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HITACHI ZEEMAN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETER AS A SELENIUM-SPECIFIC DETECTOR FOR ION CHROMATOGRAPHY

SEPARATION AND DETERMINATION OF SELENITE AND SELENATE

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SUMMARY

A Dionex ion chromatograph was interfaced with a Hitachi Zeeman graphite furnace atomic absorption spectrometer (GFAA) which functioned as a selenium-specific detector. Samples of distilled water, a synthetic river water and a Texas river water sample spiked with selenite and selenate were chromatographed and selenium detected by GFAA. The detection limit is 20 ng Se for each selenium compound Preconcentration from a maximum of 4 ml of an anion-rich water sample extends the detection limit to 5 ng Se The selenate peak broadens with increasing sulfate concentration.

INTRODUCTION

Selenium resembles sulfur chemically and is, therefore, found in native sulfur and in many sulfides. Igneous rocks have been estimated to contain an average of about 0.09 ppm of selenium. The selenium content of sedimentary rocks varies over a wide range. Weathering of such rocks mobilizes selenium in the form of selenites and selenates. The combustion of U.S.A. coals, which average 2.8 ppm of selenium, also adds selenium to the environment The most important inorganic compounds in the soil and in the water are selenites and selenates, from which a variety of organic selenium compounds are synthesized by organisms[1].

Selenium is now recognized as a nutritionally essential element However, the nutritionally required level is very close to the toxic concentration Selenium compounds have been reported to have anti-carcinogenic activity, have value against cardiovascular disease and prevent heavy metals from exerting their toxic effects These aspects of selenium have recently been reviewed[2,3].

The toxicity of selenium is very much dependent on its chemical form For

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instance, unicellular marine algae did not survive in a medium containing 10 ppm selenium in form of selenate. However, selenite was tolerated at levels as high as 100 ppm[4]. For an accurate assessment of the environmental impact of selenium, the identities and the concentrations of the selenium compounds present in a system must be known in addition to the total selenium concentration. Very little reliable information about the type of selenium compounds present in the environment is available. Considerable disagreement exists about the form of selenium in natural waters with claims for selenite[5] and selenate[6] as the predominant species. The lack of a sensitive method for the determination of selenite and selenate not requiring any chemical treatment of the sample is partly responsible for the unavailability and paucity of data Selenite can be determined quantitatively by sodium borohydride reduction to hydrogen selenide with subsequent transfer of the gaseous hydrogen selenide to an atomic absorption spectrometer for the determination of the element. Selenate is usually determined by the method used for selenite after its reduction to selenite by well-timed boiling with 4 M hydrochloric acid. Prolonged boiling may reduce selenite to elemental selenium. Moreover, the reduction of selenate to selenite is affected by the other constituents of the sample[6]. Meyer *et al.*[7] reported that the hydride reduction procedure suffers from numerous interferences Natural waters containing appreciable levels of dissolved organics had to be freed of these compounds by chromatography before selenite and selenate could be determined by the hydride technique[8]. Reviews of the analytical methods for the determination of selenium are available in the literature[1 9 10].

Although selenite and selenate can be separated by ion chromatography[11], this procedure seems to be useful only in the absence of chloride, nitrate, nitrite, phosphate, sulfate and bromide, a condition rarely encountered in the case of natural water samples. The work presented in this paper describes the separation of selenite and selenate in the presence of other anions by ion chromatography and the use of a Hitachi Zeeman graphite furnace atomic absorption spectrometer (GFAA) as a selenium-specific detector.

EXPERIMENTAL

All solutions were prepared from reagent-grade chemicals and distilled, deionized water and were stored in polyethylene bottles Stock solutions containing 1000 ppm selenium were made using Na_2SeO_3 and Na_2SeO_4. Solutions of lower concentrations were obtained daily by appropriate dilution.

