

Article

Influence of Na, K, Ca and Mg on Lead Atomization by Tungsten Coil Atomic Absorption Spectrometry

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A atomização de chumbo em atomizador eletrotérmico de filamento de tungstênio, na presença e ausência de altas concentrações de Na⁺, K⁺, Ca²⁺ e Mg²⁺, foi investigada com o objetivo de entender os processos de interferências. A atomização do chumbo foi menos comprometida por Ca²⁺ e Mg²⁺ do que por Na⁺ e K⁺. Na ausência dos concomitantes, a eficiência da atomização de chumbo foi melhorada com a presença de H₂ (10% v/v) na composição do gás de purga, durante as etapas de pirólise e atomização. As interferências causadas por Na⁺ e Ca²⁺ foram desprezíveis quando a etapa de pirólise foi realizada sem o H₂ na composição do gás de purga. Os resultados mostraram que Na⁺, K⁺, Ca²⁺ e Mg²⁺ podem estar diretamente envolvidos nas reações de competição pelo H₂ nos processos em fase condensada.

The atomization of lead in an electrothermal tungsten coil atomizer in the presence and absence of Na⁺, K⁺, Ca²⁺ and Mg²⁺ was investigated with the objective of understanding the interference processes. The lead atomization was less affected by Ca²⁺ and Mg²⁺ than by Na⁺ and K⁺. In the absence of concomitants, lead atomization efficiency was improved by the presence of H₂ (10% v/v) in the purge gas composition, during pyrolysis and atomization steps. The interference caused by Na⁺ and Ca²⁺ was negligible when the pyrolysis step was accomplished without H₂ in the purge gas composition. The results showed that Na⁺, K⁺, Ca²⁺ and Mg²⁺ are directly involved in competition reactions for H₂ in condensed phase.

Keywords: lead atomization, atomic absorption spectrometry, tungsten coil atomizer, interference

Introduction

In the last 25 years, loops, tubes, micro-tubes and coils made of tungsten or tungsten alloys have been proposed as atomizers for the determination of many elements by electrothermal atomic absorption spectrometry^{1,2}. The main features of these atomizers are simplicity, low cost, and the tungsten physical and chemical properties such as high melting point (3680 K), low specific heat (0.133 J g⁻¹ K⁻¹), low background emission and low reactivity with most of elements of analytical interest¹⁻⁴. When tungsten coils are used, a low power supply (150 W) is required and the use of cooling system is unnecessary. As a consequence, portable

electrothermal atomic absorption spectrometers are becoming a promising reality⁵⁻⁷.

There are only a few studies with metallic atomizers regarding the effect of concomitants, and practically no information on the role of the concomitants in the atomization processes. Experiments carried out by Cantle and West⁸ showed that lead was less affected by interference when it was atomized from a tungsten filament than from a graphite filament of similar dimensions. It was suggested that this behavior is related to differences in the heating rate of the atomizers. Newton and Davis⁹ studied the effects of 27 cations and anions on lead atomization in a tungsten-rhenium loop atomizer and proposed that most of the interference was dependent on the heating rate of this atomizer. It was shown that 20% (v/v) of H₂ in purge gas composition decreased the chemical interference and non-specific absorption due to concomitants.

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Chauvin *et al.*³ using a wire loop atomizer similar to that described by West *et al.*¹⁰ observed that the atomization of copper, cadmium, magnesium and beryllium was affected by concomitants probably owing to the formation of oxides and chlorides in the gas phase. It was also mentioned that the presence of SO_4^{2-} diminished the interference caused by Na^+ and K^+ .

Efforts have been made by research groups in Brazil¹¹⁻¹⁸, Chile¹⁹⁻²⁵ and USA⁵⁻⁷ to demonstrate the usefulness of 150 W tungsten coils as atomizers for ET-AAS.

The aim of the present work is to investigate the interference processes involved in lead atomization from the tungsten coil in the presence of Na^+ , K^+ , Ca^{2+} and Mg^{2+} .

