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# Determination of trace amounts of germanium by flow injection hydride generation atomic fluorescence spectrometry with on-line coprecipitation

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Received 26 June 2001; received in revised form 25 October 2001; accepted 26 October 2001

## Abstract

A method for the determination of trace amounts of germanium by hydride generation atomic fluorescence spectrometry (HG-AFS) associated on-line with flow injection (FI) coprecipitation preconcentration was described. The samples, each spiked with  $\text{Ni}^{2+}$  ( $500 \mu\text{g ml}^{-1}$ ), were introduced into the FI system using time-based injection, and mixed with a NaOH solution ( $50 \text{ g l}^{-1}$ ). Germanium was preconcentrated by coprecipitation with the generated nickel hydroxide precipitate. The precipitate is subsequently eluted with 20% (v/v) phosphate acid solution and directed into the HG-AFS system. This method is simple and rapid. The detection limit ( $3\sigma$ ) was  $0.11 \mu\text{g l}^{-1}$  and the relative standard deviation was 5.6% ( $n = 11$ ) at the  $10 \mu\text{g l}^{-1}$  level. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Flow injection analysis; Coprecipitation; Atomic fluorescence spectrometry; Germanium

## 1. Introduction

Germanium is an important element and has essential effects on human health. The methods used for the determination of trace amounts of germanium included spectrophotometry [1–3] and atomic spectrometry [4–7]. Yang and Guo [8] determined the germanium in geological samples by hydride generation nondispersive atomic fluorescence spectrometry. Hydride generation atomic fluorescence spectrometry (HG-AFS) for

the determination of germanium is simple, rapid, accurate and selective [8,9]. However, it is insufficient for the direct assay of trace amounts of germanium in some samples, therefore, a preconcentration procedure is required.

Coprecipitation by hydroxide of metals such as Al, Cd, Fe, Ga, La, and Mg has been reported for the preconcentration of trace elements [10,11]. Brindle et al. [12] have described a method for the determination of trace amounts of germanium in natural water by hydride generation atomic emission spectrometry (HG-AES) with the coprecipitation in the presence of  $\text{Mg}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . But coprecipitation in the batch mode is

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Table 1  
Operating conditions for atomic fluorescence spectrometer

PMT-voltage	320 V
Main lamp current	80 mA
Lamp ancillary electrode current	30 mA
Argon carrier gas flow rate	600 ml min <sup>-1</sup>
Atomization temperature	Low (200 °C)
Observation height	7 mm

rather tedious and time consuming. Fang et al. [13] have shown an automatic system combined with the flame atomic absorption spectrometer (FAAS) with flow injection (FI), by which trace amounts of lead can be determined with the on-line preconcentration by coprecipitation without filtration. With this system, the precipitate was collected quantitatively on the inner walls of a knotted reactor (KR), and subsequently dissolved by a stream of isobutyl methyl ketone, which was introduced directly into the burner of the AAS instrument. After that, there have been many researches on FI on-line coprecipitation technique for the preconcentration combined with atomic spectrometry [14–16], but few combined with atomic fluorescence spectrometry.

In this article a method for the determination of trace germanium by FI on-line coprecipitation preconcentration followed by HG-AFS was developed. In order to enhance the efficiency of deter-

mination and reduce the consumption of reagents, the manifold and operation program for on-line coprecipitation and hydride generation are carefully designed. Manifold parameters and chemical conditions are described in detail. The proposed method was applied to the determination of germanium in two standard reference materials. The results obtained were satisfactory.

