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Development of methodologies to determine aluminum, cadmium, chromium and lead in drinking water by ET AAS using permanent modifiers

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Abstract

In this work, methodologies were developed to determine aluminum (Al), cadmium chromium and lead in drinking water by electrothermal atomic absorption spectrometry using permanent modifiers. No use of modifier, iridium, ruthenium, rhodium and zirconium (independently, 500 μg) were tested to each one analyte through the pyrolysis and atomization temperatures curves. As the matrix is very simple, did not had occurred problems with the background for all metals. The best results obtained for cadmium and chromium was with the use of rhodium permanent modifier. For lead and aluminum, the best choice was the use of zirconium. The selection for the modifier took into account the sensitivity, form of the absorption pulse and low atomization temperature (what contributes to elevate the useful life of the graphite tube). For aluminum using zirconium permanent, the best pyrolysis and atomization temperatures were respectively, of 1000 and 2500 °C with a characteristic mass (1% of absorbance, m_o) of 19 pg (recommended of 20 pg). For cadmium, with use of rhodium the best temperatures for the pyrolysis and atomization were respectively of 400 and 1100 °C, with a symmetrical peak and with a m_o of 1.0 pg (recommended of 1.0 pg). For chromium with rhodium permanent, the best temperatures for pyrolysis and atomization were respectively of 1000 and 2200 °C, with symmetrical peak and m_o of 5.3 pg (recommended of 5.5 pg). For lead with zirconium permanent, the best temperatures for pyrolysis and atomization were of 700 and 2400 °C, with symmetrical peak and with m_o of 30 pg (recommended of 20 pg). Water samples spiked with each one of the metals in four different levels inside of the acceptable values presented recoveries always close to 100%. The detection limits were of 0.1 $\mu g\,l^{-1}$ for cadmium; 0.2 $\mu g\,l^{-1}$ for chromium; 0.5 $\mu g\,l^{-1}$ for lead and 1.4 $\mu g\,l^{-1}$ for aluminum.

Keywords: Aluminum; Cadmium; Chromium; Lead; Drinking water; ET AAS; Permanent modifiers

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1. Introduction

Aluminium (Al) is an abundant metal in the earth, it does not have any function in the human metabolism, and low concentrations (above 5.0 $\mu g\,l^{-1}$), are associated to several diseases as renal insufficiency, encephalopathy, pulmonary fibrosis, microcytic anemia and disturbances of the sleeping. Bearers of the Alzheimer's diseases present high concentrations of Al in the brain [1,2].

Cadmium is an element without physicological function in the human organism, being high toxicity in low concentrations. Trace and ultratrace determinations of cadmium in environmental and biological samples and also in human livers have become of increasing interest because the toxicity of this metal [3,4].

Chromium is an essential trace metal in both human and animals and plays an important role in the metabolism of the glucose aiding in the process of degradation of the sugar in the blood and in the lipid metabolism (mainly cholesterol) [5]. Its deficiency results in impaired glucose and lipid metabolism, owing to the poor effectiveness of insulin [6]. Excessive amounts of chromium, particularly in the more toxic Cr(VI) valence state, are detrimental to health as it may be involved in the pathogenesis of some diseases such as lung and gastrointestinal cancer [7].

For more than 4000 years, the man uses the lead under several forms. The level of contamination of the victuals produced close to the industrialized areas it is affected by the

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characteristics of the existent industries. The organisms that live in aquatic environment, capture and accumulate the lead in the water and in the sediments. The load of the existent pollutant in the vegetables is generated by the reception of the metal by the roots and by deposition on the vegetables. The lead can also be incorporate to the victuals during the industrialization processes, or in the domestic preparation, especially when ceramic utensils, lead-crystal or metallic are used [8].

