Investigation into the determination of arsenic by direct current plasma atomic emission spectrometer

by

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A thesis

presented to the Department of Chemistry

in partial fulfillment of the requirements

for the degree of

Master of Science

August 1983

Brock University

St. Catharines, Ontario

To

my wife, parents, brothers and sisters.

Abstract

Improvements have been made on the currently available hydride generator system manufactured by SpectraMetrics Incorporated, because the system was found to be unsatisfactory with respect to the following:

1. the drying agent, anhydrous calcium chloride,
2. the special sample tube,
3. the direction of argon flow through the Buchner funnel when it came to dealing with real sample, that is, with reference only to aqueous extracts of soil samples.

Changes that were made on the system included the replacement of anhydrous calcium chloride with anhydrous calcium sulphate and the replacement of the special sample tube with a modified one made from silica. Re-directing the flow of argon through the top of the Buchner funnel appeared to make the system compatible with aqueous extracts of soil samples.

The interferences from 1000 µg/mL of nickel(II), cobalt(II), iron(III), copper(II) have been eliminated with the aid of 1.4 M hydrochloric acid and 1% (weight/volume) L-cystine. Greater than 90% recovery of 0.3 µg/mL arsenic signal was achieved in each case. Furthermore, 103% of arsenic signal was accomplished in the presence of 1000 µg/mL cadmium with 5 M HCl. When each of the interferents was present in solution at 1000 ppm, a recovery of 85% was achieved by using 5 M

hydrochloric acid and 3% (weight/volume) L-cystine. Without L-cystine and when 1.4 M hydrochloric acid was used, the recoveries were 0% (Ni), 0% (Co), 88% (Fe), 15% (Cu), 18% (Cd). Similarly, a solution containing 1000 ppm of each interferent gave a zero percent recovery of arsenic.

The reduction of trivalent and pentavalent arsenic at a pH less than one has also been investigated and shown to be quantitative if peak areas are measured.

The reproducibility determination of a 0.3 μg/mL standard arsenic solution by hydride generation shows a relative standard deviation of 3.4%. The detection limits with and without Porapak Q have been found to be 0.6 ng/mL and 1.0 ng/mL, respectively.

Acknowledgements

The author is greatly indebted to Mr. I. D. Brindle for his guidance, encouragement and patience throughout this work.

Gratitude is expressed to Dr. M. Chiba and Dr. J. S. Hartman for their advice.

The author is grateful to Aaron Brindle, Mr. Tony Biernacki and Co., Mr. Jim Ross and Co., and Mr. John Vandenhoff for their help in diverse ways.

Special thanks are due to Miss J. M. Hastie for typing this thesis and for her helpfulness.

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Introduction

1. Arsenic occurrence and toxicity

The myth surrounding arsenic as a pernicious element dates as far back as the middle ages.[1] In the earth's crust, a ubiquitous arsenic mineral is the arsenopyrite, $FeS_2 \cdot FeAs_2$. Arsenic is thus present in small quantities in nearly all soils and distributed in plants, which can accumulate the element in their roots. Also human beings accumulate the element in their kidneys and livers. Man, with his technological advances and insatiable search for a better life, re-introduces the element into the environment in the form of pesticides, to combat plant diseases, and also through aerial fallout from industrial activity.[2-6]

Arsenic, which is re-introduced into the environment, could be inorganic or organic. In the inorganic form, arsenic exists in the oxide as arsenious, As_2O_3 and arsenic, As_2O_5; in the salt form as arsenite, AsO_3^{-3} and arsenate, AsO_4^{-3}; and in the acid form as arsenious, H_3AsO_3 and arsenic, H_3AsO_4. Some of the organic forms include, monomethylarsenate, $CH_3AsO_3^{-2}$; dimethylarsenate $(CH_3)_2AsO_2^{-1}$; and phenylarsenate $C_6H_5AsO_3^{-2}$, all forming the salts. The corresponding acids include methyl arsenic, $CH_3AsO(OH)_2$, dimethylarsenic, $CH_3AsO(OH)$, and phenylarsenic, $C_6H_5AsO(OH)_2$.[4,7]

According to Dagani,[4] animal studies have revealed that some arsenicals are more toxic than others, for example, arsenites, which are byproducts of copper and lead smelting, are more hazardous than arsenates, which are used

in cotton production and wood preservation. Further up the hazard list are the organic derivatives like monomethyl arsenate and dimethylarsenate.

The ultimate level of concentration and fate of this toxic element is important for the maintenance of an environment which is free from toxic chemicals. It is in light of the pernicious and useful aspects of arsenic on plants and the animal kingdom which has provided the impetus for evolving modern analytical techniques for the determination and detection of small amounts of the element. Throughout the second half of this century, all the most sensitive methods for determining arsenic have involved the conversion of arsenic to arsine.

II. The importance of generating arsenic as arsine

The advantages of the hydride generation technique were envisaged to include the following:

1. The elimination of matrix elements by selectively generating the gaseous hydride of the analyte from the sample solution. Also the possibility of gas phase interference was remote since there are a limited number of elements which would form volatile hydrides at room temperature.
2. The enhancement of sensitivity by concentrating the hydride in a trap.
3. The eradication of interferences often associated with solutions such as light scattering.

It could be deduced, therefore, that the hydride generating technique could immensely improve the detection limit of arsenic using atomic absorption spectrometry;[22] atomic emission spectrometry;[7] and atomic fluorescence spectrometry.[13,48]

III. Determination of arsenic

1. Colorimetric and spectrophotometric

Zinc and hydrochloric acid were the first to be used to generate arsine from arsenic in the trivalent state. Earlier methods of quantitating arsine were both colorimetric and spectrophotometric.

Colorimetrically, this has been accomplished by comparing the black coloration formed upon discs of dry paper impregnated with mercuric chloride with that obtained from known amounts of arsenic. This is known as the Gutzeit method.

Spectrophotmetrically, arsine has been determined by bubbling it through ammonium molybdate. The resultant arsenomolybdate is reduced with hydrazine sulphate to yield a soluble complex molybdenum blue, with an absorption maximum at 840 nm. Phosphorus yields a similar complex with ammonium molybdate and thus interferes. Arsine has also been bubbled through silver diethyldithiocarbamate to form a stable red complex in pyridine. The complex has absorption maximum at 540 nm.[17] L-ephedrine-chloroform has also been used as a solvent to substitute pyridine, which has an unpleasant odour. The complex formed in L-ephedrine-chloroform has an absorption maximum at 520 nm.[31] Antimony interferes with this method because it forms a similar complex with silver diethyldithiocarbamate. The above spectrometric methods appear to be time consuming and less sensitive. Also, Kopp[32] has cautioned on the infeasibility of this method for direct determination of organic arsenicals.

2. Atomic absorption

With the ingenious invention of atomic absorption spectrophotometer by Walsh,[33] initial optimism of determining low levels of arsenic was eclipsed because the arsenic hollow cathode lamp was less intense. There were also difficulties involved in the determination of trace quantities of arsenic by direct nebulization of arsenic solution into conventional air-acetylene flames of the atomic absorption spectrophotometer. These are due to the fact that the most sensitive arsenic absorption line, 193.7 nm, suffers from high absorption losses due to air and flame gases, let alone the correction for the scattering of light due to solid particles, and molecular absorption due to sample matrix.[34] In order to make the method feasible for the determination of trace quantities of arsenic in a large variety of materials, Oscar and Rains[23] applied a high power electrodeless discharge and a total consumption burner with an argon entrained air-hydrogen flame. A detection limit of 0.1 μg/mL was obtained in an aqueous medium free from interfering cations. Furthermore, to increase the sensitivity of the arsenic signal, Ando *et al.*[35] applied a 91 cm path length vycor cell, a ring burner, a nitrogen entrained air-hydrogen flame, which was less absorbing, and a hollow cathode lamp. A detection limit of 0.006 μg of arsenic per mL was accomplished.

A later method of quantitating arsenic was by Holak,[36] who, in lieu of the conventional aspirating method of atomic absorption, generated arsine by the zinc-hydrochloric acid method, collected in it a cold trap cooled by liquid nitrogen and swept it into an air-acetylene flame.

Holak[36] obtained a detection limit of 0.5 μg/mL and admitted that air-acetylene was not a good flame for arsenic determination, because arsenic determination was still in the same quandary as reported by Oscar and Rains.[33] In order to ameliorate the flame set back, arsenic was determined by sweeping the arsine into an electrically heated vycor glass tubing by means of argon.[11]

Subramanian and Meranger[37] have determined arsenic by chelating As(III) with ammonium pyrrolidine dithiocarbamate, followed by extraction into methyl isobutyl ketone. Extraction of total arsenic was achieved after the reduction of As(V) to As(III) with thiosulphate. The extracted arsenic complex was put directly into an electrothermal atomic absorption spectrometer and analysed. The detection limit reported for As(III) was 0.7 ng/mL. On the other hand, Ratcliffe et al.[38] have used a graphite furnace to determine arsenic in small steel samples without the need for a solvent extraction step. A detection limit of 1 ng was reported. Iverson et al.[39] have also used a pyrolytic graphite tube to determine aqueous arsenic. They attributed the precision and sensitivity of their work to the addition of nickel, which forms a non-volatile nickel arsenide at charring temperatures. The limit of detection was determined to be 2 μg/L. Total arsenic determination in shale oil and its products has been investigated by using a non-pyrolytic graphite tubing. The arsenic was extracted with tetrahydrofuran.[40] Tallman and Shaikh[23] have determined arsine species by using graphite furnace atomic absorption spectrophotometer. Detection limits were 1, 15 and 10 ng for inorganic

arsenic, monomethylarsenic acid, and dimethylarsenic acid, respectively.

3. Inductively coupled plasma emission spectrometry

Morita et al.[31] have determined arsenic compounds in biological samples in the aqueous phase by excitation with an ICP. Besides the limit of detection of 2.6 ng reported, the ICP received the eulogy of having a high sensitivity, low chemical interference, and a wider dynamic range. A hydride generation system, interfaced to an ICP for the determination of arsine has been investigated by Hahn et al.[41] A detection limit of 0.02 ng/mL was accomplished.

4. Direct current plasma emission spectrometry

A linear range of 0.8-100 μg/mL, and a detection limit of 0.08 μg/mL of arsenic have been claimed and documented through direct nebulization and subsequent determination with a DCP.[42] In addition, the hydride generation technique of analysing arsenic has been tested and a detection limit of 2 ng/mL has been reported.[43]

5. Direct current discharge emission spectrometry

A detection limit of 1 ng of arsenic has been reported by Braman et al.[8] They introduced the arsine generated into a helium direct current discharge detector and measured the resultant emission intensity at the 228.8 nm spectral line of arsenic.

6. Microwave emission spectrometry

Lichte and Skogerboe,[10] and Talmi and Bostick[28] have succeeded in determining arsenic as arsine with a microwave emission spectrometric detector. Lichte and Skogerboe[10] reported a detection limit of 5 ng whilst using the arsenic 235.0 nm line. Talmi and Bostick[28] obtained 0.25 µg/L when they determined organic arsines from water samples at the arsenic spectral line of 228.8 nm.

7. Other methods of determining arsenic

Arsenic has been determined by gas phase chemiluminescence. The procedure was based on the reaction between ozone and the hydride of arsenic. A detection limit of 0.15 ng has been documented.[44]

A procedure for x-ray fluorescence quantitation of arsenic in drinking water in concentrations as low as 0.1 µg/mL has been reported. The procedure involved chelating with ammonium pyrrolidine dithiocarbamate and subsequent extraction into chloroform.[45]

A single-sweep polarographic method of analysis has been applied to the determination of trivalent arsenic in drinking water by Whitnack and Brophy.[46] A detection limit of 4 ng/mL was reported.

Neutron activation analysis of arsenic has a limit of detection close to 1 ng.[47] However, the method is comparatively time-consuming because of the separation steps, irradiation, and decay times involved.

While single sweep and neutron activation analyses of arsenic provide adequate sensitivities, the determination involving neutron activation

represents total arsenic. Trivalent and pentavalent arsenic could not be differentiated, let alone the organic forms. With the single sweep method, a reductive step would have to be implemented to allow the determination of total arsenic. This is because the single sweep method is amenable to the determination of trivalent arsenic and not the pentavalent.

IV. Reduction and separation of arsenic in the hydride generation technique

The following reducing agents have been used to convert arsenic to arsine. They are: (a) zinc and hydrochloric acid, (b) sodium borohydride and hydrochloric acid, and (c) titanium(III) chloride, hydrochloric acid and magnesium rod.[9] The latter method has received little attention.

The use of zinc and hydrochloric acid to generate arsine has undoubtedly received widespread attention.[10-15] The authors who have used zinc and hydrochloric acid have had to reduce pentavalent arsenic with either potassium iodide and stannous chloride or potassium iodide and ascorbic acid, before ultimately reducing the trivalent form to arsine with zinc and hydrochloric acid. The added ascorbic acid prevents air oxidation of the iodide to iodine in an acidic medium. This pre-reduction step pre-supposes that pentavalent arsenic could not be converted into arsine by zinc and hydrochloric acid without the intermediate reduction step. This renders the method a rather slow process. This view has been

rebutted by Aggett and Aspell.[16] Although there were no published data in their paper, they claimed to have had the experience of generating arsine from pentavalent arsenic in connection with the silver diethyldithiocarbamate method.[17]

The most recent and popular method of generating arsine involves the use of sodium borohydride. Braman et al.[8] were the first to put the idea across and apply it to arsenic. An innovative strategy of utilizing pH differences has aided in differentiating between pentavalent and trivalent arsenic and more so the organic derivatives whilst applying sodium borohydride. This scenario has been applied by Aggett and Aspell;[16] and Braman et al.[7] Aggett and Aspell[16] have determined trivalent arsenic in the presence of pentavalent arsenic at a pH between 4 and 5. Also, both trivalent and pentavalent arsenic were determined from 5 M hydrochloric acid. The work reported by Braman et al.[7] about the determination of arsenic as arsine in an electric discharge has permitted the determination of arsenite, arsenate, methylarsenic acid, and dimethylarsenic acid in aqueous solution. Based on the pH selective reduction reactions of the trivalent and pentavalent arsenic with sodium borohydride, arsine was generated from the trivalent arsenic in the pH range 3.4-4. On the other hand, both trivalent and pentavalent arsenic were reduced at a pH less than or equal to 1 simultaneously, and the concentration of the pentavalent form determined by difference. Since then sodium borohydride has gained universal repute and superceded zinc. Siemer et al.[18] and Brodie[19] have disputed the claim that pentavalent arsenic could be reduced

quantitatively by sodium borohydride at a pH less than or equal to 1. They have, therefore, suggested that arsenic must be present in the trivalent state. This idea has been echoed by Crock and Lichte,[20] and Hobbins.[21] On the contrary, Howard and Arbab-Zavar,[22] Aggett and Aspell,[16] and Tallman and Shaikh,[23] have reported the quantitative determination of pentavalent arsenic at a pH less than 1.

This fundamental issue of whether or not to reduce pentavalent arsenic has remained latent and unresolved, because different workers have been using different experimental outlines and different hydride generating apparatuses, which are manipulated in different ways. One group has been trapping arsine in a "U" tube immersed in a liquid nitrogen, with subsequent volatization;[16,22-24] a balloon has also been used to collect arsine.[11] However, the other group eliminates the trapping stage and flushes the arsine rapidly on addition of sodium borohydride.[18,20,21,25,26] Workers who have had arsine trapped in a "U" tube immersed in a liquid nitrogen bath have reported quantitative determination of pentavalent arsenic, whilst the group which eliminates the trapping step have found it necessary to convert pentavalent arsenic to trivalent arsenic before generating arsine.

The factors affecting the rate of production of arsine are: the reduction of pentavalent or trivalent arsenic, the stripping of the arsine from the solution, and the solution viscosity. Without the "U" tube trap, area integral measurement of arsenic signal would not depend on the above factors. Nevertheless, peak height measurement of arsenic signal would be

vulnerable to the above mentioned factors. Thus, the quantitative determination of pentavalent arsenic would not differ from trivalent arsenic if the arsenic signal was measured as the area integral. However, peak height measurement would give a higher peak value with trivalent arsenic compared with pentavalent arsenic. The advantage of a "U" tube trap would be the elimination of dilution of the generated arsine by the carrier gas. Also, with the "U" tube trap, peak height or area integral measurement of the arsenic signal would be independent of the production factors. These issues have been discussed by Siemer and Koteel.[27] It is worthwhile mentioning that both groups involved in the pros and cons about the possibility of generating arsine quantitatively from pentavalent arsenic have been measuring the arsenic signal as peak height.[27]

In an attempt to increase the number of arsenicals which could be analysed, and also to improve on the reproducibility and accuracy of the hydride generation technique by repetitive analyses of each sample, Talmi and Bostick[28] separated arsenicals on a gas chromatography column. Arsenicals were extracted into either benzene or toluene. Although they claimed that diethyl ether and ethanol were more efficient extractants, these solvents were not usable with the gas chromatography column. The extraction methods did not achieve a better recovery of arsine (b.p., -55°C) and monomethyl arsine (b.p., 2°C), because the extracting solvents were maintained at room temperature. Also arsenicals were collected in a cold trap of toluene which was maintained at a temperature of -5°C with the aid of ice-ethylene glycol. The efficiency of the cold trap method,

in general, depended on the efficiency of the stripping of the arsines from the solution and the collection of the arsines by the cold trap. As a consequence, the volatile arsine, AsH_3 (b.p., -55°C) was not effectively collected. In addition, an attempt to lower the temperature of the toluene with dry ice resulted in the freezing of the toluene and blockage of the glass frit.

In order to make the collecting trap compatible with AsH_3, Odanada et al.[29] have replaced the collecting system of Talmi and Bostick[28] with n-heptane, immersed in a cold bath of dry ice and acetone (-80°C).

In order to mitigate the analysis time, an automated chromatographic method has been used for the separation of arsenite, arsenate, monomethylarsenate, dimethylarsenate, and p-aminophenylarsenate. The procedure involved the separation on an ion-exchange column and the generation of the arsines from the eluate.[30]

An ion exchange high performance liquid chromatograph has been utilized in the separation of arsenicals in biological samples.[31] The authors reported accomplishing a better resolution over conventional ion-exchange systems. However, the presence of other ions could affect the active exchange sites for the arsenicals in the ion-exchange methods.

V. Interferences affecting the hydride generation of arsenic

The generation of arsenic hydride and its promising sensitivity improvement have been plagued with interferences from foreign ions. Vogel[17] has reported the adverse effects of copper, nickel and cobalt

on the evolution of arsine. Yamamoto et al.[15] have claimed that chromium(III), manganese(II), iron(III), aluminium(III), cobalt(II), nickel(II), copper(II), zinc(I), silver(II), cadmium(II), mercury(II), sodium, potassium, magnesium and calcium did not interfere at the 250 µg/mL level. However, the maximum desirable concentrations for lead(II) and antimony(III) were 10 µg/mL, whilst that of selenium stood at 0.4 µg/mL. In addition, they mentioned that the use of potassium iodide and stannous chloride suppressed the interferences from metal ions.

A comprehensive study of the interferences from most cations and anions on arsenic and selenium has been done by Pierce and Brown.[49] They concluded that aluminium(III), chromium(II), cobalt(II), copper(II), iron(III), lead(II), nickel(II), silver(I), tin(II), vanadium(III), zinc(II) permanganate and persulphate at concentrations of 16.7 µg/mL and above, totally suppressed the arsenic analyses.

