Determination of Germanium by Atomic Absorption Spectrometry Following Volatile Hydride Generation

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A sensitive technique for determination of germanium was investigated by atomic absorption spectrometry following volatile hydride generation. Of the three types of hydride generator and atomizer systems tested, direct transfer of the generated hydride into nitrogen–hydrogen flame for atomization was found to be suitable. The sensitivity was enhanced more than 40—60% in phosphoric acid medium as compared to hydrochloric acid, malic acid, or tartaric acid media. Interference of nickel(II), gold(III), and cobalt(II) in hydrochloric acid medium was reduced by adding ethylenediaminetetraacetate as a masking reagent or replacing the acid medium by malic acid. Detection limit and relative standard deviation of ten determinations of 0.5 μg germanium(IV) in 20 ml of 0.20 M** phosphoric acid were 7 ng (S/N=2) and 4.3%, respectively, with 3 ml of 8 w/v % sodium tetrahydroborate solution. The method was applied to the determination of germanium in standard rocks, concentrations of germanium in JB-1 and JG-1 being evaluated as 1.3_1 and 1.3_2 ppm, respectively.

In the determination of germanium by atomic absorption spectrometry (AAS), it is difficult to attain high sensitivity because of production of highly stable oxide species in the flame. Dinitrogen oxide–acetylene flame is often used in combination with solvent extraction. The highest sensitivity so far reported is 0.13 ppm for 1% absorption by means of nebulizer effect.[1] Indirect AAS based on the formation of molybdogermanic acid complex has also been used because of chemical amplification.[2]

Volatile hydride generation technique has been applied to the determination of germanium by AAS,[3–6] but the sensitivity and reproducibility are inferior to those of elements such as arsenic, selenium, and antimony.[3,5] This technique was also extended to plasma emission spectrometry,[7–10] and thermal conductivity detection systems.[11]

Investigation was carried out to find suitable conditions for the determination of germanium by AAS by means of three types of hydride generation and atomization systems. Chapman and Dale[12] suggested the use of dinitrogen oxide–acetylene flame for the atomization following hydride generation. However, it was found that nitrogen–hydrogen (entrained air) flame is suitable when combined with a direct transfer type hydride generator, enabling us to use a large amount of sodium tetrahydroborate as a reductant.

The method was applied to the determination of germanium in rock samples (JB-1 and JG-1). Samples were decomposed with acid mixture; germanium was extracted into carbon tetrachloride from 9 M hydrochloric acid, and then back-extracted into water, the aqueous solutions being subjected to analysis.

Experimental

Apparatus. A Hitachi Model 170-50 type atomic absorption spectrophotometer equipped with deuterium background corrector and germanium hollow-cathode lamp (Hamamatsu TV) were used. Atomic absorption signals were recorded with a Hitachi 056 type recroder, peak height signals being used for the determination. Hydride generator and atomizer systems were used as follows.

I: Collection type hydride generator connected to nitrogen–hydrogen flame. Volatile hydride was generated with Nippon Jarrel-Ash Model ASD-1A and introduced into a nitrogen–hydrogen flame (one slot burner with 10 cm).

II: Direct transfer type hydride generator connected to heated silica tube. The hydride generator system reported by Thompson and Thomerson[5] was slightly modified, the gas being introduced into a heated silica tube (14φ×114 mm) mounted on 10 cm path air–acetylene flame burner.

III: Direct transfer type generator connected to nitrogen-hydrogen flame. A modified Hitachi hydride generator connected to a nitrogen–hydrogen flame system described in a previous paper[13] was used, the dispenser (REBURET) being replaced by another one (HANSEN 500 ml).

Conditions for the nitrogen–hydrogen flame: wavelength 256.1 nm, nitrogen flow rate 8 l min^{-1}, hydrogen flow rate 7 l min^{-1}, height of beam above burner tip 12.5 mm.

Reagents. All the reagents were of analytical grade. Deionized water was distilled twice.

Germanium(IV) stock solution (0.5 mg/ml): 0.360 g of soluble germaniumdioxide prepared by the method of Shimomura *et al.*[14] was dissolved in hot water, cooled, and diluted with water to 500 ml.

Sodium tetrahydroborate solution (8 w/v %): Sodium tetrahydrobolate(powder, Aldrich Chemical Company, Inc) was dissolved in 0.5% sodium hydroxide and filtered with 1 μm glass filter.

