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Short communication

## High-sensitivity conductivity detection in non-suppressed ion chromatography using sulfoisophthalic acid as eluent

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### Abstract

A non-suppressed ion chromatographic (IC) system for the high-sensitivity detection of common anions was developed using sulfoisophthalic acid as the eluent. The detection sensitivity was ten times higher than that using conventional non-suppressed IC with sodium phthalate as eluent, and was almost the same as that using conventional suppressed IC with a carbonate–hydrogencarbonate eluent under the same electrical conditions with a conductivity detector. Temperature regulation was very important in minimizing the baseline drift. A commercial incubator, in which a separation column and a sample injector were placed, was useful. The developed non-suppressed system facilitated the determination of low concentrations of phosphate, chloride, bromide, nitrate and sulfate at micromolar levels.

**Keywords:** Detection, LC; Conductivity detection; Sulfoisophthalic acid; Phosphate; Chloride; Bromide; Nitrate; Sulphate

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### 1. Introduction

Two kinds of pseudo peaks, the first and the second system peaks, often appear in addition to analyte peaks in non-suppressed anion-exchange chromatography [1–3]. The detection sensitivity for analyte ions depends on the detection system, the eluent composition (acid or salt) and their elution position relative to the second system peak, which originates from the change in partition equilibrium of the conjugate acid of the eluent ion between the stationary and mobile phases [2,4]. When analyte ions are eluted before

the second system peak, an acid eluent gives smaller peaks of the analytes than a salt eluent does in indirect photometric detection. In contrast, the peak intensities are increased in conductivity detection with an acid eluent. The reason for the difference in sensitivity is that the analyte ions are eluted together with part of the conjugate acid of the eluting ion distributed in the stationary phase.

In previous work [5], 0.2 mM 1,2-dihydroxybenzoic-3,5-disulfonic acid was used as an eluent for the separation of common anions with TSKgel IC-Anion-PW. Since sulfate ion, one of the important common anions, eluted on the front shoulder of the second system peak, its

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determination was difficult. Therefore, it is necessary to select some other compound that can elute sulfate ion faster than the second system peak. The volume range from the void volume to the retention volume of the second system peak can be thought as a "window" for high-sensitivity detection with acid eluents. The width of this window is mainly determined by the combination of the eluent acid and the stationary phase used.

This paper describes the selection of the eluting acid for the sensitive detection of common anions. The resulting sensitivity was compared with those of two conventional methods, non-suppressed and suppressed ion chromatography (IC).

## 2. Experimental

### 2.1. Chromatography

The IC system consisted of a Tosoh (Tokyo, Japan) CCPM pump, a Tosoh CM-8020 conductivity detector, a Rheodyne (Cotati, CA, USA) Model 7125 injector with a 100- $\mu$ l sample loop and a modified Yamato (Tokyo, Japan) IC-400 incubator (450  $\times$  400  $\times$  400 mm) as a column oven. The injector and the separation column were installed inside the incubator and connected with Teflon tubing of length 500 mm. All separations were carried out at ambient temperature (ca. 25°C) or at 30°C (controlled). The separation column was a Tosoh TSKgel IC-Anion-PW (50  $\times$  4.6 mm I.D., particle size 10  $\mu$ m) and the suppressor column used was a glass column (70  $\times$  6 mm I.D.) packed with Dowex 50W-X8 cation-exchange resin (200–400 mesh) (Dow Chemical). The flow-rate was 1.0 ml/min throughout the experiments.

### 2.2. Reagents

All chemicals were of analytical-reagent grade and used without further purification. Deionized water was passed through an Organo (Tokyo, Japan) PURIC-Z water-purification system before use. Sodium salts of *o*-sulfobenzoic, 2-naph-

thol-3,6-disulphonic and 5-sulfoisophthalic acids were purchased from Tokyo Kasei (Tokyo, Japan), and were converted into their free acids through an open column packed with Dowex 50W-X8 cation-exchange resin. Trimellitic, 4-sulphophthalic and sulfosalicylic acids were obtained from Tokyo Kasei. A 10 mM solution of each acid was prepared in advance. The eluent acidity was changed by changing the mixing ratio of the acid and the salt reagents, instead of adding strong acid or strong base. Common anions used were  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$ , which were obtained from Wako (Osaka, Japan) or Tokyo Kasei as their sodium or potassium salts.

