Bull. Chem. Soc. Jpn., 72, 2445—2449 (1999)

Determination of Ultratrace Indium in Water Sample by Electrothermal Atomic Absorption Spectrometry after Preconcentration with Solvent Extraction and Back Extraction

Hiroshi Kawaguchi,* Takashi Okamoto, Keisuke Miura, Tokuo Shimizu, and Takashi Shirakashi

Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, 7-1-2, Yoto, Utsunomiya 321-8585

(Received May 18, 1999)

A method for the determination of indium at ng dm^{-3} levels in water sample is described. Indium is extracted into carbon tetrachloride as an ion pair of (5-sulfo-8-quinolinolato) indate(III) anion with tetradecyldimethylbenzylammonium chloride, and subsequently back-extracted into 0.3 cm^3 of a nitric acid solution. The back-extracted solution, containing 100 μg cm^{-3} of palladium as a matrix modifier, is suitable for the determination of indium by electrothermal atomic absorption spectrometry. The extraction behavior of the ion associate was also compared with that of the 8-quinolinolato complex. The detection limit (3σ) for indium is 0.28 ng dm^{-3}, based on a 2000-fold preconcentration. The proposed method is applicable to the determination of indium at ng dm^{-3} levels in water sample.

The need for sensitive and reliable methods for the determination of trace elements has been recognized in analytical chemistry and/or environmental science. The determination of indium at μg g^{-1}—ng g^{-1} levels has been carried out in various samples, such as aluminum,[1—3] mineral,[4—7] and biological[8,9] samples. However, there have only been a few studies concerning the determination of indium in natural water because of its extreme low concentration (ng dm^{-3}—sub ng dm^{-3} levels). In recent years, indium has become very important in the electronics industry; for example, it has been used as InGaAsP and InP (semiconductor). Therefore, the determination of indium in water sample has become important in studies of environmental science and has been carried out using several instrumental techniques combined with preconcentration methods.[10—13]

Inductively coupled plasma mass spectrometry (ICP-MS) is a good instrumental technique for the determination of ultratrace elements in water sample on account of its high sensitivity. Orians and Boyle[10] determined the picomolar concentration (sub ng dm^{-3} level) of indium in seawater by ICP-MS. However, its determination requires a 3000-fold preconcentration with an 8-quinolinol (Hquin) chelating resin column and evaporation of the eluent.

Atomic absorption spectrometry (AAS) is an easy, rapid technique, and has been widely used for the determination of trace elements in water sample. Mohammad et al.[11] developed an on-line preconcentration method using a column of Hquin immobilized on controlled-pore glass; however, the indium concentration in natural water samples was too low for determination by flame AAS. Although electrothermal (ET) AAS is one of the most useful techniques for the determination of trace elements, there is a lack of sensitivity for indium. The poor sensitivity is caused by substantial losses of analyte from a graphite furnace before atomization due to the formation of volatile oxides. Therefore, matrix or analyte modifications with chemical reagents have been investigated. More universal modifiers for indium determination were palladium[1,4,8,13] and nickel.[6,9] Ueda and Mizui[12] studied the coprecipitation method with hafnium(IV) hydroxide for determining indium by ETAAS. It was found that hafnium(IV) hydroxide collects down to 0.5 μg dm^{-3} of indium in water sample quantitatively and that the presence of hafnium enhances the atomic absorbance of indium. Wei et al.[13] developed a selective adsorption method using activated carbon (AC) as an adsorbent and acetylacetone as a complexing agent. The resulting AC-suspension containing palladium as a matrix modifier is directly introduced into a graphite furnace and the detection limit obtained was 25 ng dm^{-3} of indium in water sample. However, these methods were not applicable to ng dm^{-3} levels of indium.

The solvent extraction method is a simple and rapid technique; in addition, high enrichment factors of more than 1000 times can be attained by extraction followed by microvolume back extraction.[14,15] In the preconcentration of indium, Hquin is used as complex-forming agents.[10,11] In this study, 5-sulfo-8-quinolinol (H_2quins) or Hquin was used as extractants. Using H_2quins with tetradecyldimethylbenzylammonium chloride (Zephiramine, Zeph), we have already reported on determination of gallium at ng dm^{-3} levels in river water.[15]

In this paper, H_2quins and Hquin were investigated for the solvent extraction and back extraction of indium so as to establish an effective method for determining indium at ng dm^{-3} levels in water sample.

