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W+Rh as Permanent Chemical Modifier in Simultaneous Atomic Absorption Spectrometry: Interference Studies on As, Cd, Pb and Se Determination

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Um estudo sistemático para verificar as interferências provocadas por Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} e PO_4^{3-} nos processos de atomização simultânea de As, Cd, Pb e Se foi realizado utilizando um espectrômetro de absorção atômica com atomização eletrotérmica. A mistura de $250 \mu g$ W + $250 \mu g$ Rh foi termicamente depositada sobre a plataforma do tubo de grafite e utilizada como modificador químico permanente. O ajuste compromissado dos parâmetros do programa de aquecimento (Tp = 650 ºC e Ta = 2200 ºC) diminuiu a eficiência de decomposição e volatilização térmica de alguns interferentes durante a etapa de pirólise, tornando a atomização simultânea de As, Cd, Pb e Se mais suscetível à interferências. Os ânions Cl^- e SO_4^{2-} causaram as interferências mais severas, enquanto NO_3^- somente afetou a atomização dos elementos estudados quando presente em elevadas quantidades ($> 27 \mu g$). O ânion PO_4^{3-} provocou uma forte interferência negativa sobre o Se. As interferências causadas pelos cátions Na^+, K^+, Mg^{2+}, Ca^{2+} afetaram principalmente o Cd, sendo que os cloretos dessas espécies provocaram interferências mais intensas do que os nitratos.

A systematic study of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} interference on the simultaneous atomization of As, Cd, Pb and Se was carried out using an electrothermal atomic absorption spectrometer. The mixture $250 \mu g$ W + $250 \mu g$ Rh was thermally deposited on the graphite tube platform and used as permanent chemical modifier. The compromised heating program adjustments (Tp = 650 ºC and Ta = 2200 ºC) diminished the thermal decomposition and volatilization efficiency of the interfering species during the pyrolysis step. The Cl^- and SO_4^{2-} anions caused the most severe interference, while NO_3^- only affected the analytes' atomization when high amounts ($> 27 \mu g$) were used. The anion PO_4^{3-} produced a strong negative interference on the Se absorbance signals. The presence of Na^+, K^+, Ca^{2+} and Mg^{2+} prejudiced mainly Cd, and the interference effects of Cl^- salts were more pronounced than NO_3^- salts.

Keywords: simultaneous atomic absorption spectrometry, interference, permanent chemical modifier

Introduction

Among the instrumental techniques available for trace and ultra-trace element determinations, atomic absorption spectrometry (AAS) occupies an outstanding position due to its high specificity, selectivity, and sensitivity, low spectral interference, and ease of operation. Despite of these attributes, its conventional mono-element operation mode restrains the analytical frequency and can be considered as the main drawback of this technique.[1] This shortcoming is aggravated for electrothermal atomic absorption spectrometry (ETAAS) due to the long extent of the heating program atomizer, typically 1 to 3 min.

Multi-element atomic absorption researches have aroused interest since the first AAS stage in order to conceive a spectrometer able to determine several elements simultaneously or *quasi* simultaneously. As result of these efforts, the simultaneous atomic absorption spectrometry (SIMAAS) technique was proposed.[2-4] Commercially introduced during the last decade, SIMAAS adjoined the multi-element capability for atomic absorption spectrometry, reducing time and costs associated with the analysis. Indeed, expressive advantages are obtained even when the spectrometer is operated in 2-element simultaneous mode: the sample and high purity reagent requirements, and the residue generation are almost reduced in 50 %, while the analytical frequency and the analytical results obtained with the same graphite tube are almost duplicated.

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At the present, the most updated commercial instrumentation is a line-source simultaneous spectrometer,[1] equipped with transversely heated graphite atomizer with integrated platform, Zeeman-effect background corrector, and solid-state detector, making possible the operation under STPF conditions.[5] This instrument allows simultaneous determinations up to six elements.[1]

SIMAAS has been used for various multi-element determinations with acceptable performance[6-26] (Table 1), keeping the main features of ETAAS: high sensitivity, low detection limits, reduced sample requirements, and the possibility to carry out *in situ* sample decomposition inside the graphite furnace. Although the increase number of multi-element procedures, reports dealing with interference studies for SIMAAS are scare so far.[12]

The mixture palladium and magnesium nitrate has been widely used for multi-element determinations by SIMAAS.[6,8-11,14,15,20,23,25] It is claimed as universal chemical modifier due to the thermal stability improvement for 21 elements.[27] Although this mixture seems to be the most suitable choice, other alternatives as rhodium-based chemical modifiers can also be explored for multi-element determinations.