Instrumentation

A Dionex Model 16 ion chromatograph was used in these investigations The 0 1-ml injection loop was replaced by a section of PTFE tubing capable of holding 1 0 ml of sample. The sample (1.0 ml) was placed on a 50 × 3 mm anion precolumn (Dionex 30008). The mobile phase (0 0080 M aqueous Na_2CO_3) was delivered at a constant flow-rate of 0.46 ml/min (pump setting 6 %). The precolumn was connected in series to a 150 × 3 mm anion separator column (Dionex 30589) and a 250 × 3 mm anion suppressor column (Dionex 30066). The effluent passed then through the conductivity detector. A PTFE tubing (0.5 mm I.D) was installed to route the effluent to the auxiliary valve 2. A similar tubing connected one port of this valve to the slider

injection valve of the ion chromatograph–GFAA interface[12][13] With the auxiliary valve 2 switch in the "on" position the effluent was routed to the GFAA, in the "bypass" position it went to waste When more than 1 ml of a sample had to be injected, the injection loop was replaced by a 150 × 3 mm anion separator column (Dionex 30232) which served as a concentrator column (Fig 1) A Hitachi Zeeman GFAA with 50-μl graphite cups equipped with an Instrument Laboratory selenium hollow cathode lamp operated at 10 mA was used as the selenium-specific detector The signals from the GFAA were recorded on a Fisher Recordal Series 5000 recorder Nitrogen at 4 l/min was utilized as the sheath gas and at 0 2 l/min as the carrier gas The carrier gas flow was stopped during the atomization cycle The expansion and response settings were 3 × The drying cycle operated at a temperature (27 A, ca. 120°C) and ramp setting (60 sec) of 6 The ashing cycle was not used The temperature setting for the atomization cycle was 9 (290 A, ca 2500°C) with a step setting of 6 (6 sec). The timer was set for an 80-sec interval between analyses
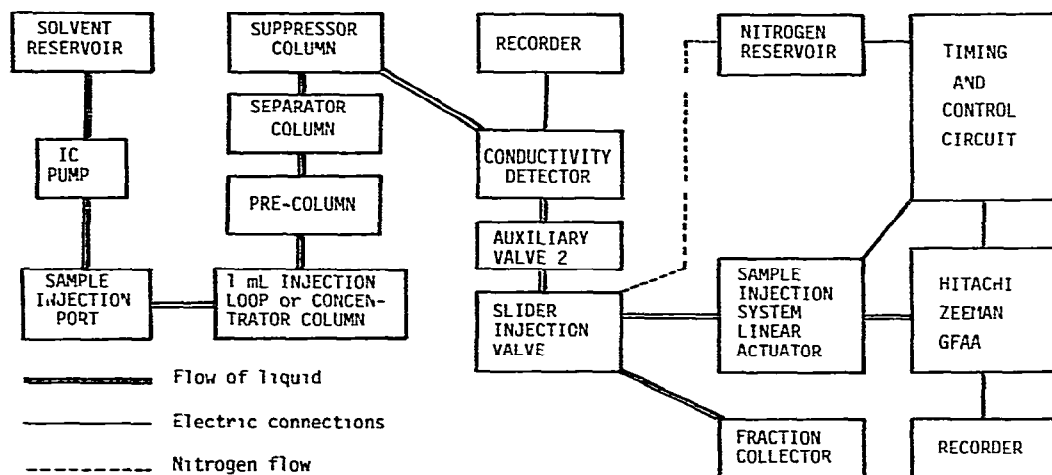

Fig 1 Block diagram for the ion chromatography–Hitachi Zeeman GFAA system

RESULTS AND DISCUSSION

Selenium concentrations in fresh waters are generally in the low ng/ml range Selenite and selenate, the most commonly encountered selenium compounds in such waters, can be separated on a Dionex 30589 anion separator column by ion chromatography. They may be detected by a conductivity detector set at high sensitivity provided that other anions are present in the samples only at comparable concentrations or concentrations lower than selenite and selenate However, the determination of selenite and selenate becomes difficult, if not impossible, when anions such as chloride, nitrate, phosphate and sulfate are present at concentrations normally encountered in fresh water unless a selenium-specific detector is used The ion chromatograph–GFAA system diagrammed in Fig. 1 makes it possible to determine selenite and selenate conveniently and reliably even in solutions containing high concentrations of other anions Fig. 2 shows the chromatograms obtained with a distilled water solution containing 600 ng/ml Se (selenite) and 600 ng/ml Se (selenate) using the

