Development of a Multi-element Hydride Generation–Inductively Coupled Plasma Mass Spectrometry Procedure for the Simultaneous Determination of Arsenic, Antimony and Selenium in Waters†

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A multi-element hydride generation–inductively coupled plasma mass spectrometry (HG–ICP-MS) method for the simultaneous determination of arsenic, antimony and selenium in water matrices has been developed. The method involves an off-line pre-reduction procedure for the reduction of Se^{VI} to Se^{IV} by HCl, combined with an on-line reduction of As^V and Sb^V to the trivalent state with thiourea and generation of the hydrides. Analytical characteristics include detection limits of 0.08 ng g^{-1} As, 0.06 ng g^{-1} Sb and 0.10 ng g^{-1} Se, linearity of four orders of magnitude and short and long term reproducibility of between 8 and 12%. Results from four reference water samples for As, Sb and Se showed data which were all within 10% of the target values. Interferences were minimal for As and Sb, whereas Cu^{2+}, and to a lesser extent Ni^{2+} and Cd^{2+}, caused signal suppression effects on Se. Advantages over an alternative, single element, HG–AFS technique include speed of analysis (by a factor of two) and elimination of the conflicting chemistry requirements, traditionally found with sequential single element hydride generation methods.

Keywords: *Simultaneous multi-element analysis; hydride generation; inductively coupled plasma mass spectrometry; water; arsenic; antimony; selenium*

Hydride generation coupled with atomic spectrometry has become a widely used analytical technique. Its popularity is due to the fact that this coupled technique is both highly selective and sensitive, produces low detection limits and, due to its ability to remove the analyte from the sample matrix, is relatively free from spectral interferences.

The efficiency of the hydride generation step is dependent upon the experimental conditions and particularly the oxidation state of the analytes.[1] When As and Sb are present as the pentavalent species they have a reduced propensity towards hydride generation (including reduction schemes involving sodium tetrahydroborate). Using this system Se, in the hexavalent state, is unable to form a hydride.[2] The lower oxidation states of As^{III}, Sb^{III} and Se^{IV} are the most favourable for the formation of the hydrides, hence a conversion of the analytes to these valencies prior to reaction with $NaBH_4$ is required. Iodide and L-cysteine can be used to reduce As^V and Sb^V to As^{III} and Sb^{III},[3] but they also reduce Se^{IV} to elemental Se which is unable to form a hydride.[4] Because of these oxidation state difficulties, few methods have been published that can be called true simultaneous hydride generation methods for these three elements.[5] As well as the oxidation state question many other experimental parameters, such as acid concentration, reaction time, reducing agent concentration, and temperature (critical

steps of any hydride generation procedure), need optimising, in turn, to establish the ideal conditions for the simultaneous determination of these analytes.

At the present time the analysis of As, Sb and Se in our laboratory is carried out using a single-element, HG–AFS system. With the analysis of over 3000 samples per annum this restriction to single-element analysis results in approximately 9000 determinations. In addition to As, Sb and Se, the instrumentation is also used for the determination of Hg. Problems are encountered when changing from one elemental system to another due to differences in the chemical strategies used. Carry-over of the reducing agents often leads to a significant decrease in sensitivity as the system is switched between elements. The time needed to flush out the system and achieve stability of response can often take a considerable time (*e.g.*, 2–3 h).

To overcome these problems a multi-element procedure using HG–ICP-MS for the determination of As, Sb and Se in water has been developed for use in a commercial laboratory environment. The method involves a pre-reduction stage of heating the sample with acid. This reduces the Se^{VI} to Se^{IV}. Thiourea is added on-line to reduce pentavalent As and Sb to the trivalent species, and then the gaseous hydrides are formed during the reaction with $NaBH_4$. Final determination is performed by use of ICP-MS. The unified sample pre-treatment leads to a streamlined system, which has dramatically reduced the analysis time and eliminated the problems when alternating between elements using the single element AFS system.

