Arsenic and Germanium Determination by Hydride Generation in the D.C. Plasma Optical Emission Spectrometer

by

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To

Franco, Anna, José, Franca, Cristina and to the

Memory of my brother Sandro

ABSTRACT

Modifications to the commercial hydride generator, manufactured by Spectrametrics, resulted in improved operating procedure and enhancement of the arsenic and germanium signals. Experiments with arsenic(III) and arsenic(V) showed that identical results could be produced from both oxidation states. However, since arsenic(V) is reduced more slowly than arsenic(III), peak areas and not peak heights must be measured when the arsine is immediately stripped from the system (approximately 5 seconds reaction). When the reduction is allowed to proceed for 20 seconds before the arsine is stripped, peak heights may be used. For a 200 ng/mL solution, the relative standard deviation is 2.8% for As(III) and 3.8% for As(V). The detection limit for arsenic using the modified system is 0.50 ng/mL.

Studies performed on As(V) standards show that the interferences from 1000 mg/L of nickel(II), cobalt(II), iron(III), copper(II), cadmium(II), and zinc(II) can be eliminated with the aid of 5 M HCl and 3% L-cystine.

Conditions for the reduction of germanium to the corresponding hydride were investigated. The effect of different concentrations of HCl on the reduction of germanium to the covalent hydride in aqueous media by means of $NaBH_4$ solutions was assessed. Results show that the best response is accomplished at a pH of 1.7. The use of buffer solutions was similarly characterized. In both cases, results showed that the

element is best reduced when the final pH of the solution after reaction is almost neutral. In addition, a more sensitive method, which includes the use of $(NH_4)_2S_2O_8$, has been developed. A 20% increase in the germanium signal is registered when compared to the signal achieved with HCl alone. Moreover, under these conditions, reduction of germanium could be accomplished, even when the solution's pH is neutral. For a 100 ng/mL germanium standard the rsd is 3%. The detection limit for germanium in 0.05 M HCl medium (pH 1.7) is 0.10 ng/mL and 0.09 ng/mL when ammonium persulphate is used in conjunction with HCl.

Interferences from 1000 mg/L of iron(III), copper(II), cobalt(II), nickel(II), cadmium(II), lead(II), mercury(II), aluminum(III), tin(IV), arsenic(III), arsenic(V) and zinc(II) were studied and characterized. In this regard, the use of $(NH_4)_2S_2O_8$ and HCl at a pH of 1.7 proved to be a successful mixture in the suppression of the interferences caused by iron, copper, aluminum, tin, lead, and arsenic. The method was applied to the determination of germanium in cherts and iron ores.

In addition, experiments with tin(IV) showed that a 15% increase in the tin signal can be accomplished in the presence of 1 mL of $(NH_4)_2S_2O_8$ 10% (m/V).

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CHAPTER 1

INTRODUCTION

A. ARSENIC GENERALITIES

Arsenic compounds are toxic. Their occurrence in the environment is wide, and a variety of relatively stable forms can be found in nature. Arsenic's oxidation states are +3, +5 and -3. Arsenic, which has been classified as a metalloid because it has characteristics of both metals and non-metals, has found extensive use for homicidal and suicidal purposes. In its sodium arsenate form Na_3AsO_4 12 H_2O, it is used in the production of printing inks, in dyeing textiles and in preparing arsenates, such as those of lead and calcium that are used as pesticides. Arsenic is still being extensively used as an herbicide in agriculture, as a silvicide in forestry, and as a wood preservative. It is currently used as a doping agent in the integrated circuit industry [1]. Its use in the fight against venereal diseases, however, has been replaced by penicillin and other antibiotics.

In many of its chemical forms arsenic is readily absorbed by the human gastrointestinal tract and its toxic effect varies in accordance with the dose and duration of intake [2].

In the environment, the pentavalent state is the primary inorganic form; however, as a result of microbiological activity some methyl arsenic compounds can be found in nature. Of these,

dimethylarsinic and dimethylarsonic acids are the most common [1]. These two compounds are also manufactured for use as selective herbicides in agriculture and forestry.

Once absorbed, arsenic compounds undergo substantial metabolic transformation. Knowledge of the processes involved in the biotransformation is relatively new and unclear [2]. According to recent studies in humans and animals, arsenic compounds can be excreted to the extent of 46% or more of the intake dose within a few days [2]. When administered orally, As(III) and As(V) appear in the urine mainly as dimethylarsinic acid (DMA) and, to a lesser extent, as monomethylarsinic acid (MMA). The same study showed that when DMA is administered orally it is excreted in the urine unchanged; however, there is some slight conversion of orally administered MMA to DMA.

Symptoms of acute arsenic poisoning include severe gastrointestinal irritation accompanied by cramps and diarrhea, scaling and pigmentation of the skin, drowsiness, poor memory, anemia and malfunction of the sensory and motor functions of the peripheral nerves.

Some studies [2] have identified arsenic as a carcinogen in humans. High incidence of lung cancer among workers has been associated with high atmospheric levels of arsenic in copper smelters. Long term exposure by dermal contact and by oral intake has resulted in skin cancer.

Due to its extremely high toxicity, arsenic has long been the subject of toxicological and environmental research. A variety of different analytical methods have been studied and

efforts have been, and still are, channelled to improve the sensitivity and detection limits. As in most chemical processes, the more that is known about reactions which cause pollution, the more intelligently, and perhaps even succesfully, the problems can be attacked.

B. GERMANIUM GENERALITIES

Germanium is a metallic element important as a semiconductor of electricity. Even though it was first suspected by Newlands (1864) as the missing member of the silicon, germanium and tin group, it was not until 1887 when the German scientist Winkler first isolated it as the sulphide GeS_2 from argyrodite $4AgS\ GeS_2$, that this was ascertained. Thereafter germanium was named in honour of Germany [3].

Germanium exhibits valences of +2, +4 and -4, with the +4 state being the more stable one. Germanium occurs in small quantities in ores of silver as well as in ores of copper and zinc [1]. Due to the rarity and high price of germanium, detailed knowledge of the chemistry of this very important element has been somewhat slow to accumulate. To this might be added the fact that since early studies showed that its properties were nearly identical to silicon and tin, its chemistry appeared to lack novelty. However, publications on inorganic and organic compounds of germanium are appearing now at an increasing rate.

Germanium finds wide application in semiconductor

devices, especially when doped with other elements such as arsenic or gallium to improve its conductivity [1]. Due to its transparency to infrared, it is also used in glass in infrared optical devices, such as windows, lenses, and prisms.

The expansion of chemical knowledge of germanium in the upcoming years will depend on the possible applications of its compounds to highly specific, possibly catalytic processes [3]. At the present time, what can be done with germanium can be accomplished more cheaply with silicon or tin compounds.

C. HYDRIDE GENERATION TECHNIQUE

1) WHY HYDRIDE GENERATION

In the past, elements such as arsenic, selenium, antimony, tellurium, etc. were difficult to measure accurately using direct solution nebulization associated with atomic spectrophotometric methods of analysis. This is primarily because optimal analytical lines for these elements lie far in the ultraviolet region of the spectrum (below 230 nm) where strong background absorption due to the commonly used flames (air-acetylene, dinitrogen oxide-acetylene) is large.

In an attempt to overcome this problem, the application of a variety of different flames was studied [4-11]. With the application of a low temperature argon (entrained air)-hydrogen flame, by Kahn and Schallis [12], the background absorption was reduced to only 15% of the available light, providing, in this

way, a much better signal to noise ratio. However, other problems due to poor vaporization characteristics caused by the lower temperature attainable by the flame, led to greater interferences associated with incomplete salt dissociation and molecular absorption.

The replacement of flames by electrothermal techniques, such as graphite furnace, resulted in other problems such as severe matrix interferences and light scattering, produced by particulate matter such as carbon. Also, analyte losses can occur, particularly for relatively volatile elements during the charring stage of the furnace program, unless matrix modification procedures are applied.

In 1969, Holak [13] generated arsine (AsH_3) by the Marsh reaction and the Gutzeit method and introduced it with a stream of nitrogen into an air-acetylene flame. In this way he was able to separate the analyte from the bulk matrix, thus reducing interferences in the flame. Since Holak's paper there have been approximately 400 publications that address the analytical application of the hydride generation technique coupled with atomic spectroscopy. Analyses have been expanded to include the generation of germane (GeH_4),arsine (AsH_3), stibine (SbH_3), plumbane (PbH_4), bismuthine (BiH_3), stannane (SnH_4), hydrogen selenide (SeH_2) and hydrogen telluride(TeH_2).

2) ADVANTAGES AND DISADVANTAGES OF HYDRIDE GENERATION

The most important advantages of hydride generation are:

a) it provides good separation and preconcentration (superior sensitivity) of the analyte from the sample matrices, thus eliminating potential chemical and/or spectral interferences commonly encountered with direct solution analysis, b) it is a more effective method of sample introduction than solution nebulization, c) it has excellent potential for multi-element analysis for atomic emission spectrophotometry and d) it is easily automated.

Among the disadvantages that should be considered are: a') strong interference effects by concomitant elements present in solution, which reduce the efficiency of hydride generation, b') wide variety of reaction conditions from which any one elemental hydride has to be generated, c') increased complexity and reduced sample throughput when collecting the hydride in a cold trap or balloon prior to atomization, d') the necessity for the analyte element to be in a form that can be readily converted to the gaseous hydride, especially in the determination of trace elements bound in biological materials.

3) REACTIONS USED IN HYDRIDE GENERATION

In the hydride generation technique, aqueous samples, properly acidified, are treated with a reducing agent to produce the volatile covalent hydride of the particular element. Thereafter, the hydride is conveyed, by means of a stream of inert gas, into the atom reservoir for its determination by either Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence

Spectroscopy (AFS) or Plasma Atomic Emission Spectroscopy (AES). One can, therefore, differentiate three basic steps in hydride generation procedures: a) the generation and volatilization of the hydride, b) the transfer of the hydride, including its collection (if applicable) and c) the atomization of the hydride and subsequent detection by any of the above mentioned systems.

Presently there are two main reactions for hydride generation. The first one, generally classified as the metal/acid reaction, uses a mixture of zinc-hydrochloric acid as shown in equation 1.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2H' \xrightarrow{E^{m+}} EH_n + H_2 \text{ (excess)} \quad (1)$$

where E is the analyte of interest and m may or may not equal n. This reaction presents, however, several drawbacks that somewhat offset the advantages of hydride generation. First, it is a rather laborious and time consuming reaction; the reaction may commonly be as long as 10 minutes, including prereduction periods. Secondly, the Zn/HCl reaction has been proven to be limited to the determination of As, Sb and Se. (occasionally Bi and Te) [14]. Finally, it is necessary to prereduce elements such as arsenic from the pentavalent to the trivalent state prior to hydride generation. Although several prereducing agents have been studied [14], a combination of $SnCl_2$ and KI has been the most widely accepted and used [14]. Due to the fact that the Zn/HCl is a rather slow reaction, it is necessary, in most cases, to trap the hydride or even condense it in a liquid

nitrogen U-tube, as described by Holak [13], prior to expulsion to the atomization cell.

A more recent and more effective method utilizes sodium borohydride(III) as the reducing agent and it is applied almost exclusively in solution form. Reduction by this method occurs as shown in equation 2,

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H' \xrightarrow{E^{m+}} EH_n + H_2 \text{ (excess)} \quad (2)$$

where E is the analyte of interest and m may or may not equal n. Braman et al. [15] were the first to use this system for the reduction of arsenic and antimony in 1972. Schmidt and Royer, cited in [14], were the first to expand its application to arsenic, bismuth, antimony and selenium by AAS. Later, the technique was extended to the determination of germanium, tin and lead [14]. Since then, $NaBH_4$ reduction has virtually replaced the metal/acid reaction for analytical methods of hydride generation.

When the heterogeneous Zn/HCl reduction system is compared with the homogeneous $NaBH_4$ system, it can be easily concluded that the latter is superior with respect to reaction yield and reaction time. Typical reaction periods range from 10 to 30 seconds. This reduces the need for trapping or collecting the hydride evolved. Another significant advantage is that hydrides of all eight elements can be generated using this reaction. Finally, this reduction system possesses a greater

advantage for automated analysis and for multielement analysis capabilities by AES than the Zn/HCl system.

In addition to the Zn/HCl reaction and the $NaBH_4$/HCl reaction, other metal-acid reactions have been investigated for the generation of arsine and other hydride forming elements. Goulden and Booksbank [16] used an aqueous slurry of aluminum powder instead of zinc to generate AsH_3, SbH_3, and SeH_2. This had the advantage of being a faster reaction than the Zn/HCl one and, therefore, more suitable for automation. In a similar fashion, Pollock and West [17] employed a mixture of magnesium metal and titanium(III) chloride reacted with HCl to generate the hydrides of As, Sb, Se, Bi and Te. However, these latter methods have received very little attention.

Ever since Braman *et al.* [15] used sodium borohydride to generate arsine, the technique has gained widespread attention, to the point that it is now the most popular and effective method for hydride generation. Originally, the use of sodium borohydride as pellets dropped into a reaction flask was the choice of many workers, until Mc.Daniel *et al.* [18] determined that the efficiency of the pellets was only 40-60% that of $NaBH_4$ solution. This resulted in a step forward towards automation. It is now customary to use an aqueous solution of $NaBH_4$ whose concentration ranges from 0.5 to 10% [14].

4) METHODS OF HYDRIDE MANIPULATION

Two different methods of hydride manipulation have been

described:

1) The hydride produced from a sample solution is directly transferred into the atomizer (direct transfer mode). This can be accomplished by using either a continuous flow system or by using a batch system.

2) The hydride is collected until evolution is completed, (i) in a container under pressure along with the hydrogen formed in the reaction or (ii) in a cold trap without the hydrogen.

In the batch system, $NaBH_4$ is added to the acidified sample and the hydride formed is stripped from the solution with an inert gas. With the continuous flow system, the sample and the $NaBH_4$ are mixed with the use of either a peristaltic pump or a pressurized reagent pumping system. The hydride is then separated in a gas-liquid separator and carried by the hydrogen to the atomizer.

A batch system, which can be automated or not, produces a transient signal, whereas the continuous flow system gives a continuous signal. The batch system gives better sensitivity; however, the continuous system can be more easily automated. Also, analysis time can be greatly reduced by this latter type. In the batch system the signal maximum depends on the analyte mass, not its concentration, and theoretically the sensitivity can be increased by applying larger volumes of sample. On the other hand, the signal produced by the continuous system is dependent upon the analyte concentration and the sample flow rate in much the same way as any solution nebulization system.

The collection mode system provides peak type signals

and sensitivity can also be further improved by separating the hydride from the excess of hydrogen produced, which acts as diluting medium. This is accomplished by the use of a cold trap.

Early procedures for hydride determinations included some form of collection of the hydrides, either in a rubber balloon [7,17,19,20], in a pressurized chamber [5,21,17,22,23,24] or in a U-tube at liquid nitrogen temperature [18,25-28] as originally described by Holak [13]. Although the trapping or condensation techniques have proven to be valuable in a great number of studies, it should be noted that, since the introduction of $NaBH_4$ as a reducing agent, the need to collect the liberated hydride has, in many cases, been eliminated. Nevertheless, it is still used to concentrate the analyte concerned so that subsequent signal responses may be sharpened. According to Chapman and Dale [21], however this is useful only for the most stable hydrides, such as AsH_3, SbH_3, BiH_3 and SeH_2.

The direct transfer mode became, therefore, more popular and a number of workers have reported on this system [8,29,30,31-33], which does not necessitate any collection of the hydride being measured.

5) HYDRIDE ATOMIZATION AND DETECTION

A variety of spectroscopic techniques have been coupled with the hydride generation reaction [14]. Since atomic absorption instrumentation is readily available in most

laboratories, the vast majority of workers have chosen this technique to atomize and detect the hydride. However, other techniques such as Atomic Fluorescence Spectrometry (AFS) and Plasma Atomic Emission Spectrometry (AES) are also gaining widespread use.

a) AAS/AFS

A variety of atomizers have been coupled with AAS and AFS. In this regard, Dalton and Malanoski [34] introduced arsine into an argon (entrained air)-hydrogen flame after collecting it in a balloon. Since then, this relatively cool and low-background flame has been used by many workers [14]. In addition to the use of flame atomizers, other systems have been used to date. These include flame-in-tube atomizers, flame heated quartz tubes, electrically heated quartz tubes, heated quartz tube fluorescence cells and graphite furnace atomizers.

Chu *et al.* [19] were the first to describe the use of an electrically heated quartz tube for the thermal decomposition of arsine in an argon atmosphere. They generated the hydride and swept it with a stream of an inert gas such as argon, nitrogen or helium into the tube. Due to the increased residence time the atoms spend in the optical path, the lower dilution by the flame gases, and the much reduced noise levels, this method was found to be twice as sensitive as atomization in an argon hydrogen flame. Numerous workers [21,35-39] have adopted the use of electrically heated quartz tubes, whose major

advantage is that the temperature can be controlled and optimized for each element.

Another flameless atom reservoir that has been gaining widespread attention is the graphite furnace atomizer. In an effort to increase sensitivity, Knudson and Christian [40] reported the use of this type of atomizer for combustion of the arsine and subsequent detection by AAS. Their work has been echoed by many others [14].

Germanium has been largely determined spectrophotometrically in the submicrogram range as the phenylfluorone complex [41]. However, such methods are usually complicated, since extraction and distillation procedures (to overcome interferences from other trace metals) generally have to be applied. Furthermore, the determination of germanium by atomic absorption spectrometry presents some difficulties due to the production of highly stable oxide species in the flame. In order to compensate for this, a dinitrogen oxide-acetylene flame is often used in combination with solvent extraction.

The high temperatures and relatively long residence times available in graphite tube atomizers have made possible some improvements in sensitivity. Johnson *et al.* [42], reported a detection limit of 0.3 ng of germanium.

Pollock and West [43] were the first to report the determination of germanium by hydride generation with $NaBH_4$. They used standard flame atomic absorption techniques and reported a detection limit near 0.5 ng/mL of Ge. The use of a silica tube within an air-acetylene flame by Thomerson and

Thompson [44] did not improve the detection limit obtained by Pollock and West [43].

Germanium has been determined in aqueous matrices by Andreae and Froelich [45], who reduced germanium(IV) with $NaBH_4$ to germane and collected it in a liquid nitrogen-cooled trap. After rapid heating of the trap, the released germane was conveyed into a modified graphite furnace and atomization was carried out at 2600 C. In this way, they obtained an absolute detection limit of 140 pg of germanium and a concentration limit of detection of 0.56 ng/L for a 250 mL sample.

Jin et al. [10] determined germanium by AAS following volatile hydride generation. They studied three types of hydride generator systems: a) a collection-type hydride generator connected to a nitrogen-hydrogen flame, b) a direct-transfer type generator connected to a flame heated silica tube and c) a direct-transfer type generator connected to a nitrogen-hydrogen flame. Of the three, the third was found to be the most suitable. They also studied the effect of diverse acids and reported an increase in the sensitivity of the germanium signal (40-60%) in phosphoric acid medium over hydrochloric acid, malic acid or tartaric acid media. The reported detection limit for germanium was 0.35 ppb for a 20 mL sample.

Halicz [46] described a method for the continuous generation of germane and the subsequent atomization in a dinitrogen oxide-acetylene flame. The procedure involved the extraction of germanium(IV) with carbon tetrachloride, which Halicz claimed could free the analysis from any other

interfering elements. He applied the method to the determination of germanium in silicate rocks, sulphide ores, carbonate rocks and soils.

The first to measure arsenic by dispersive AFS was Thompson [47], who introduced the hydrides of As, Sb, Se and Te directly into an argon-hydrogen flame and used a modulated microwave-excited electrodeless discharge lamp to excite the atom cloud. The detection limits obtained for a 15 mL sample ranged between 0.06 to 0.1 ug/L. On the other hand, Tsujii and Kuga [48] used nondispersive AFS coupled with hydride generation for the determination of arsenic. They generated the arsine by the Zn/HCl reaction and carried it into an argon hydrogen flame by a stream of argon. They used a solar-blind photomultiplier insensitive to radiation above 360 nm as detector and an electrodeless discharge lamp as the radiation source. In a later report [49], the same workers modified their reaction flask and used $NaBH_4$ to liberate the hydrides of As and Sb.

In a similar fashion, Nakahara *et al.* [50] compared the use of an argon hydrogen flame with a nitrogen hydrogen flame for the determination of arsenic using the Zn/HCl reduction system. They used a nondispersive AFS system and concluded that the former flame is more sensitive than the latter because of the higher flame temperature.

b) AES

Atomic emission has been used by numerous workers [14]

employing Direct Current Plasmas, Microwave Induced Plasmas and Inductively Coupled Plasmas as excitation sources.

The determination of arsenic and other elements by Inductively Coupled Plasma as an excitation source coupled with hydride generation is becoming widespread because of the increasing availability of many types of commercial instruments.

Thompson et al. [51,52] were the first to report the use of hydride generation coupled with ICP for the determination of As, Bi, Sb, Se and Te. They used a continuous hydride generator system, introduced the hydrides directly into the ICP, and simultaneously detected them by measuring the atomic line emission intensities. With this system they were able to improve the sensitivity and detection limits by an order of magnitude over conventional solution nebulization. Eventually they extended this procedure to the determination of Ge and Sn.

Miyazaki et al. [53] coupled a direct current plasma with the hydride generation technique for the determination of As and Sb by the Zn reduction method. They separated the hydrides from the excess hydrogen with the use of a liquid nitrogen trap and reported detection limits of 8 ng for arsenic and 40 ng for antimony in a 20 mL sample. In a later study, Panaro and Krull [54] determined total arsenic in food matrices with the use of a continuous flow hydride generator followed by direct current plasma emission spectroscopic detection. They compared this system with the continuous hydride formation-flame atomic absorption detection system and with the sequential hydride formation-flame atomic absorption detection system.

They found detection limits in aqueous solution to be 25, 10, and 0.2 ppb respectively. The better sensitivity of the latter was attributed to the fact that the sequential system actually preconcentrated all arsenic present in the sample before introduction into the flame, while the continuous approach formed hydrides as the arsenic sample continuously entered the hydride generator system.

The effect of a range of acids on the reduction of tin and germanium to their hydrides in aqueous solutions, as well as the interference effects of diverse ions in hydrochloric acid and tartaric acid media, was studied by Thompson and Pahlavanpour [55]. They used $NaBH_4$ solution in a continuous flow system coupled with ICP-AES and reported a detection limit for germanium of 0.3 ppb.

Eckhoff *et al.* [56] separated the hydrides of As,Ge and Sb on a column of Chromosorb 102. After condensation in a U tube, they introduced them into an ICP. A sequential slew scanning monochromator was used to monitor each resolved chromatographic peak at a different atomic emission wavelength. These investigators reported a detection limit for germanium of 0.2 ppb.

Several non-plasma AES detection systems have also been used for the determination of arsenic and other hydride forming elements. The use of Molecular Emission Cavity Analysis (MECA) by Belcher *et al.* [57] for the determination of As and Sb is an example of this. They produced arsine and stibine by the $NaBH_4$ method and swept them with nitrogen gas into the MECA cavity

which was placed in a nitrogen-hydrogen flame. After sample vaporization, they measured the characteristic molecular emission bands of each element.

Gas-phase-chemiluminescence was proposed for the determination of hydrides by Fujiwara *et al.* [58]. They introduced arsine and stibine, generated by the $NaBH_4$ reaction, into a flow-type furnace-hydrogen diffusion flame and measured the molecular emission peaks from arsenic and antimony as AsO and SbO respectively.

c) MULTIELEMENTAL ANALYSIS

To date, only AES and to a lesser extent AFS, can offer the analytical chemist simultaneous multielement capabilities. In particular, ICP-AES has been the most widely accepted technique for the simultaneous determination of hydride forming elements. In this regard, Thompson *et al.* [51], simultaneously generated and detected the hydrides of As, Bi, Sb, Se, and Te by ICP. They used 1% $NaBH_4$ solution in 5 M HCl to generate the hydrides and obtained detection limits in the range of 0.8 ng/mL for As to 1.0 ng/mL for Te.

More recently, Halicz and Russel [59] simultaneously determined As, Sb, Se, and Te in silicate rocks containing the noble metals and in sulphide ores by hydride generation and ICP-AES. They separated the analytes of interest from the matrix by coprecipitation with Fe(III) hydroxide at pH 2.40 and concluded that interference effects were in this way reduced to

a minimum. Since the experiments were carried out in 1:1 hydrochloric acid medium, minimum interference from iron(III) was observed.

Wolnik *et al.* [60] determined all the hydride forming elements (except Pb and Sn) along with a variety of other elements in foods by ICP-AES. The use of a tandem nebulization system, consisting of a spray chanber interconnected with a cross-flow nebulizer, was investigated. Sodium borohydride solution was aspirated through the spray chamber. The nebulized solution produced in this way was mixed with the sample solution in the cross-flow nebulizer. After mixing, the sample and the borohydride were directed towards the ICP torch. With this system the detection limit of the hydride forming elements was improved by at least one order of magnitude over conventional pneumatic nebulization systems. Detection limits for the other elements investigated remained the same as for normal solution nebulization. The detection limit achieved for germanium was 20 ppb and the one for arsenic was 3ppb. In a similar fashion, Hahn *et al.* [61] were able to achieve a detection limit of 0.6 ppb for germanium with a hydride generation/condensation system interfaced to an ICP polychromator. They simultaneously determined As, Bi, Ge, Sb, Se, and Sn and applied their method to food analysis.

All of the aforementioned procedures for simultaneous multielement analysis have proven very valuable for rapid routine analysis of a wide range of different sample types. However, sensitivity and detection limits are somewhat

compromised when the simultaneous reduction of all the hydride forming elements is carried out.

As can be seen, the analytical performance of hydride generation in these techniques will mainly depend on the type of hydride generator being used, the type of atomizer employed, the optimum experimental conditions for a given element and the particular spectrophotometric technique employed for measurement. When evaluating these techniques in terms of reported detection limit, however, attention has to be paid to the definitions of detection limit applied in each particular case.

6) CHEMICAL SPECIATION

a) ORGANIC SPECIATION

The determination of various organic forms of hydride forming elements, including arsenic, has been performed on enviromental samples and biological materials. This was done by generating inorganic and organic hydrides with $NaBH_4$ and collecting them in a liquid nitrogen cold trap. The different species can be determined by selective volatilization according to their boiling points or by separating them by gas chromatography. Braman and Foreback [62] utilized the first of these techniques for the determination of methylarsinic acid $CH_3AsO(OH)_2$ and dimethylarsinic acid $(CH_3)_2AsO(OH)$. They reduced both acids with $NaBH_4$ at pH 1-2 to their respective hydrides and detected

them by AES. Andreae et al. [63] used the second method for the determination of antimony(III), antimony(V), methylstibonic acid and dimethylstibinic acid by the $NaBH_4$ reaction under highly acidic conditions. Speciation of organic forms by hydride generation AAS or AES has also included the elements Ge, Se and Sn [14].

The determination of inorganic and methylgermanium species in aqueous matrices by a combination of hydride generation, graphite furnace atomization and AAS detection was carried out by Hambrick et al. [64]. They generated the hydrides by the $NaBH_4$ reduction and, after collection in a liquid nitrogen-cooled trap, they introduced them into a modified graphite furnace at 2700 C. The reported detection limit for inorganic germanium was 155 pg.

Braman and Tompkins [65] reported a detection limit of 0.4 ng of germanium by coupling the $NaBH_4$ reaction to a direct current discharge atomic emission detector. Reduction was carried out by adjusting the pH to 1.5 with a 10% (m/v) oxalic acid solution. They applied their system to the analysis of natural water and air particulates in the Tampa, Florida area and reported the presence of inorganic antimony and germanium, whereas organometallic compounds of either element were not detected in any of the environmental samples analyzed.

b) INORGANIC SPECIATION

Although it has been claimed that $NaBH_4$ reduction

systems do not require preliminary reduction of the element under study, the quantitative determination of some hydride forming elements has been the subject of much discussion. Since arsenic can exist in solution in two oxidation states, As(III) and As(V), several authors have studied the effect of the valence of the elements in the solution on the formation rate of the metal hydride. Some workers have added potassium iodide [14] while others have added a mixture of potassium iodide with ascorbic acid [14] to acheive prereduction before hydride generation for total determination of arsenic and selenium.

Vanloo et al . [66] have oxidized As(III) to As(V) with perchloric acid for total determination of arsenic. Aggett and Aspell [24] described a method for the selective determination of As(III) by maintaining the pH of the solution between 4 and 5. They also reported the quantitative determination of total arsenic at a pH less than 1. Hinners [67] reported that As(III) and As(V) respond similarly in HCl when sufficient sodium borohydride is used. Thompson and Thomerson [31] found that As(V) gives 90% of the signal of As(III) when a 4% m/V. sodium borohydride solution is used for reduction. Siemer and Koteel [27] reported that the often observed difference in response for As(III) and As(V) disappears when the arsine is collected into a cold trap before it is introduced into the atomizer cell. Thompson and Thoresby [68] reported that the ratio of the signals for the two oxidation states varies with the major anion present and, with the use of H_2SO_4, better consistency in the results can be achieved with a slight reduction in sensitivity.