Sodium tetrahydroborate tablet (*ca.* 0.13 g $NaBH_4$): Thirty tablets were prepared from 2 g of caoline (Fisher Scientific Co.,) and 4 g of sodium tetrahydroborate by addition of 2.5 ml of 2 M aqueous ammonia.[15] The tablet was wrapped in wafer sheet when added to the I type hydride generation vessel.

Procedure. *I*: Pipet the prescribed volume of sample solution into the reaction vessel, add an appropriate volume of acid and dilute the solution to 20 ml with water. Put a teflon coated spin bar into the vessel and set it up on the hydride generation unit. Pass nitrogen into the vessel for 20 s, turn the four-way stopcock to collection mode. Remove the cap of the reaction vessel, put sodium tetrahydroborate tablet into the vessel and replace the cap immediately. Collect the gas for 30 s, then sweep it to the nitrogen–hydrogen flame.

II: Pipet 1 ml of 8 w/v% sodium tetrahydroborate solution into the reaction vessel and set it up on the hydride

** 1M=1 mol dm^{-3}

generation unit. A plastic syringe containing 1 ml of the sample solution is inserted into the side-arm seal of the vessel. Pass nitrogen through the reaction vessel to replace air with nitrogen for 15-20 s, then inject the sample solution into the reaction vessel and carry the gas into heated silica tube with nitrogen flow rate of 2 l min^{-1}.

III: The procedure reported[13] was carried out with modification: 3 ml of 8 w/v% sodium tetrahydroborate solution was used and nitrogen was passed through the vessel with flow rate of 2 l min^{-1}.

Results and Discussion

Stability of Germanium Hydride. The stability of volatile hydride should be considered at first in the hydride generation method.[4,12,15] The effect of germanium hydride collection time in system I was examined. Figure 1 shows effect of collection time 15—300 s for 5.0 μg of germanium. Collection time 20—300 s causes no fall in sensitivity, showing that germanium hydride is stable during the course of collection. The precision of the method is not improved by altering the collection time to 30—300 s.

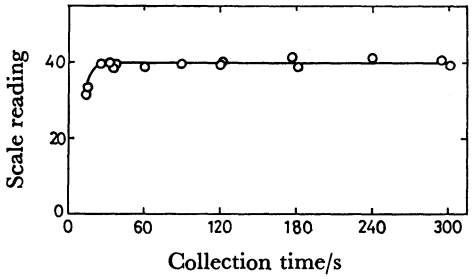

Fig. 1. Effect of collection time on the generation of germanium hydride, in system I.
Ge(IV): 5.0 μg/20 ml, acidity: 0.2 M HCl.

Atomization of Germanium Hydride. A comparison was made between nitrogen-hydrogen and argon-hydrogen flames. The former was found to be superior by *ca.* 20—30% in sensitivity of systems I and III. Sensitivity of the germanium determination by heated silica tube atomization with system II is inferior to that of flame atomization.

Effect of Acids and Acidity. Effect of acids and acidity on the relative sensitivity of germanium determination was investigated by system I for 5.0 μg germanium(IV) and system III for 0.5 μg germanium-(IV); the results are shown in Figs. 2 and 3, respectively. Concentration of acids seriously affects peak height of the signals in both types of hydride generator systems, giving maximum peak height at 0.1—0.2 M, at which acids are almost neutralized by the alkaline sodium tetrahydroborate solution. In addition to hydrochloric acid reaction medium used in volatile hydride generation with sodium tetrahydroborate, various acids can be used as reaction media, *i.e.* malic acid, tartaric acid, acetic acid, and oxalic acid (Fig. 2). Nitric acid, sulfuric acid, and phosphoric acid are also useful, but not citric acid (Fig. 2).

In system III, the effect of acid is differs somewhat from that of system I. A large difference in sensitivity

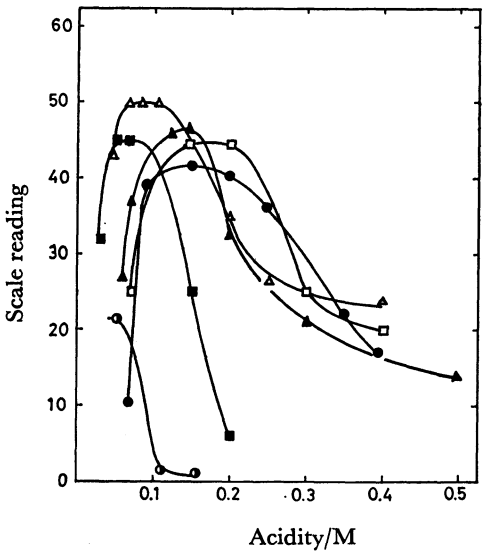

Fig. 2. Effect of acidity on the determination of germanium, in system I.
Ge(IV): 5.0 μg/20 ml, collection: 30 s, —●—: HCl, —△—: malic acid, —▲—: tartaric acid, —□—: acetic acid, —■—: oxalic acid, —◑—: citric acid.

