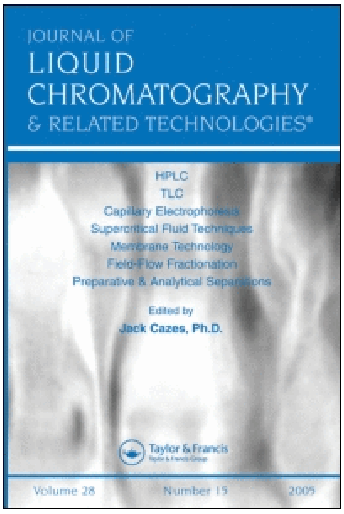

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Hu, Wenzhi , Hasebe, Kiyoshi , Reynolds, Darren Michael and Haraguchi, Hiroki(1997) 'Simultaneous Separation of Inorganic Cations and Anions by Ion Chromatography Using Strong Anionic/Zwitterionic Mixed Micelles as the Stationary Phase', Journal of Liquid Chromatography & Related Technologies, 20: 8, 1221 — 1232

To link to this Article: DOI: 10.1080/10826079708010971
URL: http://dx.doi.org/10.1080/10826079708010971

J. LIQ. CHROM. & REL. TECHNOL., 20(8), 1221–1232 (1997)

SIMULTANEOUS SEPARATION OF INORGANIC CATIONS AND ANIONS BY ION CHROMATOGRAPHY USING STRONG ANIONIC/ZWITTERIONIC MIXED MICELLES AS THE STATIONARY PHASE

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ABSTRACT

Mixed micelles obtained by mixing SDS (sodium dodecylsulfate) with Zwittergent-3-14 (N-tetradecyl-N, N-dimethyl- 3-ammonio 1-propanesulfonate) are used as a dynamic stationary phase for the simultaneous ion chromatography of inorganic cations and anions. Analyte cations are separated by the negative charges in the SDS based upon ion-exchange interactions while analyte anions are separated by both the positive and negative charges in Zwittergent-3-14 based upon simultaneous electrostatic attraction /repulsion interactions. The ratio of SDS/Zwittergent-3-14, which constitutes the stationary phase is an important factor in the determination of the retention times and elution orders of the analyte ions. The investigation of the mechanisms involved and the practical applications are discussed in this paper.

INTRODUCTION

A previous study[1] has demonstrated that a single, column, injection, eluent and detector could form the basis for the simultaneous separation of inorganic cations and anions when using a weak-positively/strong-negatively charged zwitterionic surfactant (W/S ZWITS) as the stationary phase. The mechanism involved in the simultaneous separation of the cations and anions when using a W/S ZWITS stationary phase differs to those observed for other similar 'simultaneous' IC methods.[2-10] When a W/S ZWITS stationary phase is used for IC, the analyte cations separate as a result of ion-exchange interaction while the analyte anions separate due to simultaneous electrostatic attraction and repulsion interactions.

Previously, other cations-anions separation methods[2-10] involved the use of ion exchange. When a cation-separation column and an anion separation column are used in series[2-4] then complete separation of cations and anions is achieved independently, i.e. in two stages. However, if both the cation and the anion exchangers are interspersed throughout a column[5-7] and/or if the stationary phase has both chemically bonded anionic and cationic exchangers,[7] then the separation of both cations and anions is achieved simultaneously (simultaneous IC). When chelating agents are used for the mobile phase,[8-10] the analyte cations are converted into anionic complexes and are separated along with other inorganic and/or organic anions in a single stage of anion-exchange.

The W/S ZWITS stationary phase reported in our previous study[1] was obtained by the protonation of taurine-conjugated bile surfactants using an acidic aqueous solution as the mobile phase. In this method, the mobile phase pH was extremely important for obtaining the W/S ZWITS stationary phase.

Furthermore, a simpler method which does not require protonation and which also separates inorganic cations and anions simultaneously (based on the combined effects of cation-exchange and simultaneous electrostatic attraction/repulsion interactions) is also proposed.[11] This is achieved by using a mixed micelle solution containing sodium taurodeoxycholate (NaTDC) and 3-[(3-cholamidopropyl) dimethylammonio]-1-propanesulfonate (CHAPS) as the stationary phase. NaTDC acts as a cation-exchanger and separates the analyte cations while the CHAPS acts as a simultaneous electrostatic attraction/repulsion provider and separates the analyte anions.

