Synchrotron Radiation Total Reflection for Rainwater Analysis

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Abstract. In this work Total Reflection X-Ray Fluorescence Analysis with excitation by Synchrotron Radiation (SR-TXRF) has been used for rainwater trace element analysis. The samples were collected in four different sites at Campinas City, SP, Brazil. Rainwater samples of 10 µl were added to Perspex reflector disks, dried under vacuum and analyzed for 100 s measuring time. For the calibration system standard solutions with gallium as internal standard were prepared. The detection limits obtained for K-shell lines varied from 29 ng.ml\(^{-1}\) for sulfur to 1.3 ng.ml\(^{-1}\) for zinc and copper, while for L-shell the values were 4.5 ng.ml\(^{-1}\) for mercury and 7.0 ng.ml\(^{-1}\) for lead.

INTRODUCTION

The total reflection X-ray fluorescence technique was introduced in 1971 by Yoneda and Horiuchi [1] and developed by Aiginger and Wobrauschek [2,3]. This method is based on the incidence of an X-ray beam at small angle (denoted critical angle) on the flat surface of a support or carrier (for example, quartz or Perspex) on which the sample to be analyzed is deposited. In this condition the scattering effect is minimized and thus a better peak-background ratio is obtained reducing in this way the detection limits.

The background intensity also can be reduced using linear polarization of the exciting radiation.

The most intensive X-ray source available nowadays is the synchrotron, providing outstanding properties of brilliance, linear polarization and natural collimation.

Another advantage of this technique is the small volumes required for liquid sample analysis (microliters) or small masses (micrograms) for solid samples after chemical digestion.

TXRF is especially suitable for ultra-trace analysis of pure waters such as rain and drinking water and its advantages when compared to other methods such as atomic absorption spectrometry (AAS) and inductively coupled plasma techniques (ICP-AES and ICP-MS) are the multielement determination and low cost [4].

The aim of this work is to apply the Total Reflection with Synchrotron Radiation (SR-XRF) to determine trace elements in rainwater sampling in four different sites in Campinas City, SP, Brazil.

MATERIALS AND METHODS

The quantitative analysis can be made through Equation 1, because the sample can be considered as a thin film so that absorption and enhancement effects can be neglected.

\[ I_i = S_i C_i \]  

where \( I_i \) represents the intensity (cps) for K or L X-ray line for the element \( i \); \( C_i \) the concentration (in ppm or µg.ml\(^{-1}\)) and \( S_i \) the sensitivity for this element (cps.µg\(^{-1}\).ml).

The thin film formed on the Perspex support does not have a regular geometry and therefore the X-ray intensities depend on the thin film position. This geometric effect [4,5] can be corrected computing the relative intensity for each element in relation to an internal standard added in every sample and standard.
Instrumentation

For the X-ray detection a hyperpure Ge detector with 140 eV resolution at 5.9 keV (Mn K\textsubscript{a} line) was employed, while for the excitation a white beam of synchrotron radiation [6] with 2 mm width and 1 mm height under total reflection conditions was used.

Sample and Standard Preparations

To set up the calibration curve, five standard solutions containing the elements V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Tl and Pb were prepared at different and well-known concentrations (from 0.3 to 3.8 \( \mu \text{g.L}^{-1} \)) with Ga addition as internal standard.

For the sample preparation 1 ml of each sample was taken and 10 \( \mu \text{l} \) of Ga (1025 \( \mu \text{g.ml}^{-1} \)) was added resulting in a Ga concentration of 10.148 \( \mu \text{g.ml}^{-1} \) as internal standard in the sample. Then an aliquot of 10 \( \mu \text{l} \) was pipetted onto a Perspex disk and dried in vacuum thus giving rise to a shaping thin layer of approximately 5 mm diameter (two replicates).

The samples were excited for 100 s and X-ray spectra obtained were evaluated by the software QXAS [7] in order to obtain the X-ray intensities.

Sampling Data

The site and date sampling for rainwater samples are shown in the Table 1.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Treatment Plant 1 and 2</td>
<td>Ch1-1</td>
<td>03/29/98</td>
</tr>
<tr>
<td></td>
<td>Ch1-2</td>
<td>04/29/98</td>
</tr>
<tr>
<td></td>
<td>Ch1-3</td>
<td>05/17/98</td>
</tr>
<tr>
<td></td>
<td>Ch1-4</td>
<td>06/19/98</td>
</tr>
<tr>
<td></td>
<td>Ch1-5</td>
<td>07/20/98</td>
</tr>
<tr>
<td></td>
<td>Ch1-6</td>
<td>08/03/98</td>
</tr>
<tr>
<td>Water Treatment Plant 3 and 4</td>
<td>Ch2-1</td>
<td>03/29/98</td>
</tr>
<tr>
<td></td>
<td>Ch2-2</td>
<td>08/03/98</td>
</tr>
<tr>
<td>Water Treatment Plant Capivari River</td>
<td>Ch3-1</td>
<td>03/29/98</td>
</tr>
<tr>
<td></td>
<td>Ch3-2</td>
<td>08/03/98</td>
</tr>
<tr>
<td>Water Supply Atibaia River</td>
<td>Ch4-1</td>
<td>03/29/98</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

On the bases of the measurements performed on standard solutions, the calibration curve for synchrotron radiation total reflection as shown the Figure 1 was obtained.

