Determination of trace anions in high-nitrate matrices by ion chromatography

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Abstract

An ion chromatography method was developed to determine trace anionic contamination in matrices that have a high concentration of nitrate ion. Contaminant anions of interest were separated on an IonPac AS15 high-capacity anion-exchange column and detected by suppressed conductivity detection. An EG40 eluent generator was used to prepare high-purity and carbonate-free potassium hydroxide. Using the EG40, performance at trace levels was enhanced because background conductivity decreased and retention time reproducibility improved. Trace anionic contamination from the mobile phase was minimized when using the eluent generator compared to using conventionally prepared sodium hydroxide eluents. The signal-to-noise ratio was also improved with the use of a temperature controlled conductivity cell and chromatography hardware in the microbore (2-mm) format. The eluent concentration was optimized to separate the contaminant anions from the excess of the nitrate matrix ions. The procedure was demonstrated for a solution of reagent-grade sodium nitrate and high-purity 0.7% nitric acid. Method detection limits for chloride, sulfate and phosphate of 150 μg/l and lower were achieved.   © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitric acid is a commercially important chemical. Over $1 \cdot 10^6$ lb/year are produced each year in the USA [1] (1 lb=0.454 kg). An important high-purity application is its use to etch metals in semiconductor wafers. Chloride contamination present in the nitric acid could remain on the semiconductor surface and compromise semiconductor yield and reliability [2]. There is a need for a reliable method to determine trace anions in samples containing high concentrations of nitrate ion. Traditional wet chemical methods are not sensitive and reliable enough for these demanding trace level anion determinations. Ion chromatography (IC) has been shown to be sensitive for the determination of trace anions in concentrated weak acids such as hydrofluoric, glycolic and phosphoric acids after pretreatment with an ion-exclusion separation [3]. The goal of this investigation was to develop a direct injection method for analyzing the trace anionic content of matrices that contain high concentrations of nitrate ion. To ensure the best sensitivity, we used microbore chromatography and the EG40 eluent generator.

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2. Experimental

2.1. Chromatographic system

All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-500 ion chromatograph. The system consists of a gradient pump (GP50), a conductivity detector (CD20), a liquid chromatography oven (LC30) and a thermally stabilized conductivity detector (DS3). An EG40 eluent generator equipped with an EGC-KOH cartridge was used to produce potassium hydroxide eluents. For sample loading, a Rheodyne (Cotati, CA, USA) six-port Model 9126-038 valve was fitted with a injection loop made from polyether ether ketone (PEEK) tubing. A pressurizable reservoir chamber (Dionex) large enough to accommodate the sample container was maintained at 8 p.s.i. (55 kPa) with helium to fill the sample loop with sample. A personal computer equipped with Dionex PeakNet chromatography software was used for data acquisition and instrument control.

All columns used in this study were manufactured by Dionex. A routine anion separation was demonstrated with an IonPac AS10 analytical column (250×4 mm). For the separation of trace anions in molten glass, an IonPac AG10 guard column (50×2 mm) and IonPac AS10 analytical column (250×2 mm) were used. For the determination of trace anions in high nitrate matrices, an IonPac AG15 guard column (50×2 mm) and IonPac AS15 analytical column (250×2 mm) were used. Table 1 summarizes the chromatographic conditions.

The packing material for the IonPac AS10 is composed of a highly crosslinked macroporous core with an anion-exchange latex electrostatically bonded to the surface. The core is an 8.5-μm diameter bead with a pore size of 2000 Å and consists of ethylvinylbenzene crosslinked with 55% divinylbenzene. The surface anion-exchange layer consists of 65-nm latex particles bonded to the substrate. The packing material of the IonPac AS15 is composed of a highly crosslinked macroporous core and an anion-exchange layer grafted to the surface. The substrate of the IonPac AS15 is a 9-μm diameter resin bead with a pore size of 100 Å and consists of ethylvinylbenzene crosslinked with 55% divinylbenzene.

