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

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A method for the determination of gallium at ng dm^{-3} levels in river water is described. Gallium is extracted into carbon tetrachloride as an ion pair of gallium–5-sulfo-8-quinolinol (H_2QS) chelate anion with tetradecyldimethylbenzylammonium chloride (Zephiramine), and subsequently back-extracted into 0.3 cm^3 of a nitric acid solution. The high efficiency of extraction and back extraction allows gallium to be concentrated about 5000-fold with a combined single extraction and back extraction. The back-extracted solution, containing 250 μg cm^{-3} of nickel as a matrix modifier, is suitable for the determination of gallium by electrothermal atomic absorption spectrometry (ETAAS). The detection limit (3σ) for gallium is 0.29 ng dm^{-3} based on a 1500-fold preconcentration. The concentration of dissolved gallium in river water was found to be 5.3—9.2 ng dm^{-3} by the proposed method.

The determination of certain trace elements in river water has become important in studies of river environments. Among these, studies of gallium in river water have been relatively few because of its extreme low concentration. Gallium is mainly used in the electronics industry. The increasing use of its compounds, such as GaAs (semiconductor) and GaInN (light emitting diode), has posed questions concerning its toxicity, and also requires sensitive methods for determining this element. The gallium concentration in natural water samples has been reported to be about 12 ng dm^{-3}, determined by the anion-exchange thiocyanate preconcentration coupled with spectrophotometry with Rhodamine B (CAS No-81-88-9) using 10 dm^3 of sample water.[1)]

Despite the large selection of sensitive analytical techniques for trace elements determination, atomic absorption spectrometry, particularly with the advent of the electrothermal atomization technique (ETAAS), still occupies the place of an extremely sensitive analytical technique for a large number of elements. Inductively coupled plasma mass spectrometry (ICP-MS) has superior sensitivity and ability for multielement analysis. Although the direct determination of trace elements in river water by ICP-MS has been performed,[2,3)] gallium was not determined because of spectral interference at mass 69 from doubly-ionized barium. It is therefore, thought that a direct determination of ultratrace gallium in river water is not feasible due to insufficient instrumental sensitivity and matrix interference.

Orians and Boyle[4)] determined picomolar concentrations of gallium in seawater by ICP-MS and ETAAS after 3000-fold concentration and matrix removal with an 8-quinolinol (HQ) chelating resin column and evaporation of the eluent. Mohammad et al.[5)] developed an on-line preconcentration method using a column of HQ immobilized on controlled-pore glass; however, the gallium concentration in natural water samples was too low for determination by flame AAS. Shida et al. developed a direct resin insertion technique into ETAAS for the determination of gallium in water samples. Gallium was retained as its complex with Tiron (149-45-1)[6)] or Pyrocatechol Violet (115-41-3)[7)] on an anion-exchange resin. The detection limits were 1.5 ng cm^{-3} using 5 cm^3 of sample water[6)] and 3 ng dm^{-3} using 500 cm^3 of sample water.[7)] Ueda and Mizui[8)] studied the coprecipitation of gallium with hafnium hydroxide.

Solvent extraction and back extraction methods have an advantage over other methods of preconcentration[1,4—8)] in that a higher enrichment factor is obtained by this method. The enrichment factor is dependent on the volume of the final solution when a defined volume of initial solution is used. Microvolume back extraction with 100 mm^3 of nitric acid gives excellent results for the preconcentration of ultratrace bismuth, and is well-suited for a subsequent determination by ETAAS.[9)] Bismuth is extracted into xylene as the dithiocarbamate complex and back-extracted into 20 mm^3 of fuming nitric acid and 80 mm^3 of water. An enrichment factor of 3300 times is obtainable using 400 cm^3 of sample water. In the preconcentration of gallium, HQ is used as a chelating extractant[10)] or complex-forming adsorbents.[4,5)] Ohashi et al.[11)] synthesized the alkylated HQ derivatives and studied these extraction behaviors of gallium.

In this work, HQ and its derivatives, including the alkylated HQ, were investigated for solvent extraction and back extraction of gallium. An effective extraction and back extraction of gallium was obtained using 5-sulfo-8-quinolinol (H_2QS) with tetradecyldimethylbenzylammonium chloride (Zephiramine) and nitric acid. By using the proposed method, concentration factors of 5000 can be attained, and a precise determination of gallium at ng dm^{-3} levels in river water is feasible with a 1500-fold preconcentration.

