Multielement Determination of Cadmium and Lead in Urine by Simultaneous Electrothermal Atomic Absorption Spectrometry with an End-capped Graphite Tube

Paulo R. M. CORREIA, Cassiana S. NOMURA, and Pedro V. OLIVEIRA[†]

Instituto de Química, Universidade de São Paulo, C. P. 26077, CEP 05513-970, São Paulo, SP, Brasil

A method for the multielement determination of cadmium and lead in urine is proposed by simultaneous electrothermal atomic absorption spectrometry (SIMAAS) with an end-capped transversely heated graphite atomizer (EC-THGA). The best conditions for cadmium and lead determination were obtained in the presence of $\text{NH}_4\text{H}_2\text{PO}_4$ as a chemical modifier, using 500°C and 1800°C as the pyrolysis and atomization temperatures, respectively. Urine samples were diluted 1 + 4 directly in autosampler cups with a mixture of 0.125% (w/v) Triton X-100 + 2.5% (v/v) HNO_3 + 0.31% (w/v) $\text{NH}_4\text{H}_2\text{PO}_4$. The optimized heating program was carried out in 57 s, and the instrument calibration was done with aqueous reference solutions. The use of EC-THGA increased the sensitivity of cadmium and lead by 14% and 25%, respectively. The detection limits ($n = 20$, 3σ) were $0.03 \mu\text{g L}^{-1}$ (0.36 pg) for cadmium and $0.57 \mu\text{g L}^{-1}$ (6.8 pg) for lead. The performance of EC-THGA was acceptable up to 500 heating cycles. The reliability of the entire procedure was checked with the analysis of a lyophilized urine certified reference material. The found concentrations were in agreement with the recommended values (95% confidence level).

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Introduction

The diagnosis of clinical disorders, intoxication and exposure to toxic elements is frequently evaluated by monitoring their concentrations in bodily fluids.¹⁻³ The determination of toxic metals in urine has been used for assessing occupational and environmental exposure.^{2,3} Additionally, it can be required for the clinical evaluation of potential candidates for chelation therapy based on an 8-h calcium disodium ethylenediaminetetraacetic acid (CaNa_2EDTA) mobilization test.⁴

Electrothermal atomic absorption spectrometry (ETAAS) still poses as the technique of choice for trace-element determinations in clinical samples due to its favorable features: high selectivity and sensitivity, ease of operation, minimal sample preparation, and possibility to carry out an *in situ* sample thermal decomposition during the heating program.^{1,2,5} Nowadays, the availability of simultaneous electrothermal atomic absorption spectrometry (SIMAAS), which can analyze up to six elements simultaneously, improved the analytical frequency of ETAAS, reducing costs related to instrument maintenance, sample and high purity reagent consumption.⁶⁻⁹ In spite of saving time and costs, multielement determinations carried out by SIMAAS require the adoption of compromised conditions for instrumental and experimental parameters, which can cause loss of sensitivity and damage the precision of analytical results. Therefore, chemical modifier selection and the optimization of pyrolysis and atomization temperatures are critical to evaluate a reliable method; they must be carefully

chosen while taking into account all analytes to be determined simultaneously.

The multielement determination of cadmium and lead by SIMAAS has been reported in the literature for different samples, such as aerosols and cigarette smoke,¹⁰ foodstuffs,^{11,12} whole blood,¹³⁻¹⁶ serum^{15,16} and urine.¹⁵

In comparison with the analysis of whole blood, the determination of cadmium and lead in urine presents more difficulties to be overcome. Firstly, urine from non-exposed healthy subjects contains low cadmium and lead amounts ($\text{Cd} \sim 1 \mu\text{g L}^{-1}$, $\text{Pb} \sim 15 \mu\text{g L}^{-1}$),¹⁷ and secondly, the high and variable concentration of anions and cations from sample to sample can affect the repeatability and reproducibility of the results. For instance, a huge amount of NaCl in urine samples (0.9 up to 5.1 g L^{-1})¹⁷ can cause interferences in the condensed-phase, favor the loss of the analytes as volatile halides, and change their vaporization rate during the atomization step. Taking into account these adversities, the use of Stabilized Temperature Platform Furnace (STPF) conditions is mandatory to allow atomization of the analytes under an isothermal environment in order to minimize the matrix interference.¹⁸

