TOXIC HEAVY METALS IN GROUNDWATER OF A PORTION OF THE FRONT RANGE MINERAL BELT

Partial Completion Report

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by

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ABSTRACT

Anodic stripping voltammetry and gas chromatography have been investigated with respect to their suitability for multielement analyses of trace elements in natural waters. The elements of interest in this study of toxic and esthetically undesirable elements in the regional ground waters of the Front Range Mineral Belt are arsenic, cadmium, copper, iron, lead, manganese, mercury, selenium, silver, and zinc. Atomic absorption spectrophotometry is commonly used for analysis of these elements but permits only one element to be determined at a time.

Anodic stripping voltammetry was found to be highly sensitive and suitable for determination of low concentrations of cadmium, copper, lead, manganese, and mercury. For most of these elements the reproducibility was excellent at the ppb concentration level. Compared with direct flame atomic absorption, this method was found to be more sensitive but not significantly faster despite determination of several elements per analysis.

Gas chromatography was investigated for analysis of arsenic, antimony, and selenium by generation and separation of their hydrides. The method was found to be difficult to use effectively and not sufficiently sensitive for natural water analysis.

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INTRODUCTION

A variety of toxic elements are known to occur at measurable levels in rocks and soils within regions of sulfide mineralization. Where the mineralization is sufficiently intense, mining activity brings in significant numbers of workers and their families who frequently rely on ground water for their domestic needs. In the Front Range Mineral Belt of the Colorado Rockies, the scenic terrain of the mineralized region and its close proximity to the Denver metropolitan area have also resulted in considerable development for both residential and recreational purposes. A significant proportion of this development is in unincorporated areas with no municipal water supply. There are thus many single-user domestic wells of varying depths in and near the highly mineralized zone.

This research project was initiated as a limited scale study of the quality of well waters within a portion of the Front Range Mineral Belt, and interpretation of the findings, in terms of both human hazards and the regional geology. The four specific goals of the project are as follows:

1. Sampling and chemical analysis of domestic ground water supplies in the Clear Creek basin of the Colorado Front Range. Elements included are arsenic, cadmium, copper, iron, lead, manganese, mercury, selenium, silver, and zinc.
2. Evaluation of existing analytical methods for determination of trace levels of toxic elements and development of new analytical methods where appropriate.
3. Determination of the magnitude of a possible health hazard from toxic elements in domestic supplies.

4. Analysis of the relationship of ground water quality to geology and mining activity in the Clear Creek basin.

The second objective was given priority so that suitable methods of analysis could be established for the study. This report is a summary of the investigations carried out on methodology and selection of techniques for the remainder of the project.

The principal elements of interest are known to be toxic at relatively low levels and sensitive techniques are therefore required. Maximum acceptable concentrations proposed by the Environmental Protection Agency (1) are as follows (concentrations in mg/ℓ): Ag 0.05, Cd 0.01, Hg 0.005, Pb 0.05, and Se 0.01. The U.S. Public Health Service (2) recommends the following limits for the other elements included in this study (in mg/ℓ): Cu 1.0, Fe 0.3, Mn 0.05, and Zn 5. In the cases of Fe and Mn, the limits are set mainly for esthetic reasons (taste, color, turbidity) rather than because of toxicity.

A variety of analytical methods are available for these elements and the most generally accepted procedures are adequately described in publications by certain governmental agencies and professional societies (3, 4, 5, 6). Conventional atomic absorption spectrophotometry (AAS) is widely used for determination of cadmium, copper, iron, lead, manganese, silver, and zinc, flameless atomic absorption is used for mercury, colorimetry or atomic absorption for arsenic, and colorimetry or fluorometry for selenium. Each of these methods is capable of determining one element at a time. Primary emphasis in the research reported herein was placed on examination of methods suitable for the determination of two or more elements simultaneously and in elimination of interferences which are potential sources of error in certain of the analyses.