Experimental

Apparatus. A Hitachi Model Z-7000 polarized Zeeman atomic absorption spectrometer was used. A single-element gallium hollow cathode lamp (Hamamatsu Photonics) was employed as the light source. A tube-type conventional uncoated graphite cuvette was used, since it was preferred to a pyrolytic graphite coated cuvette in gallium measurements. 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 absorbance signals were recorded at 294.4 nm, and the peak heights were taken as the analytical signals. The optimum conditions for gallium measurements were as follows: Injection volume, 20 mm^3; Drying, 80—120 °C for 30 s; Ashing, 1000 °C for 30 s; Atomization, 3000 °C for 10 s.

Reagents. A gallium 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 nickel stock solution (Kanto Chemical, 1 mg cm^{-3}, dissolving pure metal in 0.1 mol dm^{-3} nitric acid) was used as a matrix modifier. A 1.5×10^{-2} mol dm^{-3} H_2QS solution was freshly prepared by dissolving the requisite amount of H_2QS (Tokyo Kasei) in dilute aqueous ammonia before use. A 0.15 mol dm^{-3} Zephiramine solution was freshly prepared by dissolving the requisite amount of Zephiramine (Dojindo) in 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 1500-fold preconcentration of gallium is as follows.

After the pretreatments (described later), a 500 cm^3 aliquot of the sample solution was transferred into a 1000 cm^3 separatory funnel. Then, 5 cm^3 of a 1.5×10^{-2} mol dm^{-3} H_2QS solution, 5 cm^3 of a 2 mol dm^{-3} ammonium acetate solution and 5 cm^3 of a 0.15 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 10 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 gallium 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, 75 mm^3 of a 1 mg cm^{-3} nickel solution and 125 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 gallium concentration was determined by ETAAS.

The two pretreatment methods were employed before preconcentration for evaluating the speciation of gallium. Method A (Dissolved Ga): The collected sample was immediately filtered through a 0.45 µm membrane filter and acidified to 0.1 mol dm^{-3} nitric acid. Method B (Total Ga): After the collected sample was acidified to 0.1 mol dm^{-3} nitric acid, filtration was performed after one month. For all samples, preconcentration was performed within ten days after filtration.

Results and Discussion

Effect of Matrix Modifier. Gallium is one of the volatile elements exhibiting a large loss of analyte before atomization in graphite furnace AAS;[12)] a modification of the matrix by the addition of chemical reagents (nickel nitrate,[13)] nickel chloride or palladium chloride[14)]) to the furnace is necessary. In this study, nickel was used as matrix modifier because the sensitivity is slightly higher in the presence of nickel than in the presence of palladium.

The effects of the ashing and atomization temperature on the gallium absorbances were examined using an aqueous standard (50 µg dm^{-3}) of ca. 4 mol dm^{-3} nitric acid. In the presence of nickel with a nitric acid medium, the tolerable ashing temperature could be raised up to 1000 °C and the sensitivity improved by a factor of 4. At the atomization stage, the maximum peak heights were obtained at 3000 °C. The effect of the concentration of nickel was also examined. The gallium absorbances increased with increasing nickel concentration; then, a nearly constant absorbance was obtained over 0.2 mg cm^{-3}.

Extraction of Gallium from Water. The chelating behavior of H_2QS is similar to that of HQ, but the H_2QS chelates are soluble in water. An ion pair of H_2QS chelate anion with Zephiramine can easily be extracted with an organic solvent. The extracted ion associate was estimated to be $[3Z^+, [Ga(QS)_3]^{3-}]$ by a continuous variation method and a mole-ratio method using ETAAS and spectrophotometry.

The effect of an organic solvent on the extractability of gallium with H_2QS and Zephiramine was investigated by varying the solvents, such as benzene, chloroform, xylene, cyclohexane, and carbon tetrachloride. Taking into account the low solubility in water and high extractability of gallium, carbon tetrachloride was selected as a solvent for subsequent experiments.

