DETERMINATION OF GERMANIUM AT TRACE LEVELS BY CHLORIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

DETERMINATION OF GERMANIUM AT TRACE LEVELS BY CHLORIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY

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Trace amounts of germanium is determined by flame atomic absorption spectrometry by utilizing the vaporization of germanium tetrachloride. Using a continuous flow reactor, sample solution is mixed with concentrated hydrochloric acid and heated to $80^{\circ}C$ to form volatile germanium tetrachloride which can be subsequently sent to N_2O-C_2H_2 flame AAS. The necessary conditions for the volatilization of germanium tetrachloride are investigated in detail and the applicability of the method for the determination of trace amounts of germanium in real samples and standard reference materials are presented. Detection limit of the method, based on 3s, was 0.034 ng mL^{-1} using a sample of 1 mL. The precision was 0.3 %, expressed as the relative standard deviation for a germanium concentration of 1 ng mL^{-1}. Owing to the high selectivity of the proposed method, no interference effect was observed.

Keywords: Germanium; Germanium tetrachloride; Vapour generation; Atomic absorption spectrometry

ÖZ

ESER MİKTARLARDAKİ GERMANYUMUN KLORÜR OLUŞTURMA ATOMİK ABSORPSİYON SPEKTROMETRİ İLE TAYİNİ

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Eser miktarlardaki germanyum, germanyum tetra klorürün buharlaştırılması yoluyla alevli atomik absorpsiyon spektrometri kullanılarak tayin edilmiştir. Sürekli akış reaktörü kullanılarak, derişik hidroklorik asit çözeltisiyle karıştırılmış, örnek çözelti $80^{\circ}C$ ye ısıtılarak oluşan uçucu germanyum tetraklorür N_2O-C_2H_2 alevli AAS'ye gönderilmiştir. Germanyum klorürün buharlaşması için gerekli şartlar ayrıntılı olarak incelenmiş ve yöntemin gerçek örneklerde ve standart referans maddelerde bulunan eser miktarlardaki germanyumun tayinine uygulanabilirliği gösterilmiştir. Yöntemin gözlenebilme sınırı, 3s baz alınarak, 0.034 ng mL^{-1} olarak bulunmuştur. 1 ng mL^{-1} germanyum derişimi için bulunan tekrarlanabilirlik, bağıl standart sapma olarak 0.3 % dir. Önerilen yöntemin yüksek seçiciliğine bağlı olarak hiçbir girişim etkisi gözlenmemiştir.

Anahtar Sözcükler: Germanyum; Germanyum tetraklorür; Buhar oluşturma; Atomik absorpsiyon spektrometri

To My Family

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TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

CHAPTER 1

INTRODUCTION

1.1 Germanium

1.1.1 History of Germanium

Germanium is an element whose existence was predicted by Mendeleev in 1871. He predicted that the unknown element germanium should resemble silicon in its properties. He suggested the name ekasilicon (symbol Es). His predictions for the properties of germanium were remarkably close to the reality. Germanium was discovered in a mineral called argyrodite by Clemens Alexander Winkler in 1886 [1].

1.1.2 Physical and Chemical Properties of Germanium and its Compounds

Germanium is a brittle silver-gray element of group IV of the periodic table with an atomic number of 32 and atomic weight of 72.60 g mol^{-1}.

It is considered to be an element with properties between those of semimetals and metals. It can form both anions and cations [2].

In its compounds germanium the most common oxidation numbers of germanium are 2^+, 4^+ and 2^-. It is known that, divalent compounds tend to be less stable than the tetravalent ones [3]. The melting points of germanium are; 937.4°C and 2830°C, respectively [3].

The element is a gray-white metalloid, and in its pure state is crystalline and brittle, retaining its luster in air at room temperature. It is a very important semiconductor material [4].

1.1.3 Sources and Abundances

The element is commercially obtained from the dusts of smelters processing zinc ores, as well as recovered from combustion by-products of certain coals. A large reserve of the elements for future uses is insured in coal sources [5, 6]. Basic germanium minerals and basic ores from which germanium is produced are shown in Table 1.1 and Table 1.2.

Table 1.1 Basic Germanium Bearing Minerals

NAME	COMPOSITION	% GERMANIUM	COUNTRY
Argyrodite	$4Ag_2S.GeS_2$	5-7	Germany
Canfieldite	$4Ag_2S.SnS_2$	1.8	Bolivia
Enargite	Cu_3AsS_4	1.0	Western US
Germanite	$7CuS.FeS.GeS_2$	5-10	Southwest Africa
Renierite	$(Cu,Fe,Ge,As,)_xS_y$	5-7	Congo Republic
Ultrabasite	$(Pb,Ag,Ge,Sb)_xS_y$	4.0	Southwest Africa

Table 1.2 Basic Ores from Which Germanium is Produced

ORE	LOCATION	% GERMANIUM	NOTE
Sphalerite	United States	0.005-0.015	Ge present as impurity
Zinc sulfide	United States	0.001-0.01	Ge present as impurity
Pb-Zn-Cu	Southwest Africa	0.015	As germaniete and renierite
Cu-Zn Sulfides	Congo Republic	0.01	As renierite

1.1.4 Uses of Germanium and Its Toxicology

When germanium is doped with arsenic, gallium or other elements, it is used as a transistor element in thousands of electronic applications. The most common use of germanium is as a semiconductor. Germanium has many other applications including the use as an alloying agent, as a phosphor in fluorescent lamps, and as a catalyst [7].

Germanium and germanium oxide are transparent to the infrared and are used in infrared spectroscopies and other optical equipment, including extremely sensitive infrared detectors [8].

The high index of refraction and dispersion properties of its oxides have made germanium useful as a component of wide-angle camera lenses and microscope objectives [3].

The field of organogermanium chemistry is becoming increasingly important. Certain germanium compounds have low mammalian toxicity, but a marked activity against certain bacteria, which makes them useful as chemotherapeutic agents [5, 7-12].

Only germane, GeH_4, is considered as toxic, having a maximum time-weighed average of 8 hours safe exposure limit of only 0.2 ppm. The lethal dose median for GeO_2 is 750 mg kg^{-1} and that of germanium is

586 mg kg^{-1} [3]. The toxicity of specific germanium compounds usually considered more from the other part of the compound than from the germanium content. Germanium has no biological role but is said to stimulate the metabolism [12].

1.2 Vapor Generation Techniques

The generation of gaseous analytes and their introduction into different atomization cells provides an effective method for the determination of many elements. In this context, a variety of analytical methods using vapor generation are successfully employed with analytical purposes in atomic spectroscopy and a considerable number of papers published each year are devoted to this subject [13-16]. Several significant advantages over conventional pneumatic nebulization of samples are obtained.

The principal advantages can be summarized as follows:

1. The analyte transport efficiency is enhanced (approaching 100%) due to the elimination of the nebulizer/spray chamber assembly and a homogeneous vapor is delivered to the atomizer. This is of particular importance if it is compared to maximum analyte transfer efficiency not higher than 10% obtainable with a conventional nebulizer.

2. The analyte is removed from the matrix improving accuracy and an on-line preconcentration of the analyte is obtained.

3. The selectivity is higher due to a significant reduction of interferences.

4. Detection limits are lower, which is of particular interest in trace analysis and environmental studies.

5. Automation of methods can be easily achieved.

6. The possibility of speciation studies and couplings with different techniques are another advantages of vapor generation methods [16].

1.2.1 Hydride Generation

Derivatization with sodium tetrahydroborate has become the most popular method of gaseous sample introduction to atomization /excitation cells. Hydride generation (HG) was introduced around 1970 [16, 17] to overcome problems associated with the flame atomic absorption spectrometry (FAAS) determination of As and Se [16].

Dedina and Tsalev [18] classified the methods of hydride generation in two basic modes: direct transfer and collection.

Continuous flow (CF), flow injection (FI) and batch procedures are the direct transfer methods which are more used in research studies and routine analysis. On the other hand, cryotrapping methods have been more often used in speciation studies [19, 20].

Conventional acetylene-based flame systems, externally heated quartz T-tubes, heated graphite furnaces and plasmas are the atomization/excitation devices mostly used in combination with HG methods. A variety of analytical techniques have been coupled with HG methods [16].

Flame atomic absorption spectrometry (FAAS) was chosen by the majority of workers for its robustness, low instrumental and operative cost, possibility of automation, easy coupling with different techniques, as well as its availability in a great number of routine and research laboratories [16].

Among the most used combined approaches, electrothermal atomic absorption spectrometry (ETA-AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), direct current plasma (DCP), microwave induced plasma (MIP), capacitively coupled microwave plasma (CCP), direct current glow discharge and atomic fluorescence spectrometry (AFS) have been attempted in research laboratories [16].

The elements typically determined by HG are As, Bi [21], Ge, Pb [21, 22], Sb [22], Se, Sn and Te, as well as Cd and Hg (cold vapor generation) [16, 19, 21-24]. The determination of In [25], Tl [26], Cu [27] and Cd [21, 22, 28-31] by hydride generation has also been investigated. However, hydride generation is not free from interferences. The most important interference occurs with transition metals [32-34] which reduce (or eventually enhance) the analytical signal. Also concomitant effects (gas phase atomization interferences) with other elements capable of generating volatile hydrides are reported in the literature [16, 35-37]. Influence of the oxidation state (an advantage in speciation studies) and pH effects should also be considered [16].

The interferences associated with HG-AAS may be conveniently divided into three groups: spectral interferences, liquid-phase interferences and gas-phase interferences [14].

Spectral interferences are usually insignificant in this technique owing to the separation of the analyte from the matrix. Only background absorption may occur, owing to changes in the flame transparency that take place when hydride is purged into the flame. Even so, background correction is usually considered unnecessary for externally heated quartz tube atomization [38-41]

Liquid-phase interferences can occur in the liquid phase either during hydride formation or its transfer from the solution due to changes in the hydride release rate (release kinetic interferences) and/ or decrease in hydride release efficiency (release efficiency interferences).

Gas phase interferences are caused by an interferent in either volatile form or as a liquid spray. These interferences can occur on the surface or in the dead volume of the generator, the connecting tubing and/or the atomizer. They could have either direct effect (if observed only simultaneously with generation of the interferent) or a memory effect (if they persist after the remaining of the interferent generation). The usual source of interferences in the atomizer is other hydrides [14].

1.2.2 Halides (Chloride and Fluoride Generation)

Chloride and fluoride of metals and metalloids are the more convenient compounds used in derivatization processes. As, Sb, Ge, Se and Sn have volatile chlorides and this characteristic was used in the past to separate these elements from complex matrices. As an example, in 1923, Dennis and Johnson described the distillation of Ge as its tetrachloride from 6 M HCl. The possibility of vaporizing thermally stable metal chlorides is related to their boiling points. The boiling points of some of these analytes are shown in Table 1.3. Os, Pt and Ru can also be converted to volatile chlorides [17].

