# Simultaneous determination of bromide and iodide ions by capillary isotachophoresis using quaternary ammonium salts

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## Abstract

Bromide and iodide ions were determined simultaneously by capillary isotachophoresis using an aqueous electrolyte system; the separation principle was based on the ion-pairing equilibria between tetradecyldimethylbenzylammonium ion and these anions in the leading electrolyte. The interaction between iodide ion and tetradecyldimethylbenzylammonium ion was stronger than that for bromide ion. Thus complete separation of bromide and iodide ions could be obtained by using a leading electrolyte containing 1.5 m$M$ tetradecyldimethylbenzylammonium ion. The pH of the leading electrolyte was adjusted to 5.0. The relative standard deviations of the zone length for bromide and iodide ions were 1.1 and 1.2%, respectively, when mixture of 3.0 m$M$ of these ions was analysed. A 150-$\mu$l volume could be injected for the simultaneous determination of low concentrations of bromide and iodide ions.

*Keywords:* Isotachophoresis; Buffer composition; Bromide; Iodide; Quaternary ammonium compounds

## 1. Introduction

It is difficult to separate chloride, bromide and iodide ions by capillary isotachophoresis with ordinary leading electrolytes because their ionic mobilities are approximately equal in aqueous solutions [1]. The halide ions have been separated by using methanol instead of water as a solvent [2] or by complex formation with cadmium ion [3]. Madajová et al. [4] suggested the possibility of separating halide ions using the interaction with poly(vinylpyrrolidone) and applied their method to the determination of iodide ion in mineral water. In our previous paper [5] it was shown that with a leading

electrolyte containing 20 m$M$ $\alpha$-cyclodextrin (CD), iodide ions were completely separated from chloride ions but bromide ions were not. Yoshida et al. [6] demonstrated a decrease of the effective mobilities of molybdate, tungstate and vanadate ions using the ion-pairing equilibria between quaternary ammonium ions, such as tetradecyldimethylbenzylammonium and cetyltrimethylammonium ions, and these anions. Also Hine and Yagi [7] demonstrated a decrease of the effective mobilities of heptanoic acid and octanoic acid using the interaction between dodecyltrimethylammonium ion and these anions.

In this work, first the following analytical conditions were examined for the simultaneous determination of bromide and iodide ions by capillary isotachophoresis using the ion-pairing equilibria

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between the quaternary ammonium ions and these anions: type and concentration of the quaternary ammonium salt, and pH of the leading electrolyte. Then, the injection of a large volume of sample solution was examined for the determination of low concentrations of bromide and iodide ions.

# 2. Experimental

## 2.1. Apparatus

A Shimadzu (Kyoto, Japan) Model IP-2A iso-tachophoretic analyser was used with a potential gradient detector. The main column was a fluorinated ethylene–propylene (FEP) copolymer tube (15 cm× 0.5 mm I.D.), and the precolumn was a polytetra-fluoroethylene (PTFE) tube (15, 20 or 30 cm×1.0 mm I.D.). The thermostat was maintained at 20°C. A Hamilton (Reno, NV, USA) 1701-N, 1710-N or 1725-N microsyringe was used for the injection of samples into the isotachophoretic analyser. A Uni-cam Analytical Systems (Cambridge, UK) PW9421 pH meter was used. Distilled, demineralized water was obtained from a Yamato-Kagaku (Tokyo, Japan) Model WG220 automatic still and a Nihon Millipore (Tokyo, Japan) Milli-Q II system.

## 2.2. Reagents

All reagents were of analytical-reagent grade and used as received. Distilled, demineralized water was used throughout. Cetyldimethylbenzylammonium chloride (CDMBA), stearyltrimethylammonium chloride (STMA), cetyltrimethylammonium chloride (CTMA), tetradecyltrimethylammonium chloride (TDTMA), dodecyltrimethylammonium chloride (DDTMA) and sodium hexanoate were obtained from Tokyo Chemical Industry (Tokyo, Japan). Tetradecyldimethylbenzylammonium chloride (Zeph) and hydroxypropyl methylcellulose (HPMC) were obtained from Aldrich (Milwaukee, WI, USA). Tetrabutylammonium chloride (TBA) and histidine were obtained from the Nacalai Tesque (Kyoto, Japan). The abbreviations of quaternary ammonium salts are quoted from a paper by Motomizu et al. [8].

