Notes

Preconcentration/Ion Chromatography with Indirect Photometric Detection for Anions

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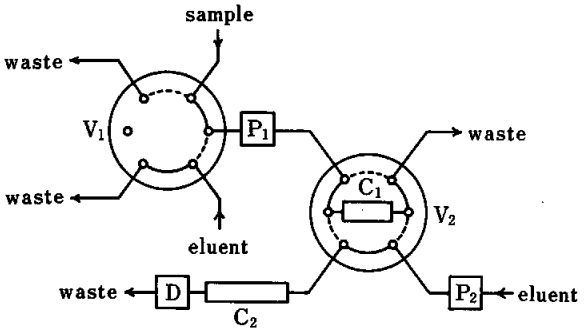
One of the major functions of ion chromatography (IC) is the simultaneous trace determination of various ions. Several systems incorporating preconcentration/IC with conductivity detection have been developed for the determination of inorganic anions.[1] Preconcentration/ion exclusion chromatography has also been reported for the determination of carboxylates.[2]

On the other hand, non-suppressed IC with indirect photometric detection (IPD)[3] provides several attractive attributes. First, this method can be performed on a conventional high-performance liquid chromatographic (HPLC) system equipped with a UV absorbance detector. Second, only common inorganic anions (as well as hydrogencarbonate[4] and carboxylates[5]) can be determined simultaneously. This method, however, has not yet been applied to trace determinations. The purpose of this study was to develop a preconcentration/IPD-IC system utilizing column-switching techniques.

Experimental

A schematic diagram of the preconcentration/IPD-IC is given in Fig. 1 along with an operation time program. The system comprised two JASCO (Tokyo, Japan) 880-PU pumps (P_1, P_2), both set at 1.0 ml/min; a Teflon low-pressure solvent selection valve (V_1); a JASCO 892-01 high-pressure switching valve (V_2); a JASCO 860-CO column oven kept at 40°C; a JASCO 870-UV absorbance detector (D) set at 260 nm; and a Shimadzu C-R1B integrator. The concentrator column (C_1, 20 mm×4.6 mm i.d., stainless-steel) was packed with Mitsubishi Kasei (Tokyo, Japan) MCI GEL SCA-03 (methacrylate, anion exchange capacity of 30 μequiv/g). The analytical column (C_2) was a Shimadzu Shim-pak IC-A1 (100 mm×4.6 mm i.d.).

Distilled-deionized water was passed through a Millipore (Bedford, MA, USA) Milli Q-II water purification system before use. Standard anion solutions were prepared by dissolving guaranteed-grade sodium salts in water, and stored in polyethylene bottles. The eluent mainly used was 2.0 mM *p*-toluenesulfonic acid, the pH of which was adjusted to 6.0 with sodium hydroxide. It was filtered with a membrane (0.45 μm) before use, and kept in a polyethylene reservoir.



Step 1 (Load the sample solution onto C_1, equilibrate C_2 with the eluent)
0 – *t* min V_1 solid; V_2 solid

Step 2 (Strip anions from C_1, transfer anions into C_2, start integrator)
t – *t*+2 min V_1 solid; V_2 dotted

Step 3 (Clean-up and equilibrate C_1 with the eluent, separate anions on C_2 and detect their elution)
t+2 – *t*+5 min V_1 dotted; V_2 dotted

Step 4 (Wash P_1 and tubing with the next sample solution, equilibrate C_1 and C_2 with the eluent, stop the integrator)
t+15 – *t*+30 min V_1 solid; V_2 dotted

Fig. 1 Schematic diagram of a preconcentration/indirect photometric detection ion chromatograph and its operation time program. *t*, sample loading time (depending on the volume).

Results and Discussion

Column-switching is a useful technique for on-line sample treatments in HPLC, as well as in IC.[6] Several preconcentration/IC systems utilizing conductivity detection have been reported. In those systems comprising two pumps and one switching valve (or one pump and two valves), the eluent flow was interrupted during the sample-loading step, and clean-up of the concentrator column was incomplete. This resulted in a base-line drift and interfering peaks, respectively. Although the set-up of our system seems to be more complex, the flow is not interrupted and C_1 is equilibrated with the eluent during the separation step. Therefore, the above-mentioned problems are not observed in our system. Moreover, any undesirable compounds having long retention times could be prevented from entering C_2 by switching V_2 while they were still retained on C_1. Thus, the present system allows only analyte ions to enter C_2.

In IPD-IC, both aromatic carboxylates and sulfonates have been popular eluents for the determination of anions.[3,7] When aromatic carboxylates, such as phthalate and benzoate, were used in the present system, a large system peak was observed after the analyte anion peaks. This was possibly due to the formation of neutral and protonated carboxylates, as was observed in non-suppressed IC.[8] This system peak was not observed when aromatic sulfonates, with a pK_a much smaller than that of carboxylates[2], were used as the eluents.

Recently, benzenedisulfonate and naphthalenedisulfonate have been widely used as eluents for IPD-IC, since these disulfonates give higher sensitivity than do monosulfonates.[8] However, the retention of the analyte anions on C_1 treated with disulfonates was much weaker than that with monosulfonates. Table 1 shows the recoveries of chloride, nitrate and sulfate from C_1 using several mono- and disulfonate eluents. The concentrations of the eluents were adjusted to 2.0 mM or 0.2 mM, so as to give similar retentions of the analyte anions. Although the three anions were recovered quantitatively using monosulfonate (benzenesulfonate, *p*-toluenesulfonate) eluents, the recoveries of chloride and nitrate ions were low when disulfonate (*m*-benzenedisulfonate, 2,6-naphthalenedisulfonate, 2-naphthol-6,8-disulfonate) eluents were used. This result suggested that large portions of the two ions had leaked from C_1 during the sample-loading step. In ion-exchange chromatography, a strongly bound ion is not easily substituted by a weaker exchanging ion at low concentrations. Thus, those disulfonate eluent ions having a stronger retention impeded the substitution of chloride and nitrate at low concentrations. Based on these results, 2.0 mM *p*-toluenesulfonic acid (pH 6.0) was used in the following experiments, and several inorganic anions and carboxylates were separately determined, as shown in Fig. 2.