Experimental

Apparatus

A SpectrAA-40 (Varian, Victoria, Australia) atomic absorption spectrometer coupled to a Varian DS-15 Data Station was used. Pb, Na, K, Ca and Mg hollow cathode lamps and a deuterium lamp source from the same manufacturer were used for measurements of atomic and background signals, respectively. The analytical wavelength was the 283.3 nm lead resonance line, selected with a spectral bandpass of 0.2 nm. All measurements were based on peak height absorbance with a 50 ms time constant. In all experiments, 10 μL of the solutions were introduced into the atomizer using a Varian autosampler.

The tungsten coil (OSRAM 150W, Munich, Germany) atomizer was fixed in two copper electrodes supported by a PTFE fitting which was inserted into a 10 cm long flow-through cell mounted in a perspex base. The whole assembly replaced the Varian GTA-96 graphite furnace as previously described¹². The tungsten coil was heated by a programmable power supply with a voltage feedback circuit (Anacom Equipments and Systems, São Bernardo do Campo, Brazil). The power supply was interfaced with the DS-15 Data Station, thereby enabling the tungsten coil furnace operation to be started by pushing the start GTA command. Argon 99.999 % (v/v) or a mixture containing 90% (v/v) Ar plus 10% (v/v) H_2 (AGA, Campinas, Brazil) flowing at 1.0 L min^{-1} were used as purge gas.

Reagents and reference solutions

All solutions were prepared from reagents of analytical. High purity de-ionized water obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout. Nitric and hydrochloric acids were purified using quartz sub-boiling stills (Kürner, Rosenheim, Germany).

A 1000 $\mu\text{g Pb}^{2+} \text{L}^{-1}$ stock solution was prepared from $\text{Pb}(\text{NO}_3)_2$ (Johnson & Matthey Chemicals, Royston, Herts., UK) in 0.014 mol L^{-1} HNO_3 . Reference solutions of 100

and 200 $\mu\text{g Pb}^{2+} \text{L}^{-1}$ were prepared by appropriate dilution of the Pb^{2+} stock solution, in 0.014 mol L^{-1} HNO_3 .

The effects of concomitants were investigated by using solutions containing up to 1000 mg $\text{Na}^+ \text{L}^{-1}$ (NaNO_3), 1000 mg $\text{K}^+ \text{L}^{-1}$ (KNO_3), 1000 mg $\text{Ca}^{2+} \text{L}^{-1}$ (CaCO_3 in HNO_3), 1000 mg $\text{Mg}^{2+} \text{L}^{-1}$ (MgO in HNO_3) in 0.014 mol L^{-1} HNO_3 all from Johnson & Matthey Chemicals. To confirm some hypothesis, 100 mg $\text{Li}^+ \text{L}^{-1}$ (LiNO_3) (Johnson & Matthey Chemicals) in 0.014 mol L^{-1} HNO_3 was used.

Additionally, a 1.0% (w/v) solution of ascorbic acid (Merck, Darmstadt, Germany) was used as a chemical modifier.

Tungsten coil temperature measurements

An optical pyrometer Marathron MR1S (Raytek Corporation, Santa Cruz, USA) was employed for tungsten coil temperature measurements at different applied voltages (1.5 - 15.0 V range). The measurements were implemented based in two wavelength ranges (750 to 1100 nm and 950 to 1100 nm)²⁶.

For applied voltages below 1.5 V, the tungsten coil surface temperatures were estimated by observing the melting point of organic and inorganic compounds. A small amount of each compound was placed onto the tungsten coil and then a voltage that would generate temperature near its melting point was applied in the tungsten coil²⁶. The experimentally observed melting points were close to the literature values. All measurements were carried out with five replicates.

Pyrolysis temperature curves

The pyrolysis temperature curves were obtained with solutions containing 100 or 200 $\mu\text{g Pb}^{2+} \text{L}^{-1}$ in absence and presence up to 100 mg L^{-1} of Li^+ , Na^+ , K^+ , Ca^{2+} or Mg^{2+} in 0.014 mol L^{-1} HNO_3 . The pyrolysis temperature curves of 5 $\mu\text{g L}^{-1}$ of Na^+ , K^+ , Ca^{2+} or Mg^{2+} in 0.014 mol L^{-1} HNO_3 were obtained by using the heating program showed in Table 1. The pyrolysis temperature curves were obtained with applied voltages varying from 0.70 (730 °C) to 1.5 V (1158 °C) during 2.0 s, the atomization step being kept constant at 13.0 V (2763 °C) for 1.0 s. By using the same conditions, pyrolysis temperature curves with solutions prepared in 1.0% (w/v) ascorbic acid medium were obtained in the absence and presence of 100 mg L^{-1} of Na^+ in 0.014 mol L^{-1} HNO_3 .

