Ion Chromatographic Determination of Anions in Environmental Samples

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ION CHROMATOGRAPHIC DETERMINATION OF ANIONS IN ENVIRONMENTAL SAMPLES

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The use of ion-exchange chromatography with an IonPac AS 14 column, 3.5 mM Na_2CO_3 / 1.0 mM $NaHCO_3$ eluent and suppressed conductivity detection provides a simple, cost-effective, fast, accurate, and highly sensitive method for the determination of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{2-}, SO_4^{2-}, and $C_2O_4^{2-}$ at low μg/L levels in environmental samples. Data on sensitivity, selectivity, accuracy, and % relative standard deviation are described. The method is suitable for many environmental applications including atmospheric aerosols (exposed on cellulose, glass fiber, and quartz filters), rainwater, cloud water, potable- and non-potable waters, and carbonated waters. Dominant components of the aerosol were SO_4^{2-}, NO_3^-, and Cl^-. Rainwater, on the other hand, has relatively very low concentrations of these three species. The wide-spread concentration range for Cl^- in variety of water samples and the high concentrations for SO_4^{2-} in drinking water are striking. Determination of the anionic composition of carbonated waters revealed a considerable variation of the individual anions.

Keywords: Ion chromatography; anions; atmospheric aerosols; rainwater; cloud water; drinking water

INTRODUCTION

In recent years, man-made emissions of atmospheric pollutants have increased considerably. It is well known that oxides of sulfur and nitrogen have long enough residence times (1–5 days) in the atmosphere to be transported to regions thousands of kilometers from the place where they were released. Water-soluble inorganic anions in suspended particulate matter are an area of growing interest with respect to the increase in pollution levels in remote and urban areas. SO_4^{2-}, NO_3^-, Cl^-, and NO_2^- are important components of atmospheric aerosols and are responsible for the acidity of wet and dry deposition. Anion like Br^- constitutes a

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hazard to public health. Knowledge of aerosol composition could help us under-
stand and trace the sources of pollutants by means of receptor models.

Another environmental problem of concern is the pollution of water by inor-
ganic species. Anions like F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{2-}, and SO_4^{2-} influence the
quality of upgraded water and can cause health risks. For example, fluoridation is
a public health issue, which raises arguments as to whether F^- should be added to
municipal water supplies. One toxic effect of F^- is the mottling of tooth enamel,
which, depending on the temperature, may occur to an objectionable degree with
concentrations in drinking water of only $0.8 - 1.6$ mg/L [1,2]. High levels of NO_3^-
are sometimes found in drinking water on farms with shallow wells. Sources of
this contaminant include municipal and industrial waste waters, refuse dumps.
animal Feed lots, septic tanks, run-off or leachate from manured or fertilized
agricultural lands, urban drainage, and biochemical nitrogen fixation. A specific
toxic effect of NO_3^- is a condition of infants called "methemoglobinemia", which
can result in mental retardation [2].

Knowledge of anion concentrations in environmental samples, thus, is as
important as the toxic metal concentrations. To date, ion chromatography is per-
haps the most suitable technique for this purpose. With the advent of suppressed
ion-exchange chromatography (IC) in the market [3], the technique has become
established as a powerful tool for the determination of inorganic anions in a wide
variety of environmental samples [4-11]. Improvements in analytical techniques
to measure increasingly lower concentrations and analyze samples of greater
complexity   are   continuously   taking   place.   Introduction   of   advanced
ion-exchange columns and membrane-based suppression has lead to obsoles-
cence of the conventional IC technology.

The aim of the this article is to present a reliable method for the simultaneous
determination of major as well as minor inorganic anions (F^-, Cl^-, NO_2^--N, Br^-,
NO_3^--N, SO_4^{2-}, and $C_2O_4^{2-}$) in various environmentally important samples viz.,
atmospheric aerosols, rainwater, cloud water, potable- and non-potable waters,
and carbonated waters by means of ion-exchange chromatography with sup-
pressed conductivity detection.

