Note

Single injection ion chromatographic analysis of both anions and cations

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(First received August 2nd, 1984; revised manuscript received August 23rd, 1984)

Ion chromatography, as developed by Small *et al.*[1], has proven to be a very useful technique for the determination of inorganic anions and cations at the ppm and sub-ppm level. The majority of the work, however, has centered on either the cations or the anions, but not the simultaneous analysis of both. One study which determined cations and anions simultaneously used a complexing agent, ethylenedinitrilotetraacetic acid, to complex the divalent metals, which were then separated and detected as anions along with the uncomplexed inorganic anions[2]. Another method for the simultaneous determination of anions and cations involves the use of a dual channel instrument with both anion columns and cation columns but only one detector[3]. Using this system, the detector must be matched with synchronal injections to efficiently observe both cations and anions. The loss of the chloride peak is possible with this system.

The technique presented here involves the use of a cation-separator column, conductivity detector, anion-separator column, anion-suppressor column, and an electrochemical detector. The output from the two detectors is monitored independently in order to observe the cations and the anions as they elute from the respective separating columns. This method does not convert the cations to anion complexes prior to separation and detection, nor does it require the switching of detectors during the middle of the analysis with the concomitant loss of peaks. The system also uses commercially available components and is easy and rapid to perform.

EXPERIMENTAL

Apparatus

The equipment and exact operating conditions used in this work are described in Table I. The instrumental set-up consists of two separator columns, two detectors and one suppressor column. The analyte flow path begins at the injection valve and proceeds to the cation separator where the cations are separated. The separated cations are then detected at the conductivity detector. After leaving the conductivity detector, the ions travel to the anion-separator column where the anions are separated, the anion-suppressor column where the previously separated and detected cations are removed, and finally to the electrochemical detector for the detection of the separated anions. The use of the electrochemical detector to detect anions in this

TABLE I

INSTRUMENTAL CONDITIONS

Instruments	Dionex Model 10 ion chromatograph
	Dionex electrochemical detector
	Houston Instruments omniscribe chart recorder
Eluent	0.0016 M Li$_2$CO$_3$ + 0.0026 M LiCH$_3$CO$_2$ · 2H$_2$O
	pH = 10.35
Flow-rate	2.3 ml/min
Electrochemical applied potential	0.4 V
Chart recorder speed	0.5 cm/min
Separator columns	
Anion separator	150 × 4 mm I.D. Dionex HPIC-AS3 anion
Cation separator	165 × 4 mm I.D. Hand packed cation column, surface
	sulfonated Bio-Beads SX2, 200–400 mesh.
Suppressor column	Dionex AFS, fiber suppressor
Injection volume	0.10 ml

manner has been described previously[4]. It would be possible to use a second conductivity meter in place of the electrochemical detector if a second meter were available.

Reagents

Stock solutions of 1000 ppm of each ion were prepared using distilled-deionized water as was the ion chromatographic eluent. The salts used were ACS certified quality. Aliquots of the stock solutions were diluted using the distilled-deionized water to the appropriate concentrations prior to injection into the ion chromatograph.

Procedure

The normal procedure for the use of the ion chromatograph was followed with the exception of the use of two separator columns in series and the placement of the electrochemical detector after the anion suppressor. The solutions were injected and the detector and recorder were adjusted appropriately to provide peaks of appropriate height.

RESULTS AND DISCUSSION

The length of columns used in this experiment is not restrictive. The lengths can be varied at will, but corresponding changes in the resolution and retention times will occur. The eluent used for this work is composed of a mixture of lithium carbonate and lithium acetate dihydrate. Various other eluents were tested including ammonium carbonates and ammonium acetates as well as various combinations of the ammonium and lithium salts. The final eluent chosen provided the best combination of resolution and retention times for all species analyzed using the analytical columns described previously.

The simultaneous separation and detection of the anionic cationic species is illustrated in Figs. 1 and 2. The figures illustrate the types of resolution that can be
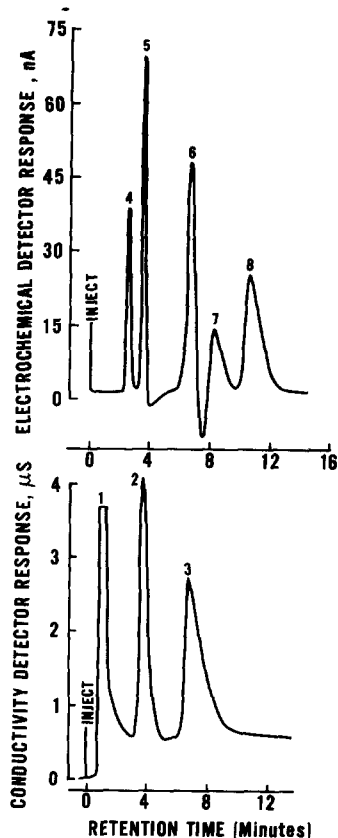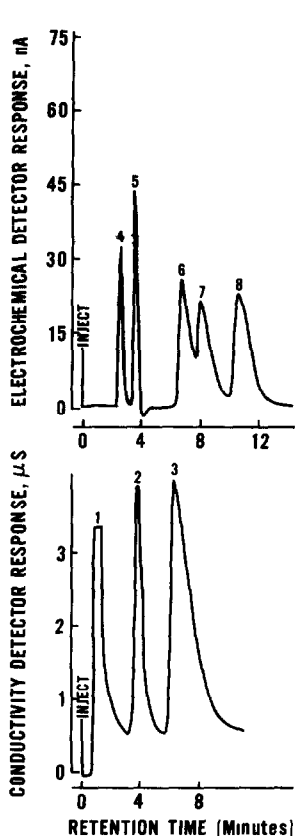
Fig. 1. Conductivity and electrochemical chromatograms of standard ion solution. 1 = Anions; 2 = Na$^+$, 100 ppm; 3 = K$^+$, 183 ppm; 4 = F$^-$, 18 ppm; 5 = Cl$^-$, 20 ppm; 6 = PO$_4^{3-}$, 346 ppm; 7 = NO$_3^-$, 99 ppm; 8 = SO$_4^{2-}$, 112 ppm.

