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DETERMINATION OF TRACE ANIONIC IMPURITIES IN CONCENTRATED INORGANIC ACIDS BY RECYCLE ION CHROMATOGRAPHY

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SUMMARY

A simple, sensitive and rapid method for determination of trace anions (chloride, nitrite, bromide, nitrate and sulphate ion) in concentrated inorganic acids (hydrochloric, nitric, phosphoric and sulphuric) has been developed. Each sample is diluted 100–400-fold in water and neutralized with sodium hydroxide. The determination is made by recycle ion chromatography to separate an objective trace anion from the coexisting anion of the sample acid. The detection limit of each anion was 0.3–0.9 ppm in the sample acid.

INTRODUCTION

Almost all of the pure chemicals have to be analyzed for the contents of inorganic impurities. Metallic impurities are determined sensitively by atomic absorption spectrometry^{1,2} and simultaneously by inductively coupled plasma-atomic emission spectrometry^{3,4}, but an universal determination method for anionic impurities is not available. Methods such as turbidimetry^{5–7}, spectrophotometry^{8–10}, ion-selective electrode potentiometry^{11,12} and other electrochemical methods¹³ have been developed for the determination of trace anions, but many of them can detect only one or a few anions, and in relatively clean samples.

Ion chromatography (IC), introduced by Small *et al.*¹⁴, is one of the most effective methods to determine trace inorganic anions, owing to its high sensitivity, rapidity and ease of operation. Many anions are determined by IC simultaneously. However, because of the low capacity of the ion exchanger used as a packing (less than 0.1 mequiv./g), anions often cause overload, and peaks become broad at relatively low concentrations (100–1000 ppm). Thus it is difficult to determine trace anions in the presence of large amounts of other anions, as the peak of an objective anion is obscured by the broad peak due to overloading. More selective detectors, *e.g.*, UV absorbance^{15,16}, electrochemical^{17,18} are available, but these cannot be used so widely for determinations of various anions.

On the other hand, recycle IC^{19–21} is a convenient method to separate a small peak which is hidden by a large peak. This paper describes a simple, sensitive and rapid

method for the determination of trace anions in concentrated inorganic acids by recycle IC.

EXPERIMENTAL

Reagents

Deionized water (Millipore RO-Q system) was used throughout the present study. A 1.0 M sodium hydroxide solution (normality factor 1.004–1.009) from Kanto was used. Other reagents and sample acids used were of reagent grade. Sample acids conformed to the Japan industrial standard (JIS)²².

Recycle IC conditions

The flow diagram of the recycle ion chromatograph system A was the same as shown in our previous report²¹. The system was equipped with a sample loop (50 μ l), an HPIC-TAC-1 concentrator column, an HPIC-AG4A guard column (50 mm \times 4 mm), an HPIC-AS4A separator column (250 mm \times 4 mm), an anion micro-membrane suppressor (AMMS) and a conductivity detector. The objective anion was collected on the concentrator column at the back of the detector.

Fig. 1 illustrates the recycle ion chromatograph system B. This system is equipped with a 1.5-ml loop (760 cm \times 0.5 mm I.D.) instead of a concentrator column as in system A, and the collection point was between the separator and the suppressor.

Sample preparation

Each sample was diluted according to Table I and neutralized with 1.0 M sodium hydroxide. Hydrochloric acid and nitric acid were neutralized with an equimolar volume of sodium hydroxide, phosphoric acid and sulphuric acid required a double equimolar volume of sodium hydroxide to be neutralized.