Methods based on the same principle were developed for many elements, using different approaches and analytical techniques. The formation of volatile species of Si, as a possible way to increase the sensitivity of their determination by ICP-AES, was studied by López Molinero [42].

Table 1.3 The Boiling Points of Some Metalloids Chlorides.

Analytes	Boiling Points
$GeCl_4$	84°C
$AsCl_3$	130°C
$SbCl_3$	223°C
$SnCl_2$	603°C

To lessen problems associated with the introduction of analytes to atomic spectrometers by continuous nebulization, Seeley and Skogerboe [43] used the halide conversion approach as a means of delivering non-volatile species to a direct current discharge for emission spectrometric measurements [44].

The total conversion of the species which undergo the reaction is expected. From this point of view, it is plausible to conclude that it is possible to vaporize thermally stable metal chlorides depending on their boiling points. According to the literature, there are more than 30 elements that can be determined by generating their volatile chlorides [44].

A low-cost method consisting of a chloride generator connected to FAAS was devised for determining Cd, Ni and Pb. The sample reacted with HCl (g) at an elevated temperature to give volatile chlorides which were transported to the atomizer using a carrier gas [16].

Silicon is another element that is susceptible to generate volatile species with hydrochloric acid under optimized generation conditions. Si was quantified in a high-purity material by the generation of $SiCl_4$ and subsequent introduction of the product into a graphite furnace for AAS determination [16].

Arsenic is one of the most studied elements in analytical chemistry due to its toxicological and environmental effects. The literature based on the hydride generation of As is larger than that devoted to many other elements. In spite of that, problems related to interferences are not solved. The determination of As as its volatile chloride offers the possibility to overcome this problem without losing sensitivity [16]. Tesfalidet and Irgum [45] developed a sensitive and selective method based on the evolution of $AsCl_3$ from trivalent As in solution by concentrated HCl.

1.3 Analytical Techniques for Determination of Germanium

1.3.1 Atomic Absorption Spectrometry

1.3.1.1 Flame Atomic Absorption Spectrometry

Flame AAS methods are not sensitive enough for the determination of germanium due to its tendency to form very stable oxide species, which prevents the efficient production of germanium atoms. A sensitivity of 2.5 μg mL^{-1} and detection limit of 1.0 μg mL^{-1} Ge were obtained with a nitrous oxide-acetylene flame [46].

Amos and Willis used different types of flames for the atomization of germanium [47]. By fuel-rich air-acetylene flame and air-hydrogen flame the sensitivity was found only as 120 μg mL^{-1}. By using nitrogen-oxygen-acetylene and nitrous oxide-acetylene flames sensitivities reached to 5.5 μg/mL and 1.5 μg mL^{-1} respectively.

Using a (1+1) water-acetone solvent system, the limit of detection was 0.5 μg mL^{-1} in nitrous oxide-acetylene flame system [48].

1.3.1.2 Electrothermal Atomic Absorption Spectrometry (ETAAS)

ETAAS is one of the most common methods for the determination of germanium. Johnson, West and Wagnall [49] used the carbon filament reservoir and graphite tube for the determination of germanium. However, the carbon filament technique was not applicable due to the inefficient atomization. The detection limit obtained by using a graphite tube is 15 ng mL^{-1}. Burns and Dadgar [50] used carbon furnace atomization for the determination of germanium in organogermanium compounds. Zhang-Li, Zhe-Ming and Xiao-Quan [51] used graphite tube with hydride generation for in-situ concentration of germanium. Natural waters containing germanium in pg mL^{-1} can be determined satisfactorily.

The determination of germanium by graphite-furnace atomic-absorption spectrometry (GFAAS) can suffer from low sensitivity and poor reproducibility due to loss of part of the germanium as GeO (starts to sublime at 1000°C), without undergoing atomization. Sohrin, Isshiki and Kuwamoto [52] eliminated the interferences caused by the formation of GeO, which improves the sensitivity, and obtained a detection limit of 2 ng mL^{-1}.

Studnick [53] studied effects of various acids and ammonium salts on the absorbance signal of germanium. Dittrich and Mandry [54] determined the germanium concentration in semiconductor materials by using several matrix modifiers in order to increase sensitivity.

Haug and Chonghua [55] obtained signals for germanium in ETAAS by using Pd or mixed Pd-Mg modifiers in dilute nitric acid solutions with a detection limit of 3 ng mL^{-1}.

Scleich and Henze [56] studied the effect of different kinds of modifiers to eliminate interferences for the determination of germanium with electrothermal atomic absorption spectrometry (ETAAS). The detection limit of this system was 20 ng mL^{-1}.

Interference effect of NaCl on the ETAAS determination of germanium was investigated and examined the performances of possible matrix modifiers such as Ni and Zn perchlorates and nitrates, nitric acid, and ammonium nitrate for the determination of germanium in matrices with high chloride content. This method was successfully applied to zinc plant samples, containing 8-15 % (w/w) NaCl [46].

1.3.2 Other Methods

Several techniques are being used for the determination of germanium in various matrices. Spectrophotometric determinations of germanium are usually based on the extraction of germanium and formation of its complexes with chromogenic reagents. 9-phenyl-2,3, 7-trihydroxy-6-fluorone (phenyl fluorone) is the most frequently used complexing reagent after extraction of germanium as germanium tetrachloride in different medium [57-60] or germanium can be separated from large amounts of zinc and sodium salts by coprecipitation with hydrous ferric oxide from an ammoniacal medium before complexation with phenyl fluorine [60]. Another extraction method, before spectrometric measurement of germanium, is the formation of molybdogermanate complexes by using of molybdogermanic acids with detection limits of 0.07 μg mL^{-1} and 1.2 μg mL^{-1} for two different studies [61, 62].

Nalini and Ramakrishna [63] obtained the detection limit 0.003 μg mL^{-1} for the spectrofluorometric determination of germanium in some geological and mineral sample. This method applied for the determination of germanium in soils, biological materials and natural waters.

Germanium can be determined polarographically, by the adsorption of Ge (IV) on mercury electrode in the form of catechol [64, 65] and pyrogallol [66] complexes with the detection limits of 1 ng mL^{-1} and 0.1 ng mL^{-1}, respectively.

Determination of germanium by neutron activation analysis is not common because of activation problems, short half-life of Ge and presence of manganese interferences.

Another frequently used method for germanium determination is the inductively coupled plasma atomic emission spectrometry (ICP-AES) due to the high sensitivity. Nadkarni and Botto [67] determined germanium in coal ash and fly ash by this method and with the use of a high-resolution spectrometer, which reduces the interferences. ICP-AES method was also be used for the determination of germanium in some plants and animals [68], food [69], human hair samples [70].

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) can also be used for germanium determinations with low detection limits. Fu-Hsiang Ko and Mo-Hsuing Yang [71] determined the concentration of germanium in urine and blood by ICP-MS with a detection limit of 0.07 ng mL^{-1}. Methylated germanium species were determined at sub parts per trillion levels by a combination of hydride generation with cold trap and ICP-MS [72].

Germanium was also determined by atomic emission spectrometric methods with detection limits of 0.1 ng mL^{-1} [73, 74].

The detection limits of the methods mentioned above for germanium determinations and detection limits of some preconcentration studies are given in Table 1.5 and 1.6 respectively.

Table 1.4 Detection Limits of Some Studies

Method	**Detection Limit (ng mL^{-1})**	**Reference No.**
Flame AAS	500	48
HGAAS	3.8	51
GFAAS	2.0	52
AFS	3.0	63
HG-ICP-AES	0.2	67
Spectrophotometry	3.0	46
Polarography	0.1	66
ICP-MS	0.07	71
MIP-HG	0.04	75

Table 1.5 Detection Limits Obtained from Some Methods Involving Preconcentration

Method	**Detection Limit ($pg\ mL^{-1}$)**	**Reference No.**
HG-GFAAS ($Pd(NO_3)_2$)	3.00 (10 mL sample)	55
DCP-HG	0.60 (1 L)	46
HG-GFAAS	0.15 (250 mL)	46
HG-ICP-MS	0.035 (7.5 mL)	74

HG: Hydride Generation
GF: Graphite Furnace
AFS: Atomic Fluorescence Spectrometry
ICP-AES: Inductively Coupled Plasma Atomic Emission Spectrometry
MS: Mass Spectrometry
MIP: Microwave Induced Plasma
DCP: Direct Current Plasma

1.4 Recent Literature Survey on Germanium Determination with Chloride Generation

Recently, three articles were reported on chloride generation (CG). The volatilization of germanium by its reaction with hydrochloric acid to produce germanium tetrachloride was explained. This compound with a boiling point of 84°C [75] can be considered sufficiently volatile to vaporize at ambient temperature.

In the first article Guo and Guo [76] reported on the volatilization of germanium tetrachloride and the determination of germanium by atomic fluorescence spectrometry. The vapor pressure of Ge tetrachloride is 0.1 atm at 21°C. This property was used to determine trace amounts of Ge by atomic spectrometry by using the vaporization of $GeCl_4$ at ambient temperature. Using an intermittent or continuous flow reactor, the sample solution was mixed with concentrated HCl to form volatile $GeCl_4$ which was subsequently introduced into an $Ar–H_2$ flame and determined by non-dispersive AFS.

In the second article, Farías and Smichowski [77] evaluated the analytical capabilities of the coupling of chloride generation (CG) with ICP-AES for the determination of Ge at trace levels. The selectivity of the method was evaluated by studying the effect of several elements on Ge signal with chloride and hydride generation using the same system. The results obtained showed that elements which are resulting in serious interferences for HG of Ge do not interfere when CG was used.

In the third article A Lopez-Molinero [78] carried out to generation of volatile germanium tetrachloride in a simple batch procedure based on the reaction between concentrated sulfuric acid and an aqueous halide solutions The analytical method shows an absolute detection limit of 0.6 ng for the injection of 200μL of sample solution. The precision expressed as the relative standard deviation was 3.2 %.

1.5 Aim of This Work

This study was undertaken to evaluate the analytical capabilities of coupling chloride generation with flame atomic absorption spectrometry for the determination of germanium at trace levels. The method was based on the generation of germanium tetrachloride at 80°C by concentrated hydrochloric acid in a continuous system and subsequent introduction of the gaseous analyte via the capillary tube of the flame AAS. After optimizing the conditions for $GeCl_4$ generation as well as the flame parameters, the method was applied for the determination of germanium in rock standard reference materials.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

i) (980 mg L^{-1} in 2% KOH) Ge (IV) solution: Aldrich. A series of standard solutions of germanium was prepared by the dilution of Ge (IV) stock solution.

ii) (1000 mg L^{-1}) Ge (IV) solution: Prepared by dissolving 0.1441 g of germanium dioxide (Aldrich) in 10 mL of 0.15 ppm of hot NaOH solution and diluting this solution to 100 mL with deionized water.

iii) (37%) Hydrochloric acid: extra pure, Merck

iv) (6 M) Hydrochloric acid solution: Prepared by diluting the (37%) hydrochloric acid (Merck).

v) (40%) Hydrofluoric acid: Aldrich

All other reagents were of analytical reagent grade. De-ionized water obtained from a Millipore water purification system was used for sample and standard preparations. All the glass and plastic wares were soaked in 10% HNO_3 for at least for 24 hours and then rinsed with de-ionized water. HCl is a corrosive reagent and should be handled with appropriate safety precautions to avoid personal damage and corrosion of the equipment.

