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Determination of Cr, Fe, Co, Ni, Cu, Zn, As and Pb in liquid chemical waste by energy dispersive X-ray fluorescence

**E. Almeida · G. A. Tavares · J. A. Bendassolli ·
V. F. Nascimento Filho**

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Abstract A method for simultaneous determination of Cr, Fe, Co, Ni, Cu, Zn, As e Pb in liquid chemical waste using Energy Dispersive X-Ray Fluorescence (EDXRF) technique was evaluated. A small sample amount (200 μL) was dried on a 6.35 μm thickness Mylar film at 60 °C and the analyses were carried out using an EDXRF spectrometer operated with an X-ray Mo tube (Zr filter) at 30 kV/20 mA. The acquisition time was 300 s and the Ga element was utilized as internal standard at 25 mg/L for quantitative analysis. The method trueness was assessed by spiking and the detection limit for those elements ranged from 0.39 to 1.7 mg/L. This method is notable because it assists the choice of the more appropriated waste treatment procedure, in which inter elemental interference is a matter of importance. In addition, this inexpensive method allows a non-destructive determination of the elements from $_{19}$K to $_{92}$U simultaneously.

Keywords EDXRF · Liquid chemical waste · Instrumental analysis · Simultaneous chemical analysis

Introduction

Concerns about chemical waste storage, treatment and disposal from industries, as well as universities and research centers, have been growing recently. Although the amount of chemical wastes from last entities is not as large as to the one from industries, their complexity and variety are much higher. In this manner, the development of a nifty, low-cost and fast analytical method for inorganic chemical waste characterization is notable.

Some methods are proposed in the literature for liquid sample analysis by EDXRF [1] either by liquid direct analysis [2–4] or by previous sample preparation, such as evaporation [5], filtration through ion exchange resin-loaded paper [6], precipitation and filtration [7–10], placed onto a paper [11] and others [12, 13].

Though the liquid direct analysis is the simpler sample preparation method in XRF, quali-quantitative analysis at trace levels is constrained inasmuch as a considerable primary X-ray scattering by the low atomic number matrix. Ekinci et al. [3] determined P, K and Ca in human milk directly; however, it was utilized 1 h per sample in the acquisition time.

On the other hand, straightforward sample preparation steps such as evaporation of a small amount on a plastic film, in which absorption and enhancement effects is neglected (thin film condition) is worthy of evaluation. This method also allows the analyte pre-concentration [2].

It is quite often to face no knowledge about liquid chemical waste composition, poor label instruction or even no label at all, in a recent chemical waste management program. The choice of the chemical treatment demands information as much as possible of waste constituents due to inter-elemental interference. So, take into account the EDXRF multielemental feature, this technique owns a great potential for being applied in this field. In addition, research centers, such as CENA/USP, whose chemical waste management program is underway, the evaluation of analytical methods for inorganic liquid chemical waste characterization is worthwhile [14].

E. Almeida (✉) · G. A. Tavares · J. A. Bendassolli ·
V. F. Nascimento Filho
Center for Nuclear Energy in Agriculture (CENA), University of São Paulo (USP), Av. Centenário, 303, Caixa Postal 96, Piracicaba, SP CEP 13400-970, Brazil
e-mail: edualm@usp.br

Experimental

Analytical standards and sample preparations

Four analytical standard sets from 0 to 500 mg/L were prepared: (1) Cr and Hg, (2) Pb and Cd, (3) Fe and Zn and (4) Ni and Sr. These analytical standards were obtained from their 1,000 and 1,005 mg/L, purchased from Aldrich Inc. and Specsol. For quantitative elemental determination, Ga internal standard was used at 25 mg/L. Two hundreds microliters was pipetted onto a 6.35 µm thickness Mylar film assembled in XRF sample cup (n. 1530—Chemplex Industries Inc.) and dried in a laboratory oven at 60 °C.

The liquid chemical waste samples were obtained from CENA/USP laboratories. The samples and *Contract Lab Program AA/ICP Interference Check Solution, mixed analytes set 3* standard (Aldrich brand) preparations followed the same procedure used for the analytical standards. They were analyzed in duplicate. This *Check Solution* standard was used for method checking.