## 3. Results and discussion

### 3.1. Selection of eluent

The desirable requirements of the eluent acid for the high-sensitivity detection in non-suppressed IC are as follows: (1) the eluting power of the acid should be strong at a lower concentration, which leads to lower background conductivity; (2) the equivalent conductivity of the eluting anion ( $\lambda_E$ ) should be significantly smaller than those of the analyte anions ( $\lambda_A$ ), which also leads to a lower background conductivity and provides a larger difference in the equivalent conductivities ( $\lambda_E - \lambda_A$ ); (3) the second system peak should appear after the analyte peaks, but within 30 min for practical use; and (4) the acid should be stable in aqueous solution for a long time.

For requirements 1 and 2, polybasic, aromatic organic acids will be candidates. Vautour et al. [6] studied the eluting power of aromatic monocarboxylic acids, and proposed *o*-sulfobenzoic acid as the strongest eluting ion at low pH. For requirement 3, the most essential one for sensitivity enhancement, acids having a large partition coefficient ( $K_d$ ) must be effective for increasing the retention volume of the second system peak. Accordingly, an acid suitable for the present purpose should be a strong electrolyte having hydrophilic functional groups. In

practice, however, it is difficult to find the optimum eluting ion theoretically owing to the lack of  $\lambda$  and  $K_d$  data for various compounds.

To find the most appropriate eluent, we studied the elution characteristics of sulfosalicylic, *o*-sulfobenzoic, 2-naphthol-3,6-disulfonic, 4-sulfophthalic, 5-sulfoisophthalic and trimellitic acids. Retention times of common anions and the second system peak with several different eluent conditions are summarized in Table 1. For the same eluent concentration (0.5 mM), 2-naphthol-3,6-disulfonic acid was the strongest eluent, giving the fastest retention time of the second system peak. This acid, at a concentration of 0.2 or 0.1 mM, satisfied the above requirements 1, 2 and 4 for the eluent, but the separation between sulfate ion and the second system peak was insufficient. 5-Sulfoisophthalic acid was the best candidate for the desired eluent, giving good separations of each analyte and the second

system peak, as shown in Fig. 1. Furthermore, the second system peak appeared within 20 min.

### 3.2. Effect of eluent acidity on the sensitivity in conductivity detection

Fig. 2 shows the effect of the degree of neutralization of 5-sulfoisophthalic acid on the peak-area responses of common anions. The horizontal axis represents the degree of neutralization of the acid, i.e., 0 and 3 mean the acid eluent and the salt eluent, respectively. The measured pH values of the eluent are given in the caption. When the acidity of the eluent is increased, the peak areas are increased for all analytes. This increase in conductivity detection is caused by the co-elution of the acid, predistributed in the stationary phase, together with each

Table 1  
Retention times of common anions and the second system peaks with several acid eluent systems

Compound	Eluent concentration (mM)	Retention time (min) <sup>a</sup>				
		Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Second system peak
5-Sulfoisophthalic acid	0.2	4.0	7.4	8.8	14.6	37.2
	0.5	3.0	4.8	5.9	9.0	17.6
	1.0	2.5	3.7	4.6	7.1	11.0
<i>o</i> -Sulfobenzoic acid	0.2	11.4	23.3 <sup>b</sup>	31.6	>65	21.5
	0.5	9.4	18.6	24.5	>65	13.6
	1.0	7.4 <sup>b</sup>	14.4	19.6	65.0	8.5
Trimellitic acid	0.5	4.9	8.0	10.0	35.6	15.5
	1.0	4.1	6.6	8.1 <sup>b</sup>	27.0	10.5
	1.5	3.9	6.0	7.4 <sup>b</sup>	22.9	9.0
Sulfosalicylic acid	0.1	4.3	6.1	7.7	23.0	15.5
	0.2	3.6	4.7	5.6	13.0	8.9
	0.5	2.5	3.5	4.2 <sup>b</sup>	6.7	5.5
4-Sulfophthalic acid	0.2	3.8	6.2	7.6	28.7	13.4
	0.5	3.1	4.7	5.4 <sup>b</sup>	13.2	6.3
	1.0	2.7	4.5 <sup>c</sup>	5.3	8.2	4.5
2-Naphthol-3,6-disulfophthalic acid	0.1	3.6	4.7	5.4	9.6 <sup>b</sup>	12.2
	0.2	2.5	3.3	3.6	4.6 <sup>b</sup>	6.0
	0.5	1.5	1.8	2.0	2.8 <sup>c</sup>	2.8