Table 1. Heating program of tungsten coil atomizer

Step	Voltage/V	Time/s	Gas flow-rate (L min^{-1})	Read
Dry	0.70	38	0.80	-
Pyrolysis	0.70 to 1.50	2	0.80	-
Atomization	13.00	1	0.80	On

Effect of concomitants and observation heights

The effect of 10, 100 and 1000 mg L^{-1} of Na^+ , K^+ , Ca^{2+}

and Mg^{2+} on the absorbance signals of $100 \mu\text{g Pb}^{2+} \text{ L}^{-1}$ was evaluated at 0.0, 1.0, 2.0, 3.0 and 4.0 mm observation heights with the filament positioned below the radiation beam. The tungsten coil was initially positioned in the center of the radiation beam and this observation height was established as the zero reference point. The observation heights were determined positioning the tungsten coil in 1.0 mm increments until 4.0 mm below the radiation beam.

Results and Discussion

Pyrolysis temperature curves

Preliminary investigations with atomization of lead in presence of Na^+ , K^+ , Ca^{2+} and Mg^{2+} , using the heating program (Table 1) with and without pyrolysis step, showed contrasting results. Either signal suppression or enhancement were observed depending on the heating program employed (Table 2). The heating program with pyrolysis produced negative interference, except in presence of 1 mg L^{-1} of Na^+ and Mg^{2+} , and 10 mg L^{-1} of Mg^{2+} when interference was slightly positive. However, these effects were opposite with a heating program without pyrolysis, except for 1000 mg L^{-1} of Ca^{2+} and Mg^{2+} . In general, Na^+ and K^+ produced the largest effects on lead atomization. Newton and Davis⁹ found similar effects when working with tungsten-rhenium loops, but they did not explain them.

Table 2. Effect of concomitants on atomization of $200 \mu\text{g Pb}^{2+} \text{ L}^{-1}$ in 0.014 mol L^{-1} of HNO_3

	Δ Peak height absorbance (%)							
	with pyrolysis*				without pyrolysis*			
	1	10	100	1000	1	10	100	1000
NaNO_3	+ 5	- 3	- 45	- 53	+ 3	+ 67	+ 73	+ 23
KNO_3	- 10	- 10	- 56	- 57	+ 20	+ 5	+ 47	+ 6
$\text{Ca}(\text{NO}_3)_2$	- 6	- 17	- 5	- 41	+ 11	+ 11	+ 11	- 35
$\text{Mg}(\text{NO}_3)_2$	+ 3	+ 9	- 8	- 34	+ 11	+ 47	+ 48	- 7

* Concomitants Concentrations: 1, 10, 100 and 1000 mg L^{-1}

The presence of Na^+ , K^+ , Ca^{2+} and Mg^{2+} (100 mg L^{-1} in 0.014 mol L^{-1} HNO_3) affected the profile of the lead pyrolysis curve (Figure 1). The pyrolysis temperature supported by lead, without chemical modifier, was $920 \text{ }^\circ\text{C}$. Above $920 \text{ }^\circ\text{C}$ neither Ca^{2+} nor Mg^{2+} changed lead atomization, and below this temperature they caused positive interference. However, interferences by Na^+ and K^+ were more severe for higher pyrolysis temperatures. The absorbance signals were drastically reduced for higher pyrolysis temperature whereas, for lower temperatures, they produced positive interferences (Figure 1).

