

SYNCHROTRON RADIATION TOTAL REFLECTION FOR RAINWATER ANALYSIS

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ABSTRACT

Total Reflection X-Ray Fluorescence Analysis excited with synchrotron radiation (SR-TXRF) has been used for rainwater trace element analysis. The samples were collected in four different sites at Campinas City, SP.

Standard solutions with gallium as internal standard were prepared for the calibration system. Rainwater samples of 10 μl were putted onto Perspex reflector disk, dried on vacuum and analyzed for 100 s measuring time.

The detection limits obtained for K-shell 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

An improvement of lower detection limits (LD) in X-ray fluorescence analysis can be achieved in some ways. Straightforward ideas to improve the LD are obviously increasing the counting time and sensitivity and reducing the background intensity. The reduction of the background intensity is achieved by applying physical phenomena such as total reflection or linear polarization of the exciting radiation or a combination of both. The most intensive X-ray source available nowadays is the synchrotron, providing outstanding properties of brilliance, linear polarization and natural collimation.

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

MATERIALS AND METHODS

The total reflection X-ray fluorescence technique was introduced in 1971 by Yoneda and Horiuchi¹ and developed by Ainginger and Wobrauschek^{2,3}. This method is based on the incidence of an X-ray beam at small angle (denominated 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. 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.

The quantitative analysis can be made through the equation 1, because the sample can be considered as thin film and so the absorption and enhancement effects can be despised.

$$I_i = S_i \cdot C_i \quad (1)$$

Where I_i represents the intensity (cps) for K or L X-ray line for the element i ; C_i the concentration (ppm or $\mu\text{g}\cdot\text{ml}^{-1}$) and S_i the sensitivity for this element ($\text{cps}\cdot\mu\text{g}^{-1}\cdot\text{ml}$).

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.

1. Instrumentation

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

2. Sample and Standard Preparations

To perform 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 $\mu\text{g}\cdot\text{L}^{-1}$) with Ga addition as internal standard to eliminate errors caused by excitation/detection geometry.

For the sample preparation was taken 1 ml of each sample and 10 μl of Ga ($1025 \mu\text{g}\cdot\text{ml}^{-1}$) was added resulting $10.148 \mu\text{g}\cdot\text{ml}^{-1}$ of Ga as internal standard in the sample. Then an aliquot of 10 μl was pipetted onto the Perspex disk and dried in vacuum shaping a thin layer with approximately 5 mm diameter (two replicates). The samples were excited for 100 s and X-ray spectra obtained were adjusted by the software QXAS⁶ in order to obtain the X-ray intensities.

3. Sampling Data

The site and date sampling for rainwater samples are showed in the table 1.

RESULTS AND DISCUSSION

1. Calibration Curve

With the standard solutions was performed the calibration curve for synchrotron radiation total reflection as showed in the figure 1.

2. Detection Limits

The detection limits were calculated by equation ^{7,8}:

$$LMD_i = 3 \cdot \sqrt{\frac{I_i(BG)}{t}} \cdot \frac{C_{Ga}}{I_{Ga} \cdot S_i} \quad (2)$$

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 adimensional sensitivity for the element i and t the measuring time.

Peak and background evaluation were done by QXAS program ⁶.

Detection limits (in $\mu\text{g.L}^{-1}$ or 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 ng.ml^{-1} for sulfur to 1.3 ng.ml^{-1} for zinc and copper. For L-shell the detection limits were 4.5 ng.ml^{-1} for mercury and 7.0 ng.ml^{-1} for lead.

3. Standard Reference Material Analysis

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 as can be see the measured values agree with the certified values.

4. Rainwater Analysis

The figure 3 presents a spectrum for rainwater sample (Ch1-4) measured by SR-TXRF for 100 seconds.

The concentrations of rainwater samples were calculated using the equation presented in the figure 1 and the results are presented in the figures 4, 5 and 6.

