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Dual Cation-Selective Membrane Tube Electrodialysis/Ion Chromatography for Halide Ions in Strongly Basic Solutions and Its Application to the Analysis of Rock Samples

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Electrodialysis pretreatment system was combined with a new dual cation-selective membrane tubes and was employed to reduce the basicity of the strongly basic sample solution prior to the ion chromatographic determination of halide ions by using a sodium salicylate solution as eluent. By using this system, large amount of cations such as sodium and potassium ions could also be removed from the sample solution through the membrane. The detection limits were 9.7, 5.4, 22.7, and 163 ng cm^{-3} and relative standard deviations at 0.5 μg cm^{-3} were 1.7, 1.2, 2.4, and 14% for fluoride, chloride, bromide, and iodide ions, respectively. Analytical results are given for rock samples fused with sodium hydroxide as a flux and afterward dissolved in water which shows strong basicity.

Ion chromatography (IC) is extensively used for the determination of both anions and cations in aqueous solutions. The multielement detection capabilities, high sensitivity, and automated aspect of IC, make it well suited for routine analysis. Trace ions in a strongly acidic or basic solution cannot be determined by direct injection into an ion chromatograph equipped with an ion exchange separation column and a conductivity detector, owing to the high background conductance of the sample and low capacity of the column. Furthermore, the analyte peaks are usually badly distorted by the high background conductance. Therefore, the solution should be diluted to alleviate the load of excess ions on the column. However, high dilution makes analysis difficult, particularly when the concentration of the analyte in the original sample is close to the instrumental detection limit. The aforementioned situations are encountered in the analyses of sample solutions of either strongly basic (prepared by alkali fusion) or strongly acidic (prepared by mineral acid digestion) nature. In order to extend IC detection capabilities to the analysis of such samples, Pettersen et al.[1] reported a pretreatment method for reducing high concentrations of sodium and hydroxide ions without dilution, for the determination of sulfate and nitrate ions. Their method was based on electrolysis in combination with one sheet of cation-exchange membrane. In our previous work, a dual anion-selective membrane tube electrodialysis system was developed for the treatment of strongly acidic samples prior to the IC determination of magnesium(II) and calcium(II).[2]

In this paper, a dual cation-selective membrane tube electrodialysis system was re-constructed and applied to the determination of halide ions in strongly basic solutions by non-suppressed or single column anion-exchange IC. During the electrodialysis, protons move from the anode electrolyte solution into the sample solution through the outer cation-selective membrane and neutralize the sample solution. Simultaneously, alkali metal ions move from the sample solution into the cathode electrolyte solution through the inner cation-selective membrane. Water is oxidized and oxygen is produced at the anode, while water is reduced to release hydrogen gas at the cathode. The purpose of this paper is to demonstrate the potentials of the system together with its application to trace fluorine and chlorine determinations in rock samples fused by sodium hydroxide.

Experimental

Chromatographic Conditions. Analyses were performed on IC system consisting of a Tosoh Model CCPD double plunger pump, a Tosoh Model TSK-gel IC-Anion-PW (4.6 mm i.d. ×5.0 cm), a Rheodyne Model 7125 injector with a 100-μl sample loop and a Tosoh Model CM-8 conductivity detector. The sensitivity of the detector was 0.5 μS cm^{-1} full scale. Chromatograms were recorded with a Tosoh Model LR4220 strip chart recorder. A mobile phase (pH 5.8) included sodium salicylate (1.0 mmol dm^{-3}). The flow-rate was 1.0 cm^{3} min^{-1}. All parts of the system in contact with fluid were non metallic except for the flow passages in the detector. From the injection loop to the detector cell, 0.25-mm bore poly(tetrafluoroethylene) (PTFE) connections were kept as short as possible to minimize the dead volume. The system was maintained at 25±0.5°C.

A Branson Model B-220 ultrasonic generator was used. The pH values were measured with a Hitachi-Horiba Model M-8L pH meter throughout.