Concentrations of aluminium in drinking waters (tap water, still mineral water and sparkling mineral water), fruit juices and soft drinks were determined using graphite furnace atomic absorption spectrometry (GFAAS) of samples processed with a HNO_3–V_2O_5 acid digestion pre-treatment. In water samples, aluminium was determined directly. The author has verified the sensitivity, accuracy and precision of the method and ruled out matrix interferences. In analyzed samples, aluminum values ranged from 4.2 to 165.3 $\mu g\,l^{-1}$ in drinking water ($n = 41$), from 49.3 to 1144.6 $\mu g\,l^{-1}$ in fruit juices ($n = 47$), and from 44.6 to 1053.3 $\mu g\,l^{-1}$ in soft drinks ($n = 88$) [9]. The differential pulse voltammetric (DPV) indirect determination of aluminium using L-dopa under alkaline conditions on a glassy carbon working electrode was studied. The method was applied to the determination of aluminium in drinking waters, synthetic renal dialysate, sodium chloride injection, blood, urine and hair samples [10].

A fast method for separation, preconcentration and determination of cadmium in drinking (source, well, tap) and water for irrigation was described. Iron(III) hexamethylenedithiocarbamate, Fe(HMDTC)3, has the role of colloid precipitate flotation collector. The determination of cadmium in final water solutions preconcentrated by flotation can be performed by flame (FAAS) or electrothermal atomic absorption spectrometry (ETAAS) [11]. In another work, cadmium concentration in different drinking water supplies of Dhaka city is reported. In this study, cadmium was extracted from water into chloroform after chelating with sodium diethyldithiocarbamate and then back extracted into water for determination by atomic absorption spectrophotometry (AAS) [12]. Subramanian et al. [13] had studied the conditions (e.g. pH, resin, particle size, foreign ions) affecting the uptake of Cd(II), Cr(III), Cu(II) and Pb(II) from aqueous solution by the SM-7 (also called XAD-7) resin. Based on these studies, a two-column method was developed to overcome the effect of complexation by humic substances. The method was successfully tested with the NBS multi-element water standard, SRM 1643d, and was subsequently applied to enrich Cd(II), Cr(III), Cu(II) and Pb(II) in 15 drinking water samples from Hamilton, Ontario. The metals were determined using graphite furnace atomic absorption spectrometry. A second national survey was done to ascertain the levels of Cd, Co, Cr, Cu, Ni, Pb, Zn, Ca, and Mg in Canadian drinking water supplies. Raw, treated, and distributed water samples collected from 71 municipal district across Canada were analyzed both by atomic absorption spectrophotometry using the direct method and by an APDC-MIBK extraction procedure [14].

The results of long-term studies made by the Department of General Chemistry, I.M. Sechenov Moscow Medical Academy, that deals with unification of methods for determining some ions of metals (lead, zinc, sodium, and potassium) in the assessment of the quality of drinking water and transfusion fluids are summarized. A procedure was developed to determine the trace impurities of zinc, lead, and silver by atomic absorption spectrometry using sorption concentration. C-80-2-aminothiazole, a new sorbent synthesized at the Research Institute of Polymers, was used to detect these ions in the drinking water [15].

In this work, some substances (no modifier, iridium, rhodium, ruthenium and zirconium permanent, 500 μg of each) were investigated to determine aluminium, cadmium, chromium and lead in drinking water by electrothermal atomic absorption spectrometry.

2. Experimental

2.1. Instrumentation

All measurements were carried out with a GBC (Victoria, Australia) 906-AA atomic absorption spectrometer, equipped with a graphite furnace and an autosampler PAL 3000 (GBC) and with a deuterium arc lamp background correction, operated under the condition recommended by the manufacturer. Integrated absorbance (peak area) was used exclusively for signal evaluation. Hollow cathod lamps for Al and Cd from GBC was operated at 10 mA, with slit of 0.5 nm in a 309.3 nm of wavelength for Al (part number (PN) 41-0101-00) and at 3 mA, with a slit of 0.5 nm in a 2288 nm for Cd (PN 41-0108-00). For Pb and Cr hollow cathode lamps from Pothron (Narren Warren, Victoria, Australia) was operated at 5 mA, with a slit of 0.5 nm in a 283.3 nm for Pb (PN 828) and at 6 mA, with a slit of 0.2 nm in a 357.9 nm for Cr (PN 812). The volume pipetted into the graphite tube was 20 μl for samples and calibration solutions. Argon, 99,996% (White Martins, Contagem, MG, Brazil), was used as sheath gas. Pyrolytic graphite coated tubes without platform (GBC) were used in all studies. The treatment of the graphite tubes with the permanent modifiers was described previously, i.e. by applying 50 μl of a 1000 $mg\,l^{-1}$ Ru, Ir, Zr or Rh solution, independently for each modifier and submitting the tube to a specific temperature program [16–18]. This procedure was repeated 10 times in order to obtain a deposit of 500 μg of the permanent modifier. The graphite furnace temperature program for the determination of all metals was optimized and showed in the Table 1.