conductivity detector set at 10 $\mu\Omega^{-1}$ full scale (Fig 2A) and the GFAA (Fig. 2B). Well-separated selenite and selenate peaks are produced by both detectors under these conditions. The two additional peaks (10 min, 18 min) are caused by chloride and sulfate. However, when a solution containing 250 ng/ml Se each of selenite and selenate, 8 μg/ml chloride, 152 ng/ml phosphate and 2 μg/ml sulfate was chromatographed, the selenite and selenate signals obtained with the conductivity detector set at 10 $\mu\Omega^{-1}$ were very poorly resolved and appeared on the high retention time-side of the off-scale peaks caused by the other anions (Fig. 3A). At somewhat higher concentrations of chloride (46 μg/ml), phosphate (0.9 μg/ml) and sulfate (11 μg/ml) demanding a lower sensitivity setting of 300 $\mu\Omega^{-1}$ on the conductivity detector, no discernible selenium signals were found in the chromatogram (Fig. 3A). However, the GFAA detector clearly shows the presence of selenite and selenate (Fig. 3B).
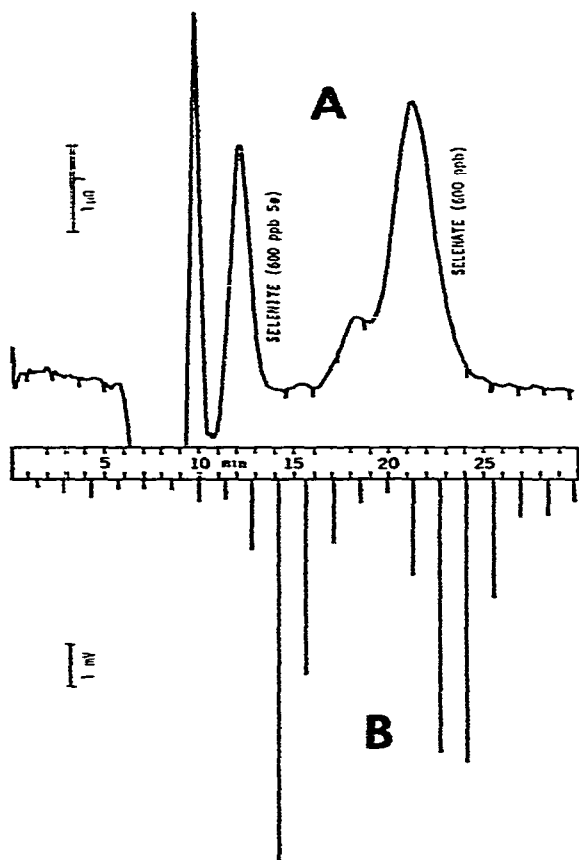

Fig. 2. The chromatograms (1-ml injection loop) of a solution of selenite and selenate recorded with (A) the conductivity detector and (B) the GFAA. ppb. The American billion (10^9) is meant.