## 2. Experimental

### 2.1. Apparatus

A AF-610 atomic fluorescence spectrometer with a commercial gas–liquid separator (Beijing Raileigh Analytic Instrument Corporation) was used under the operating conditions listed in Table 1. The flow injection analytical system applied was a JTY-1B FI multifunction solution autohandling system (Faculty of Material Science and Chemical Engineering, China University of Geosciences). Fig. 1 shows the manifold for on-line coprecipitation used in this study. The manifold program for this FI system is showed in Table 2. The precipitate collector was a Teflon micro-column with a cavity of 50 mm long and 5 mm inner diameter (i.d.) in which a piece of silk was fixed as a filtering membrane. Reacting coils,

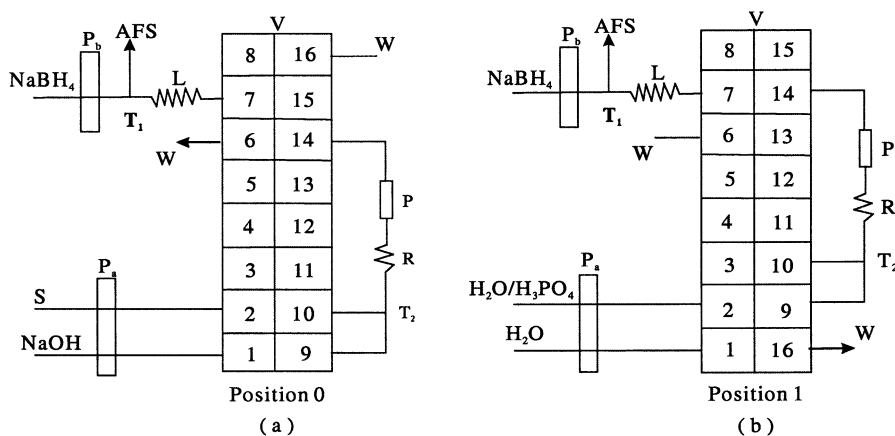


Fig. 1. Schematic diagram of the FI manifold for on-line coprecipitation–dissolution HG-AFS (a) the loading (precipitating) sequence and (b) the elution stage. P<sub>a</sub> and P<sub>b</sub>, peristaltic pumps; V, 8 channel rotary injection valve; R, reacting coil; P, precipitate collector; T<sub>1</sub> and T<sub>2</sub>, T-tube; L, sample loop; S, sample; W, waste.

Table 2  
Operating program

Step	Times (s)	Pump rate (r min <sup>-1</sup> )		Valve position	Function
		P <sub>A</sub>	P <sub>B</sub>		
0	50	50	25	0	0
1	2	2	0	0	0
2	20	20	25	0	0
3	10	10	25	0	0
4	40	40	25	0	1
5	2	2	0	0	1
6	25	25	50	90	1

The sample and NaOH solution are reacted in R, and the precipitate was collected in P  
P<sub>a</sub> stops, manually replace sample and NaOH with water  
Water is pumped to wash the tube and the precipitate  
Air is used to push out the water remaining in the tube  
V turns to position 1; P<sub>a</sub> propel the 20% H<sub>3</sub>PO<sub>4</sub> solution to dissolution the precipitate  
The eluent is replaced by water  
Both pumps are active, the eluent, pushed by water, is reacted with NaBH<sub>4</sub>; germanium is determined by HG-AFS

sample loop and connecting tubing between them were 1 mm in inner diameter.

## 2.2. Reagents

All reagents used were analytical reagent grade. Distilled water was used throughout. The germanium standard solution ( $1000 \text{ mg l}^{-1}$ ) and the nickel standard solution ( $5000 \text{ mg l}^{-1}$ ) were prepared from germanium oxide and metallic nickel, respectively. All the standard solutions were prepared by successive dilution to the required concentration just before use. A  $10 \text{ g l}^{-1}$  sodium tetrahydroborate solution was prepared by dissolving the reagent in  $2 \text{ g l}^{-1}$  sodium hydroxide solution just before use.

Twenty percent (v/v) phosphate acid solution, 10% (v/v) hydrochloric acid solution, and  $50 \text{ g l}^{-1}$  (m/v) sodium hydroxide solution were also used in this work.

## 2.3. Experimental procedure

Transfer 0.5000 g sample into a PTFE crucible, add 10 ml HF and 5 ml  $\text{HNO}_3$ , heat the solution on a hot-plate, evaporate the sample solution to incipient nearly dry. Repeat these steps and dissolve the residue in hot distilled water. Transfer this solution to a 50 ml volumetric flask and dilute to the mark with water. The sample solution and the calibration standard solutions are then measured with the given manifold program and instrument operating parameters.

