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Determination of cadmium and lead in table salt by sequential multi-element flame atomic absorption spectrometry

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Abstract

In the present paper, a simultaneous pre-concentration procedure for the sequential determination of cadmium and lead in table salt samples using flame atomic absorption spectrometry is proposed. This method is based on the liquid–liquid extraction of cadmium(II) and lead(II) ions as dithizone complexes and direct aspiration of the organic phase for the spectrometer. The sequential determination of cadmium and lead is possible using a computer program. The optimization step was performed by a two-level fractional factorial design involving the variables: pH, dithizone mass, shaking time after addition of dithizone and shaking time after addition of solvent. In the studied levels these variables are not significant. The experimental conditions established propose a sample volume of 250 mL and the extraction process using 4.0 mL of methyl isobutyl ketone. This way, the procedure allows determination of cadmium and lead in table salt samples with a pre-concentration factor higher than 80, and detection limits of 0.3 ng g^{-1} for cadmium and 4.2 ng g^{-1} for lead. The precision expressed as relative standard deviation ($n = 10$) were 5.6 and 2.6% for cadmium concentration of 2 and 20 ng g^{-1}, respectively, and of 3.2 and 1.1% for lead concentration of 20 and 200 ng g^{-1}, respectively. Recoveries of cadmium and lead in several samples, measured by standard addition technique, proved also that this procedure is not affected by the matrix and can be applied satisfactorily for the determination of cadmium and lead in saline samples. The method was applied for the evaluation of the concentration of cadmium and lead in table salt samples consumed in Salvador City, Bahia, Brazil.

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1. Introduction

The concentration of heavy metals in table salt should be rigorously controlled, considering the participation of this ingredient in the food preparations for humans. Cadmium and lead are frequently among the metals evaluated due to great toxicity these. However, the determination of these metals in these samples is complicated, considering the low concentration of the metals and the high saline content of the matrices. This way, spectroanalytical methods always request previous steps of sample preparation [1] and several pre-concentration procedures have been performed using mainly solid phase extraction as separation technique [2–4].

In the last years, several papers have been performed in order to develop the atomic absorption spectrometry as multi-element technique for determination simultaneous or sequential. Several approaches have been proposed including multi-element line sources, continuum source, multi-channel and laser-based systems [5–6]. Most of the methods were proposed for simultaneous determination using graphite furnace atomic absorption spectrometry (GF-AAS) [7,8], but papers involving flame atomic absorption spectrometry (FAAS) were also established. Farah and Sneddon proposed the simultaneous determination of copper, iron, manganese and zinc in bovine liver and estuarine sediment using flame atomic absorption spectrometry [9]. In another paper, simultaneous flame atomic absorption spectrometry was used for determination of nine metals in chromium and nickel-plating bath solutions [10]. Simplex design was used for method optimiza-

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Table 1
Analytical methods using multi-element FAAS

Elements	Matrix	Operation mode	Reference
Cu, Fe, Mn and Zn	Bovine liver and estuarine sediment	Simultaneous	[9]
Au, Cd, Cr, Cu, Fe, Ni, Pb, Pd, Sn and Zn	Chromium and nickel plating solutions	Simultaneous	[10]
	Rocks	Simultaneous	[11]
Cd, Ni and Pb	Burned and unburned crude oil	Simultaneous	[12]
Cu, Mn, Fe, Zn and Mg	Certified reference material and scrap-wood	Sequential	[13]
Cu, Pb, Cd, Co, Ni and Mn	Environmental	Sequential	[14]
Ni, Cd, Zn, Co, Fe, Mn and Cu	Potable water	Simultaneous	[15]
Co, Cu, Fe, K, Mg, Mn, Na, Ni and Zn	Manganese nodules	Simultaneous	[17]
Cu, Zn and Pb	Environmental	Simultaneous	[18]

tion for simultaneous determination of copper, iron, manganese and zinc [11]. Hammond et al. proposed a method for determination of cadmium, lead and nickel in burned and unburned Venezuelan crude oil by simultaneous FAAS [12]. Projahn et al. used the reference-element technique in order to correct the common interferences. This method was used for sequential determination of copper, manganese, iron, zinc and magnesium [13]. A method using on-line separation system and enrichment was also proposed for fast sequential determination of copper, lead, cadmium, cobalt, nickel and manganese in environmental samples by FAAS [14]. Table 1 shows several analytical methods [9–19] proposed for multi-element determination of metals using flame absorption atomic spectrometry.