EXPERIMENTAL

Sampling

Aerosol samples were collected on 20×25 cm Whatman 41 filters using
high-volume samplers. A flow rate of about 0.7 m^3 min^{-1} of air was maintained.

The 24-h samples were taken at Whiteface Mountain (WFM) and Mayville (MV) in New York State. For analysis, a 10.14-cm^2 portion of each filter was extracted in 25 or 50 mL of distilled water at 85 – 90°C for 2 h. Ambient aerosols were also collected on Glass Fiber and Quartz filters at Buffalo and Bronx in New York State, respectively. Sampling time was 24-h. Filters were cut into strips and the particulate matter was extracted from 1/12 of filter into 25 or 50 mL of distilled water after agitating in an ultrasonic bath for 30 min. For the reference samples blank filters were used to which 25 or 50 mL of deionized water had been added. Prior to injection into the column, the samples were filtered through a 0.45 μm membrane filter.

The rainwater sample was collected in a plastic bucket at Albany (ALB), New York. Cloud water samples were collected at the summit of WFM using a passive omnidirectional collector [12]. Sampling time was 15 min. Prior to sample collection, the collecting devices were rinsed thoroughly with distilled water. Samples were filtered through a 0.45 μm Nuclepore polycarbonate membrane.

Drinking water samples were from different sources in Albany, New York. A bottled water (Natural Saratoga Spring Water) and four carbonated water samples were also analyzed. Surface water samples were from the Chubb River and Engleville in New York State.

Instrumentation

The experimental system utilizes a Model DX 500/PeakNet Workstation (Dionex Corp., Sunnyvale, CA) on Chromatograph equipped with a CD 20 conductivity detector, GP 40 gradient pump, LC 20 chromatography module, and AS 40 automated sampler. The column used was an IonPac AS 14 (4 × 250 mm) separator and AG 14 guard, with a 10 μL sample loop. The IonPac AS 14 column utilizes polymeric packings and provides good peak resolution, very high efficiency, high speed, and high loading capacity compared to previous ion exchangers. Selectivity of the column is such that F⁻ and Cl⁻ are retained well away from the water dip (system dip).

The method uses 3.5 mM Na_2CO_3 / 1.0 mM $NaHCO_3$ eluent at a flow rate of 0.75 mL/min, and an Anion Self-Regenerating Suppressor (ASRS-I; 4 mm) with Auto Suppression at 100 mA in the recycle mode.

Reagents and standard solutions

All reagents were of analytical grade. Solutions were prepared with low conductivity water (< 2.0 μS/cm). Concentrations were calculated based upon the peak

areas of standards that were prepared from 1000 mg/L stock solutions. The stock solutions of the anions were prepared by dissolving the appropriate amounts of sodium or potassium salts in deionized water. Working standards were prepared daily by dilution of the stock solutions.

Quality controls

Comparison with anion standards checked against quality controls and spiked samples with known concentrations of target species confirmed the presence of anions. Field blanks and filter blanks were handled and analyzed in the same way as the samples. Anion concentrations in deionized water, in rinses of the polyethylene sample bottles and rainwater bucket, and in field and filter blanks were mostly undetectable. In cases where they were in detectable amount, field and filter blanks were subtracted.

The accuracy of calibration curves was evaluated by analyzing quality control nutrient mineral standards containing the analyte at a concentration in the low- and high-calibration range. They were obtained as concentrates from the Environmental Laboratory Approval Program (ELAP), New York State Department of Health, Albany, NY 12201, USA. For all of the anions, controls were within ± 10%. Standard Reference Material 1648 (Urban Particulate Matter – UPM) and Standard Reference Material 2694a (Simulated Rainwater) from National Institute of Standards and Technology (NIST) were also used as control samples for aerosol and water quality analyses, respectively. The percent standard deviation of measurements, evaluated on duplicate runs of several samples, was found to be better than ± 10% in most cases; also matrix spike recoveries ranged from 74% to 103%. These results are represented in Tables I and II.

