Determination of Germanium in Environmental Samples by Electrothermal Atomic Absorption Spectrometry with Continuous Flow Hydride Generation in Dilute Perchloric Acid Solution

Published in Celebration of the 10th Anniversary

NI ZHE-MING AND HE BIN

Research Centre for Eco-Environmental Sciences, Academia Sinica, Beijing, China, 100085

A method has been developed for the sensitive determination of germanium by continuous flow hydride generation electrothermal atomic absorption spectrometry with trapping in a graphite atomizer pretreated with palladium. The optimal acidities using different acids for the generation of germanium hydride were studied. Germanium was found to give a sharp analytical signal in $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, $0.15 \text{ mol l}^{-1} \text{ HNO}_3$, and $0.10\text{--}0.15 \text{ mol l}^{-1} \text{ HCl}$. Beyond these optimal acidities, significant loss of sensitivity resulted. Among the acids investigated only perchloric acid provided a wider range of acidity ($0.15\text{--}0.6 \text{ mol l}^{-1}$) giving maximum efficiency for the production of germanium hydride. Interferences from Ni, Cu, Fe, Mn and Sn on the generation of the hydride from $0.5 \text{ mol l}^{-1} \text{ HClO}_4$ were minimized by the addition of 0.1% EDTA. The characteristic mass which gave an integrated absorbance of 0.0044 s was found to be 46 pg . An absolute detection limit (3σ) of 36 pg was obtained. The method was applied successfully in the determination of germanium in coal fly ash, soil and river sediments following the decomposition of the samples by heating in a mixture of acids using a pressure bomb.

Keywords: Germanium; in situ preconcentration; continuous flow hydride generation; electrothermal atomic absorption spectrometry; perchloric acid

For the determination of germanium in coal fly ashes, the most widely employed technique is phenylfluorone spectrophotometry.¹ However, this method does not show sufficient sensitivity and a preliminary separation of germanium using 9 mol l^{-1} hydrochloric acid is required prior to determination. Recently, the trapping of germanium hydride in a palladium coated graphite furnace followed by atomization has become the method of choice due to its high sensitivity and inherent selectivity.^{2–5} Trace levels of germanium in geological and environmental samples have been reported using this method.^{2,6} Palladium treatment of the graphite tube is considered to be extremely important in enhancing the sensitivity of germanium by increasing both the efficiency of the collection of the germanium hydride and the atomization efficiency of germanium. Another factor which influences dramatically the efficiency of the production of germanium hydride is the acidity of the solution. Unlike the hydrides of arsenic, selenium, antimony and bismuth which are generated from highly concentrated hydrochloric acid solution, various acid media were used by different workers in the generation of germanium hydride. Castillo *et al.*⁷ found that the optimum medium for generating germanium hydride is 0.1 mol l^{-1} acetic acid–

sodium acetate solution (pH 4.5). Halicz⁸ reported that germanium gave a sharp analytical signal in about 0.1 mol l^{-1} hydrochloric acid solution, the same signal intensities were obtainable in 0.1 mol l^{-1} acetic acid–sodium acetate buffer solution and the analytical signal did not depend on small changes in acid concentration in acetic acid solution. Therefore, acetic acid–sodium acetate buffer was considered to be an adequate medium for the production of germanium hydride. However, in real sample analysis problems occur in carrying out hydride generation in a solution of pH 4.5 because metals such as iron, aluminum and titanium will begin to coagulate or precipitate at nearly neutral media and germanium will probably be carried away by co-precipitation or adsorption. Therefore, after digestion of the sample, germanium is extracted directly into carbon tetrachloride from 9 mol l^{-1} hydrochloric acid. The back-extraction is into distilled water before germanium hydride is generated with sodium tetrahydroborate. Brindle *et al.*⁹ suggested a medium of $0.01\text{--}0.02 \text{ mol l}^{-1}$ nitric acid for the generation of GeH_4 prior to determination by direct current plasma atomic emission spectrometry. In the presence of L-cysteine this method can be applied in the determination of germanium in metallurgical samples. Tao and Fang⁶ investigated the effect of hydrochloric acid acidity up to a concentration of 4 mol l^{-1} . The results showed that a maximum was observed between 0.10 and 0.18 mol l^{-1} , which was similar to that reported by Thompson and Pahlavanpour.¹⁰ They used 0.15 mol l^{-1} hydrochloric acid for samples with relatively simple matrices, however, 3 mol l^{-1} hydrochloric acid medium was required to achieve satisfactory recovery of germanium from complex matrices although the sensitivity was only about 20% compared with that obtained at low acidity, apparently a large percentage of the analyte was pumped to waste before being converted into the hydride.