2.2. Reagents and solutions

All chemical used were of analytical-reagent grade, unless otherwise specified. Water was de-ionized in a Milli-Q

Table 1
Temperature programs for the determination of Al, Cd, Cr and Pb in drinking waters

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml $\min^{-1}$)
1	90	3.0	2.0	250
2	140	20.0	4.0	250
3	1100 a, 400 b, 1000 c, 700 d	4.0	2.0	250
4	1100 a, 400 b, 1000 c, 700 d	0.0	2.0	0.0
5[a]	2500 a,1100 b, 2200 c, 1900 d	0.7 ad, 1.5 b, 1.1 c	2.0	0.0
6	2500	2.0	2.0	250

[a] Read in this step a = Al; b = Cd; c = Cr; and d = Pb.

system (Millipore, Bedford, MA, USA). The nitric acid was from Vetec (Rio de Janeiro, Brazil, 022844).

The following 1000 μg ml^{-1} stock solutions were used: ruthenium (Fluka, Buchs, Switzerland, No. 84033), rhodium (Fluka, No. 83722), iridium (Fluka, No. 58195) and zirconium (Aldrich, Milwaukee, WI, USA, No. 27,497–6) all in 1 mol l^{-1} hydrochloric acid. For the analytes, the following 1000 mg l^{-1} were used: aluminium from Merck (Darmstad, Germany, No. 90349698), cadmium from Spex (Edilson, NJ, USA, PLK10-Cd), chromium from Merck (No. 60186741) all in nitric acid ~0.5 mol l^{-1} and lead from Merck (No. 90361929) in ~0.3 mol l^{-1} nitric acid.

Before the use, all glasses was washed abundantly with solution of detergents, rinsed with water, maintained in bath with nitric acid 50% (v/v) for a period non inferior at 1 h and later on rinsed several times with de-ionized water. The autosampler cups were submitted to the same treatment. In all studies, the calibration was accomplished with aqueous solutions in nitric acid 0.5% (v/v).

The limit of detection (LOD, μg l^{-1}) was calculated using the equation LOD $= 3 \times S_{\mathrm{BL}}/b$, where S_{BL} was the standard deviation of 10 measurements of the blank (nitric acid 0.5% (v/v)) and b is the slope of the calibration curve.

3. Results and discussion

3.1. Pyrolysis and atomization temperature curves

All temperature optimization for the furnace programs were performed through pyrolysis and atomization temperature curves. The selection for the modifier took into account the sensitivity, forms of the absorption pulse, and low atomization temperature (what contributes to elevate the useful life of the graphite tube). The pyrolysis and atomization temperature curves were obtained for each one of the analytes, initially using the recommended atomization temperature and being selected (in agreement with the criteria described, especially sensitivity) the best temperature for pyrolysis. With these temperatures of pyrolysis fixed for each analyte, it was swept the atomization temperatures between 1000 and 2500 °C, except for Al, where the minimum temperature of appearing of the signal was in 1800 °C and for chromium, that it was in 1500 °C.