Several techniques such as polarography, anodic stripping voltammetry (ASV), neutron activation analysis, x-ray fluorescence, emission spectroscopy, mass spectrometry, and gas chromatography are capable of multi-element analyses from a single analytical procedure. Most of the techniques are impractical from one or more of the standpoints of cost of equipment, time required for analyses, sensitivity, and accuracy. Only anodic stripping and gas chromatography were considered to be of practical value for multi-element determinations in the present study.

Anodic stripping analysis is a highly sensitive analytical method for elements which can be readily electroreduced to the free metals in a mercury electrode and can then be reversibly reoxidized as the electrode is made progressively more positive. Measurement of the peak height or peak area on a current-voltage plot (or current-time plot, where time is proportional to voltage in the oxidizing portion of the cycle) is used to determine the concentration of each ion in the original solution. Not all metals can be analyzed by this technqiue, but it seemed worthy of examination for Cd, Cu, Hg, Mn, Pb, and Zn in this study.

Gas chromatography is not a conventional analytical method for elemental analysis; however, when metals can be converted into a volatile chemical form the method can be used, with certain limitations. The GC study reported herein is an examination of conversion of the metalloids As, Sb, and Se into volatile hydrides followed by their gas chromatographic separation and analysis. This technique was suggested by the recent interest in atomic absorption analysis of these elements by hydride generation followed by atomization of the free elements in an argon-hydrogen-entrained air flame.

All of the elements listed above for inclusion in the present study can be analyzed by atomic absorption procedures. The examination of anodic stripping and gas chromatography was based on the desirability of finding a rapid, sensitive, interference-free method capable of simultaneously determining several elements.

The report which follows is divided into two parts.

1) Determination of arsenic, antimony and selenium in water by gas chromatography.
2) Determination of trace concentrations of transition metals in water by anodic stripping voltammetry.

Determination of Trace Metals in Water by Anodic Stripping Voltammetry

Anodic stripping voltammetry is a highly sensitive technique for determination of metals in aqueous solution. This fact together with the capability of simultaneous multi-element analyses makes ASV a particularly attractive method for natural water analysis. The apparatus consists essentially of an electrochemical cell in which all metals of interest are reduced to the elemental state by making the cathode sufficiently negative. After electrodeposition for a predetermined period of time, the working electrode is made the anode by raising its potential at a constant rate. The metals are sequentially reoxidized as governed by their electrochemical potentials, the composition of the working electrode, and properties of the solution. The magnitude of the peak current accompanying reoxidation of a metal is normally directly proportional to the amount of metal available at the working electrode which, in turn, is directly proportional to the ionic concentration of the metal in the analyte. The working electrode is most frequently either a mercury drop or mercury film in which the free metals may dissolve.

For speed of analyses, the film electrode is preferable because of the short distance the metals must travel through the mercury before being oxidized and reentering the solution in the anodic process. Because of the longer diffusion path in a mercury drop electrode, the oxidation process must be carried out more slowly. The apparatus used in the present study utilizes a freshly deposited mercury film for each analysis. It is also designed for rapid purging of oxygen from the system to further accelerate analyses.

Apparatus

All experiments were performed on a McKee-Pedersen ElectRoCell. The ElectRoCell was used with MP-system 1000 modules as described by Clem (7). The voltammograms were recorded on a Houston Instruments recorder (Model 1511).

The reference electrode was a saturated calomel electrode, the counter electrode was platinum foil, and the working electrode was a thin film of mercury on a paraffin impregnated graphite electrode. The mercury was plated onto the electrode from solution during each analysis. Preparation of the graphite electrode consists of impregnating a graphite rod with a paraffin under vacuum. The procedure is described in the MP ElectRoCell instruction manual (8).

Reagents

All metal standards were prepared from the metals dissolved in doubly-distilled nitric acid and diluted with deionized-distilled water. All metal standard stock solutions were stored at the 1000μg/mℓ level in polyethylene bottles at a pH of 2.0 or less.

$Hg(NO_3)_2$ solution was prepared by washing triply-distilled mercury with 0.01 M nitric acid, and then dissolving the mercury in doubly-distilled nitric acid. The KCl used as supporting electrolyte was purified by recrystallization from saturated ammonia solution. All glassware and polyethylene were thoroughly acid cleaned.

