Portable Energy Dispersive X-Ray Fluorescence for Metal Determination of *in natura* Water Samples

Fluorescência de Raios X por Dispersão em Energia Portátil para Determinação de Metais em Amostras de *Água in natura*

Fábio Luiz Melquiades
State University of Center-West
Dep. of Physics
fmelquiades@unicentro.br

Paulo Sérgio Parreira, Fábio Lopes
State University of Londrina
Dep. of Physics

Carlos Roberto Appoloni
State University of Londrina
Dep. of Physics

Abstract: A portable EDXRF equipment was used to perform a qualitative and a quantitative in situ analysis of in natura water. Using this equipment 10 mL of water was directly analyzed. Detection limits, in mg L-1, for Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Hg and Pb were 12.5, 7.5, 4.9, 2.7, 2.8, 2.1, 1.6, 1.9, 3.4, 3.7, respectively, with deviation around 10%. In real samples, Fe, Zn and Pb were identified. Given the obtained results, the analytical system performance appeared to be promising

Key words: portable XRF; water; *in natura*; metal.

Resumo: Foi utilizado um equipamento portátil de EDXRF para análises qualitativas e quantitativas em amostras de água in natura, in situ. Pelo uso do equipamento uma quantidade de 10 mL de água foi analisada diretamente. Os limites de detecção, em mg L-1, para Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Hg e Pb foram 12,5, 7,5, 4,9, 2,7, 2,8, 2,1, 1,6, 1,9, 3,4 e 3.7, respectivamente com desvios da ordem de 10%. Em amostras reais, Fe, Zn e Pb foram identificados. Com base nos resultados obtidos, a performance do sistema de medidas se mostrou promissora.

Palavras-chave: XRF portátil; água; *in natura;* metal.

1. Introduction

Defining the location and extent of metal contamination in environmental systems often is a difficult task. Detailed site investigations require extensive sampling and subsequent laboratory analysis, such as Inductively Coupled Plasma Spectrometry (ICP) and Atomic Absorption Spectrometry (AAS). Samples are often collected without previous knowledge of the location, extent and composition of contamination. Due to the high cost of laboratory analysis, the amount of samples taken for analysis is limited. Zones of contamination can be missed, or, if located over or under estimated. For more detailed spatial information on the extent of contamination, sites of interest must be sampled and analyzed in repetitions[1].

One of the critical factors for successful assessment of contamination, removal and remediation operations at hazardous waste sites is a fast and appropriate analytical support to approach site samples in a timely fashion[2]. Specifically, in order to select the analytical methods to be used for water quality monitoring, the aspects of quickness, reliability, precision, accuracy, low detection limits (for trace elements determination) and low cost[3] of the analysis should be considered.

Portable Energy Dispersive X-ray Fluorescence (EDXRF) has become a common analytical technique for on-site screening and fast survey of contaminant elements in environmental samples. Field portable X-ray Fluorescence (FPXRF) is a cost effective method to increase sampling densities, which improves the reliability of decisions based on spatial models delineating the extent of contamination. A rapid, nondestructive and multi-element analysis can be performed with a portable XRF spectrometer providing near real time measurements with minimal handling of the samples, allowing for extensive, semi-quantitative analysis *in situ*.

Although EDXRF is a well established technique, portable instruments became more popular in the last years. Recent reviews [3,4,5,6,7,8] present few works with *in natura* liquid samples. So, the objective of our research has been to evaluate a portable EDXRF as a fast, *in situ* alternative technique for analysis of *in natura* water samples.

