© 1999 The Chemical Society of Japan

Determination of Ultratrace Beryllium in Natural Water by Electrothermal Atomic Absorption Spectrometry after Preconcentration with One-Drop Solvent

Tokuo Shimizu,* Keiji Ohya, Hiroshi Kawaguchi, and Yoshio Shijo

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

(Received August 24, 1998)

An effective method for the determination of beryllium at sub ng dm^{-3} levels in natural water is described. Beryllium is extracted with acetylacetone into chloroform. The organic phase is transferred to a Teflon® beaker containing a micro volume of dimethyl sulfoxide (DMSO, a high boiling-point solvent); chloroform is then removed by evaporation in a water bath (ca. 35 °C). Beryllium is concentrated in the residual DMSO and determined by electrothermal atomic absorption spectrometry. The sensitivity and stability of beryllium atomic absorption were enhanced in the presence of palladium as a matrix modifier. The detection limit (3σ) for beryllium was 0.050 ng dm^{-3}, based on a 400-fold preconcentration using 40 cm^3 of the sample water; the relative standard deviation was 1.8% (2.0 ng dm^{-3}, $n = 8$). The concentration of dissolved beryllium in natural water was found to be 0.25—0.63 ng dm^{-3} by the proposed method.

Beryllium is a highly toxic metal, which can cause extensive damage upon contact with the skin and eyes. If ingested or inhaled, it can cause dyspnea on exertion, coughing and weakness. Beryllium is mainly used in the metallurgy and nuclear industries, and is also released into the environment when coal is burned. In addition, by acidification of streams and lakes, beryllium has dissolved into the aquatic environment. Therefore, the determination of beryllium in water samples has become important in studies of environmental science. In Japan, the beryllium concentration in water samples is usually very low (ng dm^{-3}—sub ng dm^{-3} levels);[1—3] however, some acidic river waters or hot spring waters have a high beryllium concentration (μg dm^{-3}—sub μg dm^{-3} levels).[1,3—5]

Many methods for the determination of beryllium in water samples have been reported: spectrophotometry,[5—8] spectrofluorometry,[9] gas chromatography (GC),[1,10] flame atomic absorption spectrometry (AAS),[11] electrothermal (ET) AAS,[2—4,12,13] and reversed-phase high-performance liquid chromatography.[14] However, most of the above-mentioned methods do not seem to have superior sensitivity for ng dm^{-3} levels of beryllium; sufficient preconcentration techniques, such as solvent extraction, ion exchange, adsorption, and coprecipitation, are most often necessary.

The use of β-diketones, acetylacetone (2,4-pentanedione, CAS No-123-54-6),[1,2,11] and trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione, CAS No-367-57-7)[10] allowed the development of an analytical method for determining trace amounts of beryllium. Tao et al.[1] concentrated trace beryllium by extraction with acetylacetone into chloroform and by further evaporation of the solvent, determined by GC-helium microwave induced plasma emission spectrometry. We have applied the one-drop solvent preconcentration method[15] to the determination of mercury at ng dm^{-3} levels in water samples.[16] The mercury-1,5-diphenylthiocarbazone (dithizone, CAS No-60-10-6) complex is extracted into carbon tetrachloride. To the separated organic phase, a micro volume of dimethyl sulfoxide (DMSO) is added, and chloroform is removed by evaporation in order to concentrate the analyte in the residual DMSO. In this paper, to develop a simple preconcentration method having a high enrichment factor for ETAAS, the beryllium–acetylacetone complex was concentrated with a one-drop solvent.

Experimental

Apparatus. A Hitachi Model Z-7000 polarized Zeeman atomic absorption spectrometer was used. 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 234.9 nm, and the peak heights were taken as the analytical signals. The optimum conditions for beryllium measurements were as follows: Injection volume, 20 mm^3; Drying, 50—70 °C for 60 s, 100 °C for 40 s, 120—500 °C for 20 s; Ashing, 1000 °C for 15 s; Atomizing (rapid-heating atomization with an optical temperature control device), 3000 °C for 4 s.

