

Simultaneous determination of arsenite, arsenate, selenite and selenate in waters using suppressed ion chromatography with ultraviolet absorbance detection

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ABSTRACT

Using Dionex AS4A anion-exchange column, with micromembrane suppressor and UV detector at 195 nm, arsenite, arsenate, selenite and selenate can be determined simultaneously in water samples. The mole fraction of sodium carbonate in the eluent as well as eluent concentration affected the retention times especially for the divalent anions. An eluent of 2.25 mM Na₂CO₃ and 0.75 mM NaHCO₃ was found to be the most suitable for sample analysis. The responses for all ions tested was linear in 0–5 mg l⁻¹ range. The system can tolerate up to 1600 mg l⁻¹ of SO₄²⁻, before affecting arsenate peaks. Selenate peak area was not affected due to SO₄²⁻ concentration up to 2000 mg l⁻¹. The detection limits using 100-μl loop were 0.1 mg l⁻¹ for AsO₂⁻ and SeO₃²⁻ and 0.25 mg l⁻¹ AsO₄³⁻ and SeO₄²⁻.

INTRODUCTION

Metalloids especially selenium and arsenic and their derivatives can widely spread throughout the environment as a result of fuel consumption, industrial, agricultural and natural processes [1]. Although deficiencies of selenium results in selenium-responsive diseases in various animal species, the differences between essential and the toxic concentration is rather narrow [2]. Arsenic compounds represent a carcinogenic hazard in the environment. The continuing interest in tracing the fate of selenium and arsenic, led to the development of several methods for their analysis. The most common methods are: atomic fluorescence spectrometry [3,4], atomic absorption spectroscopy with hydride generator [5,6], inductively coupled plasma [7] (ICP-AES) and electrothermal graphite furnace [8], or spectrophotometry [9–11].

Because the inorganic form of these two elements exists mostly in natural waters in two oxidation states, *i.e.* Se(IV), Se(VI), As(III) and As(V), speciation becomes of particular importance. The ecological fate is also determined by the chemical form. In the afore-mentioned methods, two determinations are required. One before and the other after reduction, to measure both oxidation states. The difference between these two determinations yields the amount existed at higher oxidation states [12,13].

During the last decade the application of high-performance liquid chromatography

graphy (HPLC) for the analysis of inorganic anions (usually referred to as ion chromatography, IC) has provided a reliable, fast, convenient and sensitive alternative to many complex analytical problems. Five different low-capacity anion-exchange columns for non-suppressed ion chromatography [14] (also called single column ion chromatography, SCIC) were evaluated for inorganic anion assay [15]. SCIC was used for the assay of selenite [16], selenate [17] and arsenate [18]. However, Cl^- above 10 mg l^{-1} , SO_4^{2-} above 40 mg l^{-1} and PO_4^{3-} above 30 mg l^{-1} masked the selenite, selenate and arsenate peaks, respectively [16–18]. The use of suppressed ion chromatography [19] (SIC) offers two advantages for such applications: (1) with high pH eluents, it becomes possible to elute monovalent, divalent and even trivalent anions in a single run and reasonable time and (2) increased sensitivity due to lower background conductivity.

Conventionally, nearly all ion chromatography for inorganic anions has been done using electrical conductivity detection. However, it has been shown that many inorganic anions have suitable chromophores and their detection by an ultraviolet (UV) absorbance detector is possible [20]. The use of UV absorbance detection could provide selectivity against unwanted ionic species specially in cases where sample matrix problems exist. Since the SIC system reduced both the background conductivity as well as the UV absorbance of effluent ($2.4 \text{ mM Na}_2\text{CO}_3 + 3.0 \text{ mM NaHCO}_3$), it was possible to use the system with a UV detector [20]. Ions of fluoride, phosphate, and sulfate did not show UV absorbance whereas arsenite, arsenate, selenite, selenate and many other ions showed absorbance in this region [20].

A method for simultaneous determination of arsenite, arsenate, selenite, selenate ions has not been available. Since arsenite can not be detected by conductivity detection, an ion chromatographic method for its determination is not possible. The objective of this research was to develop a method for simultaneous determination of arsenite, arsenate, selenite and selenate using UV absorbance detection.

EXPERIMENTAL

All chemicals used in the study were of ACS reagent grade and were used as received from the suppliers.