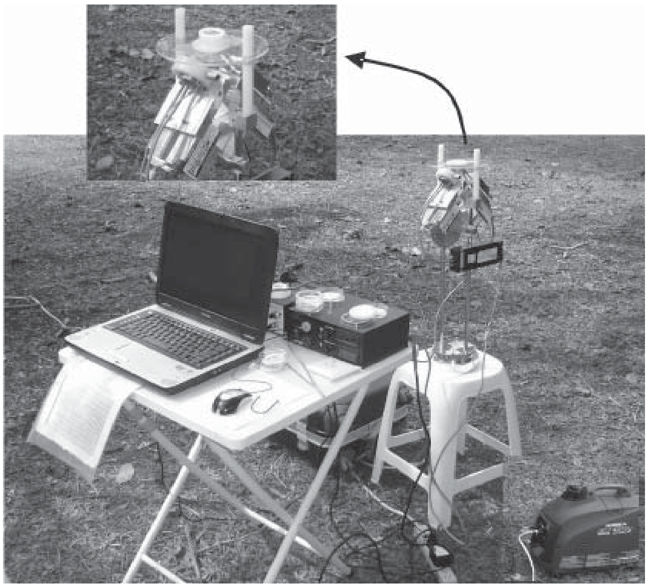
2. The experiment

Instrumentation

The EDXRF system consists in a portable X-ray tube (Ag target, 4W)[9], a Si-Pin detector (221 eV FWHM at 5.9 keV and 25 mm Be window)[10] and standard data acquisition electronics with a pocket multichannel analyzer. Figure 1 presents the complete system and the measurement geometry (45 x 45 degrees). An electric generator Honda EU10i feeds the system with stabilized energy.

The measurement conditions were: 28 kV, 10 mA and 50 mm Ag filter on the tube, Ag collimator with 3 mm diameter aperture on detector and 500 s of irradiation time.

Figure 1. Measurement system and sample geometry



Source: The authors

Sample preparation

For calibration, *in natura* standards were measured. Mono-element spiked solutions were prepared with concentrations from 10 to 50 mg L^{-1} of Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Hg and Pb.

A volume of 10 mL of the standard solution was placed in appropriated recipients for XRF analysis (Chemplex Inc.), covered with propylene film (Mylar, Chemplex Inc) for irradiation.

The validation was accomplished measuring three different multi-element standard solutions. Multi-element standard solution Sigma Aldrich 70002, multi-element standard solution Sigma Aldrich 70006 for analysis of drinking and sewage water and multi-element standard solution High Purity Inc.: Drinking Water Primary Standard (DWPS) and Drinking Water Secondary Standard (DWSS) for the analysis of drinking water.

In situ tests were performed measuring samples from Igapó Lake and Capivara River (near a car battery plant) at Londrina, Brazil. The samples were collected in a plastic beaker and 10 mL of water was placed directly in the Chemplex recipient for measurement.

Quantification procedure

Quantification was done employing fundamental parameter method. All samples and standards were measured three times each one.

Detection limits (DL) and quantification limits (QL) were obtained using the following equations (1) and (2)[11], respectively:

$$DL = \frac{3\sqrt{Bg}}{S\ t} \qquad (1)$$

$$QL = \frac{10\sqrt{Bg}}{S\ t} \qquad (2)$$

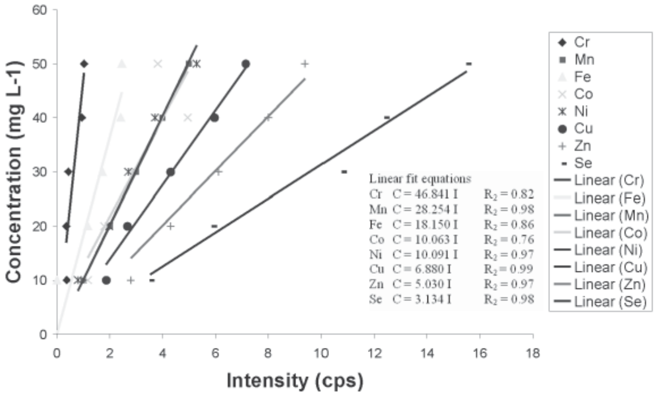
where Bg is the background counts, S the sensitivity (cps L mg^{-1}) and t the measurement time.

The obtained *spectra* were analyzed by WinQXAS software[12]..

