CHROM. 25 200

Ultratrace anion analysis of high-purity water

A column comparison

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ABSTRACT

Several vendor columns were employed in a comparison of columns aimed at optimized separation and quantitation of ultratrace (*i.e.*, high pg/ml to low ng/ml) levels of anions in high-purity water. The anionic profile of feed water will vary depending on the source; however, anions of most interest in high-purity water applications were chromatographed. The anions tested included fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, phosphate, sulfate, and oxalate. Isocratic methods were used without exception and all separations were made under chemically suppressed conditions employing a Dionex AMMS-1 suppressor with 12.5 m*M* sulfuric acid as regenerant. All eluents were prepared from either sodium carbonate–sodium hydrogencarbonate or 50% (w/w) sodium hydroxide solution. Columns evaluated in this study included Dionex AS4A, AS9, and AS10, Sarasep AN1 and AN2, and Waters IC-PAK Anion HR. Comparisons were made on the basis of chloride retention, resolution of fluoride and acetate, column efficiency on nitrite and sulfate peaks, capacity, and run time. Column durability was not thought to be an issue because of the nature of the samples. Dionex AS10, Sarasep AN2 and Waters IC-Pak Anion HR columns were deemed acceptable though no single column met every requirement.

INTRODUCTION

Over the years, two methods have emerged as on-line means of ultratrace analysis by ion chromatography. The first is merely a large volume injection technique [1,2]. In this case, between 0.5 and 2.0 ml have been successfully injected onto an ion chromatography column. The major drawback to this technique is the huge ensuing water dip that masks weakly retained species such as fluoride, acetate, and formate. The second and more popular method uses one or two switching valves and a concentrator column which is loaded off-line from the analytical column but switched in-line prior to elution of the solutes [3–5]. Large sample volumes, up to 100 ml, can be handled by this scheme as the concentrator column interstitial volume is of the

order of 0.4 ml. Concentrator column procedures are not as straightforward as they might appear. Jackson and Haddad [6] have elegantly described the complexities of this strategy.

Haddad and Heckenberg [7,8] have extensively studied factors that make up a precise and quantitative preconcentration for single-column ion chromatography (SCIC) and recommended a single pump with two high pressure switching valves. Jackson and Haddad [9] found the use of a monovalent aromatic acid at pH < 6 avoided interference by bicarbonate and provided good loading, washing, and backflushing characteristics from the concentrator column. In addition, they studied the effects of sample loading parameters [10] and ion-exchange capacity of the concentrator column [11] on achieving optimal preconcentration. Their aim was to achieve a precise and quantitative loading of the components in the sample such that these components

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would be quantitatively transferred onto the analytical column in a tight band with retention characteristics: $4 < k' < 30$ in an eluent compatible with the requirements of SCIC.

Harvey [12] evaluated several Dionex columns for a one-step gradient procedure separating eleven anions of interest in nuclear power industry applications. In particular, he cited the need to separate fluoride, acetate, formate, and chloride. Because of elution problems with hydrogencarbonate/carbonate eluents, he found the Omni-Pac PAX 100 column with a hydroxide step gradient and chemical suppression provided the needed resolution and run time for this application.

We have found the preparation of hydroxide eluents for gradient use to be somewhat tedious necessitating trap columns while maintaining a CO_2 free headspace over the eluent [13]. In addition, we have seen retention time shifts, especially for weakly retained anions, from eluent to eluent and baselines upon which it is difficult for data systems to perform integration without recalculation by the user. Also, gradients necessitate a post run requilibration period that usually requires about 10 column volumes of eluent. For these reasons, we prefer an isocratic separation with a stable and robust eluent such as hydrogencarbonate–carbonate.

Aside from the work of Harvey [12], little has been done to specify requirements for ultratrace anion applications. Our application requires the elution and separation of weakly retained anions such as fluoride and acetate as well as strongly retained anions such as sulfate in a suppression mode. The recent introduction of new IC columns of higher capacity, notably the Dionex AS10 and Sarasep AN2, may offer an advantage towards this end. In our work, the separation of fluoride, acetate, and chloride is essential. Thus, we have evaluated several low-capacity IC columns (Dionex AS4A and AS9, Sarasep AN1 and Waters IC-Pac Anion HR) along with two columns of somewhat higher capacity (Sarasep AN2 and Dionex AS10). The comparison is based on resolution of fluoride and acetate, chloride retention, total run time, and column efficiency. In addition, we desire baseline resolution of fluoride, acetate, chloride, nitrite, bromide, nitrate, phosphate, and sulfate in twenty minutes. Of less importance in our application is the selectivity of these columns towards formate and oxalate as these anions have been observed in the work of others [12].