Severe interferences from transition metals in hydride generation have been extensively studied^{11–13} and mechanisms have been proposed for these interference effects. The suppression of the analytical signal is due to the precipitation of the finely divided metal and the subsequent adsorption or decomposition of the hydride of the analyte. Increasing the concentration of the acid results in a substantial increase in the range of interference-free determination of the analyte, because of the increased solubility of the reduced metal in the strong acid. However, this approach does not seem appropriate for the determination of germanium since the absorbance decreases significantly in high acid concentrations. Various masking and chelating agents have been proposed to minimize the interferences.¹⁴ Brindle *et al.*⁹ suggested the use of L-cysteine and

L-cystine which significantly improved the tolerance to transition metals in a solution of $0.015 \text{ mol l}^{-1} \text{ HNO}_3$. Although these reagents are efficient in reducing interferences, they are relatively expensive and are not easily available in our laboratories. In the determination of bismuth in complex nickel-based alloys, by generation of the covalent hydride, Drinkwater¹⁵ used the disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) to overcome the very severe interference effects produced by the alloy matrix. Henden¹² eliminated interference from nickel, zinc, cobalt and iron in the determination of $\mu\text{g ml}^{-1}$ levels of arsenic, antimony, tin and germanium by molecular emission cavity analysis combined with hydride generation by the addition of Na_2EDTA . It was proposed that EDTA prevents or slows down the reduction or precipitate formation of the interfering ions and thus prevents or reduces the adsorption or reactive capture of the hydrides.

The aim of this study was to optimize acid concentration for the efficient generation of germanium hydride and the minimization of interference by nickel, copper and iron in the determination of sub-nanogram levels of germanium by adding Na_2EDTA .

EXPERIMENTAL

Reagents

A germanium stock solution ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving 0.1000 g of germanium metal in 5 ml of concentrated HNO_3 , followed by the dropwise addition of concentrated HF to complete dissolution. The solution was then diluted to 100 ml with de-ionized water. Working standard solutions were obtained through appropriate dilution of the stock standard solution with de-ionized water.

Sodium tetrahydroborate solution, $2\% \text{ m/v}$, was prepared daily or more frequently by dissolving NaBH_4 in de-ionized water, and was used without filtration.

Palladium chloride solution (0.100 mg ml^{-1} of Pd) was prepared by dissolving PdCl_2 in dilute nitric acid followed by dilution with de-ionized water.

Disodium salt of EDTA solution, $0.1\% \text{ m/v}$, was prepared by dissolving Na_2EDTA in de-ionized water.

All the reagents were of analytical reagent grade. De-ionized water was used throughout.