2.1.1 Preparation of 6 M Germanium Standard Solutions

Necessary amount of Ge (IV) solution was placed in 100 mL volumetric flask. 50 ml of 12 M hydrochloric acid was added and the mixture was diluted to volume with water. The final concentration of hydrochloric acid was nearly 6 M. Care was taken to avoid the loss of germanium during the operation owing to its volatilization.

2.2 Apparatus

Philips PU 9200 Atomic Absorption Spectrometer was used for measurements at 264.9 nm resonance line of germanium with band pass of 0.5 nm. The results were printed by an Epson FX-850 printer connected to the spectrometer. A Pye Unicam hallow cathode lamp with a maximum current of 20 mA was used as radiation source. A Gilson Miniplus peristaltic pump was used for the carrying of the reagents with the flow-rate 10 mL min^{-1}. A Stuart Scientific Hotplate SH3 hot plate was used for heating the water bath and also special home made ovens were designed to heat the reaction chamber in System 3 and System 4.

Nitrous oxide – acetylene flame with a 50 mm burner slot was used for the atomization. The carrier gas was Argon. The instrumental parameters for the determination of germanium are summarized in Table 2.1.

Table 2.1 Instrumental Parameters Used for the Determination of Germanium.

Light Source	Germanium Hollow Cathode Lamp
Wavelength	264.9 nm
Band Pass	0.5 nm
Lamp Current	20 mA
Flame for Atomization	Nitrous Oxide – Acetylene
Burner Slot	50 mm

2.2.1 Chloride Generation System Designs

The chemical vaporization of germanium (IV) with chloride ions is described as a means of introducing gaseous germanium into a flame for determination of germanium at trace levels. The method is based on the generation of germanium tetrachloride by concentrated hydrochloric acid. Using a reaction chamber, the sample solution was mixed with concentrated hydrochloric acid solution to form volatile germanium tetrachloride. The $GeCl_4$ generated was swept out by Ar and introduced directly to the nebulizer.

The most important part of this work was to design an appropriate reaction chamber for $GeCl_4$ generation. For this purpose, four different chloride generation systems were designed respectively. The design of the reaction chamber directly affects the precision and the accuracy of the experiment. These four systems and the the reaction chambers in each system are explained below.

System 1

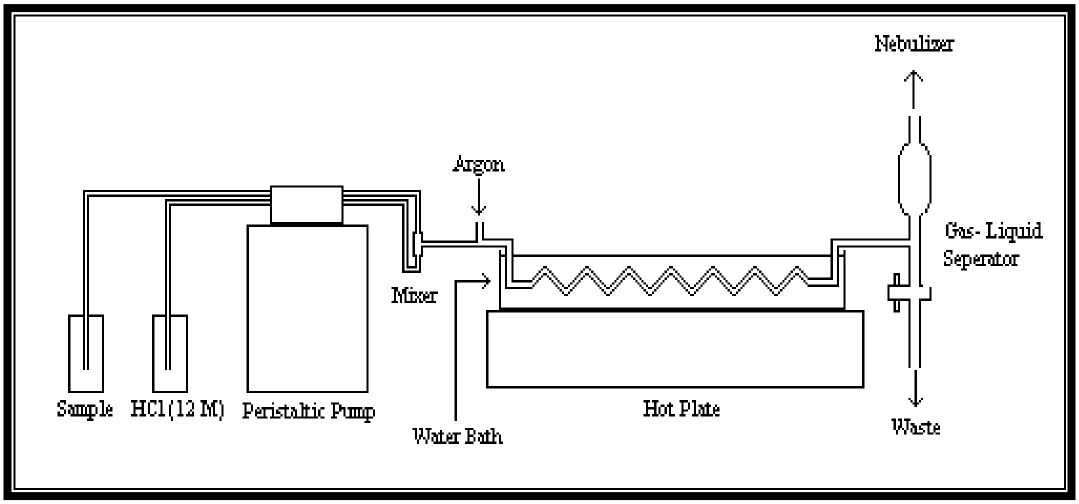

Fig. 2.1 Schematic Representation of Chloride Generation System 1

System 1 shown in Fig. 2.1 was composed of a peristaltic pump, a mixer, water bath, hot plate and a reaction chamber. The reaction chamber used in this system consisted of a reaction coil connected a gas-liquid separator. For this purpose, two reaction coils (Fig. 2.2) and three gas-liquid separators (Fig.2.3) were designed and examined. The reaction coils; knotted and coiled; were approximately 20 cm in length and 20 mL in volume.

The sample/ reagent mixture was passed to the coil in which germanium tetrachloride generation took place. Then by the use of carrier gas, the formed germanium tetrachloride was sent to the flame through the gas-liquid separator.

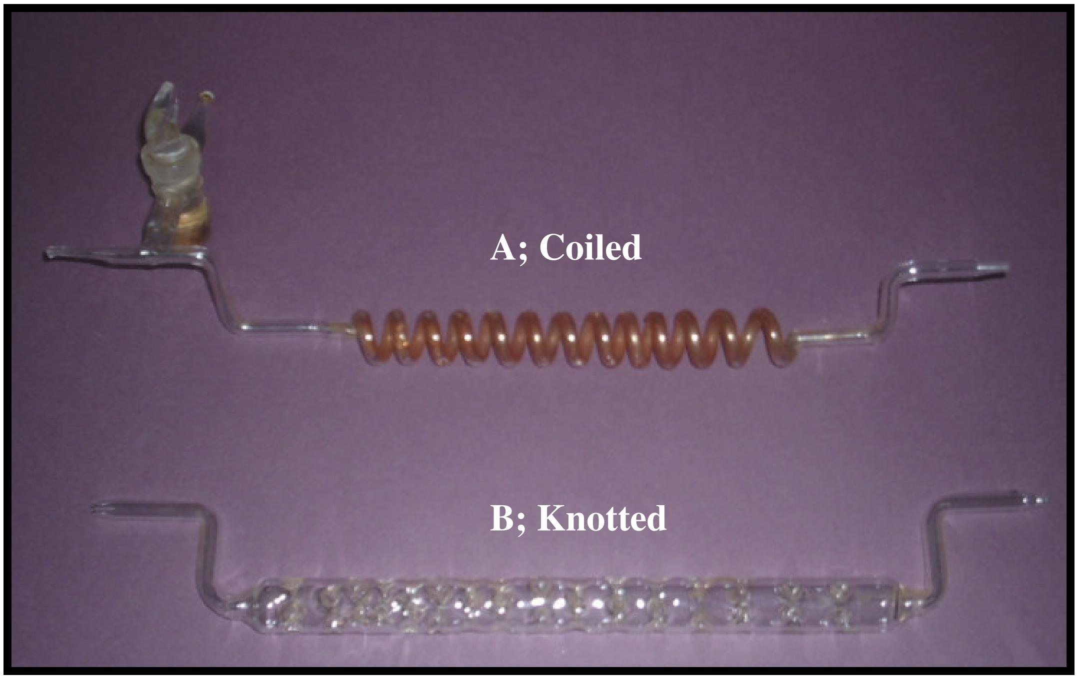

Fig. 2.2 The Reaction Coils Used in System 1 (Coiled and Knotted).

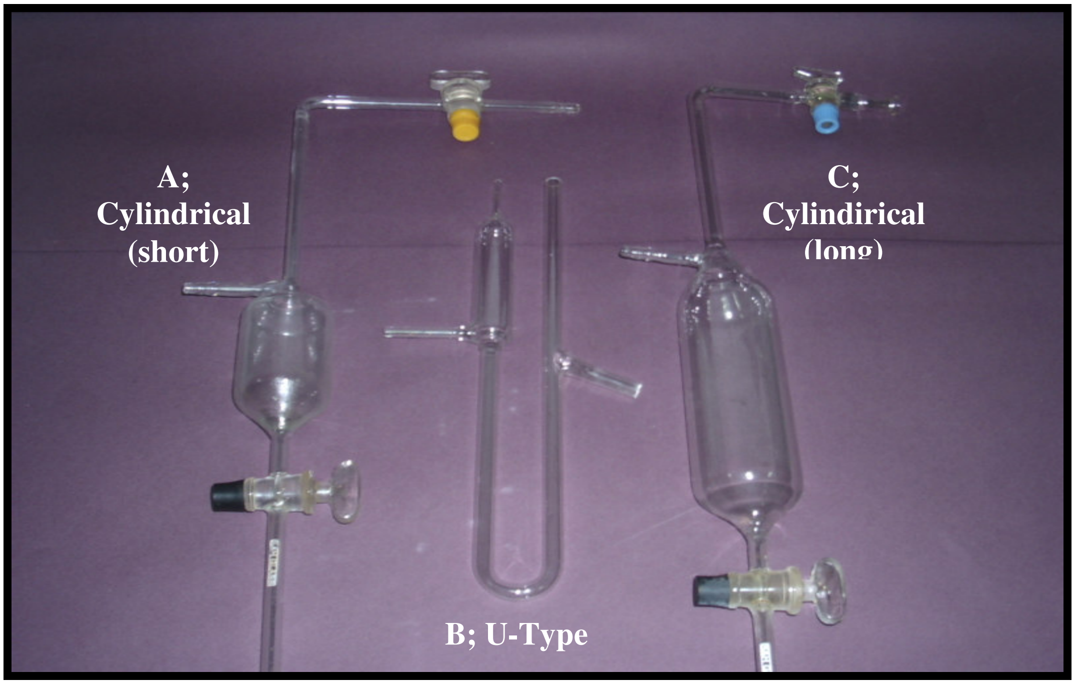

Fig. 2.3 Different Types and Sizes of Gas-Liquid Separators Used in System 1.

System 2

System 2, Fig. 2.4 was composed of a peristaltic pump, a mixer, a hot plate and a reaction chamber, Fig. 2.5. This reaction chamber contains two valves, one for carrier gas and second one to take the generated $GeCl_4$ in to the nebulizer and two inlets for sample introduction and waste. In this system no gas-liquid separator was used. The volume of the reaction chamber was about 20 mL.