Narasaki and Ikeda [69] reported the determination of As and Sb with a flow injection batch system and showed that the sensitivities of As(III) and As(V) were similar.

More recently, Anderson *et al.* [70] determined As(III) and As(V) in hydrochloric acid medium by continuous hydride generation. They reported that the signal from As(V) was 50% that of the As(III) signal. However, when a 26-turn reaction coil was inserted to increase the contact time between $NaBH_4$ and the sample to approximately 15-20 seconds, the response of As(V) increased to 95% that of As(III).

7) INTERFERENCES AFFECTING THE HYDRIDE GENERATION TECHNIQUE

Two types of interference can be distinguished in the hydride generation technique: a) matrix interference in the liquid phase of hydride generation and b) matrix interference in the gaseous phase of hydride generation (either during hydride transport or in the atomizer). However, due to the very limited number of elements that can be volatilized by this technique, the latter type of interference is usually very unlikely, with the exception of mutual interference of the hydride-forming elements [32]. Interferences inside the atomizer depend exclusively on the mechanism of atomization in a given type of atom reservoir. On the other hand, the liquid phase interferences can be ascribed to changes in the hydride generation rate (generation kinetics interferences) and/or to a decreased fraction of analyte reduced and released from the

sample solution.

The first systematic study of the effects of 48 elements on the determination of As, Bi, Ge, Sb, Se, Sn and Te was carried out by Smith [32]. In his study, he observed no interference from the alkali and alkaline earth metals. However, interferences from Cu, Ag, Au, Pt, Rh, Ru, Ni and Co were always present. Smith found that many of these interfering elements formed precipitates after the addition of $NaBH_4$ solution. He proposed that a preferential reduction of the metal ion interferent in solution to a different oxidation state or to the free metal could cause precipitation of the species. The analyte element could then be either coprecipitated with the free metal or could be adsorbed (after hydride formation) and catalytically decomposed.

Smith's findings were supported by Kirkbright and Taddia [71] who also noticed the finely dispersed black precipitate in the presence of elements such as Ni, Pb and Pt. They reported complete suppression of the arsenic signal on addition of nickel powder. Furthermore, they pointed out the fact that nickel and other group VIII elements are hydrogenation catalysts which can absorb hydrogen in large amounts. The authors also observed a decrease in interference with increasing acidity of the solution and explained that this was due to the greater solubility of the reduced interfering metal in the stronger acid.

Meyer et al. [72] reported strong interference from transition metals on the determination of selenium. However, mention of the interferent precipitation was not made. They

attributed the interference to be caused by the formation of insoluble selenides or stable complexes with the free ions of the interfering elements in solution in a secondary reaction which occurred during hydride transportation through the bulk solution. Such a gas-liquid reaction would only depend on the speed of diffusion of the hydride across the gas-liquid interface and on the concentration of the interfering ion in the solution. They also experienced a reduction in the interference from transition metals with increasing acid concentration as was reported by Kirkbright and Taddia [71].

In a comprehensive study, Pierce and Brown [73] determined the interference effects of several anions, cations and acids on the determination of As and Se by AAS. Three sample atomization techniques were investigated: Manual hydride generation with argon-hydrogen flame atomization, automated hydride generation with heated quartz tube atomization, and graphite furnace atomization. They found strong interferences for each of the three techniques used from Co and Ni, as well as from elements of the copper group, the noble metals of the palladium and platinum groups, permanganate, persulfate, dichromate, nitric acid and sulphuric acid; however, they reported that the automated system produced the least amount of interfering effects.

The interference in the gaseous phase from Sn, Pb, As, Sb, Bi, Te, and Hg in the determination of Se was studied by Dedina [74]. With the aid of ^{75}Se tracer, he found that As and Bi caused liquid phase interference while the other elements

exhibited strong gas phase interferences. He claimed that with the use of an oxygen-hydrogen flame-in-tube atomizer, the gas phase interferences could be reduced by 2-3 orders of magnitude over electrically heated quartz tube atomizers.

Welz and Melcher [75] were able to reduce by three orders of magnitude the interference caused by selenium in the determination of As(III) and As(V) by the addition of 50 mg/L of copper to the sample solution. They claimed that copper prevents the evolution of hydrogen selenide.

In a more recent work, Dittrick and Mandry [76] studied the determination of hydride forming elements (As, Sb, Se and Te) in volatile hydride-forming matrices (As, Sb, Bi, Se, Te, Ge, Sn and Pb). They were able to reduce the strong matrix interference in the liquid phase produced by Bi and Sn by matrix modification with EDTA. To diminish or avoid matrix interferences in the gaseous phase they proposed a new type of atomizer, the graphite paper tube atomizer. Temperatures as high as 2600 C can be reached; consequently, atomization is now a thermal dissociation which no longer requires hydrogen radicals. Diatomic molecules such as AsSe, AsSb, BiAs etc. are formed at temperatures below 1000 C and are dissociated above 2000 C.

Welz and Melcher [77] studied the influence of Co, Cu, Fe, and Ni on the selenium determination. With the use of a two flask system they generated hydrogen selenide from pure acid solution with $NaBH_4$ in the first flask and subsequently bubbled it through the interfering ion solution in a second flask. They

showed that the interference from these ions started to affect the determination of selenium only when the interferent was present at high concentrations (10-100 mg/L). However, when the interferents were reduced together with the Se in the same flask, the interference was 2-3 orders of magnitude more pronounced. They suggested that the interference could be greatly reduced by increasing the concentration of HCl.

The same authors [78] also studied the influence of the valency state of arsenic on the degree of signal depression caused by Cu, Fe and Ni. They showed that the interference was stronger for As(V) than for As(III) and concluded that the phenomenon was due to the slower evolution of arsine from As(V). They suggested that the precipitation of the interfering metal was more complete at the time when the arsine was evolved from As(V) than from As(III). This left, therefore, more time for the catalytic decomposition of the hydride by the finely dispersed form of the metallic species. They recommended that As(V) be reduced to As(III) with KI prior to analysis and that all determinations be carried out in 5 M HCl. The authors also demonstrated that the addition of Fe(III) in the presence of nickel further increased the range of interference-free determinations. This finding led them to the investigation of the releasing effect of Fe(III) on nickel interference on arsenic and selenium in a later report [79]. They concluded that the strong interference from nickel could be substantially reduced by using a higher acid concentration and by the addition of 2 mg of Fe(III) to the sample. According to the authors,

preferential reduction of Fe(III) to Fe(II), a reaction with a high positive reduction potential (+0.77 V), occurred thus inhibiting the precipitation of the interfering metal (Ni^{2+} to Ni^{o} -0.23 V) so that nickel would be reduced to the metal and precipitated only after all the Fe(III) had been reduced to Fe(II). In this way, less time was available for the nickel metal to catalytically decompose the generated hydride. The authors also explained that reduction of bivalent iron to the metal has an even more negative potential (-0.41 V) than the reduction of nickel ions to the metal so that no effect can be expected for this species.

In general, only those elements that can be reduced easily by $NaBH_4$ have been found to interfere with hydride generation. Many workers have tried to eliminate or reduce interferences by many different methods [14]. The most commonly used one, as previously discussed, is increasing the acidity of the reaction medium. Originally it was thought that an increase in $NaBH_4$ concentration would free the analysis from some potential interferences as well; however, this assumption has proven to be incorrect, as reported by Welz and Schubert-Jacobs [80], who extended the interference-free determination of As and Se in the presence of Cu, Ni, Fe and Co by applying a higher concentration of HCl and a lower $NaBH_4$ concentration to the sample solution. They claimed that precipitation of the interfering metal ion was less pronounced under these conditions owing to: i) better solubility of the metal in the more acidic solution, ii) formation of chloro-complexes, reducing in this

way the concentration of free ions in solution and iii) a smaller concentration of $NaBH_4$ is available to react with the interfering metal ion. The only disadvantage of this procedure, however, appears to be that the sensitivity of most hydride forming elements is greatly reduced under these conditions than at lower acid concentrations and higher $NaBH_4$ concentrations.

Other authors have studied a variety of masking agents to reduce or eliminate the interferences that plague hydride generation [14]. Among those worth mentioning are: EDTA, KI, KCN, thiosemicarbazide, 1,10-phenanthroline, tartaric acid and thiourea. The use of $La(OH)_3$ and $Fe(OH)_3$ to coprecipitate diverse interfering elements has been applied. The separation of the interferents by ion-exchange resin has been studied as well.

As can be seen, there are many interferences to which the hydride generation technique is subject. It was the purpose of this study to shed more light on the sometimes contradictory reports about the interferences caused by concomitants in the determination of As and Ge by the hydride generation technique.

D. THEORY OF ATOMIC EMISSION

When an atomic vapour is formed in an atom reservoir, a small number of atoms are transferred to an excited state by vibrationally excited gas molecules [81], as depicted below:

$$F^* + A \text{ ---- } F + A^*$$

$$A^* \text{ ----- } A + h\nu$$

where A is the atom produced in the atomic vapour, F is the flame gas molecule, A^* is the electronically excited atom and F^* is the vibrationally excited flame gas molecule.

Upon decay to its ground state (A), the atoms will emit radiation of a frequency which is characteristic of that element. The intensity of a spontaneous emission line is related to A_{ij} (the Einstein transition probability, defined as the probability that an atom in state "i" will spontaneously emit a quantum (hv) and pass to the state "j") by the following equation:

$$I_{em} = A_{ij} h\nu_o N_j \quad (3.1)$$

where N_j represents the total number of atoms in the excited state "j", h is Planck's constant and ν_o is the frequency of the spectral line at the center of the peak.

For a system in thermodynamic equilibrium, the number of atoms N_j that are in an excited state compared to the number of atoms in the ground state N_o is given by the Boltzmann distribution law:

$$N_j = (N_o g_j / g_o) \text{ Exp } [-(E_j/KT)] \quad (3.2)$$

where g_j and g_o are the statistical weights of the jth and

ground states respectively, where (g=2J+1), J is the third quantum number. E_j is the energy of the excited state, K is the Boltzmann's constant and T is the absolute temperature. Thus one can write:

$$N_j/N_o = (g_i \text{ Exp } [-(E_j/KT)])/(g_o \text{ Exp } [-(E_o/KT)]) \quad (3.3)$$

Expressing N (the total number of atoms present) as the sum of the population of all levels, i.e. $N = \Sigma_j g_j$, the equation may be rewritten as:

$$N_j/N = g_j \text{ Exp } [-(E_j/KT)]/\Sigma_j g_j \text{ Exp } [-(E_j/KT)] \quad (3.4)$$

$$= g_j \text{ Exp } [-(E_j/KT)]/F(T) \quad (3.5)$$

where F(T) is known as the partition function.

If self-absorption is neglected for a system in thermodynamic equilibrium, equation 3.1 can be expressed as:

$$I_{em} = A_{ij} h v_o (N g_j \text{ Exp } [-(E_j/KT)])/F(T) \quad (3.6)$$

A more simplified version of this formula can be obtained if one considers that virtually all the atoms remain in the ground state; thus, N, the total number of atoms, which is directly related to the concentration in solution, is aproximately equal to N_o, and equation 3.2 becomes:

$$N_j = (N g_j)/(g_o) \text{Exp } [-(E_j/KT)] \quad (3.7)$$

Equation 3.6 becomes:

$$I_{em} = (A_{ij} h v_o N g_j)/(g_o) \text{Exp } [-(E_j/KT)] \quad (3.8)$$

For practical purposes this is similar to equation 3.6. It can be, therefore, concluded that the intensity of atomic emission lines is critically dependent on temperature. It also follows that when low concentrations of analyte atoms are present (negligible self-absorption) the plot of emission

intensity against sample concentration results in a straight line.

E. DIRECT CURRENT PLASMA

A plasma is defined as "any luminous volume of gas having a fraction of its atoms or molecules ionized" [82]. Although this definition encompasses flames, it is usually applied to plasmas formed by electrical exitation.

Figure 1 shows a schematic representation of the three-electrode direct current argon plasma used in this study. The plasma jet is formed between two spectrographic carbon anodes and a tungsten cathode in an inverted Y configuration. The third electrode has been added to stabilize the discharge.

The temperature in the plasma column can be as high as 9000 K; however, due to the high plasma continuum, observation in this region is not possible. For better analytical signal-to-background ratios, the plasma has to be viewed at the angle of the Y where the temperature is approximately 6000 K.

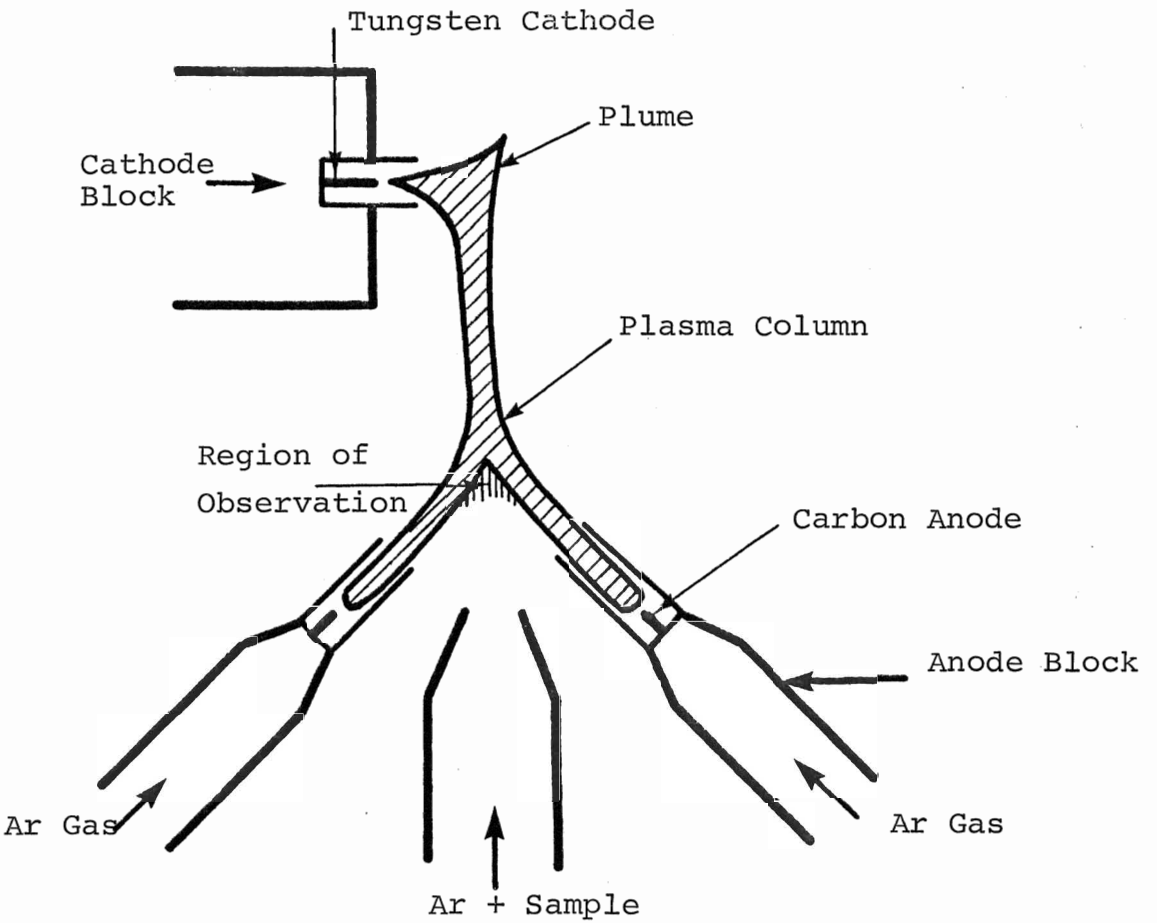


Figure 1. Schematic representation of the three electrodes D.C. Plasma source used in this study (82).

CHAPTER 2

EXPERIMENTAL

A. Apparatus

1) DCP SPECTROPHOTOMETER

A Spectraspan V DCP spectrophotometer equipped with a dynamic background compensator (DBC-33) and a Dataspan Data storage system was used throughout this work. Signals were recorded on a Fisher Recordal Series 5000 chart recorder.

2) HYDRIDE GENERATOR

Spectrametrics, a division of Smith-Kline Beckman, manufactures a sequential hydride generator which is intended to interface with the Spectraspan series of D.C. plasma emission spectrometers (fig. 2). This apparatus consists of a medium frit Buchner funnel as a reaction vessel (D), with a sintered glass platform to contain solution, a drying column packed with 8-12 mesh calcium chloride (A), a short hydrogen delay column of Porapak Q (B), a flowmeter(I) and a sample tube head (K). Nalgene tubing of 1/4 inch internal diameter and 1/16 inch wall was used for all connections. The head consists of two concentric tubes; the outer tube is perforated to allow passage of argon and, supposedly, nebulized aqueous solutions. The

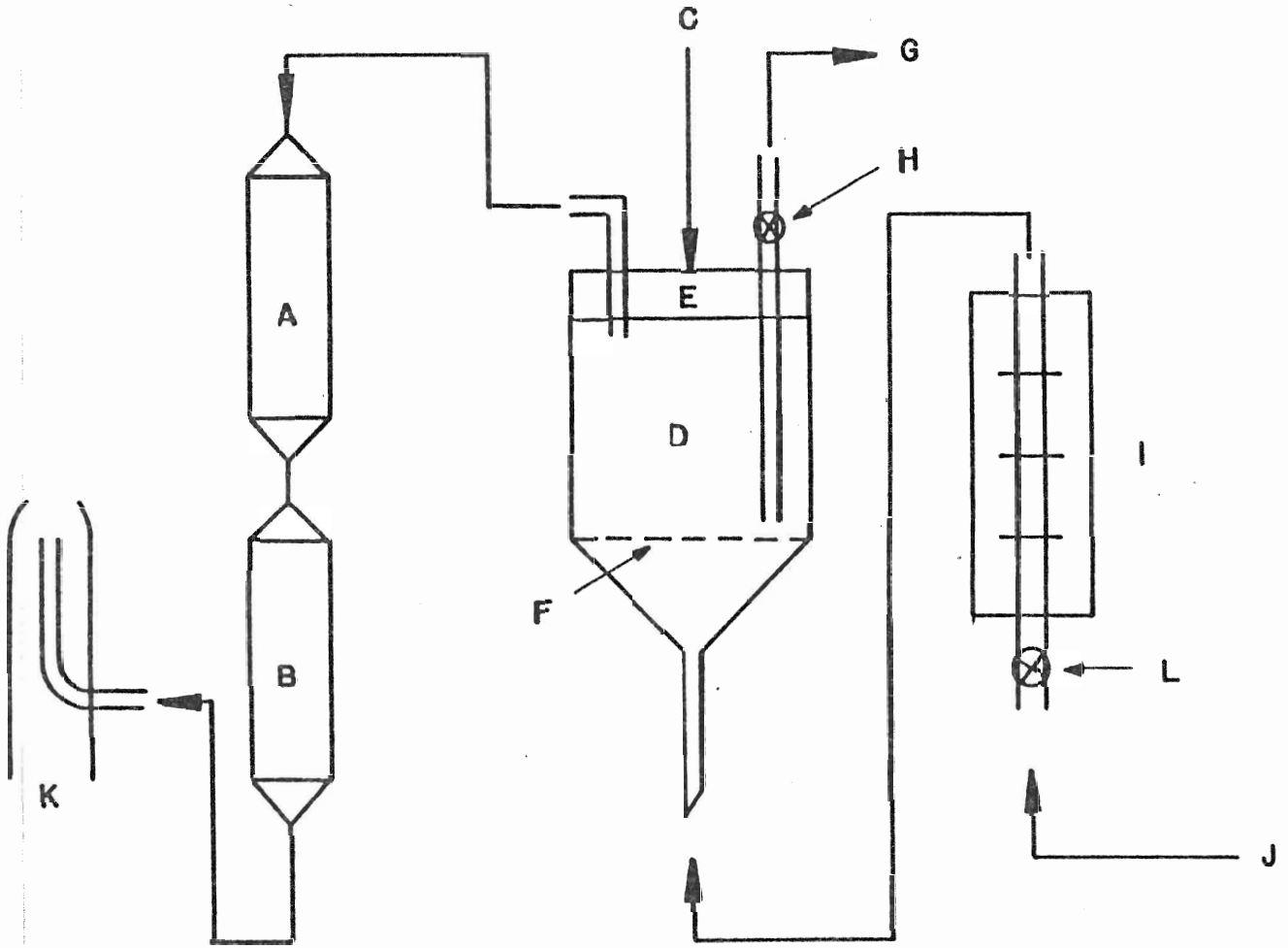


Figure 2. Schematic representation of the hydride generator. A) drying column, B) delay column, C) sample injection port, D) Buchner funnel, E) rubber stopper, F) sintered glass, G) to waste line, H) rinse valve, I) flowmeter, J) argon supply, K) sample tube head, L) purge valve

inner alumina tube is intended to transfer the hydride from the reaction vessel into the plasma. The hydride, produced by the borohydride reaction, is stripped from the reaction vessel by argon which is passed up through the Buchner frit and the solution. The hydride and hydrogen are carried, by the argon, through the drying column and the Porapak Q column, and finally through the narrow tube into the excitation zone of the plasma. The process is controlled by a series of taps (L,H) which allow the argon to flush the system as well as to empty the reaction chamber.

An early problem [83] with this apparatus was associated with the drying column. After several determinations, the calcium chloride became wet and the drying tube became impermeable to the argon. This often caused a back pressure which, on several occasions, blew off the top of the reaction vessel. The saturated calcium chloride solution also tended to drip onto the Porapak Q column which exacerbated the back pressure problem. These problems were solved [83] by substituting the calcium chloride with anhydrous calcium sulphate of 8-12 mesh, which proved to be more efficient.

Despite assertions that aqueous solutions could be aspirated through the outside cylinder of the head, this could not, in fact, be accomplished. An aqueous solution nebulized in the usual way, clogged up the small holes which perforate the outer tube and gave no signal. Thus, the methods available to the analyst to optimize the position of the head with respect to the plasma are: 1) to buy a cylinder of arsine, or other

hydride, for the purpose or 2) to perform repeated hydride generations in the hope that the position will eventually be correct. The former prospect has the advantage of a speedy set-up and the disadvantage of a particularly poisonous gas which would have to be kept in the lab in quantity. The second possibility is no better than the first. Considerable wear occurs on the electrodes if the plasma has to be turned on and off repeatedly; also, this process can be quite time consuming. These problems were solved by redisigning the sample tube, as will be seen in a later section.

3) SYRINGES

A variable volume Brinkmann Macro-Transferpettor of 10 mL capacity was used for all sample injections. However, a disposable hypodermic plastic syringe, 3 mL capacity, fitted with a micropipette tip was used to introduce solutions of $NaBH_4$ into the reaction cell.

4) SUMMARY OF OPERATING PARAMETERS

Spectrometer:	Spectraspan V (sequential)
Slits:	Entrance: horizontal 50 μm; vertical 300 μm Exit: horizontal 100 μm; vertical 300 μm
Detector:	1-1/8 inch Hamamatsu types R292, R374 and R268 (or equivalent) photomultiplier tubes (PMT).
Source:	High energy dc argon plasma, formed by a tungsten cathode and two spectrographic carbon anodes in an inverted Y configuration.
Temperature:	5500 - 6000 K
Argon Supply:	Linde welding grade-Union Carbide Canada Ltd. Tank pressure: 90 psi Sleeve pressure: 50 psi Nebulizer pressure: 26 psi Flow rate of argon through hydride generator "optimum" As: 21 mL/s Ge: 27 ml/s.
Jet Power Supply:	7 amps constant current output, low voltage (approx. 40 V) after plasma has been established.
Optical Design:	Modified Czerny-Turner using an echelle grating with 30° prism for order separation.
Wavelength:	As: 193.7 nm Ge: 303.9 nm
Operating Mode:	Active diagnostic mode using chart recorder Gain: 5-25 PMT voltage (5-9): 500-900 V Repeat: 0
Recorder:	Fischer Recordal series 5000. Chart speed: 1 inch/min Sensitivity: 10-100 mV

These were the operating conditions unless otherwise stated.

B. Chemical Reagents

The following is a list of the chemicals used in this study.

1) Acetic acid glacial (Laboratory reagent, BDH Chemicals Ltd., Toronto).

2) Ammonium germanium (IV) oxalate hydrate, 99.998% (Gold label, Aldrich Chemical Company Inc., Milwaukee, Wisconsin, USA, 53233).

3) Ammonium hydroxide (ACS reagent grade, Caledon laboratories Ltd., Georgetown, Ont. Canada).

4) Ammonium persulphate ("AnalaR", BDH Chemicals, Toronto).

5) Antifoam "B" (reagent solution, BDH Chemicals, Toronto).

6) Arsenic trioxide ("AnalaR", BDH Chemicals Ltd., Poole, England).

7) Cadmium shot (Alfa Products, Thiokol/Ventron, Andover Street, Danvers, Massachusetts, USA).

8) Calcium sulphate anhydrous (drierite-8 mesh) (Laboratory reagent, BDH Chemicals,Toronto).

9) Cobalt 50 mesh (Alfa Products, Thiokol/Ventron, Andover Street, Danver, Massachusetts, USA).

10) Copper shot (Alfa Products, Thiokol/Ventron, Andover Street, Danver, Massachusetts, USA).

11) Disodium hydrogen arsenate heptahydrate ("AnalaR", BDH Chemicals Ltd., Poole, England).

12) Germanium standard solution 1000 ppm assured for Atomic Absorption Spectroscopy (Analytical Reagent, BDH Chemicals, Toronto).

13) Hydrochloric acid ("AnalaR", BDH Chemicals, Toronto).

14) Iron wire 99.91% (Baker Analyzed Reagent, Phillipsburg, N.J., USA).

15) L-Cysteine 97% (Aldrich Chemical Company Inc., Milwaukee, Wisconsin, USA, 53233).

16) L-Cystine 99% (Sigma Chemical Company Inc., St. Louis, Missouri, USA, 63178).

17) Lead nitrate (Laboratory reagent, BDH Chemicals Ltd., Poole, England).

18) Lithium metaborate (Spectromelt A20, Merck).

19) Mercury dichloride (Chemical grade, Mallinckrodt Inc., St. Louis, Missouri, USA, 63147).

20) Nitric acid ("AnalaR", BDH Chemicals Ltd., Toronto).

21) Oxalic acid ("AnalaR", BDH Chemicals Ltd., Poole, England).

22) Phosphoric acid (Fis her Scientific Company, Fairlawn, New Jersey, USA)

23) Potassium chloride ("AnalaR", BDH Chemicals Ltd., Toronto).

24) Potassium dihydrogen orthophosphate ("AnalaR", BDH Chemicals Ltd., Poole, England).

25) Potassium persulphate (Fisher Scientific Company, Fairlawn, New Jersey, USA).

26) Silicon oxide (Johnson Matthey Chemicals Ltd., Orchard Rd., Royston, Hert. SG8 5HE, England).

27) Sodium acetate anhydrous ("AnalaR", BDH Chemicals Ltd., Toronto).

28) Sodium borohydride powdered (Fisher Scientific Co., Fairlawn, New Jersey, USA).

29) Sodium hydroxide ("AnalaR", BDH Chemicals Ltd., Toronto).

30) Thiourea ("AnalaR", BDH Chemicals Ltd., Poole, England).

31) Tin shot (Baker Analyzed Reagent, Phillipsburg, N.J., USA).

32) Zinc powder (M and B Laboratory Chemicals Ltd., Dagenham, England).

C. STOCK SOLUTIONS

1) SODIUM BOROHYDRIDE

Sodium borohydride from Fisher Scientific Co. was used as the reducing agent. A literature survey, coupled with past experience [83], indicated that the optimum concentration of freshly prepared $NaBH_4$ was found to be 4% (m/V) for arsenic analysis. In the case of germanium, solutions were prepared in the range of 2-12% (m/V). All solutions were prepared in 0.1 M NaOH to minimize decomposition and were always filtered prior to use. Solutions were prepared when needed or stored in the freezer for a maximum of one week. In each case the injection volume was 1 mL unless stated otherwise.

2) DISODIUM HYDROGEN ARSENATE HEPTAHYDRATE

A 1000 mg/L solution of arsenic(V) was prepared by dissolving 4.1642 g of $Na_2HAsO_4.7H_2O$ in 50 mL of 0.1% (V/V) nitric acid. The volume was brought to 1 L with 0.1% (V/V) nitric acid. Standard solutions of As(V) in the range 10-300 ng/mL were prepared by dilution of the aforemention standard. The final solutions were prepared in either 1.4 M or 5 M hydrochloric acid. It is perhaps worth mentioning that solutions of $Na_2HAsO_4.7H_2O$ were checked against As(III) solutions prepared from primary standard As_2O_3 by standard aspiration in the D.C. Plasma spectrophotometer. Results showed

that the disodium salt is a reliable compound for the preparation of As(V) standard solutions.