RESULTS AND DISCUSSION

Sensitivity and linearity for each of the anions were established by analysis of a mixture of anion standards with varying concentrations. Peak areas were plotted against concentrations. Good linearity was obtained between peak area and concentration over the range 0.05 – 20 mg/L for F^-, Cl^-, Br^-, SO_4^{2-}, $C_2O_4^{2-}$ and 0.005 – 2.0 mg/L for NO_2^- -N and NO_3^- -N, respectively. Correlation coefficients (r) were 0.998 or better. The method detection limit (MDL) was determined by using the procedure in USEPA Method 300.0 [13]. Seven replicate aliquots of standards were injected and the MDL were calculated as follows:

$$MDL = (t_{n-1=0.99})x(S)$$

where $t_{n-1=0.99}$ is the student's t-value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom ($t_{n-1=0.99} = 3.143$) for seven replicates) and S is the standard deviation of the replicate analyses. The calculated values of MDL for F^-, Cl^-, NO_2^--N, Br^-, NO_3^--N, SO_4^{2-}, $C_2O_4^{2-}$, and PO_4^{2-} were 0.91, 2.0, 0.40, 7.0, 0.74, 50, 90, and 40 $\mu g/L$, respectively.

TABLE I Quality controls for aerosol and different types of water samples

Sample	% Relative Standard Deviation[a]						
	F^-	Cl^-	Br^-	NO_2^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$
Simulated Rainwater	32.4	3.6	–	–	1.6	4.7	–
SRM 2694a-II	[.07]	[.98]	·		[7.2]	[10.9]	
Aerosol (WFM; 8/95)	–	6.5	–	–	0.70	0.0	–
Aerosol (Buffalo; 1/97)	–	1.2	–	–	0.54	2.2	11.5
Rainwater	–	11.6	–	5.6	5.5	5.9	–
		(95)		(100)	(91)	(94)	
Cloud Water	–	0.33	–	–	0.50	1.2	0.44
Bottled Water	10.0	0.03	–	–	0.92	0.35	–
		(90)			(95)	(97)	
Surface Water (Effluent; Chubb River)	13.8	3.8	–	5.5	7.8	7.6	–

a. Based on duplicate measurements. Values in parentheses are matrix spike recovery. Values in brackets for the Standard Reference Material are actual concentrations in mg/L found. Known values are 0.11, 0.94, 7.2, and 10.6 mg/L for F^- Cl^-, NO_3^--N, and SO_4^{2-}, respectively.

TABLE II Quality controls for carbonated waters

Type	· % Relative Standard Deviation[a]				
	F^-	Cl^-	NO_3^-	PO_4^{2-}	SO_4^{2-}
Ginger Ale (Canada Dry)	6.6	6.7 ·	5.7	9.7	0.78
Ginger Ale (Schweppes)	10.8	1.7	–	11.8	8.9
	(103)	(83)	(91)		(87)
7-Up	(101)	(81)	(90)		(90)
Mountain Dew	(76)	(74)	(77)		(84)

a. Based on duplicate measurements.
Values in parentheses are matrix spike recovery.