EXPERIMENTAL

Instrumentation

All determinations were carried out using a Perkin-Elmer ELAN 5000A ICP-MS instrument (Perkin-Elmer, Beaconsfield, UK). The on-line reduction was fully automated with the inclusion of a Perkin-Elmer FIAS 400 flow injection system. The instrumentation was computer controlled using Perkin-Elmer integrated software. The operating conditions for the ICP-MS instrument and the FIAS system are given in Tables 1 and 2, respectively. A schematic diagram of the entire HG–ICP-MS system is shown in Fig. 1.

A Tecam water-bath fitted with a Techne TE-8A thermoregulator [Techne (Cambridge) Ltd., Duxford, Cambridgeshire, UK] was used for the pre-reduction stage. Sample preparation and pre-reduction was performed using 25 ml sterilin tubes (Bibby Sterilin, Walton, Staffordshire, UK).

Reagents and Standard Solutions

All solutions were prepared with high purity deionized water (18 MΩ, Elga, High Wycombe, Buckinghamshire, UK).

Stock solutions of the elements (1000 µg g^{-1}) were prepared

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Table 1 Operating conditions for the ELAN 5000A ICP-MS

Forward power	1050 W
Carrier gas	15 l min^{-1}
Nebulizer gas	0.850 l min^{-1}
Auxillary gas	0.80 l min^{-1}
Parameter file—	
Points across peak	1
Resolution	Normal
Scanning mode	Peak hop transient
FIAS argon flow rate	0.350 l min^{-1}

	Times/ms	
Element	Replicate	Dwell
^{75}As	1200	20
^{121}Sb	1200	20
^{82}Se	1200	20

Elemental equations
Arsenic-75 = arsenic-75
Antimony-121 = antimony-121
Selenium-82 = selenium-82 − 1.001*krypton-83

Table 2 Operating conditions for the FIAS 400 flow injection system

Injection volume 200 µl

Repeat from step 2 through step 2 3 times

Step	Start read	Time/s	Speed (rpm) Pump 1	Pump 2	Valve position	Remote
Pre-sample		10	100	0	1	
1		5	100	0	1	
2		30	0	0	1	
3		2	0	0	1	X
4	X	15	0	−70	2	X
5		5	0	0	1	X
6		1	50	0	1	
Post-sample		10	100	0	1	X
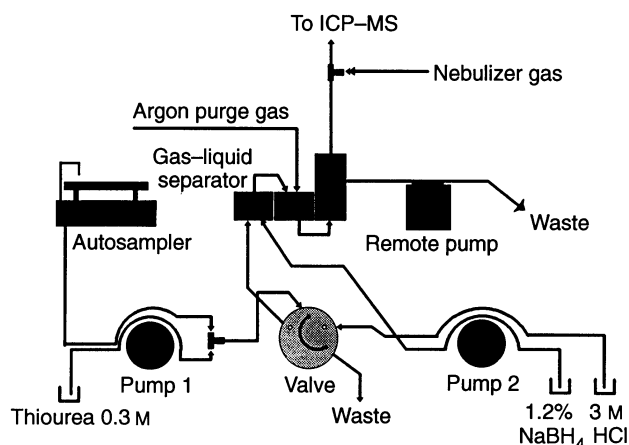
Fig. 1 Schematic diagram of the HG–ICP-MS system.

from the following salts (BDH AnalaR grade, Merck, Poole, Dorset, UK): sodium selenite (Na_2SeO_3), sodium selenate ($Na_2SeO_4 \cdot 10H_2O$), sodium arsenite ($NaAsO_2$), sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), antimony trichloride ($SbCl_3$), antimony pentachloride ($SbCl_5$). The arsenic and selenium stock solutions were prepared in 0.12 M hydrochloric acid (Baker, Phillipsburg, NJ, USA), whereas the antimony stock solution was prepared in 3 M HCl (Aristar, Merck). Working standards were prepared daily by serial dilution with 0.12 M HCl (Baker).

Sodium borohydride (Aldrich, Gillingham, Dorset, UK) 1.2% m/v was prepared weekly in 0.1 M sodium hydroxide

(Fisons, Loughborough, Leicestershire, UK). A 0.3 M solution of thiourea (Aldrich) in high purity water was prepared daily.