The rhodium-based chemical modifiers have been successfully adopted for mono-element determinations by ETAAS. The mixture of 250 μg W + 200 μg Rh was proposed as permanent chemical modifier for mono-element determinations.[28-31] The results indicated its effectiveness for As, Cd, Cu, Pb and Se, and its performance is equal or superior than that verified for the universal chemical modifier.

The use of permanent chemical modifiers allows increase the graphite tube lifetime, eliminate volatile impurities during the thermal coating process, decrease the detection limits, reduce the total heating cycle time, and minimize the high purity chemical consumption.[28]

Considering these favorable characteristics, the aim of this work is to investigate the performance of the permanent chemical modifier 250 μg W + 250 μg Rh to minimize interferences of Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^-, SO_4^{2-} and PO_4^{3} on the simultaneous atomization of As, Cd, Pb and Se. Additionally, determinations of As, Cd, Pb and Se in non-potable water using this chemical modifier are proposed.

Experimental

Apparatus

Measurements were carried out by using a SIMAA-6000 electrothermal atomic absorption spectrometer with a longitudinal Zeeman-effect background correction system, Echelle optical arrangement, solid state detector and standard THGA tube with pyrolytic coated integrated platform (Perkin-Elmer, Norwalk, CT, USA).

The spectrometer was operated in 4-element simultaneous mode using electrodeless discharge lamps for arsenic (λ=193.7 nm, i=380 mA), cadmium (λ=228.8 nm, i=200 mA), lead (λ=283.3 nm, i=450 mA), and selenium (λ=196.0 nm, i=290 mA). Solutions were delivered into the graphite tube by means of an AS-72 autosampler.

Argon 99.999% v/v (Air Liquide Brasil S/A, São Paulo, SP, Brazil) was used as protective and purge gas.

Reagent and reference solutions

All solutions were prepared with high purity de-ionized water (18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA, USA). Analytical reagent-grade HNO_3 (Synth, Diadema, SP, Brazil) was distilled in quartz sub-boiling stills (Marconi, Piracicaba, SP, Brazil). High purity standard reference solutions of arsenic (As_2O_3), cadmium ($CdCl_2$), lead [$Pb(NO_3)_2$] and selenium (SeO_2) from Tritisol (Merck, Darmstadt, Germany) were used to prepare the reference analytical solutions. The chemical modifier solutions were obtained from $Na_2WO_4.2H_2O$ (Merck) and $RhCl_3$ (Aldrich).

Cation and anion interference effects were investigated with solutions containing up to 10000 mg L^{-1} of Na^+ [$NaNO_3$, $NaCl$, Na_3PO_4 or Na_2SO_4 (Merck)], 10000 mg L^{-1} of K^+ [KNO_3 or KCl (Merck)], 5000 mg L^{-1} of Ca^{2+} [$Ca(NO_3)_2$ or $CaCl_2$ (Merck)] and 5000 mg L^{-1} of Mg^{2+} [$Mg(NO_3)_2$ or $MgCl_2$ (Merck)] in 0.1% v/v HNO_3.

Arsenic, Cd, Pb and Se were simultaneously determined in non-potable water samples with high saline content from Quality Technologies Pty Ltd (Mount Isa, Australia) using 250 μg W + 250 μg Rh as permanent chemical modifier. The samples were diluted 1:10 or 1:20 with 0.1% v/v HNO_3 for the multi-element determinations. Addition and recovery tests were performed to verify the reliability of the obtained results for As, Cd, Pb and Se determination.

Procedure

All glassware, polypropylene flasks and bottles (Nalge Company, Rochester, USA) were cleaned with detergent solution, soaking in 10% v/v HNO_3 for 24 h, rinsed with Milli-Q water and stored into a closed polypropylene container.

