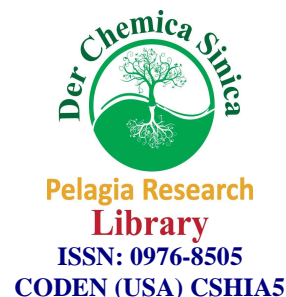




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Der Chemica Sinica, 2012, 3(4):1027-1035



Multi-element determination of bismuth, antimony, and thallium in biological samples by multi-element electrothermal atomic absorption spectrometer

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ABSTRACT

Direct and simultaneous determinations of Bi, Sb, and Tl in different biological samples using a multi-element electrothermal atomic absorption spectrometer (Perkin-Elmer SIMAA 6000) are described. Two kinds of modifiers; Pd(NO₃)₂ + Mg(NO₃)₂ mixture modifier and Ir-permanent modifier were tested. The electrothermal behaviour of the elements in single-element and multi-element mode (with and without modifiers) was studied. The pyrolysis and atomization temperatures for the simultaneous determination using the mixture modifier were 800 and 1900°C and using permanent modifier were 400 and 1800°C. The detection limits were 0.82-1.80 µg.l⁻¹ for Bi, 0.86-1.90 µg.l⁻¹ for Sb, and 1.25-12.00 µg.l⁻¹ for Tl. The Characteristic masses were 62.9-110.0 pg for Bi, 41.9-73.3 pg for Sb, and 55.0-440.0 pg for Tl. A standard reference material (Seronom Trace Elements Urine) was used to find the optimal temperature program. The reliability of the entire procedure was confirmed by analysis of certified reference materials as Trace Elements Urine Sample (from Seronom 05115459), Bovine Liver (from NIST 1577b), Pig Kidney (from BCR 186), and Tea sample (from GBW 8505). A standard additions method was used to determine Bi, Sb, and Tl in the samples simultaneously. Results of analysis of standard reference materials were in agreement with certified values.

Keywords: Simultaneous multi-element, Graphite Furnace AAS, Bismuth, Antimony, Thallium

INTRODUCTION

Graphite furnace-atomic absorption spectrometry (GFAAS) is a powerful analytical technique that has found universal application for the determination of trace metals.

Furnace atomization provides efficient volatilization/atomization and a relatively long residence time (compared to techniques using pneumatic nebulizers) which results in excellent sensitivities and detection limits. In addition, furnace atomization offers small sample size requirements, low cost of operation, simple spectra, and in situ chemical and thermal pre-treatment of samples. Historically, the biggest disadvantage of GF-AAS has been the sample analysis rate: a result of the single element nature of AAS and the slow repetition rate (an atomization every 2 to 3 min) of furnace atomization. There has been continued interest in the development of a multi-element.

GF-AAS instrument that would increase the analytical rate but retain the excellent sensitivities and detection limits of single element operation [1-8].

The availability of simultaneous electrothermal atomic absorption spectrometry (SIMAAS), which analyze up to six elements simultaneously, improved the analytical frequency of ETAAS, reducing costs related to instrument maintenance, sample and high purity reagent consumption [9-12].

In spite of saving time and costs, multi-element 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 most frequently used chemical modifiers in electrothermal atomic absorption spectrometry (ETAAS) are solutions of palladium nitrate or magnesium nitrate or mixtures of both [13-18]. It is claimed as universal chemical modifier due to the thermal stability improvement for 21 elements [19]. These modifiers are able to thermally stabilize a number of elements, allowing a high pyrolysis temperature without loss of the analytes. These modifiers and others may be previously mixed with the sample and with the analytical solutions or separately injected into the graphite tube, either before or after the sample or the analytical solution.

Alternatively, the modifier can be present in the graphite tube as a metal coating, formed by atomic sputtering or by pipetting its solution into the tube or on a L'vov platform or by soaking the tube or platform with the modifier solution and subjecting the tube to a thermal treatment. Tubes coated with Pd, Ir, and Rh were used in the determination by ETAAS of Cd, Mn, Pb, V, and Se [20] and also determination of As and Sb [21]. Good results were obtained for As, Se, and Pb using Ir-coated tubes in electrothermal vaporization-inductively coupled plasma mass spectrometry [22]. The metal-coated tubes can be cleaned *in situ* by heating, diminishing the contamination, and the same tube can be used for several determinations without recoating. 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 [23].

