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Direct and Simultaneous Determination of Bismuth, Antimony, and Lead in Biological samples by Multi-Element Electrothermal Atomic Absorption Spectrometer

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ABSTRACT

Direct and simultaneous determinations of Bi, Sb, and Pb in different biological samples using a multi-element electrothermal atomic absorption spectrometer (Perkin-Elmer SIMAA 6000) are described. Two kinds of modifiers; $Pd(NO_3)_2 + Mg(NO_3)_2$ 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 1000 and 1900^{o}C and using permanent modifier were 700 and 1800^{o}C. The detection limits were 0.75-1.71 µg.l^{-1} for Bi, 0.86-1.85 µg.l^{-1} for Sb, and 0.50-0.82 µg.l^{-1} for Pb. The Characteristic masses were 67.7-125.7 pg for Bi, 46.3-67.7 pg for Sb, and 48.9-80.0 pg for Pb. A standard reference material (Seronorm 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 Seronorm 05115459), Bovine Liver (from NIST 1577b), Pig Kidney (from BCR 186), and Pork Liver (from GBW 08551). A standard additions method was used to determine Bi, Sb, and Pb 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, Lead.

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 [1-5].

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. As a result of these efforts, the simultaneous atomic absorption spectrometry (SIMAAS) technique was proposed [6-8] and commercially introduced. 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 residue generation are almost reduced in 50 %, while the analytical frequency and the analytical results obtained with the same graphite tube are almost duplicated. SIMAAS has been used for various multi-element determinations with acceptable performance [9-22], keeping the main features of ETAAS

The mixture palladium and magnesium nitrate has been widely used for multi-element determinations by SIMAAS [9-15,19,21,22] It is claimed as universal chemical modifier due to the thermal stability improvement for 21 elements [23]. 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 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 [24].

The development and evaluation of; a fast, reliable, and comparable (in terms of detection limits and sensitivity) to the single-element analytical methodology for the simultaneous multi-element determination of Bi, Sb, and Pb in biological samples by SIMAA 6000 instrument is the aim of this work.

MATERIALS AND METHODS

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 Winlab^{TM} control software running under Microsoft Windows^{TM}. 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 from Perkin-Elmer for Bi and Sb and HCLs from Perkin-Elmer for Pb and the wavelengths for each lamp were: Bi 223.1 nm, Sb 217.6 nm, Pb 283.3 nm. The integrated absorbance of the atomic absorption signal was used for the determination.

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 HNO_3 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% HNO_3. The chemical modifier solutions used were $Pd(NO_3)_2$, $Mg(NO_3)_2$, 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} $Mg(NO_3)_2$ solution were injected into the graphite tube at 20^{o}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 [25]. 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) HNO_3 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) HNO_3.

Table 1. Temperature Program for the Metal Coating

Step	Temperature (^{o}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

The accuracy of the methods was confirmed by analyzing different certified reference materials. Samples preparation is a very important step in GFAAS [26], therefore it has been discussed for each certified material.

Trace Elements Urine Sample (Seronorm 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^{o}C for later use. Before use, the sample was diluted 1:4 with 0.2% HNO_3.

Lyphocheck Urine Metals Control–Level 1 from BIO-RAD (69061)

The same procedure was applied as Seronorm sample except that, 25 ml de-ionized water was added and the sample was diluted 1:1 before use.

Bovine Liver, Pig Kidney, and Pork Liver

The samples were digested as described by Ronald Treble [27]. Firstly, the samples were dried at 80°C for 4 hr. and stored in desiccators before use. 0.5069 g (GBW 08551), 0.5218 g (BCR-CRM 186), and 0.5129 g (NIST-SRM 1577b) dried samples were allowed to digest in 5 ml concentrated distilled HNO_3 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 [28]. 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 HNO_3 and 2 ml $HClO_4$ 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 HNO_3 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

Single-Element Mode

Without modifier

The highest pyrolysis temperatures which can be used for this group were as follows: 450, 550, and 900°C for Bi, Pb, and Sb respectively. For Bi, 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 [29].

