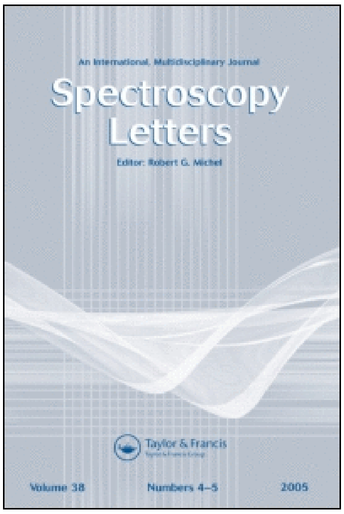

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Behavior of Volatile Elements in the Graphite Furnace in the Presence of Silver as Matrix Modifier

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ABSTRACT

The effect of silver, as an aqueous solution of $AgNO_3$, on the pretreatment and atomization behaviour of As, Cd, Bi, Hg, Pb, Sb, Se, Sn and Tl during electrothermal atomic absorption spectrometry has been investigated. The presence of silver in the graphite furnace leads to thermal stabilisation of all investigated volatile elements to allow higher pyrolysis temperatures. The maximum, loss-free, pretreatment temperatures (°C) in the presence of 100 μg Ag by atomization from the wall or from a platform are respectively: As (1500°C, –); Cd (800°C, 800°C); Bi (700°C, 700°C); Hg (250°C, –); Pb (600°C, 900°C); Sb (1200°C, 1200°C); Se (1400°C, 1400°C); Sn (1100°C, 1100°C) and Tl (1000°C, 1100°C). Also, silver facilitates a relatively low atomization temperature (°C) from the wall for Cd (1300°C), Bi (1700°C), Pb (1400°C),

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Se (1900°C) and Tl (1400°C). In addition, silver enhances the measurement sensitivity by a factor of 1.2–1.8.

Key Words: Silver modifier; ETAAS; Volatile elements.

INTRODUCTION

The electrothermal atomic absorption determination of trace volatile elements requires the use of efficient matrix modification to ensure thermal stabilisation during the pretreatment step.[1–6] Silver could be expected to be a suitable modifier for the most volatile elements because it forms thermally stable arsenide, sellenide, telluride compounds, and it is a readily reducible to the elemental state element with strong expressed amalgamation properties. However there are only few data in the literature for silver as modifier. The stabilising and enhancement effect of silver as a matrix modifier on the carbon-rod atomization of arsenic and selenium in comparison with the effect of commonly used nickel have been presented in an early paper by Sanzolone and Chao.[7] The same authors used co-extracted silver for the ETAAS determination of mercury in geological materials after solvent extraction as tetraiodomercurate (II).[8] The chloride interference on zinc determination by ETAAS with a carbon-filament atomizer has been overcome by the use of aqueous silver nitrate added as matrix modifier.[9] Norheim et al. proposed an organosilver reagent (0.5% Ag) for thermal stabilization of selenium as Se-diaminonaphthalene complex.[10] The aim of the present work was to investigate the behaviour of volatile elements in the graphite furnace in the presence of silver, in order to evaluate the efficiency of silver as a matrix modifier in the ETAAS.

EXPERIMENTAL

Apparatus

The measurements were carried out on a Perkin–Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The light sources used were hollow cathode lamps for Pb and Tl, and electrodeless discharge lamps for As, Bi, Cd, Hg, Sb, Se and Sn (Perkin–Elmer). Pyrolytically coated graphite tubes and uncoated graphite tubes with pyrolytic platforms were used as atomizers. Solutions (10 µl) were introduced into the graphite furnace using an AS-60 autosampler (Perkin–Elmer). The

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atomic absorption signals were recorded on an Anadex (Camarillo, CA, USA) printer. Only peak areas were used for quantification.

Reagents

All chemicals used were of reagent grade. Doubly distilled water was used throughout. Stock standard solutions, 1 g l^{-1} (Merck, Darmstadt, Germany), were used for the preparation of multi-element working aqueous standard solutions by appropriate dilution. The silver nitrate used for preparation of 1% (w/v) aqueous Ag solution was produced by the Institute for High Purity Substances, University of Sofia, Bulgaria.

