



Simultaneous analysis of silicon and boron dissolved in water by combination of electro dialytic salt removal and ion-exclusion chromatography with corona charged aerosol detection



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ABSTRACT

Selective separation and sensitive detection of dissolved silicon and boron (DSi and DB) in aqueous solution was achieved by combining an electro dialytic ion isolation device (EID) as a salt remover, an ion-exclusion chromatography (IEC) column, and a corona charged aerosol detector (CCAD) in sequence. DSi and DB were separated by IEC on the H⁺-form of a cation exchange resin column using pure water eluent. DSi and DB were detected after IEC separation by the CCAD with much greater sensitivity than by conductimetric detection. The five-channel EID, which consisted of anion and cation acceptors, cathode and anode isolators, and a sample channel, removed salt from the sample prior to the IEC-CCAD. DSi and DB were scarcely attracted to the anion acceptor in the EID and passed almost quantitatively through the sample channel. Thus, the coupled EID-IEC-CCAD device can isolate DSi and DB from artificial seawater and hot spring water by efficiently removing high concentrations of Cl⁻ and SO₄²⁻ (e.g., 98% and 80% at 0.10 mol L⁻¹ each, respectively). The detection limits at a signal-to-noise ratio of 3 were 0.52 μmol L⁻¹ for DSi and 7.1 μmol L⁻¹ for DB. The relative standard deviations (RSD, *n* = 5) of peak areas were 0.12% for DSi and 4.3% for DB.

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1. Introduction

Silicon plays important roles in the metabolism of plants and animals, in the aqueous environment, and in the quality of water used for various purposes. Dissolved silicon (DSi) in fresh water arises from the accumulation of diatom frustules in bottom sediment and can lead to a change of phytoplankton species in coastal seawater [1]. Several analytical methods have been used to determine the concentration of DSi in environmental water and wastewater samples. DSi often is determined in parallel with phos-

phate ion, and spectrophotometry [2–4] and separation techniques [5–8] are frequently applied. Among the latter, ion-exclusion chromatography (IEC) with post-column derivatization [5,6], ion-pair liquid chromatography [7,8], and ion-exclusion/cation-exchange chromatography (IEC/CEC) with dual detection [9] have been reported for the determination of Si dissolved in environmental and wastewater samples. In addition, the enhanced conductimetric detection of DSi by connection of two different ion-exchange columns after a cation-exchange separation column [10] and the direct determination of DSi in seawater by IEC sector field inductively coupled plasma mass spectrometry [11] have been reported.

Boron occurs naturally in the environment due to its release into air, soil, and water through weathering. It also may occur in groundwater in very small amounts. Boron is taken into the human body

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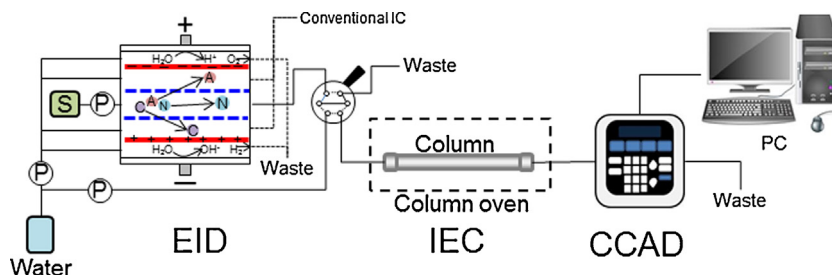


Fig. 1. Schematic illustration of the combined EID-IEC-CCAD equipment in this study.

from glass manufacturing, coal combustion, and agricultural fertilizers. In Japan, the emission limit for boron is 10 mg L^{-1} for waste water discharged into public water areas, excluding oceans [12]. The average concentration of dissolved boron (DB) in hot spring waters in Japan is around 10 mg L^{-1} . The concentration of DB in water has been determined by spectrophotometric analysis using methylene blue [13] and azomethine-H [14] and by chromatographic analysis [15–19].

Silicon and boron are metalloids that exist environmentally in water and soil and are used in semiconductor and electronic materials. Our goal is to develop a method for the simultaneous separation and determination of silicon and boron in water and soil samples in oceans, rivers, and hot springs and their surrounding areas. We seek to develop an ion chromatographic method to analyze these elements using pure water as a mobile phase by a series of pre-treatment, separation, and detection steps. Use of pure water eliminates the need for reagents apart from the sample solution and reduces post-experiment waste.

To achieve this objective we have connected an electrodiolytic ion isolation device (EID), an IEC column, and a corona charged aerosol detector (CCAD) in sequence. The EID, which was first reported by Ohira et al [20], is used to isolate DSi and DB from high concentrations of co-existing ions. IEC is used to separate the target ions eluted from the EID, and the CCAD is used to detect the ions separated by IEC.

