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Dual-column techniques for the simultaneous analysis of anions and cations

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ABSTRACT

A dual-column technique for the simultaneous analysis of anions and cations is described. The technique involves the use of the conventional ion chromatography equipment with the addition of a switching valve. Two columns (an anion and a cation column) are used as the separator columns. By using an eluent that contains both anion and cation driving ions, the simultaneous separation of anions and cations can be accomplished with one injection, one pump, and one detector. Two eluents are developed for the simultaneous analysis of anions, monovalent cations and divalent cations. The detection limits for most ions are below 400 μg/l.

INTRODUCTION

Ion chromatographic (IC) analysis of anions and cations are performed mostly independent of one another using separate columns, eluents and detectors. For samples that require the determination of both anions and cations, the use of separate methods tend to be expensive and time consuming. In order to simplify the analysis, several techniques for the simultaneous analysis of both anions and cations have been investigated. One technique uses a dual-channel instrument in which the anions and cations are determined via separate channels [1]. Using this approach, two separate pumps, eluents, columns and detectors are required. Another technique uses chemical derivatization procedures in which the cations are converted to anions and separated on the anion column, together with the common inorganic anions [2,3]. This approach requires only conventional IC equipment, however, it is limited to cations that can form anionic complexes with the eluent. Another technique uses a series of three columns and two detectors in order to perform the separation and detection [4,5]. This method uses a suppressor column to remove the cations from the system after they have been detected in the first detector and before the anions are detected in the second detector preventing peak overlap between the anions and cations. Another approach uses two columns connected in series followed by a differential conductivity detector [6]. This approach is simpler than the previous approaches, however, the ion-exchange capacities of the two columns and the ionic strength of the eluent must be carefully controlled to provide the appropriate retention times and to prevent peak overlapping between the anions and cations.

The use of a single ion-exchange column which exhibits both anion- and cation-exchange capacity has also been used. Pietrzyk and Brown [7] used a column containing alumina and silica microparticles. At an eluent pH of about 5, alumina acts as an anion exchanger and silica acts as a cation exchanger, thus allowing simultaneous separation of anions and cations. A mixed-bed ion-exchange column containing polystyrene–divinylbenzene resin with quaternary amine and sulfonic acid functionalities has also been used [8]. 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

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chromatography systems without the need for additional equipment. However, since the column is made by mixing two type of ion exchangers, column-to-column reproducibility is hard to achieve.

An improved method for the simultaneous analysis of anions such as fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate and cations such as sodium, ammonium, potassium, magnesium and calcium was developed [9]. This dual-column technique uses one injection valve, one pump, an anion column, a cation column, a switching valve and a conductivity detector. By changing the eluent composition, the simultaneous analysis of anions and monovalent cation, or anions and divalent cations can be achieved. This report extends the applications of the dual-column technique to allow simultaneous analysis of both monovalent, and divalent cations in one run along with the anions.

EXPERIMENTAL

Chromatography was performed on an Alltech (Deerfield, IL, USA) IC system which consists of a Model 325 metal-free pump, a Rheodyne 9125 metal-free injection valve (100-μl sample loop), a Model 320 conductivity detector and a Timberline (Boulder, Co, USA) 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. A Spectra-Physics (Santa Clara, CA, USA) SP 4400 Chromjet integrator was used to record all data. The Alltech Universal Anion Column (150 mm × 4.6 mm I.D., 100 mm × 4.6 mm I.D. and 50 mm × 4.6 mm I.D.) and the Alltech Universal Cation Column (100 mm × 4.6 mm I.D.) were used as the separator columns.

Reagents

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

Two eluents were used: phthalic acid and a mixture of phtalic acid and 1,2,4,5-benzenetetracarboxylic acid. Stock solution of phthalic acid (200 m*M*) was prepared by dissolving the ACS reagent-grade chemicals in methanol. This solution was diluted with deionized HPLC-grade water (Alltech) to make 5 m*M* phthalic acid eluent. Phthalic acid–benzenetetracarboxylic acid eluent was prepared by diluting the phthalic acid stock solution to 3 m*M* and adding 1,2,4,5-benzenetetracarboxylic acid to make 0.3 m*M* solution.

