

A Simple Preconcentration-Storing Technique Based on Sulfide Precipitation for Multipoint Monitoring of Mercury in Rainwater and Snow by Cold Vapor Atomic Absorption Spectrometry

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A preconcentration-storing technique that does not require any special or expensive apparatus and reagents was developed to monitor mercury in rainwater and snow at many points as simultaneously as possible. A commercially available sodium hypochlorite solution was added to the sample solution to prevent a decrease in mercury concentration after sampling. Mercury(II) ion (0.5–50 ng) in 500 mL of the sample solution was concentrated by adding zinc(II) ion and a small amount of sulfide ion and then coagulating/coprecipitating with $Zn(OH)_2$ or ZnS after reduction of residual hypochlorite by addition of hydroxylammonium chloride. The supernatant solution was discarded by decantation, and the solution including the precipitates could be stored for at least 20 days without any loss of mercury. The recoveries of mercury(II) ion from the 500 mL of the sample solutions spiked with mercury(II) ions were 99–109%, with standard deviation ranges of 3–8%, although the recovery of methylmercury(II) ion was $68 \pm 5\%$. Using this technique, the determination of mercury in rainwater and snow was demonstrated at Toyama Prefecture, Japan, from April 2004 to February 2005; mercury levels ranging from 2.7 to 33.7 ng L^{-1} were found.

In the atmospheric environment, mercury is mainly present as a gaseous elemental matter.[1–3] It has long been believed that gaseous elemental mercury has a long residence time in the atmosphere because of its low solubility in water.[1–3] Reactive gaseous mercury, which is a divalent compound, such as halogenous salts and oxides, and particulate mercury can also exist in the atmosphere[1–3] and are easily deposited with rainwater and snow by dissolution and wash-out processes.[1–3] Recently, it was reported that gaseous elemental mercury could be oxidized to reactive gaseous mercury through a reaction with ozone, sea salt aerosol, and others, resulting in deposition with rainwater and snow in some areas.[1–6] There is a possibility that the deposited mercury is bioaccumulated after its methylation in the hydrosphere,[1] and so, mercury deposition events should be monitored in many regions. It is preferable that information regarding the mercury content in rainwater and snow be obtained at multiple points as simultaneously as possible. The results obtained by multipoint monitoring can give a two-dimensional distribution of mercury in wet deposition, and this information would be useful for understanding the dynamics of mercury in an atmospheric environment.

For the determination of mercury in rainwater and snow, cold vapor atomic fluorescence spectrometry (CVAFS) combined with gold trap amalgamation is widely used because AFS is extremely sensitive for mercury detection.[7,8] On the other hand, cold vapor atomic absorption spectrometry (CVAAS) is also frequently utilized for water analysis, especially in Japan, where it has been adopted by the Japanese Industrial Standards for the determination of mercury in water.[9] However, a larger sample volume is generally required for CVAAS determination than that for CVAFS determination because AAS is less sensitive than AFS for mercury detection.[7,8,10] In multipoint monitoring, the transportation of a large volume of sample from each sampling point to an analytical laboratory might be difficult or troublesome.

In this study, we investigated a simple preconcentration-storing technique for multipoint monitoring using CVAAS. For this technique, the following requirements must be satisfied: (i) the mercury in rainwater and snow can be readily preconcentrated at, or nearby, the sampling point without any special or expensive apparatus and reagents, (ii) the preconcentrated mercury can be stored for a considerable period without any loss of mercury, and (iii) the preconcentrated mercury can be readily determined by CVAAS after transportation of the stored samples to an analytical laboratory. Gold trap amalgamation is a simple and useful preconcentration technique. However, the trap tube is relatively expensive, and contamination might occur during storage of the tube after preconcentration because of the presence of gaseous elemental mercury in the atmosphere. On the other hand, it is well known that mercury(II) sulfide is sparingly soluble in water; the solubility product constants are 2.00×10^{-53} for the black form and 4.00×10^{-54} for the red form.[11] This information prompted us to study the application of a sulfide precipitation technique to preconcentrate mercury in rainwater and snow. The preconcentration techniques for mercury(II) ion in water sample by using sulfide precipitation,[12] coprecipitation with copper sulfide,[13] and precipitate-exchange[14] on or chemofiltration[15] through a zinc sulfide layer, have been reported. However, these techniques have not been applied to CVAAS determination of mercury, which may be due to serious interference by the presence of a large amount of sulfide ion.[16–18] We found that mercury(II) ion in the sample solution could be quantitatively collected by adding small amounts of sulfide ion and

