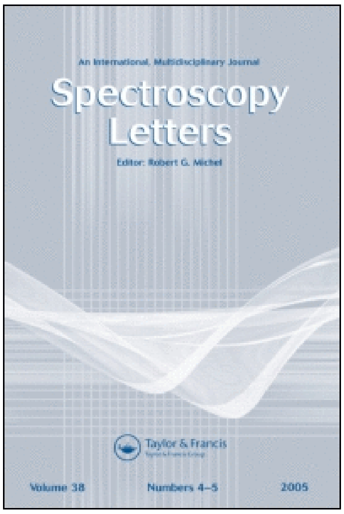

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L-Cysteine Enhanced Hydride Generation for Atomic Fluorescence Spectrometric Determination of Germanium in Geological Samples

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L-Cysteine Enhanced Hydride Generation for Atomic Fluorescence Spectrometric Determination of Germanium in Geological Samples

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ABSTRACT

L-cysteine enhanced the analytical signal in the hydride generation-atomic fluorescence spectrometric determination of germanium. In addition, it reduced or eliminated interferences from coexistent ions such as Cr (VI), Se^{4+}, Te^{4+}, Pb^{2+}, Cu^{2+}, and Ni^{+2} in aqueous analyte solutions. With L-cysteine, the tolerable limits for interferent ions were determined for Cr (VI), Se^{4+}, Te^{4+}, Pb^{2+}, Cu^{2+}, Ni^{+2}, Co^{2+}, Zn^{2+}, Fe^{3+}, As^{3+}, Sb^{3+},Pd^{2+}, Au^{3+}, Bi^{3+}, and Pt^{2+}. The proposed method was used for the determination of germanium in seven geological references samples, with analytical results in good agreement with the certified

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values. The limit of detection of the method was 0.38 μg/L (equivalent to 0.01μg/g in solid samples, assuming a sample weight of 0.5 g), and the relative standard deviation for the sample analysis ranged from 1.4% to 7.3%. The method can be used for the analysis of geological samples for germanium with concentrations ranging from 0.01μg/g to 100 μg/g.

Key Words: Germanium; Hydride generation; Atomic fluorescence spectrometry; L-Cysteine; Geological samples; Signal enchancement.

INTRODUCTION

Hydride generation-atomic fluorescence spectrometry (HG-AFS) has the major advantages of simple spectra, high sensitivity, low limits of detection (0.001 μg/L to 1 μg/L) which varies with analyte elements), high precision and accuracy, and relatively wide linear dynamic ranges (3 orders of magnitude). The commercialization of HG-AFS instruments has been a great success in China in recent years, although the worldwide commercialization of HG-AFS is not yet a reality, as opposed to the case of electrothermal atomic absorption spectrometry (ETAAS). With a commercial HG-AFS instrument, eleven elements can now be routinely measured with vapor generation, mainly hydride generation, techniques. Some instruments have two-channel capability, and can measure two elements simultaneously. The limits of detection (LODs) are at least at sub ng/mL or better, for example, several picograms per milliliter for Hg and Cd, which are better than those by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), and equivalent to or better than those by ETAAS and HG-ICP-AES. The instrumental and running costs compete very well with ICP-AES and ETAAS. Therefore, HG-AFS has been used for the determination of these trace elements in various samples.[1] It is possible to use this kind of instrument to determine additional elements via other volatile compound generation techniques, for example volatile metal derivatives.[2]

Germanium is an important trace element in the study of geochemistry. The germanium concentration is usually very low in many real samples including geological samples. Consequently, a preconcentration and/or separation step is usually employed in the determination of germanium, otherwise a very sensitive instrumental method is required for the measurements.[3–5] Besides HG-AFS, HG-ICP-AES,[6,7] HG-ICP-MS (mass spectrometry)[8] and HG-AAS (atomic absorption spectrometry)[9] have been used for the determination of germanium in geological samples.[6–9] Among these methods, HG-AFS instruments are simple, and their instrumental and running costs are relatively low, though not necessarily higher detection capability. Like ETAAS, however, the multielememt capability of HG-AFS is very limited, compared to the ICP techniques.