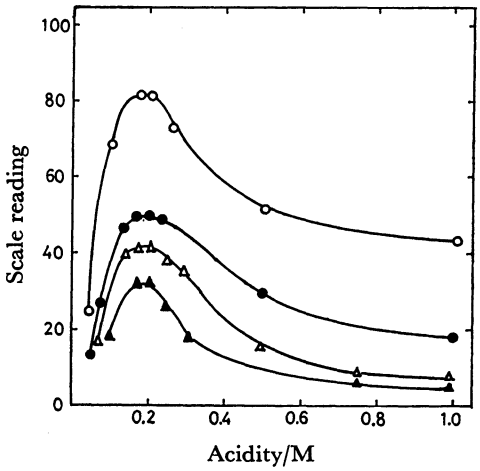

Fig. 3. Effect of acidity on the determination of germanium, in system III.
Ge(IV): 0.5 μg/20 ml, 8 w/v % $NaBH_4$: 3 ml, —○—: H_3PO_4, —●—: HCl, —△—: malic acid, —▲—: tartaric acid.

is observed with use of these acids (Fig. 3). About 40% enhancement in sensitivity is attained in 0.20 M phosphoric acid medium as compared with hydrochloric acid. The difference seems to originate from the change in reaction rate of germanium(IV) to germanium hydride.

The utility of nitric acid is different from the result of Thompson and Pahlavanpour;[10] the results of hydrochloric acid also differ. The peak height does not increase at 2—5 M hydrochloric acid.

Amount of Sodium Tetrahydroborate. In system I, the best sensitivity is attained with 0.13 g of sodium tetrahydroborate. Because of the limitation of the internal gas pressure during the course of collection, more than 0.13 g of the reductant could not be used.

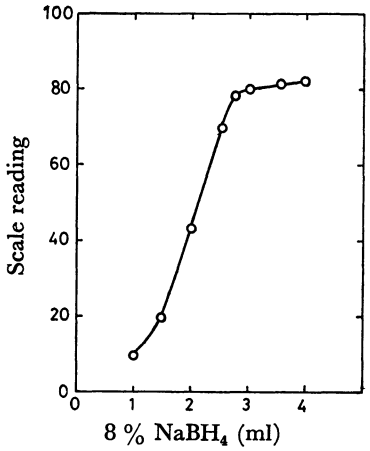

Fig. 4. Effect of the volume of tetrahydroborate solution, in system III.
Ge(IV): 0.5 μg in 20 ml of 0.2 M H_3PO_4.

Effects of the amount of sodium tetrahydroborate on germanium determination examined in system III are shown in Fig. 4, high senistivity being attained with 3—4 ml of 8 w/v% sodium tetrahydroborate solution. A relatively large amount of sodium tetrahydroborate can be treated as compared with system I. However, the use of more than 3.5 ml of 8 w/v% sodium tetrahydroborate solution sometimes caused overflow of the reaction medium. The reductant volume was fixed at 3 ml.

TABLE 1. REPRODUCIBILITY AND DETECTION LIMIT OF THE METHOD

System[a)]	Matrix	RSD[b)] %	Detection limit (S/N=2)
I	0.15 M HCl	8.3[c)]	140 ng/20 ml
	0.1 M Malic acid	7.7[c)]	
II	0.20 M HCl	4.6[d)]	
	0.20 M H_3PO_4	2.7[d)]	200 ng/ml
III	0.20 M HCl	4.5[e)]	10 ng/20 ml
	0.20 M H_3PO_4	4.3[e)]	7 ng/20 ml

a) Described in Experimental. b) Relative standard deviation calculated from ten determinations. c) Germanium taken: 5.0 μg/20 ml. d) Germanium taken: 5.0 μg/ml. e) Germanium taken: 0.5 μg/20 ml.