To verify the thermal stability of these elements in a tungsten coil atomizer, pyrolysis temperature curves for 5 mg L^{-1} of Na^+ , K^+ , Ca^{2+} and Mg^{2+} in 0.014 mol L^{-1} of

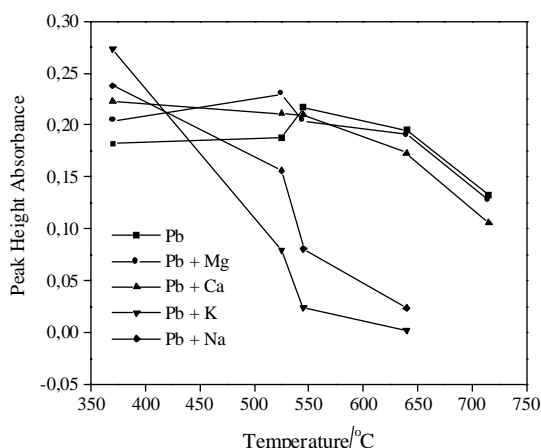


Figure 1. Pyrolysis temperature curves for $100 \mu\text{g Pb}^{2+} \text{ L}^{-1}$ with and without 100 mg L^{-1} of concomitants in 0.014 mol L^{-1} of HNO_3 ; purge gas composition: 90% v/v Ar + 10% v/v H_2 ; volume injected $10 \mu\text{L}$ and atomization temperature: $2763 \text{ }^\circ\text{C}$

HNO_3 were obtained. The pyrolysis temperature curves of these concomitants showed thermal stability over $1100 \text{ }^\circ\text{C}$ up to $1500 \text{ }^\circ\text{C}$ (Figure 2), making difficult the vaporization of the concomitants without losses of lead, that presented maximum thermal stability at $920 \text{ }^\circ\text{C}$. Moreover, the atomization of these concomitants showed a strong dependence of hydrogen (10% v/v) in the purge gas composition. The absence of hydrogen during pyrolysis or atomization steps reduced drastically the absorbance signals of these elements.

Recently, L'vov²⁷ pointed out that the most probable mechanism of atomization for alkali metals is governed by the reaction:

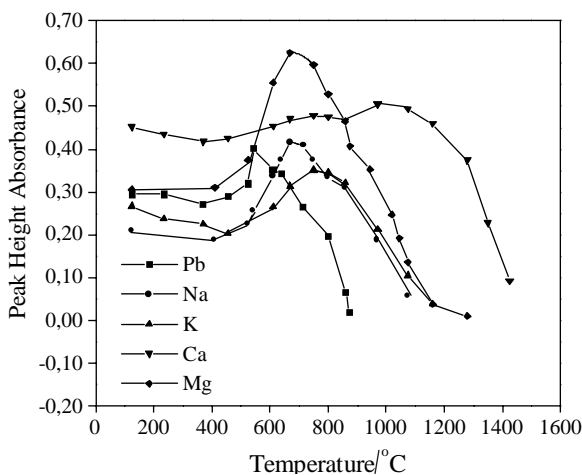
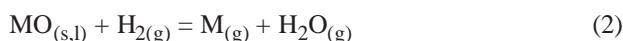


Figure 2. Pyrolysis temperature curves for $100 \mu\text{g Pb L}^{-1}$ and for 5 mg L^{-1} of Na, K, Ca and Mg in 0.014 mol L^{-1} of HNO_3 ; purge gas composition: 90% v/v Ar + 10% v/v H_2 ; volume injected $10 \mu\text{L}$ and atomization temperature: $2763 \text{ }^\circ\text{C}$

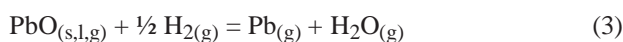
The same author also pointed out that Ca^{2+} and Mg^{2+} are atomized through the direct reduction of their oxides:



Based on these proposed mechanism, it could be assumed that the formation of monohydroxides of sodium and potassium (reaction 1) and the reduction of calcium and magnesium oxides by hydrogen in the condensed phase (reaction 2) are occurring preferentially.

It could be thought that oxide species of lead, monohydroxides of alkaline elements and oxides of alkaline-earth elements are their prevalent atomic precursors. Monohydroxide species could be formed in the condensed phase by heterogeneous reaction with hydrogen, since this gas is also essential during the pyrolysis step.

