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A novel introduction system for hydride generation-inductively coupled plasma mass spectrometry: determination of selenium in biological materials

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A novel, robust hydride generation system compatible with sample introduction with inductively coupled plasma mass spectrometry is described and applied to the determination of Se in biological tissues. A short reaction time (60 ms) and a rapid separation of the reaction products is obtained by mixing the acidified sample and the sodium borohydride reductant solution at the tip of a cross-flow nebuliser. A modified Scott spray chamber serves as a gas-liquid separator, providing 30 s wash-in and wash-out times. Analytical results generated by external calibration and isotope dilution methodologies agree well with the certified values for Se in certified biological reference materials DORM-2 and DOLT-2. Detection limits for Se and other hydride forming elements, *i.e.*, As, Sn and Sb, are below 10 ng l⁻¹ with typical precision of 2% RSD at the 10 ng ml⁻¹ level. Volatile species of Cu, Rh, Pd, Ag, In, Au, Hg, Tl and Pb are also produced, and estimated sensitivities and detection limits for these elements are reported.

Introduction

The formation of volatile hydrides of Se, As, Sb and several other elements prior to their determination by atomic spectrometric methods is an established and successful method used to enhance the concentration limit of detection for these elements.¹⁻⁸ A major shortcoming of the technique is that the presence of high concentrations of transition metals, such as Ni, Co, Cu and Fe, severely suppress the formation and release of the analyte hydride.^{7,9-12} This suppression effect and several means to overcome it have been intensively investigated for Se, as it is the element most adversely affected. Non-volatile Se species appear to be produced by a reaction between SeH₂ and reduced forms of interfering metals or their borides.^{10,13} Several approaches have been taken in an effort to overcome this effect. In general, signal suppression can be reduced by decreasing the concentration of NaBH₄ and by increasing the concentration of HCl.¹⁰ Additionally, various chelating ligands have been used as masking agents,^{7,9,11,12,14} amongst other techniques,¹⁵ in an effort to prevent the interfering metals from being reduced. Although separation of the analyte from the matrix prior to hydride generation can resolve the problem, and methods based on ion exchange¹⁶ or coprecipitation⁴ have been employed, this requires additional sample preparation. Optimising the generation conditions with special regard to the kinetics of the reaction may be used to minimise suppression effects, since Se is reduced faster than the interfering metals.¹⁶⁻²⁰ A successful approach based on this has been demonstrated using a moving bed reactor,²¹ wherein the liquid sample is dropped onto immobilised KBH₄ and the volatile products immediately removed from the reaction surface by a flow of gas. Although interference from the presence of Zn and Fe was reduced, severe effects remained from the presence of Au, Pt, Pd, Co and Ni.

Recent studies in our laboratory^{22,23} have also focused on the use of very short reaction times (below 100 ms) and rapid separation of the gaseous products. A combination of an

additional inner capillary mounted in a concentric nebuliser for simultaneous introduction of sample and reductant, as well as a spray chamber for gas-liquid separation of the product, permits sample introduction into an ICP, quartz tube atomiser or graphite furnace. Under these conditions, the suppression effects on the generation of Se hydride, arising from high transition metal concentrations, can virtually be eliminated, *i.e.*, no reduction of the Se signal is observed in the presence of 50 g l⁻¹ Ni, 25 g l⁻¹ Co or 20 mg l⁻¹ Cu.

The primary goal of the present study is to apply this concept to the determination of Se using ICP-MS, as this technique provides enhanced detection power and offers the possibility of incorporating isotope dilution capabilities as a valuable tool for the validation of this methodology. A hydride generation sample introduction system similar to that described in previous studies^{22,23} was used, although a standard cross-flow nebuliser and a Scott type spray chamber were selected for detailed study. In order to minimise the effect of interferences, a reaction time within the range investigated by Ding and Sturgeon²² was chosen. The minimisation of interferences is important for ICP-MS application since external calibrations without an internal standard are widely used for Se determination by hydride generation due to the difficulty of finding an internal standard that mimics both the hydride generation reaction and the various matrix suppression effects operative on Se. Although spray chambers have earlier been used as gas-liquid separators,²⁴⁻²⁶ a significant modification in this work was the addition of a second gas inlet to permit independent optimisation of both the gas flow rate for the nebuliser and that for the transport of the reaction products to the plasma. Experimental parameters were optimised solely for response from Se and the method was applied to its determination in two certified biological reference materials. An isotope dilution methodology was incorporated into the procedure for comparison of results generated using an external calibration approach. In addition to the usual suite of hydride forming elements, a number of other metals are also liberated as volatile species under the given conditions, opening a broad field of study aimed at utilising this new approach to vapor generation.