<sup>a</sup> Data at ambient temperature (25°C).

<sup>b</sup> Eluted on the shoulder of the second system peak.

<sup>c</sup> Overlapped completely with the second system peak.

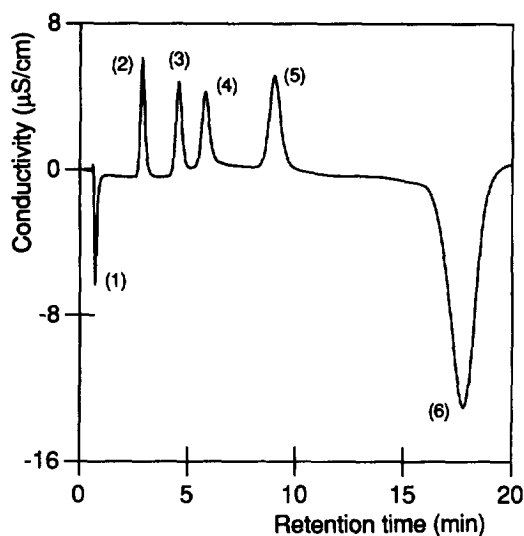


Fig. 1. Chromatogram of chloride, bromide, nitrate and sulfate at 25°C (ambient) with 0.5 mM 5-sulfoisophthalic acid. Analyte concentration: 0.1 mM each. For chromatographic conditions, see text. Peaks: 1 = first system peak; 2 =  $\text{Cl}^-$ ; 3 =  $\text{Br}^-$ ; 4 =  $\text{NO}_3^-$ ; 5 =  $\text{SO}_4^{2-}$ ; 6 = second system peak.

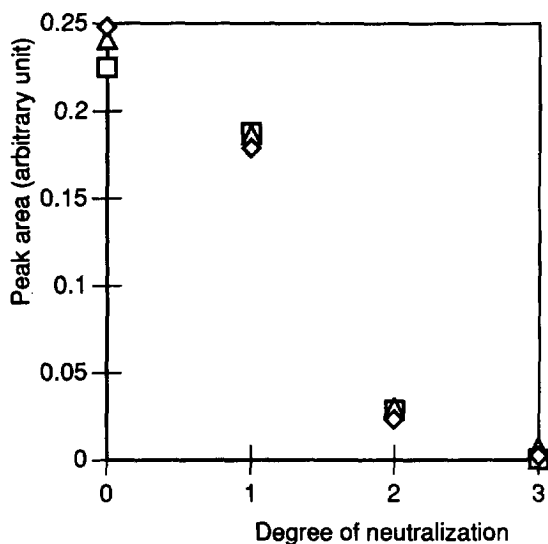


Fig. 2. Peak area vs. degree of neutralization of 5-sulfoisophthalic acid eluent. pH of the eluent: (0) 3.2; (1) 3.5; (2) 4.2; (3) 6.7. Total concentration of the conjugate acid and base: 0.5 mM. Analyte concentration: 0.5 mM each. For chromatographic conditions, see text. □ =  $\text{Cl}^-$ ; Δ =  $\text{Br}^-$ ; ◇ =  $\text{NO}_3^-$ .

analyte. A detailed explanation of this phenomenon will be presented separately [4].

