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HIGH-PERFORMANCE ION CHROMATOGRAPHY OF ANIONS

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SUMMARY

High-performance ion chromatography (HPIC) can be performed with a shorter column packed with TSK-GEL IEX-520 often at much higher efficiencies than with the other ion-exchange resins. HPIC is possible without a suppressor system, if specially designed, with a constant flow-rate pump, a temperature-controlled oven and a sensitive conductivity detector.

Polybasic acids were investigated as eluents for HPIC. The separation of chloride, bromide, iodide, thiocyanate and sulphate, of iodate, nitrite, bromate, chloride, chlorate, bromide and nitrate and of organic acids on the new column is demonstrated. The sensitivity permits the detection of as little as 10^{-10} mol of common anions and is comparable to conventional suppressed ion chromatography.

INTRODUCTION

Ion chromatography as developed by Small *et al.*[1] has allowed the rapid separation and quantitative determination of inorganic and organic anions. Despite of its many advantages, ion chromatography has some drawbacks. Organic supports are employed which are not pressure resistant and which swell in certain organic eluents. Because of the large particle size, column efficiencies are low and the broad peaks give a decreased sensitivity of detection. Only a few eluents can be used, and they must be capable of being converted into a non-conducting form in the suppressor system (*e.g.*, HCO_3^-).

Some investigations have been undertaken in an attempt to overcome these disadvantages. In particular, Gjerde and co-workers[2–4] demonstrated the use of anion chromatography with low-capacity organic anion exchangers and low-conductivity eluents.

The improved chromatographic performance demonstrated here is due essentially to three factors: (a) the use of a silica-based strong anion exchanger of small particle size (6 μm), which increases the column efficiency; (b) the use of shorter columns (50 mm), which leads to a reduction in the column void volume; and (c) the use of instrumentation with a constant flow-rate pump, a sensitive conductivity detector and a microcomputor that controls temperature, flow-rate, data analyses, etc.

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EXPERIMENTAL

Separator column

The anion exchanger used, developed by Toyo Soda (Tokyo, Japan) as TSK-GEL IEX-520, is a porous silica-based material. This material was prepared by binding quaternary aminoethyl groups on to the surface of hydrophilic packings for high-performance aqueous gel permeation chromatography (TSK-GEL G-2000SW; Toyo Soda)[5]. The packing material has a particle size of *ca.* 6 μm, a pore size of 100 Å and an ion-exchange capacity of 0.3 mequiv./g.

Apparatus

The chromatographic system (HLC-601; Toyo Soda), shown in Fig. 1 consists of the following parts:

(1) a computer-controlled pump to obtain a constant flow-rate;

(2) a sample injection valve making use of a sample loop and enabling liquid increments of 100 μl to be injected;

(3) a separator column, usually 50 × 4 mm I.D. packed with TSK-GEL IEX-520;

(4) a conductivity cell and a column arranged in a temperature-controlled oven;

(5) a conductivity detector (CM-8; Toyo Soda) with characteristic stability and high sensitivity;

(6) a microcomputer for aquisition and analyses of the outputs from the conductivity detector; and

(7) a mini-printer for outputting the analytical results.

Materials

Standard solutions of various anions (chloride, nitrate, sulphate, etc., as shown in the chromatograms) and eluent solutions were prepared from analytical-reagent grade reagents.

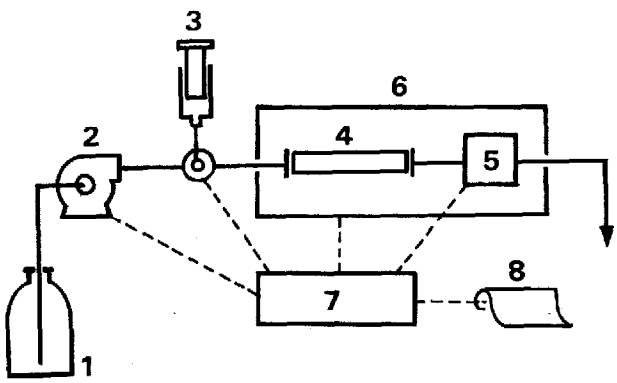

Fig. 1. Diagram of high-performance ion chromatograph. 1 = Reservoir; 2 = pump; 3 = injection valve; 4 = separator column; 5 = conductivity detector; 6 = air oven; 7 = microcomputer; 8 = printer.