# 3. Results and discussion

## 3.1. Type of quaternary ammonium salt

The effects of the type of quaternary ammonium salt in the leading electrolyte on the potential unit (PU) values for bromide and iodide ions were examined. The PU value is one of the qualitative parameters, and is defined by the equation [9]

$$PU = \frac{PG_A - PG_L}{PG_T - PG_L} \tag{1}$$

where PG is the potential gradient and the subscripts denote quantities relating to analyte (A), leading (L) and terminating (T) ions, respectively. The leading electrolyte was an aqueous solution containing 5 m$M$ hydrochloric acid, 0.01% (w/w) HPMC and 1.5 m$M$ of one of the quaternary ammonium salts shown in the Section 2.2. The pH of the leading electrolyte was adjusted to 5.0 with histidine. The terminating electrolyte was 10 m$M$ sodium hexanoate solution. Volumes of 5 μl of solutions containing 1.0 m$M$ bromide ion, 1.0 m$M$ iodide ion or their mixtures were injected into the isotachophoretic analyser. The migration current was maintained at 200 μA for the first 13 or 14 min and then reduced to 50 μA. The length of the precolumn was 15 cm. The PU values for bromide and iodide ions were zero when DDTMA or TBA were used, as shown in Fig. 1. That is to say, bromide and iodide ions were not separated from the leading ion (chloride ion). Only iodide ion was detected when STMA or TDTMA were used. Both anions were separately detected when CDMBA, Zeph or CTMA were used; the PU values for bromide and iodide ions and their differ-ence were largest when Zeph was used. These anions were completely separated with the leading elec-trolyte containing Zeph, as shown in Fig. 2. There-fore, Zeph was used in all subsequent experiments.

## 3.2. Effect of pH of leading electrolyte

The pH of the leading electrolyte containing 1.5 m$M$ Zeph was varied in the range 4.5–6.5 with histidine; no different types of counter ions were used in order to evaluate only the effect of the pH. Both PU values for bromide and iodide ions in-
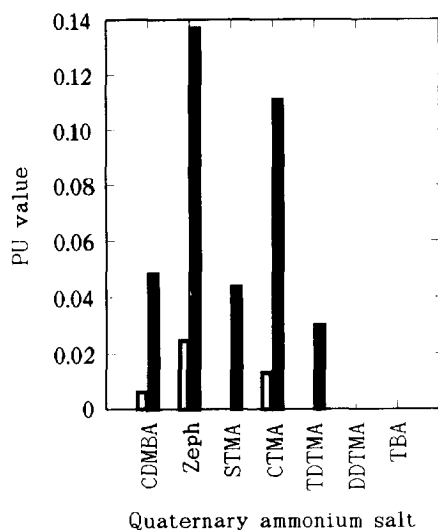
Fig. 1. Effects of the type of quaternary ammonium salt on the PU values for bromide and iodide ions. The pH of the leading electrolyte was 5.0; the concentration of the quaternary ammonium salts was 1.5 mM. (□) Br⁻; (■) I⁻.
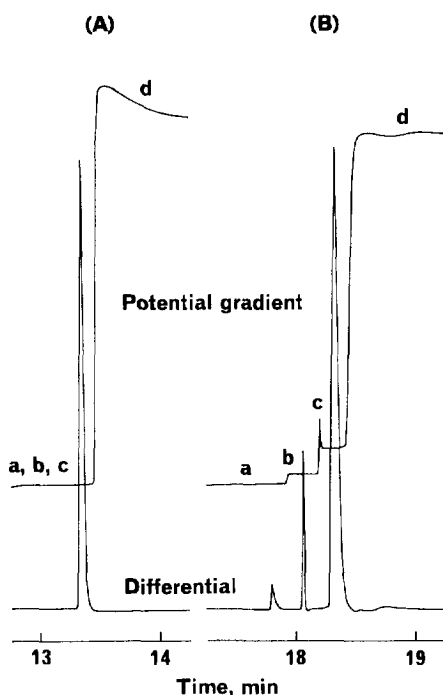