Multivariate techniques have been widely applied in the optimization of methods in analytical chemistry [20,21]. Among these, factorial design is one of the more used [22,23]. Recently, this chemometric technique was used several times for optimization of pre-concentration procedures for metal determination using FAAS [24–29].

Dithizone (diphenilthiocarbazone) is a classical reagent very used as complexing in pre-concentration procedures [30]. Several methods have been performed for determination of cadmium and lead [31–36], using solid phase extraction [31–33], liquid–liquid extraction [34,35] and also coprecipitation [36] as separation techniques.

In the present paper, a simultaneous pre-concentration procedure for the sequential determination of cadmium and lead in table salt samples using multi-element flame atomic absorption spectrometry is proposed. This method is based on the liquid–liquid extraction of cadmium(II) and lead(II) ions as dithizone complexes and direct aspiration of the organic phase for the spectrometer. The sequential determination of cadmium and lead is possible using a computer program. The optimization step was performed by a two-level fractional factorial design.

2. Experimental

2.1. Instrumentation

A Varian model SpectrAA 220 FS (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer, fitted with a deuterium background corrector, automatic switching of hollow-cathode lamps was used for the analysis. The detailed description this system is described elsewhere [13]. The cadmium and lead hollow-cathode lamps were run under the conditions suggested by the manufacture (current 4.0 and 10.0 mA). The wavelength (228.8 and 217.0 nm) bandwidth of the slit (0.5 and 1.0 nm), and burner height (13.5 mm). The flame composition was acetylene (flow rate 1.5 L min^{-1}) and air (flow rate 13.5 L min^{-1}). Nebulizer aspiration flow rate in the range of 5.0–6.0 mL min^{-1}. A Digimed DM 20 (Santo Amaro, Brazil) pH meter was also used.

2.2. Reagents and solutions

All reagents were analytical grade unless otherwise stated. Ultrapure water was obtained from an Easypure RF (Barnstedt, Dubuque, IA, USA). Nitric and hydrochloric acid were of suprapur quality (Merck). Laboratory glassware kept overnight in 10% nitric acid solution. Before use the glassware rinsed whit deionised water and dried in a dust-free environmental.

A multi-element standard solution containing 5.0 μg mL^{-1} cadmium and 10.0 μg mL^{-1} lead was prepared from 1000 μg mL^{-1} certified atomic absorption solutions of cadmium and lead (Merck).

Dithizone solution (0.125% w/v) was prepared by dissolution of 0.25 g of compound (Merck) in 200 mL of ethanol absolute (Merck).

Acetate buffer solution (pH 5.7) was prepared by dissolution of 82 g of sodium acetate (Merck) in 1 L of ultrapure water and pH adjusted with acetic acid.

2.3. General procedure

Into a separation funnel containing a sample volume of 250 mL were added 5 mL of acetate buffer solution (pH 5.7) and 4.0 mL dithizone solution (0.125%). After a fast shaking for 2 min, 4 mL of MIBK was added and the mixture was shaken again for 2 min. After equilibrium, the organic phase is separated and cadmium and lead are measured sequentially using FAAS. The same procedure was applied also for blank solutions. The analytical curve was established using (25% w/v) sodium chloride solution after five extraction steps of cadmium and lead using also dithizone.

Table 2
Factors and levels used in the factorial design

Variable	Low (−)	High (+)
pH	5.7	9.7
Dithizone mass (DM) (mg)	5	25
Shaking time for complexation (CT) (min)	0.5	4.5
Shaking time for extraction (ST) (min)	0.5	4.5

Table 3
Design matrix and the results of the two-level fractional factorial design

Exp.	pH	DM	TC	TE	Absorbance	
					Cd	Pb
1	−	−	−	−	0.2718	0.0310
2	+	−	−	+	0.3738	0.2959
3	−	+	−	+	0.6241	0.5113
4	+	+	−	−	0.5560	0.3553
5	−	−	+	+	0.6680	0.4775
6	+	−	+	−	0.5969	0.3578
7	−	+	+	−	0.6853	0.5305
8	+	+	+	+	0.6455	0.3799

DM: dithizone mass; TC: shaking time for complexation; TE: shaking time for extraction.