Figure 1 shows three chromatograms which correspond to (bottom curve) a mixture of seven standard anions; (middle curve) a sample of atmospheric aerosol collected on Glass Fiber filter at Buffalo; and (top curve) a sample of atmospheric aerosol collected on Whatman 41 filter at WFM. The optimum conditions gave good resolution and reasonable times of analysis. All samples contain Cl^-, NO_3^-, and SO_4^{2-} as major components but it is sometimes possible to detect minor peaks attributable to F^-, NO_2^-, Br^-, and $C_2O_4^{2-}$. An unknown peak at 3.08 min was also observed in aerosol samples.
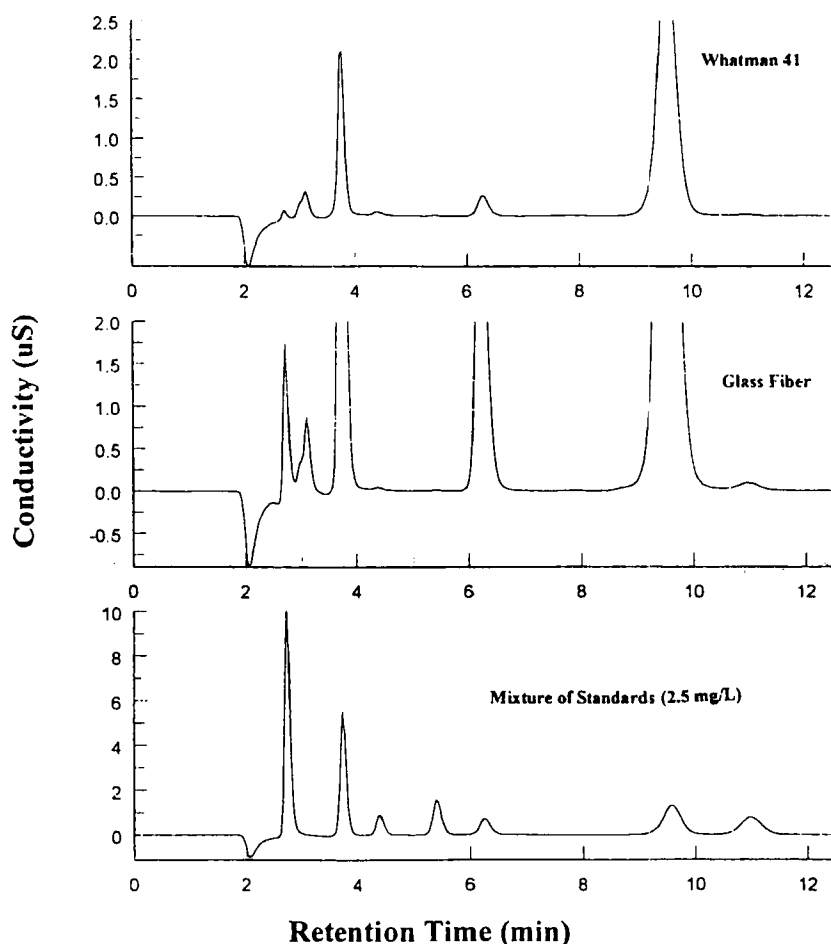
FIGURE 1 Chromatograms showing the (bottom curve) separations of seven standard anions; (middle curve) sample of atmospheric aerosol on Glass Fiber filter; and (top curve) sample of atmospheric aerosol on Whatman 41 filter. Column: AS 14; eluent: 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$; sample size: 10 µL; flow rate: 0.75 mL/min; retention time: F^- (2.73 min), Cl^- (3.73 min); NO_2^- -N (4.38 min), Br^- (5.40 min), NO_3^- -N (6.23 min), SO_4^{2-} (9.57 min), $C_2O_4^{2-}$ (10.9 min)

For a 10 µL sample volume and use of the optimum operating conditions. 50 µg SO_4^{2-}/L can easily be detected. A high-volume sampler draws about 2400 m^3 air/day. Assuming a lowest value of 1 µg SO_4^{2-}/m^3, a high-volume filter would collect 2400 µg SO_4^{2-}. Under the experimental conditions employed in this study, 0.08 µg SO_4^{2-} gets injected onto the column. This corresponds to 8,000 µg/L, which far exceeds the MDL of 50 µg SO_4^{2-}/L observed in the present study. Detection limits could be further improved by increasing the injection volume and/or decreasing the extraction volume.

