Talanta 84 (2011) 122–126

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Germanium determination by flame atomic absorption spectrometry: An increased vapor pressure-chloride generation system

Murat Kaya, Mürvet Volkan*

Department of Chemistry, Faculty of Arts and Sciences, Middle East Technical University, 06531 Ankara, Turkey

A R T I C L E I N F O

Article history:
Received 22 September 2010
Received in revised form
13 December 2010
Accepted 19 December 2010
Available online 25 December 2010

Keywords:
Germanium
Germanium tetrachloride
Flame atomic absorption spectrometry
Vapor generation
Chloride generation

ABSTRACT

A new chloride generation system was designed for the direct, sensitive, rapid and accurate determination of the total germanium in complex matrices. It was aimed to improve the detection limit of chloride generation technique by increasing the vapor pressure of germanium tetrachloride ($GeCl_4$). In order to do so, a novel joint vapor production and gas–liquid separation unit equipped with a home-made oven was incorporated to an ordinary nitrous oxide–acetylene flame atomic absorption spectrometer. Several variables such as reaction time, temperature and acid concentration have been investigated. The linear range for germanium determination was 0.1–10 ng mL^{-1} for 1 mL sampling volume with a detection limit (3 s) of 0.01 ng mL^{-1}. The relative standard deviation (RSD) was 2.4% for nine replicates of a 1 ng mL^{-1} germanium solution. The method was validated by the analysis of one non-certified and two certified geochemical reference materials, respectively, CRM GSJ-JR-2 (Rhyolite), and GSJ-JR-1 (Rhyolite), and GBW 07107 (Chinese Rock). Selectivity of the method was investigated for Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ga^{3+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, and Zn^{2+} ions and ionic species of As(III), Sb(III), Te(IV), and Se(IV).

1. Introduction

In recent years, the interest in obtaining lower limits of detection for elements with industrial and biological significance like germanium has increased. Vapor generation methods have become very popular because of their high sample throughput capability and better sensitivity obtained when compared to conventional nebulization techniques.

Germanium is among the elements that can form volatile species such as hydrides and chlorides. The reduction of germanium in a solution to the volatile germane (GeH_4, bp, 88.5 °C) by sodium borohydride and the subsequent detection of germanium hydride is known as hydride generation. Germanium determination by hydride generation coupled to flame atomic absorption spectrometry (HG-AAS) [1–3], electrothermal atomic absorption spectrometry (HG-ETAAS) [4–10], and inductively coupled plasma optical emission spectrometry (ICP-OES) [11–13] has been extensively documented. Interference effects of volatile hydride forming elements [14,15] and transition metals [15] on germanium determination by hydride generation have also been reported.

Halide volatilization, as an alternative to cold vapor and hydride generation systems, allows the extension of gaseous sample introduction techniques in atomic spectroscopy [15–18]. The principle advantage of chloride generation (CG) over hydride generation (HG) is the dramatic suppression of liquid phase interferences [15,17,18]. Generation of volatile $GeCl_4$ was achieved by mixing the sample solution with either concentrated HCl [15,17] or a H_2SO_4/NaCl mixture [18] in discontinuous [17,18] or continuous [15] flow reactors.

Volatilization of germanium in the form of germanium tetrachloride at elevated temperature is a common process applied in the recovery of germanium from germanium-bearing residues and concentrates. Germanium tetrachloride can be distilled at 90–95 °C in a chlorinated environment from the concentrates dissolved in hydrochloric acid (ca. 5–6 M HCl). Besides, dry and powdered concentrates which are heated to high temperatures (ca. 350 °C) can further be subjected to chlorine gas for the formation of the volatile chlorides of germanium. Skogerboe et al. have been pioneers of the application of chloride generation in the determination of germanium with microwave induced plasma atomic emission spectrometry [19]. They used elevated temperature volatilization of chlorides of seven elements including germanium as a sample introduction technique for their determination in atomic spectrometry. They developed a device in which the sample solutions were first dried and then heated at 850 °C for 30 s; afterward the air–HCl stream was passed over the hot sample residue surface and the germanium tetrachloride formed was sent to the microwave induced plasma atomizer. The detection limit obtained using 2 mL of sample was reported as 30 ng mL^{-1}. Lately, four studies have reported

---

[*] Corresponding author. Tel.: +90 312 2103228; fax: +90 312 2103200.
E-mail address: murvet@metu.edu.tr (M. Volkan).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.12.029

the determination of germanium via vaporization of $GeCl_4$ utilizing sensitive atomic fluorescence with an argon–hydrogen flame [17] and inductively coupled plasma optical emission spectrometric (ICP-OES) techniques [15,18,20].