Determination of bromide and nitrate ions

The prepared sample solution was subjected to the recycle system A. A fraction containing an objective anion was collected on a concentrator. This column and connection were washed with 2 ml of water. The concentrated anion was reinjected into the separator. Times to start and stop the collection were the same as the beginning

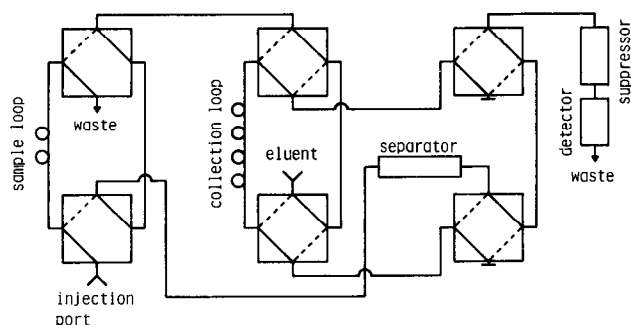


Fig. 1. Schematic diagram of recycle system B.

TABLE I
DILUTION RATIO OF SAMPLE ACIDS

Objective anion	Dilution ratio (v/v)			
	HCl	HNO ₃	H ₃ PO ₄	H ₂ SO ₄
Chloride, nitrite	—	200	400	400
Bromide, nitrate	200	—	400	200
Sulphate	100	200	400	—

and ending of an objective anion peak. Standard solutions were used to construct the calibration graph and to define the collection time of an objective anion.

Determination of sulphate ion

Recycle system A was used as above. The system-peak height of sulphate was determined previously. The peak height of an objective sulphate ion was obtained by subtracting the system-peak height from the peak height of the sample.

Determination of chloride and nitrite ion

The prepared sample solution was subjected to recycle system B. A fraction containing an objective anion was collected in a 1.5-ml loop, then reinjected into the separator. Times to start and stop the collection were 12 s earlier than those of the beginning and ending of an objective anion peak.

RESULTS AND DISCUSSION

Eluent for recycle IC

Since the aim of this study was to determine many anions in various inorganic acids, the most suitable eluent for simultaneous separation of the main acid anions was selected. Table II shows the effect of the eluent composition on the retention times of

TABLE II
EFFECT OF THE ELUENT COMPOSITION ON THE RETENTION TIMES OF ANIONS

Eluent component (mM)			Retention time (min)			
NaOH	Na ₂ CO ₃	NaHCO ₃	Chloride	Nitrate	Phosphate	Sulphate
50	0	0	2.2	4.8	— ^a	8.6
30	0	0	2.7	6.4	— ^a	20.0
10	1	0	2.1	4.7	46.0	10.6
5	3	0	1.8	3.5	13.8	5.4
0	3	0	1.9	3.8	5.0	5.4
0	2	0.5	2.0	4.0	7.2	9.5
0	2	1	2.0	4.0	6.2	8.8
0	1	4	2.2	4.5	7.2	12.9

^a Did not elute within 1 h.

chloride, nitrate, phosphate and sulphate ion. The eluent selected, 2.0 mM sodium carbonate–1.0 mM sodium bicarbonate, gave short retention times and high resolution. Increasing the concentration of this eluent decreased the retention time, but the resolution was lowered.

When using recycle system A, an objective anion was retained on the concentrator column together with anionic components of the eluent, and upon reinjection gave a peak together with system peaks. The sodium carbonate–bicarbonate eluent gave two system peaks comprising carbonate and sulphate²¹. The carbonate is likely to originate from the eluent and sulphate from the scavenger that passed through the suppressor. We thought that a sodium hydroxide eluent would give a system peak only of sulphate (from scavenger). However, it was difficult to avoid contamination of volatile anionic compounds, and some system peaks were observed (mainly carbonate, chloride and nitrite). Furthermore, since 10 mM sulphuric acid was required to suppress the sodium ion in the sodium hydroxide eluent, the resulting system-peak height of sulphate was 10-fold higher than that obtained with the sodium carbonate–bicarbonate eluent. Thus we selected the latter. The large carbonate peak was reduced by washing the concentrator column with water before reinjection^{19,21}, but interference in the determination of chloride and nitrite was still present.