The SIC system consisted of two HPLC pumps (Model LC-6A), a systems controller (SCL-6A), a UV-VIS detector (Model SPD-6AV), a data system (Model C-R3A, all Shimadzu Scientific Instruments (Columbia, MD), a conductivity detector (Waters Assoc., Milford, MA) and a HPLC injector (Model 7126, Rheodyne, Cotati, CA). The analytical column IonPac AS4A and a guard column AG5 were used with an Anion Micro Membrane Suppressor, AMMS (all columns, Dionex, Sunnyvale, CA). For the purpose of this study the system was used in a binary gradient mode to mix $3.0 \text{ mM Na}_2\text{CO}_3$ and 3.0 mM NaHCO_3 to obtain the desired Na_2CO_3 molar ratio or to mix ($2.25 \text{ mM Na}_2\text{CO}_3 + 0.75 \text{ mM NaHCO}_3$) and deionized water in desired proportions. However, the actual chromatography was isocratic. The eluents were maintained under nitrogen in order to avoid atmospheric carbon dioxide. The eluent flow-rate was kept constant at 1.7 ml min^{-1} throughout the study. The flow-rate of regenerant for AMMS ($12.5 \text{ mM H}_2\text{SO}_4$) was about 4 ml min^{-1} . The void volume of the system was 1.56 ml (or 0.92 min at 1.7 ml min^{-1}).

UV absorbance spectra were generated using a scanning spectrophotometer (Model: Lambda 6, Perkin Elmer Corp., Norwalk, CT).

RESULTS AND DISCUSSION

The absorption spectra of arsenite, arsenate, selenite and selenate in 190–230 nm range are shown in Fig. 1. It is noteworthy that the lower oxidation states of these ions exhibit relatively greater absorbance. The shortest wavelength on our detector of 195 nm was used for the detection. Other ions commonly encountered in waters, *e.g.*, nitrate and nitrite also absorb in this region but with a different absorption maxima. Fluoride, phosphate and sulfate do not show absorbance in this range [20].

A comparison of UV absorbance *vs.* electrical conductivity chromatograms of these ions in the presence of other commonly present inorganic anions (fluoride, chloride, nitrate and sulfate) is shown in Fig. 2. With UV absorbance, fluoride was not detected and sulfate appeared as a split negative peak. As expected, arsenite was not detected by electrical conductivity. Apparently, the UV absorbance not only provided a means of arsenite detection but also provided selectivity against fluoride. This was important as both the ions co-eluted very close to the void volume on this system. Consequently, UV absorption detection was used in all further work.

Optimization of chromatographic conditions

In general, increasing mole fraction of Na_2CO_3 in a 3.0 mM $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ eluent decreased the retention times of all ions tested (Fig. 3). The effect seemed to be proportional to the retention times. In other words, the retention of strongly held ions was affected relatively more than the loosely held ions. For example, increasing Na_2CO_3 fraction from 0.25 to 1.00 decreased the retention time of SeO_4^{2-} from 17.42 min to 6.15 min (a 65% decrease), whereas that of NO_3^- from 4.04 min to 2.78 min (a 31% decrease). The retention of arsenite was not affected by the eluent composition suggesting it eluted close to the void volume. Arsenate was an exception in that its retention time decreased until Na_2CO_3 mole fraction increased upto 0.50 but the retention increased again as the Na_2CO_3 mole fraction increased further beyond 0.75. This probably represents a pH effect of the eluent on the dissociation of arsenate.

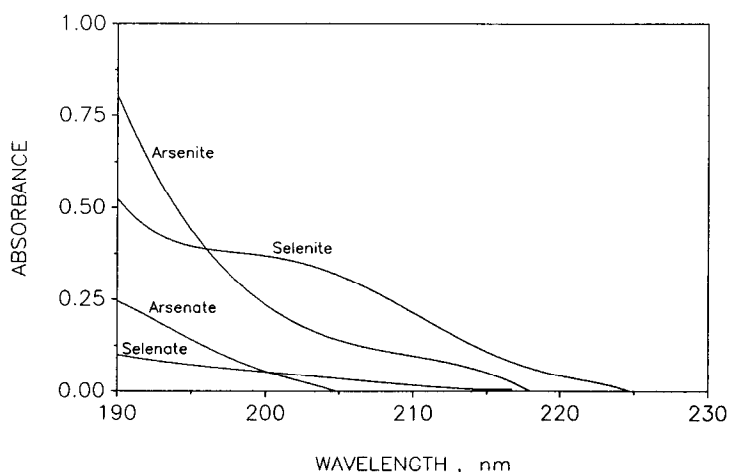


Fig. 1. Absorbance spectra of arsenite, arsenate, selenite, and selenate in 190–250 nm range (20 mg l^{-1}).