3) ARSENIC TRIOXIDE

1.3204 g of As_2O_3 was dissolved in 10 mL of 20% (m/V) potassium hydroxide. 100 mL of concentrated hydrochloric acid was added and the volume made up to 1 L with distilled water. Standard solutions of As(III) in the range 10-300 ng/mL were prepared from the above mentioned standard by appropriate dilution. Final solutions contained either 1.4 M or 5 M hydrochloric acid.

4) GERMANIUM STANDARDS

Germanium standards were prepared from two different sources: a) from ammonium germanium(IV) oxalate hydrate 99.99% purity with a certified value of analysis of 14.5% of germanium and b) from a 1000 mg/L stock standard solution of germanium, reference standard BDH assured for AAS analysis. For the preparation of standard (a) 6.8965 g of the salt were dissolved in distilled water and 1 g of high purity oxalic acid was added to stabilize the solution. The final volume was brought to 1 L with distilled water.

After preparation, standard (a) was tested against standard (b) by conventional aspiration through the DC Plasma spectrophotometer. Results showed that the certified value for

the salt is correct.

Standards in the range 1-300 ng/mL were prepared by appropriate dilution of the above mentioned standards. Final solutions contained from 0 to 5 M hydrochloric acid, depending on the study under consideration.

5) TIN STANDARD SOLUTION

High purity tin shot (1.0008 g) was dissolved in 100 mL concentrated hydrochloric acid. The solution was left overnight to dissolve and the final volume was made up to 1 L with distilled water. 100 ng/mL solutions of tin were prepared by appropriate dilution of the above mentioned standard. Final solutions contained 0.05 M hydrochloric acid.

6) METAL ION SOLUTIONS

10,000 mg/L solutions of Nickel(II), Cobalt(II), Copper(II), Cadmium(II), Iron(III), Zinc(II), Mercury(II), Lead(II), Aluminum(III), Tin(IV), Arsenic(III) and Arsenic(V) were prepared as follows:

5 g of Ni powder, 5 g of Fe wire and 5 g of Zn powder were dissolved in 40 mL of concentrated hydrochloric acid. 5 g of Co, Cu and Cd shot were dissolved separately in 40 mL of concentrated nitric acid. Approximately 6.8 g of $HgCl_2$ and 8 g of $Pb(NO_3)_2$ were dissolved separately in distilled water. For

all of the above mentioned solutions gentle heating was provided to speed up dissolution. The final volume was made up to 500 mL.

1 g of aluminum wire and 1 g of Tin shot were dissolved separately in 20 mL of concentrated hydrochloric acid. 1.3 g of As_2O_3 was dissolved in the same way as for stock solution number 3 and 4.1 g of $Na_2HAsO_4.7H_2O$ were dissolved as for stock solution number 2. The final volume for these solutions was 100 mL.

7) INTERFERENT SOLUTION FOR ARSENIC

200 ng/mL solutions of As(V) were prepared from stock solution number 1 by appropriate dilution. The final solution contained 1000 mg/L of the interfering metal ion. Solutions were prepared either in 1.4 M or 5 M hydrochloric acid, with or without the appropriate percentage of the suppressing agent, depending on the study under consideration.

8) INTERFERENT SOLUTION FOR GERMANIUM

100 ng/mL solutions of germanium were prepared from stock solution number 4 by appropriate dilution. The final solutions contained 1000 mg/L of the interfering metal ion. Solutions were brought to pH 1.7 with dilute ammonium hydroxide, with or without the appropriate percentage of the suppressing agent, depending on the study under consideration.

9) PREPARATION OF SUPPRESSANT

L-Cysteine was readily soluble in distilled water up to 15 g/100mL. The required amount was always added to the volumetric flask and shaken to dissolve. L-Cystine was dissolved in hot concentrated hydrochloric acid. A 10% (m/V) solution was prepared and the appropriate amount was pipetted into the volumetric flask containing the analyte, the interfering metal ion and the hydrochloric acid. Thiourea was dissolved in distilled water and the appropriate amount was either added directly to the volumetric flask or added to the sample aliquot in the reaction vessel. The same procedure used for thiourea was applied to potassium chloride.

10) PERSULPHATE SOLUTIONS

Persulphate solutions were originally prepared from $K_2S_2O_8$ by dissolving 3 g of the salt in 100 mL of distilled water. However, since higher concentrations could not be prepared from this salt due to its poor solubility in water, subsequent solutions were prepared from the $(NH_4)_2S_2O_8$ salt, which has a solubility of 52 g/100 mL in cold water [1].

Solutions in the range 3-30% (m/V) were freshly prepared by dissolving the salt in distilled water.

11) BUFFER SOLUTIONS

Buffer solutions were prepared by combining appropriate volumes of 1 M KH_2PO_4 and 0.3 M H_3PO_4 for pH 2 and 2 M CH_3COONa and 2 M CH_3COOH for pH 4. One milliliter aliquots of the final solutions were injected directly to the sample into the generation cell.

All the standards were stored in plastic bottles which had been presoaked in dilute nitric acid and rinsed several times with distilled water. This also applied for all the volumetric glassware used in the course of this work.

D. SAMPLE PREPARATION

1) CHERT SAMPLES

A mass of 0.100 g of finely ground chert sample from Bellevue, N.Y., was fused with 1.0 g of lithium metaborate in a platinum crucible at 1,100 C for 30 minutes. The melt was cooled, cracked out of the crucible and dissolved in 50 mL of 1 M hydrochloric acid. It required some practice to establish the right procedure for the sample dissolution. The final volume was made up to 100 mL with distilled water. Blanks of $LiBO_2$ were prepared likewise.

A standard addition method was then applied. Four 20 mL aliquots from the above mentioned solution were brought to pH

1.7 with diluted NH_4OH and transferred into four 50 mL volumetric flasks. Appropriate amounts of germanium standards were introduced in each flask so as to obtain final concentrations of 0, 2, 4 and 10 ng/ml of germanium added. The dilution factor applied aided in the suppression of foaming which was produced in the reaction vessel of the hydride generator apparatus if the more concentrated sample would have been used.

Aqueous standards in the range 0-10 ng/mL were prepared in lithium metaborate matrix. Also, a series of standards in the range 0-10 ng/mL were prepared in silicon matrix by dissolving 0.100 g of high purity SiO_2 standard in the same way as for the chert samples.

2) IRON SAMPLES

Four 0.200 g of samples of the Fer series from the Energy Mines and Resources Canada, numbers Fer-2 and Fer-4 with tentative values of germanium content of 6 and 5 ug/g respectively [85], were fused in gold-platinum crucibles with 2.0 g of lithium metaborate. The molten mixture was poured into 50 mL of 1 M hydrochloric acid and dissolved; the final volume was made up to 100 mL with distilled water. Blanks of lithium metaborate were prepared in a similar fashion. Contrary to unalloyed platinum crucibles, gold-platinum crucibles are not appreciably wetted by molten borate fusion mixtures; therefore, no problems were encountered in the dissolution of the fused iron samples as opposed to chert samples.

Since iron has been proven to interfere with germanium determinations by the hydride generation technique [68], it was decided to dilute the solution as much as possible in order to reduce to a minimum the final concentration of iron in the solution for analysis. In this regard, four 10 mL aliquots from the aforementioned solution were brought to pH 1.7 with diluted ammonium hydroxide and transferred into four 100 mL volumetric flasks. Appropriate amounts of germanium standards were introduced into each flask to obtain final concentrations of 0, 5, 10, and 20 ng/mL of germanium added. Final volumes were made up to 100 mL with distilled water. As in the case of the chert samples, the dilution factor applied here aided in the suppression of the foaming process which occurred in the reaction vessel.

A series of aqueous standards in the range of 0-20 ng/mL were prepared in lithium metaborate matrix.

E. PROCEDURE

1) HYDRIDE GENERATION PROCEDURE FOR ARSENIC

The analysis procedure was optimized for arsenic analysis. Using either tube (b) or tube (c) (fig. 4), a solution of 100 mg/L of arsenic was used to optimize or peak the instrument. During the peaking process, the purge valve (fig. 2 (L)) was kept open with an argon flow of 27 mL/sec. The nebulizer pressure was set at 26 psi, and the peristaltic pump

rollers were engaged but the pump was not turned on. Better sensitivity could be achieved this way.

Deionized water (10 mL) was introduced into the reaction cell. The chart recorder, connected to the analogue output of the computer, was started and adjusted. The rinse valve (H) was opened, the cell was emptied, and both valves (H,L) were closed again. The generator was now ready for use.

The generator can accomodate up to 10 mL of acidic samples (or standards). A suitable amount of acidified sample was introduced, via a 10 mL adjustable automatic pipet, into the cell. After sample injection, the purge valve (L) was opened and the recorder started, so that the base line could be set. The valve was closed and sodium borohydride (1.0 mL of 4% (m/V) solution) was introduced via a 3.0 mL syringe within 5 seconds. The purge valve was opened, either immediately (5 seconds) or after 20 seconds reaction, in order to study the differences in the reduction of arsenic(V) and arsenic(III) with time.

After hydride generation, the reaction vessel was rinsed several times with distilled water. Care had to be taken to wash the pipette tip through which the $NaBH_4$ solution was introduced, since a drop of the liquid would usually remain inside of it which could subsequently fall into the reaction vessel. This, of course, could produce a considerable error.

There are several concommitant problems related with this procedure which should be mentioned. Firstly, the shape of the plasma changes slightly when argon gas is flowing through the central tube (fig. 3a and 3b), so the position of the plasma

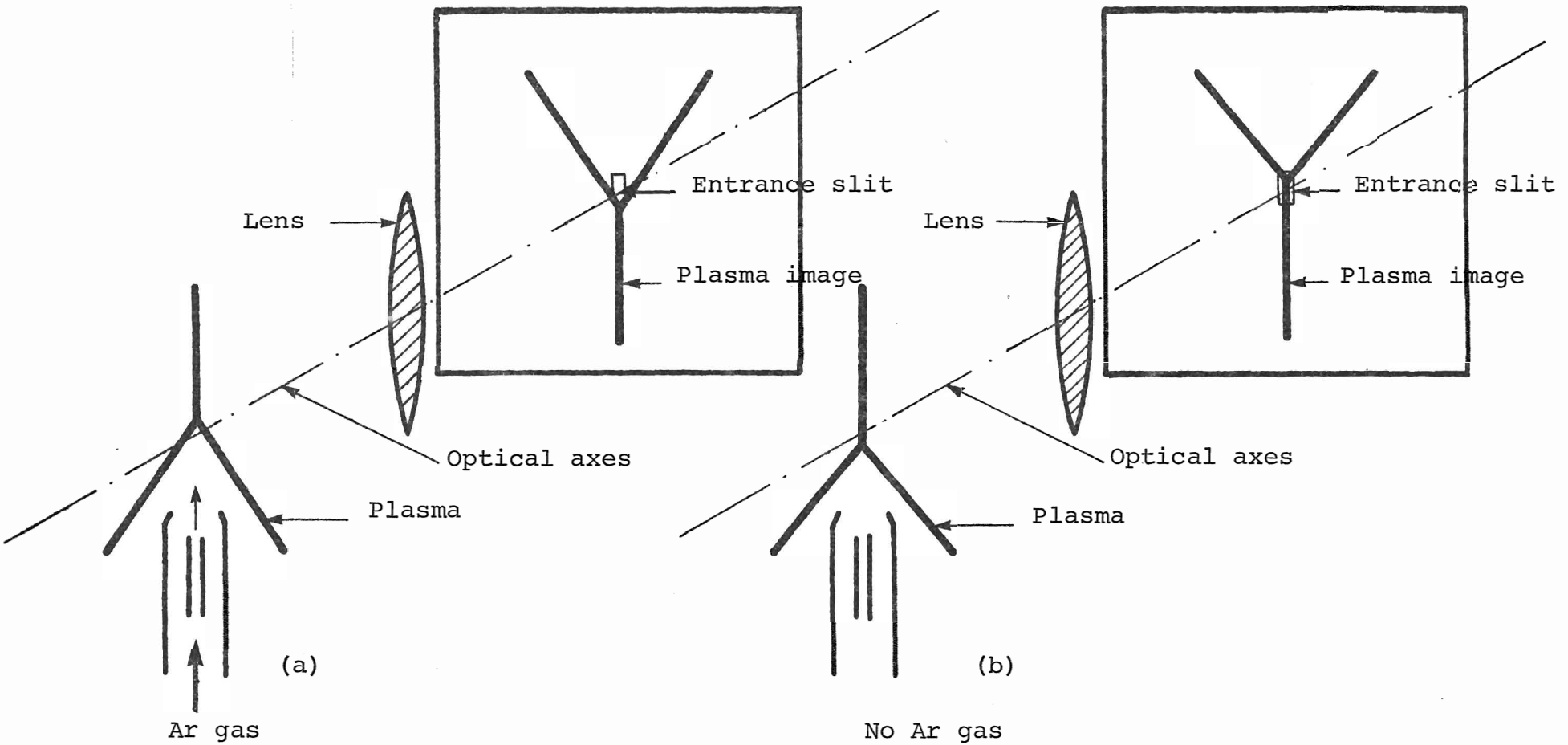


Figure 3. Schematic representation of the effect of the argon gas flow through the central tube of the sample tube head on the plasma shape. A) argon gas flowing, B) no argon gas flowing.

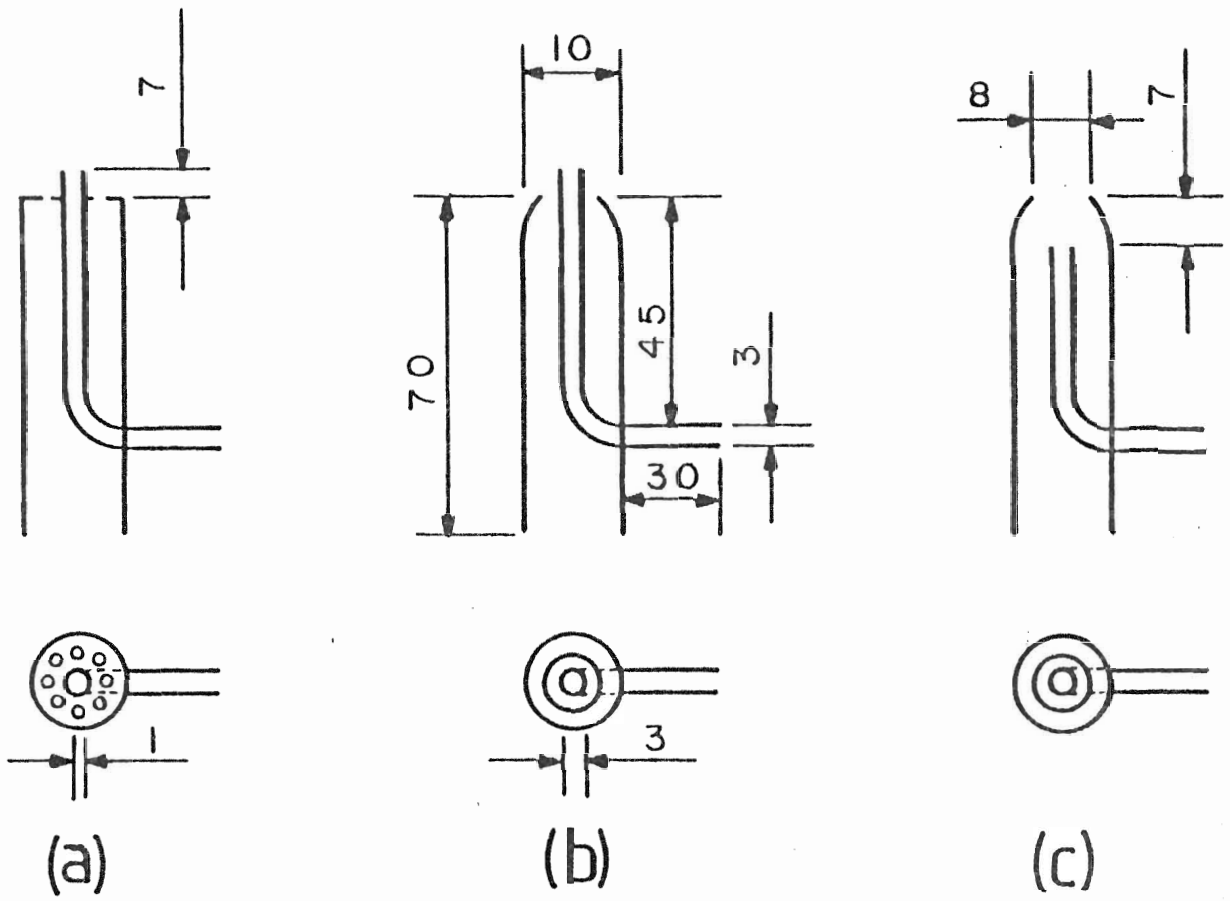


Figure 4. Schematic representation of the different sample tube heads used in this study. A) original, B) and C) modified. All dimensions in mm. All diameters are internally measured.

with respect to the slit also changes. Therefore, the base line has to be set while argon gas is flowing through the central tube. Once the base line is set and the purge valve is closed again, an immediate change in the base line, usually an increase, is produced. This is due to the emission background coming from the tail of the plasma which is now covering part of the slit.

Secondly, it is preferable to introduce the $NaBH_4$ in a single burst since a better mixing of sample and reducing agent is accomplished. It was observed that when tube (b) (fig. 4) was used, the risk of blowing out the plasma, due to the displacement of air occurring within the system (Buchner funnel) at the moment of injection of $NaBH_4$, was very high. This was not the case when tube (b) was replaced by tube (c) or (d). The latter tube is not shown in figure 4 because it was identical to tube (c), but with the inner tube 1 cm shorter. This is apparently caused by the fact that, in this case, the distance between the plasma and the end part of the inner tube is greater; therefore, the displacement of air due to the injection of $NaBH_4$ was not strong enough to extinguish the plasma. Due to this major drawback it was decided to discard tube (b), in spite of the fact that good arsenic signal response could be achieved with it.

2) HYDRIDE GENERATION PROCEDURE FOR GERMANIUM

The procedure for the hydride generation of germanium

was the same as for arsenic determinations. However, depending on the study under consideration, after sample injection, an appropriate amount of the suppressing agent, ammonium persulphate or potassium persulphate, was added directly to the sample in the reaction vessel. The peristaltic pump was, in this case, turned on because no improvement in sensitivity was observed with the pump off and better recovery of the base line could be achieved this way. Also, the reduction time was extended to 30 seconds (optimum).

3) HYDRIDE GENERATION PROCEDURE FOR GERMANIUM USING THE MICROPROCESSOR

When integrating the signal from germanium standards with the aid of the built-in microprocessor of the Spectraspan V, a rather different procedure was followed. First of all, the spectrometer was set in the integration mode of operation, the time switch was set at 15 seconds and the repeat switch was set at 1. The instrument was peaked in the same way as for procedure 1. A germanium standard (50 mg/L) was then aspirated through the nebulizer and used as the high standard to auto-range the instrument. By this means, the instrument automatically selects the gain necessary to amplify the input signal to a level corresponding to 50% full scale; following this, a high standard cycle is automatically performed. Distilled water was used as the low standard. Subsequently, 5 mL of a 100 ng/mL germanium standard was introduced into the

reaction vessel. A 1 mL of a 4% (m/V) $NaBH_4$ solution was injected. Twenty-three seconds were allowed to pass before the sample push button was depressed. After 30 seconds had elapsed (counted from $NaBH_4$ injection), the purge valve was opened and the peak recorded. After depression of the sample push button, there is a time lag of 7 seconds before the microprocessor starts to integrate the incoming signal.

CHAPTER 3

RESULTS AND DISCUSSIONS

A. MODIFICATIONS TO THE HYDRIDE SYSTEM

1) Sample Tube Heads

The most significant problem related to the modified nebulizer tube was solved by redesigning the tube. Figure 4a represents the design of the original sample tube, while figures 4b and 4c depict the new tubes made from silica and glass respectively. Tube (b) was proposed by Charles Boampong [83] and tubes (c) and (d)(not shown in fig. 3) were introduced in this work. With these new tubes, optimization of the wavelength, plasma jet position and the position of the sample tube itself could be done readily. In the particular case of tubes (c) and (d), since the inner central tubes are shorter than in tubes (a) or (b), alignment of the sample tube head with respect to the plasma could be done with the use of the same tool, provided by the manufacturer of the spectrophotometer, used to set the position of the normal tube head.

When tube (b), (c) or (d) was used, optimization of the system could be done readily by simply aspirating solutions in the normal way, with argon gas flowing through the central tube, simulating conditions of analysis.

Table I shows the results obtained for the different sample tube heads used in this study. Results were obtained

Table I. Response from a 200 ng/mL As(III) standard versus sample tube heads b,c and d.

	Peak height (cm)			
Tube Head	Mean (cm)	Standard deviation (cm)	Relative Standard deviation (%)	Number of determinations
b	9.86	0.08	0.8	4
c	9.80	0.14	1.4	4
d *	5.60	0.10	1.8	3

* Same as tube c but inner tube 1 cm shorter.

after optimization of the argon gas flow through the central tube of each sample tube head. It was decided to make tubes (c) and (d) shorter than tube (b) in order to study their influence on the arsenic signal. It can be seen that almost identical response can be achieved with either tube (b) or (c); however, if the tube is made too short (d), a decrease in the sensitivity of the arsenic signal is registered. This is due to the fact that the argon flow has to be kept at a higher rate, which causes the arsine to be dispersed and diluted more rapidly once out of the sample tube head. It is also important to mention that without some curvature at the top of the tubes (b,c,d) the plasma stability was jeopardized, and became unacceptable for the purpose of analysis. In light of the results obtained and for the reasons mentioned in section (E-1, chapter 2) it was decided to adopt the use of tube (c) and discard tubes (b) and (d).

2) Redirection Of The Hydride

In the particular case of germanium analysis, it was observed that the emission background, coming from the tail of the plasma when the purge valve (L) was closed, was considerably greater than that for arsenic analysis. This was due to the fact that the analytical emission line used for germanium (303.906 nm) lay closer to the continuum emission of the argon gas in the UV region of the spectrum than did the one for arsenic (193.7 nm). Therefore, due to this problem, good

separation between emission background and analyte peak could not be properly accomplished when following the signal with the strip chart recorder. In other words, the base line could not be achieved before the analyte peak signal was recorded. This did not present a real problem when working with high concentrations of germanium (10 ng/mL and higher) since the analyte peak was always higher than the emission background. However, when lower concentrations were used, the analyte peak showed up as a shoulder of the emission background. Increasing the chart recorder speed did not satisfactorily improve the result because a broad shoulder was then obtained. The selection of a different emission line (265.118) for germanium which lay farther away from the plasma continuum resulted in a loss of sensitivity in the germanium signal.

Since the problem is associated with the fact that the plasma shape changes when argon gas is flowing through the central tube of the sample tube head, it was thought that a change in the angle of introduction of the hydride and argon gas would solve this. Figure 5 shows the new set-up of the sample tube head. In the case of set-up (e) and (f), new glass tubes were made with the same internal diameter as for tube (c) figure 4. The tubes were then attached to the side of the sample tube holder with the aid of masking tape.

Figure 6 portrays the results obtained with each particular set-up. It can be seen that with both new arrangements a decrease in the emission background was actually accomplished; however, a decrease in sensitivity was also

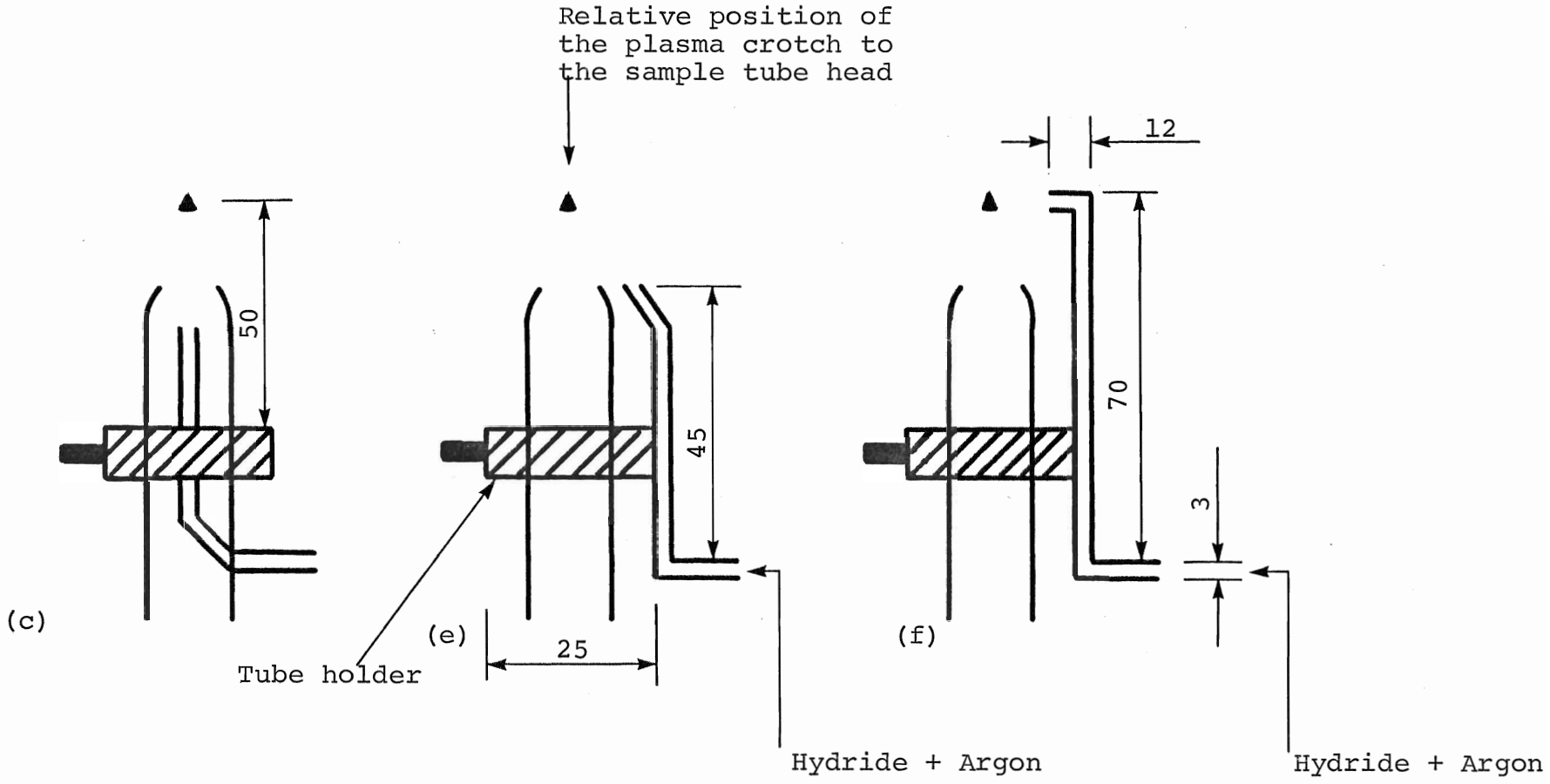


Figure 5. Schematic representation of the redirection of the hydride c) from the bottom, e) from the side, f) from the front. All measures in mm.