Analytical Procedure

All standards and samples solutions are acidified by the addition of concentrated HCl in the ratio 12.5 ml of sample to 10 ml of concentrated HCl to give a final acid concentration of 5 M. Samples are then placed in a water-bath at 80–85 °C and heated for 90 min. After pre-reduction, the solutions are allowed to cool and transferred to the ICP-MS instrumentation. There, the samples are mixed on-line with the 0.3 M m/v thiourea solution and left to react for 180 s. The sample is then reacted with the NaBH$_4$ to form the gaseous hydrides, which are swept into the ICP-MS instrument for quantification.

RESULTS AND DISCUSSION

Off-line Pre-reduction

The reduction of Se^{VI} to Se^{IV} is carried out by heating the sample with HCl. The parameters found to be critical at this stage were the acid concentration and the temperature of the water-bath.[2] A slight decrease in the acid concentration, or a drop in temperature, can result in a significantly longer heating time being required. Fig. 2 shows the effect of heating time on a Se^{VI} solution (10 ng g^{-1}). As can be seen, the signal levels off after 90 min. The Se^{IV} signal was unaffected by the length of the heating period. Best results were achieved when the sterilin sample containers were capped (but only loosely, to allow any chlorine fumes to escape). A build-up of Cl can result in the back-oxidation of Se^{IV}.[6] Recoveries of 100% were obtained for the Se^{VI} solution when compared with equivalent Se^{IV} standards.

On-line Reduction

The most commonly used reducing agents for the conversion of As^{V} and Sb^{V} to As^{III} and Sb^{III} are iodide or bromide,[7] L-cysteine[3] and thiourea.[1] The main drawback is that they all reduce tetravalent Se to its elemental state, which is unable to form the hydride. For this study the use of thiourea was investigated as an on-line reductant for As^{V} and Sb^{V}, because although thiourea is able to reduce Se^{IV} to elemental Se to a significant degree, the conversion seemed to be slower than that caused by iodide. For the complete reduction of As^{V} and Sb^{V} the concentration of the thiourea and the reaction time required were varied to establish the best set of compromise conditions. Reaction with 0.5 M thiourea brought about the reduction of As^{V} and Sb^{V} in the shortest time, but the loss of Se signal was proportionally higher. A reaction time of 180 s and 0.3 M thiourea were found to be the ideal conditions for complete reduction of As^{V} and Sb^{V} without losing a substantial amount of the Se signal (Fig. 3).

Although the concentrated HCl procedure outlined above
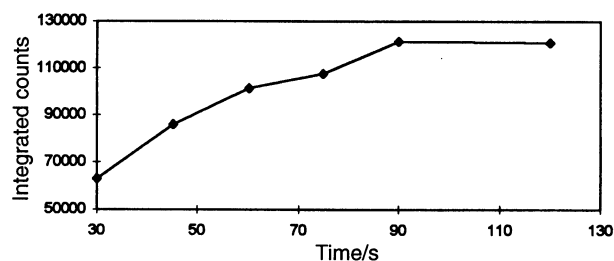
Fig. 2 Variation of Se signal with an increase in heating time. A 10 ng g^{-1} Se standard was placed in a water bath set at 80 °C and portions removed and analysed at the different intervals.
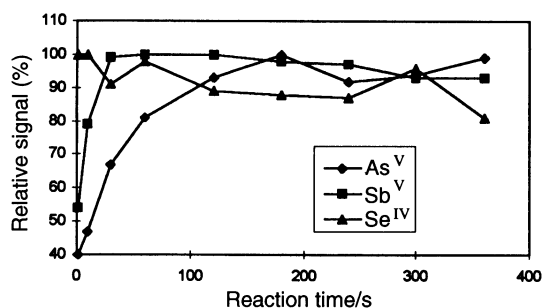
Fig. 3 Effect of reaction time with 0.3 M thiourea on As, Sb and Se signals. Variation of signal of a 10 ng g^{-1} multi-element standard in 5 M HCl, as the reaction time with thiourea increases.
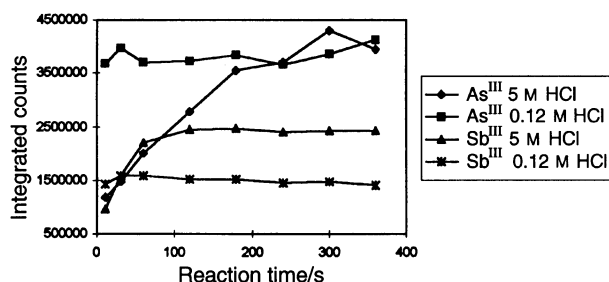