The evaluation of a fast and reliable analytical method for the simultaneous determination of ultra-trace bismuth, antimony, and thallium in biological samples by SIMAAS is the aim of this work. The effectiveness of Pd+Mg mixture modifier and Ir as a permanent modifier are considered to minimize the matrix interference and increase the sensitivity.

MATERIALS AND METHODS

Apparatus

Measurements were performed with a SIMAA 6000 system (Simultaneous Multi-element Atomic Absorption Spectrometer) equipped with a longitudinal Zeeman-effect background correction, an AS-72 autosampler, an Echelle optical arrangement, and a Solid-state detector (Perkin-Elmer GmbH, Bodenseewerk, D-88647 Überlingen). A transversely heated graphite atomizer (THGA) tubes with an integrated platform were used throughout this work. The whole system was controlled by means of AA WinlabTM control software running under Microsoft WindowsTM. High-purity argon (99.998 %, Air Liquid Deutschland GmbH) was used as the purge gas. The rate of flow of the inert gas was 250 ml.min⁻¹. This flow was stopped during atomization. The lamps used were EDLs (for Bi and Sb) and HCLs (for Tl) from Perkin-Elmer and the wavelengths for each lamp were: Bi 223.1 nm, Sb 217.6 nm, Tl 276.8 nm. The integrated absorbance of the atomic absorption signal was used for the determination. The integrated absorbance of the atomic absorption signal was used for the determination.

Reagents and Solutions

All solutions were prepared with high purity de-ionized water (18.2 MΩ) obtained from a Milli-Q water purification system (Millipore GmbH, Schwalbach, Deutschland). Analytical reagent-grade HNO₃ 65% (KMF Laborchemie Handels GmbH, Lohmer, Deutschland) was purified by sub-boiling distillation. High purity standard reference solutions (1.000 g.l⁻¹) from Bernd Kraft GmbH, Duisburg-Deutschland, were used to prepare the analytical stock solutions which are kept in a refrigerator. The reference solutions for calibration and determination were prepared daily by appropriate dilution of the stock solution with 0.2% HNO₃.

The chemical modifier solutions used were Pd(NO₃)₂, Mg(NO₃)₂, and Ir. In each measurement, 20 µl sample or standard solution, 5 µl 1.000 g.l⁻¹ Pd solution, and 3 µl 1.000 g.l⁻¹ Mg(NO₃)₂ solution were injected into the graphite tube at 20°C. In the case of the multi-element determination by using a permanent modifier, the tubes were prepared by pipetting 20 µl of a 1.000 g.l⁻¹ of Ir, as chloride, and submitting the tube to the temperature program shown in Table 1 [24]. The entire procedure, that is, the pipetting and heating, was repeated 25 times.

All glassware, micropipette tips, autosampler cups, and polypropylene containers were acid washed with 10% (v/v) HNO₃ for 24 hr. and thoroughly rinsed five times with distilled water before use. All solutions and samples were daily prepared in 0.2% (v/v) HNO₃.

Table 1. Temperature Program for the Metal Coating [24]

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (ml.min ⁻¹)
1	90	5	30	250
2	140	5	30	250
3	1000	10	10	250
4	2000	0	5	0
5	20	1	10	250

Certified Reference Materials

The accuracy of the methods was confirmed by analyzing different certified reference materials. The certified reference materials were shown in Table 2.

Table 2. Certified Reference Materials

Certified Material	LOT	Source
Trace Element Urine Sample	0511545	Seronorm
Bovine Liver	NIST-SRM 1577b	National Institute of Standards and Technology
Pig Kidney	BCR-CRM 186	Institute for Reference Materials and Measurements
Tea	GBW 08505	National Research Centre for Certified Reference Materials

Trace Elements Urine Sample (Seronom 0511545)

Exactly 5 ml de-ionized water was added to the sample and let it stand for 30 min, and then transfer it to a plastic tube. The sample was then kept in a refrigerator at -20°C for later use. Before use, the sample was diluted 1:4 with 0.2% HNO₃.