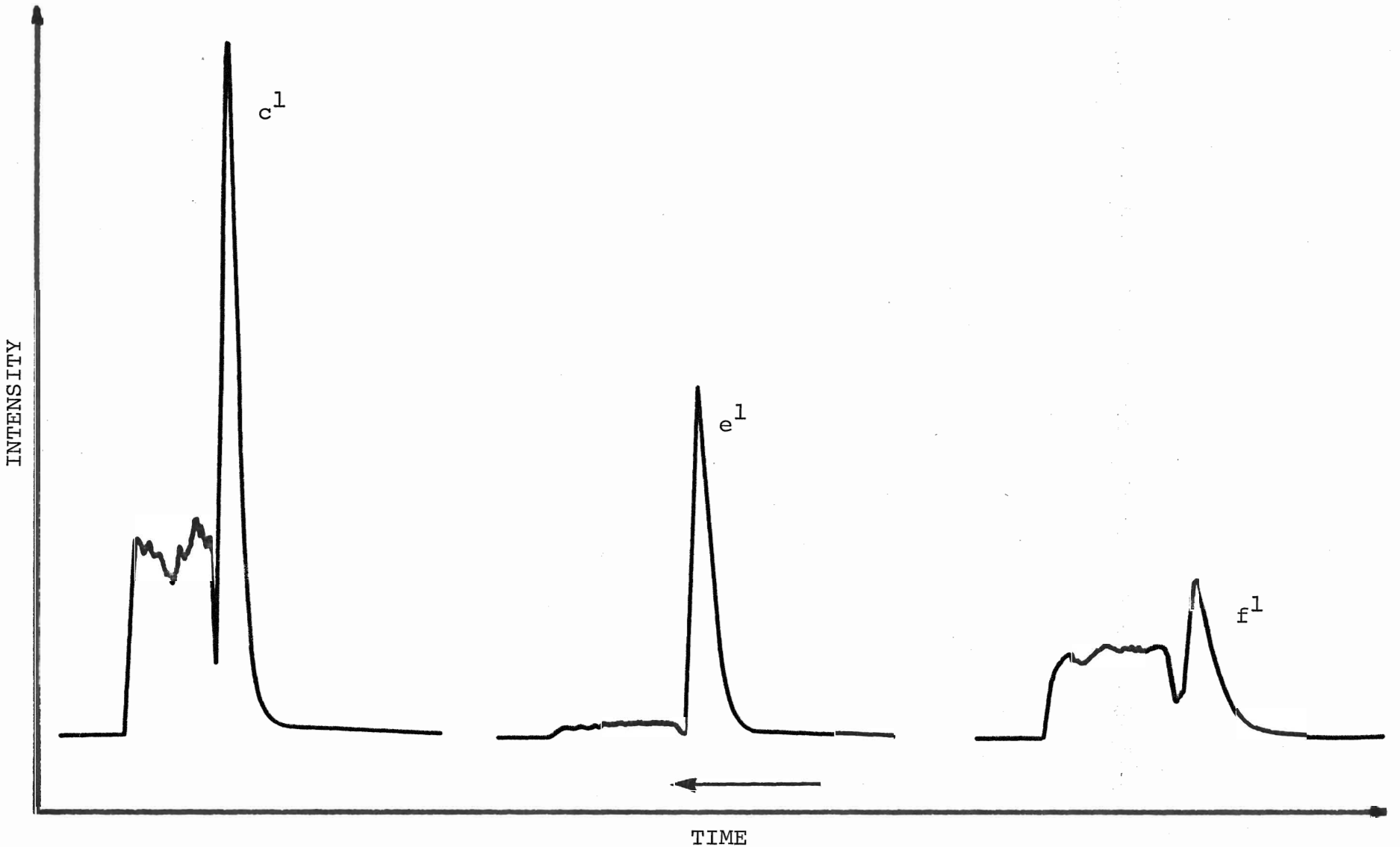


Figure 6. Response of 100 ng/mL germanium standard obtained when flushing the hydride c) from the bottom, e) from the side, f) from the front. Arrow indicates the direction of the chart recorder movement.

registered. Due to the new angle of incidence, the plasma shape does not change to the same extent as it does when sample tube head (c) is used. Consequently, the plasma tail does not cover the entrance slit completely, accounting for the reduction in the emission background level. Also, with the new set-up (e and f), the hydride travels a shorter path through the hottest region of the plasma; therefore less time is available for the exitation process to take place.

As can be seen in figure 6, set-up (f) has a greater effect on the plasma shape than does set-up (e), this is due to the fact that in this case the mixture of argon and hydride hits the plasma in a straight way and not tangentially as in set-up (e).

All of the aforementioned attempts failed to solve the problem because a reduction in sensitivity was always registered. However, by increasing the amount of porapak Q in the delay column, a better recovery of the base line, without a loss in sensitivity, could be achieved than with any of the previous methods. This arrangement proved to be valuable even for concentrations as low as 1 ng/mL; however, if very low concentrations, less than 1 ng/mL, of germanium have to be determined, the best procedure to follow still remains the standard addition method. Another possibility which was not tried in this work would be increasing the length of the tubing between the delay column and the sample tube head.

3) Signal Integration Of Germanium With The Microprocessor

As mentioned earlier, a Fisher Scientific series 5000 chart recorder was used in the course of this work to follow the transient signals from the analyte element. This is the actual procedure recommended by the manufacturer of the spectrophotometer [88]; however, a major disadvantage presents itself if an integrating chart recorder is not available for peak area measurements. If this is the case, one has to refer, therefore, to the cut and weigh method which is an inherently time consuming process.

In light of this, it was decided to determine whether it would be possible to devise a way of measuring peak areas based on the signal integration capability of the Spectraspan microprocessor. Signals processed in this digital format should give better precision than peak height measurements from strip chart records or from peak area measurements by the cut and weigh method.

The procedure followed is outlined in the experimental section; however the results obtained are shown in Table II. The average count for the blank (H_2O) was 3909. The counts due to germanium were derived by substraction of the blank signal. It can be seen that the method is not very precise since a relative standard deviation of 42% was obtained. This demostrates that integration with the microprocessor cannot be accomplished without compromising to a great extent the

Table II. Integration of the germanium signal with the built-in microprocessor of the Spectraspan V. Germanium 100 ng/mL.

Injection		Counts
1		166.8
2		91.8
3		132.8
4		82.8
5		140.8
6		142.8
7		87.8
8		262.8
	Mean	138.5
	SD	58.8
	RSD %	42%

precision of the analysis. Another disadvantage of this procedure is that peak height recordings cannot be simultaneously carried out. For these reasons no further work was pursued in this direction. The use of the chart recorder was therefore retained.

B. Arsenic Analysis

1) OPTIMIZATION OF THE ARGON GAS FLOW

Table III and Figure 7 depict the results obtained when optimizing the argon gas flow through the central tube of tube head (c). It can be seen that there is a maximun signal response at a flow rate of 21 mL/s. An increase of the flow rate over 30 mL/s would cause the plasma to go out, whereas a decrease of the flow rate below 21 mL/s would be inadequate for good peak shape signal response. The results for tube (b) were similar to those for tube (c). Tube (d) followed the same pattern, but with a reduction in sensitivity.

2) REDUCTION OF TRIVALENT AND PENTAVALENT ARSENIC

Many workers have reported on the inherently slow reduction of As(V) to arsine. In particular, Aggett and Aspell [24] reported that arsine formation from As(V) is kinetically slow and that the response increases with increasing acid concentration. It was decided to determine whether an increase

Table III. Response of a 200 ng/mL As(III) standard versus argon gas flow using the sample tube head c.

	Peak height (cm)			
Argon flow mL/s	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
15	1.02	0.04	3.9	4
21	6.91	0.04	0.6	4
27	4.68	0.10	2.1	4

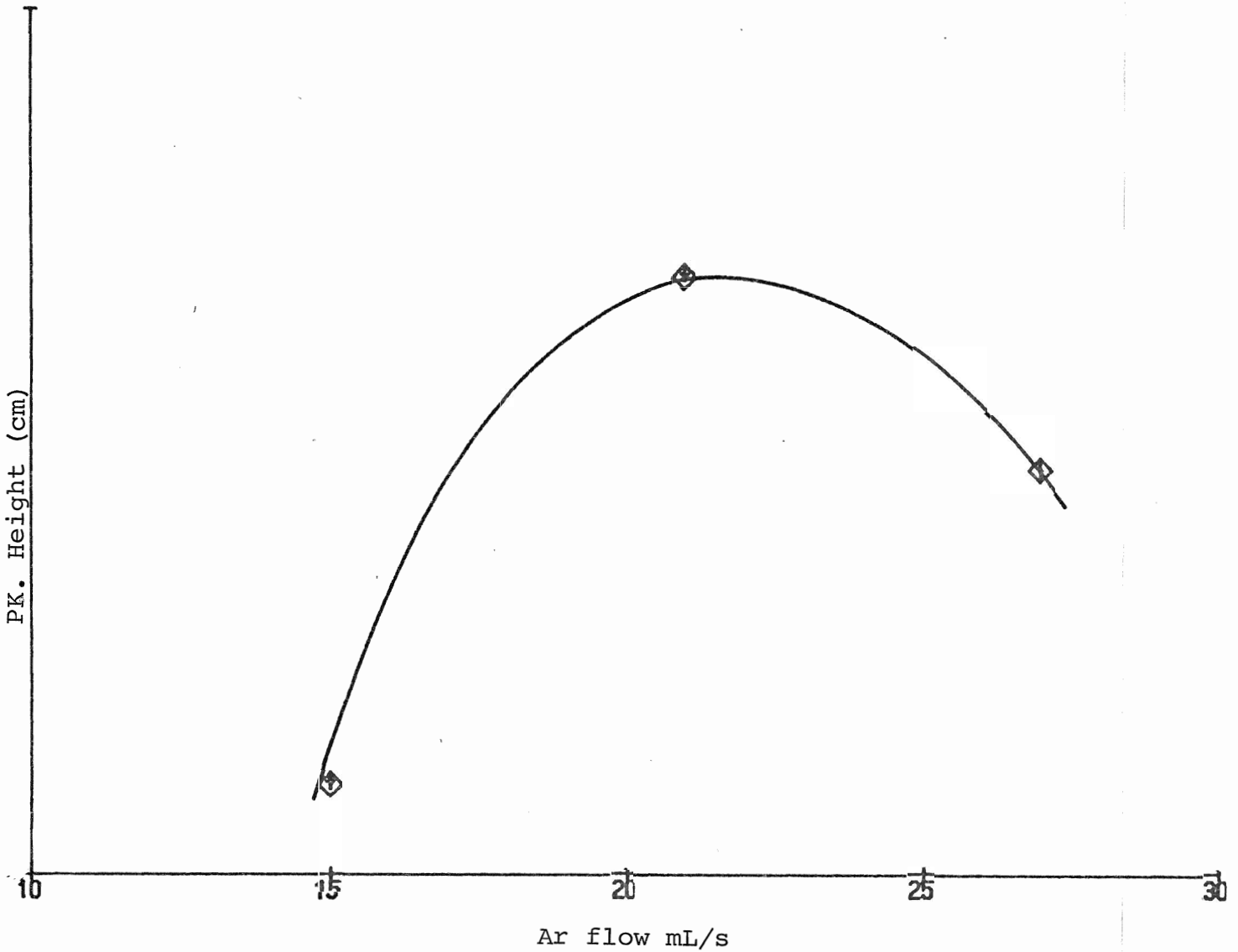


Figure 7. Response of a 200 ng/mL As(III) standard versus argon gas flow using sample tube c.

in the reduction time allowed for As(V) would result in total reduction of As(V) to arsine.

The peaks shown in Figures 8a and 8b were obtained by adding the sodium borohydride as fast as possible and rapidly flushing the system. The peaks obtained from trivalent arsenic were sharper than those peaks of pentavalent arsenic. This agrees with previous observations [24] that arsenic(III) is reduced faster than pentavalent arsenic. However, as can be seen in Table IV, when peak areas for both pentavalent and trivalent arsenic reductions were measured, no significant difference was encountered at the 95% confidence level. This is not surprising since kinetic interferences, by definition, should change the peak shape not the peak area because the analyte mass formed remains constant.

Figures 9a, 9b, and Table IV portray the results obtained when the flushing of the system was done after 20 seconds. It can be seen that the average peak height of the trivalent arsenic is equal to the average peak height of the pentavalent arsenic, which demonstrates that complete reduction of pentavalent arsenic can be accomplished by increasing the reaction time.

It can be therefore concluded that peak heights may be used when the reduction is allowed to proceed for 20 seconds before the arsine is stripped. This also demonstrates that both As(III) and As(V) can be determined in total as arsenic at pH less than or equal to 1 without the need for any prereduction step. These findings agree well with results reported by

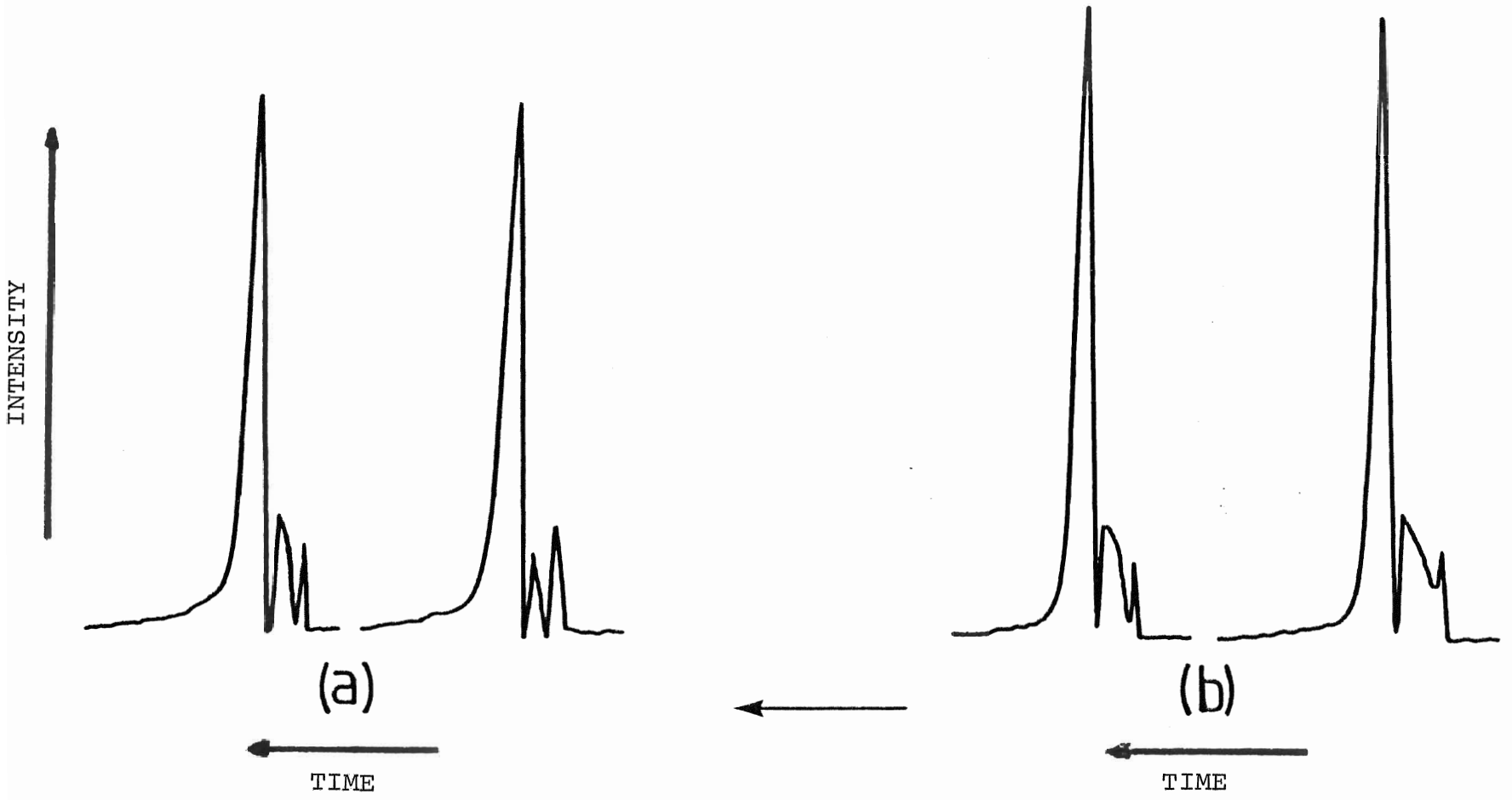


Figure 8. a) Response of 2.0 mL(200 ng/mL As(V))immediately after reaction. b) response of 2.0 mL(200 ng/mL As(III))immediately after reaction. Arrow indicates the direction of the chard recorder movement.

Table IV. Arsenic response after immediate and 20 seconds reaction for Arsenic(III) (200 ng/mL) and Arsenic(V) (200 ng/mL).

Oxidation State	Immediate Reaction Peak Area Mean*	RSD%	Peak Height Mean**	RSD%	Number of Replicates	20 Seconds Reaction Peak Area Mean*	RSD%	Peak Height Mean**	RSD%	Number of Replicates
III	28.9	3.1	9.4	2.8	4	28.3	3.4	9.4	2.8	8
V	28.3	3.3	8.4	2.9	4	28.4	2.6	9.5	3.8	8

* arbitrary units.
** measured in centimetres.

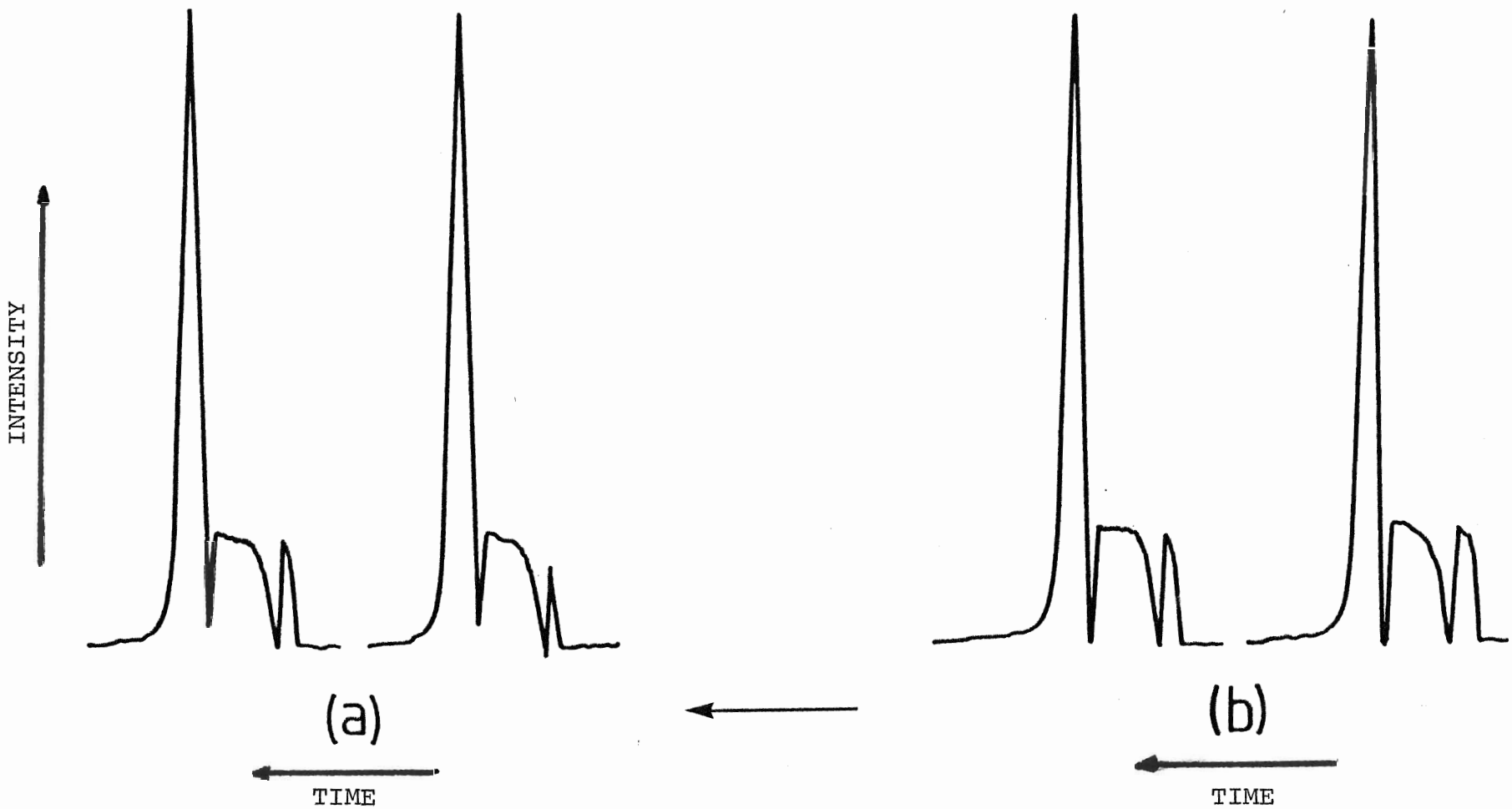


Figure 9. a) Response of 2.0 mL (200 ng/mL As(V)) after 20 sec. reaction. b) Response of 2.0 mL (200 ng/mL As(III)) after 20 sec. reaction. Arrow indicates the direction of the chart recorder movement.

Hinners [67], Aggett and Aspell [24], Tallman and Snaik [85], and Howard and Arbab-Zavar [86].

3) REPRODUCIBILITY

The reproducibility was checked by analysis of a standard solution of 200 ng/mL of arsenic(III). The results are shown in Table V. This reproducibility was tested with the modified tube (c). A relative standard deviation of 3.4% was achieved. Results indicate that analysis of arsenic can be carried out for a period of 2-3 hours without any major loss in sensitivity.

4) DETECTION LIMIT

Since some contamination of arsenic was found in the blank reagents, i.e. the hydrochloric acid and/or the sodium borohydride, the calculation of the detection limit was based on the noise level after subtraction of the blank signal. The detection limit is thus defined as twice the baseline noise. The average of the blank signal was found to be 1.00 cm at a recorder sensitivity of 10 mV. The average noise level at the same recorder sensitivity was found to be 0.50 cm. Since a 10 ng/mL standard gives a peak height of 20.50 cm, at the recorder sensitivity of 10mV, the detection limit for a 5 ml injected sample is 0.51 ng/mL. This result compares well with detection limits obtained by other workers who have used either

Table V. Response of a 200 ng/mL of arsenic(III) standard with respect to time.

Time (min)	Peak Height (cm)
3	21.4
5	20.9
11	20.3
19	20.2
28	21.7
32	19.4
36	21.1
43	20.8
48	20.3
56	21.1
59	19.8
64	20.4
68	19.4
108	20.8
113	20.3
118	20.5
126	20.6
132	20.1
136	19.5
140	20.1
144	19.4
147	19.4

Mean: 20.3 ± 0.7

RSD: 3.4%

AAS or AES.

5) CALIBRATION CURVES

The detection limit associated with arsenic determination, using the direct current plasma through solution nebulization, has been reported to be 80 ng/mL [87]. It therefore became expedient to evaluate the hydride generator system below this concentration. It was also important to compare the efficiency of the hydride generator system when using both the special sample tube head manufactured by Spectrametrics Inc. and the modified sample tube head (c) designed in our laboratories. The data are shown in Tables VI and VII and plotted in Figure 10. It can be concluded that modifications made to the system have resulted in a large increase, over 100%, in the sensitivity of the arsenic signal reponse, particularly in the range of 20 to 200 ng/mL.

6) EFFECT OF POTASSIUM PERSULPHATE ON THE ARSENIC SIGNAL

Since it was observed that the use of potassium persulfate aided in the reduction of germanium to germane, it was decided to study its effect on the reduction of As(III) and As(V) to arsine.

The results shown in Table VIII demostrate that persulfate has a depressive effect on recovery of both valency states of arsenic. The effect is stronger for arsenic(V) than

Table VI. Response of arsenic standards using the special sample tube head (a) [83].

As ng/mL	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
10 *	11.97	0.34	3.0	5
30 **	2.36	0.04	2.0	3
50 **	2.75	0.04	1.0	3
80 **	3.85	0.10	3.0	3
100 **	4.25	0.08	2.0	3
200 **	7.20	0.26	3.0	3

* Measured at recorder sensitivity of 10 mV

** Measured at recorder sensitivity of 100 mV.

Table VII. Response of arsenic(III) standards using the modified sample tube head (c).

As ng/mL	Peak height (cm) Mean (cm)	Standard deviation (%)	Relative standard deviation (%)	Number of determinations
10*	13.35	0.08	0.9	3
20**	2.60	0.07	2.7	4
30**	3.70	0.10	2.7	3
50**	5.43	0.09	1.5	3
70**	7.00	0.30	4.3	3
80**	8.80	0.36	4.1	3
100**	11.68	0.47	4.0	3
200**	19.34	0.35	1.8	3

* Measured at recorder sensitivity of 10 mV

** Measured at recorder sensitivity of 100 mv.

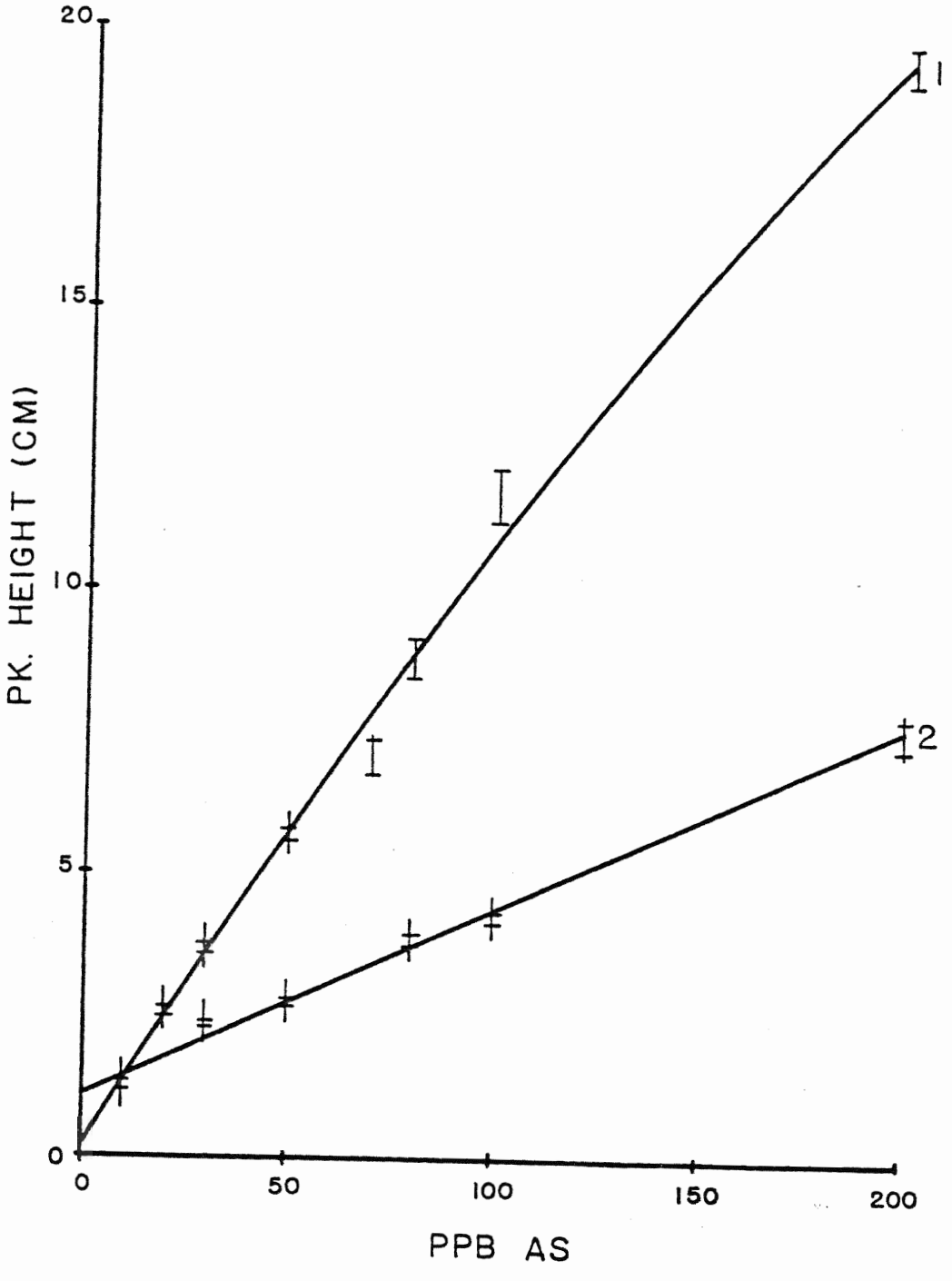


Figure 10. Calibration curves for: (1) arsenic with modified sample tube head (c), and (2) arsenic with original sample tube head (a) (83). All measurements based on a 2 mL injection.

Table VIII. Percent recovery of arsenic from different media.

Oxidation state	% Recovery		
	1.4 M HCl	1.4 M HCl 3mL PS 3%	No HCl 3mL PS 3%
As(III)	100	40	11
As(V)	100	15	2

PS, Potassium persulfate.

for arsenic(III). This might be due to the fact that potassium persulphate consumes borohydride at a faster rate, inhibiting the production of arsine.

7) INTERFERENCE STUDY

As mentioned earlier, many workers [14] have used complexing agents to correct for the interference produced by transition elements in the hydride generation technique.

In 1983, Charles Boampong [83] studied the use of different acid concentrations and complexing agents in an effort to free the analysis of arsenic from the interferences produced by 1000 mg/L of nickel, cobalt, iron, copper, and cadmium. The results are summarized in Table IX. It can be seen that he accomplished 85% recovery of the arsenic signal from a mixture of 1000 mg/L of each of the aforementioned elements in 5 M hydrochloric acid and 3% (m/V) L-cystine. However, individual recoveries were not determined. It was therefore decided to assess the percent recovery of arsenic from solutions containing each individual interferent element under the same conditions of analysis.

First of all, it was necessary to pin-point the worst case, that is, to determine which valency state of arsenic was more subject to interference from the previously mentioned transition elements.

Secondly, in order to shorten the analysis time and to simplify the sample preparation procedure, the use of L-cysteine

Table IX. Percent recovery of arsenic(V) from different media.

	% Recovery					
	From Reference [83]					This work
Matrix	1.4M HCl	1.4M HCl 3% TH	1.4M HCl 1% L-C	5M HCl	5M HCl 3% L-C	5M HCl 3% L-C
Ni	0	94	95	-	-	100
Co	0	93	94	-	-	83
Fe	88	94	100	-	-	96
Cu	15	58	95	99	-	94
Cd	18	58	36	103	-	90
Zn	-	-	-	-	-	109
Hg	-	-	-	-	-	60
Mixture of 1000 mg/L each of Ni, Co, Fe, Cu, and Cd.	-	-	-	-	85	81

was also studied. The main reason for this was that L-cysteine is very soluble in water, whereas L-cystine is soluble in concentrated hot hydrochloric acid. The results portrayed in Tables X and XI demonstrate that there is a strong depressing effect of L-cysteine in the signal recovery of both As(III) and As(V).

