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PRECONCENTRATION AND SEPARATION OF INORGANIC SELENIUM ON DOWEX 1X8 PRIOR TO HYDRIDE GENERATION–ATOMIC ABSORPTION SPECTROMETRY

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Summary—Exchange reactions between inorganic selenium species and chloride were studied on Dowex 1X8. The concentration exchange constants were determined with the batch technique at room temperature and used to predict the chromatographic enrichment and separation of tetra- and hexavalent selenium. A procedure for the determination of total selenium after digestion with permanganate and anion exchange preconcentration was also developed. The enrichment techniques were applied to the determination of Se(IV) and total dissolved selenium in drinking water and fresh water using flow injection hydride generation–atomic absorption spectrometry (HG–AAS). Results agreed with those obtained in a HG–AAS system where selenium was preconcentrated as hydrogen selenide in a trap at liquid nitrogen temperature.

Despite the very sensitive analytical techniques available for selenium[1–8] it is seldom possible to make direct determinations at the concentration levels present in natural waters. The total selenium concentrations found in Swedish lake water and drinking water are generally below 0.2 μg/l.[1,9] This means that the analyte has to be preconcentrated prior to its determination. Several preconcentration procedures have been described in the literature, *e.g.* decrease of sample volume by evaporation,[2] coprecipitation reactions,[10] derivatization followed by extraction into a small volume of an organic solvent,[3] *in-situ* collection of hydrogen selenide in a graphite furnace[4] or in a trap at liquid nitrogen temperature.[1] With the growing interest in speciation analysis of trace elements like selenium, the need for efficient preconcentration and separation procedures increases.

Use of ion exchange techniques offers the following possibilities.

(1) Decreased limits of detection. The limit of detection for selenium after hydride generation in spectrometric systems without preconcentration is approximately 0.1 μg/l[11,12] and thus generally too high for selenium speciation in waters. Preconcentration in a cold trap lowers the detection limit by a factor of about 50[1] and adequate sensitivity is obtained, but the equipment becomes more complicated with the cold trap included. Hence preconcentration by ion exchange combined with a standard HG–AAS system is an attractive alternative.

(2) Separation of Se(IV) and Se(VI). Selenium(VI) is usually determined after reduction to Se(IV) in boiling hydrochloric acid and thus obtained as the difference between a determination of Se(IV) + Se(VI) and a determination of Se(IV). The separation of the two oxidation states will increase the accuracy in the determination of Se(VI), especially when the ratio of Se(IV) to Se(VI) is large. Direct determination by ion chromatography at the concentration levels normally present in waters does not seem possible due to lack of sensitivity.[13]

(3) Removal of interferents. Resins based on crosslinked polystyrene adsorb dissolved organic material from natural waters.[3] Such organic material can cause severe interference in the determination of selenium.[14] Provided that the interferences to do not co-elute with the selenium, the use of an ion exchanger will lead to samples less prone to be affected by concomitants.

The separation of Se(IV) and Se(VI) has been demonstrated by several authors using paper chromatography,[15] high performance ion chromatography[16] and ordinary ion exchange

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chromatography.[5,17–19] Separation by ion exchange chromatography is also useful where the sample matrix prevents the direct determination of selenium.[7,20] Losses of Se(IV) have, however, been reported on Dowex 2.[21]

A number of papers describe applications of ion exchangers in the determination of selenium in natural waters. Selenium(IV) has been separated from Se(VI)[6] and interfering iron.[7] Zhang *et al.*[22] incorporated an anion exchange column in a flow injection system for the preconcentration and determination of Se(IV) at pH 5. Itoh and coworkers[23] have studied the selective preconcentration of Se(IV) on an anion exchanger modified with bismuthiol-II or its sulfonic acid derivative. Oyamada *et al.*[24] used Dowex 1X4 in the hydroxide form to preconcentrate Se(IV) and Se(VI) with subsequent simultaneous elution of both species. Boegel and Clifford[25] described a method for the industrial purification of water contaminated with selenium. After oxidation with chlorine, Se(VI) was adsorbed on Amberlite IRA-458 at pH 1.5 from hydrochloric acid solutions. Only in the work by Tanzer and Heuman[8] conditions were such, that in addition to preconcentration, Se(IV) and Se(VI) were quantitatively separated from each other.