Precision and Sensitivity. Precision and sensitivity of germanium determination in system I—III were compared. The results are given in Table 1. System I is conventional, but its precision and sensitivity are not so good as that of system III. Precision is improved in system II as compared with system I, but not sensitivity. The highest sensitivity was attained in system III; detection limit of 7 ng/20 ml (=0.35 ppb) is more sensitive than 50 ng/13 ml (=4 ppb) reported by Smith,[6] the highest sensitivity so far reported by AAS.

Influence of Foreign Ions. The influence of various foreign ions on the determination of germanium(IV) (0.5 μg) were examined in system III. The results are shown in Table 2. The ions showing strong suppression in 0.2 M hydrochloric acid medium were paradium(II), nickel(II), gold(III), and cobalt(II). Suppression was also observed in the presence of 50 μg of volatile hydride forming elements such as arsenic(III), antimony(III), and selenium(IV) in the same medium, 250 μg of bismuth(III) not interfering. The interference was not eliminated significantly except selenium(IV) by addition of potassium iodide; coexistence of 100 μg of selenium(IV) was tolerable by addition of 1 ml of 40% potassium iodide solution in hydrochloric acid.

TABLE 2. EFFECTS OF FOREIGN IONS ON THE DETERMINATION OF GERMANIUM
(Results given are percentage changes in absorbance for 0.5 μg of germanium(IV) in systemIII.)

Ion	Added (μg)	Acid reaction matrix[a)] 0.2 M-HCl[b)]	0.2 M-H_3PO_4	0.2 M-H_3PO_4 +EDTA[c)]	0.2 M-Malic acid
Ni(II)	20	−74	−60	0	0
	100	−97	—	0	0
Pd(II)	3	−66	−90	−90	−11
Au(III)	20	−55	−27	0	−19
	60	−70	—	−30	−34
Co(II)	60	−24	0	0	0
	250	−65	0	0	0
Cd(II)	125	−35	−30	−5	−40
Fe(III)	1400	−20	0	0	0
	2800	−37	0	0	0
As(III)	50	−9	−15	−15	−9
Sb(III)	50	−30	−30	−30	—
	250	−50	—	−54	−56
Se(IV)	50	—	−25	−25	—
	125	−31	—	—	−11

a) Volume of test solution, 20 ml; 3 ml of 8 w/v % sodium tetrahydroborate solution was added as a reductant. b) The following are tolerable: Sn(II), Pb(II), Te(IV) (50 μg coexistence); Bi(III)(250 μg coexistence); Hg(II), Ca(II), Mg(II), Mn(II, VII), Ru(III), Mo(VI), V(V), Cr(III, VI), Al(III) (500 μg coexistence); Cl^-, Br^-, NO_3^-, SO_4^{2-}, CH_3COO^-, SiO_3^{2-}, BO_3^{3-}, IO_3^-, ClO_4^-, Na^+, K^+ (2500 μg coexistence). c) 0.25 M EDTA2Na 1 ml was added.

The influence of foreign ions on the determinations in phosphoric acid medium was almost the same as that of hydrochloric acid, but the interference by cobalt(II) and iron(III) is much more reduced than that of hydrochloric acid medium (Table 2).

In malic acid reaction medium, interference caused by nickel(II), gold(III), cobalt(II), zinc(II), or iron(III) is less than that of hydrochloric acid medium as shown in Table 2. Malic acid is superior to other organic acids such as tartaric acid and lactic acid as regards the influence of nickel(II); coexistence of 100 μg of nickel(II) caused no loss of sensitity in 0.2 M malic acid. However, 70% sensitivity suppression took place in 0.2 M tartaric acid, and 95% in 0.2 M ractic acid.

Addition of EDTA to reaction medium is effective for eliminating the interference of nickel(II), gold(III), cadmium(II), and zinc(II) as shown in Table 2. Addition of EDTA to phosphoric acid medium is suitable for the determination of germanium(IV) in

view of sensitivity and influence of foreign ions.

Determination of Germanium in Standard Rocks. The method was applied to the determination of germanium in standard rocks JB-1 and JG-1. Samples were decomposed by the following methods.