Electrodialysis Apparatus. An electrodialysis system comprised an electrodialysis cell, a constant dc current electric source (0.9 A), a relative conductivity monitor, a Tokyo Rikakikai Model MP-3 2-channel peristaltic pump, an M & S Instruments Model JR magnetic stirrer and a gas–liquid separator. A Tosoh Model IE-Labo was utilized for the electric source and monitor. A tip for a Gilson Pipetman Model P-1000 digital micropipette was used as gas–liquid separator when it received the sample droplets free of carbon dioxide gas which was flushed out automatically. With the exception of ion exchange membrane tubes and gas–liquid separator, the rest of the mechanism and components related to electrodialysis are the same as described in the literature.[2] However, as shown in Fig. 1, the configuration was rearranged to suit the determination of anions. The design of the electrodialysis cell, utilized a Tosoh cation-selec-

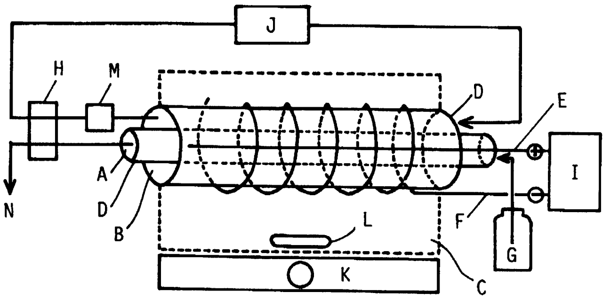

Fig. 1. Schematic diagram of electrodialysis system. A, anode electrolyte solution channel; B, sample channel; C, cathode electrolyte solution; D, cation-selective membrane tube; E, anode; F, cathode; G, anode electrolyte solution; H, 2-channel peristaltic pump; I, electric source; J, relative conductivity monitor; K, magnetic stirrer; L, stirring bar; M, gas–liquid separator; N, waste.

tive membrane tube (1.00 mm i.d. ×2.25 mm o.d. ×30 cm), containing a platinum wire (0.3 mm o.d. ×40 cm), inserted inside a Tosoh cation-selective membrane tube (2.00 mm i.d. ×2.38 mm o.d. ×30 cm). A stainless-steel wire (0.50 mm o.d. ×2.0 m) was coiled around the outer membrane tube and held negative with respect to the central conductor. Inlet/outlet liquid connections were made with silicone rubber tees. A sample solution flowed in the outer channel, while an anode electrolyte solution flowed in the inner channel. Other parts of the system were connected with PTFE tubings (1.0 mm i.d.).

Electrodialysis Procedure. The sample channel was filled with an aliquot of sample solution (ca. 2.5 cm^3). This solution was then circulated at a flow-rate of 5.0 cm^3 min^{-1}, and the anode electrolyte solution was also pumped at the same flow-rate. Subsequently, platinum and stainless-steel wire electrodes were connected to the source to start the electrodialysis. The relative conductivity was monitored throughout the dialysis. After the electrodialysis, the neutralized sample was collected from the system for analysis.

Reagents. De-ionized water was prepared in our laboratory using an Advantec Toyo Model GSU-901 water purification system. The conductivity of the water was less than 0.05 μS cm^{-1}. All reagents were of analytical-reagent grade and were used without further purification.

A mobile phase was prepared by diluting 0.16 g of sodium salicylate (Yoneyama Yakuhin Kogyo) to 1000 cm^3 with the de-ionized water followed by filtering through a membrane filter (Millipore) of 0.45 μm pore size. Dissolved gases in the mobile phase were removed under vacuum with the ultrasonic generator. The pH of the mobile phase was 5.8. The standard stock solutions of halide ions were prepared by dissolving their sodium salts (Kanto Chemical) in water. Working standard solutions were prepared by stepwise dilution of the stock solutions with water.

