FLOW INJECTION DETERMINATION OF Se(IV) AND Se(VI) IN FRESHWATERS USING PRECONCENTRATION ON A QUATERNARY AMINE ANION EXCHANGE RESIN, HYDRIDE GENERATION AND ICP-AES DETECTION

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A microcolumn containing the anionic exchange resin, Benson BA-X10®, has been used in a flow injection manifold for the on-line preconcentration of Se(IV) and Se(VI) from freshwaters. Good separation was achieved for selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) using 0.08 M and 0.6 M ammonium nitrate eluents respectively with ICP-AES detection. For the more sensitive and selective determination of Se(IV), this species was eluted with ammonium nitrate (0.08 M) and acidified on-line prior to hydride generation. The volatile hydride was passed through a membrane gas-liquid separator and detected by ICP-AES. The limit of detection (3s, n =6) with a 1ml sample loop was 10 $\mu g\ l^{-1}$ at 196.026 nm and the reproducibility was 4.6% (n=6) for a 30 $\mu g\ l^{-1}$ standard. The NIST SRM 1643c (Trace Metals in Water) was analysed for Se(IV) and the result (11.2 ± 1.4 $\mu g\ l^{-1}$) compared well with previously reported data (10.6 $\mu g\ l^{-1}$). Total inorganic Se was also determined after off-line pre-reduction of Se(VI) and the result (13.5 ± 1.1 $\mu g\ l^{-1}$) was in good agreement with the certificate value (12.7 ± 0.7 $\mu g\ l^{-1}$).

Keywords: Selenium speciation, preconcentration, inductively coupled plasma-atomic emission spectrometry, hydride generation, freshwater, flow injection.

1. INTRODUCTION

Selenium is an essential trace element for mammals, including man, but it also has the lowest tolerance value of all essential elements [1]. In the environment Se exists in many forms, including seleno-amino acids and seleno-enzymes, (e.g. glutathione peroxidase, which prevents oxidative

damage to cells [2]), that are readily transformed into dimethylselenide (DMS) and dimethyldiselenide (DMDS) [3], and inorganic Se(IV) and Se(VI), of which the latter is highly toxic. In freshwaters the mean concentration of total Se is 0.2 $\mu g\ l^{-1}$ and the typical range is 0.01 - 5 $\mu g\ l^{-1}$ with Se(IV) being the predominant inorganic species in most surface waters [4].

Hydride generation (HG) coupled with ICP-AES is commonly used for the direct detection of Se(IV) and for the determination of Se(VI) after pre-reduction [5,6]. For speciation studies HPLC is the laboratory method of choice for separating selenium species prior to HG-ICP-AES detection and a variety of column types have been used for this purpose [7-11], including Benson BA-X10®, a quaternary amine based anionic exchange resin [11]. For environmental studies there is also a need for relatively simple techniques that combine in situ sample collection and preconcentration with the ability to separate Se(IV) and Se(VI).

This paper therefore describes an FI manifold incorporating a low pressure Benson BA-X10® resin microcolumn for the preconcentration and separation of inorganic Se species in freshwaters. The manifold is coupled with hydride generation and ICP-AES detection for the preconcentration (up to 2 h at 0.5 ml min^{-1}) and quantification of Se(IV).

2. EXPERIMENTAL

2.1. Reagents

All chemicals were of reagent grade unless otherwise stated and all solutions were prepared fresh each day in de-ionised water (18 $M\Omega\ cm^{-1}$) from a Milli-Q analytical reagent grade water purification system (Millipore, Bedford, MA, USA) and stored prior to use in acid leached 100 ml polypropylene graduated volumetric flasks. 1000 mg l^{-1} stock solutions of Se(IV) and Se(VI) were prepared by dissolving 0.3331 g and 0.4625 g of sodium selenite and sodium selenate respectively (Merck BDH, Poole, Dorset, U.K.) in water.