Fig. 4 Effect of acid concentration on As^{III} and Sb^{III} signals. Differences in hydride formation of a 10 ng g^{-1} Sb^{III} standard in 0.12 M HCl compared with a 10 ng g^{-1} Sb^{III} standard acidified to 5 M HCl.

does not reduce As^V and Sb^V to their trivalent states, we did find that the high concentration of acid seemed to affect the ability of As^{III} and Sb^{III} to form the hydrides in the proposed system. A solution of As^{III} and Sb^{III} prepared in 0.12 M HCl and heated for 90 min at 80–85 °C gave a consistent signal regardless of the reaction time with the 0.3 M thiourea (Fig. 4). However, the same solution heated in 5 M HCl gave signals which were dependent on the thiourea reaction time, mimicking the behaviour of the pentavalent species. The signal for the As^{III} standard acidified to 5 M HCl equalled that of the standard prepared in 0.12 M HCl. The signal for the 5 M HCl Sb^{III} standard exceeded that of the standard prepared in 0.12 M HCl. This suggests that although the Sb was present at the lower oxidation state in 0.12 M HCl this acid concentration was not ideal for Sb hydride generation (Fig. 4).

Interferences

Several elements, in particular the transition metals, have been found to interfere with the generation of hydrides.[1,8] As thiourea has been used as an interference suppresser in other hydride generation systems, its effectiveness in the proposed method was investigated. A study of the effect of the most common interferents was carried out. A 10 ng g^{-1} multi-element standard was spiked with a variety of interferents at 1, 10 and 100 µg g^{-1} (Table 3). The results are expressed as a percentage of the signal without interferent. Precision data, expressed as an RSD of the three replicates performed for each solution, have also been included here. As can be seen, the biggest interference was caused by Cu (100 µg g^{-1}) on Se. The signal has decreased by 53% from that obtained for the Se standard with no added Cu. This may be caused by adsorption of the hydride by metal precipitates present in the solution.[1,8] Cd and Ni also had an adverse effect on the Se signal, but to a lesser extent. As and Sb were generally unaffected by the interferents examined.

Analytical Performance

A typical injection profile for a 200 µl 10 ng g^{-1} multi-element standard is shown in Fig. 5. Using the present parameter file conditions (Table 2), the linearity of the system was found to be up to 25 ng g^{-1} for As and 50 ng g^{-1} for Sb and Se. This linearity can be increased by desensitizing the detector at specific masses by utilizing the Perkin-Elmer OmniRange software option.

Reproducibility was measured by analysing 10 consecutive determinations of a 10 ng g^{-1} multi-element standard, followed by several further determinations over a 4 h period. The short and long term stability of the analytes under these conditions, expressed as RSDs, are 8 and 12% for As, 9 and 12% for Sb, and 7 and 10% for Se, respectively.