A 0.01 mol dm^{-3} sulfuric acid and a 0.1 mol dm^{-3} sodium hydroxide solution were used as the anode and the cathode electrolyte solutions, respectively.

Sodium hydroxide of special grade (Kanto Chemical) was used in sample fusion.

Analysis of Rock Samples. For the determination of chlorine, bromine, and iodine, each 1 g of the powdered rock samples was fused with 5 g of the flux in a nickel crucible. The fusion cake was dissolved in 150 cm^3 of water by heating and stirring for 1 h in a water bath, and was allowed to stand overnight. Polymerized silicic acids and metal hydroxides were sufficiently precipitated during this procedure. The mixture was filtered through a filter (Nucleopore; 47 mm o.d., 0.45 μm pore size, pre-washed with water). The filtrate was made to the required volume of 250 cm^3 with water.

For the determination of fluorine, alkali fusion was carried out in the same manner as described above. Into a 50-ml steam distilling flask, the resulting fusion cake was placed and to it, 1 cm^3 of phosphoric acid and 30 cm^3 of sulfuric acid were added. The flask was maintained at a temperature in the range 140—150 °C, and steam was introduced into it and the distillate was collected in a 250-cm^3 volumetric flask, containing 25 cm^3 of 10 mol dm^{-3} sodium hydroxide solution. Fluoride ion was steam distilled as fluorosilicic acid and condensed as sodium fluoride in the flask. After 1 h, the volume of distillate collected was about 220 cm^3. The sample was diluted with the water to the volume in 250-cm^3 volumetric flask. It is 1 mol dm^{-3} with respect to sodium hydroxide.

Results and Discussion

Ion Chromatographic Separation. Separation behavior of inorganic and organic anions have been discussed. Matsushita et al.[3)] reported that monovalent inorganic anions were completely separated with a 1 mmol dm^{-3} tartaric acid (pH 3.2) or 10 mmol dm^{-3} potassium benzoate (pH 6.6) solution as eluent. Fritz et al.[4)] also measured the relative retention times of various anions with different acid eluents, and reported that salicylic acid was a powerful eluent for late-eluting anions.

In our experiment, several organic acid solutions were investigated as eluent for the selective and sensitive determination of halide ions from the view point of analyte separations among them and hydroxide ion. The organic acids have to be soluble enough in water to be used and partially dissociated to provide an anion concentration sufficient to push analyte anions down the column. However, the acid must be partly in the molecular form so that the blank level becomes enough low to amplify the analyte signal. The organic acids (1 mmol dm^{-3}, pH 5.0 adjusted by a sodium hydroxide solution) examined as eluent, were citric acid, fumaric acid, ethylenediaminetetraacetic acid (EDTA), tartaric acid, succinic acid, salicylic acid, *p*-hydroxybenzoic acid, and benzoic acid. Table 1 lists the retention times of halide ions obtained by using these eluents. Separation of all four halide ions could be achieved with these eluents tested here, if the analyte ions were dissolved in the de-ionized water. When citric acid, fumaric acid, EDTA, tartaric acid, and succinic acid were used as eluent, however, the overlap of fluoride and chloride ions by hydroxide ion and water dip made these analyses unacceptable, especially when more basic samples were analyzed. On the other hand, the aromatic

Table 1. Retention Times of Halide Ions with 1 mmol dm^{-3} Different Acid Eluents (pH 5.0)

