Determination of Trace Amount of Lead in Natural Water by Isotope Dilution - Inductively Coupled Plasma Mass Spectrometry

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Isotope dilution-inductively coupled plasma mass spectrometry (ID-ICP-MS) was applied to the determination of lead in natural water, and its precision was compared to that of the conventional calibration method. Trace amount of lead in natural water was preconcentrated using a chelating resin of Chelex 100 before ID-ICP-MS, where the preconcentration factor of 50 was obtained. The concentrations of lead were 26.1 pg/g and 266 pg/g for the certified river reference materials (JAC 0031) and the pond water sample, respectively, with the RSD less than 1%.

Keywords ICP-MS, isotope dilution, lead, natural water.

Isotope dilution (ID) analysis is noted for its extremely high precision.¹⁻² ID analysis does not require the use of external calibration standards and quantitative recoveries in the measurements, and the analytical results are hardly affected by losses and errors during sample pretreatment procedures. Thus, ID analysis is of great advantage in the determination of trace elements in environmental samples, when the complete recoveries of analytes during sample pretreatment are very difficult to be obtained because of their low concentrations. ID analysis is mainly used for highly precise analysis with thermal ionization mass spectrometry (TIMS). TIMS, which is essentially a single element detection method, requires very complicated sample pretreatment procedure, great skill in measurement, and extended analytical time, although it provides precise and accurate measurement of isotope ratios of analytes.

Inductively coupled plasma mass spectrometry (ICP-MS) has been becoming one of the most conventional analytical methods for the determination of trace elements in various kinds of samples.^{3,4} ICP-MS provides many excellent analytical features such as low detection limit at the pg/ml level for many elements, a wide dynamic range (ng/ml - pg/ml), multielement detection capability, and rapid analysis. In addition, ICP-MS has expanded the application of isotope dilution (ID) analysis to various analytical

fields,⁵⁻⁹ because ICP-MS provides simple sample pretreatment, easy operation, and high sample throughput for ID analysis.

The precise determination of lead is very important from the viewpoint of the environmental sciences, because lead is a toxic element, but it is widely used in industry.¹⁰ However, its concentration levels in unpolluted natural water are too low to be determined precisely. In the present study, hence, ID-ICP-MS was applied to the determination of lead in natural water, and its precision was compared to that of the conventional calibration method.

Experimental

Instrumentation

An ICP-MS instrument of model SPQ8000A from Seiko Instrument Inc. (Tokyo) was employed for the determination of trace amount of lead in natural water as well as measurement of the isotope ratios of lead. The operating conditions were as follows: rf power 1.0 kW, plasma gas flow rate 16 l/min, auxiliary gas flow rate 1.0 l/min, carrier gas flow rate 1.0 l/min, and sampling height 12 mm from the top of the load coil.

Chemicals

All solutions were prepared with de-ionized water purified using a MilliQ system (Millipore, Bedford, MA, USA). All chemicals used were of analytical reagent grade. A chelating resin of Chelex 100 (100-200 mesh, Bio Rad Laboratories, Richmond, CA, USA) was used for the concentration of trace amount of lead in the water samples. Before use, the resin was rinsed sequentially with 5 M hydrochloric acid, 2 M nitric acid and pure water in order to eliminate concomitant elements. Ammonium acetate solution was prepared with mixing acetic acid and aqueous ammonia solution.

The enriched spike of ^{206}Pb was the certified reference material (NIST SRM 983) which was issued from National Institute of Standards and Technology (NIST, USA). A portion (0.1 g) of NIST SRM 983 was dissolved in 100 ml of 0.1 M nitric acid, and the accurate concentration of the spike solution was determined by the reversed ID-ICP-MS, using a reference metal solution with the natural isotopic abundance. The certified reference material for the natural isotopic abundance of lead (NIST SRM 981) was used for mass calibration of the ICP-MS instrument. The isotopic abundances of NIST SRM 981 and 983 are listed in Table 1.

Lead standard solutions for calibration were prepared by dissolving aliquot of $1000\text{ }\mu\text{g ml}^{-1}$ of the stock solution for atomic absorption spectrometry in 0.1 M nitric acid solution.

Samples

The certified river reference materials (JAC 0031 and JAC 0032) issued from the Japan Society for Analytical Chemistry were analyzed in order to evaluate the analytical procedures employed here. The JAC 0031 reference material is the natural river water sample and the JAC 0032 reference material is the spiked river water sample. The natural pond water and the natural river water samples analyzed in the present experiment were obtained from the Kagamiga-ike pond in the Nagoya university campus and the Kiso river in Bisai city in Nagoya prefecture, respectively.