CONCLUSIONS

The elements Ca, S, Fe, Zn and Hg 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 significative 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 is compared the Ch2-1 and Ch2-2 samples, sampling in the same site but in a different dates, 03/29/98 and 08/03/98, respectively, can be verified that the values for the Ch2-2 sample are higher than 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

1. Y. YONEDA, T. HORIUCHI, "Optical flats for use in X-ray spectrochemical micro-analysis". *Rev. Sci. Instrum.*, 42, 1069 (1971).
2. H. AIGINGER, P. WOBRAUSCHEK, "A method for quantitative X-ray fluorescence analysis in the nanogram region". *Nucl. Instr. Meth.*, 114, 157-158 (1974).
3. P. WOBRAUSCHEK, H. AIGINGER, "Total reflection fluorescence spectrometric determination of elements in ng amounts". *Anal. Chem.*, 47, 852 – 855 (1975).
4. W. LADISICH, R. RIEDER, P. WOBRAUSCHEK, "Quantitative total reflection X-ray fluorescence analysis with monoenergetic excitation". *John Wiley & Sons Ltd.*, (1994).
5. R. KLOCKEMKÄMPER, A. VON BOHLEN, "Elemental analysis of environmental samples by total reflection fluorescence": A review. *X-ray Spectrom.*, 25: 156 - 162, (1996).
6. Quantitative X-ray Analysis System (QXAS) software package, IAEA, Vienna.
7. L. A. CURIE, "Limits for quantitative detection and quantitative determination". *Anal. Chem.*, 40(3): 586 - 593, (1968).
8. W. LADISICH, R. RIEDER, P. WOBRAUSCHEK, H. AIGINGER, "Total reflection X-ray fluorescence analysis with monoenergetic excitation using rotating anode X-ray tubes". *Nucl. Instr. Meth. in Phys. Res.*, 330 A: 501 - 506, (1993).

FIGURES AND TABLES

Table 1 - Site and date sampling for rainwater samples.

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

Table 2 – Measured and certified values in the standard reference material (Drinking Water Pollutants)

Element	Concentration ($\mu\text{g.ml}^{-1}$)	
	Certified Value	Measured Value
Cr	10.00±0.49	9.74±0.09
As	10.00±0.49	10.05±0.14
Se	5.00±0.05	5.00±0.25
Ba	100.00±0.53	99.98±0.53
Pb	10.00±0.49	9.86±0.61

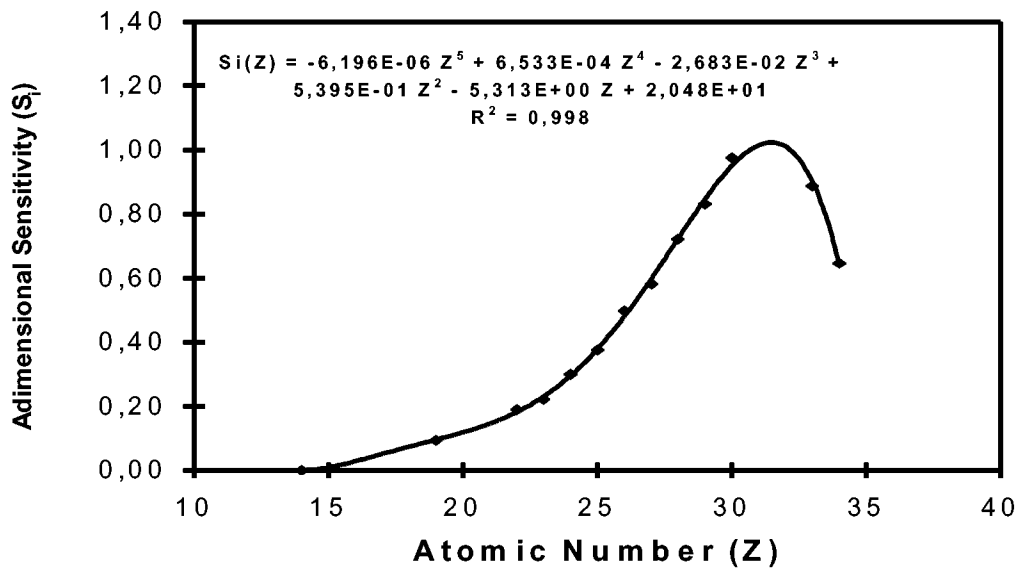


Figure 1. Adimensional sensitivity curve for Synchrotron Radiation X-ray Total Reflection.