Eluent[b]	pK_a	Retention time/min[a]			
		F^-	Cl^-	Br^-	I^-
Citric acid	3.1, 4.8, 6.4	1.1	2.7	5.8	25.8
Fumaric acid	3.0, 4.4	1.3	3.1	6.4	26.8
EDTA	2.0, 2.7, 6.2, 10.3	1.4	3.6	8.6	21.0
Tartaric acid	3.0, 4.4	1.6	4.2	9.1	40.3
Succinic acid	4.2, 5.6	2.2	5.4	12.4	56.1
Salicylic acid	3.0	3.3	4.8	6.8	16.8
p-Hydroxybenzoic acid	4.6	5.9	10.5	17.0	51.7
Benzoic acid	4.2	8.0	15.0	26.8	—[c]

a) Chromatographic conditions: column, IC-Anion-PW; flow-rate, 1.0 cm^3 min^{-1}; injection volume, 100 mm^3; electroconductivity detector range, 5.0 μS cm^{-1} full scale. b) At pH 5.0 the acids are predominantly in an anionic form. c) Very long retention time.

carboxylic acid such as *p*-hydroxybenzoic acid and benzoic acid took longer time to elute iodide ion. By adopting salicylic acid, the excellent separation of the four solutes were achieved with a shorter analysis time than those obtained by adopting other aromatic carboxylic acid eluents. Moreover, weakly basic samples could be analyzed with minimum overlap caused by hydroxide ion.

The effectiveness of the salicylic acid eluent to extrude halide ions from the separation column will depend on several factors. A higher percentage of ionization means that a higher concentration of the acid anions is available to move analyte anions down to the column. This depends on the pH of the eluent. Figure 2 shows the effect of pH of the salicylic acid (pK_a 3.0) on the retention times of halide ions. Except fluoride ion, the retention times of the analyte ions decreased as the pH of the eluent increased (up to pH 5) and then became almost constant for each analyte ion within the tested pH range 5—9. In this experiment, pH 5.8 was selected as the pH of the eluent for practical convenience, because the eluent solution shows pH ca. 5.8 when it is 1 mmol dm^{-3} with respect to sodium salicylate. More-

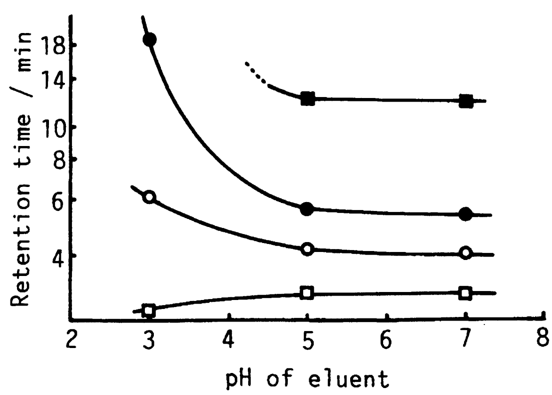

Fig. 2. Effect of pH of the salicylate eluent on retention time. □, fluoride; ○, chloride; ●, bromide; ■, iodide. See text for chromatographic and detection conditions.

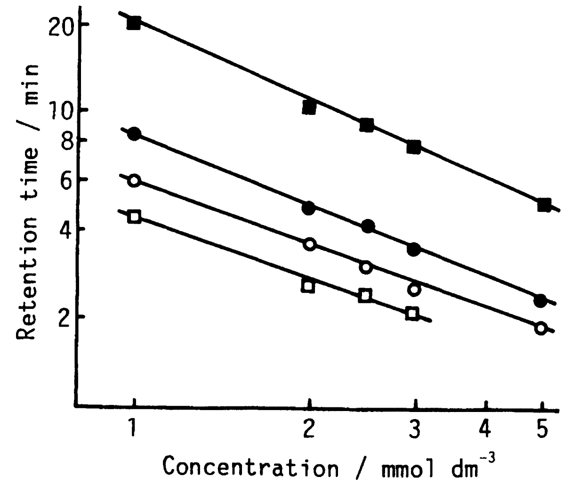

Fig. 3. Relation between retention time and concentration of the salicylate eluent. □, fluoride; ○, chloride; ●, bromide; ■, iodide. See text for chromatographic and detection conditions.