The EID consists of five components including a sample channel, cation and anion acceptors, and two electrode isolators, which are composed of a combination of regenerated cellulose and ion-exchange membranes. The EID can quantitatively extract strong acid anions (e.g., NO_3^- , SO_4^{2-}) onto an anion acceptor, positive side, and strong base cations (e.g., Li^+ , K^+) onto a cation acceptor, negative side, with a potential of 10–30 V. Large molecules, particulates, and neutral compounds are not extracted into the anion and cation acceptors, because of the size-selective separator membrane and the absence of electric field effects on non-ionic chemical forms. Until now, the EID was successfully applied to quantitative transfer the analyte from sample solutions. Heavy metals in plasma [21] and anions in a single drop of whole blood [22] have been transferred into acceptor solutions and directly introduced into analyzers. The EID is used here to remove strong acid anions, typically at high concentration ($\sim 100 \text{ mmol L}^{-1}$), from a sample solution to determine very weak acid anions. Electrodialytic salt removal was reported in our previous study of protein determination with electrospray ionization mass spectrometry [23], where a miniature, capillary scale ($\sim 1 \mu\text{L min}^{-1}$) three-layer device with ion separators and cation and anion exchange membranes was used to separate salts from proteins. In the present study, we propose to separate and detect very weak acid anions in the presence of strong acid anions.

IEC, which was first reported by Wheaton and Baumann [24] and aggressively developed by Tanaka et al. [25–27], and many researchers [28–33], separates weak acid anions such as carbonate by elution with pure water. Because the limiting equivalent conductances of aliphatic carboxylate and carbonate ions are very low,

they are difficult to detect by conductivity, as typically employed in IC and IEC. Weak acid anions can be separated and detected using suppressed conductimetric detection IC with an alkaline eluent having a pH greater than the corresponding pK_a values [34].

The CCAD, which was developed by ESA Biosciences Inc. (Chelmsford, USA), consists of atomization, charging, and detection steps and is applicable to the detection of semi-volatile and non-volatile analytes [35,36]. Based on the nature of the CCAD, we have adopted it for the sensitive detection of non-volatile weak acid anions having very low conductimetric responses.

In this study, the combined EID-IEC-CCAD methodology is used to achieve the selective and sensitive analysis of total silicon and boron dissolved in aqueous solution by a sequential process that involves isolation from co-existing salts, separation, and detection. Here, the separations are achieved using pure water only as eluent for all processes, because it is attractive in terms of very low background levels in detection and ease of waste treatment. The sensitivity of DSi and DB detection by CCAD is compared to that of strong acid anions such as chloride and sulfate. The separation and determination of DSi and DB in artificial seawater and hot spring water samples using pure water eluent is described as an example application.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade and were purchased from Wako (Osaka, Japan). Solutions were prepared by dissolving reagents in pure water to a concentration of 0.1 mol L^{-1} . Dilutions were made as needed using pure water obtained from a Millipore Simpli Lab with Sim Pak 1 (Millipore, MA, US). Feed solutions to ion acceptors and cathode/anode isolators and eluents in IEC were all prepared with pure water. The standard sample consisted of an aqueous solution of inorganic ions [10 mmol L^{-1} HCl, 10 mmol L^{-1} H_2SO_4 , 10 mmol L^{-1} KNO_3 , 1 mmol L^{-1} silicon standard solution (Na_2SiO_3 in Na_2CO_3) (1 mmol L^{-1} Si), and 0.25 mmol L^{-1} $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (1 mmol L^{-1} B)] at appropriate concentrations.

2.2. Apparatus

The ion chromatographic separations of DSi and DB used a Shimadzu LC 20 AD solution pump, a Shimadzu CTO-20AC column oven, and a Tosoh CD-8020 conductivity detector. The CCAD was a Corona™ CAD™ (Thermo Fisher Scientific Inc., Waltham, MA, US) unit. Operating conditions of the CCAD were as follows: N_2 gas flow rate, 1.53 L min^{-1} ; N_2 gas flow ratio, 0.54; corona voltage, 2.25 kV; corona current, 1.0 μA ; ion trapping voltage, 20.2 V; and N_2 gas pressure, 35 psi. The other analytical conditions were as follows: eluent flow rate, 0.6 mL min^{-1} ; column temperature, 40°C ; and injection volume, $30 \mu\text{L}$. A schematic illustration of the combined EID-IEC-CCAD system used in this study is shown in

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