Experimental

Apparatus. A Hitachi Model Z-7000 polarized Zeeman atomic absorption spectrometer was used. A single-element indium

hollow cathode lamp was employed as the light source. A tube-type pyrolytic graphite coated cuvette was used. Argon was used as a sheath gas at a flow rate of 3.0 dm^3 min^{-1} and a carrier gas (internal gas) at 0.2 dm^3 min^{-1}. The carrier gas flow was interrupted during the atomization stage. The absorbance signals were recorded at 325.6 nm, and the peak heights were taken as the analytical signals. The optimum conditions for indium measurements were as follows: Injection volume, 20 mm^3; Drying, 80—120 °C for 30 s, 150 °C for 30 s, 150—200 °C for 30 s; Ashing, 1500 °C for 30 s; Atomizing (rapid-heating atomization with an optical temperature control device), 2700 °C for 7 s.

Reagents. An indium working solution was prepared from a stock solution (Kanto Chemical, 1 mg cm^{-3}, dissolving pure metal in 1 mol dm^{-3} nitric acid) by dilution with 0.1 mol dm^{-3} nitric acid. A palladium stock solution (Kanto Chemical, 1 mg cm^{-3}, dissolving pure metal in 1 mol dm^{-3} nitric acid) was used as a matrix modifier. A 4.0×10^{-2} mol dm^{-3} H_2quins solution was freshly prepared by dissolving the requisite amount of H_2quins (Tokyo Kasei) in dilute aqueous ammonia before use. A 0.1 mol dm^{-3} Zephiramine solution was freshly prepared by dissolving the requisite amount of Zephiramine (Dojindo) in water before use. A 4.0×10^{-2} mol dm^{-3} Hquin solution was freshly prepared by dissolving the requisite amount of Hquin (Kanto Chemical) in dilute nitric acid and subsequent dilution with water before use. All other chemicals were of analytical reagent grade. Distilled, deionized water was further purified using a Millipore Milli-Q system.

Procedure. The recommended procedure for 2000-fold preconcentration of indium using H_2quins–Zeph system is as follows.

An 800 cm^3 of sample solution was transferred into a 1000 cm^3 separatory funnel. Then, 1 cm^3 of a 4.0×10^{-2} mol dm^{-3} H_2quins solution, 8 cm^3 of a 2 mol dm^{-3} ammonium acetate solution and 4 cm^3 of a 0.1 mol dm^{-3} Zephiramine solution were successively added. The pH of the solution was adjusted to 5.0 by the addition of aqueous ammonia. After the addition of 16 cm^3 of carbon tetrachloride, the mixture was shaken by hand for 5 min. After 30 min for phase separation, the organic phase was collected in a 30 cm^3 centrifuge tube. After centrifuging, a 12 cm^3 aliquot of the organic phase was transferred into another centrifuge tube. The back extraction of indium was carried out using 100 mm^3 of concentrated nitric acid (60%) for 3 min, after which the mixture was centrifuged for 10 min. Then, 30 mm^3 of a 1 mg cm^{-3} palladium solution and 170 mm^3 of water were added and the contents were shaken for 3 min. After centrifuging for 10 min, the organic phase was sucked up through a Teflon® tube (0.3 mm i.d.). Then, the back-extracted solution was transferred into a collection vial and the indium concentration was determined by ETAAS.

In the case of a 1500-fold preconcentration using Hquin system, a 600 cm^3 of sample solution was transferred into a 1000 cm^3 separatory funnel. Then, 1.5 cm^3 of a 4.0×10^{-2} mol dm^{-3} Hquin solution and 6 cm^3 of a 2 mol dm^{-3} ammonium acetate solution were successively added. The pH of the solution was adjusted to 6.0 by the addition of aqueous ammonia. After the addition of 12 cm^3 of carbon tetrachloride, the mixture was shaken by hand for 5 min. After 30 min for phase separation, the organic phase was collected in a 30 cm^3 centrifuge tube. After centrifuging, a 9 cm^3 aliquot of the organic phase was transferred into another centrifuge tube. The back extraction of indium and ETAAS measurement were the same as mentioned above.