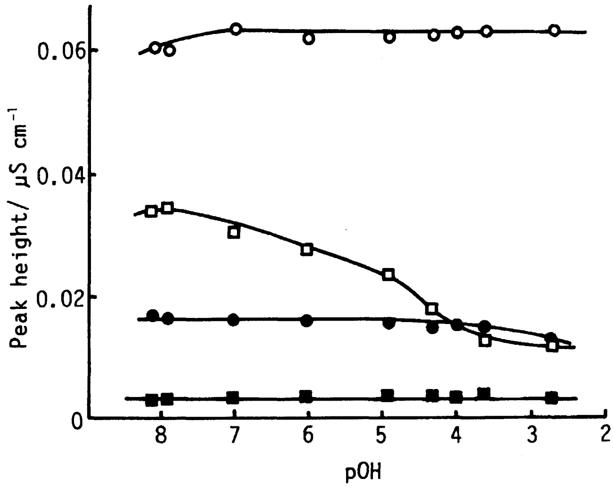

Fig. 4. Effect of pOH on peak height of halide ions. Sample, a 1 mol dm^{-3} sodium hydroxide solution containing halide ions of each 2.0 μg cm^{-3}. See text for chromatographic and detection conditions.

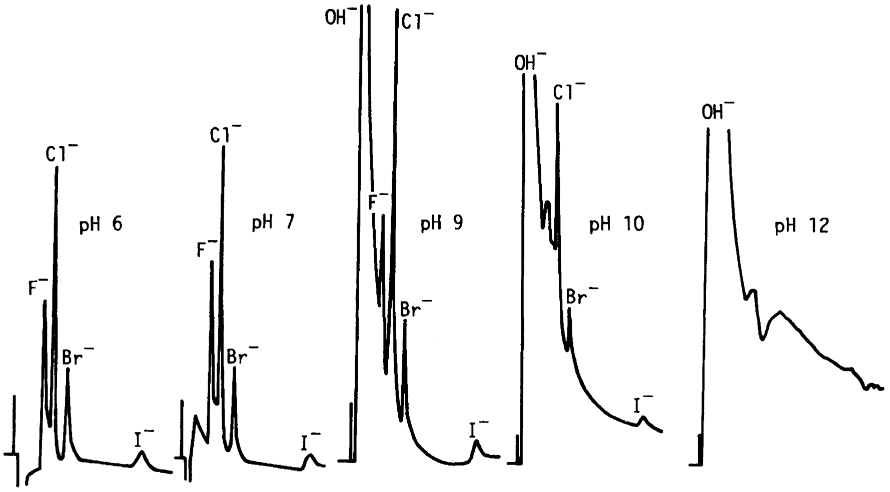

Fig. 5. Chromatogram of halide ions. Samples are the same as those in Fig. 4. See text for chromatographic and detection conditions.

Table 2. Analytical Results of Rock Samples[a)]

Sample	Found[b)]/$\mu g\,g^{-1}$	Recommended[c)]/$\mu g\,g^{-1}$
	Fluorine	
JG-1a (Granodiorite)	449±20	450
JR-1 (Basalt)	993±11	942
JB-2 (Ryolite)	99±10	101
	Chlorine	
JG-1a (Granodiorite)	86±22	(67)[d)]
JR-1 (Basalt)	940±26	920
JB-2 (Ryolite)	264±26	240

a) Geological Survey of Japan rock reference samples. b) Mean ± ave. dev., 3 results. c) Recommended value in reference.[6)] d) Reported value in reference.[7)]

over, the fluctuation in retention time could be minimized even if a weakly basic sample is introduced into the IC system. As for the effect of the sodium salicylate concentration on the retention times, Fig. 3 shows these results. When a lower concentration of the eluent was adopted, an easier separation between hydroxide ion and halide ions was achieved. Therefore, a 1.0 $\mathrm{mmol\,dm^{-3}}$ sodium salicylate solution was used as the optimum eluent.