In the HG atomic spectroscopic techniques (HG-AS), gaseous phase and liquid phase chemical interferences still exist although the measurements are conducted after the analyte hydrides are separated from the sample matrices.[10,11] Sometimes, therefore, a separation step such as precipitation is still needed for the elimination of the matrix interferences.[12] It is interesting to note that the HG-DCP-AES (hydride generation-direct current plasma-atomic emission spectrometry) signals of arsenic, antimony, germanium, tin, and lead can be significantly enhanced by separately aspirating a solution of easily ionized elements into the DCP when the hydrides are atomized and excited inside the plasma.[13] Apparently, a more convenient way is desired to eliminate the interferences and meanwhile to enhance the sensitivity. In recent years, it has been found that L-cysteine can enhance the analytical signal of HG-AS for some elements, and suppress the matrix interferences.[14–18] This effect of L-cysteine has not yet been tested for the determination of any elements in usually complicated geological samples by HG-AFS. In this paper, therefore, the versatile reagent L-cysteine was used to enhance the HG-AFS signal and to eliminate the interference in the analysis of geological samples for germanium. The experimental conditions were optimized first. Together with the enhancement effect, the interference of 16 coexisting ions was studied in detail. Finally, the proposed analytical procedure was applied to the determination of germanium in seven geological reference samples, with germanium levels ranging from 0.4 μg/g to 12.4 μg/g in the solid samples.

EXPERIMENTAL

Instrument and Reagents

A commercial atomic fluorescence spectrometer (model: AFS-2202, Beijing Haiguang Instrument Co., Beijing, P. R. China) was used for the experiments described in this paper. The instrument can work in a simultaneous two-channel mode or one channel mode. The light source is coded hollow cathode lamps (HCLs), i.e., two HCLs are pulse-powered alternately, providing emission lines from the two HCLs, alternately. The emission light beams from the HCLs are focused on to a quartz atomizer for the excitation of atomic fluorescence of analyte atoms. In this experiment, a germanium high intensity HCL (Beijing Institute of Vacuum and

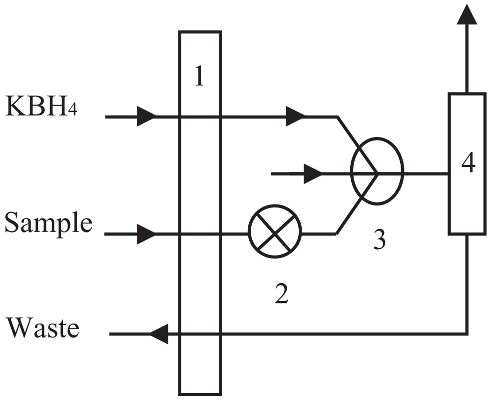

Figure 1. A schematic diagram of the intermittent hydride generation reactor/sampler. 1—pump; 2—valve; 3—reactor; 4—gas/liquid separator.

Electronics, Beijing, P. R. China) was used. A hydride-generator is used to generate the hydride of the analyte element, which is subsequently introduced to the quartz atomizer with an argon flow. The hydrogen flowing with argon and the hydride produced from the hydride-generation reaction, is ignited with an electrically heated wire to form an argon-hydrogen flame in the quartz atomizer for the atomization of the hydrides. The resultant fluorescence is focused, via a non-dispersive optical system, onto a photomultiplier tube (PMT), and followed by the amplification of the signal and data processing with a computer. The hydride generation atomic fluorescence spectrometer (HG-AFS) is routine for the measurement of 11 elements, i.e., As, Sb, Bi, Hg, Se, Te, Sn, Ge, Pb, Zn, and Cd. Usually, $NaBH_4$ or KBH_4 is used as a reducing reagent. The HG system is a manufacturer-designed, computer-programmable, intermittent hydride generation reactor, as shown in Figure 1 schematically. The optimized instrumental conditions for the determination of germanium are listed in Table 1.

Table 1. Optimal-working program for the intermittent flow sampler/reactor.

Step	Rotation speed (rps)	Time (s)	Repetition time	Reading	Stop
0	80	8	1	N	N
1	0	5	1	N	N
2	100	15	1	Y	N
3	0	5	0	N	Y

A germanium working standard solution (1 mg/L) was prepared from a stock germanium standard solution (10 mg/L), both in the medium of 0.5% NaOH. KBH_4, 25 g/L in the medium of 0.10 mol/L KOH, was freshly prepared daily prior to use. All the reagents used in the experiment were of analytical grade or better. Sub-boiled de-ionized water was used for cleaning and dilutions. A series of standard solutions with concentrations of 1, 3, 5, 10, 50, 100 Ge μg/L in the medium of 4 mol/L H_3PO_4+1 mol/L H_2SO_4+0.09% (m/v) L-cysteine were prepared from further dilution of the working standard solution.

