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Note

Determination of organic acids in highly alkaline solutions

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Since its introduction by Small *et al.*[1], ion chromatography has been developed into a rapid and sensitive means for determining ions in aqueous solution, especially inorganic anions. Ion chromatography differs from conventional ion-exchange chromatography in that a low-capacity ion-exchange column, eluents of low concentration and conductivity detection are used. Although the method is effective for the determination of anions in relatively pure solutions such as river waters, complicated pre-treatment operations are necessary when analysing anions in industrial solutions such as brines and sodium hydroxide solutions, because high salt solutions disturb the equilibrium in the low-capacity column, and large salt peaks sometimes interfere in the separation[2].

Many reports on the separation of organic anions by conventional ion-exchange chromatography with spectrophotomeric detection have been published[3–6]. One of the features of the method is that it is applicable to various industrial samples because of the stable equilibrium in the column. However, there have been few reports on the determination of anions in highly alkaline solutions with direct injection of the samples.

In this paper a liquid chromatographic procedure suitable for the determination of organic anions in highly alkaline solutions is described. First the injected sample is introduced into the pre-treatment column, which is packed with a strong sulphonic acid-type cation-exchange resin (H-type) where sodium or alkali metal cations are exchanged. Subsequently, the exchanged neutral sample is introduced into the separation column and the organic anions are eluted. The eluting anions are detected by monitoring at 210 nm. In this work the gel used in both the pre-treatment and the separation columns was the same. In spite of the direct injection of highly alkaline solutions, the difficulties associated with that of high salt solutions were not observed. This liquid chromatographic procedure is applicable to determinations of other compounds, for example, cations in highly acidic solutions.

EXPERIMENTAL

All chemicals and reagents were of analytical-reagent grade and were used without further purification. Deionized water was used throughout.

A flow diagram of the procedure is shown in Fig. 1. Liquid chromatographic

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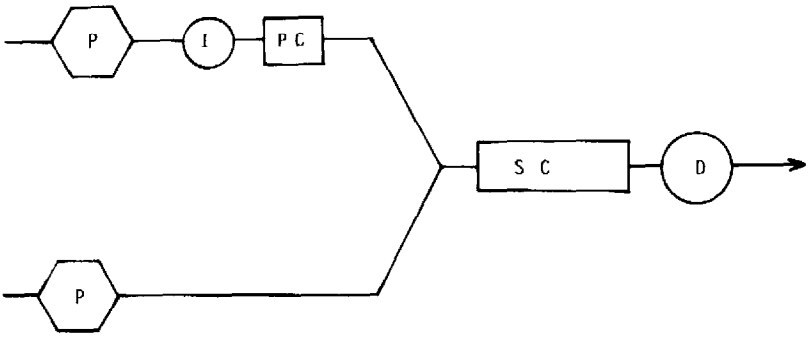

Fig. 1. Schematic flow diagram of on-line pre-treatment system. P = pump; PC = pre-treatment column; SC = separation column; D = detector; I = injector.

separation was performed on a system consisting of a CCPM pump (two heads, metal-free; Toyo Soda), a Rheodyune 7125 injector with a 100-μl loop and a UV-8000 variable-wavelength detector (Toyo Soda). A detection wavelength of 210 nm was employed and peak integrations were carried out using a CP-8000 data station (Toyo Soda). The separation column was 10 cm × 8 mm I.D. and the pre-treatment column was a 1 cm × 8 mm I.D. glass column. The gel packed in these columns was TSK-gel SCX (10 μm) and the cation-exchange capacity was almost 4.2 mequiv./g. After breakthrough of the alkaline material in the pre-treatment column, it was washed with 0.2 vol.-% phosphoric acid solution for 2 h at a flow-rate of 1 ml/min.

Under the usual chromatographic conditions, 0.2 vol.-% phosphoric acid solution was pumped at a flow-rate of 0.2 ml/min as the mobile phase. Deionized water was also pumped to the injector at a flow-rate of 0.8 ml/min.