At ordinary temperature and pressure, germanium tetrahydride (GeH_4) is in gas form whereas germanium tetrachloride is present as vapor. Germanium tetrachloride, with a boiling point of 84 °C, was considered sufficiently volatile at room temperature and consequently recent studies on chloride generation have been carried out at ambient temperature similar to hydride generation. Detection limits reported so far [15,17,18] for the determination of germanium through chloride formation at room temperature are in the range of 3.0–0.25 ng mL^{-1}.

The aim of the present study was to improve the detection limit of the chloride generation technique by increasing the vapor pressure of germanium tetrachloride. The vapor pressure of $GeCl_4$ is only 0.1 atm at 27 °C [14] and it can simply be improved 10-fold by heating the solution to its boiling point temperature [21]. The stability of the plasma can easily be affected by the large amount of gases produced during chloride generation at high temperature [20]. Regarding its inherent stability and robustness, flame is much more convenient compared to plasma as an atomizer for vapor generation systems. The proposed method was based on the generation of germanium tetrachloride at 80 °C by concentrated hydrochloric acid in an intermittent system and subsequent introduction of the gaseous analyte through the nebulizer to a nitrous oxide–acetylene flame for AAS detection. A new vapor generation–gas separation unit was designed and the variables affecting vapor generation were optimized. The analytical capability of the chloride generation-FAAS system for the determination of germanium at trace levels was investigated.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical reagent grade unless otherwise stated. De-ionized water obtained from a Millipore Elix 5 water purification system was used for the preparation of sample and standard solutions. Stock AAS solutions of Ge (IV) and potential interfering metal ion solutions were purchased from Aldrich as 1000 mg L^{-1} solutions. For the measurements, samples, standards, and standards containing interfering ions were all prepared in 6 M HCl. Since HCl is a corrosive reagent, specific care should be taken when handling all solutions.

2.2. Instrumentation

A Philips PU9200 flame atomic absorption spectrometer equipped with a deuterium background correction system was used for the measurement of the germanium signal. Nitrous oxide–acetylene flame was used for AAS detection. Fine tune the alignment of the flame was done by aspirating the highest concentration standard into the flame. The rate of fuel and burner position (horizontal and vertical) were adjusted until a maximum absorbance was observed. Besides, the pink color of the flame can be considered as a visual indication of the correct gas combination. The optimum flow rates of N_2O and C_2H_2 and position of burner head were used throughout all the experiments. N_2O and C_2H_2 flow rates used in the measurements were given in Table 1. The possibility of flashback problem is more severe in case of nitrous oxide–acetylene flame. It is advised to obey all the regulations stated in the manual of the instrument regarding ignition procedures and operating conditions for the nitrous oxide–acetylene flame strictly. The instrument should not be left unattended unless the flame is extinguished. A germanium hollow cathode lamp with an analytical wavelength of 265.1 nm was used as the light source. The lamp's current was 20 mA and bandpass was 0.5 nm. The intermittent manifold used to generate the volatile $GeCl_4$ was based on the use of a home-made oven, mixer, cylindrical reaction chamber (10 cm in length and 40 cm^3 in volume), and a Gilson Minipuls peristaltic pump as shown in Fig. 1. The glass cylindrical reaction chamber design had 4 valves. The sample and reagent mixture was loaded into the system via valve 1 and the carrier argon gas via valve 2. Valve 3 was used for the connection to the atomizer and valve 4 was utilized for the waste. The reaction chamber provides efficient mixing and heating of the sample and 12 M HCl, separation of the $GeCl_4$ from the liquid, mixing of the gaseous product with the carrier gas, and discarding of the waste. The glass reaction chamber is a compact system and only the glass valves are prone to leakage. So, the valves were strengthened by using silicon wax and teflon gaskets. The condition of the valves was inspected frequently and the gasket parts were changed periodically. The heater (150 W) part of the oven was made of ceramic and a copper wire, and was controlled with a GE-XDD1DC096 type digital controller. A PT 100 type thermocouple was used for screening the temperature of the surface of the reaction chamber. The variation in temperature was about ±3 °C. For sample digestion a Milestone Ethos Plus Labterminal 800 microwave oven was used.

