Simultaneous analysis of anions and cations by single-column ion chromatography

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ABSTRACT

   A new technique for the simultaneous analysis of anions and cations is described. The technique involves the use of the existing single column ion chromatography equipment with the addition of a switching valve. An anion and a cation column are used as the separator column. Three eluents are developed to allow simultaneous separation of anions and monovalent cations or anions and divalent cations. A simultaneous analysis of anions such as fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate, and cations such as sodium, ammonium, potassium, rubidium, magnesium, calcium, and barium can be accomplished in approximately 20 to 30 min depending on the number of ions present in the sample. The detection limits for most ions are less than 500 μg/l.

INTRODUCTION

   Ion chromatography, as originally developed by Small *et al.* [1], has been used extensively in many laboratories for the determination of inorganic anions and cations. The majority of the anion and cation analyses have been performed using separate columns and eluents. Recently, the simultaneous analysis of both anions and cations has been explored. One technique uses a dual channel instrument with two different eluents, injectors, columns, and detectors [2]. A single injection, with dual columns and a single detector on a dual channel instrument, has also been used [3]. Another technique utilizes one injector, one eluent, several columns (anion, cation and an anion suppressor column) and two detectors connected in various configurations [4,5]. This enables the detectors to independently monitor the anions and cations as they elute from the respective columns.
   A single column approach for the simultaneous analysis of anions and cations has also been used. One technique uses a complexing agent as the eluent [6,7]. Using this method, metal ions are converted into anionic complexes and are separated along with the other inorganic anions on an anion separator column. Another technique uses a mixed bed ion-exchange column. Pietrzyk and Brown [8] used a column containing alumina and silica microparticles. At the eluent pH used, alumina provides anion-exchange sites and silica provides cation-exchange sites, thus allowing simultaneous separation of anions and cations. A mixed bed ion-exchange column contain-

ing polystyrene divinyl benzene resin with quaternary amine and sulfonic acid functionalities has also been used [9]. By using an eluent that contains both anion and cation eluting ions, the simultaneous separation of inorganic anions and cations can be performed with one injection, one pump, one column and one detector. The advantage of this approach is that the analysis can be accomplished using existing single-column ion chromatography (SCIC) systems without the need for additional equipment. However, experiments in our laboratory indicated that one major problem with this technique is the difficulty in manufacturing a reproducible column when a new batch of material is used. The ion-exchange capacity of the anion and cation exchangers varies from batch to batch. Therefore, the ratio of the anion to the cation exchanger has to be modified each time a new batch of material is used.

The technique presented here uses one injection, one pump, an anion column, a cation column, a switching valve, and a conductivity detector. The configuration of the system is shown in Fig. 1. By changing the eluent composition, the simultaneous analysis of anions and monovalent cation, or anions and divalent cations can be achieved.

EXPERIMENTAL

The ion chromatograph used in this work was an Alltech/Wescan metal-free ion chromatography system (Alltech, Deerfield, IL, USA). It consists of an Alltech
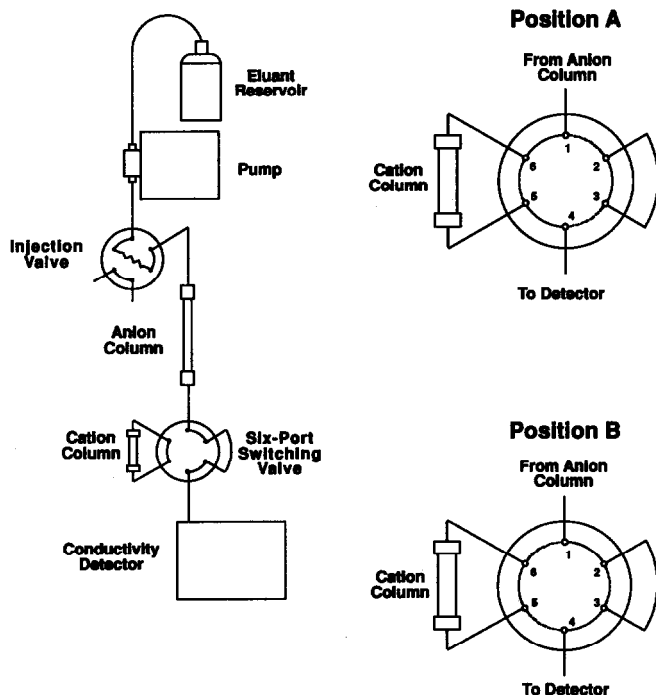

