Application of Flow Injection Analysis to the Determination of Germanium

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A rapid and simple flow injection analysis for the determination of germanium (Ge) is described. Ge is reacted with phenylfluorone in a mixing coil (0.5 mm i.d. × 300 cm) at 40 °C, and the developed color is measured at 508 nm. The calibration graph is linear over the concentration range of 0.04—10 μg ml^{-1} (2—500 ng). Interference by various foreign substances, amino acids and vitamins, was investigated. Satisfactory results were obtained by the proposed method. The method was applied to a commercially available Ge-containing health beverage.

Keywords germanium; determination; flow injection analysis; phenylfluorone; health beverage

Introduction

Several methods have been proposed for the determination of germanium (Ge). The most widely used method for the determination of Ge is spectrophotometry using phenylfluorone reagent with[1,2] or without[3] a surface-active agent. The authors have previously reported an improved spectrophotometric determination of Ge using phenylfluorone reagent, involving sample degradation in oxygen combustion flasks.[4]

In the present paper, the application of phenylfluorone reagent was extended to provide a rapid and simple analytical method for Ge by flow injection analysis (FIA). The new method was employed to evaluate samples of a health beverage.

Experimental

Reagents and Solutions Phenylfluorone reagent for Ge was obtained from E. Merck (Darmstadt, G. F. R.). The original Ge solution used was a 0.2 M KOH-alkaline solution of potassium germanate (1000 ppm Ge, Kanto Chemical Co.) prepared as a reagent for atomic absorption spectrophotometry. Thiamine hydrochloride, riboflavine, pyridoxine hydrochloride, ascorbic acid and cholesterol were obtained from Wako Pure Chemicals (Tokyo, Japan). HCl·EtOH solution was prepared by dissolving 0.43 ml of hydrochloric acid in 100 ml of ethanol. Phenylfluorone solution was prepared by dissolving 0.05 g of phenylfluorone in 100 ml of HCl·EtOH as a stock solution, and then 4 ml of the solution was diluted to 100 ml with HCl·EtOH as a working solution prior to use.

Apparatus The analytical flow system is shown in Fig. 1. Hitachi 635 pump and a Japan Technicon Corporation autoanalyzer type III were employed, with flow rates of 0.42 and 0.50 ml/min. A Rheodyne sample injector (50-μl loop) was used. The detector was a Shimadzu SPD-6AV UV-visible spectrophotometer with an 8-μl flow cell, the wavelength being set at 508 nm. The reaction coil was Teflon tubing (0.5 mm i.d. × 300 cm), immersed in a constant-temperature oil bath at 40 °C.

Calibration Curve A stock solution of Ge (100 ppm) was prepared by diluting the original Ge solution (1000 ppm) ten times with HCl·EtOH. Several aliquots of different concentrations of Ge standard solutions were prepared by diluting 0 to 1.0 ml of the diluted Ge solution with HCl·EtOH to 10 ml, respectively. Fifty microliters of each sample solution was injected into the FIA system, and the absorbance was measured from the peak height five times for each sample.

Examination of Interfering Substances Thiamine hydrochloride, riboflavine, pyridoxine hydrochloride, ascorbic acid and cholesterol solutions (1×10^{-4} M) were prepared in HCl·EtOH. The first and second working solutions (1×10^{-5} and 1×10^{-6} M) containing a test substance (1×10^{-5} and 1×10^{-6} M) and Ge (300 ng/50 μl) were prepared by mixing each 1×10^{-4} M solution with the original Ge solution and diluting with ethanol.

Determination of Ge in Commercially Available Ge-Containing Health Beverage One milliliter of commercially available Ge-containing health beverage was diluted to 100 ml with HCl·EtOH, and 50 μl of the sample solution was injected into the FIA system. The absorbance was measured at 508 nm. As the blank test, 50 μl of water–HCl·EtOH (1 : 9, v/v) solution was injected into the same system instead of the sample solution, and the absorbance measured was used to correct the observed values. The determination of Ge was also carried out by the standard addition method. One hundred microliters of Ge-containing health beverage was diluted to 500 μl with HCl·EtOH. To each 100 μl of the diluted sample solution, 25, 50, 200 or 300 μl of diluted germanium solution (Ge, 100 ppm, 100 ng/μl) was added, and the solution was made up to exactly 500 μl with HCl·EtOH. The subsequent procedures were as before.