Table 1
Optimized parameters used for the determination of $GeCl_4$.

Sample flow-rate	10 mL min^{-1}
Reagent flow-rate	10 mL min^{-1}
Sample acidity	6 M HCl
Reagent solution	12 M HCl
Reactor volume	40 cm^3
Carrier gas flow-rate (Ar)	400 mL min^{-1}
Reaction period	1 min
N_2O-C_2H_2 (flame) flow-rate	4.8–2.1 L min^{-1}
Reaction temperature	80 ± 3 °C
Tubing size (sample and reagent)	3 mm (id)
Tubing size (nebulizer)	0.056 mm (id)

2.3. Procedure

Sample solution and 12 M HCl were pumped separately with a flow rate of 10 mL min^{-1} and merged just prior to valve 1 of the

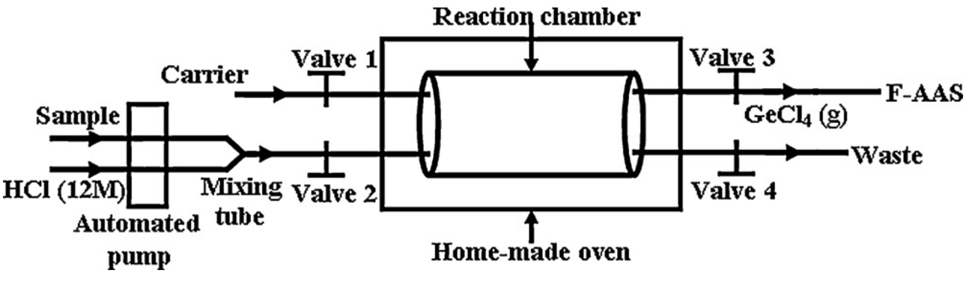

Fig. 1. Schematic representation of the chloride generation system used for Ge determination.

reaction chamber; during sampling, only valve 1 was in the open position. In order to determine the optimum time (6 s), the optimum flow rate of the peristaltic pump for a specific tubing size was determined and fixed. A specific volume of solution was introduced into the system and the period of time necessary for the solution to reach the reactor was measured with a chronometer at this flow rate. This measurement was repeated several times with different volumes of solutions in order to construct a conversion table for finding the precise time required to deliver the necessary volume. The condition of the tubing was inspected frequently and changed periodically. An automated system was used to stop the pump after 6 s. At the end of the sampling period (6 s), the pump was switched off, valve 1 was closed, and the mixture was kept in the closed reaction chamber for 1 min. Afterwards, the $GeCl_4$ gas that accumulated in the upper part of the reactor was swept to the nebulizer by argon carrier gas by opening valves 2 and 3 only. After the measurement period, the carrier gas was also used to discard the waste from the cell and to purge the whole cell for 30 s in order to dehumidify the reactor and the tubing connected to the nebulizer; for this stage, only valves 2 and 4 were open. The flow rate limit of the flow meter used in the measurements was in the range of 100–600 mL min^{-1} with 100 mL min^{-1} increments. Argon gas flow was examined within this range and 400 mL min^{-1} was obtained as the optimum value. At higher carrier gas flow rates (500, 600 mL min^{-1}) signal intensity was decreased probably owing to the dilution effect. However, even at these flow rates the flame was stable. In fact the robustness of the flame (even nitrous oxide–acetylene flame) compared to plasma makes it more suitable to gaseous sample introduction. For FAAS measurements, a 5 cm slot nitrous oxide–acetylene burner head was used. The optimized conditions are summarized in Table 1.

2.4. Optimization of HCl concentration

To investigate the effect of HCl concentration on germanium tetrachloride generation, HCl concentration of a 4 ng mL^{-1} germanium solution was varied in the range of 3–10 M while keeping the acidity of the reagent solution constant at 12 M. Similarly, the variation in the signal of 4 ng mL^{-1} germanium solution prepared in 6 M HCl was examined with variation in the HCl concentration of the reagent solution in the range of 8–12 M.