Procedure

Fig. 1 shows the system configuration. This technique consists of 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. At this position, 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

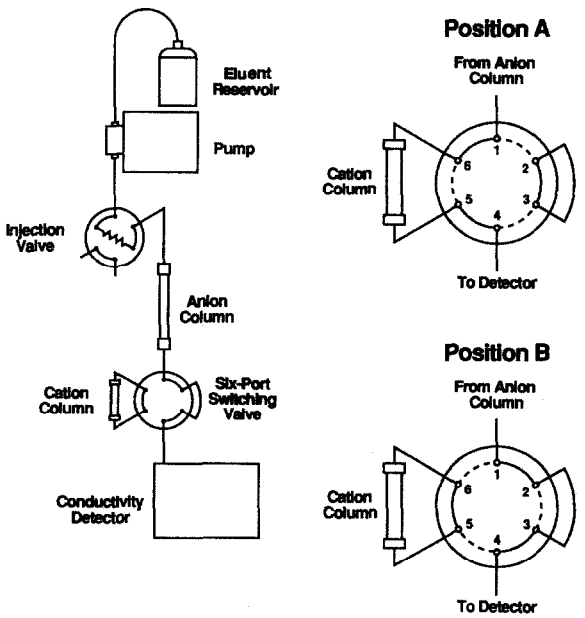

Fig. 1. Instrument configuration for the simultaneous analysis of anions and cations. At position A, the eluent is passed through both anion and cation columns. At position B, the cation column is bypassed.

A redirecting the eluent to separate the cations that are retained at 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 with the valve at position B (the cation column is bypassed). 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 total 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 total 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, automatically using an electronically actuated switching valve and data system.

RESULTS AND DISCUSSION

In the earlier works, three eluents were developed to separate anions and monovalent cations, or anions and divalent cations [9]. The simultaneous separation of both monovalent and divalent cations along with the anions could not be achieved using these eluents. The goal of this work was to develop a method for the simultaneous determination of anions, monovalent cations and divalent cations. The determination of both group I and group II cations is important in a variety of samples.

The two most important criteria when developing a simultaneous method for analyzing anions and cations are choosing the appropriate column and eluent. The column must be able to separate the species of interest. The eluent must be able to elute both the anions and the cations of interest. When a conductivity detector is used, the difference in the equivalent conductance between the eluent and the solutes must be as large as possible in order to observe the signals. The only column that is capable of separating both monovalent and divalent cations under isocratic condition is the silica-based polymer-coated stationary phase developed by Schomburg *et al.* [10]. The Alltech Universal Cation Column which is packed with similar stationary phase (silica-based column coated with polybutadiene–maleic acid copolymer) was used to separate the cations. Anions are separated on the Universal Anion Column. This column, which is packed with hydroxyethylmethacrylate-based anion exchanger, has been shown to be useful for the separation of anions using a wide variety of eluents [11].

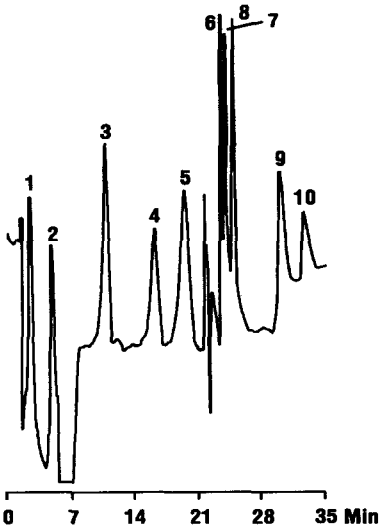

Fig. 2. Simultaneous analysis of anions, monovalent cations and divalent cations using 5 m*M* phthalic acid eluent. Column: Alltech Universal Anion Column (150 mm × 4.6 mm I.D.) and Alltech Universal Cation (100 mm × 4.6 mm I.D.). Eluent flowrate: 1.0 ml/min. Detector: conductivity, 1.0 μS full scale. Peaks: 1 = fluoride (10 ppm); 2 = phosphate (20 ppm); 3 = chloride (10 ppm); 4 = bromide (20 ppm); 5 = nitrate (20 ppm); 6 = sodium (6 ppm); 7 = ammonium (4 ppm); 8 = potassium (12 ppm); 9 = magnesium (3 ppm); 10 = calcium (5 ppm).