Although a number of inorganic cations and anions were successfully separated when using the two aforementioned stationary phases,[1,11] nitrate, a very important and common inorganic ion, could not be separated nor detected using either the W/S ZWITS stationary phase or NaTDC/CHAPS mixed stationary phase. When a W/S ZWITS stationary phase is used nitrate is separated from the other analyte ions, however, its retention time is very close to that of water. When UV-Visible detection is used, its UV absorbance is obscured by the negative UV absorbance of water.[1]

When the NaTDC/CHAPS stationary phase is used, nitrate ions were co-eluted with the mono-valent cations.[11] Unfortunately, the conditions which determine the separation abilities during this particular type of IC analysis were not investigated in previous studies.[1,11]

To further improve the separation abilities of simultaneous IC a new type of stationary phase is used. This is obtained by immobilizing a mixed micelle of SDS (sodium dodecylsulfate, a strong negatively charged surfactant) with Zwittergent-3-14 (N-tetradecyl-N, N-dimethyl-3-ammonio-1-propanesulfonate, a strong/strong zwitterionic charged surfactant).

Present studies have demonstrated that by careful selection of the strongly charged surfactants which are used as the stationary phase, the separation abilities of the simultaneous IC technique are vastly improved. Present experimental results also show that the elution order of the analyte ions can be manipulated by adjustment of the SDS/Zwittergent-3-14 ratio in the stationary phase. This provides a new and convenient approach for avoiding technical problems such as elutionoverlapping, which are often encountered in the IC of target ionic species in a concentrated salt matrix. The investigation of the separation mechanism and the practical applications of this new proposed method are outlined in this paper.

EXPERIMENTAL

Apparatus

The HPLC system used in this study was a Shimadzu (Kyoto, Japan) LC-6A system. It was equipped with an LC-7A pump, a SIL-6A auto injector, a SCL-6A system controller and an UV-visible detection (SPD-M6A). ODS packed columns (L-Column, 46 X 250 mm, Chemical Inspection & Testing Institute, Tokyo, Japan) were used as the support columns for the preparation of SDS/Zwittergent-3-14 mixed micellar stationary phase. A commercial cation separation column, Shim-pack IC-C3 (4.6 X 100 mm, Shimadzu), and anion separation column, Shim-pack IC-A3 (4.6 X 150 mm, Shimadzu) were also used for conventional IC measurements.

Materials

Sodium dodecylsulfate (SDS) and N-tetradecyl-N, N-dimethyl-3-ammonio-1-propanesulfonate (Zwittergent-3-14) were used to prepare a stationary phase for the simultaneous IC of inorganic cations and anions. These were obtained from Wako (Osaka, Japan) and Calbiochem (La Jolls, CA, USA), respectively. Inorganic salts, which were used as the standard analytes were also obtained from Wako, all reagents were used as received.

Stationary Phase Preparation

Aqueous solutions containing mixtures of SDS and Zwittergent-3-14 were passed through the ODS-packed columns for 60 minutes using a flow rate of 1.0 mL/min. These columns were then conditioned with an aqueous solution containing 2.0 mM cerium (III) chloride for at least 60 minutes using the same flow rate.

RESULTS AND DISCUSSION

The concentration of the mobile phase ions, flow rate of the mobile phase, and the ratio of SDS/Zwittergent-3-14 which is immobilized on the ODS surfaces, will determine the resolution abilities. To detect both analyte cations and anions using a single UV-visible detector, UV-absorbing anions were chosen as the typical analyte anions and were detected directly while analyte cations were detected 'indirectly'. Indirect UV absorption is based upon the

