

**ION CHROMATOGRAPHY OF COMMON ANIONS
BY USE OF A REVERSED-PHASE COLUMN
DYNAMICALLY COATED
WITH FLUORINE-CONTAINING SURFACTANT**

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ABSTRACT

A method with unusual selectivity has been developed for determination of common anions such as chloride, bromide, nitrite, sulfate, phosphate, and iodide. The method uses with reversed-phase columns (graphite carbon and ODS), coated with fluorine-containing surfactant, and conductivity detection. A graphitized carbon column was selected for this study because of its high chemical stability, reliability, and reproducibility. Separation of common anions was achieved in 12 min. Calibration plots of peak area against anion concentrations were linear in the range 1–15 $\mu\text{g mL}^{-1}$ for Cl^- , 1–20 $\mu\text{g mL}^{-1}$ for Br^- and SO_4^{2-} , and 3–20 $\mu\text{g mL}^{-1}$ for I^- and NO_3^- , with good correlation coefficients ($r^2 = 0.9922$). Detection limits calculated for a signal-to-noise ratio (S/N) of 3 ranged from 0.76 to 0.98 $\mu\text{g mL}^{-1}$. The reproducibility of retention times was varied from 0.28 to 0.45 relative standard deviation (RSD,%) and reproducibility of chromatographic peak areas was 2.13–3.25 (RSD,%). The method was successfully applied to the determination of anions in acid rain and related natural waters, including rain, river, and underground water.

INTRODUCTION

Ion chromatography (IC) has been widely used as a useful and powerful tool for analysis of anionic and cationic components in waters related to acid rain [1,2]. Continuous analysis of the ionic components of acid rain water is important for estimation of the effect of the acidification of natural and urban environments caused by acid rain. It is strongly believed

that acid rain is a widespread environmental pollution problem in Europe, North America, and East Asia, including Japan. It is worth developing a suitable approach for monitoring acid rain and related environmental waters. A variety of methods have been proposed for determination of anions in natural waters, but few of them are rapid, sensitive, and accurate. Ion chromatography (IC) is the most popular and powerful tool for analysis of environmental samples [3–6], because of its high accuracy and reliability. Chemically suppressed IC has been recently recognized by the US Environmental Protection Agency (EPA) as the method of choice for determination of anions in natural water. Tanaka et al. have published several papers on the determination of anions and cations in acid rain water by use of ion-exclusion/cation exchange chromatography on a weakly acidic cation-exchange resin and a weakly acidic anion-exclusion column [7–9]. Although ODS columns have usually been used for determination of anions, ODS has the disadvantage of low chemical resistance and stability because the silica base tends to dissolve under alkaline conditions, which makes such columns incompatible with the mobile phase used with suppressed conductivity detection. Graphitized carbon columns have unique properties compared with silica-based packing materials and ion-exchangers, the matrices of which are organic polymers. Carbon columns are resistant to the strongly acid or alkaline mobile phases and free from swelling in organic solvents. Hoyosa [10] showed that the molecules in graphitized carbon columns have no localized electrons (i.e. they are neutral), except for induced effects, and that the carbon particles had a homogeneous surface [11]. Okamoto et al. used a combination of tetrabutylammonium hydroxide and acetonitrile to optimize the separation of common anions such as F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} , HPO_4^{2-} , and I^- [12]. Nagashima et al. investigated the determination of anions using a graphitized carbon column dynamically coated with cetyltrimethylammonium (CAT) ions [13]. Separation of common anions was complete within 30 min.

Our aim in the work discussed in this communication was to demonstrate the effectiveness of a reversed-phase carbon column coated with a fluorine-containing surfactant for rapid separation of anions. Most reported methods for separation of anions have been achieved by use of cationic surfactant; to the best of our knowledge anionic fluorine-containing surfactants such as that used in this work have not previously been applied for separation of anions. Use of a sulfosalicylic acid mobile phase enabled appropriate resolution with non-suppressed conductivity detection for common anions. After investigation of the effects of different chromatographic

conditions complete separation was achieved within 12 min. We analyzed a series of water samples, to evaluate the technique for real applications. The results obtained by use of this chromatographic system were unexpected, and unusual selectivity was demonstrated in the chromatographic separation of inorganic anions.