In this case, one hypothesis to explain the negative interference caused by Na^+ and K^+ would be the competition for the hydrogen present in the purge gas, which was necessary for lead, sodium and potassium atomization. These processes could affect the dissociation of lead oxide in the condensed or vapor phase:



To show the competition of hydrogen during pyrolysis step, an experiment was carried out without hydrogen in the purge gas composition during pyrolysis or atomization steps. The interference of Na^+ and Ca^{2+} in lead atomization was suppressed when pure argon 99.999% (v/v) atmosphere was used during the dry and pyrolysis steps and a mixture of 90% (v/v) Ar plus 10% (v/v) H_2 was used in the atomization step. Besides, using a mixture of 90% (v/v) Ar plus 10% (v/v) H_2 during the dry and pyrolysis steps and pure argon 99.999% (v/v) in the atomization step, the interference persisted (Table 3).

To confirm the hypothesis that the interference processes were related to the formation of monohydroxides

species, an experiment was also carried out with Li^+ and ascorbic acid. This element was chosen considering that its monohydroxide is easily formed²⁸ and thus the interference should manifest more critically.

The lead pyrolysis temperature curves in the presence of Li^+ (Figure 3) showed, as expected, that atomization suppression was much more pronounced, confirming the hypothesis that lead atomization is affected by a competition process for hydrogen, since monohydroxide species of Na^+ , K^+ and Li^+ are formed during dry and pyrolysis steps. Lead pyrolysis temperature curves in presence of 10 fold less Li^+ than Na^+ or K^+ , presented more severe interference even at low pyrolysis temperatures. Figure 3 shows that in presence of 10 mg Li^+ L^{-1} , the lead analytical signal was strongly attenuated and disappeared with 100 mg Li^+ L^{-1} for all applied voltages. Monohydroxides of alkaline metals are more stable than oxides, and LiOH is the most stable²⁸. The more stable the monohydroxide species, the more pronounced is the interference of the alkaline element, which explains why 10-100 fold less Li^+ , affected more drastically the lead pyrolysis temperature curve when compared to Na^+ and K^+ . According to these results, similar interference effects for those elements that depend on the presence of hydrogen in the purge gas composition for their atomization are expected.

The influence of a reducing agent was also confirmed by adding ascorbic acid to solutions containing lead or lead and 100 mg Na^+ L^{-1} (Figure 4). Interferences were not observed for temperatures lower than 800°C. For higher temperatures, the Na^+ interference in a medium containing ascorbic acid was always lower than that without this compound, because the thermal decomposition of ascorbic acid leads to the formation of CO and hydrogen²⁹, increasing the reducing characteristics of the medium. Consequently, more hydrogen was available.

Table 3. Effect of purge gas composition on atomization of 100 μg Pb L^{-1} in the presence and absence of 100 mg L^{-1} of Na^+ or Ca^{2+} in 0.014 mol L^{-1} of HNO_3 .

Step	Purge Gas Composition*	HNO_3	100 mg L^{-1} Na^+	100 mg L^{-1} Ca^{2+}
dry	90% Ar + 10% H_2			
pyrolysis	90% Ar + 10% H_2	0.205±0.006	0.033±0.007	0.139±0.010
atomization	90% Ar + 10% H_2			
dry	99.999% Ar			
pyrolysis	99.999% Ar	0.103±0.001	0.109±0.007	0.126±0.008
atomization	90% Ar + 10% H_2			
dry	90% Ar + 10% H_2			
pyrolysis	90% Ar + 10% H_2	0.141±0.008	0.015±0.011	0.024±0.007
atomization	99.999% Ar			