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coagulating with zinc(II) hydroxide and/or coprecipitating with partly formed zinc(II) sulfide. Furthermore, the collected mercury(II) ions could be stored for at least 20 days without any loss of mercury after the supernatant solution was discarded by decantation. The mercury could be readily determined by CVAAS without interference from the sulfide ion after the dissolution of the precipitate and the addition of a small amount of potassium permanganate. The coagulation/coprecipitation step is tedious in the sulfide precipitation technique because of the addition of hydrochloric acid or bromine monochloride solution, which is widely used to prevent mercury-loss in a sample solution during sampling.[7,8] This problem was solved by using a commercially available sodium hypochlorite solution instead of hydrochloric acid or bromine monochloride solution.

This paper describes the optimum conditions for a preconcentration-storing technique using sulfide precipitation. The investigation into the sampling of rainwater and snow for multipoint monitoring based on sulfide precipitation-CVAAS determination is also reported.

Experimental

Apparatus. A Perkin-Elmer FIMS-400 mercury analysis system (cold vapor atomic absorption spectrometry based on the flow injection technique, FI-CVAAS) and a Hitachi 180-80 polarized Zeeman atomic absorption spectrometer (flame-type) were used to measure mercury and zinc, respectively. The pH was measured by using a Horiba F-22 pH meter. A Nippon Instruments MA-2 mercury analyzer (cold vapor atomic absorption spectrometry combined with a gold trap amalgamation, GTA-CVAAS) and a Hiranuma HG-1 mercury analyzer (cold vapor atomic absorption spectrometry) were also utilized for optimization of preconcentration and sampling conditions.

Reagents. A commercially available stock solution of mercury(II) ions (50 mg L^{-1}, Kanto Kagaku) was used. A stock solution of methylmercury(II) ions (50 mg L^{-1} Hg) was prepared by dissolving methylmercury(II) chloride (Aldrich) in distilled-deionized water. These solutions were diluted to the desired concentration in each experiment. A sodium hypochlorite solution (practical grade) was purchased from Wako Pure Chemical Industries; the concentration of sodium hypochlorite as determined by iodometric titration[19] was 11.4%w/v. A zinc(II) ion solution (10 g L^{-1} Zn) was prepared by dissolving zinc(II) chloride (guaranteed reagent grade, Wako Pure Chemical Industries) in a small amount of distilled-deionized water and 1 mL of concentrated sulfuric acid and diluting the mixture to 100 mL with distilled-deionized water. A sulfide solution (1 g L^{-1}) was also prepared by dissolving sodium sulfide nonahydrate in distilled-deionized water. All of the other reagents used were of guaranteed or analytical reagent grade.

Procedures. Sampling: The rainwater and snow used for this study were sampled on the rooftop of the Faculty of Engineering, University of Toyama (Toyama Prefecture, Japan). A fluorinated narrow-mouth bottle (fluorinated high-density polyethylene, Nalgene) and a polyethylene funnel were used for the sampling of rainwater. A polypropylene container (W440 × L740 × H350 (mm)) was also utilized for the sampling of falling snow. All of the apparatus used for the samplings was immersed in an approximately 3 mol L^{-1} nitric acid solution for at least 24 h and then rinsed with distilled-deionized water before use.[20] The snow samples were melted at room temperature in a tightly covered container. After taking a 500 mL sample of the rainwater or of the melted snow, approximately 0.5 mL of the sodium hypochlorite solution was added to the sample as soon as possible. Some of the sample solutions were filtered by suction using a hydrophilic PTFE membrane filter (Nihon Millipore, Omnipore membrane, pore size of 0.45 μm, diameter of 47 mm) before the sodium hypochlorite solution was added. The sample solution was allowed to stand for a day before preconcentration.

Preconcentration and Storage: To 500 mL of the sample solution containing 0.5–50 ng of mercury(II) ion (Hg_i ng) and hypochlorite, 3 mL of 2%w/v hydroxylammonium chloride solution was added for reduction of residual hypochlorite. Then, 0.1 mL of the sulfide solution and 2 mL of the zinc(II) ion solution (Zn_i mg) were added, and 2.5 mL of a 1 mol L^{-1} sodium hydroxide solution was slowly dropped to the solution for approximately 5 min to form the precipitate. After the precipitate had settled, the supernatant solution (approximately 490 mL) was discarded slowly by decantation; in this operation, some loss of the precipitate was permitted. The solution containing the precipitate was transferred to a 50 mL polyethylene centrifuge tube or borosilicate glass vial and capped tightly. It was then stored at room temperature.

