



# Precise determination of dissolved silica in seawater by ion-exclusion chromatography isotope dilution inductively coupled plasma mass spectrometry



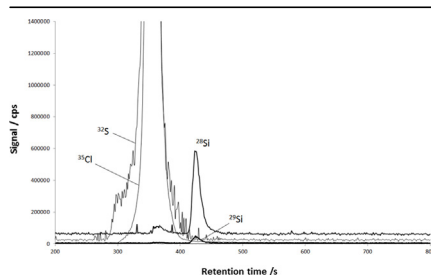
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## HIGHLIGHTS

- One  $\text{mg kg}^{-1}$  level of dissolved silica in seawater was determined precisely (0.5 %).
- Silicon background problem was minimized to yield a BEC value of  $3 \text{ ng g}^{-1}$ .
- Good precision of isotope ratio measurement was achieved in  $m/\Delta m = 4000$  of ICP-MS.
- Developed method has been applied to production of three levels of seawater CRMs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ion exclusion chromatograph (IEC) isotope dilution (ID) inductively coupled plasma mass spectrometry (ICP-MS) (IEC-ID-ICP-MS) was developed for measurement of dissolved silica in seawater, which was applied to production of certified reference materials (CRMs) of three concentration levels of nutrients (high, medium and low levels). IEC-ICP-MS has been employed to separate dissolved silica from seawater matrix. In the present study, in order to solve substantial problems due to spectral interference in ICP-MS and to improve the accuracy of IEC-ICP-MS beyond standard addition or conventional calibration methods, ID method was coupled with ICP-sector field mass spectrometry (operated under medium resolution, *i.e.*,  $m/\Delta m = 4000$ ). In addition, effects of various operating parameters in ICP-MS on a silicon background level were also investigated to obtain lower background equivalent concentration (BEC). As a result,  $3 \text{ ng g}^{-1}$  of the BEC and 0.5 % of relative standard uncertainties were achieved in the analyses of dissolved silica in seawater samples at concentration levels from  $4.0 \text{ mg kg}^{-1}$  to  $0.8 \text{ mg kg}^{-1}$  as silicon. The developed method was successfully validated by analyses of an artificial seawater containing a known amount of silicate and the seawater certified reference material MOOS-2 produced by the National Research Council Canada.

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## 1. Introduction

To investigate the cycle of nutrients (*i.e.*, nitrate, nitrite, phosphate and dissolved silica) in seawater over a long period and at difference places has been of importance in the field of oceanography, because the nutrients are the sources for

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phytoplankton to maintain its biological activity. The Joint Global Ocean Flux Study (JGOFS) proposed that concentrations of the nutrients in seawater at several sea areas should be measured with high precision of 1–3 % in order to clarify the role of the ocean in global carbon and nutrient cycles [1,2]. For that purpose production of certified reference materials (CRMs) of seawater for nutrient analysis has been desired. As for CRMs for the nutrient analysis, MOOS-2 produced by the National Research Council Canada (NRCC) is the only one, in which four kinds of nutrients were certified with expanded uncertainties (coverage factor 2) of 3–6 %. Such relatively large uncertainties make its use for monitoring the changes in nutrient concentrations at different oceans and times difficult. In addition, the concentration of each nutrient in oceans in the world has a wide distribution, i.e., the distribution of dissolved silicate in the Atlantic Ocean is from  $10 \mu\text{mol L}^{-1}$  to  $30 \mu\text{mol L}^{-1}$  [3] and that in the Pacific Ocean is from  $0.6 \mu\text{mol L}^{-1}$  to  $176 \mu\text{mol L}^{-1}$  [4]. To solve this problem, the National Metrology Institute of Japan (NMIJ) has started to develop CRMs with three concentration levels of nutrients, which are expected to support measurements along the proposal of the JGOFS.

There are many publications on the analysis of dissolved silica in seawater, employing inductively coupled plasma mass spectrometry (ICP-MS) [5], inductively coupled plasma optical emission spectrometry [6,7], flow injection analysis [8–10], and absorption spectrometry [11–13]. The determination of dissolved silica in seawater by ion-exclusion chromatography ICP-MS (IEC-ICP-MS) was reported by Hioki et. al [5], who used a quadrupole type ICP-mass spectrometer and achieved the detection limit of  $0.08 \mu\text{mol L}^{-1}$  ( $2.3 \text{ ng g}^{-1}$  as silicon). The relative standard deviation of 6 sample measurements by IEC-ICP-MS with standard addition calibration was about 1.45 %.

For further improvement of IEC-ICP-MS, the combination with the isotope dilution (ID) method was newly considered. In contrast with standard addition method or conventional calibration one, the ID method leads directly to analytical results through both weighing of samples and enriched-isotope spike materials and measuring of the molar ratio of analyte isotopes in a blend of sample and isotope spike. Therefore the ID is regarded as one of primary methods of measurements traceable to the International System of Units (SI).