Solutions containing 311 ng/ml Se (selenite) and 276 ng/ml Se (selenate) and alkali metal salts of common anions were chromatographed using both detectors to determine interferences caused by these anions. The concentrations of anions in mg/l depressing the selenium signals by 5% relative to those obtained in the absence of the
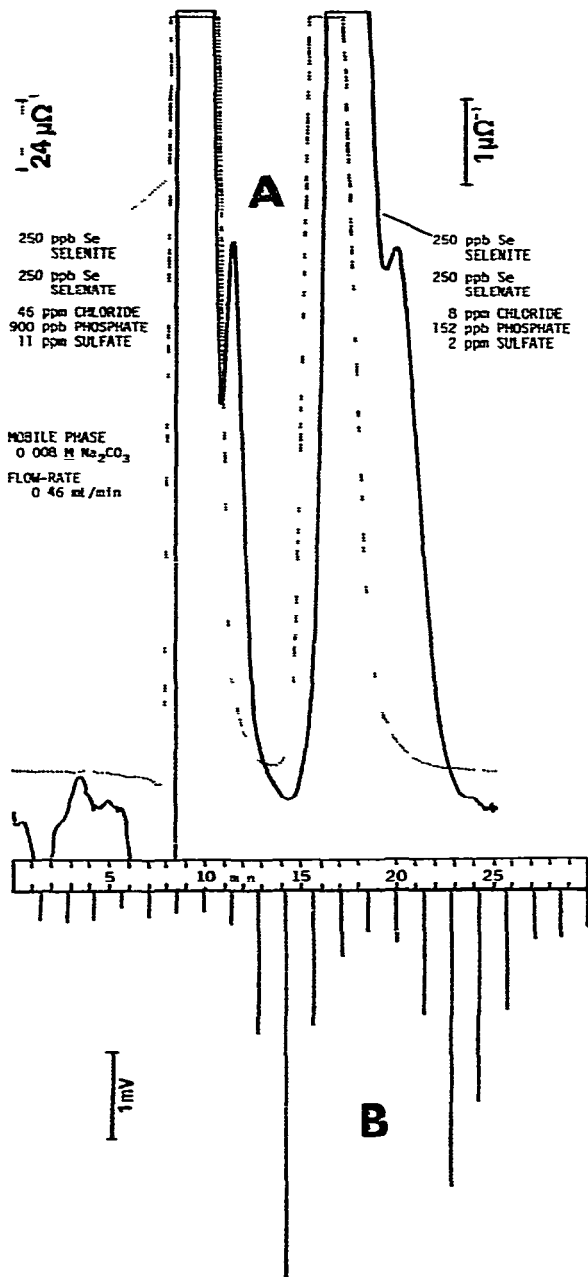
Fig. 3. The chromatograms (1-ml injection loop) of solutions containing selenite, selenate, chloride, phosphate and sulfate recorded with (A) the conductivity detector and (B) the GFAA.

anion are listed in Table I. Chloride, nitrite, nitrate and bromide interfere seriously with the determination of selenite, and the presence of sulfate makes the quantitation of selenate almost impossible when the conductivity detector is used With the

TABLE I

THE EFFECT OF COMMON ANIONS ON THE INTENSITIES OF THE SELENIUM SIGNALS

Interfering anion	*Salt added*	*Concentration of the interfering anion in mg/l which reduces the Se signal by 5%*			
		Conductivity detector		*GFAA*	
		Se (selenite)*	*Se (selenate)**	*Se (selenite)**	*Se (selenate)**
F⁻	NaF	93	220	>311	>276
Cl⁻	NaCl	1 5	>276	>311	>276
Br⁻	KBr	1 5	83	>311	>276
NO₂⁻	NaNO₂	0 6	>276	>311	>276
NO₃⁻	NaNO₃	3 1	69	>311	>276
PO₄³⁻	Na₂HPO₄	77	27	>311	>276
SO₄²⁻	Na₂SO₄	93	0 3	>311	>276

* The selenium concentrations were 311 $\mu g/l$ Se (selenite) and 276 $\mu g/l$ Se (selenate) The 1 0-ml injection loop was used.

GFAA, no interferences were observed at anion concentrations 10^3 times the Se (selenite) or Se (selenate) levels.

The calibration curve for the determination of selenite and selenate by ion chromatography–GFAA was constructed by plotting the sums of the GFAA signal intensities[14] generated by each one of the selenium compounds *versus* the quantities of selenium, injected as selenite or selenate. The calibration curve (Fig. 4) is linear up to 700 ng Se, the largest quantity investigated for each of the two selenium compounds. The calibration points have average deviations of 10%, or less. Within experimental error, the signals are not dependent on the form of selenium, making it possible to use the same calibration curve for selenite and selenate. The calibration curve contains data obtained at different times and with different graphite cups from solutions of the selenium compounds in distilled water and in synthetic river water, indicating that the GFAA is not influenced by other anions and operates reliably. Data with much smaller deviations have been obtained when the experiments were performed over a short period of time with the same graphite cup.