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Table 1 HG-ICP-MS hardware and operating parameters

<i>Hydride generation—</i>	
Sample uptake rate	0.8 ml min ⁻¹
Sample acidity	1 M HCl
NaBH ₄ flow rate	0.8 ml min ⁻¹
NaBH ₄ solution	1.0% (m/v) NaBH ₄ , with 0.1% (m/v) NaOH
<i>ICP-MS—</i>	
Rf power	1000 W
Plasma gas flow rate	15 l min ⁻¹
Intermediate gas flow rate	2.6 l min ⁻¹
Shear gas flow rate	0.200 l min ⁻¹ (0.5 l min ⁻¹) ^a
Make-up gas flow rate	0.500 l min ⁻¹ (0.15 l min ⁻¹) ^a
Scanning mode	Peak hopping
Dwell time	50 ms
No. of sweeps per replicate	30
No. of replicates	5
Measurements per peak	1
Resolution	0.8 u

^aFor Meinhard-type nebuliser.

Experimental

Instrumentation

The ICP mass spectrometer was a Perkin-Elmer Sciex (Concord, Ontario, Canada) Model ELAN 5000, operated under the conditions shown in Table 1. A quartz torch and alumina injector tube were used. Two hydride generation systems were examined. The design of the first was based on a Meinhard type concentric nebuliser, fabricated in-house from pyrex. A quartz capillary tube (hand drawn, 4 cm long × 0.15 mm id × 0.3 mm od) was inserted into the sample introduction channel to permit mixing of the sample and reductant solutions just prior to nebulisation, as described earlier.^{22,23} This design was selected to minimise aerosol formation while maximising the response from the generated hydride. The second system was based on a commercial Gem TipTM cross-flow nebuliser (Perkin-Elmer, Norwalk, CT). To provide a small, well-defined mixing zone for the hydride generation reaction with this device, a narrow TeflonTM tube was inserted into this nebuliser tip through the TeflonTM sample introduction tube, as illustrated in Fig. 1, thereby forming concentric channels for the introduction of both sample and NaBH₄ solutions (outer tube dimensions: 1.8 mm od × 1.2 mm id; inner tube dimensions: 0.88 mm od × 0.58 mm id). The resulting volume of the mixing zone was approximately 1.6 µl, resulting in a residence time of the sample in the reaction zone of approximately 60 ms for a combined reactant flow of 1.6 ml min⁻¹. The concentric nebuliser provided similar reaction conditions. A second gas inlet was added to a quartz double-pass Scott spray chamber to permit optimisation of the nebuliser gas independently of the total carrier gas entering the plasma. The flow rate of Ar introduced through

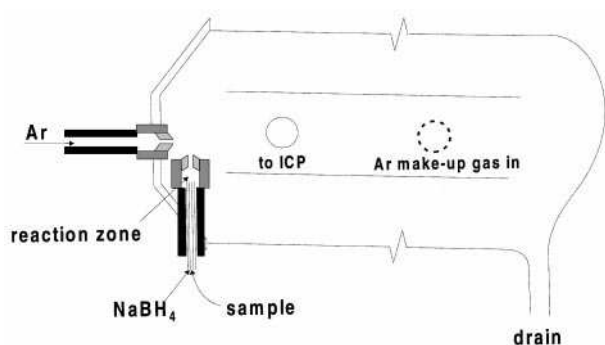


Fig. 1 Schematic of modified Scott spray chamber and cross-flow nebuliser containing reaction zone of 1.6 µl volume (figure not to scale).

this inlet (“make-up gas”) was maintained by an external mass flow controller. The optimum torch position was found to be advanced by 2 mm compared to the standard position. The orifice of the injector tube is thus in line with the first loop of the induction coil. The sampling depth (the distance between the coil and the sampling cone) remained at 10 mm.

A CEM (Matthews, NC, USA) MDS-2100 microwave digester was used for closed vessel high pressure sample dissolution.

Reagents and solutions

All chemicals used were of reagent grade unless otherwise stated. A 500 mg l⁻¹ stock solution of Se(IV) was prepared by dissolving sodium selenite (99%, BDH Chemical Ltd., Poole, England) in 1 M hydrochloric acid. A stock solution of 1.41 mg l⁻¹ enriched ⁸²Se was prepared by dissolving the elemental powder (Oak Ridge National Laboratory) in a minimum volume of nitric acid. The oxidation state of Se in this solution was +4. Stock solutions for other elements were prepared from commercially available standards or by dissolution of high purity metals. Hydrochloric and nitric acids were purified in-house by sub-boiling distillation of analytical-reagent grade feedstock in a quartz still prior to use. Distilled, de-ionised water (DDW) was obtained from a Barnstead Nanopure system (Barnstead/Thermolyne, Dubuque, IA, USA). Solutions of NaBH₄ (Alfa Chemicals Inc., Newburyport, MA, USA) were prepared daily at a concentration of 1% (m/v) in 0.1% (m/v) NaOH (BDH Inc., Toronto, ON, CA). Certified reference materials DORM-2 (Dogfish Muscle Tissue) and DOLT-2 (Dogfish Liver Tissue) were obtained from the Institute for National Measurement Standards, National Research Council of Canada.