Reagents. A beryllium working solution was prepared from a stock solution (Kanto Chemical, 1 mg cm^{-3}, dissolving pure metal in 0.5 mol dm^{-3} nitric acid) by dilution with 0.1 mol dm^{-3} nitric acid. Acetylacetone (Dojindo) was used without further purification. All the chemicals used were of analytical reagent grade. Distilled, deionized water was further purified using a Millipore Milli-Q water purification system.

Procedure. The recommended procedure for the 400-fold preconcentration of beryllium is as follows.

After pretreatments (described later), a 40 cm^3 aliquot of the sample solution was transferred into a 50 cm^3 stoppered centrifuge tube. Then, 500 mm^3 of a 4 mol dm^{-3} ammonium acetate solution, 400 mm^3 of a 0.2 mol dm^{-3} EDTA solution, and 40 mm^3 of acetylacetone were successively added. The pH of the solution was adjusted to 5.5 by the addition of a 5 mol dm^{-3} sodium hydroxide solution. After the addition of 2 cm^3 of chloroform, the mixture was shaken for 15 min. After centrifuging for 1 min, the organic phase was separated with hydrophobic filter paper (ADVANTEC 2S, 125 mm) to a 10 cm^3 Teflon® beaker containing 80 mm^3 of DMSO, whose weight was measured in advance. The extracting solvent, chloroform, was removed by evaporation in a water bath at ca. 35 °C. The beaker plus residual DMSO was weighed again; then, 10 mm^3 of a 1 mg cm^{-3} palladium solution and 10 mm^3 of water were added. The beryllium concentration was determined by ETAAS; the absorbance was corrected if an excess loss of DMSO was observed.

The two pretreatment methods were employed before preconcentration. Method A (Dissolved Be): 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 Be): After the collected sample was acidified to 0.1 mol dm^{-3} nitric acid, filtration was performed after 4 weeks (river water) or 7 weeks (sea water). For all samples, preconcentration was performed within 10 d after filtration.

In the case of Method B, since the beryllium content was too high, the preconcentration factor was decreased to 160 or 80 times by reduction in the volume of sample solution used.

Results and Discussion

Effect of Matrix Modifier. Beryllium acetylacetonate is one of the volatile complexes[17] exhibiting a large loss of analyte before atomization in ETAAS. In a previous study,[16] the sensitivity and stability of mercury atomic absorption were enhanced in the presence of DMSO and dithizone due to a matrix modification. In this study, matrix modifiers, such as magnesium nitrate, nickel nitrate, and palladium nitrate, were investigated. Among them, palladium nitrate was the best for beryllium sensitivity in a DMSO solution, and the highest permissible ashing temperature was raised to 1500 °C. The beryllium absorbances increased with increasing palladium concentration; then, a nearly constant absorbance was obtained over 0.1 mg cm^{-3}. With an ashing temperature of 1000 °C, the sensitivity was improved by a factor of 3.7 over that in the absence of a matrix modifier.

The effect of the DMSO concentration in an aqueous solution was also investigated in the presence of palladium, and it was found that a nearly constant absorbance was obtained over 30% v/v.

Extraction of Beryllium from Water. The effect of the pH on the extraction of beryllium was studied using 40 cm^3 of water spiked with 40 pg of beryllium in the absence of EDTA as a masking agent. As shown in Fig. 1, the optimum pH range is 4—11 for the extraction of beryllium. The value of pH$_{1/2}$ in benzene was reported to be 2.45,[17] and beryllium was extracted quantitatively over wide pH ranges (even in weakly basic solutions). However, in the case of the evaporation method under reduced pressure,[1] the optimum pH range was reported to be 5.5—5.7 in the presence of EDTA. A decrease above pH 6 was due to complex formation with EDTA. Therefore, the extraction of beryllium was carried out at pH 5.5 in a subsequent study.

