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Note

High-performance liquid chromatography of inorganic and organic anions using ultraviolet detection and an amino column

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Silica-based high performance liquid chromatography (HPLC) has been used only sparingly for routine analysis of inorganic anions. With the advent of variable-wavelength detectors, those anions which absorb below 254 nm can be analyzed.

Ion-exchange techniques have been used on inorganic systems[1] utilizing a conductivity detector after removing the background conductance of the eluent; however, chromatography obtained with polymer-based ion exchangers is not normally as efficient as that obtained on micro-particulate supports[2]. Richards[3] showed that organic anions could be separated on cation-exchange resins by ion exclusion.

Inorganic anions have been determined on reversed-phase systems after derivatization to organic species[4]. Using ion-pair formation, inorganic anions have been separated on a cyano column[5]. Anions were determined using tetrabutylammonium hydroxide as an ion-pairing reagent on a reversed-phase column[6]. Nitrate and bromide were determined in foodstuffs using an amino column[7]. The purpose of the present work is to expand the use of an amino column to the analysis of various organic and inorganic anions.

EXPERIMENTAL

Chemicals

Inorganic chemicals used were reagent grade available from J. T. Baker (Philipsburg, NJ, U.S.A.) All organic acids were of technical grade or better. Water used to prepare eluents was deionized and filtered through a 0.45 μm membrane filter.

HPLC conditions

The liquid chromatograph used consisted of an Altex Model 100A pump, a Rheodyne Model 7010 injection valve equipped with a 20-μl loop, a LC-55 (Perkin Elmer) variable-wavelength detector and a Sargent Model SRG recorder.

The column used throughout this work was a 250 × 4.6 mm I.D. Zorbax® NH_2 (DuPont Instruments, Wilmington, DE, U.S.A.). The eluent consisted of 0.03 *M* H_3PO_4 (J. T. Baker) adjusted to pH 3.2 with NaOH. Flow-rate was 2.0 ml/min. Detection was by UV at 205 nm for all chromatograms except Fig. 4, which was monitored at 214 nm. Detector sensitivity was 0.1 a.u.f.s. Column pressure was 1500 p.s.i. and operating temperature was 25°C.

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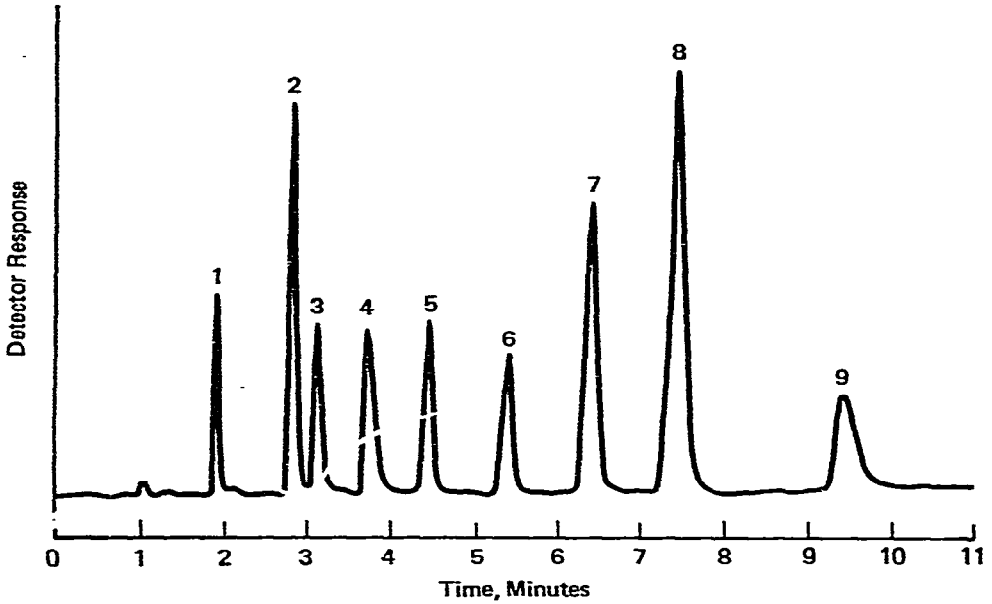

Fig. 1. Separation of acetate (1), acrylate (2), glycolate (3), formate (4), nitrite (5), bromide (6), nitrate (7), iodate (8) and dichloroacetate (9). Columns, Zorbax NH_2 (250 × 4.6 mm I.D.); mobile phases, 0.03 *M* H_3PO_4 adjusted to pH 3.2 with NaOH; flow-rate, 2.0 ml/min; temperatures, 25°C; detection, UV at 205 nm and 0.1 a.u.f.s.; pressure, 1500 p.s.i. Injected sample was prepared in water to give concentrations of 25–100 μg/ml.

TABLE I

RETENTION TIMES AND DETECTION LIMITS OF INORGANIC AND ORGANIC ANIONS

Columns, Zorbax NH_2, eluent, 0.03 *M* H_3PO_4, pH 3.2, at 2.0 ml/min. The calculations were performed using chromatograms obtained at a 5-mV full scale setting.