Lead is also a volatile element. After the drying step, PbO is formed as a decomposition of the lead nitrate or hydrolysis of the chloride. Pb atoms are formed from the reduction of PbO which is favourable at 1040 K [30]. Double peak has been observed for Pb. Double peaks for Pb and other relatively volatile metals, such as Cd and Zn, have been reported for a variety of sample types and atomizer designs [31-35]. Several researchers have studied the Pb system and have offered some theoretical models for the production of double peaks. McLaren and Weeler [32] proposed that the two peaks observed for Pb result from the formation of the massicot and litharge dimorphic of PbO on the atomizer surface. It is assumed that these two dimorphic forms of PbO can be formed on the surface of the atomizer during the pyrolysis step and that this is the cause of the double peaks that occur for Pb. Both Fuller [36] and Regan and Warren [33] have reported that the condition of the graphite surface has an affect on the extent to which interferences are observed. The implication is that two distinct release mechanisms lead to the two peaks observed for Pb and that the condition of the graphite surface, i.e., whether the furnace is new or old, determines the extent to which either mechanism occurs. Holcombe et al. [35] have concluded that the presence of O_2 in a graphite atomizer can have a profound effect on the atomizer surface, which in turn changes the release mechanism for Pb. It has been suggested that the formation of atomic vapour of the analyte is often preceded by the reduction of the metal oxide by the graphite surface. Two major types of active sites on graphite provide different mechanisms for PbO reduction and Pb vaporization. Deactivation of these sites by the chemisorptions of O_2 causes a shift to the secondary release mechanism. The two release mechanisms account for the double peaks and appearance temperature shifts which are observed for Pb.

Sb is thermally stable up to 500°C and above this temperature the absorption signal starts to decrease gradually with increasing temperature. L. Pszonicki [37] 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 lowest atomization temperatures were: 1300, 1400, and 1700°C for Bi, Pb, and Sb respectively

Table 2. Pyrolysis and atomization temperatures in the single-element determinations

Element	Pyrolysis Temperature (°C)			Atomization Temperature (°C)		
	Without	Pd+Mg	Ir	Without	Pd+Mg	Ir
Bi	450	1100	1200	1300	1800	1900
Pb	550	1000	1200	1400	1900	1900
Sb	900	1300	1500	1700	1900	2100

With modifier

As the difference in the thermal stability is increased, as the difficulty to find compromised conditions between these elements is increased. The use of matrix modification increases the stability of the volatile element which permits the use of higher pyrolysis and atomization temperatures. This will lead to a common temperature program for a wide variety of elements.

With $Pd(NO_3)_2 + Mg(NO_3)_2$ *Modifier*

A comparison was made between the maximum pyrolysis temperatures for thermal pre-treatment without loss of elements in the absence of chemical modifier or in the presence of Pd-Mg (5 µg Pd + 3 µg Mg) modifier. The results are given in Table 2.

The pyrolysis temperature of the volatile elements Bi, Pb, and Sb were 400-650°C higher in the presence of Pd+Mg modifier than those obtained with no modifier which are similar to those reported by Welz et al. [38]. 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. At higher atomization temperatures, the diffusion losses of these elements are higher so that lower integrated absorbances are obtained [37]

The optimized pyrolysis and atomization temperatures in the presence of this modifier have been used to determine the characteristic masses and detection limits for the elements. The results are shown in the Table 3. The detection limits were calculated as three times the standard deviation of ten replicate measurements of each blank.

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

Element	LOD (µg.l^{-1})				Characteristic mass (pg)			
	Single		Multi		Single		Multi	
	Pd+Mg	Ir	Pd+Mg	Ir	Pd+Mg	Ir	Pd+Mg	Ir
Bi	0.46	0.50	0.82	1.25	67.7	73.3	80	73.3
Sb	0.29	0.63	0.75	0.94	41.9	46.3	44.0	55.0
Pb	0.32	0.17	0.50	0.53	46.3	48.9	48.9	51.8

With Ir-permanent Modifier

Iridium is rather a refractory element with high melting (2410°C) and boiling (4527°C) points. These temperatures are significantly higher than the corresponding figures for palladium usually employed as universal chemical modifier (1552 and 2927°C) [38]. Tsalev et al. [40] have found that during a simulated clean-out step, Ir losses start at temperatures higher than 2200°C. Therefore, Ir absorbance signals were much more strongly depressed on pyrolytically coated platforms than were those of Pd. This means that Ir is better retained on the graphite surface, making it a promising permanent modifier.

In this work, the tube was coated with 500 µg Ir by pipetting 20 µl of a 1.000 g.l^{-1} solution of Ir, as chloride, and submitting the tube to the temperature program shown in Table 1. The entire procedure was repeated 25 times.