Sample preparation

All sample preparations were conducted in a clean room providing a class 10 working environment. The biological tissues were digested by adding 5 ml nitric acid to 250 mg of the sample in a TeflonTM vessel. Enriched isotope spikes of ⁸²Se were added at this time for the isotope dilution experiments. The vessels were sealed and heated in the microwave oven under the following conditions: 5 min at a pressure of 1.4 bar (20 lb in⁻²) and 60% power; 5 min at 2.8 bar (40 lb in⁻²) and 60% power; 10 min at 5.9 bar (85 lb in⁻²) and 70% power; and 15 min at 8.3 bar (120 lb in⁻²) at 80% power. After cooling, the vessels were opened and placed on a hot plate in a clean hood where they were evaporated to dryness with the aid of an infrared lamp. In order to convert all Se to Se(IV), 1 ml hydrochloric acid and 1 ml DDW were added to dissolve the residue and the solution was again evaporated on the hot plate to near dryness. A 1.5 ml volume of nitric acid was then added and the solution was diluted to 25 ml with DDW in a volumetric flask. It is to be noted that there is a possibility of re-oxidation of some of the Se(IV) back to Se(VI) during the course of the experimental investigation. Apart from a possible loss in sensitivity, this will have no effect on results generated using isotope dilution techniques, but may lead to low results for solutions analysed *via* external calibration. Prior to the determination of Se, the DORM-2 and DOLT-2 samples were further diluted 5- and 10-fold, respectively, with 1 M HCl.

Procedures

All ICP-MS measurements were made using the general parameters given in Table 1, unless otherwise stated. Measurements of Se were performed using the ⁷⁷, ⁷⁸ and ⁸² isotopes. Quantification of Se in the reference materials DORM-2 and DOLT-2 was done by external calibration (EC) using both ⁷⁷Se and ⁸²Se isotopes as well as by isotope dilution (ID-ICP-MS) following addition of enriched ⁸²Se spikes. A quantity of ⁸²Se

was spiked into the samples in an effort to obtain a ratio of $^{78}\text{Se}/^{82}\text{Se}$ near 1 in the final solution. ^{77}Se was monitored in order to ascertain the extent of any interference by polyatomic $^{40}\text{Ar}^{37}\text{Cl}^+$ co-generated during the sample introduction process. Procedural blank concentrations determined by ID-ICP-MS were all below the detection limit and therefore no correction to the sample was required.

Experiments designed to detect volatile species of other metals utilised a multi-element solution containing Mg, Al, Si, Cu, Pb, As, Se, Sn, Sb, Rh, Pd, In, Au, Tl, Hg, Ag. All solutions were prepared in 1 M HCl and, unless specified otherwise, 1% (m/v) NaBH_4 was used for reduction of all elements. A shear gas flow rate of 0.2 l min^{-1} was optimised for the production/separation of volatile species from the solution immediately at the nebuliser tip. This clearly differs from typical conditions used for maximum aerosol generation efficiency when analysing solutions using conventional pneumatic nebulisation. However, the possibility that a small fraction of the sample solution was transported to the plasma in the form of an aerosol could not be completely excluded. In order to estimate the contribution any such aerosol fraction may have made to signal response, the NaBH_4 solution was replaced with 1 M HCl, to eliminate hydride generation, and the experiment was repeated under otherwise unchanged conditions.

Results and discussion

As the use of these nebulisers was to supply analyte hydride vapor to the ICP without the corresponding transport of an aerosol fraction, their operational characteristics were far removed from the conventional in that the “nebuliser” gas flow rates are significantly lower. A minimal contribution from the transport of any aerosol fraction served to minimise potential space charge interferences in the extraction region arising from the high levels of sodium ion. The term “shear gas” is used instead of “nebuliser gas” throughout this study because of the different function it serves, *i.e.*, to effect a rapid gas-liquid separation of the volatile analyte species rather than form a transportable aerosol. In such a case, the shear gas flow rate must be lower than standard nebuliser gas flow rates. Transport of the analyte hydride from the spray chamber is then facilitated with the addition of a separate “make-up” gas such that their total volume flow rate is compatible with the inner gas flows normally used for ICP-MS operation.