## 3. Results and discussion

### 3.1. Design of precipitate collector

In reported on-line coprecipitation systems, a KR was often used to collect the precipitate. Tao and Hansen [15] have argued that the KR had two important functions: first, it promoted radial mixing of the sample and reagent, providing reproducible conditions for the precipitation process, and secondly, it acted as a collector of the precipitate. In order to improve the sensitivity, more samples should be introduced and the pre-

Table 3

Comparison of different precipitate collectors

Precipitate collector	Fluorescence intensity	RSD (% , $n = 10$ )
Knotted reactor	306	7.5
PTFE cavity	823	3

cipitate should be collected completely as well, therefore, longer KR was needed. As a result, the system became time consuming.

In this work, a polytetrafluoroethylene (PTFE) micro-column with a  $50 \text{ mm} \times \varnothing 5 \text{ mm}$  cavity in which a piece of silk membrane being fitted was used as precipitate collector. With this collector, more precipitate could be collected completely and more samples were allowed. Table 3 showed the fluorescence intensity of  $10 \mu\text{g l}^{-1}$  germanium solution obtained with different precipitate collectors.

### 3.2. Optimization of chemical variables

In the determination of germanium by hydride generation method, different medium affect the hydride generation. The influences of phosphate acid, sulfuric acid, nitric acid, hydrochloric acid and tartaric acid on the determination of germanium were studied. The results showed that germanium in 20% phosphate acid could produce maximum fluorescence signal. Therefore, 20% phosphate acid solution was used to dissolve the precipitate.

Under certain conditions, germanium could be coprecipitated by  $\text{Cd}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Co}(\text{OH})_2$  or  $\text{Ni}(\text{OH})_2$ . When  $\text{Ni}(\text{OH})_2$  was used as coprecipitant, germanium could be absorbed quickly and completely. Further experiment showed there was no influence on the determination of germanium even when the  $\text{Ni}^{2+}$  concentration was  $1000 \text{ mg l}^{-1}$ .  $\text{Ni}(\text{OH})_2$  was used as coprecipitant in this work. The effect of NaOH and  $\text{Ni}^{2+}$  concentration were shown in Figs. 2 and 3 The NaOH concentration and the  $\text{Ni}^{2+}$  concentration used in this work were 50 and  $500 \text{ mg l}^{-1}$ , respectively.

Immerging the reacting coil into hot water, faster and larger particles of precipitate could be

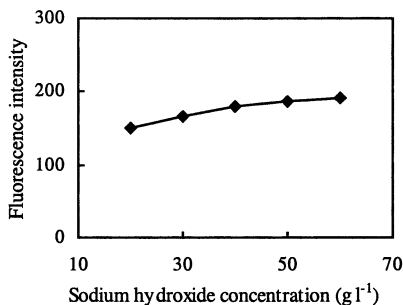


Fig. 2. Effect of NaOH concentration.

obtained. Therefore, the precipitate could be collected more completely and the fluorescence intensity was increased significantly. In addition, heating the eluent could speed the dissolution of precipitate, and the signal also could be increased. The effect of temperature on coprecipitation of Ge was investigated, and the results showed that the fluorescence intensity was maximal and stable when the temperature exceeded 80 °C. The reacting coil was immersed in boiled water in this work.

### 3.3. Optimization of FI variables

The flow rate and the enrichment time of samples were optimized. When flow rate of the sample varied from 1.5 to 3.0 ml min<sup>-1</sup>, there was no obvious influence on the fluorescence intensity, but the signal decreased with increasing pumping rates when it exceeded 3.0 ml min<sup>-1</sup> as shown in Fig. 4. At the same time, the fluorescence intensity

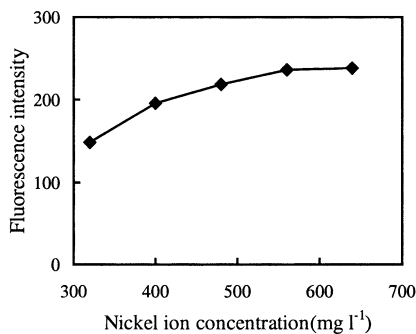


Fig. 3. Effect of the nickel ion concentration.