No exchange constants for selenium have, to our knowledge, been reported for a strongly basic ion exchanger. This makes the rational use of ion exchange chromatography for the preconcentration and separation of selenium in the analysis of natural waters difficult. In this work exchange constants on Dowex 1X8 have been determined. Procedures for the preconcentration and separation of Se(IV) and Se(VI) based on these constants have been worked out. They were applied to the determination of Se(IV) and total dissolved selenium in waters with HG–AAS. The results are compared with those obtained in a HG–AAS system where selenium was preconcentrated as hydrogen selenide in a cold trap.

EXPERIMENTAL

Apparatus

The instrumentation for HG–AAS in a flow injection system was the same as described elsewhere.[12] The cold trap system,[1,3] was slightly modified. The original photomultiplier tube was replaced by the more UV-sensitive tube R-955 (Hamamatsu) and the power supply was replaced by the EDL System 2 (Perkin-Elmer) which allows the deuterium background corrector to be used with the Perkin-Elmer 3100 spectrometer.

A Metrohm Titroprocessor 636 equipped with the 635 titration stand was used for chloride determinations.

A Perkin-Elmer 2380 atomic absorption spectrometer operated in the flame mode was used for determination of iron in the water samples.

The reduction of eluted Se(VI) was carried out in calibrated borosilicate glass test tubes heated in a purpose built aluminium block thermostatted to 105°.

The ion exchanger tube was constructed from borosilicate glass. It consisted of a wide cylindrical funnel (volume $\approx$ 70 ml) sealed onto a 200 mm long and 8 mm i.d. tube having a 1 mm drawn out bore tip. Flow was controlled by a clamp around a small piece of PVC tubing connected to the tip.

Chemicals, reagents and ion exchange resin

Analytical grade chemicals from Merck were used unless otherwise stated. Demineralized, distilled water passed through a Millipore three filter cartridge system (Milli-Q water) was used throughout.

Standard stock solution of Se(IV), 1 g/l, in dilute nitric acid was checked as described previously.[12] Further standards were made by dilution and contained 2 ml/l of concentrated hydrochloric acid. Acid-free standard solutions of Se(IV) and Se(VI), used in the determination of exchange constants, were prepared by dissolving sodium selenite pentahydrate and sodium selenate decahydrate (BDH), respectively, in Milli-Q water and standardized against a Se(IV) standard solution.

Sodium tetrahydroborate (Fluka) solution, 0.5% (w/v), was prepared and purified as described previously.[1]

Indicator solution, 0.03% (w/v). Dissolve methyl red in 60 ml of ethanol and dilute to 100 ml with Milli-Q water.

Ammonium buffer solution, pH 9. Dissolve 2.12 g of ammonium chloride and 1.55 g of 25% (w/w) ammonia in water and dilute to 250 ml.

Hydrogen peroxide 3% (w/w). Prepare by dilution of suprapur Perhydrol®.

Potassium permanganate, 1% (w/v). Prepare by dissolution in water.

Hydrochloric acid, 37% (w/w). Dilute 1:1 and deaerate prior to use in the cold trap system.

Ion exchange resin, Dowex 1X8 chloride form, 100–200 mesh (Serva).

Water samples

Water samples were collected in acid leached polyethylene bottles, filtered through 0.45 μm membrane filters (Millipore) and stored refrigerated. The samples were immediately analysed for Se(IV) using the cold trap system and, in addition, total iron, pH and chloride were determined.

Ion exchange resin

Fines were removed by decantation and the resin (100 g) washed with 200 ml of 1*M* sodium hydroxide followed by Milli-Q water to neutral. Conversion into chloride form was achieved by washing with 200 ml of 1*M* hydrochloric acid. After extensive rinsing with Milli-Q water the resin was dried over night at 50° and then conditioned over calcium chloride hexahydrate and its saturated solution in a desiccator. The water content of the conditioned resin was determined after drying at 105° over night.

Any presence of selenium in the resin was determined after digestion with a mixture of nitric, perchloric and sulfuric acid or the magnesium nitrate–nitric acid–hydrochloric acid method.[26]

The capacity of the resin was determined by potentiometric titration after elution of chloride with 1*M* sodium perchlorate.

Column preparation

One gram (dry weight) of the conditioned resin was slurried in water, packed between plugs of quartz wool and washed with 10 ml of 1*M* hydrochloric acid followed by 25 ml of Milli-Q water. When Se(IV) was to be preconcentrated, the resin was finally washed with 20 ml of ammonium buffer solution (0.001*M*, pH 9). Prior to preconcentration of Se(VI) the resin was washed with 10 ml of 0.025*M* hydrochloric acid.