Table 1
Chromatographic conditions for trace anions in high-nitrate matrices

Application	Standard separation	Molten glass	High-nitrate matrices
Guard column	None	IonPac AG10 (50×2 mm)	IonPac AG15 (50×2 mm)
Analytical column	IonPac AS10 (250×4 mm)	IonPac AS10 (250×2 mm)	IonPac AS15 (250×2 mm)
Eluent	50–124 mM Sodium hydroxide in 30 min	10–200 mM Sodium hydroxide from 7 to 27 min	48 mM Potassium hydroxide step to 100 mM for 20 min equilibrate for 20 min at 48 mM
Eluent flow-rate	1 ml/min	0.25 ml/min	0.20 ml/min
Injection volume	20 μl	10 μl	1 μl
Detection	Suppressed Conductivity	Suppressed Conductivity	Suppressed Conductivity
Trap column	ATC-1 (4 mm) (24×9 mm)	ATC (2 mm) (35×4 mm)	ATC-1 (4 mm) (24×9 mm) ATC (2 mm) (35×4 mm)
Suppressor	AMMS (4 mm)	AMMS (2 mm)	ASRS (2 mm)
ASRS current	500 mA	300 mA	50 mA
Temperature	Ambient	Ambient	Ambient

An anion self-regenerating ultra suppressor (ASRS) from Dionex was used to reduce the conductivity of the eluent for the trace AS15 applications [4]. The ASRS was operated in the external water or gas assisted recycle mode to lower the level of the baseline noise [5]. The AS10 separations were performed with a Dionex anion micromembrane suppressor. The column and suppressor in the microbore format were connected with 0.005-in. I.D. (0.125 mm) PEEK tubing. The lengths of the connecting tubing were kept as short as possible to minimize system void volume and ensure efficient 2-mm column operation. Care was taken to evenly cut tubing ends to avoid introducing any unwanted void volume.

Anion trap columns (ATCs) were used to strip trace contaminants from the eluent or deionized water. These columns contain a high-capacity anion-exchange resin in the hydroxide form. For eluent pretreatment, a 4-mm ATC-1 (24×9 mm) column was used with the AS10 separation, whereas a 2-mm ATC (35×4 mm) column was used for the molten glass application. For the AS15 separation, both a 2- and 4-mm ATC were used. The 4-mm ATC was placed between the GP50 outlet and the EGC-KOH cartridge inlet and the 2-mm ATC was placed between the EG40 degas unit outlet and the injection valve inlet. The ATCs were initially prepared for use by flushing at 2 ml/min with 200 ml of 2 M sodium hydroxide followed by 100 ml of deionized water at the same flow-rate. The ATCs were periodically regenerated using this procedure.

2.2. Chemicals, solutions and samples

Reagent-grade chemicals were used for standard and eluent preparation. Samples of trace metal grade 70% (w/w) nitric acid (J.T. Baker, Phillipsburg, NJ, USA) and reagent-grade sodium nitrate (Fisher, Pittsburgh, PA, USA) were analyzed as samples. Sodium hydroxide, 50% (w/w) from Fisher was used to prepare bottle-based sodium hydroxide eluents. Deionized water with a specific resistance of 17.8 MΩ cm or greater from a deionized water purification system was used to prepare all eluents, reagents, and standards.

Anion standards (1000 mg/l) for the analytes of interest were from Dionex and Fisher. Working standards were prepared by further diluting the 1000 mg/l standards to the range expected for the anions of interest. Dilute working standards were prepared weekly. Increasing concentrations of chloride, sulfate and phosphate were added into the water used to dilute 70% (w/w) nitric acid to 0.7% (v/v). Containers presoaked with deionized water, which had a specific resistance of 17.8 MΩ cm or greater, were used to store concentrated acid samples and standards. Polyethylene containers were used to store standards, whereas PTFE containers were used for storage of the concentrated nitric acid samples.

3. Results and discussion

An anion-exchange column for determining trace anions in samples with high nitrate should ideally have two characteristics. The column should have sufficient capacity for the high-nitrate matrix and should strongly retain nitrate. The IonPac AS10 column has both of these characteristics. The high anion-exchange capacity of 170 μequiv. for this column makes it an excellent match for this application. Nitrate is the last eluting anion when using a sodium hydroxide gradient on the AS10. Shown in Fig. 1 is a separation of an anion standard at low mg/l with the 4 mm IonPac AS10. A sodium hydroxide gradient from 50 to 124 mM at 1 ml/min was used for this separation.