Data for aerosol samples on Whatman 41 filters at WFM and MV are presented in Table III. SO_4^{2-}, NO_3^-, and Cl^- are the dominant anionic species of the aerosols. Concentrations of Br^- and $C_2O_4^{2-}$ in the atmosphere are very low and fall near the detection limits. In general, a seasonal variation in the concentrations emerges with higher concentrations in summer than in spring or winter. Concentrations of SO_4^{2-} and NO_3^- at WFM during summer were approximately 17 times higher and 5 times lower, respectively, than those found (SO_4^{2-} = 0.54 µg/m^3; NO_3^- = 0.38 µg/m^3) at a mountain site in southern Nevada [14]. Our data for MV during winter are in the range of those reported by Cadle et al., [15] for particulate SO_4^{2-} (2.54 µg/m^3) and NO_3^- (0.78 µg/m^3) in northern Michigan. It is likely that these anions present in the aerosol are from anthropogenic sources. The lack of considerable sources within the region indicates that these anions were transported from the heavily industrialized Ohio River Valley area. Large amounts of SO_2 and NO_x are emitted from the coal-fired power plants in this area and are thus available for conversion and transport downwind.

TABLE III Anion concentrations for aerosol samples on Whatman 41 filter

Site	Date	Concentration (µg/m^3)						
		F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$
WFM	1/95	–	0.077	–	–	–	0.188	–
WFM	3/95	0.014	0.768	0.010	0.016	0.067	4.62	–
WFM	8/95	0.004	0.175	–	–	0.076	9.55	–
MV	1/95	–	0.090	–	–	0.409	2.77	–
MV	3/95	0.003	0.200	–	–	0.465	5.57	–
MV	8/95	–	0.340	0.010	–	0.263	1.30	–

Results of the analyses on Glass Fiber and Quartz filters are shown in Table V. Dominant species observed in the aerosol were SO_4^{2-}, NO_3^-, Cl^-, and $C_2O_4^{2-}$. Small concentrations of F^-, NO_2^-, and Br^- were also found in few samples. Con-

centrations of these anions are higher at the Buffalo site than at the Bronx site. Examination of the different seasons revealed a higher Cl⁻ concentration in winter than in spring or summer, and a higher $C_2O_4^{2-}$ concentration in summer than in spring or winter. Higher Cl⁻ concentrations at the two sites during winter become understandable considering the road salts used during the winter season. Relative to the Bronx, high Cl⁻ in winter at Buffalo is not surprising since the latter has much more snow.

TABLE IV Anion concentrations in ambient aerosols

Site	Date	Type	Concentration (µg/filter)						
			F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$
Buffalo	1/97	Glass Fiber	–	5450	–	–	2216	15086	323
Buffalo	3/97	Glass Fiber	38.4	2744	–	10.8	911	10391	194
Buffalo	7/97	Glass Fiber	–	506	–	–	2027	15377	–
Bronx	1/97	Quartz	–	226	4.8	–	132	7943	155
Bronx	3/97	Quartz	–	66	7.2	–	234	9287	159
Bronx	8/97	Quartz	–	42	–	–	149	8135	412

TABLE V Concentration of anions in different types of water

Type	Concentration (mg/L)						
	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$
Rainwater	0.005	0.155	0.018	–	0.163	1.53	–
Cloud Water	0.005	0.055	–	–	0.012	3.54	–
Cloud Water	0.003	0.247	–	–	2.27	10.4	–
Cloud Water	0.001	0.745	–	–	5.97	32.1	2.28
Drinking Water	0.026	23.2	–	–	0.013	11.1	–
Drinking Water	0.024	23.1	–	–	0.007	11.4	–
Drinking Water	0.056	31.7	–	–	0.734	45.3	–
Drinking Water	0.057	33.3	–	–	0.733	47.8	0.151
Bottled Water	0.017	35.9	–	–	0.646	15.9	–
Surface Water (Effluent; Chubb River)	0.025	39.5	0.165	–	3.57	15.8	–
Surface Water (Engleville)	0.040	0.899	–	–	0.044	3.24	–