Determination of exchange constants

The temperature was 20 ± 2° in all experiments. Duplicate determinations were made at all chloride concentrations. pH was checked at the start and end of an experiment. Further details of the conditions are given in Table 1.

One gram (dry weight) of the conditioned resin and 100.0 ml of a 1.00 μM selenium solution were added to an Erlenmeyer flask. The pH was adjusted with 0.2*M* sodium hydroxide when needed. The flask was closed and the solution stirred gently for 12 hr. A portion of the aqueous phase was then filtered through a 0.45 μm membrane filter. Hexavalent selenium was reduced by boiling in 4*M* hydrochloric acid. The selenium concentration in the aqueous phase was determined with the flow injection system.

Preconcentration

The recommended volumes pertain to selenium concentrations in the range 0.025–0.2 μg/l. The amount of resin is 1.00 g (dry weight). The flows during preconcentration and elution are approximately 2 and 1 ml/min, respectively.

Preconcentration of Se(IV). To a 100 ml sample add 2 drops of indicator solution and while deaerating with nitrogen, add dropwise 6*M* hydrochloric acid followed by 1*M* acid until a stable pink colour is observed. Continue deaerating for 10 min. Add 0.4 ml of ammonium buffer solution, mix and pass the sample through the column. Elute selenium with 7.5 ml of 1*M* hydrochloric acid.

Preconcentration of Se(VI). Make the sample 0.025*M* with respect to hydrochloric acid and deaerate with nitrogen. Pass a 100 ml portion of the sample through the column. Elute Se(VI) with 7.5 ml of 5*M* hydrochloric acid into a test tube and mix thoroughly. Heat the tube in the thermostatted aluminium block for 90 min, cool and adjust the volume to 7.5 ml.

Preconcentration and separation of Se (IV) *and Se*(VI). Pretreat and preconcentrate at pH 9 as for Se(IV). After preconcentration, elute Se(IV) with 10 ml of 0.025*M* hydrochloric acid. Then elute Se(VI) with 7.5 ml of 5*M* hydrochloric acid.

Sample preparation for determination of total dissolved selenium

To a 100 ml portion of the sample, add 2 drops of indicator solution. While deaerating

Table 1. Experimental conditions and results from determinations of the exchange constants for tetra- and hexavalent selenium on Dowex 1X8

Selenium species	pH	[Cl] (*mM*)	Exchange constant ($\times 10^2$ (range))*
$HSeO_3^-$	5.0 ± 0.2	1, 4,7	10.7–11.4
SeO_3^{2-}	10.1 ± 0.1	5, 10, 25, 40	1.2–1.5
$HSeO_4^-$	1.3–5.6	20, 40	≈350
SeO_4^{2-}	6.1 ± 0.1	15, 25, 40	8.6–9.3

*Constants for $HSeO_3^-$ and $HSeO_4^-$ are dimensionless. Constants for SeO_3^{2-} and SeO_4^{2-} expressed as *M*/(mol/kg).

with nitrogen add 6*M* hydrochloric acid until the colour changes to pink followed by another portion of acid to adjust pH to 2. Transfer the sample to a 250 ml beaker. Add 3 ml of the permanganate solution and some boiling stones. Cover the beaker with a watch glass. Heat and boil gently on a hot plate for 30 min.

Ion exchange preconcentration. While the sample is still boiling, remove excess permanganate by dropwise addition of hydrogen peroxide. When all manganese dioxide has disappeared, cool and adjust the volume to about 100 ml. Preconcentrate the sample as described for Se(VI).

Cold trap preconcentration. After the oxidation step with permanganate, add 40 ml of concentrated hydrochloric acid and continue boiling for 1 hr. Cool and transfer to a 250 ml volumetric flask. Dilute to volume with Milli-Q water.

Determination of selenium

Cold trap system.[1,3] Use a total volume of 30 ml and evaluate from a calibration curve established from acid matched standards containing not more than 5 ng of Se(IV).

Flow injection system.[12] Use a 0.5 ml injection loop and evaluate from a calibration curve established from acid matched standards of Se(IV), 0–5 μg/l.