Fig. 1 shows the pyrolysis and atomization temperature curves for aluminium in drinking water. The best results were obtained using zirconium permanent with temperatures of 1000 and 2500 °C and a characteristic mass (1% of absorbance), of 19 pg (recommended by the manufactures without modifier use in nitric acid 0.2% (v/v) of 20 pg). With this modifier, the peak is very symmetrical and return to the baseline in 2 s. For cadmium (Fig. 2), the best result were obtained with rhodium permanent, with best temperatures of 400 and 1100 °C, with a symmetrical peak that return to the baseline in 2 s and with a characteristic mass of 1.3 pg (recommended of 1.0 pg). For chromium (Fig. 3), the best conditions were obtained using rhodium permanent, with symmetrical peak that return to the baseline in 2 s and with a characteristic mass of 5.3 pg (recommended of 5.5 pg) and with best temperatures of 1200 and 2200 °C. In Fig. 4, was shown the pyrolysis and atomization temperature curves for lead. The best results were obtained using zirconium permanent, with temperatures of 700 and 2400 °C for pyrolysis and atomization, respectively. The peak shape is very definite and return to the baseline in 1 s of atomization.

For Al (Fig. 1), it is evident the improvement in sensitivity with the use of permanent zirconium, the double or more than with the use of the other modifiers. Besides, it is

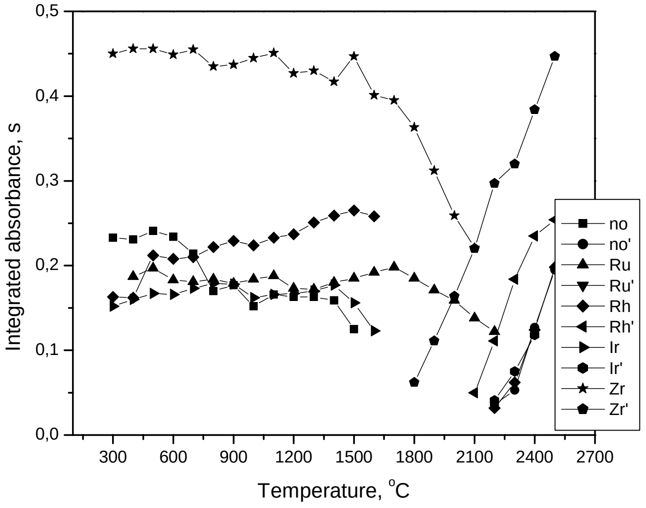

Fig. 1. Pyrolysis and atomisation temperature curves for 2 ng of Al in drinking water using different modifiers.

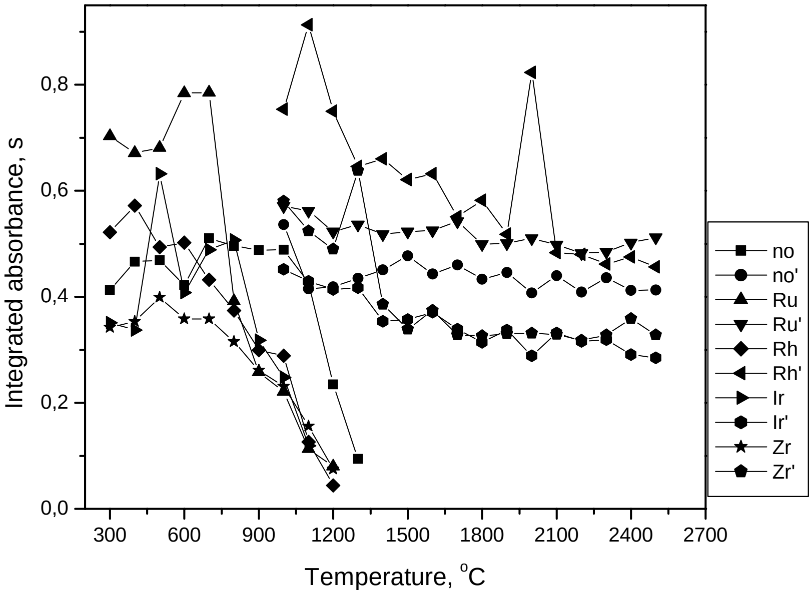

Fig. 2. Pyrolysis and atomisation temperature curves for 0.2 ng of Cd in drinking water using different modifiers.