Measurements: The precipitate in the tube or vial was dissolved by adding 1 mL of concentrated hydrochloric acid. The solution was diluted to approximately 25 mL with distilled-deionized water, and 20 μL of a 5%w/v potassium permanganate solution was added. The atomic absorbance of mercury ($Hg_{f(abs)}$) and zinc ($Zn_{f(abs)}$) was measured by FI-CVAAS and flame atomic absorption spectrometry (FAAS), respectively, using the operating conditions shown in Table 1.

Calculation of Mercury Content: The ratio of the amount of mercury (Hg_i ng) contained in 500 mL of the initial sample solution to the amount of added zinc(II) ion (Zn_i mg) was equal to the ratio of the concentration of mercury(II) ions (Hg_f ng L^{-1}) to that of zinc(II) ions (Zn_f mg L^{-1}) in the solution after the preconcentration; therefore, the mercury content (Hg_i ng) in the sample solution was calculated by using the following equation:

$$Hg_i = Zn_i \times Hg_f/Zn_f. \quad (1)$$

Since Hg_f (ng L^{-1}) and Zn_f (mg L^{-1}) are in proportion to the $Hg_{f(abs)}$ and $Zn_{f(abs)}$ obtained for the measurements, respectively, Eq. 1 can be written as follows:

Table 1. Operating Conditions for FI-CVAAS and FAAS

FI-CVAAS	
Wavelength	253.7 nm (Hg)
Signal	Peak Height
Sample loop	1 mL
N_2 gas flow	50 mL min^{-1}
Carrier	3%v/v HCl
Reductant	1.1%w/v $SnCl_2$
Pump speed	120 rpm
Read time	20 s
Replicate	3 times
FAAS	
Wavelength	307.6 nm (Zn)
Lump current	10 mA
Slit	1.3 nm
Flame	Air–C_2H_2
Air	160 kPa
C_2H_2	20 kPa

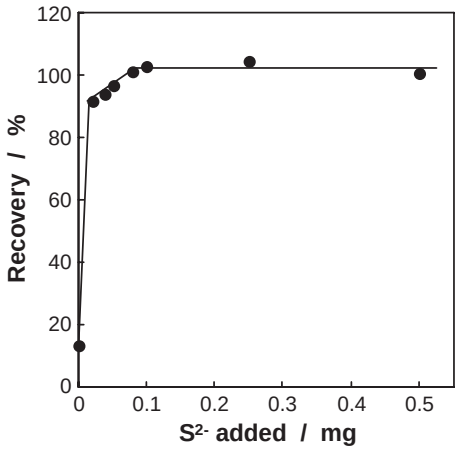

Fig. 1. Effect of addition of sulfide ion on the recovery of mercury(II) ion. Sample, rainwater; sample volume, 500 mL; Hg^{II}, 10 ng, Zn^{II}, 20 mg; 1 mol L^{-1} NaOH, 2.5 mL. The measurement of mercury was carried out according to the procedure recommended.

$$\begin{aligned} Hg_i &= Zn_i \times \{(Hg_{f(abs)} - b)/a\}/\{(Zn_{f(abs)} - b')/a'\} \\ &= (a'/a) \times Zn_i \times \{(Hg_{f(abs)} - b)/(Zn_{f(abs)} - b')\}, \end{aligned} \quad (2)$$

where a and a' are the slopes of calibration curves of mercury (L ng^{-1}) and zinc (L mg^{-1}), and b and b' are the absorbances of mercury and zinc in the blank solution, respectively. In this method, a calibration curve, which means the relationship between the amount of mercury(II) ions and the ratio of the atomic absorbance of mercury to that of zinc, was prepared according to the procedure using 500 mL of mercury(II) ion-spiked water; a blank, using distilled-deionized water as a sample solution, was run using the same procedure as that used for the sample solution.

Results and Discussion

Preconcentration and Storage. Sulfide Precipitation: When sulfide ion was added to 500 mL of a solution containing 50 ng of mercury(II) ion, the formation of mercury(II) sulfide was not visually observed, and the mercury(II) ion in the solution could not be separated. By adding zinc(II) ions and a sodium hydroxide solution, however, mercury(II) ion could be collected with the precipitate formed in the solution. Since the recovery of the mercury(II) ions was less than 20% without the addition of sulfide ion, as shown in Fig. 1, the collection efficiency of mercury(II) ion seemed to be improved by the coagulation of mercury(II) sulfide with zinc(II) hydroxide and/or coprecipitation of mercury(II) ion with partly formed zinc(II) sulfide. The recovery of the mercury(II) ions increased as the added amount of zinc(II) ion was increased and became a quantitative value in the range of 20–40 mg of zinc(II) ions; the presence of zinc(II) ions up to at least 30 mg did not affect the determination of mercury(II) by FI-CVAAS. As shown in Fig. 1, the necessary amount of sulfide ion for the quantitative recovery of mercury(II) ion was more than 0.08 mg. In this method, 20 mg of zinc(II) ions and 0.1 mg of sulfide ion were used.