Optimisation of parameters for Se determinations

As is evident from the above, one of the critical parameters to be considered for this sample introduction process is the shear gas flow, which deserves close inspection with the systems used. A two-dimensional optimisation was therefore undertaken for both nebuliser systems. Fig. 2a–c shows results obtained with the cross-flow nebuliser. Highest sensitivity for ^{82}Se (Fig. 2a) can be achieved over a broad range (0.1 to 0.4 l min^{-1}) of shear gas flow rates provided the make-up gas flow is sufficient to result in a total gas flow exiting the spray chamber of approximately 0.7 l min^{-1} . This is typical of the flow rate necessary for efficient operation of nebuliser systems for sample introduction for ICP-MS.²⁷ In order to identify conditions which minimise interference from $^{40}\text{Ar}^{37}\text{Cl}^+$ on ^{77}Se in a Cl-containing solution, data from the same experiment were evaluated with respect to m/z 75, *i.e.*, the signal from $^{40}\text{Ar}^{35}\text{Cl}^+$. Results, displayed in Fig. 2b, serve to identify different regions of operation of the system, *i.e.*, those which produce efficient nebulisation of the sample, thereby producing a transportable aerosol phase, and those that likely reflect the simple transport of a chlorine containing vapor-phase species. The latter conditions are achieved, as expected, at relatively low shear gas flow rates, in the range 0.25 – 0.35 l min^{-1} . At low shear gas flow rates aerosol formation should be significantly

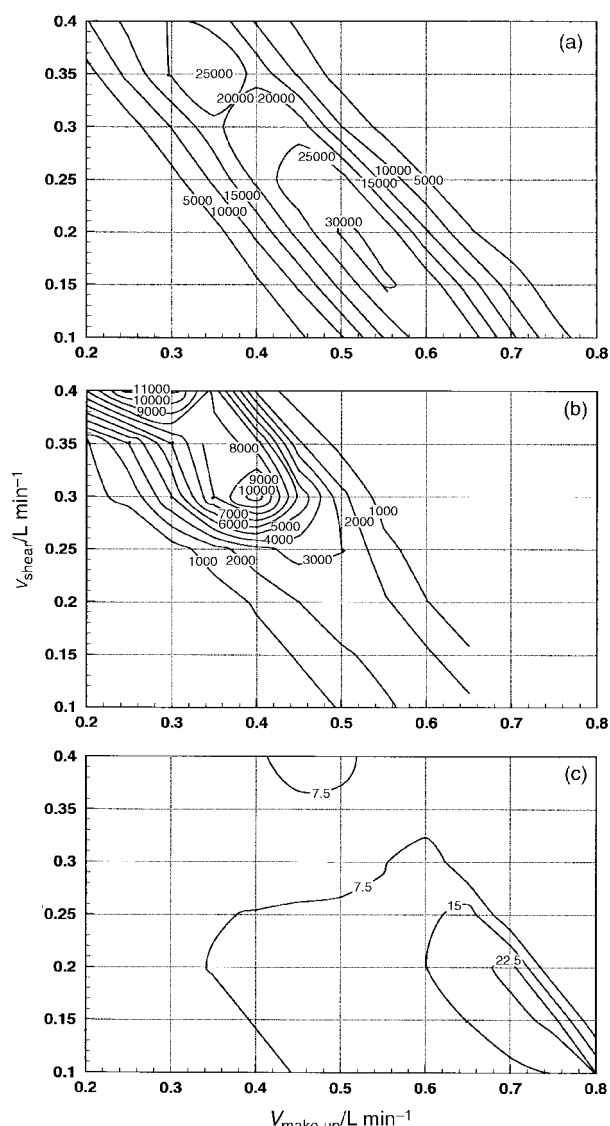


Fig. 2 Response surfaces for the cross-flow nebuliser. (a) ^{82}Se using a solution of $10 \mu\text{g l}^{-1}$ Se(IV) and 1 M HCl reacting with 1% (m/v) NaBH_4 ; (b) for $^{40}\text{Ar}^{35}\text{Cl}^+$ in 1 M HCl; (c) ratio of ^{82}Se to the signal at m/z 75 resulting from $^{40}\text{Ar}^{35}\text{Cl}^+$.

reduced and, as a consequence, the transport of droplets to the ICP can be assumed to be negligible. The broad region of flat response for m/z 75 probably arises as a consequence of the relatively high vapor pressure of HCl. Note that the total gas flow rate necessary for maximum response remains relatively constant at 0.7 l min^{-1} . The optimum signal-to-background ratio occurs under conditions which maximise analyte vapor formation and transport while minimising the aerosol contribution. A plot of the response surface for ^{82}Se vs m/z 75, shown in Fig. 2c, suggests that the device should be operated, as expected, under conditions of low shear gas flow rate and high make-up gas flow rate, approximately 0.2 and 0.7 l min^{-1} , respectively, for quantitation of ^{77}Se . In such circumstances, the contribution of $^{40}\text{Ar}^{37}\text{Cl}^+$ from a solution of $10 \mu\text{g l}^{-1}$ Se and 1 M HCl is approximately 3% of the total signal measured at m/z 77. Although this is too high to permit direct analysis of seawater with this approach, it suffices for this preliminary study. Further refinement of the sample introduction technique should improve this situation. Since ^{78}Se and ^{82}Se were the isotopes of interest for this study, the conditions evident in Fig. 2a were selected for optimum response, *i.e.*, shear and make-up gas flow rates of 0.2 and 0.5 l min^{-1} , respectively, since $^{40}\text{Ar}^{37}\text{Cl}^+$ is of no concern for this determination. These