The optimum pyrolysis and atomization temperatures obtained from pyrolysis and atomization curves for these elements are listed in Table 2. For, Bi, Pb, and Sb higher pyrolysis temperatures; compared to that with Pd+Mg modifier, can be used. Also, higher atomization temperatures, especially for Sb, are required 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). At higher atomization temperatures, diffusion losses of elements are higher so that lower integrated absorbances are obtained; hence, the m_o values are higher than those obtained with The 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.

Multi-Element Determinations

As in any multi-element technique, SIMAAS requires compromised conditions, e.g., chemical modifier, pyrolysis and atomization temperatures, which can lead to significant sensitivity deterioration. In spite of instrumental advancements and the use of STPF conditions, the majority of the multi-element methods performed by SIMAAS are limited for few elements due to the difficulties to find out a more universal set of adjustments for the experimental and instrumental parameters. Even so, for 2-element operating mode, the time, reagent, and sample consumption are significantly reduced.

With Pd+Mg Modifier

The dependence of Bi, Sb, and Cd absorbance on the pyrolysis temperature at 1900°C atomization temperature was studied. The pyrolysis and atomization curves were made using the following concentrations: 100 ppb Bi, 100 ppb

Sb and 40 ppb Pb in 0.2% HNO_3 in the presence of 5µg Pd and 3µg Mg as a modifier. In order to determine all three elements simultaneously, 1000^{o}C was chosen as an optimum pyrolysis temperature. Similarly, the effects of atomization temperature on the atomic absorbance are studied. The effect of the atomization temperature was studied at the pyrolysis of 1000^{o}C. 1900^{o}C has been chosen as the optimum atomization temperature for all three elements. This optimized temperature program has been used to determine the characteristic masses and detection limits for these elements in the multi-element mode .These values are compared with those in the single-element mode and shown in Table 3.

With Ir Permanent Modifier
The thermal behaviour of the elements was evaluated using pyrolysis and atomization curves of 100 ppb Bi, 100 ppb Sb, and 40 ppb Pb obtained in the presence of 500µg iridium which is thermally deposited on the graphite tube platform. The pyrolysis and atomization curves obtained for each element are presented. The effect of pyrolysis temperature on the atomic absorption was studied at atomization temperature of 2000^{o}C. A pyrolysis temperature of 1200^{o}C was selected for the simultaneous determination of Bi, Sb, and Pb. The effect of atomization temperature was studied at pyrolysis temperature of 1200^{o}C. An atomization of 2000^{o}C was chosen as the optimum for the simultaneous determination of these elements. The values of characteristic masses and detection limits in the multi-element mode compared with single-element mode are presented in Table 3.

The Effect of the Urine Matrix 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 our 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.

With 5µg Pd + 3µg Mg modifier
The diluted reference material (1:4) has been spiked with 80 ppb Bi, 80 ppb Sb, and 40 ppb Pb. 20 µl diluted spiked reference material has been injected with 5µg Pd + 3µg $Mg(NO_3)_2$ as a modifier into the atomizer each time during this study. The dependence of Bi, Sb, and Pb absorbance on the pyrolysis temperature at 1900^{o}C atomization temperature was studied and shown in Figure 1. The atomic signal for Pb and Bi remained approximately constant till the pyrolysis temperature reached 1000^{o}C and then started to decrease. For Sb, the atomic signal was almost constant till 1300^{o}C then started gradually to decrease. In order to determine all three elements simultaneously, 1000^{o}C was chosen as an optimum pyrolysis temperature. Similarly, the effects of atomization temperature on the atomic absorbance are studied and shown in Figure 1. The effect of the atomization temperature was studied at the pyrolysis of 1000^{o}C. For Bi, the atomic absorption signal increased with increasing the temperature as the atomization temperature varied from 1100-1500^{o}C and then started to decrease gradually due to increased diffusional losses of analyte atoms under high atomization temperatures. For Pb, the atomic absorption signal increased with increasing atomization temperature and had its maximum at atomization temperature between 1400-1600^{o}C and then started to decrease. Sb atomic absorption signal had its maximum at approximately 1900^{o}C atomization temperature. By taking into account the atomic signal, 1900^{o}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.

