PIXE Protocol Setup for Cluster Analysis of Archeological Samples

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Abstract. Ion Beam Analysis techniques were developed and utilized for applications in the domain of archeology at the accelerator laboratory of the Lebanese Atomic Energy Commission. Our first aim was to set up a suitable experimental protocol using "Proton Induced X-ray Emission" technique, in order to have accurate and relatively fast measurements for the analysis and the study of archeological objects, mainly ceramics. The first experimental protocol was done using two runs at 1 MeV and 3 MeV. It showed satisfactory results when it was applied to Roman amphora from Beirut and helped to establish a database of Beirut amphora production. The second one was more advantageous since it is time consuming by using just one run at 3 MeV with a pinhole filter as x-ray absorber. It had the same ability as the previous one by doing accurate PIXE measurements and showed the similar satisfactory results. Consequently, a classification study based on the elemental composition and on multivariate statistical techniques will be performed in order to determine possible provenance of the studied archeological objects.

1. Introduction

Since 1999 a particle accelerator, located at the Lebanese Atomic Energy Commission, has been devoted to elemental analysis in different domains of application: archeology, environment and materials science. Several nuclear analytical techniques are performed, such PIXE, RBS, PIGE, NRA, ERDA and others. Indeed the first application of the setup in archeology concerned the study of Beirut ceramic products. In view of the considerable Lebanese heritage, a special attention was focused on the PIXE applications in archeology, which its capability in the field was proven many times. The opportunity of our work is to establish locally, in Lebanon, a powerful analytical technique that archeologists need sometimes to resolve some problems. In fact, the elemental composition determination provided by PIXE, will be used in a multivariate statistical program to identify and classify into groups the studied objects. It is assumed that objects in the same group have the same provenance.

It is known that "Particle Induced X-ray Emission" is a suitable technique to the study of archeological objects because it is sensitive, multi-elemental, relatively fast and non destructive [1, 2]. Comparing to other analytical techniques that require sample digestion, chemical extraction and some other preparation before analysis, the PIXE advantages are enhanced when a considerable quantity of objects are present. The setup of an experimental protocol capable to do accurate measurements using PIXE technique was necessary to establish in order to provide elemental analysis of archeological objects.

Two experimental setup protocols were established, experimented and will be discussed later in more details through the measurement of different samples.

2. Experimental

2.1. Target preparation

The selected ceramics were chosen from pre-groups already established according to archeological-typological criteria. The surface layers of the sherds were removed, as they are more liable to present alterations in their composition due to chemical exchanges with the surrounding soil. Samples were heated for one hour at 950°C, and then left to cool down in the oven. This process was designed to eliminate the organic elements and the humidity, which normally constitute 2-3% of our samples. After crushing into an agate mortar, the collected powder was pressed into pellets with a hydraulic press. The grain size is less than 20 µm, which was far smaller than the beam size (~2 mm), and hence a better homogeneity of the analyzed sample is achieved. A borax powder, from behind and around the edges, was pressed with the ceramic powder in order to improve the adhesion of the obtained pellet and to keep it free of cracks. The obtained dimensions of the pellets were 2-cm in diameter and 1 mm in thickness. In order to avoid a charge build-up at the surface during the analysis, the sample was covered, using an adapted carbon deposition evaporator, by a very thin ultra pure Carbon layer (<10 µg/cm^2).

2.2. Experimental Set-up

The elemental composition of the archeological ceramics was measured by the conventional in vacuum PIXE, using the accelerator facility at the Lebanese Atomic Energy Commission [3]. It's a tandem Pelletron from NEC of 1.7 MV, model 5SDH, with an Alphatross RF ion source.
The spot diameter of the beam on the target was about 2-4 mm, defined by a Ta antiscatter collimator. In the PIXE chamber, the beam hits the target under normal incidence. The PIXE scattering chamber, which contains the X-ray detector, is equipped with a wheel target holder (up to 16 samples) monitored by PC through a stepping motor. X-ray emission from targets is detected using an Ortec Si(Li) detector (SLP-06165 model) with 30 mm² active area, 12.7 µm thick Be window, and 170 eV measured FWHM energy resolution at 5.9 keV, placed at 135° to the beam direction. The Si(Li) detector calibration and the solid angle determination were performed using a set of appropriate radioactive sources and via the analysis of a set of MicroMatter thin film standards. The beam current, on the target, was measured via a 20 cm length graphite faraday cup electrically isolated from the analysis chamber and located in the beam direction at 1 cm behind the target. An Ortec charge integrator, connected to an Ortec digital counter-timer, measured the beam charge deposited on the target. The suppression of secondary electrons, emitted from the target, was realized by holding the target between two appropriate aluminum circular wires biased at –400 Volts. The bias voltage was optimized in order to have less than ± 2 % difference between the current measured directly by the Faraday cup (without sample) and the one measured on the sample.