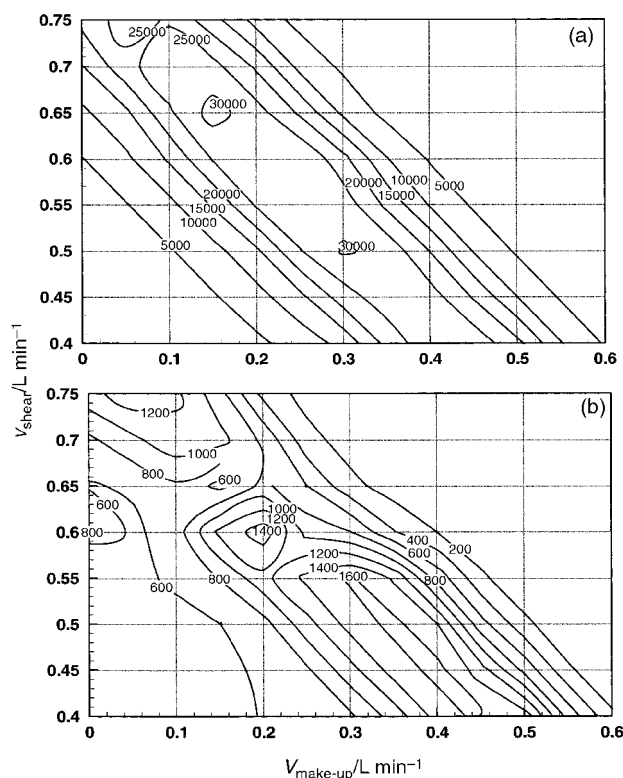


Fig. 3 Response surfaces for the Meinhard-type nebuliser. (a) ^{82}Se using a solution of $10\ \mu\text{g l}^{-1}$ Se(IV) and 1 M HCl reacting with 1% (m/v) NaBH_4 ; (b) for $^{40}\text{Ar}^{35}\text{Cl}^+$ in 1 M HCl.

were subsequently used for all further studies with this nebuliser.

Fig. 3a and b illustrates similar data for the optimisation of the concentric nebuliser. Again, a broad range of gas flow rate combinations which satisfy a total flow of $0.8\ \text{l min}^{-1}$ is evident for optimal response from ^{82}Se . Examination of Fig. 3b shows that, unlike the modified cross-flow nebuliser, there is no apparent optimum position indicative of significant aerosol formation and transport. This is to be expected, based on the initial design criteria used for this nebuliser. The region of maximum response occurs over a broad range of shear gas flows, suggesting that this signal is due to vapor-phase transport of HCl at a total gas flow rate of $0.8\ \text{l min}^{-1}$. This conclusion is also supported by the fact that the signal intensities in this system are 5- to 10-fold smaller than those shown in Fig. 2b under conditions conducive to efficient aerosol formation and transport. Owing to this, the optimum signal-to-background (figure not shown) conditions are established principally by the response from ^{82}Se alone, suggesting an operating condition of $0.65\ \text{l min}^{-1}$ for shear gas and $0.15\ \text{l min}^{-1}$ for the make-up gas. Although enhanced signal-to-background and generally higher sensitivity for ^{82}Se are both evident with this nebuliser system, it was abandoned in favour of the cross-flow device. The relatively high flow rate of reactant solutions through this glass Meinhard type nebuliser resulted in a destructive oscillation of the inner capillary, whereby the tip of both channels would erratically erode and alter the response with long term operation. Construction of the device from alternative (polymeric) materials should serve to eliminate this problem and work is now in progress to accomplish this.