Anion	*Retention time (min)*	*Calculated detection limit* (μg/ml)*
Acetate	1.9	15
Acrylate	2.8	2
Glycolate	3.1	18
Formate	3.7	18
Nitrite	4.5	0.4
Bromide	5.5	0.5
Nitrate	6.4	0.3
Iodate	7.4	1.0
Dichloroacetate	9.4	16
Iodide	5.5	0.5
Propionate	1.9	16
Bromate	6.2	3
Trichloroacetate	11.6	20
Thiocyanate	3.6	–

* Calculated as three times baseline peak-to-peak random noise level.

RESULTS AND DISCUSSION

An example of the separations obtained is shown in Fig. 1. The estimated detection limits, together with the observed retention times, are listed in Table I.

The mechanism of separation is weak base ion exchange. Thus, changes in pH of the eluent dramatically affect retention times, because of varying degrees of pro-

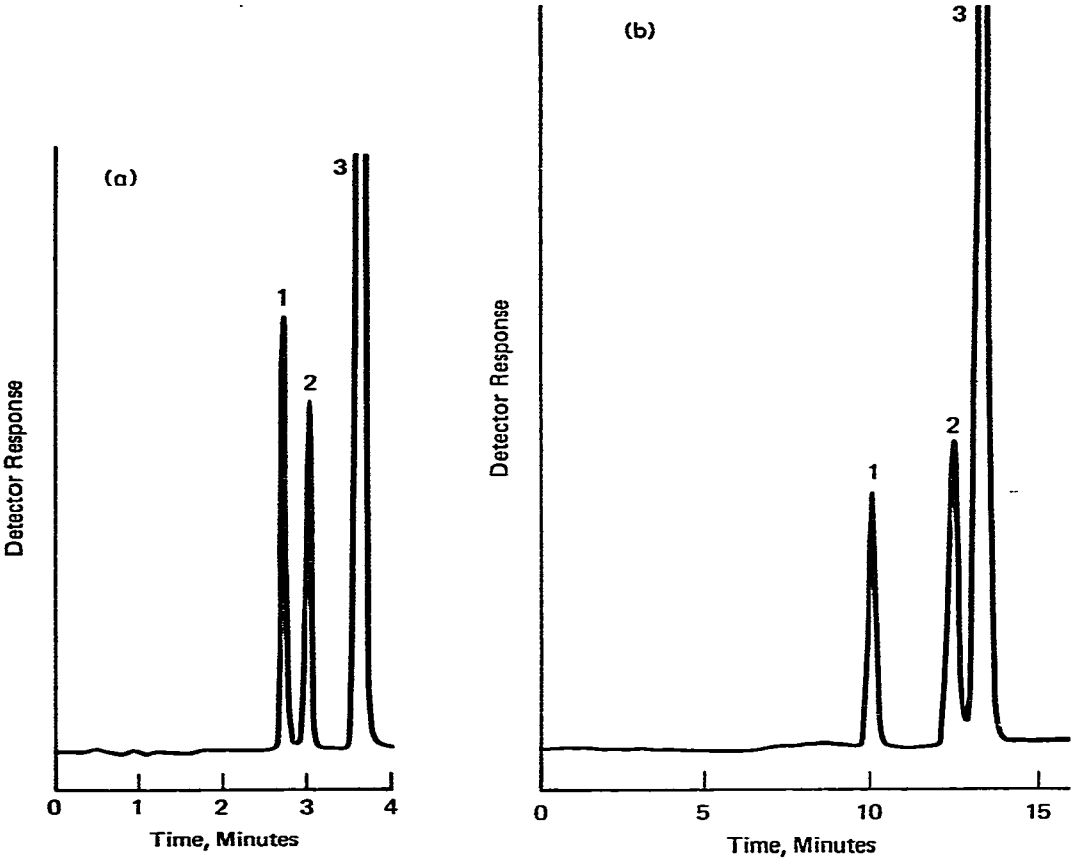

Fig. 2. (a), Separation of nitrite (1), bromide (2) and nitrate (3), showing the effect of pH on retention times. Mobile phase. 0.03 *M* H_3PO_4 adjusted to pH 5.0 with NaOH. Injected sample was prepared in water to give concentrations of 10 μg/ml for nitrite and bromide and 35 μg/ml for nitrate. Other conditions as in Fig. 1. (b), As (a), except mobile phase: 0.03 *M* H_3PO_4 adjusted to pH 2.8 with NaOH.

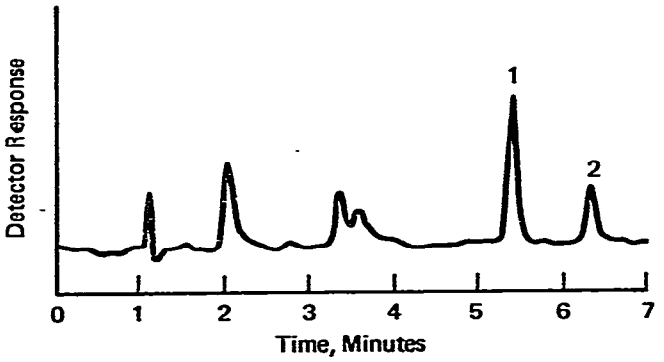

Fig. 3. Separation of bromide (1) and nitrate (2) in 95% sulfuric acid. Injected sample was prepared by diluting 1 ml in 1 ml of water. Other conditions as in Fig. 1.

tonation of the amino functionality (Fig. 2a and b). Column efficiencies obtained were in the range of 4000 theoretical plates, calculated at a capacity factor of 4.5 for bromide ions. The separation technique was applied to the analysis of real samples.

