Anion-exchange enrichment and spectrophotometric determination of traces of gallium in natural waters

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Anreicherung durch Anionenaustausch und spektralphotometrische Bestimmung von Galliumspuren in Meerwasser

Summary. Traces of Ga in sea and fresh water have been enriched by anion-exchange from an acidified sample in the presence of thiocyanate. Gallium adsorbs strongly on a column of Amberlite CG 400 and can be stripped with a NaOH-NaCl solution. Gallium in the effluent is purified by anion-exchange from HCl and determined spectro-photometrically with Rhodamine B as colour reagent. The combined method allows to determine traces of Ga in sea water as well as fresh water on a 10 l sample basis. The standard deviation is about 17% at a Ga level of 0.01 µg/l.

Introduction

Little information is available on the occurrence of Ga in natural waters. The determination of Ga in these waters entails a concentration step, because of the extreme low concentration of Ga involved. Several preconcentration techniques, including coprecipitation on aluminium hydroxide [1] or ferric hydroxide [2] and solvent extraction of 4-(5-chloro-2-hydroxyphenylazo)resorcinol complex [3] or dithiocarbamate complex [4] have been reported. However, nothing is known about the enrichment of Ga by ion-exchange from a large volume of water samples. Anion-exchange in acid thiocyanate media has been applied to analyses of natural water samples for some traces of metals [5] such as Mo, V, Co, Ag, U, Cd-Co-U, Zn and Ti, but the capability of this method is not known for ultratraces of Ga in sea and fresh waters. In this work it will be demonstrated that anion-exchange thiocyanate preconcentration coupled with spectrophotometry with Rhodamine B provides a convenient means for determining traces of Ga in sea and non-saline water samples.

Experimental

Reagent and apparatus

Gallium stock solution. Dissolve a known quantity of Ga metal (99.99%, Wako Pure Chemical Industries, Tokyo) in 6 mol/l HCl and dilute to yield 1310 µg of Ga(III) per ml of 0.1 mol/l HCl.

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Rhodamine B solution. Dissolve 0.5 g of Rhodamine B (Wako) in 100 ml of distilled-demineralized water.

Ion-exchange column A. Slurry 5.0 g of Amberlite CG 400 in the SCN⁻ form (100–200 mesh) with water and pack in a conventional column (i.d. 2.5 cm).

Ion-exchange column B. Slurry 2.0 g of Amberlite CG 400 in the Cl⁻ form (100–200 mesh) with water and pack in a column (i.d. 1.0 cm). Spectrophotometric measurements were made with a Hitachi 100-10 spectrophotometer in a 5 cm glass cell.

Determination of the distribution coefficient

Weigh out 1.0 g each of the air-dried Amberlite CG 400 in the SCN⁻ form and place in an Erlenmeyer flask with ground glass stopper. To the flask add 41.0 ml of liquid phase, which consists of 40.0 ml of 0.5 mol/l NaCl-0.1 mol/l HCl solution of varying thiocyanate concentration and 1.0 ml of Ga standard solution (0.0188 mmol Ga ml⁻¹ in 0.1 mol/l HCl). Shake the mixtures for about 20 h at room temperature. After the phase separation, determine Ga in the filtrate spectrophotometrically [6] and obtain the distribution coefficient Kd according to:

$$Kd = \frac{\text{amount of Ga in resin phase/g of resin}}{\text{amount of Ga in solution phase/ml of solution}} \cdot$$

Procedure

Filter the sea water or fresh water through a Millipore Filter (0.45 µm pore). Take five 2 l aliquots and add 17 ml of HCl and 152 g of NH₄SCN to each aliquot to yield 0.1 mol/l in HCl and 1 mol/l in NH₄SCN. Load the mixture onto the top of the column A and pass down the column at a flow rate of 5 ml min⁻¹. Repeat the same procedure five times so that 10 l of sample is passed through the column. Wash the column with 250 ml of 0.1 mol/l HCl-1.0 mol/l NH₄SCN solution. Strip the Ga adsorbed by elution with 60 ml of 1.0 mol/l NaOH-1.0 mol/l NaCl solution. Add 20 ml of HNO₃ to the effluent and destruct the thiocyanate by gentle heating. Add 12 ml of 1 : 1 H₂SO₄ to the solution and evaporate to dryness. Dissolve the residue in 75 ml of 4 mol/l HCl and pass it down the column B, previously conditioned with 4 mol/l HCl. Wash the column with 20 ml of 4 mol/l HCl.

Table 1. Distribution coefficients [ml/g] of Ga on Amberlite CG-400 (SCN^- form) in thiocyanate media

	NH_4SCN (mol/l)				
	1.0	0.30	0.10	0.030	0.010
I	4.5×10^3	9.6×10^2	1.0×10^2	9.9	3.6
II	4.0×10^3	8.4×10^2	1.2×10^2	15	2.5

I	0.1 mol/l HCl − x mol/l NH_4SCN − 0.5 mol/l NaCl media
II	0.1 mol/l HCl − x mol/l NH_4SCN media

Table 2. Effect of diverse ions

Metal ion	Added (μg)	Ga (μg) Added	Ga (μg) Found	Relative error (%)
Bi(III)	2.08×10	1.64	1.65	0.6
Cd(II)	1.21×10^2	1.64	1.63	− 0.6
Co(II)	3.42×10^2	1.64	1.63	− 0.6
Cu(II)	1.00×10^3	1.64	1.82	11.0
	6.67×10^2	1.64	1.72	4.9
Fe(III)	8.36×10^3	1.64	2.06	25.6
	4.18×10^3	1.64	1.69	3.0
Hg(II)	8.70×10^2	1.64	1.61	− 1.8
Pb(II)	1.04×10^3	1.64	1.64	0.0
Sb(III)	2.90×10^2	1.64	1.64	0.0
Tl(I)	1.71×10	1.64	2.21	34.8
	5.13	1.64	1.71	4.3
Zn(II)	3.85×10^3	1.64	1.64	0.0

Strip the absorbed Ga by elution with 30 ml of 0.1 mol/l HCl. Determine Ga in the effluent spectrophotometrically with Rhodamine B as the reagent [6].