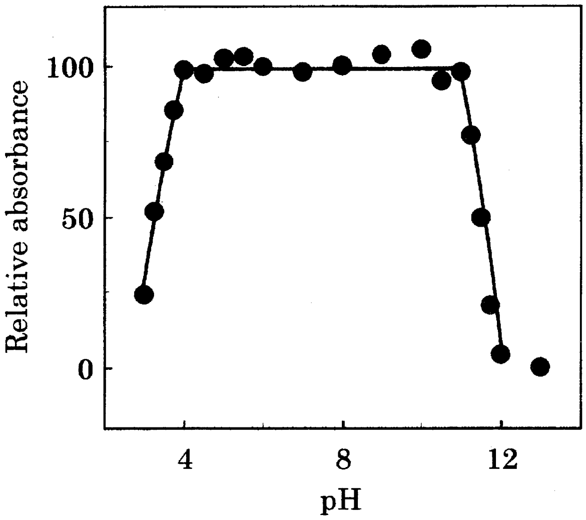

Fig. 1. Effect of pH on the extraction of 40 pg of beryllium from 40 cm^3 of water. Chroloform, 2 cm^3; DMSO solution, 0.1 cm^3 (80 mm^3 of DMSO+10 mm^3 of 1 mg cm^{-3} Pd+10 mm^3 of water).

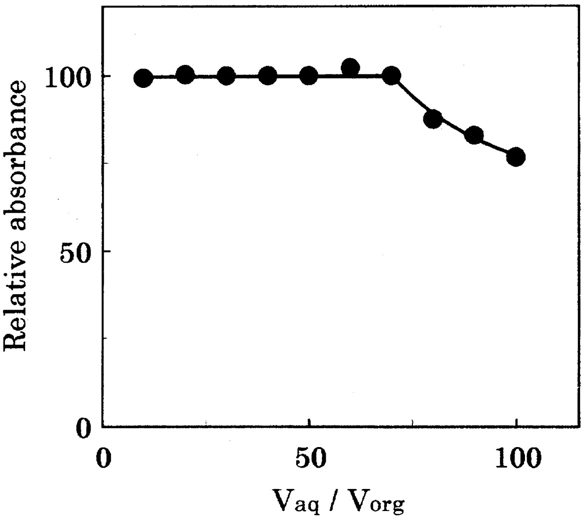

Fig. 2. Effect of the volume ratio of aqueous to organic phase on the extraction of beryllium. Be, 40 pg; Chroloform, 2 cm^3; DMSO solution, 0.1 cm^3.

The effect of the acetylacetone concentration in the aqueous phase on the extraction of beryllium was studied in the range 0.05—20$\times$10^{-3} mol dm^{-3}. The recovery of beryllium abruptly increased along with an increase in acetylacetone, and reached almost a constant value of over 1$\times$10^{-3} mol dm^{-3}. On the basis of this result, subsequent extraction was carried out at an acetylacetone concentration of 10$\times$10^{-3} mol dm^{-3}.

The shaking time for the extraction of beryllium was investigated, and it was found that the extraction of beryllium was achieved within 5 min.

Preconcentration with One-Drop Solvent. The evaporation of a large volume of extracting solvent in a water bath is a time-consuming step. Kaneko et al.[15] have removed

Table 1. Influence of Foreign Ions on the Determination of Beryllium in Sea Water

Ions	Concentration/ng cm^{-3}				
Al^{III}	0	0	5	25	50
Ti^{IV}	0	0	1	5	10
V^{V}	0	0	1.5	7.5	15
Mn^{II}	0	0	2	10	20
Fe^{III}	0	0	3	15	30
Co^{II}	0	0	0.08	0.4	0.8
Ni^{II}	0	0	2	10	20
Cu^{II}	0	0	3	15	30
Zn^{II}	0	0	5	25	50
Ga^{III}	0	0	0.03	0.15	0.3
Mo^{VI}	0	0	10	50	100
Cd^{II}	0	0	0.05	0.25	0.5
Ba^{II}	0	0	30	150	300
Pb^{II}	0	0	0.03	0.15	0.3
Artificial sea water	None	Add	Add	Add	Add
Relative absorbance[a)]					
a	100	100.7	97.0	85.9	74.1
b	—	101.9	100.3	95.7	97.8