Two standard solutions containing concentrations of dissolved metals comparable to those found in acid mine drainages in the Clear Creek drainage (9) were synthesized. The composition of these mine drainage waters should be characteristic of the most adverse possible well water contaminations in the area. Dilutions of the mixed standards were used in testing for sensitivity and freedom from interferences in the ASV analyses. Standard A contained high concentrations of sulfate and chloride, whereas Standard B contained no chloride and lower sulfate. Nitrates, oxides, and carbonates were used in preparation of standard B, with the exception of iron which was prepared from $FeSO_4 \cdot 7H_2O$. Composition of the elements of interest for these standards are shown in Table 1.

Procedure

The general analytical procedure used is described by Clem (7). A 15-ml sample at pH 2.5 (3.5 for Mn analyses) was pipetted into the cell. 0.2 ml of 2.0 M KCl and 0.2 ml of 0.133 mg/ml $Hg(NO_3)_2$ solution was added (repipeter). The solution was deoxygenated by rapidly rotating the cell while flowing in nitrogen at a high flow rate. Plating was then carried out for 5 minutes while the cell was rotated in alternating directions in order to stir the solution.

TABLE 1

Composition of Mixed Standards

Standard A

Element	Concentration (μg/ml)
Na	40
K	16
Ca	360
Mg	300
Fe	800
Mn	300
Zn	160
Cu	100
Cd	2
Pb	1
As	2
($SO_4^=$)	4,000
($Cl^=$)	463

Standard B

Element	Concentration (μg/ml)
Na	40
K	16
Ca	360
Mg	300
Fe	800
Mn	300
Zn	150
Cu	100
Cd	5
Pb	8
As	2
Ag	5
($SO_4^=$)	1,400

The plating voltage was maintained constant at a level dependent upon the metals being analyzed. The elctrode was stripped (made progressively more anodic) at a rate of 1.2 volts/minute. The stripping process was stopped when the working electrode reached +0.40 volts with respect to the reference electrode. At this point, if the method of standard additions was used, microliter volumes of appropriate standard solutions were added as "spikes" and the analysis was repeated. In all solutions analyzed the metals being determined were present in the concentration range from 1.0 to 200 ng/ml.

Results

Samples were analyzed by both the standard additions method and by use of calibration curves. The results of analyses by the two methods are presented along with results obtained by atomic absorption in Tables 2-5.

The stripping process in the analyses is carried out to a sufficiently high voltage to completely strip the mercury from the working electrode subsequent to stripping the metals dissolved in it. Since a mercury-free electrode is therefore available at the start of each analysis, the electrode may be used for determination of mercury in the sample. The procedure is modified to the extent of omitting the addition of mercury to the sample and using a plating potential of -0.2 volt with respect to the calomel reference electrode. The mercury is then stripped and its peak height measured. Results of mercury analyses on standard samples are shown in Table 6. The concentration of Hg in most samples is much less than is required for the ASV analysis of other metals. However, after completion of an Hg analysis, an aliquot of standard mercury solution may be added and the analysis for other metals can then be performed on the same solution.

Discussion

The anodic stripping method of analysis proved to be a highly sensitive and reliable method for determination of Cd, Cu, Hg, Mn, and Pb in natural and synthetic waters. The precision of the method was generally excellent and good agreement was obtained with atomic absorption analyses of the same samples by other investigators. The agreement between analyses performed by standard additions and by use of standar curves was excellent, with the exception of manganese analyses. Internal agreement between the two ASV methods was generally somewhat better than agreement between ASV and AAS. There appears to be little justification for use of the much more time consuming standard addition method for the samples we have analyzed. It is quite possible, however, that other types of samples would have significant interference problems that would necessitate use of standard additions, at least for random checks.

Good linearity between peak height and concentration was obtained over the ranges tested. An upper limit to the linear response was not evaluated. Figures I-A, I-B, and IC are calibration curves obtained for Cu, Pb, and Cd, respectively.