Cadmium and lead have similar thermal features, and are usually stabilized by $\text{NH}_4\text{H}_2\text{PO}_4$ ^{11,13,15} or $\text{Pd} + \text{Mg}$.^{12,14,19} For this reason, these chemical modifiers are the most indicated choices for the simultaneous determination of cadmium and lead by SIMAAS. Alternatively, permanent chemical modifiers can be used due to the elimination of volatile impurities during the thermal coating process, an increase of the graphite tube lifetime, and shortening the heating program.^{20,21} A mixture of $250 \mu\text{g W} + 200 \mu\text{g Rh}$ has been successfully applied to trace element determinations over a wide range of samples, including biological and clinical materials.²¹⁻²⁴

The evaluation of a fast and reliable analytical method for the

[†] To whom correspondence should be addressed.
E-mail: pvolivei@iq.usp.br

simultaneous determination of ultra-trace cadmium and lead amounts in urine samples from non-exposed healthy subjects by SIMAAS is the aim of this work. The effectiveness of Pd + Mg, $\text{NH}_4\text{H}_2\text{PO}_4$ and a mixture of 250 μg W + 200 μg Rh as a chemical modifier, and the adoption of end-capped graphite tubes are critically considered to minimize the matrix interference and increase the sensitivity.

End-capped transversely heated graphite atomizers (EC-THGA) are frequently used to determine volatile elements by ETAAS.^{25,26} The end-caps reduce the diffusional losses and increase the residence time of the atom cloud during the atomization step. It has been verified that an increase in the sensitivity for cadmium and lead using EC-THGA, compared with the standard transversely heated graphite atomizers (THGA).²⁵⁻²⁷ Therefore, EC-THGA should be tested for the simultaneous determination of cadmium and lead in urine.

Experimental

Apparatus

All simultaneous measurements for cadmium and lead were performed with a SIMAA-6000 electrothermal atomic absorption spectrometer equipped with a longitudinal Zeeman-effect background correction system, an Echelle optical arrangement and a solid-state detector (Perkin-Elmer, Norwalk, CT, USA). End-capped transversely heated graphite tubes (EC-THGA) with an integrated platform were used throughout this work. A standard THGA tube was used to compare the analytical performance obtained for both atomizers. Electrodeless discharge lamps were adopted as radiation sources for cadmium ($\lambda = 228.8$ nm; $i = 230$ mA) and lead ($\lambda = 283.3$ nm; $i = 450$ mA). The analytical reference and sample solutions were delivered into the graphite tube by means of an AS-72 autosampler. Argon 99.996% (v/v) (Air Liquide Brasil S/A, São Paulo, SP, Brazil) was used as a protective and purge gas.

Reagents and solutions

High-purity deionized water (18.2 M Ω cm), obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used to prepare all solutions. Analytical reagent-grade HNO_3 (Synth, Diadema, SP, Brazil) was distilled in quartz sub-boiling stills (Marconi, Piracicaba, SP, Brazil). Triton X-100 (Merck, Darmstadt, Germany) was used as a surfactant agent.

Analytical reference solutions were prepared by successive dilution of 1000 mg L^{-1} cadmium and lead Tritisol stock solutions (Merck). Chemical modifier solutions were obtained from high-purity reagents: $\text{Pd}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ Suprapur salts (Merck), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Merck) and RhCl_3 (Sigma, St. Louis, MO, USA). All solutions were stored in decontaminated polypropylene bottles (Nalge Company, Rochester, NY, USA).