Flow Rate: 1.0 L min^{-1}

Pyrolysis temperature: 920 °C; Atomization temperature: 2763 °C

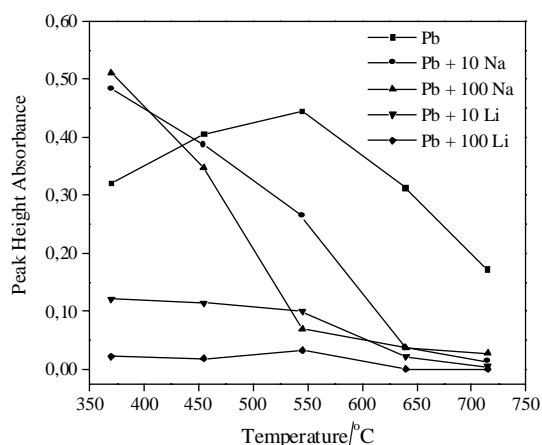


Figure 3. Pyrolysis temperature curves for 200 $\mu\text{g Pb L}^{-1}$ with and without 10 or 100 mg L^{-1} of Li or Na in 0.014 mol L^{-1} of HNO_3 ; purge gas composition: 90% v/v Ar + 10% v/v H_2 ; volume injected 10 μL and atomization temperature: 2763 $^\circ\text{C}$

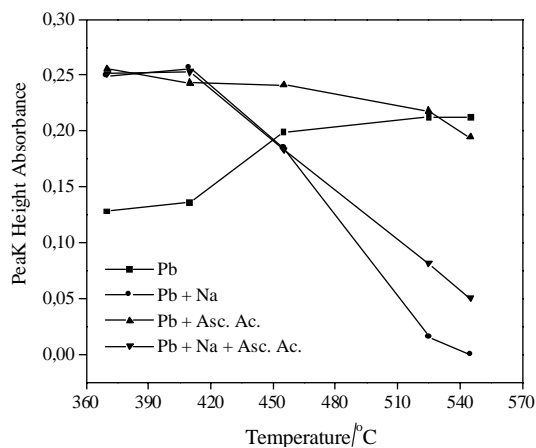


Figure 4. Pyrolysis temperature curves for 100 $\mu\text{g Pb mL}^{-1}$ with 1% w/v of ascorbic acid and 100 $\text{mg Na}^+ \text{L}^{-1}$ in 0.014 mol L^{-1} HNO_3 ; purge gas composition: 90% v/v Ar + 10% v/v H_2 ; volume injected 10 μL and atomization temperature: 2763 $^\circ\text{C}$.

Gilchrist *et al.*³⁰ proposed the occurrence of reaction (3) in a graphite tube, where the hydrogen in the purge gas would react with oxygen and other oxidant species, forming lead atoms in the gas phase. So, it can be suggested that the decrease of lead absorbance signal (Figure 1), in the presence of alkaline elements, was partially due to the lack of hydrogen during pyrolysis and atomization steps. In other words, it is supposed that lead atomization efficiency is related to hydrogen availability during the pyrolysis and atomization steps, and that this availability would depend on the presence of other species that also react with hydrogen, such as the alkaline elements, that may form stable monohydroxide species^{27, 30}.

In spite of the non-isothermal environment around the coil, the interference effect was slightly affected by changing the observation height (Figure 5). It can be supposed that the lower lead absorbance signal for higher observa-