Bovine Liver and Pig Kidney

The samples were digested as described by Ronald Treble [25]. Firstly, the samples were dried at 80°C for 4 hr. and stored in desiccators before use. 0.5218 g (BCR-CRM 186), and 0.5129 g (NIST-SRM 1577b) dried samples were allowed to digest in 5 ml concentrated distilled HNO₃ for a period of 72 hr. at room temperature. The digested/acidified samples were transferred into 50 ml volumetric flask and diluted to the mark with de-ionized water. Before use, each sample was diluted as required.

Tea Sample

The sample was digested as described by Yin Ming [26]. The sample firstly was dried at 80°C for 4 hr. in a clean oven and stored in desiccators before use. A sample portion of 1.0217 g was weighed into a beaker and moistened with pure water. 10 ml HNO₃ and 2 ml HClO₄ were added in sequence. After standing overnight, the sample was evaporated to nearly dry on a hotplate at 200°C. The resulting residue was treated with 0.5 ml concentrated HNO₃ and some water, and then heated gently for 5 min. till the solution turned clear. This solution was rinsed into a 50 ml volumetric flask and diluted to the mark with de-ionized water. The sample was diluted as required before use.

RESULTS AND DISCUSSION

Optimization Using Aqueous Solutions

The optimization conditions were studied using 100 ppb aqueous solution for each element in 0.2% HNO₃ without modifier, in the presence of 5 µg Pd+ 3 µg Mg as a modifier and in the presence of 500 µg iridium as permanent modifier (which was thermally deposited on the graphite tube platform).

Pyrolysis and atomization curves were carried out in order to define the compromise conditions for simultaneous determination of Bi, Sb, and Tl, since in simultaneous detection the heating program of the atomizer is the same or all analytes. The pyrolysis temperature is limited by the most volatile element, but should ideally be as high as possible in order to assurance the matrix elimination. On the other hand, the atomization temperature should be lower as possible to avoid faster graphite tube deterioration, but it is limited by the more refractory element.

Without modifier, the highest pyrolysis temperatures which can be used for these elements were: 450°C for Bi and Tl and 900°C for Sb. On the other hand, the lowest atomization temperatures were: 1300°C for Bi, 1400°C for Tl, and 1700°C for Sb. For Bismuth, bismuth oxide Bi_2O_3 (which is formed after the drying step) is reduced to a volatile suboxide at active sites on the graphite surface which is further reduced to metallic Bi upon colliding with the surface again. The volatile suboxide is responsible for metal losses during pyrolysis step [27]. Also for Thallium, Hahn *et al.* [28] investigated the effect of oxygen on the reactions of Thallium and they found the loss of Tl is due to the formation of volatile Thallium suboxide, which is formed during the reduction of thallium trioxide by carbon in the graphite furnace. For Antimony, L. Pzsonicki [29] suggested that antimony present in the solution in the form of antimonous acid and decomposed during the drying and early pyrolysis stages to oxide and successively reduced to elemental antimony that sublimes at temperatures above 500°C.

The mixture of palladium and magnesium nitrate has been widely used for simultaneous multi-element determinations by SIMAA 6000. It is claimed as universal chemical modifier due to thermal stability improvement for 21 elements [19]. The pyrolysis temperatures of these elements (Bi, Sb, and Tl) were 350-650°C higher in the presence of Pd+Mg modifier than those obtained with no modifier (800°C for Tl, 1100°C for Bi, and 1300°C for Sb). The stabilizing effect of this modifier on these elements, which results from the formation of a chemical compound or of an inter-metallic phase and/or from an imbedding effect, is not limited to the pyrolysis step but also increases the atomization temperature (1600°C for Tl, 1800°C for Bi, and 1900°C for Sb). At higher atomization temperatures, the diffusion losses of these elements are higher so that lower integrated absorbances are obtained.