Solution manipulations were conducted in a class-100 laminar flow bench (Veco, Campinas, Brazil) to avoid airborne contamination. Reference solutions containing

Table 1. Multi-element analytical procedures developed by SIMAAS

Element	Sample	Chemical modifier	LD (mg L^{-1})	m_0 (pg)	Ref.
Mn Se	Serum	Pd + Mg	0.65 5.0	6.0 46	6
Cu Fe Zn	Serum	-	4.0 2.2 0.4	26 16 2.7	7
As Cu Mn Sb Se	Drinking water	Pd + Mg	0.7 0.2 0.6 0.3 0.9	39 17 60 43 45	8
Al As Cu Fe Mn Ni	Fuel ethanol	Pd + Mg	1.2 2.5 0.2 1.6 0.2 1.1	37 73 31 16 45 9.0	9
Bi Pb	Wine	Pd + Mg	- 0.9	- 45	10
Cu Mn Mo	Sea water	Pd + Mg and 5% H$_2$	0.4 0.7 1.2	- - -	11
Cr Mn	Urine	Mg	0.08 0.16	7.8 4.6	13
Cd Pb	Wine	Pd + Mg	0.03 0.8	0.6 33	14
As Cd Ni Pb	Atmosferic particulate matter	Pd + Mg	0.26 0.02 0.97 4.3	37 2.2 28 1400	15
Al Cr Cu Mn	Urine	Pd + 5% H$_2$	0.06 0.05 0.08 0.06	- - - -	16
Cr Mo V	Bismuth tellurite optical crystals	-	1.1 4.9 6.7	7.5 20 58	17
Cd Pb	Foodstuffs	NH$_4$H$_2$PO$_4$ + Mg	0.04 0.93	1.5 37	18
As Bi Sb Se Te	Water	Ir	0.82 0.04 0.26 0.29 -	177 91 107 90 -	19
Cd Cr Cu Ni Pb	Potable and surface water	Pd + Mg	0.1 1 1 1 1	- - - - -	20
Mo V	Seawater	NH$_4$H$_2$PO$_4$ + Mg	0.35 0.32	- -	21
Cr Ni	Serum	-	0.05 0.2	- -	22
Cd Pb	Blood	NH$_4$H$_2$PO$_4$	0.2 4.5	- -	22
Cd Pb	Urine	NH$_4$H$_2$PO$_4$	0.06 2.6	- -	22
Cu Mn	Seawater	Pd + Mg	0.07 0.10	1.5 37	23
Cd Pb Co Cu	Soil and sediment	-	0.001 0.1 0.05 0.02	0.44 22 22 35	24
Cd Pb	Whole blood	Pd + Mg	- -	- -	25
Co Mn	Urine	Mg	0.18 0.09	- -	26

2.5 μg L^{-1} of Cd^{2+} + 50 μg L^{-1} of As^{3+}, Pb^{2+} and Se^{4+} in 0.1% v/v HNO$_3$, with and without the concomitant species, were used for the heating program optimization and for the interference studies. These solutions were prepared directly in the autosampler cups by dilution (1:1) of the stock reference solution, containing 5.0 μg L^{-1} of Cd^{2+} + 100 μg L^{-1} of As^{3+}, Pb^{2+} and Se^{4+} in 0.1% v/v HNO$_3$, with blank or interfering solutions.

The permanent chemical modifier 250 μg W + 250 μg Rh was obtained according to the thermal coating process described in the literature.[28] The heating program was optimized with pyrolysis and atomization temperature curves in absence and presence of the mixture 250 μg W + 250 μg Rh as chemical modifier. The instrumental adjustments and the heating program for the graphite tube are showed in Table 2.

The influence of increasing amounts of Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and PO$_4^{3-}$ in the analytes' absorbance signals was verified. The concomitant amounts (cations and anions) added to the analytical reference solutions were based on cation concentration, ranging from 50 to 5000 mg L^{-1}. The interference studies of cations were executed using NO$_3^-$ and Cl$^-$ salts, while for anions were used only Na$^+$ salts.

