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Determination of inorganic anions in salt solutions by ion chromatography using C_{18} reversed-phase columns coated with cetyltrimethylammonium

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ABSTRACT

A simple and sensitive method using ion chromatography is described for the determination of I^-, SCN^-, NO_2^- and $S_2O_3^{2-}$ as impurities in inorganic analytical-reagent grade chemicals. Aqueous solutions of individual salts containing matrix anions (5–20 g/l) were prepared and analyzed directly for trace impurities. Good chromatograms of trace anions were obtained without interference by matrix ions. C_{18} reversed-phase columns coated with cetyltrimethylammonium (CTA^+), with either high or low capacity, a mobile phase mixture (pH 5.8) of sodium chloride (0.1 *M*) and sodium phosphate buffer (0.005 *M*), and ultraviolet (225 nm) and amperometric (+1.0 V *vs.* Ag/AgCl) detection systems were used. The detection limits for different impurities in the solutions were 0.002–0.06 mg/l.

INTRODUCTION

Recently, efforts have been made to develop an improved method for the separation and detection of trace anions in concentrated salt solutions by ion chromatography (IC). For the separation of anions, the use of C_{18} reversed-phase columns has become of increasing interest not only because of their good chromatographic efficiency but also the flexibility in choosing eluents and ion-pair reagents [1–6]. Especially columns coated permanently with ion-pair reagents such as cationic surfactants can be used as "fixed-site" anion-exchange columns. The anion-exchange capacity can be adjusted by controlling the conditions of column coating for practical applications. An increase in exchange capacity improved the mutual separation between anions without any changes to the elution order [5,6]. When using coated columns, however, the selection of the mobile phase and the detection method are the most important features and are being improved continuously.

In a previous paper [7], we reported the determination of μg/l levels of iodide in 100 μl of sea water using a conventional IC column, 0.1 *M* NaCl solution as eluent, and UV and amperometric (with a glassy carbon electrode) detection, without interference from excess of anions, especially chloride. NaCl is UV-transparent and electroinactive on a glassy carbon electrode and the separation of different anions was in accordance with the theoretical predictions for ion-exchange reactions [8]. However, the IC column could not be applied to μg/l levels of nitrite and nitrate in sea water (100 μl), because of incomplete separations owing to the low exchange capacity of the column. Separation was

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successfully achieved using a C_{18} reversed-phase column (silicone-coated silica packing) coated with cetyltrimethylammonium (CTA^+), which has a high exchange capacity (0.25 mequiv. per column) [5]. The silicone-coated C_{18} reversed-phase column is resistant to alkaline samples (*e.g.*, sea water, pH *ca.* 8) and retains the chromatographic efficiency of the silica-based packings [9]. The observed anion-exchange capacity of a coated column (150 mm × 4.6 mm I.D.) was in the range 0–0.4 m*M* depending on the amount of CTA^+ attached [5]. Thus, iodide in sea water was also determined using a CTA^+-coated column with low capacity [6].

In this study, the determination of anionic impurities in the presence of various matrix anions was examined by direct ultraviolet (UV) and amperometric detection; the anionic impurities examined included iodide, thiocyanate, nitrite and thiosulfate in analytical reagent-grade inorganic salts such as $NaIO_3$, KCN, Na_2SO_4, NaBr and $NaNO_3$. CTA^+-coated C_{18} (AG 120) reversed-phase columns with high and low capacities were employed for the separation of various analyte anions. As the matrix anions, IO_3^-, NO_3^- and Br^-, have UV absorption, complete separation of the analyte anions is essential. With the exception of Br^-, a glassy carbon electrode is electroinactive for matrix ions whereas a silver electrode is electroactive for Cl^- present in the mobile phase and Br^- and CN^- in the matrix [10].

EXPERIMENTAL

Apparatus

The IC system consisted of a Tosoh Model CCPM pump, a Rheodyne Model 7125 injector with a 100-μl sample loop, a Hitachi Model L-4200 UV detector, Yanagimoto Models VMD-101A and P-1000 amperometric detectors with a glassy carbon working electrode and a Tosoh Model CP-8000 chromato-processor.