Results and Discussion

Effect of Matrix Modifier. As described above, indium exhibits a large loss of analyte before atomization. In this study, nickel nitrate and palladium nitrate were investigated as matrix modifier and palladium was selected because the sensitivity improved about 2 times higher than that obtained with nickel.

The effects of the ashing and atomization temperature on the indium absorbances were examined using an aqueous standard (25 μg dm^{-3}) of ca. 4 mol dm^{-3} nitric acid. In the presence of palladium with a nitric acid medium, the tolerable ashing temperature could be raised up to 1750 °C and the sensitivity was greatly improved. At the atomization stage, the maximum and nearly constant absorbance was obtained at over 2700 °C. The effect of the concentration of palladium was also examined. The indium absorbances increased with increasing the palladium concentration; then, a nearly constant absorbance was obtained over 50 μg cm^{-3}.

Extraction of Indium from Water. An ion pair of (5-sulfo-8-quinolinolato) indate(III) anion with Zephiramine can be easily extracted into carbon tetrachloride. The extracted ion associate was estimated to be $[3Zeph^+, [In(quins)_3]^{3-}]$ by a continuous variation method and a mole-ratio method using spectrophotometry. Since the chelating behavior of Hquin is identical to that of H_2quins, the extraction of indium with Hquin was also investigated.

The effect of the pH on the extraction of indium was studied using 20 cm^3 of water spiked with 10 ng of indium. As shown in Fig. 1, the optimum pH range using H_2quins is 4.5—9.0 for the extraction of indium. In the case of the Hquin system, the optimum pH range is 5—10, which was similar to that of the H_2quins system. Therefore, the extraction of indium was carried out at pH 5.0 (H_2quins–Zeph system) or 6.0 (Hquin system).

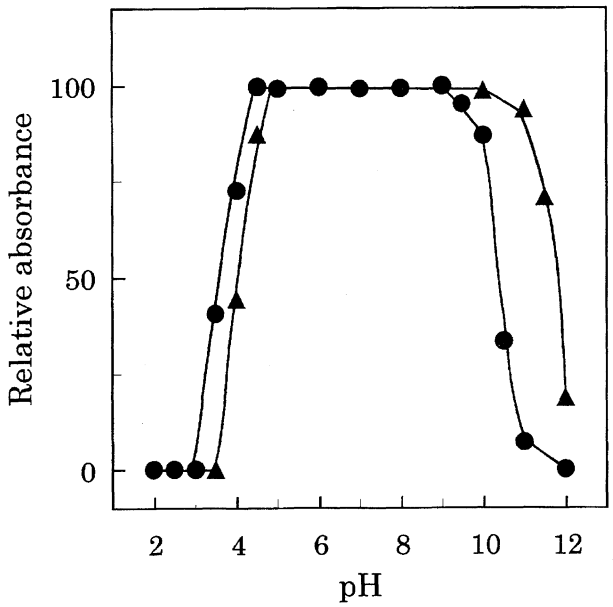

Fig. 1. Effect of pH on the extraction of indium from 20 cm^3 of water. H_2quins (●); Hquin (▲). In 10 ng; Carbon tetrachloride, 4 cm^3; Back extraction solution, 300 mm^3 (100 mm^3 of concd HNO_3+30 mm^3 of 1 mg cm^{-3} Pd+170 mm^3 of water).

The effect of the H_2quins concentration in the aqueous phase on the extraction of indium was investigated. The results are shown in Fig. 2. When the Zephiramine concentration was 2.0×10^{-2} mol dm^{-3}, the maximum relative absorbance of indium was achieved at an H_2quins concentration of 5.0×10^{-5} mol dm^{-3}. However, the complete extraction of indium was achieved at an H_2quins concentration of 2.0×10^{-4} mol dm^{-3} and a Zephiramine concentration of 2.0×10^{-3} mol dm^{-3}. The effect of the Zephiramine concentration in the aqueous phase on the extraction of indium was also studied. The results are shown in Fig. 3. When the H_2quins concentration was 2.0×10^{-3} mol dm^{-3}, the maximum relative absorbance of indium was achieved at a Zephiramine concentration of 2.0×10^{-3} mol dm^{-3}. However, the complete extraction of indium was achieved at a Zephiramine concentration of 2.0×10^{-3} mol dm^{-3} and an H_2quins concentration of 2.0×10^{-4} mol dm^{-3}. Therefore, subsequent extraction was carried out at an H_2quins concentration of 2.0×10^{-4} mol dm^{-3} and a Zephiramine concentration of 2.0×10^{-3} mol dm^{-3}.