Experimental measurements were made with at least three replicates and based on integrated absorbance throughout this work.

Results and Discussion

When ETAAS is used for mono-element determinations, all experimental and instrumental parameters are optimized for only one analyte. Consequently, the best optimized pyrolysis and atomization temperatures are used in the heating program, minimizing condensed- and gas-phase interference.[3] On the other hand, the adoption of compromised conditions for multi-element determinations by SIMAAS are mandatory. The heating program temperatures and chemical modifier must be carefully selected to achieve the best atomization efficiency for all the analytes. In general, the most volatile analyte determines the pyrolysis temperature while the least volatile analyte determines the atomization temperature. Despite of these adverse temperatures, the use of a transversely heated atomizer with integrated platform offers optimum conditions for both volatile and non-volatile elements.[3] Add to that, STPF conditions adoption and the use of an appropriate chemical modifier have guaranteed similar performance of SIMAAS in comparison to mono-element ETAAS. This fact reinforces that the success of any atomic absorption spectrometer for simultaneous determination depends on using STPF conditions.

Simultaneous heating program optimization

The characteristic masses (m_o) and the best pyrolysis and atomization temperatures for As, Cd, Pb and Se obtained by SIMAAS in absence and presence of the 250 μg W + 250 μg Rh are presented in Table 3 and compared with mono-element ETAAS data indicated in the literature.[29,30] It can be observed an agreement between the results obtained by SIMAAS with those obtained by mono-element ETAAS (Table 3). The higher pyrolysis temperatures achieved for Cd, Pb and Se using SIMAAS were probably due to the higher Rh mass deposited on the graphite tube surface (250 μg). However, this data are in

Table 2. Spectrometer settings and heating program parameters for the multi-element detection of As, Cd, Pb and Se

	Spectrometer setup			
	Arsenic	Cadmium	Lead	Selenium
Wavelength (nm)	193.7	228.8	283.0	196.0
Bandpass (nm)	0.7	0.7	0.7	0.7
Lamp current (mA)	380	200	450	290
Read time (s)	4.0	2.0	3.0	4.0
	Heating progam for the THGA			
Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow rate (mL min^{-1})
	10 μL of sample or analytical reference solution injection			
Drying I	110	10	5	250
Drying II	130	10	10	250
Pyrolysis	650^a	10	15	250
Atomization	2200^a	0	4	0
Cleaning	2200	1	4	250

^{a}Optimized condition for As, Cd, Pb and Se in presence of 250 μg W + 250 μg Rh as permanent chemical modifier; Total program time: 69s; Injection temperature: 20°C.

Table 3. Characteristic masses (m_0), pyrolysis (T_p) and atomization (T_a) temperatures for 25 pg Cd + 500 pg As, Pb and Se in 0.1% v/v HNO_3 in absence and presence of 250 μg W + 250 μg Rh as permanent chemical modifier

Analyte	Parameter	Chemical modifier		
		None	W+Rh[a]	W+Rh[b]
As	m_0 (pg)	74	35	39
	T_p (°C)	500	1500	1200
	T_a (°C)	2100	2200	2100
Cd	m_0 (pg)	1.2	1.8	1.1
	T_p (°C)	300	650	500
	T_a (°C)	1200	1400	1200
Pb	m_0 (pg)	25	43	30
	T_p (°C)	500	900	800
	T_a (°C)	1200	1600	1800
Se	m_0 (pg)	87	68	42
	T_p (°C)	400	1300	1200
	T_a (°C)	1800	2000	2000

[a]Results for the multi-element determination of As, Cd, Pb and Se by SIMAAS; [b]Results for the mono-element detemination As, Cd, Pb and Se(29,30).

discordance with previous work, which indicates that masses higher than 200 μg are not recommended due to the sensitivity decrease (about 15% for each analyte).[28]

The higher characteristic masses for Cd, Pb and Se in comparison with mono-element ETAAS (Table 3), can be related to the compromised conditions adopted for the simultaneous determination. The necessity to consider compromised adjustments imposes 650 °C as pyrolysis temperature, due to the low thermal stability achieved for Cd in presence of W+Rh.