40 pg-Be/40 cm^3, 400-fold preconcentration. a) Relative to 100 for absorbance of beryllium alone without masking agent. In the absence (a) or presence (b) of EDTA as masking agent. Composition of the artificial sea water (in g dm^{-3}) is Na$^+$: 11.03, Mg^{2+}: 1.33, Ca^{2+}: 0.42, K$^+$: 0.39, Sr^{2+}: 0.013, Cl$^-$: 19.84, SO$_4{}^{2-}$: 2.77, Br$^-$: 0.067, BO$_3{}^{3-}$: 0.028, and F$^-$: 0.0014.

Table 2. Influence of Foreign Ions on the Determination of Beryllium 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
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
Ga^{III}	0	0	0.1	0.5	1
Mo^{VI}	0	0	0.6	3	6
Cd^{II}	0	0	1	5	10
Ba^{II}	0	0	10	50	100
Pb^{II}	0	0	1	5	10
Artificial river water	None	Add	Add	Add	Add
Relative absorbance[a)]					
a	100	95.0	79.6	43.3	29.3
b	—	98.4	101.7	101.5	101.5

40 pg-Be/40 cm^3, 400-fold preconcentration. a) Relative to 100 for absorbance of beryllium alone without masking agent. In the absence (a) or presence (b) of EDTA as masking agent. Composition of the artificial river water (in mg dm^{-3}) is Ca^{2+}: 7.41, Na$^+$: 6.5, Mg^{2+}: 1.87, K$^+$: 1.20, NH$_4{}^+$–N: 0.05, SO$_4{}^{2-}$: 11.97, Cl$^-$: 6.39, NO$_3^-$–N: 0.26, PO$_4{}^{3-}$: 0.02, and SiO$_2$: 19.0.

Table 3. Analytical Results of Beryllium in Natural Water

Sample	Be found/ng dm^{-3}	
	Method A	Method B
Sea water		
Hitachi[b)]	0.25 ± 0.02[a)]	1.35 ± 0.02
Isozaki[c)]	0.32 ± 0.03	1.04 ± 0.03
River water		
Kinu[d)]	0.63 ± 0.03	3.79 ± 0.05

Method A: Collected sample was immediately 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 4 weeks (river water) or 7 weeks (sea water). a) Mean ± standard deviation, $n = 4$. b) Hitachi, Ibaraki Pref. c) Hitachinaka, Ibaraki Pref. d) Utsunomiya, Tochigi Pref.

chloroform at 60 °C; however, the beryllium-acetylacetonate volatilized at such a high temperature. Therefore, the evaporation temperature was controlled to be below 35 °C, and the volume of chloroform was limited to 2 cm^3.

The extraction of beryllium in various volume ratios of the aqueous to organic phase was studied. As shown in Fig. 2, quantitative extractions of beryllium were attained with a volume ratio of the aqueous to organic phase of less than 70 : 1. Since beryllium was finally concentrated in 0.1 cm^3 of a DMSO solution, a concentration factor of 1400 can consequently be achieved.

Recovery, Detection Limit, and Precision. The recovery of 40 pg of beryllium from 40 cm^3 of water using the proposed method was found to be 105.3±5.4% ($n = 5$) by a comparison of the absorbance obtained for beryllium in the final solution of the analytical procedure and for beryllium added to an aliquot of the final blank solution.