EXPERIMENTAL

Reagents

Reagent-grade water from a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout this work. Sodium carbonate and sodium hydrogencarbonate were standard reference materials obtained from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA). Sodium hydroxide, 50% (w/w), was Fisher certified reagent (Fisher Scientific, Fair Lawn, NJ, USA). Sulfuric acid used to prepare regenerant was ULTREX Ultrapure reagent (J.T. Baker, Phillipsburg, NJ, USA). Sodium nitrate used to measure column capacities was reagent-grade material (EM Industries, Cherry Hill, NJ, USA). Anion standards for fluoride, chloride, nitrite, bromide, nitrate, and sulfate were prepared from certified 1000 μg/ml stock solutions (Alltech, Deerfield, IL, USA). The oxalate standard was prepared from J.T. Baker primary standard oxalic acid, formate from reagent grade sodium formate (Aldrich, Milwaukee, WI, USA), and acetate from suprapure sodium acetate (Alfa/Johnson Matthey, Ward Hill, MA, USA).

Instrumentation

All column test chromatograms were performed on a Dionex 4500i, polyether ether ketone (PEEK) version (Dionex, Sunnyvale, CA, USA) with a Spectra-Physics 8875 autosampler (Spectra-Physics, Fremont, CA, USA) and 20-μl loop. Sulfuric acid regenerant at 12.5 mM concentration was delivered with a Dionex AutoRegen module. The Dionex system was controlled and data acquired with a Dionex AutoIon 450. The columns and corresponding eluents used in this study are found in Table I. Flow-rates used with all columns was 1.0 ml/min. A Waters 600E pump (Millipore, Milford, MA, USA) equipped with a Rheodyne 9125 metal-free injector valve (Rheodyne, Cotati,

TABLE I

ANION-EXCHANGE COLUMN SPECIFICATIONS

Columns	Manufacturer	Dimensions (mm)	Particle size (μm)	Eluent
IonPac AS4A	Dionex	250 × 4	15	1.4 mM Carbonate, 1.3 mM hydrogencarbonate
IonPac AS9	Dionex	250 × 4	15	1.5 mM Carbonate, 0.56 mM hydrogencarbonate
IonPac AS10	Dionex	250 × 4	8.5	90 mM Hydroxide
AN1	Sarasep	250 × 4.6	8	1.4 mM Carbonate, 1.3 mM hydrogencarbonate
AN2	Sarasep	250 × 4.6	8	1.6 mM Carbonate, 2.1 mM hydrogencarbonate
IC-Pak Anion HR	Waters	75 × 4.6	6	1.2 mM Carbonate, 1.1 mM hydrogencarbonate

CA, USA) was used with a Kratos 783 variable-wavelength UV detector (Applied Biosystems, Ramsey, NJ, USA) at 245 nm (this wavelength was chosen to provide a 0.7 AU response with 10 mM nitrite) to measure column capacities. A Waters 590 pump and events unit controlled a Waters solvent switching valve and an Eldex Model E series B sample pump in the trace enrichment studies. Data acquisition for the Waters systems was made with a Nelson 2600 through series 760 interfaces.

Column capacity studies

Columns were converted to the hydroxide form by pumping with 1 M sodium hydroxide for 1 h. The excess base was pumped out with water until the conductivity dropped to 1 μS. The column was connected directly between the 9125 valve and the UV detector with a minimum of 0.010 inch I.D. PEEK tubing. While pumping water at 1.0 ml/min, the data system was started simultaneously with a switch from water to 10 mM sodium nitrite. An S-shaped curve was obtained and the time required to achieve 90% of the absorbance in the upper plateau region was determined for t (*i.e.*, the nitrate break-through time) in the equations below. The choice of 90% absorbance was somewhat arbitrary but reflected the fact that some of the curves were not symmetrical in shape. The delay volume due to the column alone, V_M, was obtained by measuring the time required for an injected

water dip to elute from the column after conversion of the resin to the nitrite form. The system delay volume $(V_D)_{TOT}$ could be measured by removing the column, replacing with a zero-dead volume fitting, and repeating the eluent switching experiment. After returning to water, the delay volume between the injector and detector, $(V_D)_{INJ}$, was obtained by injecting 25 μl of nitrite into water and measuring the time to the beginning of the nitrite response. Pump flow rates were verified gravimetrically with each measurement. The column capacity could then be calculated from the following relationship.

$$Ft = (V_D)_{TOT} + V_M - (V_D)_{INJ} + C/E$$

Solving the above equation for C, the capacity, one obtains

$$C = [Ft - (V_D)_{TOT} - V_M + (V_D)_{INJ}]E$$

In the above equations C is the column capacity in μequiv., E is the eluent concentration in mM, F is the flow-rate in ml/min, t is the time to achieve 90% maximum absorbance in min, and the volume quantities are defined in the text above and are in ml.