Sample Preparation

Samples of 0.1 to 0.5 g were accurately weighed into Teflon crucibles with an analytical balance. To each of the samples, 10 ml HF, 5 ml HNO_3, and 1 ml 50% H_2SO_4 were added, then the crucibles with covers were put on a hot plate. The crucibles were heated gradually from low temperature to high temperature (around 250 °C), and eventually to the point that the white fumes of sulfuric acid appeared. Then, the crucibles were removed from the hot plate to cool down before their walls and covers were rinsed with sub-boiled deionized water. The crucibles were reheated to the white fume point. After cooling, 5 ml of 8 mol/L H_3PO_4 was added. Again, the crucibles were put back onto the plate, and heated to boil gently for about one minute. Finally, 2.5 ml of 0.35% (m/v) solution of L-cysteine was added, and the sample solutions were quantitatively transferred to 10 ml test tubes and diluted to the mark with sub-boiled deionized water when the crucibles were cooled down. The supernatant was used for the instrumental measurements.

RESULTS AND DISCUSSION

Selection of Acid-Medium

The effects of hydrochloric acid, sulfuric acid and phosphoric acid were investigated on the atomic fluorescence signal of germanium. The results were shown in Figure 2. It can be seen that phosphoric acid was the best and hydrochloric acid the worst in terms of signal size. Since sulfuric acid was involved in the sample digestion step, a mixed acid solution of 4 mol/L H_3PO_4 and 1 mol/L H_2SO_4 was selected for the rest of the work. In addition, phosphoric acid is helpful in restraining the interference from alkaline earth metals, iron, mercury and molybdenum ions.

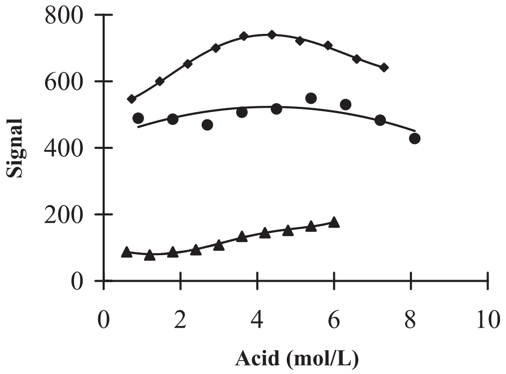

Figure 2. Effects of acids and their concentrations on the germanium atomic fluorescence signal. ◆H_3PO_4; ●H_2SO_4; and ▲HCl.

Amount of KBH_4

The effect of the amount of potassium borohydride, KBH_4, on the fluorescence intensity of germanium was carefully tested. The experimental results showed that the optimal range of the reducing reagent was 25 to 30 g/L of KBH_4. The concentration of KBH_4 used in later experiments was 25 g/L in the basic medium of 0.10 mol/L KOH.

Amount of L-Cysteine

It was found that the fluorescence intensity of germanium reached a maximum when 2.5 ml of 0.35% (m/v) of L-cysteine was added to the analyte solution. The signal was enhanced by about 30%. Although this enhancement effect is not impressive, a further benefit of using L-cysteine is its capability of suppressing interferences from coexisting ions, as detailed in the next section. It is believed that L-cystein reacts with BH_4^- through -SH and forms a complex, BH_3-S-R^-, which increases the formation rate of germanium hydride and therefore the atomic fluorescence intensity of germanium.[15]

Interference of Co-existing Ions

In the determination of germanium by HG-AFS, the interference is mainly from the elements of Groups VIIIB, IB and IIB in the periodic table of elements. In the early phase of hydride formation, these elements form highly dispersed free metal atoms (preferential reduction of the interferent ions) or metal boronide precipitates, which adsorb or catalytically decompose germanium hydride, thus suppressing the atomic fluorescence of germanium.[11] Other hydride-forming elements, such as arsenic, antimony, tin and selenium, may form compounds with other elements including germanium in the gaseous phase of the low-temperature argon-hydrogen flame, and interfere with the determination of germanium.[10,19]

It has been reported that L-cysteine can enhance the atomic fluorescence of germanium, and suppress the chemical interferences from transition metal ions such as Cu^{2+}, Co^{2+}, and Ni^{2+}.[14] The interferences from Cr (VI), Pd^{2+}, Te^{4+}, As^{3+}, and Sb^{3+}were studied in detail. When the amounts of these elements exceeded the tolerable limits, 4, 4, 6, 15, and 3 μg for Cr (VI), Pd^{2+}, Te^{4+}, As^{3+}, and Sb^{3+}, respectively, the interferences were significant. When L-cysteine was used, the tolerable limits for the coexisting ions, Cr (VI), $Pd^{2+}$and Te^{4+}, were dramatically increased to 300, 120, and 300 μg, respectively. This resulted from the high reducing capability of L-cysteine ($E^0 = 0.076$ V), which reduces Cr (VI), $Pd^{2+}$and $Te^{4+}$to Cr (III), Pd^0 and Te^0 before KBH_4 reduces the analyte element, thus eliminating the interference. However, with L-cysteine, the tolerable limit for $As^{3+}$and Sb^{3+}were only doubled to 30 and 6 μg, respectively. This is probably because the L-cysteine cannot reduce $As^{3+}$and $Sb^{3+}$to As^0 and Sb^0. As shown in Figure 3, Sb^{3+} leads to positive interference as oppose to other interferent ions, for which the mechanism is still unknown. With L-cysteine, the tolerable limits for other coexisting ions, Cu^{2+}, Co^{2+},