RESULTS AND DISCUSSION

The ion exchange resin

Only the chloride form of Dowex 1X8 was used in the experiments. The conditioned resin contained about 11% of water and the capacity was 3.2 meqv./g (dry weight). Due to the very low selenium concentrations investigated, it is necessary to select a selenium-free resin. An old batch, first used, leaked selenium on washing with hydrochloric acid after standing for some time in water only. Analysis showed that it contained about 0.2 μg Se/g. Apparently the selenium is present in the structure which continuously degrades. No detectable amounts of selenium were found in fresh batches of resin, however.

Boegel *et al.*[25] reported losses of Se(VI) on Dowex 1X8 below pH 2. This was explained as due to spontaneous reduction of selenate to selenite by the high concentration of hydrochloric acid within the resin phase. In order to investigate this, we performed the following experiment: Dowex 1X8 was contacted with 1 μ*M* selenate solutions in 0.01*M* hydrochloric acid for 4 days. The resin and the solution were then analysed for Se(IV). The amounts of Se(IV) did not exceed those expected from the 0.1% selenite originally present in the selenate stock solution. Hence the determination of the exchange constants were not affected by redox reactions.

The exchange constants

The amount of selenium which needs to be collected on the ion exchanger prior to HG–AAS determination is <1 nmol. Hence the loading of the ion exchanger will be very small, if 1 g of resin is used. The exchange constants were therefore determined only for low mole fractions of selenium on the resin. The batch technique was used and no concentration changes were observed after 6 hr of equilibration. The experimental conditions were chosen so that the exchange equilibria were shifted towards the resin phase. Hence an analysis of the aqueous phase for selenium is sufficient to provide the data needed for the calculation of the exchange constants.

The following equilibria pertain to the exchange processes

$$HSeO_3^- + R^+Cl^- \rightleftharpoons R^+HSeO_3^- + Cl^- \quad (1)$$

$$SeO_3^{2-} + 2R^+Cl^- \rightleftharpoons R_2^+SeO_3^{2-} + 2Cl^- \quad (2)$$

$$HSeO_4^- + R^+Cl^- \rightleftharpoons R^+HSeO_4^- + Cl^- \quad (3)$$

$$SeO_4^{2-} + 2R^+Cl^- \rightleftharpoons R_2^+SeO_4^{2-} + 2Cl^- \quad (4)$$

In order to simplify the presentation charges are often omitted and the following abbreviations will be used;

$$X = SeO_4^{2-} \text{ or } SeO_3^{2-},\ HX = HSeO_4^-$$
$$\text{or } HSeO_3^- \text{ and } H_2X = H_2SeO_3$$

The concentration exchange constants corresponding to reactions (1)–(4) are

$$K_{Cl}^{HX} = \frac{[HX]_R[Cl]}{[Cl]_R[HX]} \quad (5)$$

$$K_{2Cl}^{X} = \frac{[X]_R[Cl]^2}{[Cl]_R^2[X]} \quad (6)$$

Concentrations in the aqueous phase in mol/l [*M*] and in the resin phase [subscript R] in mol/kg dry resin. The protonation constants of X will be denoted by β_1^H and β_2^H.

The total concentrations of selenium in the two phases are

$$[X]_{tot} = [H_2X] + [HX] + [X] \qquad (7)$$

$$[X]_{R,tot} = [HX]_R + [X]_R \qquad (8)$$

Combining equations (5)–(8) and introduction of the expressions for the protonation constants yields

$$\begin{aligned}[X]_{R,tot} = {} & [X]_{tot}(K_{Cl}^{HX}\beta_1^H[H^+][Cl]_R[Cl]^{-1} \\ & + K_{2Cl}^{X}[Cl]_R^2[Cl]^{-2})(1+\beta_1^H[H^+] \\ & + \beta_2^H[H^+]^2)^{-1} \qquad (9)\end{aligned}$$

After a measurement of $[X]_{tot}$ and $[H^+]$ all other quantities in equation (9) are known except the exchange constants.

Exchange of selenite. The acid dissociation constants of selenous acid are $pK_1 = 2.6$ and $pK_2 = 8.2$.[26] Hence at pH 10, X will predominate with very little HX present, whereas at pH 5, HX will dominate with very little H_2X and X present. Under the respective conditions, equation (9) reduces to equations (5) or (6) which were used to calculate the results for Se(IV) in Table 1.

Exchange of selenate. The acid dissociation constant of the hydrogen selenate ion is about $0.01/M$ [$pK = 2$]. Hence the selenate ion predominates at pH > 5. The results for K_{2Cl}^X presented in Table 1 were obtained at pH 6.1 and calculated from equation (6).