An application of this separation is the analysis of molten glass in a solution of 0.8% hydrofluoric acid and 1.3% nitric acid. A proprietary glass sample was heated to a liquid sate and then placed in hydrofluoric and nitric acid to dissolve both the glass and the additives. The concentrated solution was diluted 1:10 in deionized water and analyzed using a 2 mm IonPac AG10 and AS10 as shown in Fig. 2. An eluent of 10 mM sodium hydroxide was maintained for 7 min to elute the excess of fluoride ion. A gradient of 10 to 200 mM sodium hydroxide from 7 to 27 min was used to separate the analytes of interest from the excess of nitrate and fluoride ion. The microbore format was chosen for this analysis to allow the suppression of the 200 mM sodium hydroxide final eluent concentration.
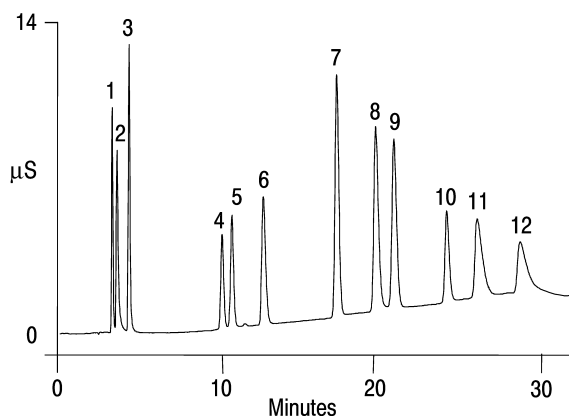
Fig. 1. Routine gradient anion separation with the IonPac AS10. Peaks: 1=fluoride (1.2 mg/l); 2=acetate (30 mg/l); 3=formate (5 mg/l); 4=selenite (10 mg/l); 5=chloride (1.8 mg/l); 6=nitrite (9 mg/l); 7=sulfate (10 mg/l); 8=oxalate (10 mg/l); 9=selenate (10 mg/l); 10=phosphate (9 mg/l); 11=bromide (10 mg/l); 12=nitrate (6 mg/l). Sample volume: 20 μl; analytical column IonPac AS10 (250×4 mm); detection: suppressed conductivity; eluent: 50–124 mM sodium hydroxide, eluent flow-rate: 1 ml/min.
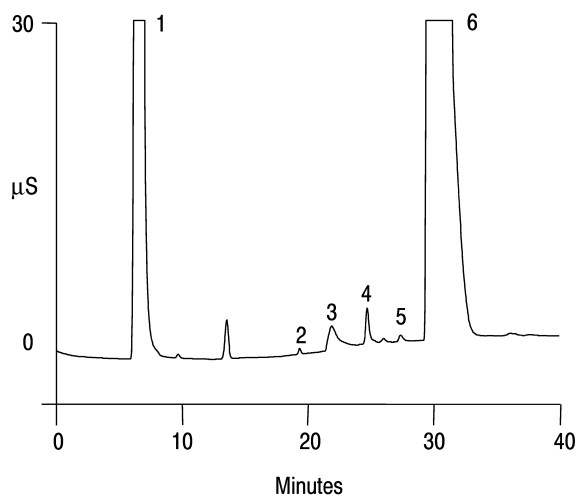
The newly developed IonPac AS15 anion-exchange column was investigated for trace anion determinations. It has higher capacity that the IonPac AS10 column (56 μequiv. for the 250×2 mm AS15 vs. 43 μequiv. for the 250×2 mm AS10) and the KOH eluents used with this column could be generated by the EG40. Nitrate elutes before phosphate when using the standard 33 mM potassium hydroxide eluent as shown in Fig. 3a. However when the eluent concentration was increased to 48 mM potassium hydroxide, the selectivity of the column changed. The retention of multivalent ions such as phosphate, sulfate and carbonate are affected more by the increase in eluent strength than the monovalent nitrate ion [6]. Nitrate elutes last using 48 mM potassium hydroxide with good separation of the other anions of interest as shown in Fig. 3b. These
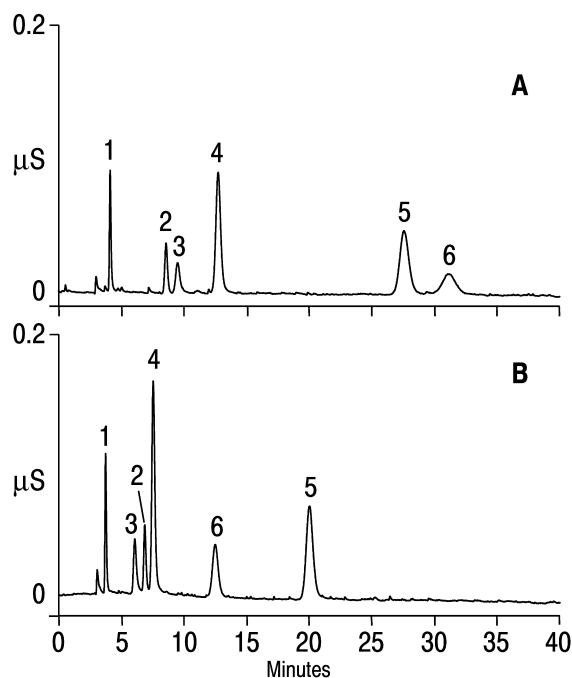