The atomization temperatures for all analytes were also increased in presence of the W+Rh permanent modifier (Table 3), for Cd (1400 °C) and Pb (1600 °C) were lower than those verified for As (2200 °C) and Se (2000 °C). The atomization temperature selection for the simultaneous heating program (2200 °C) was based on the As thermal behavior. This is also the maximum temperature recommended for the heating program in order to avoid loss of deposited Rh by vaporization.[28] The adoption of higher temperatures for the atomization and/or cleaning steps impairs the W+Rh coating lifetime.

Anion interference

The effect of Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} on the simultaneous atomization of As, Cd, Pb and Se are showed in Figure 1. The results were expressed as absorbance ratios calculated between absorbance signals with and without the anions.

The interference effect of Cl^- in ETAAS has been largely
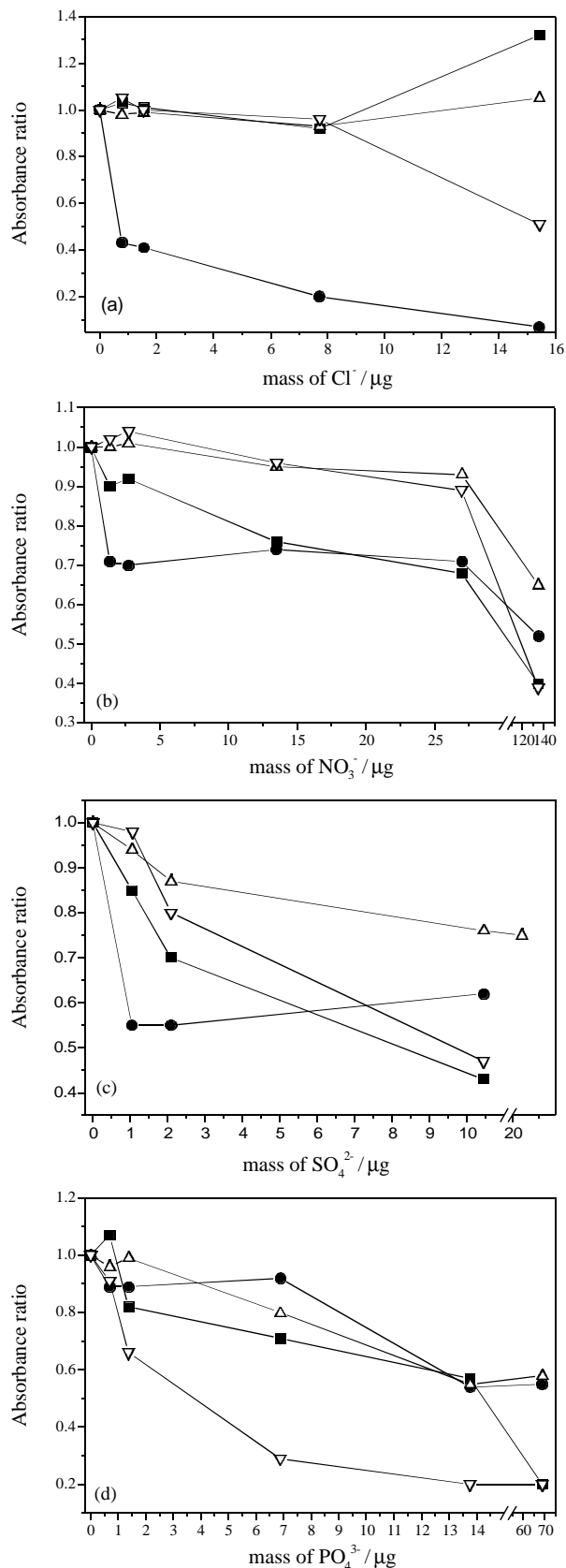
Figure 1. Interference effect of (a) $NaNO_3$ (b) NaCl, (c) Na_2SO_4 and (d) Na_3PO_4 on atomization of 25 pg Cd + 500 pg As, Pb and Se (■ As, ● Cd, △ Pb, ▽ Se).