On the other hand, the same Tables show the results obtained for the interference of 1000 mg/L of cadmium in the recovery of As(III) and As(V). As can be seen, the worst case was found to be As(V). This finding agrees well with results obtained by Welz and Melcher [78] who reported stronger interference for As(V) than for As(III) from copper, iron and nickel. All further studies concerning this work were, therefore, performed with As(V).

Table IX summarizes the recoveries obtained for arsenic with 1.4 M HCl and 3% L-cystine in the presence of 1000 mg/L each of the interferent elements. It can be concluded that this method may be used in the determination of arsenic by the hydride generation technique even when high concentrations of some interfering elements are present.

Table X. Percent recovery of arsenic(III) from different media.

	% Recovery	
	1% L-c	1% L-C
Matrix	1.4M HCl	1.4M HCl
Cd	12	76

L-c, L-cysteine.

L-C, L-cystine.

matrix, 1000 mg/L

Table XI. Percent recovery of arsenic(V) from different media.

	% Recovery	
	1% L-c	1% L-C
Matrix	1.4M HCl	1.4M HCl
Cd	11	33

L-c, L-cysteine.

L-C, L-cystine.

Matrix 1000 mg/L.

C. GERMANIUM ANALYSIS

Since good results were achieved in the determination of arsenic using the hydride generation technique, it was decided to evaluate the performance of the system using another hydride forming element. In this regard, germanium was selected for two reasons. Firstly, relatively little information on the hydride generation of this element has been accumulated to date. Secondly, the determination of germanium in chert samples, which are thought to contain low concentrations of the element, appeared to be an attractive application of this technique.

Original work was carried out using similar experimental conditions as for arsenic analysis; that is, 1 M hydrochloric acid and $NaBH_4$ 4% (m/V) were employed.

1) OPTIMIZATION OF THE $NaBH_4$ 4% (m/V) VOLUME OF INJECTION.

The volume of $NaBH_4$ was optimized by keeping the reaction time constant at 30 s, the argon flow at 21 mL/s and the volume of analyte solution at 5.0 mL. Table XII and figure 11 show the results obtained. It can be clearly seen that 1.0 mL provided the best signal response. When larger volumes were injected, a considerable decrease in the signal was registered. This could have been caused, on one hand, by the fact that higher volumes of hydrogen gas were produced in the reaction, thereby diluting the hydride to a greater extent. Secondly, the injection of a bigger volume of $NaBH_4$ produced a greater

Table XII. Response of 100 ng/mL germanium versus volume of sodium borohydride 4% (m/V) injected.

$NaBH_4$ (mL)	Peak height (cm) Mean (cm)	Standard deviation(cm)	Relative standard deviation (%)	Number of measurements
0.5	9.33	0.32	3.4	5
1.0	11.45	0.21	1.8	6
2.0	3.33	0.30	9.0	3
3.0	1.95	0.05	2.6	2

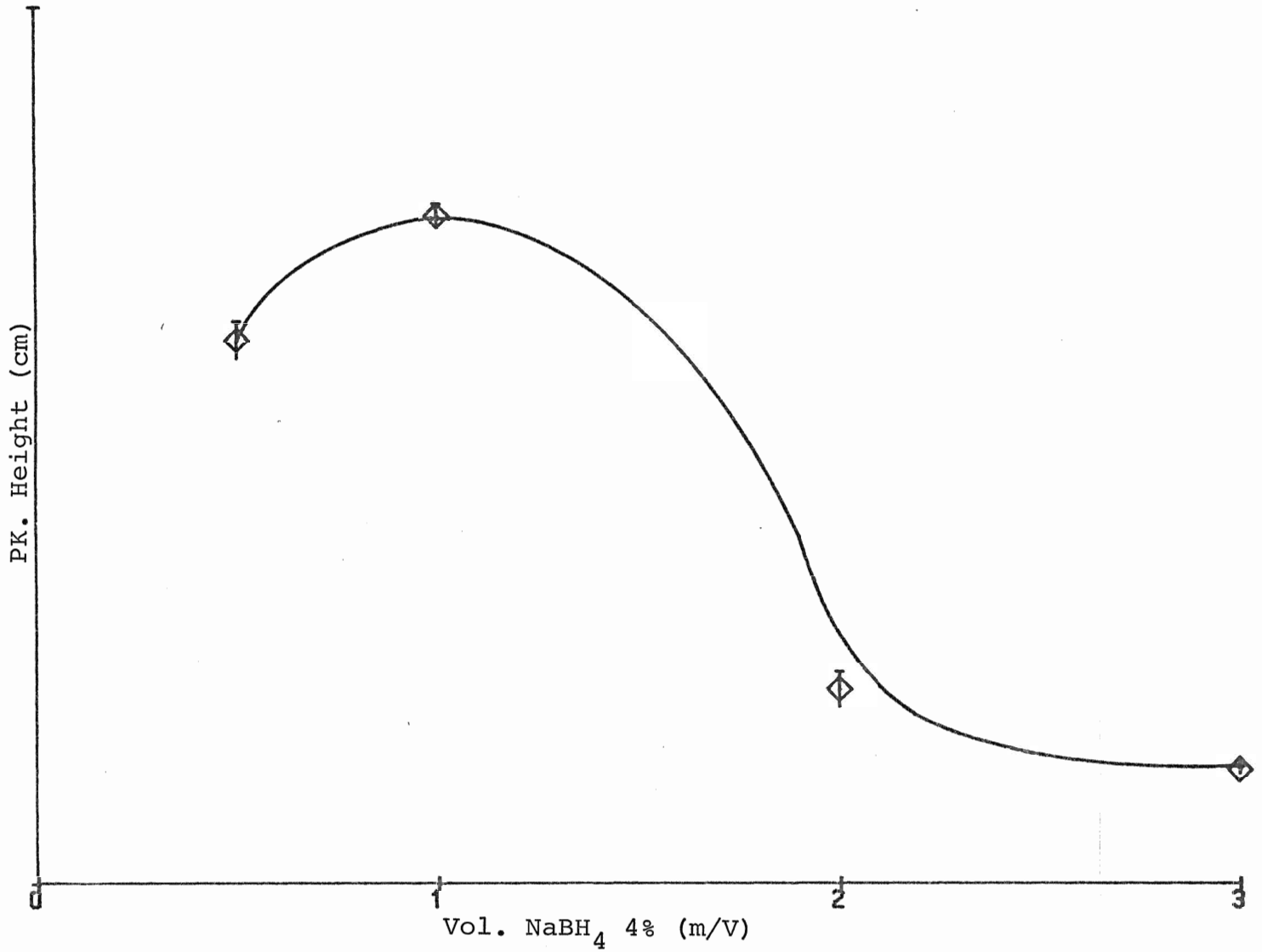


Figure 11. Response of 100 ng/mL germanium versus volume of sodium borohydride.

displacement of the gases inside the reaction vessel, which may have caused part of the hydride to be diluted before the purge valve was opened. It is, therefore, very important to optimize the conditions in terms of $NaBH_4$ volume and concentration when the experimental conditions are varied.

2) OPTIMIZATION OF THE ARGON GAS FLOW

The argon gas flow was subsequently optimized. Table XIII and figure 12 portray the results. The best signal was achieved with a flow rate of 30 mL/s. However, at this rate the plasma stability was jeopardized: therefore a compromise in sensitivity was taken and 27 mL/s was adopted as the optimum argon gas rate.

3) OPTIMIZATION OF THE REACTION TIME

The reaction time was optimized by keeping the aforementioned optimized parameters constant. Table XIV and figure 13 summarize the results obtained. No major improvement in the germanium signal could be achieved after 20 seconds of reaction. Although the best value was registered at a reaction time of 60 s, it was decided to compromise the sensitivity in order to save on analysis time, thus a reaction time of 20 s was used as the optimum value.

Table XIII. Response of 100 ng/mL germanium standard versus argon gas flow rate.

	Peak height (cm)			
Argon flow rate mL/s	Mean (cm)	Standard deviation(cm)	Relative standard deviation (%)	Number of measurements
15	1.83	0.06	3	3
21	2.73	0.08	3	3
27	2.82	0.10	4	3
30	2.90	0.17	6	2

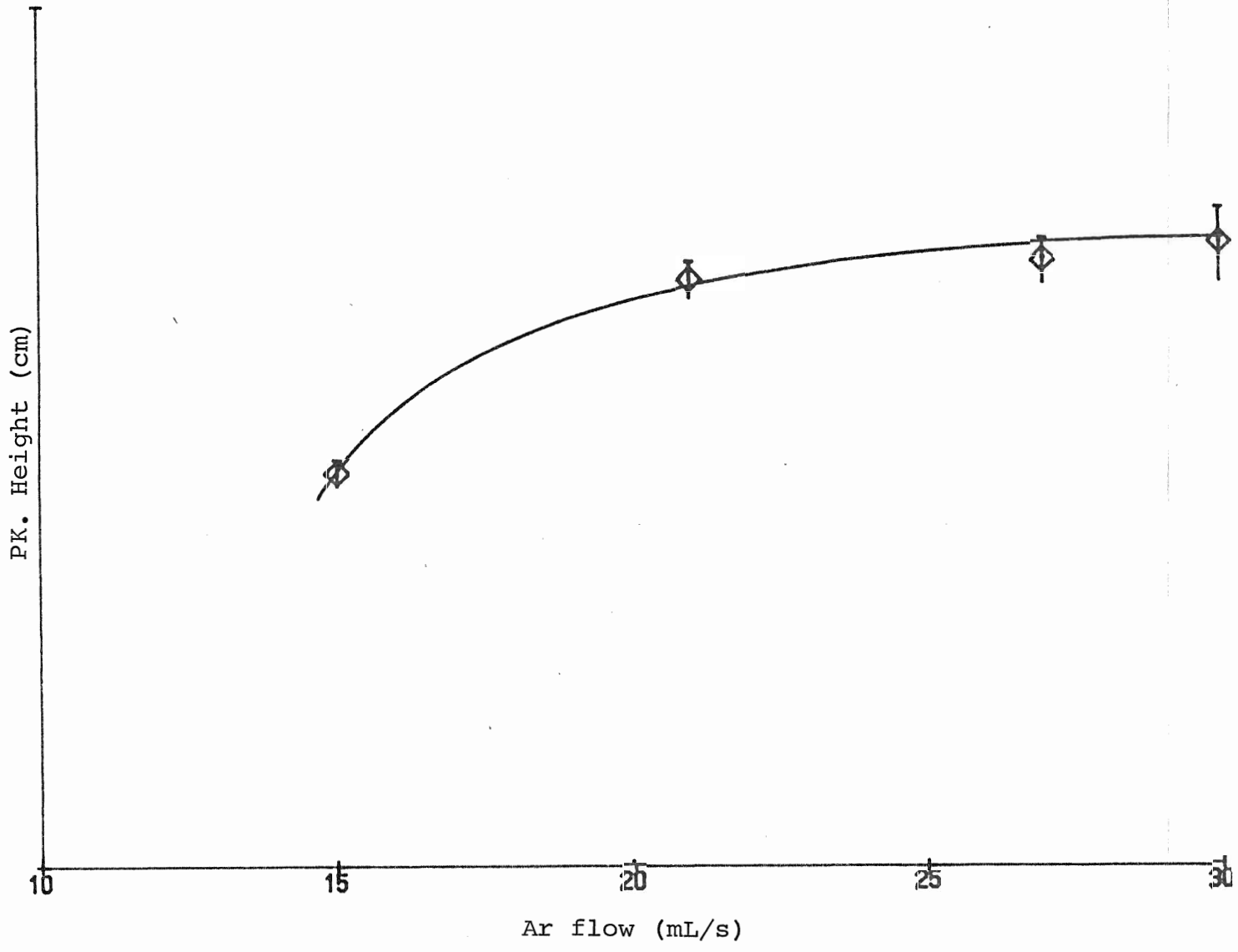


Figure 12. Response of 100 ng/mL germanium versus argon gas flow rates.

Table XIV. Response of a 100 ng/mL germanium standard versus reaction time in seconds.

	Peak height (cm)			
Time (s)	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
10	2.47	0.06	2.3	4
20	2.50	0.01	0.5	4
30	2.50	0.05	2.0	4
40	2.63	0.11	4.0	5
60	2.68	0.04	1.3	2
120	2.55	0.07	2.8	2

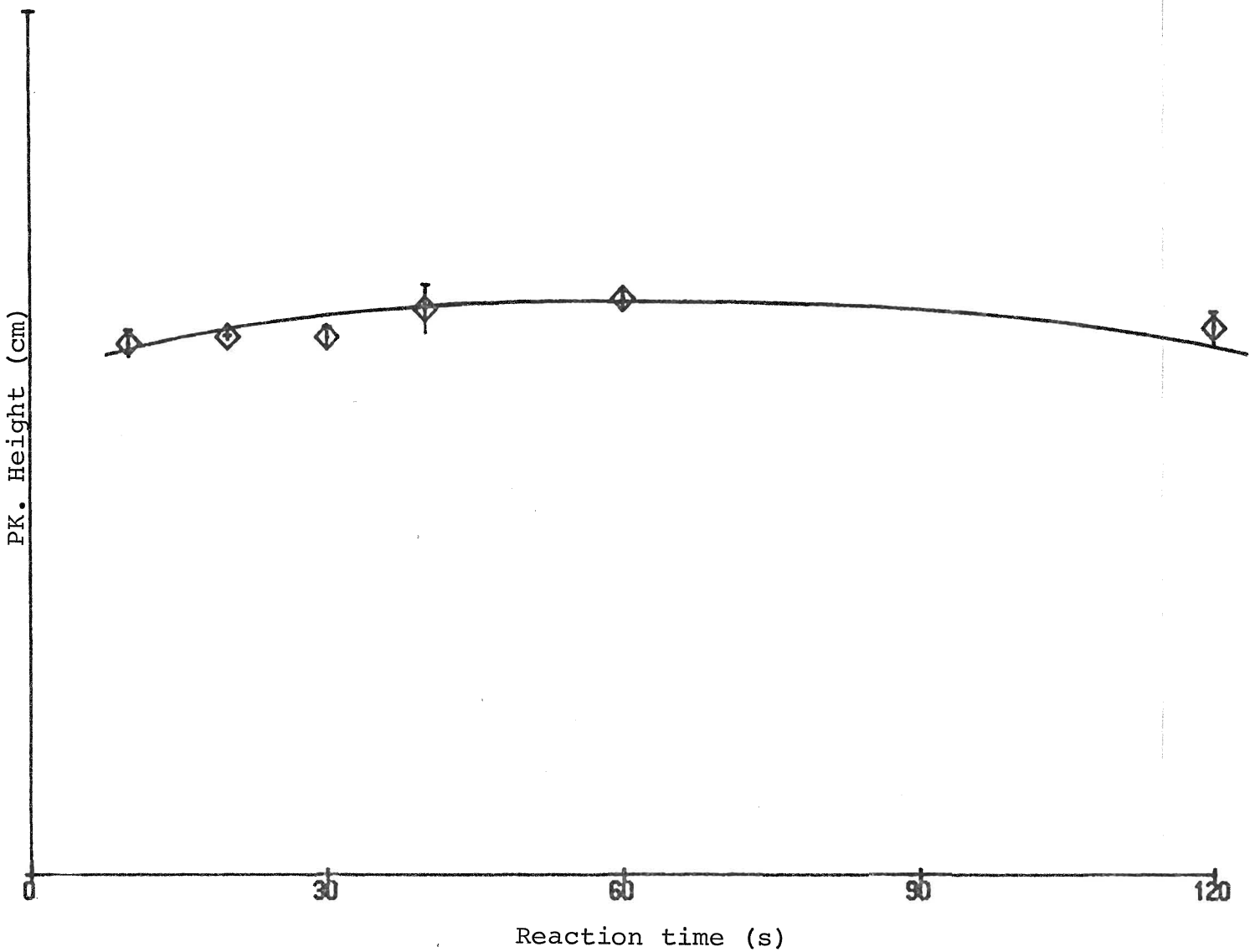


Figure 13. Response of 100 ng/mL germanium standard versus reaction time in seconds.

4) EFFECT OF CALCIUM SULPHATE AND PORAPAK Q ON THE GERMANIUM SIGNAL.

As mentioned earlier, a drying column, containing $CaSO_4$, and a delay column, containing Porapak Q, are interfaced between the reaction vessel and the sample tube head. According to the manufacturer of the hydride generator, the Porapak Q is used to slow down the generated hydride and separate it from the excess hydrogen gas. The results shown in Table XV indicate that a considerable decrease in the signal was registered when no porapak Q was used. This leads one to the conclusion that without Porapak in the delay column, the hydride is diluted with the excess hydrogen, thus accounting for the reduction in sensitivity.

It is also worth noting that no signal was registered from a blank solution which was run after injection of a germanium standard. This suggested that no appreciable amounts of germane were absorbed by the Porapak Q.

5) INTERFERENCE FROM ARSENIC(III) AND ARSENIC(V).

Once optimization of the aforementioned parameters was carried out, the effect of different concentrations of As(III) and As(V) on the germanium signal was assessed.

It should be kept in mind that reaction conditions for the hydride generation of both elements , As and Ge, were, at

Table XV. Response of 100 ng/mL germanium standard versus packing material in the drying and delay columns.

	Peak height (cm)			
Packing material	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
A	2.07	0.10	5.0	3
B	4.33	0.19	4.4	3

A, Calcium sulphate alone.

B, Calcium sulphate and Porapak Q.

this point in time, the same.

Smith [32] reported 50% suppression of the germanium signal when 100 mg/L of As(III) was present in solution. In the reported work, the germanium concentration used was 2 mg/L in 1 M HCl and $NaBH_4$, in pellet form, was used as the reducing agent. On the other hand, Jin et al. [10] recovered 81% of the germanium signal from a 50 mg/L solution of As(III) in 0.2 M HCl. Reduction was carried out with 3 mL of 8% (m/V) $NaBH_4$ solution.

The results given in Tables XVI and XVII and in Figures 14 and 15 show that no interference from As(III) and As(V) up to 1000 mg/L was encountered in this study.

When comparing the results previously mentioned, it should be remembered that $NaBH_4$ pellets have been proven to be 40 to 60% less efficient than $NaBH_4$ solutions. Secondly, arsine generation proceeds at a faster rate than germane generation. Consequently, this might suggest that when using $NaBH_4$ pellets as the reducing agent, the reduction of arsenic to arsine outperforms the reduction reaction of germanium to germane. Therefore less reducing agent is available for the complete reduction of germanium. Moreover, one would expect the interferences to decrease at higher acid concentrations.

6) EFFECT OF SUBSEQUENT ADDITIONS OF 4% $NaBH_4$ ON THE GERMANIUM SIGNAL.

It was observed that a residual signal, Figure 16,

Table XVI. Response of 100 ng/ml germanium versus increasing concentrations of arsenic(III).

As(III) mg/L	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of measurements
0	3.78	0.08	2.0	3
0.1	3.71	0.01	0.4	4
0.5	3.89	0.22	5.6	4
1	4.25	0.17	4.0	4
10	3.84	0.17	4.4	3
100	3.93	0.19	4.8	4
500	3.83	0.17	4.5	4
1000	3.89	0.17	4.5	3

Table XVII. Response of 100 ng/mL germanium standard versus increasing concentration of arsenic(V).

	Peak height (cm)			
As(V) mg/L	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
0	5.93	0.15	2.6	3
500	6.08	0.24	3.9	4
1000	6.03	0.16	2.7	4

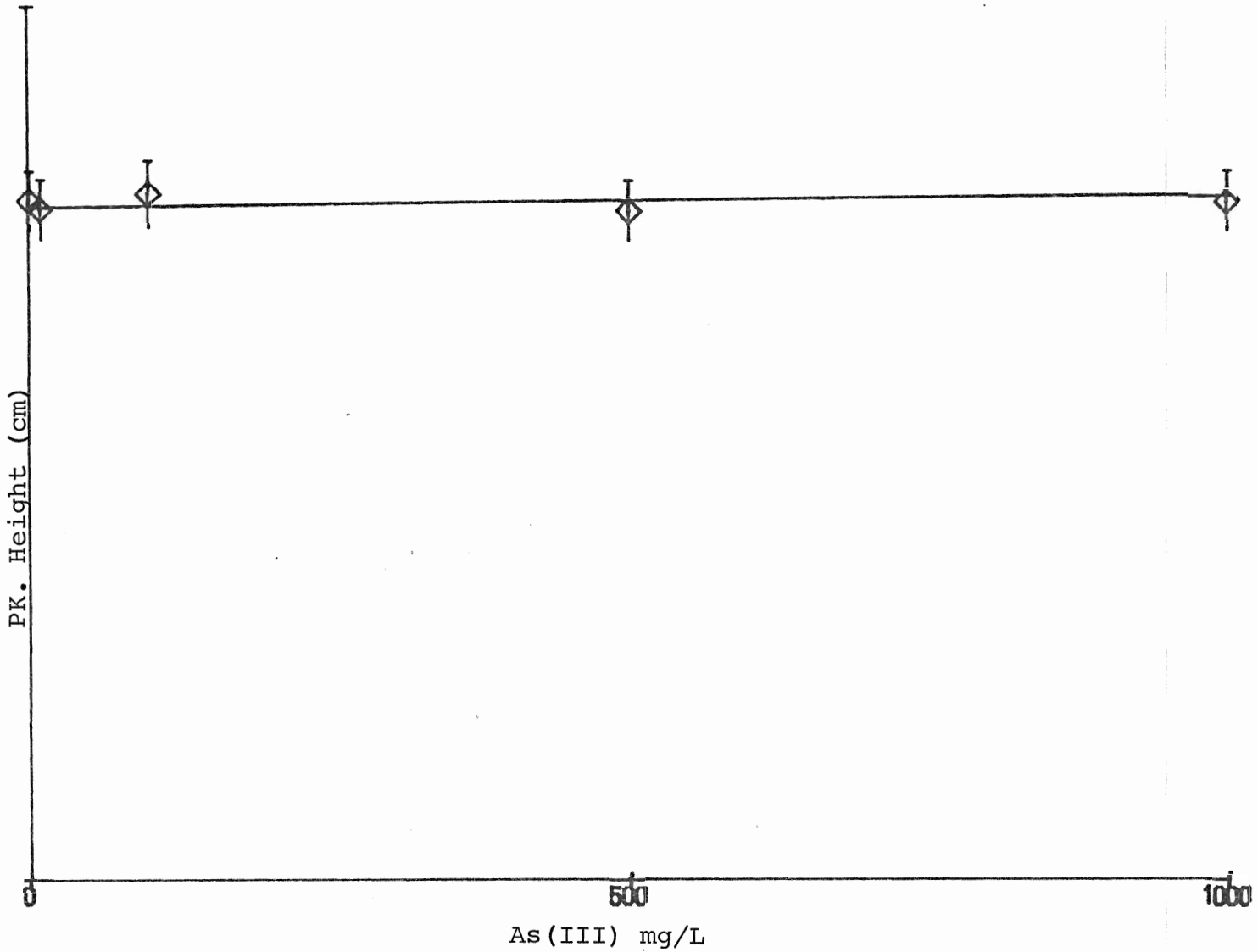


Figure 14. Response of 100 ng/mL germanium versus increasing concentrations on arsenic(III).

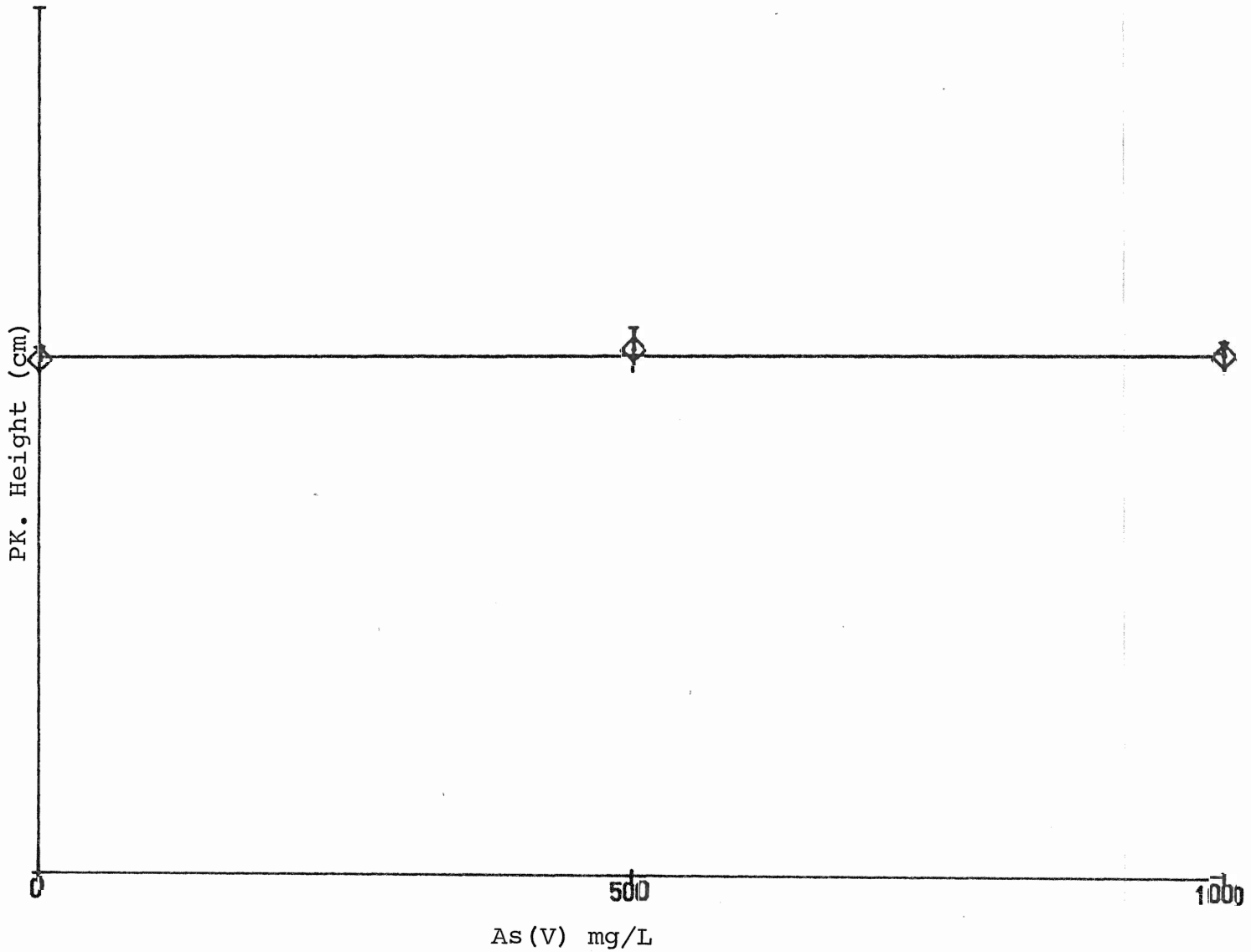


Figure 15. Response of 100 ng/mL germanium versus increasing concentrations of arsenic(V).