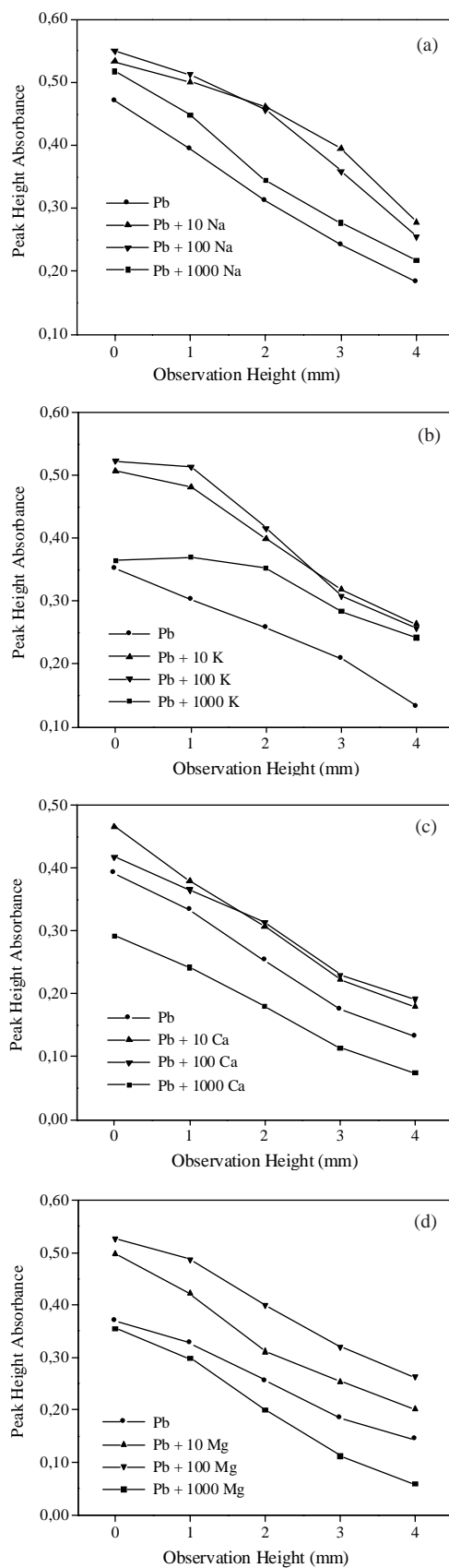


Figure 5. Influence of observations heights on atomization of 100 $\mu\text{g Pb}^{2+} \text{L}^{-1}$ with and without 10, 100 and 1000 mg L^{-1} of concomitants in 0.014 mol L^{-1} HNO_3 : (a) Na, (b) K, (c) Ca and (d) Mg.

tions heights is due to the dilution of the vapor cloud into the flow-through cell. With the exception of K^+ and Mg^{2+} (1000 mg L⁻¹ and 0.0 observation height), lead curves showed similar behavior in the presence and in absence of the concomitants. In general, lower concentration of concomitants (10 and 100 mg L⁻¹) and higher concentration (1000 mg L⁻¹) caused increase and decrease, respectively, of the lead analytical signal (Figure 5). These effects were always observed for lower pyrolysis temperatures. Probably, the presence of sodium, potassium, calcium and magnesium (10 and 100 mg L⁻¹) change the kinetics of the lead atomization, increasing the absorbance signal. For higher concentration of the concomitants (1000 mg L⁻¹) lead occlusion can be occurring.

The processes occurring in the condensed phase seemed to be dominant. It can be verified from Figure 5 that interferences were not critically affected by the gas phase temperature, leading to the conclusion that the above mentioned processes occur predominantly in the condensed phase. This was also confirmed by experiments in which lead and the alkaline elements were introduced simultaneously, but physically separated in the tungsten coil. The results showed no occurrence of interferences in the gas phase, confirming the condensed phase hypothesis.

These results showed that the understanding of the atomization processes in the W coil atomizer needs new paradigms to better explaining them. The fast heating rate, the non-isothermal ambient and the use of hydrogen in the purge gas exert a pronounced effect on the mechanism of atomization and these effects still require a full interpretation.

Acknowledgments

We thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP Processo 1995/5782-7) and Financiadora de Estudos e Projetos (PRONEX) for financial support. We are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for fellowship of P. V. Oliveira and F. R. P. Rocha and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for fellowships F. J. Krug, J. A. Nóbrega, M. M. Silva and Z. F. Queiroz.

References

1. Suzuki, M.; Ohta, K. *Prog. Anal. At. Spectrosc.* **1983**, *6*, 49.
2. Nóbrega, J. A.; Silva, M. M.; Oliveira, P. V.; Krug, F. J.; Baccan, N. *Quím. Nova* **1995**, *18*, 555.
3. Chauvin, J. V.; Davies, D. G.; Hargis, L. C. *Anal. Lett.*