Another elaborate work by Smith,[50] has unveiled copper, silver, gold, platinum, palladium, rhodium, ruthenium, nickel and cobalt as strong interferents. Also, mutual interferences were reported to have been observed among volatile hydrides forming elements in the gaseous phase. The effect of selenium on arsenic has been reported by Welz and Melcher.[51] Although the concentrations of cobalt(II), nickel(II), zinc(II), iron(III), bismuth(III), cadmium(II), copper(II) and silver(I) were not mentioned, 0.01 M EDTA was used to eliminate their interference effect on arsine generation.[52] Bedard and Kerbyson[5,53] utilised lanthanum hydroxide as a collector to isolate arsenic from a copper matrix and they subsequently

dissolved the residue in order to determine arsenic as arsine. Potassium thiocyanate has been used to attenuate the interferences from nickel.[54]

Kirkbright and Taddia[55] have applied masking agents such as 1,10-phenanthroline and thiosemicarbazide to minimise interferences from high concentrations of copper, nickel, platinum and palladium. The interferences by cobalt(II), iron(III), manganese(VII), nickel(II), antimony(III), sodium(I), potassium(I), calcium(II), magnesium(II), chromium(VI), copper(II) and zinc(II) have been examined in the following media: 5 M hydrochloric acid, 0.5 M acetate buffer (pH 4) and 1 M citrate buffer (pH 4). The effect of 1000 µg/mL of cobalt(II), manganese(VII) and nickel(II) could not be overcome in the presence of 5 M hydrochloric acid. With the acetate buffer, there was some success in masking 10 µg/mL of cobalt(II), copper(II) and iron(III). However, the acetate buffer could not efficiently mask 1000 µg/mL of nickel(II), zinc(II), cobalt(II), copper(II) and iron(II). No data were presented on the efficiency of the citrate buffer.[16]

Studies by Peacock and Singh [56] have also revealed that cobalt(II), nickel(II), platinum(II), copper(II), silver(I) and gold(I) interfere tremendously with the determination of arsenic as arsine. Despite the limited success they claimed to have found with ethylenediaminetetraacetic acid (EDTA), triphenyl phosphine, trimethyl phosphite, cyanide, thiocyanate, fluoride, dimethyl glyoxime, dipyridyl, o-phenanthroline and diethylammoniumdithiocarbamate as suppressants, they emerged with thiourea, which they mentioned was the panacea for all the interferences from these

metals. Peacock and Singh[56] concluded that 0.7 g of thiourea could overcome the interferences from 100 mg of copper, silver, cobalt and nickel.

Investigations into the interferences by nitric acid, iron(III), nickel(II), cobalt(II) and copper(II) on arsine generation have been conducted by Nakahara et al.[26] They claimed that 0.1 M nitric acid interfered with arsine generation. However, 1% potassium iodide was added to overcome the interfering effect from 0.1 M nitric acid. In addition, 12 M hydrochloric acid was applied to overcome the interfering effect from 1% of iron. Furthermore, a solution of composition, 6 M hydrochloric acid, 10% malic acid and 1% potassium iodide was not the antidote to the interfering effects from 1000 μg/mL level of nickel and cobalt. However, 6 M hydrochloric acid and 10% malic acid was used to produce 100% recovery of arsine in the presence of 1000 μg/mL of copper.

VI. Theory of atomic emission in a plasma

An atom of an element, after undergoing excitation, decays to its ground state with the emission of radiation of a frequency which is characteristic of that element. To obtain the highest sensitivity in plasma emission spectrometry, the temperature of the plasma should be high. This can be seen from the terms of the Boltzmann distribution equation

$$N_m^* = N_m \frac{g_i}{F(T)} e^{-E_i/kT} \qquad (1)$$

where N_m^* is the number of excited atoms of species m in the plasma, N_m is the number of free m atoms in the plasma, g_i is the statistical weight degeneracy of the excited atomic state, F(T) is the partition function of the atom over all states, E_i is the energy of the excited state, K is the Boltzmann constant, and T is the absolute temperature. Equation 1 shows that the higher the temperature of the plasma, the greater the number of excited atoms.

The intensity of the emitted radiation is given by the equation

$$I_{em} = h\nu_0 N_m^* A_T \qquad (2)$$

where I_{em} is the total intensity radiated by the atoms in the plasma, h is Planck's constant, ν_0 is the frequency of the peak of the spectral line under observation, A_T is the Einstein coefficient (number of transitions each excited atom undergoes per second).

Putting N_m^* from Equation 1 into Equation 2,

$$I_{em} = h\nu_0 A_T N_m \frac{g_i}{F(T)} e^{-E_i/kT}$$

N_m is directly related to the concentration in solution.

Thus, the intensity of atomic emission is dependent on temperature, and at low concentrations when self-absorption is negligible, a plot of intensity versus sample concentration is linear.

VII. Two point calibration of intensity measurement

With this procedure, the direct current plasma atomic emission spectrometer sets up a calibration by measuring the intensities of two standard solutions (a high standard and a low standard) that have known concentrations of the element to be analysed. From the data, the system develops a straight line calibration curve for that element, and uses the curve to convert subsequent intensity measurements into concentration values.

Experimental Section

I. Apparatus

1. Direct current plasma

The direct current plasma atomic emission spectrometer used in this work was the SpectroSpan V, manufactured by Spectrametrics Incorporated, U. S. A. The heart of the system, the spectrometer unit itself, consists of a jet assembly and power supply; optics and detector module; a computer and an operator control panel.

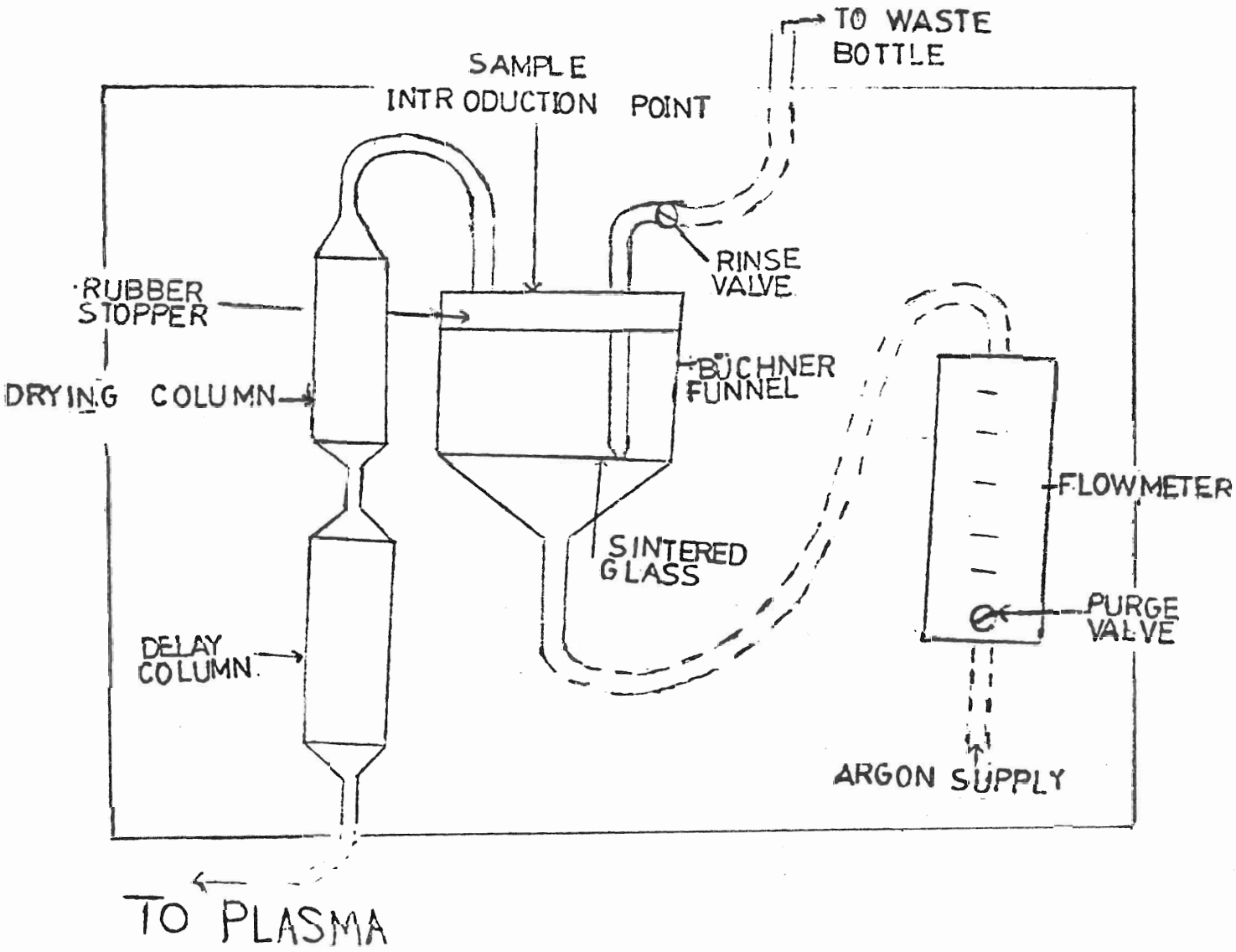
The instrument was equipped with an automatic sampler unit, a dynamic background compensator (DBC-33), a photographic attachment, a printer, and a dataspan. A detailed description of the SpectroSpan V emission spectrometer and the use of the instrument for both quantitative and qualitative analyses are in the operator's manual.[42] In connection with the hydride generator, a recorder was connected to the spectrometer in order to measure emission signals as peak heights.

2. Hydride generator

The apparatus for the generation of arsine is illustrated in Figure 1. The generator accessory was manufactured by Spectrametrics Incorporated. Instructions for assembling and operating the system were provided by the manufacturer.[43]

The major components of the generator were a 60 mL Buchner pyrex funnel reaction cell with a sintered glass platform to contain solution;

Figure 1. The hydride generation apparatus



a plastic drying column, with internal diameter 3/5" and 5½" long; a plastic hydrogen delay column, with internal diameter 3/5" and 5½" long; a flowmeter and valves; and a special sample introduction tube, which replaced the standard Spectrajet sample tube. All components were mounted for easy accessibility and visibility on a resistant frame of high density polyethylene. Nalgene tubing of ¼" internal diameter and 1/16" wall was used for all connections.

Argon from the nebulizer regulator of the Spectrajet was split, so that half was directed through the generator and the other half followed its normal flow through the nebulizer to the sample tube. The side arm of the sample introduction tube was connected to the bottom of the hydrogen delay column containing Porapak Q. Finally, the rinse valve was connected to a suitable waste container, the drying column was filled with anhydrous calcium chloride desiccant to prevent water from getting onto the Porapak Q. Problems which were encountered with the calcium chloride, special sample tube, and the Porapak Q led to some changes which are discussed under the heading "Modifications to the Hydride Generator".

3. Hypodermic plastic syringes

One and 10 mL disposable hypodermic plastic syringes fitted with micro-pipette tips were used to introduce solutions 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 Hammamatsu types R292, R374 and R268 (or equivalent) photomultiplier tubes (PMT)
Source:	High energy dc argon plasma, formed by a tungsten cathode and two carbon anodes in an inverted "Y" configuration.
Temperature:	6000°-7000°K
Argon Supply:	Linde welding grade-Union Carbide Canada Ltd.
	Tank pressure: 90 psi
	Sleeve pressure: 50 psi
	Nebulizer pressure: 14 psi
	Flow rate of argon through hydride generator: 12.5 ml/min
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:	193.7 nm
Operating Mode:	Active diagnostic using chart recorder
	Gain: 14-20
	PMT voltage (8): 900 V
	Repeat: 0

Recorder: Fisher Recordall series 5000.

Chart speed: 1 cm/min

Sensitivity: 1 mV-10V

These were the operating conditions unless otherwise stated.

II. Chemical Reagents

Below is a list of the names, grades and manufacturers of the chemicals which were used.

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

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

(c) Sodium hydroxide ("AnalaR", BDH Chemicals Ltd., Poole, England).

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

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

(f) Calcium chloride, 8-12 mesh (Laboratory reagent, BDH Chemicals, Toronto).

(g) Anhydrous calcium sulphate (Drierite-8 mesh) (Laboratory reagent, BDH Chemicals, Toronto).

(h) Powdered sodium borohydride (Fisher Scientific Co., Chemical manufacturing division, Fair Lawn, New Jersey, U. S. A. 07410)

(i) L-Cystine 99% (Aldrich Chemical Company Inc., Milwaukee, Wisconsin, U. S. A. 63233)

(j) Thiosemicarbazide (Chemical Service, Media, Pennsylvania, U. S. A.)

(k) 1,3-Diethyl-2-thiourea (Chemical Service, Westchester, Pennsylvania, U. S. A. 19380)

(l) Diethyldithiocarbamic acid (Sigma Chemical Company, P. O. Box 14504, St. Louis, Missouri, U. S. A. 63178)

(m) Triphenylphosphine (Laboratory reagent, Britich Drug House Ltd., BDH Laboratory Chemical Division)

(o) 1,10-phenanthroline monohydrate (Aldrich Chemical Company Inc., Milwaukee, Wisconsin, U. S. A. 63233)

(p) Tris-(isobutyl)phosphorus sulphide (Cyanamid, Welland, commercial sample).

(q) Cobalt-50 mesh, Nickel powder, Copper shot and Cadmium shot (Alfa Products, Thiokol/Ventron, Division 152, Andover Street, Danvers, Massachusetts, U. S. A.)

(r) Iron wire (99.91%, Baker Analysed Reagent)

(s) Antifoam "B" (Reagent solution, BDH Chemicals, Toronto)

III. Stock Solutions

(1) Sodium borohydride

4% (weight/volume) of sodium borohydride was prepared with boiled and cooled deionized water. The resultant solution was kept in a closed plastic bottle to avoid absorption of carbon dioxide from the atmosphere. One pellet of sodium hydroxide was added to every 50 mL solution to stabilize it. Solutions were prepared when needed or stored in the freezer for a maximum of two weeks. Whenever a solution was stored, it was allowed to reach room temperature before being used.

(2) Disodium hydrogen arsenate heptahydrate

A solution of concentration of 1000 µg/mL of arsenic was prepared by dissolving 4.1642 g of disodium hydrogen arsenate heptahydrate in 50 mL of 0.1% (volume/volume) nitric acid in a 150 mL beaker. The resultant solution was transferred into a liter volumetric flask and the volume made to the mark with 0.1% (volume/volume) nitric acid. The stock solution was changed every month.

(3) Arsenic trioxide

1.3204 g of arsenic trioxide was dissolved in 10 mL of 20% (volume/volume) potassium hydroxide in a 150 mL beaker. 100 mL of concentrated hydrochloric acid was added. The resultant solution was transferred into a liter volumetric flask and the solution made to the mark with deionized water. The final solution was 1000 µg/mL.

(4) Metal ion solutions

2000 μg/mL stock solutions of nickel(II), cobalt(II), copper(II), cadmium(II) and iron(III) were prepared as follows: 2 g of nickel powder was put into a 150 mL beaker and 20 mL of concentrated hydrochloric acid added. The mixture was warmed on a hotplate to facilitate dissolution. Similarly, 2 g of cobalt, approximately 2 g of copper and cadmium shots were dissolved in 20 mL of concentrated nitric acid. However, 2 g of iron wire was dissolved in 20 mL of concentrated hydrochloric acid. Heat was applied in the cases of copper, cadmium and iron to speed up dissolution. All stock solutions were stored in a plastic bottle that had been pre-soaked in 2% (volume/volume) nitric acid for 24 hours. They were further washed several times with deionized water.

(5) Standard solutions

The appropriate concentrations of arsenic were prepared from the stock solution by dilution. The final solution contained 12% (volume/volume) hydrochloric acid.

(6) Interferent solutions

A 0.3 ppm solution of arsenic(V) was prepared from the stock solution. The final solution contained 1000 ppm of the interfering metal ion, 12% (volume/volume) hydrochloric acid and with or without the appropriate percentage of the suppressing agent.

(7) Preparation of suppressants

Thiourea was readily soluble in both deionized water and acidified deionized water. The amount needed was always added directly to the volumetric flask as the solid and shaken to dissolve.

L-Cystine was not soluble in deionized water but was soluble in hot hydrochloric acid. In a typical case of preparing 1% volume/volume of L-Cystine, 1 g of the powder was put into a 150 mL beaker. 12 mL of concentrated hydrochloric acid was added. The mixture was brought to boiling on a hot plate. Immediately, the mixture was slightly diluted with deionized water. The mixture was then stirred with a glass stirring rod until the L-cystine was dissolved. At this juncture the solution was taken from the hot plate and allowed to cool. If the solution was cooled too fast or used too soon, it precipitated out. It would require some practice to establish a strategy for the dissolution of the L-cystine.

IV. Hydride generation procedure

A solution of 1000 µg/mL of arsenic was used to optimise or peak the instrument via the standard Spectrajet sample tube. After this, the plasma jet was taken off and the standard Spectrajet sample tube was replaced with the special sample introduction tube. The apparatus was assembled and connected to the Spectrajet as shown in Figure 1.

Both rinse and purge valves were closed, the nebulizer pressure set at 14-18 psi, and the peristaltic pump was engaged but not turned on. The computer was set into the active diagnostic mode [1] and the repeat set to zero. Finally, the PMT and gain were adjusted accordingly.

10 mL of deionised water was next introduced into the reaction cell. The purge valve was opened, and the flow was set at 12.5 ml/min. The jet position was then adjusted so that the entrance slit sat just inside the excitation region (crook of the "V"). The chart recorder, connected to the analogue output of the computer was started and adjusted. The rinse valve was opened, the cell emptied, and both valves were closed.

10 mL of sample (or standard) was introduced into the cell. 1.0 mL of 4% (weight/volume) of sodium borohydride was introduced via a 1 mL syringe within 5 seconds. Introducing the sodium borohydride in a single burst should have been the best strategy, but the plasma went off any time that attempt was made. After 30 seconds, the purge valve was opened and the peak recorded. The rinse valve was opened when the pen of the recorder returned to the baseline and the reaction cell was emptied. Deionized water was used to rinse the cell. The valves were closed and the system was ready for the next sample or standard.

Results and Discussion

I. Spectral line intensities

The principal measurement obtained from the direct current plasma atomic emission spectrometer is the emitted spectral line intenisty. Two different ways were used to measure the intensities of different concentrations of arsenic at a wavelength of 193.7 nm.

The first type, whose measurements are shown in Table 1, was accomplished by applying the two point calibration procedure.[42]

The second type, however, was achieved by utilizing the dynamic background compensator. When the dynamic background compensator is in operation, a refractor plate located behind the entrance slit is set into incremental rotation. The scans of 33 points which were generated were used to describe the shape of the spectrum and the central position along the wavelength axis. The data shown in Table 2 were obtained by measuring the spectral line intensity at the central position. All these measurements and the plotting of spectra were done by the Data Span.

The differences in the magnitude of the intensities of solutions of the same concentration (Tables 1 and 2) confirms the fact that the two processes of measuring the spectral line intensities are entirely different. The two point calibration process yields relative values, which are dependent on the intensities of the high and low standard solutions used in setting the two point calibration. The intensities obtained using the dynamic background compensator are absolute.