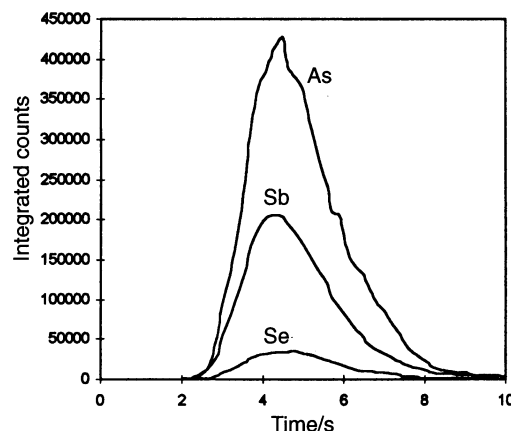One of the requisites of the proposed method is that it

Fig. 5 Typical signal profile of a 10 ng g^{-1} As, Sb and Se multi-element standard mixture: 200 µl injection volume.

Table 3 Effect of interferents on As, Sb and Se signals—10 ng g^{-1} multi-element standard spiked with the interferents at 1, 10 and 100 µg g^{-1}. Results expressed as a percentage of the result without interferent

| | Interferent concentration/µg g^{-1} | | | | | | | | |
| | As | | | Sb | | | Se | | |
Interferent	1	10	100	1	10	100	1	10	100
Cu^{2+}	94	95	95	94	95	96	89	95	47
RSD (%)	3.6	3.7	2.4	4.5	2.8	2.5	4.3	3.0	2.4
Cd^{2+}	94	97	94	91	93	91	90	84	83
RSD (%)	1.0	3.2	3.4	2.2	3.4	3.1	0.8	4.6	2.8
Ni^{2+}	94	95	99	92	87	92	84	78	83
RSD (%)	7.0	4.9	2.5	4.1	2.9	2.6	5.8	6.7	4.8
Pb^{2+}	102	96	114	96	96	97	96	97	99
RSD (%)	4.5	2.1	1.1	0.6	0.8	1.3	4.6	2.1	6.6
Fe^{3+}	94	95	102	87	82	92	89	90	93
RSD (%)	6.6	6.4	6.8	3.9	5.4	3.9	9.4	4.9	6.1

Table 4 Accuracy data from Water Research Centre inter-laboratory reference waters. All concentrations are in ng g^{-1}

	As		Sb		Se	
Sample	Obtained	Expected	Obtained	Expected	Obtained	Expected
AQUACHECK 85	24.9	24.1	2.78	2.81	3.21	3.13
AQUACHECK 93	27.9	27.0	3.00	3.10	3.25	3.00
AQUACHECK 101–5	23.9	22.0	8.50	8.40	4.11	4.30
AQUACHECK 101–5A	38.7	36.0	5.35	5.30	4.63	4.20

Table 5 Recovery results from spiked water samples—obtained by spiking the samples at 10 ng g^{-1} with As, Sb and Se

	Recovery (%)		
Sample	As	Sb	Se
1	101	97	102
2	116	105	108
3	105	107	98
4	107	97	88

would be able to comply with the present Water Supply (Water Quality) Regulations 1989[9] (present limits are 50 ng ml^{-1} for As and 10 ng ml^{-1} for Sb and Se). Although many compromises had to be made in the development of the method, the detection limits of 0.08, 0.06 and 0.10 ng g^{-1} for As, Sb and Se, respectively (calculated as 3σ based on 10 determinations of the blank) are well below the required levels.

To check on the accuracy of the method a number of Water Research Centre (WRC) spiked Aquacheck reference solutions were analysed (Table 4). As can be seen the results are very acceptable, with agreement falling within 10% of the WRC declared spike values. Some typical water samples (drinking and bore waters) submitted to the laboratory were spiked with As, Sb and Se at approximately the 10 ng g^{-1} level. The samples were analysed using the multi-element method and recovery values calculated (given in Table 5). All recovery results were encouraging, with over 90% of the values falling within 10% of the expected amount.

CONCLUSIONS

A method has been successfully developed for the simultaneous determination of As, Sb and Se in water. Problems associated with using a single element HG–AFS instrument for the analysis of different analytes, each with different chemical strategies, is no longer an issue due to a unified sample pre-treatment methodology. The HG–ICP-MS method produces savings in analysis time of 50% over the single element HG–AFS method. This rapid analysis time, compared with the single element approach, leads to improvements in efficiencies and increased productivity, welcome in any commercial laboratory environment.

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