RESULTS AND DISCUSSION

TSK-gel SCX is a strong cation-exchange resin consisting of totally porous sub-10 μm particles. Two retention mechanisms, ion exclusion and reversed-phase adsorption, are reported primarily to influence the retention behaviour of organic acids on cation-exchange resins[7–10]. Organic acids with low pK_a values are separated on this type of column principally by an ion-exclusion mechanism, whereas organic acids with higher pK_a values such as acetic acid, which exists predominantly in the undissociated form at the mobile phase pH, are separated by adsorption on the relatively non-polar stylene–divinylbenzene resin backbone[5].

A typical chromatogram of a standard sample containing 50 ppm each of formic acid acetic acid and 100 ppm of propionic acid in deionized water obtained with the present system is shown in Fig. 2. These three acids could be separated and determined in 7 min. Inorganic anions such as nitrate and sulphate were eluted rapidly and the first large solvent front peak corresponded to these inorganic anions. The separation of the acids was clear in spite of the use of the two-column system. The small volume of pre-treatment column and the efficient mixing of the carrier and the mobile phase enabled effective separations to be achieved.

The linearity of calibration graphs was examined. Linear graphs with intercept

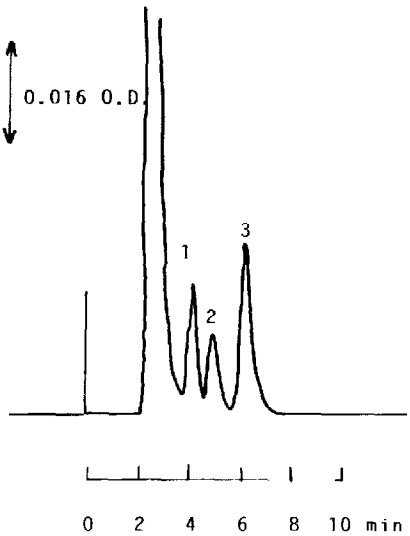

Fig. 2. Separation of acids in pure water. 1, Formic acid (50 ppm); 2, acetic acid (50 ppm); 3, propionic acid (100 ppm). Flow-rate of carrier, 0.8 ml/min; flow-rate of eluent, 0.2 ml/min; injection volume, 100 μl.

close to zero were obtained throughout, as is usual with a one-column system. The dynamic range was 0–200 ppm for the above acids, which would be adequate for their determination in industrial samples.

The precision of the liquid chromatographic procedure was evaluated by running five repeated analyses of a series of standard samples (in deionized water). Table I summarizes the results. The relative standard deviations were 0.5–1.7%, which are satisfactory. These good results may be due the high quality of the pump delivery system.

A typical chromatogram of the acids in 1 *M* sodium hydroxide solution is shown in Fig. 3a. In spite of direct injection of a highly alkaline solution, these acids could be separated and determined as in Fig. 2. Much of the sodium could be eliminated with high efficiency in the pre-treatment column. A typical chromatogram when the pre-treatment column was omitted is shown in Fig. 4. A suitable separation could not be achieved and it took too long to obtain a stable baseline again. This result suggests that the two-column system may be favourable for the determination of the acids in industrial samples.

TABLE I

REPRODUCIBILITY OF THE INJECTION OF ACIDS IN PURE WATER

Acid	*Peak area*	*Relative standard deviation (%)*	*Peak height*	*Relative standard deviation (%)*
Formic	1.58	1.13	7.56	1.35
Acetic	1.12	1.64	4.60	1.37
Propionic	3.40	1.26	10.94	0.45