The recoveries of mercury(II) ion from the spiked distilled-deionized water and rainwater samples ranged from 99 to 109% at pH 9.0–11.5. The recovery of methylmercury(II) ion was also investigated; for the measurement, CVAAS in an alkaline medium was used.[21] The recoveries of methylmercury(II) ion from the spiked distilled-deionized water and rainwater samples ranged from 14 to 15% at pH 9.0–11.9. From these results, it is clear that sulfide precipitation is a powerful technique for preconcentrating mercury(II) ions; however, it cannot be used for the quantitative collection of methylmercury(II) ion.

Simplification of Operation: Since the pH adjustment in and the separation of precipitate from the solutions are tedious and time-consuming, these operations were simplified.

During the preconcentration, no strict adjustment of the pH in the solution was needed because the recovery of mercury(II) ion was quantitative over the wide pH range described above. In this method, when 2.5 mL of a 1 mol L^{-1} sodium hydroxide solution was added to 500 mL of some water samples in order to form a precipitate, the pH values (mean ± standard deviation) were 11.05 ± 0.07 for distilled-deionized water ($n = 126$), 11.03 ± 0.06 for well water ($n = 19$), 10.68 ± 0.08 for mineral water (Volvic, $n = 19$), 10.98 ± 0.03 for rainwater ($n = 23$), and 11.06 ± 0.03 for snow-melted water ($n = 19$). The mercury(II) ion spiked in each solution could be quantitatively recovered over this pH range. The precipitate that formed was sometimes a little too fine when the sodium hydroxide solution was added rapidly, which was troublesome for the consecutive separations of the precipitate. To overcome this problem, 2.5 mL of a 1 mol L^{-1} sodium hydroxide solution was slowly added over approximately 5 min.

For the separation of the precipitate, filtration was generally used. However, the recovery of mercury(II) ion was extremely low when the precipitate was filtered by using suction with the membrane filter required in this method. The mercury(II) ions might have remained on the filter because the dissolution of mercury(II) sulfide is difficult in common mineral acids such as hydrochloric and nitric acids.[22,23] Decantation[24,25] was therefore used to separate the precipitate. The precipitate could not be completely recovered by using the decantation, which meant that the mercury(II) ions, which were coagulated and/or coprecipitated with the precipitate, was lost along with the precipitate. However, the loss of mercury could be corrected based on the ratio of the amount of zinc(II) ions in the final solution after preconcentration to the amount of zinc(II) ions added to the initial sample solution. For the correction, the following requirements must be satisfied: (i) zinc(II) content in the initial sample solution must be negligibly small, (ii) zinc(II) ion added to the initial sample solution must be quantitatively precipitated, and (iii) after the decantation, the lost amount of mercury must be proportional to the lost amount of zinc(II). The zinc content in rainwater and snow used for the investigations was much smaller than the added amount of zinc(II) ion in the proposed method. The recoveries of zinc(II) ions from the distilled-deionized water and rainwater samples were almost 100% in the pH range of 9.0–11.5. Figure 2 shows the relationship between the atomic absorbance of mercury and that of zinc obtained by measuring the solution after preconcentration. In this experiment, 20 mg of zinc(II) ions was added to 500 mL of distilled-deionized water or rainwater spiked with 10 ng of mercury(II) ion, and the precipitate was formed by adding the sodium hydroxide solution.