The effect of the Hquin concentration in the aqueous phase on the extraction of indium was studied. As shown in Fig. 4, the complete extraction of indium was achieved at an Hquin concentration of 1.0×10^{-4} mol dm^{-3}. Therefore, extraction was carried out at an Hquin concentration of 1.0×10^{-4} mol dm^{-3}.

The shaking time for the extraction of indium with H_2quins and Hquin systems was investigated. A shaking time of 5 min was found to be sufficient to achieve the extraction equilibrium of indium.

Back Extraction of Indium from the Organic Phase. Indium in the organic phase can be easily back-extracted with nitric acid. The effect of the amount of concentrated nitric acid (60%) on the back extraction of indium from carbon tetrachloride into the aqueous phase was investigated. The back extraction of indium from 3 cm^3 of carbon tetrachloride, extracted as In–H_2quins–Zeph ion associate and In–Hquin chelate, was carried out with 25—200 mm^3 of concentrated nitric acid in a centrifuge tube. After shaking, the mixture was centrifuged; then, 30 mm^3 of 1 mg cm^{-3} palladium solution and water were added until the total volume was 300

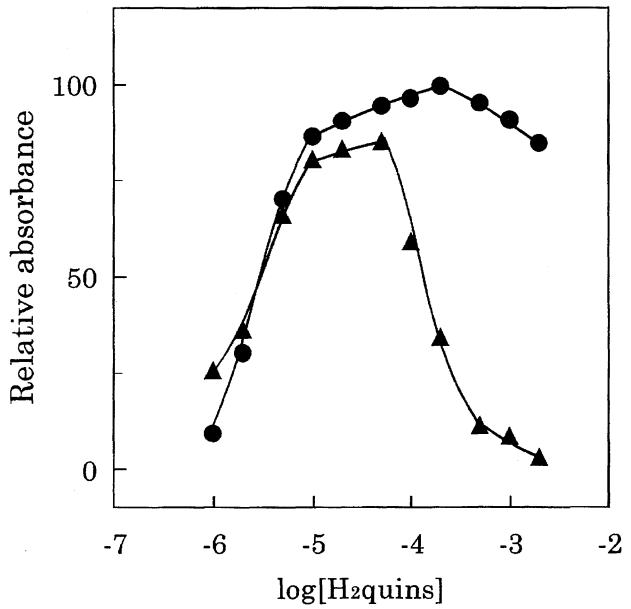

Fig. 2. Effect of H_2quins concentration on the extraction of indium from 20 cm^3 of water. Zeph concentration, 2.0×10^{-3} mol dm^{-3} (●) or 2.0×10^{-2} mol dm^{-3} (▲); In, 10 ng; Carbon tetrachloride, 4 cm^3; Back extraction solution, 300 mm^3.

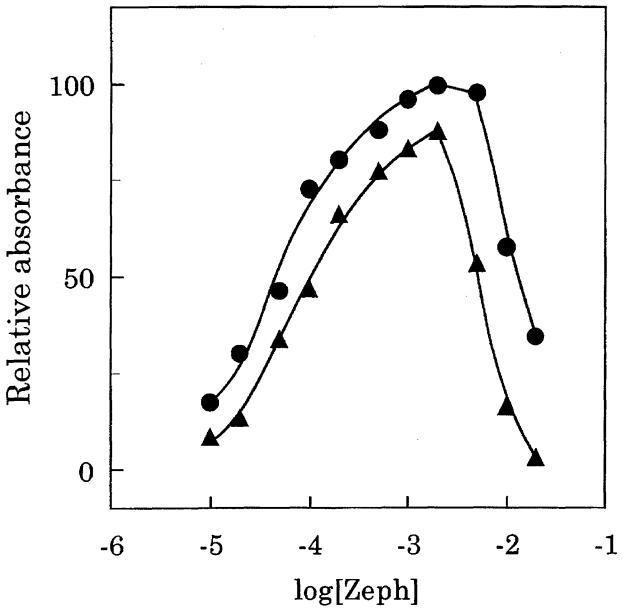

Fig. 3. Effect of Zephiramine concentration on the extraction of indium from 20 cm^3 of water. H_2quins, 2.0×10^{-4} mol dm^{-3} (●) or 2.0×10^{-3} mol dm^{-3} (▲); In, 10 ng; Carbon tetrachloride, 4 cm^3; Back extraction solution, 300 mm^3.