RESULTS AND DISCUSSION

The thermal behaviour of As, Cd, Bi, Pb, Sb, Se, Sn and Tl is studied in the presence of Ag as modifier (10 μl, $AgNO_3$ at a concentration of 10,000 μg ml^{-1}) through the construction of pretreatment and atomization curves. The results obtained are depicted at Figure 1. The data have been blank corrected. As can be seen, silver provides substantial thermal stabilisation for all the investigated elements. More detailed information on the maximum applicable pyrolysis temperature, for a loss-free pre-treatment, is given in Table 1. The high pre-treatment temperatures achieved with silver as modifier (1500°C for As, 700°C for Bi, 800°C for Cd, 1400°C for Se, 1500°C for Sn, 1000°C for Tl) could be explained by the formation of thermally stable compounds as silver arsenide, silver selenide, silver telluride.[11] Also, it might be assumed that fast low temperature reduction of $AgNO_3$ to elemental Ag takes place. The atomization curves (Figure 1) constructed for all studied elements showed that, despite the high concentration of the introduced silver modifier, relatively low atomisation temperatures should be used for complete analyte atomization (Table 1). Further, the integrated absorbance signals for Cd, Pb and Tl in the case of wall atomization were lower at atomization temperatures higher than the optimized temperature. Perhaps silver transforms, by catalytic reduction, these analytes into a reactive, elemental and highly dispersed form. Another change in the behaviour of the volatile elements studied is the observed delay in the appearance time of the signals, and the change of their shape, broadening. This is probably a result of the slower evaporation of the analytes from the Ag amalgam, and is indirect evidence for the assumption that silver acts also as a physical modifier to ensure the atomization of the analytes in more nearly isothermal conditions. An essential observation is the increase in the integrated absorbance value for Bi, Hg, Se (1.2 fold); As,

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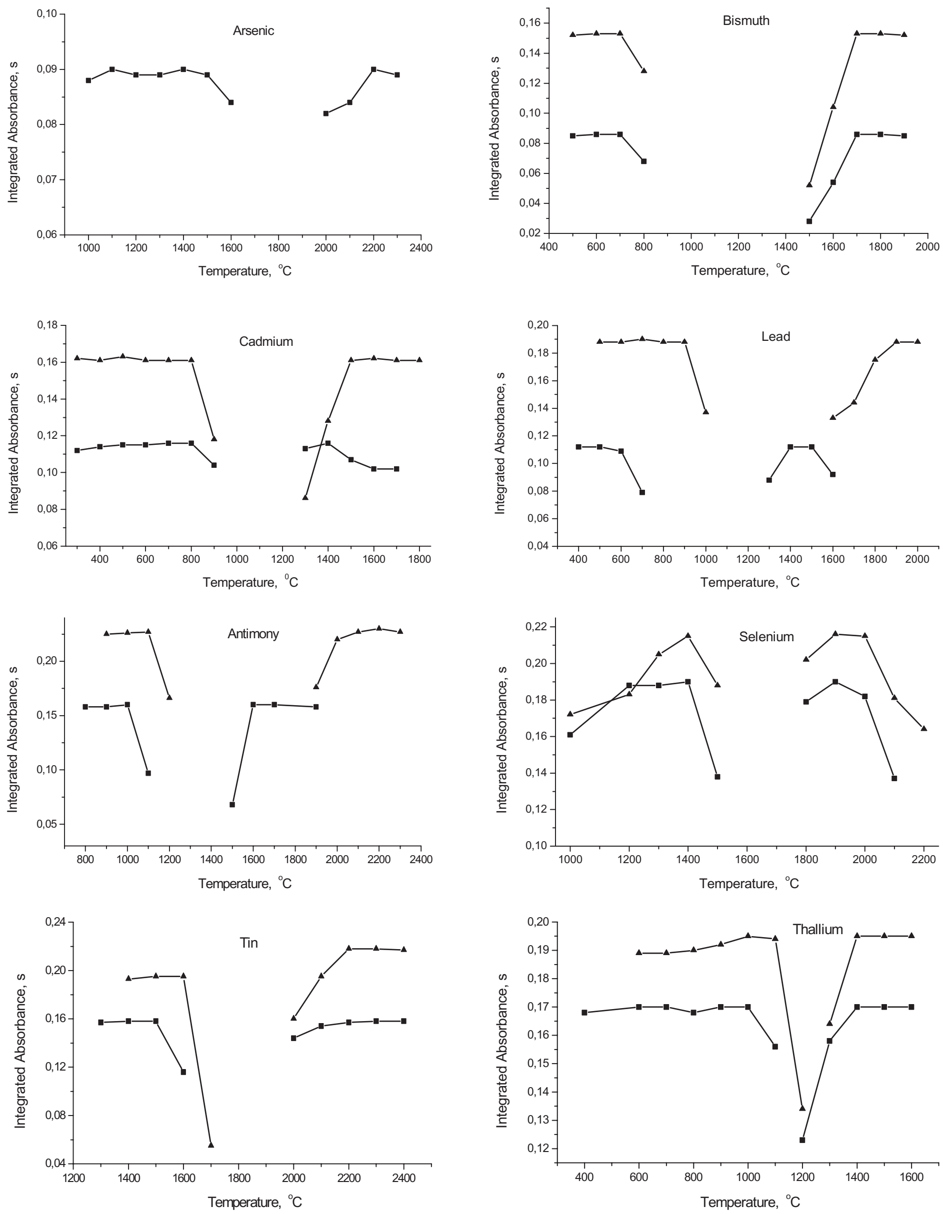