EXPERIMENTAL

Reagents and Samples

Sodium fluoride, sodium chloride, sodium bromide, potassium iodide, sodium nitrite, sodium nitrate, ammonium sulfate, and phosphoric acid were purchased from Merck (Darmstadt, Germany). All reagents were of analytical grade. The commercially available surfactant EF-132 (*N*-[3-(perfluorooctanessulfonamide)propyl]-*N,N,N*-trimethylammonium iodide, $C_8F_{17}SO_2NHC_3H_3N^+(CH_3)I^-$, MW 726) was purchased from Jemco (Japan).

All samples of acid rain and other water samples were collected in or near the city of Seto in central Japan. All samples were passed through a 0.45 μm membrane filter before chromatographic analysis.

Chromatography

Dionex (Sunnyvale, CA, USA) equipment with an LC25 column oven were used. Chromatographic data were processed by use of Fujitsu FMV-Biblo software resident in a notebook computer. Two reversed-phase columns were used for separation of inorganic anions, a 100 mm \times 4.6 mm i.d. Hypercarb column packed with 5 μm particles of graphitized carbon and an ODS column. Both columns were coated with fluorine-containing surfactant, and were operated at 40°C. The mobile phases used for IC were 0.26 mM sulfosalicylic acid with the graphitized carbon column and 0.8 mM sodium carbonate–1.0 mM sodium bicarbonate with the ODS column. The flow rate was 1.0 mL min⁻¹, and the injection volume 50 μL . The conductivity detector was used both suppressed and non-suppressed.

Method of Preparing the Separation Column Coated with Fluorine-Containing Surfactant

The two columns were washed with deionized water for 2 h at flow rate of 1.0 mL min⁻¹. The columns were coated with fluorine-containing surfactant by passing an aqueous solution of standard EF-132 (0.5 mM,

200 mL) through the column at a flow rate of 1.0 mL min⁻¹ for 2 h. After dynamic coating, each column was washed with de-ionized water for 2 h, and then conditioned with mobile phase at a constant flow rate of 1.0 mL min⁻¹ until a steady baseline was obtained. The columns were then used for separation of common anions.

RESULTS AND DISCUSSION

Effect on Retention Behavior of Fluorine-Containing Surfactant in Coating Solution

The surface of graphite contains no surface functional groups, hence porous graphite is expected to be a highly reproducible material. In addition, graphite is extremely unreactive and is not affected by aggressive mobile phases such as strong acids and bases. Porous graphitic carbon is also hydrophobic and the surface is suitable for dynamic coating then preparation of different phases [14]. The effect on retention behavior of the concentration of surfactant used for permanent coating was tested in the range 0.25–1.0 mM. When 0.26 mM sulfosalicylic acid was used as mobile phase efficient separation of common anions was accomplished when the graphitized carbon column was coated with 0.5 mM surfactant. Because the surfactant was strongly adsorbed on the surface of the stationary phase, there was no need to add surfactant to the mobile phase. EF-132 surfactant was not removed during at least six months use with acidic and alkaline mobile phases. When silica gel columns were coated in the same way as the graphitized carbon column it was observed that the coating was removed after approximately ten injections when sodium carbonate–sodium bicarbonate was used as mobile phase.

Effect of the Concentration of Sulfosalicylic Acid in the Mobile Phase

Sulfosalicylic acid was used by Tanaka et al. for simultaneous ion-exclusion/cation-exchange separation of anions and cations on weakly acidic cation-exchange resin [15]. Acidic mobile phase was used also for the simultaneous separation of mono- and divalent cations on weakly acidic cation-exchange resins [1,9]. Sulfosalicylic acid, which is both strongly acidic and hydrophobic in nature, was used in this investigation for separation of inorganic anions on a carbon column coated with fluorine-containing surfactant. Sulfosalicylic acid contains three functional groups when diluted, two of these (sulfonic and carboxylic) are dissociated and surrounded by

negative charges and so its hydrophobic absorption and influence on the retention of acids can be neglected. Because the stationary phase contains tetraalkylammonium, however, ion interaction (i.e. formation of ion pairs) with sulfosalicylic acid may occur. This could be the reason for separation of acids. The effect of the concentration of sulfosalicylic acid in the mobile phase on the retention volumes (V_R) of the anions was investigated to optimize the separation conditions. Different concentration of sulfosalicylic acid from 0.26 to 0.51 mM was studied to determine the optimum concentration. V_R values of the anions decreased as the concentration of sulfosalicylic acid in the mobile phase was increased. Relationships between the retention volumes of the anions and sulfosalicylic acid concentration are shown in Fig. 1. For sulfosalicylic acid concentrations from 0.26 to 0.51 mM V_R values remain almost constant; 0.26 mM sulfosalicylic acid was therefore used throughout these experiments.