Fig. 2. Isotachopherograms for bromide and iodide ions. The pH of the leading electrolyte was 5.0. (A) Without Zeph; (B) with 1.5 mM Zeph. (a) Cl⁻; (b) Br⁻; (c) I⁻; (d) C₅H₁₁COO⁻.
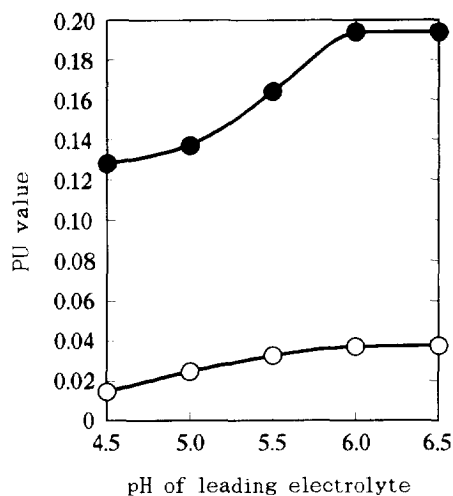


Fig. 3. Effect of pH of the leading electrolyte on the PU values for bromide and iodide ions. The concentration of Zeph was 1.5 mM. (○) Br⁻; (●) I⁻.

creased with pH up to pH 6.0, and then almost levelled off, as shown in Fig. 3. Isotachopherograms of the solution containing 1.0 mM iodide ion are shown in Fig. 4. Only one zone of iodide ion was obtained with the use of leading electrolyte adjusted to pH 5.0. On the other hand, two zones, other than the main zone corresponding to iodide ion, were observed when the pH was 5.5 or above. This may suggest the existence of some ionic species other than iodide ion. In our previous paper [10], where periodate ion was analysed by isotachophoresis, two zones were observed using histidine hydrochloride as the leading electrolyte; on the other hand, only one zone of periodate ion was obtained using hydrochloric acid with β-alanine as the leading electrolyte. Therefore, the above phenomena observed at pH of 5.5 or above might be some effect of histidine. The length of the main zone decreased and those of the other zones increased with the pH of the leading electrolyte. Therefore, pH 5.0 was adopted as the optimum pH of the leading electrolyte for the determination of bromide and iodide ions.

### 3.3. Effect of concentration of Zeph

The concentration of Zeph in the leading electrolyte adjusted to pH 5.0 was varied in the range 0.5–2.5 mM. Bromide ion was not detected when the
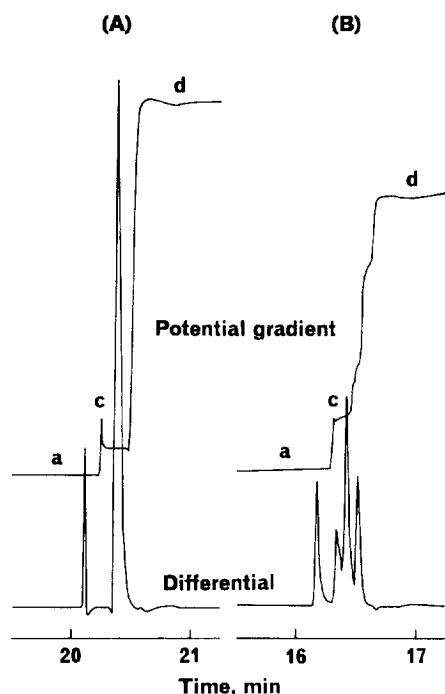
**(A)**                    **(B)**



Fig. 4. Isotachopherograms for iodide ion. The concentration of Zeph was 1.5 m$M$. (A) pH 5.0; (B) pH 6.5. Zone symbols are the same as in Fig. 2.

Zeph concentration was 1.0 m$M$ or below and was detected when it was 1.5 m$M$; the PU value for bromide ion was almost constant when the Zeph concentration was 1.5–2.5 m$M$. On the other hand, iodide ion was detected when the Zeph concentration was 0.5 m$M$; the PU value for iodide ion increased with the Zeph concentration up to 1.0 m$M$, but then almost levelled off. Some zones, other than the main zone corresponding to iodide ion, were observed when the Zeph concentration was 2.0 m$M$ or above, in a similar manner as described in Section 3.2. The length of the main zone decreased and those for the other zones increased with the Zeph concentration. Therefore, 1.5 m$M$ was selected as the Zeph concentration in the leading electrolyte.