To check the reproducibility of the ion chromatography–GFAA technique 1-ml aliquots of a solution containing 500 $\mu g/l$ of selenium each in the form of selenite and selenate were chromatographed six times. The sum of the GFAA peak heights were averaged. The relative standard deviations for selenite and selenate signals were 8.8 and 9.6%, respectively.

The detection limit of the ion chromatography–GFAA system, defined as the quantity of selenium either as selenite and selenate producing GFAA signals, the sum of which is equal to twice the average deviation of the background signals, was found to be 20 ng Se with the use of the 1-ml injection loop. Although natural waters in seleniferous regions may contain several mg/l of selenium, most unpolluted fresh water and sea water samples do not have more than a few ng Se/ml (ref. 1). The present U.S.A. standard for drinking water lists 10 ng/ml Se as the upper acceptable limit[15].

To improve the detection limits, experiments in which selenite and selenate
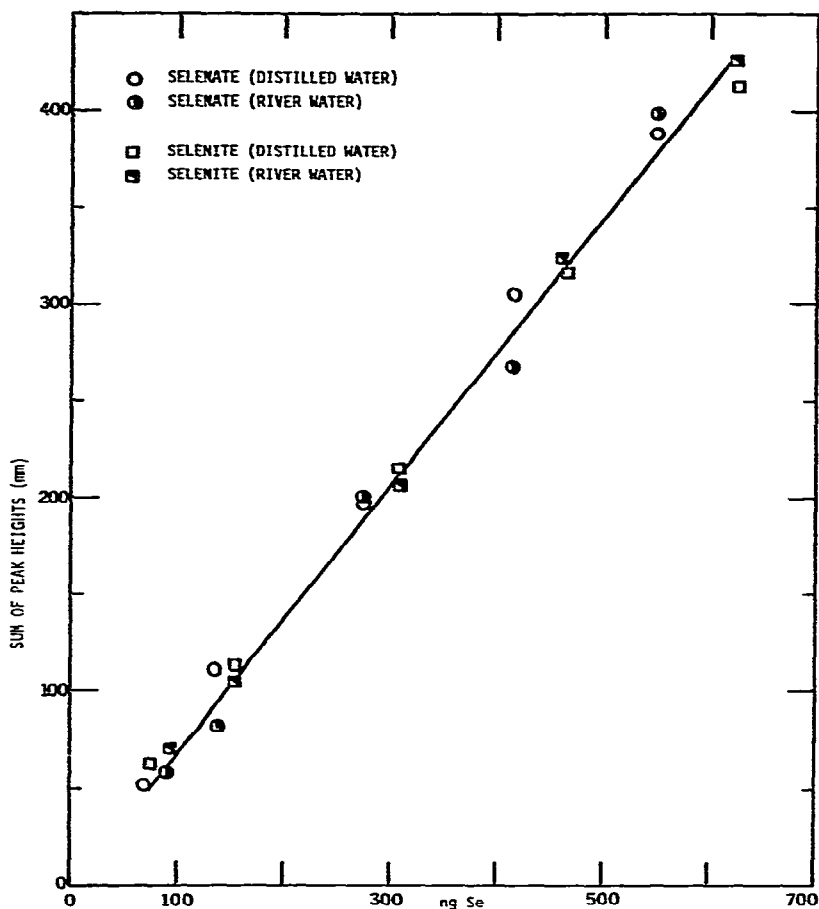
Fig. 4 Calibration curve for the determination of selenite and selenate by ion chromatography–GFAA

were concentrated on a 150 × 3 mm Dionex 30589 anion separator column replacing the 1 0-ml sample loop were performed. Various volumes of solutions in deionized water containing 1–6 ng/ml each of selenium in form of selenite and selenate were passed through the concentrator column The selenium compounds retained on the column were chromatographed under the conditions employed in the experiments with the 1 0-ml sample loop. The recoveries of selenium, relative to the results obtained with more concentrated solutions containing the same quantities of selenium, but introduced via the sample loop, are summarized in Table II When volumes of solutions containing a quantity of selenium in the form of selenite or selenate equal to or less than six times the detection limit of 20 ng Se were injected, the GFAA gave recoveries between 80 and 84%. At larger quantities, the recoveries were above 90% and were the same for the GFAA and the conductivity detector. The volume passing through the concentrator column does not influence the results within the volume range from 20 to 100 ml.