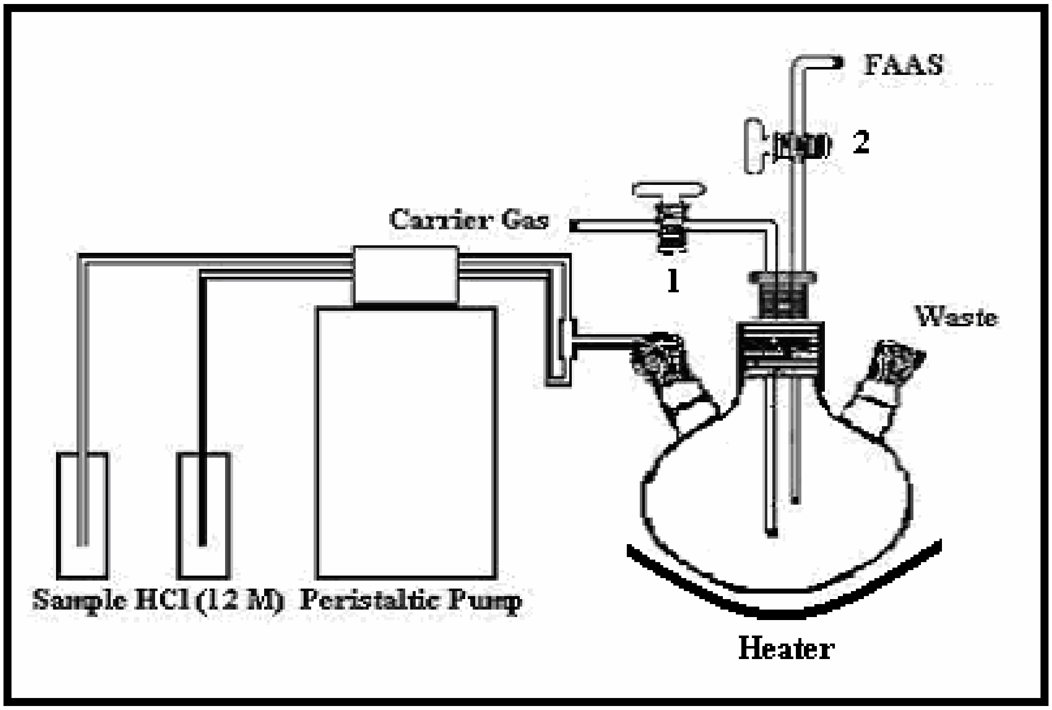

Fig. 2.4 Schematic Representation of Chloride Generation System 2

Fig. 2.5 The Reaction Chamber Used in System 2.

System 3

In System 3, Fig. 2.6 peristaltic pump was not used, instead the sample introduction was performed using a 5-mL syringe. The reaction chamber which is shown in Fig. 2.7 had four valves. Valve 1 was for sample and reagent introduction, valve 2 for carrier gas, valve 3 was for sending the germanium tetrachloride in to the flame and valve 4 for waste. No gas-liquid separator was used. The volume of the reaction chamber was about 20 mL. The reaction chamber was heated by a special home-made oven. The oven was designed in a way to cover the container part of the reaction chamber for homogeneous heating.

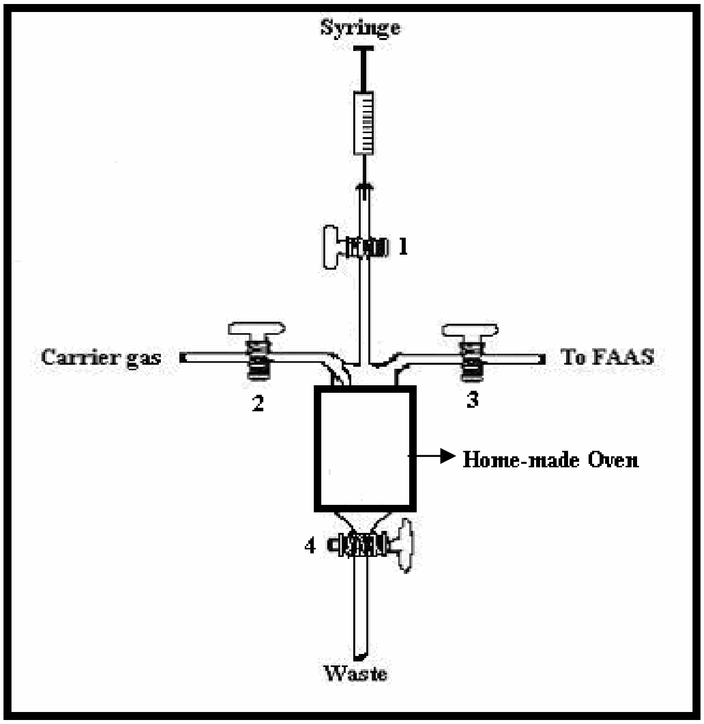

Fig. 2.6 Schematic Representation of Chloride Generation System 3.

Fig. 2.7 The Reaction Chamber Used in System 3.

System 4.

System 4 consisted of a peristaltic pump, a mixer, a home-made oven and a cylindrical reaction chamber, Fig. 2.8. The designed reactor had 4 valves. Valve 1 was used for introduction of the sample and reagent mixture and valve 2 for carrier gas. Valve 3 was used for the connection to the detector and valve 4 for waste. The lenght of the reactor was 10 cm and had a radius of 4 cm. No gas-liquid separator was used.

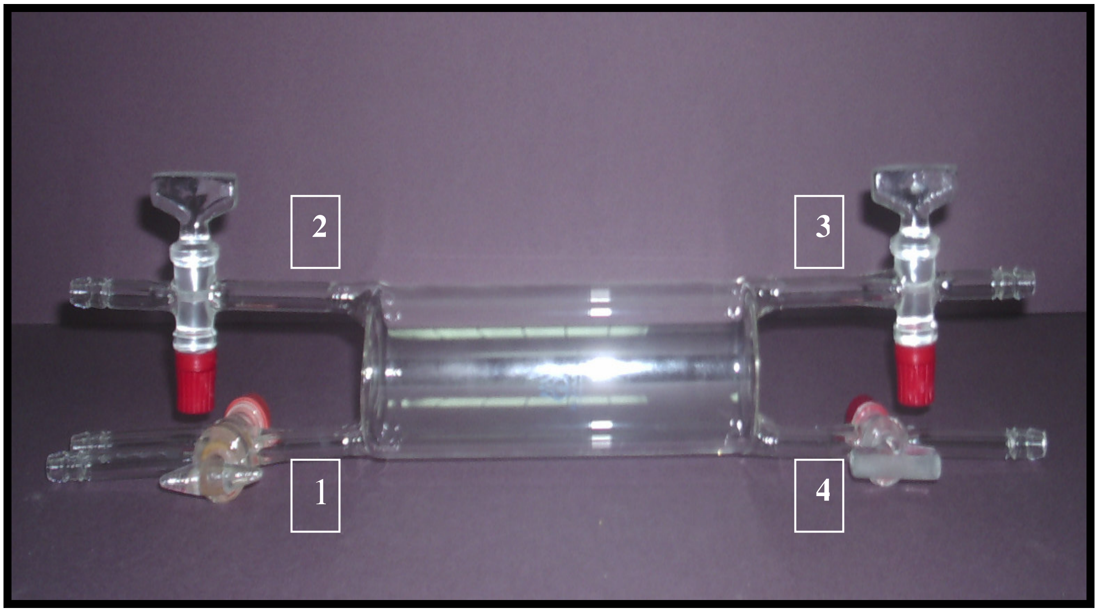

Fig. 2.8 The Reaction Chamber Used in System 4.

The home- made oven shown in Fig. 2.9 was used to heat System 4.

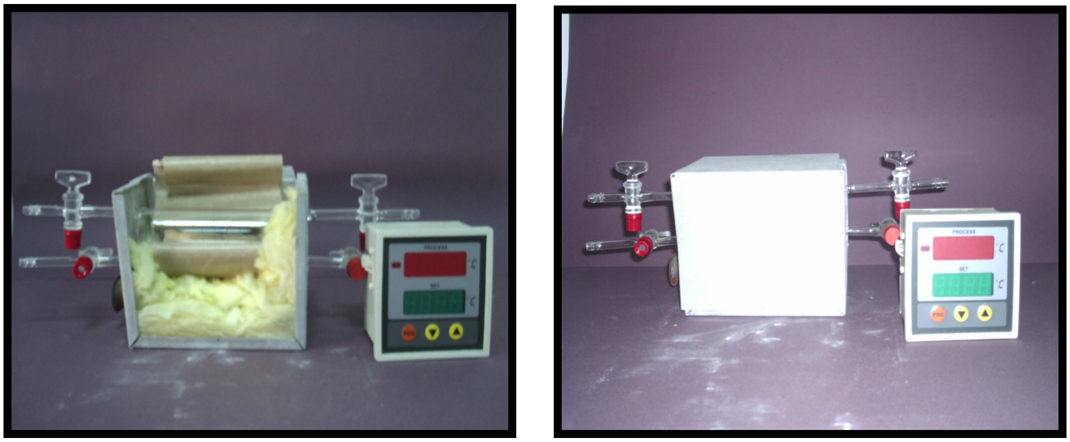

Fig. 2.9 The Home-Made Oven Used in System 4.

The heater part of the oven was made with ceramic soil and copper wire. Its power is 150 watt. The temperature of the heater was controlled with

GE-XDD1DC096 type digital controller. PT 100 type thermocouple was used to read temperature the surface of reaction chamber.

System 4, Fig. 2.10 was chosen for the determination of germanium as germanium tetrachloride.

2.2.2 Recommended Procedure for the Determination of Germanium with CG-FAAS

The systems consisted of a peristaltic pump by which the sample and 12M HCl were pumped separately to the reaction chamber with a flow rate of 10 mL min^{-1}. After merging of the streams the mixture was then transferred to the reaction chamber which was about 10 cm in length.

During measurements, sampling time was set at 6 seconds. At the end of sampling period the peristaltic pump was switched off and the mixture was kept about 1 minute in the reaction chamber for the completion of formation of germanium tetrachloride generation.

The formed $GeCl_4$ gas which was accumulated at the upper part of the reactor was swept to the nebulizer by use of argon carrier gas. The solution part at the bottom of the reactor was pumped to the waste with carrier gas and the whole cell was purged with argon for 30 seconds to dry the reactor and the tubing connected to the nebulizer.