EDXRF spectrometer

The excitation was carried out using a Mo X-ray tube (PW 1316/92 model, Philips brand), operated with Zr filter and at 30 kV and 20 mA. Acquisition time was 300 s for analytical standards and sample analyses. It was utilized an X-ray acrylic holder for X-ray sample cup support, whose geometry was 45° between sample surface and excitation X-ray beam and the same angle comparing the sample to detector surfaces.

The X-rays were detected by a Si(Li) semiconductor detector, SLP-06165-P model, manufactured by EG&G Ortec. It was coupled to an amplifier (672 model) and multichannel pulse analyzer (ACE$^{\mathrm{TM}}$ model). The X-ray spectra were deconvoluted by AXIL software [15]. The analytes from $_{24}$Cr to $_{38}$Sr were analyzed by Kα X-rays and $_{48}$Cd, $_{80}$Hg and $_{82}$Pb analyzed by Lα X-rays. To minimize the scattering X-ray from the sample, an Al collimator with 5 mm internal diameter was placed on the detector.

Elemental quantitative analyses

For EDXRF quantitative analyses with internal standard addition, the intensity of the analyte X-ray I_i is related to its concentration by Eq. 1 [16]:

$$R_i = S'_i \cdot C_i \tag{1}$$

in which

$$R_i = \frac{I_i}{I_{\mathrm{Ga}}} \cdot C_{\mathrm{Ga}} \tag{2}$$

and

$$S'_i = \frac{S_i}{S_{\mathrm{Ga}}} \tag{3}$$

where R_i = relative intensity of analyte i (mg/L); S_i and S_{Ga} = analytical sensitivities (cps L/mg) to analyte i and Ga, respectively; S'_i = relative sensitivity to element i (unitless); C_i and C_{Ga} = concentrations (mg/L) of analyte i and element Ga, respectively; I_i and I_{Ga} = lines X-ray line intensities (cps) for analyte i and element Ga, respectively.

Limit of detection (LD)

The LD was calculated using Eq. 4 [16]:

$$\mathrm{LD} = 3\sqrt{\frac{I_{i(\mathrm{BG})}}{t}}\,\frac{C_{\mathrm{Ga}}}{I_{\mathrm{Ga}}S'_i} \tag{4}$$

where LD = limit of detection (mg/L); $I_{i(\mathrm{BG})}$ = background intensity of analyte i (cps); and t = acquisition time (s).

Trueness

The trueness was evaluated by spiking one hundred microgram (100 µL of the 1,000 mg/L primary standard solution) of Cr, Co, Cu, Zn, As and Pb in 1 mL of the sample. To avoid diluting the sample considerably, it was spiked three elements per sample only.

Results

Figure 1 shows a liquid chemical waste X-ray spectrum containing Zn mainly from a laboratory at CENA. The argonium X-ray peak is due to its atmosphere presence and the Ga one accounts for its use as internal standard (added in the samples). Considering EDXRF technique parameters utilized in this work, it was possible to determine K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb, Hg and Pb simultaneously, evaluated through Kα X-ray lines, unless the last two elements evaluated by Lα X-ray lines.

Actually, in case of interest and by using appropriated analytical standards, the elements Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Bi, Th, and U might also be determined through their L X-ray lines. This wide screening potential in liquid chemical waste samples demonstrates that multi-elemental and simultaneous ED-XRF is a suitable analytical technique for this matrix characterization.

Besides that, the liquid chemical waste screening using EDXRF is notable for choosing the more appropriated waste treatment method. It is quite common in these methods the inter-elemental interference (e.g. chemical

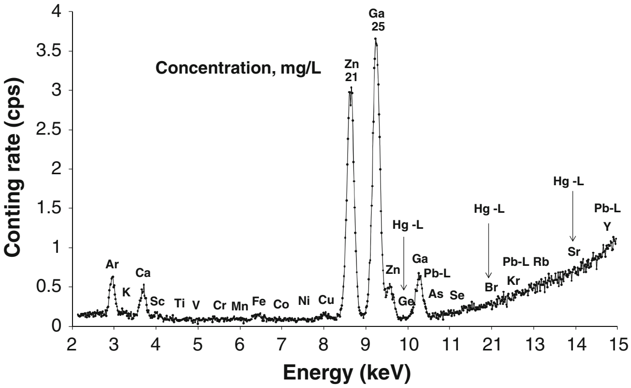

Fig. 1 X-ray spectrum of a liquid chemical waste sample from a laboratory at CENA containing Zn mainly. The argonium X-ray peak is due to its atmosphere presence and Ga one accounts for its use as internal standard (added in the samples)