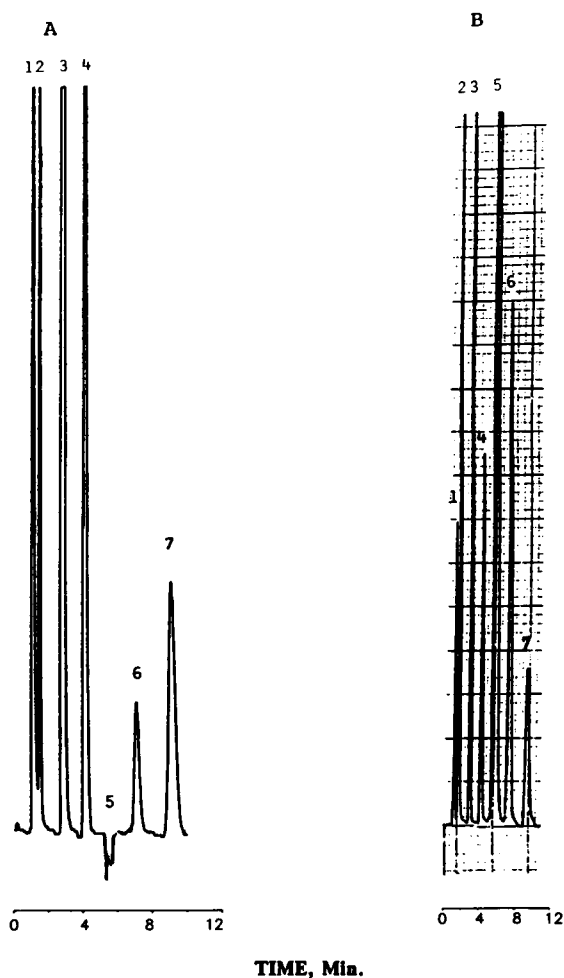


Fig. 2. Comparison between UV absorbance (A) and electrical conductivity detection (B). Peak identification: 1 = arsenite in A and fluoride in B; 2 = chloride; 3 = nitrate; 4 = selenite; 5 = sulfate; 6 = selenate; 7 = arsenate.

An increase in the Na_2CO_3 mole fraction from 0.75 to 1.00, increased the eluent pH from 10.2 to 10.6. This would increase the mole fraction of trivalent AsO_4^{3-} from 0.05 to 0.18 [21] and thus resulting in a stronger retention. Based on the information shown in Fig. 3, a Na_2CO_3 mole fraction of 0.75 was chosen for further work.

A decrease in the eluent strength ($\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ concentration), at a Na_2CO_3 mole fraction of 0.75, increased the retention times of all ions (Fig. 4). However, the slight improvement in resolution due to increased retention times was negated by longer analysis time. Therefore, an eluent concentration of 3.0 mM was chosen. Under these conditions the total analysis time was about 12.0 min.

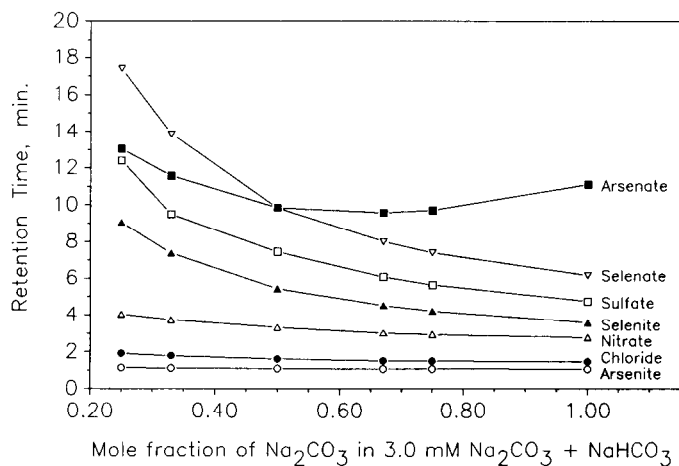


Fig. 3. Effect of eluent composition on the retention times of anions.