investigated.[3] The use of chemical modifier is important to avoid loss of volatile chlorides during pyrolysis step. In this work, the pronounced effect observed from 0.8 μg Cl$^-$ on Cd absorbance signal can be attributed to the volatilization of cadmium chloride during the pyrolysis step at 650 °C (Figure 1a). Nevertheless, Cd loss was not observed when lower pyrolysis temperatures (< 500 °C) were used. Probably, the formation and volatilization of $CdCl_2$ occurred before the interaction between Cd and Rh on the graphite tube surface. It can be concluded that Cl$^-$ ions, even in low amounts, damaged the thermal stabilization obtained for Cd in presence of the W+Rh as permanent chemical modifier. Similar behavior was observed for low masses of NO_3^- (1.3 mg) and SO_4^{2-} (1.0 mg), which also reduced the Cd absorbance signal (Figures 1b-1c). The increase of Cl$^-$, NO_3^-, SO_4^{2-} masses did not cause any expressive change in the Cd absorbance ratios. On the contrary, the initial decrease of the Cd ratio was not observed in presence of PO_4^{3-} (Figure 1d), probably due to the increase in the thermal stabilization of this element. The synergistic effect between W+Rh and PO_4^{3-} was efficient to stabilize Cd at 650 °C. Cadmium and Pb form very stable oxyphosphorous compounds[3] and, for this reason, $NH_4H_2PO_4$ is usually used as chemical modifier for these elements.

The effect of SO_4^{2-} on As and Se was more pronounced than on Pb atomization (Figure 1c). For the latter, the effect of Na_2SO_4 is aggravated in strong acid solutions.[32] The

lower integrated absorbance observed for Se can be explained by molecular interference, which occurs due to the vaporization of SO_4^{2-} decomposition products, such as SO_3, SO_2, and SO.[33-35] Arsenic exhibited strong signal suppression in presence of the SO_4^{2-} (Figure 1c). This effects can be attributed to the interactions between As and Na_2SO_4 and the resulting decomposition products, particularly sulfide species.[36]

Selenium suffered more strong interference in presence of PO_4^{3-} (Figure 1d). Additionally, As was the most affected analyte by NO_3^- (Figure 1b). It can be supposed that the low pyrolysis temperature adopted for the simultaneous heating program (650 °C), impaired the adequate formation of the atomic precursors for As.

Cation interference

The performance of 250 μg W + 250 μg Rh to overcome the interference caused by Na$^+$, K$^+$, Mg^{2+} and Ca^{2+} on the simultaneous atomization of As, Cd, Pb and Se atomization are showed in Table 4. The results were expressed as absorbance ratios calculated between the absorbance signal with and without the cations.

In general, chloride salts caused more pronounced interference than nitrate salts. Cadmium was the most affected analyte, mainly in presence of alkaline ions (Table 4). The interference for all analytes was negligible only in

Table 4. Absorbance ratios for 25 pg Cd + 500 pg As, Pb and Se in presence of Na$^+$, K$^+$, Mg^{2+}, Ca^{2+} as chloride and nitrate salts

| Mass (μg) | | Absorbance ratio | | | | | | | |
| | | Cl$^-$ salt | | | | NO$_3^-$ salt | | | |
		As	Cd	Pb	Se	As	Cd	Pb	Se
Na$^+$	0.5	1.0	0.43	0.98	1.0	0.90	0.71	1.0	1.0
	1	1.0	0.41	0.99	1.0	0.92	0.70	1.0	1.0
	5	0.92	0.20	0.93	0.96	0.76	0.74	0.95	0.96
	10	1.3	0.07	1.0	0.51	0.68	0.71	0.93	0.89
	50	-	-	-	-	0.40	0.52	0.65	0.39
K$^+$	0.5	1.1	0.39	0.86	0.95	1.0	0.79	0.99	1.0
	1	1.1	0.36	0.85	0.95	1.0	0.77	0.97	0.99
	5	1.0	0.36	0.69	0.86	1.0	0.68	0.92	0.96
	10	0.94	0.12	0.64	0.71	0.91	0.50	0.84	0.92
	50	-	-	-	-	0.56	0.67	0.46	0.37
Mg^{2+}	0.5	0.97	0.89	0.96	0.89	1.0	0.93	0.99	0.98
	1	0.99	0.79	0.89	0.96	1.1	0.96	1.0	1.0
	5	1.0	0.70	0.78	1.0	1.0	0.95	0.96	1.0
	10	1.1	0.38	0.62	1.0	0.98	0.84	0.95	0.98
	25	1.1	0.05	0.40	1.0	0.87	0.86	0.95	0.88
Ca^{2+}	0.5	0.92	0.89	0.86	0.89	0.92	0.91	1.0	0.96
	1	0.87	0.82	0.84	0.89	1.0	0.90	1.0	1.0
	5	0.85	0.66	0.82	0.87	1.1	0.77	1.1	1.0
	10	0.71	0.44	0.71	0.78	0.93	0.53	0.89	0.91
	25	0.62	0.40	0.71	0.77	0.87	0.64	0.93	0.91