2.5. Sample preparation

0.200 g of rock sample was transferred into a PTFE vessel, and an acid mixture of 5 mL of H_2SO_4, 5 mL of HF, and 10 mL of HNO_3 was added with swirling in order to obtain a homogeneous solution. The microwave digestion procedure applied was as follows: 500 W for 5 min at 100 °C, 500 W for 5 min at 150 °C, 600 W for 5 min at 200 °C, and 700 W for 60 min at 200 °C. Then 30 mL of 5% boric acid solution was added to the digested samples in order to get rid of the effect of the hydrofluoric acid in the final solution. Finally, the samples were diluted to 100 mL and each sample was run in triplicate.

3. Results and discussion

3.1. Improvement of the chloride generation system

In this study, a similar flow system to those utilized in the ambient temperature volatilization of germanium tetrachloride was used [15,17,18] for the introduction of germanium to the atomizer. Hydrochloric acid was used as the chlorinating reagent and the vapor formed was sent to the nitrous oxide–acetylene flame. In the earlier stages of the study, a heated coil reactor attached to a gas liquid separator was used for the production of the germanium tetrachloride. However, due to the condensation of $GeCl_4$ gas produced on the surface of the gas–liquid separator, a new cylindrical glass chloride generation separation unit was designed as shown in Figs. 1 and 2. A laboratory-made temperature controlled mini oven was used to maintain a constant temperature at the entire surface of the reactor. In this system, the volatilized gas was separated from the liquid during heating and it was easily swept to the atomizer with an argon gas flow passing through the upper part of the container. The large volume of the container (40 mL) provided sufficient space for the accumulation of the gas formed over the solution. Hence, the chloride generation–separation unit also acted as a collection unit. All the parameters affecting germanium tetrachloride generation were optimized to achieve the best sample introduction efficiency. Reaction chambers of different shapes and volumes (10–60 cm^3) were designed and examined during the studies. The optimum signal was obtained with the reaction chamber volume of 40 cm^3.

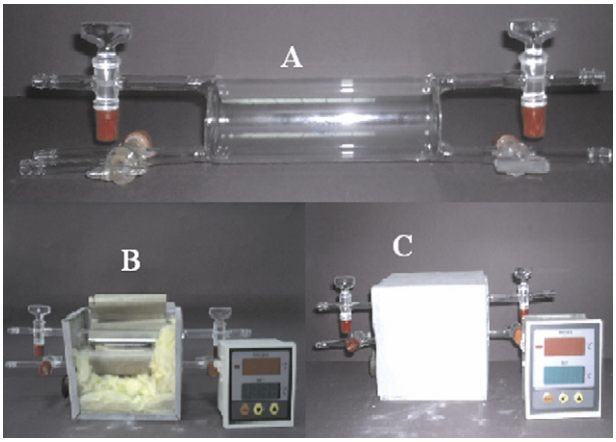

Fig. 2. Chloride generation system used in this work. (A) Cylindrical glass chloride generation separation unit, (B) inside view of the laboratory-made oven, and (C) outside view of the chloride generation system.

3.2. Optimization of the conditions for the volatilization of germanium tetrachloride

3.2.1. The effect of HCl concentration on the volatilization of germanium tetrachloride

The importance of HCl concentration in chloride generation systems is well documented in previous publications [15,17]. In these studies, the HCl concentration of the standard solution was varied in the range of 3–9 M and it was concluded that if the concentration of HCl in reagent solution was kept at 12 M the maximum signal was obtained with a solution prepared in 6 M HCl. A continuous decrease in signal has been reported at HCl concentrations higher than 6 M, which was explained by the loss of analyte during sample preparation due to the volatility of $GeCl_4$ even at ambient temperature. On the other hand, only a small fraction of Ge was found to be present in germanium tetrachloride form at HCl concentration levels less than 5 M [15,17]. In order to investigate the effect of HCl concentration on the volatilization of $GeCl_4$ at high temperature (80 °C), the HCl concentrations in the sample (or standard) and the reagent solutions were optimized. Optimum signals were obtained when the HCl concentrations in the sample and reagent solutions were 6 M and 12 M, respectively. Therefore, 9 M HCl concentration in the final solution, which resulted in the highest $GeCl_4$ vapor production, was adopted as the optimum HCl concentration in this study.