Column

A Shiseido Capcellpak C_{18} (AG 120) reversed-phase column (150 × 4.6 mm I.D., particle size 5 μm, octadecyl-bonded silica gel already precoated with silicone polymer) was used. The column was equilibrated with 1 m*M* cetyltrimethylammonium chloride (CTAC) in water–methanol mixtures (80:20 and 56:44, v/v) at 20°C. The CTA^+-coated columns were employed for the separation of analyte anions. CTAC and high-performance liquid chromatographic grade methanol, both obtained from Katayama Chemical, were used as received.

Sample and mobile phase preparation

Inorganic salts of analytical-reagent grade were obtained from Katayama Chemical and were used without treatment. Ion-free distilled water was used throughout for preparing solutions. The concentration of matrix anions in the stock solutions prepared was IO_3^- 20 g/l ($NaIO_3$), CN^- 10 g/l (KCN), SO_4^{2-} 40 g/l (Na_2SO_4), Br^- 20 g/l (NaBr) and NO_3^- 20 g/l ($NaNO_3$). Dilute sample solutions both with and without the added analyte (0.01–0.5 mg/l) were analyzed directly. Mobile phase (pH 5.8) consisting of 0.1 *M* NaCl and 0.005 *M* sodium phosphate buffer (0.5 m*M* Na_2HPO_4 and 4.5 m*M* NaH_2PO_4) was prepared from stock solutions.

RESULTS AND DISCUSSION

Use of CTA^+-coated column with low capacity

Anionic impurities in analytical reagent-grade chemicals such as $NaHCO_3$, NaOH and Na_2CO_3 have been determined by IC with conductivity detection [11,12]. After removing Na^+ by the "dual ion-exchange method", anionic impurities in the resulting solutions (H_2CO_3, H_2O) with lower conductivity were determined. However, it is difficult to remove the matrix anions effectively, together with Na^+ or K^+, for the present samples by chemical pretreatment. Recycle IC (also known as the reinjection method) is capable of separating a small impurity peak from a large sample peak. Anionic impurities in inorganic acids have been determined by recycle IC with conductivity detection after their dilution with ion-free distilled water followed by neutralization with NaOH [13]. Similarly, the determination of sub-mg/l levels of nitrite in sea water has been achieved using recycle IC with conductivity detection [14]. This system, however, requires valve switching during analysis, which causes a decrease in the detectability owing to peak broadening by reinjection and long retention times of the analyte anions. In this study, a direct and sensitive method for the detection of anionic impurities in various salt solutions was examined using UV and amperometric detection methods.

Analytical reagent-grade sodium iodate and potassium cyanide usually contain iodide and thiocyanate, respectively, as impurities. Figs. 1 and 2 show the separation of I^- and SCN^- in their respective reagents (IO_3^-, 10 g/l; SCN^-, 5 g/l) on a CTA^+-coated C_{18} reversed-phase column with low capacity (0.06 mequiv. per column). The coating solution employed was 1 m*M* CTA^+ solution in water–methanol (56:44, v/v) [6]. The retention times for I^- and SCN^- were identical with those obtained for solutions spiked with 0.2 mg/l of I^- and SCN^-, respectively (dashed line). The use of 0.1 *M* NaCl as mobile phase eliminated the interference of faster eluting species. Further, 0.1 *M* NaCl stabilized the sorbed CTA^+ and improved the long-term use of the coated column [5,15]. The chromatograms were obtained by UV (225 nm) and amperometric (+1.0 V *vs.* Ag/AgCl) detection as reported [6]. The iodate peak with UV absorptivity did not interfere with I^- and separate peaks were observed. Similarly, with amperometric detection only the I^- peak was observed (Fig. 1B) and IO_3^-, which is amperometry inactive, was eliminated.

Good chromatograms were obtained for SCN^- in KCN solution even though the sensitivity of SCN^- for amperometric detection was increased with multiple injection of the sample. This may be due to the activation of the glassy carbon electrode surface by CN^-. Determination of the analytes was effected using calibration graphs (0–1 mg/l) and the standard addition (0.1–0.5 mg/l) method using peak areas. Peak areas of the analyte ions remained constant on addition of salts whereas the peak heights decreased rapidly [5,6].