Samples and certified reference material

Fresh urine samples were collected from laboratory personnel directly in disposable polypropylene containers (Sarstedt, Nümbrecht, Germany) and frozen at -20°C for until one week prior to the multielement cadmium and lead determination. SeronormTM Trace Elements in Urine from Sero AS (Billingstad, Norway) was used to check the reliability of the entire proposed analytical method. It was supplied in lyophilized form and reconstituted by dissolving the vial total content with high-purity deionized water.

Table 1 Instrumental parameters and heating program for the simultaneous determination of Cd and Pb in urine

	Spectrometer setup	
	Cadmium	Lead
Wavelength (nm)	228.8	283.3
Bandpass (nm)	0.7	0.7
Lamp type ^a	EDL	EDL
Lamp current (mA)	230	450
Integration time (s)	3	3

Step	EC-THGA Heating program			
	Temperature/ $^\circ\text{C}$	Ramp/ s	Hold/ s	Argon flow rate/ ml min^{-1}
Drying I	130	10	10	250
Pyrolysis	500	10	20	250
Atomization	1800	0	3	0
Cleaning	2200	1	3	250

a. EDL: Electrodeless discharge lamp.

Total heating program time: 57 s.

Sample volume, 12 μL ; injection temperature, 100°C ; pipet speed, 50%.

Procedure

All glassware and polypropylene flasks were cleaned with a detergent solution, soaked in 10% (v/v) HNO_3 for 24 h, rinsed with Milli-Q water and stored in a closed polypropylene container. The autosampler cups were cleaned with a nitric acid vapor steam, as described in the literature.²⁸ All solution and sample manipulations were conducted in a laminar flow bench (Veco, Campinas, SP, Brazil) to avoid airborne contamination. The instrumental conditions and the heating program for the graphite tube are given in Table 1.

A solution containing 1 $\mu\text{g L}^{-1}$ Cd^{2+} and 10 $\mu\text{g L}^{-1}$ Pb^{2+} in 0.1% (w/v) Triton X-100 + 2% (v/v) HNO_3 was used to verify the thermal behavior of the analytes and to optimize the heating program parameters. Pyrolysis and atomization temperature curves were simultaneously obtained for cadmium and lead in the presence of the following chemical modifiers: (1) a mixture of 250 μg W + 200 μg Rh thermally deposited as a permanent modifier, following the coating procedure described in the literature,²¹ (2) 5 μg Pd + 3 μg Mg¹⁹ and (3) 25 μg $\text{NH}_4\text{H}_2\text{PO}_4$ introduced in the solution form. A diluted urine solution (1 + 4) in 0.1% (w/v) Triton X-100 + 2% (v/v) HNO_3 was used to evaluate the matrix constituent effects on the cadmium and lead thermal stability.

Analytical reference solutions for the spectrometer calibration were prepared directly in the autosampler cups. An aliquot of 240 μL of the stock analytical reference solutions containing 0.625 up to 10 $\mu\text{g L}^{-1}$ Cd^{2+} and 6.25 up to 100 $\mu\text{g L}^{-1}$ Pb^{2+} was diluted with 960 μL of 0.125% (w/v) Triton X-100 + 2.5% (v/v) HNO_3 . When the conventional phosphate modifier was used, the diluent also contained 0.31% (w/v) $\text{NH}_4\text{H}_2\text{PO}_4$. The urine samples were diluted (1 + 4) as described for the analytical reference solutions. An Eppendorf micropipette (Brinkmann Instruments, Westbury, USA) was used to measure the volumes and to mix the diluted reference solutions and urine samples.

Twelve urine samples were analyzed with and without the addition of 0.25 $\mu\text{g L}^{-1}$ Cd^{2+} + 2.5 $\mu\text{g L}^{-1}$ Pb^{2+} and 0.5 $\mu\text{g L}^{-1}$ Cd^{2+} + 5.0 $\mu\text{g L}^{-1}$ Pb^{2+} .

All measurements were made with at least three replicates and based on the integrated absorbance.

Fig. 1 Pyrolysis and atomization temperature curves for cadmium (a) and lead (b) in the presence of diluted urine (1 + 4).

