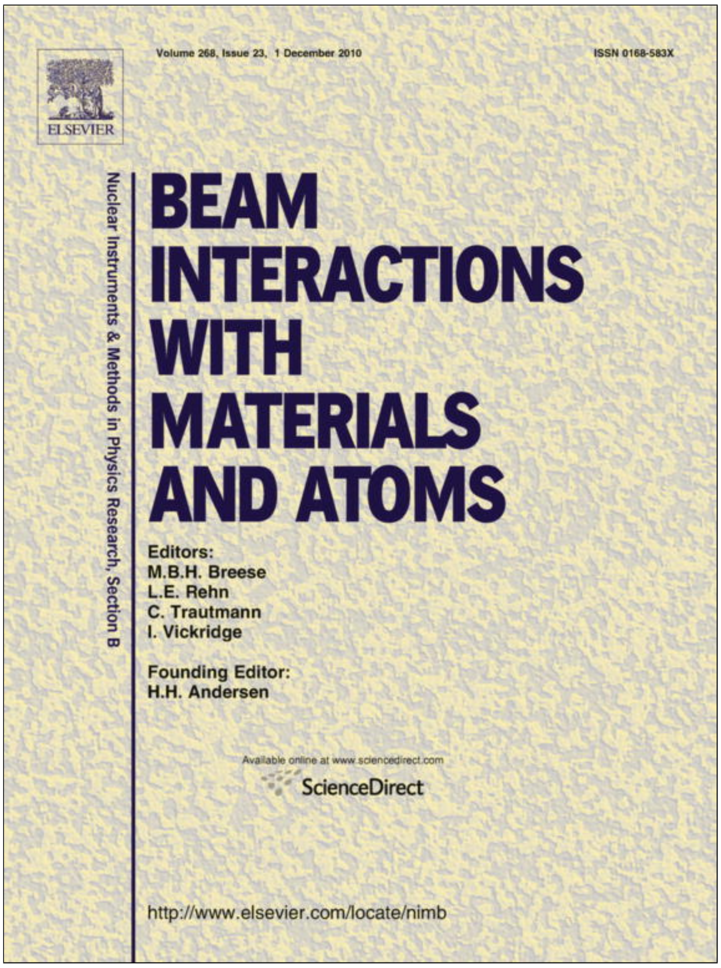
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Short Communication

Total reflection X-ray fluorescence analysis using polycapillaries. A comparison with conventional setups

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ABSTRACT

The possibility of producing parallel X-ray beams with low divergence by means of half monolithic polycapillaries gives the impression to be useful in total reflection X-ray fluorescence (TXRF) experiments. On one hand, the use of polycapillaries facilitates the alignment and the setup of the experiment. As expected, the spectra registered in the experiment shown low background and good signal–noise ratio. On the other hand, the intensity of photons on the samples when polycapillaries are employed is lower than in other configurations, which produces a loss of efficiency for the excitation of the sample mainly for light elements. In this work, different TXRF experiments were carried out and the minimum detection limits attained were compared with the ones obtained from TXRF using polycapillaries. The results indicate that the decrease of intensity produced by polycapillaries is imposing when detection limits are analyzed. Nevertheless, detection limits are better than conventional XRF. The possibility of employing non-symmetrical polycapillaries could eventually improve the detection limits so as to be equivalent to the conventional TXRF setups.

1. Introduction

Recently, the capabilities of the X-ray fluorescence (XRF) and micro-X-ray fluorescence spectroscopy (μXRF) were expanded by the use of X-ray lenses. At present, most of the X-ray lenses used in XRF experiments with conventional sources are mainly glass capillaries and polycapillaries. Glass capillaries are small tapered tubes in which photons travel along the capillary by total reflection on the inner wall. Polycapillaries are more complex systems formed by hundreds or, usually, thousands of monocapillaries that accept photons from an emitting point and concentrate the emerging photons in a focal spot. Semi-lens polycapillaries or double-focus polycapillaries are used in different geometries [1].

Semi-lens polycapillaries are special lenses that collect photons from a focal spot and produce an emerging parallel beam, and conversely, collect photons from a parallel beam and concentrates the photons in a focal spot. These kinds of lenses are particularly appropriated to perform total reflection X-ray fluorescence analysis because their capability of producing a homogeneous beam with very low divergence.