Similar experiments were performed using a synthetic water sample simulating river water and containing 277 µg/ml chloride, 69 µg/ml sulfate, 5.4 µg/ml phosphate,

TABLE II

RECOVERY OF SELENITE AND SELENATE FROM DEIONIZED WATER SOLUTIONS USING THE ION CHROMATOGRAPHY–GFAA SYSTEM WITH A 150 × 3 mm ANION SEPARATOR COLUMN FOR THE CONCENTRATION OF THE SELENIUM COMPOUNDS

Selenium compound	ml injected	ng Se injected	GFAA		Conductivity detector	
			ng Se found*	% Se recovered	ng Se found*	% Se recovered
Selenite	20 0	124	99 ± 5	80 ± 4	114 ± 4	92 ± 3
Selenate		110	92 ± 9	84 ± 9	105 ± 2	95 ± 1
Selenite	30 0	186	170 ± 5	91 ± 3	171 ± 5	92 ± 2
Selenate		165	144 ± 5	87 ± 3	157 ± 5	95 ± 3
Selenite	50 0	311	300 ± 10	96 ± 3	296 ± 6	95 ± 2
Selenate		276	269 ± 8	97 ± 3	268 ± 3	97 ± 1
Selenite	80 0	149	136 ± 8	91 ± 5	142 ± 2	95 ± 1
Selenate		132	122 ± 7	92 ± 6	125 ± 4	95 ± 3
Selenite	100 0	311	294 ± 8	95 ± 6	298 ± 5	95 ± 1
Selenate		276	281 ± 6	102 ± 4	268 ± 4	96 ± 1
Selenite	100 0	100	84 ± 5	84 ± 5	95 ± 2	95 ± 1
Selenate		100	83 ± 8	83 ± 8	92 ± 2	92 ± 1

* Average ± average deviation from triplicate experiments

85 μg/ml Na$^-$, 5.0 μg/ml K$^+$, 2 0 μg/ml NH$_4^+$, 80 μg/ml Ca^{2+} and 17.4 μg/ml Mg^{2+}. Aliquots of this solution were spiked with selenite and selenate. passed through the concentrator column, and chromatographed The results in Table III show that pre-concentration is not possible from more than 4 ml of solution under the chromatographic conditions employed. The recovery of selenium decreases to unacceptable levels when more than 5 ml of solution are passed through the pre-concentration column. This decrease is specially noticable for selenate (Table III). The competition between the selenium compounds and the other anions, present in much higher concentrations, for the active sites on the column materials prevents the complete retention of

TABLE III
RECOVERY OF SELENITE AND SELENATE FROM SYNTHETIC RIVER WATER* BY ION CHROMATOGRAPHY–GFAA AFTER PRE-CONCENTRATION ON A 150 × 3 mm DIONEX ANION SEPARATOR COLUMN

ng Se (selenite) in ml solution	ng Se found	Recovery (%)	ng Se (selenate) in ml solution	ng Se found	Recovery (%)
622 ng/1 ml	640 ± 115	103 ± 2	552 ng/1 ml	509 ± 9	97 ± 2
622 ng/2 ml	670 ± 16	108 ± 2	552 ng/2 ml	497 ± 15	95 ± 4
622 ng/4 ml	622 ± 6	100 ± 2	552 ng/4 ml	548 ± 18	104 ± 3
311 ng/5 ml	280 ± 6	90 ± 2	276 ng/5 ml	230 ± 10	83 ± 4
373 ng/6 ml	319 ± 8	86 ± 2	331 ng/6 ml	240 ± 21	73 ± 7
435 ng/7 ml	380 ± 11	87 ± 3	386 ng/7 ml	270 ± 26	70 ± 7
500 ng/10 ml	410 ± 10	82 ± 2	500 ng/10 ml	305 ± 21	61 ± 4
500 ng/20 ml	400 ± 13	80 ± 3	500 ng/20 ml	255 ± 32	51 ± 7