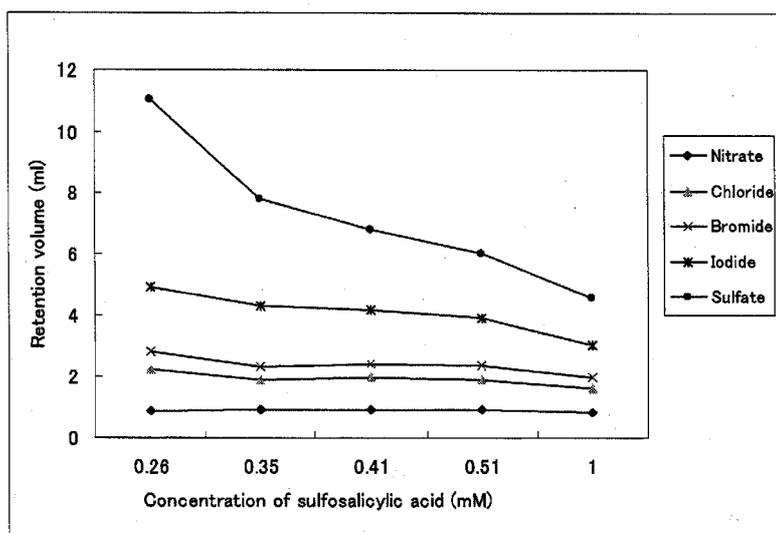


Fig. 1

Effect of sulfosalicylic acid concentration on the retention volumes (V_R) of common anions

Effect of Organic Modifier in Retention Time

It is well known in ion chromatography that addition of an organic modifier produces sharper peaks, reduces retention times, and facilitates phase transfer. In this study, the results obtained were different – addition of modifiers, for example methanol (10–15%), to the sulfosalicylic acid

mobile phase had no significant effect on the chromatographic separation. The life-time of the column coating was, moreover, reduced dramatically when methanol was added to the mobile phase. Methanol was, therefore, excluded from the mobile phase.

Chromatogram of Anions on Graphitized Carbon Column Coated with Fluorine-Containing Surfactant

Figure 2 shows a typical chromatogram obtained from a standard mixture of five inorganic anions, Cl^- , Br^- , NO_3^- , I^- , and SO_4^{2-} by use of the reversed-phase carbon column coated with fluorine-containing surfactant and elution with 0.26 mM sulfosalicylic acid as mobile phase. The reasonable chromatogram obtained shows it is possible to use this column for analysis of anions.