Apparatus

A Perkin-Elmer Model 4000 atomic absorption spectrometer and a Model HGA-400 graphite furnace with deuterium background correction were employed for the measurement of germanium absorbance under the condition of 'gas stop'. A high intensity germanium lamp (General Research Institute of Non-Ferrous Metals, Beijing, China) was used as the line source. A spectral slit-width of 0.7 nm was used to isolate the 265.0 nm resonance line. Pyrolytic graphite coated graphite tubes were used throughout; the sample introduction port was enlarged to a diameter of 2.5 mm with a drill bit for the insertion of the quartz tube connected to the outlet of the hydride generator HG-100.¹⁶ Hydride generation was accomplished in continuous mode in a mixing cell by using two channels of a peristaltic pump to deliver sample and sodium tetrahydroborate(III) solutions to the generator at 12 ml min^{-1} . The mixing and reaction of the solutions as well as the separation of gaseous hydride and liquid were accomplished simultaneously in the cell. A piece of 4 mm i.d. silicone rubber tubing was used for the connection between the outlet of the hydride generator and the quartz tube. The tip of the quartz tube was inserted through the sample introduction port at the centre of the tube, to contact the opposite interior wall. The generated hydride was stripped from the solution by an argon gas stream flowing at 720 ml min^{-1} and

was adsorbed on the inside wall of the palladium-treated graphite tube. The furnace program is presented in Table 1.

Sample Decomposition

A 0.1 g portion of finely ground sample was weighed into a 30 ml Teflon container, and 2 ml of nitric acid (65%), 1 ml of hydrofluoric acid (42%) and 1 ml of perchloric acid were added in sequence. The container was then covered with Teflon and placed in a stainless-steel bomb. The bomb was sealed tightly with a screw closure to avoid gas leakage and placed in an oven. The oven temperature was raised to 170°C over 0.5 h and kept at this temperature for 7 h . The bomb was taken out of the oven and cooled down to room temperature. The Teflon container was taken out of the stainless-steel bomb and the Teflon cover was removed. The container was heated on a hot plate and the solution was evaporated until fumes of perchloric acid nearly disappeared. The residue was dissolved in several ml of 0.01 mol l^{-1} nitric acid, the solution was transferred into a 25 ml volumetric flask and diluted to the mark with 0.01 mol l^{-1} nitric acid. An aliquot (about 0.5 ml) of the solution was transferred into a 10 ml calibrated flask and diluted to the mark with 0.5 mol l^{-1} perchloric acid. The diluted solution was used to generate the germanium hydride.

RESULTS AND DISCUSSION

Acidity Conditions

The efficiency of the generation of GeH_4 in various acid solutions at different concentrations was studied. The results are presented in Fig. 1. The optimal acidities for maximum efficiency were found to be 0.05 , 0.15 , 0.1 – 0.15 and 0.15 – 0.06 mol l^{-1} for H_2SO_4 , HNO_3 , HCl and HClO_4 , respectively. Perchloric acid was found to have a plateau of absorbance at 0.15 – 0.6 mol l^{-1} , which is easier to control than the other acid media with which small changes around the optimum acidity

Table 1 Furnace programme for Ge

Step	Temperature/ $^\circ\text{C}$	Time/s		Procedure
		Ramp	Hold	
1	130	1	50	Injection of Pd solution and drying
2	800	1	80	Injection into quartz tube, hydride generation
3	2300	0	5	Removal of quartz tube, atomization
4	2650	1	3	Cleaning of the graphite tube

Fig. 1 Effect of acid concentration on the integrated absorbance for 1 ng of Ge, where: A, HClO_4 ; B, HCl ; C, HNO_3 ; and D, H_2SO_4

result in an apparent decrease in absorbance. As shown in Fig. 2, there is a plateau for germanium absorbance in acetic acid–sodium acetate buffer solution at pH 2.5–4.5 with similar sensitivity as observed from 0.15–0.6 mol l⁻¹ perchloric acid. Perchloric acid was preferred since the sample was decomposed using perchloric acid and it was more convenient to generate the hydride from the same acid medium directly following sample decomposition rather than adjusting the pH of the solution by introducing sodium acetate and acetic acid. Furthermore, in the near neutral solution of pH 4, iron, aluminum and titanium will probably coagulate and precipitate with the risk of carrying away the trace germanium. Since the amount of tolerable interferences can be increased by increasing the acid concentration of the solution for measurement, 0.5 mol l⁻¹ HClO₄ solution was chosen for the generation of germanium hydride.