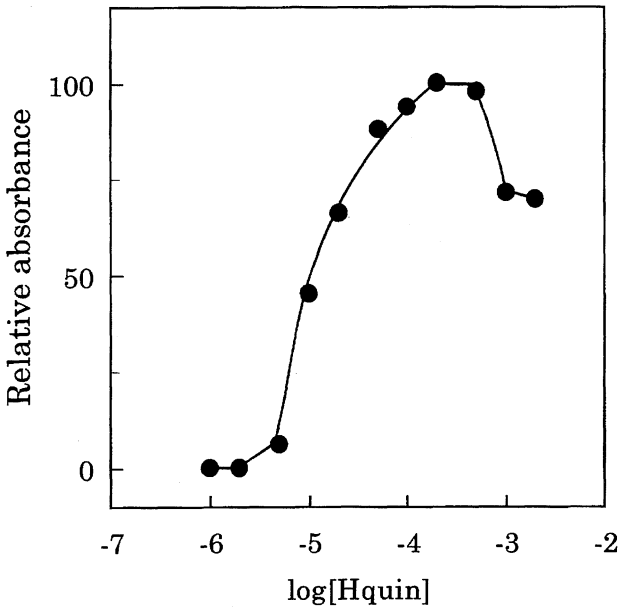

Fig. 4. Effect of Hquin concentration on the extraction of indium from 20 cm^3 of water. In, 10 ng; Carbon tetrachloride, 4 cm^3; Back extraction solution, 300 mm^3.

mm^3; the mixture was shaken again. After centrifuging, the aqueous phase was collected and used for ETAAS measurements. Complete back extraction of In–H_2quins–Zeph ion associate was obtained when the volume of concentrated nitric acid (60%) was 75 mm^3 or more. In the case of In–Hquin chelate, complete back extraction was obtained when the volume of concentrated nitric acid (60%) was 100 mm^3 or more.

The shaking time for the back extraction of indium was also examined. Complete back extraction of In–H_2quins–Zeph ion associate was obtained by shaking for more than 30 s. In the case of In–Hquin chelate, shaking for more than 3 min was necessary for complete back extraction.

Effect of the Aqueous to Organic Phase Volume Ratio. The extraction and back extraction of indium with H_2quins–Zeph system in various volume ratios of aqueous to organic phase were studied. All operations were carried out according to the procedures described above, except for the volume ratio of the two phases. As shown in Fig. 5a, relative absorbance of indium steeply decreases with increase of a volume ratio of the aqueous to the organic phase above 10 : 1 when the extraction of indium was carried out at an H_2quins concentration of 2.0×10^{-4} mol dm^{-3} and a Zephiramine concentration of 2.0×10^{-3} mol dm^{-3}. When the H_2quins and Zephiramine concentration were 5.0×10^{-5} and 5.0×10^{-4} mol dm^{-3}, respectively, a quantitative extraction of indium was attained with a volume ratio of the aqueous to the organic phase of less than 75 : 1. On the other hand, Fig. 5b shows that a quantitative back extraction of indium was attained with a volume ratio of the aqueous to the organic phase of less than 1 : 75. On the basis of these results, more than 1000-fold concentration was carried out at an H_2quins concentration of 5.0×10^{-5} mol dm^{-3} and a Zephiramine concentration of 5.0×10^{-4} mol dm^{-3}.