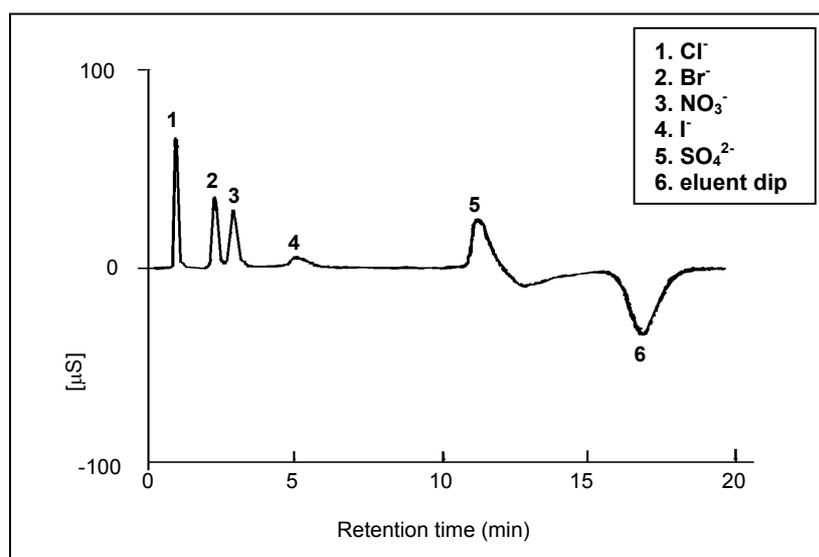


Fig. 2

Anion-exchange chromatogram obtained from common anions ($10 \mu\text{g mL}^{-1}$) on a reversed-phase carbon column coated with fluorine-containing surfactant and eluted with 0.26 mM sulfosalicylic acid. Column conditions: flow rate 1.0 mL min^{-1} , column temperature 40°C , injection volume $50 \mu\text{L}$, non-suppressed conductivity detection. Peaks: 1. Cl^- , 2. Br^- , 3. NO_3^- , 4. I^- , 5. SO_4^{2-} , 6. eluent dip

A most interesting aspect of this separation was the unusual selectivity for Γ^- relative to that for SO_4^{2-} . Haddad and Jackson have obtained unusual selectivity for Γ^- relative to SO_4^{2-} when using 0.5 mM ammonium citrate (pH 6.5) as mobile phase with a methacrylate anion-exchange column (Waters IC Pack A or TSK gel IC PW, 50 mm \times 4.6 mm, i.d., 30 $\mu\text{equiv g}^{-1}$) [16]. One possible contribution to this behavior could be direct interaction between the anions and the graphitized carbon column phase [17]. Another possible cause could be reduced hydrophobic interaction between Γ^- and the fluorinated surfactant.

System Peak

The chromatogram obtained from separation of the inorganic anions contains a negative eluent dip after elution of all the anions. System peaks usually occur in anion-exchange non-suppressed IC. A good discussion of system peak has been given by Haddad and Jackson [18], who indicated that the origin of this peak could be a consequence of:

1. disturbance of column equilibria as a result of injection of the sample;
2. elution of a specific anion; and
3. specific chemical interaction occurring in some mobile phases.

In our study the dip occurred after complete elution of inorganic anions and did not interfere with or overlap the anion peaks.

Chromatogram of Anions on ODS Column Coated with Fluorine-Containing Surfactant

Figure 3 shows a typical chromatogram obtained from a standard mixture of the five anions Cl^- , Br^- , NO_3^- , SO_4^{2-} , and HPO_4^{2-} by use of the ODS column coated with fluorine-containing surfactant and elution with an aqueous solution containing 0.8 mM NaHCO_3 and 1.0 mM Na_2CO_3 . It shows that all the five inorganic anions were separated under these conditions. The chromatographic system obtained was excellent for anion analysis. From Fig. 3 it is apparent that SO_4^{2-} was eluted before HPO_4^{2-} . Although the cause of this unusual selectivity for the anions is not yet clear, it might be because of a direct interaction between anions and the ODS phase or because of reduced hydrophobic interaction.

Behavior of Some Anions on the Coated Graphitized Carbon Column

Nitrite and fluoride were injected on to the coated graphitized carbon column for separation with the five inorganic anions previously sepa-

