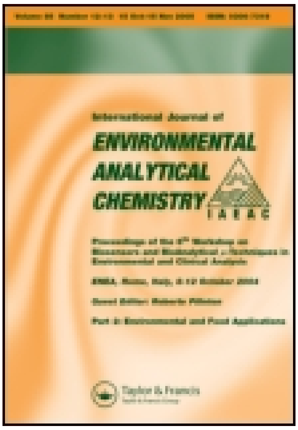

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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To cite this article: Junling Bai, Hirotsugu Minami, Hirotoshi Sakagami, Kanako Mantoku, Ikuo Atsuya, Nobuo Takahashi, Atsushi Tanaka, Kazuo Jin & Takayoshi Kawai (2011): Development of determination method of trace nickel in natural water by ID-oxygen added nitrogen-MIP-MS with direct measurement of liquid-liquid extracted organic phase, International Journal of Environmental Analytical Chemistry, 91:9, 811-820

To link to this article: http://dx.doi.org/10.1080/03067311003782641

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 9, 10 August 2011, 811–820

Development of determination method of trace nickel in natural water by ID-oxygen added nitrogen-MIP-MS with direct measurement of liquid–liquid extracted organic phase

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(*Received 5 October 2009; final version received 12 February 2010*)

This work introduces the development of a novel determination method of trace nickel (ng l^{-1} level) in natural water samples. Nickel in the water samples is liquid–liquid extracted into methyl isobutyl ketone (MIBK) as nickel-diethyldithiocarbamate (DDTC) complex, and isotope dilution-oxygen added nitrogen-microwave induced plasma mass spectrometry (ID-oxygen added nitrogen-MIP-MS) is conducted by direct measurement of the liquid–liquid extracted organic MIBK phase. The accuracy of the proposed method was confirmed by analysing certified reference materials (NRC NASS-5 seawater, NRC SLRS-3 riverine water and NRC SLRS-4 river water), and the analytical results obtained were in good agreement with the certified values. The detection limit for nickel is 1.3 ng l^{-1} when the water sample is 50 times concentrated. The precision as RSD is $<4\%$. The proposed method was applied to clarify the concentration-depth vertical profiles of nickel in Lake Mashu, Japan, as the Baseline Station of the United Nations GEMS/Water (Global Environment Monitoring System/Water) Programme.

Keywords: nickel; natural water; isotope dilution; liquid–liquid extraction; microwave induced oxygen added nitrogen plasma mass spectrometry; Lake Mashu

1. Introduction

Nickel is one of the most important elements in environment-monitoring projects such as the United Nations GEMS/Water (Global Environment Monitoring System/Water) Programme [1] since nickel is emitted into the air by the combustion of fossil fuels such as oil and coal [2–5]. Fossil fuel combustion could be a serious source of nickel contamination in water via the air, thus increasing the water environmental burden. Nickel is a moderately toxic element, but it can cause allergic reactions, and certain nickel compounds are found to be associated with nasal and lung cancer [6,7]. In order to assess the input of nickel from the air, at least two distinct approaches should be carried out, i.e. the

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067311003782641
http://www.informaworld.com

determination of nickel in environmental waters and the chemical analysis of nickel compounds in air particulate matter [8]. This study thus focuses on nickel in natural water samples. The concentration of nickel in natural water has been reported to be as low as sub-μg l^{-1} levels (0.12–0.70 μg l^{-1} in open ocean water) [9]. Therefore, the use of a highly sensitive and accurate analytical method for the determination of nickel in natural water samples is important. In order to establish an analytical method for the determination of nickel in natural water samples, the previously reported detection limit values of commonly used instrumental analyses were as follows: (1) inductively coupled plasma atomic emission spectrometry (ICP-AES): 0.2 μg l^{-1} [10]; (2) graphite furnace atomic absorption spectrometry (GF-AAS): 0.1–0.4 μg l^{-1} [10]; and (3) inductively coupled plasma mass spectrometry (ICP-MS) and microwave induced plasma mass spectrometry (MIP-MS): 0.0005–0.01 μg l^{-1} [10]. From the perspective of the detection limit, plasma mass spectrometry such as ICP-MS and MIP-MS is suitable for the determination of trace nickel in natural water samples.