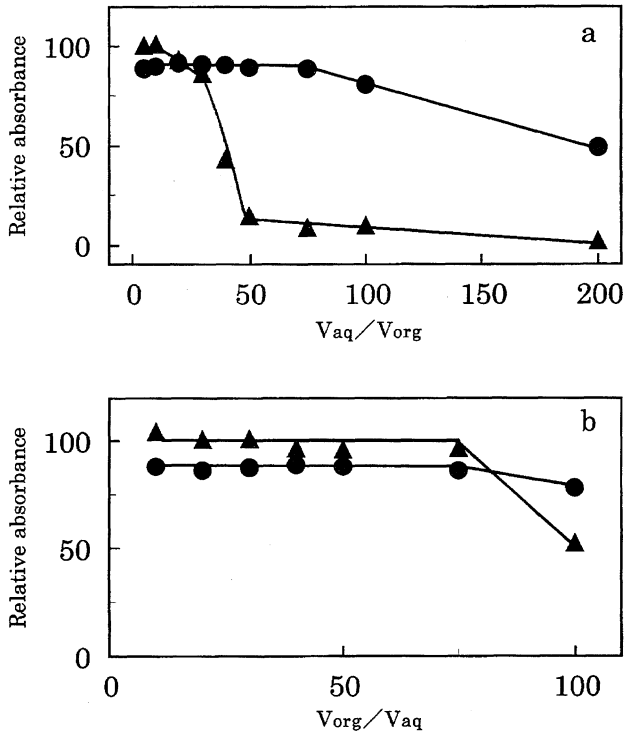

Fig. 5. Effect of the volume ratio of aqueous to organic phase on the extraction of indium with H_2quins (a), and organic to aqueous phase on the back extraction of indium (b). H_2quins, 5.0×10^{-5} mol dm^{-3}, Zeph, 5.0×10^{-4} mol dm^{-3} (●); H_2quins, 2.0×10^{-4} mol dm^{-3}, Zeph, 2.0×10^{-3} mol dm^{-3} (▲). In, 10 ng; Back extraction solution, 300 mm^3.

The extraction and back extraction of indium with Hquin system in various volume ratios of aqueous to organic phase were also examined. The results are shown in Figs. 6a and 6b. Quantitative extractions of indium were attained with a volume ratio of the aqueous to the organic phase of less than 50 : 1 for the first extraction and 1 : 30 for the back extraction.

Detection Limit and Interference. The linear calibration curve for 2000-fold preconcentration with H_2quins–Zeph system was obtained over the range of 0 to about 16 ng dm^{-3} in the initial solution. The indium concentration corresponding to 1% absorption (absorbance = 0.0044) was 0.89 ng dm^{-3}. The detection limit, defined as three times the standard deviation of the blank signals (n = 10), was 0.28 ng dm^{-3}. The relative standard deviation for eight replicate determinations of 12 ng dm^{-3} level was 2.4%.

The linear calibration curve for 1500-fold preconcentration with Hquin system was obtained over the range of 0 to about 25 ng dm^{-3} in the initial solution. The indium concentration corresponding to 1% absorption was 1.1 ng dm^{-3}. The detection limit was 0.95 ng dm^{-3}. The relative standard

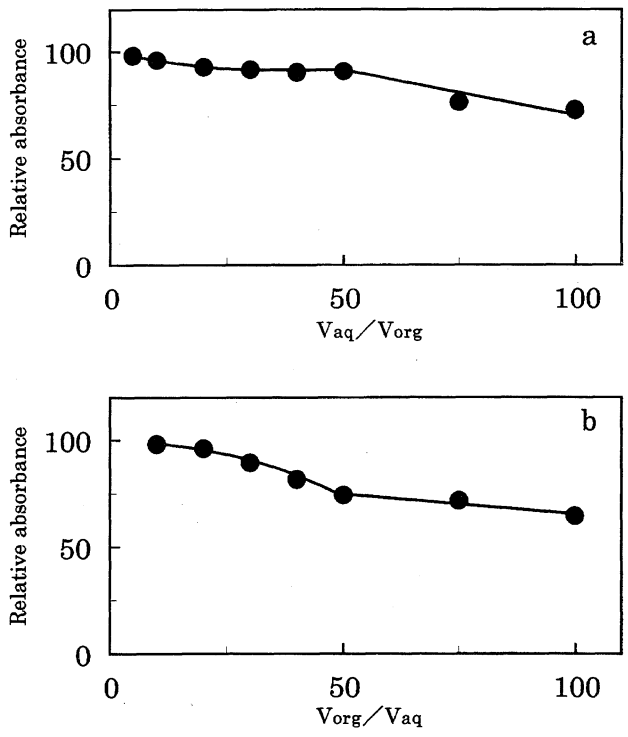

Fig. 6. Effect of the volume ratio of aqueous to organic phase on the extraction of indium with Hquin (a), and organic to aqueous phase on the back extraction of indium (b). In, 10 ng; Hquin, 1.0×10^{-4} mol dm^{-3}; Back extraction solution, 300 mm^3.