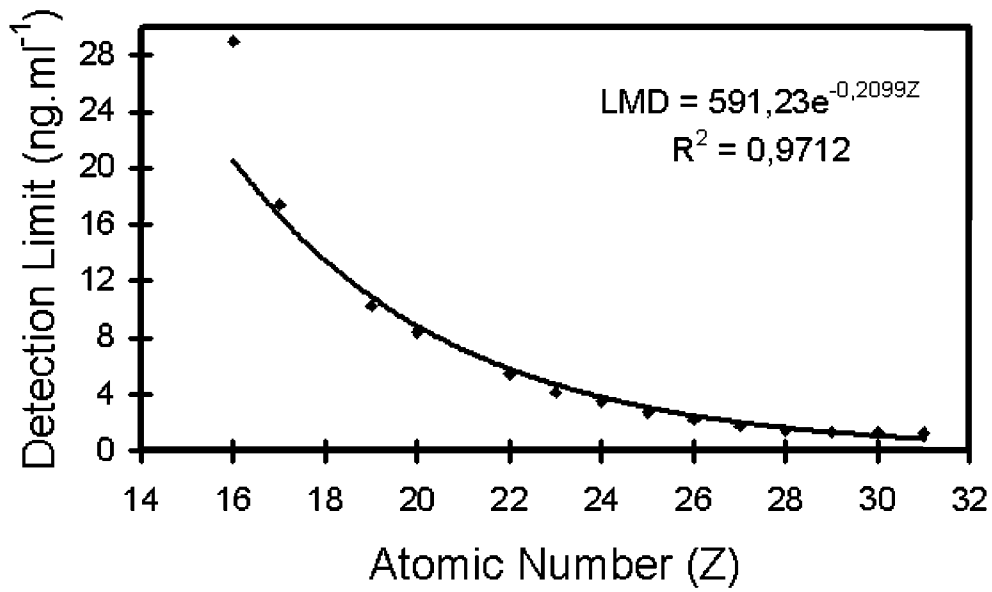


Figure 2. Detection Limit for Synchrotron Radiation Total Reflection (SR-TXRF) for 1000 s.

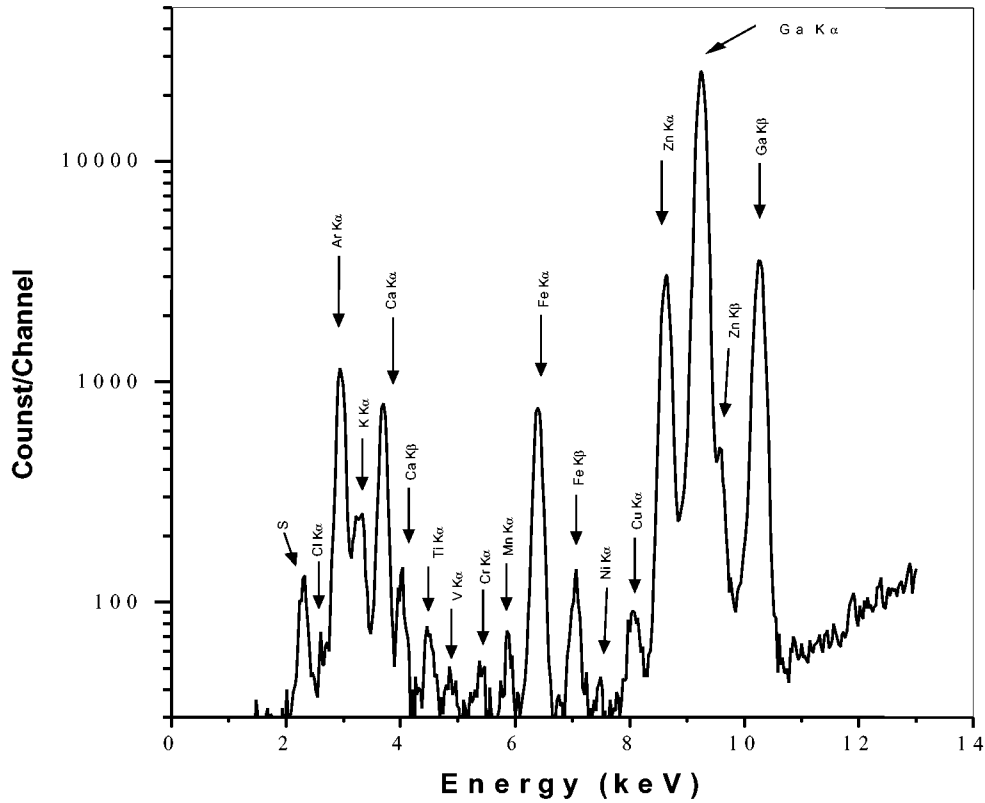


Figure 3. Characteristic X-ray spectrum rainwater (Ch1-4) measured by 100 s with SR-TXRF.

