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Rapid and Direct Determination of Bi, Sb, and Cd in Biological Samples by Multi-Element Graphite Furnace Atomic Absorption Spectrometer

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ABSTRACT

Direct and rapid procedures for the electrothermal atomic absorption spectrophotometric determination of Bi, Sb, and Cd 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. For Seronorm urine, Lyphocheck urine, Bovine liver, Pig kidney, Pork liver, and Tea, the samples were diluted (1:4, v/v), (1:1, v/v), (1:9, v/v), (1:29, v/v), (1:3, v/v), (1:4, v/v), respectively, with 0.2% HNO_3 which were then introduced directly into the furnace. The detection limits were 0.90-1.5 $\mu g.l^{-1}$ for Bi, 0.79-1.3 $\mu g.l^{-1}$ for Sb, and 0.01-0.025 $\mu g.l^{-1}$ for Cd. The Characteristic masses were 73.3-88 pg for Bi, 46.3-67.7 pg for Sb, and 1.7-3.3 pg for Cd. The reliability of the procedures is checked by analyzing certified reference materials. A standard additions method was used to determine Bi, Sb, and Cd in the samples simultaneously. Results of analysis of standard reference materials were in agreement with certified values.

Introduction

The accurate determination of bismuth, antimony, and cadmium in environmental, biological, and food samples is of importance because of the toxicity of these elements and their compounds [1]. As these elements are usually present at low levels in most biological samples, sensitive analytical techniques are required, such as flame atomic absorption spectrometry [2], atomic fluorescence spectrometry [3], inductively coupled plasma mass spectrometry [4], or inductively coupled plasma optical emission spectrometry [5]. Electrothermal atomic absorption spectrometry (ET-AAS) is a suitable and widely used technique for the determination of trace elements due to its selectivity, simplicity, high sensitivity, and its capability for direct determination in various matrices [6-13].

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 [14-17]. The direct and simultaneous determination of several trace elements is particularly advantageous for routine laboratories because of the saving of time and minimum sample preparation that is required.

The most frequently used chemical modifiers in electrothermal atomic absorption spectrometry (ETAAS) are solutions of palladium nitrate or magnesium nitrate or mixtures of both [18-23]. It is claimed as universal chemical modifier due to the thermal stability improvement for 21 elements [24]. 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 [25] and also determination of As and Sb [26]. Good results were obtained for As, Se, and Pb using Ir-coated tubes in electrothermal vaporization–inductively coupled plasma mass spectrometry [27]. 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 [28].

The evaluation of a fast and reliable analytical method for the simultaneous determination of ultra-trace bismuth, antimony, and cadmium 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.

Experimental

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 Winlab™ control software running

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under Microsoft Windows™. 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 and the wavelengths for each lamp were: Bi 223.1 nm, Sb 217.6 nm, Cd 228.8 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 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 [29]. 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 [29]

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

Certified Reference Materials

The accuracy of the methods was confirmed by analyzing different certified reference materials.

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 (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, Pork Liver, and Pig Kidney

The samples were digested as described by Ronald Treble [30]. Firstly, the samples were dried at 80^{o}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 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 [31]. The sample firstly was dried at 80^{o}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^{o}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

Optimization Using Aqueous Solutions

The optimization conditions were studied using 100 ppb aqueous solution for (Bi and Sb) and 2 ppb for Cd in 0.2% HNO_3 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 Cd, 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.

The optimum pyrolysis and atomization temperatures have been used to determine the characteristic masses and detection limits and the results are shown in Table 2.