Suppressor and scavenger for recycle IC

The system peak from sulphate was minimized by the use of an AMMS and 2.5 mM sulphuric acid as a scavenger. In our previous study²¹ an anion fibre suppressor (AFS) and 50 mM dodecylbenzenesulphonic acid (DBS) as a scavenger were used. Since the AMMS had a higher efficiency of cation suppression, and caused smaller diffusion of analyte than did the AFS, the former was used in this study. Sulphuric acid was used as a scavenger because the AMMS did not suppress cations sufficiently with DBS as a scavenger.

Recycle IC system

The recycle system B was developed to cancel any system peak. As system A concentrated an objective anion together with other anions on the top of the concentrator, eluent was pumped in the reverse direction to that for the collection. The system B collected separated anions with the same matrix as the eluent. Eluent was pumped in the same direction as that used for the collection.

Times to start and stop the collection in system A were the same as the beginning and ending of an objective anion peak, because the analyte was collected just behind the detector cell. In system (B), since the objective anion was collected just behind the separator column, and it took 12 s to flow from the back of the separator to the detector, collection times were 12 s earlier than the beginning and ending of an objective anion peak.

The peak heights of reinjected anions in recycle systems A and B were 95–98 and 30–35%, respectively, of the peak height obtained by conventional IC. The low recovery in system B resulted from diffusion caused by passing the separator twice without any concentration procedure.

Determination of trace anions in inorganic acids

Fig. 2a shows a chromatogram of diluted phosphoric acid (1/400). A broad peak

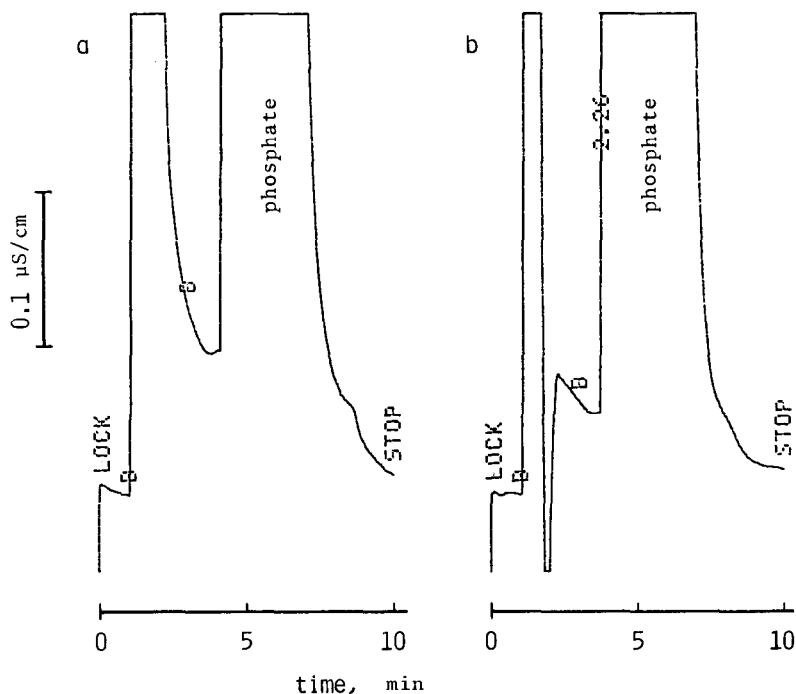


Fig. 2. Chromatograms of diluted orthophosphoric acid (1/400): (a) without neutralization; (b) neutralized with sodium hydroxide.

appeared just behind a water dip and interfered with the determination of trace chloride and nitrite even though recycle system B was used. We believe that this broad peak is due to carbonate that is extruded by a large amount of phosphate. The same phenomenon was observed for other acids. This broad peak disappeared upon neutralization of sample acids with sodium hydroxide as shown in Fig. 2b. The neutralization was not needed for the determination of anions by recycle system A, but was necessary to avoid damage of the separator column by acidic samples.

Fig. 3 shows an example of chromatograms in which 30 ppm of bromide in concentrated hydrochloric acid were determined by recycle system A. Fig. 4 shows an example of the determination of 6.0 ppm of chloride and 7.8 ppm of nitrite in concentrated phosphoric acid by recycle system B. Both systems were effective in separating and determining hidden peaks of analyte behind a large peak of sample acid.