Results and Discussion

Evaluation of the chemical modifier efficiency

The pyrolysis and atomization temperatures were selected from temperature curves obtained simultaneously for cadmium and lead in the presence of 5 µg Pd + 3 µg Mg, 25 µg NH₄H₂PO₄ and a mixture of 250 µg W + 200 µg Rh as a permanent chemical modifier (Fig. 1). A diluted urine (1 + 4) spiked with 12 pg Cd²⁺ and 120 pg Pb²⁺ was used to check the thermal behavior of cadmium and lead in the presence of the sample matrix.

The best pyrolysis temperatures obtained for cadmium were 400°C, 500°C and 550°C in the presence of W + Rh, NH₄H₂PO₄ and Pd + Mg, respectively (Fig. 1a). The performance of W + Rh as a permanent chemical modifier was worst than that reported in the literature for other samples.²¹ The interaction between the sample and the modifier coated in the platform impaired the analyte-Rh contact. Thus, the analyte was more susceptible to combine with any matrix concomitants, such as chloride ions. The conventional co-injection of a chemical modifier in solution form with the sample seemed to be more successful. The mixing process is more efficient, and improves the analyte-modifier contact.

A similar pattern was also verified for lead and 600°C, 650°C and 800°C were the best pyrolysis temperatures obtained for W + Rh, NH₄H₂PO₄ and Pd + Mg, respectively (Fig. 1b). Nevertheless, the setup of a compromised condition for the pyrolysis step requires taking into account the thermal behavior of the more volatile element to be simultaneously determined. As a consequence, the cadmium thermal behavior must be considered instead of lead.

The atomization temperatures for cadmium and lead were selected based on the integrated absorbance and the

Table 2 Recoveries (%) obtained for the addition of 12 pg Cd²⁺ and 120 pg Pb²⁺ in the presence of the tested chemical modifiers

Urine sample	W + Rh		Pd + Mg		NH ₄ H ₂ PO ₄	
	Cd	Pb	Cd	Pb	Cd	Pb
I	73	83	84	89	97	97
II	75	76	86	93	94	105
III	84	89	90	91	100	95
Mean	77 ± 6	83 ± 7	87 ± 3	91 ± 2	97 ± 3	99 ± 5

repeatability of three consecutive signals (Fig. 1). In presence of NH₄H₂PO₄, 1600°C and 1800°C were the more appropriated values for cadmium and lead, respectively. When Pd + Mg was used, the selected temperatures were 1500°C for cadmium and 1900°C for lead. For the mixture W + Rh as a permanent chemical modifier, the best results were obtained by using 1500°C and 1600°C for cadmium and lead, respectively. The atomization temperature selection for multielement determinations by SIMAAS must consider the thermal behavior of the less volatile element to be simultaneously determined. Thus, the lead thermal behavior is the limiting condition to select the atomization temperature to be adopted.

In presence of diluted urine (1 + 4), the more adequate compromise conditions obtained for achieving the determination of cadmium and lead were: $T_p = 400^\circ\text{C}/T_a = 1600^\circ\text{C}$ for the mixture W + Rh, $T_p = 500^\circ\text{C}/T_a = 1800^\circ\text{C}$ for NH₄H₂PO₄ and $T_p = 550^\circ\text{C}/T_a = 1900^\circ\text{C}$ for Pd + Mg, where T_p is the pyrolysis temperature, and T_a the atomization temperature.

Besides enhancing the thermal stability of the analytes, the chemical modifier should minimize any interfering effect caused by the sample matrix. The recoveries obtained for the addition of 12 pg Cd²⁺ and 120 pg Pb²⁺ to three randomly selected urine samples are shown in Table 2. These results were obtained for all tested chemical modifiers, under the best heating conditions for each one.

The low recoveries obtained for the mixture W + Rh as a permanent chemical modifier indicated that the analyte-Rh interaction was not sufficient to reduce the interference caused by the concomitants. On the other hand, both chemical modifiers introduced in solution form showed better recovery results (Table 2). The mixing process between the analyte and the modifier was less efficient when a permanent chemical modifier was used and, probably, its performance was damaged for volatile elements in the presence of complex matrices. The performance of Pd + Mg was acceptable for cadmium and lead, but the adoption of NH₄H₂PO₄ presented the best results (Table 2) and ensured the possibility to carry out an instrument calibration with aqueous standards.