Response linearity and detection limits

The UV absorbance response, of all four ions over the concentration range (0–5 mg l⁻¹, 100-μl injections) tested, was linear (Fig. 5). The detection limits (signal-to-noise ratio of 3.0) using 100-μl injections were measured as: arsenite, 0.1 mg l⁻¹; selenite, 0.1 mg l⁻¹; selenate, 0.25 mg l⁻¹; arsenate, 0.25 mg l⁻¹. Lower detection limits should be possible with the use of larger injection volumes and/or a concentrator column. Concentrator columns have been used to lower detection limits by enabling the researcher to load as much as 20-ml sample [16].

Effect of sample matrix

A sample concentration of SO₄²⁻ greater than 50 mg l⁻¹ has been a major problem during selenate assay with SCIC [17] and SIC [22]. Selenate signal was

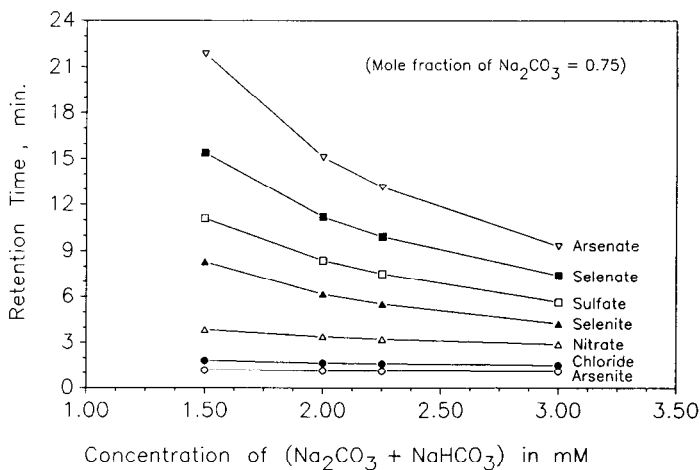


Fig. 4. Effect of eluent concentration on the retention times of anions.

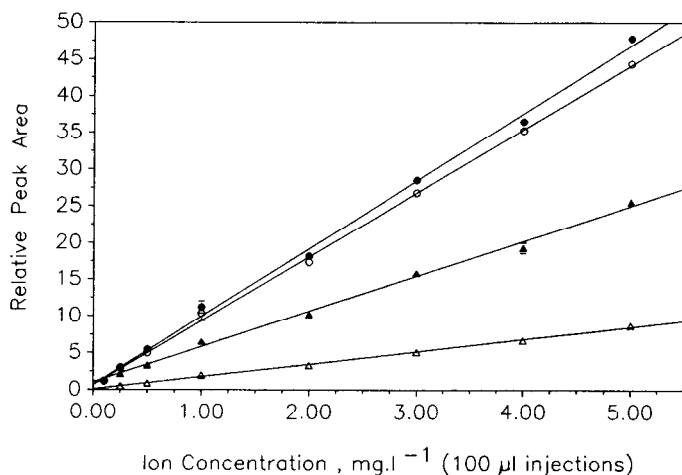


Fig. 5. Linearity of UV absorbance response for selenite, arsenite, selenate, and arsenate. ● = Selenite ($y = 0.7023 + 9.244x, r = 0.9988$); ○ = arsenite ($y = 0.6265 + 8.741x, r = 0.9995$); ▲ = arsenate ($y = 1.0453 + 4.804x, r = 0.9978$); △ = selenate ($y = 0.8693 + 1.689x, r = 0.9989$).

reduced by 5% and 19% in the presence of 0.3 mg l^{-1} with SIC [23] and 60 mg l^{-1} SO_4^{2-} with SCIC [17], respectively, using conductivity detection. Removal of SO_4^{2-} ions from sample to reduce its concentration, prior to assay, has also been tested with little success. For example, cation-exchange resin in barium form [17] and chemical treatment of sample with barium formate [17] and barium hydroxide [22] has been tried to reduce the SO_4^{2-} concentration. Such sample treatment resulted in slight