The results of the determination of trace anions in hydrochloric, nitric, phosphoric and sulphuric acids are shown in Tables III–VI. Chloride and nitrite were determined simultaneously by recycle system B. Bromide and nitrate were determined simultaneously, and sulphate was determined separately by recycle system A. The recoveries of each anion were in the range of 95–103% with a relative standard deviation (R.S.D.) of 0.4–5.2%.

To determine sulphate by recycle system A, the system-peak height of sulphate should first be determined. Since the system-peak height had high reproducibility, the

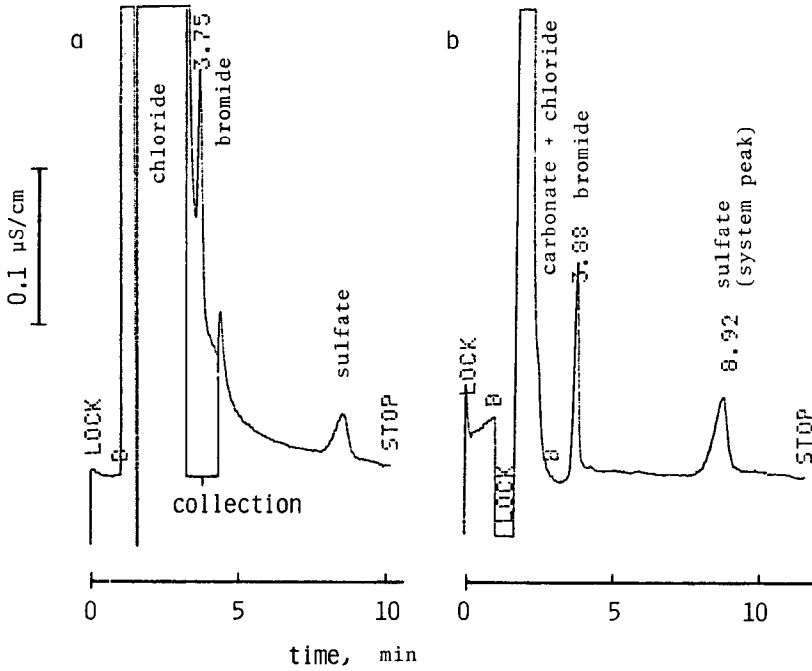


Fig. 3. Determination of bromide ion (30 ppm) in concentrated hydrochloric acid by recycle system A. The chromatograms show (a) collection, (b) reinjection.

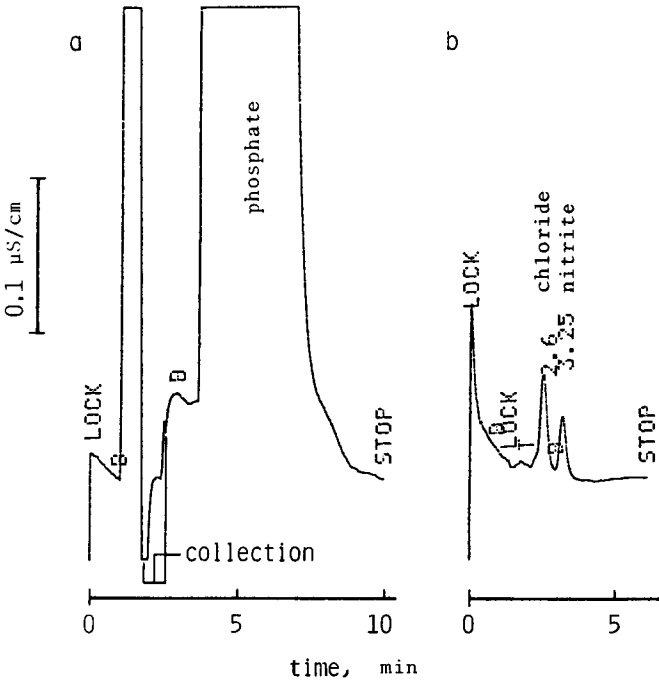


Fig. 4. Determination of chloride ion (6.0 ppm) and nitrite ion (7.8 ppm) in concentrated orthophosphoric acid by recycle system B. The chromatograms show (a) collection, (b) reinjection.