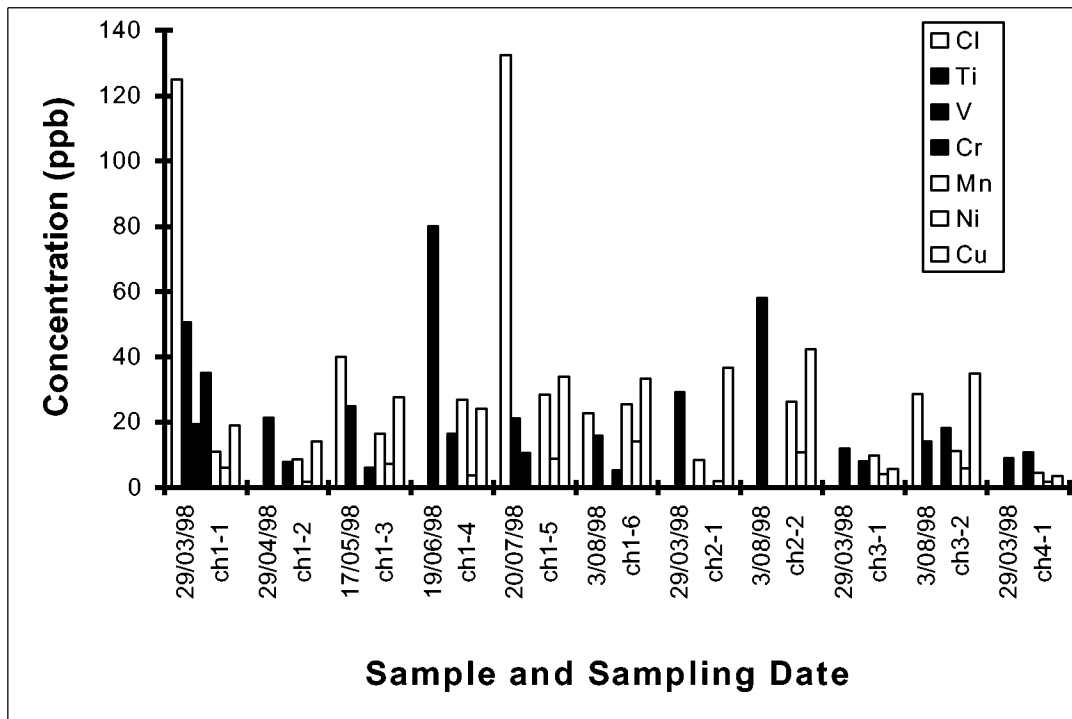


Figure 4. Concentrations of Cl, Ti, V, Cr, Mn, Ni and Cu for rainwater samples.

