Preconcentration of Gallium by Coprecipitation with Synthetic Zeolites Prior to Determination by Electrothermal Atomic Absorption Spectrometry

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Synthetic zeolites were dissolved in nitric acid, and the resulting solution used as a coprecipitant for the preconcentration of trace amounts of gallium in water samples prior to determination by electrothermal atomic absorption spectrometry (ETAAS). The gallium preconcentration conditions and the ETAAS measurement conditions were optimized. Gallium was quantitatively concentrated with the zeolites coprecipitate from pH 6.0 to 8.0. The coprecipitate was easily dissolved in nitric acid, and an aliquot of the resulting solution was introduced directly into a tungsten metal furnace. The atomic absorbance of gallium in the resulting solution was measured by ETAAS. An ashing temperature of 400°C and an atomizing temperature of 2600°C were selected. The calibration curve was linear up to 3.0 µg of gallium and passed through the origin. The detection limit ($S/N \geqq 3$) for gallium was 0.08 µg/100 cm^3. The relative standard deviation at 1.0 µg/100 cm^3 was 3.0% (n = 5). The proposed method has been successfully applied to trace gallium analysis in environmental water samples.

Introduction

Electrothermal atomic absorption spectrometry (ETAAS) has been widely used for trace metal ions analysis. The variable preconcentration methods, such as flotation, solvent extraction, solid phase extraction (SFE) and ion exchange, were generally associated with ETAAS in order to improve the detection limit and separate the target metal ions from the matrix.

Coprecipitation is one of the more effective preconcentration method for trace metal ions in water samples, and several coprecipitants, such as hydroxides of indium,[1] hafnium,[2,3] iron,[4-6] zirconium,[7,8] lanthanum,[9] nickel,[10] and magnesium,[11] gallium phosphate,[12] cobalt ammonium pyrrolidinedithiocarbamate (APDC),[13] nickel diethyldithiocarbamate (DDTC),[14] iron tetramethylenedithiocarbamate (TMDM),[15] nickel-8-quinolinol/1-nitroso-2-naphthol,[16] and chitosan,[17] have been reported. Similarly, SFE is also an effective preconcentration method, and several adsorbents, such as ion-exchange resin, chelating resin and activated carbon, have been used. Synthetic zeolites are extensively used in adsorption, ion-exchange and separation processes, due to their unique structural properties. Moreover, synthetic zeolites have been employed as useful catalysts and detergent builders and for purification processes, such as air decontamination and gas sweetening. On the other hand, synthetic zeolites are dissolved in some acids, such as nitric acid, hydrochloric acid and sulfuric acid, because the synthetic zeolite structure is composed of aluminum oxide and silicon oxide. Nevertheless, concerning synthetic zeolites as useful materials, there have been few reports for on application of synthetic zeolites as preconcentrating trace metal ions.[18] When an acid solution containing dissolved synthetic zeolite was added to water samples containing trace metal ions and the pH of the sample solution was neutralized, alumino-silicate amorphous precipitates were formed and metal ions were concentrated from the sample solution into these precipitates.

Although gallium is important for use in the semiconductor industry, gallium particles and gallium compounds, such as gallium arsenide, have been identified as potential health hazards. Therefore, from an environmental standpoint, the need for sensitive and reliable methods for determining trace concentrations of gallium has become apparent in various fields. ETAAS is an effective analytical method for the determination of trace amounts of gallium. Further, solvent extraction,[19] adsorption,[20] ion exchange,[21] membrane,[22] and coprecipitation,[23] have been used to preconcentrate gallium prior to ETAAS analysis in order to improve the detection limit. However, there have been no reports on the use of a synthetic zeolite as a coprecipitant for gallium. This paper describes the fundamental conditions for the coprecipitation of gallium using a synthetic zeolite and for the ETAAS analysis of trace gallium in water samples.

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Table 1 Instrumental operating conditions for gallium determination by tungsten metal furnace atomic absorption spectrometry

Element	Ga
Wavelength	294.36 nm
Background correction	D_2
Slit width	0.5 nm
Lamp current	8 mA
Sheath gas	Ar: 3.0 dm^3 min^{-1}
	H$_2$: 1.0 dm^3 min^{-1}
Cuvette	U-type tungsten metal board
Injection volume	10 μl
Measurement mode	Peak height
Drying	130°C/30 s
Ashing	400°C/20 s
Atomization	2600°C/4 s
Cleaning	2800°C/5 s

Fig. 1 Effect of the pH on the recovery of gallium from a sample solution. (●) 2.0 cm^3 of 1.0% synthetic zeolite solution; (○) 10.0 cm^3 of 10.0% aluminium nitrate solution; gallium, 1.0 μg/100 cm^3; adsorption time, 15 min.