To determine ionic species in the eluent, dissociation constants of 5-sulfoisophthalic acid were determined by measuring the UV absorption spectra of the acid at several different pH values, and  $\text{p}K_2 = 2.0$  and  $\text{p}K_3 = 3.2$  were obtained ( $\text{p}K_1 \ll 1$ ). Since the pH of 0.5 mM 5-sulfoisophthalic acid was 3.2, the ionic composition was concluded to be a mixture of its divalent and trivalent anions. In such a case, it is very difficult to estimate theoretically the magnitude of the sensitivity enhancement, although the increase in sensitivity for analyte peaks can be estimated in a diprotic strong acid eluent system [4]. In any case, it is clear that the sensitivity of common anions is enhanced substantially.

### 3.3. Influence of column temperature

The partition equilibrium of the acid molecule between the stationary and the mobile phases is severely influenced by the column temperature. Particularly in the determination of anions at low concentrations, an undulating chromatographic baseline caused by injection of sample solutions at different temperatures often made precise determinations impossible. In this work, a commercial incubator of large inside capacity was used to control the temperature of the chromatographic line after the pump through the inlet of the detector. Solvent reservoirs can also be placed inside the oven, if necessary. An improved chromatogram obtained at 30°C is shown in Fig. 3.

### 3.4. Comparison with conventional detection methods

The detection sensitivity and the chromatographic reproducibility of the proposed IC system were compared with those of two conventional IC systems, suppressed IC with 1.0 mM  $\text{Na}_2\text{CO}_3$ –1.0 mM  $\text{NaHCO}_3$  and non-suppressed IC with 1.0 mM disodium phthalate (pH 7.0). The term detection sensitivity is used here for the intrinsic sensitivity to the chemical system or

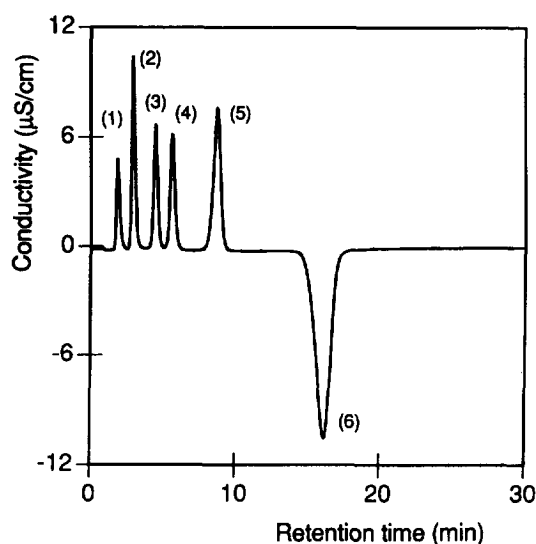


Fig. 3. Chromatogram of six common anions with 0.5 mM 5-sulfoisophthalic acid. The counter cation of the analyte anions was hydrogen ion. Peaks: 1 =  $\text{H}_2\text{PO}_4^-$ ; 2 =  $\text{Cl}^-$  and  $\text{NO}_2^-$ ; 3 =  $\text{Br}^-$ ; 4 =  $\text{NO}_3^-$ ; 5 =  $\text{SO}_4^{2-}$ ; 6 = second system peak. Analyte concentration: 0.1 mM each. column temperature: 30°C. For other conditions, see text.

method, and is independent of the performance of the detector and the data processor used. Therefore, the conductivity detector was used under fixed electrical conditions (gain and conductivity range) throughout all experiments. The separation of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (0.01 mM each, 100- $\mu\text{l}$  injection) was carried out seven times for each IC system. The results are summarized in Table 2. Under the same electrical conditions of a conductivity detector, the peak areas with the proposed acid eluent were approximately ten times larger than those with the phthalate eluent, and were almost the same as those in suppressed IC. The relative standard deviations for peak area were almost the same with all three IC systems.