A typical chromatogram of a sample of cloud water (top curve) is shown in Figure 2. F⁻, Cl⁻, NO₃⁻, SO₄²⁻, and C₂O₄²⁻ were identified with an unknown peak at 3.07 min. Figure 3 depicts the chromatograms of a sample of bottled water (lower curve) and a sample of drinking water (upper curve). Concentrations of F⁻, Cl⁻, NO₃⁻, and SO₄²⁻ present in the bottled- and drinking- water were high enough to be determined with a good degree of sensitivity.
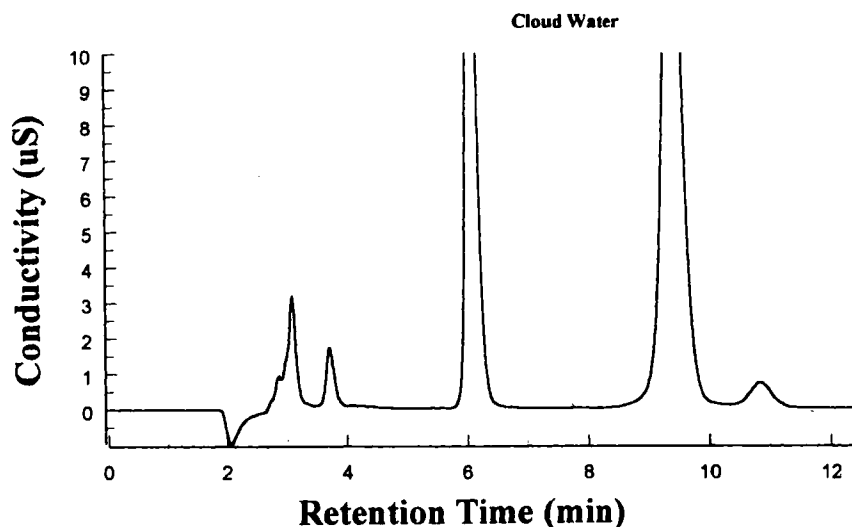
Cloud Water

FIGURE 2 Chromatogram of a sample of cloud water

Table V summarizes the results of the anion measurements in rainwater, cloud water, potable-, and non-potable waters. SO_4^{2-}, NO_3^-, and Cl⁻ dominate the inorganic composition of the rainwater. The levels observed were of the same order of magnitude as found in precipitations in the northeast [16–18]. SO_4^{2-} and NO_3^- accounted for 82% and 8.7%, respectively, of the acid ions in rain. Observed SO_4^{2-} and NO_3^- in rainwater is due to scavenging of both particulate SO_4^{2-} and NO_3^- as well as gaseous SO_2 and HNO_3. An NO_2^-/NO_3^- ratio of 0.11 was found, indicates that NO_2^- is only a minor species in rainwater and its contribution to rainwater acidity is negligible. SO_4^{2-} and NO_3^- represent the dominant acidic inputs to the cloud water provided by H_2SO_4 and HNO_3. Cloud water SO_4^{2-} and NO_3^- concentrations at WFM were similar to values reported from locations in New England [19, 20] but were much higher than the values reported for Washington State [21]. Cloud water concentrations of major anions were generally 1.6 to 37 times greater than in rainwater. The SO_4^{2-} to NO_3^- ratio was about 5 and 9.4 for cloud water and rainwater.
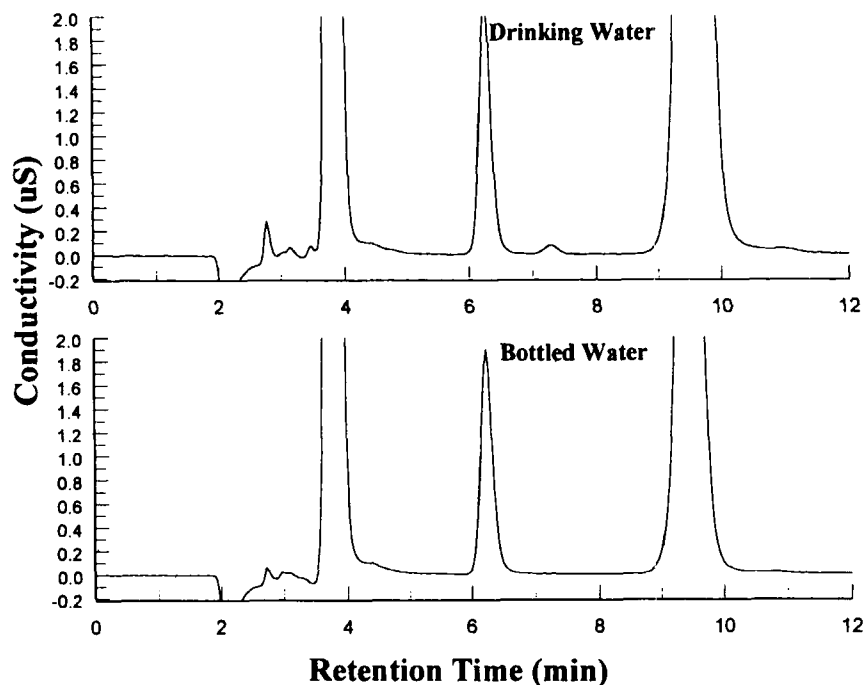
FIGURE 3 Chromatogram of a sample of bottled water (bottom curve) and a sample of drinking water (top curve)