Working solutions were prepared by diluting the respective stock solutions with water. Sodium tetrahydroborate solution (2.75% m/v) was prepared immediately prior to use by dissolving 2.75 g $NaBH_4$ (98%) (Aldrich Gillingham, Dorset, U.K.) in water. Solutions of HCl (4 mol l^{-1}) were prepared by dilution of Aristar grade HCl (Merck BDH) with water. Benson BA-X10® resin (Benson Polimeric Inc., Reno, Nevada, USA) consisted of 15 - 25 μm beads functionalised with a quaternary amine group and supplied in the chloride form. The resin (1.003 g) was washed with 100 ml of 1.0 M NaOH and then with water until the washings were neutral. It was then slurry packed into a PEEK microcolumn (Phase Sep, Deeside, Clwyd, UK) with dimensions of 50 mm length and 2.4 mm i.d. The theoretical column capacity was 1.1 meq ml^{-1}. The retained Se species were eluted with various concentrations of ammonium nitrate (98%) (Aldrich) in water.

2.2. Instrumentation and Procedures

A schematic diagram of the FI manifold is shown in Fig. 1. Reagent solutions were pumped through the microcolumn using a 4 channel peristaltic pump (Gilson Minipuls 3, Villiers-le-Bel, France) with water as the carrier. Discrete volumes of sample (1.0 ml) and eluent (0.5 ml) were injected into the carrier stream using Rheodyne 5041 PTFE rotary injection valves (Rheodyne Inc., Cotati, CA). The column eluent was then acidified by merging with a stream of 4 mol l^{-1} HCl pumped at 0.5 ml min^{-1} using 0.025" i.d. Tygon® peristaltic pump tubing (Life Sciences International (UK) Ltd, Basingstoke, UK).

A second 4 channel peristaltic pump was used to merge this stream with the tetrahydroborate solution. The flow rate of the acidified stream was 1.0 ml min^{-1} and the tetrahydroborate had a flow rate of 1.0 ml min^{-1}. The gas-liquid separator consisted of a Perkin Elmer manifold assembly (Perkin Elmer Corp., Newark, CT) with a 1 μm PTFE membrane (Schleicher and Schuell, Dassel, Germany). The total flow rate into the gas-liquid separator was 2.0 ml min^{-1}. Argon flow (175 ml min^{-1}) was controlled via a rotameter and the nebuliser flow of the instrument was used as the make-up gas. The gas-liquid separator was drained at 3.0 ml min^{-1} using 0.06" i.d. Tygon® pump tubing. Peak areas were calculated using FigP®.

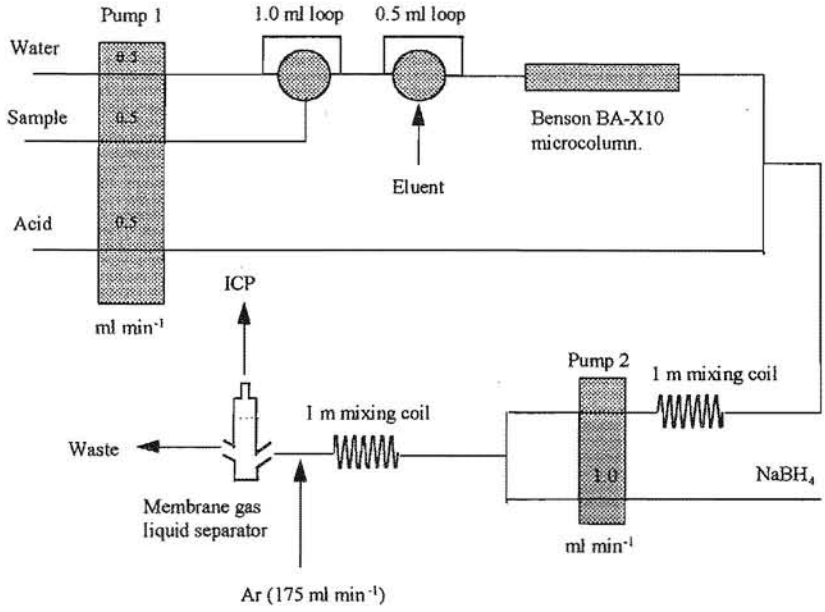

Fig. 1 Schematic diagram of the FI manifold incorporating hydride generation and ICP-AES detection.