The effect of the pH on the extraction of gallium was studied using 20 cm^3 of water spiked with 20 ng of gallium. As shown in Fig. 1, the optimum pH range is 4—9 for the extraction of gallium. The decrease in the relative absorbance of gallium above pH 9.5 is due to a depression of gallium extraction along with the formation of a hydroxo complex of gallium, $[Ga(OH)_4]^-$. The extraction of gallium was therefore carried out at pH 5.0 in a subsequent study.

The effect of the H_2QS concentration in the aqueous phase on the extraction of gallium was investigated. The results are shown in Fig. 2. When the Zephiramine concentration was 1.5×10^{-2} mol dm^{-3}, the maximum relative absorbance of gallium was achieved at an H_2QS concentration of 7.5×10^{-6} mol dm^{-3}. However, the complete extraction of gallium was achieved at an H_2QS concentration of 1.5×10^{-4} mol dm^{-3} and a Zephiramine concentration of 1.5×10^{-3} mol dm^{-3}. The effect of the Zephiramine concentration in the aqueous phase on the extraction of gallium was also studied. The results are shown in Fig. 3. When the H_2QS concentration was 1.5×10^{-3} mol dm^{-3}, the maximum relative absorbance of gallium was achieved at a Zephiramine concentration of about 7.5×10^{-3} mol dm^{-3}. However, the complete extraction of gallium was achieved at a Zephiramine concentration of 1.5×10^{-3} mol dm^{-3} and an H_2QS concentration of 1.5×10^{-4} mol dm^{-3}. On the basis of these results, subsequent extraction was carried out at an H_2QS concentration

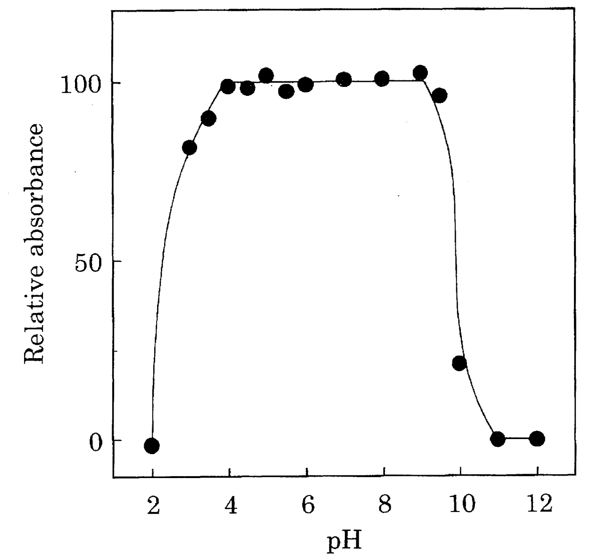

Fig. 1. Effect of pH on the extraction of gallium. Ga, 20 ng; Back extraction solution, 300 mm^3 (100 mm^3 of concd HNO_3 + 75 mm^3 of 1 mg cm^{-3} Ni + 125 mm^3 of water).

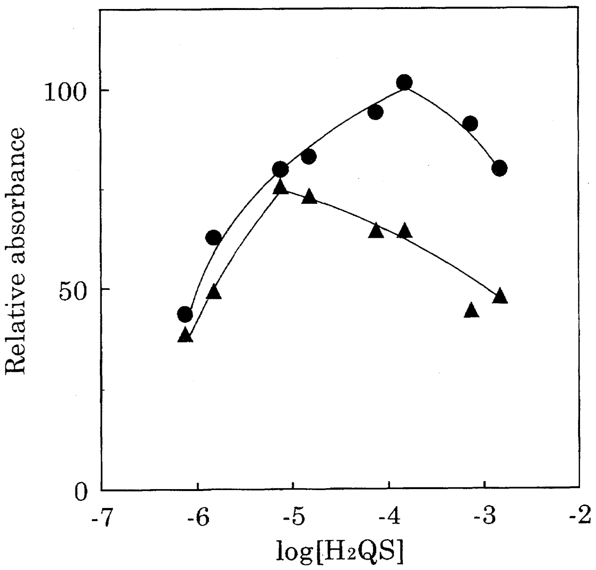

Fig. 2. Effect of H_2QS concentration on the extraction of gallium. Zeph. concentration, 1.5×10^{-3} mol dm^{-3} (●) or 1.5×10^{-2} mol dm^{-3} (▲); Ga, 20 ng; Back extraction solution, 300 mm^3.

of 1.5×10^{-4} mol dm^{-3} and a Zephiramine concentration of 1.5×10^{-3} mol dm^{-3}.