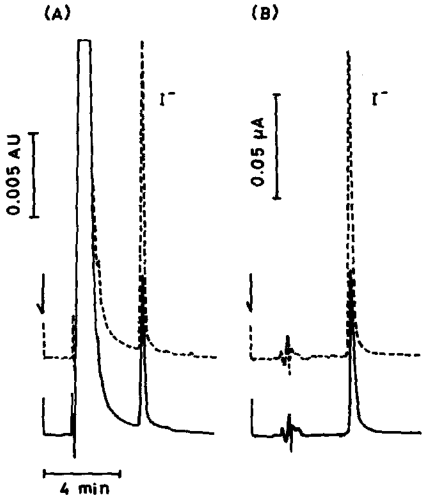

Fig. 1. Ion chromatograms of sodium iodate solution (10 g/l IO_3^-, solid line) and the solution spiked with 0.2 mg/l of I^- (dashed line). Column, Capcellpak C_{18} coated with 1 m*M* CTA^+ in water–methanol (56:44, v/v); mobile phase, 0.1 *M* NaCl–0.005 *M* sodium phosphate buffer (pH 5.8); detection (A) UV, 225 nm; (B) amperometry, +1.0 V (*vs.* Ag/AgCl); flow-rate, 1.0 ml/min; sample volume, 100 µl.

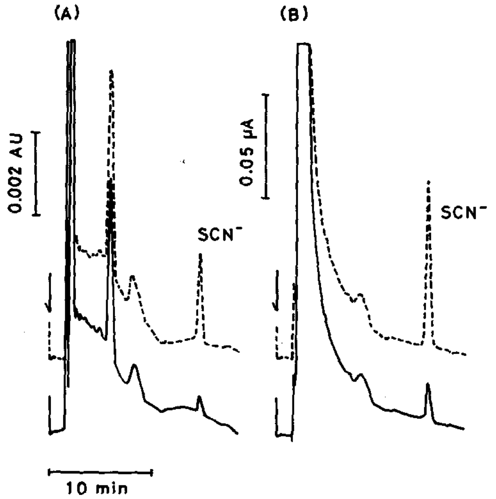

Fig. 2. Ion chromatograms of potassium cyanide solution (5 g/l CN^-, solid line) and the solution spiked with 0.2 mg/l of SCN^- (dashed line). Conditions as in Fig. 1.

The results are summarized in Table I. With good agreement between the two detection methods, detection limits of 0.005 mg/l for I^- and 0.015 mg/l for SCN^- (signal-to-noise ratio 2) were observed.

Use of CTA^+-coated column with high capacity

The presence of nitrite and thiosulfate as impurities in inorganic salts such as sodium sulfate, sodium nitrate and sodium bromide was examined. A column coated with 1 m*M* CTA^+ in water–methanol (80:20, v/v) (anion-exchange capacity 0.25 mequiv. per column) was used as reported [5] for the separation of NO_2^- and $S_2O_3^{2-}$. Fig. 3 shows chromatograms of Na_2SO_4 solutions (SO_4^{2-} 20 g/l) unspiked (solid line) and spiked (dashed line) with 0.05 mg/l of NO_2^- and 0.1 mg/l of $S_2O_3^{2-}$. Compared with $S_2O_3^{2-}$, NO_2^- was relatively more sensitive for both UV and amperometric detection. The detection conditions were as reported [5]. The presence of

TABLE I

RESULTS FOR IMPURITIES IN INORGANIC SALT SOLUTIONS

Mean results ± standard deviations for five determinations. The results were obtained using a calibration graph and (in parentheses) by the standard addition method.

Reagent	I^- (mg/l)		SCN^- (mg/l)	
	UV	Amperometry	UV	Amperometry
$NaIO_3$ (10 g/l IO_3^-)	0.18 ± 0.01[a] (0.18 ± 0.01)	0.18 ± 0.01 (0.22 ± 0.01)	–	–
KCN (5 g/l CN^-)	–	–	0.043 ± 0.010 (0.054 ± 0.010)	0.043 ± 0.002 (0.046 ± 0.002)

[a] The certificate value of I^- in the solution was < 0.23 mg/l.

large amounts of SO_4^{2-} did not interfere with NO_2^-.