Table 2. The Characteristic mass and Detection Limits with different Modifiers

Element	LOD (µg.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	0.82	1.0	67.7	73.3	80.0	73.3
Sb	0.29	0.63	0.75	1.06	41.9	46.3	44.0	51.8
Cd	0.007	0.0058	0.0085	0.0067	2.1	1.70	2.5	1.96

* At 700^{o}C pyrolysis and 1900^{o}C atomization temperatures

** At 700^{o}C pyrolysis and 2100^{o}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.

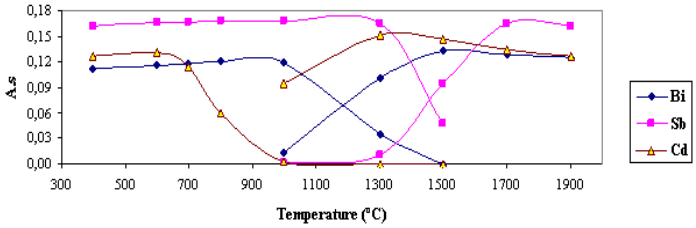

Fig. 1. Pyrolysis and atomization curves of Bi, Sb, and Cd in diluted urine sample with Pd+Mg modifier

With Pd+Mg Modifier

The diluted reference material (1:4) has been spiked with 80 ppb Bi, 80 ppb Sb, and 2 ppb Cd. 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 Cd absorbance on the pyrolysis temperature and atomization temperature was studied and shown in Fig 1. The absorption peaks of the elements at the optimum pyrolysis and atomization temperatures are shown in Figure 2.

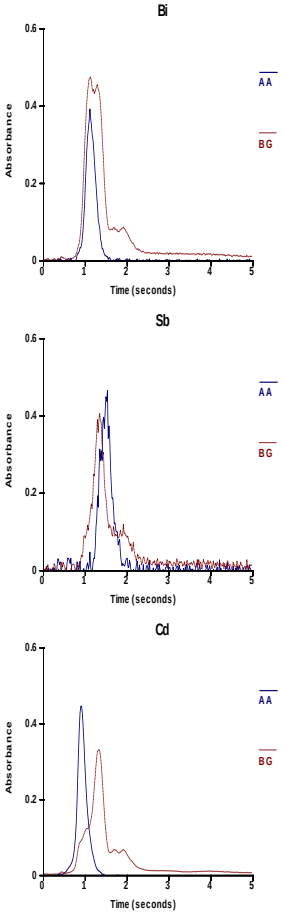

Fig. 2. Peak signals for multi-element determination in diluted urine sample with Pd+Mg modifier

With Ir-Permanent Modifier

The 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 2 ppb Cd. 20 µl diluted spiked reference material has been injected into the atomizer each time during this study. The dependence of Bi, Sb, and Cd absorbance on the pyrolysis temperature and atomization temperature was studied and shown in Fig 3. The absorption peaks of the elements at the optimum pyrolysis and atomization temperatures are shown in Figure 4.

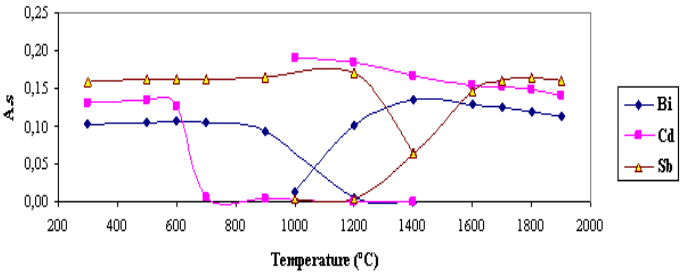

Fig. 3. Pyrolysis and atomization curves of Bi, Sb, and Cd in diluted urine sample with Ir modifier

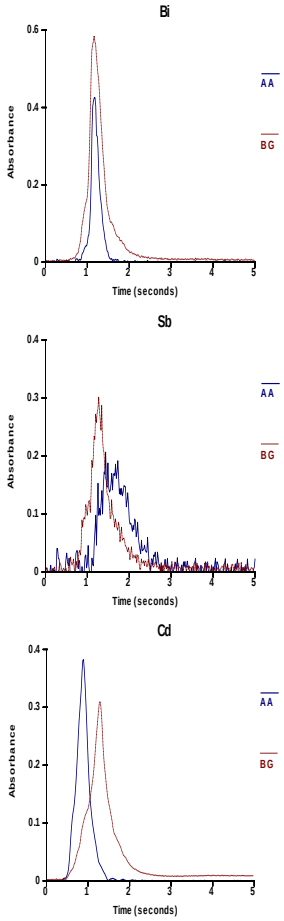

Fig. 4. Peak signals for multi-element determination in diluted urine sample with Ir modifier

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% 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.

