Technical note

# An off-line automated preconcentration system with ethylenediaminetriacetate chelating resin for the determination of trace metals in seawater by high-resolution inductively coupled plasma mass spectrometry

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HIGHLIGHTS

- A novel automated off-line preconcentration system for trace metals was developed.
- Nine trace metals were quantitatively preconcentrated and determined by HR-ICP-MS.
- The single-step preconcentration effectively removed major cations of seawater.
- The procedural blanks and detection limits were at the lowest levels.
- Reference seawater samples and vertical profiles were analyzed successfully.

GRAPHICAL ABSTRACT
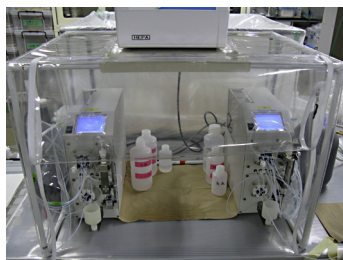
ABSTRACT

A novel automated off-line preconcentration system for trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in seawater was developed by improving a commercially available solid-phase extraction system SPE-100 (Hiranuma Sangyo). The utilized chelating resin was NOBIAS Chelate-PA1 (Hitachi High-Technologies) with ethylenediaminetriacetic acid and iminodiacetic acid functional groups. Parts of the 8-way valve made of alumina and zirconia in the original SPE-100 system were replaced with parts made of polychlorotrifluoro-ethylene in order to reduce contamination of trace metals. The eluent pass was altered for the back flush elution of trace metals. We optimized the cleaning procedures for the chelating resin column and flow lines of the preconcentration system, and developed a preconcentration procedure, which required less labor and led to a superior performance compared to manual preconcentration (Sohrin et al. [5]). The nine trace metals were simultaneously and quantitatively preconcentrated from ∼120 g of seawater, eluted with ∼15 g of 1 M $HNO_3$, and determined by HR-ICP-MS using the calibration curve method. The single-step preconcentration removed more than 99.998% of Na, K, Mg, Ca, and Sr from seawater. The procedural blanks and detection limits were lower than the lowest concentrations in seawater for Mn, Ni, Cu, and Pb, while they were as low as the lowest concentrations in seawater for Al, Fe, Co, Zn, and Cd. The accuracy and precision of this method were confirmed by the analysis of reference seawater samples (CASS-5, NASS-5, GEOTRACES GS, and GD) and seawater samples for vertical distribution in the western North Pacific Ocean.

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# 1. Introduction

Trace elements and their isotopes (TEIs) in the ocean are important as tracers in oceanography, micronutrients and/or toxins in biogeochemistry, and proxies in paleoceanography [1]. Recently, an international research program of the marine biogeochemical cycles of TEIs, referred to as GEOTRACES, was commenced to determine the distributions of key TEIs (such as Al, Mn, Fe, Cu, Zn, Cd, and Pb) and to clarify their sensitivity toward changing environmental conditions [2,3]. While high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is a powerful technique in the multi-elemental determination of trace metals, major constituents of seawater interfere with the precise determination [4]. In our previous paper, we reported a single-step and quantitative preconcentration of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb from open-ocean water, based on solid-phase extraction using a NOBIAS Chelate-PA1 resin (Hitachi High-Technologies) [5]. This resin consists of hydrophilic polyhydroxymethacrylate beads functionalized with ethylenediaminetriacetic acid and iminodi-acetic acid [6]. Ethylenediaminetriacetate is an analogue of ethylenediaminetetraacetate and a strong ligand for trace metals. In addition, NOBIAS Chelate-PA1 has certain advantages, including the effective removal of alkali and alkaline earth metals, low blanks of trace metals, and chemical and physical stability. We applied this method for oceanographic studies of trace metals in the Indian Ocean [7], the Bering Sea [8], and the Arctic Ocean [9]. The utilization of NOBIAS Chelate-PA1 is growing worldwide, not only for GEOTRACES key trace metals [10–13] but also for rare earth elements [13–17], Bi [18], Th [19], U [20], and isotopic ratios of trace metals [21–23]. Our original method was based on a manual manifold, which required skillful and uninterrupted operation. Here, we report a new automated preconcentration system with NOBIAS Chelate-PA1 for the quantitative recovery of nine trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb). Three methods using automated preconcentration systems with NOBIAS Chelate-PA1 have been reported thus far. One method was based on a seaFAST system (Elemental Scientific) for the on-line flow-injection ICP-MS determination of Mn, Fe, Co, Ni, Cu, and Zn [11]. Another method utilized a house-made, off-line pre-concentration system for Mn, Co, Ni, Cu, Cd, and Pb [12]. The final method was based on a Dionex ICS3000 chromatograph for the off-line preconcentration of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Cd, Ag, Pb, and rare earth elements [13]. While these methods utilized small volumes of seawater (9–38 mL), our system can handle a larger sample volume and can reduce the relative concentrations of blanks and interferents. In addition, while the reported methods adopted in-line pH adjustments, the sample pH in this method was adjusted off-line for a precise pH control. We utilized ~120 g of seawater, quantitatively recovered the nine metals, and realized the lowest levels of blanks, concentrations of interferents, and detection limits.