Experimental

Apparatus

The analysis was conducted using an atomic-absorption spectrometer (SAS-7500; Seiko Instruments, Inc.) connected to an electrothermal atomizer (PS-200; Seiko Instruments, Inc.); the furnace was a High-capacity U-Type metal board (50 μl) made of tungsten. A L-233 single-element hollow-cathode lamp (L-233; Hamamatsu Photonics Inc.) of gallium and a deuterium lamp were used for atomic-absorption measurements and background corrections, respectively. X-ray diffraction (XRD) patterns of the precipitate and the residue on the tungsten metal furnace were recorded using the Rigaku RAD-B system. A scanning electron microscope (SEM) (JSM-5499LUS; Japan Spectroscopic Co.) was used to record images of the precipitate and the surface of the tungsten metal furnace. A centrifugal separator (H-11C Type; Kokusan) and a test tube mixer (TM-152; Iwaki glass) were used to separate the coprecipitate from the sample solution and to dissolve the coprecipitates, respectively. A pH meter (M-8L; Horiba Co.) and a magnetic stirrer (SR-50; ADOVANTEC Co.) were used for pH control of the sample solution and to age the gallium/synthetic coprecipitates, respectively.

Reagents

Ultra-pure water (out put of 18 MΩ cm), obtained from a Puric-S system (Organo), was used to prepare all of the solutions.

A 1.0 w/v% zeolite solution was prepared by dissolving 5.0 g of synthetic zeolite A-4 (Wako Pure Chemical Industries, Ltd.) in 500 cm^3 of 1.0 mol dm^{-3} nitric acid. This solution contained 10 mg of zeolite in 1.0 cm^3 of 1.0 mol dm^{-3} nitric acid.

A gallium solution was prepared by diluting a 1000 ppm (1000 μg cm^{-3}) atomic-absorption standard (Wako Pure Chemicals) with water, as required.

All other reagents used were of analytical reagent grade.

General procedure

To a sample solution (100 cm^3) containing less than 3.0 μg of gallium, 2.0 cm^3 of a 1.0 w/v% zeolite solution was added, and the pH of the solution was adjusted to pH 7.0 with a diluted sodium hydroxide solution or diluted hydrochloric acid. Then, the coprecipitate was formed and the gallium was collected into this coprecipitate. The mixture solution was stirred for 15 min by a magnetic stirrer in order to age the coprecipitate. The
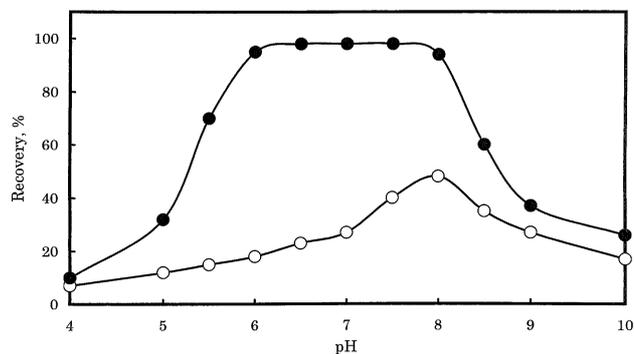
mixture solution was allowed to stand for 15 min in order to settle the coprecipitate. After the coprecipitate had settled, the majority of the supernatant was decanted off. The remaining solution was then transferred into a stoppered centrifuge tube. The solution was centrifuged at 4000 rpm in order to separate the coprecipitates from the supernatant. The supernatant was removed and discarded, the remaining coprecipitate was subsequently dissolved in 1.0 cm^3 of 2.0 mol dm^{-3} nitric acid, and was then made up to 2.5 cm^3 with water exactly. The obtained solution was then stirred using a test-tube mixer; a 10 mm^3 aliquot of the solution was injected into the tungsten metal furnace using a micropipette. The atomic absorbance of gallium was measured under the operating conditions listed in Table 1. A blank sample was run using water, according to the same procedure. In this investigation, the signal from a blank was extremely small, and the blank could be neglected.