The direct determination of sub-μg l^{-1} levels of nickel by ICP-MS equipped with a reaction cell using 10-times dilution seawater was reported [11]. However, positive errors caused by spectral interference by $^{44}Ca^{16}O$ on ^{60}Ni were reported when using ICP-MS, not only without a reaction cell [12] but also ICP-MS equipped with a reaction cell [13]. These reports suggest that the separation of nickel from the matrix of the water sample must be carried out to achieve accurate analyses.

Many methods for separating nickel from the matrix have been reported, including co-precipitation methods [14,15], chelating resins [16–20] and liquid–liquid extraction after the formation of chelate compounds [21,22]. The accuracy of the analytical results determined by these methods is, however, critically influenced by variations in the recovery of the analyte during the separation processes. Therefore, a more accurate calibration method, the accuracy of which is not affected by variation in the recovery of analyte, such as isotope dilution (ID), is necessary. Sturgeon *et al.* and Mykytiuk *et al.* have reported the determination of 0.4 μg l^{-1} levels of nickel in seawater samples using ID-spark source mass spectrometry after an ion exchange pre-concentration and separation process [23,24]. However, the method requires a large capital outlay and can process only relatively few samples per day, making routine use unfeasible. McLaren *et al.* reported the determination of 0.3 μg l^{-1} levels of nickel in seawater samples by ID-ICP-MS after separation and pre-concentration with silica-immobilised 8-hydroxyquinolin [25–27]. However, Beauchemin *et al.* reported problems with inaccuracy that were caused by spectral interference after pretreatment using the silica-immobilised 8-hydroxyquinolin [28].

In our study, nickel in natural water samples was separated and extracted into the methyl isobutyl ketone (MIBK) phase as nickel-diethyldithiocarbamate (DDTC) complex by liquid–liquid extraction, which can eliminate calcium-based spectral interference since calcium is not extracted as DDTC complex [29].

An MIP-MS was developed and placed on the market by Hitachi (Japan) in the early 1990s. Oishi *et al.* and Okamoto have reported on the characteristic behaviour of nitrogen-MIP-MS [30,31]. The most important characteristic of nitrogen-MIP-MS for nickel analysis with liquid–liquid extraction separation is that the direct measurement of the extracted organic MIBK phase containing nickel-complex is possible when oxygen is added to the nitrogen-MIP. Kato *et al.* reported ID-ICP-MS analysis of a 2 μg l^{-1} level (*ca.* 100 times higher than that we attempted to determine in our study) of nickel in a water sample after liquid–liquid extraction using chloroform [32]. However, they needed to evaporate chloroform since this organic solvent could not be measured directly by Ar-ICP and redissolve the residue containing nickel using acids before measurements, which might cause potential contamination.

This work introduces the development of a novel determination method of trace nickel (ng l^{-1} level) in natural water samples by ID-oxygen added nitrogen-MIP-MS with direct measurement of the liquid–liquid extracted MIBK phase containing Ni-DDTC complex. The proposed method was applied to clarify the concentration-depth vertical profiles of nickel in Lake Mashu, Japan, as the Baseline Station of the United Nations GEMS/Water (Global Environment Monitoring System/Water) Programme.

2. Experimental

2.1 *Apparatus*

A Hitachi P-7000 MIP-MS (Hitachi, Japan) was used to measure the nickel isotope ratio ($^{60}Ni/^{62}Ni$) in order to carry out an ID analysis of nickel. Typical operating conditions for oxygen added nitrogen-MIP-MS are given in Table 1. Platinum sampler and Pt-coating skimmer cones were used. A Hitachi Z-8230 polarised Zeeman flame-atomic absorption spectrometry (FAAS) was used to measure nickel absorbance to fix nickel-extraction conditions. A model Seacat SBE 19-03 (Sea-Bird Electronics, USA) Conductive-Temperature-Depth-profiling (CTD) was used to measured water temperature at different depths in Lake Mashu, Japan.