Fig. 2. Determination of anions from molten glass. Sample: molten glass in 0.8% hydrofluoric acid, 1.3% nitric acid, diluted 1:10 in water. Peaks: 1=fluoride; 2=chloride (2.3 mg/l); 3=carbonate; 4=sulfate (12.0 mg/l); 5=phosphate (16.8 mg/l); 6=nitrate. Sample volume: 10 μl; analytical column IonPac AS10 (250×2 mm); guard column IonPac AG10 (50×2 mm) detection: suppressed conductivity; eluent: 10 mM sodium hydroxide, gradient: 10–200 mM sodium hydroxide from 7 to 27 min, eluent flow-rate: 0.25 ml/min.

Fig. 3. Analysis of aqueous standard with the IonPac AS15. Peaks: 1=fluoride (60 μg/l); 2=chloride (90 μg/l); 3=carbonate; 4=sulfate (450 μg/l); 5=nitrate (600 μg/l); 6=phosphate (450 μg/l). Sample volume: 1 μl; analytical column IonPac AS15 (250×2 mm); guard column IonPac AG15 (50×2 mm) detection: conductivity; suppression: ASRS, external water mode; eluent: (a) 33 mM potassium hydroxide (b) 48 mM potassium hydroxide, eluent flow-rate: 0.20 ml/min. Eluent source: EG40 eluent generator.

conditions are a good match for trace anion determinations in high-nitrate matrices.

The columns and suppressor used in this method are in the microbore format (2 mm). Microbore chromatography yields a fourfold enhancement in sensitivity when compared to separation in the 4-mm standard bore format for the same injection volume. The slower flow-rate results in reduced mobile phase consumption. A DS3 detection stabilizer was used to minimize the effects of cell drift and temperature fluctuations.

An EG40 eluent generator was used to produce high-purity potassium hydroxide (KOH) eluent for this analysis [7,8]. The current applied by a programmable current source determines the concentration of the KOH. A KOH cartridge in the EG40 contains K^+ ion electrolyte solution and a KOH generation chamber connected by a cation-exchange connector. The EG40 can generate eluents that are free of carbonate contamination and therefore have lower background conductivity. These features enabled the delivery of hydroxide eluent that was low in anionic contamination.

The method steps to 100 mM KOH for 20 min to elute any residual nitrate left in the column when eluting samples containing high concentrations of nitrate. For the last 20 min of the method the eluent concentration returns to 48 mM KOH to equilibrate the column for the next injection. This method was used to determine the anionic contamination of nitrate salts. A solution of 7000 mg/l sodium nitrate was analyzed by this method. The sample was prepared by dissolving 0.9597 g of reagent-grade sodium nitrate (NaNO$_3$, formula mass 84.99) in 100 ml of deionized water. Fig. 4 shows an analysis of this sample and determined 38 μg/l chloride and 17 μg/l sulfate.

We applied the method to the analysis of anionic contaminants in trace metal grade 70% nitric acid. To ensure that the column was not overloaded by the nitrate ion the 70% (w/w) nitric acid was diluted to 0.7% (v/v) with deionized water. Fig. 5 shows a chromatogram for the analysis of 0.7% (v/v) nitric acid. The large nitrate matrix is well separated from the anions of interest. An injection volume of 1 μl of 0.7% nitric acid minimizes the amount of nitrate loaded onto the column set while maximizing the amount of contaminant ions. A trace amount of
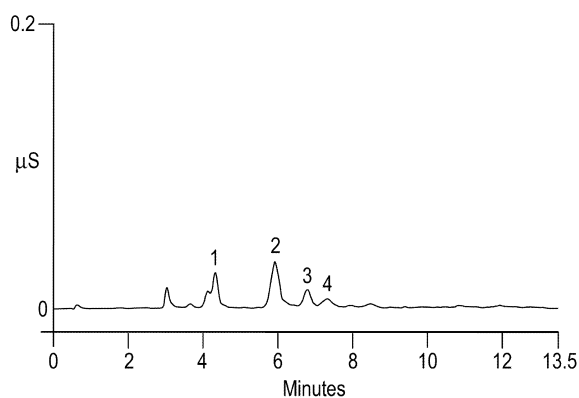