### 3.4. Determination of bromide and iodide ions

Regression equations relating zone-length response ($y$; mm) to concentration ($x$; 0–0.5 m$M$)

were: $y = 11.7x + 0.4$ (correlation coefficient 0.9998) for bromide ion; $y = 9.9x + 0.6$ (0.9997) for iodide ion using the leading electrolyte containing 1.5 m$M$ Zeph and adjusted to pH 5.0. The recording speed was adjusted to 40 mm/min. The length of the precolumn was 20 cm. Table 1 summarizes the limits of detection (LODs) and the relative standard deviations (R.S.D.s) of the PU value and zone length for bromide and iodide ions. LOD is defined as three times the standard deviation of the standard solution containing 3.0 m$M$ bromide and iodide ions. When 5-μl volumes of solutions containing various concentrations of bromide and iodide ions were injected and analysed by use of the calibration graphs, the error was ±10% or below. Calibration graphs for bromide and iodide ions were linear up to 5.0 and 50 m$M$, respectively. A mixed zone with the leading ion was observed when the concentration of bromide ion was 6.0 m$M$ or above.

### 3.5. Determination of low concentrations of bromide and iodide ions

In general, it is necessary to increase the injection volume when an analyte concentration in sample solutions is low. The volume of sample injected into the isotachophoretic analyser was varied in the range 5–100 μl. A solution of 0.10 m$M$ bromide ion or 0.10 m$M$ iodide ion was used as sample. Both calibration graphs were linear up to 75 μl. The regression equations relating zone-length response ($y$; mm) to injection volume ($x$; 5–75 μl) for bromide and iodide ions were $y = 0.208x + 0.9$ (correlation coefficient 0.9999) and $y = 0.194x - 0.7$ (0.9994), respectively. Migration was stopped at the injection volume of 100 μl because of the unusual

Table 1
Detection limits and relative standard deviations of PU values and zone length for bromide and iodide ions

| Sample[a] | LOD (m$M$) | R.S.D. (%)[b] | |
|---|---|---|---|
| | | PU value | Zone length |
| Br | $9.8 \cdot 10^{-2}$ | 3.8 | 1.1 |
| I | $1.1 \cdot 10^{-1}$ | 2.6 | 1.2 |

[a] 3.0 m$M$ Br$^-$ + 3.0 m$M$ I$^-$.
[b] Number of determinations, 8.

increase of migration voltage. The maximum injection volume was 75 μl in the present conditions. Linear calibration graphs were obtained for lower concentrations of bromide and iodide ions with the injection of 75 μl of standard solutions. The concentrations of these anions were 1/20 of those for the 5-μl injection. The regression equations were: $y = 163x - 0.4$ ($0 \leq x \leq 0.25$ mM, correlation coefficient 0.9994) for bromide ion; $y = 135x$ (1.0000) for iodide ion. The slopes of these equations for bromide and iodide ions were almost equal to those of the equations obtained by injecting 5 μl of the standard solutions respectively, if the concentrations were converted to the absolute amounts injected into the analyser. The LODs and R.S.D.s for bromide and iodide ions are shown in Table 2. LOD is calculated from the standard deviation of the standard solution containing 0.15 mM bromide and iodide ions. The R.S.D. of the PU value for bromide ion was relatively large. This seems to be due to the small PU value for bromide ion. Various concentrations of bromide and iodide ions were determined by injecting 75-μl volumes of solutions. The error was ±6.0% or below, as evident in Table 3.

### 3.6. Further increase of injection volume

As described above, it was impossible to inject 100 μl of sample solution. The possibility of further increasing injection volume was examined. Usually a PTFE tube (30 cm×1.0 mm I.D.) was used to connect the terminating-electrolyte reservoir and the injection block in the analyser (shaded tube in Fig. 5). At first a sample solution injected into the analyser is kept within the shaded tube. If a larger volume of PTFE tube can be used in this part, an

Table 2
Detection limits and relative standard deviations of PU values and zone length for low concentrations of bromide and iodide ions

| Sample[a] | LOD (mM) | R.S.D. (%)[b] | |
|---|---|---|---|
| | | PU value | Zone length |
| Br⁻ | 4.0·10⁻³ | 7.8 | 0.93 |
| I⁻ | 4.1·10⁻³ | 3.9 | 0.94 |

[a] 0.15 mM Br⁻ +0.15 mM I⁻.
[b] Number of determinations, 8.