Today, TXRF has reached an important development. Several applications in all kind of samples are published each year and many special devices are commercially available [2,3]. The capability of polycapillaries of producing highly parallel beams opens the possibility of performing TXRF experiments in a simpler and more efficient manner, keeping similar detection limits as the ones obtained with other methods.

In this work we performed TXRF measurements in different samples using conventional TXRF systems and special setups using polycapillaries. A conventional X-ray tube was used as excitation source, and a high resolution angular stage was used for TR positioning. The detection system consists of an energy dispersive Si-PIN detector, a fast amplifier and a standard multichannel analyzer. In order to perform a direct comparison of the different methods employed, the same samples and reflectors were used in all the measurements. By means of the calculation of minimum detection levels the different configurations were compared.

2. Experimental

The experiments were carried out using an Mo X-ray tube Philips model 1830 with a long fine focus oriented as a point source. The Mo anode was in the horizontal plane with a focus dimension of 0.4 mm × 8 mm. The direction of the maximum intensity of the X-ray beam pointed down at 6° from the horizontal plane. The maximum power supply of the X-ray generator was 3 kW.

Fluorescent radiation was collected with a Si-PIN detector Amptek XR100 and an MCA. The X-ray detector was positioned

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perpendicular to the excitation beam along the vertical axis. The distance from the entrance window of the detector and the surface sample was 15 mm.

Three different configurations were arranged for TXRF experiments: a standard setup with white beam and slits, a beam-guide system [4], and a setup with a one-focus lens. The experimental configurations are shown in the Fig. 1. For all of them a highly polished silicon wafer was used as a substrate of the samples.

For the standard setup a horizontal slit of 0.1 mm was placed over the maximum intensity of the excitation beam at 200 mm from the output windows of the X-ray tube. The substrate sample was put on a motorized goniometer. Its movements were controlled by a personal computer with an angular resolution of 0.1 mrad.

For the experimental setup with the beam guide (BG) [4] a horizontal slit of 1 mm was disposed over the maximum intensity of the excitation beam at 200 mm from the output windows of the X-ray tube. Basic characteristics and the working principle of BG are described in detail by Sánchez [4]. In short, BG consists of two reflectors separated by spacers in order to allow the transmission of photons in the middle space by total reflection processes (see Fig. 1). One reflector is larger than the other, the open extreme of it is used as sample holder. The gap between reflectors is larger than the coherence length for X-rays, which means that no standing waves are produced inside the guide. Photons entering the BG propagate inside it by total reflection and reach the sample area after none, one, three, five, or $2n + 1$ reflections. The beam guide was placed at the end of a horizontal slit on the motorized goniometer controlled by a personal computer. In this way the BG could be aligned in an easily and with a high degree of precision.

The system with a lens used a home-made half monolithic glass polycapillary (HMP) composed of 3000 monocapillaries. The characterization of this lens was done in the LNLS using a specific procedure described elsewhere [5]. The focal distance was 40 mm with a focal dimension of 0.09 mm, a transmission efficiency of 30% and a gain of 20. The lens was mounted on a precision manual-controlled four-axis stage (up–down, left–right, horizontal rotate, and vertical rotate) Newport model Cat.LP-05A. The focus of the HMP was placed on the anode of the X-ray tube in order to produce a parallel beam with low divergence. The cross section of the emerged beam was circular with 10 mm of diameter and a divergence of only 3 mrad. As in the conventional setup, the substrate sample was put on the motorized goniometer to simplify the alignment procedure.

To obtain the minimum detection limits (MDL) for each experimental setup, a multielemental standard sample was prepared. Standard aqueous solutions of Cl, Ti, Cr, Mn, Co, Cu and As at 2000 ppm (Tritisol, Merck, Darmstadt, Germany) were used. In first step, 0.2 ml of each standard solution was pipetted onto a clean and polished silicon wafer. After that, the wet sample was dried at 60 °C during 4 h in electrical oven. As a result, a standard sample on a Si(1 1 1) wafer with 0.4 mg of Cl, Ti, Cr, Mn, Co, Cu and As was obtained.

