Improvements on Calcium Rich Materials Analysis by External PIXE using Selective Absorbers

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ABSTRACT

For Particle Induced X-ray Emission Spectroscopy (PIXE) and X-ray Fluorescence Technique (XRF), the analysis of materials rich in one or two elements may present some difficulties due to high counting rates and saturation effects in X-ray detectors. In this case, it is possible to use selective absorbers in order to reduce the intensity of the major elements with low attenuation for the X-rays of other elements of the material. Using selective absorbers, the detection limits and the sensitivity are increased. For Ca rich materials (cements, shells, bone, teeth and stucco, for instance), the high intensity of Ca X-rays interferes with the detection of lighter and heavier elements. Cl, Ar and Ag compounds are good candidates for Ca selective absorbers, but only Ag and Ar may have a practical absorber thickness. A selective absorber for Ca X-rays combining thin Ag films and a flux of Ar-He was tested at an external beam setup for PIXE measurements. In this work, the improvement on X-ray detection is shown.

Keywords: X-ray absorber, PIXE, external beam, stucco, bone remains, sea shells, teeth, cement.

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1. INTRODUCTION

For analytical techniques based in X-ray detection, such as Particle Induced X-ray Emission Spectroscopy (PIXE) [1] and X-Ray Fluorescence (XRF) [2], the analysis of materials rich in one or two elements may present some difficulties due to high counting rates and saturation effects in X-ray detectors. In this case, it is possible to use selective absorbers in order to reduce the intensity of the major elements with low attenuation for the X-rays of other elements of the material [3-4]. Detection limits and the sensitivity are increased by selective absorbers. A selective absorber may be solid, liquid or gaseous. The most important limitation for the use of X-ray selective absorbers is the X-ray signals in the spectra from secondary fluorescence in the absorber. Then, the concentrations of common elements in the analyzed sample and in the absorber cannot be measured. For this reason, selective absorbers must have high purity.

Since Ca has a high X-ray production cross section, for calcium rich materials, such as cements, shells, bone, teeth and stucco, the high intensity of Ca X-rays interferes with the detection of lighter and heavier elements than calcium due to pile-up and long tails effects [5]. Since these materials have an important role in biomaterial science, medicine, odontology, archaeology, paleoclimate and biology, the improvement on the analysis of these kind materials by X-rays detection is relevant and necessary.

2. SELECTIVE ABSORBERS FOR CALCIUM

A suitable selective absorber must have a high X-ray mass attenuation coefficient at the X-rays energy of the major element and its absorption edge at lower energy [3-4]. Figure 1 shows the X-ray mass energy-absorption coefficients as a function of the X-ray energy for Cl, Ar and Ag [6]. Calcium X-rays energies are also included. It is clear that these elements fit the previous condition. Then compounds of these materials are good candidates for calcium selective absorbers. To obtain a 90% of Ca X-rays attenuation it is necessary to use absorbers with the following thicknesses: 1.6μm of Ag, 1.8 cm of Ar (with a density...
of 0.00165g/cm³), 15 µm of NaCl, 72 µm of a saturated solution of NaCl and 44 µm of HCl (at 40%). From these calculations, only Ag and Ar may have a practical absorber thickness.

On the other hand, the corresponding X-ray transmissions for light elements are shown in figure 2. Ar and Ag absorbers present the highest X-ray transmissions, but the transmission of K in Ar is very low. Calculations show that Ar and Ag are the most suitable materials for calcium selective absorbers.

### 3. EXPERIMENTAL

Ag absorber was prepared by evaporation. 3.5 µm Mylar foils were glued to metallic washers and then Ag was deposited using a typical evaporation chamber at 5.10⁻⁵ torr. The thickness of the Ag layer is controlled changing the distance from the evaporation point. Using several washers, a layer thickness of (1.63±0.10) µm and other thicknesses may be obtained. The thickness was measured with a Si detector by the attenuation of Ca-Kα X-ray emission from a CaCO₃ pellet irradiated by a W X-ray tube (45 kV, 0.3mA, 3 min) with and without absorber. For the Ar absorber, a controlled flux of gas at the detection path of the detector was used instead of a bottle of gas with thin Mylar windows. In this way it is possible to modify the parameters of absorption by changing the Ar flux rate.

### 4. RESULTS

An external beam setup was used to test the absorbers [7]. Figure 3 shows the experimental setup at the Si detector. A 3 MeV proton beam was used to irradiate a calcium rich reference material of cement (NIST1880a). The solid absorber was set at the detector window while the Ar flux was blown into a conical cap. In order to control the X-ray absorption in the air atmosphere and in the Ar absorber, a controlled He flux was mixed with the Ar flux.

Several configurations were tested. Using only the Ag absorber, the light elements detection improves significantly, but pileup effects are still important. When only Ar is used, most of the X-ray signals are attenuated. Ar flux must be diluted in He in order to decrease the X-ray absorption. The 1.6 µm Ag absorber with a He flux gives rise to good...
detection results but the best results are obtained with a thinner Ag absorber (1.2 µm) if the He flux is mixed with the Ar flux. The experimental parameters depend mainly on the sample composition, but He/Ar flux rate may reach 25 or more. Figures 4 show the improvement on X-ray detection using the Ag absorber and the Ar-He flux. Lighter and heavier elements than Ca are easily detected and pile-up and long tail effects were reduced. High purity CaCO$_3$ and hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) pellets were irradiated and only a low Ar secondary fluorescence was observed in the spectra. The Ca/background and S/background signal ratios increments are 55% and 65%, respectively. The increase of Fe/background signal is more than 125%.

Figure 4. PIXE spectra of Portland cement (NIST 1880a) without absorber and with the absorber of Ag and Ar-He flux.

5. CONCLUSION

A selective absorber for calcium rich materials using a combination of thin Ag films and a flux of argon and helium was successfully implemented for external beam PIXE measurements. The detection of lighter and heavier elements was significantly improved. The experimental parameters of X-ray absorption may be changed and controlled as a function of the Ca sample composition for an optimal analysis. This absorber setup may be modified for in vacuo analysis. The analysis of light elements in calcium rich materials, such as cements, shells, bone, teeth and stucco, will benefit of this absorber for many applications.

ACKNOWLEDGMENTS

The authors thank K. López, F. Jaimes and J.G. Morales for their technical collaboration during the PIXE measurements and J.C. Pineda and M. Galindo for the preparation of X-ray absorbers at the laboratory. This research has been supported by UNAM DGAPA PAPIIT grant IN403302.

REFERENCES


Proceedings of the 10th International Conference on Particle Induced X-ray Emission and its Analytical Applications, Portorož, Slovenia, June 4-8, 2004