Unfortunately, K_{Cl}^{HX} must be determined from measurements on solutions which contain HX and X in comparable concentrations. Measurements were made in mixtures of hydrochloric acid and sodium chloride. Two series of experiments were performed and the medium was varied from pure hydrochloric acid to pure sodium chloride while the total chloride concentration was kept constant at 0.02 *M* and 0.05*M*, respectively. Our data were not accurate enough to permit a simultaneous determination of K_{2Cl}^X, K_{Cl}^{HX} and β_1^H, [$\beta_2^H = 0$]. The contribution from $[X]_R$ to $[X]_{R,tot}$ was therefore calculated and subtracted from $[X]_{R,tot}$ and the difference attributed to $[HX]_R$. In this calculation $K_{2Cl}^X = 0.09$ and $\beta_1^H = 40/M$ [$pK_1 = 1.6$] were used. There is a considerable scatter in the reported values of β_1^H. The value used here is based on the extensive data of Nair as recalculated in Ref. 27. The value of $K_{Cl}^{HSeO_4}$ obtained varied between 2 and 5 with a strong covariation between the calculated value of the exchange constant and the protonation constant used in the calculation. Together they will, however, reproduce the experimental results.

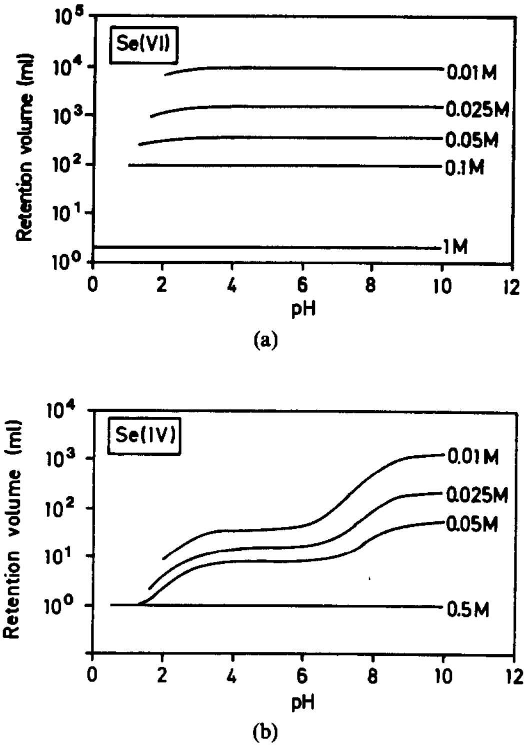

Fig. 1. Predicted retention volumes for tetra- and hexavalent selenium on Dowex 1X8 as a function of pH. Calculations based on the exchange constants in Table 1. Molar concentrations refer to chloride. Amount of resin: 1 g, void volume: 0.8 ml.

The retention volumes, V_R, of tetra- and hexavalent selenium as a function of pH and chloride concentration were calculated from

$$V_R = V_M + wK_D \qquad (10)$$

Where *w* is the weight of the ion exchanger and V_M the volume of the mobile phase in the column. The distribution ratio of selenium is denoted by K_D. The loading of the resin with selenium will be very small in an analytical application, hence the concentration of chloride in the ion exchanger phase will be equal to its capacity, *Q*. K_D can be found from

$$K_D = \frac{\alpha_1[H^+][Cl^-]^{-1} + \alpha_2[Cl^-]^{-2}}{1+\beta_1^H[H^+]+\beta_2^H[H^+]^2} \qquad (11)$$

with $\alpha_1 = K_{Cl}^{HX}\beta_1 Q$ and $\alpha_2 = K_{2Cl}^X Q^2$. Calculated retention volumes for a 1 g column ($V_M = 0.8$ ml/g and $Q = 3.2$ mmol/g) are shown in Fig. 1. It can be concluded that for solutions low in chloride, preconcentration of Se(IV) requires pH > 8 while Se(VI) is more uniformly retained between pH 1 and 10. Separation of the two oxidation states can be achieved in a 0.025*M* hydrochloric acid medium. It can also be concluded that only samples of moderate chloride concentration will allow preconcentration of selenium. This limits the practical use of the enrichment procedures to fresh waters and similar matrices. It also requires that any pretreatment steps in the analytical procedure, such as conservation or digestion of the sample, do not add large amounts of chemicals. Use of a counter ion with less affinity to the ion exchanger, *e.g.* acetate,[22] would increase the retention volumes and thus facilitate the enrichment. We did not make any experiments with acetate or other weak bases as counter ions, since we wanted to use pH as a tool for obtaining a reasonably sharp separation of Se(IV) and Se(VI).