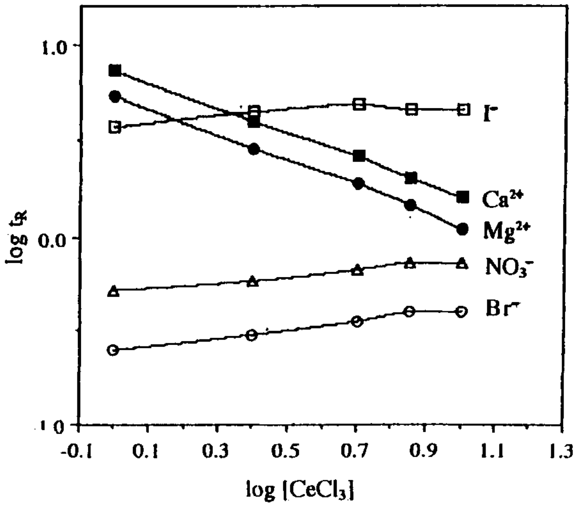

Figure 1. The relationship between the logarithms of the adjusted retention times of analyte ions (log t_R) and the logarithms of $CeCl_3$ concentration (log[$CeCl_3$]) in the mobile phase. Column: ODS-packed column (46 X 250 mm) coated with SDS/Zwittergent-3-14 (20/40, mM/mM). Mobile phase: $CeCl_3$. Flow rate: 1.0 mL/min. Sample injection volume: 20 μL. Detection UV-visible at 253 nm.

measurement of the decreased UV-absorbency of the mobile phase. When non-UV absorbing analytes are eluted from the stationary phase, the UV-absorbency of the mobile is diluted by the eluting analyte, resulting in a negative signal. Cerium (III) are UV-absorbing ions commonly used as the mobile phase ions when detecting inorganic cations using the indirect UV-absorption method.

Five aqueous solutions containing, (i) 1. 0, (ii) 2. 5, (iii) 5. 0, (iv) 7.0 and (v) 10, mM of cerium (III) chloride were prepared and respectively used for the mobile phase to investigate the effects of mobile phase concentration on the retention behavior of the analyte ions. An aqueous solution containing 1.0 mM each of $MgBr_2$, $Ca(NO_3)_2$ and CaI_2 was chosen to represent a 'typical' sample. Adjusted retention times were calculated as the difference between the observed retention time of the analyses and the void time (t_o) of the column. The relationships between the logarithms of the adjusted retention times of Mg^{2+}, Ca^{2+}, Br^-, NO_3^-, and I^- and the logarithms of cerium (III) chloride concentration are shown in Figure 1. The values of the logarithms for the adjusted retention times of the analyte cations linearly decreased with increasing concentration of $CeCl_3$ in the mobile phase. For this, the separation of the analyte cations is achieved as a result of ion exchange interactions.[12]

On the contrary, the value of the logarithms for the adjusted retention times of the analyte anions are initially increased with increasing concentration of $CeCl_3$ in the mobile phase. However at around 7.0 mM concentration of $CeCl_3$ the logarithmic values stabilized and remained almost constant. These experimental results suggest that the separation for the analyte anions is not based on ion-exchange interactions.

It was initially mentioned in our previous paper that when a strong positively/negatively charged zwitterionic stationary phase is used for the IC of inorganic anions, the retention time of the analyte ions is increased with increasing concentration of mobile phase ions.[13] The IC of ionic chemicals while using a strong positively/negatively-charged zwitterionic stationary phase is a new approach proposed by the present authors.[14-16] When analyte ions are passed through a stationary phase where the positive and negative charges are fixed in close proximity, i.e., the zwitterionic stationary phase, both of the analyte cations and anions will receive electrostatic attraction and repulsion from the stationary phase, simultaneously. This results in an extremely weak electrostatic affinity between the analyte ions and the stationary phase. The effective distribution of the analyte ions between the stationary phase and the mobile phase can be achieved without the need for ion-exchange. The IC of ions based on simultaneous electrostatic attraction and repulsion interactions is termed electrostatic IC.[14]

For ion-exchange IC, the retention time of the analyte ions is decreased with increasing concentration of mobile phase ions. The potential for ion-exchange is increased by increasing the concentration of replacing ions present in the mobile phase. For electrostatic IC, the retention time of the analyte ions is increased with increasing concentration of the mobile phase ions due to the following; when a strong positively/negatively charged zwitterionic stationary phase is conditioned with a mobile phase containing electrolytes (ions), a moving (mobile) electrical double layer consisting of the mobile phase ions is created with the stationary phase. The levels of the mobile phase ions in the moving electrical double layer are proportional to the concentration of mobile phase ions. This becomes critical when the concentrations of the mobile phase ions are at sufficiently high levels. The separation of analyte ions while using a strong positively/negatively charged zwitterionic stationary phase which has been conditioned with a mobile phase containing the electrolytes, requires an effective distribution of the analyte ions between the mobile phase and the moving electrical double layer. The distribution rate of the analyte ions decreases with increasing levels of mobile phase ions that are initially involved in the moving electrical double layer. This results in longer retention times for the analyte ions with increasing concentration of the mobile phase ions.