2.4. *Optimization strategy*

The optimization step was carried out using a two-level fractional factorial design [22,23]. Considering the pre-concentration procedure proposed, the variables chosen for optimization were: pH, dithizone mass (DM), shaking time after addition of dithizone (CT) and shaking time after addition of solvent (ET). Maximum and minimum levels of each factor (Table 2) were established according to the data from previous papers. Table 3 shows the factorial design matrix, using absorbance for cadmium and lead as analytical response. All the experiments were carried out in random order, using a solution volume of 250 mL of a sample solution of concentration 25% (w/v) contained 3 μg of cadmium and 25 μg of lead.

3. Results and discussion

3.1. *Optimization of the pre-concentration procedure using factorial design*

For optimization of the pre-concentration procedure was performed a fractional factorial design (2^{4-1}), involving the followings variables: pH, mass of dithizone, shaking time after addition of dithizone and shaking time after addition of solvent, using absorbance as analytical response as Table 3. The factorial design demonstrated that these variables in the studied levels were not statistically significant. This result can be easily explained considering previous works, which used dithizone for pre-concentration of lead and cadmium. The pH recommended for this procedure is 5.7 considering that the dithizone selectivity decreases with increase of pH, because other metal ions can react also with dithizone. The dithizone mass of 5 mg, shaking time after addition of dithizone of 2 min and shaking time after addition of solvent of 2 min were established in the general procedure (Figs. 1 and 2).

3.2. *Analytical characteristics*

The proposed procedure using sequential multi-element flame atomic absorption spectrometry showed linearity within the concentration range 0.98–40 ng g^{-1} for cadmium and 14–400 ng g^{-1} for lead. The precision expressed as relative standard deviation (RSD) ranged from 5.6 to 2.6% for cadmium concentration of 2 and 20 ng g^{-1}, respectively, and from 3.2 to 1.1% for lead concentration of 20 and 200 ng g^{-1}, respectively. The limits of detection (LD) and quantification

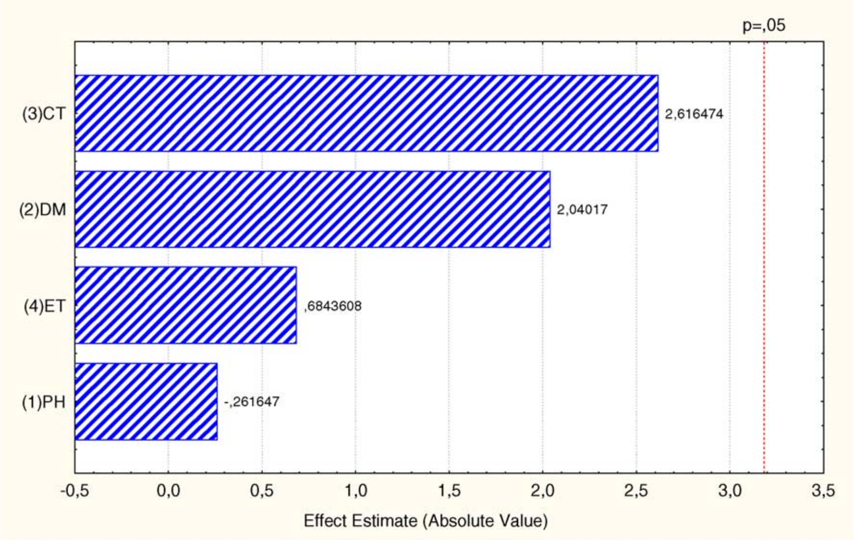

Fig. 1. Pareto chart for fractional factorial design—cadmium results.