4. Berndt, H.; Schaldach, G. *J. Anal. At. Spectrom.* **1988**, *3*, 709.
5. Parsons, P. J.; Qiao, H.; Aldous, K. M.; Mills, E.; Slavin, W. *Spectrochim. Acta* **1995**, *50B*, 1475.
6. Sanford, C. L.; Thomas, S. E.; Jones, B. T. *Appl. Spectrosc.* **1996**, *50*, 174.
7. Batchelor, J. D.; Thomas, S. E.; Jones, B. T. *Appl. Spectrosc.* **1998**, *52*, 1086.
8. Cattle, J. E.; West, T. S. *Talanta* **1973**, *20*, 459.
9. Newton, J. A.; Davis, D. G. *Anal. Chem.* **1975**, *47*, 2003.
10. West, M. H.; Molina, J. F.; Yuan, C. L.; Davis, D. G.; Chauvin, J. V. *Anal. Chem.* **1979**, *51*, 2370.
11. Giné, M. F.; Krug, F. J.; Sass, V. A.; Reis, B. F.; Nóbrega, J. A.; Berndt, H. *J. Anal. At. Spectrom.* **1993**, *8*, 243.
12. Silva, M. M.; Silva, R. B.; Krug, F. J.; Nóbrega, J. A.; Berndt, H. *J. Anal. At. Spectrom.* **1994**, *9*, 361.
13. Krug, F. J.; Silva, M. M.; Oliveira, P. V.; Nóbrega, J. A. *Spectrochim. Acta* **1995**, *50B*, 1469.
14. Silva, M. M.; Krug, F. J.; Oliveira, P. V.; Nóbrega, J. A.; Reis, B. F.; Penteadó, D. *Spectrochim. Acta* **1996**, *51B*, 1925.
15. Silva, M. M.; Arruda, M. A. Z.; Krug, F. J.; Oliveira, P. V.; Queiróz, Z. F.; Gallego, M.; Valcárcel, M. *Anal. Chim. Acta* **1998**, *368*, 255.
16. Lima, E. C.; Krug, F. J.; Nóbrega, J. A.; Nogueira, A. R. A. *Talanta* **1998**, *47*, 613.
17. Luccas, P. O.; Nóbrega, J. A.; Oliveira, P. V.; Krug, F. J. *Talanta* **1999**, *48*, 695.
18. Lopes, G. S.; Nogueira, A. R. A.; Oliveira, P. V.; Nóbrega, J. A. *Anal. Sci.* **1999**, *15*, 165.
19. Bruhn, C. G.; Ambiado, F. E.; Cid, H. J.; Woerner, R.; Tapia, J.; Garcia, R. *Anal. Chim. Acta* **1995**, *306*, 183.
20. Bruhn, C. G.; Ambiado, F. E.; Cid, H. J.; Woerner, R.; Tapia, J.; Garcia, R. *Quím. Anal.* **1996**, *15*, 191.
21. Bruhn, C. G.; Neira, J. Y.; Valenzuela, G. D.; Nóbrega, J. A. *J. Anal. At. Spectrom.* **1998**, *13*, 29.
22. Bruhn, C. G.; Neira, J. Y.; Valenzuela, G. D.; Nóbrega, J. A. *Talanta* **1999**, *48*, 537.
23. Bruhn, C. G.; Neira, J. Y.; Guzmán, M. I.; Darder, M. M.; Nóbrega, J. A. *Fresenius J. Anal. Chem.* in press.
24. Bruhn, C. G.; Nóbrega, J. A. *Química & Indústria* **1998**, *37*.
25. Neira, J. Y.; Bruhn, C. G.; Valenzuela, G. D.; Nóbrega, J. A. *Quím. Nova* **1998**, *21*, 490.
26. Oliveira, P. V.; Queiroz, Z. F.; Krug, F. J.; Lima, E. C.; Nóbrega, J. A.; 5th Rio Symposium on Atomic Spectrometry, Cancun, Mexico, 1998.
27. L'Vov, B. V. *Spectrochim. Acta* **1997**, *52B*, 1.

28. Alkemade, C. T. J.; Lollander, T.; Snelleman, W.; Zeegers, P. J. T. *Metal Vapours in Flames*; Pergamon Press; London, 1982.
29. Byrne, J. P.; Chakrabarti, C. L.; Gilchrist, G. F.; Lamoureux, M. M.; Bertels, P. *Anal Chem.* **1993**, *65*, 1267.
30. Gilchrist, G. F. R.; Chakrabarti, C. L.; Cheng, J.; Hugles, D. M. *J. Anal. At. Spectrom.* **1993**, *8*, 623.

Received: August, 5, 1999

FAPESP helped in meeting the publication costs of this article.