Fig. 4. Determination of trace anions in 7000 mg/l sodium nitrate. Peaks: 1=unidentified; 2=carbonate; 3=chloride (38 μg/l); 4=sulfate (17 μg/l). Sample volume: 1 μl; analytical column IonPac AS15 (250×2 mm); guard column IonPac AG15 (50×2 mm) detection: conductivity; suppression: ASRS, external water mode; eluent: potassium hydroxide 48 mM from 0 to 15 min, 100 mM from 15 to 35 min and 48 mM from 35 to 55 min, eluent flow-rate: 0.20 ml/min. Eluent source: EG40 eluent generator.

chloride was detected in this sample as shown in the detailed view in Fig. 6.

To verify proper quantification of analytes in the nitric acid matrix the method of standard additions was used. A spiked standard was prepared by adding aqueous standards of fluoride, chloride, sulfate and phosphate to the concentrated nitric acid as described in the Experimental section. Fig. 7 shows a spiked 0.7% nitric acid sample containing 65 μg/l fluoride, 105 μg/l chloride, 460 μg/l sulfate and 433 μg/l
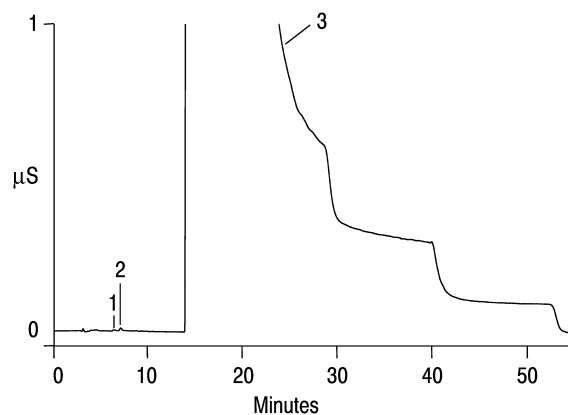

Fig. 5. Determination of trace anions in 0.7% nitric acid. Peaks: 1=carbonate; 2=chloride (38 μg/l); 3=nitrate. Chromatographic conditions as in Fig. 4.
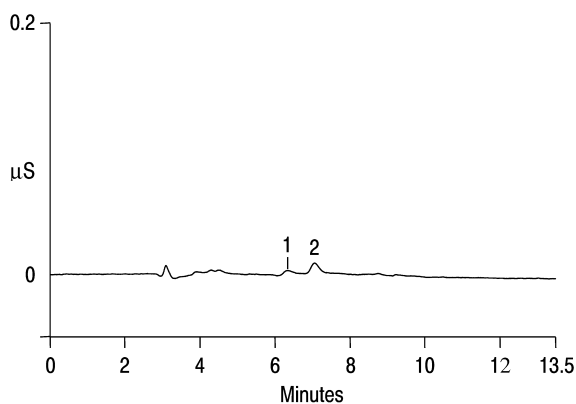
Fig. 6. Determination of trace anions in 0.7% nitric acid. Detail of Fig. 5. Chromatographic conditions as in Fig. 4.
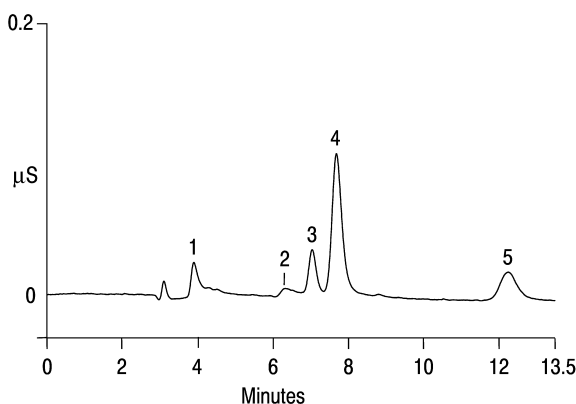

Fig. 7. Spiked sample of 0.7% nitric acid. Peaks: 1=fluoride (65 μg/l), 2=carbonate, 3=chloride (105 μg/l), 4=sulfate (460 μg/l) and 5=phosphate (433 μg/l). Chromatographic conditions as in Fig. 4.

phosphate. Spikes of 20, 200 and 320 μg/l chloride; 45, 150, 900 and 1500 μg/l sulfate and phosphate yielded coefficient of determination (r^2) values greater than 0.99. A spike of 90 μg/l chloride, 450 μg/l sulfate and 450 μg/l phosphate in 0.7% nitric acid

yielded recoveries between 86 and 109%. The calibration and spike/recovery results are summarized in Tables 2 and 3, respectively.