Results and Discussion

Ge(IV)–phenylfluorone complex has a low solubility in water or aqueous ethanol, so that cetyltrimethylammonium bromide,[2] gelatin,[1] gum arabic,[1] or sodium lauryl sulfate are commonly used as dispersants.

The authors focused on the determination of Ge by FIA without using those dispersing agents to simplify the flow system; Ge-containing sample solution was injected directly into the continuous flow system, and the reaction of Ge with phenylfluorone was performed in the reaction coil at 40 °C. The reaction mixture was monitored at 508 nm. A longer reaction path resulted in higher absorbance; the most suitable length of tubing was 300—330 cm. The use of tubing longer than 4 m resulted in diffusion of the injected

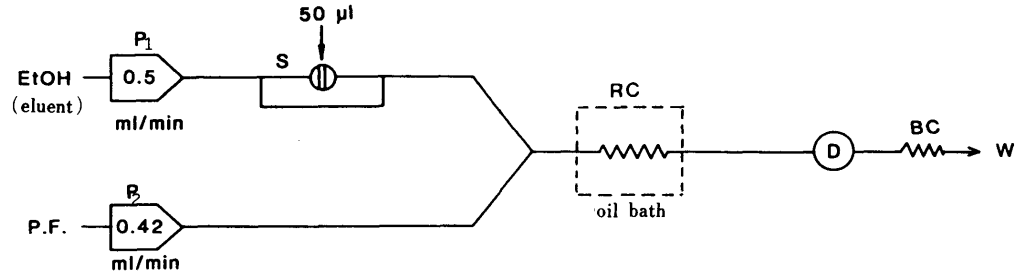

Fig. 1. Schematic Diagram of Flow Injection System

P_1, pump 1; P_2, pump 2; P.F., phenylfluorone solution containing 0.05 M hydrochloric acid (6.2×10^{-5} M); S, sample injector, 50 μl loop; R.C., reaction coil, 0.5 mm i.d. × 300 cm, 40 °C; D, spectrophotometric detector, 508 nm; B.C., back pressure coil; W, waste.

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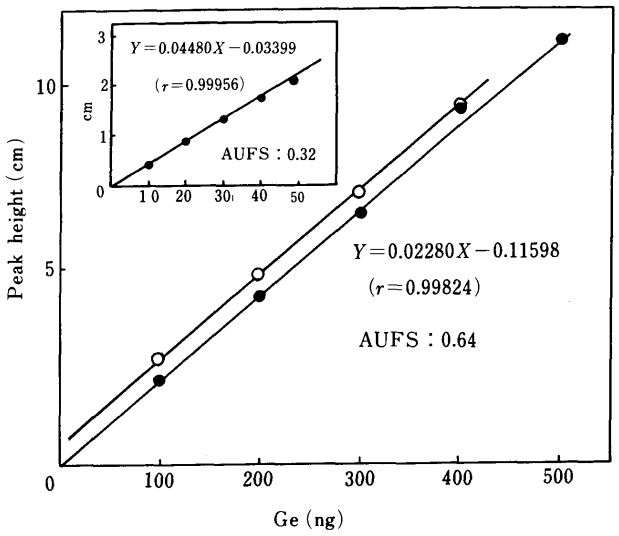

Fig. 2. Calibration Curves of Ge and of Ge and Sn

Injection volume, 50 μl; ●—●, germanium; ○—○, germanium and tin.