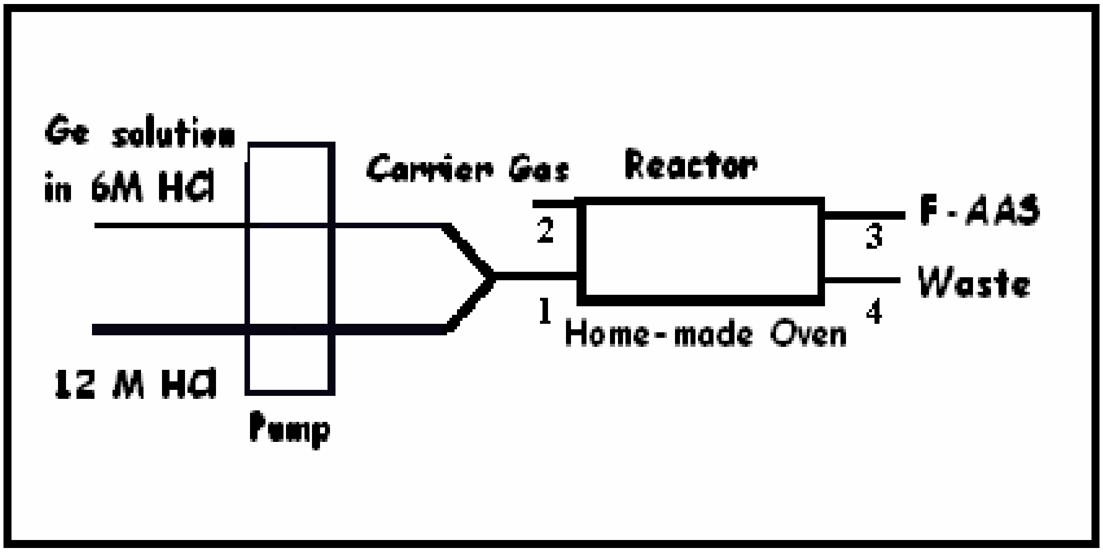

Fig. 2.10 Schematic Representation of Chloride Generation System 4.

Fig. 2.11 Chloride Generation System 4 Coupled with FAAS.

2.3 Experimental Conditions

The experimental conditions are summarized in Table 2.2

Table 2.2 Experimental Conditions Used Through the Experiment.

Parameter	**Value**
Carrier gas (Ar) flow-rate	400 mL min^{-1}
Peristaltic pump flow-rate	10 mL min^{-1}
Fuel flow-rate	4.8 mL min^{-1}
Reaction Time	1 min.
Reaction Temperature	80°C

2.4 Operational Procedures

In order to obtain better results, some parameters, such as; effects of the sample and reagent acidity, flow rate of gases, reaction temperature and reaction time were optimized and also the interference effects of foreign ions on germanium tetrachloride production were studied. Unless stated otherwise the experimental conditions given in Table 2.2 was used throughout the following optimization studies.

2.4.1 Influence of HCl Concentration in the Sample Solution on Germanium Signal

1 $\mu g \, L^{-1}$ solutions of Ge (IV) were prepared in 3 -10 M of HCl solutions as sample solutions. In these studies, 12 M HCl was used as a carrier solution.

2.4.2 Influence of HCl Concentration in the Carrier Solution on $GeCl_4$ Generation

HCl solutions in various concentrations (8 -12 M) were used as carrier solution. In this studies, 1 $\mu g \, L^{-1}$ solutions of Ge (IV) were prepared in 6 M HCl was used as sample solution.

2.4.3 Studies on the Effect of Carrier Gas Flow Rate

The flow rate of the carrier gas was controlled by a Cole- Parmer flowmeter which was calibrated for the carrier gas with a home-made soap-bubble flowmeter. The optimum gas flow rate was determined by using 1 $\mu g \, L^{-1}$ solutions of Ge (IV) prepared in 6 M HCl sample solution and 12 M HCl as a carrier solution.

2.4.4 Effect of Reaction Period on $GeCl_4$ Formation

The optimum reaction time for the formation of germanium tetrachloride was investigated by heating the sample and carrier solution mixture in various time intervals (10 s-5 min). In these studies, 1 μg L^{-1} Ge (IV) solutions which were prepared in 6 M HCl were used as sample solutions and 12 M HCl was used as a carrier solution.

2.4.5 Effect of Reaction Temperature on $GeCl_4$ Formation

The effect of reaction temperature on germanium tetrachloride production was investigated by changing the temperature of the heater in the range of 30-100°C. In these studies, 1 μg L^{-1} Ge (IV) solutions which were prepared in 6 M HCl were used as sample solutions and 12 M HCl was used as a carrier solution.

2.4.6 Gas Formation Efficiency Studies

The chloride generation efficiency of the reactor was tried to be measured. In these studies, different volumes of 0.01 μg mL^{-1} of Ge (IV) prepared in 6 M HCl was used as sample solution and 12 M HCl was used as a carrier solution. On the contrary to the usual measurements, the sample solutions remaining in the reactor was not discarded and its germanium content was measured 3 times.

2.4.7 Studies on the Interference Effects of Foreign Ions

The interference effects of As (III), Cd (II), Co (II), Cu (II), Fe (III), Ga (III), Hg (II), Ni (II), Pb (II), Sb (III), Se (IV), Sn (II) were studied. Different ions were added one by one to the sample solutions containing 1 µg L^{-1} germanium. Their final concentrations were in the range of 50-500 mg L^{-1}, Table 3.2. All the tests were carried out at optimum acidity unless stated otherwise. In general, the acidities of the added solutions were negligible as compared to the test solution.

2.5 Sample Dissolution Procedure

This method provides the acid digestion of the sample in a closed vessel rotor using temperature controled microwave heating.

Approximately 0.200 g of sample was transferred to a PTFE beaker and then 5 mL of concentrated H_2SO_4, 5 mL of concentrated HF and 10 mL of concentrated HNO_3 were added in a PTFE vessel. The solution were swirled to homogenize it. The vessel was closed and introduced in to the rotor segment. Then the segment was inserted into the microwave cavity and the temperature sensor was connected then the microwave program, which is shown in Table 2.3, was run.

Table 2.3 The Microwave Program

Step	Time	Temperature	Microwave power
1	3 minutes	100°C	Up to 1.000 W
2	3 minutes	150°C	Up to 1.000 W
3	3 minutes	200°C	Up to 1.000 W
4	2 hours	200°C	Up to 1.000 W

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Optimization of the Conditions for the Volatilization of Germanium Tetrachloride

It is crucial to optimize the chloride generation conditions for the specific system in use. The design of the reactor and the selection of the operating conditions determine the performance of the coupling. Good long-term precision and accurate results also require strict control of the operating parameters.

Chemical and physical parameters affecting germanium chloride generation were optimized individualy while other parameters were fixed at their optimum value in order to obtain maximum gas evolution by using System 4.

3.1.1 Chemical Parameters

The efficiency and the rate of germanium tetrachloride generation strongly depends on the HCl concentration of the medium. In our studies no other external source of chloride was used. Hence the amounts of HCl in the reaction chamber was controlling two important parameters: The acidity and the chloride concentration of the medium. In order to optimize the final concentration of HCl in the mixture, the HCl concentration in the sample and the carrier solutions should be optimized.

3.1.1.1 Influence of HCl Concentration in the Sample Solution on Germanium Signal

The HCl concentration of the carrier was fixed as 12 M and the effect of HCl concentration of sample solution on the germanium tetrachloride generation was investigated in the concentration range of 3 to 10 M, (Figure 3.1). As can be seen from the figure, maximum signal was obtained at 6 M HCl concentration. At higher and lower concentration of HCl in the sample solution, lower germanium signals were obtained. At HCl concentrations less than 5 M, the decrease in Ge signal was probably due to the conversion of only small fraction of Ge present in the sample into germanium tetrachloride. Whereas at hydrochloric acid concentration higher than 7 M, continuous drop in the Ge signal could possibly be attributed to the loss of analyte during the preparation of the samples because of the volatility of $GeCl_4$ even at ambient temperature. Consequently, 6 M hydrochloric acid concentration was chosen as optimum for the sample solution.

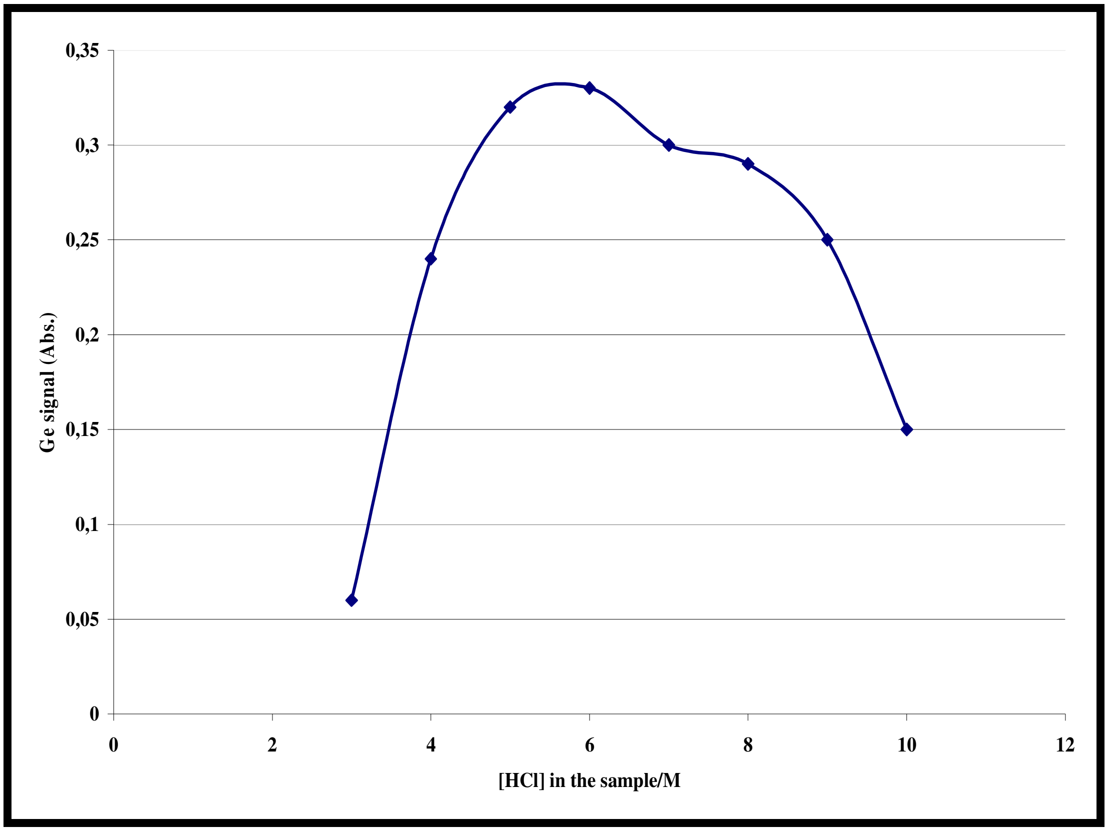

Fig. 3.1 Influence of Sample Acidity on $GeCl_4$ Production (Ge, 1µg L^{-1}, 5 mL)

3.1.1.2 Influence of HCl Concentration in the Carrier Solution on $GeCl_4$ Generation

To investigate this fact, a series of hydrochloric acid solutions were prepared covering a range of 8-12 M HCl as carrier solution. Figure 3.2 shows the change in the signal of 1µg L^{-1} germanium solution prepared in 6 M HCl with the change in HCl concentration of carrier solution.