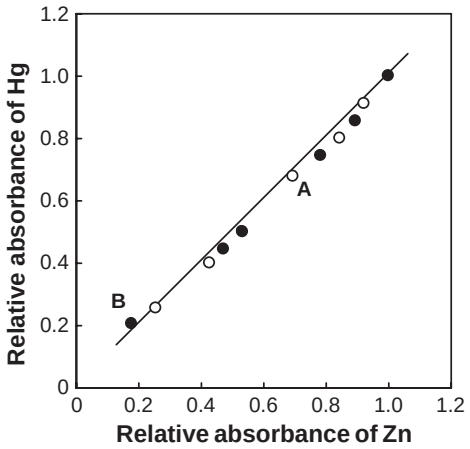

Fig. 2. Relationship between the relative absorbance of zinc and that of mercury after preconcentration. Sample, distilled-deionised water (A) and rainwater (B); sample volume, 500 mL; Hg^{II}, 10 ng; S^{2-}, 0.1 mg; Zn^{II}, 20 mg; 1 mol L^{-1} NaOH, 2.5 mL. The mercury(II) and zinc(II) ions in the solution were measured after a portion of the formed precipitate was discarded by decantation.

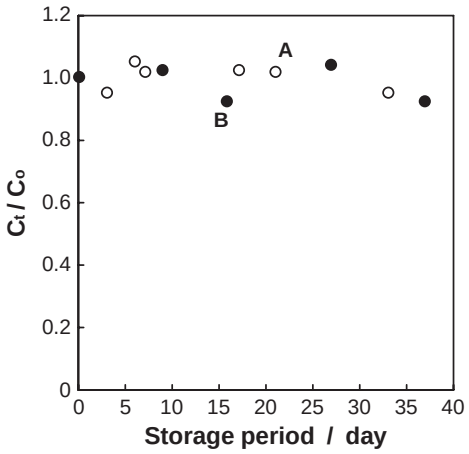

Fig. 3. Effect of storage period after preconcentration on the determination of mercury(II) ions. Sample, distilled-deionized water (A) or rainwater (B); sample volume, 500 mL; Hg^{II}, 10 ng; S^{2-}, 0.1 mg; Zn^{II}, 20 mg; 1 mol L^{-1} NaOH, 2.5 mL; storage apparatus, 50 mL polyethylene centrifuge tube. C_0, C_t: The concentration of Hg before and after storage for t days, respectively.

After standing for approximately 1 h, a portion of the precipitate was intentionally discarded with the mother liquor. The absorbance of mercury, which was proportional to the amount of mercury(II) ions in the solution, correlated significantly to that of zinc(II) ions. From these results, the three requirements mentioned above were satisfied. By using decantation, the procedure for separating the precipitate was extremely simple and rapid.

Storage Period. Since it would be useful for multipoint monitoring of mercury in rainwater and snow to be able to store the sample for a considerable period without any contamination or loss of mercury, the storage period was investigated. The precipitate remaining in the solution after the decantation was transferred to a 50 mL polyethylene centrifuge tube, and the tube was stored in our laboratory at room temperature after being tightly capped. As shown in Fig. 3, no significant loss of mercury was observed for up to at least 20 days; almost the same results were obtained when a borosilicate glass vial was used as a storage bottle. The amount of the mercury(II) ions decreased as the storage period was lengthened when the precipitate was dissolved before storage. These results show that the sample must be stored without dissolution of the precipitate after preconcentration, and storage of the tube in a sealed polyethylene bag would be effective to prevent contamination.

Sampling. Addition of NaClO Solution: Since the concentration of mercury(II) ion decreases when the sample solution has been allowed to stand for a considerable period after the sampling, hydrochloric acid or bromine monochloride solution is generally added.[7,8,26] Although they were shown to be effective in the method using sulfide precipitation, the formation of the precipitate was troublesome and time-consuming because the addition of a large amount of sodium hydroxide solution was required. Therefore, a sodium hypochlorite solution, which can be readily purchased, was used.

The effectiveness of sodium hypochlorite solution was investigated using GTA-CVAAS. Decrease in the mercury(II) ion concentration was prevented by adding more than 0.1 mL of sodium hypochlorite solution to 500 mL sample solution. When 0.5 mL of sodium hypochlorite solution was added to 500 mL of the rainwater or snow-melted water sample and the sample solution was then allowed to stand for a day, the absorbance, which was standardized to that of blank solution, was almost the same as that obtained by adding bromine monochloride solution.[7] There was little change up to 5 days after the addition of sodium hypochlorite solution. Also, the absorbance remained the same even when the sodium hypochlorite solution was added up to at least 3 days after the sampling. In this method, 0.5 mL of sodium hypochlorite solution was added to the rainwater and snow-melted water samples as soon as possible after the sampling, and the sample solutions were allowed to stand for a day before preconcentration.

When mercury(II) ion in the solution containing the hypochlorite was concentrated by sulfide precipitation, the recovery of mercury(II) ion was extremely low due to the oxidation of sulfide ion by the residual hypochlorite.[18,21] The recovery was improved by adding hydroxylammonium chloride solution to reduce the residual hypochlorite. In this method, 3 mL of 2%w/v hydroxylammonium chloride solution was added before preconcentration.