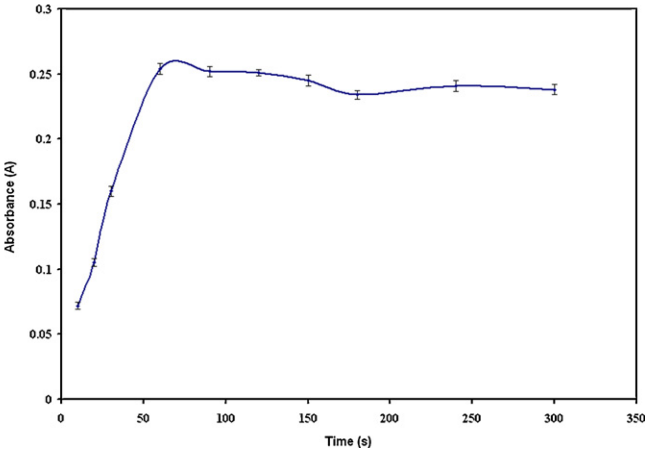

Fig. 3. Effect of reaction period on the 4 ng mL^{-1} germanium signal.

3.2.2. *Effect of reaction period on $GeCl_4$ formation*

The reaction period was defined as the time interval in which the mixture of germanium and HCl solution was heated in the reaction chamber. The optimum reaction period for the formation of germanium tetrachloride was investigated in the range of 10 s to 5 min using 4 ng mL^{-1} germanium solutions. As can be seen from Fig. 3, the signal reaches a plateau after 1 min of heating. Thus, 1 min was chosen as the reaction period throughout this study.

3.2.3. *Effect of reaction temperature on $GeCl_4$ formation*

The experiments performed at room temperature resulted in quite low signals; therefore, it was decided to investigate the effect of reactor temperature on germanium tetrachloride generation. The temperature settings of the mini oven were altered in the range of 30–100 °C for 4 ng mL^{-1} germanium solution. The results are shown in Fig. 4. As expected, the enhancement in the signal became steady after 80 °C. Therefore, a reactor temperature of 80 °C was chosen. However, lower temperatures leading to depressed sensitivities can also be used where higher concentrations are concerned.

3.3. *Signal characterization*

The amount of Ge (IV) volatilized could be related to the area and/or peak height of the signal. Peak area and peak height were examined during the preliminary work. The precision of peak height measurements was better than that of area measurements. Afterwards peak widths at half maximum height of the signals were evaluated and it was found that they were also very reproducible. Only the area corresponding to the tailing part of the signal was showing small variations as displaced in Fig. 5. Presumably the complete removal of the $GeCl_4$ gas from the reactor was taking place at different time intervals. Therefore, peak height was chosen as the analytical response for further experiments.

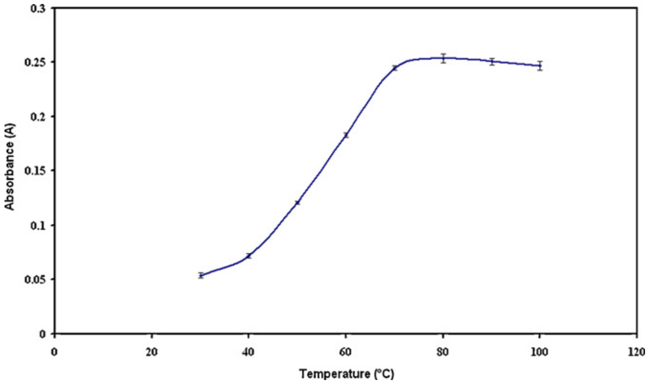

Fig. 4. Effect of reactor temperature on the 4 ng mL^{-1} germanium signal.

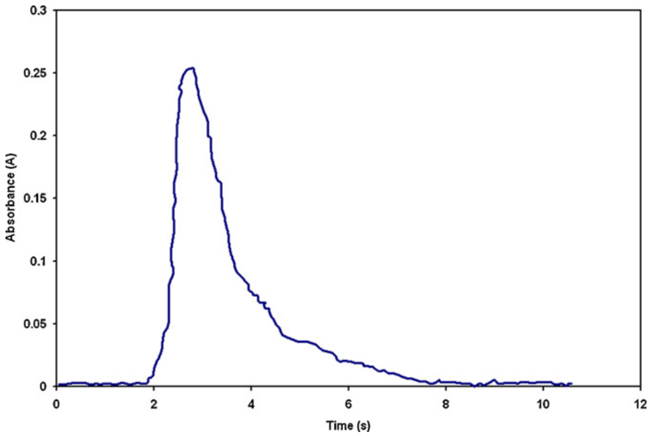

Fig. 5. A sample signal obtained by the introduction of a germanium solution containing 4 ng mL^{-1} Ge.