Procedure A: Germanium separation process developed by Schneider and Sandell,[16] Onishi,[17] Argollo and Schilling[18] was appleid with a slight modification: Weigh 0.5 g of rock samples in Uniseal decomposition vessel. Add 2 ml of 9 M sulfuric acid, 1 ml of concentrated nitric acid, and 5 ml of 46% hydrogen fluoride. Seal the vessel immediately, put the vessel in air bath for 2 h at 100 °C. After cooling, take off the cap of the decomposition vessel and heat it on a hot plate until fuming of sulfuric acid begins. Transfer the contents into the separation funnel, add 15 ml of 9 M hydrochloric acid and shake for 10 min with an electric shaker. Add 10 ml of carbon tetrachloride and shake for 3 min. Separate each phase and transfer the carbon tetrachloride phase to another separation funnel. Repeat the procedure by adding another 10 ml of carbon tetrachloride into the first separation funnel. Add second carbon tetrachloride phase to previous carbon tetrachloride phase, and wash the phase with 5 ml of hydrochloric acid. Separate each phase, transfer the carbon tetrachloride phase to another separation funnel and add 10 ml of water. Shake for 5 min, then separate each phase. The aqueous solutions were subjected to germanium determination by the proposed method (system III, phosphoric acid matrix). Blank solution was prepared by the same preparation as above. Recovery of germanium was checked by adding standard germanium(IV) solution into Uniseal vessel with sample and carrying out the same procedure described above.

Procedure B: Procedure without germanium separation as in Procedure A was carried out until the decomposition step of the sample in air bath. After cooling the reaction vessel, add 80 ml of 4% boric acid in order to mask excess fluoride ion and transfer the solution to a 100 ml volumetric flask, and add water to the mark. The prescribed volume of the sample solution was subjected to germanium determination by means of standard addition technique (in phosphoric acid containing EDTA). Blank solution was also prepared by the same procedure as above.

The analytical results are given in Table 3. Recovery of 85—95% germanium in Procedure A (both for JB-1 and JG-1) agreed with that of other rock samples.[17] The germanium contents of JB-1 and JG-1 corrected with recovery percent agreed with those by Argollo and Scilling[18] attained by neutron activation analysis. Results obtained by Procedure B were somewhat inaccurate. However, the technique is very simple, rapid, and an average of two or three multiple sample determinations gives almost the same result as that by Procedure A (Table 3). A large discrepancy of germa-

Table 3. Determination of germanium in standard rocks

Sample	Taken (g)	Ge Added (μg)	Pretreatment[a]	Ge Found			Reported (ppm)
				μg[b]	ppm	ppm corrected[c]	
JB-1	0.502		A	0.56_7	1.1_3	1.2_8	0.7[d]
	0.510		A	0.56_0	1.2_7	1.4_4	0.22±0.03[e]
	0.507		A	0.55_0	1.0_8	1.2_3	1.33[f]
	0.502		A	0.50_0	1.2_0	1.3_6	
	0.517		A	0.56_7	1.1_0	1.2_5	
				av.:	1.1_6	1.3_1 (RSD 6.6%)	
	0.517	0.50	A	1.0_5	90%	Recovery[g]	
	0.510	1.00	A	1.4_5	86%	av. 88%	
	0.296		B		1.3		
	0.249		B		1.0	av. 1.2_3 ppm	
	0.138		B		1.4		
JG-1	0.508		A	0.63_3	1.2_5	1.4_4	1.2[d]
	0.510		A	0.58_3	1.1_4	1.3_1	1.7±0.5[e]
	0.513		A	0.58_0	1.1_3	1.3_0	1.32[f]
	0.505		A	0.59_7	1.1_8	1.3_6	
	0.503		A	0.56_0	1.1_1	1.2_8	
	0.503		A	0.53_3	1.0_6	1.2_2	
				av.:	1.1_5	1.3_2 (RSD 5.7%)	
	0.513	0.50	A	1.0_4	90.6%	Recovery	
	0.506	0.50	A	1.0_0	84.2%	av. 87.4%	
	0.180		B		1.5		
	0.228		B		1.3	av. 1.3_3 ppm	
	0.218		B		1.2		

a) Described in the text. b) Mean of two determinations. c) Calculated from recovery test. d) Ref. 19. e) Ref. 18. g) Calculated from average amount of germanium.

nium content is observed in the results of JB-1 between 1.3_3 ppm in this work and 0.22 ± 0.03 ppm by Ohta and Suzuki.[20] They decomposed 2—3 g of the sample at a time, but this seems too much for complete decomposition.

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