RESULTS AND DISCUSSION

Column efficiency

The column used has approximately the same inner diameter as a conventional column (4 mm), but is shorter (only 50 mm long). The smaller particles result in much higher efficiencies per unit column length, thereby permitting greater efficiency to be achieved with the shorter column.

Fig. 2 shows the relationship between eluent flow-rate and height equivalent to a theoretical plate (HETP) for the TSK-GEL IEX-520 column at flow-rates ranging from 0.1 to 5.0 ml/min. The maximum plate number of 25,000 plates/m was obtained for the sulphate peak eluted at a flow-rate of 0.8 ml/min. Of course, in order to realize fully this higher performance the appropriate high-performance instrumentation must be used.

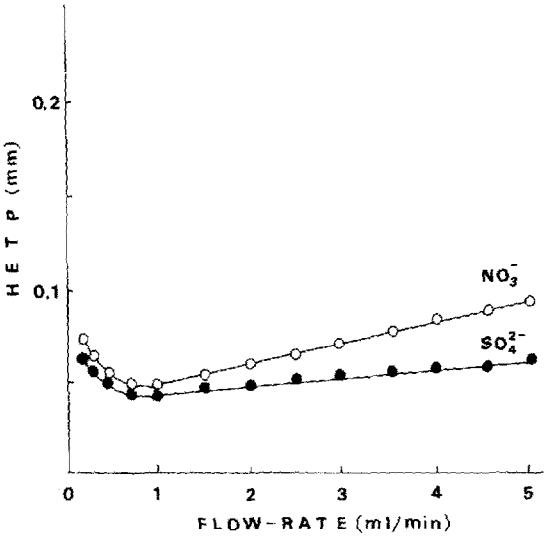

Fig. 2. Effect of flow-rate on the plate height for TSK-GEL IEX-520 column. Eluent, 1 m*M* potassium citrate, pH 5.2.

System performance

The ion chromatograph used was improved in terms of flow-rate precision, temperature control, detector sensitivity and automation capability. Several advantages result from the combined use of the shorter column and with the appropriate instrumentation: (1) significantly improved chromatographic performance (plates/metre); (2) improved baseline stability; (3) increased sensitivity; and (4) very high resolution.

A microcomputer-controlled pump is not simply a quick-return reciprocal pump, but high speed suction is controlled by a microcomputer, which, as shown in Fig. 3, made it possible to minimize the change in pumping pressure.

Another factor is the influence of temperature on conductivity. The temperature coefficient of conductivity is approximately 2%/°C which requires very close control of the eluent temperature if the background noise is to be minimized. The shorter

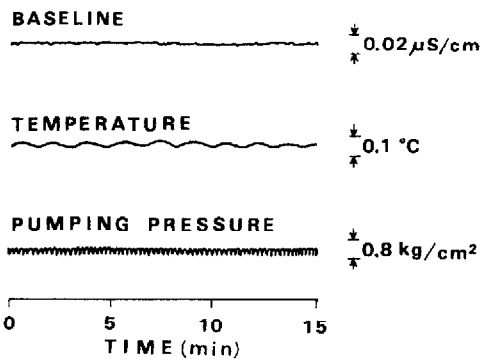

Fig. 3. Baseline stability with control of the temperature and pumping pressure. Eluent, 1 m*M* potassium phthalate, pH 6.5; flow-rate, 1.0 ml/min; oven temperature, 30°C.

column and the detector cell are enclosed in a small temperature-controlled oven to prevent temperature fluctuations.

In order to obtain direct conductivity detection without a suppressor system, a high-sensitivity conductivity detector was designed and tested. The measurement cell of this detector is composed of five ring electrodes: active electrodes, detection electrodes and a guard electrode. Two active electrodes and a guard electrode make it possible to reduce the polarization effect and external noise. With the appropriate conditions as shown in Fig. 3, the noise level of the conductivity is lower than 0.02 μS/cm. The baseline stability is considerably improved in comparison with the other commercial conductivity detectors. The sensitivity permits the detection of as little as 10^{-10} mol of common anions, such as chloride, nitrate and sulphate and seems to correspond to that of conventional ion chromatography.

Eluent

The eluents used in anion chromatography must have two properties: they must be capable of eluting the desired species and they must have a conductivity sufficiently low to permit conductivity detection. We found that salts of polybasic acids such as citric and tartaric acids were suitable developing reagents. In most instances, 10^{-3} *M* polybasic acid in the pH range 3.0–7.0 was found to be most useful. Table I lists the elution times for each of seven anions from 50 × 4 mm I.D. column packed with 6-μm TSK-GEL IEX-520 anion exchanger of exchange capacity 0.3 mequiv./g at a flow-rate of 1.2 ml/min. Elution times such as those given in Table I are useful in that they give the order in which the various anions are eluted and suggest which anions can be separated from each other.