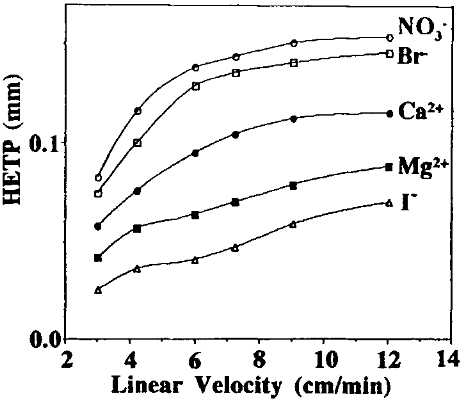

Figure 2. Relationship between HETP and the linear velocity for a strong anionic/zwitterionic mixed micellar stationary phase. Mobile phase: 5.0 mM $CeCl_3$. Conditions are the same as described in Figure 1.

To investigate the effects of flow rate on the theoretical plate heights (HETP) of the column, the flow rate of the mobile phase was incremented from 0.5 mL/min to 2.0 mL/min (3.01 cm/min to 12.04 cm/min). An aqueous solution containing 5.0 mM $CeCl_3$ was used for the mobile phase. As the experimental results in Figure 2 show, the HETP of this column depends on the flow rate of the mobile phase in a similar way as conventional packed columns.[17] The optimum flow rate which allowed for high resolution and a relatively short analytical time was found to be 1.0 mL/min (6.02 cm/min).

Three aqueous solutions, containing (i) 40 mM Zwittergent-3-14 and 10 mM SDS, (ii) 40 mM Zwittergent-3-14 and 20 mM SDS, and (iii) 40 mM Zwittergent-3-14 and 40 mM SDS, were prepared as SDS/Zwittergent-3-14 mixed micellar stationary phases. An aqueous solution containing Mg^{2+}, Ca^{2+}, Ba^{2+}, Br^-, NO_3^-, I^- and SCN^- was prepared and used to represent a 'typical' sample. This sample was then analyzed using the three respective stationary phases. When the concentrations of Zwittergent-3-14 and SDS in the mixed micellar stationary phase preparatory solutions are 40 and 10 mM respectively, Br-, NO_3^-, I^-, SCN^-, Mg^{2+}, Ca^{2+} and Ba^{2+} can be base-line separated and the divalent cations elute between NO_3^- and I^- (Figure 3A). However, when the concentrations of SDS were increased to 20 mM (Figure 3B) and 40 mM (Figure 3C), the retention times of the analyte cations are increased while the retention times of the analyte anions are decreased. The increased and decreased retention times of respective analyte cations and anions results in elution overlapping and a change in elution order.