observed that the atomization temperature curve has similar behavior for all the studied modifiers, or be the sensitivity increases always with the increase of the temperature. For the use of permanent rhodium, the temperature of appearance of the signal is the more lower (1800 °C) with equal sensitivity increase with the temperature up to 2500 °C, the maxim studied temperature, avoiding the use of higher temperatures than can compromise the useful life of the graphite tube. For Cd, it is well observed by Fig. 2 that with rhodium in a low atomization temperature (1100 °C) it is obtained the best sensitivity. With increase of the atomization temperature, the sensitivity falls being finally almost similar to the use of ruthenium or without modifier above 2100 °C. For the other modifiers the sensitivity changes very a little with the increase of the temperature (it is almost formed a plateau in all studied temperature ranges). For Cr, the same tendency observed for Al occurred. The measure that increases the atomization temperature the signal increases for all the modifiers and without modifier, except for the rhodium use. In this case, it is obtained a maximum sensitivity in 2200 °C and above this value the sensitivity falls. Another interesting fact is that using permanent ruthenium was not obtained a peak but a plateau in the whole range of studied temperatures, the baseline does not return even in 10 s of atomization. For Pb, occur a behavior relatively similar for the not modifier use and ruthenium, rhodium and permanent zirconium, with

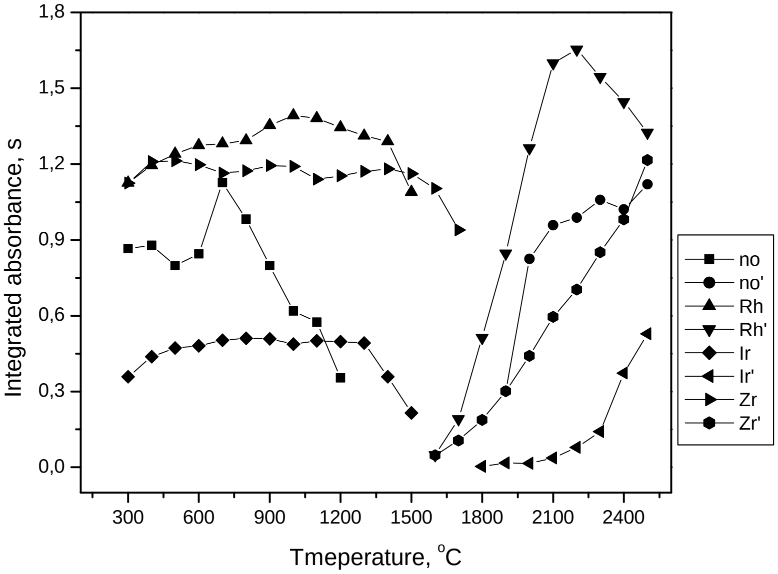

Fig. 3. Pyrolysis and atomisation temperature curves for 2 ng of Cr in drinking water using different modifiers.

Table 2
Characteristic masses (pg), obtained in the best condition of temperatures (for pyrolysis and atomization)

Analyte	No modifier[a]	Zirconium	Rhodium	Iridium	Ruthenium	Recommended
Al	50	19	33	34	36	20
Cd	1.2	2.2	1.0	2.0	1.6	1.0
Cr	7.9	7.2	5.3	17.0	–	5.5
Pb	33.0	30.0	36.2	65.2	33.0	20.0

[a] According with recommended conditions by the manufacturer.

Table 3
Analytical characteristics for the determination of Al, Cd, Cr and Pb in drinking water using zirconium or rhodium permanent modifier

Analyte	m_o (pg)	LOD (μg l^{-1})	R.S.D. ($n = 3$) (%)	r^2	Calibration range (μg l^{-1})	Maximum value[a] (μg l^{-1})
Al	19	1.4	<7	0.996	5–200	100
Cd	1.0	0.1	<5	0.996	1–10	5
Cr	5.3	0.2	<4	0.997	5–100	50
Pb	30	0.5	<12	0.997	1–20	10

[a] According to the Brazilian legislation [19].

sensitivity a little better and a better defined peak for this last one. For the use of permanent iridium the sensitivity is less of the half that for zirconium and with an irregular peak.