Since an analyte solution resulting from a sample digestion with HNO_3 may contain residual and varying amounts of HNO_3 , the influence of different acids on response was examined. A 5 M HCl solution was chosen for comparison, since it is a commonly used concentration for hydride generation and was examined in previous studies.^{22,23} Fig. 4

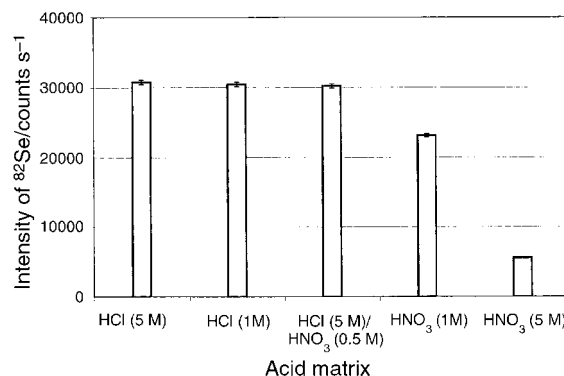


Fig. 4 Response for $10\ \mu\text{g l}^{-1}$ Se(IV) in different acid matrices. The error bar indicates the standard deviation.

summarises results for the cross-flow nebuliser, from which it is evident that the same sensitivity is obtained in either 5 M or 1 M HCl or even in a mixture of 0.5 M HCl and 0.5 M HNO_3 . In 1 M HNO_3 alone, the sensitivity is reduced to 76% of that realised with 1 M HCl. This result, comparable to that reported by Ding and Sturgeon²² who utilised a concentric nebuliser, highlights the superiority of this approach over earlier studies wherein the signal for Se is completely suppressed in the presence of 0.5 M HNO_3 –2 M HCl when using a conventional hydride generation system.²⁸

Figures of merit for Se, As, Sn and Sb

Detection limits and precision for Se, As, Sn and Sb, determined under standard conditions using both nebulisers, are summarised in Table 2. Values comparable to those reported in other studies utilising hydride generation^{1,4,29–31} are achieved and in all cases are limited by the purity of the reagents rather than by the sensitivity of the system. Stability was examined by monitoring the response from a solution of $10\ \mu\text{g l}^{-1}$ of As, Se, Sn and Sb at 5 min intervals over the course of one hour of constant operation. With the cross-flow nebuliser, the drift in response amounted to approximately 5%. Table 2 quantitatively summarises the “short term” (5 replicates, 30 s) RSD achieved over the course of one hour (12 measurements at 5 min intervals). The stability of the signals is comparable to that achieved with conventional solution introduction using a pneumatic nebuliser, and typically a precision of the individual measurements with median values of the relative standard deviation below 2% was found (see Table 2). This represents a significant improvement over conventional continuous hydride introduction systems, which are often characterised by 5–10% RSD for Se at this concentration.¹ An additional, important advantage over conventional hydride generation systems is the rapid signal equilibration and washout times, illustrated for As, Se and Sb in Fig. 5. Signals from a $10\ \mu\text{g l}^{-1}$ solution require approximately 30 s to achieve a steady-state response from the moment the solution reaches the spray chamber, and a return to 1% of the maximum occurs within approximately 30 s.

The effect of NaBH_4 concentration on response was also examined. Signal intensities for all four analytes generated using 0.5% (m/v) NaBH_4 (containing 0.05% NaOH) were approximately 60% of those obtained with 1% (m/v). When 5% (m/v) NaBH_4 (containing 0.1% NaOH) was used, response for As, Se, Sn and Sb was reduced to 35, 10, 65 and 65%, respectively, of their optimal values achieved with 1% (m/v) NaBH_4 . Although lower reagent concentrations may be favourable for minimisation of potential interferences from transition metals,¹⁰ the short reaction time used here is not conducive to optimum response. Decreased recoveries with the higher concentration of NaBH_4 may have as their origin an increase in the amount of sodium reaching the plasma,

Table 2 Analytical figures of merit (cross-flow nebuliser)

Isotope	Sensitivity ^a /counts l s ⁻¹ μg ⁻¹	LOD ^b /μg l ⁻¹	BEC ^c /μg l ⁻¹	Relative standard deviation (<i>n</i> = 5)		
				Min (%)	Median (%)	Max (%)
⁷⁵ As	14000	0.007	0.18	0.40	1.4	3.8
⁸² Se	21000	0.010	0.070	0.72	1.6	3.0
¹¹⁸ Sn ^d	64000	0.008	0.17	0.56	1.7	3.6
¹²¹ Sb ^d	40000	0.005	0.051	0.74	1.2	2.0

^aTheoretical sensitivity calculated assuming 100% abundance. ^bLimit of detection: 3σ criterion, based on three measurements (each of 5 replicates) of a blank solution. ^cBackground equivalent concentration. ^dBased on 12 measurement intervals over a one hour stability study of continuous signal generation.

suppressing the degree of analyte ionisation. Clearly, additional studies are needed in order to interpret these results more fully.