Results and Discussion

Optimum conditions for coprecipitation

Gallium was concentrated from the sample solution into the alumino-silicate precipitate when the zeolite solution was added and the pH was adjusted to the neutral range. In order to determine the optimum pH for coprecipitation, the recovery of gallium was investigated in the pH range from 4.0 to 10.0 with a 100 cm^3 sample solution containing 1.0 μg of gallium according to the procedure described above. The results are shown in Fig. 1. The gallium was almost completely recovered at pH values ranging from 6.0 to 8.0; hence, the pH was adjusted to 7.0 for further experiments. The recovery of gallium decreased below pH 6.0, because the precipitate formation was incomplete in the lower pH range; thus, gallium could not be completely collected. Similarly, the recovery of gallium decreased above pH 8.0, because the part of the coprecipitate (*i.e.* aluminum hydroxide) dissolved at a higher pH range due to the amphoteric properties of aluminum. Furthermore, the atomic weight % of aluminum decreased both in the lower and higher pH ranges based on elementary analysis. The X-ray powder diffraction patterns, the scanning electron microscope (SEM) images of the original zeolite A and the obtained alumino-silicate precipitate are shown in Fig. 2, respectively. Although zeolite A has a cube-centered crystal structure, the precipitate did not. Furthermore, the X-ray diffraction (XRD) patterns of the zeolite A and the precipitate are shown in Fig. 2. The composition formula of zeolite A and the precipitate are Na$_2$O·Al$_2$O$_3$·2SiO$_2$
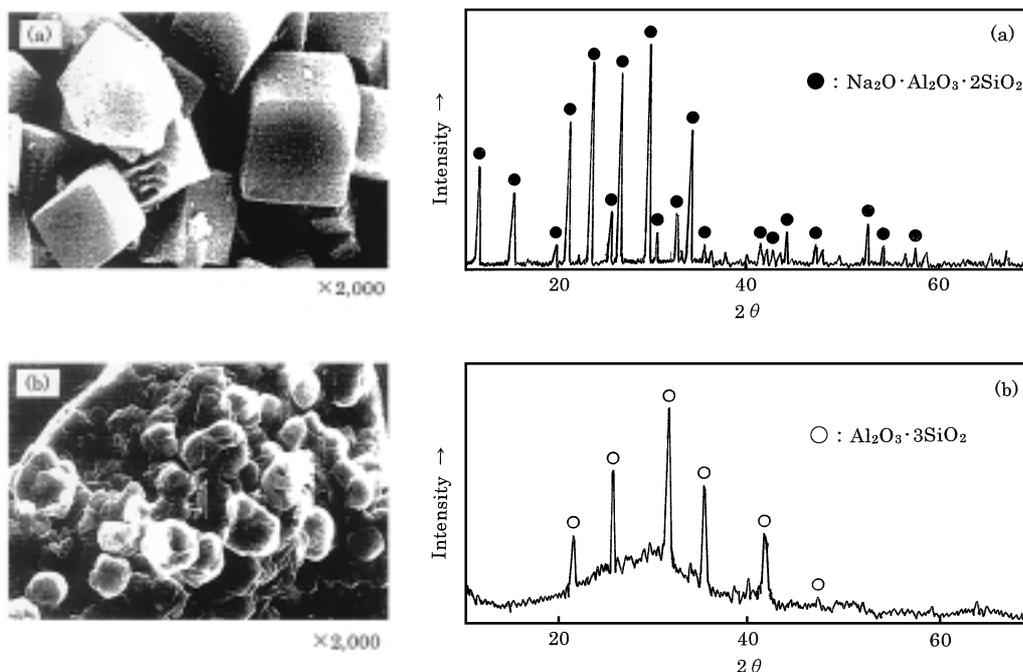
Fig. 2   SEM photographs and XRD patterns of the A-4 synthetic zeolite and its precipitate. (a) A-4 synthetic zeolite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), (b) precipitate ($Al_2O_3 \cdot 3SiO_2$).

and $Al_2O_3 \cdot 3SiO_2$, respectively. In these results, zeolite A was dissolved in acid and the obtained zeolite solution formed an alumino-silicate precipitate. The composition of this precipitate ($Al_2O_3 \cdot 3SiO_2$) was different compared to that with zeolite A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), and gallium was effectively concentrated in this precipitate.

Aluminum hydroxide has generally been used as a coprecipitant for cadmium and phosphate, and aluminum oxide is one of the primary elements mainly constituting zeolite A. The recovery of gallium was incomplete when aluminum hydroxide was used as the coprecipitant, instead of a zeolite solution. In addition, a large amount of aluminum hydroxide was required to recover gallium. These results are shown in Fig. 1. Consequently, the zeolite solution was found to be more effective for gallium recovery than aluminum hydroxide in the proposed procedure.

