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## WATER AND SEDIMENT ANALYSIS OF TOURISTIC PLACES IN GUARAPUAVA, PR USING A PORTABLE EDXRF SYSTEM

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### ABSTRACT

The use of the Energy Dispersive X Ray Fluorescence (EDXRF) have increasingly been applied for *in situ* trace metal analysis in different kinds of samples. Results of a monitoring sampling, in the winter and summer of 2008, respectively, from 6 touristic places in Guarapuava, PR city are presented. The work consisted on the use of a portable EDXRF system constituted by a X-ray tube to excite the samples, a Si-Pin detector, a holder for the excitation-detection system and samples positioning, with the standard data acquisition electronics to register the spectra. The water samples were filtered in membranes for suspended particulate matter retention. After this, APDC precipitation methodology was applied for sample preconcentration with posterior filtering in membranes. So, the dissolved and non dissolved metal fractions were determined separately. Sediment samples were dried at 60 C for 24h and sieved through 60 mesh. Micromatter standards were used for sensitivity determination for membranes samples. For sediments 5 multi-element standards were used and calibration curves were constructed. For water membrane measurements, Fe concentration was quantified from  $0.026 \pm 0.004$  to  $5.1 \pm 1.0$ , in  $\text{mg L}^{-1}$ . For sediments, considering all the sampling locations, Mn, Cu, Sr, Y and Nb were identified qualitatively, and it was possible to quantify the following range of elements and concentrations,  $\text{mg Kg}^{-1}$ : Ca (1977 – 10162), Ti (12494 – 22320), Fe (36972 – 88452), Zn (73 – 185) and Zr (158 - 960). The performance of the equipment was very good and the results are quite satisfactory for portable equipment.

### 1. INTRODUCTION

The growth of world population in this century, accompanied by an increase in industrial plants, have brought several problems for the environment, including body water contamination and consequently the ground sediment by organic and inorganic waste produced by the own population[1].

Waste disposal containing metal species in water, even in small concentrations, cause environmental problems such as changes in the physicochemical characteristics of water.

Metals exert toxic effects on the food chain and can cause various disorders to human health. They may also reduce the ability of environment self-restoration due to the toxic effect on the microorganisms responsible for organic matter decomposition in water, causing the deterioration of their quality [2,3].

The contamination of aquatic environment by heavy metals can not be judged solely based on the levels found in water. Due to the closeness of the relationship between the quality of sediment and water quality, contaminated sediments can serve as a source of diffuse pollution of long duration, even if water pollution is significantly reduced[4,5].

Energy Dispersive X-ray Fluorescence (EDXRF) has been largely used for trace metal analysis in different environmental samples[6]. The objective of this work is to quantify the heavy metals present in water and sediment samples, collected in some touristic places of Guarapuava city, state of Paraná, through the technique of EDXRF using portable equipment.

## **2. MATERIAL AND METHODOS**

### **2.1. Sampling place**

Water samples were collected in July and December, 2008, at six touristic places of Guarapuava. Sediment samples from the same points were collected only in December. The sampling points were: Parque das Crianças (Pq Crianças), Lagoa das Lágrimas (Lg Lágrimas) and 3 points in the Parque do Lago (Lg P1, Lg P2, Lg P3) in the urban area of the city. The last point is placed in a district, 10 km far away from the city, called Parque do Jordão (Pq Jordão).

### **2.2. Sample Preparation**

The procedure for water samples preparation consist in the filtering of one liter of sample for suspended matter retention, using 0.45  $\mu\text{m}$  pore size ester cellulose membranes. In the percolate sample is applied a preconcentration procedure.

The preconcentration is essential for water samples quantification. In this case was used the direct precipitation methodology by adding APDC as chelating agent. The procedure consist in adjusting the pH for 4 of 300 mL of sample. So 1 mL of a freshly prepared 2 % APDC solution is added and the solution is stirred for 10 minutes. After this, it is filtered in 0,45  $\mu\text{m}$  pore size ester cellulose membranes[7]. The membranes were irradiated for elements identification.

Sediment samples from the margins of lakes and rivers were collected with a plastic shovel and stored in plastic bags. All the samples were dried in an oven at 60°C for 48h. In the sequence they were macerated with an agate mortar and pistil, and then sieved in a stainless steel sieve of 250 $\mu\text{m}$  thick. For EDXRF analysis, 3g of sample was placed in a specific recipient covered with Mylar film for irradiation.