Tetrahydroborate Concentration

The dependence of the integrated absorbance of germanium (2 ml of 0.5 ng ml⁻¹ solution) on the tetrahydroborate concentration in 0.5 mol l⁻¹ HClO₄ under continuous flow mode is shown in Fig. 3. As the integrated absorbance remains constant in 1.5–5% NaBH₄ solution when 2 ml of germanium solution is introduced, 2% solution was used throughout the experiment. Although peak height gave double the sensitivity than integrated absorbance, the latter provided better precision in measurement especially in the analysis of real samples. Therefore, integrated absorbance was measured in our experiments.

Fig. 2 Effect of pH of acetic acid–sodium acetate buffer solution on the integrated absorbance for 1 ng of Ge

Fig. 3 Effect of NaBH₄ concentration (% m/m) on the integrated absorbance for 1 ng of Ge

Gas Flow Rate

Argon carrier gas was used to strip and transport the hydrides into the atomizer. According to Tao and Fang⁶ the effects from the carrier gas flow rate were negligible, the amount of hydrogen generated during the reaction was sufficient for transporting the germane into the furnace, so that no carrier gas was used in their experiment. However, our results show that the stripping of germane from the hydride generator into the furnace is complete only when the argon flow rate is maintained at 590–850 ml min⁻¹ (Fig. 4), with the stripping time kept at 50s. The difference in results may probably be attributed to the different modes of hydride generation. In their flow injection mode, the total volume of reaction coil and gas–liquid separator was assumed to be much smaller than the hydride generator we used in the continuous mode.

Trapping Temperature

There was no difference in the integrated absorbance when the trapping temperature was adjusted from 200 to 850 °C (Fig. 5). But at a temperature lower than 600 °C, the background absorption was significant during atomization and contributed to the integrated absorbance when the deuterium arc corrector was not used. At a temperature higher than 800 °C no background absorption was observed and no background correction was required.

Interference Study

The interference effects of metals like nickel, copper, manganese, tin and iron on the generation of germanium were studied and the results are shown in Fig. 6. With the addition of 0.1% EDTA solution these metals could be tolerated in amounts of

Fig. 4 Effect of argon flow rate (ml min⁻¹) on the integrated absorbance for 1 ng of Ge

Fig. 5 Trapping (atomization temperature 2300 °C) and atomization (trapping temperature 800 °C) curves of Ge on palladium treated tubes

Fig. 6 Influence of nickel, copper, manganese, tin and iron on the determination of Ge: A, with and B, without EDTA

10^2 – 10^4 greater than that of germanium. The presence of EDTA improved the interference tolerance 2–4 times. We tried to increase the concentration of EDTA to improve the results but did not succeed, as higher concentrations of EDTA tended to precipitate in slightly acid solution. The effect of EDTA is most obvious in the analysis of real samples as indicated in Table 2. Without adding EDTA the recoveries of germanium ranged from 14 to 74% depending on the sample type, while complete recovery could be achieved with the addition of EDTA in the analysis of coal fly ash, soil and river sediment, indicating that the suppression effects from the matrix components had been eliminated.

Analytical Performances

The characteristic mass, defined as the mass of analyte which provides an integrated absorbance of 0.0044 s was found to be 46 pg. The absolute detection limit of germanium based on the variability of the reagent blank was found to be 36 pg. The precision of the method was 2.5% for 1 ng of germanium ($n=7$). The regression equation for the calibration curve is $y=0.095x+0.003$ with a correlation coefficient of 0.9992, where x =analyte mass (ng) and y =integrated absorbance.

The efficiency of the collection system was evaluated as 89.9% comparing the characteristic mass determined with that determined by direct-injection electrothermal atomic absorption spectrometry (ETAAS).