The linear calibration curve for 400-fold preconcentration was obtained over the range of 0 to 4 ng dm^{-3}. The beryllium concentration corresponding to 1% absorption (absorbance = 0.0044) was 0.036 ng dm^{-3}. The detection limit, defined as three times the standard deviation of the blank signals ($n = 10$), was 0.050 ng dm^{-3}. The relative standard deviation for eight replicate determinations of 2.0 ng dm^{-3} level was 1.8%. The blank levels in the final blank solutions were low (absorbance = ca. 0.01) and the reproducibility of the signal from beryllium was satisfactory.

Interference. The interference of various metal ions in the determination of beryllium was investigated with a mixture of metal ions at concentrations approximately equal to, or exceeding, those normally found in natural water. The results are given in Tables 1 and 2. Many elements form acetylacetone complexes,[17)] but interferences are negligible, except for aluminum and iron. Relatively large amounts of aluminum and iron showed serious interferences. However, with the addition of EDTA, their interferences were considerably masked.

Analysis of Natural Water. The concentrations of beryllium in sea water and river water samples were determined according to the proposed method using the standard addition method of calibration. The analytical results are given in Table 3. The analytical values obtained from Method B (Total Be) were extremely higher than those of Method A (Dissolved Be). This was because beryllium dissolved out from suspended or particulate matter in the acidified samples during storage.

The proposed method can be successfully applied to the determination of sub $\mathrm{ng\,dm^{-3}}$ levels of beryllium in natural water, and allows simple handling of small volumes of samples and considerable saving in reagents. The detection limit reported here is far lower than those reported for ETAAS combined with the adsorption method using activated carbon (0.6 $\mathrm{ng\,dm^{-3}}$)(2) or silica fibres (0.3 $\mathrm{ng\,dm^{-3}}$),(3) and the coprecipitation method using hafnium hydroxide (6.25 $\mathrm{ng\,dm^{-3}}$).(13)

References

1) H. Tao, A. Miyazaki, and K. Bansho, *Anal. Sci.*, **4**, 299 (1988).

2) T. Okutani, Y. Tsuruta, and A. Sakuragawa, *Anal. Chem.*, **65**, 1273 (1993).

3) I. Nukatsuka, K. Sakai, R. Kudo, and K. Ohzeki, *Analyst*, **120**, 2819 (1995).

4) A. Sato and N. Saitoh, *Bunseki Kagaku*, **26**, 747 (1977).

5) I. Nukatsuka, T. Ohba, H. Ishida, H. Sato, K. Ohzeki, and R. Ishida, *Analyst*, **117**, 1513 (1992).

6) H. Dong, M. Jiang, G. Zhao, and M. Wang, *Anal. Sci.*, **7**, 69 (1991).

7) M. C. Valencia, S. Boudra, and J. M. Bosque-Sendra, *Analyst*, **118**, 1333 (1993).

8) M. C. Valencia, S. Boudra, and J. M. Bosque-Sendra, *Anal. Chim. Acta*, **327**, 73 (1996).

9) F. Capitan, E. Manzano, A. Navalon, J. L. Vilchez, and L. F. Capitan-Vallvey, *Analyst*, **114**, 969 (1989).

10) C. I. Measures and J. M. Edmond, *Anal. Chem.*, **58**, 2065 (1986).

11) J. Korkisch, A. Sorio, and I. Steffan, *Talanta*, **23**, 289 (1976).

12) P. Lagas, *Anal. Chim. Acta*, **98**, 261 (1978).

13) J. Ueda and T. Kitadani, *Analyst*, **113**, 581 (1988).

14) L. Shoupu, Z. Mingqiao, and D. Chuanyue, *Talanta*, **41**, 279 (1994).

15) E. Kaneko, H. Hoshino, and T. Yotsuyanagi, *Chem. Lett.*, **1992**, 955; *Bunseki Kagaku*, **42**, 753 (1993).

16) T. Shimizu, K. Ohya, and Y. Shijo, *Bunseki Kagaku*, **43**, 971 (1994).

17) K. Ueno, T. Imamura, and K. L. Cheng, "Handbook of Organic Analytical Reagents," 2nd ed, CRC Press, Florida (1992), p. 101.