With Ir Permanent Modifier
The 500µg 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 40 ppb Pb. 20 µl diluted spiked reference material has been injected into the atomizer each time during this study. The dependence of Bi, Sb, and Pb absorbance on the pyrolysis temperature at 1900^{o}C atomization temperature was studied and shown in Figure 3. The atomic signal for Pb remained approximately constant till the pyrolysis temperature reached 700^{o}C and then decreased rapidly. For Bi and Sb, the atomic signal was almost constant till 800^{o}C and 1200^{o}C, respectively, then started gradually to decrease. A decreased in the pyrolysis temperature comparing with the determination of these elements in the aqueous solution (1200, 1200 and 1500^{o}C for Pb, Bi, and Sb, respectively) can be seen. C. G. Magalhães et al. [41] found that with iridium applied in solution together with the urine sample, the best pyrolysis temperature was 900^{o}C but the sensitivity was analogous with that obtained using Pd+Mg modifier. They [41] found also that with Ir+Rh permanent modifier that the best pyrolysis temperature was 900^{o}C. Using W+Rh permanent modifier, Oliveira et al. [42] reported 400^{o}C as the best pyrolysis temperature for the determination of Cd in urine sample. E. Bulska et al. [43] determined Sb in biological samples using different types of modifiers and fond that iridium stabilized antimony to higher temperature when compared with palladium, but significant decrease in absorbance value of 23% was observed. In order to determine all three elements simultaneously, 700^{o}C was chosen as an optimum pyrolysis temperature. The effect of the atomization temperature was studied at the pyrolysis of

700°C. For Bi, the analytical atomic absorption was high at 1300°C and the signal peak was too broad. Above 1300°C the signal peak start to become sharper and the integrated absorbance value to decrease gradually. For Pb, the atomic absorption signal increased with increasing atomization temperature and had its maximum at atomization temperature between 1500-1700°C and then started to decrease. Sb atomic absorption signal had its maximum at approximately 1800°C atomization temperature. For the simultaneous determination of the elements, 1800°C was chosen as an optimum atomization temperature. The signal absorption peaks at the optimum pyrolysis and atomization temperatures are shown in Figure 4.

Figure 1. Pyrolysis and atomization curves for multi-element determinations using Pd + Mg modifier in spiked diluted urine sample

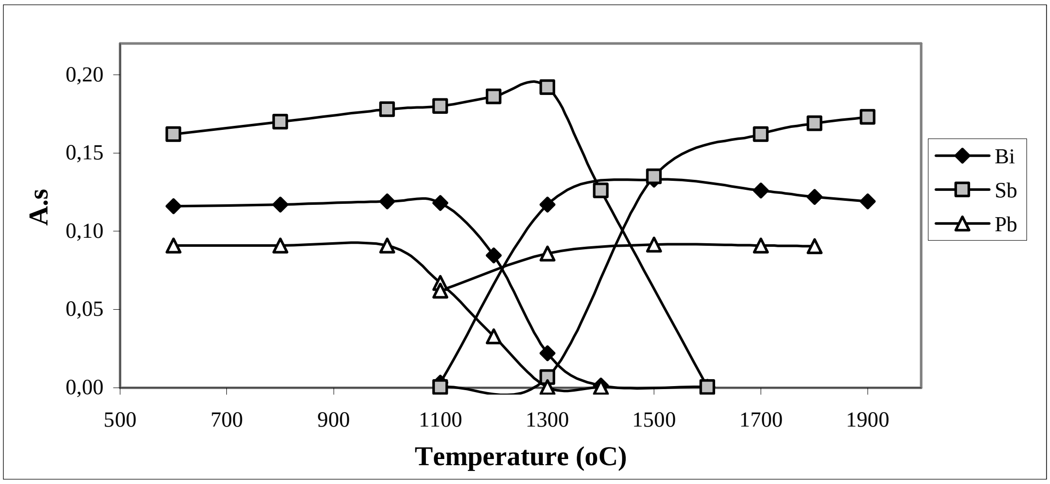
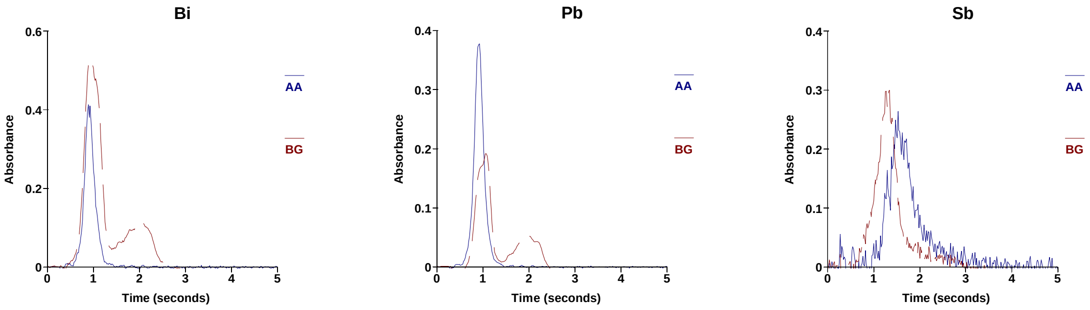