3. PIXE protocols

Two PIXE protocols were used to determine the elemental composition of ceramic samples in order to provide cluster analysis for provenance studies. A comparison between the two protocols was necessary in order to choose the most appropriate one regarding the accuracy and the time of the measurements. As application, the first protocol was used in a first study on Roman amphora from Beirut and showed satisfactory results. It allowed the determination of an elemental composition database of Beirut ceramic product at the Roman period [4]. The second protocol was applied to the provenance study of Byzantine amphora from Beirut and showed also adequate results using the already established database [5]. In fact, the elemental composition of the most abundant elements (10 to 20) was used in multivariate statistical techniques, in particular the cluster analysis.

3.1. Two runs measurement

Prior to the analysis of the studied archeological samples, some reference materials such as the two Geo-standards DR-N and BE-N are analyzed by PIXE, as thick targets, as a quality control for our experimental setup. PIXE measurements were carried out in order to determine almost 20 elements. The different prepared samples were exposed to a proton beam at two different energies:

(a) 1 MeV, without any x-ray absorber in front of the detector, for matrix determination (Fig.1a), which is constituted by major and minor elements (Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe). Tentative measurements, for V and Cr, were performed as well, but were not further used due to low precision and accuracy. However, the use of more appropriate filters showed a better and acceptable determination for these elements. Consequently, this determination required a third acquisition for the same sample, which is not appropriate for the study of a large number of objects; therefore a compromise between time of analysis, which constitutes a part of the experimental protocol, and necessary elements needed for classification is obtained by the elimination of these two elements. Due to the close distance between the target and the detector, a beam current of 0.4 nA and an acquisition time of about 10 minutes were enough for the analysis. The total integrated charge for each sample was 0.2 μC and the count rate did not exceed 500 counts/sec.

(b) 3 MeV to determine the heavier elements (Fig.1b) with $Z = Z_{Fe}$. In the case of ceramics, they are usually the trace elements such as Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Ba, Pb and others. An Al filter of 250 μm of thickness was positioned in front of the detector entrance in order to absorb the low energy X-rays emitted by the major elements. To get good statistics within a reasonable time of acquisition (~10 minutes), the beam current was increased to ~100 nA. Thus, the total integrated charge was 60 μC and the count rate was found to be less than 1000 counts/sec.