In addition an ICP-sector field mass spectrometer was employed so as to avoid spectral interferences. In IEC-ICP-MS employing a quadrupole mass spectrometer, the ratio of background signal at 28 amu to that at 29 amu disagrees with the natural isotope ratio of  $^{28}\text{Si}/^{29}\text{Si}$  (19.685) because these signals consist of both silicon itself come from an introduction system of ICP-MS and interfering ion species due to plasma gas and/or solvent such as  $^{14}\text{N}_2^+$ ,  $^{12}\text{C}^{16}\text{O}^+$ ,  $^{14}\text{N}_2\text{H}^+$  and  $^{12}\text{C}^{16}\text{OH}^+$ , which are not distinguishable each other for a same mass. In particular the background from the interfering ion species would easily fluctuate with an elapsed time in a chromatogram. Therefore, the interference had better be reduced by using a sector field mass spectrometer to keep the background level stable.

However, the analysis of silicon by ICP-MS suffers from possibly higher silicon background because the sample introduction system

of ICP-MS normally employs quartz devices. The background equivalent concentration (BEC) of silicon could reach  $100 \text{ ng g}^{-1}$  under a general operating condition. Although the silicon resulting from the sample can be distinguished from the background silicon by the coupling of IEC with ICP-sector field mass spectrometer, it would be desirable to reduce the background level as low as possible to obtain better precision of peak area. This enables to determine dissolved silica in a range from  $0.04 \text{ mg kg}^{-1}$  to  $4 \text{ mg kg}^{-1}$  (as silicon; hereinafter, the concentration of dissolved silica is expressed as the mass fraction of silicon) contained in a wide variety of seawater. Therefore, in the present study, the influences of various operating parameters in ICP-MS on both the silicon background level and the net signal intensity resulting from a silicon standard solution were also investigated to find the operating condition yielding better precision of isotope ratio measurement in IEC-ICP-MS.

The present study is the first application of IEC-ID-ICP-MS to determine dissolved silica in seawater; it was partly presented in the annual meeting of the Japan Society for Analytical Chemistry [14].

## 2. Experimental

### 2.1. Seawater sample

The three levels of seawaters used in the present study are listed in Table 1. The labels of H, M and L mean high, medium and low concentration levels of nutrients, respectively. As for M-Level seawater appropriate amounts of the three sources of seawaters listed in Table 1 were blended so as to give a similar composition to seawater of the Atlantic Ocean. Each production process for the three levels of seawaters was as follows: (i) filtration of raw material with a membrane filter, (ii) sterilization by autoclave treatment, (iii) subdivision into high-density polypropylene bottles with an inner volume of 110 mL, (iv) labeling and (v) sealing by aluminum zip bags. All processes were done in a clean room.

### 2.2. Instrumentation

The ICP-sector field mass spectrometer used in the present study is an Element 2 (Thermo Fisher Scientific Inc., Bremen, Germany), equipped with a PFA nebulizer with sample uptake rate of  $450 \mu\text{L min}^{-1}$  in a self-aspiration mode and a double pass-PFA spray chamber developed for stable isotope ratio measurement [15]. The mass spectrometer was operated in a medium resolution mode ( $m/\Delta m = 4000$ ), because the signals of  $^{28}\text{Si}^+$  (27.976927) and  $^{29}\text{Si}^+$  (28.976495) overlapped with those of  $^{14}\text{N}_2^+$  (28.006148) and  $^{12}\text{C}^{16}\text{O}^+$  (27.994915),  $^{14}\text{N}_2\text{H}^+$  (29.013973) and  $^{12}\text{C}^{16}\text{OH}^+$  (29.002740), where each number in parentheses indicates atomic or molecular weight [16].

The detector was switched from a pulse counting mode to an analog mode over the signal range of 4,000,000 count per second (cps). In the analyses of H-Level and M-Level seawaters, the detector worked in the analog mode, so the conversion factor between two modes was checked at each measurement.

**Table 1**  
List of seawater materials planned for NMIJ CRMs.

Concentration level of dissolved silica	Abbreviation for seawater	Approximate concentration of dissolved silica ( $\text{mg kg}^{-1}$ )	Source of material
High	H-Level	4.0	Seawater from the nutrient maximum layer (3000 m depth) in the Pacific Ocean
Medium	M-Level	0.8	Blended seawater of (1) 690 m depth one of the Arctic Sea, (2) 1500 m depth one of the Atlantic Ocean, and (3) 397 m depth one of the Suruga-wan Bay
Low	L-Level	0.036	Seawater from the surface layer in the Pacific Ocean

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