Trace enrichment studies

The Eldex pump had a bubble trap placed on the inlet tubing just prior to the pump head. This pump was operated at a flow-rate of 1.50 ml/min. A single switching valve design [3,4], where the solutes are backflushed from the concen-

TABLE II

TRACE ENRICHMENT PROGRAM

Time (min)	Event or action
0.0	Flush lines to injector valve with the sample (analytical column off-line)
5.0	Load sample on the concentrator column (analytical column off-line)
8.0	Backflush the solutes onto the analytical column and data acquisition
10.0	Rotate valve back to load
33.0	End run and data acquisition

trator column, was employed and controlled by the events unit of the Waters 590 pump. A Dionex AS9 was used as the concentrator column and loaded with water sample for 3.0 min. Most applications typically preconcentrate 10 to 30 ml of sample; however, we prefer smaller volumes, of the order of 5 ml, to help minimize spreading of weakly retained anions along the concentrator column [5,10]. Between samples, the inlet line to the Eldex pump was purged with the next sample by opening the bubble trap and allowing several milliliters to run to waste as the solvent inlet line provides the greatest dead volume between samples. The anions were eluted by backflushing the concentrator column for 2.0 min onto the analytical column. The program sequence may be found in Table II. The analytical column was either a Dionex AS9 or a Sarasep AN2 (Sarasep, Santa Clara, CA, USA). A Dionex AMMS-1 suppressor was used with 12.5 mM sulfuric acid delivered at 2 ml/min pneumatically with helium. A Dionex CDM-2 was employed as detector. Samples were collected in polypropylene bottles that had been presoaked in high-purity water overnight [4].

RESULTS AND DISCUSSION

There are several desirable features for a routine analytical method for the determination of trace anions in water. These applications require pg/ml to low ng/ml level detection limits for anions. Preferably, the method will be isocratic. This eliminates the need for column re-

equilibration associated with running gradients, thus increasing sample throughput. A run time of less than 20 min is desirable. A robust method, in particular, a stable easily maintained eluent, is also needed.

There are ten anions that are commonly measured in high-purity water applications: fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, phosphate, sulfate and oxalate. In our experience, we have observed all of these with the exception of formate and oxalate. Chloride is always seen at some level. This may be a combination of sampling and the ubiquitous nature of chloride. Because of this, k' for chloride of at least 1.0 for adequate retention is essential.

Acetate is frequently observed in our applications and at exceptionally high levels (hundreds of ng/ml). Because of its weak retention, separation from fluoride is important. Thus, a column that gives resolution between fliuoride and acetate of at least 1.0 is desirable.

In addition to the above criteria, there are other features that are important although not specific requirements for this method; *viz.*, columns providing good efficiency (*i.e.*, >15 000 plates/m) and good peak shapes. Also, if possible in this hypothetical isocratic run, baseline resolution of all ten components would be an ideal feature.

Table III gives a compilation of the columns with emphasis on retention of fluoride, chloride, and the last eluting anion. Figs. 1–6 are chromatograms of the ten anions on each column. Only three columns meet the criteria of $k' \geq 1.0$ for chloride (Dionex AS10, Sarasep AN2 and Waters Anion Pak HR). In fact, the Waters

TABLE III

RETENTION OF SELECTED ANIONS

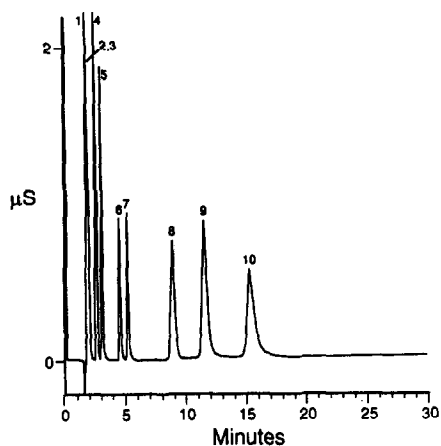| Columns	V_0	$k'(F)$	$k'(Cl)$	k' (last)
Dionex AS4A	1.6	0.20	0.70	8.62
Dionex AS9	1.4	0.17	0.74	11.2
Dionex AS10	2.4	0.30	2.28	10.2
Sarasep AN1	2.9	0.46	0.83	4.82
Sarasep AN2	3.0	0.52	1.02	6.17
Waters HR	1.3	1.00	2.40	13.3