FIGURE 1. Adimensional sensitivity curve for Synchrotron Radiation X-ray Total Reflection

The detection limits were calculated by equation [8,9]:

\[
LMD_i = 3 \left( \frac{I_i(BG)}{I_{Ga}} \right) \sqrt{\frac{C_{Ga}}{S_i t}}
\]

where \( I_i(BG) \) is the background intensity for the element \( i \); \( I_{Ga} \) the internal standard intensity (Ga); \( C_{Ga} \) the internal standard concentration (Ga), \( S_i \) the relative sensitivity for the element \( i \) and \( t \) the measuring time.

Detection limits (in \( \mu \text{g.L}^{-1} \) or \( \text{ng.ml}^{-1} \)) for synchrotron radiation total reflection, calculated using the equation above, were extrapolated for 1000 seconds measuring time (figure 2).

As can be visualized in this figure, the detection limits obtained for K-shell changed from 29 \( \text{ng.ml}^{-1} \) for sulfur to 1.3 \( \text{ng.ml}^{-1} \) for zinc and copper. For L-shell the detection limits were 4.5 \( \text{ng.ml}^{-1} \) for mercury and 7.0 \( \text{ng.ml}^{-1} \) for lead.

FIGURE 2. Detection Limit for Synchrotron Radiation Total Reflection (SR-TXRF) for 1000 s.

The concentrations of rainwater samples were calculated using the equation presented in Figure 1 and the results are presented in Figures 3 and 4.

\[
S_i(Z) = -6.196 \times 10^{-6} Z^5 + 6.533 \times 10^{-4} Z^4 - 2.683 \times 10^{-2} Z^3 + 5.395 \times 10^{-1} Z^2 - 5.313 \times 10^0 Z + 2.048 \times 10^1 \\
R^2 = 0.998
\]
Reflection X-ray Fluorescence (SR-XRF)

FIGURE 3: Concentration (ppm) of S, Cl, Ca, Zn, Fe and Ni for seawater samples by Spectroscopy Radiation Total
Figure 4. Concentration (ppm) of K, Ni, Mn, Cu, Cr and V for different samples by synchrotron radiation total reflection X-ray fluorescence (SR-TXRF).
A standard reference material (Drinking Water Pollutants - Aldrich- 41,393-3) containing Cr, As, Se, Ba and Pb was analyzed in order to test the procedure. Table 2 shows the results and it can be seen that the measured values agree well with the certified values.

**TABLE 2.** Measured and certified values in the standard reference material (Drinking Water Pollutants)

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified Value</th>
<th>Measured Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>10.00±0.49</td>
<td>9.74±0.09</td>
</tr>
<tr>
<td>As</td>
<td>10.03±0.49</td>
<td>10.05±0.14</td>
</tr>
<tr>
<td>Se</td>
<td>5.00±0.05</td>
<td>5.00±0.25</td>
</tr>
<tr>
<td>Ba</td>
<td>100.00±0.53</td>
<td>99.98±0.53</td>
</tr>
<tr>
<td>Pb</td>
<td>10.04±0.49</td>
<td>9.86±0.61</td>
</tr>
</tbody>
</table>

As can be seen by the table 1 the accuracy of this method is about 3% and the precision about 2%. In general, the detection limits values obtained are in good agreement with those reported by other workers in different synchrotron radiation facilities [4, 5, 10, 11].

**CONCLUSIONS**

The elements Ca, S, Fe and Zn presented the highest concentrations in every sample. Comparing the Ch1-1, Ch2-1, Ch3-1 and Ch4-1 samples collected in the same day (03/29/98) and different sites was not observed a significant variation for the same element but for the other three samples, Ch1-6, Ch2-2 and Ch3-2, sampling in 08/03/98, can be observed a small variation in the concentration for the same element.

When the Ch2-1 and Ch2-2 samples are compared, which were sampled at the same site but on different dates (03/29/98 and 08/03/98) it can be noted that the values for the Ch2-2 sample are higher than for the Ch2-1 sample. The same fact happened for the Ch3-1 and Ch3-2 samples, collected in the same date cited above.

This can be explained by the fact of August be a rainier month than March, thus, the particulate material present in the atmospheric is higher and when it rains this material is dragged together rainwater, resulting in a higher concentrations in the sample.

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**REFERENCES**