### 3.5. Problems with acidic eluents

Since the acid eluents have high background conductivity in comparison with the neutralized eluents, the signals from the detector cannot be amplified electrically as sensitively as in sup-

Table 2  
Peak areas, their reproducibilities and detection limits of four common anions in three different IC systems

Analyte	Eluent					
	0.5 mM 5-sulfoisophthalic acid without suppressor (233 $\mu\text{S}/\text{cm}$ ; 0.47 $\mu\text{S}/\text{cm}$ ) <sup>a</sup>		1.0 mM disodium phthalate (pH 7.0) without suppressor (193 $\mu\text{S}/\text{cm}$ ; 0.44 $\mu\text{S}/\text{cm}$ ) <sup>a</sup>		1.0 mM $\text{Na}_2\text{CO}_3$ - 1.0 mM $\text{NaHCO}_3$ with suppressor (11 $\mu\text{S}/\text{cm}$ ; 0.19 $\mu\text{S}/\text{cm}$ ) <sup>a</sup>	
	Area <sup>b</sup>	D.L. <sup>c</sup> (M)	Area <sup>b</sup>	D.L. <sup>c</sup> (M)	Area	D.L. <sup>c</sup> (M)
$\text{Cl}^-$	0.230 (3.1%)	$2.1 \cdot 10^{-8}$	0.0194 (4.4%)	$2.2 \cdot 10^{-7}$	0.236 (1.3%)	$0.9 \cdot 10^{-8}$
$\text{Br}^-$	0.210 (3.0%)	$3.1 \cdot 10^{-8}$	0.0198 (4.2%)	$3.1 \cdot 10^{-7}$	0.224 (4.2%)	$1.4 \cdot 10^{-8}$
$\text{NO}_3^-$	0.210 (3.0%)	$4.0 \cdot 10^{-8}$	0.0180 (4.2%)	$4.4 \cdot 10^{-7}$	0.200 (2.3%)	$1.9 \cdot 10^{-8}$
$\text{SO}_4^{2-}$	0.412 (2.7%)	$2.7 \cdot 10^{-8}$	0.048 (1.4%)	$2.1 \cdot 10^{-7}$	0.484 (2.1%)	$1.1 \cdot 10^{-8}$

Column temperature, 30°C; analyte concentration, 0.01 mM each; for chromatographic conditions, see text.

<sup>a</sup> Background conductivity and baseline noise.

<sup>b</sup> Values in parentheses are R.S.D.s ( $n = 7$ ).

<sup>c</sup> Detection limit ( $S/N = 3$ , 100- $\mu\text{l}$  injection).

pressed IC. Therefore, the present method with the 5-sulfoisophthalic acid eluent does not give the same sensitivity as suppressed IC. In Table 2, the detection limits at  $S/N = 3$  with the present apparatus are shown for comparison.

Under the proposed elution conditions, phosphate ion was eluted before chloride ion, and the peak of nitrite ion overlapped with that of chloride ion, as shown in Fig. 3, while both phosphate and nitrite ions were eluted after chloride ion with the phthalate eluent ( $\text{pH} > 4$ ). At such a low pH (3.2), 90% of phosphate exists as dihydrogenphosphate ion and 50% of nitrite is undissociated. The peak area of nitrite ion was only 40% of that of chloride ion at the same concentration, probably owing to the partial dissociation and the partial decomposition of  $\text{HNO}_2$  at low pH [7]. The separation of  $\text{Cl}^-$  and  $\text{NO}_2^-$  will be improved by using another stationary phase of different selectivity in the ion-exchange reaction.

### 3.6. Effect of sample acidity

In Fig. 3, the first system peak does not appear. The reason is that the analyte ions were

prepared from their free acids [4]. This facilitated the precise determination of fast-eluting ions, as the baseline is so flat. In addition, if a sample solution contains the eluent acid at the same concentration as in the eluent, the second system peak can be eliminated while maintaining the highly sensitive analyte peaks. The developed non-suppressed IC system facilitates the determination of micromolar levels of common anions, and is useful for routine analyses such as in environmental analysis.

### References

- [1] P.E. Jackson and P.R. Hadad, *J. Chromatogr.*, 346 (1985) 125.
- [2] H. Sato, *Anal. Chem.*, 62 (1990) 1567.
- [3] H. Sato and H. Watanabe, *React. Polym.*, 17 (1992) 1.
- [4] H. Watanabe and H. Sato, in preparation.
- [5] H. Sato, *Anal. Chim. Acta*, 206 (1988) 281.
- [6] G. Vautour, M.C. Mehra and V.N. Mallet, *Mikrochim. Acta*, I (1990) 113.
- [7] W.F. Koch, *Anal. Chem.*, 51 (1979) 1571.