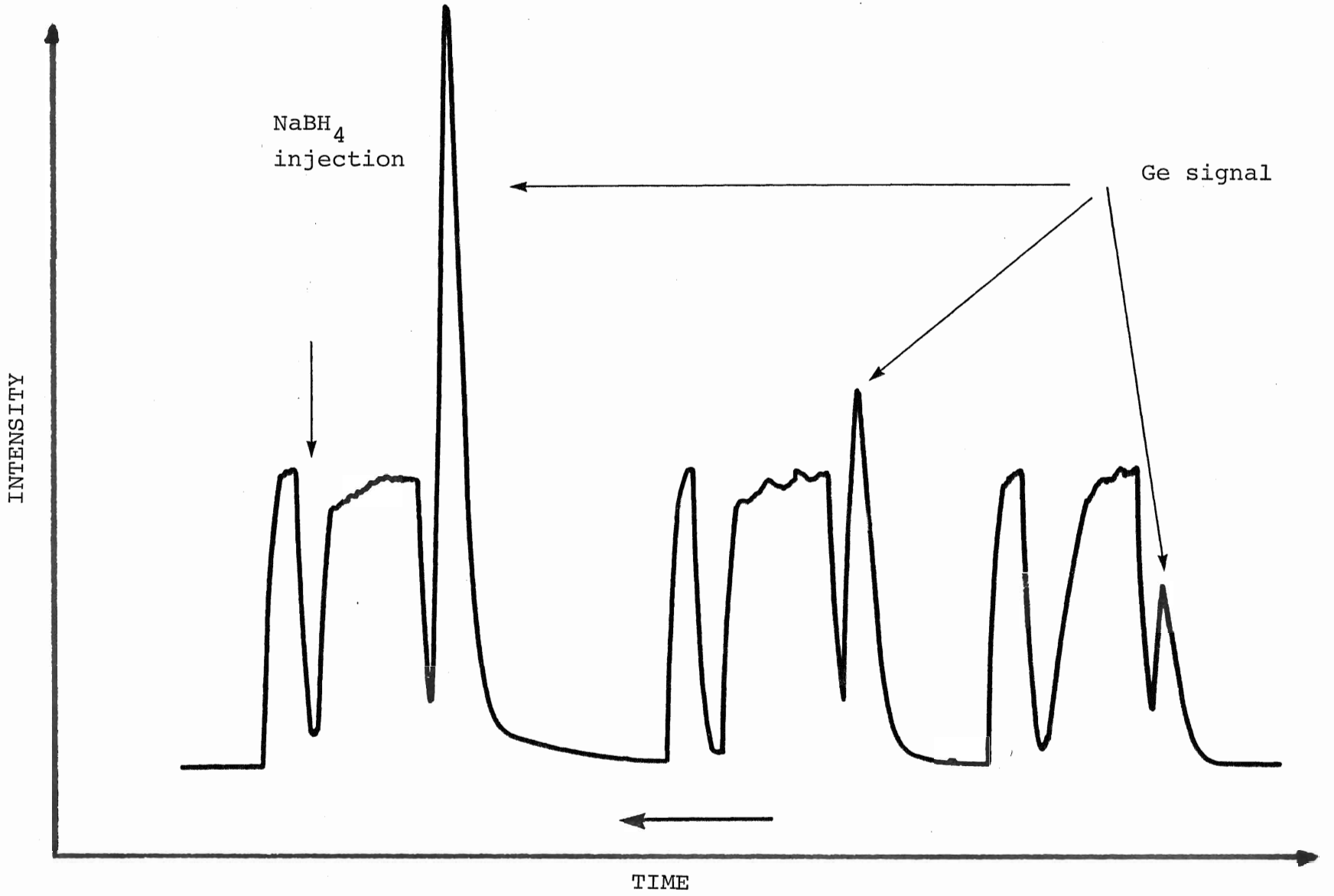


Figure 16. Response of 100 ng/mL germanium standard in 1 mL HCl after subsequent additions of 1 mL $NaBH_4$ 4% (m/V). Arrow indicates the direction of the chart recorder movement.

appeared after consecutive additions of 1 mL of $NaBH_4$ 4% (m/V) to samples which had been already reacted once. This suggested that reduction of germanium was not completed after the addition of the first milliliter of reducing agent. This behaviour would also explain why no interference from arsenic was encountered. In other words, since only 50% of the total germanium is being recovered, the effect of arsenic in the remaining portion of the analyte cannot be assayed. In an effort to solve the problem, higher volumes of reducing agent were injected but, as mentioned earlier, no improvement was accomplished. On the contrary, a decrease in the germanium signal was registered. The results were indicative of the fact that, due to the high concentration of hydrochloric acid (1 M) in the solution for analysis, the $NaBH_4$ was decomposed too quickly. As a result, the rest of the sample could not react and produced no hydride. This agrees with findings by Agterdenbos and Bax [89] who have shown that within 10 ms of mixing the alkaline $NaBH_4$ solution with the acid sample solution, the reducing agent is decomposed. It was therefore necessary to optimize the $NaBH_4$ concentration.

7) GERMANIUM SIGNAL VERSUS $NaBH_4$ CONCENTRATION.

Table XVIII and Figure 17 summarize the results obtained when different concentrations of reducing agent were used. The injected volume was 1 mL in each case . It can be seen that a maximum value was obtained with a concentration of 8% (m/V). This was due to the fact that more borohydride was present to

Table XVIII. Response of 100 ng/mL germanium standard versus increasing concentrations of sodium borohydride.

$NaBH_4$ %	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2	8.70	0.36	4.0	3
4	11.83	0.43	3.6	4
8	13.86	0.77	5.5	4
12	10.75	0.21	2.0	2

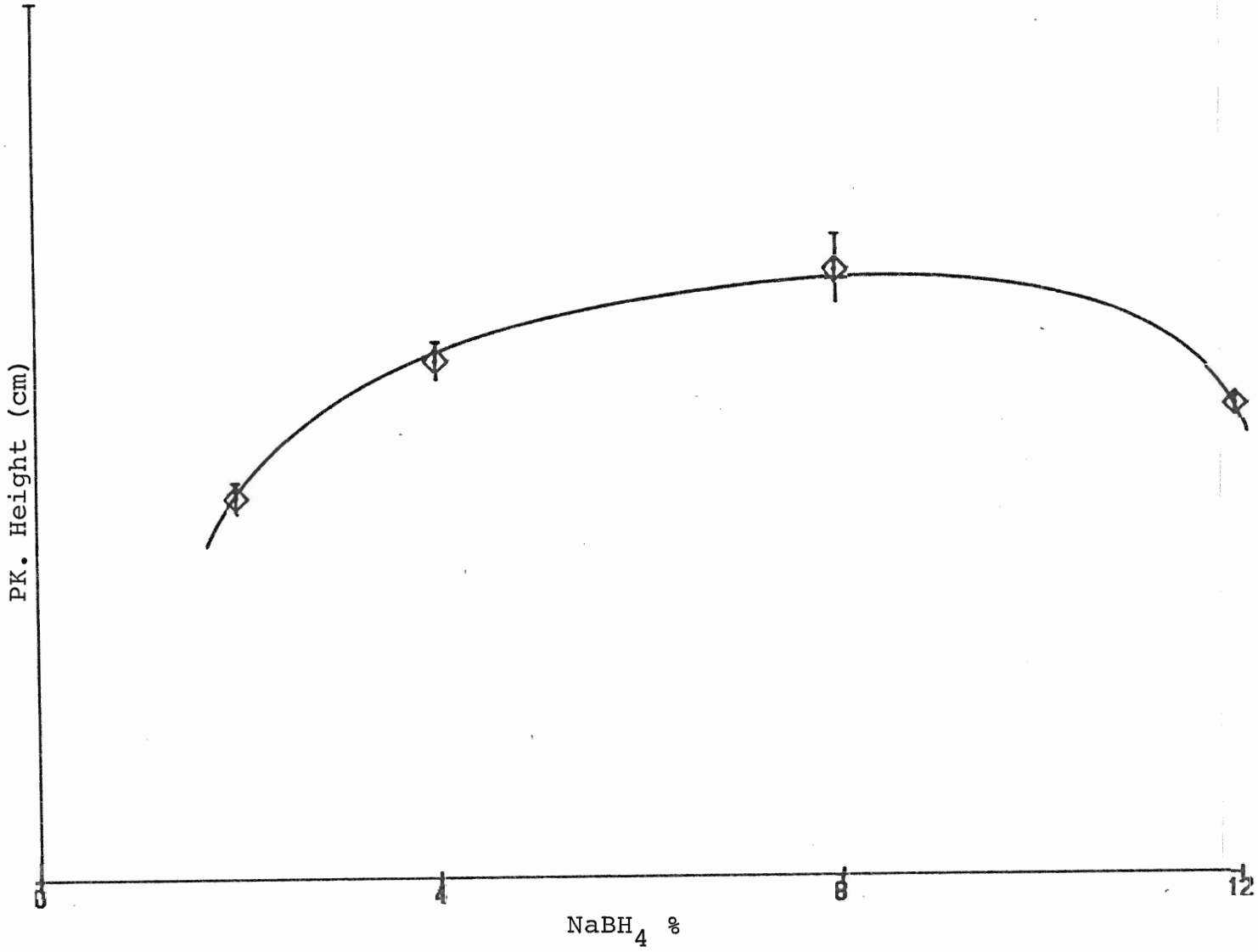


Figure 17. Response of 100 ng/mL germanium standard versus increasing concentrations of sodium borohydride.

react with the sample and therefore a higher yield of hydride was obtained. The decrease in signal produced by the 12% solution could be explained, once again, in terms of the big dilution effect caused by the excess hydrogen evolved in the reaction. When subsequent injections of 8% $NaBH_4$ were performed on the same sample, residual peaks as in the previous case were still observed. The only difference, as it was expected, was that the subsequent peaks were smaller. Also, the injection of more than 1 mL of the reducing agent at a time resulted in a decrease of the germanium signal.

One conclusion can be made; that is, as it stands,the method could be used in combination with a collection mode hydride generator system, where repetitive injections of the reducing agent can be carried out.

Since the system used in the course of this work was a direct-transfer batch-type system, it became expedient to optimize the concentration of hydrochloric acid in the solution for analysis.

8) GERMANIUM SIGNAL VERSUS HYDROCHLORIC ACID CONCENTRATION.

In order to save on the expensive reducing agent, a sodium borohydride concentration of 4% (m/V) was selected for this study. Table XIX and Figure 18 show the reponse of a 100 ng/mL germanium standard (5.0 mL)in different concentrations of HCl. It can be seen that the germanium signal increased with decreasing acid concentration, reaching a point of diminishing

Table XIX. Response of 100 ng/mL germanium versus HCl concentration.

Molarity HCl	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
0.000	0.00	0.00	0.0	2
0.025	7.40	0.99	13.0	2
0.050	23.00	0.53	2.3	3
0.100	20.06	0.84	4.0	3
0.200	15.63	0.81	5.0	3
0.500	10.24	0.69	6.7	4
1.000	7.59	0.47	6.2	2
5.000	7.67	0.74	9.7	2

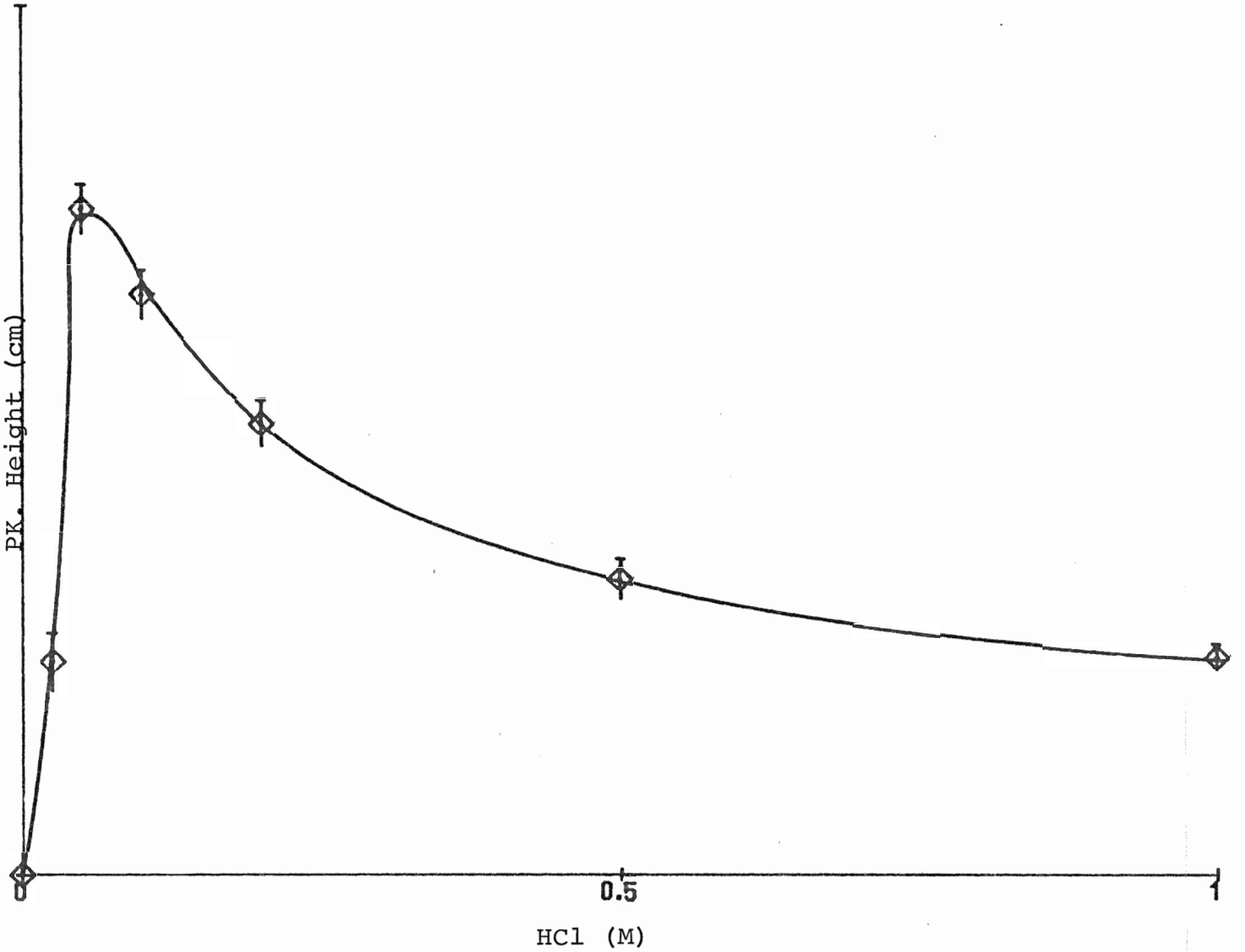


Figure 18. Response of 100 ng/mL germanium versus HCl concentration.

return at a concentration of 0.05 M. This concentration corresponds to a pH of 1.7 when measured experimentally. These findings compare well with results obtained by Thompson and Pahalavampour [55] who reported a maximum sensitivity of the germanium signal in 0.10 M hydrochloric acid. The slight discrepancy between results may be accounted for by the fact that these authors used a continuous hydride generator system.

It was observed, as was expected, that in the cases where HCl concentrations were greater than 0.2 M, large residual signals appeared with subsequent injections of the reducing agent. However, in the cases where HCl concentrations were less than 0.1 M, only a small residual signal was achieved after consecutive injections of $NaBH_4$. This, however, was not conclusive, due to the fact that the sample solution was already basic (pH 7-8) when the second injection was performed and, as can be seen from the results in Figure 18, no hydride evolution would take place, even after 60 s reaction, when the solution's pH was not acidic. In this regard, when more HCl was added to the solution, which had been reacted once, a series of peaks were observed as depicted in Figure 19.

The tailing of the peak became longer at lower acid concentrations, suggesting that more analyte reacted and that reduction became a longer process. This was also supported by the observation that effervescence continued for a longer period of time at lower acid concentrations than at higher acid concentrations. For this reason, the reaction time for these experiments was increased to 30 s.

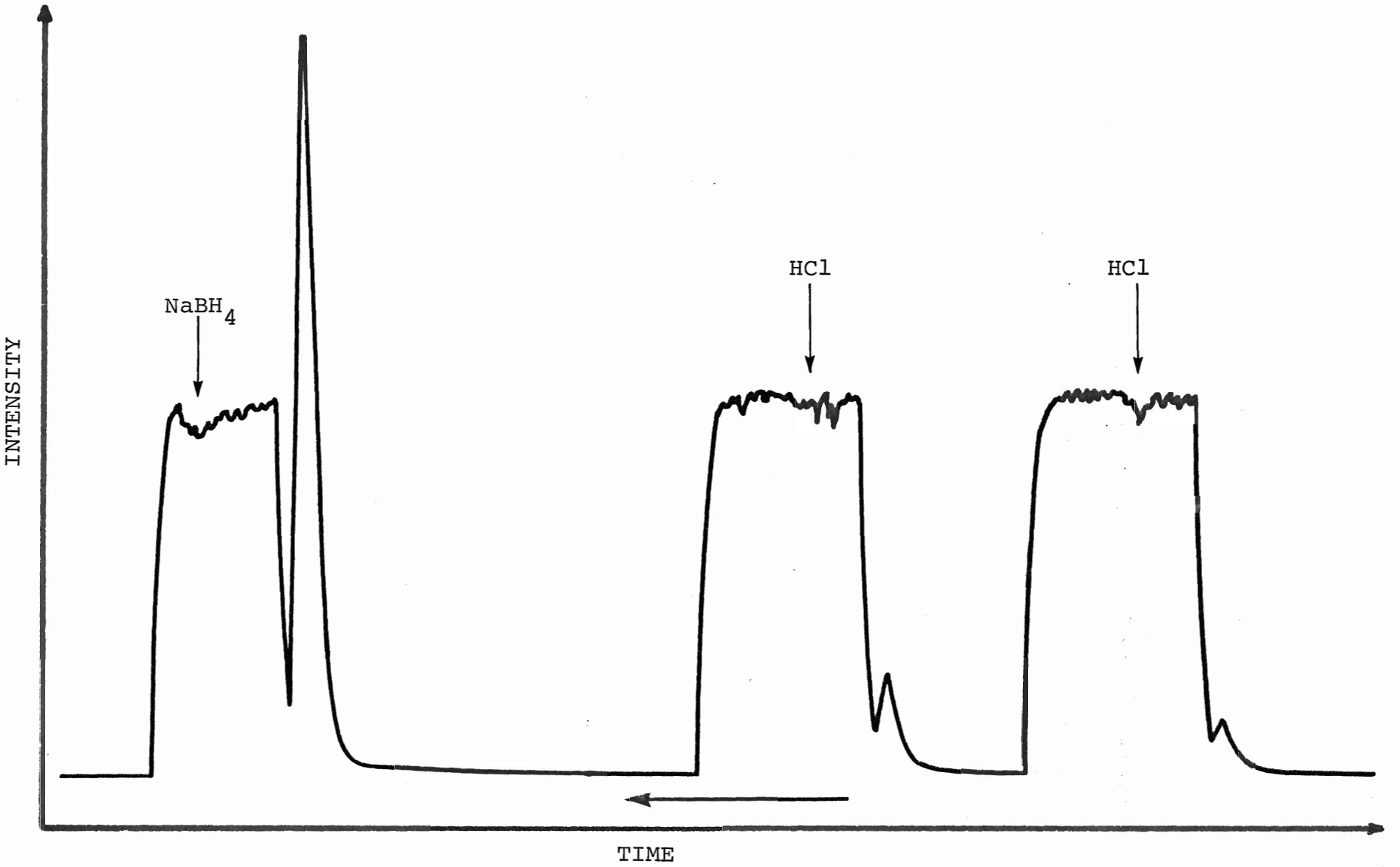


Figure 19. Response of 100 ng/mL germanium standard at pH 1.7 reacted once with 1 mL of $NaBH_4$ 4% (m/V) to which subsequent additions of HCl have been made. Arrow indicates the direction of the chart recorder movement.

In light of the results obtained , it can be concluded that reduction of germanium to germane is not fully accomplished under either condition of analysis; however, under these new conditions (0.05 M HCl + 1 mL $NaBH_4$ 4% (m/V)), 60% increase in the germanium signal can be accomplished when compared to the signal achieved in 1 M HCl. A way to determine the percent yield of the reduction accurately would be to analyze the reacted solution by Graphite Furnace A.A.S.

9) GERMANIUM SIGNAL VERSUS BOROHYDRIDE CONCENTRATION

Table XX and Figure 20 summarize the results obtained when optimizing the $NaBH_4$ concentration. The volume of reducing agent injected was 1 mL in all cases and the HCl concentration kept at 0.05 M. The best response was obtained at a concentration of 4% $NaBH_4$. Once again, it can be seen that an excess of borohydride has a negative effect on the germanium signal which, according to previous observations, is due to the dilution of the hydride with the hydrogen gas.

10) GERMANIUM SIGNAL VERSUS BUFFER SOLUTIONS

It is a well known fact [14] that the efficiency of the hydride generation technique is strongly dependent on the pH at which the reaction is performed. Since the borohydride solution is basic, the pH after the addition of the borohydride can be much higher than the initial pH.

Table XX. Response of 50 ng/mL germanium versus sodium borohydride concentration.

$NaBH_4$ %	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2	9.70	0.40	4.1	3
4	21.40	0.99	4.6	3
8	20.68	0.98	4.7	3
12	11.75	0.64	5.4	3

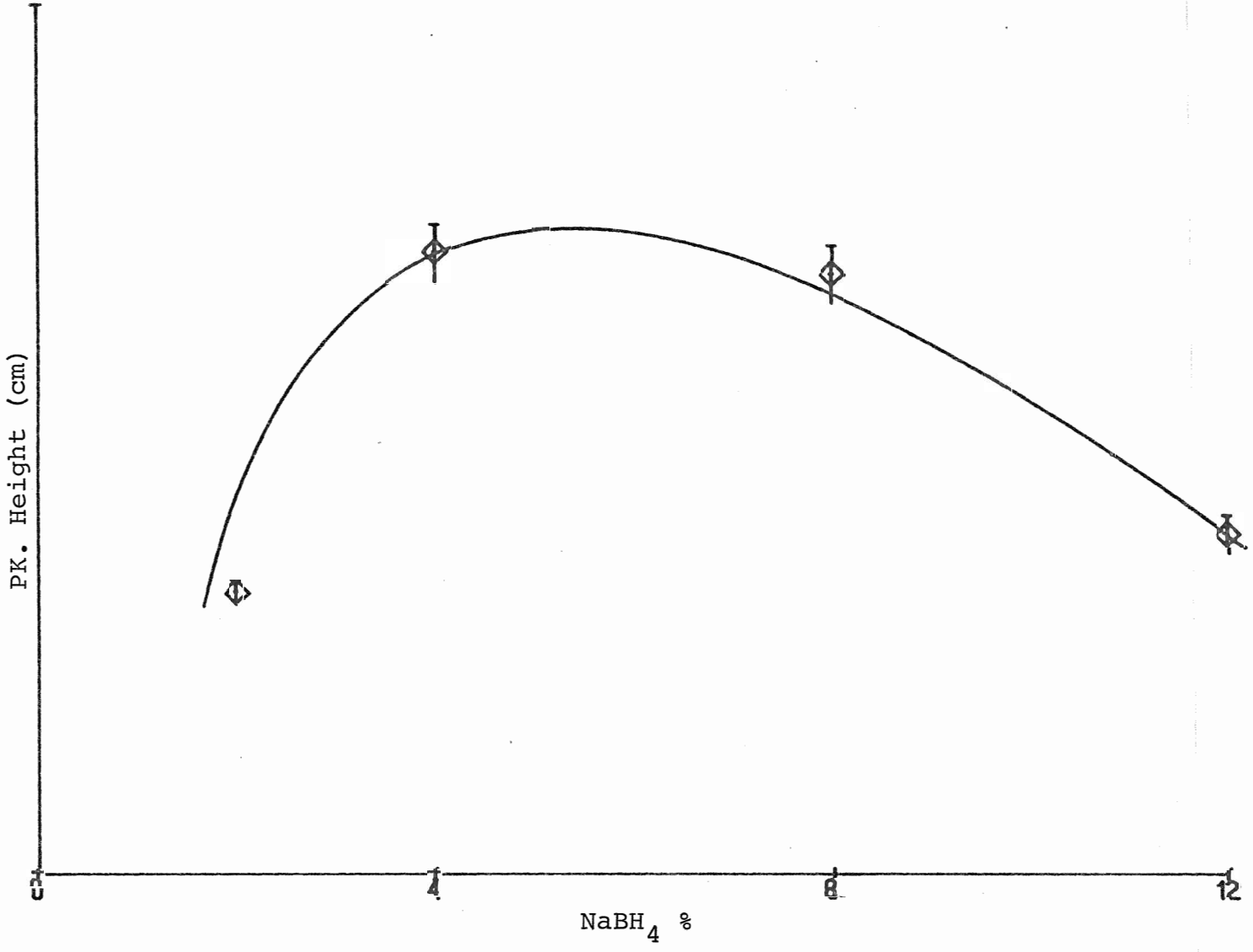


Figure 20. Response of 50 ng/mL germanium versus sodium borohydride concentration.

It was decided, therefore, to study the effect of buffer solutions on the reduction of germanium. Two buffer solutions were studied: acetate buffer at pH 4 and phosphate buffer at pH 2. The efficiency of both of these systems was compared with the response obtained in the 0.05 M HCl medium.

Other workers have used a number of buffer solutions for a similar purpose. Andreae and Froelich [45] studied the use of TRIS, oxalate, maleate, phosphate and strong acids (HCl, H_2SO_4). They observed that the reaction efficiency was significantly lower at both high and low pH and that a broad maximum of the reaction yield exists in the near neutral 4-6 pH range. The authors selected the TRIS-HCl system at a concentration of 0.095 M in the final solution for routine work because it displayed adequate buffering capacity in the desired pH range. They used a collection mode system and introduced the hydride into a graphite furnace atomizer.

Braman and Tompkins [65] investigated the use of oxalate at pH 1.5, phthalate at pH 4 and unbuffered distilled water. They obtained a low yield from the unbuffered solution, pH 5-6, and a better yield from the oxalate buffer, pH 1.5, than with the phathalate system at pH 3-4. A collection mode system was also used in this study.

Table XXI portrays the results obtained in this work. Better recovery was accomplished with the phosphate buffer at pH 2 (pH 4 after reaction) than with the acetate buffer at pH 4 (pH 5.5 after reaction). Nonetheless, an excessive amount of foaming was observed when the acetate buffer was used. The

Table XXI. Response of 50 ng/mL germanium standard versus 0.05 M hydrochloric acid (pH 1.7), acetate buffer (pH 4), and phosphate buffer (pH 2).

	Peak height (cm)			
Medium	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
A	16.63	0.25	1.5	3
B	8.70	0.60	7.0	2
C	9.60	0.20	2.1	2

A, 0.05 M Hydrochloric acid.

B, Acetate buffer (no HCl).

C, Phosphate Buffer

addition of Antifoam B did not particularly improve this.

In both cases, a residual signal was recorded after the subsequent addition of reducing agent to the samples which had been already reacted once. The signal produced with 0.05 M HCl still remained the highest.

It might be concluded that when the pH of the solution remains too low, a pH less than 5, the hydrolysis of the $NaBH_4$ proceeds much more rapidly than hydride formation.

11) EFFECT OF POTASSIUM PERSULPHATE ON THE GERMANIUM SIGNAL

Jin and Taga [35] as well as Castillo *et al.* [90] have studied the effect of different oxidizing agents, such as $K_2Cr_2O_7$, $KMnO_4$, H_2O_2, and $(NH_4)_2S_2O_8$, on the hydride generation of plumbane PbH_4. Both groups concluded that better recovery of the analyte atom was accomplished in the presence of such agents. Jin and Taga [35] reported a recovery factor of greater than 80% with the use of ammonium persulphate, whereas Castillo *et al.* [90] reported a 97.5% recovery with the use of the same oxidizing agent. The effect was attributed to the oxidation of lead to a metastable tetravalent state before conversion into plumbane.

In light of the aforementioned facts, it was decided to study the effect of persulphate on the reduction efficiency of germanium. Table XXII summarizes the results obtained when 3 mL of $K_2S_2O_8$ (3% (m/V)) was injected into germanium standards with and without HCl. It can be seen that a 25% increase in the

Table XXII. response of 100 ng/mL germanium standard in different media.

	Peak height (cm)			
Medium	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
A	12.18	0.27	2.2	3
B	9.74	0.29	3.0	3
C	11.85	0.07	0.6	4
D	8.95	0.49	5.5	2

A, No HCl + 3 mL of Potassium persulphate 3% (m/V).

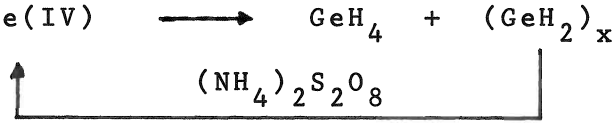
B, 0.05 M HCl only.

C, 0.05 M HCl + 3 mL of potassium persulphate 3% (m/V).

D, Phosphate buffer + 3 mL of potassium persulphate 3% (m/V).

germanium signal was accomplished with the use of persulphate compared to the signal obtained with HCl alone. The signal also increased when the phosphate buffer was used; however, subsequent peaks appeared after the injection of more reducing agent.

The mechanism responsible for this behaviour is yet not clear. However, a possible explanation may reside in the fact that some $(GeH_2)_x$ is formed in the course of the reaction with $NaBH_4$ [88] causing the persulphate to act on the polymer and to oxidize Ge(II) to Ge(IV). Thus, this would displace the equilibrium towards the right hand side as GeH_4 leaves the solution. The overall reaction is depicted below.



The signal achieved when no HCl was present was slightly bigger than the one obtained with 0.05 M HCl and persulphate. However, recovery of the base line was accomplished more quickly with the latter system. In other words, the tailing of the peaks obtained without HCl was considerably longer than the one produced by the other two methods. This, of course, presented the disadvantage that the analysis time had to be increased. For this reason the HCl/persulphate mixture was taken as the optimum solution for analysis.

The volume of 3% persulphate was also optimized.

Results are given in Table XXIII and Figure 21. A decrease in the germanium signal was registered at both high and low volumes of persulphate. The effect of different concentrations of HCl in the presence of 3 mL of persulphate was also assessed. It can be seen from Table XXIV and Figure 22 that the behaviour is similar to the one observed when HCl alone is present, as depicted in Figure 18. However, reduction could be accomplished, in this case, when no HCl was present, that is, when the pH was near neutral. No attempts were made to determine the percent yield of the reaction under these new conditions.