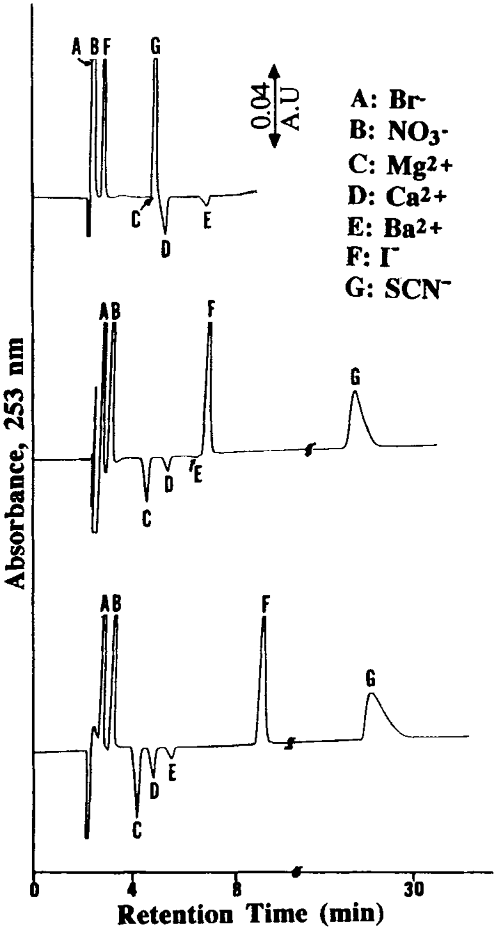

Figure 3. Chromatograms of an aqueous solution containing Br$^-$, NO$_3^-$, I$^-$, SCN$^-$, Mg^{2+}, Ca^{2+} and Ba^{2+} obtained using the SDS/Zwittergent-3-14 mixed micellar stationary phases. Ratio of SDS/Zwittergent-3-14 concentration is 10/40 (A), 20/40 (B) and 40/40 (C), mM/mM. In Figure 3B, the negative peak due to Ba^{2+} is partly obscured by the positive peak due to I$^-$. In Figure 3C, Br$^-$ is not baseline separated from NO$_3^-$; the negative peak due to Mg^{2+} is completely obscured by the positive peak due to SCN$^-$. Flow rate of the mobile phase: 1.0 mL/min. Other conditions are the same as described in Figure 1.

For a certain ODS-packed column, the total amount (maximum) of SDS and Zwittergent-3-14 found in the stationary phase is a constant. By increasing the concentration of SDS in the preparatory solution containing 40 mM Zwittergent-3-14 the amount of SDS immobilized on the stationary phase is increased. This results in a decrease in the amount of Zwittergent-3-14 immobilized in the stationary phase. The retention times for the analyte cations and anions are proportional to the levels of SDS and the level of Zwittergent-3-14, respectively, in the stationary phase. By adjustment of the SDS/Zwittergent-3-14 ratio in the solutions (stationary phase) the retention time and/or the elusion order of the analyte ions can be manipulated.

While using the Zwittergent-3-14/SDS (40/10, mM/mM) mixed micellar coated stationary phase and 5.0 mM $CeCl_3$ mobile phase, the mono-valent cations elute with a zero retention time (void time). Subsequently, this provides a simple and convenient method for the determination of divalent cations and UV-visible absorbing inorganic anions in a concentrated salt matrix. To illustrate this, sea water diluted ten-fold with pure water, was directly injected into the IC system and magnesium, calcium and iodide ions were simultaneously determined. The cations and the magnesium ions are easily detected, however, the iodide ions were not detected, due to the low concentration of iodide found in sea water (sub-μM levels). Figure 4 shows the chromatogram of a real sea water sample spiked with iodide.

An aqueous solution containing 10μM each of $CaBr_2$, $Ca(NO_3)_2$, CaI_2 and $Ca(SCN)_2$, 40 μM $MgCl_2$ and 40 μM $BaCl_2$ was analyzed ten times to test the reproducibility and the detectability of this method. The standard deviation (in %) was found to be 0.73, 0.45, 0.52, 0.55, 0.52, 0.42 and 0.43 for the retention times and 0.85, 0.55, 0.55, 0.53, 0.62, 0.52 and 0.61 for the concentration (peak areas) of Br^-, NO_3^-, Mg^{2+}, Ca^{2+}, Ba^{2+}, I^- and SCN^-, respectively. The detection limit for Br^-, NO_3^-, Mg^{2+}, Ca^{2+}, Ba^{2+}, I^- and SCN^-, using a signal to noise ratio of 3, was found to be 0.60, 0.65, 6.1, 6.3, 7.2, 5.5, and 6.3 μM, respectively.

Tap water was directly analyzed using this IC system. As the chromatogram in Figure 5 shows, the UV-absorbing anion, nitrate, and divalent cations, magnesium and calcium, were simultaneously detected. The concentrations of NO_3^-, Mg^{2+} and Ca^{2+} that were found in tap water were 0.026, 0.61 and 0.57 mM, respectively. This tap water was also analyzed using the conventional anion-separation and cation-separation IC, respectively (the measurement was achieved under the conditions as recommended by the manufacturer). The concentration of NO_3^- was found to be 0.029 mM, using a conventional anion-separation IC.

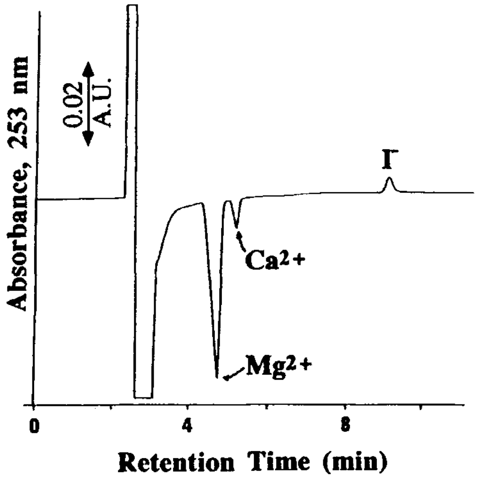

Figure 4. Chromatogram of 10-fold diluted real sea water spiked with 0.1 mM of I^-. Data obtained using a SDS/Zwittergent-3-14 mixed micellar stationary phase, conditions are the same as described in Figure 3A.