The order of elution of iodide and thiocyanate ions is different to that reported for styrene-based anion exchangers. These two anions, in spite of their smaller hydration energies and polarities, elute relatively faster and are well resolved. It may be pointed out that matrix effects apart from the ion-exchange effect are exerted on a styrene-based anion exchanger.

Another factor that affects the order of elution of anions is the pH of the eluent. If the elution pH of a polybasic acid such as citric and tartaric acids is increased, the elution power increases substantially. If the pH of the eluent is made more acidic than the usual 5.0–7.0, the elution power is decreased because some of the eluent anions can be converted into a molecular acid.

TABLE I

ELUTION TIMES (min) OF ANIONS ON TSK-GEL IEX-520 COLUMN

Eluent concentration, 1 m*M*; pH, 6.5.

Anion	*Eluent*					
	Citrate	*Sulpho-benzoate*	*Phthalate*	*Tartrate*	*Salicylate*	*Benzoate**
Cl^-	1.5	1.5	1.5	1.5	3.1	5.5
NO_2^-	1.6	1.6	1.6	1.9	3.4	7.4
Br^-	1.8	1.8	1.9	2.3	4.1	9.5
NO_3^-	2.0	2.1	2.2	2.7	4.4	10.7
I^-	4.0	4.3	4.6	6.3	7.6	—**
SCN^-	5.8	7.0	7.5	11.5	10.5	—**
SO_4^{2-}	5.0	10.1	10.3	14.0	18.5	—**

* pH 5.5.
** Very long elution times.

Fig. 4 shows elution times for anions using citrate eluents of different pH. At pH 4.5 much of the eluent is in the monovalent form, whereas at pH 5.5 the divalent citrate anion predominates. The results indicate that much more rapid elution is obtained with the eluent containing a divalent anion. Some anions will exist in different protonated forms, depending on the eluent pH. Thus phosphate can be present as $H_2PO_4^-$ or HPO_4^- according to the pH.

Separation

Figs. 5–7 show some typical examples of the system using a TSK-GEL IEX-520 column. Fig. 5 shows a chromatogram of chloride, bromide, iodide, thiocyanate and sulphate anions with 1 m*M* citrate as the eluent. The total analysis times is 15 min. The analysis of thiocyanate ion in human saliva was performed successfully

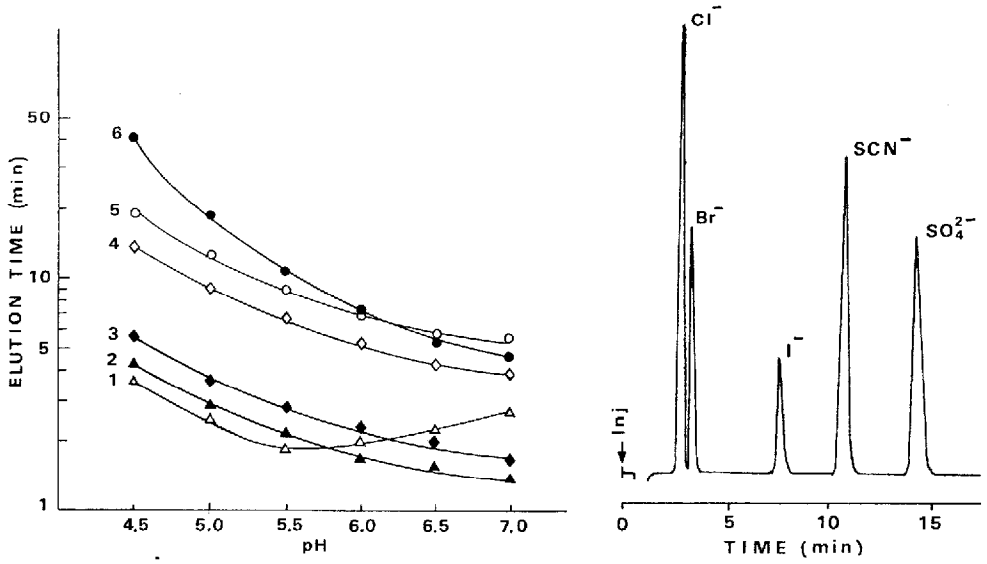

Fig. 4. Effect of eluent pH on elution time. Eluent, 1 m*M* potassium citrate; flow-rate, 1.2 ml/min; oven temperature, 30°C. Anions: 1 = phosphate; 2 = chloride; 3 = bromide; 4 = iodide; 5 = thiocyanate; 6 = sulphate.