Figure 2, in conjunction with Table 1, shows a profile which would make the two point calibration method useful for the measurement of arsenic in deionized water between 0.2 μg/mL and 0.8 μg/mL. However, the measurement would be less accurate because of the non-linearity of the region between 0.2 μg/mL and 0.8 μg/mL.

The intensities shown in Table 2 do not increase linearly with increasing concentrations of arsenic between the blank (deionized water) and 1 μg/mL. However, the little information that could be gained in Figure 3-14 is mainly qualitative.

Figures 3 and 4 show distinct peaks for 100 μg/mL and 10 μg/mL of arsenic respectively. Figure 5 depicts two peaks which appear to be on the verge of separation. Nevertheless, a comparison of the blank (deionized water) spectrum and those of 1.0 μg/mL, down to 0.1 μg/mL of arsenic reveals that there is no clear peak present at the central peak position, but, rather, the arsenic emission shows up as a shoulder on a prominent peak. This peak is also present in the deionized water spectrum and could be due to C_2, OH or CH bands. One conclusion is definitely possible, that is, below 1 μg/mL of arsenic the presence of arsenic in deionized water cannot be qualitatively indicated by using the dynamic background compensator.

The discontinuities associated with Figures 6 and 8 are a feature which occasionally occurs during a sample run. In addition, all the spectra in Figures 3-14 were magnified by operating in the appropriate programme mode in the Dataspan. They are about five times the original spectra.

Table 1. Response, measured as intensity (w/s) in relation to arsenic concentration (μg/mL), using the two point calibration procedure.

Concentration of arsenic (μg/mL)	Number of integrations	Spectral line intensity range (w/s)	Mean (w/s)	Standard deviation (w/s)	Relative standard (%) deviation
Blank	5	4183-4255	4223	27.0	0.6
0.2[x]	5	4216-4282	4264	38.0	0.8
0.2	5	4295-4339	4315	17.5	0.3
0.3	5	4243-4339	4286	30.9	0.7
0.4	5	4247-4350	4321	37.9	0.8
0.5	5	4339-4378	4355	16.2	0.4
0.6	5	4354-4419	4380	26.3	0.6
0.7	5	4379-4445	4420	22.2	0.5
0.8[y]	5	4435-4481	4460	15.3	0.3

[x]low concentration

[y]high concentration

Figure 2. Relationship between spectral line intensity (w/s) and arsenic concentration (µg/mL), using the two point calibration procedure.
--- two point (instrumental calibration
—— experimental calibration

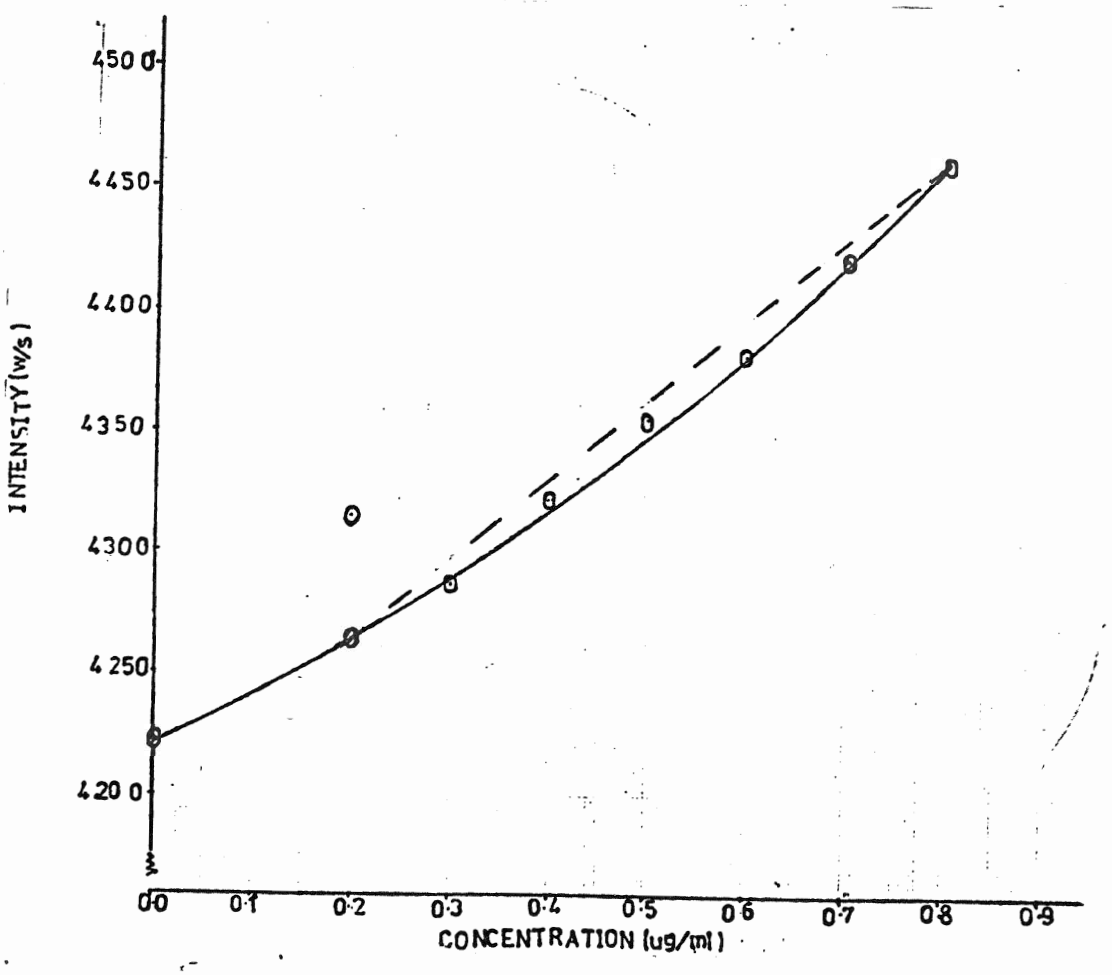


Table 2. Relationship between arsenic concentration and the spectral line intensity at peak centre using the dynamic background compensator.

Concentration of arsenic (µg/mL)	Spectral line intensity at peak centre (w/s)
Blank (deionized water)	118
0.1	120
0.2	125
0.3	145
0.4	142
0.5	137
0.6	71
0.7	129
0.8	88
1.0	109
10.0	295
100.0	1976