Fig. 1. Ten anions separated on a Dionex AS4A column. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks: 1 = fluoride; 2 = acetate; 3 = formate; 4 = chloride; 5 = nitrite; 6 = bromide; 7 = nitrate; 8 = phosphate; 9 = sulfate; 10 = oxalate.
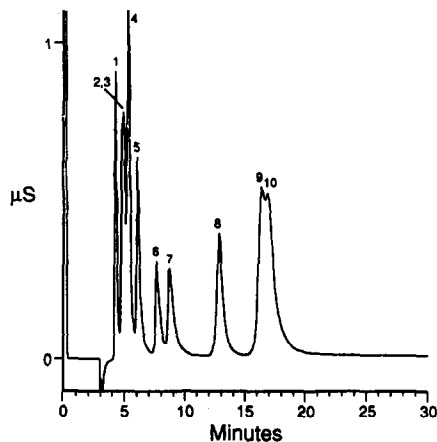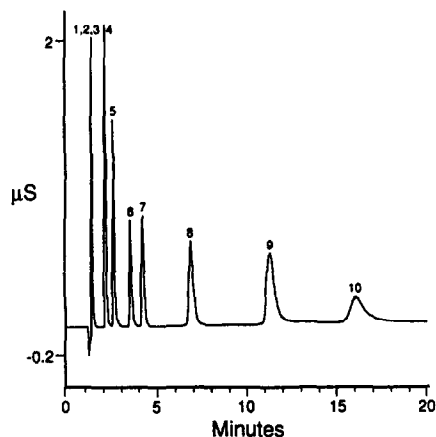

Fig. 2. Ten anions separated on a Dionex AS9 column. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks as in Fig. 1.
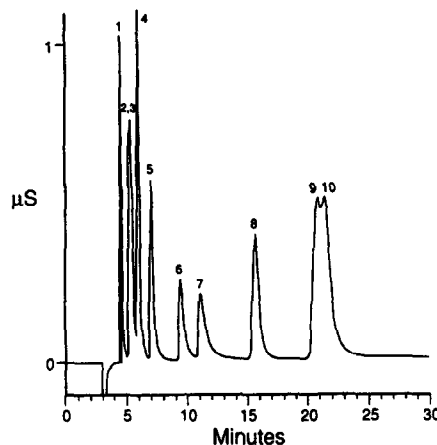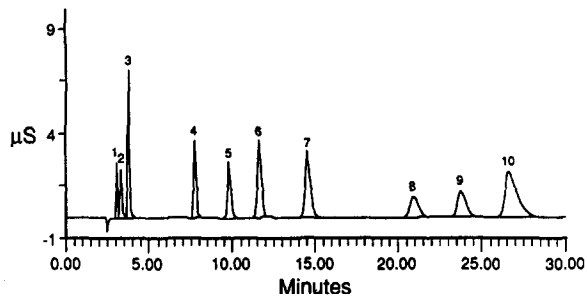

Fig. 3. Ten anions separated on a Dionex AS10 column. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks: 1 = fluoride; 2 = acetate; 3 = formate; 4 = chloride; 5 = nitrite; 6 = sulfate; 7 = oxalate; 8 = phosphate; 9 = bromide; 10 = nitrate.

Fig. 4. Ten anions separated on a Sarasep AN1 column. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks as in Fig. 1.

Fig. 5. Ten anions separated on a Sarasep AN2 column. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks as in Fig. 1.

column shows appreciable retention of fluoride ($k' = 1.0$). The criteria for a run time <20 min is met or nearly met by all the columns studied under the conditions of Table I.