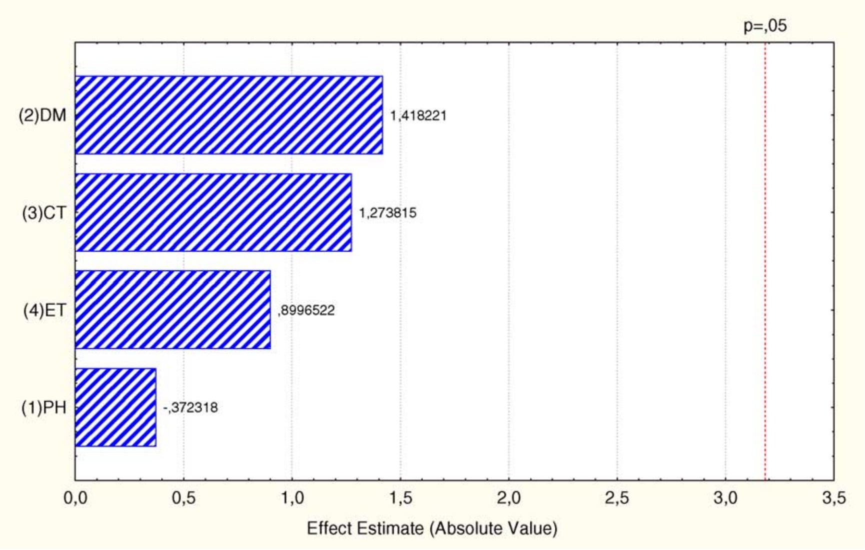

Fig. 2. Pareto chart for fractional factorial design—lead results.

(LQ) were determinate as IUPAC recommendation [37] for sample solution of 250 mL. For cadmium LD and LQ were 0.29 and 0.98 ng g^{-1} and for lead were 4.2 and 14 ng g^{-1}, respectively. The experimental pre-concentration factors, calculated considering the ratio of the slopes of the analytical curves with and without pre-concentration, were 86 for cadmium and 99 for lead.

3.3. *Effect of other metal ions*

In order to evaluate the effect of other metal ions in the pre-concentration procedure, a volume of 250 mL of sample solution containing cadmium (4 μg L^{-1}), lead (40 μg L^{-1}) and other ions (200 μg L^{-1}) was prepared and analyzed by the proposed method. Results showed that nickel(II), chromium(VI), cobalt(II), zinc(II), aluminum(III), iron(III), manganese(II), mercury(II), copper(II), molybdenum(VI) and vanadium(V) in this concentration do not interfere in the determination of cadmium and lead by this procedure.

3.4. *Application*

The proposed procedure was applied for cadmium and lead determination in several table salt samples collected in Salvador City, Bahia, Brazil in 2004. The results for 10 samples analyzed are shown in Table 4. In it can be seen that the cadmium content varied from 1 to 7 ng g^{-1}, and lead content varied from 33 to 106 ng g^{-1}. For five samples, addi-

Table 4
Determination of cadmium and lead in several table salt samples ($n = 3$)

Sample	Cd (ng g^{-1})			Pb (ng g^{-1})		
	Added	Found	Recovered (%)	Added	Found	Recovered (%)
1	0	<LQ[a]	–	0	62 ± 5	–
	2.0	2.0 ± 0.2	100	40	103 ± 5	103
2	0	<LQ	–	0	49 ± 3	–
	2.0	2.2 ± 0.2	110	40	88 ± 5	980
3	0	1.0 ± 0.1	–	0	<LQ	–
	2.0	3.0 ± 0.1	100	20	34 ± 2	115
4	0	1.3 ± 0.1	–	0	33 ± 1	–
	2.5	3.5 ± 0.2	88	50	83 ± 2	100
5	0	7.3 ± 0.9	–	0	<LQ	–
	5.0	12.4 ± 0.2	102	25	27 ± 2	108
6	–	4.3 ± 0.3	–	–	85 ± 3	–
7	–	2.9 ± 0.3	–	–	59 ± 4	–
8	–	2.8 ± 0.1	–	–	61 ± 4	–
9	–	3.8 ± 0.2	–	–	83 ± 1	–
10	–	1.5 ± 0.1	–	–	106 ± 5	–

[a] Below limit of quantification.

tion/recovery tests were performed and the recovery values achieved are in the range from 88 to 110% for cadmium and 98 to 115% for lead. These results demonstrated that the proposed procedure could be satisfactorily used for analysis of table salt samples. The achieved results for cadmium and lead in the analyzed samples were lower than the maximum permissible limits in Brazil, which are 0.5 and $2\,\mu g\,g^{-1}$ for cadmium and lead, respectively [38].

4. Conclusions

A fractional factorial design made possible the optimization step more fast.

The dithizone reagent allowed a procedure for simultaneous pre-concentration of cadmium and lead using liquid–liquid extraction as separation technique.

The fast sequential mode is a good alternative for multielement determination using flame atomic absorption spectrometry.

The proposed procedure was applied for determination of cadmium and lead in several table salt samples collected in Salvador City, Bahia, Brazil, and the achieved results were always less than the maximum permissible limits in Brazil.

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