Table 3
Analytical results for bromide and iodide ions

| Mixture | Added (mM) | | Found (mM) | | Error (%) | |
|---|---|---|---|---|---|---|
| | Br⁻ | I⁻ | Br⁻ | I⁻ | Br⁻ | I⁻ |
| 1 | 0.050 | 0.050 | 0.052 | 0.048 | +4.0 | −4.0 |
| 2 | 0.050 | 0.25 | 0.047 | 0.25 | −6.0 | 0.0 |
| 3 | 0.10 | 0.10 | 0.098 | 0.099 | −2.0 | −1.0 |
| 4 | 0.10 | 0.20 | 0.097 | 0.20 | −3.0 | 0.0 |
| 5 | 0.15 | 0.15 | 0.15 | 0.15 | 0.0 | 0.0 |
| 6 | 0.20 | 0.10 | 0.20 | 0.094 | 0.0 | −6.0 |
| 7 | 0.25 | 0.050 | 0.25 | 0.047 | 0.0 | −6.0 |

increase of the injection volume up to more than 100 μl can be obtained [11]. Therefore, the PTFE tube (30 cm×1.0 mm I.D.) was replaced by a PTFE tube (30 cm×2.0 mm I.D.). In addition, the length of the precolumn was increased to 30 cm. The standard solution containing 0.10 mM bromide ion or 0.10 mM iodide ion was injected into the analyser with a volume of 50–150 μl. Both calibration graphs were linear up to 150 μl. The regression equations for bromide and iodide ions were $y = 0.215x + 1.1$ (correlation coefficient 0.9996) and $y = 0.196x$ (0.9999), respectively. The slopes of these equations for bromide and iodide ions were almost equal to those of the equations obtained by injecting 5–75 μl of the standard solutions, respectively. When a 150-μl volume of the mixed solution of 0.10 mM bromide and iodide ions was injected and analysed, the errors for bromide and iodide ions were +0.6 and −3.7%, respectively.
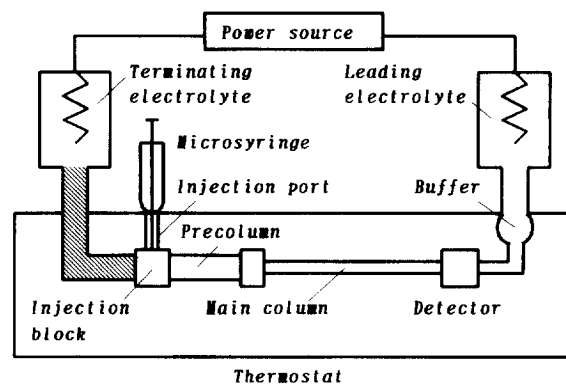


Fig. 5. Schematic diagram of the analyser used in this experiment.

The use of the ion-pairing equilibria between tetradecyldimethylbenzylammonium ion and bromide and iodide ions was effective for the isotachophoretic determination of these anions. The modification in the analyser described above was also effective for the increase of the injection volume to determine low concentrations of these anions by capillary isotachophoresis.

## Acknowledgments

## References

[1] Chemical Society of Japan, Kagaku Binran, Maruzen, Tokyo, 3rd ed., 1984, p. II 460.

[2] J.L. Beckers and F.M. Everaerts, J. Chromatogr., 51 (1970) 339.

[3] P. Boček, I. Miedziak, M. Deml and J. Janák, J. Chromatogr, 137 (1977) 83.

[4] V. Madajová, E. Turcelová and D. Kaniansky, J. Chromatogr., 589 (1992) 329.

[5] K. Fukushi and K. Hiiro, J. Chromatogr., 518 (1990) 189.

[6] H. Yoshida, M. Hida and M. Taga, J. Chromatogr., 325 (1985) 179.

[7] T. Hine and T. Yagi, Proc. 11th Symp. Capillary Electrophoresis, Tokyo, December, 1991, Japan Discussion Group of Electrophoretic Analysis, Japan Soc. Anal. Chem. Tokyo, 1991, p. 5.

[8] S. Motomizu, S. Hamada and K. Toei, Bunseki Kagaku, 32 (1983) 648.

[9] H. Miyazaki and K. Kato, Tosoku-Denki-Eido-Ho (Isotachophoresis, in Japanese), Kodansha Scientific, Tokyo, 1980, p. 30.

[10] K. Fukushi and K. Hiiro, J. Chromatogr. A, 684 (1994) 343.

[11] S. Kobayashi, pers. comm.