The shaking time for the extraction of gallium was investigated and found that the extraction equilibrium of gallium was achieved within 3 min.

Back Extraction of Gallium from the Organic Phase. Gallium 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 gallium from carbon tetrachloride into the aqueous phase was investigated. The back extraction of gallium from 3 cm^3 of carbon tetrachloride, extracted as the ion associate, was carried out with 25—200 mm^3 of concentrated nitric acid in a centrifuge tube. After shaking, the mixture was centrifuged; then, 75 mm^3 of 1 mg cm^{-3} nickel solution and water were added until the total volume was 300 mm^3; the mixture was shaken again. After centrifuging, the aqueous phase was collected and used for ETAAS measurements. Complete back extraction was obtained when the volume of concentrated nitric acid (60%) was 75 mm^3 or more.

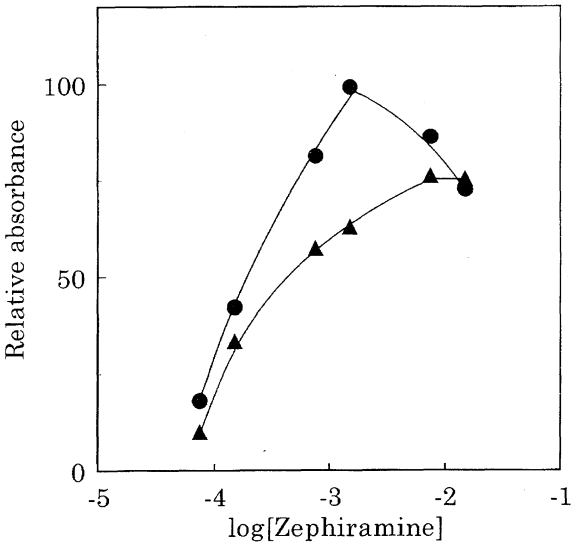

Fig. 3. Effect of Zephiramine concentration on the extraction of gallium. H_2QS, 1.5×10^{-4} mol dm^{-3} (●) or 1.5×10^{-3} mol dm^{-3} (▲); Ga, 20 ng; Back extraction solution, 300 mm^3.

The shaking time for the back extraction of gallium was investigated. Complete back extraction of gallium was obtained by shaking for more than 1 min. For subsequent work, a concentrated nitric acid volume of 0.1 cm^3 and a shaking time of 3 min were selected.

Effect of the Aqueous to Organic Phase Volume Ratio. The extraction and back extraction of gallium 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. The results are shown in Fig. 4. Quantitative extractions of gallium were attained with a volume ratio of the aqueous to the organic phase of less than 75 : 1 for the first extraction and 1 : 75 for the back extraction. A concentration factor for gallium from water of about 5.0×10^3 can consequently be achieved by a combined single extraction and back extraction.

Detection Limit and Precision. The linear calibration curve for 1500-fold preconcentration was obtained over the range of 0 to about 80 ng dm^{-3} in the initial solution. The detection limit, defined as three times the standard deviation of the blank signals ($n = 10$), was 0.29 ng dm^{-3}. The relative standard deviation for eight replicate determinations of 30 ng dm^{-3} level was 2.6%. The blank levels in the back-extracted solutions were very low and the reproducibility of the signal from gallium was satisfactory. Gallium concentrations at ng dm^{-3} levels in water can be determined using concentration factors of more than 10^3.