Resolution of four pairs of closely eluting anions is given in Table IV. The pair of primary interest (fluoride and acetate) are well resolved on the Dionex AS10, Sarasep AN2 and Waters columns. The latter two actually meet the criteria of resolution of 1.0 or greater. Resolutions of formate/acetate and sulfate/oxalate are poor on the Sarasep AN2 column but of far less importance because of the absence of for-
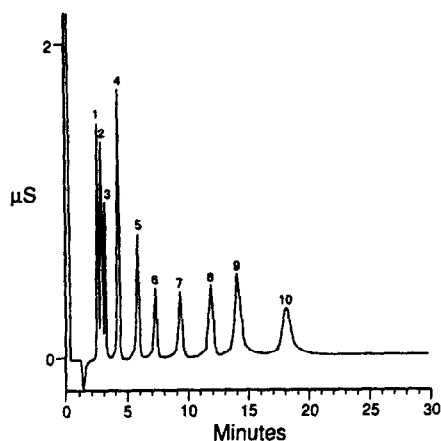
Fig. 6. Ten anions separated on a Waters IC-Pak Anion HR column. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks as in Fig. 1.

mate and oxalate in these samples. Other applications may require separation of the latter two anions from acetate and sulfate, respectively. Viewing the chromatograms obtained on each

column, only the Dioxex AS10 and Waters Anion Pak HR column are capable of resolution of all ten anions. Haddad *et al.* [14] found the Waters column to be superior to others used in SCIC based on a number of criteria.

Table V compares efficiencies of the columns as calculated from the width at half-height. For the most part, all columns meet the somewhat arbitrary conditions of 15 000 plates/m. The Dionex AS10 column has an exceptionally high efficiency. This may be due to the design of this pellicular/macroporous packing [15]. The peak shapes exhibited on all columns are excellent except for the Waters column where the peaks are exceedingly asymmetrical with uncharacteristic shoulders on the front and back of each peak. This column is not normally used with carbonate-type eluents and because of its methacrylate structure may be subject to some hydrolysis at high pH, although this was not confirmed in this study.

A recent example from our laboratory will

TABLE IV

RESOLUTION OF SELECTED PAIRS OF ANIONS

Column	R_s(OAc/F)	R_s(OAc/COO)	R_s(NO$_3$/Br)	R_s(SO$_4$/oxalate)
Dionex AS4A	0.39	0.58	2.50	4.45
Dionex AS9	0.00	0.00	2.98	4.42
Dionex AS10	0.88	1.88	2.37	4.79
Sarasep AN1	2.87	0.10	1.58	0.35
Sarasep AN2	2.17	0.26	1.89	0.61
Waters HR	1.39	1.54	4.04	3.66

TABLE V

COLUMN EFFICIENCIES AND CAPACITIES

Column	N (nitrite)[a]	N (sulfate)[a]	Capacity
Dionex AS4A	22 000	16 000	40
Dionex AS9	14 000	14 000	38
Dionex AS10	44 000	36 000	140
Sarasep AN1	16 000	25 000	39
Sarasep AN2	15 000	21 000	61
Waters Anion HR	18 000	18 000	41

[a] All units are plates/m. Calculation based on the following equation: $N = 5.54 \ (t_R/w_h)^2$, where w_h is the peak width at half-height.
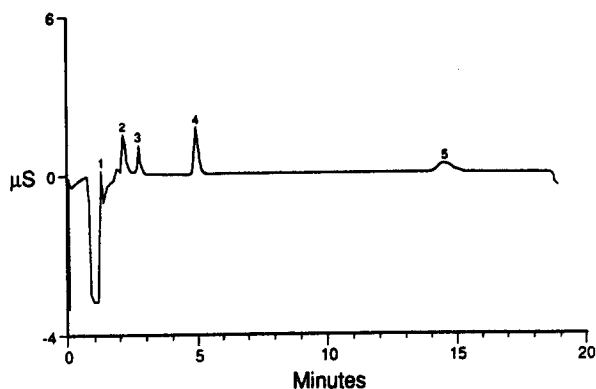
Fig. 7. Trace enrichment of standard on Dionex AS9. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = nitrate; 5 = sulfate.
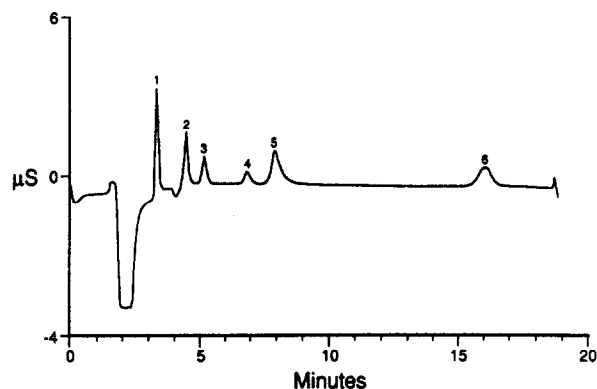