# 2. Materials and methods

## 2.1. Reagents and materials

Deionized water (MQW) purified with a Milli-Q Integral 5 system (Millipore) was used to prepare all solutions. Ultra-high purity reagents, including HCl, $HNO_3$, acetic acid (HOAc), and $NH_3$ (Optima Acids, Fisher Scientific or TAMAPURE AA-10, Tama chemicals), were used for the solution preparation and analysis. Standard solutions of trace metals were prepared from 1000 mg $L^{-1}$ standard solutions (Wako Pure Chemical). All solutions were prepared on a weight basis in a clean room (class 1000).

Low-density polyethylene (LDPE) bottles (Nalge Nunc) were used for sample storage and solution preparation. The bottles were cleaned in a clean hood and the operator wore polyethylene gloves (Saniment, AS ONE) to avoid contamination. The bottles and caps
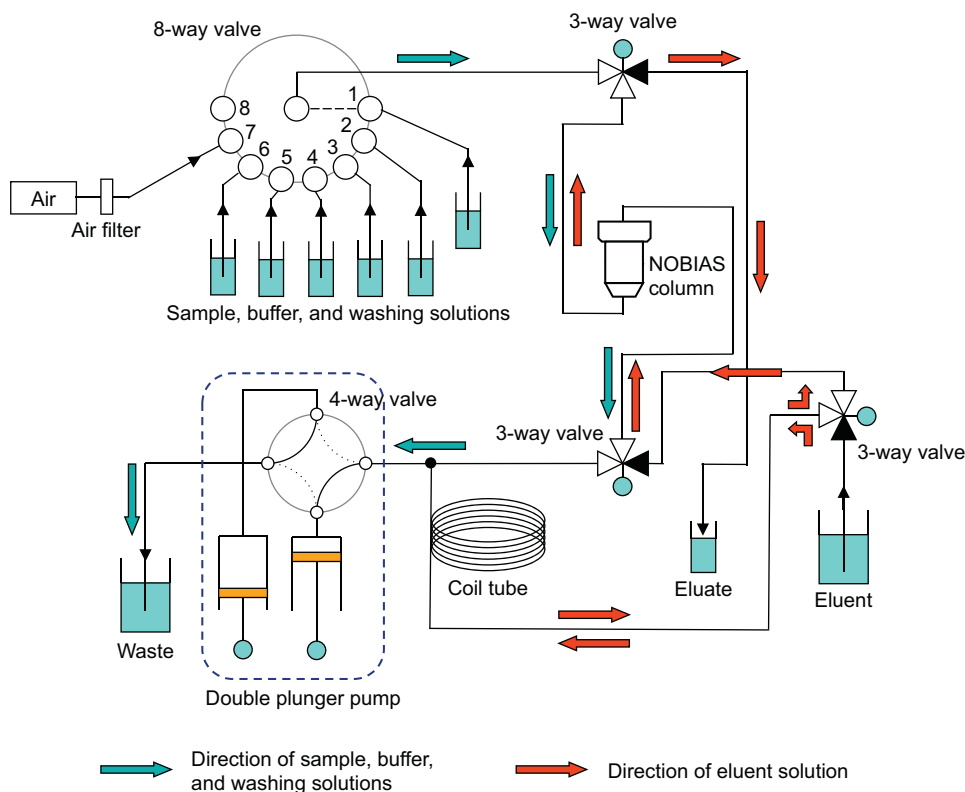


Fig. 1. Manifold schematic of the modified automated concentration system. The sending unit, a possible source of contamination, is shown in the box with the broken line.