Table 5. Analysis and recovery test results for the simultaneous determination of As, Cd, Pb and Se in non-potable water samples

| | | Concentration (μg L^{-1}) | | | |
		As	Cd	Pb	Se
Dilution 1:10	Sample A	23.3 ± 10	61.8 ± 10	382 ± 11	-
	Ref. Value	21.6 ± 3.2	58.9 ± 13.6	296 ± 51	-
	Recovery (%)	91	85	86	105
Dilution 1:20	Sample B	260 ± 21	291 ± 21	501 ± 81	181 ± 20
	Ref. Value	226 ± 7	235 ± 5	507 ± 9	190 ± 15
	Recovery (%)	96	106	98	108

presence of Mg^{2+} as nitrate salt. For this reason, $Mg(NO_3)_2$ is usually used as chemical modifier alone or combined with other substances. When magnesium chloride was tested, the interfering effect was more pronounced for all analytes (Table 4). These results highlighted the interfering effect of chloride anion.

Non-potable water analysis and figures of merit

Two non-potable water samples from Quality Technologies Pty Ltd (Mount Isa, Australia) used for interlaboratorial calibration were analyzed using the optimized heating program (Table 2) and the mixture of 250 μg W + 250 μg Rh as permanent chemical modifier. The results of the simultaneous determination of As, Cd, Pb and Se (Table 5) are in agreement with the interlaboratorial values (95% confidence level). Addition and recovery tests showed results between 85% and 108% for all analytes. It was possible to determine As, Cd, Pb and Se simultaneously in non-potable water samples considering 1:10 and 1:20 as dilution factor.

Detection limits for As (3.2 μg L^{-1}), Cd (0.03 μg L^{-1}), Pb (0.70 μg L^{-1}), and Se (3.0 μg L^{-1}) were calculated based on the variability of the 10 blank solution measurements according to 3 S_{blk}/m, where S corresponds to the blank measurement standard deviation and m is the calibration curve slope. Characteristic masses obtained for As, Cd, Pb and Se were 35 pg, 1.8 pg, 43 pg, and 68 pg, respectively. Under these optimized conditions, the performance of the W+Rh permanent chemical modifier was acceptable until 250 heating cycles, when the loss of sensitivity for all analytes indicated the W+Rh coating degradation. The same graphite tube was re-coated twice and their lifetime was increase to 750 heating cycles.

Conclusions

According to this study, the simultaneous determination of As, Cd, Pb and Se with the mixture of 250 μg W + 250 μg Rh as permanent chemical can be subject to interference effects in high saline matrices. The volatile analytes, such as Cd, imposes low pyrolysis temperatures (< 650 °C) when multi-element determinations are executed by SIMAAS. The decomposition and volatilization of Na^+, K^+, Ca^{2+} and Mg^{2+} salts only occur when higher pyrolysis temperatures are adopted. With the pyrolysis temperature used in the heating program (650 °C) concomitants are volatilized with analytes, increasing the interference processes. The negative interference observed for As, Cd, Pb and Se can be related to losses by volatilization, due to the inappropriate formation of intermetallic compounds and/or solid solution between the analytes and the permanent chemical modifier.

Acknowledgments

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