Determination of Se in biological tissues

The determination of Se in biological tissues following microwave digestion has previously been shown to be unreliable with hydride generation using external calibration due to matrix suppression effects.¹ A comparison of results by external calibration (without using an internal standard) with those from a determination using the isotope dilution technique thus provides a sensitive test for matrix interferences. The results of these efforts are summarised in Table 3, which also permits comparison of the data with certified concentrations for this element. The five replicate samples of both reference materials represent five individual sample digestions. No significant difference is evident for the two calibration strategies, and all results are within the certified range for both nebulisers. Acceptable results were also obtained using external calibration with the ⁷⁷Se isotope following minor correction (3%) for the blank (samples 1a and 2a). Despite the use of non-optimal shear and make-up gas flows for the measurement of this isotope (Fig. 2c), reproducible data can be achieved. A few subtle points are also evident in the data that merit additional discussion. Because the final sample preparation step involved addition of HNO₃ to the samples, a slow process of re-oxidation of the Se(IV) to Se(VI) may have been initiated. Sub-samples were first diluted with HCl and then analysed using the Meinhard nebuliser system; several weeks later the same sub-samples were analysed using the cross-flow nebuliser system. Data generated using EC methodology for DORM-2 are biased slightly low for the cross-flow system, possibly as a consequence of the extended period of time during which enhanced oxidation of the Se(IV) occurred in this solution (note that this effect would have no influence on results generated using ID techniques). Re-oxidation of Se(IV) would be less apparent with the DOLT-2 sub-samples as they

were initially diluted to a greater extent with HCl prior to their analysis.

Although a previous study based on a conventional hydride generation system revealed that recovery of Se in DOLT-2 was only 26%, due to severe matrix effects,¹ it is not possible to directly compare such performance with that obtained here since the high sensitivity with the present arrangement permitted sub-samples to be diluted a further 5- to 10-fold prior to analysis, thereby alleviating any potential interferences. However, based on earlier reported performance characteristics for this new hydride generation approach,^{22,23} it may be assumed that transition metal interferences were probably significantly attenuated.

Response from transition and noble metals

Several transition metals have been shown to form volatile species by reaction with NaBH₄, including Cd,^{32–34} Cu,^{32,35} and Au, Zn and Co.³² Based on these reports, a broad range of elements was tested for potential response and the results are summarised in Table 4. In addition to elements such as In,³⁶ Tl³⁷ and Pb,³⁸ which are known to form volatile hydrides, or Hg which forms a cold vapour, these additional elements show promising sensitivity and precision under the tested conditions. This can only be rationalised by their formation of volatile species through reaction with NaBH₄. In an attempt to exclude the possibility that the observed signals were caused by a fine aerosol fraction transported to the ICP, the contribution from such an aerosol was measured separately by replacing the NaBH₄ with 1 M HCl. The aerosol fraction typically contributed to less than 0.5% of the total signal, supporting the hypothesis that a volatile species of the analyte is indeed formed as a result of a chemical reaction. This is consistent with the conclusions drawn earlier from the data in Fig. 2 and 3. The composition of an aerosol should reflect the relative composition of the solution from which it was generated. A purely physical enhancement of the transport efficiency by formation of an even finer aerosol in the presence of NaBH₄ and/or its decomposition products would be expected to affect all elements to a similar degree, the only exception being those forming stable hydrides or generating a cold vapor. This was not found in subsequent experiments wherein the solution was spiked to contain elements such as Mg, Al and Si.

Volatile species of these transition and noble metals could be present as a cold vapor or a gaseous hydride, depending on the element, and further investigations must be made to discern their nature. Although such compounds appear to be quite unusual, they are well-known in inorganic chemistry as the spectroscopic properties of the diatomic gaseous hydrides of Ag, Au, Cu, Pd, Pt and Tl have been investigated since the sixties.^{39,40} Due to the immediate separation of the reaction products from the solution, even unstable metal hydrides (or atomic vapors) appear to be released into the gas phase and subsequently transported to the ICP with substantial efficiency. The efficiency of formation of these volatile species has not been optimised, but it is anticipated that there will be a kinetic dependence on experimental variables. It is further evident

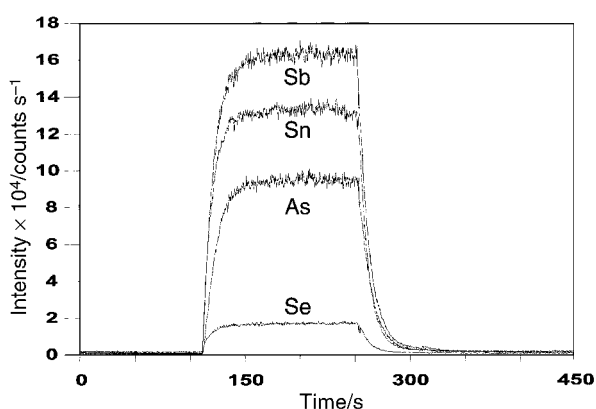


Fig. 5 Uptake and washout performance for introduction of a solution containing 10 μg l⁻¹ As(III), Se(IV), Sn and Sb.