It has been reported that the retention and separation of monovalent cations on the polybutadiene–maleic acid copolymer-coated stationary phase is achieved through conventional cation-exchange mechanisms, while divalent cations are separated through coordination with maleic acids [10,12]. Effective eluents for the separation of cations on this stationary phase are organic acids such as citric, phthalic and salicylic, which are capable of forming complexes with calcium and magnesium [10]. A mixture of nitric acid and ethylenediaminetetraacetic acid has also been used [12]. Experiments in our laboratory showed that the isocratic separation of monovalent and divalent cations can also be accomplished using nitric acid, hydrochloric acid and trifluoroacetic acid. Therefore, complexing eluent is not required to achieve these separations. Since phthalic acid is the most common eluent used with the Universal Anion Column, phthalic acid was chosen as the eluent for the simultaneous anion/cation analysis in this study. Fig. 2 shows the chromatogram of the anion and cation standards using 5 m*M* phthalic acid as the eluent. Using this eluent, fluoride phosphate, chloride, bromide, nitrate, sodium, ammonium, potassium, magnesium and calcium are separated and detected simultaneously. Phthalate is the driving ion for the anions, hydronium ion is the driving ion for the monovalent cations and the divalent cations are retained and separated through the formation of coordination complexes with phthalic acid and maleic acid on the stationary phase. Since the equivalent conductance for the anions is higher than the equivalent conductance for phthalate ion, anions are detected as positive peaks. However, the equivalent conductance for the cations is lower than the equivalent conductance for the hydrogen ion (phthalic acids); thus, the cation peaks are detected as negative peaks (decrease in conductance). The polarity of the detector is reversed after the valve is switched back from position B to position A to make the cation peaks appear as positive peaks. At the pH of the eluent (approximately 2.8) used, phosphate is present as dihydrogenphosphate and eluted between fluoride and chloride. At this pH, phthalate is present mostly in -1 charge and not capable of eluting divalent anions such as sulfate. The separation of some real samples using this eluent are shown in Fig. 3. The apple and grape juices are diluted and filtered through the Anotop IC (Alltech) disposible syringe filters before injection. Cereal sample was extracted with deionized HPLC-grade water and filtered through a syringe filter before injection. As shown in Fig. 3A and B, acetate can also

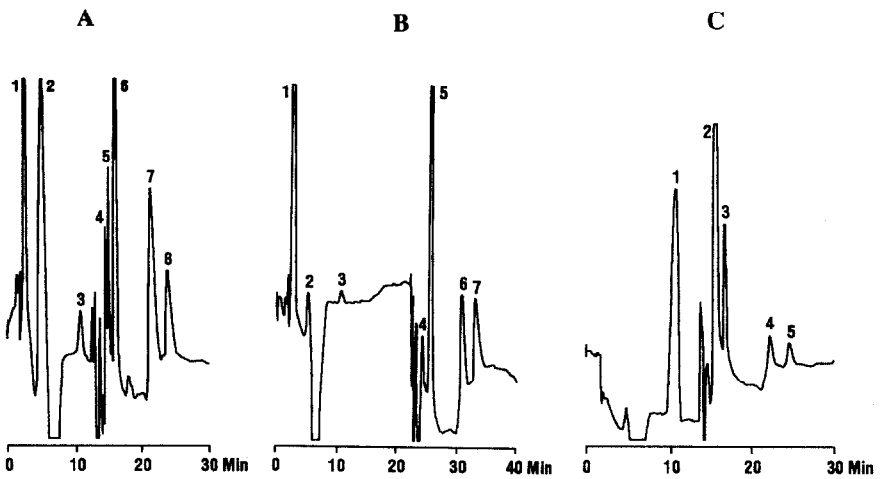

Fig. 3. Simultaneous separations of anions and cations in grape juice, apple juice and cereal using 5 m*M* phthalic acid eluent. Other chromatographic conditions as in Fig. 2. (A) Grape juice; peaks: 1 = fluoride; 2 = phosphate; 3 = chloride; 4 = sodium; 5 = ammonium; 6 = potassium; 7 = magnesium; 8 = calcium. (B) Apple juice; peaks: 1 = fluoride; 2 = phosphate; 3 = chloride; 4 = sodium; 5 = potassium; 6 = magnesium; 7 = calcium. (C) Cereal; peaks: 1 = chloride; 2 = sodium; 3 = potassium; 4 = magnesium; 5 = calcium.