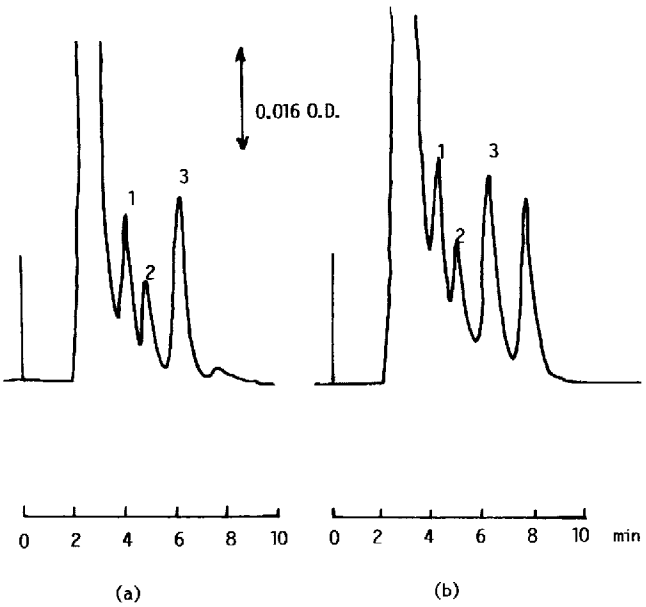

Fig. 3. Separation of acids in 1 *M* NaOH solution: (a) with the fresh pre-treatment column; (b) with the "breakthrough" pre-treatment column. 1, Formic acid (50 ppm); 2, acetic acid (50 ppm); 3, propionic acid (100 ppm). Conditions as in Fig. 2.

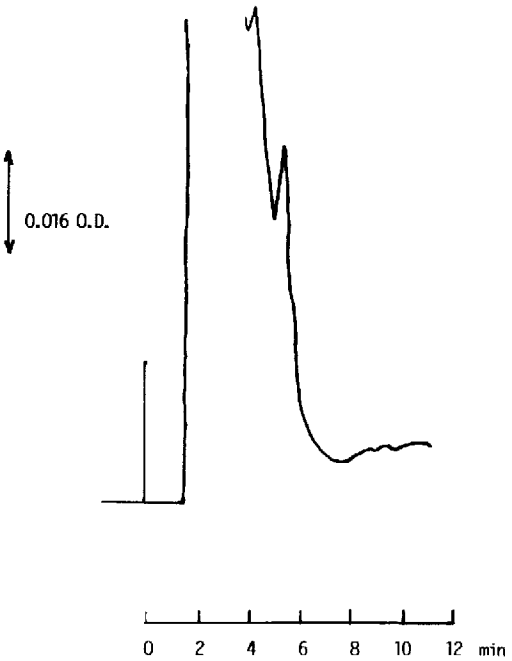

Fig. 4. Chromatogram of the acids in 1 *M* NaOH solution without the pre-treatment column. Conditions as in Fig. 2.

TABLE II

REPRODUCIBILITY OF THE INJECTION OF ACIDS IN 1 *M* SODIUM HYDROXIDE SOLUTION

Acid	*Peak area*	*Relative standard deviation (%)*	*Peak height*	*Relative standard deviation (%)*
Formic	1.51	2.66	7.45	0.67
Acetic	1.15	0.97	4.85	1.03
Propionic	3.56	1.02	11.35	2.37

Table II summarizes the results of reproducibility experiments on the highly alkaline solution. The sample solution contained 50 ppm each of formic acid and acetic acid and 100 ppm of propionic acid in 1 *M* sodium hydroxide solution. The peak height and area were almost the same as those in the former instance. This result suggests that the on-line pre-treatment in the flow stream was effective and neutralization of sodium in the pre-treatment column did not affect the separation. The relative standard deviations were as low as in the former instance.

One of the major problems of this system is "breakthrough" of the pre-treatment column on passing through highly alkaline sample solutions. Before injection of alkaline samples the column is totally in the $-SO_3H$ form, but once the samples have been injected it is partly exchanged to the $-SO_3Na$ form and the exchange capacity for alkaline solutions is diminished. When 100 μl of 1 *M* sodium hydroxide solution were injected five times, the capacity of the pre-treatment column was reduced and a clear separation could not be achieved. The "fifth" chromatogram is shown in Fig. 3b. The front peak became larger and the unknown peak after propionic acid also became larger. Hence formic and acetic acids could not be determined. The unknown peak is currently under investigation.

CONCLUSION

With deionized water as the carrier and phosphoric acid solution as the mobile phase, organic acids in highly alkaline solutions could be determined without any pre-treatment. Sodium could be easily excluded using the cation-exchange gel column. Although the system consisted of two pumps and two columns, very rapid and precise separations could be achieved. The results make the system particularly suitable for the determination of organic acids in industrial sample solutions.

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