Measurements. Dissolution of Precipitate: Zinc(II) hydroxide could be readily dissolved in common mineral acids such as hydrochloric and nitric acids. Hydrochloric acid was used to dissolve the precipitate because it was also used for the carrier in FI-CVAAS. The precipitate remaining in the solution could be dissolved by adding 1 mL of more than 0.5 mol L^{-1} hydrochloric acid; 1 mL of concentrated hydrochloric acid was used in this method because of the rapid dissolution of the precipitate. Mercury(II) ions in the solution after dissolution with hydrochloric acid were difficult to detect in the measurement due to sulfide interference during the reduction process for mercury(II) ions.[16–18] However, the interfer-

ence was dramatically reduced by adding 20 μL of 5%w/v potassium permanganate solution as an oxidizing reagent; the presence of up to at least 0.5 mg of sulfide ion did not interfere with the determination of mercury(II) ions.

Optimum Conditions for Measurements: The operating conditions for FI-CVAAS were optimized. A sample loop of 1 mL was used based on sensitive measurements. The highest atomic absorbance was obtained at a nitrogen gas flow rate of 50 mL min^{-1}. For the carrier and reducing agent solutions, almost constant absorbance was obtained in 0–10%v/v hydrochloric acid and 0.5–10%w/v tin(II) chloride solutions, respectively. From these results, the conditions were fixed as shown in Table 1.

In the method proposed here, the amount of zinc(II) ions in the solution after preconcentration must be measured, and therefore, FAAS was used. Although the zinc(II) ion concentration in the solution after preconcentration was relatively high, the amount of zinc(II) ions could be determined without dilution at an analytical wavelength of 307.6 nm. A straight relationship was obtained up to 2000 mg L^{-1} of zinc(II) ions without any interference. Other optimized conditions are summarized in Table 1.

Calibration Curve: The relationship between the amount of mercury(II) ions in the sample solution and the ratio of the atomic absorbance of mercury to that of zinc in the final solution after preconcentration was investigated. A straight line was obtained in the range of 0.5–50 ng of mercury(II) ion in 500 mL of the sample solution. This result indicates that the amount of mercury(II) ions in the initial sample solution can be determined based on Eq. 2. For the experiments, this relationship was used as a calibration curve. The detection limit, defined as 3 times the standard deviations obtained from 10 replicate determinations of the blank, was 0.14 ng of mercury in 500 mL of the sample solution.

Application to Analyses of Rainwater and Snow. Effect of Diverse Ions: The influence of some diverse ions which are often found in rainwater and snow was examined. The mercury(II) ion concentration was determined within a 10% error in the presence of each of the following: 10 mg L^{-1} of Na^+, K^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-}; 5 mg L^{-1} of NO_3^-; 1 mg L^{-1} of Fe^{3+}; and 0.3 mg L^{-1} of Al^{3+}. The concentration of each ion was nearly equal to or slightly higher than that in general rainwater and snow.[27,28]

Recovery from Spiked Water Samples: The recovery of mercury(II) ions in the rainwater samples spiked with 10 or 50 ng of mercury(II) ions was also investigated, and for comparison, the recovery from spiked distilled-deionized water was also examined. The recoveries (mean ± standard deviation, $n = 5$) were $105 \pm 8\%$ for 10 ng and $109 \pm 4\%$ for 50 ng of mercury(II) ion in rainwater and $99 \pm 5\%$ for 10 ng and $100 \pm 3\%$ for 50 ng in spiked distilled-deionized water. These results show that the method proposed here will be useful for analyses of rainwater and snow. The recovery of methylmercury(II) ion from the distilled-deionized water spiked with 50 ng of methylmercury(II) ion was $68 \pm 5\%$ ($n = 5$) when preconcentration using sulfide precipitation was carried out after the addition of sodium hypochlorite solution. Since the recovery of methylmercury(II) ion was low without sodium hypochlorite solution, the increase in the recovery is due to the decomposition of methylmercury(II) ion to mercury(II) ion upon addition of sodium hypochlorite solution. However, the recovery of methylmercury(II) ion could not be improved by increasing the amount of added sodium hypochlorite solution. In general, the content of methylmercury(II) ion in rainwater and snow is extremely small,[1,2,29–31] which suggests that the contribution of methylmercury(II) ion to the value obtained in this method is not very large. The method using sodium hypochlorite solution was compared with the method using bromine monochloride solution in the determination of mercury in a rainwater sample. The results ($n = 3$) were 7.8 ± 0.3 ng L^{-1} for sodium hypochlorite solution and 7.5 ± 0.7 ng L^{-1} for bromine monochloride solution. In addition, a comparison analysis of well water which was sampled at the Faculty of Engineering, University of Toyama, was also carried out, and the results ($n = 3$) were 4.0 ± 0.7 ng L^{-1} for sodium hypochlorite solution and 4.5 ± 0.8 ng L^{-1} for bromine monochloride solution.