In order to produce comparative results, the same excitation conditions were used in all the experiments. The X-ray tube was operated at 45 kV and 25 mA and the multielemental standard sample was measured in air atmosphere. The acquisition live time of the Si-PIN detector was 1000 s in all cases.

3. Data analysis and results

The spectra were analyzed with the AXIL program [6] in order to reproduce a typical data analysis in a TXRF experiment. All the spectra were fitted using the same background model, peak corrections, and other artifacts like escape peaks and sum peaks. Fig. 2 shows a spectrum of the sample using the standard configuration for TXRF.

MDL were calculated according to the following usual [7]:

$$\mathrm{MDL}_i = \frac{3C_i}{I_i}\sqrt{\frac{I_{Bi}}{t}} \tag{1}$$

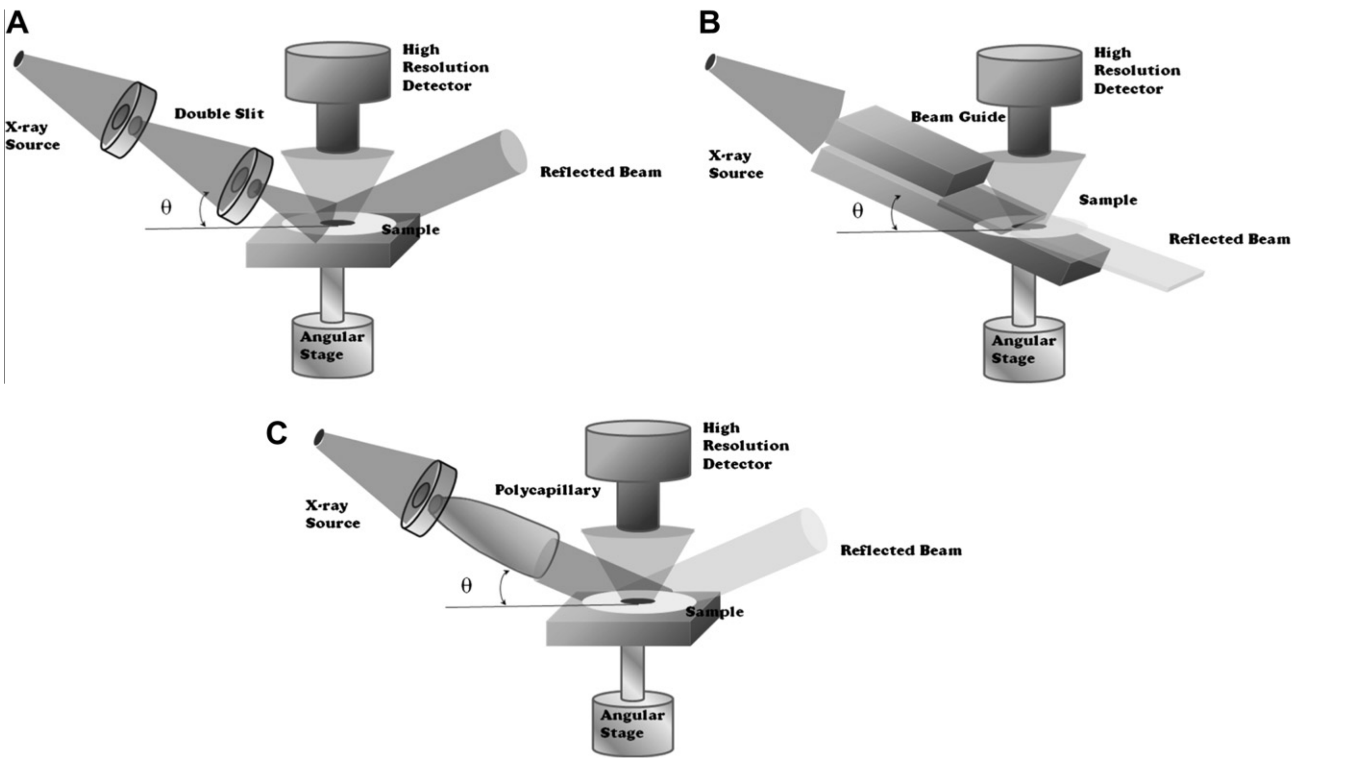

Fig. 1. Experimental TXRF setups used in this work. (a) Conventional setup, (b) setup with a beam guide, and (c) setup with a half monolithic glass polycapillary.