Figs. 4 and 5 show chromatograms of unspiked NaBr and $NaNO_3$ (Br^- 5 g/l, NO_3^- 5 g/l; solid line) and spiked (dashed line) solutions containing 0.05 mg/l of NO_2^- and 0.1 mg/l of $S_2O_3^{2-}$, respectively. Altough Br^- showed a response in UV and amperometric detection, it did not interfere in the detection of the analyte anions. The sensitivity of NO_2^- in $NaNO_3$ solution was high and remained unaffected by the presence of matrix NO_3^-. The peak height of NO_2^- added to Na_2SO_4 solution was lower than those in NaBr and $NaNO_3$, presumably owing to the difference in concentration of the matrix ions. Detection limits in NaBr solution (Br^- 5 g/l), for example, were 0.004 mg/l (UV) and 0.002 mg/l (amperometric detection) for NO_2^- and 0.06 mg/l (UV) and 0.01 mg/l (amperometric detection) for $S_2O_3^{2-}$. Only NO_2^- (0.004 mg/l, UV and amperometric detection) in $NaNO_3$ solution (NO_3^- 5 g/l) was determined.

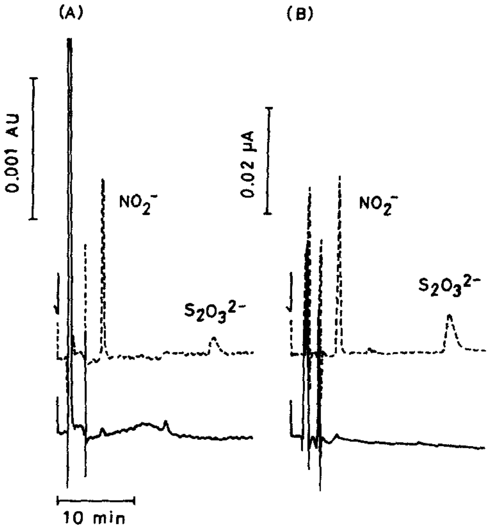

Fig. 3. Ion chromatograms of sodium sulfate solution (20 g/l SO_4^{2-}, solid line) and the solution spiked with 0.05 mg/l NO_2^- and 0.1 mg/l $S_2O_3^{2-}$ (dashed line). Column, Capcellpak C_{18} coated with 1 m*M* CTA^+ in water-methanol (80:20, v/v). Other conditions as in Fig. 1.

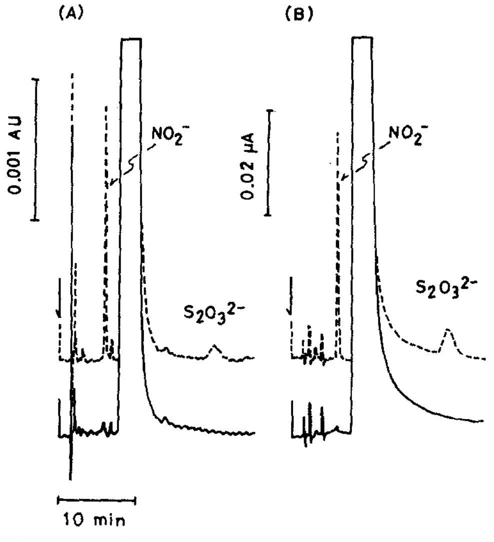

Fig. 4. Ion chromatograms of sodium bromide solution (5 g/l Br^-, solid line) and the solution spiked with 0.05 mg/l NO_2^- and 0.1 mg/l $S_2O_3^{2-}$ (dashed line). Conditions as in Fig. 3.

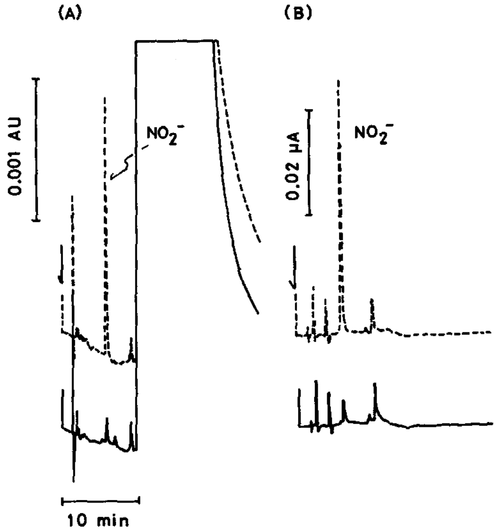

Fig. 5. Ion chromatograms of sodium nitrate solution (5 g/l NO_3^-, solid line) and the solution spiked with 0.05 mg/l NO_2^- (dashed line). Conditions as in Fig. 3.

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