2.3. Operating Conditions for ICP-AES

Se was monitored at 196.026 nm using an ICP-AES with a segmented-array, charge coupled device detector (Optima 3000, Perkin Elmer Corp., Newark, CT). Detector conditions were optimised for rf power, viewing height and nebuliser flow rate with an on-board multivariate optimisation program, using a 10 mg l^{-1} Se(IV) standard in Milli-Q with a continuous flow rate of 1.0 ml min^{-1}. The optimised conditions are given in Table 1.

Table 1. Operating Conditions for ICP-AES

RF Power	1250 W	Nebuliser Flow Rate	0.9 l min^{-1}
Viewing Height	6 mm	Auxiliary Flow Rate	0.5 l min^{-1}
Analytical Line	196.026 nm	Plasma Flow Rate	15 l min^{-1}
Sample Flow Rate	1.0 ml min^{-1}		

2.4. Preparation of the Benson BA-X10® Microcolumn

Benson BA-X10® resin was obtained in the chloride form and conditioned prior to packing. Resin (1.003 g) was weighed onto a glass sinter, rinsed under vacuum with 100 ml of 1.0 mol l^{-1} NaOH, then washed with water until the pH of the washings was neutral. The resin was then converted to the nitrate form by washing with 120 ml of 0.002 M HNO_3, rinsed with water and stored as a slurry in water. A PEEK microcolumn (Phase Sep, Deeside, Clywd, UK) of dimensions 50 mm x 4.6 mm i.d. was sealed at one end with a frit and the slurry slowly pumped into the column using a peristaltic pump. Connections to the column were sealed with PTFE tape.

3. RESULTS AND DISCUSSION

3.1. Optimisation of FI Separation Conditions

Initial studies involved optimisation of the conditions for the retention of Se(IV) and Se(VI) from water and their elution with ammonium nitrate. To optimise these eluent concentrations 1 mg l^{-1} Se standards were prepared by dilution from 1000 mgl^{-1} stock solutions, 1 ml sample volumes injected and preconcentrated on the column and the column rinsed with water. For Se(IV) elution ammonium nitrate solutions in the range 0.02 - 0.16 M were used and for Se(VI) elution ammonium nitrate solutions in the range 0.08 - 1.0 M were used. After 5 min, 0.5 ml of eluent was injected and after 10 min a second aliquot of eluent was injected to ensure total elution of analyte and to condition the column. Prior to the introduction of the next sample the column was rinsed for 3 min with water. Each sample was analysed in triplicate at each eluent concentration.

As can be seen from Figs. 2 and 3, the optimum ammonium nitrate concentrations for Se(IV) and Se(VI) elution were 0.08 M and 0.6 M respectively. There was no Se(VI) elution with 0.08 M ammonium nitrate and therefore complete resolution of the two selenium species was achieved. Sample pH, when buffered with suitable amounts of dilute nitric acid or sodium hydroxide had no effect on analyte retention in the pH range 2 - 9.

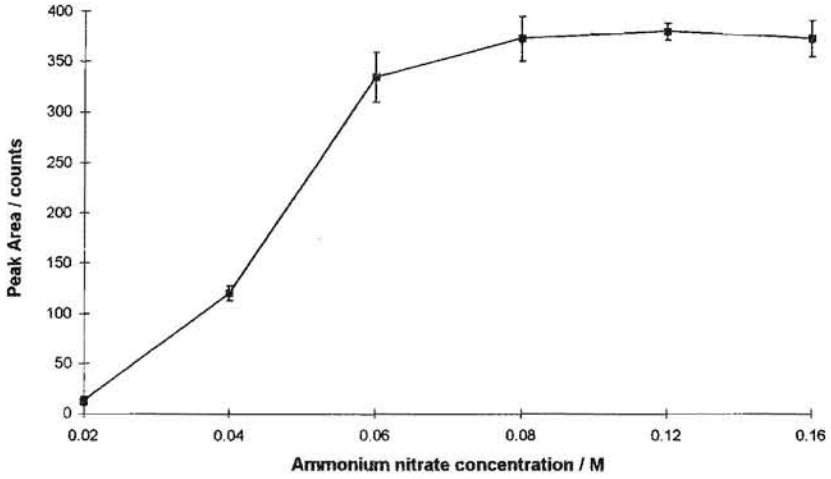

Fig.2 Effect of ammonium nitrate concentration on elution of 1 mg l^{-1} of Se(IV) from the microcolumn.