2.2 *Reagents and materials*

The high-purity water was made by a Milli-Q ultra pure water system (Milli-Q gradient purity system equipped with an Elix pure water system, Millipore Co., Japan). A nickel standard solution was prepared by diluting a commercially available nickel standard solution (Wako Pure Chemical Co., Japan; $Ni(NO_3)_2$ in 0.1 M HNO_3, 1000 mg l^{-1}). A ^{62}Ni spike solution was prepared by dissolving a ^{62}Ni stable isotope (metal powder form, ^{62}Ni: 97.81%, Oak Ridge National Laboratory, USA) in a high purity nitric acid (Ultra pure, Kanto Chemical Co., Japan). The accurate nickel concentration of ^{62}Ni solution was

Table 1. Instrument conditions for ID-MIP-MS.

Plasma conditions	
Frequency	2.45 G Hz
Microwave power	1.3 k W
Plasma nitrogen gas flow rate	13 l min^{-1}
Carrier nitrogen gas flow rate	1.3 l min^{-1}
Plasma oxygen gas flow rate	100 ml min^{-1}
Sampling cone	Pt, 0.8 mm orifice
Skimmer cone	Pt coated Cu, 0.4 mm orifice
Measurement parameters	
Dwell time	50 ms
Number of sweeps	1500
Points per peak	1
Number of replicates	5

determined by inverse isotope dilution method using commercially available nickel standard solution.

A diethyldithiocarbamate solution (DDTC solution, 1%, w/v) was prepared daily by dissolving AAS grade sodium diethyldithiocarbamate trihydrate (Wako Pure Chemical Co., Japan) in water. MIBK (Wako Pure Chemical Co., Japan) was used as solvent. Diammonium hydrogen citrate (Wako Pure Chemical Co., Japan) for AAS was used. Ammonia solution (28%, Ultra pure, Kanto Chemical Co., Japan) was used to adjust pH of the solutions. A dimethylglyoxime (DG) ethanol solution (1%, w/v) was prepared by dissolving special grade dimethylglyoxime (Wako Pure Chemical Co., Japan) in ethanol. All reagents are used without further purification.

Certified reference materials of trace metals in seawater (NRC NASS-5), in estuarine water (NRC SLRS-3) and in river water (NRC SLRS-4) issued from National Research Council of Canada (Ottawa, Ontario, Canada) were used to confirm the accuracy of the proposed method. All of the natural water samples collected were acidified using nitric acid after sampling to preserve trace metals in solution.

All the bottles, volumetric flasks, beakers, etc. employed in this study were made of PFA (polytetrafluoroethylene-perfluoro alkyl vinyl ether copolymer) or PTFE (polytetrafluoroethylene). Materials that came into contact with the water samples and all reagents we used were acid-cleaned before use. In order to prevent the contamination, the preparation of solutions and the extraction procedure were carried out on a clean bench (class < 10) placed in a clean room (class < 1000). The sample solution placed in a clean bench (class < 10) was introduced into the MIP-MS.

2.3 *Separation and pre-concentration of nickel in water samples by the liquid–liquid extraction*

A 250 ml portion of the water sample was taken in a PFA bottle. An appropriate portion (50–250 µl) of ^{62}Ni isotope solution (*ca.* 0.8 mg l^{-1}) was added to the water sample. The spiked sample solution was heated on a hotplate heater at *c.* 80°C overnight to achieve isotope equilibrium, and it was then transferred to a 500 ml PFA separating funnel. A 25 ml portion of diammonium hydrogen citrate solution (10%, w/v) was added to the funnel, and the pH of the solution was adjusted to pH 8–10 by the addition of ammonia solution. In order to avoid contaminating by dipping a pH electrode into the solution, pH measurement was carried out using an isolated 500 µl portion of the solution. A 10 ml portion of the DDTC solution (1%, w/v) was then added to the funnel. Finally, 10 ml of MIBK was added to the funnel, which was then shaken for 20 min by an auto-shaker and allowed to stand for a few minutes. The organic phase (final volume of MIBK after shaking was *ca.* 4–5 ml) was then separated. The concentration factor during this procedure was 50–60.