Preconcentration Procedure

The river water sample was filtrated through a $0.45\text{ }\mu\text{m}$ membrane filter just after sampling, and then a proper amount of nitric acid was added to the sample to adjust the pH to ca. 1. The certified river reference materials had been already filtrated and acidified to pH 1. A proper amount of spike solution

was added to 500 ml samples of each river water, and let them stand for 24 h to reach the isotopic equilibria.

After being in equilibrium state, the pH of the spiked sample solutions were adjusted to pH 6 with acetic acid and aqueous ammonia solution. After adding 0.4 g of Chelex 100 resin, the sample solutions were stirred with the magnetic stirrers for 2 h. The resin in each sample solution was collected on a glass filter. The matrix elements of Na, K, Ca, and Mg, which were partially adsorbed onto the resin, were eliminated by rinsing with 15 ml of 1 M ammonium acetate solution (pH 6.0). The resin was further rinsed with pure water to remove the adsorbed ammonium acetate. Lead collected on the resin was eluted with 10 ml of 2 M nitric acid solution. Consequently, the 50-fold concentrated solution was obtained and provided to the ICP-MS measurement.

Isotope dilution analysis

In isotope dilution analysis, an analyte concentration is determined with the measurement of the isotope ratio of the spiked sample. The concentration of analyte X is calculated from the following formula:

$$X = \frac{(A_s - R \times B_s)K}{R \times B_N - A_N}$$

Here, A_N is the natural abundance of the reference isotope, A_s the abundance of the reference isotope in the spike solution, B_N the natural abundance of the spike isotope, B_s the abundance of the spike isotope in the spike solution, K the concentration of the analyte element in the spike solution, R the

Table 1 Certified isotope abundances of NIST SRM 981 and SRM 983

	NIST SRM 981 (Natural abundance)	NIST SRM 983 (Enriched abundance)
^{204}Pb	1.4255 ± 0.0012	0.0342 ± 0.0020
^{206}Pb	24.1442 ± 0.0057	92.1497 ± 0.0041
^{207}Pb	22.0833 ± 0.0027	6.5611 ± 0.0025
^{208}Pb	52.3470 ± 0.0086	1.2550 ± 0.0022

Table 2 Comparison of isotope abundance ratios

	Measured value by ICP-MS (a)	Certified value of SRM 981 (b)	Correction factor (b/a)
$^{204}\text{Pb}/^{206}\text{Pb}$	0.0593 ± 0.0006	0.0590	0.995
$^{207}\text{Pb}/^{206}\text{Pb}$	0.911 ± 0.005	0.915	1.004
$^{208}\text{Pb}/^{206}\text{Pb}$	2.135 ± 0.007	2.168	1.015

isotope ratio in the spiked sample solution.

The isotope ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ were measured for ID analysis. The isotope ratio of $^{204}\text{Pb}/^{206}\text{Pb}$ was not adopted, for it was too small to be measured precisely.

In ID analysis, the precision of the analysis depends to some extent on the value of the measured isotope ratio, R . An optimum ratio may theoretically minimize the analytical error introduced by propagation of the errors of the isotope ratio measurements. The optimum ratio of Pb isotopes is 3.3, which is calculated from the error magnification factor. Then, a target value of the measured isotope ratio of 3-4 was chosen. Before ID-ICP-MS analysis, the concentration levels of Pb in the samples analyzed were determined semi-quantitatively by ICP-MS, in order to decide a proper amount of the spike solution added to each sample solution.

Measurement procedure for isotope ratio

Before and after the isotope ratio measurement of each sample, the isotope ratios of NIST SRM 981 were measured 10 times in order to correct mass discrimination of ICP-MS and to evaluate the error of isotope ratio measurement. If the relative standard deviation of the 20 measurements for SRM 981 was more than 1%, the data obtained were rejected. The measurement scheme was as follows; NIST SRM 981 was measured 10 times, the reference solution for the determination of the natural abundance ratio 10 times, the spiked sample 10 times, and NIST SRM 981 10 times, again.