Sample Analysis

In order to demonstrate the reliability of the proposed method, it was applied to the analysis of Coal fly ash, (GBW 08401)

and Tibetan soil (GBW 08302) reference samples (Research Centre for Eco environmental sciences, Chinese Academy of Sciences), and River sediment (GSD-1 and GSD-2), and Geological material (GSR-1) reference samples (Ministry of Geology, China), containing minor constituents of iron, aluminium and titanium. The values obtained for germanium compared well with the reference values. In order to examine any systematic errors associated with the determination, 1 ng of germanium was spiked for the recovery study, the results indicate that the spiked germanium can be recovered quantitatively when EDTA is added.

CONCLUSION

The efficiency of GeH_4 generation in 0.15 – 0.6 mol l^{-1} perchloric acid was found to be about 90% evaluated by comparing the characteristic mass determined with that of the direct-injection ETAAS. The sensitivity for germanium determination could be enhanced by one order of magnitude with use of *in situ* preconcentration. The trapping of GeH_4 on a Zr-coated graphite tube was found to be unsuccessful though in the direct introduction method this tube gives a much higher sensitivity for germanium as compared with that obtained from a standard graphite tube.¹⁷ The mechanism of the trapping of GeH_4 on palladium coated graphite tubes is not quite clear and is the subject of further investigation.

This work was supported by the National Natural Science Foundation of China under Grant No. 29170240.

Table 2 Determination of Ge in reference samples

Sample	Concentration of analyte/ $\mu\text{g g}^{-1}$		Recovery (%)	
	Found*	Reference value	With EDTA	Without EDTA
Coal fly ash GBW 08401	6.24 ± 0.22	6.0	104	74.0
Tibetan soil GBW 08302	1.07 ± 0.02	—	105	14.0
River sediment GSD-1	1.04 ± 0.04	1.3	102	44.6
River sediment GSD-2	1.79 ± 0.08	1.7	101	67.5
Geological material GSR-1	1.90 ± 0.07	1.9	98	74.0

* Mean value $\pm$ standard deviation ($n=6$)

REFERENCES

- 1 Donaldson, E. M., *Talanta*, 1984, **31**, 997.
- 2 Zhang, L., Ni, Z.-m., and Shan, X.-q., *Spectrochim. Acta. Part B*, 1989, **44**, 751.
- 3 Doidge, P. S., Sturman, B. T., and Rettberg, T. M., *J. Anal. At. Spectrom.*, 1989, **4**, 251.
- 4 Sturgeon, R. E., Wille, S. N., Sproule, G. I., Robinson, P. T., and Berman, S. S., *Spectrochim. Acta. Part B*, 1989, **44**, 667.
- 5 Haug, H. O., and Chonghua, J., *J. Anal. At. Spectrom.*, 1990, **5**, 215.
- 6 Tao, G.-h., and Fang, Z.-l., *J. Anal. At. Spectrom.*, 1993, **8**, 577.
- 7 Castillo, J. R., Lanaja, J., and Aznárez, J., *Analyst*, 1982, **107**, 89.
- 8 Halicz, L., *Analyst*, 1985, **110**, 943.
- 9 Brindle, I. D., Le, X.-c., and Li, X.-f., *J. Anal. At. Spectrom.*, 1989, **4**, 227.
- 10 Thompson, M., and Pahlavanpour, B., *Anal. Chim. Acta*, 1979, **109**, 251.
- 11 Welz, B., and Melcher, M., *Analyst*, 1984, **109**, 569.
- 12 Henden, E., *Analyst*, 1982, **107**, 872.
- 13 Brindle, I. D., and Le, X.-c., *Anal. Chim. Acta*, 1990, **229**, 239.
- 14 Yan, X.-p., and Ni, Z.-m., *Anal. Chim. Acta*, 1994, **291**, 89.
- 15 Drinkwater, J. E., *Analyst*, 1976, **101**, 672.
- 16 Yan, X.-p., and Ni, Z.-m., *J. Anal. At. Spectrom.*, 1991, **6**, 483.
- 17 Gao, Y.-q., and Ni, Z.-m., *Huaxue Xuebao*, 1982, **40**, 1021.

Paper 5/02424B

Received April 18, 1995

Accepted May 23, 1995