2.4 *Measurement of the isotopic ratio (^{60}Ni/^{62}Ni) to determine the concentration of nickel by ID-MIP-MS*

Prior to the measurement of the sample solution, 0.14 M nitric acid and then MIBK were introduced to wash the inside the tube, spray chamber, etc. of the MIP-MS for a few minutes. Then, the analytical blank were measured at ion counts $m/z = 62$ and 60, the spike and reference isotopes, respectively. ^{60}Ni/^{62}Ni in a sample solution containing ^{62}Ni spike was obtained after subtracting the ion counts of the analytical blank obtained just before the sample measurement. The nickel concentration in the sample water was calculated by an equation described by Minami *et al.* as follows [33]:

$$\mathrm{C = w_n M_s\,(A_s - RB_s)/\,w_s W\,(RB_n - An)}$$

where R is the obtained isotopic ratio (^{60}Ni/^{62}Ni), which is corrected for mass discrimination by using nickel standard solution, C is the concentration of nickel in the sample (in ng ml^{-1}), w_n is the atomic weight of natural nickel (58.6934) [34], w_s is the atomic weight of spiked nickel (61.9404), M_s is the amount of spiked nickel (in ng), A_s is the abundance of ^{60}Ni in the spike (0.0086), B_s is the abundance of ^{62}Ni in the spike (0.9781), A_n is the abundance of ^{60}Ni in natural nickel (0.262231) [34], B_n is the abundance of ^{62}Ni in natural nickel (0.036345) [34], and W is the volume of the sample (in ml).

2.5 *Lake water sampling*

Lake water samples were collected in Lake Mashu (Japan), which is the Baseline Station of the United Nations GEMS/Water Programme. Lake Mashu samples are used to determine a representative nature baseline level, and there is no inflow river, no hotel/road at the lakeside, and no settlement/factory in catchment area. A continuous monitoring of water temperature using CTD revealed that the entire lake water mixes completely twice a year [35]. The basic information of Lake Mashu is as follows: (1) area: 19.2 km^2; (2) altitude of surface: 315 m; (3) water depth (average/deepest): 146 m/212 m; and (4) inner volume: 2.9×10^9 m^3.

Lake Mashu samples were collected using a Go-Flo sampler made of PVC. As no metallic part is contained in this sampler, it is suitable for the sampling for trace metals analysis. The interior of the fluorine-resin-coated sampler was cleaned by acid before use. Water samples were collected in June 2008 (0.3 m, 1.5 m, 10 m, 50 m, 100 m, 200 m) and August 2007 (200 m, 205 m, 210 m) at 43°35′02″ N, 144°32′03″ E in Lake Mashu. Lake water was transferred from the sampler to the acid-cleaned PFA bottles immediately after collection. It was placed in a cold box on board and then brought into a clean room as soon as possible. Samples of all depths were acidified in the clean room. All the samples were stored at 4°C until use.

3. Results and discussion

3.1 *Selection of the ligand*

The requirements of the ligand used in this study were that: (1) it could form a stable complex with nickel; (2) spectroscopic interfering metals, especially calcium, must not be extracted to MIBK phase; (3) a high-purity reagent containing negligible levels of nickel is commercially available; and (4) spectroscopic interfering molecular ions must not be produced in the oxygen-added nitrogen MIP. In order to select the ligand, preliminary experiments were carried out by using DG, which was one of the most common ligands for nickel. When DG was used as a ligand, however, rapid and critical sensitivity suppression was found; this reduction was thought to be caused by the introduction of the MIBK phase containing large amounts of DG to the plasma. When DDTC was used as a ligand, the suppression of the signal was not observed at all. The difference between these phenomena was based on the solubility of the ligands (DG and DDTC) in MIBK.

In order to evaluate the contamination level of nickel in reagent solutions containing DDTC, diammonium hydrogen citrate and ammonia solution, the analytical blank values determined by the proposed method using the reagent solutions with and without purification (the DDTC solution was shaken with two-folds of 10 ml of MIBK to remove contaminating nickel) were compared, and no difference was found.

3.2 *Effects of pH of aqueous phase and mass of DDTC on liquid–liquid extraction of nickel*

As the ID method was used in this study, the extraction rate basically had no influence on the accuracy. Therefore, the optimal pH for nickel extraction and the optimal mass of DDTC were examined not from the perspective of accuracy but from the perspective of sensitivity.