3.4. *Analytical performance characteristics*

Figures of merit were evaluated using aqueous germanium standard solutions under the optimized conditions. Blank corrected data were used in all calculations. The analytical response was found to be linear between 0.1 ng mL^{-1} and 10 ng mL^{-1} Ge (IV) with the slope of 0.0599 (absorbance/(ng mL^{-1})) and R^2 of 0.998. The relative standard deviation obtained for nine independent replicates of 1 ng mL^{-1} germanium standard solution was 2.4% and the detection limit (3 s) of the chloride generation-nitrous oxide acetylene FAAS system was 0.01 ng mL^{-1}. The mean absorbance for blank measurements was 0.007 A (for 10 replicates).The total time required for one cycle was 3 min. So measurement frequency was 20 samples per hour. The chloride generation system proposed in this study could be coupled to other more powerful but fragile plasma type atomizer systems (ICP-OES, ICP-MS) through, for example, the use of headspace SPME sampling as proposed by Guo et al. [20]. Considering the detection limits obtained by other sensitive systems, such as electrothermal atomizer ETA [22], hydride generation – ETA [9], and direct ICP-MS [23] methods for the determination of germanium, the proposed method provides a very low detection limit with a normal nitrous oxide–acetylene flame atomizer.

3.5. *Evaluation of interferences*

The selectivity of the method was determined by studying the effect of potential interfering ions on the Ge signal obtained with the chloride generation AAS system. All tests were carried out under optimum operating conditions. The results are depicted in Table 2. Variations over ±5% in the analytical signal of 4 ng mL^{-1} Ge (averages of the triplicate determination) in the presence of foreign ions were considered to indicate interference. The boiling points of some of the thermally stable metal chlorides like germanium are as follows: $AsCl_3$, 130 °C; $SbCl_3$, 223 °C; $SnCl_2$, 603 °C; $SnCl_4$, 114 °C. The possibility of gas phase interferences from $AsCl_3$ and $SnCl_4$ in the heated system used in this study was investigated. As can be seen from Table 2, at an interferent to analyte mass ratio of 50,000, no interference on germanium signal was observed.

It has been stated by Guo and Guo [17] that chloride generation is really an interference free method in the presence

Table 2
Effect of potential interferents on the determination of 4 ng mL^{-1} Ge by chloride generation-FAAS.

Variation in Ge signal (%)		
Element	Con. (mg L^{-1})	Chloride Generation
As^{III}	50	+2
Cd^{II}	50	−1
Co^{II}	500	+1
Cu^{II}	500	−2
Fe^{III}	500	+1
Ga^{III}	50	+1
Hg^{II}	50	−1
Ni^{II}	500	+2
Pb^{II}	50	+3
Sb^{III}	50	+2
Se^{IV}	50	+3
Sn^{II}	50	−2
Te^{IV}	50	−2
Zn^{II}	500	+2

Ge concentration was 4 ng mL^{-1}. Negative and positive signs mean decrease or increase in the signal, respectively.

Table 3
Determined concentration of Ge in certified and noncertified reference materials.

Sample	Ge concentration (μg g^{-1})
Rock (GBW 07107)[a]	
Ge (found)	2.9 ± 0.1
Ge (certified)	3.1
Rock (GSJ-JR-1)[a]	
Ge (found)	2.1 ± 0.1
Ge (certified)	1.88
Rock (GSJ-JR-2)[b]	
Ge (found)	1.9 ± 0.1
Ge (noncertified)	1.88

[a] Student's *t*-test was applied at 95% confidence level and no differences were observed for Rock (GBW 07107) and Rock (GSJ-JR-1) samples (*N* = 3).

[b] Student's *t*-test was applied at 80% confidence level and no difference was observed for Rock (GSJ-JR-2) sample (*N* = 3).

of well-known interfering species of hydride generation. Similar behavior was also observed in this study. Hence, the method is expected to be suitable for the trace analysis of a diverse range of samples.

3.6. *Application of the chloride generation method to the analysis of real samples*

The applicability of the proposed method was checked by the analysis of one non-certified and two certified geochemical reference materials: CRM GBW 07107 (Chinese Rock), GSJ-JR-1 (Rhyolite), and GSJ-JR-2 (Rhyolite). The results given in Table 3 were in good agreement with the certified values. The concentrated acids used in the digestion process were further examined for their effect on the signal by comparing the blank and standard solutions in the presence and absence of these acids. No difference was observed for the signals of blank and standard solutions in either case and so it was concluded that the acids used for digestion had no effect on the signal.