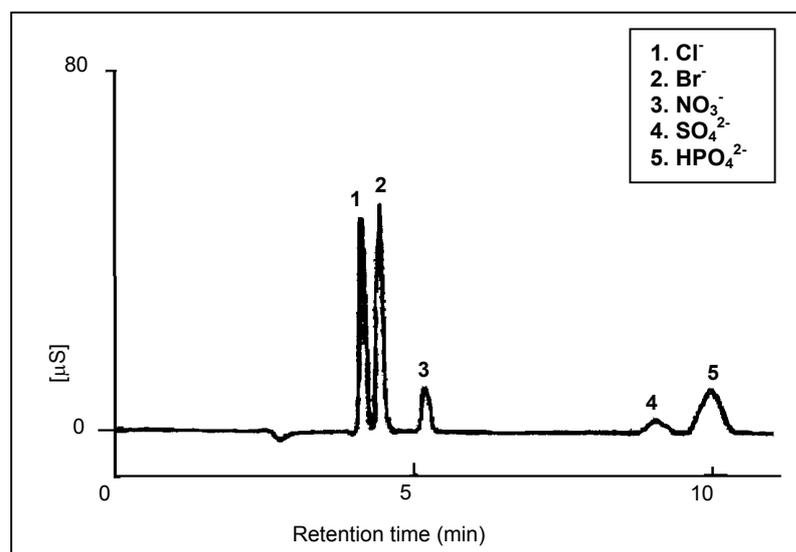


Fig. 3

Anion-exchange chromatogram obtained from common anions ($5 \mu\text{g mL}^{-1}$) on a reversed-phase ODS column coated with fluorine-containing surfactant and eluted with 0.8 mM NaHCO_3 – $1.0 \text{ mM Na}_2\text{CO}_3$, pH 8.2. Column conditions: flow rate 1.0 mL min^{-1} , column temperature 40°C , injection volume $50 \mu\text{L}$, suppressed conductivity detection. Peaks: 1. Cl^- , 2. Br^- , 3. NO_3^- , 4. SO_4^{2-} , 5. HPO_4^{2-}

rated. It was observed that nitrite was not eluted; it is possible it was decomposed/oxidized by the acidic mobile phase. Similarly fluoride (F^-) was not eluted, or maybe it passed unnoticed. This may be because the retention time of F^- depends on mobile phase pH; it may also be because of chemical interaction of the ion with the fluorine-containing coating on the surface of the column. Figures 2 and 3 show that monovalent anions were eluted earlier than divalent anions from coated ODS and carbon columns; this gave the impression that a typical anion-exchange interaction was occurring.

Analytical Performance

Linear calibration plots of peak area against concentration of inorganic anions were obtained. Linearity ranges, correlation coefficients, regression equations, and detection limits ($S/N = 3$) were summarized in Table I. The correlation coefficients for the anions varied from 0.9848 to 0.9982. Detection limits of common anions were between 0.76 and $0.98 \mu\text{g mL}^{-1}$.

These detection limits are suitable for monitoring anions in acid rain and related natural waters, including rain, river, and underground waters.

Table I

Calibration data obtained for the anions by use of the carbon column coated with fluorine-containing surfactant, elution with 0.26 mM sulfosalicylic acid, and use of conductivity detection

Anion	Linear range ($\mu\text{g mL}^{-1}$)	Regression equation	Correlation coefficient (r^2)	Detection limit ($S/N = 3$; $\mu\text{g mL}^{-1}$)
Cl^-	1–15	$Y = 43146X + 74009$	0.9963	0.98
Br^-	1–20	$Y = 114846X - 88726$	0.9908	0.76
I^-	3–20	$Y = 25866X - 27685$	0.9982	3.3
NO_3^-	3–20	$Y = 14546X - 76667$	0.9911	0.99
SO_4^{2-}	1–20	$Y = 147017X + 172946$	0.9848	0.99

The reproducibility of retention times and peak areas under optimum elution conditions are reported in Table II. Relative standard deviations (RSD,%) were calculated for ten chromatographic runs for each anion. The values obtained were between 2.13 and 3.25% and between 0.25 and 0.45% for peak areas and retention times, respectively.

Table II

Relative standard deviation of peak areas and retention times for anions eluted with 0.26 mM sulfosalicylic acid from the reversed-phase carbon column coated with fluorine-containing surfactant

Anion ($5 \mu\text{g mL}^{-1}$)	Peak area RSD (%)	Retention time RSD (%)
Cl^-	3.25	0.45
Br^-	2.52	0.36
I^-	3.15	0.33
NO_3^-	2.93	0.28
SO_4^{2-}	2.13	0.42

Application to Water Samples

The anion-exchange method using a carbon column coated with fluorine-containing surfactant was successfully applied to environmental samples. Acid rain water was injected and three common anions (Cl^- , NO_3^- , SO_4^{2-}) were separated. The chromatogram is presented in Fig. 4.