Concentrations of F^-, Cl^-, NO_3^-, and SO_4^{2-} in drinking- and bottled-water (Table V) were found to be considerably lower than the USEPA's recommended MCL (Maximum Contaminant Level) [22] for F^- (2.0 mg/L), Cl^- (250 mg/L), NO_3^- -N (10 mg/L), and SO_4^{2-} (250 mg/L).

The main anionic components of surface water are Cl^-, SO_4^{2-}, and NO_3^- (Table V). Their concentrations are higher in surface water than in rainwater.

TABLE VI Anion concentrations in carbonated waters

Type	Concentration (mg/L)				
	F^-	Cl^-	NO_3^-	PO_4^{2-}	SO_4^{2-}
Ginger Ale (Canada Dry)	2.49	12.9	1.05	0.931	6.59
Ginger Ale (Schweppes)	2.11	29.1	0.255	0.745	49.2
7-Up	1.46	36.9	0.464	–	56.7
Mountain Dew	1.52	32.2	0.715	3.74	52.4

In Figure 4 the chromatograms corresponding to a mixture of F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{2-}, and SO_4^{2-} (bottom curve) and a sample of carbonated water (top curve) are shown. Carbonate was eluted (3.15 min) away from the water dip. An unknown peak at 4.8 min was observed. Results of the carbonated water analysis are listed in Table VI. Ranges of concentration of F^-, Cl^-, NO_3^-, PO_4^{2-}, and SO_4^{2-} in these waters were 1.46 – 2.49 mg/L, 12.9 – 36.9 mg/L, 0.255 – 1.05 mg/L, 0.745 – 3.74 mg/L, and 6.59 – 56.7 mg/L, respectively.

CONCLUSIONS

The salient features of this analytical method are: 1) high detection sensitivity (1 – 10 μg/L) without preliminary concentration; 2) high selectivity and speed in complicated mixtures (10 ions can be analyzed during a 12-minute period); 3) simultaneous determination of a number of inorganic and organic ions; 4) small sample volume required (10 μL); 5) determination of both micro- and macro-components of the sample owing to the linear dependence of the conductivity signal over a wide range of concentrations (5 μg/L – 20 mg/L); 6) simple pretreatment for analysis; 7) good reproducibility; 8) complete automation of analysis; 9) high tolerance for foreign ions; and 10) cost-effectiveness, particularly when used for multiple-anion analysis.