Fig. 3 illustrates the determination of bromide and nitrate in 95% sulfuric acid. The sample was diluted by placing 1.0 ml of acid in 1.0 ml of water prior to injection. Brine solution (20% NaCl) was analyzed for organic and inorganic ions by injecting the solution neat (Fig. 4).

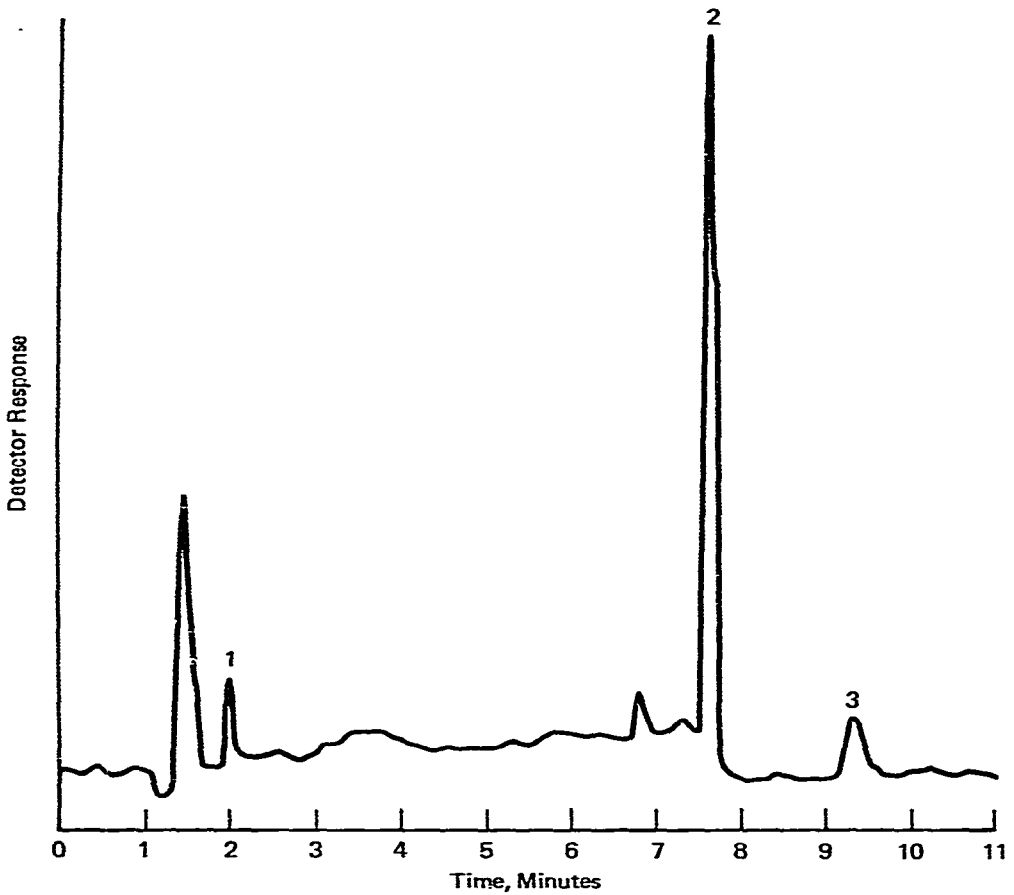

Fig. 4. Separation of anions in 20% NaCl solution. Sample was injected neat. Detection, UV at 214 nm and 0.1 a.u.f.s. Other conditions as in Fig. 1. Peaks: 1 = acetate; 2 = bromate; 3 = dichloroacetate.

CONCLUSIONS

A sensitive method for organic and inorganic ions that respond in the UV region has been expanded. It offers an advantage over previously available procedures in that separations can be obtained on commercially available columns, and samples high in UV-transparent ions, such as chloride and sulfate, can be analyzed with ease. The variety of ions separated is an indication of the broad applicability of this technique.

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REFERENCES

1 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.* 47 (1975) 1801.
2 L. R. Snyder and J. J. Kirkland, *Introduction To Modern Liquid Chromatography*, Wiley, New York, 2nd ed., 1979, p. 414.
3 M. J. Richards, *J. Chromatogr.*, 115 (1975) 259.
4 G. L. Wheeler and P. F. Lott, *Microchem. J.*, 19 (1974) 390.
5 R. N. Reeve, *J. Chromatogr.*, 177 (1979) 393.
6 I. Molnár, H. Knauer and D. Wilk, *J. Chromatogr.*, 201 (1980) 225.
7 U. Leuenberger, R. Gauch, K. Rieder and E. Baumgartner, *J. Chromatogr.*, 202 (1980) 461.