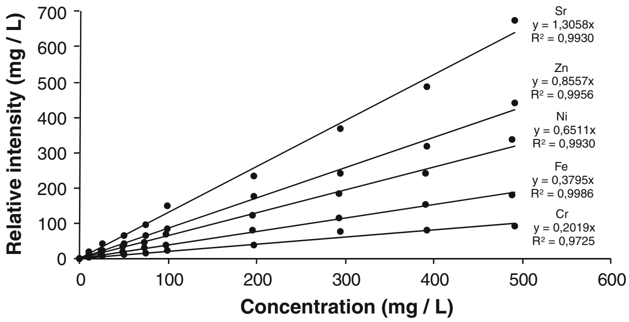

Fig. 2 Analytical curve plots for Cr, Fe, Ni, Zn and Sr

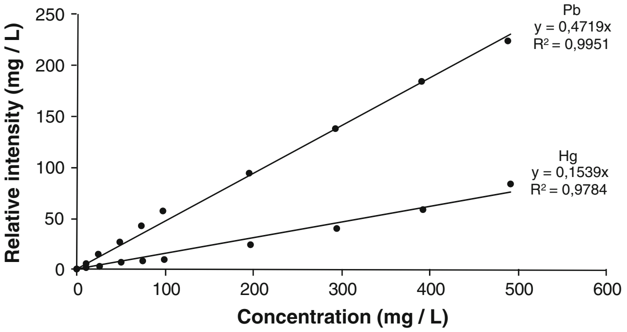

Fig. 3 Analytical curve plots for Pb and Hg

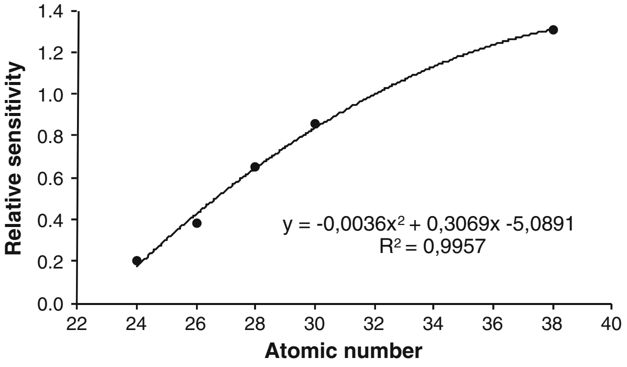

Fig. 4 Relative sensitivity dependence of atomic number evaluated by Kα lines

equilibrium displacement). So, the more knowledge of sample contents, the more adequate will be the choice of waste treatment. Moreover, EDXRF does not need gas carrier to run the analyses as opposed to others spectrochemical techniques. So, EDXRF presents a relative low-cost per sample. In addition, the sample volume required (1 mL) in this EDXRF method is relatively small, much less than the normal one demanded in other ordinary spectrochemical techniques (around 5 mL for multi-elemental running).

Figure 2 shows the analytical curves for Cr, Fe, Ni, Zn and Sr. Figure 3 shows the analytical curves for Pb and Hg (Lα lines).

The linearity of the relative sensitivity and elemental concentration from 0 up to 500 mg/L is worthy of note. For X-ray fluorescence spectroscopy technique it is expected that linearity would continue even at higher concentration, however, to avoid matrix effect (mainly absorption one), the concentration range for the analytical standard was limited up to five hundreds mg/L. It is worthy to mention that the Resolution n. 899 of Brazilian Regulation ANVISA [17], recommends at least a set of five standards at different concentrations for analytical curves. In our work, it was used nine standards at different concentrations.