Anodic stripping voltammetry is a reliable technique in the hands of a competent analyst. Careful control of conditions is mandatory and frequent standards should be run to assure that performance of the working electrode has not been impaired. In the McKee-Pedersen method used, it was found that the electrode

Table 2

Determination of Cu in mixed standards and in well waters by anodic stripping voltammetry (ASV) and atomic absorption spectrophotometry (AAS).

Sample	Actual Conc. (ng/ml)	Conc. by ASV (ng/ml)		Conc. by AAS (ng/ml)
		Std. Add.	Calib. Curve	
1/1000 Std. A	100.0	93.3		
1/1000 Std. B	100.0	95.3		
016A		223	232	240
018A		54.0	54.1	50
025A		554	543	600
040A		676	664	620

Table 3

Determination of Pb by ASV and AAS

Sample	Actual Conc. (ng/ml)	Conc. by ASV (ng/ml)		Conc. by AAS (ng/ml)
		Std. Add.	Calib. Curve	
1/1000 Std. A	1.0	0.91		
1/1000 Std. B	8.0	7.4		
016A		1.2	1.2	1
018A		1.4	1.3	1
019A		1.3	1.2	1
021A		2.4	2.5	2
025A		4.1	3.8	4
027A		3.2	3.3	3

Table 4
Determination of Cd by ASV and AAS

Sample	Actual Conc. (ng/ml)	Conc. by ASV (ng/ml) Std. Add.	Conc. by ASV (ng/ml) Calib. Curve	Conc. by AAS (ng/ml)
1/1000 Std. A	2.0	2.1		
1/1000 Std. B	5.0	5.1		
016A		73.8	83.7	80
018A		1.1	.9	1
021A		1.1	1.1	1
025A		151.	158.	170
040A		86.5	89.4	80

Table 5
Determination of Mn by ASV and AAS

Sample	Actual Conc. (ng/ml)	Conc. by ASV (ng/ml) Std. Add.	Conc. by ASV (ng/ml) Calib. Curve	Conc. by AAS (ng/ml)
1/1000 Std. A	300	332		
1/1000 Std. B	300	326		
016A		3,760	3,250	4,000
025A		11,700	9,200	10,000
040A		20,800	17,500	19,000

Table 6
Determination of Hg in Standard Samples by ASV

Actual Conc. (ng/ml)	Conc. Found (ng/ml) Standard Additions	Conc. Found (ng/ml) Calibration Curve
1.0	1.2	1.0
5.0	5.0	5.0
25.0	25.6	27.2
50.0	48.9	47.4
100.0	96.7	107.3

performance would occasionally show an abrupt deterioration for reasons which were not apparent. Although upper concentration limits were not determined in this study, ASV has been found by other investigators to be useful primarily in the sub-ppm concentration range. It is particularly useful as a technique for analysis in the ng/l (ppb) concentration range where flame atomic absorption is not sufficiently sensitive. It was found to be a somewhat more time consuming and demanding analytical method than AAS at concentrations where either technique is usable.