The absorbance peaks obtained for cadmium and lead in the presence of the tested chemical modifier are presented in Fig. 2. The effects of urine concomitants can be evaluated by comparing the peaks obtained from aqueous solution (I) with those obtained in the presence of urine (II). The atomization kinetic was changed for cadmium when NH₄H₂PO₄ and Pd + Mg were used as chemical modifiers (Figs. 2b – 2c). This behavior was also verified for lead in the presence of the mixture W + Rh and Pd + Mg (Figs. 2d – 2e). Considering the achieved thermal stabilization for the analytes, the effectiveness for reducing interference caused by the matrix concomitants, and the peak absorbance shapes under compromise conditions, NH₄H₂PO₄ was selected for the multielement determination of cadmium and lead in urine.

Fig. 2 Cadmium and lead absorbance peaks for an aqueous solution (I) and urine samples (II) with the addition of 12 pg Cd^{2+} (a, b, c) and 120 pg Pb^{2+} (d, e, f) in the presence of the tested chemical modifier.

Analytical figures of merit

The spectrometer was calibrated using aqueous standard solutions ranging from 0.125 up to $2.0 \mu\text{g L}^{-1}$ for cadmium and from 1.25 up to $20 \mu\text{g L}^{-1}$ for lead in 0.1% (w/v) Triton X-100 + 2% (v/v) HNO_3 + 0.31% $\text{NH}_4\text{H}_2\text{PO}_4$. The optimized heating program and instrumental conditions are indicated in Table 1. The slopes and regression coefficients obtained from the calibration graphs were $(5.12 \pm 0.04) \cdot 10^{-2} \text{ s L } \mu\text{g}^{-1}$ and 0.9998 ± 0.0007 for cadmium; $(2.40 \pm 0.01) \cdot 10^{-3} \text{ s L } \mu\text{g}^{-1}$ and 0.9999 ± 0.0004 for lead.

The characteristic masses calculated from the calibration curves and based on the integrated absorbance were 1.0 pg (RSD = 0.8%) for cadmium and 22 pg (RSD = 1.7%) for lead. The increase in the sensitivity due to the use of an end-capped graphite tube was estimated by a comparison of the calibration graph slopes when end-capped and standard graphite tubes were used. The ratio $S_{\text{END}}/S_{\text{STD}}$, where S_{END} is the slope for the end-capped tube and S_{STD} is the slope for the standard tube, was calculated for both analytes. It was observed an increase of 14% and 25% for the cadmium and lead sensitivity, respectively.

The detection limits were calculated considering the variability of 20 consecutive measurements of 0.1% (w/v) Triton X-100 + 2% (v/v) HNO_3 + 0.31% $\text{NH}_4\text{H}_2\text{PO}_4$, according to $3S_{\text{blk}}/m$, where S_{blk} is the standard deviation of blank measurements and m is the calibration curve slope. The obtained values were $0.03 \mu\text{g L}^{-1}$ (0.36 pg) for cadmium and $0.57 \mu\text{g L}^{-1}$ (6.8 pg) for lead. The detection limits were also estimated in the presence of a low-level certified material (Urine blank SeronormTM Trace Elements in Urine). The found

Table 3 Analysis and recovery test results for the simultaneous determination of cadmium and lead in 1 + 4 urine samples and a certified reference material ($n = 3$)