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. Higher pyrolysis temperatures; compared to that with Pd+Mg modifier, can be used (1000°C for Tl, 1200°C for Bi, and 1500°C for Sb). Also, higher atomization temperatures, especially for Sb, are required (1600°C for Tl, 1900°C for Bi, and 2100°C for Sb) and this means more stabilization effect with this modifier will be obtained. Broad absorbance, compared with Pd+Mg modifier, for Sb has been observed. At the same time, there are decreases in the sensitivity for these elements which can be a result from the higher atomization temperature that have been used with this modifier comparing with the other modifier (Pd+Mg modifier). The optimum pyrolysis and atomization temperatures have been used to determine the characteristic masses and detection limits and the results are shown in Table 3.

Table 3. The Characteristic mass and Detection Limits with different Modifiers

Element	LOD ($\mu\text{g}\cdot\text{l}^{-1}$)				Characteristic mass (pg)			
	Single-Element		Multi-Element		Single-Element		Multi-Element	
	Pd+Mg	Ir	Pd+Mg*	Ir**	Pd+Mg	Ir	Pd+Mg*	Ir**
Bi	0.46	0.50	0.75	1.50	67.7	73.3	73.3	73.3
Sb	0.29	0.63	0.71	1.06	41.9	46.3	41.9	51.8
Tl	0.86	0.43	1.40	1.25	62.9	62.9	67.7	73.3

* At 800°C pyrolysis and 1900°C atomization temperatures

** At 1000°C pyrolysis and 2000°C atomization temperatures

Study the Effect of Urine Sample on the Multi-Element Determination

In our work, we have used standard reference urine sample from Seronorm (LOT 0511545) to study the effect of the matrix on the pyrolysis and atomization curves of the simultaneous multi-element determination of these elements. Since the concentrations of most elements in the reference material were high, we have diluted it (1:4), which has also reduced the concentration of the interferences. The resulting temperature program has been used to evaluate the concentrations of the elements in different types of reference materials.

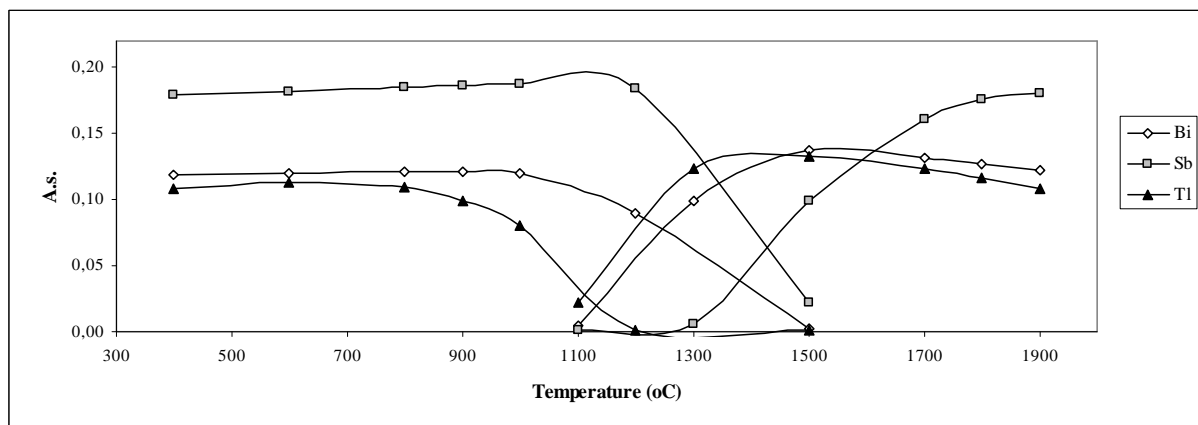


Fig. 1. Pyrolysis and atomization curves of Bi, Sb, and Tl in diluted urine sample with Pd+Mg modifier

With Pd+Mg Modifier

The diluted reference material (1:4) has been spiked with 80 ppb Bi, 80 ppb Sb, and 80 ppb Tl. 20 μ l diluted spiked reference material has been injected with 5 μ g Pd + 3 μ g Mg(NO₃)₂ as a modifier into the atomizer each time during this study. The dependence of Bi, Sb, and Tl absorbance on the pyrolysis temperature and atomization temperature was studied and shown in Fig 1. Pyrolysis temperature was tested between 400 and 1500 °C with a constant atomization temperature of 1900 °C.