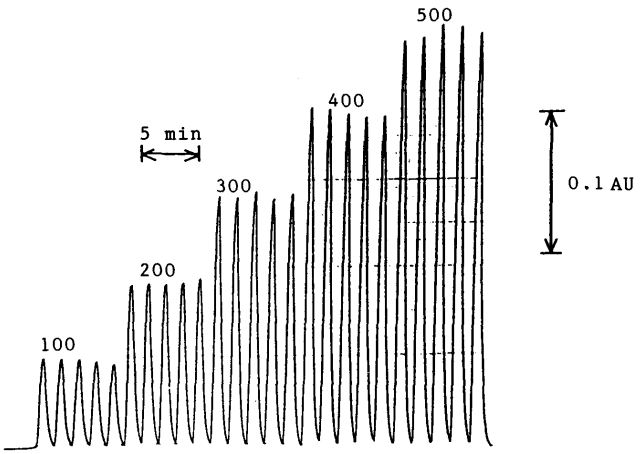

Fig. 3. Typical Signal Peaks for Several Concentrations of Ge Standard Solution

sample zone in the carrier stream. The oil bath was kept at 40 °C, since at temperatures above 40 °C the peak height decreased.

The calibration curves were constructed by using the diluted germanium solution (100 ppm, 100 μg/ml). The regression curve was linear over the range of Ge content of 2—500 ng, as shown in Fig. 2. The regression equation was $Y=0.02280X-0.11598$; correlation coefficient (r) 0.99824.

When Ge standard solutions were repeatedly injected, satisfactory reproducibility was obtained, as shown in Fig. 3. The relative standard deviation for 100—500 ng of Ge did not exceed 2%.

Several kinds of amino acids and vitamins presumably contained in health beverages were examined to see whether they interfered with the reaction of Ge and phenylfluorone (Table I). Thiamine hydrochloride decreased the color intensity of Ge sample solution by 14% at 1×10^{-5} M, and by 9% at 1×10^{-6} M. Ascorbic acid at the concentrations of 1×10^{-5} and 1×10^{-6} M caused no decrease in absorbance.

Table I. Effect of Addition of Foreign Substances on the Response in the Ge–Phenylfluorone Reaction[a]

Substance added	Relative response	
	10^{-5} M	10^{-6} M
Lysine	1.080	0.970
Tryptophan	1.022	1.009
Glycine	1.000	0.974
Thiamine	0.864	0.909
Riboflavine	0.914	0.975
Pyridoxine	0.914	0.968
Ascorbic acid	1.010	1.022
None	(1.000)	(1.000)

a) Ge concentration was adjusted to 300 ng/50 μl.

Riboflavine and pyridoxine hydrochloride caused a decrease in absorbance by 9% at 1×10^{-5} M and by 3% at 1×10^{-6} M. Consequently, the coexistence of small amounts of these interfering substances did not markedly influence the Ge·phenylfluorone color development.

Lysine and tryptophan caused a slight increase in absorbance at 10^{-5} M, while at 10^{-6} M no significant effect was observed for either amino acid. No decrease in absorbance was observed at those concentrations of glycine.

In addition to Ge, several metals react with phenylfluorone to form colloidal complexes. There is a possibility that foreign elements are contained in health foods or beverages. The effect of the coexistence of tin (Sn), a heavy and toxic metal on the color development of Ge phenylfluorone has been investigated. The Sn phenylfluorone complex shows one-fifth of the absorbance of the Ge phenylfluorone complex (Fig. 2).

The proposed method was applied to the determination of Ge in a commercially available health beverage. As another approach for the determination of Ge, the standard addition method was employed. The content of Ge in the beverage was estimated as 87.0 μg/ml by the proposed FIA method, and as 80.0 μg/ml by the standard addition method.

The detection limit was 1 ng for Ge at a signal-to-noise ratio of 2. The detection limit is comparable to that obtained with hydride generation atomic emission spectrometry.[5]

One of the advantages of the present method is that substances coexisting in health food or beverages do not seriously interfere with the analysis of Ge at the expected concentration.

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References

1) D. T. Burns and D. Dadgar, *Analyst*, **105**, 75 (1980).
2) E. M. Donaldson, *Talanta*, **31**, 997 (1984).
3) J. Aznárez, P. Moneo, J. C. Vidad and F. Palacios, *Analyst*, **110**, 747 (1985).
4) M. Nakano, C. Sekiguchi, H. Wakabayashi and K. Shimada, *Bunseki Kagaku*, **33**, 188 (1984).
5) I. D. Brindle and C. M. C. Ponzoni, *Analyst*, **112**, 1547 (1987).

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