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Note

Non-suppressed determination of cations and anions using a differential conductivity detector

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The analysis of anions and cations in one injection has been an area of recent active research interest. The original work in this area converted the cations into anion complexes and these complexes were then detected along with the anions[1]. Since this original paper was published, two alternative techniques have been developed which do not require conversion of the cations into anion complexes prior to detection. One of these techniques uses a series of three columns and two detectors in order to perform the separation and detection[2–4]. 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. The second method relies on indirect photometric detection principles to accomplish the detection[5]. This method uses indirect photometry at two different wavelengths to distinguish the cations from the anions in a manner that results in detector-assisted separation and discrimination. The method described in this report uses two columns in series followed by a differential conductivity detector to affect the separation and detection of the cations and anions in the sample. The advantages of this system over the previous systems include a simplified flow schematic and direct detection of the ions of interest.

EXPERIMENTAL

Equipment
       The equipment used in this research and the flow schematic are given in Table I and Fig. 1, respectively. The following modifications were made to the Tracor 965 photoconductivity detector for this particular application. The Tracor 965 photoconductivity detector is a differential measurement detector and as such has a stream splitter immediately preceeding the reaction coil and the detector. This stream splitter was removed and placed in line between the pump and the injection valve. As a result of placing of the stream splitter in this position, one eluent path becomes the sample line and the other eluent path becomes a reference line. It is important to place a dummy column or some other type of flow restriction in the reference line in order to equalize back pressure in the two paths and thus equalize eluent flow. The high-intensity UV lamp in the Tracor 965 photoconductivity detector was not used during this research.

TABLE I

DESCRIPTION OF COMPONENTS

Pump:	Tracor Model 955
Eluent:	0.004 M lithium hydrogen phthalate
Flow-rate:	3.0 ml/min
Splitter:	30% of flow to dummy column and 70% of flow to injection valve
Injection volume:	0.020 ml
Cation column:	Wescan 269-024 cation column
Anion column:	Vydac 302 IC4.6 anion column
Dummy column:	Vydac 302 IC4.6 anion column
Detector:	Tracor 965 photoconductivity detector, used as a differential conductivity detector.
Recorder:	Linear Instruments 1200 chart recorder.

Chemicals

All solutions were prepared using distilled–deionized water. All reagents and standards were prepared using reagent-grade chemicals.

The lithium hydrogen phthalate eluent was prepared from equimolar amounts of lithium hydroxide and phthalic acid. The solution was either allowed to stand overnight or heated gently to provide complete reaction of the slightly soluble phthalic acid. Usually a 10 mM stock solution of lithium hydrogen phthalate was prepared and was diluted to the working concentration as needed.
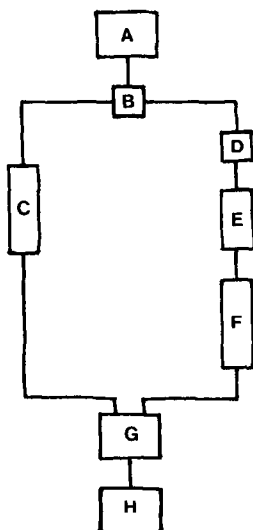

Fig. 1. Flow schematic of the ion chromatographic system used in this research. The letters correspond to the following parts of the system (see Table I for complete description): A = pump; B = stream splitter; C = dummy column; D = injection valve; E = cation column; F = anion column; G = conductivity detector; H = chart recorder.

Procedure

The normal procedure for the use of high-performance liquid chromatography equipment was followed at all times and all equipment was used as designed with the exception of the detector modifications outlined above.