Figure 1. Thermal pre-treatment and atomization curves; ■—wall atomization; ▲—platform atomization.

Table 1. Maximum pyrolysis temperature (°C) for loss-free pretreatment (Step 2) of the analytes and optimum atomization temperatures (Step 3) with silver as matrix modifier (10 μl 10 g l^{-1}Ag).

	Wall atomization		Platform atomization	
Analyte	Step 2	Step 3	Step 2	Step 3
As	1500 (15, 10)	2200 (0, 3)	–	–
Bi	700 (7, 10)	1700 (0, 3)	700 (7, 10)	1700 (0, 3)
Cd	800 (8, 10)	1300 (0, 3)	800 (8, 10)	1500 (0, 3)
Hg	250 (5, 10)	900 (1, 9)	–	–
Pb	600 (6, 10)	1400 (0, 4)	900 (10, 10)	1900 (0, 3)
Sb	1000 (10, 10)	1600 (0, 3)	1100 (12, 10)	2100 (0, 3)
Se	1400 (15, 10)	1900 (0, 3)	1400 (15, 10)	1900 (0, 3)
Sn	1500 (15, 10)	2200 (0, 3)	1600 (16, 10)	2200 (0, 3)
Tl	1000 (10, 10)	1400 (0, 4)	1100 (12, 10)	1400 (0, 4)

Cd, Te, Tl (1.4 fold); Pb (1.8 fold) with silver, in comparison with aqueous standard solutions of the analytes (for As, Hg and Se in comparison with palladium as matrix modifier: 10 μl 5 ppm Pd for Hg, and 10 μl 300 ppm Pd for As, Se). Also, this is probably due to atomization of the analytes after the stabilization of the furnace temperature. In this way silver modifier seems to play the role of a platform.

Insignificant differences were observed in the thermal behaviour of Bi, Se and Tl i.e. the same optimal pyrolysis and atomization temperature were obtained as for platform atomization. Significantly different is the behaviour of lead. Platform atomization in presence of silver as matrix modifier

Table 2. Maximum loss-free pretreatment temperatures (°C).

	Modifier					
Analyte	Pd	Pd + Zr	Pd + W	Pd + Mg	Pd + V	Ag
As	1200	1300	1300	1200	1450	1500
Bi	1200	1200	1200	1200	1200	700
Cd	–	–	–	–	800	800
Hg	350		–	–	–	250
Pb	800	900	900	1000	1000	900
Sb	1200	1300	1300	1300	1400	1100
Se	1100	1300	1300	1100	1400	1400
Sn	1200	1300	1300	1400	1400	1600
Tl	1000	1000	1000	900	1100	1100

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ensures higher, by 300°C, loss-free pretreatment temperature (900°C). Higher by 500°C is the required atomization temperatures for Pb (1900°C) and for Sb (2100°C) and by 200°C (1500°C) for Cd (Figure 1, Table 1).

Unexpectedly platform atomization with silver modifier is inappropriate for As and Hg—as lower sensitivity and lower reproducibility were observed. However for lead, selenium, thallium and tin a 1.4 fold enhancement in sensitivity was obtained.

CONCLUSION

Silver has potential as a matrix modifier in ETAAS when determining the analytes As, Bi, Cd, Hg, Pb, Sb, Se, Sn, Tl (see Table 2). This modifier is relatively cheap, shows low blank values, ensures high loss-free pretereatment temperatures and higher measurement sensitivity . One disadvantage is the contamination of the graphite furnace with silver.

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