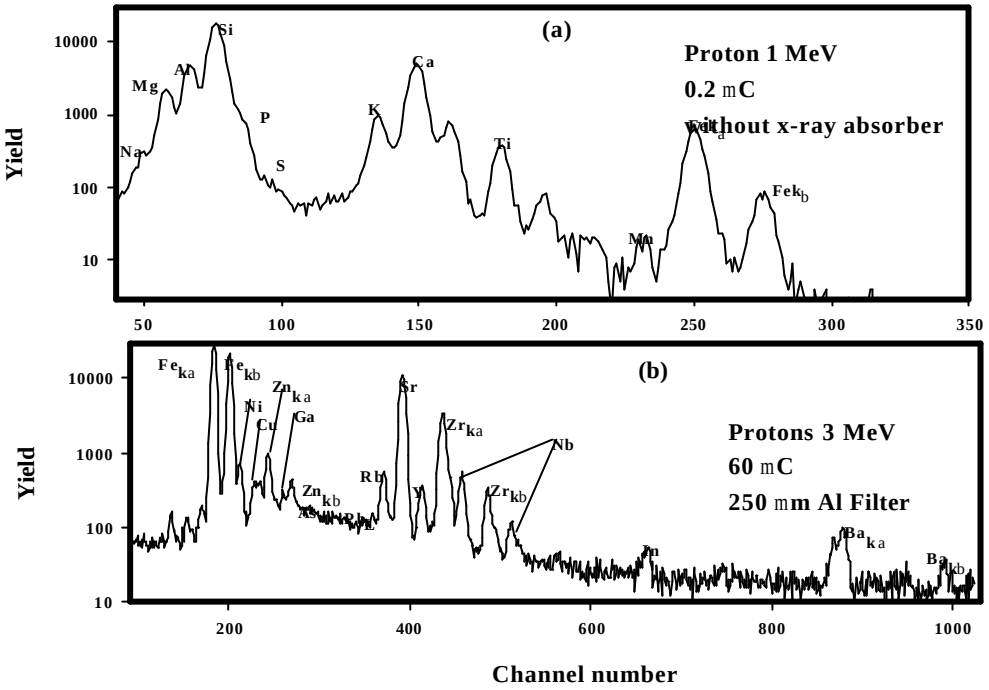

Fig. 1: X-ray spectrum of a ceramic object, which shows the major and trace elements at respectively: (a) 1 MeV and (b) 3 MeV of proton beam.

Samples were classified into groups of similar elemental composition by hierarchical cluster analysis (Fig. 3). Cluster analysis was applied to standardized data, using Euclidian distance as distance measure and unweighted pair-group centroid as linkage rule. Twelve elements (Mg, Al, Si, K, Ca, Ti, Fe, Ni, Zn, Rb, Sr, Zr) were taken into account in the classification. Some elements were not considered, such as V and Cr, for analytical reasons and also in the case of Ba because its concentration may have been altered during the burial of the sherds.

3.2. One run measurement

The second protocol, which was developed later, consisted on the use of one-run PIXE, instead of two, for time consuming in order to analyze a large number of samples in due time. This procedure allowed both the lighter (10< Z< 27) and heavier elements (Z >26) to be analyzed simultaneously. Indeed, the so-called funny filter (a filter with a tiny hole drilled at its center) is an x-ray absorber foil that is placed in front of the Si(Li) detector. This absorber has only a small effect on the less intense higher energy x-rays, but it stops most or all the intense low energy x-rays except for those that pass through the pinhole [6]. The result is a spectrum where both low and high energies X-rays are accumulated.
The use of the Al pinhole filter provided 22 elements in one spectrum (Fig. 3): (i) Na, Mg, Al, Si, P, Ca, K, Ti, Mn and Fe as major and minor elements, and (ii) V, Cr, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb and Pb as trace elements.

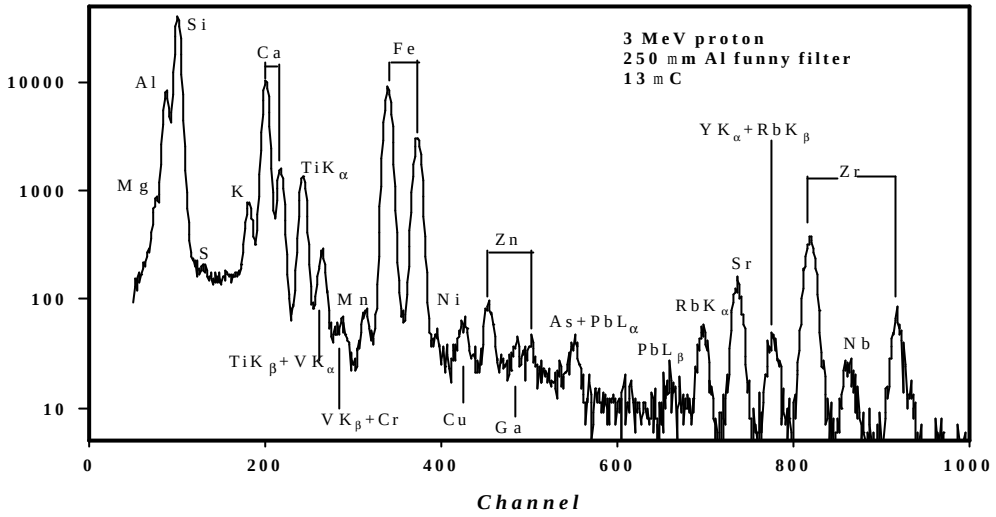

Fig. 2: PIXE spectrum of a Byzantine amphora from the Beirut 002 site and corresponding to the second group B. The prepared sample was bombarded with 3 MeV protons and a 250 µm Al funny filter was placed in front of the Si(Li) detector, as X-ray absorber