The relationship between nickel concentration in the MIBK phase and pH of the aqueous phase before liquid–liquid extraction were discussed using FAAS and MIP-MS. Nickel standard solutions, 500 $\mu g\,l^{-1}$ and 10 $\mu g\,l^{-1}$, were extracted under different pH, and the respective nickel concentrations in the MIBK phase were measured by FAAS and MIP-MS, respectively. The nickel concentration (DDTC-Ni complex concentrations) remained almost maximum and constant in the pH range 8–10. Therefore, in this study, pH 8–10 was used for nickel extraction. The optimal mass of DDTC was investigated in the same way, and the optimal mass chosen was 40 mg DDTC for a 100 ml sample.

3.3 *Determination of nickel in certified reference materials by the proposed method*

Table 2 shows the analytical values for nickel in certified reference materials (seawater: NRC NASS-5, riverine water: NRC SLRS-3, river water: NRC SLRS-4). The analytical values determined by the proposed ID-MIP-MS were in good agreement with the certified values without diluting the samples, even the seawater sample, which shows an immense advantage in sensitivity. The accuracy of the proposed method for sub $\mu g\ l^{-1}$ nickel determination was then confirmed.

Table 2. Analytical results for nickel in the seawater reference material NASS-5, river water reference material SLRS-4 and riverine water reference material SLRS-3 by ID-MIP-MS (Mean of replicate measurements of a sample with 95% confidence level).

	NRC NASS-5		NRC SLRS-4		NRC SLRS-3	
	Seawater reference material		River water reference material		Riverine water reference material	
Element	Found Value ($\mu g\ l^{-1}$)	Certified Value ($\mu g\ l^{-1}$)	Found Value ($\mu g\ l^{-1}$)	Certified Value ($\mu g\ l^{-1}$)	Found Value ($\mu g\ l^{-1}$)	Certified Value ($\mu g\ l^{-1}$)
Ni	0.269 ± 0.008 ($n = 10$)	0.253 ± 0.028	0.72 ± 0.01 ($n = 20$)	0.67 ± 0.08	0.82 ± 0.03 ($n = 5$)	0.83 ± 0.08

3.4 *Detection limit and precision*

The detection limit of ^{60}Ni in organic phase is calculated based on standard deviation of blank solution after the proposed pre-concentration procedure and the slope of a calibration curve obtained by determining the extracted MIBK phase of the standard solutions. The value of the detection limit is $1.3\,\mathrm{ng\,l^{-1}}$ (50 times pre-concentration) when 3σ definition is used. The relative standard deviation (RSD) of the proposed method for the determination of nickel is 2.8–3.7% ($n = 5$–20). Thus, the proposed method can be used to assess trace nickel (ng $\mathrm{l^{-1}}$ level) in natural water samples including seawater samples.

3.5 *Determination of nickel in Lake Mashu as the Baseline Station of the United Nations GEMS/Water Programme*

Lake Mashu, Japan is the Baseline Station of the United Nations GEMS/Water Programme [1]. From the viewpoint of global environmental monitoring of pollution by halogenated organic compounds [36–38], organochlorine pesticides such as benzene hexachloride (BHC) in the water of Lake Mashu have been analysed since the early 1980s, after the enforcement of regulations on manufacture and sale/adihibition of BHC in 1972 in Japan. As a result, a steady annual decrease of the concentrations of BHC isomers in Lake Mashu water has been detected since the adhibition of BHC was forbidden in a neighbouring country in 1984 [36,38]. This means that the BHC was atmospherically transported to Japan across the ocean between Japan and a neighbouring country. This result strongly suggests that other chemicals, such as nickel, that are atmospherically transported to Japan from neighbouring countries should be detected by using water samples from Lake Mashu, since it is the Baseline Station located in Japan.