RESULTS AND DISCUSSION

One of the key aspects necessary to obtain maximum sensitivity with this technique is the use of the differential measurement conductivity detector. In this manner, the relatively high conductance of the eluent can be subtracted in the detector so that only the analyte ions are actually observed at the detector output. The nature of the signal and the type of resolution which can be expected are illustrated in Fig. 2. This chromatogram shows the separation of a three-component mixture of ammonium chloride, potassium nitrate and sodium sulfate.
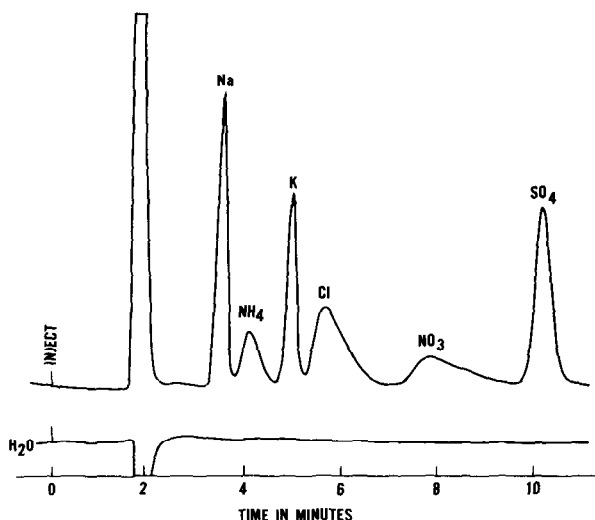

Fig. 2. Separation of a mixture of ammonium chloride, potassium nitrate and sodium sulfate. Peaks: peak at 2 min = system peak; Na = sodium ion (15 ppm); NH_4 = ammonium ion (15 ppm); K = potassium ion (15 ppm); Cl = chloride ion (25 ppm); NO_3 = nitrate ion (25 ppm); SO_4 = sulfate ion (25 ppm).

The selection of the eluent used in this analysis was based upon the following criteria. First, the eluent must be able to be prepared easily and with minimal chance for contamination from extraneous ions which might alter the eluent strength or provide interference peaks. Second, the lithium ion was chosen as the cationic component of the eluent due to the lack of analytical interest in the ion chromatographic measurement of lithium, especially when compared to sodium, potassium and ammonium. Other cationic components are possible, but since lithium is more weakly retained than the main species of interest, it will provide the best resolution. Third, the phthalate ion was selected as the anionic component of the eluent due to the

widespread use of various phthalate species in anionic ion chromatography. Other anion components are possible, such as benzoic acid, and may prove to be advantageous in other situations.

Detection limits for this system are equivalent to those obtained in normal cation or anion chromatography using a non-suppressed system. Solutions with concentrations below 1 part-per-million (ppm) can be routinely analyzed provided proper laboratory skill and precautions are employed. The linearity of this technique is, again, typical of that for single-column ion chromatography. Solutions of two to three orders of magnitude differences in concentration can be quantified using a linear calibration curve. The upper limit on the linear operating range is governed by the capacity of the column and resulting overloading of the column when solutions of relatively high concentrations are used (such as those approaching 100 ppm). The lower limit on the linear operating range is governed by the signal-to-noise ratio as well as the sharpness of the peak and the limiting ionic conductance of the ions. For species such as sulfate which have a relatively broad peak shape, the lower limit is slightly below 1 ppm. For species such as sodium with a sharp peak and relatively high equivalent conductance, the lower limit for the linear operating range is approximately 0.1 ppm. This technique is reproducible and provides good precision in the analysis. Typical precision is approximately 1% relative standard deviation (R.S.D.) for the repetitive injection of multiple ion-containing sample. Day-to-day precision and multiple-operator precision are close to 2% R.S.D.

Several potential variations of this technique, based upon the use of the serial columns and a single detector, can be designed. One of the more obvious is to heat one of the columns in order to increase the elution speed of either the cations of the anions. This is the only effective method for altering the elution characteristics of the cations without significantly affecting the anions or *vice versa*.

The main advantages of this system are listed below:

(1) Only commercially available components are used.

(2) The system uses only one detector and relies on chemical separation of the species and not on detector differentiation of the cationic and anionic species, and

(3) The analysis is rapid, needing only 15 min to completely separate a six-component mixture.

The potential uses of a system such as the one described here would seem to be those systems where a large number of repetitive samples were analyzed and where a constant, but not excessive, number of ions are to be determined.

ACKNOWLEDGEMENT

REFERENCES

1 M. Yamamoto, H. Yamamoto and Y. Yamamoto, *Anal. Chem.*, 56 (1984) 832.
2 V. K. Jones and J. G. Tarter, *J. Chromatogr.*, 312 (1984) 456.
3 V. K. Jones and J. G. Tarter, *Am. Lab.*, 17, No. 7 (1985) 48.
4 V. K. Jones, S. F. Frost and J. G. Tarter, *J. Chromatogr. Sci.*, 23 (1985) 442.
5 Z. Iskandarani and T. E. Miller, Jr., *Anal. Chem.*, 57 (1985) 1591.