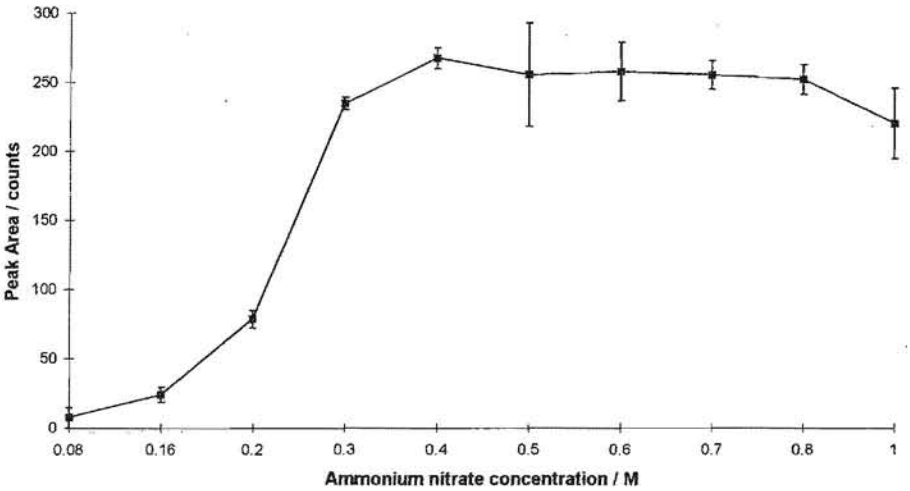

Fig.3 Effect of ammonium nitrate concentration on elution of 1 mg l^{-1} of Se(VI) from the microcolumn.

The detection limits (3s of the blank) for Se(IV) and Se(VI) were 100 μg l^{-1} and 130 μg l^{-1} respectively, with a 1 ml sample loop, which are unsuitable for the direct determination of Se species in natural waters. Nonetheless the results demonstrate the efficiency of inorganic Se preconcentration and speciation using a FI approach, which is well suited to field deployment.

3.2. Optimisation of Hydride Generation

A hydride generation (HG) system was incorporated in the FI manifold described above to increase the sensitivity for the determination of Se(IV) in water. The concentrations of $NaBH_4$ and HCl and argon flow rate through the membrane gas-liquid separator were optimised without the column in place and with a continuous sample flow rate of 1 ml min^{-1}.

Formation of the gaseous hydride of Se(IV) takes place in acidic solution [12] and optimisation of the HCl concentration was carried out using a 1 mg l^{-1} solution of Se(IV) in water and a $NaBH_4$ concentration of 0.75 % m/v pumped at 1.0 ml min^{-1}. The argon flow rate through the membrane separator was 250 ml min^{-1}. This optimisation was carried out by continuously mixing acid in the range 0.3 - 5.0 M at a flow rate of 0.5 ml min^{-1} with the sample. The response levelled off at 1.5 - 5.0 M and a concentration of 2.0 M was used for all subsequent experiments.

The effect of sodium tetrahydroborate on peak height was optimised by introducing concentrations in the range 0.25 - 5.25 % m/v at 1.0 ml min^{-1} into the acidified Se(IV) stream and the response showed a maximum at 2.75% m/v which was used for all subsequent experiments. As expected, lower argon flow rates allowed more time for hydride removal from the aqueous phase, thus increasing sensitivity. The optimum argon flow rate was 175 ml min^{-1} because lower flow rates caused plasma instability, even with 0.9 l min^{-1} of make up gas introduced into the nebuliser.

When using the optimised HG conditions, plasma conditions were re-optimised and found to be unchanged from those stated above. Using these optimised conditions with continuous sample introduction (no preconcentration), the limit of detection was 19.0 μg l^{-1} for Se(IV).

3.3. Flow Injection coupled with Hydride Generation and ICP-AES Detection

The FI manifold shown in Fig. 1 was used for the preconcentration of Se(IV) from water using the optimised separation and HG conditions. Calibrations were linear over the range 0 - 750 $\mu g\ l^{-1}$ with a regression coefficient (r^2) of 0.9987. The detection limit (3s of the blank) for Se(IV) with a 1 ml sample loop and 0.5 ml eluent loop (preconcentration factor of 2) was 10 $\mu g\ l^{-1}$ and the RSD was 7.3% (n=6) at 30 $\mu g\ l^{-1}$.

