SR-TXRF Detection Limit Reduction Using Thin Polymer Film Substrates

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Three different substrates for the analysis of liquid samples by Total Reflection X-Ray Fluorescence with Synchrotron Radiation (SR-TXRF) were investigated and compared: Lucite (Perspex), Kimfoil and Mylar. Dry targets were prepared by pipetting 5 μl aliquotes of the liquid samples (synthetic standards and fresh water samples) on the different substrates. A five fold reduction of the continuous background and a corresponding reduction of the elementary detection limits were observed when thin polymer film substrates were used instead of the common thick Perspex substrate.

1 Introduction

Total Reflection X-Ray Fluorescence (TXRF) is a multielementary technique for the determination of trace elements [1] widely used in environment research (plants, soil, air.) [2-4] and also for water analysis [5-7]. TXRF is a fast, economic and relatively simple method for the simultaneous determination of elements with atomic number higher than 11, and detection limits in the range of 10 μg/l (ppb) [8].

Differently from the common XRF, Total Reflection x-ray Fluorescence needs a smooth substrate (support) for the deposition of the samples and for the proper reflection of the incoming X-ray beam. The substrate must be dense and uniform, chemically inert and free of impurities, show no fluorescence peaks in the energy range of interest, and be physically stable in the X-ray beam [9]. In general, quartz or Lucite (Perspex) substrates are used. In spite of being the ideal substrate for X-ray reflection, quartz presents some significant disadvantages due to the fluorescence of Si X-rays which interferes with Si determination in the sample. Quartz is also expensive, though it can be reused after careful cleaning, which may also introduce contaminants [1,7]. Lucite substrates, though not as good as quartz, are cheap and disposable, and therefore most used in TXRF analysis. Constituted only by H, C and O, whose X-rays are usually not detected, Lucite sheets are supplied already polished and with little contaminants [7,10].

Thin polymer films, like Kimfoil and Mylar are commonly used as substrates in PIXE analysis yielding very low detection limits [11]. In this work, these materials were tested for Synchrotron TXRF analysis, comparing them with the commonly used Lucite substrate. It was probed if a reduction in the Minimum Detection Limit (MDL) could be attained. Thin film substrates will also enable the analysis of the same sample by PIXE and by TXRF, providing direct comparisons of both analytical methods.

2 Materials and methods

2.1 SR-TXRF

In the SR-TXRF technique, an intense, polarized and well collimated Synchrotron Light Beam is guided at a critical angle ($< 0.1°$) on a smooth substrate where the sample to be analyzed has been deposited. At these conditions the Rayleigh and Compton scattering effects, that would otherwise rise the continuous background in the x-ray spectrum are minimized, and detection limits of the order of μl^{-1} (ppb) of the original liquid sample, can be reached. Usually 5 to 50 μl of a digested sample is placed on the substrate and dried at room temperature (or at most, in a warm oven, $< 40°C$), resulting in a thin film sample with mass ranging from 10^{-6} to 10^{-9} g with less than 5 mm of diameter. Due to the small thickness of the sample and the high energy of X-rays used, absorption and reinforcement effects can be disregarded hence corrections for matrix effects are unnecessary.

In TXRF, the elementary concentration C_i of element i in the liquid sample can be calculated using $I_i = \alpha.L. = C_i.S_i$, where I_i is the characteristic x-ray fluorescent yield, S_i is its corresponding sensitivity and L the average Synchrotron Light intensity on the sample. The parameter α accounts for experimental dilution factors (or losses during pipetting), solid angle and illumination corrections that may vary from sample to sample. The parameter α can be cancelled out by adding in to the liquid sample a small volume of an element in solution with a know concentration, as an internal standard, hence assuming it should not occur naturally in the samples [12,13]. Defining V_s the volume of

the internal standard with concentration C_s, added to a liquid sample with volume V from which an aliquot has been pipetted, the measured concentration of element i is given by

$$C_i = \frac{I_i}{I_s} \frac{S_s}{S_i} C_s \frac{V_s}{V} \qquad (1)$$

where the subscript *s* represents the element used as an internal standard. This relation is now independent on the Synchrotron Light intensity and experimental uncertainties during pre-concentration and pipetting.

Elementary Minimum Detection Limits (MDL) are directly related to the intensity of the continuous background under the characteristic x-ray peak [14]. MDL with three standard deviation confidence interval, were calculated using

$$C_M DL = \frac{3\sqrt{BG}}{I_s} \frac{S_s}{S_i} C_s \frac{V_s}{V} \qquad (2)$$

where $\sqrt{BG}$ is the sum of the counts of the continuum under (FWHM) the characteristic peak.