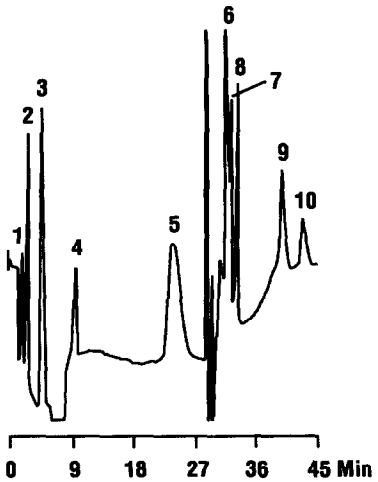

Fig. 4. Simultaneous analysis of anions, monovalent cations and divalent cations using 3 m*M* phthalic acid–0.3 m*M* benzenetetracarboxylic acid eluent. Column: Alltech Universal Anion Column (100 mm × 4.6 mm I.D.) and Alltech Universal Cation (100 mm × 4.6 mm I.D.). Eluent flow-rate: 1.0 ml/min. Detector: conductivity, 1.0 μS full scale. Peaks: 1 = fluoride; 2 = phosphate; 3 = chloride; 4 = nitrate; 5 = sulfate; 6 = sodium; 7 = ammonium; 8 = potassium; 9 = magnesium; 10 = calcium.

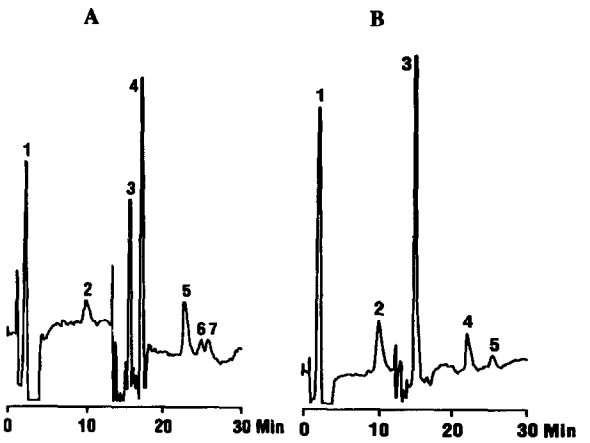

Fig. 5. Simultaneous separation of anions and cations in orange juice and bottled drinking water using 3 m*M* phthalic acid–0.3 m*M* benzenetetracarboxylic acid eluent. Column: Alltech Universal Anion Column (50 mm × 4.6 mm I.D.) and Alltech Universal Cation column (100 mm × 4.6 mm I.D.). Eluent flow-rate: 1.0 ml/min. Detector: conductivity, 1.0 μS full scale. (A) Orange juice; peaks: 1 = chloride; 2 = sulfate; 3 = sodium; 4 = potassium; 5 = magnesium; 6 = iron; 7 = calcium. (B) Bottled drinking water; peaks: 1 = chloride, 2 = sulfate; 3 = sodium; 4 = magnesium; 5 = calcium.

be analyzed in the same run. If fluoride is present in the sample, it will coelute with acetate. Phosphate and nitrite will also coelute under this condition. Other organic acids such as citric and maleic may also present in fruit juices. At the eluent pH used, they are not ionized and eluted in the column void volume. The total analysis time in Fig. 3B is approximately 10 min. longer than the total analysis time in Fig. 3A. This is an example of poor timing in step 3, where the valve was not switched immediately after all the anions are eluted. In Fig. 3C, since chloride is the only anion present in the sample, the valve was switched from position B back to position A immediately after the chloride is eluted. This reduces the total analysis time from 35 to 25 minutes.