Figure 3. Wavelength scan of 100 µg/mL of arsenic

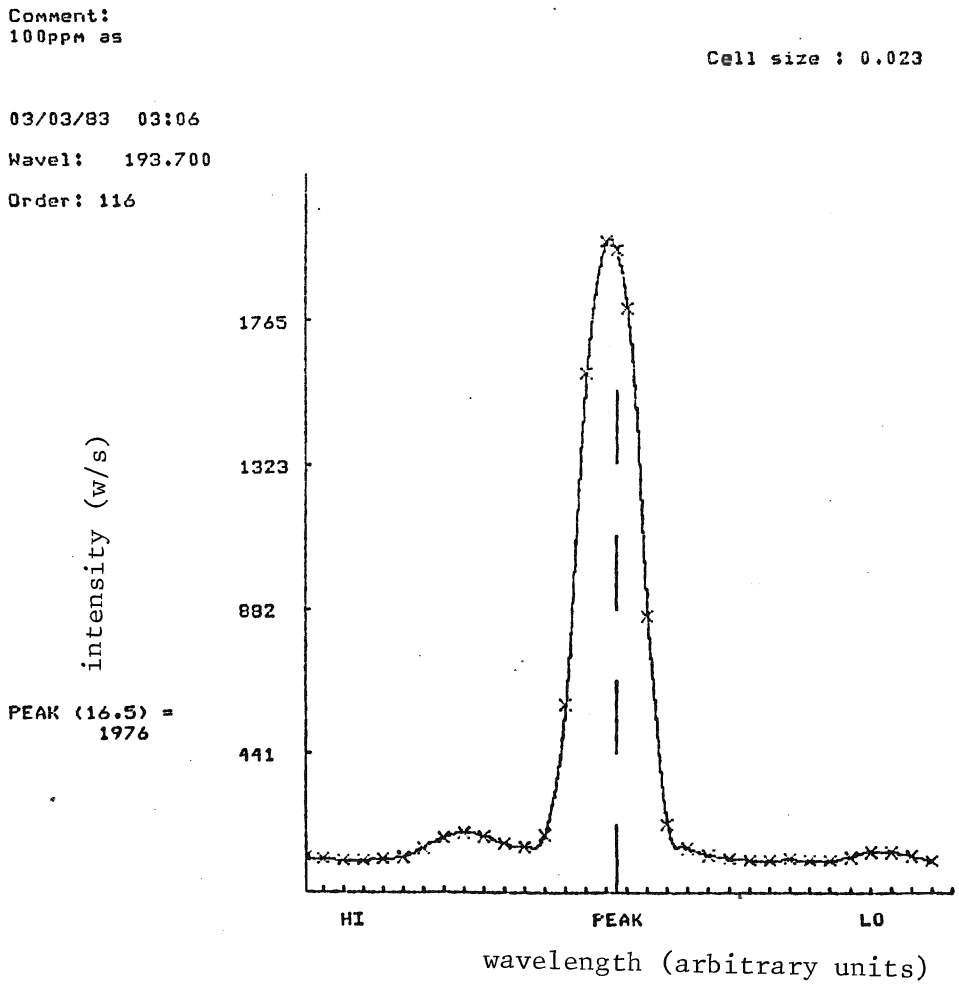


Figure 4. Wavelength scan of 10 µg/mL of arsenic

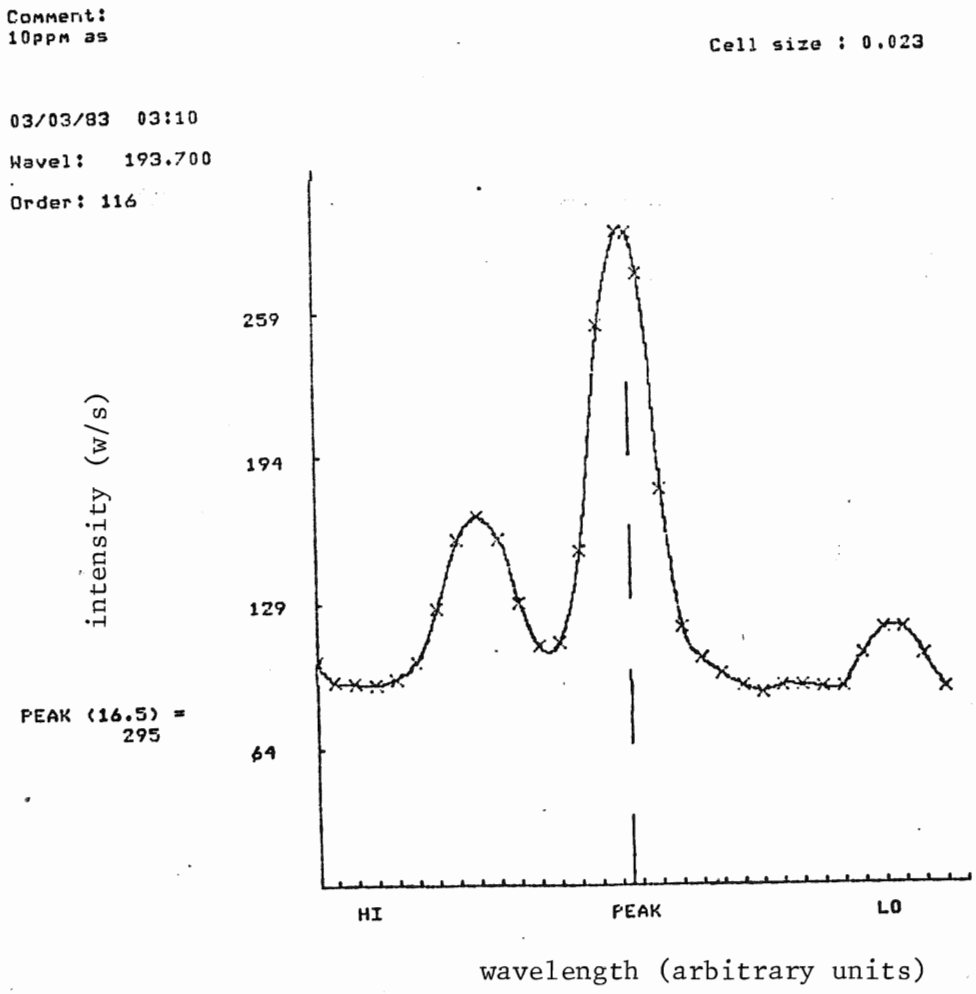


Figure 5. Wavelength scan of 1 µg/mL of arsenic

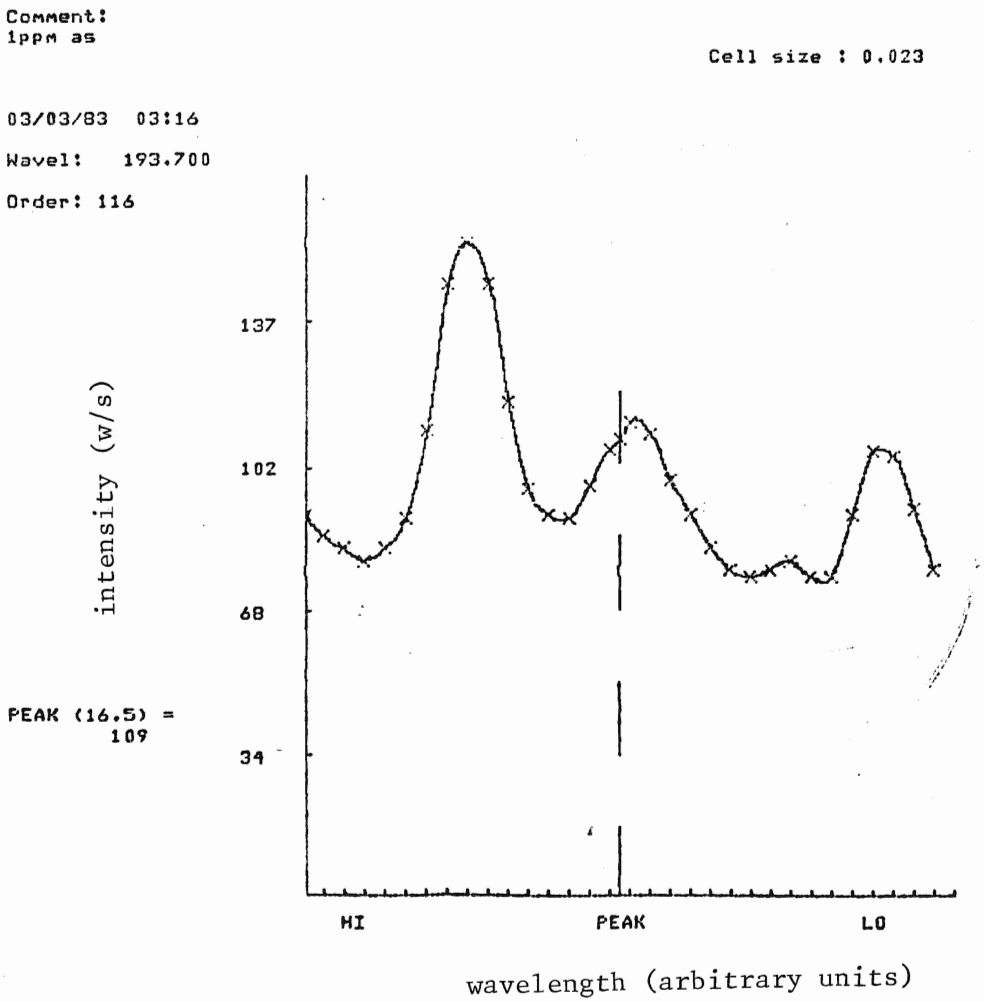


Figure 6. Wavelength scan of 0.8 µg/mL of arsenic

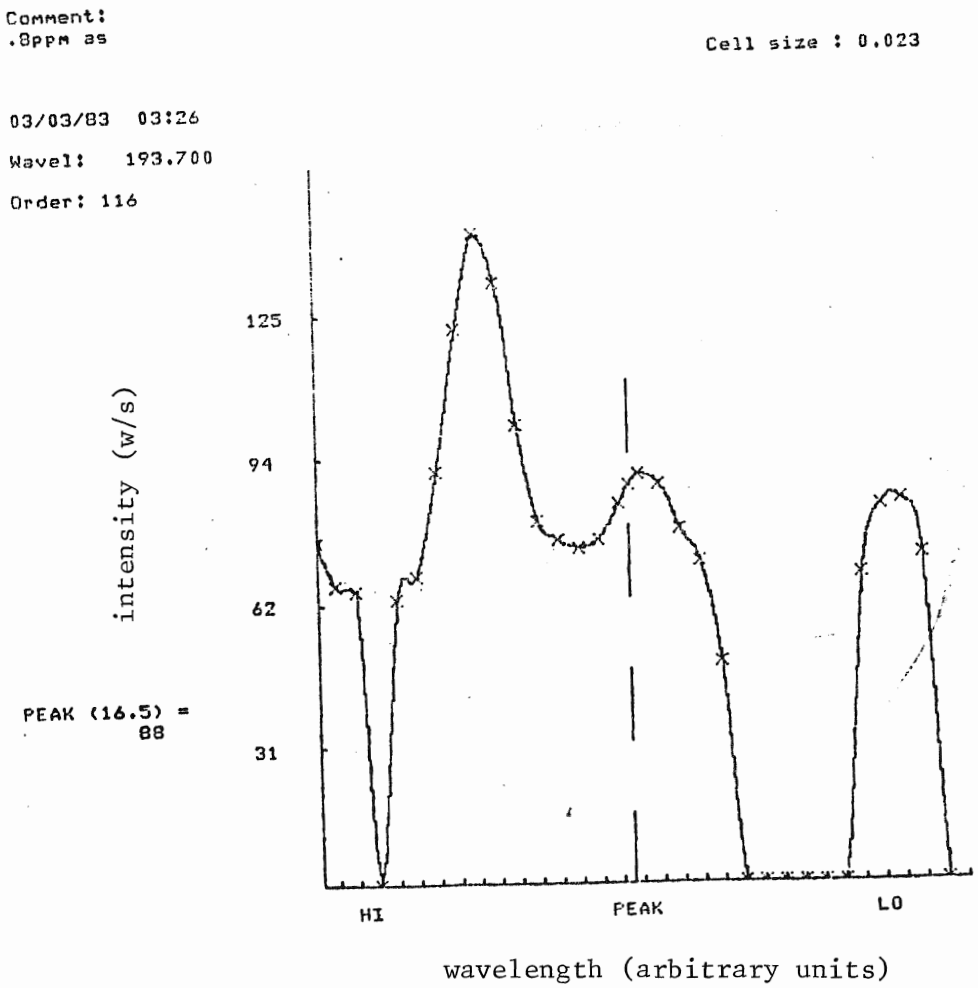


Figure 7. Wavelength scan of 0.7 µg/mL of arsenic

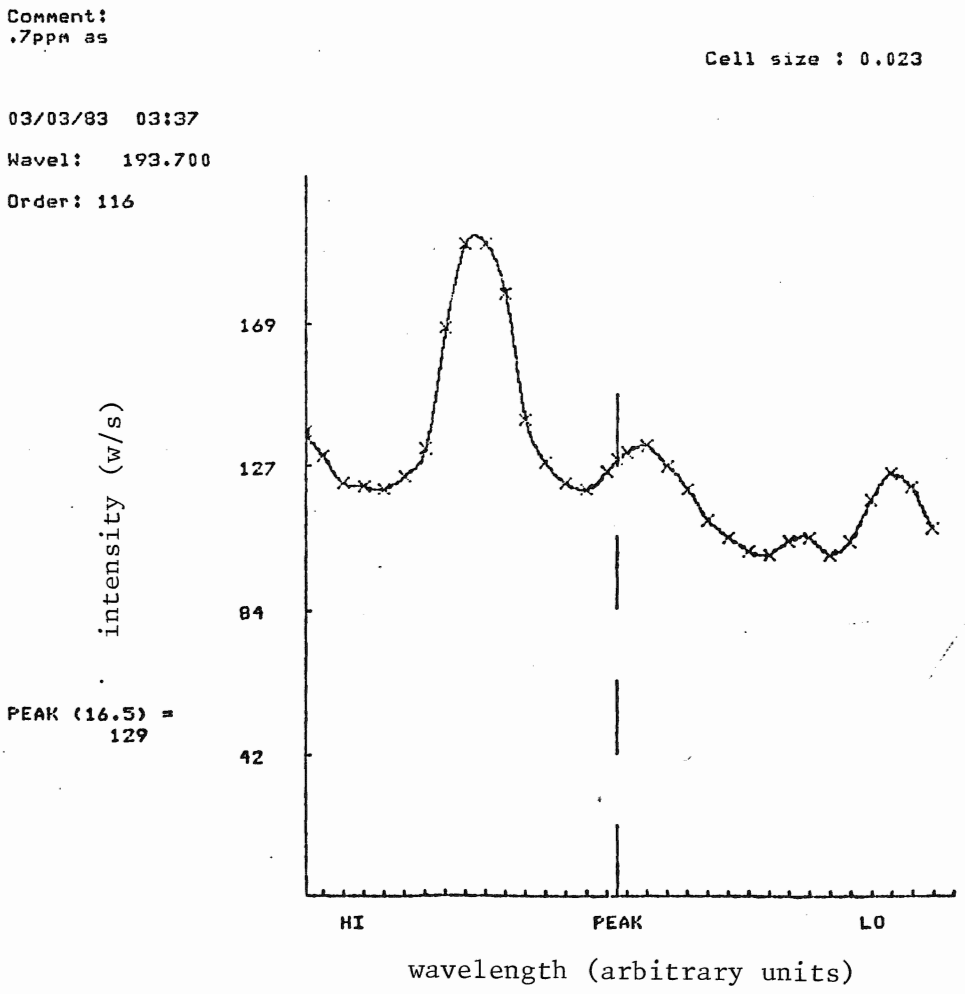


Figure 8. Wavelength scan of 0.6 µg/mL of arsenic

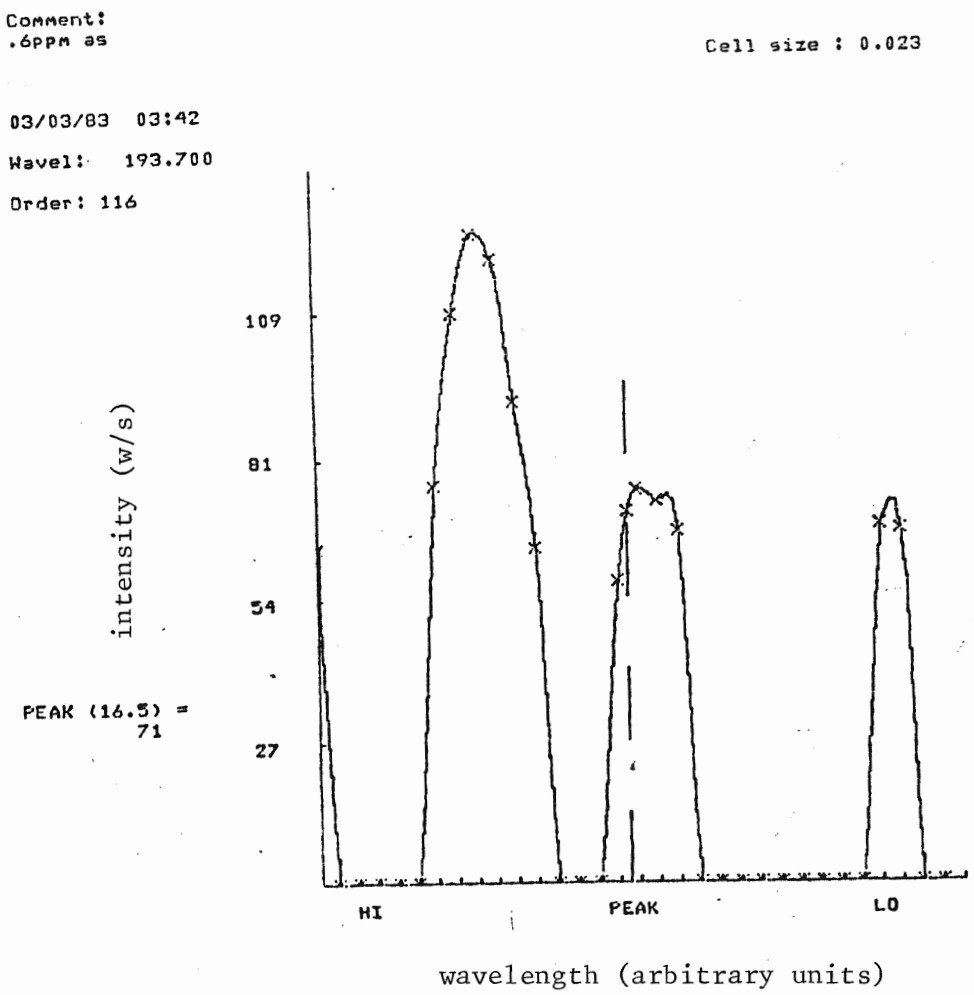


Figure 9. Wavelength scan of 0.5 µg/mL of arsenic

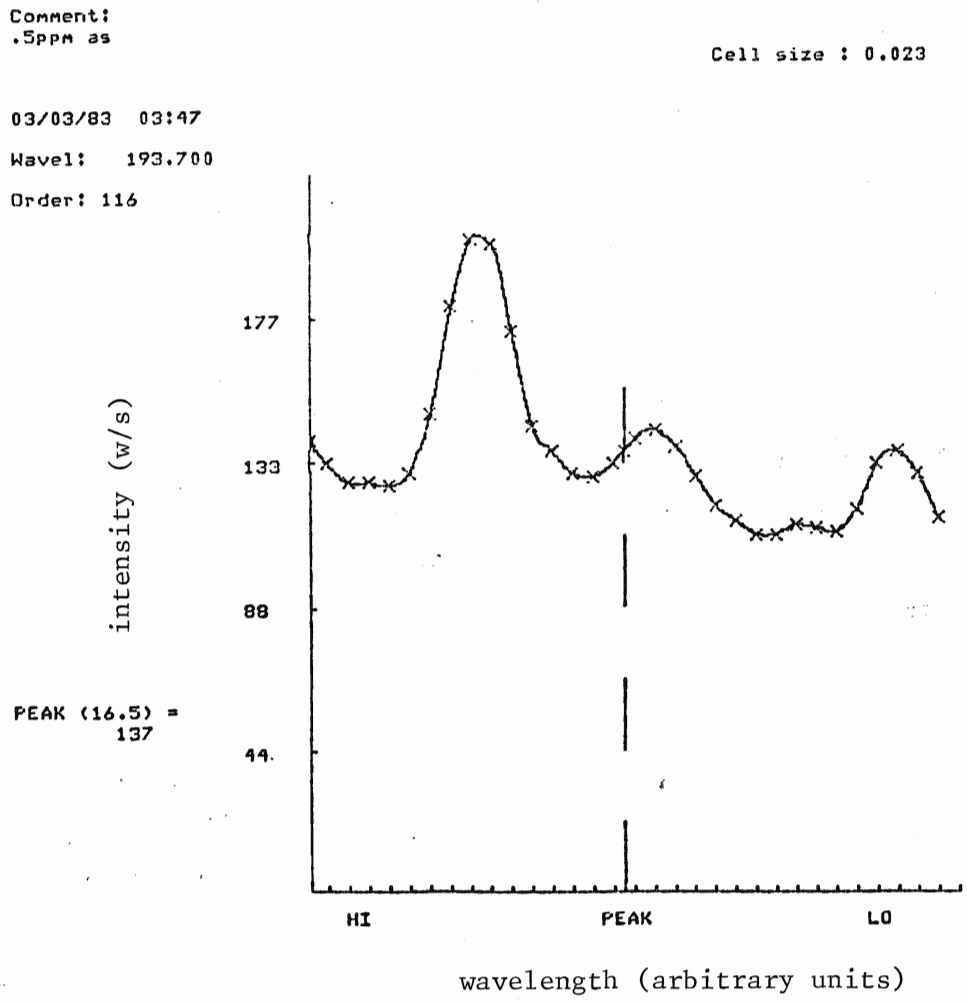


Figure 10. Wavelength scan of 0.4 µg/mL of arsenic

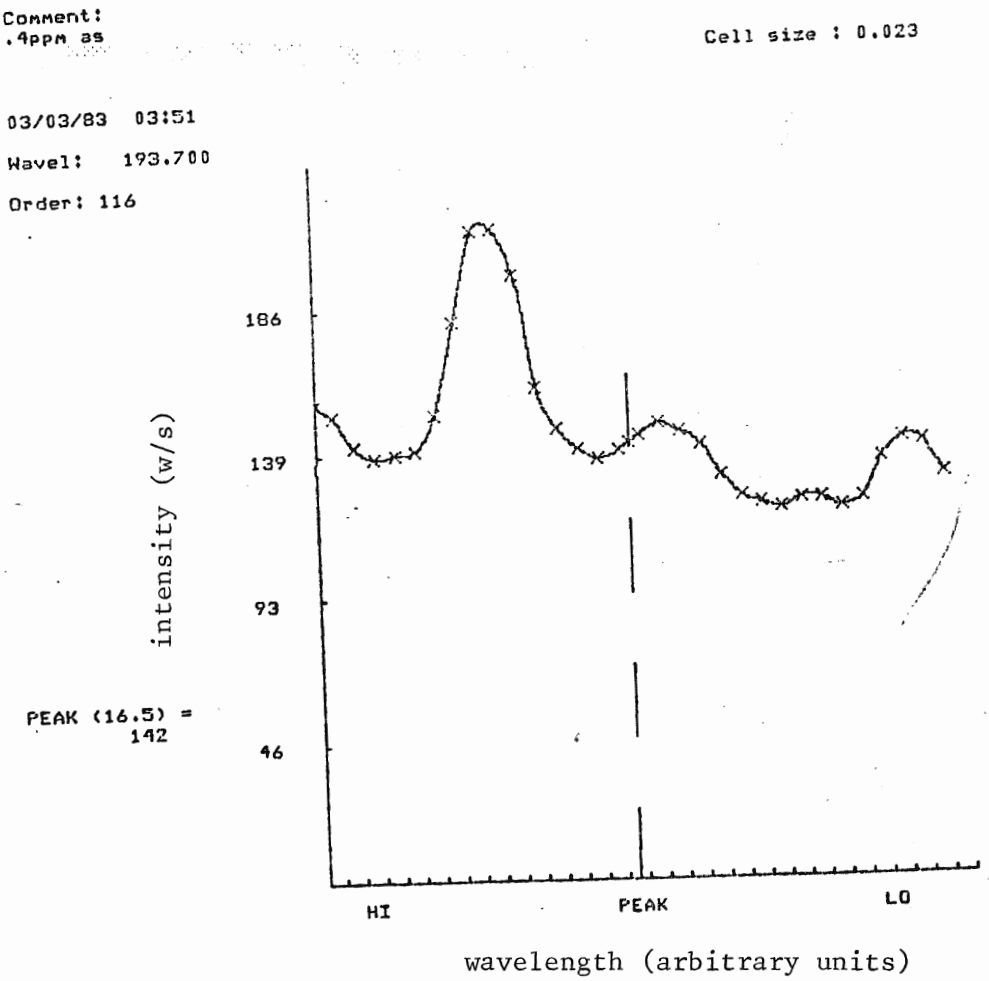


Figure 11. Wavelength scan of 0.3 µg/mL of arsenic

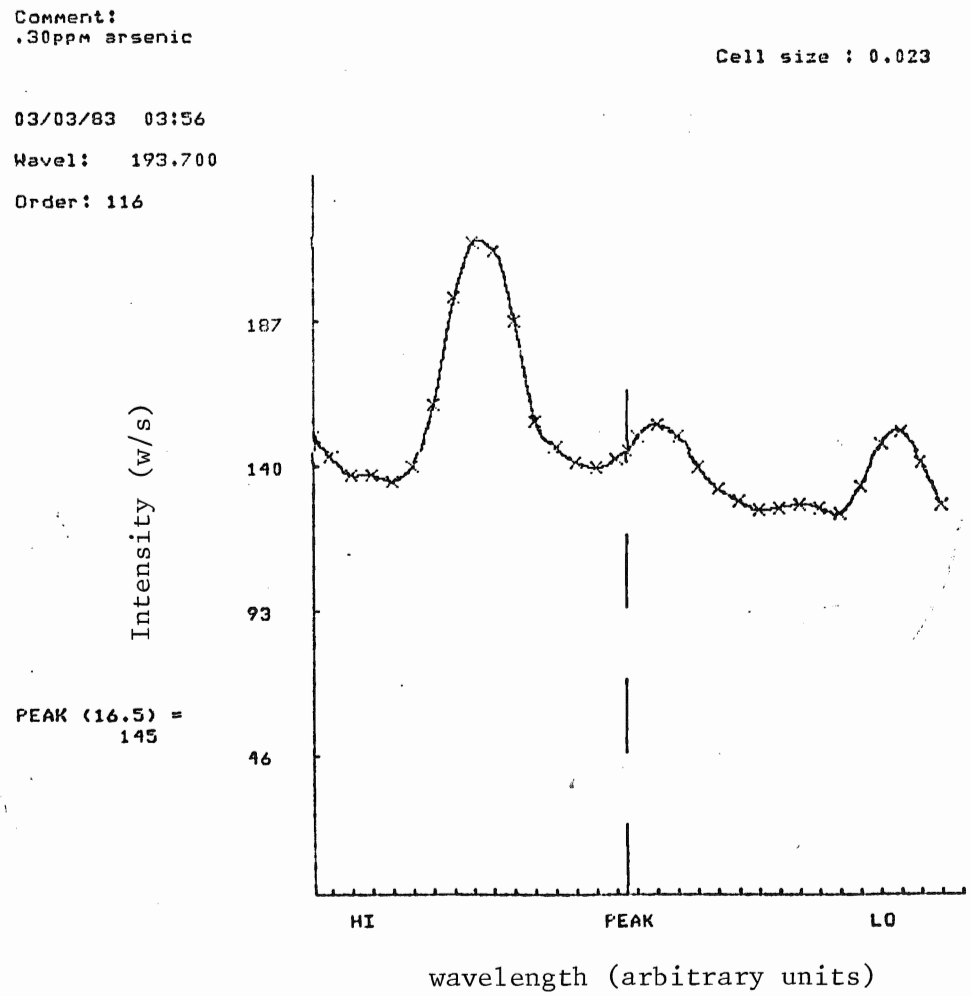


Figure 12. Wavelength scan of 0.2 µg/mL of arsenic

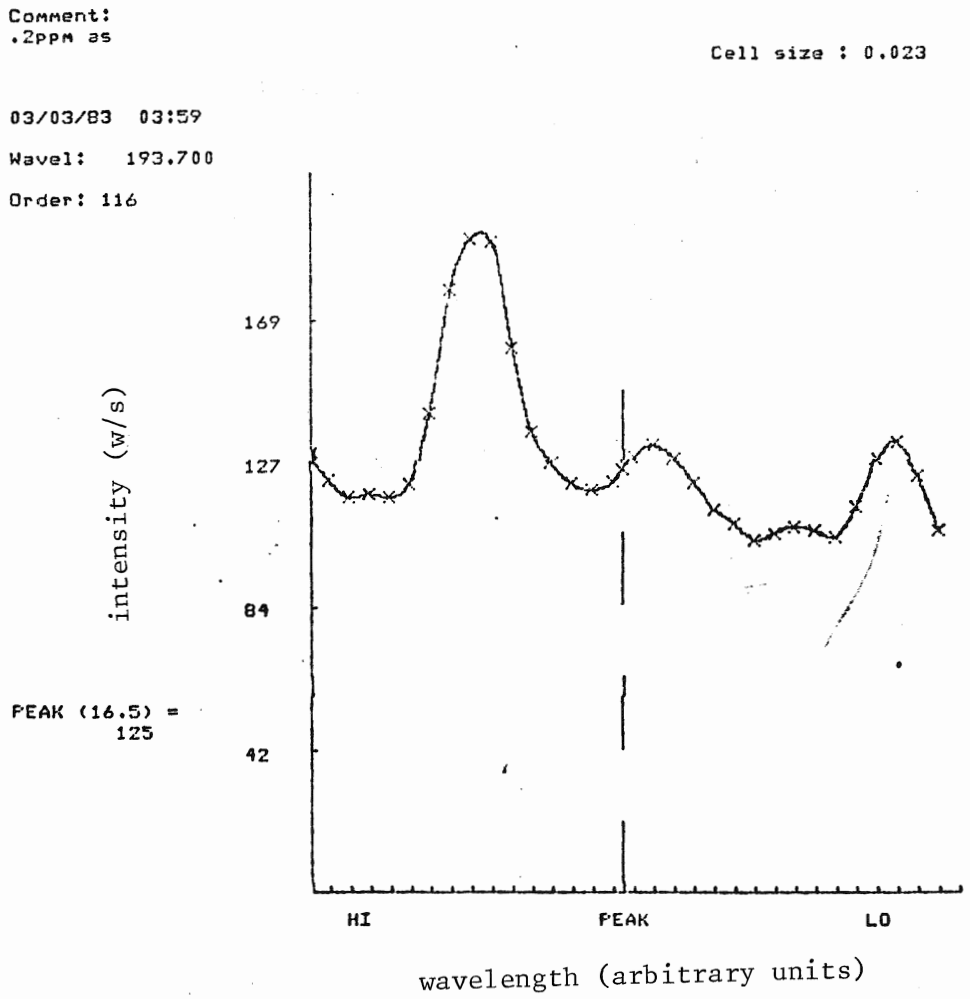


Figure 13. Wavelength scan of 0.1 µg/mL of arsenic

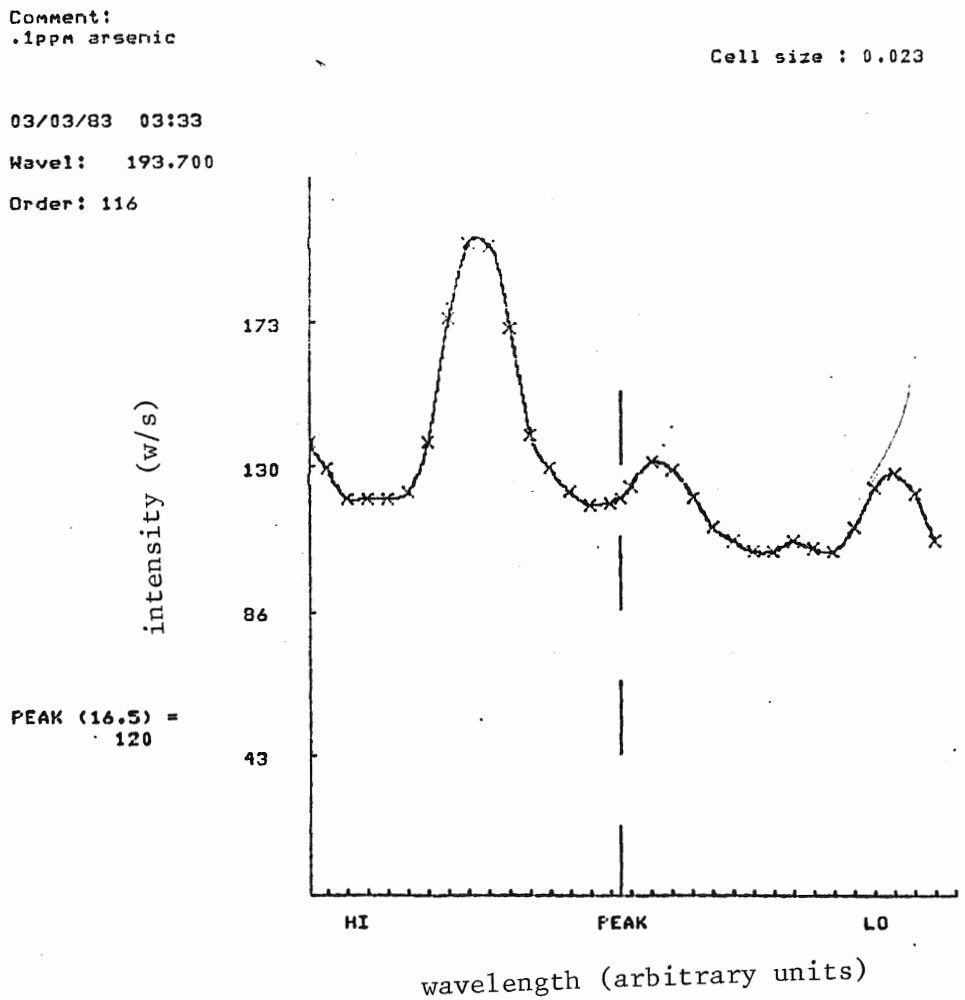
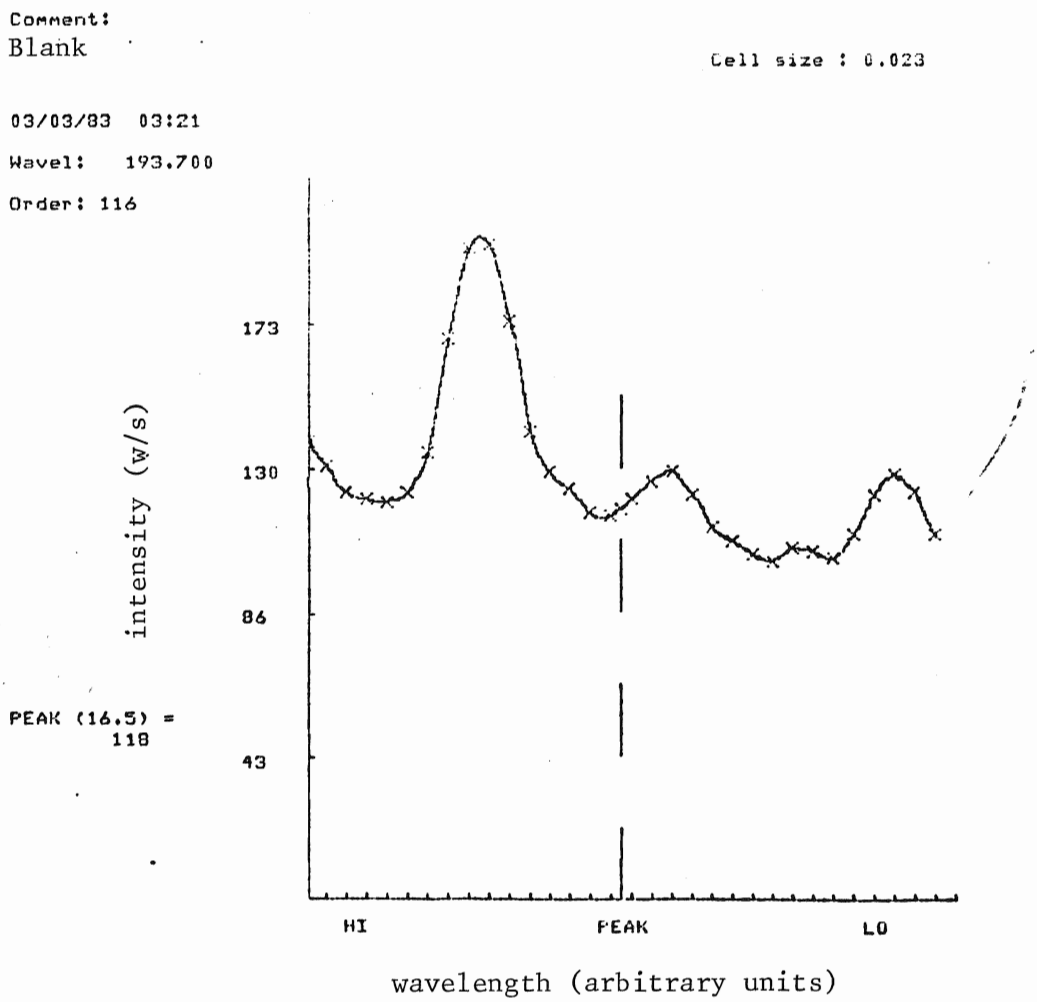


Figure 14. Wavelength scan of deionized water (blank)



II. Optimisation of the hydride generator

The flow of argon at a rate of 12.5 mL/min through the hydride generator, the sample volume of 10 mL, and the reaction of 30 seconds were adhered to, as directed by the manufacturer. Brief investigations into the above parameters revealed an increase in the sensitivity of the arsenic signal with increasing flow rate. However, above 12.5 cc/min the plasma became very unstable and sometimes extinguished. In addition, the efficiency of the drying agent diminished because more aerosol was being carried onto it.

The effect of time which had to expire before purging the generator after the addition of sodium borohydride to a pentavalent arsenic solution was immaterial between 15 and 60 seconds with respect to the peak heights. An increase in the arsenic signal was also observed when the sample volume was changed from 15 mL to 10 mL. However, 15 mL was found to be incompatible with the drying agent.

Furthermore, there was no change in the response of the arsenic signal when the acid concentration was varied from 1.4-4.0 M hydrochloric acid. This is shown in Table 3. This was expected, since, according to Bsaman et al., arsine could be generated quantatively from both trivalent and pentavalent arsenic provided the acid concentration was equal to or less than pH 1. Table 4 indicates that as the volume of 4% (weight/volume) of sodium borohydride was increased from 0.5 mL to 1.0 mL, the arsenic response increased. Nevertheless, the response began to fall when the volume was 2.0 mL or 3.0 mL. This was because of excessive foaming.

Table 3. The effect of acid concentration on the sensitivity of 0.4 μg/mL of arsenic.

Hydrochloric acid concentration (Molarity)	Peak height (cm)				
	Range (cm)	Number of measurements	Mean (cm)	Standard deviation (cm)	Relative standard deviation
1.4	11.48-12.00	3	11.79	0.22	1.8
3.0	11.30-12.30	3	11.80	0.40	3.4
4.0	10.72-12.60	3	11.67	0.78	6.6

Table 4. The effect of volume of 4% (weight/volume) of sodium borohydride on the sensitivity of 0.3 μg/mL of arsenic

Volume (mL)	Peak height (cm)				
	Range (cm)	Number of measurements	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)
0.5	7.60-7.80	3	7.70	0.08	1.0
1.0	9.40-9.50	3	9.46	0.04	0.4
2.0	8.70-9.00	3	8.86	0.12	1.4
3.0	5.87-6.70	3	6.35	0.35	5.5

III. Studies on the reduction of trivalent and pentavalent arsenic

With the hydride generator used in this experiment, the arsine which was generated by the addition of sodium borohydride was flushed from the solution with the aid of argon. It was therefore expedient to investigate whether there were differences in signals measured as peak heights, produced from trivalent and pentavalent arsenic at a pH less than or equal to 1 as reported by Siemer et al.,[18] Brodie,[19] Crock and Lichte,[20] and Hobbins.[21]

Aggett and Aspell[16] have outlined a scheme for the reduction of trivalent and pentavalent arsenic to arsine, and it is as follows:

$$As(V) \xrightarrow{\text{reduction}} As(III) \qquad (1)$$