Fig. 5. Chromatogram of 5 ppm of chloride, 10 ppm of bromide, 10 ppm of iodide, 10 ppm of thiocyanate and 10 ppm of sulphate. Eluent, 1 m*M* potassium citrate, pH 5.2; flow-rate, 1.2 ml/min; oven temperature, 30°C; injection volume, 100 μl.

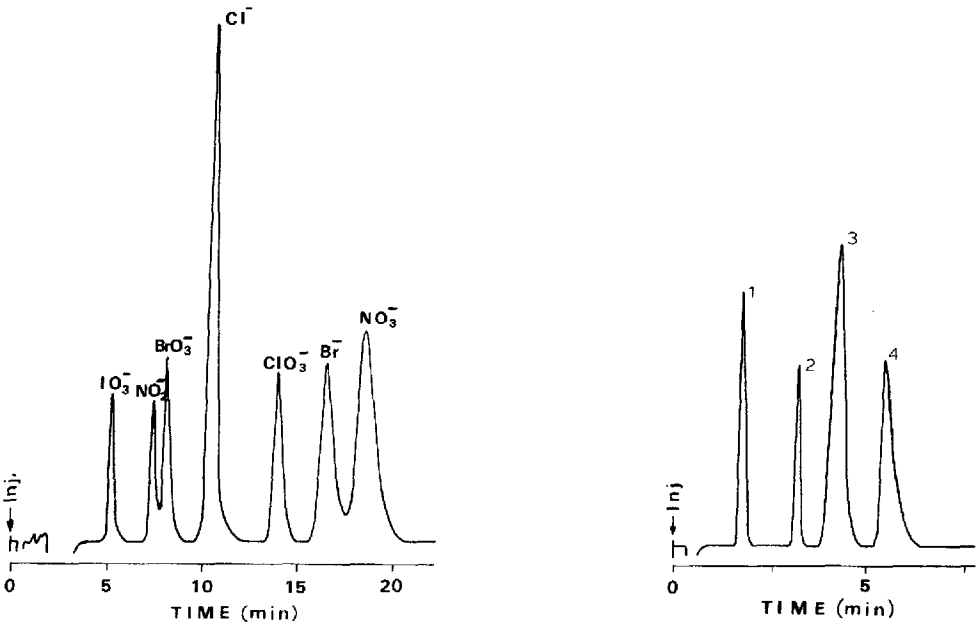

Fig. 6. Chromatogram of 10 ppm of iodate, 10 ppm of nitrite, 10 ppm of bromate, 10 ppm of chloride, 10 ppm of chlorate, 10 ppm of bromide and 10 ppm of nitrate. Eluent, 1 m*M* tartaric acid, pH 3.2; flow-rate, 1.5 ml/min; oven temperature, 30°C; injection volume: 100 μl.

Fig. 7. Chromatogram of 5 ppm of acetic (1), 5 ppm of lactic (2), 5 ppm of formic (3) and 5 ppm of benzoic (4) acids. Eluent, 1 m*M* potassium phthalate, pH 4.4; oven temperature, 30°C; injection volume, 100 μl.

under the conditions shown in Fig. 5. As a result of several experiments, we found that the saliva of a smoker has a thiocyanate concentration five times greater than that of a non-smoker.

Fig. 6 shows a chromatogram of iodate, nitrite, bromide, chloride, chlorate, bromide and nitrate anions. Tartaric acid as the eluent gives an excellent separation of easily eluted anions and the sensitivity is several times better than that which can be obtained with sodium and potassium tartrate. The detection limit of bromide ion is 0.2 μg/ml. Potassium bromate is used as an oxidizing agent and it has been suspected of being carcinogenic. The proposed technique has enabled the analysis of bromate in food and blood after appropriate pre-treatment[6].

Fig. 7 shows a chromatogram of acetic, lactic, formic and benzoic acids with phthalate as the eluent. These organic acids are very weakly retained on the TSK-GEL IEX-520 column, and therefore a 1 m*M* phthalate eluent adjusted to pH 4.4 should be used. With the proposed method, it proved feasible to determine acetic acid in fermentation alcohols by direct injection after filtering through a 0.22-μm filter.

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