Analyses of Rainwater and Snow: Determination of mercury in rainwater and snow was carried out over different periods from April 2004 to February 2005. The results are summarized in Fig. 4. The concentration of mercury varied irregularly in the range of 2.7–33.7 ng L^{-1}. For some samples, the rainwater or snow filtered before the addition of sodium hypochlorite solution was also analyzed. In this case, only the dissolved mercury could be determined; the amount of the partic-

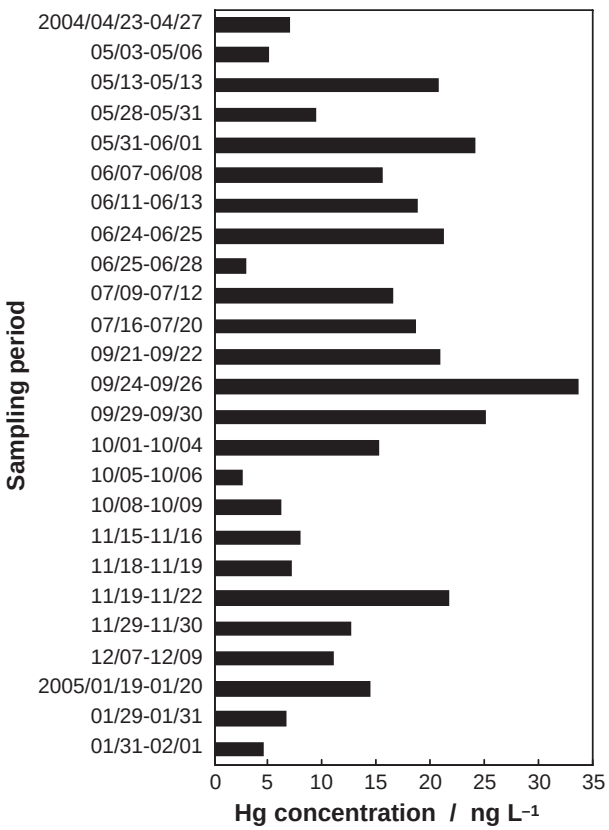

Fig. 4. Results for the determination of mercury in rainwater and snow. Sample volume, 500 mL. The rainwater and snow were sampled on the rooftop of the Faculty of Engineering, University of Toyama (Toyama Prefecture, Japan).

Table 2. Results for the Determination of Hg in Rainwater and Snow with or without Filtration

Sampling period	Hg concentration[a)]/ng L^{-1}	
	Non-filtration	Filtrate
2004/10/05–10/06	2.7 ± 0.7	1.3 ± 0.1
10/08–10/09	6.1 ± 0.5	4.0 ± 0.2
11/29–11/30	12.6 ± 1.1	0.4 ± 0.0
2005/01/19–01/20	14.6 ± 1.4	7.0 ± 0.5
01/31–02/01	4.7 ± 1.8	2.2 ± 0.3

a) Mean $\pm$ standard deviation ($n = 3$).

ulate mercury in the rainwater or snow could be calculated by subtracting the amount of mercury in the filtrate from the amount of mercury without filtration. The results are shown in Table 2. Although the ratio of the particulate mercury varied, the ratio was mostly larger than 0.5. These results suggest that the particulate mercury plays an important role in the wet deposition of mercury at this sampling point.

Conclusion

In this study, a preconcentration-storing technique based on sulfide precipitation was developed to determine mercury in rainwater and snow. Mercury(II) ions ranging from 0.5 to 50 ng in 500 mL of sample solution could be readily concentrated without any special or expensive apparatus and reagents although the recovery of methylmercury(II) ion was less than 70%. The fact that the concentrated mercury(II) could be stored for up to 20 days without any loss of mercury is also attractive. Concentrated mercury(II) ions could be readily determined by using FI-CVAAS and FAAS. This technique would be useful for multipoint monitoring of mercury in rainwater and snow. Mercury can be preconcentrated and stored at each sampling area, and the samples after preconcentration can be transported periodically to an analytical laboratory where both CVAAS and FAAS are available. This technique would enhance knowledge of the dynamics of mercury in an atmospheric environment.