$$As(III) \xrightarrow{\text{hydride transfer}} AsH_3 \qquad (2)$$

It is conceivable from the above reaction steps that there is a time lag between the reduction of trivalent and pentavalent arsenic to arsine.

The peaks shown in Figure 15 were obtained by adding the sodium borohydride as fast as possible and quickly flushing the system as soon as the pen of the recorder started to move up. The peaks obtained from the trivalent arsenic were sharper than those peaks of pentavalent arsenic. Since the pentavalent arsenic gave broad peaks, peak height measurement would be inherently less accurate. From the peaks in Figure 15, one conclusion is certain; that is, trivalent arsenic was reduced faster than the pentavalent arsenic. When the peaks in Figure 15 were cut and weighed, the average weight of the trivalent arsenic peak was

5.72 mg with standard deviation of 0.58 mg, whilst that of the pentavalent arsenic peak was 6.24 mg with standard deviation of 0.53 mg. Figure 16 represents the flushing of the arsine 30 seconds after the addition of sodium borohydride. The peak height of the pentavalent arsenic looks greater than that of trivalent arsenic. The "baby peaks" of the trivalent arsenic trace could account for the decrease.

Ideally, the average peak height of the trivalent arsenic in Figure 15 should be equal to the average peak height of the pentavalent arsenic in Figure 16. This equality is expected, since the latter does not show either signs of peak broadening or the symptoms of "baby peaks" as depicted in Figure 16 by the trivalent arsenic. On the contrary, the average peak height of the pentavalent arsenic in Figure 16 looks less than that of the trivalent arsenic in Figure 15. This discrepancy could be due to the diffusion of arsine around the rubber stopper, fitted to the Buchner funnel, during the time that 30 seconds was being allowed to elapse.

The means and estimates of the standard deviation of the weighed peaks of the trivalent and pentavalent arsenic in Figure 15 were compared by using the t-test. For 10 measurements and 8 degrees of freedom, the calculated t-value was 1.31 and the t-value from the student's table was 1.86 at the 90 percent confidence level. Thus, since calculated t value is less that that from the student's table, there is no significant difference between the mean of the weights of the trivalent and pentavalent arsenic peaks. Therefore, it can be concluded that both trivalent and

pentavalent arsenic can be reduced quantitatively at pH less than 1. However, this statement would have been questioned if the arsenic signals in Figure 15 were measured as peak heights. The weights of trivalent and pentavalent arsenic, including the t-test formula are shown in the Appendix.

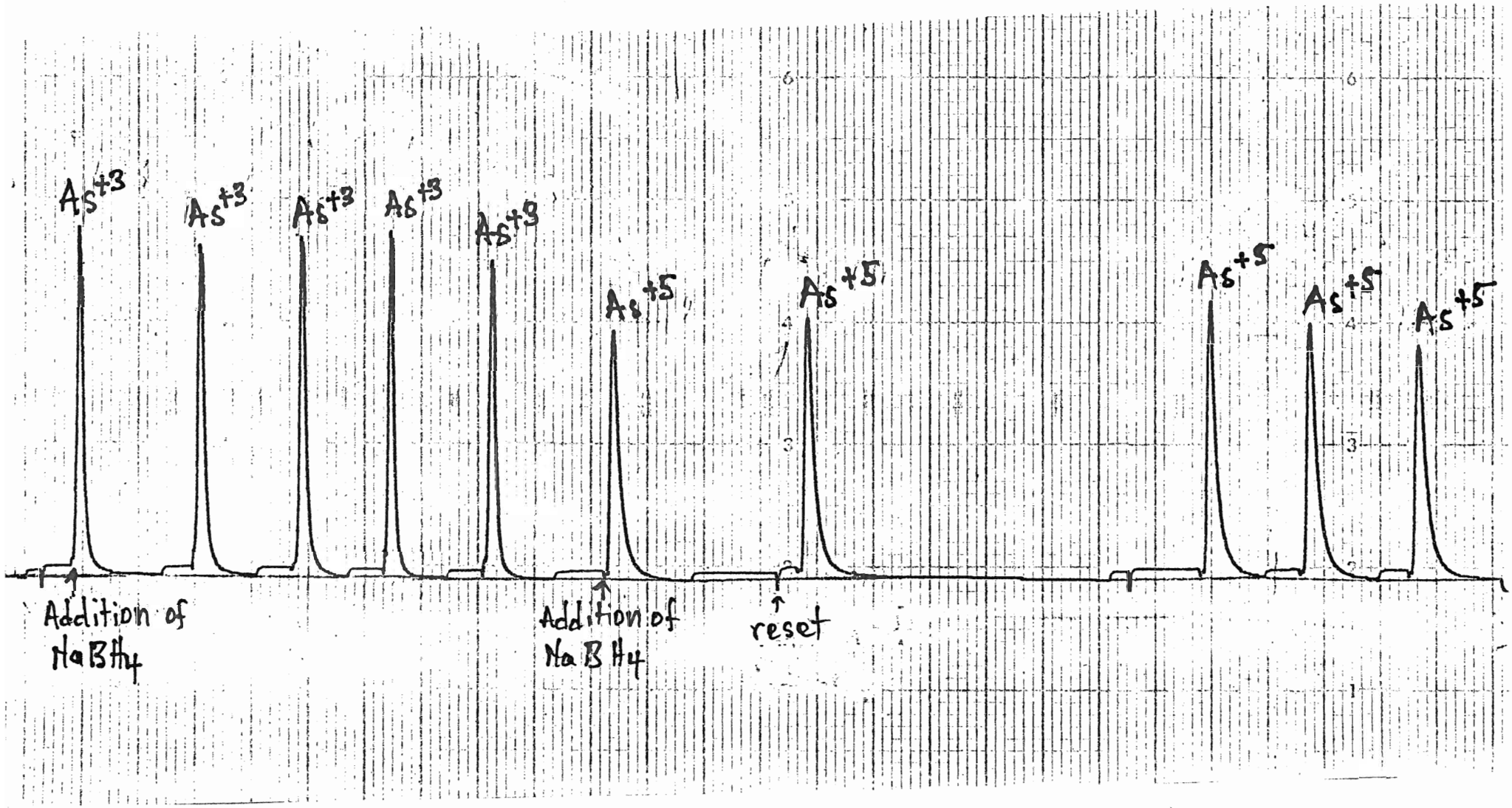


Figure 15. The response of 0.3 µg/mL of trivalent and pentavalent arsenic, when the hydride generator system was flushed immediately after the addition of sodium borohydride.

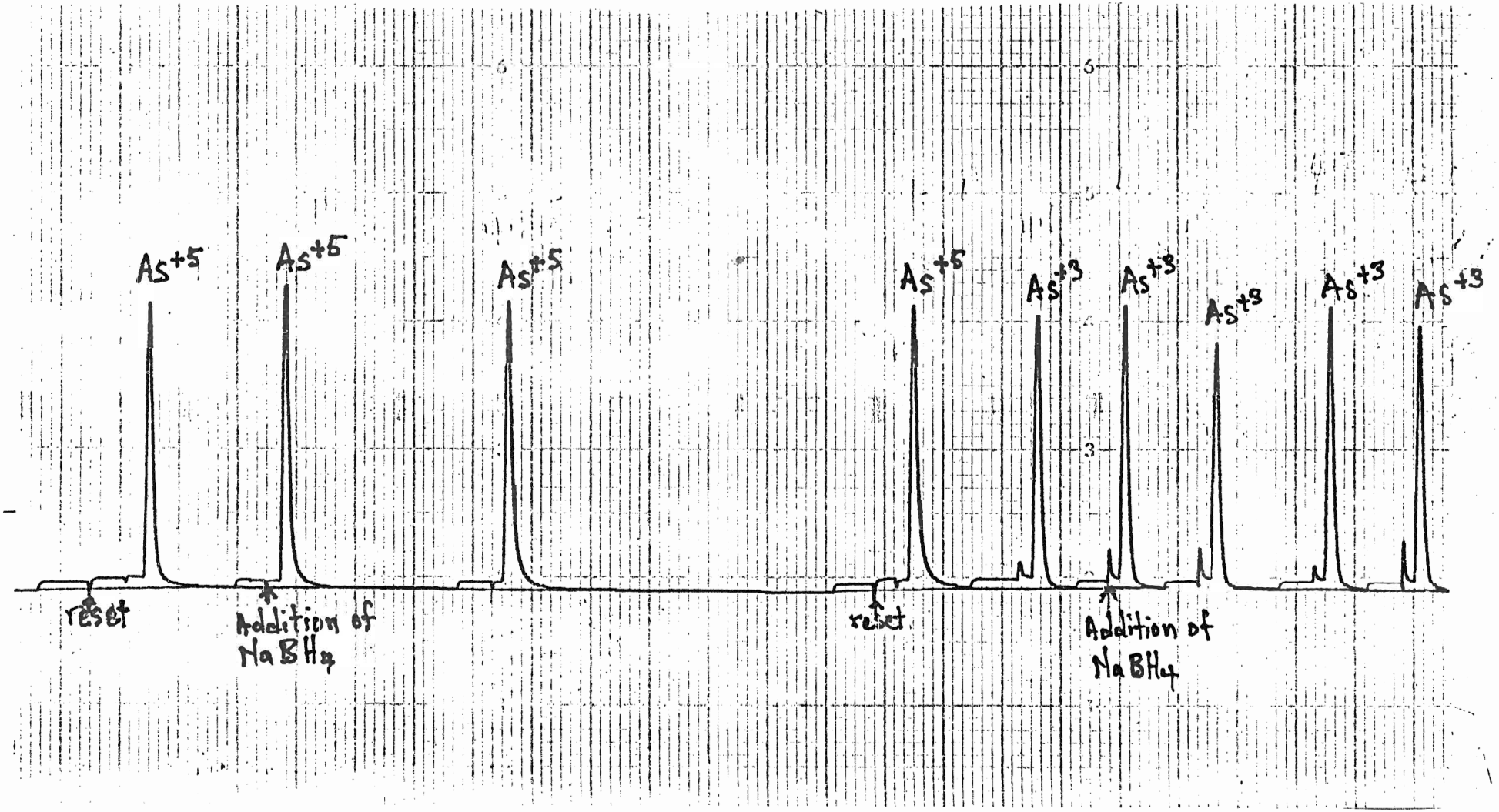


Figure 16. The response of 0.3 µg/mL of trivalent and pentavalent arsenic, when 30 seconds was allowed before flushing the hydride generator, after the addition of sodium borohydride.

IV. Modifications to the hydride generator

1. The special sample tube

There were three concommitant problems associated with interfacing the hydride generator to the direct current plasma SpectraSpan V. The first was with the special sample tube for the hydride generator shown in Figure 17A. The special sample tube could not be used to optimise the wavelength and the plasma position on the entrance slit. This was because there was flooding of aerosols at the top of the semi-open tube. As a consequence, the regular sample tube used for the determination of elements in solution was used to optimise the instrument and then replaced with the special hydride generator sample tube. The consequences of this interchange were:

(a) The plasma was positioned at the entrance slit by eyeballing when the special sample tube was in position. This made the system vulnerable to operator errors.