In order to determine sulfate in the same run, another eluent was developed. Phthalic acid may be used at a higher pH in order to elute sulfate. However, at higher pH, the carboxyl functional groups on the cation column becomes more ionized and will strongly retain the monovalent and divalent cations. In order to be able to elute the cations, low-pH must be used. Benzenecarboxylic acids have been shown to be a useful eluent for separating anions in non-suppressed IC [13]. Tetraprotic acids such as 1,2,4,5-benzenetetracarboxylic acid can be effective eluents for divalent anions even at low pH values. Fig. 4 shows the separation of anions and cations using 3 m*M* phthalic acid–0.3 m*M* benzenetetracarboxylic acid as the eluent. Benzenetetracarboxylic acid is added to increase the strength of the eluent for eluting divalent anions. Using this eluent, fluoride, phosphate, chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium and calcium can be analyzed in the same run in approximately 45 min. When a smaller number of ions present in the sample, the total analysis time can be shorten by using a shorter column as shown in Fig. 5A and B. In Fig. 5, only chloride and sulfate are separated on the anion column. In addition to the cations mentioned earlier, iron(II) can also be analyzed in the same run. As with the 5 m*M* phthalic acid eluent, the polarity of the detector must be reversed after the valve is switched back from position B to position A to make the cation peaks positive.

A slight baseline shift occurs when the cation column is switched in and out of the flow stream. This baseline shift may be due to differences in the distri-

TABLE I

LINEAR REGRESSION ANALYSES AND SIMPLE CORRELATION COEFFICIENTS OF THE POTASSIUM NITRATE AND CALCIUM BROMIDE CALIBRATION PLOTS

y represents the peak area; c represents the concentration of ions.

Ions	Regression equation	Correlation coefficient (r)
Nitrate	$y = 0.39 + 0.08c_{\text{nitrate}}$	1.00
Potassium	$y = 0.25 + 0.10c_{\text{potassium}}$	1.00
Bromide	$y = -0.06 + 0.06c_{\text{bromide}}$	1.00
Calcium	$y = -0.03 + 0.20c_{\text{calcium}}$	1.00

bution coefficient for the eluent components on the anion and cation stationary phases [14]. When the cation column is bypassed, an ion-exchange equilibrium is established between the anion driving ion and the anion exchanger. When the valve is switched, a second equilibrium is established between the cation driving ion and the cation exchanger, thus, a baseline shift results. However, this shift does not adversely affect 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 potassium nitrate (0–100 ppm nitrate) and calcium bromide (0–100 ppm bromide) using 5 mM phthalic acid as the eluent are listed in Table I. These results are comparable to those obtained in normal anion and cation chromatography 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 II lists the relative standard deviations (R.S.D.) for seven replicate injections using 5 mM phthalic acid eluent. The R.S.D. ranged from 0.60 to 3.00%. This is, again, comparable to single-column IC analysis of anions and cations using separate columns and eluents.

TABLE II

REPRODUCIBILITY OF THE SIMULTANEOUS SYSTEM USING 5 mM PHTHALIC ACID ELUENT

Ions	Concentration (ppm)	R.S.D. (%) ($n=7$)
Fluoride	10	1.05
Chloride	10	2.90
Bromide	20	1.90
Nitrate	12	3.00
Potassium	19	1.30
Magnesium	3.2	2.02
Calcium	5.0	0.60

TABLE III

DETECTION LIMITS WITH 5 mM PHTHALIC ACID ELUENT

Ions	Detection limits (μg/l)
Fluoride	50
Phosphate	0.28
Chloride	300
Bromide	380
Nitrate	560
Potassium	20
Magnesium	40
Calcium	14

The detection limits for various ions (expressed as minimum detectable concentration) with 5 mM phthalic acid eluent 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. The detection limits for most ions are less than 0.4 mg/l.

CONCLUSIONS

The technique developed in this study is useful when the determination of both anionic and cationic fractions of the sample are required. Instead of performing two chromatographic analyses using two different eluents, this technique offers a simpler, cheaper, and faster method for the determination of anions and cations. Only conventional IC equipment with the addition of a switching valve is required. Using 5 mM phthalic acid eluent, fluoride, phosphate, chloride, bromide, nitrate, lithium, sodium, ammonium, potassium, magnesium and calcium can be analyzed simultaneously. The 3 mM phthalic acid–0.3 mM benzenetetracarboxylic acid eluent allows for the determination of fluoride, phosphate, chloride, nitrate, sulfate, lithium, sodium, ammonium, potassium, magnesium, iron and calcium. One major advantage of this method is that it allows the analyst to minimize the run time depending on the nature of the sample.

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