Fig. 1. Instrument configuration for the simultaneous analysis of anions and cations. At position A, the eluent is passed through both anion and cation columns. At position B, the cation column is bypassed.

Model 325 metal-free pump, a Rheodyne 9125 metal-free injection valve(100-μl sample loop), a Alltech Model 320 conductivity detector, and a Timberline column heater. The temperature of the column heater and the conductivity detector cell was maintained at 35°C. A Rheodyne Model 9000 metal-free switching valve combined with the Alltech universal valve actuator was used to direct the eluent flow through or around the cation separator column. All data were recorded on a Spectra-Physics (Santa Clara, CA, USA) SP 4400 Chromjet integrator. The Alltech Universal Anion Column (150 × 4.6 mm I.D.) and the Wescan Cation/R Column (100 × 3.2 mm I.D.) were used as the separator columns.

Reagents

Only reagent-grade chemicals (Aldrich, Milwaukee, WI, USA) were used for standard and eluent preparations.

Three different eluents were used: lithium *p*-hydroxybenzoate, lithium hydrogenphthalate, and lithium hydrogenphthalate–ethylenediamine combination. Stock solutions of *p*-hydroxybenzoic acid (pHBA) (100 mM) and phthalic acid (100 mM) were prepared by dissolving the ACS-reagent-grade chemicals in methanol. Lithium *p*-hydroxybenzoate eluent was prepared by diluting the stock solution to 5 mM and adjusting to pH 7.8 with lithium hydroxide. Lithium hydrogenphthalate eluent was prepared by diluting the stock solution to 4 mM and adjusting to pH 4.5 with lithium hydroxide. Lithium hydrogenphthalate–ethylenediamine eluent was prepared by diluting the stock solution to 4 mM, adding concentrated solution of ethylenediamine to make 1 mM ethylenediamine solution, and adjusting the pH to 4.5 with lithium hydroxide.

Procedure

Fig. 1 shows the system configuration. This technique involves three steps. Step 1, at position A where the eluent is passed through both anion and cation columns, a sample is injected. Since cations are not retained on the anion column, they will rapidly pass through the anion column. Step 2, once the cations reach the inlet of the cation column, the valve is switched to position B, where the cation column is bypassed, trapping the sample cations at the inlet of the cation column. All the anions are separated and detected by the conductivity detector. Step 3, when all the anions have eluted from the anion column, the valve is switched back to position A to separate the cations that are retained on the inlet of the cation column.

The timing of step 2 is very important. If the valve is switched too early, the cations may not reach the cation column. The cations that do not reach the cation column will not be separated and pass rapidly through the anion column in the void volume. If the timing is delayed too long, the cations may be separated on the cation column and eluted along with the other anions. This may cause peak overlapping (anion and cation) and inaccurate results. The exact time to switch the valve in step 2 can be determined easily by injecting an anion standard on an anion column (the cation column is bypassed, or both the cation column and the switching valve may be removed from the system). Since cations are not retained on the anion column, they will pass rapidly through the anion column in the column void volume along with other non-retained components. The first peak (solvent peak) on a chromatogram is attributed to these non-retained components. The retention time at which the solvent

peak returns to baseline is used as the exact time to switch the valve from position A to position B. The timing for step 3 is not as critical as step 2. The valve may be switched at any time after all the anions are eluted from the anion column. The retention time for the cations (and the whole analysis time) is dependent on the timing of step 3. If the valve is switched immediately after all the anions are eluted, the retention times for the cations (and the whole analysis time) will be shorter. If it is delayed, the retention times and the whole analysis time will be longer. The switching valve may be operated manually, or once the proper timing is determined, an electronically actuated switching valve and data system may be used.