Figure 2. Absorbance signals of diluted spiked urine sample at 1000°C pyrolysis and 1900°C atomization with Pd + Mg modifier in multi-element determinations



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 antimony in the urine sample from Seronorm. The sample was diluted (1:4, v/v) with 0.2% HNO_3 and 20µl of the sample was injected for each measurement. 5µl of 1.00 $g.l^{-1}$ Pd and 3µl 1.00 $g.l^{-1}$ $Mg(NO_3)_2$ 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.

Figure 3. Pyrolysis and atomization curves for multi-element determinations using Ir permanent modifier in spiked diluted urine sample

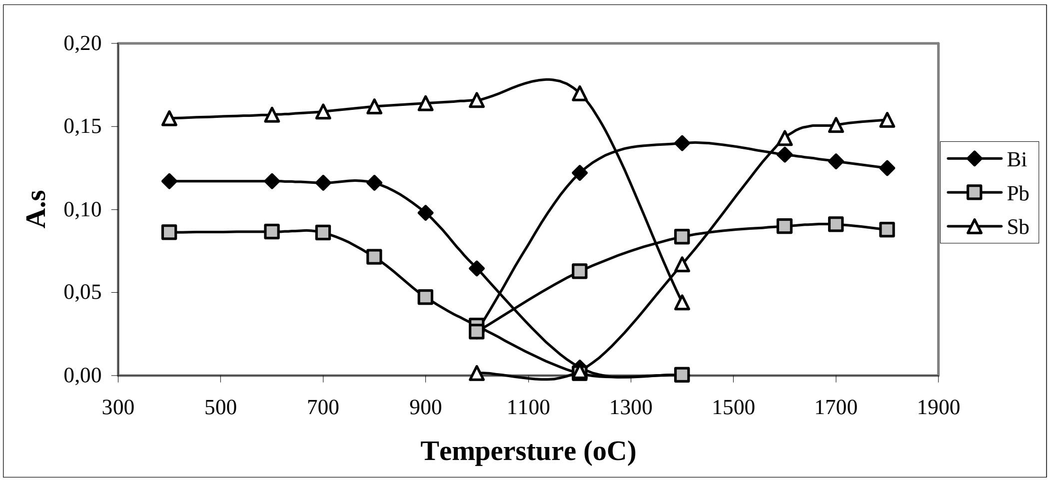
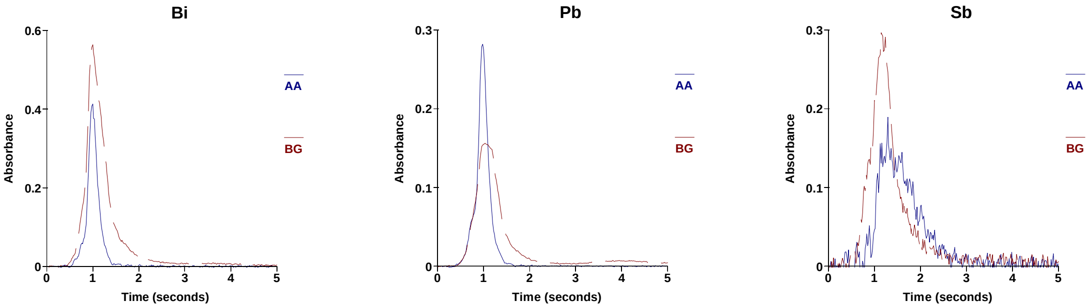


Figure 4. Absorbance signals of diluted spiked urine sample at 700°C pyrolysis and 1800°C atomization with Ir permanent modifier in multi-element determinations



With Pd+Mg modifier
The standard addition curves with good linearity (R^2 = 0.9977, 0.9989, and 0.9998 for Bi, Sb, and Pb, 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 98.6, 104.4, and 103.7 % for Bi, Sb, and Pb, 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 = 0.9999, 0.9997, and 0.9996 for Bi, Sb, and Pb, 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 110.4, 101.3, and 99.3 % for Bi, Sb, and Pb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

Lyphocheck Urine Metals Control–Level 1 from BIO-RAD (69061)
The sample was diluted (1:1, v/v) with 0.2% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 $g.l^{-1}$ $Pd(NO_3)_2$ and 3 µl of 1.00 $g.l^{-1}$ $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified value for bismuth; therefore, the sample has spiked with bismuth before the dilution.