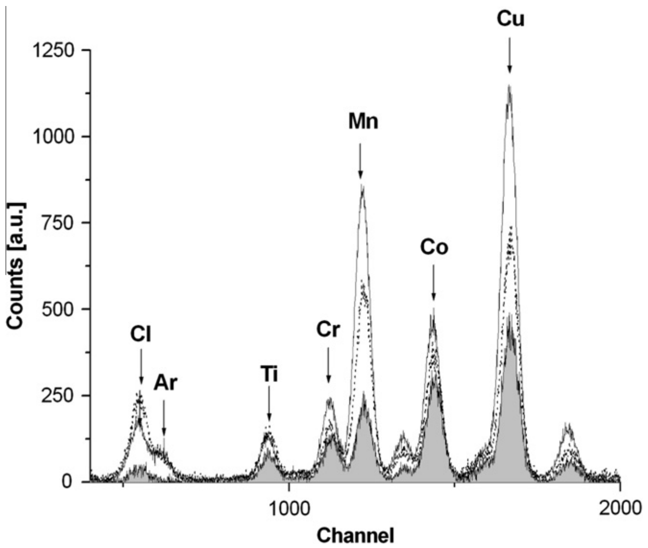

Fig. 2. Spectra of the sample using the three configuration for TXRF. The curve with fill area corresponds to the polycapillary setup. The dot and solid curves correspond to the BG and standard setup respectively.

where MDL_i is the detection limit for element i, C_i is the mass concentration for element i, I_{Bi} and I_i are the measured background and fluorescence intensities of element i, and t is the measured live time.

Fig. 3 shows minimum detection limits obtained for the three configurations of TXRF experiments. Simulation programs indicate that polycapillaries suppress the soft part of the incident spectrum [8]. It is caused by the X-ray absorption by the polycapillary material that acts in a selective way as a function of the photon energy, removing the softer energetic components more effectively. Besides, these simulation programs predict that the high-energy components are slightly reduced by polycapillaries formed by cylinder-shaped channels. To corroborate this hypothesis, the conventional XRF spectra of a sample of white acrylic resin (Vaicel, Vaicril S.A.) with and without the polycapillary were recorded. Both spectra were obtained under the same experimental conditions described in a previous paper of some of the authors [5]. In Fig. 4 the ratio of the XRF spectrum with the lens to the XRF spectrum

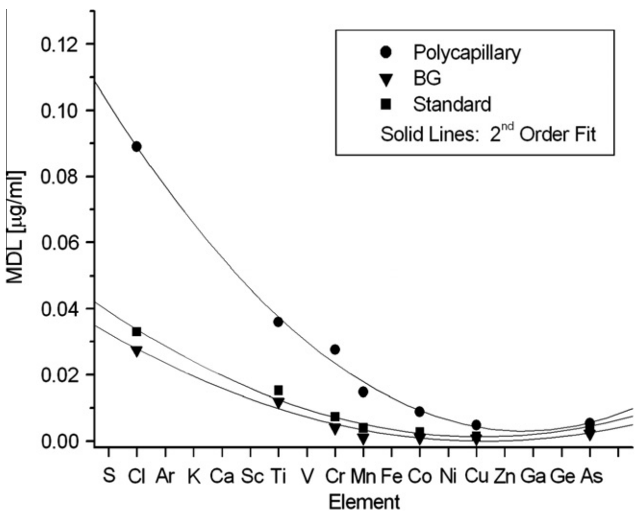

Fig. 3. Minimum detection limits obtained for the three configurations of TXRF experiments.