RESULTS AND DISCUSSION

The goal of this work was to develop a simple method for simultaneous separation of anions and cations using existing SCIC equipment. Since using a mixed-bed column is unreliable due to the poor column to column reproducibility, separate anion and cation columns were used. A switching valve was added to the system to direct flow of the eluent.

Three eluents were developed to separate anions and monovalent cations, and anions and divalent cations. Fig. 2 shows the chromatograms of the anion and cation standards using these eluents. By using 5 mM lithium p-hydroxybenzoate, pH 7.8, fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate, sodium and potassium are separated and detected simultaneously. The valve is switched from position A to position B at 1 min 50 s and switched back to position A after all the anions are eluted from the column. p-Hydroxybenzoate was chosen as the eluent for anions because it is one of the most useful eluents in SCIC. It has lower equivalent conductance than most inorganic anions and is capable of eluting both monovalent and divalent anions in one run. Lithium was chosen as the cation eluent because its selectivity for the resin is close to that of sodium, ammonium and potassium. Also, lithium is not commonly found in most samples. Due to the pH of the eluent, ammonia exist in the molecular (neutral) form and was not retained on the cation column or detected by the conduc-
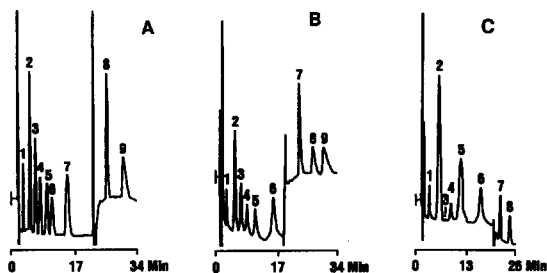

Fig. 2. Chromatograms of standard ions using various eluents. (A) 5 mM lithium p-hydroxybenzoate, pH 7.8; peaks: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate; 6 = phosphate; 7 = sulfate; 8 = sodium; 9 = potassium. (B) 4 mM lithium hydrogenphthalate, pH 4.5; peaks: 1–5 as in (A); 6 = sulfate; 7 = sodium; 8 = ammonium; 9 = potassium. (C) 4 mM lithium hydrogenphthalate–1 mM ethylenediamine, pH 4.5; peaks: 1–5 as in (A); 6 = sulfate; 7 = magnesium; 8 = calcium. Column: Alltech Universal Anion Column (150 × 4.6 mm I.D.) and Wescan Cation/R column (100 × 3.2 mm I.D.). Eluent flow-rate: 1.0 ml/min. Detector: conductivity.

tivity detector. Since ammonium is not detected, it is possible to detect sodium and potassium ions in the presence of high concentrations of ammonium.

In order to determine ammonium simultaneously with the anions, another eluent, 4 mM lithium hydrogenphthalate, pH 4.5 was developed. At pH 4.5, all the ammonia present is in the ammonium form, with the necessary charge for retention on the cation column and detection by the conductivity detector. Using this eluent, fluoride, chloride, nitrite, bromide, nitrate, sulfate, sodium, ammonium and potassium can be analyzed simultaneously, as shown in Fig. 2. The valve is switched from position A to position B at 2 min 10 s and switched back to position A after all the anions are eluted from the anion column. Like pHBA, phthalate was chosen because of its low equivalent conductance and is capable of eluting both monovalent and divalent anions in one run. Since the pH of the eluent is low, phosphate is eluted in the column void volume (solvent peak).