12) EFFECT OF ARSENIC(III) AND ARSENIC(V) ON GERMANIUM SIGNAL

Since the reaction conditions (0.05 M HCl, 3 mL of $K_2S_2O_8$ 3% (m/V) + 1 mL of $NaBH_4$ 4% (m/V)) at this point in time were different than the original ones (1 M HCl, 1 mL of $NaBH_4$ 4% (m/V)), it was decided to restudy the effect of As(III) and As(V) on germanium reduction under the new conditions.

Table XXV portrays the results obtained. While no effect could be observed for As(V), a 25% decrease in the germanium signal was produced by the presence of 1000 mg/L of As(III). The addition of 3 mL of $K_2S_2O_8$ did not improve the results.

Table XXIII. Response of 100 ng/mL germanium standard versus volume of 3% (m/V) potassium persulfate.

PPS 3% mL	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
1	8.43	0.72	8.6	4
2	10.87	0.45	4.2	4
3	11.16	0.11	1.0	4
5	10.23	0.40	3.9	3

PPS, Potassium persulphate.

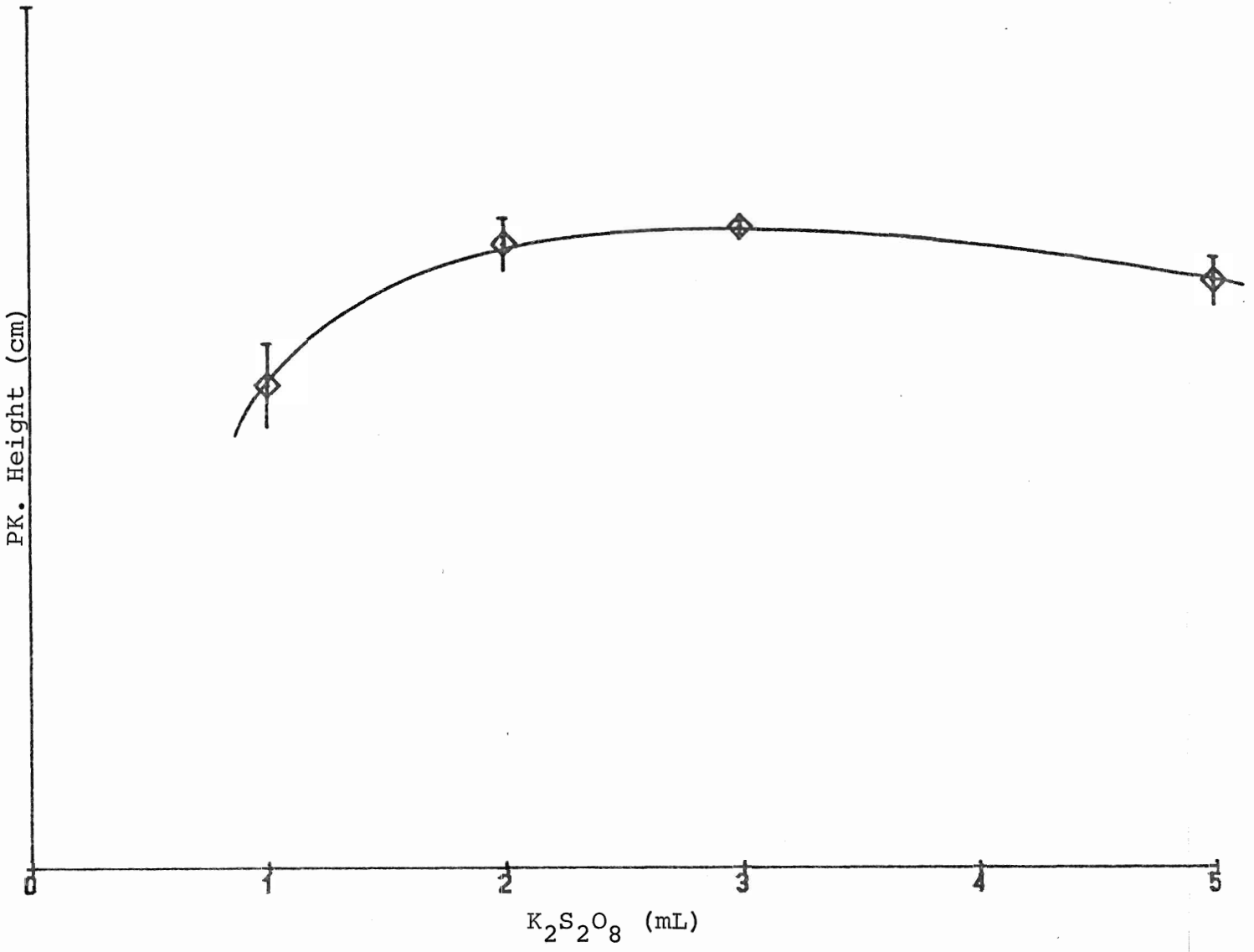


Figure 21. Response of 100 ng/mL germanium standard versus volume of 3% (m/V) potassium persulphate.

Table XXIV. Response of 100 ng/mL germanium standard, 3 mL of 3% (m/V) potassium persulfate versus HCl concentration.

	Peak height (cm)			
Molarity HCl	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
0.00	22.27	0.30	1.3	3
0.05	21.67	0.95	4.4	3
0.50	3.95	0.49	12.5	3
0.10	3.48	0.11	3.1	2

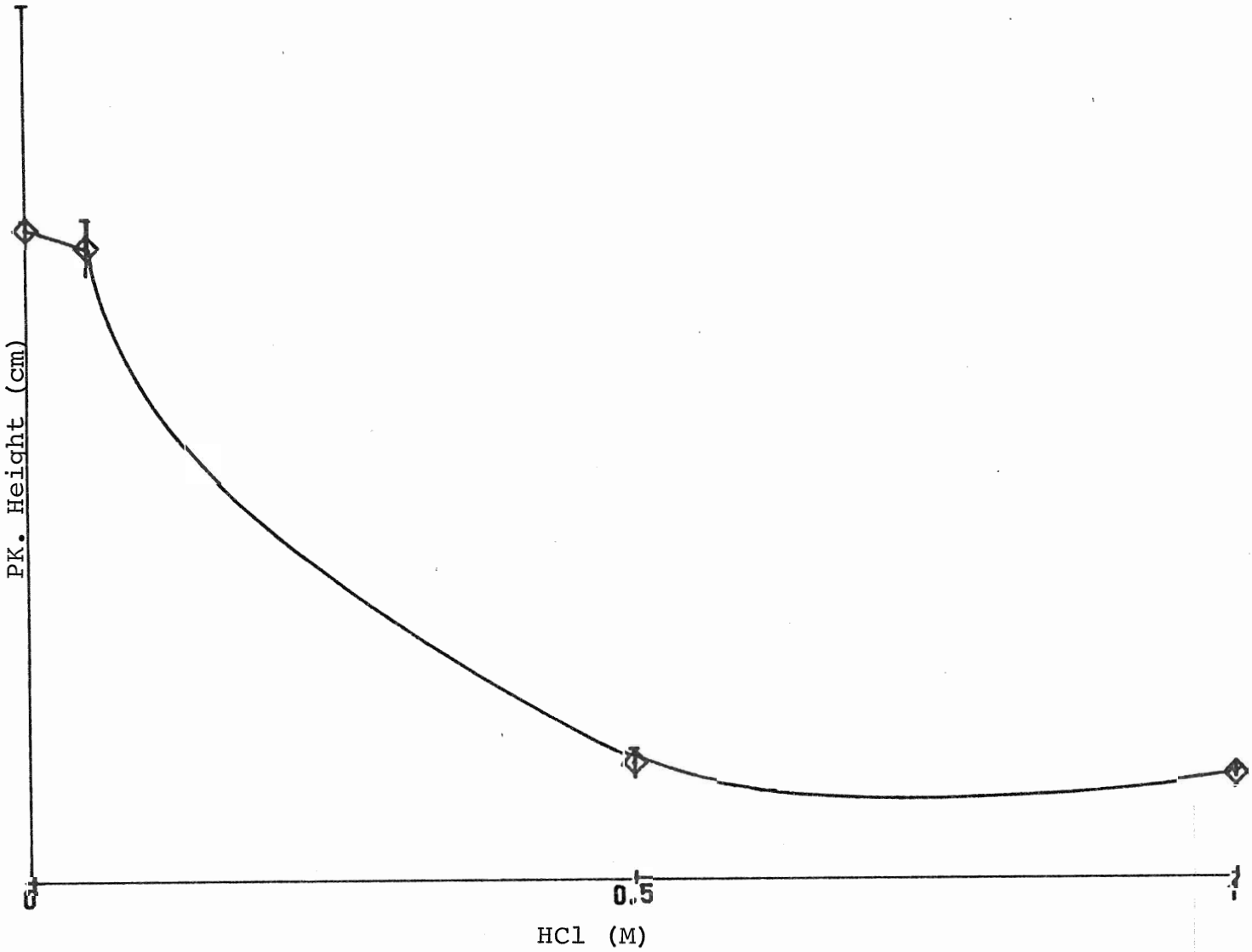


Figure 22. Response of 100 ng/mL germanium standard, 3 mL of 3% (m/V) potassium persulphate versus HCl concentration.

Table XXV. Germanium recovery (%) from 1000 mg/L of As(III) and As(V) in different media.

	Ge recovery %		
	Medium		
Interferent		pH 1.7	No HCl
1000 mg/L	pH 1.7	3 mL PPS 3 %	3 mL PPS 3 %
As(III)	77	74	75
As(V)	95	96	93

PPS, Potassium persulphate.

13) EFFECT OF AMMONIUM PERSULPHATE ON THE GERMANIUM SIGNAL

As mentioned in the experimental section, $K_2S_2O_8$ is not very soluble in water; therefore, the effect of higher concentrations of persulphate on the germanium recovery was established with the use of $(NH_4)_2S_2O_8$. No difference in the germanium signal was observed when identical concentrations of either salt were used. Table XXVI and Figure 23 summarize the results. It can be seen that at higher concentrations of persulphate, the signal decreased. This was possibly due to $NaBH_4$ being decomposed more quickly by the persulphate. This was supported by the fact that the reaction proceeded more violently once the reducing agent was injected.

At lower persulphate concentrations, the signal also decreased; however, tailing of the peak increased suggesting that the amount of analyte being reduced might remain constant.

14) EFFECT OF BOROHYDRIDE AND PERSULPHATE ON THE GERMANIUM SIGNAL

It became necessary to establish the optimum conditions for germanium reduction in 0.05 M HCl in terms of $(NH_4)_2S_2O_8$ and $NaBH_4$ concentrations. Results are given in Tables XXVII, XXVIII XXIX and Figure 24. It can be observed that high concentrations of both reagents had a negative effect on the germanium signal. The addition of 1 mL of $NaBH_4$ 4% (m/V) and 1 mL of $(NH_4)_2S_2O_8$ 10% (m/V) resulted in the best signal response.

Table XXVI. Response of 100 ng/mL germanium standard versus ammonium persulfate concentration.

APS %	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
5	14.57	1.03	7.0	3
10	15.64	0.46	3.0	4
15	14.00	0.30	2.2	3
20	12.80	0.78	6.0	3

APS, Ammonium persulphate.

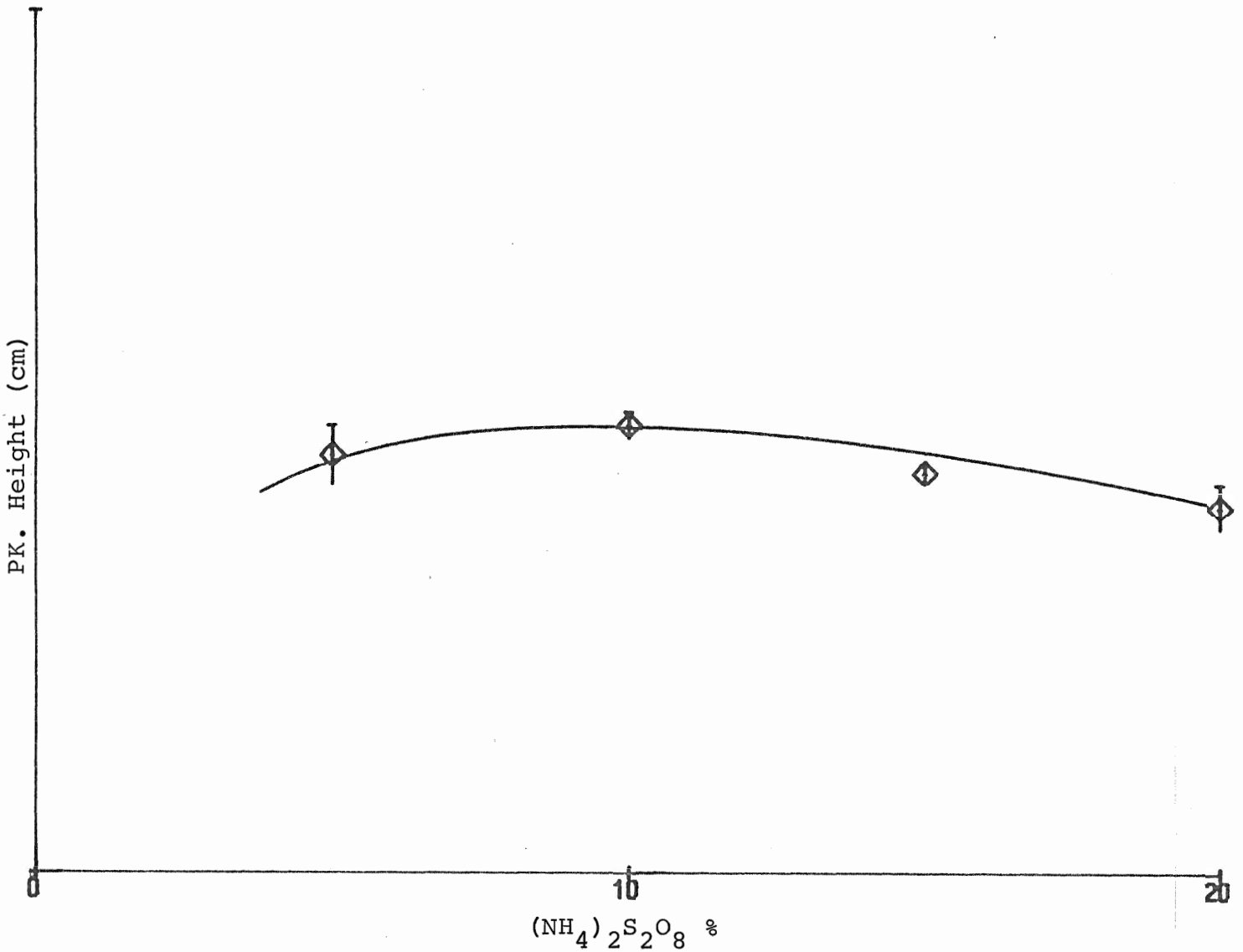


Figure 23. Response of 100 ng/mL germanium standard versus ammonium persulphate concentration.

Table XXVII. Response of 100 ng/mL germanium standard in 1 mL of 10% (m/V) ammonium persulfate versus sodium borohydride concentration.

	Peak height (cm)			
$NaBH_4$ %	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2	14.87	0.47	3.1	4
4	15.64	0.46	2.9	4
8	13.68	0.26	1.9	3
12	12.67	0.10	1.0	3

Table XXVIII. Response of 100 ng/mL germanium standard in 1 mL of 5% (m/V) ammonium persulfate versus sodium borohydride concentration.

$NaBH_4$ %	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2	13.74	0.36	2.6	3
4	14.57	0.26	1.8	3
8	12.84	0.25	1.9	3

Table XXIX. Response of 100 ng/mL germanium standard in 1 mL of 15% (m/V) ammonium persulfate versus sodium borohydride concentration.

$NaBH_4$ %	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of measurements
2	7.60	0.11	1.4	3
4	14.00	0.10	0.7	3
8	10.63	0.11	1.0	3

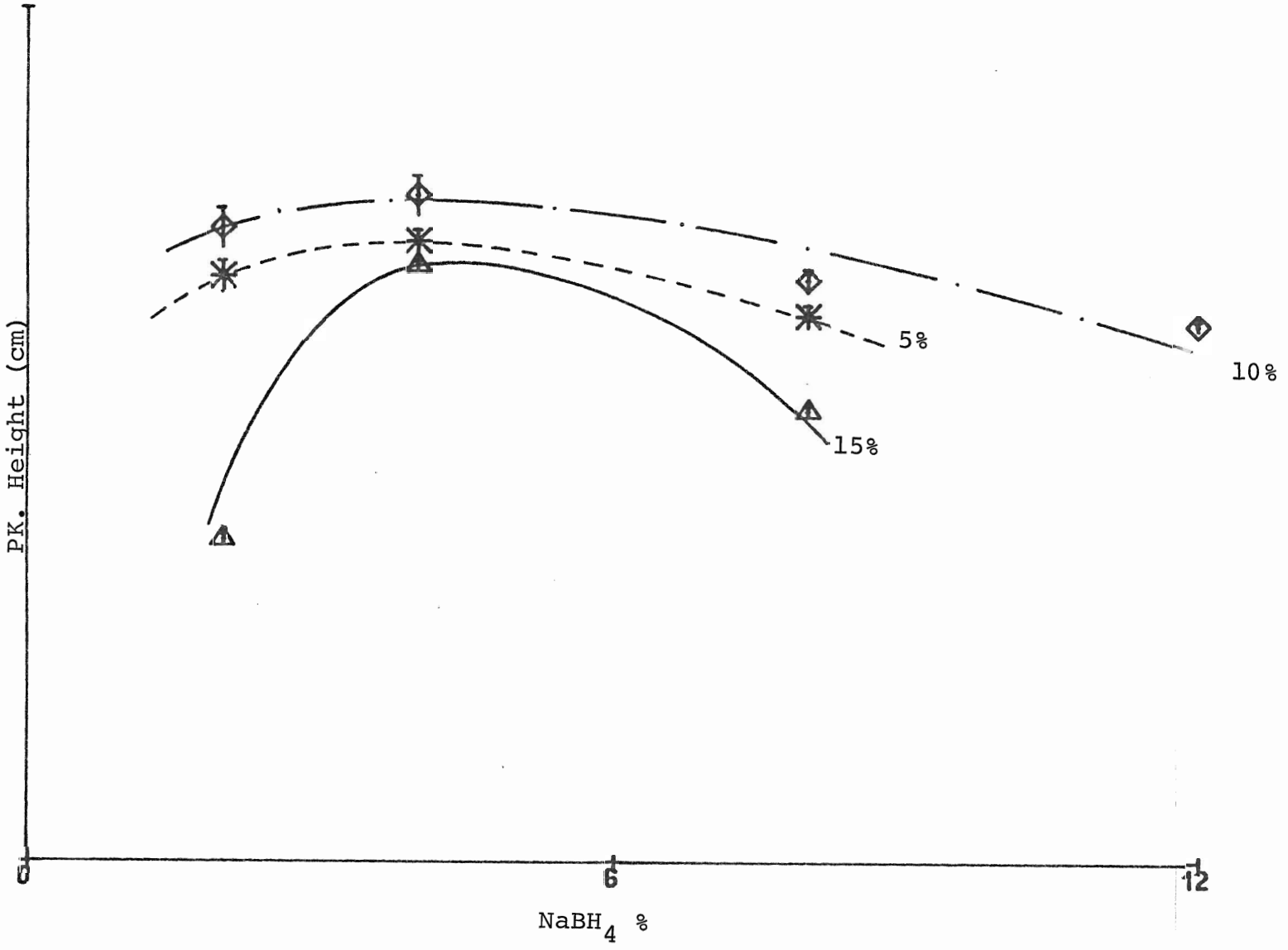


Figure 24. Effect of ammonium persulphate on the signal response of 100 ng/mL germanium standard in 0.05 M HCl versus $NaBH_4$ concentration.

15) GERMANIUM SIGNAL VERSUS REACTION TIME

The response of a 100 ng/mL germanium standard versus time was evaluated in 0.05 M HCl and 10% ammonium persulphate. Table XXX and Figure 25 portray the results obtained. It can be seen that the signal increased with time; however, after 30 s no improvement could be accomplished. Therefore, 30 s was taken as the optimum value.

16) REPRODUCIBILITY

The reproducibility of the germanium analysis was tested in 0.05 M HCl and 1 mL of ammonium persulphate 10% (m/V) solution. Results are given in Table XXXI. A relative standard deviation of 3% was achieved for eight determinations over a period of two hours, starting from the time of the first injection.

17) DETECTION LIMIT

The detection limit was evaluated with HCl alone and with the mixture HCl/persulphate by injection of a 1 ng/mL germanium standard. Since no contamination was encountered on the blank reagents, the calculation of the detection limit was based on the noise level. The average noise level at a recorder sensitivity of 10 mV was found to be 0.50 cm. The average peak

Table XXX. Response of 100 ng/mL germanium standard versus time in seconds.

	Peak height (cm)			
Time (s)	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
10	12.68	0.25	1.9	2
20	14.80	0.57	3.8	3
30	17.60	0.22	1.6	2
40	17.25	0.35	2.0	2
50	17.08	0.74	4.3	2
80	15.90	0.42	2.7	2

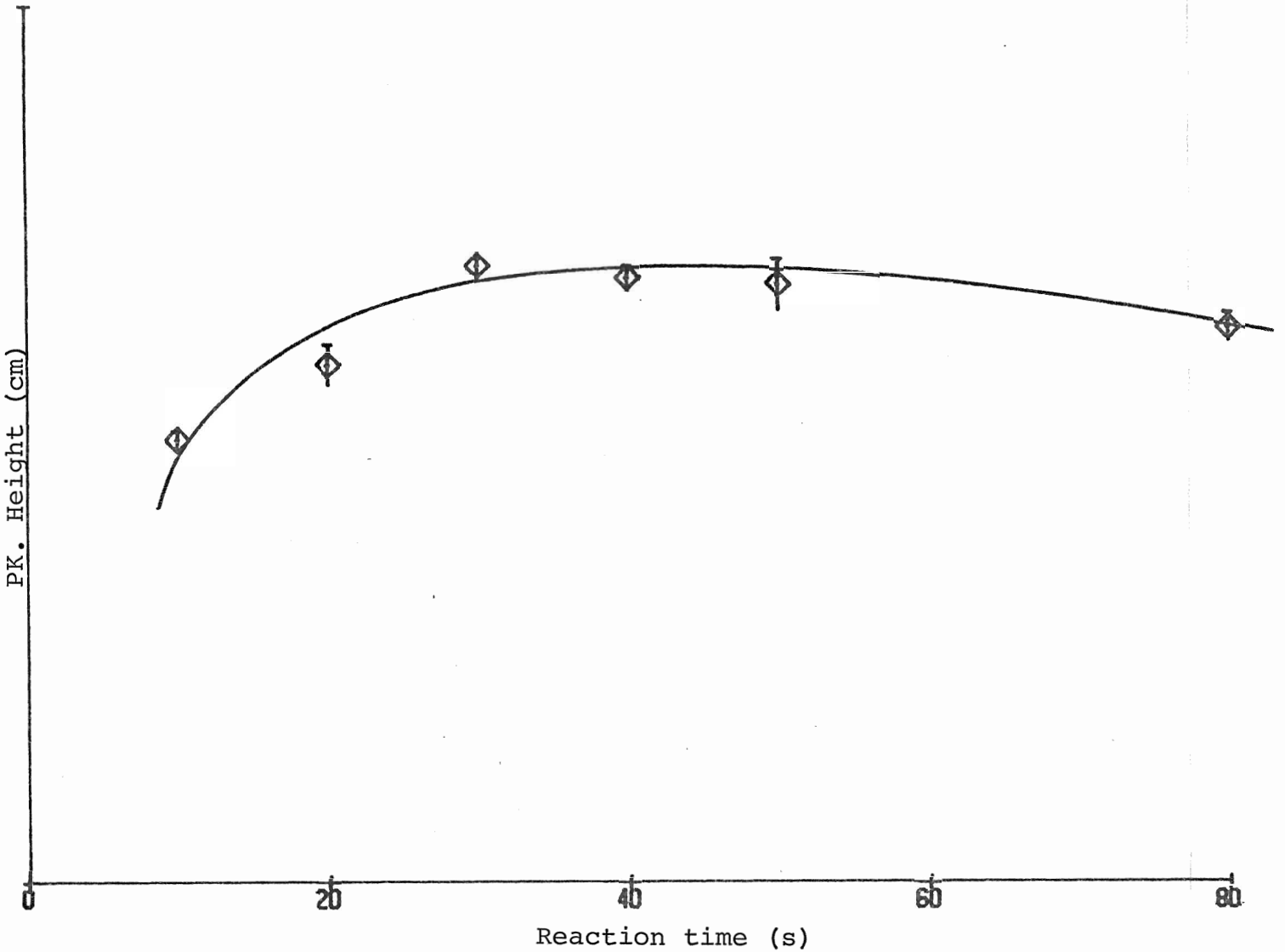


Figure 25. Response of 100 ng/mL germanium standard versus time in seconds.

Table XXXI. Variation of 100 ng/mL germanium signal with time.

Time (min)		Peak height (cm)
0		16.20
5		16.40
10		16.10
15		16.10
20		15.70
80		15.40
85		15.50
90		15.15
120		15.20
	Mean	15.69
	SD.	0.46
	RSD %	3.0

height of the germanium standard in HCl alone was 9.66 cm while the average peak height of the same standard with 1 mL of $(NH_4)_2S_2O_8$ 10% (m/V) was 11.00 cm. The detection limit for a 10 mL injected sample was 0.10 ng/mL and 0.09 ng/mL respectively.

18) CALIBRATION CURVES

The linear dynamic range associated with germanium determinations using the Direct Current Plasma through solution nebulization has been reported to be 0.1-1000 mg/L [84]. The response of germanium standards, using the hydride generation technique, was evaluated in the range 0.02-100 mg/L.

Three calibration curves were constructed: one containing 0.05 M HCl alone, one containing 0.05 M HCl and persulphate and finally one containing persulphate alone. Tables XXXII, XXXIII, XXXIV and Figure 26 summarize the results obtained. It can be seen that in all cases the response was linear in the range studied. However, as was expected, the best sensitivity was accomplished when ammonium persulphate was used.

19) CHERT SAMPLES

Following the procedure outlined in the experimental section, three samples were prepared. A standard addition method, in the range 0-10 ng/mL, was applied to one of the samples. Results are given in Table XXXV. A calibration curve of aqueous standards containing the appropriate amounts of blank

Table XXXII. Response of germanium standards using 0.05 M HCl and 1 mL of 10% (m/V) ammonium persulfate.

Ge ng/mL	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2*	1.71	0.03	1.8	2
5*	4.33	0.04	1.0	3
10*	8.25	0.07	1.0	2
50**	4.20	0.11	2.7	4
100**	8.61	0.11	1.3	4

* Measured at recorder sensitivity of 10 mV

** Measured at recorder sensitivity of 100 mV.

Table XXXIII. Response of germanium standards using 0.05 M HCl only.

Ge ng/mL	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2*	1.32	0.01	0.8	3
5*	3.53	0.01	0.3	3
10*	6.70	0.01	0.2	3
50**	3.36	0.09	2.7	4
100**	6.62	0.11	1.7	4

* Measured at recorder sensitivity of 10 mV

** Measured at recorder sensitivity of 100 mV.

Table XXXIV. Response of germanium standards using 1 mL of 10% (m/V) ammonium persulfate only.

