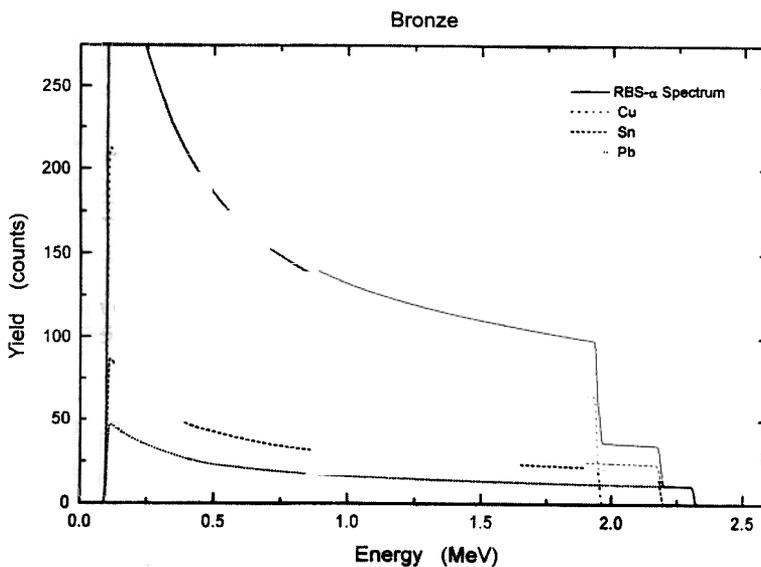


Figure 10b. Typical spectrum of backscattered α -particles ($E_i = 2.5$ MeV) on a bronze artefact (Cu 78 %; Sn 18 %; Pb 4 %).

⁽¹²⁾ Demortier, G., 'IBA applications to ancient metallic items' in *Applications of ion beam analysis techniques to arts and archaeometry* (M. A. Respalda and J. Gómez-Camacho, eds.). Secretariado de Publicaciones Universidad de Sevilla, Seville, 1996, pp. 91–114.