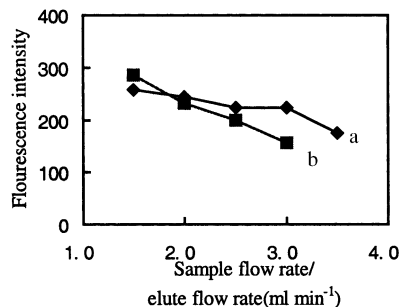


Fig. 4. (a) The effect of the sample flow rate and (b) the effect of elute flow rate.

increased with longer sample enrichment time. Fig. 5 showed the effect of enrichment time on the fluorescence intensity of germanium. The flow rate of the sample applied in this work was 3.0 ml min<sup>-1</sup>, and the sample enrichment time was 60 s.

The effect of the elute flow rate was studied, also shown in Fig. 4. Considering the time consumption and the sensitivity of this procedure, we chose 2.5 ml min<sup>-1</sup> as the flowing rate for dissolvent.

### 3.4. Interference

Interferences due to coexisting ions on the determination of 10 µg l<sup>-1</sup> of germanium were studied. Upto 100 mg l<sup>-1</sup> of Pb, Fe, Co, Cd, Cu, Ag, Al and 1000 mg l<sup>-1</sup> of In, Ba, Cr, As, Bi, Sb did not interfere in the FIA-HG-AFS determination of Ge.

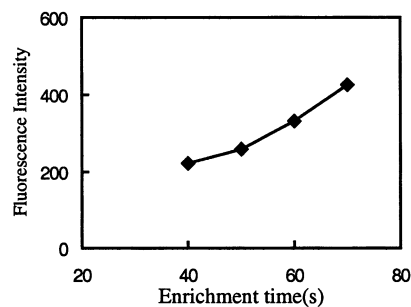


Fig. 5. Effect of the enrichment time.

Table 4

Performance data for the on-line coprecipitation–dissolution preconcentration HG-AFS system

Calibration graph, 0–8 $\mu\text{g l}^{-1}$ of R germanium	
Regression equation	
[Fluorescence intensity versus concentration ( $\mu\text{g l}^{-1}$ )]	$y = 21.25 \times + 2$
Correlation coefficient	$r = 0.9991$
Sampling frequency	$24 \text{ h}^{-1}$
Enrichment factor	11
Detection limit ( $3\sigma$ )	$0.11 \mu\text{g l}^{-1}$
Relative standard deviation ( $10 \mu\text{g l}^{-1}$ of Ge, $n = 11$ )	5.6%
Sampling consumption	2.1 ml
20% $\text{H}_3\text{PO}_4$ consumption	1.7 ml

Table 5

Analysis of reference material ( $\omega(\text{Ge})/\mu\text{g g}^{-1}$ ,  $n = 5$ )

Sample	Recommended value	Found	RSD (%)
GBW07302	1.70	2.06	3.7
GBW07308	0.94	0.98	4.3

### 3.5. Performance of the on-line coprecipitation–dissolution preconcentration system

Characteristic performance data of the on-line coprecipitation–dissolution preconcentration system are presented in Table 4. For a precipitate collection (sampling) time of 50 s and a sampling frequency of  $24 \text{ h}^{-1}$ , an enrichment factor of 11 was obtained. The detection limit ( $3\sigma$ ) was  $0.11 \mu\text{g l}^{-1}$  and the relative standard deviation (RSD) was 5.6% ( $n = 11$ ) at the  $10 \mu\text{g l}^{-1}$  level.

The proposed method was applied to the determination of Ge in two standard reference materials. Analytical results in Table 5 show that the values found for Ge are in good agreement with the certified values.

### Acknowledgements

The authors thank The Hubei Key Laboratory of Waste Geological Disposal and Environment Protection for financially supporting this work.

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