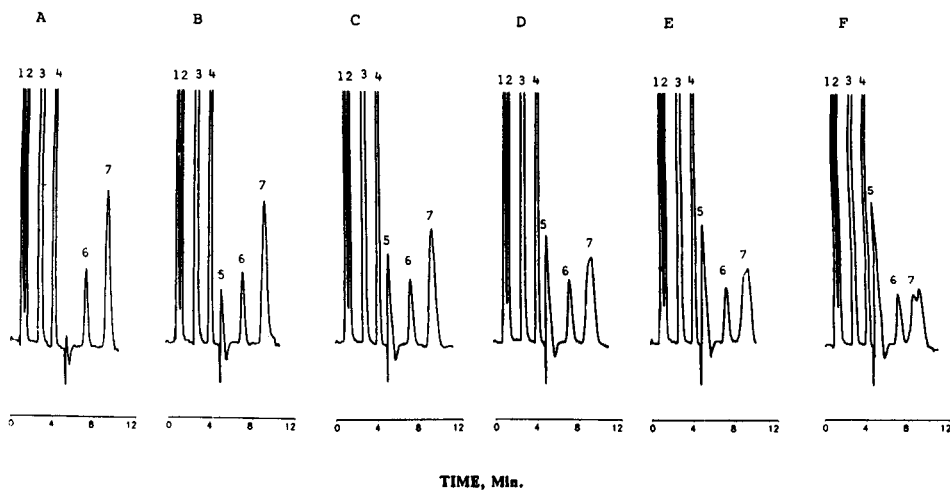


Fig. 6. Effect of high sulfate concentration on the separation and detection of arsenite (1), selenite (4), selenate (6), and arsenate (7) in the presence of chloride (2), nitrate (3), and sulfate (5). Sample composition (mg l^{-1}): chloride, 100; nitrate, 10; arsenite, 20; selenite, 20; selenate, 20; arsenate, 20. Sulfate concentration (mg l^{-1}): A, 400; B, 800; C, 1200; D, 1400; E, 1600; F, 2000.

TABLE I

RELATIVE PEAK AREAS AND RETENTION TIMES FOR ARSENATE AND SELENATE (BOTH AT 20 mg l⁻¹) IN THE PRESENCE OF DIFFERENT SO₄²⁻ CONCENTRATIONS (20 μl INJECTIONS)

Sulfate (mg l ⁻¹)	Selenate ^a		Arsenate ^b	
	Time (min)	Peak area (%)	Time (min)	Peak area (%)
400	7.33	100	9.36	100
800	7.28	103	9.33	98
1200	7.27	100	9.32	100
1400	7.27	102	9.34	97
1600	7.24	102	9.33	96
2000	7.23	100	8.78, 9.42	(50 + 45) = 95

^a Peak number 6 in Fig. 6.

^b Peak number 7 in Fig. 6.

improvement in resolution but the selenate signal was reduced. In our system, increasing concentration of SO₄²⁻ in samples did not affect the peaks of ions with retention times shorter than SO₄²⁻ (AsO₂⁻, Cl⁻, NO₃⁻, SeO₃²⁻). The peak heights of ions that eluted after SO₄²⁻, i.e., AsO₄³⁻ and SeO₄²⁻, were decreased; however, the retention times and peak areas were not effected significantly (Fig. 6 and Table I). When SO₄²⁻ concentration was increased beyond 1400 mg l⁻¹, a distortion of arsenate peak was observed. The effect was so pronounced that at 2000 mg l⁻¹ SO₄²⁻, the arsenate peak appeared forked and two separate peaks were detected (Fig. 6). Interestingly, the peak area (sum of both peaks) was affected only slightly (Table I). The peak for selenate was normal even at 2000 mg l⁻¹ SO₄²⁻. The high SO₄²⁻ mass injected probably saturated the column and disturbed the column equilibrium such that the peaks following were distorted. The use of a diluter (weaker strength) eluent would probably reduce the peak distortion simply by allowing more time for stationary phase re-equilibration in between the peaks. These data show that the ions in question can be effectively quantitated in the presence of 1400 mg l⁻¹ and perhaps up to 2000 mg l⁻¹ SO₄²⁻. The increasing concentrations of SO₄²⁻ reduced the apparent resolution between AsO₄³⁻ and SeO₄²⁻. However, baseline separation (100% practical resolution) was achieved even at the highest SO₄²⁻ level tested (Fig. 6). The interference due to high concentration of Cl⁻ was not tested but it can be effectively removed by the use of cation-exchange resin in silver form [16].

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