Acknowledgements

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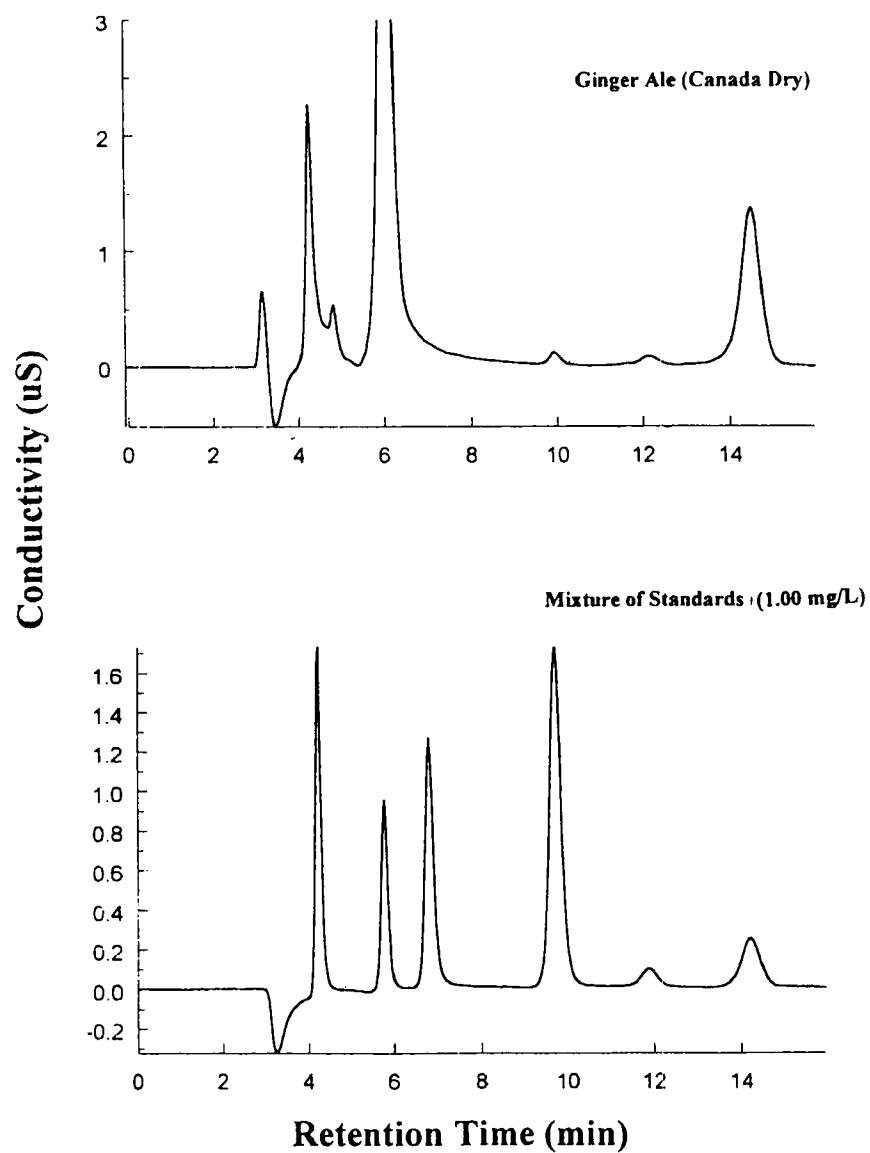
Conductivity (uS)

Ginger Ale (Canada Dry)

Mixture of Standards ˈ(1.00 mg/L)

Retention Time (min)

FIGURE 4 Chromatogram of (bottom curve) a mixed standard of F⁻ (4.22 min), Cl⁻ (5.77 min); NO_2^--N (6.80 min), NO_3^--N (9.72 min), PO_4^{2-}(11.9 min), SO_4^{2-} (14.2 min) and (top curve) a sample of carbonated water

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