3. Results and discussion

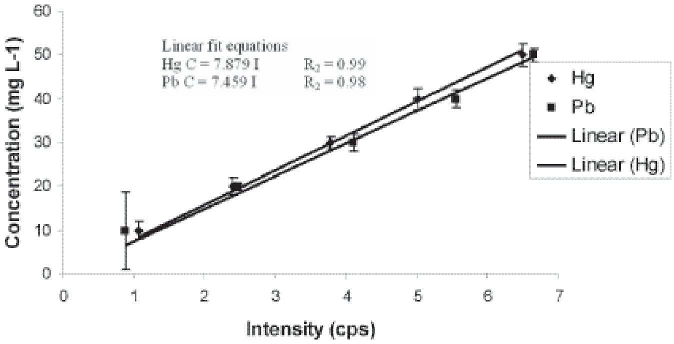
Calibration curves are presented in figures 2 and 3. The values for DL and QL, within 95% confidence level, are shown in table 1.

Figure 2. Calibration curves for in natura water standards for Kα X-ray lines (Linear fit). Standard deviation in each point ranges from 5% to 15%



Source: The authors

Figure 3. Calibration curves for in natura water standards for Lα X-ray lines (Linear fit)



Source: The authors

Table 1. Detection limits and quantification limits for in natura water with a portable EDXRF system. Values, in mg L^{-1}, within 95% confidence level deviation

Element	Detection Limit	Deviation	Quantification limit	Deviation
Cr	12.5	1.5	41.8	4.9
Mn	7.5	0.8	24.8	2.7
Fe	4.9	0.5	16.3	1.8
Co	2.7	0.3	9.1	0.9
Ni	2.8	0.2	9.5	0.8
Cu	2.1	0.2	7.0	0.7
Zn	1.6	0.2	5.4	0.6
Se	1.9	0.1	6.2	0.4
Hg	3.4	0.2	11.5	0.8
Pb	3.7	0.4	12.4	1.2

Source: The authors

The results for the multi-element standards, in order to verify the accuracy of the methodology, are shown in table 2. The standards have the following elements: Sigma Aldrich 70002 (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Tl, Zn); Sigma Aldrich 70006 (Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Tl, V, Zn); Standard HP: DWPS (Ag, As, Ba, Cd, Cr, Pb, Hg, Se); DWSS (Cu, Fe, Mn, Zn).

Table 2. Results of the multi-element standards for methodology validation. Values in mg L^{-1}

Standard 7000		
Element	**Certified Concentration**	**Measured Concentration**
Cr	47.5 - 52.5	43.4 - 65.0
Mn	9.5 - 10.5	16.2 - 24.4
Fe	9.5 - 10.5	7.5 16.9
Co	9.5 - 10.5	5.2 - 14.8
Ni	47.5 - 52.5	45.3 - 60.1
Cu	9.5 - 10.5	9.8 - 14.4
Zn	9.5 - 10.5	11.3 - 12.3
Pb	95 - 105	91.1 - 99.3

Standard 70006		
Element	**Certified Concentration**	**Measured Concentration**
Mn	9.5 - 10.5	7.1 - 33.9
Fe	95 - 105	71.8 - 96.4
Co	9.5 - 10.5	6.8 - 11.8
Ni	19 - 21	17.7 - 24.1
Cu	19 - 21	19.1 - 22.5
Zn	95 - 105	75.8 - 85.4
Se	95 - 105	74.2 - 82.2
Pb	38 - 42	35.7 - 74.3

(Continua...)

(Continuação...)

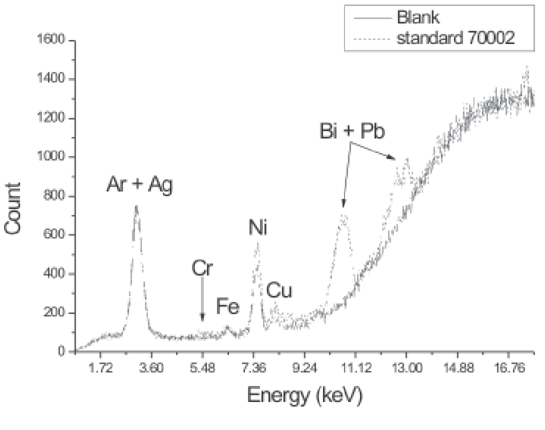
	Standard DW	
Element	**Certified Concentration**	**Measured Concentration**
Cr	95 - 105	79.3 - 111.5
Mn	47.5 - 52.5	41.6 - 51.0
Fe	91 - 105	75.2 - 102.0
Cu	47.5 - 52.5	44.7 - 48.4
Zn	47.5 - 52.5	75.8 - 85.4
Se	95 - 105	39.7 - 46.9
Hg	19 - 21	13.99 - 23.1
Pb	95 - 105	7.1 - 88.1

(Conclusão...)