### 2.3. EDXRF Quantification Procedure

The relationship between the fluorescence intensity of characteristic  $K\alpha$  or  $L\alpha$  line and the concentration of an element in the sample is given by the fundamental parameters equation, Eq. 1:[8]

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

in which  $I_i$  is the characteristic X-rays net intensity (cps),  $C_i$  is the concentration ( $\mu\text{g.g}^{-1}$ ),  $S_i$  the elementary sensitivity of the analyzed element  $i$  ( $\text{cps.g}^{-1}.\text{cm}^2$ ) and  $A$  is the absorption factor.

For water samples quantification, mono-element standards membranes of polycarbonate from MicroMatter were irradiate for sensitivity determination. Were measured K, Ca, Ti, Cr, Fe, Co, Ni, Cu, Zn, Ga, As, Se and Br standards.

For sediment samples quantification, 5 clay and soil multi-element standards were measured (IAEA375, IPT51, IPT57, IPT134 e PTXRF04). The standards were measured *in natura* and calibration curves were obtained for each element.

The measurement system was the PXRF-LFNA-02, which comprises a Si-PIN detector (221 eV FWHM at 5.9 keV and 25  $\mu\text{m}$  Be window) (Amptek Inc.)[9], coupled to a pre-amplifier, both thermoelectrically cooled, a high voltage source with amplifier, multichannel analyzer and a notebook for data acquisition and evaluation. The samples excitation was done with a mini X-ray tube (Ag target, 4 W) (Moxtek Inc.)[10]. The whole system is portable and can be used in the sampling place.

The measurement conditions were: 28 kV, 10  $\mu\text{A}$  and 50  $\mu\text{m}$  Ag filter at the tube output. Ag collimator with 3 mm diameter aperture at the detector entrance and 500 s of irradiation time.

## 3. RESULTS

### 3.1. Water sample results

Fe, Ni and Cu were quantified in the water samples. Nickel concentration was between 0.02 and 0.04  $\text{mg L}^{-1}$ , and for copper just one value besides detection limit, ( $0.003 \pm 0.001$ )  $\text{mg L}^{-1}$ . Iron was found in all samples as show Table 1.

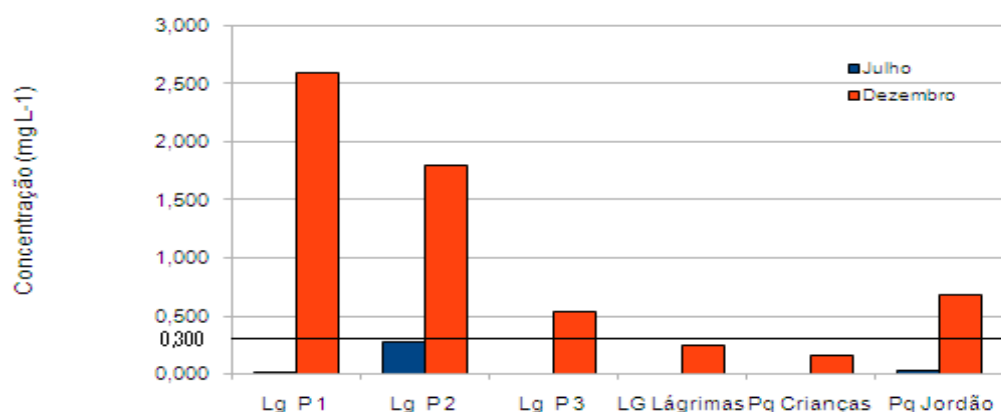
Maximum permitted values by Brazilian Environmental Commission (CONAMA)[11], for class 1 water is: dissolved Fe ( $0.3 \text{ mg L}^{-1}$ ), Ni ( $0.025 \text{ mg L}^{-1}$ ), Cu ( $0.009 \text{ mg L}^{-1}$ ).

**Table 1. Iron concentration values, in  $\text{mg L}^{-1}$ . Deviation with 95% confidence level. (SPM) Suspended particulate matter, (DM) dissolved matter.**

Sampling points	July		December	
	MPS	MD	MPS	MD
Lg P 1	$0.268 \pm 0.091$	$0.026 \pm 0.004$	$2.430 \pm 0.320$	$2.588 \pm 0.440$
Lg P 2	$0.278 \pm 0.063$	$0.278 \pm 0.063$	$2.976 \pm 0.980$	$1.800 \pm 0.35$
Lg P 3	$>0.040$	$0.007 \pm 0.006$	$3.362 \pm 0.430$	$0.542 \pm 0.060$
LG Lágrimas	$0.106 \pm 0.010$	$0.005 \pm 0.002$	$2.430 \pm 0.320$	$0.250 \pm 0.08$

Pq Crianças	0.135±0.013	0.008±0.002	2.802±0.300	0.160±0.030
Pq Jordão	0.225±0.044	0.040±0.010	5.134±1.020	0.674±0.150

Figure 1 show that, the highest concentrations for Fe, independent on the samples point, was in December. Lg P1, Lg P2, Lg P3 and Parque do Jordão presented concentration levels of dissolved Fe over the maximum limit, noting contamination.