As can be seen from the figure, the best response was obtained when 12 M HCl was used as the carrier solution.

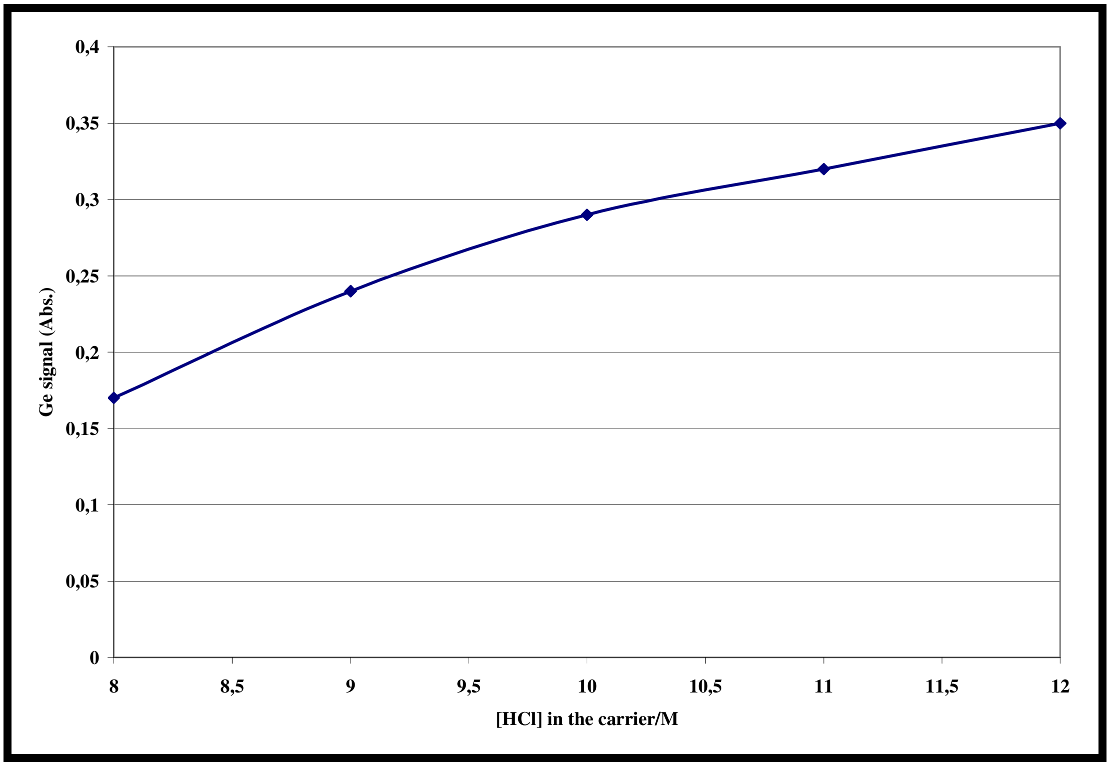

Fig. 3.2 Influence of Carrier Acidity on $GeCl_4$ Production (Ge, 1µg L^{-1}, 5 mL)

3.1.2 Physical Parameters

Physical parameters were optimized using a 4 mL sample of 1 μg L^{-1} of germanium in 6 M hydrochloric acid and 12 M hydrochloric acid as carrier solution.

3.1.2.1 Optimization of Sample and Carrier Flow Rates

The same size of tubings were used both for sample and carrier solutions. When the sampling tube of the peristaltic pump has a particular inner diameter, the amount of solution delivered to the system can simply be adjusted by changing the rotation rate and the sampling time. To evaluate the effect of the pump speed, the acidified sample and the carrier solution were pumped over a range of 4 to 11 mL min^{-1} The pressure developed were too high at higher flow rates. The best signals for germanium were obtained with flow rates between 9 to 11 mL min^{-1}. We have chosen 10 mL min^{-1} as the optimum flow rate in this study. However, when better detection limits are not required, lower or higher rates can be used in order to reduce time consumption.

3.1.2.2 Optimization of Carrier Gas Flow Rate

Argon carrier gas flow rate of 400 mL min^{-1} was selected in this work. A higher carrier gas flow rate would decrease the intensity owing to the dilution effect while a lower value would increase the memory effect.

3.1.2.3 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 were 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 minutes. The results are shown in the Figure 3.3. As can be seen from the figure, after 1 minute of reaction period, the germanium signal reaches a plateau. Thus 1 minute was chosen as the reaction period throughout this study.

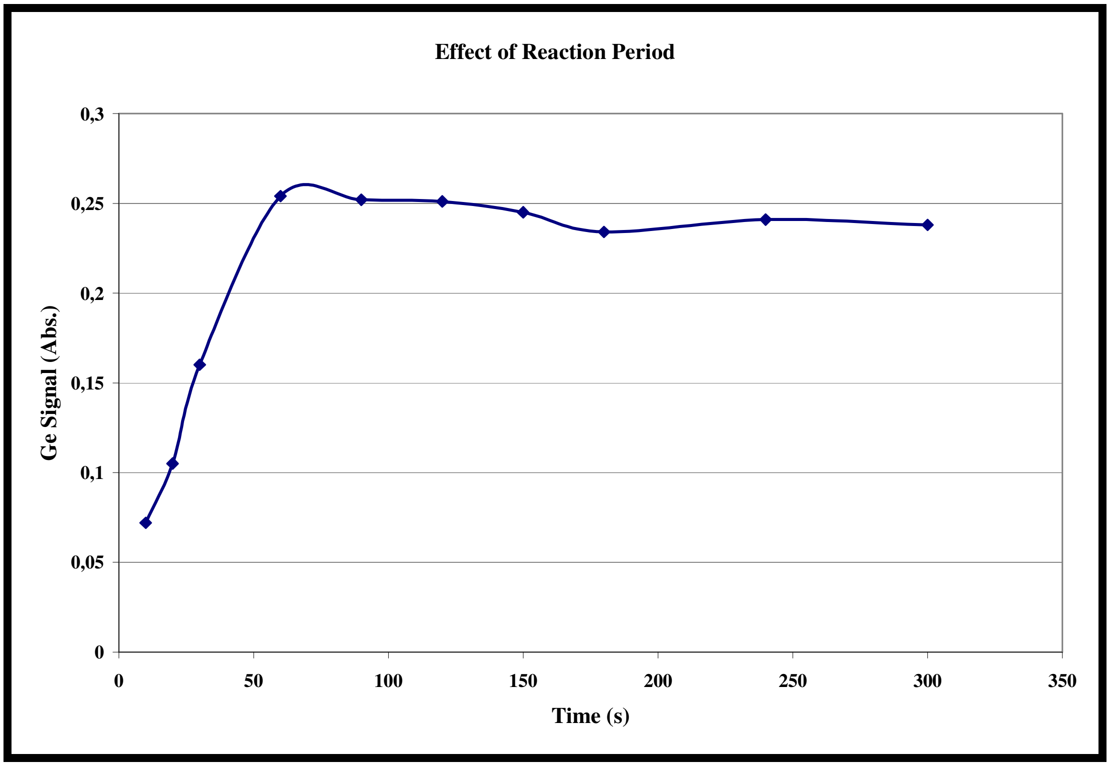

Fig. 3.3 Effect of Reaction Period (Ge 1µg L $^{-1}$, 4 mL)

3.1.2.4 Effect of Reaction Temperature on $GeCl_4$ Formation

The effect of reactor temperature on germanium tetrachloride production was investigated. Previously the experiments were performed at room temperature resulting in quite low signals. Thus, we decided to heat the reaction coil to increase the chloride generation efficiency. Heating was done in the range of 30-100°C. The results are shown in the Figure 3.4.

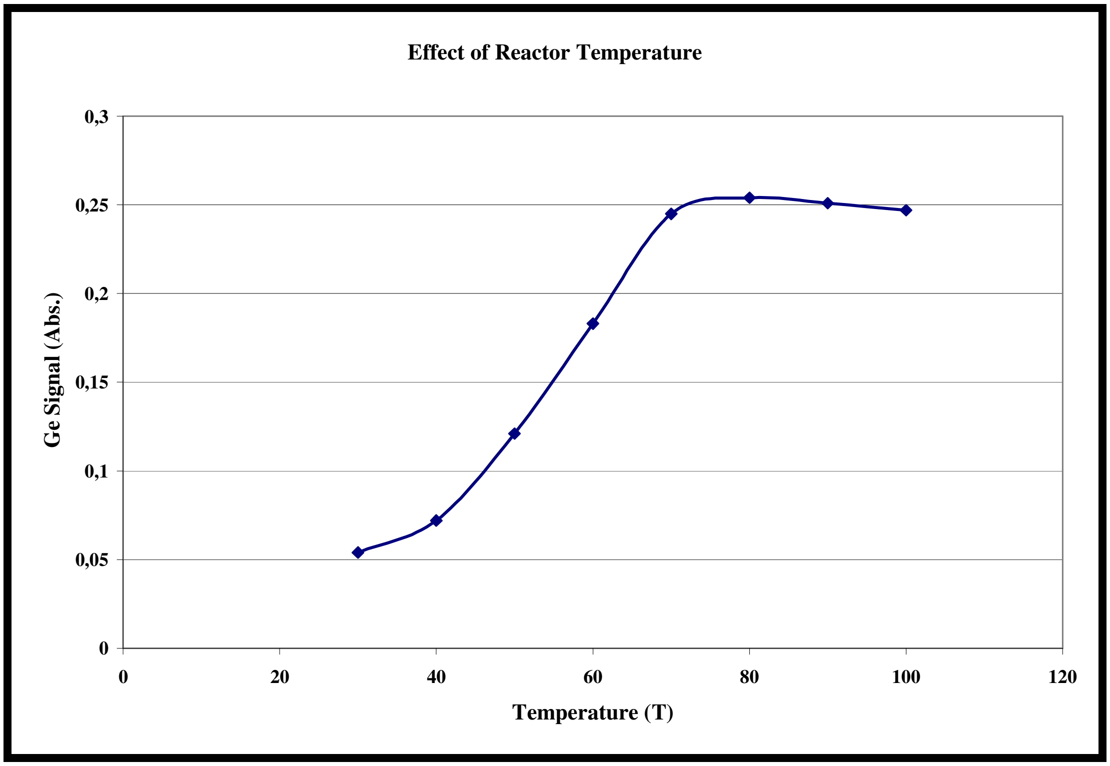

Fig. 3.4 Effect of Reactor Temperature (Ge 1µg L $^{-1}$, 4 mL)

As expected, the highest signal was obtained at 80°C which is almost equal to the boiling point of germanium tetrachloride (84°C) and stayed steady afterwards. Therefore the reactor temperature was chosen as 80°C.

