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INDIRECT PHOTOMETRIC DETECTION OF INORGANIC ANIONS USING ANTHRAQUINONE-DISULFONATE AS VISUALIZATION AGENT

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ABSTRACT

Signal enhancement of inorganic anions has been achieved by indirect photometric detection with anthraquinone-disulfonate as visualization agent in liquid chromatography. The separation was conducted using a 50 x 4.6 mm I.D. separation column packed with LIC-10-SA1 and detected at 264 nm using a UV-spectrophotometer detector. The calibration curve for analytes tested were linear up to the concentration of 10 mM. The present method improved the sensitivity of the analytes tested by a factor of 10-20.

Key words: Anthraquinone-disulfonate, inorganic anions, indirect detection, ion chromatography.

INTRODUCTION

Ion chromatography has been widely applied to the determination of inorganic ions as well as organic ions since it was initiated by Small *et al.* [1]. Indirect photometric detection is one of the detection methods employed in ion chromatography, in which the analyte ions displace the UV-absorbing mobile phase ions, resulting in a depression of the background signal[2-4]. The sensitivity achieved by the indirect photometric detection is affected by the molar absorptivity of the eluent ion and the noise level; the higher the molar absorptivity, the better detection limit[5]. In order to achieve better sensitivity, packing with smaller ion-exchange capacity should be employed, allowing the use of lower concentration of eluent. The eluent concentration is primarily adjusted by consideration of the retention time of the analytes.

In the previous work[6] disodium 2,6-anthraquinone-disulfonate (2,6-AQDS) was employed as the visualization agent for microcolumn ion chromatography. The detection limits of inorganic anions were improved because of its larger molar absorptivity {5.5×10^4 $(molL^{-1})^{-1}$ cm^{-1} at 258 nm}.

The concentration detection limits of chloride, nitrate and sulfate were 0.91 – 1.6 μM at S/N = 3, corresponding to mass detection limits of 18-32 fmol. It was found that the mass detection limits achieved by microcolumn LC system were remarkable, but the concentration sensitivity was not still satisfactory. It is expected that the concentration detection limits can be further improved by using conventional-size column because the injection volume can be increased to as much as 0.1 mL.

This work describe signal enhancement of anions such as chloride, nitrate and sulfate by ion chromatography with indirect photometric detection using conventional-size columns and 2,6-AQDS as the visualization agent.

EXPERIMENTAL

Apparatus

The liquid chromatograph comprised an 880-PU HPLC pump (Jasco, Tokyo, Japan), a UVIDEC-100-V UV Detector (Jasco), a 50 x 4.6 mm I.D. An IC-10-SA1 separation column (Denki Kagaku Keiki, Tokyo, Japan), a loop injector with an injection volume of 21 μL, and a Chromatopac C-R4AX data processor (Shimadzu, Kyoto, Japan). The stationary phase employed was a strong anion exchanger and its base material was a styrene-divinylbenzene copolymer. The flow rate of the mobile phase was 1.0 mL min^{-1}. The injector was prepared from a model 7000 six-way switching valve (Rheodyne, Cotati, CA, USA). The detector was operated at 264 nm, and its time constant was kept at 1.0 sec. The separation column was immersed in a water-bath to minimize variations of the column temperature. UV spectra of the UV absorbing agent were obtained by using an UV-210 A double beam spectrophotometer (Shimadzu). The experiments were carried out at room temperature (20-25 °C). The pH of the mobile phase was measured by using an IM-20E Ion Meter (TOA Electronic, Tokyo, Japan). The ion-exchange capacity of the column was measured from the breakthrough curve by using sodium nitrate solution as the eluent. The column employed in this work possesses an ion-exchange capacity of 4.9×10^{-6} equivalent per column.

Reagents

Guaranteed reagent-grade solvents and reagents were obtained from Nacalai Tesque (Kyoto, Japan), unless otherwise stated. The reagents were employed without any further treatment as received. Purified water was prepared from

laboratory-made distilled water by using a Milli-Q Plus system (Millipore, Molsheim, France). The mobile phase was prepared from the purified water, acetonitrile and 2,6-AQDS (Tokyo Chemical Industry, Tokyo, Japan). The mobile phase was degassed in an ultrasonic bath under vacuum condition prior to use.