The necessary amounts of the 1.0 w/v% zeolite solution (this solution containing zeolite A 10 mg/cm^3) for the coprecipitation was examined using a 100 cm^3 sample solution containing 1.0 μg of gallium, according to the proposed procedure. More than 1.5 cm^3 of a 1.0 w/v% zeolite solution should be added for the quantitative collection of gallium. However, the volume of the coprecipitate increased with an increase in the addition volume of the zeolite solution. In order to dissolve a large quantity of coprecipitates, a large volume and a high concentration of acid are required. Unfortunately, these are not effective for the preconcentration and measurement conditions, since the large volume of the resulting solution gave a low preconcentration rate, and the high concentration of acid caused a deterioration of tungsten metal furnace. Accordingly, the small volume of the precipitate is effective for the coprecipitation method. On the other hand, the presence of large amounts of silicon gave a negative effect for the absorbance of gallium. Silicon is the main component of the coprecipitant of this proposed method. Therefore, 2.0 cm^3 of a 1.0 w/v% zeolite solution was employed for further procedure.

Other conditions, such as the stirring time and the standing time, were also investigated, and the optimum conditions for the coprecipitation of gallium with the zeolite solution were determined and used in further experiments.

Separation and dissolution of the coprecipitate

The coprecipitate was separated from the mother solution by centrifugation, because the obtained coprecipitate was swelling and difficult to separate by filtration.

The coprecipitate must be dissolved prior to ETAAS measurements. The solubility of the coprecipitate decreased with decreasing concentrations of nitric acid, and the coprecipitate did not dissolve when 0.1 mol dm^{-3} nitric acid was employed. Although the coprecipitate easily dissolved with high concentrations of nitric acid, deterioration of the tungsten metal furnace progressed. Furthermore, although the small volume of the dissolving solution gave a high preconcentration rate, the dissolving solution was viscous.

Consequently, the coprecipitate was dissolved in 1.0 cm^3 of 2.0 mol dm^{-3} nitric acid and subsequently diluted to 2.5 cm^3 with water.

Optimization of the instrumental operating conditions

It is important to examine several measurement conditions for ETAAS in order to achieve sufficient atomization of the analyte element. The optimum conditions for measuring the atomic absorbance of gallium were investigated using a 2.5 cm^3 volume of the dissolved coprecipitate solution according to the proposed procedure. Initially, the effect of the ashing temperature was investigated by varying the temperature from 200 to 900°C, and other conditions were kept constant, as given in Table 1. The results of this experiment are summarized in Fig. 3. An almost constant absorbance was obtained at a heating temperature in the range of 300 to 600°C. The absorbance was observed to decrease at below 300°C, attributable to incomplete thermal decomposition of the matrix in the ashing stage. The
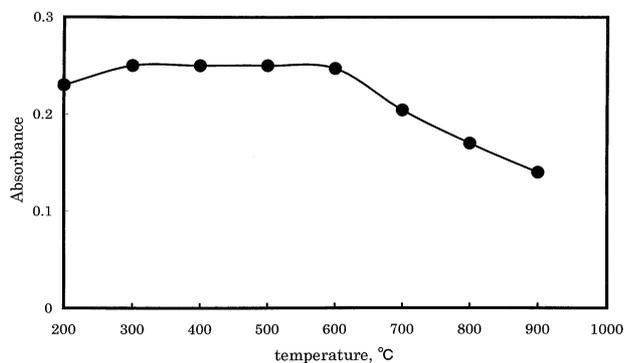
Fig. 3   Effect of the ashing temperature on the atomic absorbance of gallium by the proposed procedure.

Table 2   Effect of foreign ions

Ion	Amount/μg	Recovery, %
Na(I)	1000	98
K(I)	1000	97
Mg(II)	500	95
Ca(II)	500	98
Al(III)	500	95
Mn(II)	500	98
Fe(III)	100	97
Cr(III)	100	96
Co(II)	100	99
Ni(II)	100	97
Cu(II)	100	97
Zn(II)	10	95
Sr(II)	10	95
Cd(II)	10	99
Pb(II)	10	97
Bi(III)	10	96

Gallium amount 1.0 μg, samle volume 100 cm^3, pH 7.0, 2.0 cm^3 of 10% zeolite solution.