The correlations between relative intensity and concentration for Cr and Hg (R^2 equal to 0.9725 and 0.9784, respectively) were not as good as the other elements. For Cd evaluation, the method proposed was less appropriated (R^2 equal to 0.9638), probably due to its low L X-ray line sensitivity and absorption effect at its 3.134 keV Lα X-ray line. For this element, it is recommended the use of an X-ray tube with a higher atomic number target (e.g. W), allowing the choice of Kα Cd X-ray line.

With reference to Ga internal standard use, without its correction the analytical curves for Sr and Pb presented R^2 equal to 0.9138 and 0.9690, however, their value of R^2 rose to 0.9930 and 0.9951, respectively, taking into account the internal standard. The most important reason for using internal standard was due to the asymmetric sample dryness on the Mylar film. Conversely, Ga correction was less critical for Fe, Zn and Ni.

Figure 4 shows the plot of Kα X-ray line relative sensitivity versus the atomic number. Insofar as knowing the correlation of these two variables, it was possible to determine the relative sensitivity of other chemical elements such as Mn, Co, Cu, Ge, As, Se, Br and Rb, even though, none of these elements were present in the analytical standard sets.

Table 1 Limits of detection (LD, mg/L) for Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb, Sr, Hg and Pb, considering 300 s for acquisition time

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Br	Rb	Sr	Hg	Pb
LD (mg/L)	1.7	1.1	0.90	0.64	0.51	0.44	0.39	0.39	0.42	0.46	0.52	0.70	0.86	2.6	0.92

Table 2 Spike recoveries (%) for Cr, Fe, Co, Ni, Cu, Zn, As and Pb

	Cr	Fe	Co	Ni	Cu	Zn	As	Pb
Recoveries (%)	85	62	97	76	88	92	105	99

Table 3 Cr, Mn, Co, Ni, Cu, Zn and Pb concentration values (mg/L, mean ± one standard deviation) obtained by EDXRF method and the certificated ones (provided by Aldrich)

	Cr	Mn	Co	Ni	Cu	Zn	Pb
EDXRF	53.6 ± 1.0	47.2 ± 1.9	43.8 ± 1.3	92.2 ± 1.3	44.4 ± 0.9	98.2 ± 0.7	113 ± 4
Certificate	50	50	50	100	50	100	100

Table 1 shows the limit of detection LD for Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb, Sr, Hg and Pb, considering 300 s for acquisition time.

There are some EDXRF methods for liquid analysis utilizing precipitation and filtration procedures in which lower limits of detection is obtained [7–10]. However, these methods are much more time-consuming and elaborate. In addition, due to the fact that the complex agent of choice is effective for only a certain group elements, and besides that, it is quite common to face no previous knowledge of chemical waste elemental content, these features constrain the utilization of precipitation and filtration procedures in liquid wastes analysis.

Table 2 shows the spike recovery (%) for Cr, Fe, Co, Ni, Cu, Zn, As and Pb. These elements were those ones under evaluation in a LTR/CENAs waste lot. Because of that, it not verified the recoveries for the other elements. The spike recovery verifies the analyte method trueness. The method trueness of all elements was satisfactory (80–120%), except for Ni.

Though the elements Mn, Ge, Se, Br, Rb, Sr and Hg might be also determined, they were not included in the title and the abstract because it was not carried out any trueness test for them.

In order to check the method it was analyzed the *Contract Lab Program AA/ICP Interference Check Solution, mixed analytes set 3* standard, purchased from Aldrich. The analysis was ran in duplicate. Table 3 presents the Cr, Mn, Co, Ni, Cu, Zn and Pb concentration values obtained by EDXRF method and the certificated ones (provided by Aldrich).

Conclusions

This method has shown a great potential for liquid chemical waste characterization. Due to simplicity, fast, simultaneous and multi-elemental features of the EDXRF, this technique is suited for the analysis of this sort of sample inasmuch as the important role of the inter-elemental interference in liquid chemical waste treatment. Moreover, it is also quite common to face chemical waste without any knowledge of major, minor and trace constituents, in which an analytical "screening" is recommended. Other advantage is the small sample volume required (1 mL) in this EDXRF method. In addition, for being a non-destructive analytical technique, the samples might be analysed as many times as it requires.

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