Fig. 2. Conductivity and electrochemical chromatograms of standard ion solution. 1 = Anions; 2 = Na$^+$, 105 ppm; 3 = K$^+$, 115 ppm; 4 = F$^-$, 20 ppm; 5 = Cl$^-$, 30 ppm; 6 = Br$^-$, 13 ppm; 7 = PO$_4^{3-}$, 167 ppm; 8 = SO$_4^{2-}$, 93 ppm.

observed. The simultaneous separation takes considerably less time than the separate analysis of cations and anions. The analysis time for the simultaneous separation takes approximately 12 min, with the cations eluting in 8 min and the anions in 12 min. With the separate analysis of cations and anions, an average elution time for cations is about 12 min[5] and an averge elution time for the anions is approximately 8 min[6]. Even though these analysis times are approximately the same as for the simultaneous analysis, consideration must be given to the fact that if only one system is used, the analysis time will more than double since time will be spent changing the cation components with the anion components. If two systems are used the time will approximate the time required for the simultaneous separation, but with the simultaneous separation technique only one system is used thus any additional systems will be available for other work.

TABLE II

RETENTION TIMES FOR VARIOUS ANIONS AND CATIONS

Ion	Retention time (min)
Fluoride	2.7
Chloride	3.7
Nitrite	4.4
Bromide	6.8
Nitrate	7.2
Phosphate	8.3
Sulfite	9.8
Sulfate	11.2
Sodium	2.9
Potassium	5.0
Rubidium	8.7
Cesium	11.6

The retention times for various anionic and cationic species are given in Table II. Most species elute within 12 min using the system described here. Since there is no re-equilibration period or system modification to be made between injections, as many as five injections can be made in a 1-h period. The ammonium ion was not observed in this experimentation due to the pH involved in the eluent. The pH of 10.35 results in over 99.9% of the ammonium being in the form of ammonia which does not respond to conductivity detection. This will provide a means for the detection of sodium and potassium ions in the presence of a large excess of ammonium ions.

Using the Dionex Model 10 ion chromatograph did provide some problems when attempting to perform this work. The Model 10 is equipped with single piston pulsed pumps. These pumps cause severe pump noise in the system. Accordingly, many of the detection limits reported here (Table III) are pump noise limited rather than limited by detector stability or extent of conductivity change. It is assumed that the detection limits of the cations, the species most affected by the pump noise due to the close proximity of the conductivity detector to the pump, will be significantly lower if a pulseless pump is used. A small amount of band broadening may be ob-

TABLE III

DETECTION LIMITS FOR SELECTED IONS

Ion	Detection limit (mg/l)
Fluoride	0.4
Chloride	0.3
Bromide	0.1
Phosphate	1.2
Sulfate	1.1
Sodium	5
Potassium	5

TABLE IV

REPRODUCIBILITY FOR SIMULTANEOUS SYSTEM

Ion	Retention time (min)			Peak height (cm)		
	$\bar{X}$	Range	R.S.D. (%)	$\bar{X}$	Range	R.S.D. (%)
Sodium	2.9	2.8–3.0	3.2	7.8	7.5–8.1	2.5
Potassium	5.0	4.3–5.4	9.5	4.1	4.0–4.2	1.9
Fluoride	2.6	2.5–2.7	2.6	7.6	7.4–7.9	3.7
Phosphate	8.3	8.2–8.4	0.9	0.5	0.4–0.5	8.9

served. The loss of resolution is inconsequential when compared to the savings in time and equipment which result.

A standard solution was analyzed to ascertain the stability of the system as well as to determine the reproducibility. Table IV shows the results of the analysis of the same solution with injections every hour for an 8-h day. These results indicate that the system is quite stable and capable of precise work. The large R.S.D. (%) for the potassium ion can be explained by the fact that the potassium peak is a rather rounded peak making retention time measurements a little more difficult than for a sharp peak like fluoride. The large R.S.D. (%) for the phosphate ion peak is due to the small nature of the peak which was being measured and the increased uncertainty in accurately making small measurements.

ACKNOWLEDGEMENTS

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