For Tl and Bi, the atomic signal was almost constant till 800°C and 1100°C, respectively, then started gradually to decrease. For Sb, the atomic absorption remained almost constant until 1200°C and then gradually decreased. In order to determine all three elements simultaneously, 800°C was chosen as an optimum pyrolysis temperature. Atomization temperatures were studied from 1100 to 1900 °C at a constant pyrolysis of 800°C. For Bi, had its maximum at atomization temperature between 1500-1600°C and then started to decrease gradually. Tl atomic absorption signal had its maximum between 1400-1500°C. For Sb, the atomic absorption signal increased with increasing atomization temperature and had its maximum at 1900°C. By taking into account the atomic signal, 1900°C was chosen as an optimum atomization temperature for the simultaneous determination of the elements. The absorption peaks of the elements at the optimum pyrolysis and atomization temperatures are shown in Figure 2.

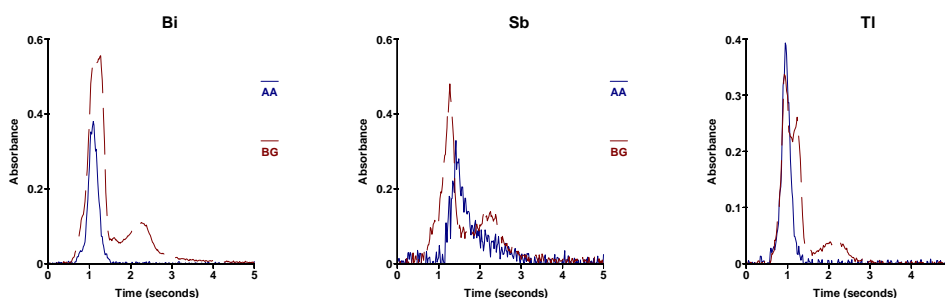


Fig. 2. Peak signals for multi-element determination in diluted urine sample with Pd+Mg modifier

With Ir-Permanent Modifier

The 500 μ g iridium was thermally deposited on the graphite tube platform and used as permanent modifier. The diluted reference material (1:4) has been spiked with 80 ppb Bi, 80 ppb Sb, and 80 ppb Tl. 20 μ l diluted spiked reference material has been injected into the atomizer each time during this study. The dependence of Bi, Sb, and Tl absorbance on the pyrolysis temperature and atomization temperature was studied and shown in Fig 3. Pyrolysis temperature was tested between 250 and 1400 °C with a constant atomization temperature of 1900 °C. For Tl and Bi, the atomic signal was almost constant till 400°C and 800°C, respectively, then started gradually to decrease. For Sb, the atomic absorption remained almost constant until 1300°C and then gradually decreased. In order to determine all three elements simultaneously, 400°C was chosen as an optimum pyrolysis temperature. Atomization temperatures

were studied from 1000 to 1900 °C at a constant pyrolysis of 400°C. For Bi, had its maximum at atomization temperature between 1400-1500°C and then started to decrease gradually. Tl atomic absorption signal had its maximum between 1300-1500°C. For Sb, the atomic absorption signal increased with increasing atomization temperature and had its maximum at 1800°C. By taking into account the atomic signal, 1800°C was chosen as an optimum atomization temperature for the simultaneous determination of the elements. The absorption peaks of the elements at the optimum pyrolysis and atomization temperatures are shown in Figure 4.