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References

1 O. Lindqvist, H. Rodhe, *Tellus* **1985**, *37B*, 136.
2 K. Marumoto, M. Sakata, *Chikyu Kagaku (Geochemistry)* **2000**, *34*, 59.
3 A. Carpi, *Water, Air, Soil Pollut.* **1997**, *98*, 241.
4 C. Seigneur, J. Wrobel, E. Constantinou, *Environ. Sci. Technol.* **1994**, *25*, 1589.
5 S. E. Lindberg, S. Brooks, C.-J. Lin, K. J. Scott, M. S. Landis, R. K. Stevens, M. Goodsite, A. Richter, *Environ. Sci. Technol.* **2002**, *36*, 1245.
6 I. M. Hedgecock, G. A. Trunfio, N. Pirrone, F. Sprovieri, *Atmos. Environ.* **2005**, *39*, 7217.
7 U. S. Environmental Protection Agency, Method 1631, Revision E: Mercury in water by oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, North Carolina, **2002**.
8 S. Lindberg, S. Vermette, *Atmos. Environ.* **1995**, *29*, 1219.
9 Japanese Industrial Standards, K0102, Testing Methods for Industrial Wastewater, Tokyo, **1998**.
10 C. Vandecaseele, C. B. Block, *Modern Methods for Trace Element Determination*, Wiley, Chichester, **1993**, pp. 164–165.
11 *CRC Handbook of Chemistry and Physics*, 74th ed., ed. by D. R. Lide, CRC Press, Boca Raton, FL, **1993–1994**, pp. 8–49.
12 M. F. El-Shahat, A. G. Hamza, M. M. Abdel-Badei, *Microchem. J.* **1986**, *34*, 242.
13 G. R. Doshi, S. N. Joshi, *Indian J. Technol.* **1987**, *25*, 371.
14 A. Disam, P. Tschöpel, G. Tölg, *Fresenius' Z. Anal. Chem.* **1979**, *295*, 97.
15 R. Sitko, B. Zawisza, Z. Mzyk, *J. Anal. At. Spectrom.* **2006**, *21*, 13.
16 Y. Umezaki, K. Iwamoto, *Bunseki Kagaku* **1971**, *20*, 173.
17 T. Kamada, Y. Hayashi, T. Kumamaru, Y. Yamamoto, *Bunseki Kagaku* **1973**, *22*, 481.
18 S. Kagaya, T. Nishimura, K. Hasegawa, *Fresenius' J. Anal. Chem.* **1999**, *363*, 112.
19 G. D. Christian, *Analytical Chemistry*, 5th ed., Wiley, New York, **1994**, pp. 711–714.
20 F. Fang, Q. Wang, J. Li, *Sci. Total Environ.* **2004**, *330*, 159.
21 S. Kagaya, Y. Kuroda, Y. Serikawa, K. Hasegawa, *Talanta* **2004**, *64*, 554.
22 N. Mikac, D. Foucher, S. Niessen, J.-C. Fischer, *Anal. Bioanal. Chem.* **2002**, *374*, 1028.
23 R. Fernandez-Martinez, M. I. Rucandio, *Anal. Bioanal. Chem.* **2005**, *381*, 1499.
24 J. Ueda, S. Kagaya, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1496.
25 S. Kagaya, S. Kosumi, J. Ueda, *Anal. Sci.* **1994**, *10*, 83.
26 N. S. Bloom, E. A. Crecelius, *Mar. Chem.* **1983**, *14*, 49.
27 C. Reimann, P. de Caritat, *Chemical Elements in the Environment*, Springer, Berlin, **1998**, p. 36; **1998**, p. 78; **1998**, p. 126; **1998**, p. 176; **1998**, p. 196; **1998**, p. 212.
28 T. Ozeki, T. Ihara, T. Okada, R. Kikuchi, N. Ogawa, *Bunseki Kagaku* **2004**, *53*, 1427.
29 Y.-H. Lee, A. Iverfeldt, *Water, Air, Soil Pollut.* **1991**, *56*, 309.
30 R. P. Mason, W. F. Fitzgerald, G. M. Vandal, *J. Atmos. Chem.* **1992**, *14*, 48.
31 V. L. St. Louis, J. W. M. Rudd, C. A. Kelly, L. A. Barrie, *Water, Air, Soil Pollut.* **1995**, *80*, 405.