RESULTS AND DISCUSSION

The separation of a mixture of chloride, nitrate and sulfate on the LIC-10-SA1 column was carried out using 30 μM 2,6-AQDS dissolved in aqueous acetonitrile (10%, v/v) as the eluent. 5 μM of each analyte ion is indirectly detected at 264 nm. Actually, negative peaks were observed for the analyte ions. It is seen that the analyte anions are well separated, and the system peaks slightly interfere with chloride. The amount of each analyte ion injected was *ca.* 1 nmol. Although the optimum wavelength to achieve better sensitivity was 258 nm, the background absorbance of 30 μM 2,6-AQDS at that wavelength was much larger than 1. Considering the background absorbance, 264 nm was as the wavelength. The background signal of the eluent and its noise level under the above conditions were 1.5 and 3.5×10^{-5} AU, respectively. The dynamic reserve, defined as the ratio of the background signal to noise level[7], was calculated to be 4.3×10^4. The separation of these anions could be achieved within 10 min, e.g., the retention times of chloride, nitrate and sulfate were 2.0, 2.7 and 8.2 min, respectively. However, it took a long time to stabilize the baseline, when the eluent concentration was lower than 30 μM. Moreover, the stability of the retention times and the peak height were also poor when the 2,6-AQDS concentration was lower than 30 μM.

The reproducibility of the retention time and peak height of the analyte ions for five successive measurements under the above conditions are 0.5 to 1.2% and 2.0 to 2.2%, respectively.

Figure 1 shows the calibration curves of chloride, nitrate and sulfate.. It is found that the curves are linear up to the concentration of 10 μM. The concentration detection limit at S/N = 3 were 44, 72 and 140 nM for chloride, nitrate and sulfate ions, respectively, corresponding to 1.6, 4.5 and 13 ng mL^{-1}. On the other hand, the mass detection limits were 0.92, 1.5 and 2.9 pmol, corresponding to 33, 94 and 280 pg. The concentration detection limits were improved by a factor of 10-20 compared with those achieved by microcolumn LC system[6], whereas the mass detection limits were deteriorated by a factor of 50-90. For the determination of ions in environmental water samples, the concentration sensitivity plays an important role. This means that the present conventional LC system will give a better approach for water analysis.

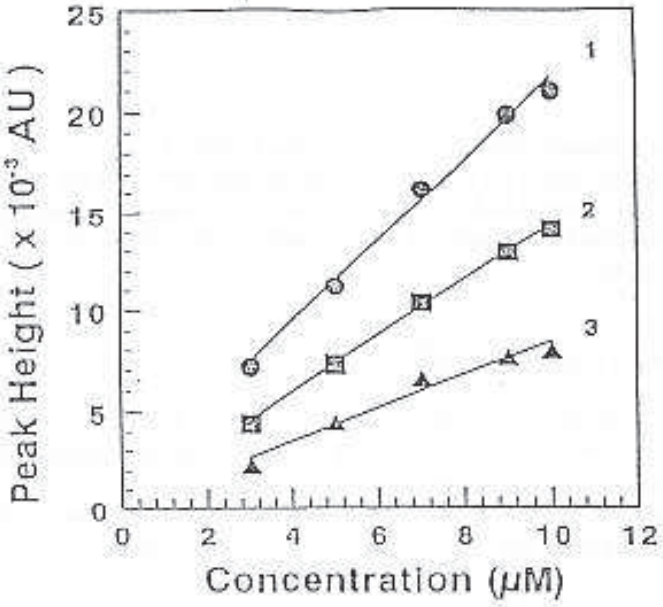

Figure 1. Calibration curves for the determination of chloride, nitrate and sulfate. Analytes: 1 = chloride, 2 = nitrate and 3 = sulfate.

The present method was successfully applied to the determination of chloride, nitrate and sulfate present in water samples. A chromatogram for tap water is demonstrated in Figure 2. The concentrations of chloride, nitrate and sulfate in tap water were determined to be 32, 22 and 15 μM, respectively, corresponding to 1.1, 1.4 and 1.5 μg mL^{-1}.

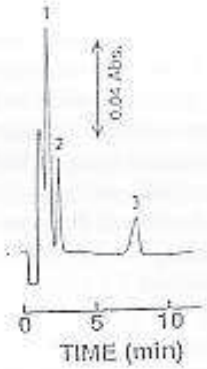

Figure 2. Separation of anions in tap water. Analytes as in Figure 1. Sample: 21 μL of local tap water.

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