Table 3   Determination of gallium in water samples

Sample	Added/μg	Found/μg	Recovery, %
River water[a]	—	N.D.	—
(Kitakamigawa,	0.5	0.48	96
Iwate-pref.)	1.0	0.98	97
Well water[a]	—	N.D.	—
(Funabashi, Chiba-	0.5	0.49	98
pref.)	1.0	0.95	95
Spring water[a]	—	N.D.	—
(Kimitsu, Chiba-	0.5	0.48	97
pref.)	1.0	0.95	96
Lake water[a]	—	N.D.	—
(Noziriko, Nagano-	0.5	0.50	100
pref.)	1.0	0.98	99
Experimental waste	—	N.D.	—
water[a]	0.5	0.51	102
(Mimomi campus,	1.0	1.01	101
Nihon University)			
Boler wastewater[a]	—	N.D.	—
(Mimomi campus,	0.5	0.48	98
Nihon University)	1.0	0.96	97
Plating factory waste	—	0.28	—
water[b]	0.5	0.75	97
(Chiba, Chiba-pref.)	1.0	1.25	95

N.D. $\leqq$ 0.08 μg gallium.
a. Sample volume, 100 cm^3.
b. Sample volume, 10 cm^3.

absorbance also decreased above 600°C; this decrease is thought to be due to a considerable amount of gallium volatilized before the atomization stage. Secondly, the effect of the atomization temperature was investigated over a temperature range of 1400 to 3000°C. A constant and maximum absorbance was obtained at an atomization temperature in the range of 2500 to 2800°C. Considering these observations, an ashing temperature of 400°C and an atomization temperature of 2600°C were selected for gallium analysis.

In general, a tungsten metal furnace can be used repeatedly (about 500 times) when a common aqueous sample solution is injected. However, in this proposed procedure, the tungsten metal furnace could not be used more than 200 times because the residues remained on the surface of the tungsten metal furnace. After repeated measurements of over 200 times, the analytical accuracy decreased and the measurement error increased. Furthermore, these residues could not be physically removed by cleaning. From an analysis of the X-ray diffraction (XRD) patterns of the residue, the residue was assumed to be an aluminum oxide.

Therefore, the tungsten metal furnace was exchanged before the measurements reached 200 times in this proposed procedure.

Calibration curve and detection limit

The relationship between the absorbance and the concentration of gallium was examined using the proposed procedure for a 100 cm^3 sample solution. A straight line passing through the point of the origin was obtained up to 3.0 μg of gallium. The relative standard deviation obtained from five repeated measurements was 3.0% for 1.0 μg of gallium. The detection limit ($S/N \geqq 3$) was 0.08 μg in the initial sample solution.

The influence of the sample size was investigated by varying the volume of a sample solution containing 1.0 μg of gallium. A quantitative recovery was obtained using the proposed procedure over the 100 – 300 cm^3 range. The recovery decreased above the 300 cm^3 range, and was about 60% when a 500 cm^3 sample solution was employed. Because the formation of the precipitate was incomplete, gallium was not concentrated with this precipitate. However, a quantitative recovery was obtained by addition of 8.0 cm^3 of a 1.0 w/v% zeolite solution and the 500 cm^3 of the sample solution. Thus, use of a 500 cm^3 sample solution gave a concentration factor of 250.

Interference

According to the proposed procedure, the effect of foreign ions on the recovery of gallium was investigated for a 100 cm^3 sample solution containing 1.0 μg of gallium and coexisting ions. The tolerance limit was taken as the concentration of foreign ions resulting in an error of ± 5% recovery. The experimental results are given in Table 2. Common cations, such as Mg(II), Ca(II), Cu(II), Na(I) and K(I), did not interfere with the recovery of gallium at a concentration of 100 to 1000 times gallium. Similarly, other cations, such as Fe(III), Al(III), Mn(II), Co(II) and Ni(II), did not interfere with the recovery at a concentration of 10 to 100 times. These results demonstrate that the proposed procedure can be used to quantitatively

recover trace amounts of gallium from general water samples.

Applications

To evaluate the usefulness of the proposed method, it was applied to the analysis of gallium from water samples, such as river water, hot spring water and industrial waste water. The samples were filtered through a membrane filter (pore size; 0.45 μm) to remove any suspended matter, and the acidity was adjusted to 1 mol dm^{-3} with nitric acid for storage. The results are listed in Table 3. The trace amounts of gallium from the plating factory waste water could be determined by this proposed method. However, gallium was not detected from other water samples, because the gallium concentration would be extremely low. The actual gallium levels in these water samples are estimated to be lower than 0.08 μg/100 cm^3. In addition, the recovery of gallium from water samples spiked with gallium was examined by the standard-addition method. The quantitative recovery of gallium was obtained for water samples.

In conclusion, this proposed method can be successfully applied to the determination of trace amount of a gallium in water samples.

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