TABLE III
RECOVERY OF TRACE ANIONS IN CONCENTRATED HYDROCHLORIC ACID

Objective anion	Concentration (ppm)		Recovery (%)	R.S.D. (%)	n
	Added	Found			
Bromide	0	19.24	—	0.82	4
	6.45	25.77	101.2	0.54	6
Nitrate	0	0.10	—	5.22	4
	5.0	5.12	100.4	1.05	6
Sulphate	0	1.97	—	4.93	4
	10.0	12.30	103.3	2.02	6

TABLE IV
RECOVERY OF TRACE ANIONS IN CONCENTRATED NITRIC ACID

Objective anion	Concentration (ppm)		Recovery (%)	R.S.D. (%)	n
	Added	Found			
Chloride	0	1.62	—	4.73	4
	3.0	4.58	98.7	3.17	5
Nitrite	0	0.00	—	0	4
	3.89	3.78	97.2	2.81	5
Sulphate	0	1.89	—	4.28	4
	10.0	12.20	103.1	1.69	6

TABLE V
RECOVERY OF TRACE ANIONS IN CONCENTRATED PHOSPHORIC ACID

Objective anion	Concentration (ppm)		Recovery (%)	R.S.D. (%)	n
	Added	Found			
Chloride	0	0.00	—	0	3
	3.0	2.92	97.3	2.83	5
Nitrite	0	0.00	—	0	3
	3.89	3.85	99.0	2.53	5
Bromide	0	0.00	—	0	4
	6.45	6.49	100.6	2.01	6
Nitrate	0	0.00	—	0	4
	5.0	5.12	102.4	1.74	6
Sulphate	0	12.48	—	4.37	4
	10.0	22.76	102.8	0.39	6

TABLE VI
RECOVERY OF TRACE ANIONS IN CONCENTRATED SULPHURIC ACID

Objective anion	Concentration (ppm)		Recovery (%)	R.S.D. (%)	n
	Added	Found			
Chloride	0	0.91	—	4.45	4
	3.0	3.75	94.7	2.93	5
Nitrite	0	0.00	—	0	4
	3.89	3.78	97.2	2.19	5
Bromide	0	0.00	—	0	4
	6.45	6.55	101.6	1.13	6
Nitrate	0	0.00	—	0	4
	5.0	4.84	96.8	1.54	6

lower determination limit was less than that obtained by system B. Sulphate was determined by system B without any system peak, but the recovery was *ca.* 30%.

We could not determine data for phosphate because the recovery of phosphate by recycle system A was 70–75% even for standard phosphate in the absence of any other anion. Furthermore, the recovery of phosphate by conventional IC was reduced by the coexistence of large amounts of other anions.

Table VII shows the detection limit of anionic impurities in concentrated inorganic acids by recycle IC. The value for sulphate was defined as three times the standard deviation of the system-peak height, and those for other anions were defined at a signal-to-noise ratio of 3. Each value was lower or equivalent to the limit of anionic impurities according to JIS²². An objective anion would be separated completely from very large amounts of coexisting anions by repeated recycling, and thus the detection limits might be improved.

TABLE VII
DETECTION LIMITS OF TRACE ANIONS IN CONCENTRATED ACIDS BY RECYCLE ION CHROMATOGRAPHY

Sample acid	Detection limit (ppm)				
	Chloride	Nitrite	Bromide	Nitrate	Sulphate
HCl	—	— ^a	0.50	0.41	0.32
HNO ₃	0.25	0.49	— ^a	—	0.54
H ₃ PO ₄	0.42	0.82	0.70	0.57	0.91
H ₂ SO ₄	0.39	0.77	0.32	0.26	—

^a No data.

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