(b) The position of the special sample tube had to be adjusted a couple of times before a good signal could be accomplished. It was merely a question of trial and error.

These problems were resolved by making a new sample tube from silica. The modified sample tube head is shown in Figure 17B. With this modified sample tube head, the optimisation of the wavelength, plasma jet position and the position of the sample tube head itself could be done readily.

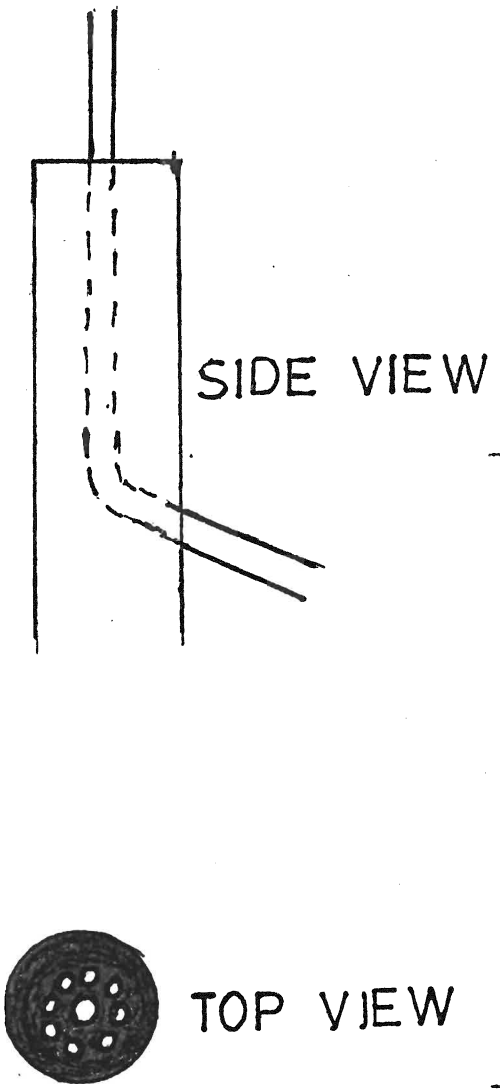


Figure 17A. Original special hydride generator sample tube head.

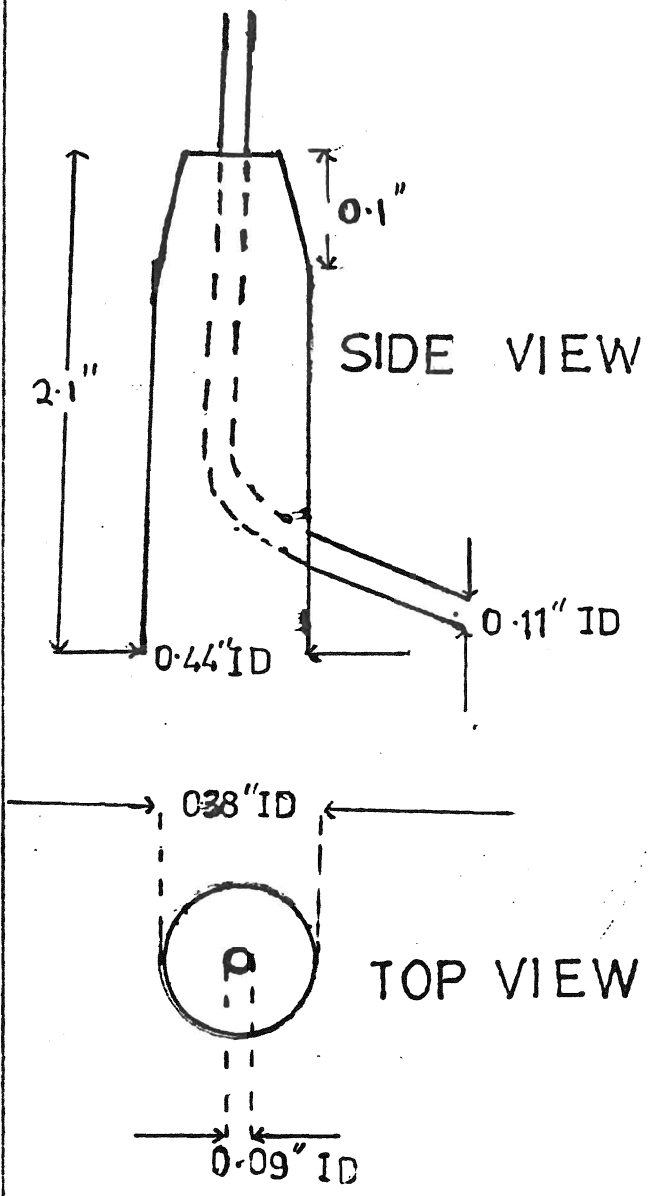


Figure 17B. Modified hydride generator sample tube head

2. Calcium chloride and Porapak Q

A second setback was due to the calcium chloride, which was supposed to stop water vapour from getting onto the Porapak Q, and the Porapak Q itself, which was supposed to separate the arsine from the excess hydrogen, which was presumed to disrupt the plasma. The calcium chloride was replaced with an anhydrous calcium sulphate of 8-12 mesh size. This was necessitated by the fact that as soon as the calcium chloride got wet, it got stuck together and inhibited the flow of gas through the system. This inhibition could create a severe back pressure, which would push the rubber stopper out from the Buchner funnel.

Although the calcium sulphate did not stick together as the calcium chloride, some water vapour found its way onto the Porapak Q. Whenever the Porapak Q got wet, it caused lower signal response and poor reproducibility. However, as can be seen from Figure 18, when the Porapak Q was dried, it yielded better signal response compared with the situation where it was removed completely from the line. In Figure 19A, the peaks which are marked with "X" were obtained from a reaction between hydrochloric acid and sodium borohydride. These peaks were generated after the analyses of 10 ng/mL of arsenic with dry Porapak Q in position. However, Figure 19B shows the absence of peaks when the blank analysis was carried out first, before analysing any standard concentration of arsenic. Comparing the two figures, it could be said that the Porapak Q adsorbs some arsine which comes off later. In addition, no residual peaks were observed when the porapak Q was taken off completely, as would have been expected to happen with respect to Figure 19A.

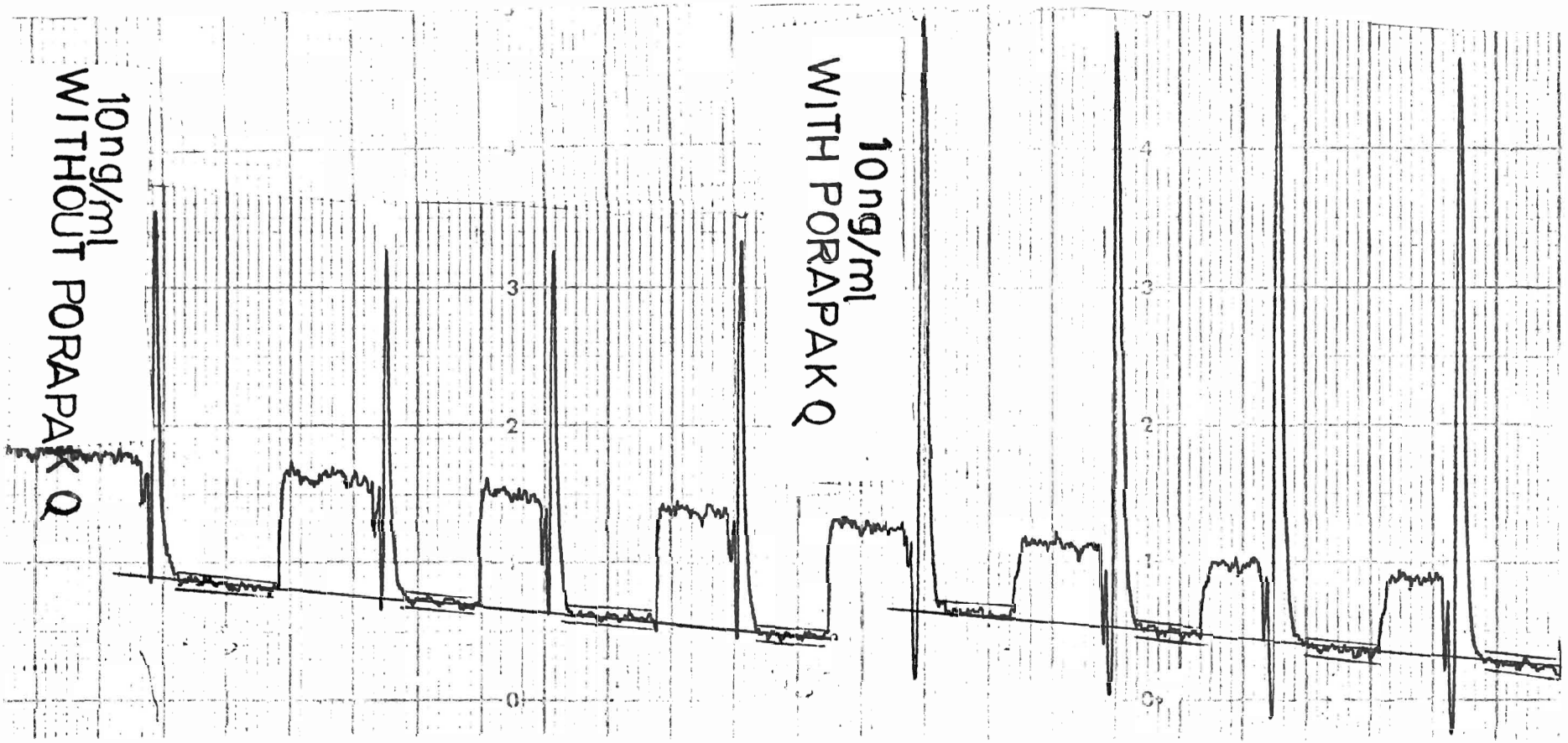
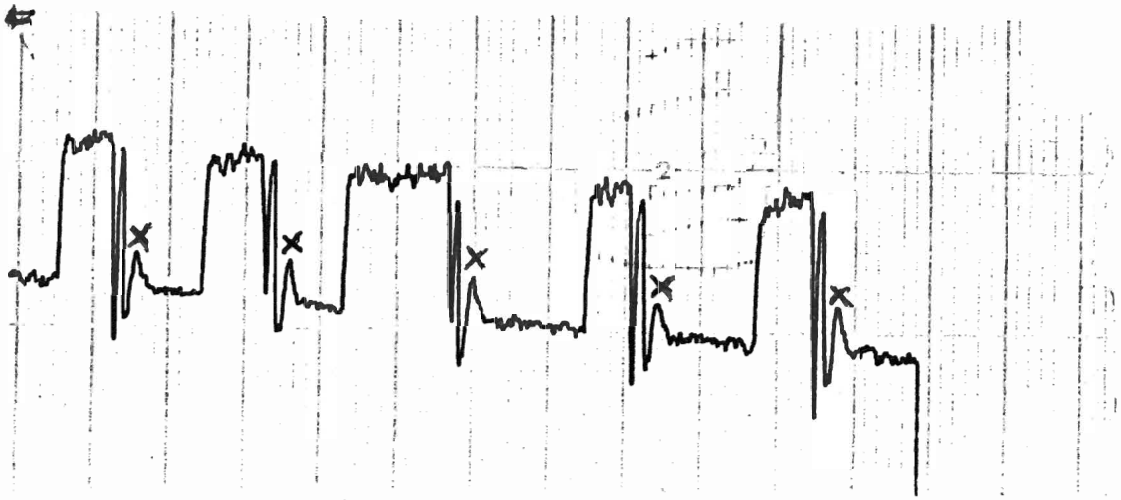


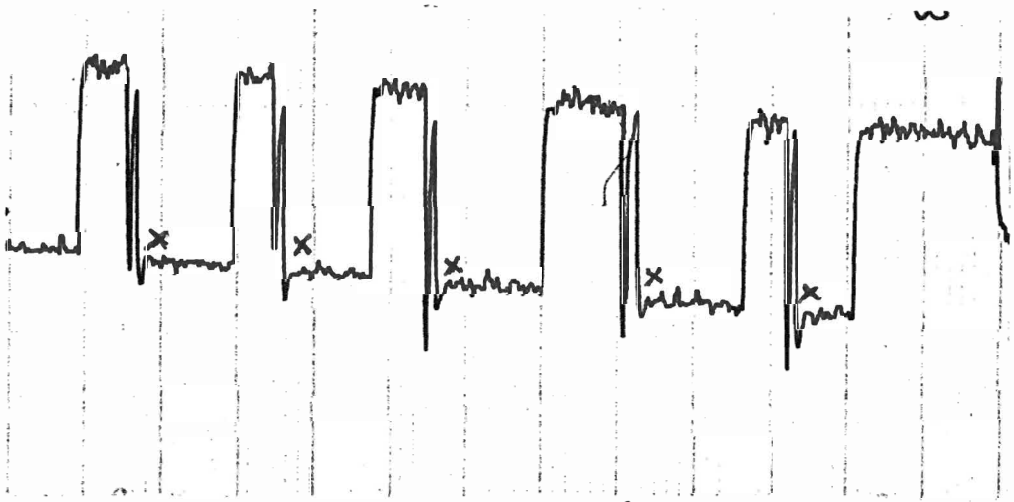
Figure 18. Differences in signal response of 10 ng/mL of arsenic without Porapak Q and with Porapak Q

Figure 19A. Traces of response of arsine from Porapak Q when the blank was run after a 10 ng/mL arsenic(V) concentration.



Note: The letter X indicates arsenic peaks or where they were expected to be.

Figure 19B. Traces of the response of arsine from Porapak Q when the blank was run as the first sample



Note: The letter X indicates arsenic peaks or where they were expected to be.

3. Soil samples

Soil samples from the Canada Centre for Mineral and Energy Technology were extracted with nitric acid, sulphuric acid, perchloric acid and hydrofluoric acid by the method of Crock and Lichte.[58] Analyses of soil sample extracts for arsenic were not compatible with the way the argon was passed through the bottom of the Buchner funnel in order to carry arsine to the plasma. There was always foaming. The foaming being described here was technically different from foaming obtained with detergents. What actually happened was that very small and slow breaking bubbles were formed as opposed to very large and fast breaking bubbles which were normally encountered. Whenever this, so-called, foaming occurred, there was severe depression of signals. The assistance of antifoam "B" could not stop the foaming but rather escalated it. Brief experiments indicated that just a drop of the antifoam "B" was enough to suppress completely the signal from 10 ng/mL of arsenic. This was because the antifoam "B" itself produced the same type of bubbles encountered with soil samples.

It was attempted to re-direct the direction of the flow of argon through the Buchner funnel as shown in Figure 20, because that approach did not result in the foaming of soil sample extracts. Figure 21 shows the peaks which were obtained when 300 ng/mL standard arsenic solution in 1.4 M hydrochloric acid was analysed. The peaks labelled A represent the passing of argon through the bottom of the Buchner funnel, whilst peaks labelled B represent the passing of argon in a manner as shown in Figure 20. The two peaks labelled B in Figure 21 were lower in peak height because the stripping of the arsine from the solution was slower. There was no significant difference in the area measurements between peaks A and B at 99.9% confidence level using the t-test.

Figure 20. Illustration of the re-direction of the flow of argon through the Buchner funnel.

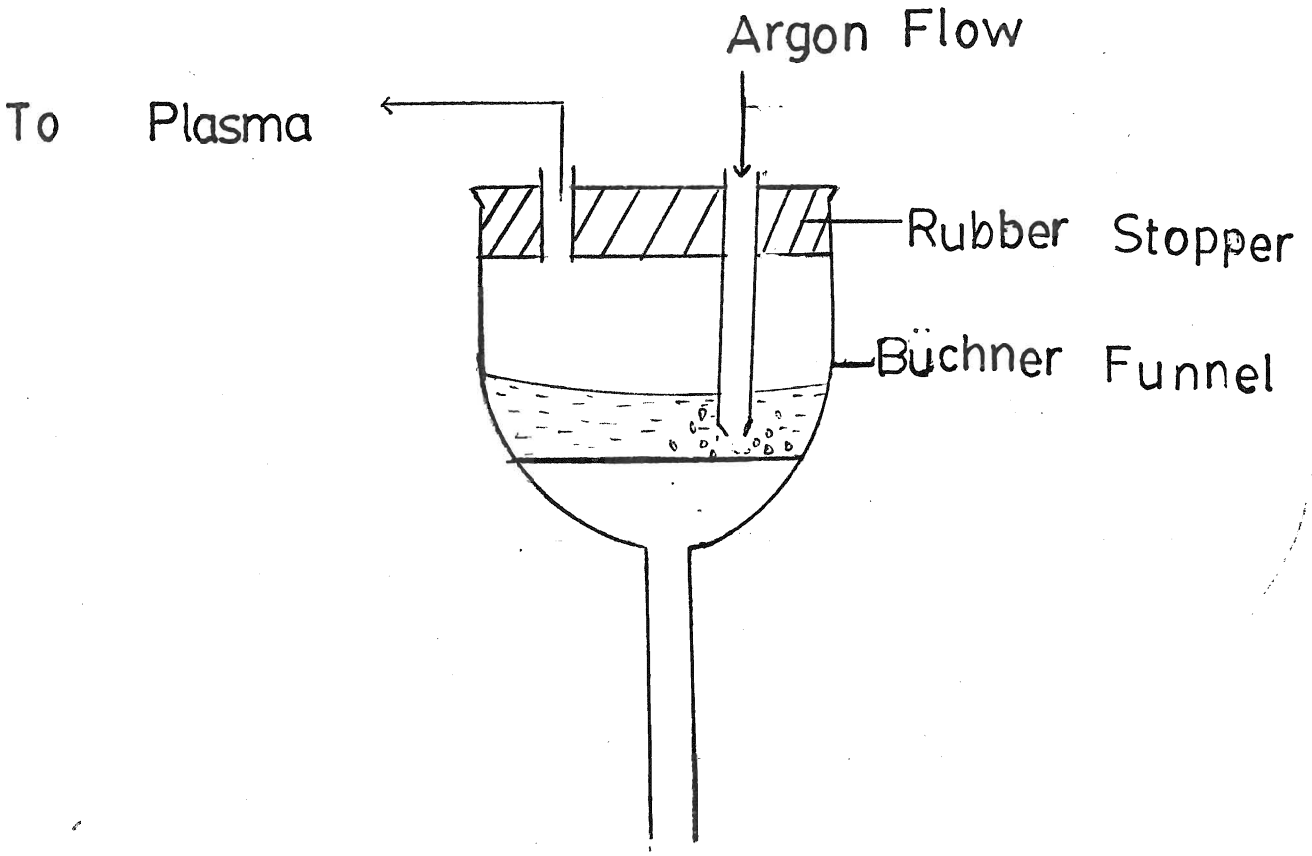
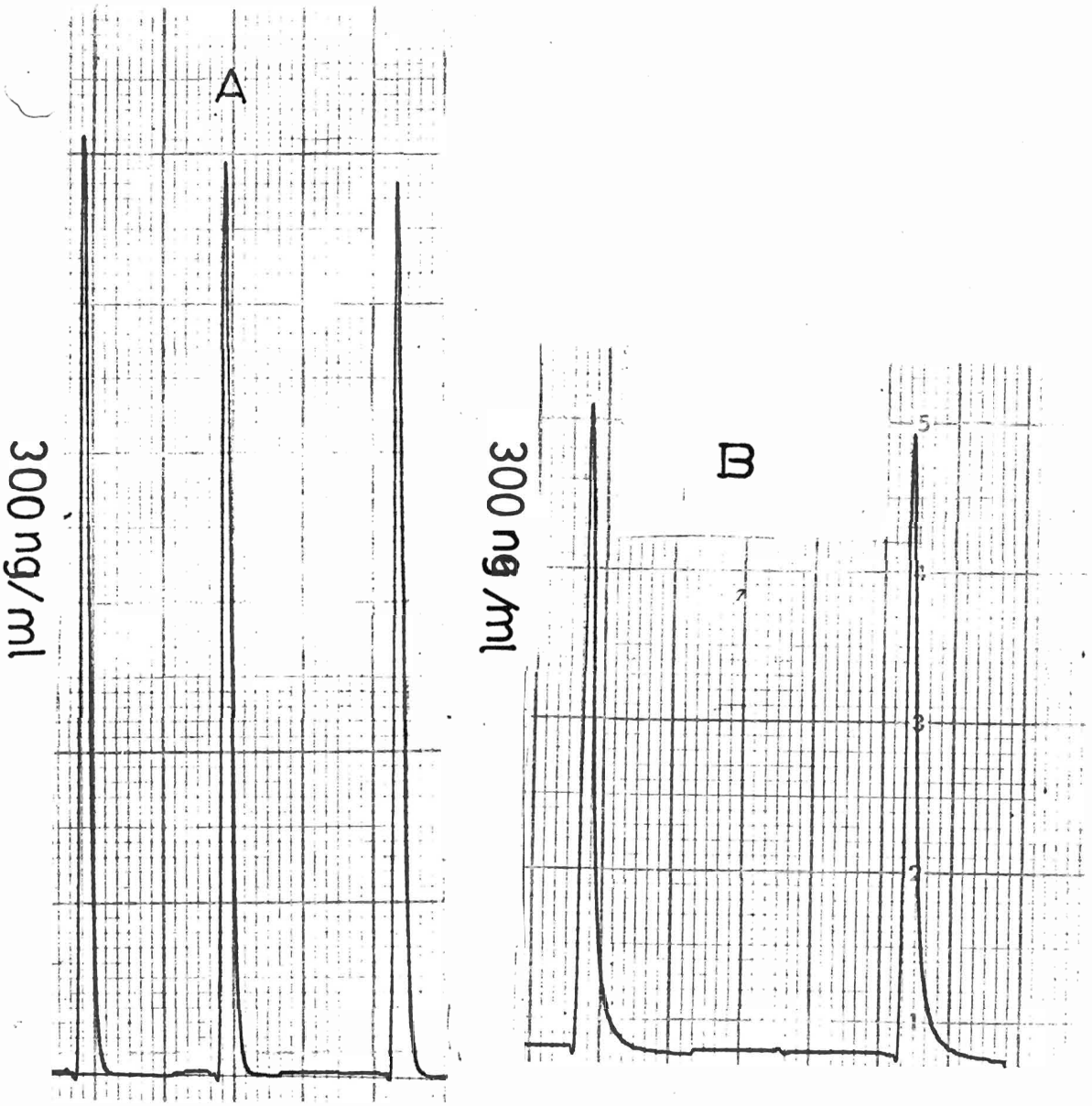