Since levels of Se are generally very low in freshwaters, and a minimum of sample treatment is desirable when studying speciation, it is advantageous to preconcentrate the sample *in situ* for subsequent laboratory analysis. This approach minimises the potential for sample contamination, sample loss or changes in composition and has been successfully applied to the preconcentration and speciation of mercury [13] and chromium [14]. The ability of the Benson column to retain Se(IV) quantitatively over extended periods of preconcentration time has therefore been investigated.

A 10 $\mu g\ l^{-1}$ Se(IV) standard in water was preconcentrated off-line (in the field) for 5, 15, 30, 60 and 120 min and the microcolumn returned to the laboratory and incorporated in the FI manifold described above. Preconcentration was linear with respect to time (r^2=0.9917) with a sample flow rate of 0.5 ml min^{-1}. 60 ml of sample was therefore preconcentrated in 2 h and eluted with 0.5 ml of eluent to give a preconcentration factor of 120. Uncertainties for periods of preconcentration of 30 and 120 min were 7.7% and 2.5% respectively (n=3). The approach reported here thus has considerable potential for *in situ* preconcentration and speciation studies (using ammonium nitrate elution) of Se in freshwaters. It is not suitable for saline waters however due to the deleterious effect of the higher ionic strength on retention of Se .

3.4. Freshwater SRM Analysis

A standard reference material (NIST SRM 1643c - Trace Elements in Water), certified for total inorganic selenium at 12.7 $\pm$ 0.7 $\mu g\ l^{-1}$, was analysed by the method of standard additions. 25 ml aliquots of the SRM were spiked with small volumes of 1 mg l^{-1} Se(IV) to give spiked standards at

20, 40 and 80 μg l^{-1}. A 5 ml sample loop was used instead of a 1 ml loop to provide increased sensitivity and each standard was analysed in triplicate. The standard addition graph was linear in the range 0 - 80 μg l^{-1} ($r^2 = 0.999$) and the SRM was found to contain 11.2 ± 1.4 μg l^{-1} Se(IV) which is in good agreement with a previously reported value of 10.6 μg l^{-1} obtained using AFS detection [11].

In order to determine total inorganic Se in the SRM, Se(VI) was pre-reduced using a method previously reported by Brimmer *et al.*[15]. Concentrated HCl (100 ml; 12 M) was then added to 100 ml of the SRM to give a 6 M solution in an acid washed conical flask (250 ml). This was sealed and fully immersed in a water bath maintained at 90°C for 30 min. The sample was allowed to cool for 1 h and then analysed immediately to minimise losses from back oxidation to Se(VI). This procedure created a highly acidic sample solution, which was buffered on-line with 0.1 M potassium sulphate (AnalaR) in order to protect the column. The on-column pH was 4.2. The buffer solution was directed to waste via a switching valve and water was pumped to the detector. After sample loading the column was rinsed for 1 min to remove residual buffer and the valve was switched and the eluent directed to the detector. Retained Se(IV) was eluted as described above. Determination of total inorganic Se was carried out as described above for Se(IV) using a 5 ml sample loop and spiked standards at 20, 40 and 80 μg l^{-1}. Calibration was linear ($r^2 = 0.993$) and the sample found to contain 13.5 μg l^{-1} ± 1.1 μg l^{-1} total inorganic selenium which compares well with the certified value of 12.7 ± 0.7 μg l^{-1}. By difference, Se(VI) was present in the SRM at 2.3 ± 1.2 μg l^{-1}.

4. CONCLUSIONS

An FI method incorporating a Benson BA-X10® resin microcolumn has been developed for the preconcentration and separation of inorganic selenium species in water using ammonium nitrate as the eluent. The method has been successfully coupled with hydride generation and ICP-AES detection for the sensitive (LOD of 10 μg l^{-1}) and direct determination of Se(IV), with Se(VI) determined indirectly after pre-reduction. Good agreement for Se(IV) and total inorganic Se was obtained for the NIST SRM 1643c. This column method can also be used for in situ preconcentration (up to 120X) of Se species from freshwaters.

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