deviation for eight replicate determinations of 20 ng dm^{-3} level was 4.1%.

The effect of foreign ions included natural water samples was examined. A number of common ions tested were found not to cause severe interference. However, 50 μg of iron showed serious interferences with the determination of 10 ng amount of indium and resulted in a decrease in atomic absorbance of indium. The dissolved iron concentrations usually found in Kinu river water ranged from 4 to 8 μg dm^{-3} by a direct ETAAS determination. Taking into account the preconcentration factor and the detection limit, the H_2quins–Zeph system was applied to a real sample analysis.

Analysis of Water Sample. The determination of indium was performed by the proposed H_2quins–Zeph system for a water sample from Kinu river (Utsunomiya, Tochigi Pref.) using the standard addition method. The collected water sample was immediately filtered through a 0.45 μm membrane filter and acidified to 0.1 mol dm^{-3} nitric acid. From the non-spiked river water, indium was not detected because of its extremely low concentration (sub ng dm^{-3} level).

The availability of the proposed method in river water matrix was confirmed by the recovery test of 8 ng dm^{-3} of indium spiked to the river water. The recovery of indium was 97.5±4.0% (n = 4).

The proposed method, H_2quins–Zeph system, is applicable to the determination of ng dm^{-3} levels of indium in water sample. Carbon tetrachloride is recognized as one of the ozone-depleting substances, and the application of it is to be restricted or forbidden in the near future. Instead of carbon tetrachloride, xylene can be used as the extracting solvent, which has been confirmed experimentally.

References

1 Y. Shijo, E. Yoshimoto, S. Sakurai, T. Shimizu, and Y. Kawamata, *Anal. Sci.*, **10**, 277 (1994).

2 S. V. Vartak and V. M. Shinde, *Talanta*, **45**, 925 (1998).

3 Dianjie Ma, Y. Okamoto, T. Kumamaru, and E. Iwamoto, *Anal. Sci.*, **15**, 193 (1999).

4 Shan Xiao-quan, Ni Zhe-ming, and Yuan Zhi-neng, *Anal. Chim. Acta*, **171**, 269 (1985).

5 K. Itsuki, H. Yagasaki, and H. Fujinuma, *Bunseki Kagaku*, **34**, T109 (1985).

6 R. Kuroda, T. Wada, T. Soma, N. Itsubo, and K. Oguma, *Analyst*, **115**, 1535 (1990).

7 Chang Xijun, Li Yanfeng, Su Zhixing, Zhang Guangyao, and Luo Xingyin, *Anal. Lett.*, **29**, 1861 (1996).

8 G. Schlemmer and B. Welz, *Spectrochim. Acta, Part B*, **41B**, 1157 (1986).

9 S. Imai, M. Harada, T. Tanaka, and Y. Hayashi, *Anal. Sci.*, **13**, 837 (1997).

10 K. J. Orians and E. A. Boyle, *Anal. Chim. Acta*, **282**, 63 (1991).

11 B. Mohammad, A. M. Ure, and D. Littlejohn, *J. Anal. At. Spectrom.*, **8**, 325 (1993).

12 J. Ueda and C. Mizui, *Anal. Sci.*, **4**, 417 (1988).

13 Jinshan Wei, Qian Liu, and T. Okutani, *Anal. Sci.*, **10**, 465 (1994).

14 Y. Shijo, M. Mitsuhashi, T. Shimizu, and S. Sakurai, *Analyst*, **117**, 1929 (1992).

15 H. Kawaguchi, T. Shimizu, T. Shirakashi, and Y. Shijo, *Bull. Chem. Soc. Jpn.*, **71**, 647 (1998).