Since lithium is a monovalent cation, it is capable of eluting monovalent cations only at the concentration used in these eluents. To analyze anions and divalent cations, a lithium hydrogenphthalate–ethylenediamine combination was developed. Ethylenediamine was chosen as the eluent for cations because it is a commonly used eluent for separating divalent cations in SCIC [10]. Phthalate is the eluent for anions. Lithium hydroxide was added to bring the pH of the eluent to 4.5 since phthalic acid, pH 4.5 is the commonly used eluent for separating anions on the anion column used for this study. Since the equivalent conductance for magnesium and calcium are lower than the equivalent conductance of ethylenediamine, the peaks are detected as negative peaks (decrease in conductance). The polarity of the detector is reversed after the valve is switched in step 3 to make the magnesium and calcium peaks positive. By using this eluent, fluoride, chloride, nitrite, bromide, nitrate, sulfate, magnesium and calcium can be analyzed simultaneously as shown in Fig. 2C. The valve is switched from position A to position B at 2.00 min and is switched back to position A after all the anions are eluted from the anion column. At the same time, the polarity of the detector is reversed.

The position of the anion and cation columns may be reversed. As shown in Fig. 3, the cations are eluted first if the cation column is placed before the anion column. In this analysis, the valve is switched from position A to position B at 1 min 30 s.

Fig. 3. Chromatogram of standard ions using lithium p-hydroxybenzoate after the position of the anion and cation columns is reversed. Other chromatographic conditions are shown in Fig. 2. Peaks: 1 = sodium; 2 = potassium; 3 = fluoride; 4 = chloride; 5 = nitrite; 6 = bromide; 7 = nitrate; 8 = phosphate; 9 = sulfate.
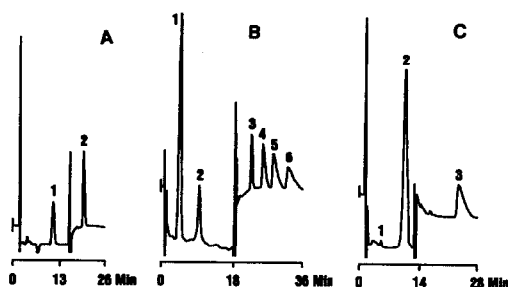
Fig. 4. Simultaneous separations of anions and cations. (A) Pharmaceutical pentapeptide sample using lithium *p*-hydroxybenzoate eluent; peaks: 1 = phosphate; 2 = sodium. (B) Working standard containing rubidium ion using lithium hydrogen phthalate eluent; peaks: 1 = chloride; 2 = nitrate; 3 = sodium; 4 = ammonium; 5 = potassium; 6 = rubidium. (C) Barium nitrate solution using lithium hydrogenphthalate–ethylenediamine eluent; peaks: 1 = chloride; 2 = nitrate; 3 = barium. Other chromatographic conditions are shown in Fig. 2.

Fig. 4 shows the separation of a pharmaceutical sample (pentapeptide) and standard solutions containing additional ions. In addition to the common inorganic anions and cations, the determination of rubidium and barium are also possible as shown in Fig. 4B and C, respectively.

A slight baseline shift occurs when the cation column is switched in and out of the flow data. This baseline shift may be due to differences in the distribution coefficient for the eluent components on the anion and cation stationary phases [11]. When the cation column is bypassed, an ion-exchange equilibrium is established between the anion driving ion (*p*-hydroxybenzoate or phthalate) and the anion exchanger. When the valve is switched, a second equilibrium is established between the cation driving ion (lithium and/or ethylenediamine) and the cation exchanger, thus, a baseline shift results. However, this shift does not adversely effect the linearity or precision of this method. Linear regression analyses and simple correlation coefficients of the calibration plots of peak area against ionic concentration for sodium nitrate using lithium hydrogen phthalate eluent are listed in Table I. These results are comparable to the well known analysis of anions and cations using separate columns and eluents.