Figure 21. The response of 300 ng/mL of arsenic when the direction of argon flow was through the bottom of the Buchner funnel (A) and the response of 300 ng/mL of arsenic when the direction of argon flow was through the top of the Buchner funnel (B).



V. Reproducibility

The reproducibility was checked by analysing a standard solution of 0.3 μg/mL of arsenic. The results are shown in Table 5. This reproducibility was tested with the Porapak Q and the special sample tube. A relative standard deviation of 3.4% was accomplished. The reset button was pressed after each determination. This was done when the recorder sensitivity was set at 0.1 V. However, when the recorder was set at a sensitivity of 10 mV, the reset button was pressed in between four or five determinations. This was necessary because the recorder pen changed its position anytime the reset button was pressed.

VI. Detection Limit

Since there was no arsenic signal response from the blank reagents, i.e., hydrochloric acid and sodium borohydride the calculation of the detection limit was based on the noise level. The detection limit is thus defined as twice the base line noise. The average of the noise level was found to be 2.8 mm, at recorder sensitivity of 10 mV. Therefore, from Table 8, which represents the calibration of arsenic when the Porapak Q was removed from the line, 10 ng/mL gives a peak height of 57.8 mm, at recorder sensitivity of 10 mV. Thus the detection limit is 1 ng/mL.

Similarly, from Table 9, which also represents the calibration of arsenic, when the Porapak Q was dried and in position, 10 ng/mL gives a peak height of 95.2 mm, the detection limit is 0.6 ng/mL.

Table 5. Variation of 0.3 μg/mL arsenic signal with time

Time (minutes)	Peak height (cm)
0	7.50
6.6	7.20
10.5	6.70
17.2	7.75
21.8	7.10
27.4	6.05
32.0	6.70
42.5	6.60
46.5	6.40
49.9	6.29
54.3	7.60
57.4	5.95
60.8	5.80
64.5	6.70
67.6	5.69
70.8	5.70
74.7	5.40
79.6	6.55
84.6	6.10

mean = 6.52

standard deviation = 0.22

relative standard deviation = 3.4%

VII. Calibration curves

When it was realised that the nature of the calibration curve below 0.8 μg/mL of arsenic was not linear, the hydride generation method was put into test. In Table 6, the concentrations 0.1 μg/mL-0.3 μg/mL were run at recorder sensitivity of 0.1 V, while 0.4 μg/mL-0.8 μg/mL were run at 1.0 V. Figure 22 shows a better linear response compared with the curve in Figure 2. The two Figures, 22 and 2, were obtained with the same concentrations of arsenic.

The detection limit associated with arsenic determination, using the direct current plasma through solution nebulization has been reported to be 0.08 μg/mL.[42] It therefore became expedient to evaluate the hydride generator apparatus below this concentration. In Table 7, the concentrations 10 ng/mL-30 ng/mL were run at recorder sensitivity of 10 mV, and 50 ng/mL-400 ng/mL were run at 0.1 V. The calibration curve in Figure 23 in association with Table 7, represents a measure of the efficiency of the hydride generator system when the Porapak Q was in position, and also when the special sample tube, manufactured by Spectrametrics Inc was in use. Although the calibration line in Figure 23 has a wide linear range, up to 300 ng/mL, it took a long time to get the special sample tube at right position. This was due to problems which have been discussed under "Modifications to the hydride generator".

It was found that wet Porapak Q could inhibit the arsenic signals, so it was decided to eliminate it from the hydride generator system. After implementing this change, another calibration curve was prepared

Table 6. Response, measured as peak height (cm) in relation to arsenic concentration (μg/mL), using the special sample tube head and Porapak Q

Concentration (μg/mL)	Peak height (cm)				
	Range (cm)	Number of measurements	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)
0.1[a]	4.90-5.15	3	5.03	0.10	2.0
0.2[a]	9.30-9.90	3	9.66	0.26	3.0
0.3[a]	13.20-15.10	3	13.96	0.81	6.0
0.4[b]	1.96-1.80	2	1.74	0.05	3.0
0.5[b]	2.20-2.25	3	2.22	0.02	1.0
0.6[b]	2.50-2.90	3	2.63	0.19	7.0
0.8[b]	3.20	3	3.20	0.00	0.0

[a]Concentrations were measured at recorder sensitivity of 0.1 V

[b]Concentrations were measured at recorder sensitivity of 1.0 B

Figure 22. Relationship between peak height (cm) and arsenic concentration (µg/mL), using the special sample tube head and Porapak Q

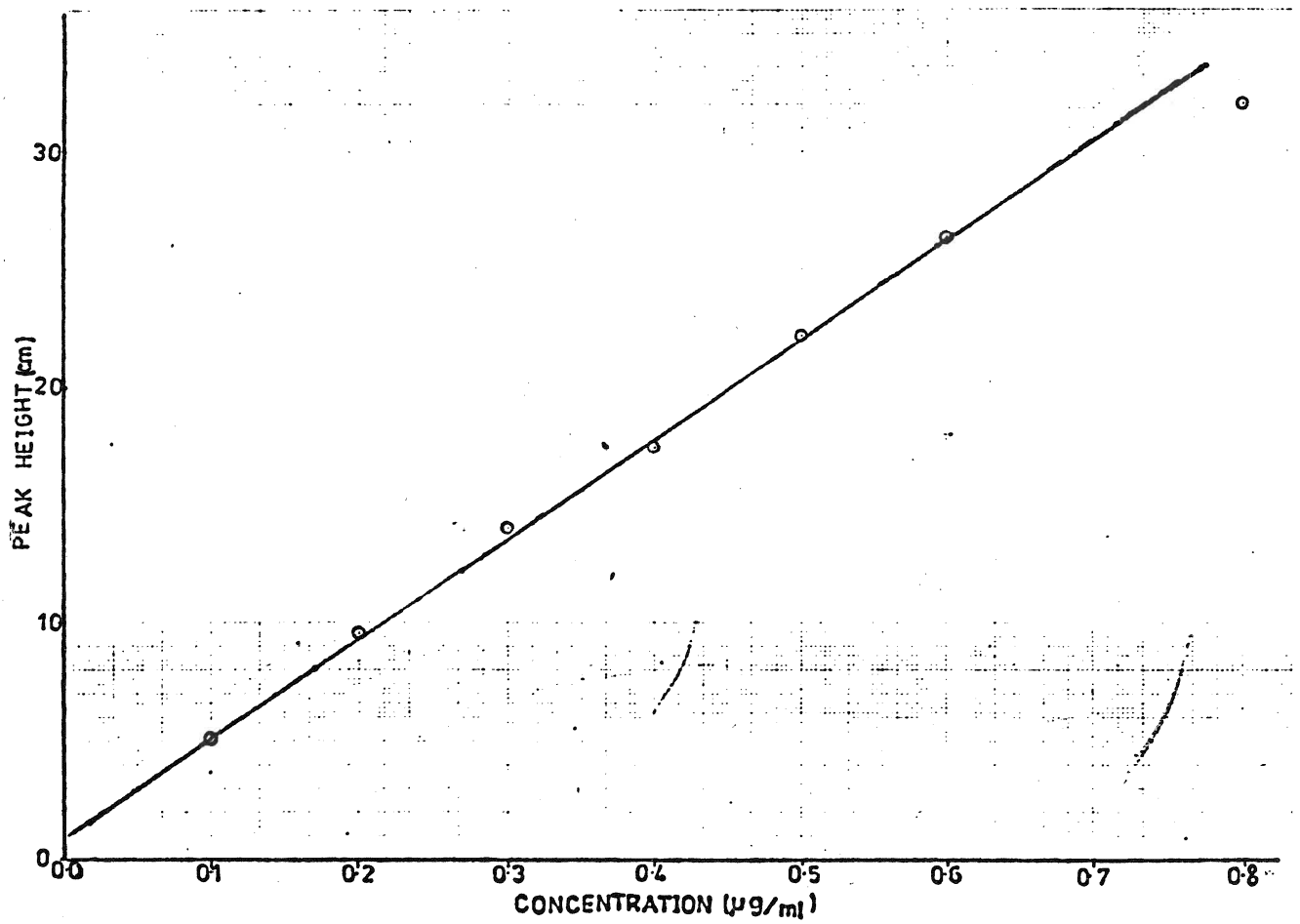


Table 7. Response, measured as peak height (cm) in relation to arsenic concentration (ng/mL), with special sample tube head and Porapak Q

Concentration (ng/mL)	Peak height (cm)				
	Range (cm)	Number of measurements	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)
10[a]	11.50-12.50	5	11.97	0.34	3.0
30[a]	2.30-2.40	3	2.36	0.04	2.0
50[b]	2.70-2.80	3	2.75	0.04	1.0
80[b]	3.75-4.00	3	3.85	0.10	3.0
100[b]	4.15-4.35	3	4.25	0.08	2.0
200[b]	7.20-7.85	3	7.53	0.26	3.0
300[b]	9.90-10.90	3	10.35	0.40	4.0
400[b]	11.30-12.40	3	11.83	0.45	4.0

[a]Concentrations were measured at recorder sensitivity of 10 mV

[b]Concentrations were measured at recorder sensitivity of 0.1 V

Figure 23. Relationship between peak height (cm) and arsenic concentration (ng/mL), using the special sample tube head and Porapak Q.

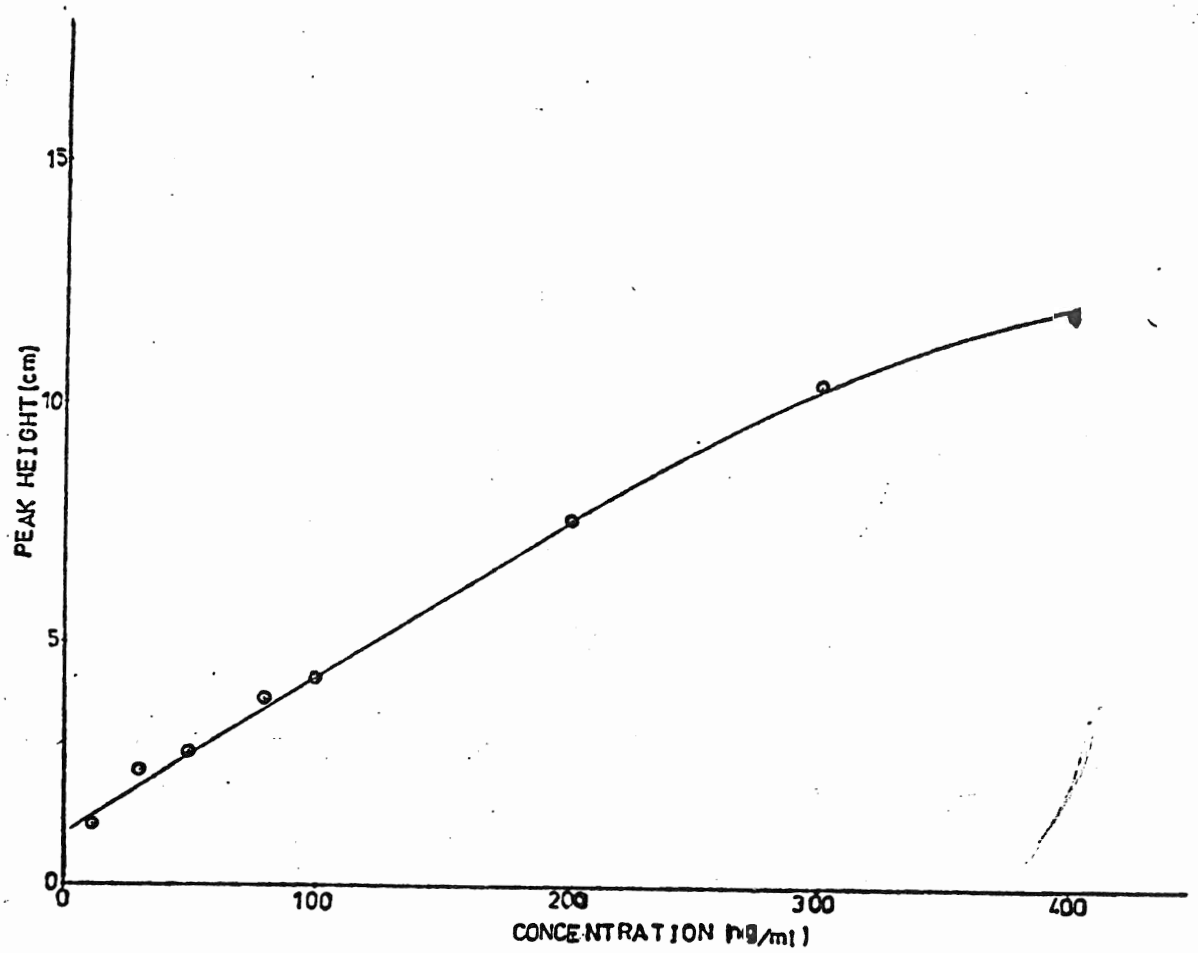


Table 8. Response, measured as peak height (cm) in relation to arsenic concentration (ng/mL), with modified sample tube head, but no Porapak Q

Concentration (ng/mL)	Peak height (cm)				
	Range (cm)	Number of measurements	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)
10[a]	5.50-6.10	4	5.78	0.21	4.0
20[a]	11.70-12.30	3	11.92	0.26	2.0
30[a]	19.90-20.30	3	10.30	0.19	1.0
50[b]	2.53-2.90	3	2.68	0.16	6.0
70[b]	3.61-3.90	3	3.77	0.12	3.0
80[b]	3.90-4.00	3	3.96	0.05	1.0
100[b]	4.70-4.75	3	4.72	0.02	1.0
200[b]	8.20-8.50	3	8.33	0.12	1.0
300[b]	10.10-10.60	3	10.36	0.20	2.0
400[b]	12.85-13.00	3	12.92	0.05	1.0

[a]Concentrations were measured at recorder sensitivity of 10 mV

[b]Concentrations were measured at recorder sensitivity of 0.1 V

Figure 24. Relationship between peak height (cm) and arsenic concentration (ng/mL), using the modified sample tube head but no Porapak Q