A systematic study was undertaken on reference materials such as IAEA SL-1 and two geostandards BE-N and DR-N, received as powder form and prepared in the same way of our studied samples, in order to choose the most appropriate funny filter (type, thickness and hole diameter) for such study. While it is reasonably straightforward to characterize a normal foil as x-ray absorber, this is not the case for a funny filter. A well calibration of the detection system (filter thickness, hole diameter, Beryllium window thickness, solid angle or geometry) was done in order to have no energy dependence of the so-called H value. It was found that a 250 µm thick Al funny filter with a hole diameter of about 0.3 mm, offered a good detection sensitivity for most of the elements of the reference standards, analyzed as thick targets, such as the IAEA SL-1, and the geo-standards BE-N, and DR-N (Table 1). Furthermore, the fractional hole size, a characteristic parameter which is the ratio between the hole area and the surface of the whole filter seen by the detector, was determined experimentally and found to be equal to 0.295%. This essential determination was realized by analyzing a set of thin film standards (Micromatter® reference material) covering x-ray energies from 1.4 keV to 25 keV. For the geostandard reference materials and comparing to the two-acquisitions protocol using 1 MeV and 3 MeV, the certified and measured values showed satisfactory results, within 5 %, for most of the above mentioned elements. In addition, the limits of detection (LOD) were significantly improved for V (106 vs. 448 ppm) and Cr (44 vs. 117 ppm). In contrast, the use of the funny filter caused deterioration of the detection limit for Na, and hence a consequent quantification for such low content was less accurate. Nevertheless, this Na determination was not necessary for the cluster analysis, since the Na determination was just used to complete the elemental composition to 100%.

	DRN		BE-N			DR-N		BE-N	
Majors	cv	mv	cv	mv	Traces	cv	mv	cv	mv
Na_2O	3.05	2.52	3.28	3.36	Ni	15	11	275	277
MgO	4.49	3.84	13.56	11.01	Cu	51	56	74	63
Al_2O_3	17.89	17.82	10.39	11.59	Zn	148	155	124	113
SiO_2	53.97	54.42	39.41	39.71	Ga	22	20	18	14
P_2O_5	0.26	0.27	1.08	1.21	Rb	75	75	48	51
K_2O	1.74	1.7	1.43	1.61	Sr	408	440	1413	1538
CaO	7.20	7.31	14.31	14.91	Y	29	25	31	28
TiO_2	1.11	1.15	2.69	2.67	Zr	128	115	273	281
MnO	0.22	0.25	0.21	0.16	Ba	393	472	1057	1053
Fe_2O_3	9.91	10.5	13.25	13.26	Pb	56	62	4	6

Table 1. Comparison of the certified values cv (after normalized to 100%) and the measured values mv, of major (%) and trace elements (ppm) for DR-N and BE-N standards, using 3 MeV protons and Al "funny filter".

3.3. Cluster analysis

The PIXE spectra were processed with the Gupix package (Guelph PIXE software package) [7]. This program is based on the fundamental parameter approach including x-ray production cross sections, x-ray attenuation coefficients, proton stopping powers, detector efficiency, collected charge and geometry effects to produce an output of elemental concentrations in ppm. Then, cluster analysis was performed, using a multivariate statistical program, to group together objects that have similar elemental compositions. It used the Gupix data matrix, containing the sample identification as columns and the chemical elements or characteristics as rows. The data was standardized before clustering, with the formula given in Eq. (1) [8], to make all characteristics contribute equally to the discrimination process.

$$Z_{ij} = \frac{X_{ij} - \overline{X}_i}{S_i} \quad (1)$$

where Z_{ij} are the elements of the new matrix, X_{ij} the elements of the original data matrix, $\overline{X}_i$ the average of elements per attribute and S_i the standard deviation.