Some elements such as Mn, Fe and Co in Sigma Aldrich standards are close to the quantification limit and were not determined with good accuracy. Quantification of Zn, Se and Pb was affected by system limitations and interference of other elements that make the deconvolution of peak areas with good precision difficult. However, in figures 4, 5 and 6 it can be seen that the qualitative identification is possible. The elements Al, B, Be were not quantified because the measurements were done in air atmosphere. The Ag tube target hinders Ag and Cd verification. Due to its low concentration in the standards, Ba and Ca were not identified.

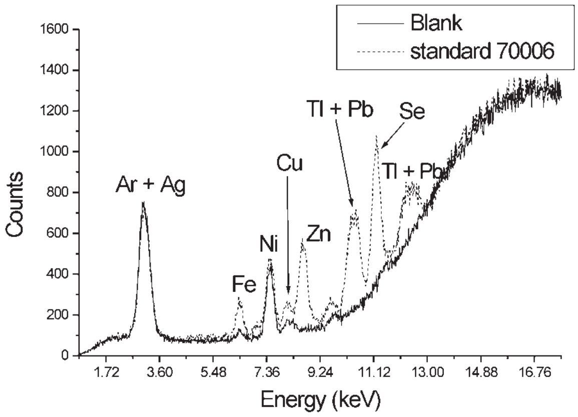
The results could have been improved if the measurement time had been increased. However, as the analysis was performed *in situ*, keeping the measurement time as low as possible allowed for the results to be obtained fast.

Figure 4. Spectra *of the multi-element standard 70002*



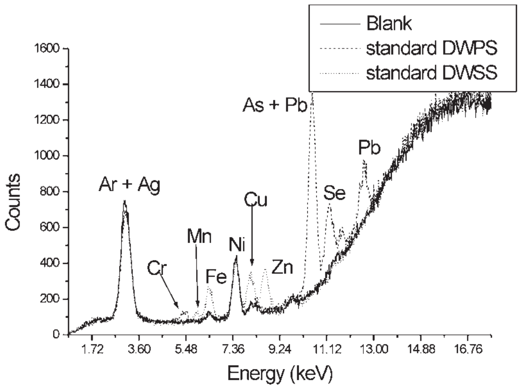
Source: The authors

Figure 5. Spectra *of the multi-element standard 70006*



Source: The authors

Figure 6. Spectra *of the multi-element standard DWPS and DWSS*



Source: The authors

As one may verify in all *spectra*, there is a Ni contamination because of an internal Ni rod that holds the Si PIN crystal[13], so nickel is an element that is always present in the *spectra*. The Ar K line is due to air and Ag L lines are due to the Ag filter.

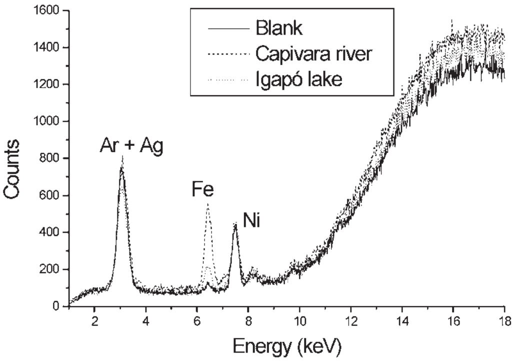
Two samples were analyzed *in situ* and the results are in table 3. Figure 7 shows both *spectra*. Just iron was possible to be determined above the quantification limit. At Capivara river, the concentration value for Pb and Zn were 4.07±0.87 and 3.76±0.56, respectively.