Results and discussion

The high concentration of NaCl in sea water makes it difficult to achieve quantitative enrichment of traces of metals by ion-exchange. Therefore, we attempted to obtain information on the adsorbability of Ga from saline water (0.5 mol/l NaCl solution). The distribution coefficient data on the adsorption of Ga from thiocyanate media with and without NaCl are given in Table 1 as a function of thiocyanate concentration. The coefficient increases with increasing concentration of thiocyanate, reaching values as high as 4500 ml/g at 1 mol/l thiocyanate solution, nearly irrespective of the presence and absence of NaCl. In contrast, Ga does not adsorb on the anion-exchange resin from 1 − 2 mol/l HCl, though the coefficient increases to about 10^5 ml/g in 7 mol/l acid [7]. From 1 mol/l thiocyanate solution the coefficient will be sufficiently high to concentrate traces of Ga on 5 g resin column from 10 l water samples, because the retention volume will be as high as 22.5 l under the given conditions.

The elution condition is an important factor for achieving effective enrichment. We found that the adsorbed Ga can be easily removed by elution of 60 ml of 1 mol/l NaOH-1 mol/l NaCl solution.

Considerable numbers of metals form thiocyanate complexes, which may adsorb on the anion-exchange resin

Table 3. Recovery of Ga from saline (0.5 mol/l NaCl) and non-saline waters

Sample (l)	Ga (μg) added	found				average
Saline water						
10	164	165	156	166		162 ± 6
10	1.64	1.55	1.60	1.59		1.58 ± 0.03
10	0.0 .	0.02_2	0.02_7	0.03_7		$0.02_9 \pm 0.00_8$
Non-saline water						
5	4.10	4.14	4.05	4.10	4.08	4.09 ± 0.04
10	1.64	1.64	1.69	1.53		1.62 ± 0.08
10	0.0	0.03_7	0.02_6	0.01_5		$0.02_6 \pm 0.01_1$

$\pm$ Values for the average represent the standard deviation

Table 4. Determination of Ga in sea and lake waters

Sample taken (l)	Ga (μg) added	found	Content in original sample (μg/l)
Sea water[a]			
10	0.0	0.12	0.012
10	0.0	0.14	0.014
10	0.0	0.13	0.013
10	0.33	0.43	0.010
10	0.66	0.79	0.013
			av.0.012 ± 0.002
Lake water[b]			
10	0.0	0.13	0.013
10	0.0	0.14	0.014
10	0.0	0.13	0.013
10	0.33	0.43	0.010
10	0.66	0.75	0.009
			av.0.012 ± 0.002

[a] Collected at the Kamoike Harbor, Kagoshima Bay, on October 5, 1987. Salinity 32.79‰

[b] Collected at the Ikeda Lake, Kagoshima, on October 23, 1987

[8]. However, the elution with NaOH-NaCl is selective for amphoteric ions such as Ga or anionic species like molybdate and tungstate [9]. Results of the interference study with Rhodamine B are listed in Table 2, where metal ions are chosen which react with Rhodamine B and also are as abundant as or more abundant than Ga in sea water. Assuming even the same behaviour as Ga in anion-exchange enrichment and elution steps, the metal ions 30 times as abundant as their actual concentration do not interfere with the determination of Ga. Therefore, the further separation of metal ions, which interfere with the determination of Ga is not necessary. However, the elution yields considerable amounts of Na_2SO_4, so we used a one-step purification of Ga by anion-exchange in 4 mol/l HCl (column B). Gallium adsorbs on the column from 4 mol/l HCl and is recovered by elution with 30 ml of 0.1 mol/l HCl. In Table 3 the results are shown of the determination of Ga in saline solution (0.5 mol/l NaCl) and non-saline water on a 10 l and in one case on a 5 l sample basis. As can be seen, the recoveries of Ga are very good. The overall blank levels for 10 l of saline and non-saline (distilled) water are 0.02_9 μg Ga (average of three determinations) and 0.02_6 μg Ga (average of three deter-

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minations), respectively. Based on these observations, the present method may provide a sound basis for the determination of Ga in natural waters. Repeated determinations of Ga in a sea water and a lake water sample were accomplished on a 10 l basis with and without the addition of a known amount of Ga. Results are compiled in Table 4. The added trace Ga is recovered quantitatively from 10 l of sample waters. Relative standard deviation ($n = 5$) is 17% for the determination of gallium both in sea and lake waters at a level of 0.012 μg l^{-1}.

In the present method the final determination is not limited to spectrophotometry, but other sensitive methods such as graphite furnace atomic absorption spectrometry may be used so that the sample volume may be reduced to some extent. The apparent drawback of the present method is to take considerable time to accomplish the enrichment ($\sim$ 30 h for 10 l sample). However, the ion-exchange column enrichment is actually a non-attendant procedure, being performed without attention for the 10 l sample treatment. Several columns are allowed to run simultaneously. We used usually three parallel columns, so that the average enrich-

ment time may be reduced to ca. 10 h per sample. The number of the enrichment columns can be increased as desired.

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