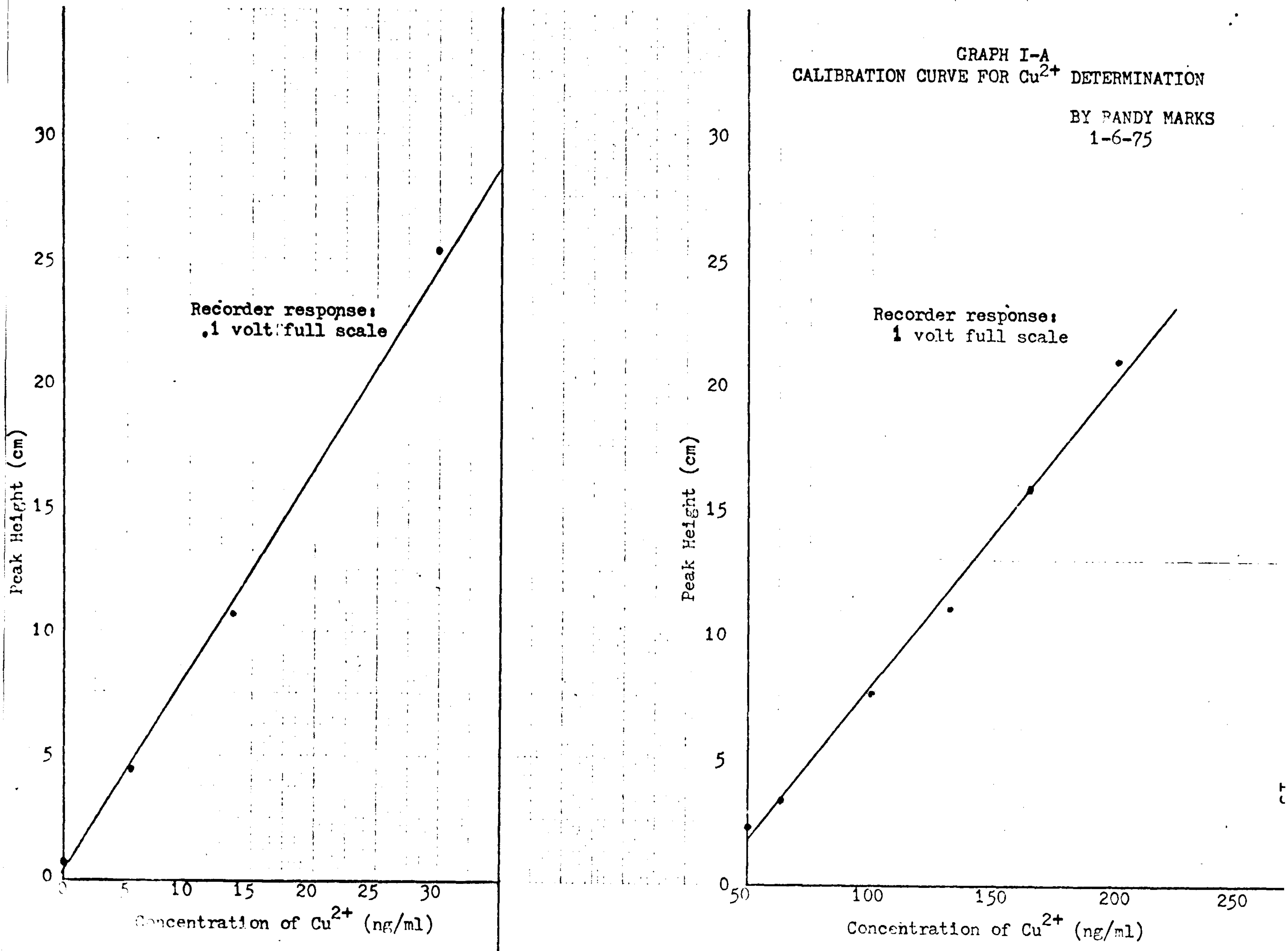
Determination of Metalloids in Water by Gas Chromatographic Analysis of Their Hydrides

Arsenic, antimony, selenium, bismuth, germanium, tellurium, and tin can be reduced in aqueous solution to their hydrides in the presence of a reducing agent sufficiently strong to generate hydrogen by reaction with water or hydronium ion. Several reducing agents have been used with varying degrees of success. These include finely divided zinc (usually in combination with potassium iodide and stannous chloride), magnesium metal in combination with titanium trichloride, and sodium borohydride.

