Multielement determination of trace metals in seawater by ICP-MS with aid of down-sized chelating resin-packed minicolumn for preconcentration

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Abstract

The multielement determination of trace metals in seawater was carried out by inductively coupled plasma mass spectrometry (ICP-MS) with aid of a down-sized chelating resin-packed minicolumn for preconcentration. The down-sized chelating resin-packed minicolumn was constructed with two syringe filters (DISMIC 13HP and Millex-LH) and an iminodiacetate chelating resin (Chelex 100, 200–400 mesh), with which trace metals in 50 mL of original seawater sample were concentrated into 0.50 mL of 2 M nitric acid, and then 100-fold preconcentration of trace metals was achieved. Then, 0.50 mL analysis solution was subjected to the multielement determination by ICP-MS equipped with a MicroMist nebulizer for micro-sampling introduction. The preconcentration and elution parameters such as the sample-loading flow rate, the amount of 1 M ammonium acetate for elimination of matrix elements, and the amount of 2 M nitric acid for eluting trace metals were optimized to obtain good recoveries and analytical detection limits for trace metals. The analytical results for V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U in three kinds of seawater certified reference materials (CRMs; CASS-3, NASS-4, and NASS-5) agreed well with their certified values. The observed values of rare earth elements (REEs) in the above seawater CRMs were also consistent with the reference values. Therefore, the compiled reference values for the concentrations of REEs in CASS-3, NASS-4, and NASS-5 were proposed based on the observed values and reference data for REEs in these CRMs.
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1. Introduction

Nowadays, inductively coupled plasma mass spectrometry (ICP-MS) has become one of the most powerful analytical techniques for trace element analysis with high sensitivity as well as with wide linear dynamic range and simultaneous multielement detection capability [1,2]. However, weak tolerance to dissolved salts and polyatomic interferences is the principal disadvantage of ICP-MS, and makes it difficult to perform direct injection analysis of seawater containing ca. 3% of dissolved salts. Furthermore, the concentrations of most trace metals in seawater are extremely low at $pg\,mL^{-1}$ levels [1]. In order to overcome these difficulties, various methods such as solvent extraction [3,4], coprecipitation [5–8], and chelating resin adsorption [9–21] have been developed for preconcentration of trace metals in seawa-

ter. Among them, the chelating resin adsorption technique is the most promising approach because of no use of harmful organic solvent and low risk of contamination.

Recently, the present authors have reported a chelating resin-packed minicolumn for preconcentration of trace metals in seawater [22], where trace metals in 50 mL of original seawater sample were concentrated into 2.5 mL of 2 M nitric acid (final solution). It has been proved that the minicolumn is a convenient preconcentration device for trace metals in seawater as well as in mineral waters prior to the determination by the ICP-MS instrument equipped with a conventional concentric nebulizer [22,23].

A MicroMist nebulizer is now commercially available as a micro-sampling device, which can be operated efficiently at very low solution uptake rates (down to $sub\text{-}mL\,min^{-1}$) [24]. Then, the simultaneous multielement determination may be performed using only 0.1–0.2 mL of sample solution with the MicroMist nebulizer. Thus, the combined system of ICP-MS with a MicroMist nebulizer is expected to be a next generation

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Table 1
Operating conditions with micro-sampling and concentric nebulization for ICP-MS instrument

Operating parameters	Operating conditions	
	Micro-sample nebulization	Conventional concentric nebulization
Plasma conditions		
Incident power (kW)	1.3	1.3
Coolant gas flow rate (L min^{-1})	Ar 15.0	Ar 15.0
Auxiliary gas flow rate (L min^{-1})	Ar 1.0	Ar 1.0
Carrier gas flow rate (L min^{-1})	Ar 1.0	Ar 1.0
Sampling depth (mm from load coil)	5.5	9
Nebulizer	MicroMist	Conikal
Sample uptake rate (mL min^{-1})	0.1	1
Data acquisition		
Measurement mode	Peak hopping	Peak hopping
Dwell time (ms/point)	50	50
Data point (points/peak)	3	3
Number of scans	100	100

analytical method for the multielement determination of trace metals in seawater, if a proper preconcentration technique is established.

In the present paper, hence, a downsized syringe-driven chelating resin-packed minicolumn was developed to obtain the large preconcentration factors for trace metals in seawater, i.e., from 50 mL of original seawater to 0.5 mL of analysis solution. Then, the experimental parameters were optimized for the multi-element determination by micro-sampling ICP-MS. The present analytical method was validated by analyzing seawater certified reference materials (CRMs; CASS-3, NASS-4, and NASS-5) issued by the National Research Council of Canada (NRCC).

2. Experimental

2.1. Instrumentation

An ICP-MS instrument (Agilent HP 4500, Yokogawa, Tokyo, Japan) was used for the multielement determination of trace metals in seawater, which was equipped with a MicroMist nebulizer (AR35-1-FM01E, Glass Expansion Pty Ltd., West Melbourne, Australia). This micro-sampling ICP-MS system allowed us to determine 40 trace metals with less than 0.5 mL of analysis solution. The operating conditions for micro-sampling ICP-MS are summarized in Table 1, all of which were optimized for each instrumental parameter. For comparison, the operating conditions for conventional ICP-MS with a concentric nebulizer (Conikal, AR35-1-FC1E, Glass Expansion Pty Ltd.) are also given in Table 1. A syringe pump (KDS200, KD Scientific, MA, USA), which could flow the solution at the adjustable flow rate automatically, was used for *on-line* monitoring of the signal profiles for trace metals and matrix elements with ICP-MS as well as for passing the rinsing solutions through the column.

2.2. Chemicals and samples

Nitric acid, acetic acid and aqueous ammonia solutions of electronics industry grade were purchased from Kanto Chem-

icals (Tokyo, Japan). The multielement standard solutions for making the working calibration curves were prepared by diluting the single-element standard stock solutions (1000 μg mL^{-1}) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). The multielement standard solutions were prepared in three groups, as is shown in Table 2, in which Ge, In, Re, and Tl were added as the internal standard elements to be 10 ng mL^{-1} each. The Chelex 100 resin in 200–400 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). Before packing the chelating resin into the minicolumn, the resin was cleaned by soaking in fresh 5 M HCl, which was changed daily for 5 days. The resin was collected on a G4 glass filter, and after rinsing with 2 M nitric acid and pure water, it was kept in a 0.1 M of ammonium acetate at pH 6.0. Pure water used throughout the present experiment was prepared by a Milli-Q purification system (Element A-10, Nihon Millipore Kogyo, Tokyo, Japan).

Three kinds of seawater CRMs (CASS-3, NASS-4, and NASS-5) were purchased from NRCC. Coastal seawater sample collected from the shore near the Take Island (Gamagori, Aichi Prefecture, Japan) was used for optimizing the experimental conditions of the present preconcentration method. It was filtered with a membrane filter (pore size 0.45 μm) and acidified to pH 1 with concentrated nitric acid.

Table 2
Multielement standard solutions for calibration[a]

Group	Element	Concentration (ng mL^{-1})
Group I	V, Co, Pb	50
	Dy, Ho, Er, Tm, Lu	5
Group II	Cu, Zn, Cd	50
	La, Ce, Pr, Nd, Yb	5
Group III	Mn, Ni, Mo	50
	Y, Sm, Eu, Gd, Tb, U	5

[a] Each of the multielement standard solutions contains Ge, In, Re, and Tl (10 ng mL^{-1} each) as internal standard elements.