Method detection limits (MDLs) were calculated to be 41 μg/l chloride, 104 μg/l sulfate and 120 μg/l phosphate using an ordinary least-squares regression analysis in a matrix of 0.7% nitric acid. Semiconductor and Equipment and Materials International (SEMI) guidelines for the maximum level of chloride, sulfate and nitrate in 70% nitric acid is 50 μg/l [9]. The method we have developed is not able to meet the SEMI guidelines but to our knowledge represents the most sensitive direct injection method possible with current IC technology.

The same sample of 0.7% nitric acid that was analyzed by the EG40 in Fig. 5 was also analyzed using sodium hydroxide eluents prepared by the conventional method. Significantly higher amounts of chloride and sulfate as well as an unknown contaminant were detected as shown in Fig. 8. The reason that less anionic contaminants were detected with the EG40 over the bottle system is most likely due to the EG40's ability to produce high-purity eluents. This suggests that bottle eluents have anionic contaminants that are eluted by the nitric acid samples.

If concentrations above 0.7% nitric acid are analyzed with this method run times can become long. The run time increases to over 2 h for an injection of 7.0% nitric acid under these conditions because of the time required to rinse the columns of excess nitrate. It is also likely that contaminant anions would not be completely recovered for a 1 μl injection of 7% nitric acid. Based on the 67.5 μequiv. capacity for the AG15 and AS15 2 mm columns; it may be possible to analyze a 1 μl sample of 4.0% nitric acid with this method. A 1 h run time for a 1 μl injection of 0.7% nitric acid represents the best compromise for the most sensitivity for the analytes of interest with a reasonable run time.

Table 2
Calibration results for trace anions in 0.7% (v/v) nitric acid

Anion	Data points	r^2	Slope	Intercept	Dynamic range (μg/l)
Chloride	9	0.9977	13.5±0.55	−0.01±0.009	30–300
Sulfate	9	0.9986	15.3±0.41	−0.02±0.024	45–1500
Phosphate	12	0.9982	43.3±1.31	0.013±0.026	45–1500

Table 3
Spike/recovery of trace anions in 0.7% nitric acid[a]

Anion	Sample (μg/l)	Standard addition (μg/l)	Found – sample (μg/l±SD)	Recovery (%)
Chloride	32±3.2	90	77±1.9	86
Sulfate	–	450	491±8.7	109
Phosphate	–	450	459±16	102

[a] For $n=7$.

4. Conclusion

A microbore direct injection method has been developed for the determination of trace anions in high nitrate matrices. An EG40 eluent generator was used to prepare high-purity and carbonate-free potassium hydroxide. This improved performance for trace level analysis over conventional bottle-based hydroxide eluents. Sensitivity to the low μg/l level in 0.7% nitric acid and solutions of nitrate salts up to 7000 mg/l was demonstrated with good recovery. Further work could involve the use of a two-dimensional heart-cutting technique to enhance sensitivity required for trace applications.
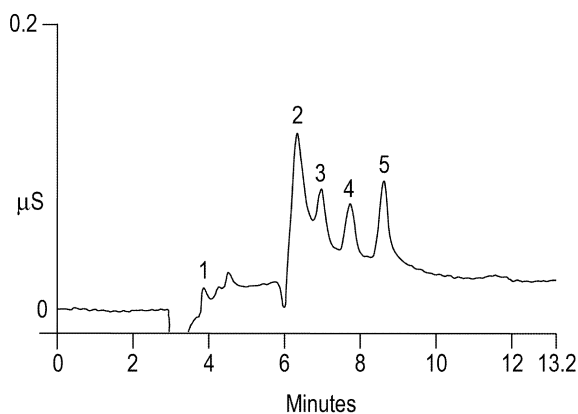

Fig. 8. Determination of trace anions in 0.7% nitric acid with bottle eluent. Peaks: 1=fluoride; 2=carbonate; 3=chloride (88 μg/l); 4=sulfate (127 μg/l); 5=unidentified. Sample volume: 1 μl; analytical column IonPac AS15 (250×2 mm); guard column IonPac AG15 (50×2 mm) detection: conductivity; suppression: ASRS, gas assisted recycle mode; eluent: sodium hydroxide 48 mM from 0 to 15 min, 100 mM from 15 to 35 min and 48 mM from 35 to 55 min, eluent flow-rate: 0.20 ml/min.

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