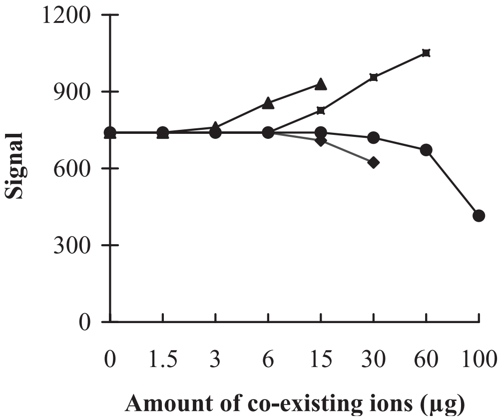

Figure 3. The interference of As^{3+} and Sb^{3+} with the measurements of the atomic fluorescence signal of germanium. ◆As^{3+}; ● As^{3+} with L-cysteine; ▲Sb^{3+}; and ■ Sb^{3+} with L-cysteine.

Ni^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Au^{3+}, Bi^{3+}, Se^{4+}, $Hg^{2+}$and Pt^{2+}, were 30 mg, 15 mg, 20 mg, 300 mg, 300 mg, 50 mg, 50 μg, 50 μg, 250 μg, 50 μg and 100 μg, respectively, with recoveries ranging from 97% to 100%. All the tolerable limits reported in the paper were based on the analyte amount of 0.40 μg Ge in 10 ml analyte solution. However, it should be pointed out that the absolute ratio of interference to analyte element is not always the most important consideration, since interferences can often be eliminated by dilution in many applications of atomic spectrometric techniques if the sensitivity is high enough.[20,21]

Limit of Detection, Precision, Linear Dynamic Range, and Sample Analysis

The limit of detection (LOD), 0.38 μg/L, was obtained by 12 measurements of a blank solution, and calculated based on three times the standard deviation of the blank measurements. This LOD is equivalent to 0.01μg/g in solid samples, assuming a sample weight of 0.5 g. The relative LOD for germanium is better than that by ETAAS (0.8 μg/L, assuming 20 μL sampling volume) and that by ICP-AES (20 μg/L). It should be pointed out that the instrumental and the running costs of the HG-AFS are much lower than ICP-AES or ETAAS. The six-point calibration curve can be linear, at least, up to 100 μg/L, with a correlation coefficient of 0.9995. The precision of the proposed procedure was 1.7%, based on the relative standard deviation of 12 measurements of a real sample (GBW07105). The method was used for the analysis of seven certified geological reference materials, with the analytical results listed in

Table 2. Analytical results of germanium for standard reference geological samples.

Sample no.	Certified (μg/g)	Found* (μg/g)	RSD (%)**	RE (%)***
GBW07305	1.4 ± 0.4	1.39 ± 0.02 (4)	1.4	− 1
GBW07310	0.4 ± 0.06	0.46 ± 0.03 (3)	6.5	15
GBW07404	1.9 ± 0.4	1.87 ± 0.07 (4)	3.5	− 2
GBW07103	0.98 ± 0.23	0.91 ± 0.07 (4)	7.3	− 7
GBW07105	3.1 ± 0.4	3.25 ± 0.07 (3)	2.1	5
GBW07234	0.93	0.89 ± 0.02 (3)	2.8	− 4
GBW07239	12.4	12.6 ± 0.23 (4)	1.8	2

*average ± standard deviation (number of measurements).
**RSD = relative standard deviation.
***RE = relative error.

Table 2. The relative standard deviation for the analysis of the seven samples was found to be from 1.4% to 7.3%. The Student's t-test at 95% confidence level shows that there is no significant difference between the certified values and the measured values by the proposed method. The relative errors are less than 7% for all the samples except for GBW07310, which has the lowest germanium concentration. Assuming that the maximum and minimum sample weights are 0.5 g and 0.1 g, respectively, and that 10 times dilution is allowed for samples of high germanium concentration, the method is suitable for the determination of germanium in geological samples with concentrations ranging from 0.01 to 100 μg/g, estimated from the linear range of the calibration curve.

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