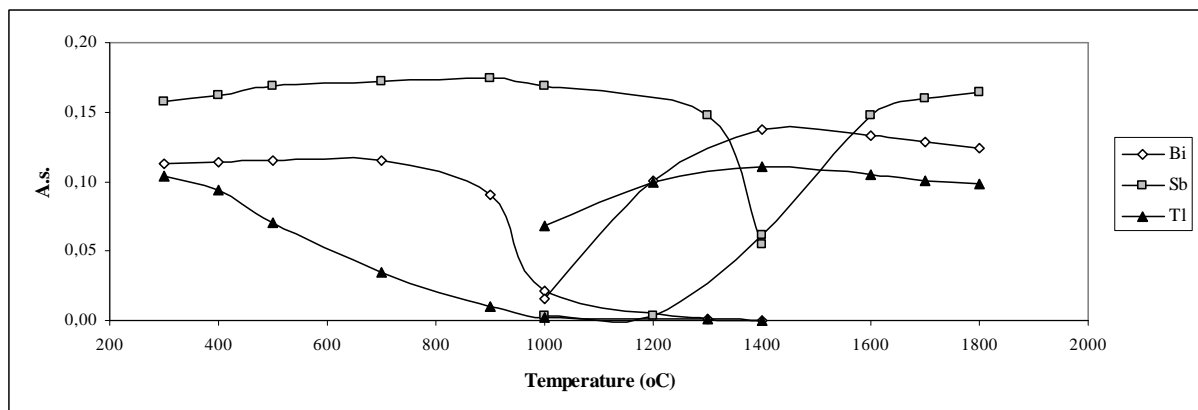


Fig. 3. Pyrolysis and atomization curves of Bi, Sb, and Tl in diluted urine sample with Ir modifier

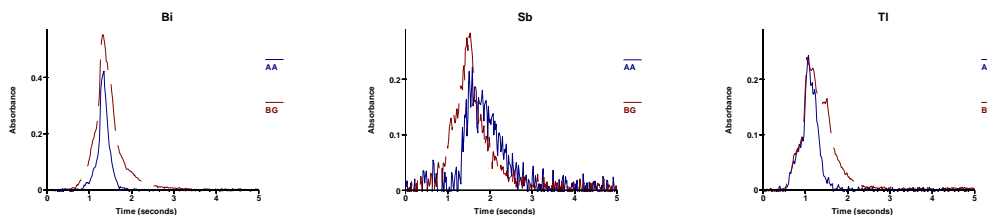


Fig. 4. Peak signals for multi-element determination in diluted urine sample with Ir modifier

Analysis of Certified Reference Materials

Number of certified reference materials was used to test the simultaneous determination methodologies that we have developed. The optimum pyrolysis and atomization temperatures that have been developed using urine matrix were used to analyze the reference materials. The standard addition curves were used to analyze the reference materials. The peak area of the atomic absorption signal was used for the determination and each experimental value is the average of five determinations. Detection limits were calculated as three times the standard deviation of ten replicate measurements of the blank.

Trace Element Urine Sample from Seronorm (0511545)

We have used two types of modifiers; the mixture of Pd and Mg and Ir as a permanent modifier, in the multi-element determination of bismuth, Lead, and thallium in the urine sample from Seronorm. The sample was diluted (1:4, v/v) with 0.2% HNO₃ and 20µl of the sample was injected for each measurement. 5µl of 1.00 g.l⁻¹ Pd and 3µl 1.00 g.l⁻¹ Mg(NO₃)₂ were injected also with the sample into the graphite tube. In the case of the permanent modifier, the Ir was deposited into the graphite tube in a separate step.

With Pd+Mg modifier

The standard addition curves with good linearity ($R^2 = 0.9994, 0.9996, \text{ and } 0.9991$ for Bi, Sb, and Tl, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 4. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 101.5, 95.5, and 111.2 % for Bi, Sb, and Tl, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

With Ir permanent modifier

The standard addition curves with good linearity ($R^2 = 0.9998, 0.9994, \text{ and } 0.9998$ for Bi, Sb, and Tl, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 4. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 109.5, 110.1, and 122.0 % for Bi, Sb, and Tl, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

Bovine Liver from National Institute of Standards and Technology (NIST-SRM 1577b)

The sample was diluted (1:100, v/v) with 0.2% HNO_3 . For each measurement, 20 μl of the diluted sample, 5 μl of 1.00 g.l^{-1} $\text{Pd}(\text{NO}_3)_2$ and 3 μl of 1.00 g.l^{-1} $\text{Mg}(\text{NO}_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified value for bismuth and thallium and the amount of antimony was below the detection limits; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity ($R^2 = 0.9996, 0.9998, \text{ and } 0.9999$ for Bi, Sb, and Tl, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified values in Table 4. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 100.9, 100.0, and 103.1 % for Bi, Sb, and Tl, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

Table 4. The results of simultaneous determination of Bi, Sb, and Tl in different certified materials