With Pd+Mg modifier

The standard addition curves with good linearity (R^2 = 0.9987, 0.9986, and 0.9989 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 97.5, 102.2, and 95.1 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

With Ir permanent modifier

The standard addition curves with good linearity (R^2 = 0.9997, 0.9996, and 0.9997 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 109.5, 106.5, and 110.5 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

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 = 0.9995, 0.9998, and 0.9996 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 102.5, 104.5, and 103.0 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

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

The sample was diluted (1:9, 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 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 = 0.9999, 0.9994, and 0.9998 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 100.0, 96.2, and 98.0 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

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

The sample was diluted (1:29, 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 values for bismuth and antimony; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9999, 0.9996, and 0.9996 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 100.7, 92.9, and 100.7 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

Pork Liver from National Research Centre for Certified Reference Materials (GBW 08551)

The sample was diluted (about 1:3, 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 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, 0.9999, and 0.9999 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 97.5, 100.0, and 98.5 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

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

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°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 = 0.9999, 0.9997, and 0.9999 for Bi, Cd, and Sb, 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 3. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 102.2, 103.0, and 96.4 % for Bi, Cd, and Sb, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 3.

Conclusion

Simultaneous Multi-Element Atomic Absorption Spectrometer (SIMAA 6000) can be used to determine groups of elements (up to six) simultaneously 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.

Table 3. The results of simultaneous determination of Bi, Sb, and Cd in different certified materials

Sample		Bi	Sb	Cd
Seronorm With Pd+Mg modifier	Con. Found (µg l^{-1})	19.6	95.0	4.7
	Con. Certif. (µg l^{-1})	20.1	99.9	4.6
	DL (µg l^{-1})	0.86	1.1	0.015
	CM (pg)	62.9	62.9	2.1
	% RSD**	12.3	3.7	2.1
Seronorm With Ir modifier	Con. Found (µg l^{-1})	22.0	110.4	4.9
	Con. Certif. (µg l^{-1})	20.1	99.9	4.6
	DL (µg l^{-1})	1.5	1.3	0.025
	CM (pg)	88	62.9	1.8
	% RSD**	3.6	5.7	2.4
BIO-RAD 69061	Con. Found (µg l^{-1})	12.3	16.9	6.9
	Con. Certif. (µg l^{-1})	12.0*	16.4	6.6
	DL (µg l^{-1})	1.0	0.92	0.017
	CM (pg)	73.3	67.7	2.5
	% RSD**	7.6	5.9	0.2
Bovine Liver NIST 1577b	Con. Found (µg l^{-1})	5.0	4.9	0.25
	Con. Certif. (µg l^{-1})	5.0*	5.0*	0.26
	DL (µg l^{-1})	1.0	0.94	0.01
	CM (pg)	73.3	55.0	3.0
	% RSD**	4.0	1.5	1.5
Pig Kidny BCR 186	Con. Found (µg l^{-1})	14.6	14.6	1.3
	Con. Certif. (µg l^{-1})	14.50*	14.50*	1.4
	DL (µg l^{-1})	1.0	0.79	0.016
	CM (pg)	73.3	46.3	2.4
	% RSD**	5.5	4.2	0.3
Pork Liver GBW 08551	Con. Found (µg l^{-1})	1.95	1.97	0.034
	Con. Certif. (µg l^{-1})	2.00*	2.00*	0.034
	DL (µg l^{-1})	1.0	1.0	0.017
	CM (pg)	73.3	58.7	1.7
	% RSD**	4.8	2.9	2.9
Tea GBW 8505	Con. Found (µg l^{-1})	2.53	2.41	0.034
	Con. Certif. (µg l^{-1})	2.50*	2.50*	0.033
	DL (µg l^{-1})	0.90	1.10	0.011
	CM (pg)	88.0	62.9	3.3
	% RSD**	7.3	7.3	5.5

* **Added**

** **For five replicates**

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