In this paper, in order to assess the input of nickel into Lake Mashu from the air, the clarification of the concentration-depth vertical profiles of the trace nickel (tens of ng $\mathrm{l^{-1}}$ level) in Lake Mashu was conducted by using the proposed ID-MIP-MS. Figure 1 shows the nickel concentration-depth vertical profiles of Lake Mashu in June 2008 (closed circles). Water samples of Lake Mashu were collected both above and below the thermocline (2 m), which was determined by continuous monitoring of water temperature using CTD. This is the first report of the concentration-depth vertical profiles of nickel in Lake Mashu. These results show that the concentrations of nickel in the shallow layers (0.3 m: $0.076 \pm 0.003\,\mathrm{\mu g\,l^{-1}}$, and 1.5 m: $0.038 \pm 0.002\,\mathrm{\mu g\,l^{-1}}$) were higher than those in the intermediate layers (10 m: $0.015 \pm 0.001\,\mathrm{\mu g\,l^{-1}}$, 50 m: $0.017 \pm 0.001\,\mathrm{\mu g\,l^{-1}}$, and 100 m: $0.020 \pm 0.003\,\mathrm{\mu g\,l^{-1}}$). This figure also shows that the concentration of nickel in the bottom water (200 m: $0.054 \pm 0.002\,\mathrm{\mu g\,l^{-1}}$) was higher than those in the intermediate layers. The finding that the concentration of nickel in the bottom water (200 m) was higher than that at 100 m might be the result of a nickel supply from a hot spring on the lake floor [35], since the concentration of nickel in the bottom lake water increased with both the depth (up to deepest: 212 m) and temperature of the lake water as shown in Figure 2 (sampled in August 2007). The concentrations of nickel in the intermediate depth water (10 m, 50 m and 100 m) were constant values; the average value ($0.017\,\mathrm{\mu g\,l^{-1}}$) of the concentration of nickel at 10, 50 and 100 m was comparable to the reported value ($0.027\,\mathrm{\mu g\,l^{-1}}$) obtained in the early 1980s using ICP-AES measurement after 500-times concentration using chelating resin [39].

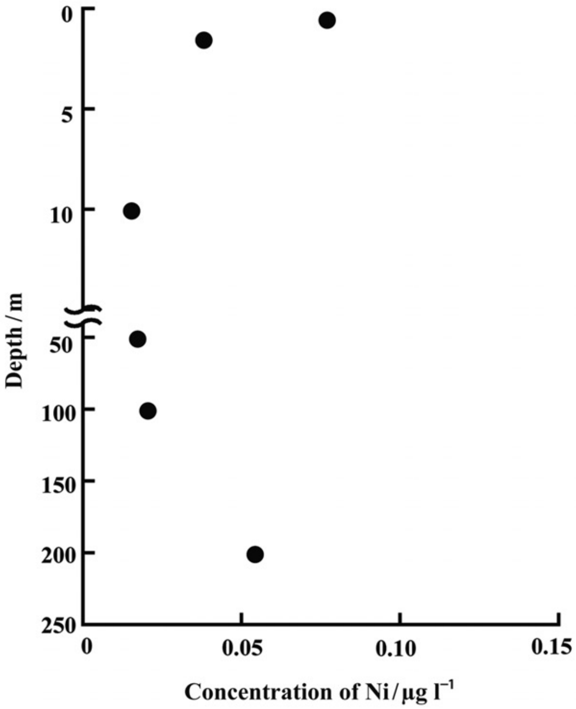

Figure 1. Ni concentration-depth profiles of Lake Mashu water sampled in June 2008. Five replicate measurements were made for each water sample.

A continuous monitoring of the relationship between water temperature and water depth using CTD revealed that the entire lake water mixes completely twice a year (spring and late autumn) [35]. It means that the concentration of nickel should be the same between the surface water and the bottom water during the mixing period. In 2007 and 2008, the entire water mixing was confirmed by CTD before the lake water sampling. As Lake Mashu has no inflow rivers, the fact that the concentration of nickel in the shallow layers (0.3 m and 1.5 m) above the thermocline (2 m) was higher than those at intermediate depths (10 m, 50 m and 100 m) suggests a nickel supply from the atmosphere. However, further study such as the characterisation of the nickel chemical species, should be carried out.