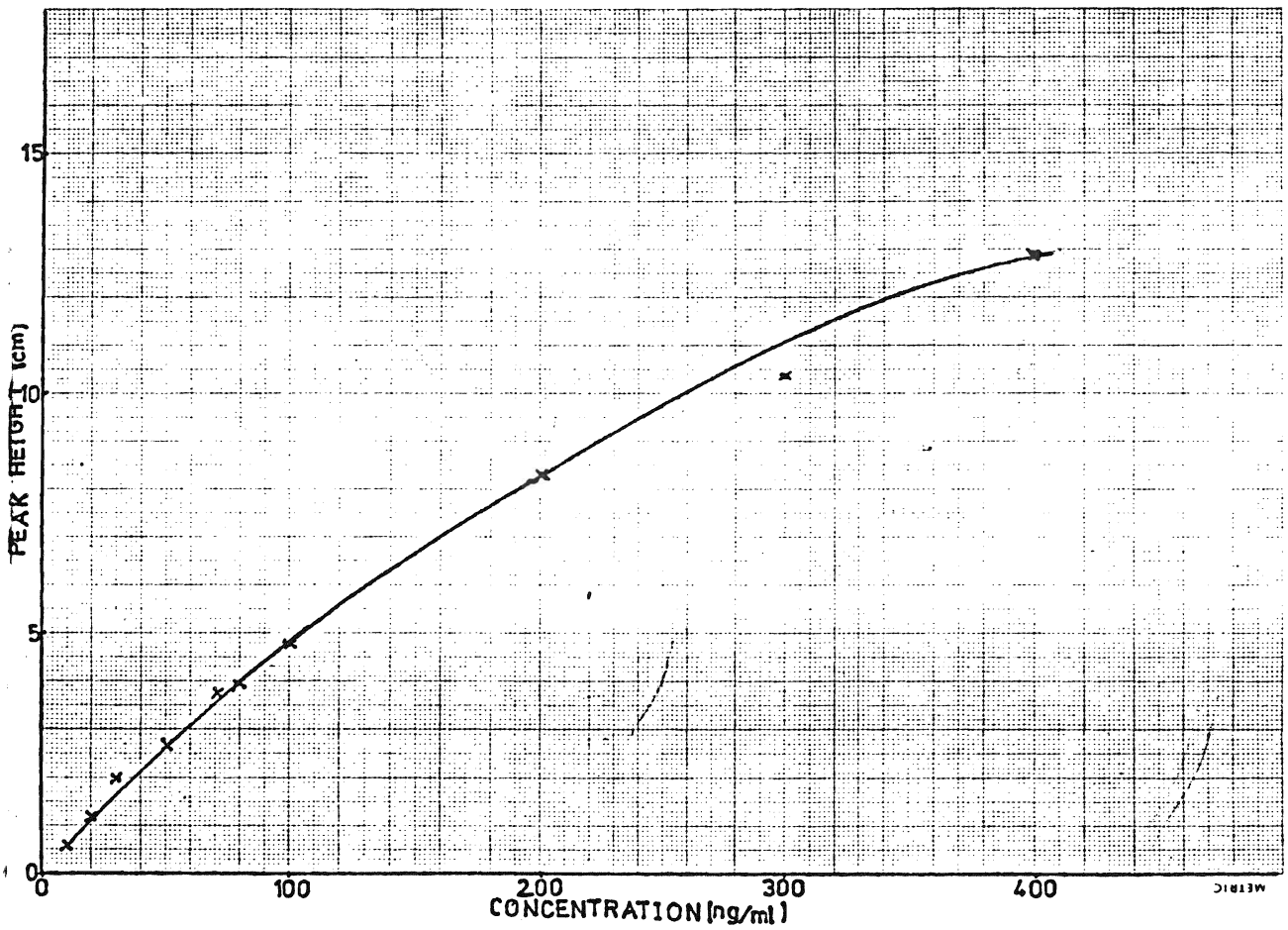


Table 9. Response, measured as peak height (cm) in relation to arsenic concentration (ng/mL), with modified sample tube head and Porapak Q

Concentration (ng/mL)	Peak height (cm)				
	Range (cm)	Number of measurements	Mean (cm)	Standard deviation (cm)	Relative standard deviation (%)
10[a]	9.40-9.70	4	9.52	0.13	1.0
20[a]	16.60-17.60	3	17.13	0.41	2.0
30[b]	2.45-2.50	3	2.47	0.02	1.0
50[b]	3.60-3.70	3	3.63	0.06	1.6
70[b]	4.60-4.84	3	4.74	0.11	2.0
80[b]	5.40-5.55	3	5.48	0.06	1.0
100[b]	5.98-6.00	3	6.01	0.01	1.0
200[b]	11.00-11.20	3	11.10	0.08	1.0
300[b]	12.95-13.60	3	13.25	0.28	2.0
400[b]	16.45-17.20	3	16.85	0.28	2.0

[a]Concentrations were measured at recorder sensitivity of 10 mV

[b]Concentrations were measured at recorder sensitivity of 0.1 V

Figure 25. Relationship between peak height (cm) and arsenic concentration (ng/mL), using modified sample tube head and dry Porapak Q

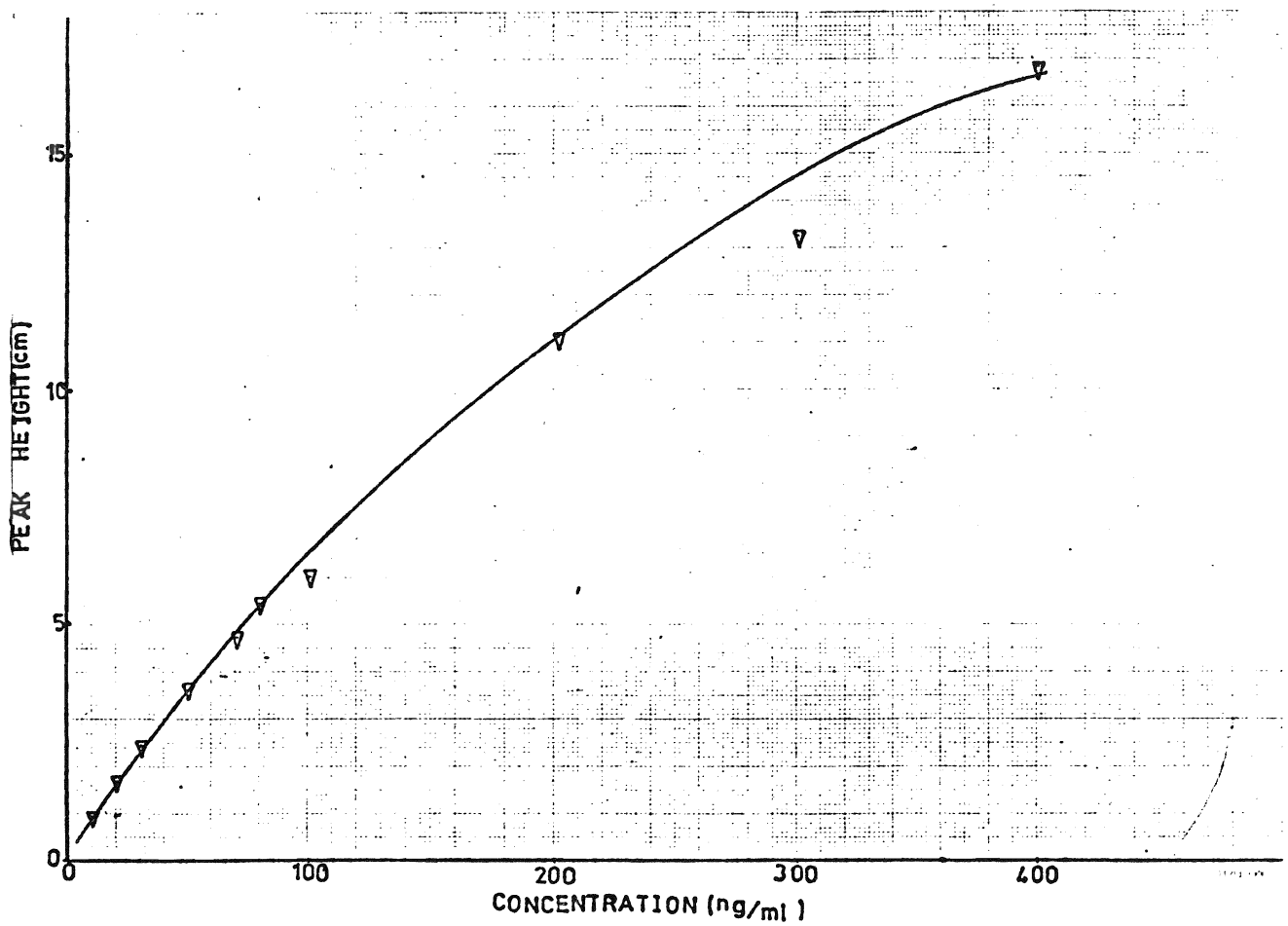
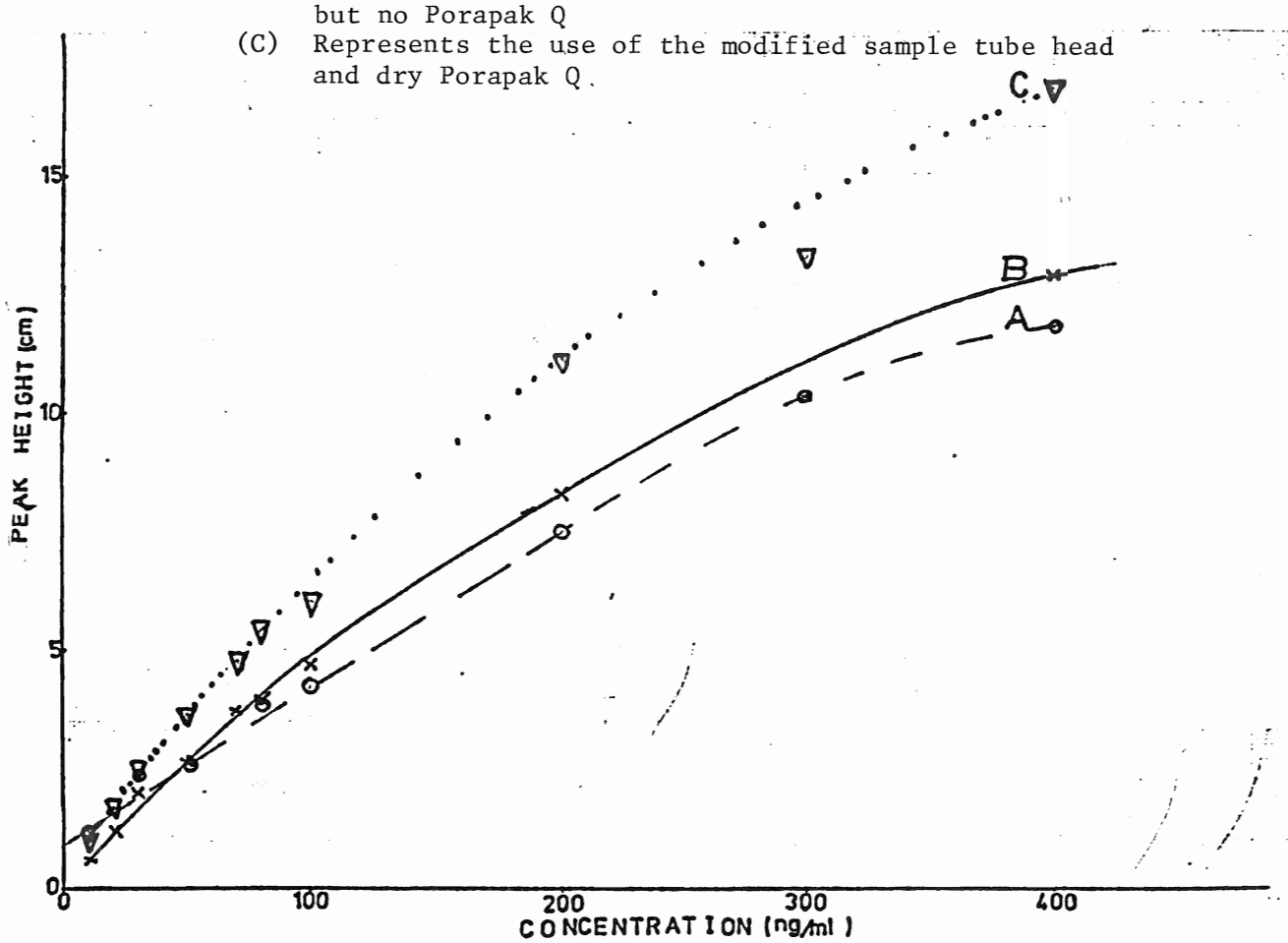


Figure 26. Relationship between peak height (cm) and arsenic concentration (ng/mL)
(A) Represents the use of the special sample tube head and Porapak Q
(B) Represents the use of the modified sample tube head but no Porapak Q
(C) Represents the use of the modified sample tube head and dry Porapak Q.



in order to assess the hydride generator. In this particular case, the modified sample tube shown in Figure 17B was used. The results are shown in Table 8 and Figure 24. In Table 8, concentrations 10 ng/mL-30 ng/mL were run at recorder sensitivity of 10 mV, and 50 ng/mL-400 ng/mL were run at 0.1 V.

Lastly, it was decided to appraise the modified sample tube and Porapak Q, which was dried. Table 9 and Figure 25 depict the results.

Figure 26 shows all the three curves in Figures 23, 24 and 25. It can be concluded from Figure 26 that a combination of the modified sample tube and a dried Porapak Q can increase the sensitivity of the arsenic signal.

VIII. Interference studies

Two theories have been put forward by Kirkbright and Taddia,[55] and Smith[50] to explain the interferences from metal ions on the generation of arsine from arsenic. Kirkbirght and Taddia have observed complete suppression of arsenic signal in the presence of powdered nickel. They also stated that elements such as nickel adsorb hydrogen in large quantities compared with their own weight. Smith has said, "Preferential reduction of the metal ion interferent in solution to a different valency state or to the free metal can cause precipitation of that valency species that can either co-precipitate the metal of interest, adsorb the volatile hydride formed, catalytically decompose it or slow down or completely stop its evolution from solution."

On one hand, potassium thiocyanate has been used to produce 87% recovery of arsenic in the presence of 1000 μg/mL of nickel.[54] On the other hand, it has been used by Peacock and Singh to recover 84%, 83% and 83% of arsenic in the presence of cobalt, nickel and copper, respectively.

A suppressant which could overcome the interference effects from 1000 μg/mL of copper(II), nickel(II), cadmium(II), iron(III) and cobalt(II) individually and also when all were put together was investigated. The cornerstone of the investigation was that any suppressant which formed a precipitate with any of the metal ions under consideration was unacceptable, because the formation of a precipitate would not only require filtration, which would increase analysis time, but also the problem of adsorption and co-precipitation of arsenic would have to be resolved.

Potassium thiocyanate was not considered in this work because of the precipitate it forms with copper and cadmium: Neither was potassium iodide considered, because of its formation of a precipitate with copper. Furthermore, diethyldithiocarbamaic acid (sodium salt) and 1,10-phenanthroline formed a precipiate with copper and cadmium. Thiosemicarbazide also formed a precipitate with copper. Ethylenediaminetetraacetic acid was found to be less efficient because of its limited solubility and pH dependent efficienty. However, 1,3-diethyl-3-thiourea, 1-phenyl-3-thiosemicarbazide, tris-(isobutyl)phosphorus sulphide, and triphenyl phosphine were eliminated on the grounds that they were insoluble in acidified deionized water.

According to Nakahara *et al.*[26] 6 M hydrochloric acid, 1% potassium iodide, and 10% malic acid gave 65% recovery of 0.03 μg/mL of arsenic in

Table 10. Summary of the interference studies on hydride generation of 0.3 µg/mL of arsenic

Composition and concentration of metal ions	Suppressants				
	1.4 M hydrochloric acid*	1.4 M hydrochloric acid and 3.0% (wt/vol) thiourea	1.4 M hydrochloric acid and 1% (wt/vol) cystine	5 M hydrochloric acid	5 M hydrochloric acid and 3.0% (wt/vol) cystine
1000 µg/mL nickel	0	94	95	--	--
1000 µg/mL cobalt	0	93	94	--	--
1000 µg/mL iron	88	94	100	--	--
1000 µg/mL copper	15	58	95	99	--
1000 µg/mL cadmium	18	58	36	103	--
A mixture of 1000 µg/mL of nickel, cobalt, iron, copper and cadmium	0	--**	--	--	85

Results are percent recoveries
* 1.4 M hydrochloric acid is approximately equal to 12% (volume/volume).
** -- indicates not tested

the presence of 1000 µg/mL of copper; 75% recovery was accomplished in the presence of 6 M hydrochloric acid; and 100% recovery was noted in the presence of 6 M hydrochloric acid and 10% malic acid. The trend clearly shows that potassium iodide has a negative impact on the efficiency of 6 M hydrochloric acid and 10% malic acid. The adverse effect of potassium iodide is compatible with the fact that it forms a precipitate with copper in solution.

The recoveries obtained when hydrochloric acid concentration (which is equivalent to approximately 1.4 M) was used as the suppressant are summarized in Table 10. These results are not similar to the 5% and 55% recoveries of arsenic in the presence of about 1000 µg/mL of cobalt and copper, respectively, as have been reported by Dornemann and Kleist.[57] The reason is probably because they used 5 mL of 5% (weight/volume) of sodium borohydride on 8.3 ng/mL of arsenic in 1 M hydrochloric acid, as opposed to 1 mL of 4% (weight/volume) of sodium borohydride on 0.3 µg/mL of arsenic in 1.4 M hydrochloric acid used in the present studies.

The work by Dornemann and Kleist[57] showed a constant recovery of 5% of arsenic in the presence of approximately 500, 1000, 2000, 4000 and 5000 µg/mL of cobalt. The trend is indicative of the fact that they did not apply background correction which could have been caused by scattering from hydrogen. This correction was necessary since they used an atomic absorption spectrometer in their studies. However, they have also utilized pyridine-2-aldoxime to overcome interferences from 1000 µg/mL. or higher of metal ions of cobalt, nickel, copper and iron.

Based on the prognosis by Peacock and Singh about the possibility of using thiourea to overcome the interferences from higher concentrations of copper, silver, cobalt and nickel, thiourea was evaluated. According to Table 10, 3.0 % (weight/volume) of thiourea recovered 94%, 93% and 94% of 0.3 µg/mL of arsenic in the presence of nickel, cobalt and iron, respectively, while 58% was recovered in the presence of both copper and cadmium.

One intriguing observation with copper was the disappearance of its blue colour, and the formation of a clear solution on the addition of thiourea. The solution turned cloudy later. The cloudy solution was allowed to stand for a while, and the resultant precipitate was filtered. Mass spectrometric analysis indicated that the precipitate was pure sulphur. Investigation showed that the copper(II) was reduced to copper(I).

Cystine proved more potent compared with thiourea. The recoveries of arsenic are shown in Table 10. However, it produced 36% recovery of arsenic in the presence of cadmium.

Aggett and Aspell[16] have used 5 M hydrochloric acid to suppress the interference effect from 1000 µg/mL of copper. This, they attributed to the formation of chloro complex. When the idea was tested, it produced 99% recovery of arsenic. This was further extended to overcome the interference from 1000 µg/mL of cadmium. A recovery of 103% of arsenic was obtained.

Finally, 5 M hydrochloric acid and 3% (weight/volume) of cystine were utilized to yield a recovery of 85% of arsenic in the presence of a mixture of 1000 μg/mL of nickel, cobalt, iron, copper and cadmium. Thus, so far, a combination of hydrochloric acid and L-cystine can be used to resolve the interferences from nickel, cobalt, iron, copper and cadmium.

IX. Recommendations

Because of the so-called foaming which occurred with soil samples, antifoam "B", and large use of the sodium borohydride, the reactor should be re-designed. The new design should direct the argon through the top and centre of the reactor. The tubing carrying the argon could be fitted to a glass tube with a fritted glass at the end.

Also, an all glass apparatus would prevent the possibility of arsine diffusing into the rubber before it is flushed.

The interferences from other hydride forming elements such as bismuth, selenium, tellurium and tin on arsenic hydride have been reported by Smith.[50] Further work should therefore be carried out to resolve the above issue.

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Appendix

The weights of the trivalent arsenic peaks in Figure 15 were (X), 5.6, 4.8, 6.6, 6.0 and 5.6 mg. The $\bar{X}$ was 4.72 mg and the estimated standard deviation was 0.58 mg. The weights of the pentavalent arsenic peaks were (Y), 6.7, 5.6, 5.6, 6.8, and 6.5 mg. The mean $\bar{Y}$ was 6.24 mg and the estimated standard deviation was 0.53 mg.

$$t_{calculated} = \frac{|\bar{X} - \bar{Y}|}{S\sqrt{\frac{1}{n_x} + \frac{1}{n_y}}} \qquad (1)$$

S = pooled standard deviation of Y and X

n_x = number of X measurements

n_y = number of Y measurements

$$S = \sqrt{\frac{\sum(X_i - \bar{X})^2 + \sum(Y_i - \bar{Y})^2}{n_x + n_y - 2}}$$