The standard addition curves with good linearity (R^2 = 0.9999, 0.9999, and 0.9999 for Bi, Sb, and Pb, 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 101.7, 100.0, and 100.7 % for Bi, Sb, and Pb, 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 used without dilution. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 g.l^{-1} $Pd(NO_3)_2$ and 3 µl of 1.00 g.l^{-1} $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20^{o}C. No certified value for bismuth 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, and 0.9997 for Bi, Sb, and Pb, 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 106.0, 102.0, and 113.6 % for Bi, Sb, and Pb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

Pig Kidney from Institute for Reference Materials and Measurements (BCR-CRM 186)
The sample was used without dilution. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 g.l^{-1} $Pd(NO_3)_2$ and 3 µl of 1.00 g.l^{-1} $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20^{o}C. No certified values for bismuth and antimony; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9996, 0.9998, and 0.9998 for Bi, Sb, and Pb, 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 103.0, 101.3, and 113.2 % for Bi, Sb, and Pb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 4.

Pork Liver from National Research Centre for Certified Reference Materials (GBW 08551)
The sample was diluted (about 1:4, v/v) with 0.2% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 g.l^{-1} $Pd(NO_3)_2$ and 3 µl of 1.00 g.l^{-1} $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20^{o}C. No certified values for bismuth and antimony; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9997, 0.9999, and 0.9998 for Bi, Sb, and Pb, respectively) were used to determine 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 102.8, 103.8, and 101.6 % for Bi, Sb, and Pb, 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% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 g.l^{-1} $Pd(NO_3)_2$ and 3 µl of 1.00 g.l^{-1} $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20^{o}C. No certified values for bismuth and antimony; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9996, 0.9994, and 0.9999 for Bi, Sb, and Pb, 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 101.4, 98.4, and 94.6 % for Bi, Sb, and Se, 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.

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

Sample		Bi	Sb	Pb
Seronorm With Pd+Mg modifier	Con. Found (µg l^{-1})	20.8	104.3	41.8
	Con. Certified (µg l^{-1})	20.1	99.9	40.3
	DL (µg l^{-1})	0.92	1.07	0.53
	CM (pg)	67.7	62.9	51.8
	% RSD**	13.3	4.5	2.1
Seronorm With Ir modifier	Con. Found (µg l^{-1})	22.2	101.2	40.0
	Con. Certified (µg l^{-1})	20.1	99.9	40.3
	DL (µg l^{-1})	1.33	1.85	0.67
	CM (pg)	97.8	67.7	48.9
	% RSD**	17.9	6.4	8.7
Bio-Rad	Con. Found (µg l^{-1})	12.2	16.4	14.5
	Con. Certified (µg l^{-1})	12*	16.4	14.4
	DL (µg l^{-1})	0.75	0.86	0.60
	CM (pg)	73.3	62.9	58.7
	% RSD	6.7	4.1	2.6
Bovine Liver NIST 1577b	Con. Found (µg l^{-1})	10.6	10.2	1.5
	Con. Certified (µg l^{-1})	10*	10*	1.32
	DL (µg l^{-1})	1.00	1.26	0.50
	CM (pg)	73.3	46.3	48.9
	% RSD**	10.3	3.4	8.9
Pig Kidny BCR 186	Con. Found (µg l^{-1})	10.30	10.13	3.60
	Con. Certified (µg l^{-1})	10*	10*	3.18
	DL (µg l^{-1})	1.00	1.40	0.56
	CM (pg)	73.3	58.7	55
	% RSD**	6.3	2.1	5.2
Pork Liver GBW 8551	Con. Found (µg l^{-1})	41.1	41.5	5.56
	Con. Certified (µg l^{-1})	40*	40*	5.47
	DL (µg l^{-1})	1.09	1.13	0.50
	CM (pg)	80	55	48.9
	% RSD**	6.3	2.2	6.8
Tea GBW 8505	Con. Found (µg l^{-1})	50.7	49.2	20.5
	Con. Certified (µg l^{-1})	50*	50*	21.66
	DL (µg l^{-1})	1.71	1.17	0.82
	CM (pg)	125.7	48.9	80
	% RSD**	12.5	10.0	8.0

* *Added*
** *For five replicates*

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