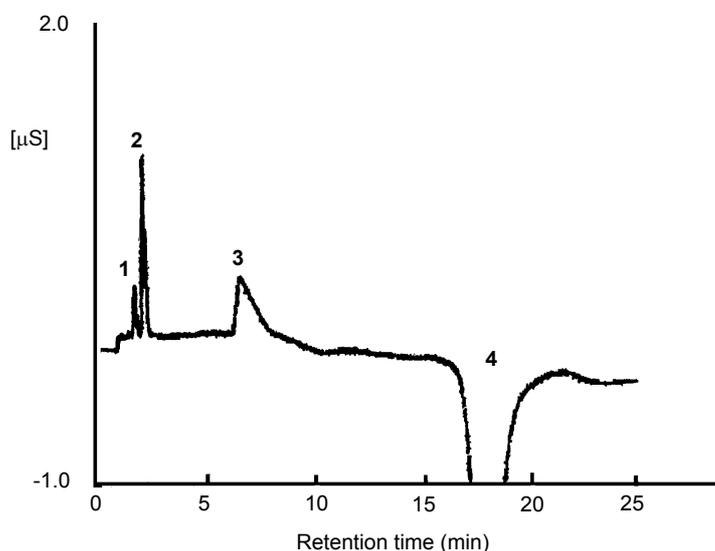


Fig. 4

Anion-exchange chromatogram obtained from anions in acid rain water on a reversed-phase carbon column coated with fluorine-containing surfactant and eluted with 0.26 mM sulfosalicylic acid. Column conditions: flow rate 1.0 mL min^{-1} , column temperature 40°C , injection volume $50 \text{ }\mu\text{L}$, non-suppressed conductivity detection. Peaks: 1. Cl^- , 2. NO_3^- , 3. SO_4^{2-} , 4. eluent dip

CONCLUSION

A chromatographic method with unusual selectivity has been developed for determination of common inorganic anions. The ions were successfully separated on both carbon and ODS columns coated with fluorine-containing surfactant. Organic modifier added to the eluent was without effect on the retention behavior of the anions. Monovalent ions were eluted before divalent ions from both columns, implying that separation was mainly based on an anion-exchange mechanism. The unexpected selectivity toward the inorganic anions was exploited in the successful application of the method to the determination of inorganic anions in environmental water samples, including acid rain and river and underground waters. The main advantage of the carbon column was its high chemical stability – the column was used for approximately six months without any significant damage.

REFERENCES

- [1] P.R. Haddad and P.E. Jackson, *Ion Chromatography – Principles and Applications*, Elsevier, Amsterdam, 1990
- [2] D.T. Gjerde and J.S. Fritz, *Ion Chromatography*, Hüthig, New York, 2nd edn, 1987
- [3] W.T. Frankenberger Jr, *J. Chromatogr.*, **504**, 211 (1990)
- [4] S. Carrozzino and F. Righini, *J. Chromatogr. A*, **706**, 227 (1995)
- [5] V. Cheam, *Analyst*, **117**, 1137 (1992)
- [6] N. Gros and B. Gorenc, *J. Chromatogr. A*, **770**, 119 (1997)
- [7] S.-M. Kwon, K.-P. Lee, K. Tanaka, and K. Ohta, *J. Chromatogr. A*, **85**, 79 (1999)
- [8] K. Tanaka, K. Ohta, P.R. Haddad, J.S. Fritz, K.-P. Lee, K. Hasebe, and A. Ieuji, *J. Chromatogr. A*, **850**, 311 (1999)
- [9] K. Tanaka, K. Ohta, P.R. Haddad, and J.S. Fritz, *J. Chromatogr. A*, **804**, 179 (1998)
- [10] H. Hosoya, *Kotaibuturi*, **33**, 181 (1998)
- [11] L.I. Monser and G.M. Greenway, *Anal. Commun.*, **33**, 105 (1995)
- [12] T. Okamoto, A. Isozaki, and H. Nagashima, *J. Chromatogr. A*, **800**, 239 (1998)
- [13] H. Nagashima and T. Okamoto, *J. Chromatogr. A*, **855**, 261 (1999)
- [14] T. Hanai, *J. Chromatogr. A*, **989**, 183 (2003)
- [15] K. Tanaka, K. Ohta, P.R. Haddad, and J.S. Fritz, *J. Chromatogr. A*, **884**, 167 (2000)
- [16] P.R. Haddad and P.E. Jackson, *Ion Chromatography*, Elsevier, 1991, Fig. 4.9, p. 89
- [17] C. Elfakir, P. Chaimbanlt, and M. Dreux, *J. Chromatogr. A*, **829**, 193 (1998)
- [18] P. Haddad, Jackson, *Ion Chromatography*, Elsevier, 1991, Section 4.6, pp. 123–127