Indeed, cluster analysis was applied to standardized data, using Euclidean distance defined in Eq. (2) as the distance measure and unweighted pair-group centroid as the linkage rule [9]. The smaller the Euclidean distance based on m chemical elements is, the better the linkage is between two objects j and j', hence the greater the probability for belonging to the same origin [10].

$$d^2_{j,j'} = \sum_{i=1}^{m} (Z_{ij} - Z_{ij'})^2 \quad (2)$$

Figure 3 shows the statistical classification of Roman amphorae from Beirut including local reference materials and “carrot” amphorae found in Gaul (south of France). Once can see that some of the 'carrot' and Reynolds Type 72 amphorae were of Beirut products, which highlight the role of Beirut city in the Mediterranean trade in the Roman period.

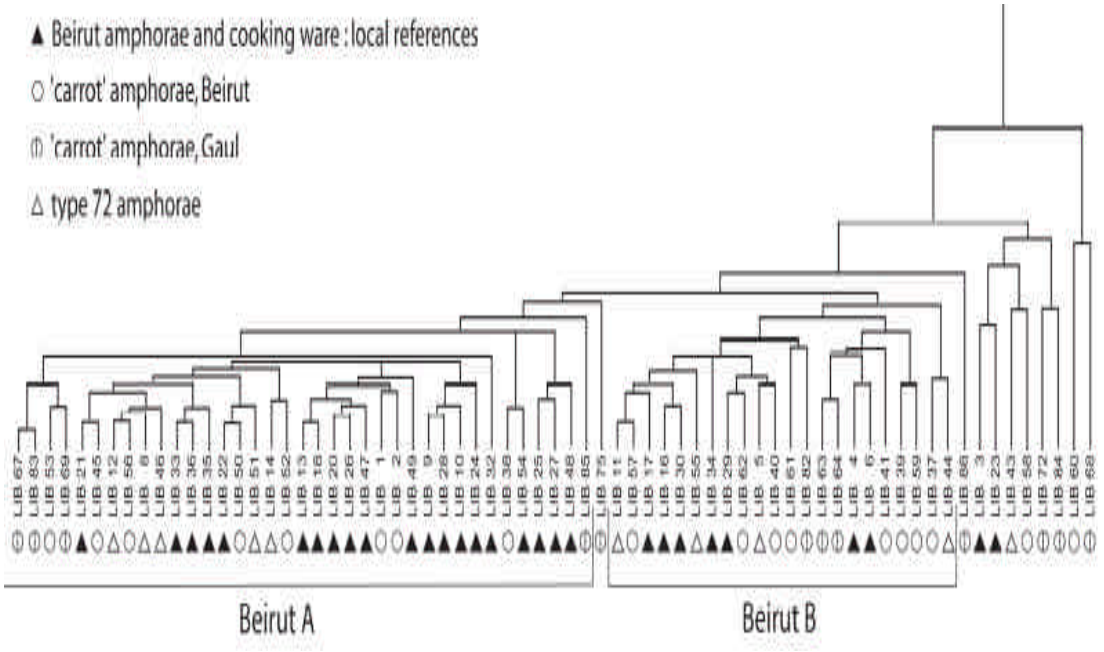

Fig.3: Classification of Roman amphorae from Beirut and from Gaul: Beirut reference samples for local production, ‘carrot’ and Reynolds type 72 amphorae (see symbols chart). The hierarchical cluster analysis was applied to standardized concentrations of 12 elements. The compositional groups are underlined and the reference samples are indicated by black triangles.

4. Conclusion

In this paper, we presented the in vacuum PIXE set-up optimized, at the IBA laboratory in Lebanon, for the analysis of archaeological ceramics. The elemental composition of the different archeological samples, analyzed as thick targets, was determined successfully in one run using a 3 MeV proton beam with a 250 µm thick Al funny filter as X-ray absorber. The comparison with the typical experimental protocol of PIXE, using two runs at respectively 1 and 3 MeV, showed a similarity of the results within 5%. Moreover, the sensitivity to detect V and Cr was improved, unlike Na for which the detection limit was worsened. Therefore, there is an important time saving aspect particularly when a considerable amount of material is to be analyzed. This means reducing time necessary for PIXE measurements as well as for spectra processing.

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