Table 3. Concentration results, mg L^{-1}, for the two points analyzed

Element	Capivara River	Igapó Lake
Cr	< 15.7	< 12.7
Mn	< 9.4	< 7.6
Fe	225±29	62.6±8.6
Co	< 3.4	< 2.8
Ni	< 3.5	< 2.9
Cu	< 2.5	< 2.1
Zn	QI	< 1.6
Se	< 2.1	< 1.9
Hg	< 3.9	< 3.5
Pb	QI	< 3.8

QI = Qualitative Identification (DL < concentration value < QL)

Figure 7. Spectra *of real samples analyzed in situ*



Source: The authors

The obtained results are satisfactory for a portable instrument, provided an acceptable standard deviation around 30%[14]. Our research featured a standard deviation within 95% confidence, between 7% and 14% for almost all of the concentration results, which is quite below the 30% accepted in the literature.

4. Conclusions

The obtained detection limits for *in natura* samples (magnitude order of 10^1 mg L^{-1}) are above the national and international established values. In the case of Brazilian legislation[15] the magnitude order for the maximum permitted values range from 10^{-2} to 10^1 mg L^{-1}. On the other hand, the analysis is fast and does not demand sample preparation. So, if an element is detected, this indicates that it is over the maximum established value.

The accuracy and precision of the results are satisfactory considering *in situ* analysis with portable equipment. Portable EDXRF methodology provided both qualitative and quantitative information about site contamination.

In situ analysis should be considered when characterizing large areas that require the sampling of many populations, when confirming removal activities at sites exhibiting large contaminant variability, and also for industrial application of liquid characterization and waste water effluents.

Acknowledgements

The authors are grateful to the Fundação Araucária de Apoio ao Desenvolvimento Científico e Tecnológico do Paraná (009/2005-5402) and to the Conselho Nacional de Desenvolvimento Tecnológico, CNPq (470662/2004-2), for the financial support.

References

[1] V.J. Kirtay, J.H. Kellum and S.E. Apitz, Wat. Sci. Tech., *37*, 141 (1998).

[2] J.D. Kalnicky and R. Singhvi, J. Hazard. Mater. *83*, 93 (2001).

[3] F.L. Melquiades and C.R. Appoloni, J. Radioanal. Nucl. Chem. *262,* 533 (2004).

[4] H. Xiandeng, H. Yihua and B. T. Jones, Appl. *Spectros*. Rev. *39,* 1 (2004).

[5] P. J. Potts, A.T. Ellis, P. Kregsamer, C. Streli, C. Vanhoofd and M. Weste and P. Wobrauschekc, J. Anal. At. *Spectrom. 20*, 1124 (2005).

[6] P. J. Potts, A.T. Ellis, P. Kregsamer, C. Streli, C. Vanhoofd and M. Weste and P. Wobrauschekc, J. Anal. At. *Spectrom. 21*, 1076 (2006).

[7] O.T. Butler, J.M. Cook, C.F. Harrington, S.J. Hill, J. Rieuwerts and D.L. Miles, J. Anal. At. *Spectrom.*, *21*, 217 (2006).

[8] O.T. Butler, J.M. Cook, C.F. Harrington, S.J. Hill, J. Rieuwerts and D.L. Miles, J. Anal. At. *Spectrom.*, *22*, 187 (2007).

[9] Operating Manual. Miniature Bullet X ray Tube, Moxtek Inc. 2003.

[10] Operating manual. XR-100CR x-ray detector system and PX2CR power supply / shaper, Amptek Inc. 1998.

[11] L.A. Currie, Anal. Chem. *40*, 586 (1968).

[12] Software WinQxas, http://www.iaea.or.at/programmes/ripc/physics/faznic/winqxas.htm. At 25/08/2008

[13] P. Kump, M. Necemer and Z. Rupnik, *Report IAEA/AL/130 Attachment 5.10* Vienna; 2001.

[14] P. Kump, M. Necemer and Z. Rupnik. *Report IAEA-TECDOC-1456*. Vienna; 2005.

[15] BRASIL. Ministério do Meio Ambiente, Conselho Nacional do Meio Ambiente. *Resolução n 375, de 17 de março de 2005.* Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências. Brasília, 2005.