Optimization of Electrodialysis Conditions. The electrodialysis conditions were optimized using a 1.0 $\mathrm{mol\,dm^{-3}}$ sodium hydroxide test solution containing different halide ions of 2.0 $\mathrm{\mu g\,cm^{-3}}$ each. During dialysis, water is oxidized to release oxygen gas at the anode, while at the cathode, it is reduced to release hydrogen gas. Bubbles of oxygen and hydrogen gas can be removed easily by stirring the cathode electrolyte solution with the magnetic stirrer and by sucking the anode electrolyte solution with the peristaltic pump. At the same time, sodium ions migrate from the sample solution through the cation-selective membrane into the cathode electrolyte solution. Also, protons migrate from the anode electrolyte solution into the sample solution thereby neutralizing it and carbon dioxide gas is liberated when carbonated are involved in the sample. The liberation of carbon dioxide was a serious problem especially in the analysis of practical samples such as rock materials. In order to expel carbon dioxide bubbles, a plastic tip for digital micropipette was utilized as gas–liquid separator. Sample droplets were collect down in the wider part of the tip, and were sucked and recirculated by the peristaltic pump. By doing so, carbon dioxide bubbles were completely removed. The inner membrane did not allow halide ions to enter into the anode electrolyte solution.

Within approximately 10 min, the pH of the sample solution decreased to 5.8—7.0, and further dialysis was not advisable. This is because gradual penetration of the analyte ion from the sample to the anode electrolyte solution was apt to occur. Incomplete dialysis caused an overlap of the fluoride peak with hydroxide ion peak. Figure 4 shows the dependence of peak height of halide ions in IC on the pOH, which represents the degree of neutralization by electrodialysis. Figure 5 shows a typical ion chromatogram obtained at different pH.

Sensitivity and Precision. Under the operating conditions summarized in the experimental section, the upper limit of the linear response was 10 $\mathrm{\mu g\,cm^{-3}}$ for all halide ions examined here. The detection limits were 9.7, 5.4, 22.7, and 163 $\mathrm{ng\,cm^{-3}}$ for fluoride, chloride, bromide, and iodide ions, respectively. The detection limit was defined as the concentration required to give a signal-to-noise ratio equal to 3. The relative standard deviations at 0.5 $\mathrm{\mu g\,cm^{-3}}$ for five replicate determinations were 1.7, 1.2, 2.4, and 14% for fluoride, chloride, bromide, and iodide ions, respectively.

Application to Practical Samples. According to the recommended procedure, the accuracy of the proposed method was examined by analyzing JGS (the Geological Survey of Japan) rock reference samples. Since samples could be contaminated with halide ions during analysis, halogen contents of sodium hydroxide flux of different grades and manufacturers were determined before use. The reagent having the lowest halogen contents was selected and used in this study. Negligible amounts of fluoride, bromide, and iodide were found in the reagent. The chloride content of the blank was observed to be 5.0 ± 0.7 $\mu g\,g^{-1}$. This value contains chloride impurity of the reagent and chloride contamination from the environment during the electrodialysis process. The analytical results of the JGS rock reference samples obtained are in good agreement with the recommended values (Table 2). Regarding bromine and iodine, their concentrations were too low to be determined.

Despite its high concentration, fluorine was not detected. However, this was not because electrodialysis or IC but the sample was not decomposed, hence no free fluoride ion in the solution. Therefore, an additional pretreatment, that is, steam distillation was carried out for the determination of fluorine. The method of steam distillation is well known and is an established procedure in solution absorption spectrophotometry for the analysis of water samples.$^{5)}$ By the distillation described in the experimental section, fluoride ion was separated from the matrix of the rock samples. Then, the electrodialysis procedure was carried out to neutralize the sodium hydroxide matrix. As Table 2 shows, the results which were obtained with the calibration curve method were in good agreement with the certified values. Therefore, the proposed method is applicable to the determination of trace anions in strongly basic solutions such as alkali fusion samples.

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