Sample	Analyte		Recovery, %			
	Cadmium ^a / $\mu\text{g L}^{-1}$	Lead ^a / $\mu\text{g L}^{-1}$	Cd spike/pg		Pb spike/pg	
			3	6	30	60
CRM	5.10 ± 0.03	83.0 ± 0.5	—	—	—	—
A	ND ^b	4.2 ± 0.1	104	102	105	100
B	0.45 ± 0.04	7.7 ± 0.1	92	92	88	97
C	0.25 ± 0.05	3.7 ± 0.2	112	102	108	101
D	0.40 ± 0.04	7.8 ± 0.4	104	94	103	95
E	ND ^b	ND ^b	104	98	112	108
F	0.30 ± 0.05	4.4 ± 0.4	92	98	93	102
G	0.45 ± 0.06	6.5 ± 0.3	88	88	96	94
H	0.25 ± 0.04	6.5 ± 0.5	96	92	90	90
I	0.35 ± 0.03	4.0 ± 0.5	88	94	95	92
J	ND ^b	ND ^b	97	106	96	114
K	0.70 ± 0.05	9.2 ± 0.3	91	96	103	90
L	ND ^b	8.5 ± 0.2	90	88	88	85
Mean	—	—	97 ± 8	96 ± 6	98 ± 8	97 ± 8

a. Recommended values for CRM ($\mu\text{g L}^{-1}$): Cd = 5.0 and Pb = 85.

b. Not detectable.

values were $0.05 \mu\text{g L}^{-1}$ (0.60 pg) for cadmium and $0.61 \mu\text{g L}^{-1}$ (7.3 pg) for lead, considering 20 consecutive measurements.

The performance of the end-capped graphite tube was acceptable up to 500 heating cycles, under the optimized conditions. Considering the simultaneous determination of cadmium and lead, it was possible to have up to 1000 analytical results with the same atomizer, lowering the costs associated with the replacement of graphite parts. Nevertheless, the use of EC-THGA beyond its lifetime damaged the analytical results: poor precision for triplicate measurements was observed (RSD > 10%) and the end-caps were worn down. As a consequence, diffusional losses were increased and the sensitivity decreased for both analytes. Regarding the heating cycle time, it was possible to have 50 simultaneous determinations per hour.

Cadmium and lead determination in urine

A certified reference material (CRM) from Sero AS (SeronormTM Trace Elements in Urine) and twelve volunteers' urine samples were used to evaluate the reliability of the simultaneous procedure. The found cadmium and lead concentrations and the recoveries obtained with spiked samples are given in Table 3.

The analysis of CRM showed values in agreement with the certified cadmium and lead concentration at the 95% confidence level. The volunteers' urine samples were spiked with two different concentrations of cadmium (0.25 and $0.50 \mu\text{g L}^{-1}$) and lead (2.5 and $5.0 \mu\text{g L}^{-1}$). The obtained recoveries were satisfactory (Table 3) and confirmed the minimization of interferences caused by the matrix constituents, when $\text{NH}_4\text{H}_2\text{PO}_4$ was adopted as a chemical modifier.

Conclusions

SIMAAS can be successfully adopted for the multielement cadmium and lead determination in urine from non-exposed healthy subjects. The sensitivity achieved by using an end-capped transversely heated graphite atomizer ensured the possibility to detect ultra-trace amounts of both analytes,

making possible the determination of reference values for unexposed populations.

The chemical modifier selection is critical and the minimization of interference effects caused by sample matrix must be taken into account as well as the stabilization obtained for the analytes. All tested chemical modifiers increased the thermal stability of cadmium and lead in the presence of urine. On the other hand, only 25 µg of $\text{NH}_4\text{H}_2\text{PO}_4$ ensured the possibility to carry out the instrument calibration with aqueous standard solutions.

The analytical frequency was increased due to the short heating program developed for the graphite tube (57 s). Considering the simultaneous determination of two elements, it was possible to carry out 50 heating cycles per hour. The simplified sample treatment before the analysis (a unique dilution step with $\text{NH}_4\text{H}_2\text{PO}_4$ + Triton X-100 + HNO_3) also contributed to diminish the total time of the analysis. The possibility to have up to 500 heating cycles with the same graphite tube reduces the analytical costs related to any graphite parts replacement. Multielement determinations by SIMAAS also lower the high-purity reagent requirement and residue generation during the analysis.

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