4. Conclusion

The use of ID-oxygen added nitrogen-MIP-MS with direct measurement of liquid–liquid extracted organic phase could greatly enhance the technique's ability to determine tens of ng l^{-1} levels of nickel in water samples, because it provides improvements in accuracy by using the ID method as well as the elimination of potentially interfering calcium-based polyatomic species. The proposed method was applied to clarify the concentration-depth vertical profiles of nickel in Lake Mashu as the Baseline Station of the United Nations GEMS/Water Programme. The results we obtained suggested the possibility that the

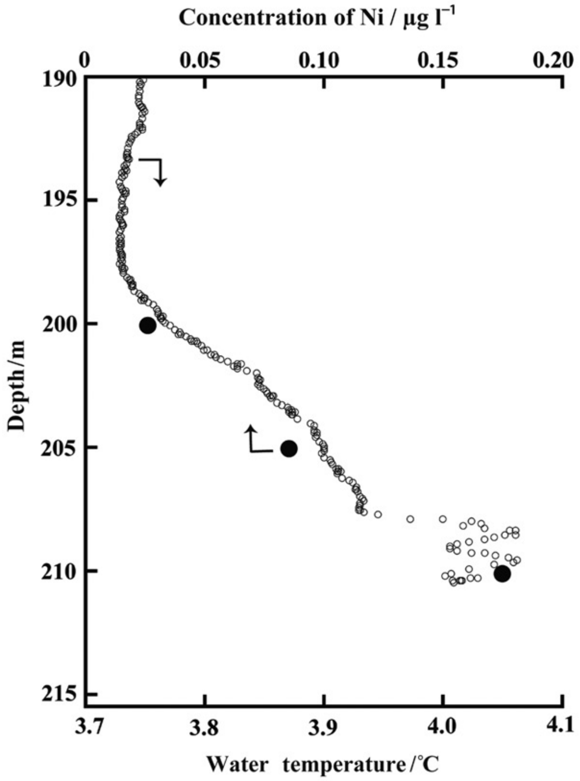

Figure 2. Ni concentration-depth profiles of Lake Mashu water sampled in August 2007. Closed circles, Ni concentration. Open circles, water temperature (measured by CTD). Five replicate measurements were made for each water sample.

proposed method could be used to check for signs of anthropogenic atmospherically derived pollutions of not only agrichemicals such as BHC but also of nickel, particularly in Lake Mashu, the only Baseline Station of the United Nations GEMS/Water Programme located in Japan.

References

[1] United Nations GEMS/Water Programme, http://www.gemswater.org/.

[2] F.E. Huggins, G.P. Huffman, W.P. Linak, and C.A. Miller, Environ. Sci. Technol. **38**, 1836 (2004).

[3] T. Okuda, S. Nakao, M. Katsuno, and S. Tanaka, Atmos. Environ. **41**, 7642 (2007).

[4] E.G. Pacyna, J.M. Pacyna, J. Fudala, E.S. Jastrzab, S. Hlawiczka, D. Panasiuk, S. Nitter, T. Pregger, H. Pfeiffer, and R. Friedrich, Atmos. Environ. **41**, 8557 (2007).

[5] S.L. Tsai and M.S. Tsai, Resour. Conserv. Recycl. **22**, 163 (1998).

[6] E. Denkhaus and K. Salnikow, Crit. Rev. Oncol. Hemat. **42**, 35 (2002).

[7] H. Liu, X. Shi, M. Costa, and C. Huang, Mol. Cell. Biochem. **279**, 45 (2005).

[8] S. Shimada, T. Toyoda, and K. Tsunemi, Bunseki Kagaku **58**, 159 (2009).

[9] Y. Sohrin and K. Isshiki, *Chemistry of Sea and Lake* (in Japanese) (Kyoto University Press, Kyoto, 2005).

[10] C. Vandecasteele and C.B. Block, editors, *Modern Methods for Trace Element Determination* (John Wiley & Sons, Chichester, 1993).

[11] P. Leonhard, R. Pepelnik, A. Prange, N. Yamada, and T. Yamada, J. Anal. At. Spectrom. **17**, 189 (2002).