Results and Discussion

Precision of isotope ratio measurement

The precision of the isotope ratio measurements depended on the concentration of lead in the samples, as shown in Fig. 1, which was obtained by the measurement of the natural abundant lead solutions. The dependence of the relative standard deviation RSD on the concentration of lead was almost the same, when the isotope ratios of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ were measured. However, that of $^{204}\text{Pb}/^{206}\text{Pb}$ was rather worse because of the low abundance of ^{204}Pb . It appeared that the RSD saturated to a certain value at 0.001 ng/ml, as the signal and blank intensities were almost equal at the concentration level. The RSD was less than 0.5%, when the concentration of lead was more than 1 ng/ml. The concentrations

Fig.1. Dependence of precision of isotope ratio measurement on Pb concentration

of lead in the measured solutions for ID analysis were chosen to be about 10 ng/ml, which corresponded to about 8×10^4 counts of ions, because such ion intensity was suitable for the precise signal intensity measurement in ICP-MS. The concentrations of lead in the sample solutions were roughly adjusted to about 10 ng/ml before the ID-ICP-MS measurement by the preconcentration or the proper dilution. Therefore, the analytical precision of the present method was expected to be less than 1%, which was calculated from the error magnification factor.

Mass discrimination

The abundance ratios of Pb isotopes obtained in the measurement of NIST SRM 981 were compared with those calculated from the certified values in Table 2. The correction factors were also shown in Table 2. The abundance ratios observed by ICP-MS were slightly different from the certified values because of mass discrimination effect. The analytical errors introduced by mass discrimination were less than 2%, even if there was no correction for mass discrimination. However, in order to carry out the precise analysis in the present study, the abundance ratios were corrected by the correction factors, which were obtained by measuring NIST SRM 981 before and after the measurements of the samples, mentioned in a previous section. When the RSD of the measurements of NIST SRM 981 was more than 1%, the data obtained at that time were rejected in the present study.

Table 3 Analytical results for lead in the spiked river reference material and pond water

Sample	Isotope ratio	Found		Certified value (ng/g)
		ID-ICP-MS (ng/g)	Calibration (ng/g)	
River reference material (JAC 0032)	$^{208}\text{Pb}/^{206}\text{Pb}$	9.90 ± 0.06	10.1 ± 0.1	9.9 ± 0.2
	$^{207}\text{Pb}/^{206}\text{Pb}$	9.93 ± 0.15		
Pond water (the Kagamiga-ike pond)	$^{208}\text{Pb}/^{206}\text{Pb}$	0.266 ± 0.002	0.25 ± 0.02	---
	$^{207}\text{Pb}/^{206}\text{Pb}$	0.267 ± 0.005		

Table 4 Analytical results for lead in the river reference material and river water

Sample	Isotope ratio	Found		Certified value (ng/g)
		ID-ICP-MS (ng/g)	Calibration (ng/g)	
River reference material (JAC 0031)	$^{208}\text{Pb}/^{206}\text{Pb}$	26.1 ± 0.2	25 ± 5	26 ± 3
	$^{207}\text{Pb}/^{206}\text{Pb}$	27.2 ± 0.8		
River water (the Kiso river)	$^{208}\text{Pb}/^{206}\text{Pb}$	35.7 ± 0.4	---	---
	$^{207}\text{Pb}/^{206}\text{Pb}$	34.8 ± 0.5		

Analysis of natural water

Lead in the certified river water reference materials of JAC 0032 and the pond water sampled from the Kagamiga-ike pond were determined by both ID-ICP-MS and the conventional calibration ICP-MS. The results are shown in Table 3. JAC 0032 was analyzed without preconcentration, because its Pb concentration level was high enough to be directly determined by ICP-MS. The analytical results for JAC 0032 obtained by both the methods were well coincident with each other and well agreed with the certified value. The analytical precisions of both ID-ICP-MS and the conventional calibration method were good enough to determine Pb within RSD 1%. This is because such concentration levels are quite suitable for the ICP-MS measurement, as can be seen in Fig. 1. The analytical results for the pond water were also coincident with each other. At this concentration level, however, the precision of ID-ICP-MS was much better than that of the conventional method.

The analytical results for the certified river water reference materials of JAC 0031 and the river water sampled from the Kiso river are shown in Table 4. The analytical result for JAC 0031 obtained by both the methods was coincident with each other and in good agreement with the certified value. The precisions represented as RSD were less than 1%, even when the several pg/g levels of Pb were determined, although that of the conventional calibration method was 20%. Pb in the Kiso river water was also determined as 35 pg/g with the RSD of about 1.5%. It should be noted here that Pb in the water samples can be precisely determined even at the 10 pg/g level

by ID-ICP-MS in cooperation with chelating resin preconcentration.

In conclusion, the Pb concentrations in river water samples were in the range of 10 to 50 pg/g levels, while that in the Kagamiga-ike pond sample was 266 pg/g. These results indicate that ID-ICP-MS is the most promising method for the precise determination of lead in natural water.

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