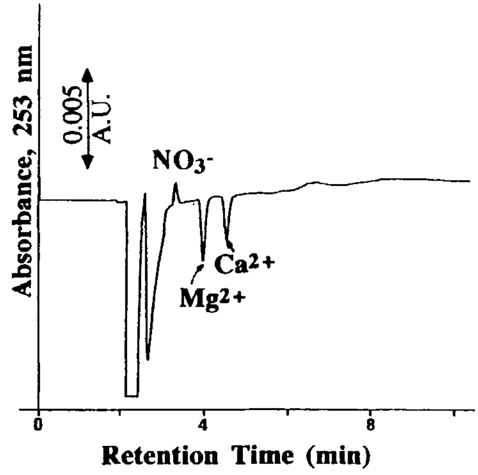

Figure 5. Simultaneous determination of UV-Visible inorganic anions and divalent cations in tap water. Separation conditions are the same as described in Figure 3A.

The concentrations of Mg^{2+} and Ca^{2+} were found to be 0.59 mM and 0.58 mM, respectively, using a conventional cation separation IC. Hence, good agreements on the analytical results obtained using the present method and the conventional IC were obtained. Although, using conventional IC techniques other inorganic ions, such as Na^+, K^+, NH_4^+, Cl^-, and SO_4^{2-} can also be measured along side Mg^{2+}, Ca^{2+} and NO_3^-, two analytical stages are required for cations and anions respectively. On the contrary, Mg^{2+}, Ca^{2+} and NO_3^- were measured simultaneously using the proposed IC system, and analysis was achieved using a single sample injection and a single IC system. The separation-ability of the proposed IC system could further be improved by using a more effective anionic/zwitterionic mixed micellar stationary phase. It is also possible to further improve the separation/detection abilities by using a more appropriate detection method

REFERENCES

1. W. Hu, H. Haraguchi, Anal. Chem., **66**, 765 (1994).

2. V. K. Jones. J. G. Tarter, J. Chromatogr., **312**, 456 (1984).

3. J. G. Tarter. J. Chromatogr. Sci., **27**, 462 (1989).

4. R. Saari-Nordhaus, J. M. Anderson, Jr., J. Chromatogr., **549**, 257 (1991).

5. D. J. Pietrzyk, D. M. Brown, Anal. Chem., **58**, 2554 (1986).

6. D. M. Brown, D. J. Pietrzyk, J. Chromatogr., **466**, 291 (1989).

7. D. J. Pietrzyk, S. M. Senne, D. M. Brown, J. Chromatogr., **546**, 101 (1991).

8. M. Yamamoto, H. Yamamoto, Y. Yamamoto, S. T. Ikushige, Anal. Chem., **56**, 832 (1984).

9. S. Matsushita, J. Chromatogr., **312**, 327 (1984).

10. D. Yan. G. Schwedt, J. Chromatogr., **516**, 383 (1990).

11. W. Hu, A. Miyazaki, H. Haraguchi, Anal. Sci., **11**, 999 (1995).

12. J. H. Knox, G. R. Laird, J. Chromatogr., **122**, 17 (1976).

13. W. Hu, H. Haraguchi, Anal. Chim. Acta, **285**, 335 (1994).

14. W. Hu, T. Takeuchi, H. Haraguchi, Anal. Chem., **65**, 2204 (1993).

15. W. Hu, H. Tao, H. Haraguchi, Anal. Chem., **66**, 2514 (1994).

16. W. Hu, A. Miyazaki, H. Tao, A. Itoh, T. Umemura, H. Haraguchi, Anal. Chem., **67**, 3713 (1995).

17. J. Weiss, **Ion Chromatography**, Second Edition, VCH Inc., Weinheim, Germany, p . 22, 1995.

Received July 28, 1996
Accepted October 10, 1996
Manuscript 4227