* Composition (mg/l): Na$^+$ 85, K$^+$ 5 0, NH$_4^+$ 2.0, Mg^{2+} 17.4, Ca^{2+} 80, Cl$^-$ 277, SO$_4^{2-}$ 69, phosphate 5.4
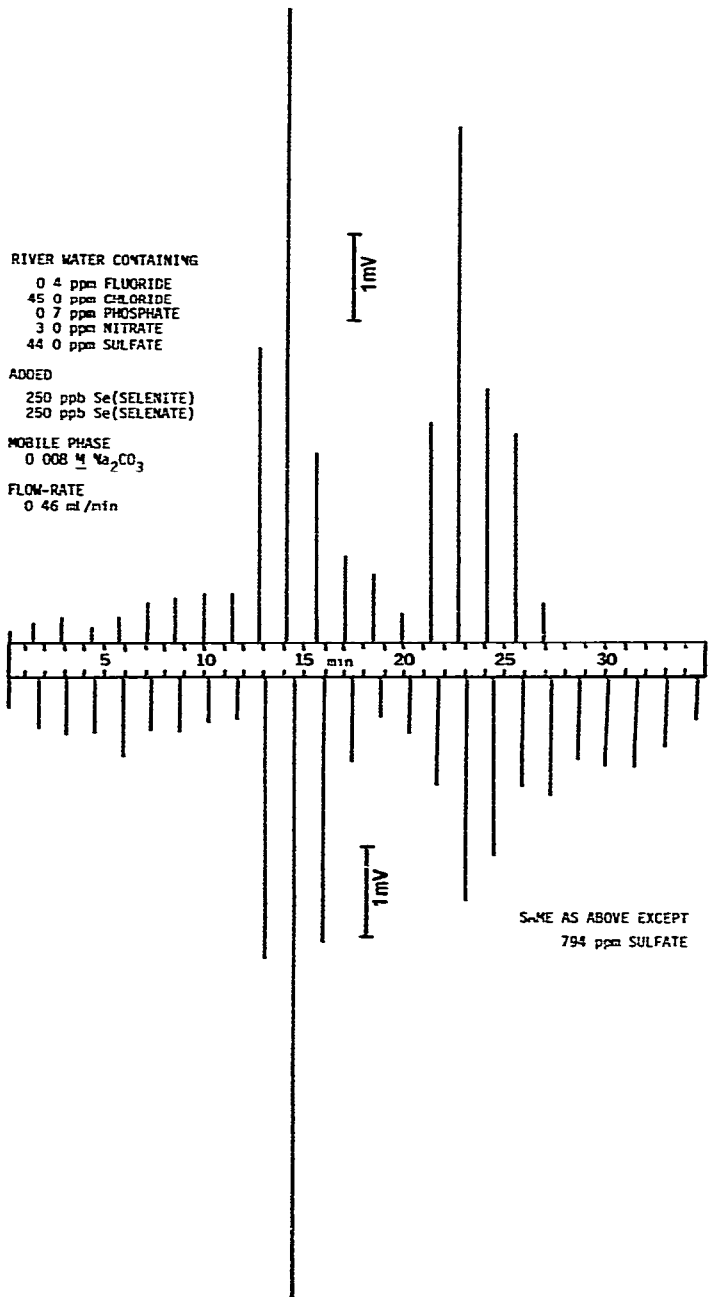
Fig. 5. The chromatograms (1-ml injection loop) of river water spiked with selenite, selenate and sulfate, and recorded with the GFAA.

selenite and selenate on the concentrator column when more than 4 ml of solution are injected. In addition, the selenate peaks become increasingly broad with increasing sulfate concentration as shown in the chromatograms of two samples of a Texas river

A

SYNTHETIC RIVER WATER

277 ppm CHLORIDE
69 ppm SULFATE
5 ppm PHOSPHATE

400 ppb Se(SELENITE)
400 ppb Se(SELENATE)