Sample		Bi	Sb	Tl
Seronorm With Pd+Mg modifier	Con. Found ($\mu\text{g l}^{-1}$)	20.4	95.4	10.3
	Con. Certified ($\mu\text{g l}^{-1}$)	20.1	99.9	9.26
	DL ($\mu\text{g l}^{-1}$)	1.07	1.25	1.31
	CM (pg)	62.9	73.3	55
	% RSD**	8.2	3.6	9.3
Seronorm With Ir modifier	Con. Found ($\mu\text{g l}^{-1}$)	22.0	110.0	11.3
	Con. Certified ($\mu\text{g l}^{-1}$)	20.1	99.9	9.26
	DL ($\mu\text{g l}^{-1}$)	1.8	1.9	1.25
	CM (pg)	88	62.9	73.3
	% RSD**	14.4	9.1	14.9
Bovine Liver NIST 1577b	Con. Found ($\mu\text{g l}^{-1}$)	50.5	50.0	51.5
	Con. Certified ($\mu\text{g l}^{-1}$)	50*	50*	50*
	DL ($\mu\text{g l}^{-1}$)	0.82	0.86	1.62
	CM (pg)	80	41.9	67.7
	% RSD**	5.5	2.6	4.3
Pig Kidney BCR 186	Con. Found ($\mu\text{g l}^{-1}$)	14.57	14.54	14.22
	Con. Certified ($\mu\text{g l}^{-1}$)	14.50*	14.50*	14.50*
	DL ($\mu\text{g l}^{-1}$)	0.82	1.00	1.75
	CM (pg)	80	48.9	73.3
	% RSD**	4.5	3.4	8.8
Tea GBW 8505	Con. Found ($\mu\text{g l}^{-1}$)	2.66	2.40	2.50
	Con. Certified ($\mu\text{g l}^{-1}$)	2.50*	2.50*	2.50*
	DL ($\mu\text{g l}^{-1}$)	1.50	1.50	12.00
	CM (pg)	110.0	62.9	440
	% RSD**	10.60	13.10	68.20

* Added

** For five replicates

Pig Kidney from Institute for Reference Materials and Measurements (BCR-CRM 186)

The sample was diluted (1:30, v/v) with 0.2% HNO₃. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 g.l⁻¹ Pd(NO₃)₂ and 3 µl of 1.00 g.l⁻¹ Mg(NO₂)₃ modifier solution were injected into the graphite tube at 20°C. No certified values for bismuth, antimony, and thallium; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity ($R^2 = 0.9997, 0.9998, \text{ and } 0.9996$ for Bi, Sb, and Tl, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified values in Table 4. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 100.5, 100.3, and 98.0 % for Bi, Sb, and Tl, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

Tea sample from National Research Centre for Certified Reference Materials (GBW 08505)

The sample was diluted (about 1:5, v/v) with 0.2% HNO₃. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 g.l⁻¹ Pd(NO₃)₂ and 3 µl of 1.00 g.l⁻¹ Mg(NO₂)₃ modifier solution were injected into the graphite tube at 20°C. No certified values for bismuth, antimony, and thallium; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity ($R^2 = 0.9999, 0.9994, \text{ and } 0.9995$ for Bi, Sb, and Tl, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 4. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 102.6, 95.8, and 100.0 % for Bi, Sb, and Tl, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

CONCLUSION

Simultaneous Multi-Element Atomic Absorption Spectrometer (SIMAA 6000) can be used to determine groups of elements (up to six) simultaneously, by using 2-operating and 4-operating modes, if the temperature program has been carefully optimized taking into account all analytes to be determined. A universal powerful matrix modifier should be used in order to increase the stability of the elements (especially the volatile elements). All tested chemical modifiers increased the thermal stability of the elements. The Pd+Mg mixture modifier stabilizes the high and mid volatile elements. Ir coating of the tube or platform extend significantly the tube lifetime. Also, Ir coating is not time-consuming and so the proposed methodology is a useful analytical tool for routine analysis. The detection limits values of the multi-element determination were higher than those of the single-element which is mainly as a result of decreasing the lamp intensities in the multi-element mode compared to the single-element mode. Another effect which could cause the higher detection limits is the use of higher atomization temperature.