3.1.2.5 Type of Reactor

Four different reactors were designed, tested and compared. The whole measurement unit including the reactor is called as system. All of the systems were explained in the experimental part. It was found that the results obtained by a System 1, System 2 and System 3 were poorer in precision and sensitivity than that obtained by System 4 (Table 3.1). The reactor design in System 4 ensures the homogeneous mixing of the reactants, and thus better results were obtained. So this reactor was preferred and used for further experiments because of its sensitivity, simplicity in construction and flexibility in use.

In System 1, a reaction coil, connected to a gas- liquid separator was used as the reactor. The main problem of this system was poor reproducibility. The signal obtained in the second measurement was always lower than the first one. The reason for this decrease was the condensation problem of $GeCl_4$ on the cold surface of the gas- liquid separator which was not heated. In order to obtain a reproducible signal, the system has to be completely dried before each cycle. The extra drying step increased the experiment period and reagent consumption. Besides the chloride generation efficiency of the system was quite low. In order to minimize these problems, new reaction coils and gas- liquid separators having various sizes and shapes (shown in Figure 2.2 and Figure 2.3) were designed and examined. However, the modification did not succeed in removing all the problems completely so a new system (System 2) was designed.

In System 2, three-neck rounded bottom flask was used as a reactor to prevent the problems arised from the gas- liquid separator and the reaction coil used in the first system. However, additional difficulties were arised.

A) The reactor design was not resistant to high pressure formed inside due to the formation of gaseous $GeCl_4$ and also due to carrier gas introduced to the system externally. Thus, analyte losses due to the gas leakages from the joint part were observed.

B) The design was not suitable for a continuous measurement. In order to discharge the waste the reactor has to be separated into pieces and built up again before each cycle which was also time-consuming.

C) The system could not be heated effectively so condensation problem could not be removed properly. These problems revealed the necessity for a new design.

In System 3, the reactor in System 2 was modified and designed as a unique part in order to prevent the gas leakage formed due to high pressure and an extra valve was added to discharge the waste easily. Still it was not a continuous system; sample was delivered to the reactor by utilizing a septum and a syringe. We obtained an increase in the signal but the gas formation efficiency was still low. The system could not be heated effectively and again the time and reagent consumptions were high.

There upon, lastly we designed System 4. In this system, a home- made oven, Fig. 2.9, was used for the heating process that enabled effective and complete heating so the condensation problem reduced to a minimum. Waste could be easily discharged from the system and the system could easily be dried by passing carrier gas for a short period. By this way, time and reagent consumption was reduced and the sensitivity of the system was improved appreciably compared to the formerly designed systems.

Table 3.1 Comparison of the Designed Systems

System	1	2	3	4
***Sensitivity**	0.120 A (10 mL)	0.180 A (10 mL)	0.520 A (10 mL)	1.914 A (2.5 mL)
Total Analysis Time	15 min.	15 min.	10 min.	≤ 3 min.

* Absorbance value obtained for 1 mg L^{-1} germanium aqueous solution at optimized conditions, for each reactor.

3.1.2.6 Atomizer (N_2O-C_2H_2 Flame)

Air-acetylene flame was tried for germanium determination, since it is safer, less expensive, and less noisy compared to nitrous oxide-acetylene flame. As it is stated in the literature no signal was observed even for high concentration of germanium (500 mg L^{-1}). Therefore high temperature N_2O-C_2H_2 (3000° C) flame was selected [46].

3.2 Signal Characterization

The amount of Ge (IV) volatilized could be related to the area and/or peak height of the signal. The peak height measurement is simpler and more reproducible than the peak area, so peak height was the parameter chosen as the analytical response. To investigate the peak shape printer outputs of four signals with various absolute concentrations are given in Figure 3.5.

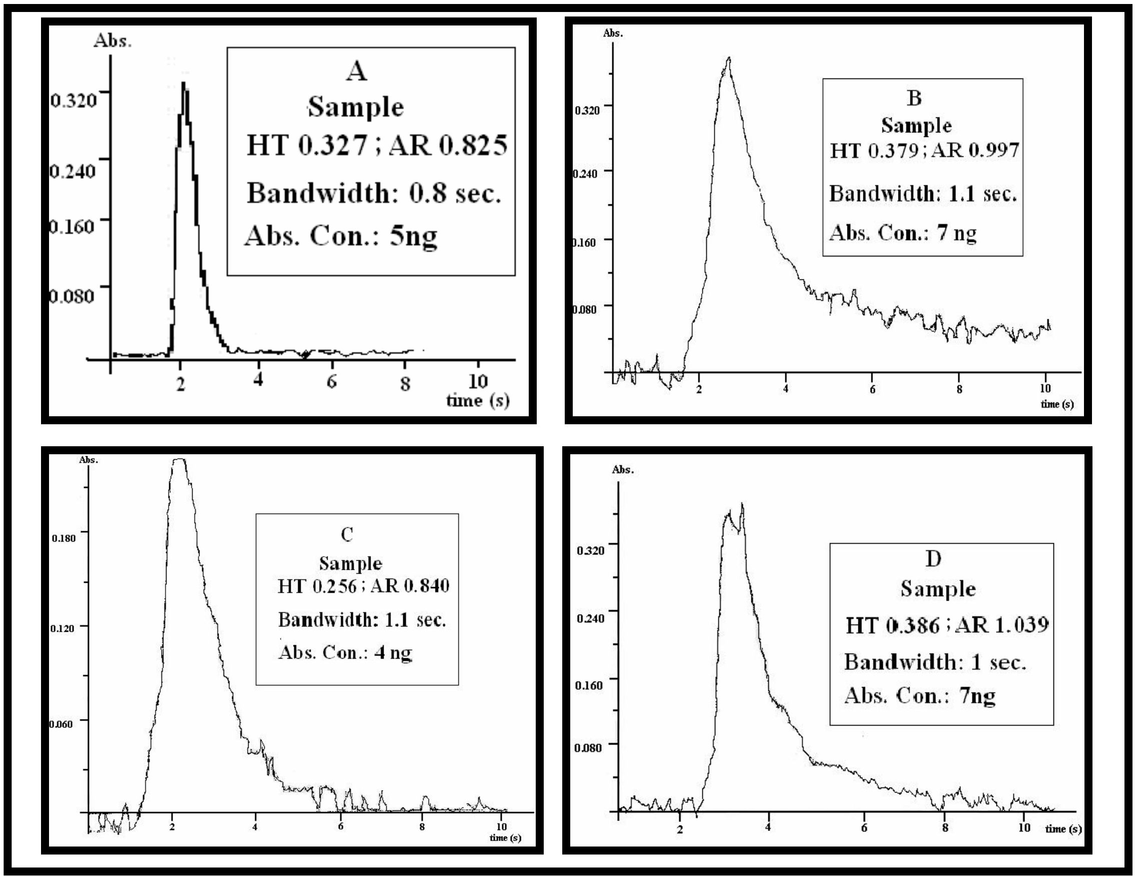

Fig. 3.5 The sample analytical signals obtained for 1 μg L^{-1} Ge solutions with different sample volumes

(HT; peak height, AR; peak area, Bandwith; the width of the peak at half of the maximum height.)

3.3 Sensitivity and Linear Working Range

The performance of the method was evaluated by preparing a calibration graph. Under the previously deduced optimum conditions, different concentrations were sent into the reaction vessel for the Ge determination by flame atomic absorption spectrometry (FAAS). A detection limit of 0.034 µg L^{-1} was obtained by using FAAS and the relative standard deviation obtained by analyzing nine independent replicates of a solution was 0.3 % for a germanium concentration of 0.1 µg L^{-1}. The analytical response was found to be linear up to 10 ng. Ge (IV) using the equation y= 0.0572x + 0.0175, with a regression coefficient of 0.0998 y. The height of the germanium absorption peak at 264.9 nm in arbitrary units was shown by y and x is the concentration of Ge (IV) in solution in ng as absolute concentration.

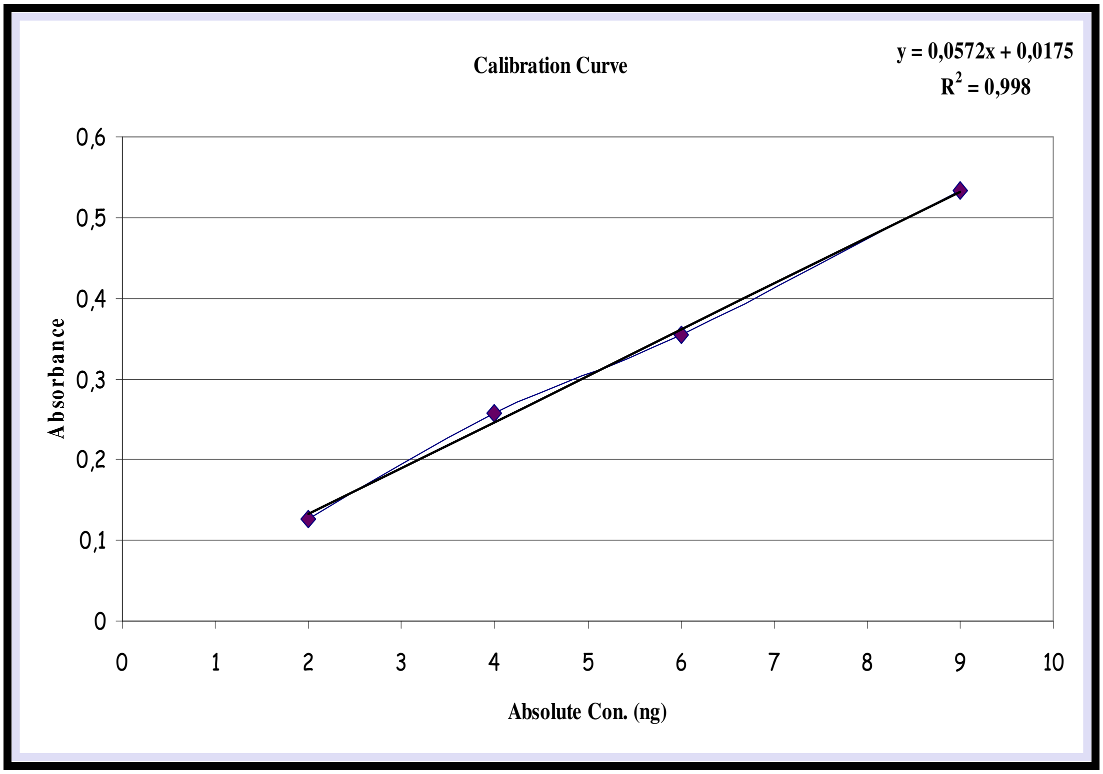

Fig. 3.6 Calibration Graph Obtained Using Different Concentation Standards of Ge Prepared in 6 M HCl.