Ge ng/mL	Peak height (cm) Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
2*	1.58	0.04	2.5	4
5*	4.46	0.09	2.0	3
10*	8.68	0.13	1.5	3
20*	15.73	0.16	1.0	3
50**	4.45	0.03	0.7	3
100**	8.53	0.04	0.5	3

* Measured at recorder sensitivity of 10 mV

** Measured at recorder sensitivity of 100 mV.

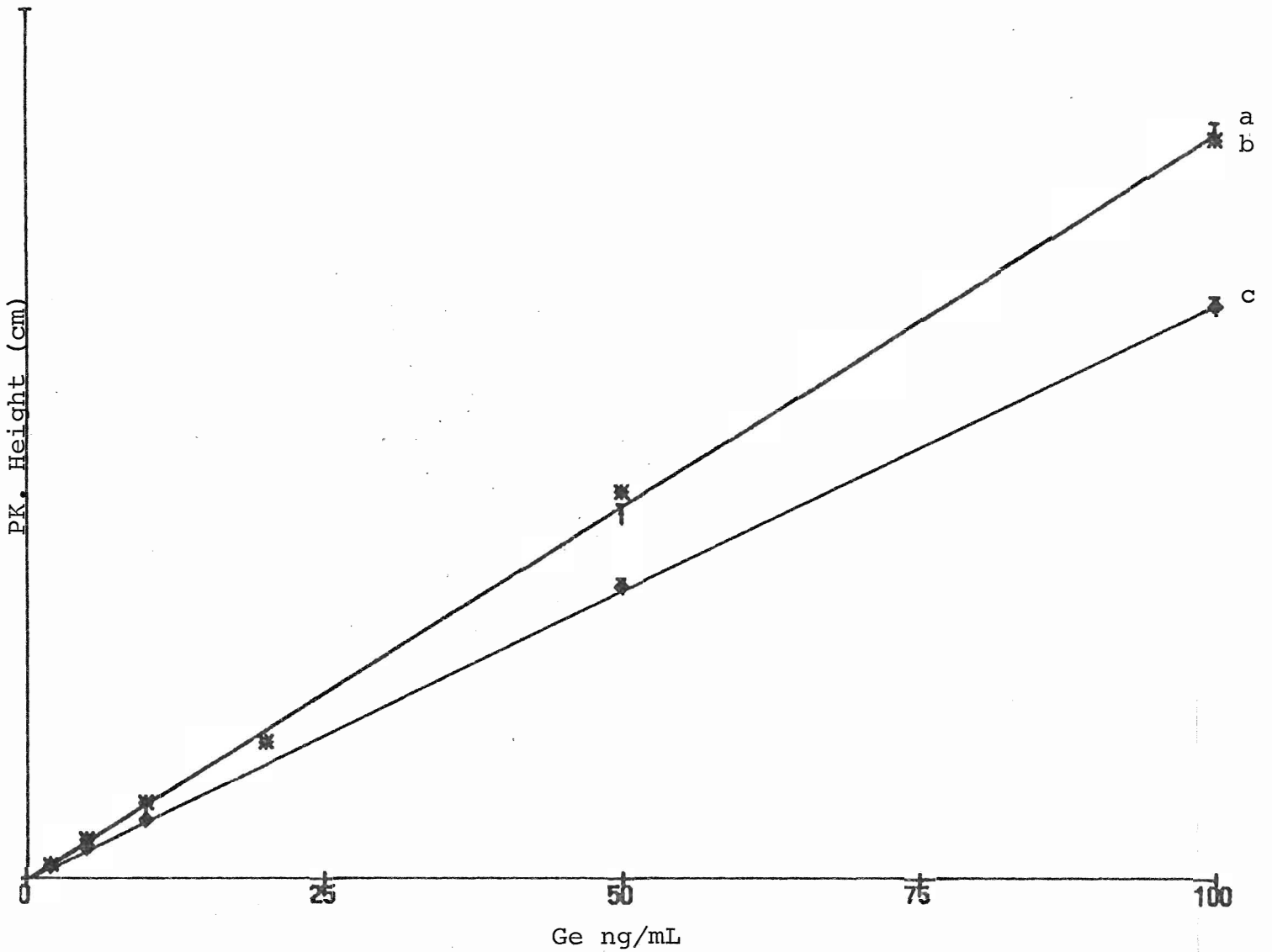


Figure 26. Calibration curves for germanium standard in different media. a) 0.05 M HCl + 1 mL ammonium persulphate 10% (m/V), b) 1 mL ammonium persulphate 10% (m/V) alone, c) 0.05 M HCl alone. Note: Curves a and b are superimposed.

Table XXXV. Standard addition method for the determination of germanium in cherts, using 1mL of 10% (m/V) ammonium persulfate and pH 1.7.

	Peak height (cm)			
STD addition	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
S-0	0.32	0.07	2.1	4
S-2	2.01	0.01	0.7	5
S-4	3.45	0.06	2.3	3
S-10	8.79	0.22	3.4	4

All standards measured at a recorder sensitivity of 10 mV

reagents was run in conjunction with the sample. Results are shown in Table XXXVI. In addition, a calibration curve in the same concentration range, containing the same amount of Si and blank reagents as the sample solutions, was constructed. Results obtained are depicted in Table XXXVII.

Due to the dilution factor applied to the samples and standards, no foaming problems were associated with the determinations. The volume of standards and samples injected was always 10 mL. Prior to injection of $NaBH_4$, 1 mL of ammonium persulphate 10% (m/V) was added directly into the reaction vessel.

Figure 27 summarizes the results obtained in all cases. It can be seen that, since the curves are parallel to each other, no interference can be ascribed to either silicon or lithium. This is not surprising because no interference has ever been reported for these two elements in the hydride generation technique [14]. Since this was the case, the germanium content of the two remaining samples was assessed using the aqueous standard calibration curve. Table XXXVIII portrays the results obtained.

20) IRON SAMPLES

The procedure applied to the iron samples was the same as that used for the chert samples; however, in this case, a standard addition method in the range 0-20 ng/mL was applied to one of the samples. This is depicted in Table XXXIX. An

Table XXXVI. Response of aqueous germanium standards using 1mL of 10% (m/V) ammonium persulfate and 0.05 M HCl for the determination of germanium in cherts.

	Peak height (cm)			
Ge ng/mL	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
0	0.00	0.00	0.0	2
2	1.70	0.04	2.2	3
4	3.12	0.16	5.0	3
10	8.40	0.13	1.6	4

All standards measured at recorder sensitivity of 10 mV

Table XXXVII. Response of germanium standards in SiO_2 matrix using 1 mL of 10% (m/V) ammonium persulfate and pH 1.7.

	Peak height (cm)			
SiO_2 std addition	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
Si-0	0.00	0.00	0.0	2
Si-4	3.33	0.20	6.0	4
Si-10	8.28	0.35	4.2	4

All standards measured at a recorder sensitivity of 10 mV

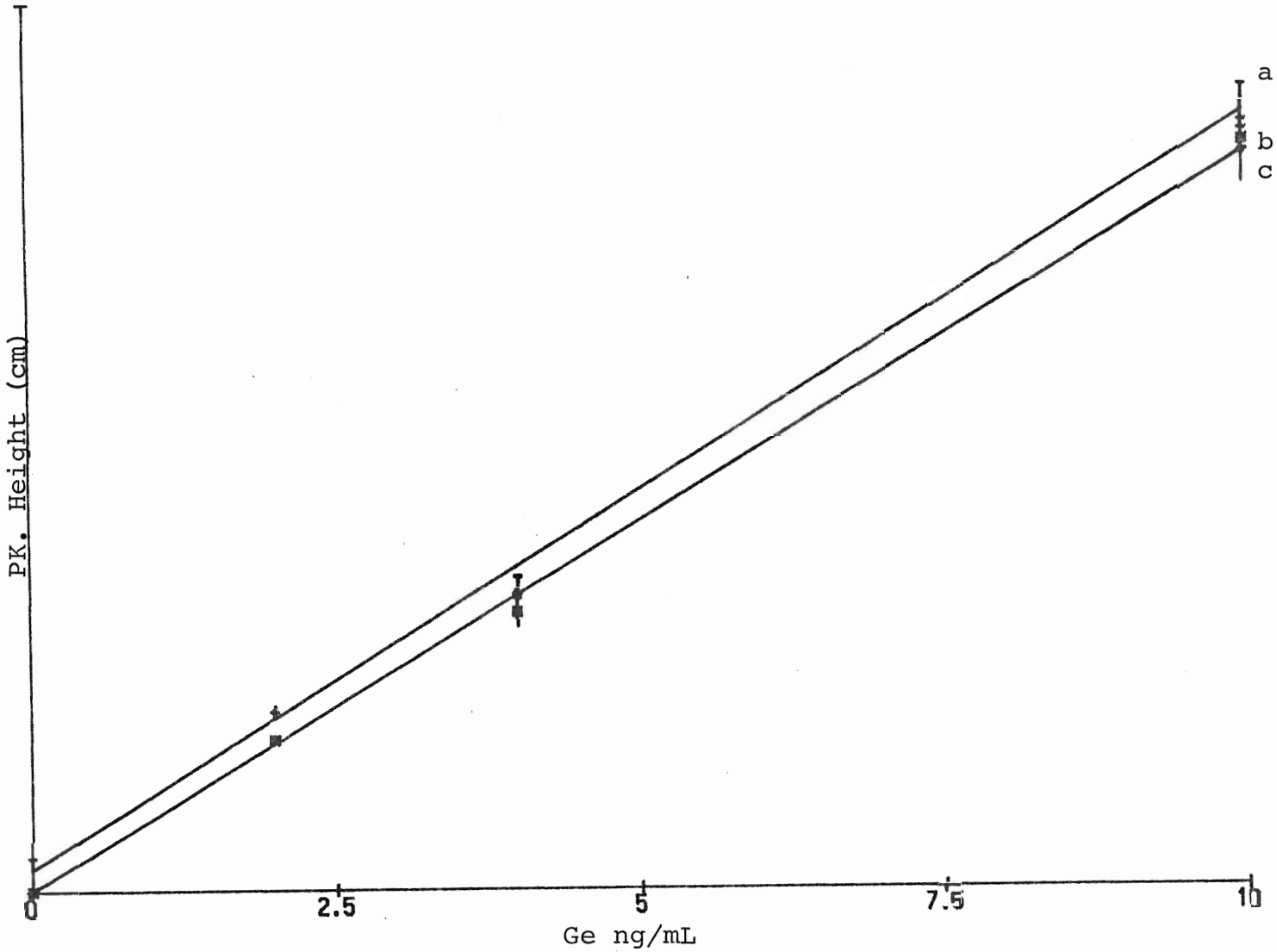


Figure 27. Standard addition method for the determination of germanium in chert samples a) sample, b) aqueous standards, and c) aqueous standards in silicon matrix.
Note: Curves a and b are superimposed.

Table XXXVIII. Results for chert samples.

Sample	Weight	Ge found μg/g	average	SD	RSD %
1*	0.11058	1.22			
2	0.11971	1.29	1.27	0.04	3.4
3	0.10875	1.30			

* Sample to which standard addition method was applied

Table XXXIX Standard addition method for the determination of germanium in iron samples, using 1 mL of 10% (m/V) ammonium persulphate and pH 1.7

	Peak height (cm)			
STD addition	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
S-0*	3.00	0.14	4.7	3
S-5*	10.98	0.04	0.3	3
S-10*	20.15	0.07	0.4	3
S-20**	3.35	0.18	5.4	3

* measured at recorder sensitivity of 10 mV.

** measuredat recoreder sensitivity of 100 mV.

aqueous standard calibration curve containing the appropriate amounts of blank reagents was run in conjunction with the sample curve. Results are given in Table XL.

According to the results depicted in Figure 28, no interference due to iron was encountered in the determination. This was due mostly to two reasons: a) the concentration of iron in the solution for analysis was low (estimated to be less than 200 mg/L) and b) the use of ammonium persulphate, as will be seen later, aided in the suppression of interferences due to iron.

Results for the samples analyzed are given in Table XLI. The technique used to determine the tentatively assigned values included in Table XLI was Spark Source mass spectrometry. The results obtained indicate that the method used in this work has great potential for the determination of low concentrations of germanium in minerals and ores. Nonetheless, the accuracy and precision of this method should still be assessed against a certified standard reference material.

21) INTERFERENCES

Thompson and Pahlavanpour [55] studied the interference effects of diverse ions in the hydride generation of germanium in 0.1 M HCl and in 1% (m/V) tartaric acid media by ICP. They reported strong interfering effects from iron(II), iron(III), nickel(II), cobalt(II), zinc(II), copper(II), and cadmium(II) at a concentration of 10 mg/L and higher in 0.1 M HCl. However,

Table XL. Response of aqueous germanium standards using 1 mL of 10% (m/V) ammonium persulphate and 0.05 M HCl pH 1.7 for the determination of germanium in iron samples.

	Peak height (cm)			
Ge ng/mL	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
0*	0.00	0.00	0.0	2
5*	7.53	0.03	0.4	5
10*	15.03	0.55	3.6	5
20**	2.98	0.04	1.2	5

* measured at a recorder sensitivity of 10 mV.

** measured at a recoreder sensitivity of 100 mV.

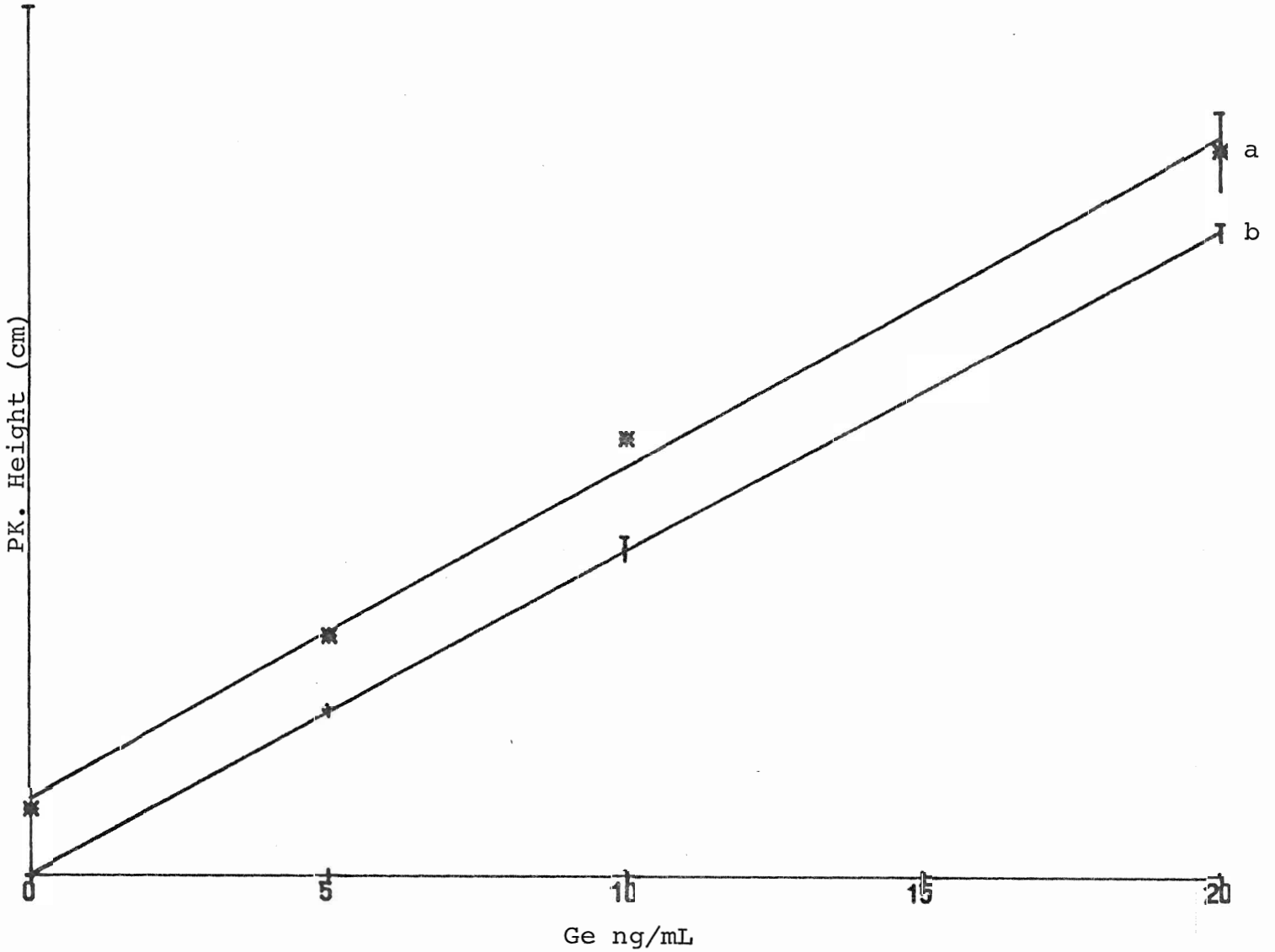


Figure 28 Standard addition method for the determination of germanium in iron samples a) sample, b) aqueous standards.

Table XLI. Results for iron samples.

Sample	Average Ge found μg/g	SD	RSD%	Assigned values μg/g [84]
Fer-2	8.9	0.1	1.1	6.5
Fer-4*	7.8	0.1	1.3	5.2

* Sample to which standard addition method was applied.

they were able to reduce the interferences caused by iron and cadmium by the use of 1% (m/V) tartaric acid. The interferences produced by the remaining ions could not be properly overcome by this means.

Jin et al. [10] studied the effect of nickel(II), palladium(II), gold(III), cobalt(II), cadmium(II), iron(II), arsenic(III), antimony(III) and selenium(IV) on the determination of germanium by AAS. Four different acidic media were investigated: a) 0.2 M HCl, b) 0.2 M H_3PO_4, c) 0.2 M H_3PO_4 + EDTA and d) 0.2 M malic acid. Strong suppression of the germanium signal was observed in system (a) from As(III), Ni(II), Au(III) and Co(II) at concentrations of 20 mg/l and higher. The influence of the foreign ions in system (b) was similar to that of system (a), but better recoveries were achieved in the cases of Fe(III) and Co(II) when they were present in concentrations of 1000 mg/L and 250 mg/L respectively. In system (d) the interferences caused by Ni(II), Au(III), Co(II), Zn(II) and Fe(II) were less pronounced than in system (a). System (c) proved to be the most effective medium for eliminating the interferences from Ni, Au, Cd, Pd and Se.

In the course of this work, interferences from iron(II), copper(II), lead(II), mercury(II), aluminum(III), tin(IV), nickel(II), cobalt(II), zinc(II), cadmium(II) arsenic(III) and arsenic(V) were studied and characterized.

The cornerstone of the investigation was based on the use of ammonium persulphate as an oxidizing agent. In other words, it was thought that persulphate could aid in the

suppression of the interferences caused by the aforementioned elements. For this purpose, solutions containing 100 ng/mL of germanium(IV) and 1000 mg/L of the interfering element were prepared. The pH of the solutions was adjusted to 1.7 with dilute ammonium hydroxide. Subsequently, 5 mL samples were injected into the reaction vessel and the appropriate amount of suppressing agent was introduced and mixed with the sample prior to the addition of 1 mL of $NaBH_4$ 4% (m/V). No heat was provided at any time. Table XLII portrays the results obtained when different concentrations of ammonium persulphate were added to the solutions in the presence of diverse ions.

The signal obtained in cases (b), (c), (d), (e) and (f) was always compared with the signal achieved with a pure standard (100 ng/mL) at pH 1.7 to which 1 mL of $(NH_4)_2S_2O_8$ 10% (m/V) had been added. The same applies for the rest of the results obtained in this work. However, the signal obtained in case (a) Table XLII, was measured aginst the signal produced by a germanium standard in HCl alone. Results given are the average of at least two determinations.

It can be seen that 1 mL of $(NH_4)_2S_2O_8$ 10% (m/V) resulted in the best combination since good germanium recoveries were achieved in the presence of Fe, Cu, Pb, and Al. In the case of Sn, the best recovery occurred at a concentration of 5%.

Increasing the concentration of persulphate resulted in a decrease in the signal recovered from most of the interfering elements except Ni, Co, Zn, Cd and As. In these cases, the recovery increased and remained constant with increasing

Table XLII. Effect of diverse ions on recovery of germanium in different media.

	Ge recovery (%)						
	Medium	(a)	(b)	(c)	(d)	(e)	(f)
Matrix	Ref[55]	pH 1.7	1 mL APS 5 %	1 mL APS 10 %	1 mL APS 30 %	2 mL APS 30 %	3 mL APS 30 %
Fe(III)	1	16	42	95	60	32	-
Cu(II)	1	Nd	75	85	39	33	-
Pb(II)	70	84	100	109	50	-	-
Hg(II)	107	101	89	91	68	-	-
Al(III)	60	80	88	93	42	-	-
Sn(IV)	-	27	106	61	60	-	-
Ni(II)	1	Nd	-	0.4	0.8	1	-
Co(II)	1	Nd	Nd	1	10	9	8
Zn(II)	1	Nd	-	29	41	58	57
Cd(II)	40	17	-	20	32	34	34
As(III)	-	74	-	74	100	-	-
As(V)	-	95	-	96	-	-	-

APS, Ammonium persulphate.
Interferent always 1000 mg/L.
The pH of all media always 1.7 (0.05 M HCl) except for Ref [55] (0.10 M HCl).
- , Not determined.
Nd , Not detectable.

concentration of persulphate. The worst results were obtained with Ni and Co for which only 1% and 10% recovery could be achieved respectively.

Except for Al and Fe, which gave white and brown precipitates due to $Al(OH)_3$ and Fe_2O_3 (hydrated) respectively, the rest of the elements produced black precipitates upon addition of the reducing agent when 5% persulphate or less was added. An intriguing phenomenon was observed when the 10% solution was used; after addition of $NaBH_4$, the black precipitate would initially appear, but then disappeared by the time the purge valve was opened. No precipitate was observed, at any time and for all cases, when the persulphate concentration was 30% or higher. This fact eliminates, therefore, the possibility of the formation of insoluble compounds of germanium with the interfering element. Evidently, this cannot provide a possible explanation of the interfering effect caused by some of the elements studied.

According to the results obtained, it appears that persulphate is indeed able to oxidize the interfering elements to their highest valency states (no black precipitate is observed). In spite of this fact, the interfering effects for some of the elements studied seems to be persistent.

The low results obtained in the presence of Fe, Cu, Pb, Hg, Al, and Sn, in case (d) of Table XLII, are to be ascribed to the fact that some $NaBH_4$ has been preferentially consumed by the excess of ammonium persulphate. One should recall that increasing the concentration of persulphate results in a

decrease of the germanium signal and in a more vigorous reaction. This might be better illustrated by considering mercury as an example. Basically no interference from this element is observed in cases (b) and (c), Table XLII. However, in case (d) the recovery factor decreases to only 68% of the total signal. Since the only difference between cases (b), (c) and (d) is the amount of persulphate that has been added to the sample solution, it may be concluded that the depression is caused by the excess of persulphate added. Recovery factors should be assessed in these cases by comparing the signal obtained with the interfering solution against a pure standard analyzed under the same conditions. The differences registered in the recovery factors of the elements within the same case (vertical columns) might be ascribed to the differences in the consumption rate of persulphate due to $NaBH_4$, to the interfering element in question and to the kinetics of each particular reaction.

The results obtained for Ni and Co seem to suggest that the interfering effect from these ions cannot be attributed to the adsorption and catalytic decomposition of the hydride by the precipitated metal ion, since better recoveries would then be accomplished. Similarly, preferential consumption of the reducing agent by the interfering ions, is not likely to be the causative process, because, as mentioned earlier, it has been proven that only a very small percentage of the $NaBH_4$ is used to generate the hydride [89]. Secondly, reduction of the metal ions is not taking place (no black precipitate).

The results obtained for Sn(IV) were peculiar as well. The recovery decreased with increasing persulphate; however, the fact that better recovery could be accomplished in 5% persulphate than at higher concentration may have arisen from the fact that reduction of Sn under persulphate conditions is a very favourable process. As will be seen later, an enhancement of the Sn signal can be achieved with the use of persulphate. This suggests that preferential reduction of Sn to the hydride by $NaBH_4$ may take place, resulting in a lower recovery of germane.

It is apparent, therefore, that complicated kinetic and thermodynamic processes are responsible for the effects observed in this work. A more complete study should be carried out in which the concentration of persulphate and interfering element should be studied in a wider range and in shorter intervals.

In an effort to eliminate or reduce the interferences produced by Cd, Ni, Co, and Zn, the use of thiourea was investigated. Table XLIII depicts the results obtained. Poor results were accomplished when thiourea was used alone; however, when it was used in conjunction with persulphate better recovery was achieved for all of the elements. Nickel still remained the worst case since only a 20% recovery could be accomplished. Increasing the amount of thiourea did not improve the results for Cd and Ni, whereas a slight increase for Co and Zn was registered.

It should be pointed out that the results shown in Table XLIII for the recovery of germanium using 3% T.H. and 1 mL

Table XLIII. Effect of diverse ions on recovery of germanium in different media.

	Ge recovery (%)				
	Medium				
Matrix	3 % T.H.	3 % T.H. 1 mL APS 5 %	3 % T.H. 1 mL APS 10 %	3 % T.H. 1 mL APS 30 %	5 % T.H. 1 mL APS 10 %
Cd(II)	1	31	56	19	52
Ni(II)	2.5	-	20	8	18
Co(II)	-	-	32	-	43
Zn(II)	-	-	46	48	50

APS, Ammonium persulphate.

T.H., Thiourea.

Matrix always 1000 mg/L

pH always 1.7.

-, Not determined.

$(NH_4)_2S_2O_8$ 10% (m/V) were obtained by adding the suppressant directly into the reaction vessel following sample injection prior to reduction with $NaBH_4$. On the other hand, the results given in Table XLIV, for the same combination, were obtained by mixing the thiourea directly into the volumetric flask during standard preparation. The persulphate was added into the reaction vessel after sample injection. Since results agree well with one another, the possibility of dilution or heterogeneity effects that might be produced by adding the reagents to the sample in the reaction vessel can be disregarded.

As discussed earlier, some authors have proposed that elements such as Cd can form chloro complexes [14]. This causes the analyte element to be freed from the interfering effect. In this regard, the use of a 4% and 8% (m/V) solution of KCl was investigated. Results are given in Table XLIV. It can be seen that no improvement in the germanium recovery could be accomplished under either condition. Moreover, the use of persulphate in combination with KCl did not improve the results.

Following Welz and Melcher's theory [79] of preferential reduction, the use of an easily reducible element was investigated in an attempt to reduce the interference produced by Cd. Mercury was selected because, as can be seen in Table XLII, it does not have a suppressive effect on the germanium signal. Secondly, its reduction potential is more positive (+0.79 V) than the reduction potential of cadmium (-0.40 V).

Table XLIV. Effect of cadmium on recovery of germanium in different media.

	Ge recovery (%)				
	Medium				
Matrix	4% KCl	8% KCl	4% KCl 1 mL APS 10%	8% KCl 1 mL APS 10%	3% T.H. 1 mL APS 10%
Cd(II)	22	18	22	19	53

APS, Ammonium persulphate.

T.H., Thiourea.

KCl, Potassium chloride.

Matrix 1000 mg/L.

pH always 1.7.

Table XLV shows the results obtained. It can be seen that good recovery can be accomplished in the presence of Hg. Again, the addition of persulphate did not improve the results. Although complicated kinetic processes have to be taken into account, the trend indicates that preferential reduction might actually take place; however, a better way of assessing this, would be by carrying out further experiments in the presence of various concentrations of cadmium and mercury.

The use of L-cystine, which proved very successful in the arsenic analysis, could not be assessed in the case of germanium because the L-cystine precipitated out of the solution when the pH was brought to 1.7. As in the analysis of arsenic, L- cysteine had a negative effect on the germanium signal.

Table XLV. Effect of cadmium on recovery of germanium in different media.

	Ge recovery%				
	Medium				
Matrix	1 g/L Hg	2g/L Hg	1 g/L Hg 1mL APS 5%	1 g/L Hg 1mL APS 10%	1g/L Hg 2mL APS 10%
Cd(II)	52	58	49	52	34

APS, Ammonium persulphate.

Hg, Mercury

Matrix 1000 mg/L

pH always 1.7

D. TIN ANALYSIS

1) EFFECT OF AMMONIUM PERSULPHATE ON THE TIN SIGNAL

Since the use of ammonium persulphate proved to be very valuable in the hydride generation of germanium, it was decided to study its effect on the reduction of tin to its corresponding hydride.

The reaction conditions for the reduction of this element were not fully optimized. However, a literature survey showed that the optimum conditions , in terms of pH and $NaBH_4$ concentration, lay very close to the ones for germanium analysis. Preliminary work was carried out in 0.05 M HCl. For this purpose, a 100 ng/mL tin(IV) standard was reduced with 1 mL of $NaBH_4$ 4% (m/V). Experiments were performed with and without the presence of ammonium persulphate. Results are given in Table XLVI. It can be seen that a 15% increase in the tin signal can be achieved in the presence of persulphate. Due to the lack of time, no further work was pursued in this direction.

Table XLVI. Response of a 100 ng/mL tin standard in different media.

	Peak height (cm)			
Medium	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)	Number of determinations
A	14.27	0.38	2.6	4
B	16.78	0.11	0.6	4

A, 0.05 M HCl alone.

B, 0.05 M HCl + 1 mL $(NH_4)_2S_2O_8$ 10% (m/V).

E. CONCLUSIONS

The increased sensitivity, resulting from the changes made to the system, seems to be very attractive for arsenic and germanium determination with the D.C. Plasma. The applicability of this system to other hydride-forming elements is of interest.

The method is also very easy to use, once the initial technique is attained. Probably the most important aspect of all is that the apparatus can be constructed at low cost by any competent glass blower.

This work has demonstrated that both As(III) and As(V) can be determined in total as arsenic at pH less than or equal to 1 without the need for any prereduction step.

The interference from a variety of different elements was studied. Results showed that the best way of overcoming them is by making use of L-cystine. Its use as a releasing agent in the interference-free determination of other hydride-forming elements should be considered.

An increase in the sensitivity of germanium analysis was registered when ammonium persulphate was used in combination with $NaBH_4$. The optimum conditions for reduction, for a 5-10 mL sample, were found to be pH 1.7, 1 mL of $(NH_4)_2S_2O_8$ 10% (m/V) and 1 mL $NaBH_4$ 4% (m/V). Interferences from other elements should be investigated and characterized. The use of persulphate should be retained and the effect produced by different concentrations of the interfering elements should be assessed. Solutions of persulphate should be prepared in close concentration ranges, so that a better understanding of the

processess involved in the interfering effects and their suppression can be obtained.

In addition, the application of persulphate to tin analysis proved very promising. Further work should, therefore, be carried out and conditions should be optimized.

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