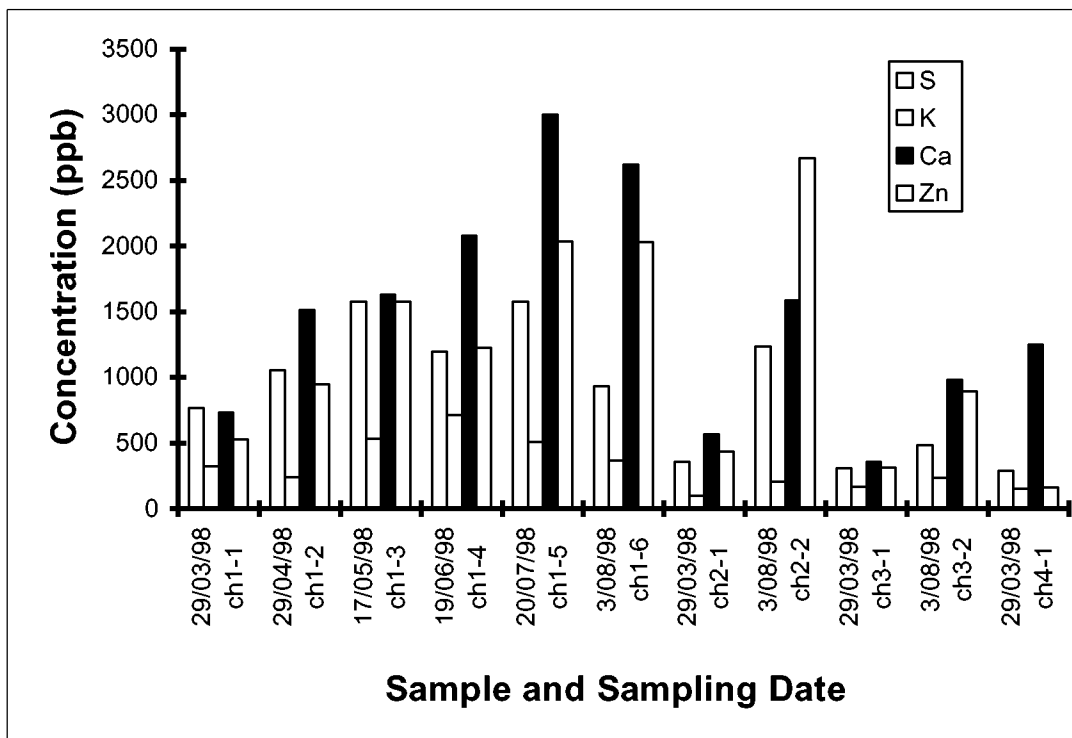


Figure 5. Concentrations of S, K, Ca and Zn for rainwater samples.

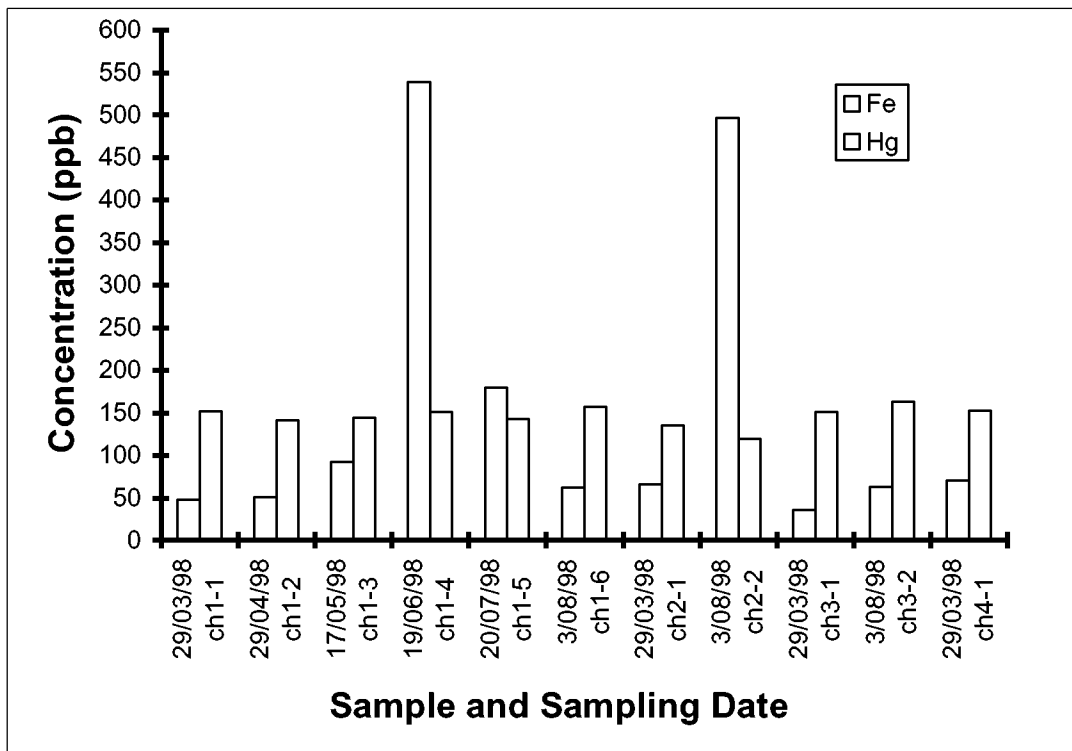


Figure 6. Concentrations of Fe and Hg for rainwater samples.