**Figure 1. Dissolved Fe concentration values, in mg L<sup>-1</sup>. The black line highlights the maximum permitted values established by CONAMA[[11].**

### 3.2. Sediment sample results

As was expected the intensity of the peaks in the spectra was more pronounced in sediment samples compared to water ones. Table 2 shows the concentration of elements in each sample. It was possible to quantify Ca, Ti, Fe, Zn and Zr. The elements Mn, Cu, Sr, Y and Nb were identified qualitatively due to the absent of standards for calibration curves construction.

**Table 2. Concentration results (mg kg<sup>-1</sup>) for the elements found in sediment samples from touristic places in Guarapuava,PR. Deviation with 95% confidence level.**

	Lg P1	Lg P2	Lg P3	Pq jordão	LG Lagrimas	Pq Crianças
Ca	6860±932	10162±2532	< 574	1977±508	< 574	8250±1437
Ti	17991±1665	12494±3059	12534±942	14719±891	22320±385	13730±274
Mn	QI	QI	QI	QI	QI	QI
Fe	49183±5732	36972±3120	57387±6754	88452±36586	57330±3944	60447±963
Cu	QI	QI	NI	QI	NI	QI
Zn	185±49	88±9	103±2	88±4	73±11	108±22
Sr	QI	QI	QI	QI	QI	QI
Y	QI	QI	QI	QI	QI	QI
Zr	423±148	342±200	792±225	158±34	960±144	416±7
Nb	QI	QI	QI	QI	QI	QI

QI – Qualitative identification; NI – Non identified

#### 4. CONCLUSIONS

With portable EDXRF equipment it was possible to determine the presence of several elements in water and sediment samples. The accuracy of the measurements is good considering a portable system.

For water samples it was noted a Fe contamination in the second sampling. For sediment samples there are no official levels established by CONAMA and it was not shown the presence of heavy metals in any samples.

#### REFERENCES

1. A.E.S. Vives, “Estudo da remoção de metais pesados em sistemas de tratamentos de água por TXRF”. *Proceedings of V Mostra acadêmica da Unimep Santa Barbara D’Oeste*, **1**, 1-5 (2007).
2. R.P. Gambrell, “Trace and Toxic Metals in Wetlands A Review”, *Journal of Environmental Quality*, **23**, 883-891 (1994).
3. S. E Triesdell, and V. T. Breslin, “Characterization and Leaching of Elements from Municipal Solid Waste Compost” *Journal of Environmental Quality*, **24**, 827-833 (1995).
4. A. E. S Vives, S. M. B Brienza, “Emprego de Fluorescência de Raio X dispersiva para avaliação da poluição por metais pesados em amostras de água e sedimentos de lagos”, *Proceeding of VI National Meeting on Nuclear Applications*, Rio de Janeiro, **1**, 1-11(2002).
5. N.M.Hassan, P.E. Rasmussen, E. Dabek-Zlotorzynska, V. Celo, H. Chen, “Analysis of Environmental Samples Using Microwave-Assisted Acid Digestion and Inductively Coupled Plasma Mass Spectrometry: Maximizing Total Element Recoveries” *Water Air Soil Pollut.* **178**, 323-334 (2007).
6. F.L. Melquiades, C.R. Appoloni, “Application of XRF and field portable XRF for environmental analysis” *J. Radioanal. Nucl. Chem.* **262**, 533-541 (2004).
7. F.L. Melquiades, P.S. Parreira, M.J. Yabe, M.Z. Corazza, R. Funfas, C.R. Appoloni, “Factorial design for Fe, Cu, Zn, Se and Pb preconcentration optimization with APDC and analysis with a portable X-ray fluorescence system” *Talanta* **73**, 121-126 (2007).
8. E.P. Bertin, *Principles and practice of X-ray spectrometric analysis*. Plenum Press, London (1975).
9. Operating manual – XR-100CR x-ray detector system and PX2CR power supply / shaper, Amptek Inc., 1998
10. Operating Manual – Miniature Bullet X ray Tube, Moxtek INC, 2003.
11. Brazilian National Environmental Commission (CONAMA), resolution n°. 357, 23p, (2005).