[12] A. Itoh, K. Iwata, S. Ji, T. Yabutani, C. Kimata, H. Sawatari, and H. Haraguchi, Bunseki Kagaku **47**, 109 (1998).

[13] H. Louie, M. Wu, P. Di, P. Snitch, and G. Chapple, J. Anal. At. Spectrom. **17**, 587 (2002).

[14] H. Sawatari, E. Fujimori, and H. Haraguchi, Anal. Sci. **11**, 369 (1995).

[15] H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, and H. Haraguchi, Bull. Chem. Soc. Jpn. **69**, 1925 (1996).

[16] T. Sumida, T. Nakazato, and H. Tao, Bunseki Kagaku **52**, 619 (2003).

[17] N.G. Beck, R.P. Franks, and K.W. Bruland, Anal. Chim. Acta **455**, 11 (2002).

[18] S. Hirata, Y. Ishida, M. Aihara, K. Honda, and O. Shikino, Anal. Chim. Acta **438**, 205 (2001).

[19] S. Hirata, T. Kajiya, M. Aihara, K. Honda, and O. Shikino, Bunseki Kagaku **52**, 1091 (2003).

[20] Y. Zhu, A. Itoh, and H. Haraguchi, Bull. Chem. Soc. Jpn. **78**, 107 (2005).

[21] S.J. Santosa, S. Tanaka, and K. Yamanaka, Fresenius' J. Anal. Chem. **357**, 1122 (1997).

[22] S.J. Santosa, S. Tanaka, and K. Yamanaka, Environ. Monitor. Assess. **44**, 515 (1997).

[23] R.E. Sturgeon, S.S. Berman, J.A.H. Desaulniers, A.P. Mykytiuk, J.W. McLaren, and D.S. Russel, Anal. Chem. **52**, 1585 (1980).

[24] A.P. Mykytiuk, D.S. Russell, and R.E. Sturgeon, Anal. Chem. **52**, 1281 (1980).

[25] J.W. McLaren, A.P. Mykytiuk, S.N. Willie, and S.S. Berman, Anal. Chem. **57**, 2907 (1985).

[26] D. Beauchemin, J.W. McLaren, A.P. Mykytiuk, and S.S. Berman, Anal. Chem. **59**, 778 (1987).

[27] D. Beauchemin, J.W. McLaren, A.P. Mykytiuk, and S.S. Berman, J. Anal. At. Spectrom. **3**, 305 (1988).

[28] D. Beauchemin and S.S. Berman, Anal. Chem. **61**, 1857 (1989).

[29] H. Freiser and G.H. Morrison, Annu. Rev. Nucl. Sci. **9**, 221 (1959).

[30] K. Oishi, T. Okumoto, T. Iino, M. Koga, T. Shirasaki, and N. Furuta, Spectrochim. Acta **49 B**, 901 (1994).

[31] Y. Okamoto, J. Anal. At. Spectrom. **9**, 745 (1994).

[32] T. Kato, S. Nakamura, and M. Morita, Anal. Sci. **6**, 623 (1990).

[33] H. Minami, W. Cai, T. Kusumoto, K. Nishikawa, Q. Zhang, S. Inoue, and I. Atsuya, Anal. Sci. **19**, 1359 (2003).

[34] J.R. De Laeter, J.K. Böhlke, P. De Bièvre, H. Hidaka, H.S. Peiser, K.J.R. Rosman, and P.D.P. Taylor, Atomic Weights of the Elements: Review 2000, Pure Appl. Chem. **75**, 683 (2003).

[35] Y. Nojiri, T. Kawai, and A. Otsuki, Res. Rep. Natl. Inst. Eviron. Stud. Jpn. **126**, 25 (1990).

[36] H. Shiraishi, T. Kawai, and A. Otsuki, Res. Rep. Natl. Inst. Eviron. Stud. Jpn. **36**, 43 (1982).

[37] A. Otsuki, J. Environ. Inf. Sci. **14**, 25 (1985).

[38] *GEMS/Water Lake Mashu Monitoring Data Book* (National Institute for Environmental Studies, Japan, 2004).

[39] Y. Nojiri, T. Kawai, A. Otsuki, and K. Fuwa, Wat. Res. **19**, 503 (1985).