Next, the influence of the flow rate and sample-loading volumes on the recoveries of analyte anions (chloride, bromide, nitrate and sulfate) was examined. When 40 ml of the above-mentioned anion mixture (each 5.0×10^{-7} M) was loaded at flow rates of between 0.25 ml/min and 2.0 ml/min, they were quantitatively recovered. When constant amounts of these four anions (each 1.0×10^{-8} mol) were loaded at volumes between 5 and 100 ml, they were all quantitatively recovered without any peak broadening. This suggests that loading a sample volume of over 100 ml is possible.

Figure 3 shows calibration curves of the four ions in the 1.0×10^{-9} M to 1.0×10^{-7} M range. These concentrations were below the detection limits (10^{-6} M range) obtained from by IPD-IC without preconcentration. Linear calibration curves were observed for chloride (r=0.9999)

Table 1 Anion recoveries[a]

Eluent	Recovery, %		
	Chloride	Nitrate	Sulfate
Benzenesulfonate, 2.0 mM	96	96	99
p-Toluenesulfonate, 2.0 mM	94	97	99
m-Benzenedisulfonate, 0.2 mM	23	73	98
2,6-Naphthalenedisulfonate, 0.2 mM	b	67	95
2-Naphthol-6,8-disulfonate, 0.2 mM	5	3	100

a. Mean values of three experiments. Twenty milliliters of the mixture of three ions (each 5.0×10^{-7} M) was loaded.
b. The quantification was disturbed by an unknown peak.

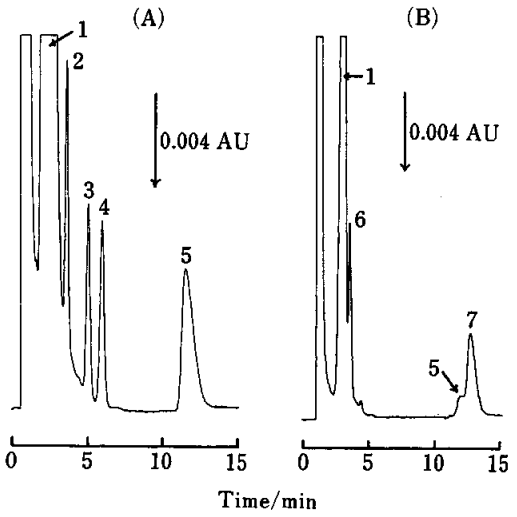


Fig. 2 Chromatograms of (A) inorganic anions and (B) carboxylates. Sample: (A) a 100 ml mixture of chloride, bromide, nitrate and sulfate (each 1.0×10^{-7} M); (B) 20 ml of butyrate and tartrate (5.0×10^{-7} M). Peaks: 1, hydrogencarbonate; 2, chloride; 3, bromide; 4, nitrate; 5, sulfate; 6, butyrate; 7, tartrate.

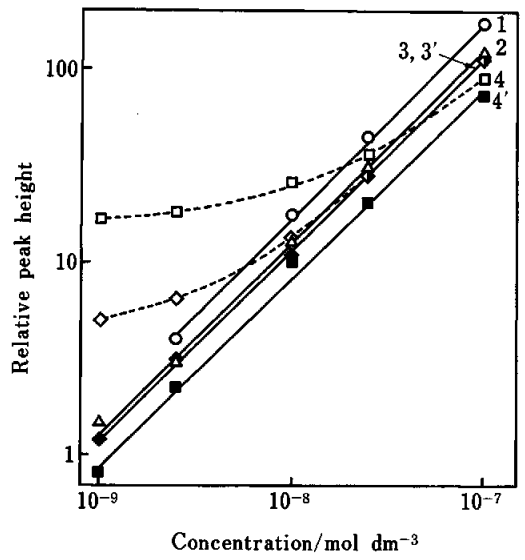


Fig. 3 Calibration curves. Sample: a mixture of chloride, bromide, nitrate and sulfate. Loading volume: 100 ml. Lines: 1, chloride; 2, bromide; 3, nitrate; 4, sulfate; 3′ and 4′, background-corrected lines of 3 and 4, respectively.

and bromide (r=1.0000), although the nitrate and sulfate curves were not linear at lower concentrations. One possible reason for this may be due to impurities in either the sample containers or *p*-toluenesulfonic acid. Small peaks of nitrate and sulfate were observed when water was loaded following purification. In addition, sulfate anions may be present in *p*-toluenesulfonic acid. By correcting the peak heights using the background levels of nitrate (2.8×10^{-9} M) and sulfate (2.0×10^{-8} M), the two curves were made to be linear (r=0.9999 for nitrate, r=0.9991 for sulfate), as shown in Fig. 3.

In Fig. 2, the large hydrogencarbonate peak, eluting before the chloride peak, originates from the carbon dioxide dissolved in the sample solution; the height of this peak increases with increasing sample volume. Interference by the hydrogencarbonate peak in the trace-level determination of the chloride was greatly reduced by the addition of 2.0 mM *p*-toluenesulfonic acid to the sample solution. This effect might be attributable to the reduction of the pH. On the other hand, it has been reported that hydrogencarbonate can be determined by a combination of the system proposed here if nitrogen is bubbled through the eluent[4], even though it was difficult to obtain a linear calibration curve below 10^{-6} M.

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