4. Conclusion

The present investigation was undertaken with the objective of improving the sensitivity and detection limit of the chloride generation method through the use of elevated temperature volatilization of germanium tetrachloride in an intermittent flow system for the direct determination of germanium in complex matrices. A detection limit (0.01 ng mL^{-1}) at least an order of magnitude lower compared to that of ambient temperature chloride generation systems reported so far (3.0–0.25 ng mL^{-1}) was achieved. The novel chloride generation–separation unit investigated provides a simple, rapid, sensitive, and reliable means of germanium determination using an ordinary nitrous oxide–acetylene flame atomizer.

The application of the method to a variety of geological samples clearly demonstrated its accuracy. The precision expressed as the relative standard deviation for nine replicates of a 1 ng mL^{-1} germanium solution was found to be 2.4%. The chloride generation system proposed in this study can also be coupled to other more powerful but fragile plasma type atomizer systems (ICP-OES; ICP-MS) through, for example, the use of headspace SPME sampling as proposed by Guo et al. [20] to result in further enhanced detection limits.

Acknowledgments

The authors would like to express sincere thanks to Prof. Dr. O. Yavuz Ataman from Middle East Technical University Chemistry Department for his valuable discussions. This study was funded by the Middle East Technical University (METU-BAP).

References

[1] J.R. Castillo, J. Lanaja, J. Aznarez, Analyst 107 (1982) 89.
[2] A.E. Boyukbayram, M. Volkan, Spectrochim. Acta, Part B 55 (2000) 1073.
[3] K. Jin, H. Terada, M. Taga, Bull. Chem. Soc. Jpn. 54 (1981) 2934.
[4] G.A. Hambrick III, P.N. Froelich Jr., M.O. Andreae, B.L. Lewis, Anal. Chem. 56 (1984) 421.
[5] M.O. Andreae, P.N. Froelich Jr., Anal. Chem. 53 (1981) 287.
[6] H.O. Haug, J. Chonghua, J. Anal. Atom. Spectrom. 5 (1990) 215.
[7] B. Hilligsøe, J.E.T. Andersen, E.H. Hansen, J. Anal. Atom. Spectrom. 12 (1997) 585.
[8] N. Zhe-Ming, H. Bin, J. Anal. Atom. Spectrom. 10 (1995) 747.
[9] H.A. Roels, J.P. Buchet, J. Environ. Monit. 3 (2001) 67.
[10] M.A. Anwari, H.U. Abbasi, M. Volkan, O.Y. Ataman, Fresenius J. Anal. Chem. 355 (1996) 284.
[11] M. Grotti, C. Lagomarsino, R. Frache, J. Anal. Atom. Spectrom. 20 (2005) 1365.
[12] E. Bolea, F. Laborda, J.R. Castillo, R.E. Sturgeon, Spectrochim. Acta, Part B 59 (2004) 505.
[13] C. Rigby, I.D. Brindle, J. Anal. Atom. Spectrom. 14 (1999) 253.
[14] P. Smichowski, S. Farías, Microchem. J. 67 (2000) 147.
[15] S. Farías, P. Smichowski, J. Anal. Atom. Spectrom. 14 (1999) 809.
[16] S. Tesfalidet, K. Irgum, Anal. Chem. 60 (1988) 2031.
[17] X.-w. Guo, X.-m. Guo, Anal. Chim. Acta 330 (1996) 237.
[18] A.L. Molinero, A. Villareal, D. Andia, C. Velilla, J.R. Castillo, J. Anal. Atom. Spectrom. 16 (2001) 744.
[19] R.K. Skogerboe, D.L. Dick, D.A. Pavlica, F.E. Lichte, Anal. Chem. 47 (1975) 568.
[20] X. Guo, Z. Mester, R.E. Sturgeon, Anal. Bioanal. Chem. 373 (2002) 849.
[21] R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 52nd ed., CRC Press, New York, 1971–1972, p. B93.
[22] D.Q. Xu, G.P. Guo, J. Anal. Atom. Spectrom. 10 (1995) 753.
[23] F.H. Ko, M.H. Yang, J. Anal. Atom. Spectrom. 11 (1996) 413.