Table 3 Determination of Se in certified biological reference materials

		Result ^b /μg g ⁻¹		Certified value ^c /μg g ⁻¹	
Sample number	Calibration ^a	Cross-flow	Meinhard		
DORM-2					
1	EC (⁸² Se)	1.39 ± 0.02	1.47 ± 0.01	1.40 ± 0.09	
2	EC (⁸² Se)	1.39 ± 0.01	1.46 ± 0.01		
1a	EC (⁷⁷ Se)	1.37 ± 0.01	1.40 ± 0.01		
2a	EC (⁷⁷ Se)	1.37 ± 0.01	1.40 ± 0.02		
3	ID (⁷⁸ Se/ ⁸² Se)	1.47 ± 0.01	1.43 ± 0.01		
4	ID (⁷⁸ Se/ ⁸² Se)	1.46 ± 0.01	1.43 ± 0.01	6.06 ± 0.49	
5	ID (⁷⁸ Se/ ⁸² Se)	1.47 ± 0.01	1.44 ± 0.02		
DOLT-2					
1	EC (⁸² Se)	5.53 ± 0.04	5.64 ± 0.06		
2	EC (⁸² Se)	6.09 ± 0.04	5.86 ± 0.10		
1a	EC (⁷⁷ Se)	5.48 ± 0.04	5.58 ± 0.06		
2a	EC (⁷⁷ Se)	6.03 ± 0.02	5.62 ± 0.07		
3	ID (⁷⁸ Se/ ⁸² Se)	6.00 ± 0.01	5.85 ± 0.04		
4	ID (⁷⁸ Se/ ⁸² Se)	5.92 ± 0.01	5.68 ± 0.07		
5	ID (⁷⁸ Se/ ⁸² Se)	5.96 ± 0.01	5.72 ± 0.04		

^aEC=external calibration; ID=isotope dilution. ^bResults present mean and one standard deviation. ^cUncertainties for the certified values are 95% confidence intervals.

Table 4 Elements forming volatile species and estimated detection limits (cross-flow)

Isotope	Sensitivity of volatile species ^a / counts l s ⁻¹ μg ⁻¹	Concentration of the test solution/μg l ⁻¹	BEC/μg l ⁻¹	RSD (5 replicates) (%)	Detection limit ^b / μg l ⁻¹
⁶⁵ Cu	860	100	0.22	14	0.038
¹⁰³ Rh	930	100	0.031	9.0	0.009
¹⁰⁶ Pd	990	100	0.023	9.3	0.003
¹⁰⁷ Ag	3400	250	0.010	0.7	0.012
¹¹⁵ In	740	111	0.017	11	0.003
¹⁹⁷ Au	290	91	0.014	10.8	0.004
²⁰² Hg	18000	8.8	0.074	0.6	0.001
²⁰⁵ Tl	470	135	0.026	7.5	0.019
²⁰⁸ Pb	230	100	0.22	8.3	0.041

^aTheoretical sensitivity calculated assuming 100% abundance of measured isotope (to facilitate comparison amongst various elements). ^b3σ, based on three measurements (each of 5 replicates) of a blank solution.

from these observations that there is a difference in the kinetics of formation of the volatile adducts of these elements and their complete reduction to the micro-particulate form. It is only in the latter phase that they are capable of inducing the classical interferences reported for transition metals suppressing signals from the conventional hydride forming elements.

It is interesting to note that this additional suite of elements comprises several of those detected as atomic species in solution following their reduction by NaBH₄.⁴¹ For most of these elements, the sensitivities and detection limits are, at the present time, comparable to those attained with conventional pneumatic nebulisation sample introduction. Since the experimental conditions of reagent concentrations, choice of acid and reaction time were optimised only for the determination of Se, it is very likely that further improvements regarding signal stability and sensitivity for these other elements can be achieved.

Conclusions

Determination of Se in two biological certified reference materials has demonstrated the viability of this new sample introduction technique. The system can be constructed from simple, commercially available equipment, and routine operation is comparable to the handling of solutions. No problems were encountered with respect to the detection of other elements known to form stable hydrides (As, Sb, Sn) or for Hg as a cold vapor.

The formation of volatile species of transition and noble metals by reaction with NaBH₄ was noted for a large number of elements. Data (not presented), suggest that the technique

may be utilised analytically for the determination of these transition and noble metals in biological samples, and through variation of the experimental conditions, further improvements in analytical performance are likely.

Additional studies with the concentric nebuliser are warranted, owing to the enhanced sensitivity and low background from aerosol transport with this system. The full versatility of this sample introduction methodology may be achieved through sequential optimised detection of both the hydride forming elements and those introduced *via* the usual aerosol formation process.

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