Division of Environmental Chemistry <u>– Hydrospheric Environment Analytical Chemistry</u>–

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Prof SOHRIN, Yoshiki (D Sc)



Assoc Prof UMETANI, Shigeo (D Sc)



Assist Prof NORISUYE, Kazuhiro (D Sc)



Techn Staff MINAMI, Tomoharu (D Eng)

Students

TAKANO, Shotaro (D1) YAMAMOTO, Jun (D1) FUJISAKA, Hiroaki (M2) ICHIWAKI, Shouhei (M2) KAWAHARA, Shimpei (M1) KONAGAYA, Wataru (M1)

Visitor

Dr HO, Tung-Yuan Research Center for Environmental Changes, Academia Sinica, Taiwan, 13 July

Scope of Research

- (i) Biogeochemistry of trace elements in the hydrosphere: Novel analytical methods are developed for trace metals and its isotopes. Distribution of trace elements in the hydrosphere and its effects on ecosystem are investigated. The study also covers hydrothermal activity, deep biosphere and paleocean.
- (ii) Ion recognition: Novel ligands and ion recognition system are designed, synthesized and characterized.

KEYWORDS

Analytical Chemistry Marine Chemistry Trace Elements Stable Isotopes Metal Ion Recognition



Selected Publications

Norisuye, K.; Sohrin, Y., Determination of Bismuth in Open Ocean Waters by Inductively Coupled Plasma Sector-Field Mass Spectrometry after Chelating Resin Column Preconcentration, *Analytica Chimica Acta*, **727**, 71-77 (2012).

Nakagawa, Y.; Takano, S.; Firdaus, M. L.; Norisuye, K.; Hirata, T.; Vance, D.; Sohrin, Y., The Molybdenum Isotopic Composition of the Modern Ocean, *Geochemical Journal*, 46, 131-141 (2012).

Cid, A. P.; Nakatsuka, S.; Sohrin, Y., Stoichiometry among Bioactive Trace Metals in the Chukchi and Beaufort Seas, *Journal of Oceanography*, 68, 985-1001 (2012).

Okamura, H.; Ikeda-Ohno, A.; Saito, T.; Aoyagi, N.; Naganawa, H.; Hirayama, N.; Umetani, S.; Imura, H.; Shimojo, K., Specific Cooperative Effect of a Macrocyclic Receptor for Metal Ion Transfer into an Ionic Liquid, *Analytical Chemistry*, **84**, 9332-9339 (2012).

Tsurubou, S.; Umetani, S.; Komatsu, Y., Separation of Alkaline Earth Metal Ions with a Strongly Acidic Cation Exchange Resin Using the Diazapolyoxabicyclic Ligand as an Ion Size Selective Masking Reagent, *Solvent Extraction Research and Development, Japan*, **19**, 177-181 (2012).

Stoichiometry among Bioactive Trace Metals in the Arctic Ocean

The distribution of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater was investigated in the Chukchi and Beaufort Seas in September 2000. The unfiltered and filtered seawater samples were used for determination of total dissolvable metal (TDM) and dissolved metal (DM), respectively. The concentrations of TDAl, TDMn, TDFe, TDCo, and TDPb varied substantially in the study area. The high concentrations occurred at stations near the Bering Strait, in the Mackenzie delta, and above reductive sediments on the shelf and slope. These elements were mostly dominated by labile particulate species, such as Fe-Mn oxides and species adsorbed on terrestrial clay. DCo was correlated with DMn over the study area. TDNi, TDCu, TDZn, and TDCd showed relatively small variations and were generally dominated by dissolved species. There was a moderate correlation between DCd and phosphate for all samples, whereas there were no significant correlation between the other DMs and nutrients. TDNi and TDCu showed a remarkable linearity for most stations except those near the Bering Strait. These results suggest that biogeochemical cycling including uptake by phytoplankton and remineralization from settling particles has only minor control over the distribution of trace metals in this area. Using the present data, the annual input of bioactive trace metals from the Bering Strait and the Mackenzie River was estimated. Also the trace metal compositions of major water masses were evaluated. The DM/P ratios were significantly different from those for Pacific deep water and Bering Sea water, suggesting substantial modification of the trace metal compositions of seawater in the study area.



Figure 1. Observation in the Arctic Ocean during the R/V Mirai MR00-K06 cruise in September 2000.

High-Throughput Method for the Determination of Bismuth in Open Ocean Waters

Bismuth is a unique and useful tracer for the input of volcanogenic and/or anthropogenic materials to the surface oceans and also for vertical processes in the ocean. However, the number of oceanic data is scarce and little is known about the marine biogeochemical cycle of this element. It is necessary to develop a method that satisfies high throughput as well as high precision, good accuracy, and low blank and detection limit. We have developed a novel low-blank method for the analysis of bismuth in open ocean waters based on preconcentration using an ethylenediaminetriacetic acid (EDTriA) chelating resin column followed by determination with inductively coupled plasma sector-field mass spectrometry (ICPSFMS). A sample is siphoned into and drains through the column with the flow rate being kept constant by using a water bath device. Bi in 250 mL of acidified seawater is extracted onto the column in this process and eluted with 2 mL of 3 M HNO₃ followed by 3 mL of ultra-high purity water. The concentration of Bi in the eluate is measured by ICPSFMS. The benefits of the present method relative to others are its simplicity, a smaller amount of seawater, and lower blanks and detection limits at fmol kg⁻¹ levels. Another advantage is that it allows a simultaneous run of large numbers of samples depending on the number of column lines.



Figure 2. The preconcentration system. (a) Pipetting of solutions for conditioning, removal of sea salt and elution. (b) Steady-flow siphonic transport of seawater samples using the flotation device. H is the water level difference of a sample solution between the bottle and column.