A series of experiments were carried out using standard solutions of selenium in sodium chloride to test the conclusions from Fig. 1. As can be seen from Table 2, Se(IV) and Se(VI) were quantitatively taken up from a solution of 0.02*M* in chloride. This concentration is expected to be an upper limit for the anion concentration of fresh water samples. The results also demonstrate that 0.025*M* hydrochloric acid is a suitable eluent for the separation of the two oxidation states. A hydrochloric acid concentration of 5*M* was found convenient for the elution of Se(VI). This concentration elutes Se(VI) quantitatively in 7.5 ml and is, at the same time, the proper medium for reduction of Se(VI) to Se(IV). Lowering the elution volume to 5 ml of hydrochloric acid resulted in losses but the recovery of selenium was never less than 90%.

Table 2. Preconcentration and separation of Se(IV) and Se(VI). Synthetic samples pH 9, [Cl] = 0.020*M*, sample volume 100 ml. Selenium(IV) eluted with 10 ml of 0.025*M* hydrochloric acid. Selenium(VI) eluted with 7.5 ml of 5*M* hydrochloric acid. Average and standard deviation of four replicates

Selenium taken (*ng/l*)		Selenium found (*ng/l*)			
Se(IV)	Se(VI)	Se(IV)	(%)	Se(VI)	(%)
200	27	203 ± 4	101	27 ± 2	100
200	54	198 ± 5	99	53 ± 5	98
200	108	198 ± 1	99	107 ± 2	99
200	216	200 ± 2	100	212 ± 4	98
50*	50	51 ± 2	102	50 ± 4	100

*After removal of carbon dioxide from samples 0.020*M* in HCO_3^-.

Digestion procedure

Oxidation with permanganate was found to be the most suitable method for digestion of the water samples prior to ion exchange preconcentration. Acid digestion with permanganate quantitatively converts inorganic selenium to the hexavalent state. However, permanganate is known not to destroy all types of organic material including selenonium compounds,[1,28] which might be present in natural waters. The concentration of such compounds in fresh water appears, however, to be low.[1,8,23] The method is rapid and excess reagent can easily be removed. Since Mn^{2+} is formed the reagent does not contribute to the loading of the ion exchanger. For this reason hydrogen peroxide is preferred to oxalate in the removal of excess permanganate. Manganese dioxide particles adsorbed on the glass wall is preferably rinsed down into the solution prior to the addition of peroxide. The hydrogen peroxide should be added carefully to avoid losses by spray in the rather violent reaction. Small traces of manganese dioxide remained in some digests after 5 min of boiling but this did not affect the subsequent steps in the procedure. A blank signal from the digestion step, corresponding to ≤5 ng/l selenium, was recorded with the cold trap system.

Possible alternatives to permanganate include UV-irradiation or digestion with peroxodisulphate.[1] UV-irradiation demands proper control of pH to ensure selenium being present in only one oxidation state.[29] Peroxodisulphate converts selenium to Se(VI) and releases selenium from trimethyl selenonium[1] but is reduced to sulphate which will subsequently load the resin.

Applications to fresh waters

One of the major ions in fresh water is the hydrogen carbonate ion, which is enriched on the ion exchange column. On elution by acid, a substantial volume of carbon dioxide is evolved that upsets the resin column. This prevents elution into a small volume which is essential for a high enrichment factor. Elution of adsorbed selenium species can be made by salt solutions for instance, a sodium perchlorate solution in order to avoid gas formation. However, the presence of a fairly high concentration of a salt caused a decrease in the sensitivity of the HG–AAS determination. The effect on the sensitivity was a function both of the nature and concentration of the salt. Presence of carbon dioxide causes a spectral interference in the

Table 3. Comparison of preconcentration techniques on fresh water samples. Total dissolved selenium after digestion with permanganate at pH 2 and recovery of 50 ng/l of Se(IV) added to the samples. Average and standard deviation (ng/l) of four determinations

		Preconcentration technique			
		Anion exchange		Cold trap	
Sample location	Sample type	Se(IV)	Total Se	Se(IV)	Total Se
Institute	Drinking water*	62 ± 2	199 ± 8	59 ± 3	196 ± 7
Alunda	Well water	52 ± 3	130 ± 4	48 ± 3	136 ± 6
Funbo	Lake water	52 ± 3	140 ± 6	47 ± 2	141 ± 6
Lunsen	Surface run-off	45 ± 2	46 ± 2	48 ± 2	46 ± 2
Ekoln	Lake water	51 ± 2	140 ± 4	49 ± 3	144 ± 16

*10 ± 1 ng/l Se(IV) from direct determination with the cold trap system.