Fig. 9. Trace enrichment of standard on a Sarasep AN2. Eluent is 2.0 mM sodium carbonate and 2.5 mM sodium hydrogencarbonate at 1.0 ml/min. Peaks: 1 = fluoride; 2 = chloride; 3 = nitrite, 4 = bromide; 5 = nitrate; 6 = sulfate.

serve to illustrate the importance of acetate and fluoride resolution. A chromatogram of a five-anion standard (fluoride, chloride, nitrite, nitrate and sulfate) on a Dionex AS9 column is shown in Fig. 7. Note the fluoride peak eluting from the inverted tail of the water dip. A sample run at that time showed a large peak at the retention time of fluoride; see Fig. 8. This peak was initially reported as fluoride to the customer. On further discussion with the customer, the possibility of so large a fluoride contaminant in the water purification system seemed remote. Running an acetate standard, an identical retention time with fluoride was confirmed.

The Sarasep AN2 column was designed with this high-purity water application in mind. In Fig. 9, six anions (fluoride, chloride, nitrite, bromide, nitrate and sulfate) are separated on the Sarasep AN2 column. Note the fluoride is well out of the water dip. On the date this standard was run, another sample containing the unknown peak that eluted at the retention time of fluoride on the Dionex AS9 column was received. Fig. 10 shows this chromatogram and clearly the large anion in the sample is not fluoride. An acetate standard showed a good retention time and peak shape match with this unknown peak.
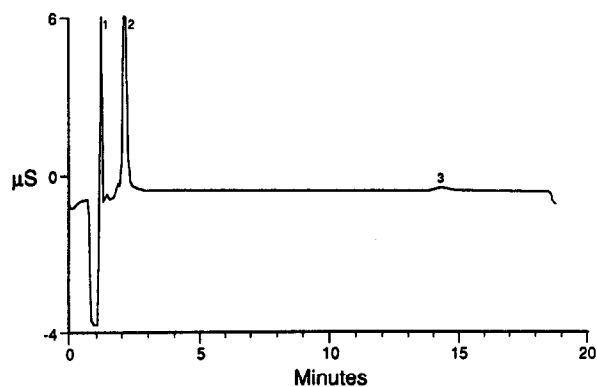

Fig. 8. Trace enrichment of ultrapure water on a Dionex AS9. Conditions can be found in Table I. The flow-rate is 1.0 ml/min. Peaks: 1 = unknown; 2 = chloride; 3 = sulfate.
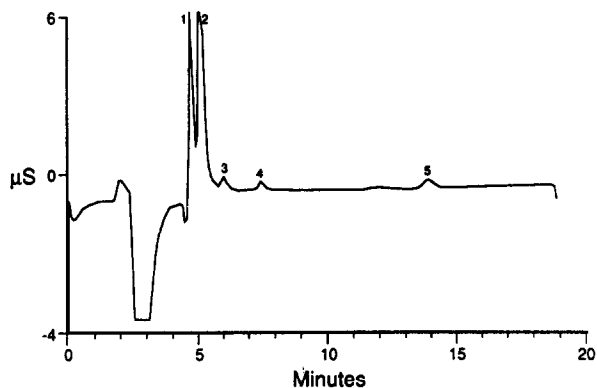

Fig. 10. Trace enrichment of ultrapure water on a Sarasep AN2. Conditions as in Fig. 9. Peaks: 1 = unknown; 2 = chloride; 3 = bromide; 4 = nitrate; 5 = sulfate.

CONCLUSIONS

Six commercially available columns were studied to determine suitability for a high-purity water analysis. Traditional IC columns that are used to separate the seven anions of primary interest in general IC applications (fluoride, chloride, nitrite, bromide, nitrate and sulfate) were not suitable in an isocratic mode for this high-purity water application. New columns that combine excellent fluoride retention with reasonable elution of the last peak are far superior in this regard. An additional criterion of importance is resolution of weak organic acids such as acetate from fluoride. Three vendor columns were found to be suitable for most criteria, although no column fulfilled all. Sodium hydrogencarbonate and sodium carbonate eluents are preferred in suppressed IC because they are easily prepared and stable. The salts are available from NIST providing a traceable source. It must be stressed that each application will have its own requirements. For example, if oxalate and formate are impurities of interest, the Sarasep AN2 column will not adequately resolve these from sulfate and acetate, respectively.

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