MOBILE PHASE
0 008 N Na_2CO_3

FLOW-RATE
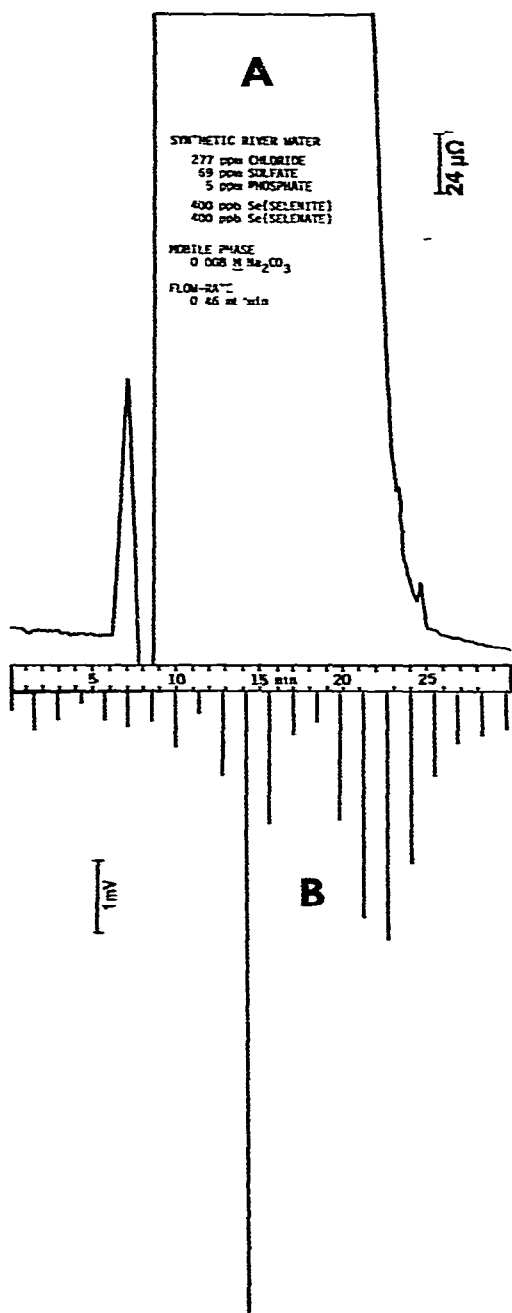0 46 ml min

24 µS

5   10   15 min   20   25

1mV

B

Fig. 6. The chromatograms (1-ml injection loop) of synthetic river water spiked with selenite and selenate, and recorded with (A) the conductivity detector and (B) the GFAA.

water, one spiked to contain 794 mg/l of sulfate (Fig 5) With this limited capability of pre-concentrating selenite and selenate, the detection limits of the ion chromatography–GFAA system can be lowered to approximately 5 ng/ml.

To furnish an example of the advantage of GFAA as the selenium-specific detector for ion chromatography a chloride- and sulfate-rich synthetic river water sample spiked with selenite and selenate to achieve a concentration of 400 ng/ml Se from each of the selenium compounds was chromatographed using the conductivity detector and the GFAA The high concentrations of chloride and sulfate generate a signal which obliterated any conductivity detector response to selenium. The signals from the GFAA are not influenced by the other anions present in the solution (Fig 6)

While investigating the recovery of selenite and selenate added to tap water, most of the selenite was found to have been converted to selenate. When the tap water had been boiled before selenite and selenate were added, selenite was not converted to selenate Additional experiments showed that the chlorine in the water is the oxidizing agent.

CONCLUSION

The ion chromatography–GFAA system described in this paper is capable of separating and quantitatively determining selenite and selenate in the presence of large excesses of other anions with a detection limit of 20 ng Se using the 1-ml injection loop. Pre-concentration of the selenium compounds on an anion separator column from anion-rich water samples is limited to volumes of 4 ml or less providing detection limits of approximately 5 ng Se. Selenite and selenate can be pre-concentrated from 100-ml distilled water solutions providing a detection limit of 0.2 ng Se. The use of pre-concentration columns of higher capacity could lead to an improvement of the detection limit for the analysis of anion-rich water samples

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