In Table 2 was shown the characteristic masses for the four analytes investigated in this work in each modifier. The data without modifier use were obtained with the conditions recommended by the manufacturer, that is, with temperatures of atomization of 2500 °C for Al, 1800 °C for Cd, 2500 °C for Cr and 2000 °C for Pb. Except for Pb where the optimized temperature with permanent Zr was higher (2400 °C) and for Al that was the same recommended (2500 °C), for Cd and Cr the optimized values were lower comparatively to those recommended (atomization temperatures optimized in 1100 °C for Cd and 2200 °C for Cr). It can be observed that the results obtained for the characteristic masses for the recommended conditions do not reproduce the data suggested by the manufacturer. This can be due to the equipment that already are in using a many years.

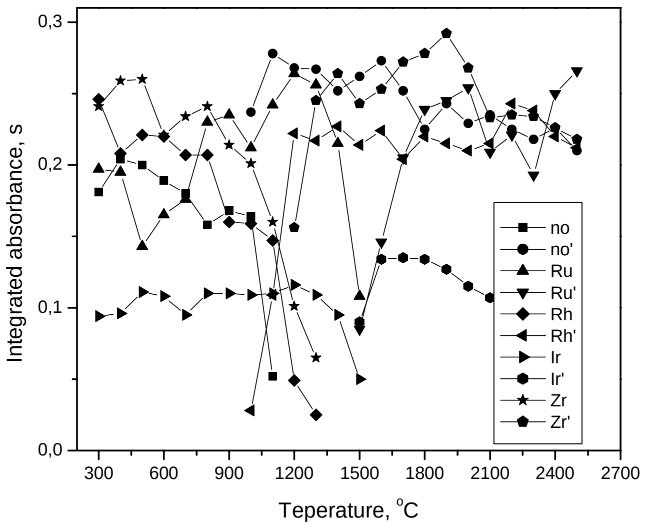

Fig. 4. Pyrolysis and atomisation temperature curves for 2 ng of Pb in drinking water using different modifiers.

3.2. Analytical figures of merit

Calibration curves using aqueous solutions (in 0.5% of nitric acid) were constructed following the procedure described under Section 2 and by applying the temperature program given in Table 1.

The analytical characteristic for the determination of the four investigated metals in drinking water are show in Table 3.

Recovery experiments were carried for each element in drinking water with the optimized pyrolysis and atomization temperatures and with the proposed modifier. The recoveries were determined from three replicates and are shown in Table 4. To determine the recovery for each analyte, the

Table 4
Recovery of Al, Cd, Cr and Pb added to drinking water against aqueous calibration curves

Expected concentration (μg l^{-1})	Recovery (%)	R.S.D. ($n = 3$)
Al		
50	103	0.5
100	102	1.1
150	98	0.9
200	101	1.8
Cd		
2.5	88	4.5
5	101	1.5
7.5	96	2.5
10	95	0.9
Cr		
25	106	3.2
50	106	2.2
75	101	1.0
100	97	0.6
Pb		
5	109	3.0
10	96	6.5
15	111	12.0
20	98	5.2

concentrations of the analytes in the drinking water were determined and discounted from values of the same samples spiked with different concentrations of each metal.

It was verified that the recoveries for all analytes investigated in this work in all levels are always close to 100%, indicating acceptable accuracy. The standard deviations were usual for graphite furnace analysis.

The lifetime of the graphite tubes were of at least of 360 cycles of atomization using zirconium permanent and of 450 cycles for rhodium permanent and were obtained processing an analytical solution at 20 or 30 cycles of atomization inside the studies until that the absorbance value falls in more than 20%.

4. Conclusions

Aluminium and lead can be determined with sensitivity, accuracy and precision in drinking water using zirconium as permanent modifier. Recoveries of spiked drinking water samples in four levels for each analyte showed values close to 100%. Cadmium and chromium are best determined employing rhodium as permanent modifier. Recoveries of spiked samples in four levels showed values close to 100%, indicating acceptable accuracy of the proposed methodology. The lifetime of the graphite tubes were at least of 360 for zirconium and 450 for rhodium use.

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