2.2 Instrumentation

The SR-TXRF measurements were carried out using the polychromatic X-ray beam, with maximum energy of 20 keV, of the XRF line, at the National Laboratory of Synchrotron Light (LNLS), located in Campinas-SP [15]. A HP-Ge X-ray detector with 165 eV FWHM resolution was used. AXIL program was used for X-ray spectrum processing [16].

2.3 Sample preparation

The water samples used for analysis were prepared at the *Universidade Estadual do Oeste do Paraná*, UNIOESTE. The samples were collected from the Toledo River (PR) and acidified with HNO_3 to pH = 2, to preserve their constituent elements. Through open air evaporation at 85 ^{o}C, the samples were pre-concentrated to a five-fold reduction of volume. Samples were spiked with 11.6 ppm of Y as an internal standard. A 5 μl the resulting solution was pipetted on 2.5 μm thick Kimfoil or 10μm thick Mylar film, both stretched on plastic rings (ϕ 25mm, 2mm thick), and 3mm thick Lucite disks, and left to dry at ambient temperature in a laminar flow bench. The Mylar and Kimfoil films are made of 100% polyester thus composed only by C, H, and O, have high transparency, are chemically neutral and present low heavy metal contaminations. These polymers are not affected by oils or greases and keep their clarity, flexibility and hardness until 150°C.

3 Results and discussion

Figure 1 shows three X-ray spectra of the same sample on the three different substrates, using the SR-TXRF system. The normalization was made by the internal standard used. The presence of the elements Ta and Ar are due to the experimental setup (Ta from the X ray collimators and Ar from

the air). Although not as reflective as the Lucite substrates, the experimental conditions for TXRF using thin polymer films were acceptable and easy to achieve. It is worthwhile to notice the lower continuous background of the spectra (all taken with the same approximate counting rate) for the samples on polymer films leading to an approximate 2-fold lower detection limit.
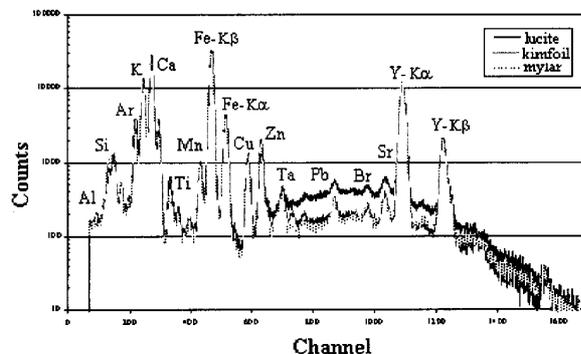

Figure 1. Comparison of the TXRF spectra for the same water sample on different substrates.

In Fig. 2 the detection limits of the three substrates are compared. An important remark is that the detection limits refer to the original liquid samples, thus including the 5 fold reduction in their values, consequence of the pre-concentration, as described above.
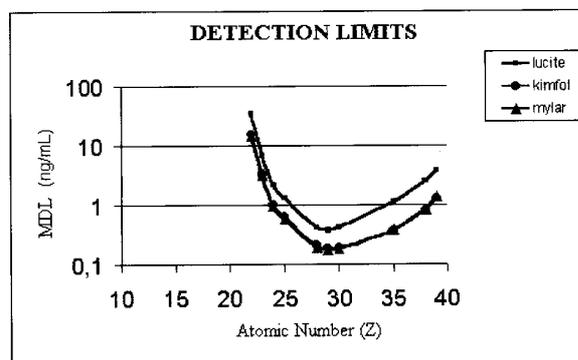

Figure 2. Curve of the detection limit comparing the different substrates.

4 Conclusions

Substrates of thin polymer film have shown to be suitable for TXRF analysis, although not as polished or dense, as the commonly used acrylic substrates recommended in the specialized literature. With its use, a reduction in the detection limit of a factor of 2 was observed, when compared with the Lucite substrate (Fig 2).

The slight differences in the intensity of the X-ray signal for the trace elements in the samples, which can be seen in Fig. 1, may be an effect of the preferential orientation of the polymer films, result of the manufacturing process. Differences in adhesion and crystallization of the pipetted

liquid on the different substrates may also have occurred, as a result of the differences in the drying process on each substrate. These effects have yet to be investigated.

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