HG–AAS method.[1] Therefore carbon dioxide must always be removed and it was found best to make this removal as the first step in the procedure. The adopted pH adjustment with the methyl red indicator and deaeration worked well, see Table 2. The indicator is strongly bound to the resin and is difficult to elute. A new column was therefore prepared for each enrichment of Se(IV) from fresh water. When total selenium was determined, the indicator was destroyed in the digestion step and the column could then be used for a large number of preconcentrations.

A preliminary analysis with the cold trap system showed detectable concentrations of Se(IV) only in the drinking water, 10 ng/l. In order to study the ion exchange procedure we chose to spike all samples with 50 ng/l of Se(IV). The results from the proposed ion exchange procedures for Se(IV) and total selenium agree very well with those obtained by cold trap preconcentration. The added Se(IV) is recovered with no significant losses and the observed total concentrations are in line with previous reports for Swedish waters.[1,9] However, preliminary results using water samples high in dissolved organic carbon indicate losses of Se(IV) from preconcentration at pH 9. This disturbance is more or less overcome by filtration of the sample through XAD-8 at pH 2 prior to the preconcentration step. The relative standard deviation of the methods is about 5% in the range 50–200 ng/l. The detection limit is 5 ngSe/l. No results are given for Se(VI) because interferences have been observed in the reduction step for some waters and these disturbances will be subjected to a separate study.

The total concentrations of iron in the water samples were 0.02–1.06 mg/l. On adjustment of pH to about 9 prior to the preconcentration of Se(IV) no formation of a precipitate could be observed. Since the solubility of iron(III) hydroxides are extremely small, the iron was evidently present in a strongly complexed form which did not affect the preconcentration step. Presence of free or loosely bound iron interfered in this step, however. Addition of 5 mg/l of iron(III) to standard solutions of Se(IV) resulted in precipitate formation at pH 9 and poor recoveries of selenium. Neither increased contact time with the eluant nor increased eluant volume gave reproducible results. Removal of iron on a cation exchange resin (Dowex 50) at pH 4 also failed due to poor adsorption of the iron species. However, if this step can be carried out at pH 2, iron will probably be more efficiently separated from selenium. With a subsequent adjustment of the effluent pH to 9 the preconcentration might be successful. As a whole, recoveries varying between 70 and 100% were obtained in the experiments with iron, despite various efforts to secure quantitative results.

The concentrations of chloride were low and together with hydrogen carbonate and sulphate the total anion concentrations in Swedish fresh waters are generally below 5 meqv./l.[30]

CONCLUSIONS

The exchange constants determined in this work provide necessary information for designing preconcentration and separation methods for selenium by ion exchange chromatography. The proposed procedures will allow an accurate determination of the element down to about 25 ng/l by the standard HG–AAS method in samples of low or moderate chloride concentration. Thus most fresh waters can be analysed. The method requires only simple and cheap equipment, but it involves a few additional steps. It should, however, be quite easy to automate the preconcentration and separation steps. Even with the simple equipment used here, the steps can be run largely unattended. The construction of the exchanger columns with a narrow-bore tip prevents the column from running dry. With a carefully cleaned glass surface volumes added to the column are recovered with a high reproducibility and hence no volume adjustments are necessary. For instance, 5.00 ± 0.02 ml were collected as eluate when 5.00 ml were added to the column. The removal of carbon dioxide is the most labour-intensive step for which no easy alternative was found.

Metal ions, which can change the sensitivity of the HG–AAS step, are removed in the preconcentration step, but disturbing anions, such as the nitrite ion,[31] might accumulate. In order to reach preconcentration factors of 10–20, the eluate volumes must be small. This makes application of the method of standard additions, which is used to take care of a varying sensitivity, difficult. However, the proposed procedures tend to normalize the matrices so that calibration curves established from acid-matched standards can be used for evaluation of the concentrations.

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