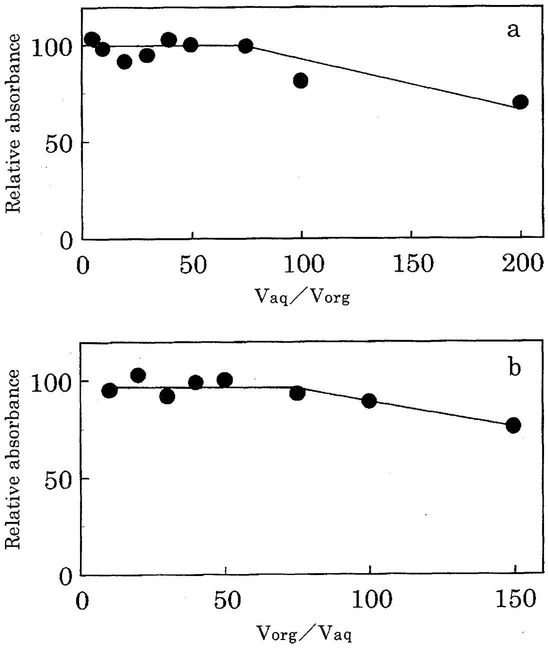

Fig. 4. Effect of the volume ratio of aqueous to organic phase on the extraction of gallium (a), and organic to aqueous phase on the back extraction of gallium (b). Ga, 20 ng; Back extraction solution, 300 mm^3.

Interference. The interference of various metal ions in the determination of gallium was investigated with a mixture of metal ions at concentrations approximately equal to, or exceeding, those normally found in river water. The results are given in Table 1. The mixture of metal ions tested was found not to cause severe interference with the determination of gallium.

Analysis of River Water. The concentrations of gallium in three river water samples were determined according to the proposed method using the standard addition method of calibration. The results are given in Table 2. The concentrations of spiked gallium varied from 4 to 24 ng dm^{-3} for a 1500-fold preconcentration and from 25 to 150 ng dm^{-3} for a 600-fold preconcentration. The analytical values obtained from Method B (Total Ga) were higher than those of Method A (Dissolved Ga). This was because gallium dissolved out from suspended or particulate matter in the acidified samples during storage. The precision (relative standard deviation) ranged from 1.8 to 4.3% for dissolved gallium and from 3.4 to 8.2% for total gallium.

Table 1. Influence of Foreign Ions on the Determination of Gallium in River Water

Ions	Concentration/ng cm^{-3}				
Al^{III}	0	0	400	2000	4000
Ti^{IV}	0	0	3	15	30
V^{V}	0	0	1	5	10
Cr^{III}	0	0	1	5	10
Mn^{II}	0	0	5	25	50
Fe^{III}	0	0	670	3350	6700
Co^{II}	0	0	0.2	1	2
Ni^{II}	0	0	0.3	1.5	3
Cu^{II}	0	0	5	25	50
Zn^{II}	0	0	10	50	100
Mo^{VI}	0	0	1	5	10
Pb^{II}	0	0	3	15	30
Artificial river water	None	Add	Add	Add	Add
Relative absorbance	100	103.5	97.2	88.4	88.3

20 ng-Ga/20 cm^3-artificial river water. Composition of the artificial river water (in mg dm^{-3}) is Ca^{2+}: 7.41, Mg^{2+}: 1.87, Na$^+$: 6.5, K$^+$: 1.20, $SO_4{}^{2-}$: 11.97, Cl$^-$: 6.39, $PO_4{}^{3-}$: 0.02, $NH_4{}^+$-N: 0.05, $NO_3{}^-$-N: 0.26, and SiO_2: 19.0.

Table 2. Analytical Results of Gallium in River Water

Sample	Ga found/ng dm^{-3}	
	Method A	Method B
Kinu river$^{c)}$	7.0±0.3$^{a)}$	37.3±1.9$^{b)}$
Watarase river$^{d)}$	5.3±0.1	7.9±0.3
Kusaki dam$^{e)}$	9.2±0.2	35.4±2.9$^{b)}$

Method A: Collected sample was filtered through 0.45 μm filter and acidified to 0.1 mol dm^{-3} nitric acid. Method B: Collected sample was acidified to 0.1 mol dm^{-3} nitric acid. Filtration was done after one month. a) Mean±standard deviation, $n=4$. b) Obtained by 600-fold preconcentration using 200 cm^3 of sample water. The other values were obtained by 1500-fold preconcentration. c) Utsunomiya, Tochigi Pref. d) Ashio, Tochigi Pref. e) Azuma, Gunma Pref.

The proposed method can be successfully applied to the determination of ng dm^{-3} levels of gallium in river water. The proposed method can be used for the preconcentration and determination of other group 13 elements, indium and thallium, and this work is in progress.

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