A standard solution containing various anions and cations was analyzed to determine the reproducibility of the method using one of the eluents developed. Table

TABLE I

LINEAR REGRESSION ANALYSES AND SIMPLE CORRELATION COEFFICIENTS OF THE SODIUM NITRATE CALIBRATION PLOTS

Lithium hydrogenphthalate was used as eluent.

Ions	Regression equation[a]	Correlation coefficient (r)
Nitrate	$y = -0.024 + 0.011C_{Nitrate}$	0.998
Sodium	$y = -0.005 + 0.010 C_{Sodium}$	0.999

[a] y represents the peak area and C represents the concentration of ions (ppm).

TABLE II

REPRODUCIBILITY OF THE SIMULTANEOUS SYSTEM USING LITHIUM HYDROGEN-
PHOSPHATE ELUENT

Ions	Concentration (ppm)	R.S.D. (%)[a]
Fluoride	10	2.27
Chloride	20	0.76
Nitrite	20	1.58
Bromide	20	1.46
Nitrate	20	0.89
Sulfate	30	1.24
Sodium	45	0.38
Ammonium	5	1.16
Potassium	19	2.00

[a] Relative standard deviation, $n = 9$.

II lists the relative standard deviations (R.S.D.) (%) for nine replicate injections using lithium hydrogenphthalate eluent. The R.S.D. ranged from 0.38 to 2.27%. This is comparable to SCIC analysis of anions and cations using separate columns and eluents.

The detection limits for various ions (expressed as minimum detectable concentration) with the three eluents developed in this study are shown in Table III. The numbers were obtained based on a 100 μl injection volume and were calculated as a threefold signal-to-noise ratio at the baseline ($S/N = 3$). The detection limits for most ions are less than 0.5 ppm.

Since the valve can be switched from position B back to position A immediately after all the anions are eluted from the anion column, this technique allows the analyst to minimize the run time depending on the nature of the sample. For example, if the sample contains only chloride and sodium, the valve may be switched from

TABLE III

DETECTION LIMITS WITH VARIOUS ELUENTS

Ions	Lithium p-hydroxybenzoate (ppm)	Lithium hydrogenphthalate (ppm)	Lithium hydrogenphthalate–ethylenediamine (ppm)
Fluoride	0.15	0.12	0.17
Chloride	0.12	0.17	0.16
Nitrite	0.14	0.15	0.16
Bromide	0.43	0.40	0.54
Nitrate	0.40	0.40	0.41
Phosphate	1.50	–	–
Sulfate	0.67	0.96	1.04
Sodium	0.38	0.25	–
Ammonium	–	0.12	–
Potassium	0.40	0.36	–
Magnesium	–	–	0.13
Calcium	–	–	0.30

position B to position A after the chloride peak and the total run time will be reduced from 25 min to approximately 10 min.

The main area of application of this technique will be the analysis of water samples [rain water, tap water, ground water, well water, and seawater (brine)], pharmaceutical samples, food products, and any other matrix where information on the anionic and cationic fractions of the sample are required. Instead of performing two chromatographic analyses using two different eluents, this technique offers a simpler and faster method for the simultaneous determination of anions and cations.

CONCLUSIONS

The system described here simplifies the simultaneous determination of anions and cations, requiring only conventional IC equipment with the addition of a switching valve. Various ions can be determined in 20 to 30 minutes depending on the number of ions present in the sample. Using lithium p-hydroxybenzoate eluent, fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate, sodium and potassium can be analyzed simultaneously. Since ammonium is not detected, it is also possible to detect sodium and potassium ions in the presence of high concentrations of ammonium. Fluoride, chloride, nitrite, bromide, nitrate, sulfate, sodium, ammonium and potassium can be analyzed using lithium hydrogen phthalate eluent. Lithium hydrogenphthalate–ethylenediamine eluent allows for the determination of anions (fluoride, chloride, nitrite, bromide, nitrate and sulfate) and divalent cations (magnesium, calcium and barium). This technique allows the analyst to minimize the run time depending on the nature of the sample.

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