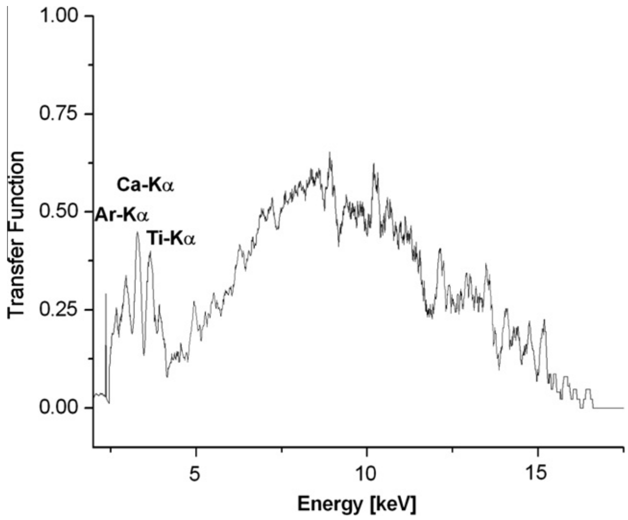

Fig. 4. Transfer function of the polycapillary half lens given by the ratio of the XRF spectrum with the lens to the XRF spectrum without the lens.

without the lens is shown. The suppression of the soft and hard part of the incident spectrum becomes evident.

Thus, the natural band-pass nature of polycapillaries explain the increase of the MDL for light elements observed in the TXRF setup with the HMP. Probably the TXRF setup with the BG has the same absorption effect but at lower level, because the observed MDL is better for light elements.

4. Conclusions

The results show good detection limits for all the configurations, especially in the range from Cr to As. Regarding the different configurations, we verified that the use of polycapillaries facilitates the alignment and the setup of the experiment. In this sense, polycapillaries presents the same advantages as beam-guide. Polycapillaries have a natural band-pass that improves the excitation conditions in the range of 4–10 keV. This reduces MDL in this range. However, as the density of photons per square cm is reduced to produce a parallel beam, the intensity of photons on the sample is significantly lower than in other configurations. This implies a loss of efficiency for the excitation of the sample, hence increasing detection limits.

Our experimental results show that the excitation efficiency of a conventional half-polycapillary with circular cross section is worse than traditional setups. It is expected because the photon intensity accepted by the sample in total reflection geometry with conventional half-polycapillary is extremely poor. The sample accepts about 10 mm by few micrometers, so most of the cross section of the beam does not strike the sample. It is desirable to employ a specific polycapillary in order to produce an asymmetric parallel beam. It is a technological challenge because the present polycapillary manufacture processes only produce symmetric lenses.

An interesting point to observe is that the standard configuration, i.e., a collimated white-beam that excite the sample at glancing angle, shows almost the same MDL than the beam-guide configuration in the range of Cr–Zn. This could be a result of the combination of better excitation and a more efficient emission of characteristic radiation in this range for the standard methods, reaching similar detection limits as beam guides.

References

[1] M.A. Kumakhov, Capillary optics and their use in X-ray analysis, X-ray Spectrom. 29 (2000) 343–348.

[2] A. von Bohlen, Total reflection X-ray fluorescence and grazing incidence X-ray spectrometry—tools for micro- and surface analysis. A review, Spectrochim. Acta B64 (2009) 821–832.

[3] M. West, A.T. Ellis, P.J. Potts, C. Streli, C. Vanhoof, D. Wegrzynek, P. Wobrauschek, Atomic spectrometry update. X-ray fluorescence spectrometry, J. Anal. At. Spectrom. 24 (2009) 1289–1326.

[4] H.J. Sánchez, Total reflection X-ray fluorescence analysis using plate beam-guides, Nucl. Instrum. Methods B194 (2002) 90–95.

[5] R.D. Perez, H.J. Sánchez, M. Rubio, C.A. Perez, Characterization of homemade X-ray polycapillaries, X-ray Spectrom. 37 (2008) 646–652.

[6] P. Van Espen, K. Janssens, J. Nobels, AXIL-PC, software for the analysis of complex X-ray spectra, J. Chemometr. Intell. Lab. Syst. 1 (1986) 109–114.

[7] P. Wobrauscheka, P. Kregsamera, W. Ladisicha, R. Riedera, C. Streli, Total-reflection X-ray fluorescence analysis using special X-ray sources, Spectrochim. Acta B48 (1993) 143–151.

[8] V. Rossi-Albertini, B. Paci, A. Generosi, S.B. Dabagov, O. Mikhin, M.A. Kumakhov, On the use of polycapillary structures to improve laboratory energy-dispersive X-ray diffractometry and reflectometry, Spectrochim. Acta B62 (2007) 1203–1207.