3.3.1 Gas Formation Efficiency Studies

The results of studies for chloride generation efficiency are shown in Table 3.2. Under optimum conditions, different volumes of 0.01 μg mL^{-1} Ge aqueous solutions concentration were sent into the reaction vessel for the Ge determination by flame atomic absorption spectrometry. 1st run represents the absorbance values measured when the $GeCl_4$ from the sample solution was directly sent to the flame. Normally, the liquid part remained in the reactor was discarded. But, to measure the efficiency, it was kept in the reactor and a fresh argon gas sent to the system for each measurement. 2nd and 3rd runs represent the result of the successive measurements of the germanium content of the leftovers with FAAS.

As can be seen from the table, the absorbance values measured at the 3rd run are almost identical to the blank value. However the measurements at the 2nd run shows that 13-14% of the total germanium were left in the solution. Thus it was concluded that the efficiency of the system at optimized conditions (Table 2.2) was around 84-86%. The term of efficiency covers the competence of the reactor for converting germanium into $GeCl_4$ and also transportation of the formed $GeCl_4$ in to the flame.

Table 3.2 Gas Formation Efficiency Studies for 0.01 µg mL^{-1} Ge solutions

Sample	**1st (A)**	**2nd (A)**	**3rd (A)**	**Blank(A)**	**Total Loss**
1. (2 mL)	0.400	0.053	0.024	0.018	**14%**
2. (3mL)	0.597	0.080	0.027	0.021	**14%**
3. (2mL)	0.486	0.070	0.029	0.023	**16%**
4. (3mL)	0.543	0.078	0.021	0.016	**15%**

3.4 Evaluation of Interferences

Since the germanium tetrachloride distillation method was originally used as a specific method for the separation of germanium from the other elements, it can be expected that the proposed method which utilizes the same principle will also be highly selective. The selectivity of the method was presented by studying the effect of interferences on the Ge signal obtained with chloride generation AAS system. All tests were carried out under optimum operating conditions. Averages of the triplicate determination of 1 µg L^{-1} are shown in the Table 3.3. Variations over ± 5% in the analytical signal of 1 µg L^{-1} Ge in the presence of foreign ions were considered as interference.

Transition metals are serious interferents in the hydride generation technique of germanium determination. Hydride formed reacts with transition metals that have been reduced and precipitates in a colloidal form in the presence of tetrahydroborate [33]. The results of the interference study clearly showed that elements such as Co (II), Cu (II), Fe (III) and Ni (II) that are serious interferences in the hydride generation of germanium (95% reduction in the HG signal [76]) did not interfere when the chloride generation was used.

It was reported that arsenic trichloride is the only species that can be distilled at the same hydrochloric acid concentration [32]. Hence it was expected that As (III) may give interfere effect. As can be seen from the Table 3.3 at interferent to ratio of 50000, arsenic did not interfere with the germanium signal. If it did interfere, oxidation of As (III) to As (V) could handle the problem.

Similarly well known hydride forming elements such as Sb (III), Se (IV), Sn (II) and Te (IV) that showed moderate (5-45% reduction in the signal) interference effects with hydride generation system [76] did not give interference in chloride generation system.

Table 3.3 Effect of Potential Interferents on the Determination of 1 μg L^{-1} Ge by CG-FAAS

		Variation in Ge signal (%)	
Element	**Con. (mg L^{-1})**	***HG [43]**	**CG**
As (III)	50	0	+2
Cd (II)	50	-30	-1
Co (II)	500	-95	+1
Cu (II)	500	-95	-2
Fe (III)	500	-95	+1
Ga (III)	50	-20	+1
Hg (II)	50	-20	-1
Ni (II)	500	-95	+2
Pb (II)	50	-40	+3
Sb (III)	50	-35	+2
Se (IV)	50	-45	+3
Sn (II)	50	-5	-2
Te (IV)	50	-15	-2
Zn (II)	500	-45	+2

*Germanium concentration was 0.1 mg L^{-1}.

The avoidance of the use of tetrahydroborate, as in the present chloride generation method, has a direct effect on the reduction of interferences and is a very important advantage to highlight.

The interference studies showed that the proposed method is interference free in the presence of the tested elements. For this reason, CG method is promising for application to analysis of germanium in different types of samples including those which have low Ge concentrations and complex matrixes.

3.5 Analytical Performance

Two previously reported chloride generation techniques explained in the introduction section (1.4) are compared with the one that is proposed in this study in terms of their analytical performances. The analytical characteristics of the methods are given in Table 3.4.

Table 3.4 Comparison of Analytical Performances of the Hyphenated Techniques CG-ICP-AES and CG-AFS and CG-FAAS.

Parameter	**CG-ICP-AES [77]**	**CG-AFS [76]**	**CG-FAAS (This work)**
***Sample Volume**	0,6 mL	0,6 mL	1 mL
****Conc. of Reagent**	1.0 x 10^{-2} mg L^{-1}	1.0 x 10^{-1} mg L^{-1}	1.0 x 10^{-4} mg L^{-1}
Detection Limit (3s)	0.25 ng mL^{-1}	0.5 ng mL^{-1}	0.034 ng mL^{-1}
Precision (% RSD)	5.5	0.8	0.3
*****N**	10	5	10

*Volume of the sample used in the measurement

**Concentration of the reagent measured for the detection limit calculations.

*** Number of replicates (N)

Just like germanium hydride, the atomization of $GeCl_4$ is quite difficult. As it was mentioned in the atomizer section (3.1.2.6), germanium signal was observed only with N_2O- Acetylene flame. In the other chloride generation techniques mentioned in Table 3.4, more sensitive and efficient atomization techniques were used. Despite this fact the detection limit obtained in this study is 7 fold and 15 fold lower than that of Ref. 77 and Ref. 76 respectively. The detection limit of the method can be further improved by increasing the sample volume and by introducing a collection step.

3.6 Application to the Analysis of Real Samples

In order to demonstrate the accuracy of the proposed method, it was applied to the analysis of one certified and two reference materials: Chinese Rock (CRM GBW 07107) and GSJ-JR-1, GSJ-JR-2 rock samples. The results given in Table 3.5 were in good agreement with the certified values.

Table 3.5 Determination of Ge in Environmental Reference Materials

Sample	**Ge concentration** (μg g^{-1})
*__Rock (GBW 07107)__	
Ge (found)	2.9±0.1
Ge (informative)	3.1±0.1
Rock (GSJ-JR-1)	
Ge (found)	2.1±0.1
Ge (informative)	2.4±0.4
Rock (GSJ-JR-2)	
Ge (found)	1.9±0.1
Ge (informative)	2.1±0.3

*Certified sample

Student t-test was applied at 99% cofidence level and no difference was observed.

3.7 Future Work

The designed system will be further modified by utilizing a 5-way distribution valve for sample introduction. Also, it is planned to design a completely automated system by using the home-made flow injection analysis system constructed in our laboratory. Besides, the detection limit of the method will be improved by introducing a collection step.

CHAPTER 4

CONCLUSION

Under optimized conditions, germanium tetrachloride can be completely volatilized from high concentration hydrochloric acid solutions. A low cost continuous flow method of germanium determination based on this fact was developed in this study. The sample reacted with hydrochloric acid, at 80°C to give germanium tetrachloride which was transported to nitrous oxide- acetylene flame atomizer using argon gas.

This method was developed as an alternative to the widely used hydride generation methods. The proposed method is more selective and similar simplicity in operation when compared to the hydride generation techniques. The principle advantage of chloride generation (CG) over hydride generation (HG) is the dramatic suppression of liquid phase interferences.

The effects of well known potential interferants for hydride generation on germanium signal of chloride generation were evaluated. Transition metals like Co, Cu, Fe, and Ni which diminish the germanium signal 95 % at interferant to analyte ratio of 5000 utilizing hydride generation did not cause any adverse effect on germanium signal obtained with chloride generation at interferant to analyte ratio of 500.000.

N_2O-Flame atomic absorption spectrometer was chosen in our study, instead of more potent atomizer like ICP, due to its availability in a great number of routine and research laboratories. The sensitivity of the N_2O-Acetylene flame AAS system is not adequate to use with the previously proposed ambient temperature chloride generation system. Thus, we proposed completely new chloride generation system, very similar in operation to HG-AAS (N_2O-Acetylene) system and equipped with a heating unit. Therefore the purposed technique can easily be adopted by any laboratory for routine germanium determination. Besides it seems promising for coupling to the other atomic spectrometric detectors.

The absolute detection limit of the proposed system is 0.034 ng (0.034 µg L^{-1}) for 1 mL sample which is lower than the detection limit of a hydride generation system used in our laboratories which is 0.213 ng (0.085µg L^{-1} for 25 mL sample) and also the detection limits of the previously proposed chloride generation systems utilizing more powerful atomizer units (0.25 ng- 0.5 ng). Detection limit of the method can be improved further by using trap system.

In order to demonstrate the accuracy of the proposed method, it was applied to the analysis of one certified and two reference rock samples. The results are in good agreement with the certified values.

In our opinion, further developments are required in order to fully utilize the potential and advantages of chloride generation and to extend the use of this method to other analytes.

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APPENDIX

Table 1. Certified Values of Constituents of GBW 07107-Rocks and Geological Materials (All values are expressed in mg kg^{-1} (parts per million) on a dry weight basis)

Analyte	Certified Value
Ge	3.1
As	1.4
Cd	0.033
Co	21
Cu	42
Fe(III) oxide, total	76000
Ga	26
Hg	0.01
Ni	37
Pb	8.7
Sb	0.17
Se	0.078
Sn	2
Te	0.023
Zn	55

Table 2. Certified Values of Constituents of GSJ-J1-Rock Materials (All values are expressed in mg kg^{-1} (parts per million) on a dry weight basis)

Analyte	Certified Value
Ge	2.4
As	15.9
Cd	0.017
Co	0.65
Cu	1.4
Fe(III) oxide, total	-
Ga	17.6
Hg	0.008
Ni	0.66
Pb	19.1
Sb	1.43
Se	0.0059
Sn	2.7
Te	-
Zn	30

Table 3. Certified Values of Constituents of GSJ-J2-Rock Materials (All values are expressed in mg kg^{-1} (parts per million) on a dry weight basis)

Analyte	Certified Value
Ge	2.1
As	19.5
Cd	0.019
Co	0.4
Cu	1.4
Fe(III) oxide, total	-
Ga	18.2
Hg	0.0002
Ni	0.84
Pb	21.9
Sb	1.83
Se	0.0026
Sn	3.2
Te	-
Zn	27.42