REFERENCES

- [1] J. Savory and M. R. Wills, *Clin. Chem.*, **1992**, 38, 1565
- [2] K. Elsherif and M-H Kuss, *Der Chim. Sin.*, **2012**, 3, 727
- [3] Abdul Jameel A., Sirajudeen J. and Mohamed Mubashir M. M., *Der Chem. Sin.*, **2012**, 3, 210
- [4] Ameh E. G and Akpah, F.A, *Adv. in App. Sci. Res.*, **2011**, 2 , 33
- [5] Ogbonna O, Jimoh W.L, Awagu E. F. and Bamishaiye E.L., *Adv. in App. Sci. Res.*, **2011**, 2 , 62
- [6] Indrajit Sen, Ajay Shandil and Shrivastava V. S., *Adv. in App. Sci. Res.*, **2011**, 2 , 161
- [7] D. L. Tsalev, *J. Anal. At. Spectrom.*, **1993**, 9, 405
- [8] G. Komarmoy-Hiller, *Anal. Chem.*, **1999**, 71, 338R
- [9] J. Sneddon, B. D. Farah, and K. S. Farah, *Microchem. J.*, **1993**, 48, 318
- [10] K. S. Farah and J. Sneddon, *App. Spectrosc. Rev.*, **1995**, 30, 351
- [11] B. Radziuk, G. Rodel, H. Stenz, H. Becker-Ross, and S. J. Florek, *J. Anal. At. Spectrom.*, **1995**, 10, 127
- [12] P. R. Correia, E. Oliveira, and P. V. Oliveira, *Anal. Chim. Acta*, **2002**, 458, 321
- [13] Correia, P. R. M.; Oliveira, E.; Oliveira, P. V.; *Talanta* **2002**, 57, 527.
- [14] A. Filho, V. R.; Fernandes, K. G.; Moraes, M.; Neto, J. A G.; *Atom. Spectros.* **2002**, 23, 7.
- [15] Oliveira, A P.; Moraes, M.; Neto, J. A G.; Lima, E. C.; *Atom. Spectros.* **2002**, 23, 39.
- [16] Fernandes, K. G.; Moraes, M.; Neto, J. A G.; Nóbrega, J. A.; *Analyst* **2002**, 127, 157.
- [17] Thomaidis, N. S.; Manalis, N.; Viras, L.; Lekkas, T. D.; *Int. J. Environ. Anal. Chem.* **2001**, 79, 121.

- [18] Feuerstein M.; Schlemmer, G.; *Atom. Spectros.* **1999**, 20, 149.
- [19] Welz, B.; Schelemmer, G.; Mudakavi, J. R.; *J. Anal. Atom. Spectrom.* **1992**, 7, 1257
- [20] Radameyer, C.; Radziuk, B.; Romanova, N.; Skaugset, N. P.; Skogstad, A.; Thomassen, Y. *J. Anal. At. Spectrom.*, 1995, **10**, 739.
- [21] Bulska, E.; Jedral, W. *J. Anal. At. Spectrom.*, 1995, **10**, 49.
- [22] Pozebon, D.; Dressler, V. L.; Curtius, A. J. *J. Anal. At. Spectrom.*, 1998, **13**, 7
- [23] Lima, E. C.; Krug, F. J.; Jackson, K.W.; *Spectrochim. Acta* **1998**, 53B, 1791.
- [24] D. L. Styrus, L. J. Prell, and D. A. Redfield, *Analytical Chemistry*, 63(**1991**), 508
- [25] R. G. Treble, T. S. Thompson, and H. R. Lynch, *BioMetals*, 11(**1998**), 49
- [26] Yin Ming and Li Bing, *Spectrochimica Acta*, 53B(**1998**), 1447
- [27] M-V German, H. Lothar, M. Hans, W. Wolfgang, and J-R Dimitri, *J. Anal. Atom. Spectrom.*, **1995**, 10, 777-783
- [28] L. Hahn, G. Müller-Vogt, and W. Wendel, *J. Anal. Atom. Spectrom.*, **1993**, 8, 223
- [29] L. Psonicki and J. Dudek, *J. Anal. Atom. Spectrom.*, **1999**, 14, 1755-1760