The classical method for determination of arsenic in water involves the generation of arsine, AsH_3, by reduction of trivalent arsenic with zinc in acidic solution (10, 11). Potassium iodide and stannous chloride are usually added to help reduce the arsenic. The generated arsine is then absorbed in a solution of silver diethyldithiocarbamate with which it reacts to form a soluble red product having an adsorption peak at about 535 nm. The absorbance

GRAPH I-A
CALIBRATION CURVE FOR Cu^{2+} DETERMINATION

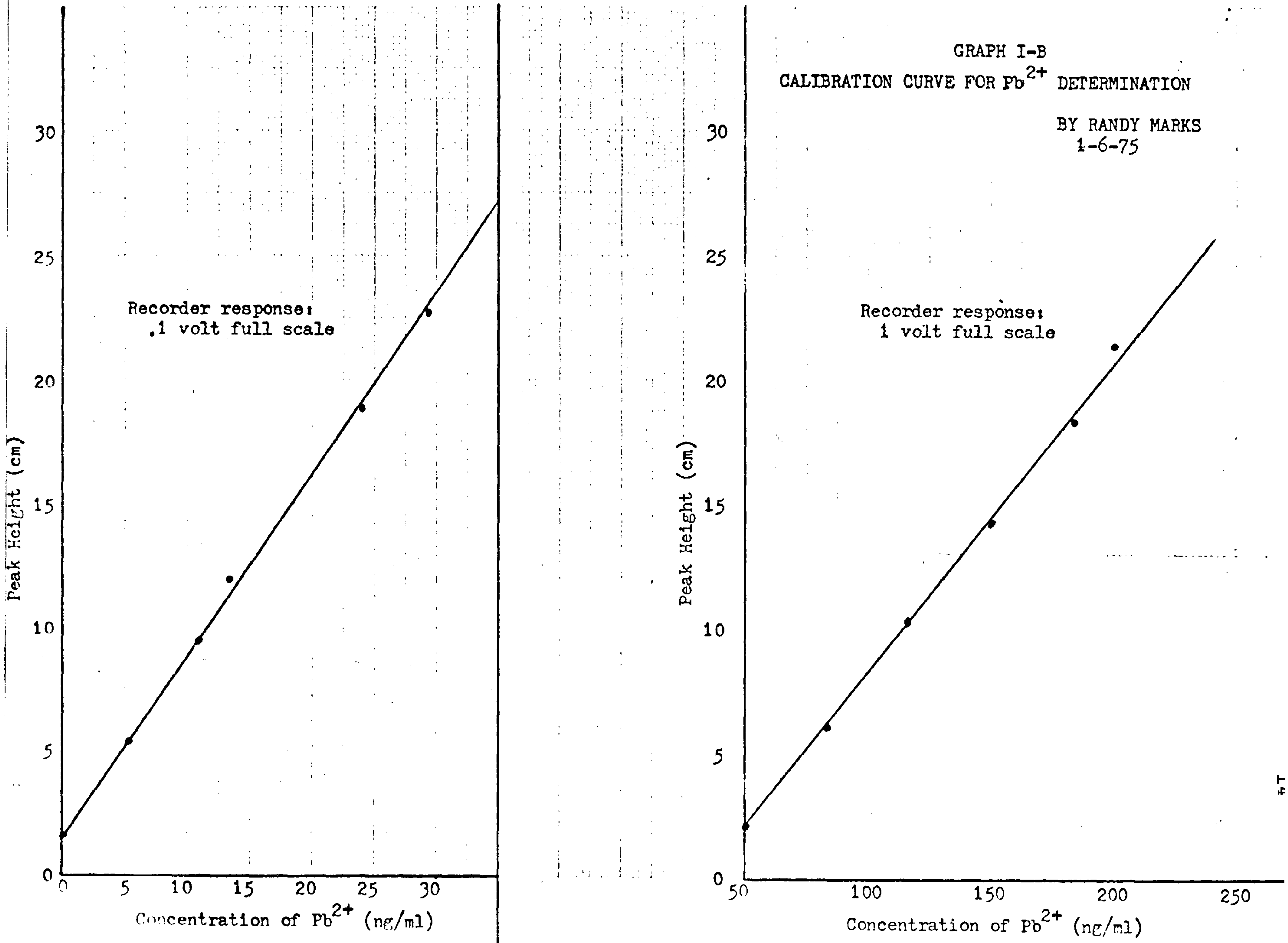
BY RANDY MARKS
1-6-75



GRAPH I-B

CALIBRATION CURVE FOR Pb^{2+} DETERMINATION

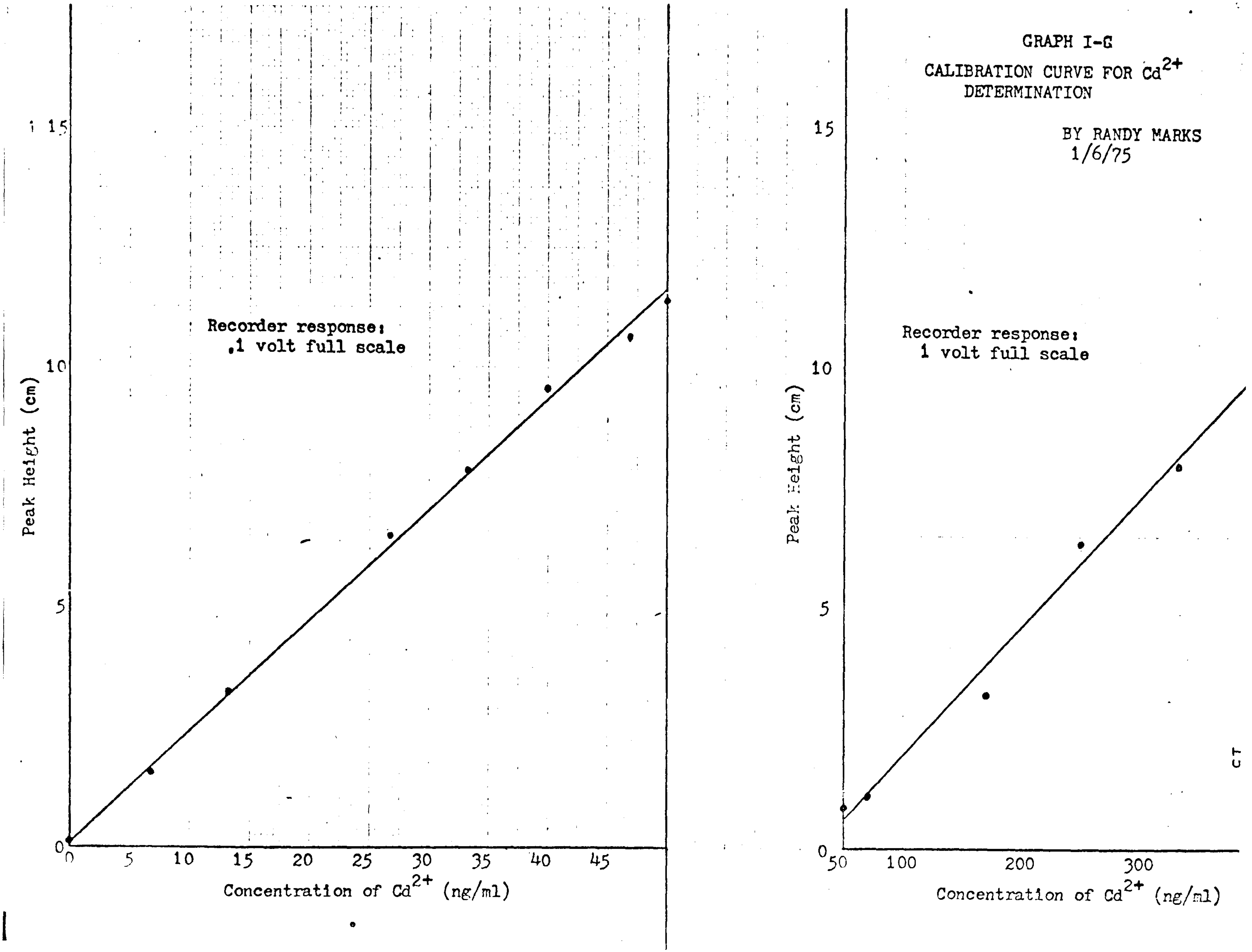
BY RANDY MARKS
1-6-75



GRAPH I-G

CALIBRATION CURVE FOR Cd^{2+} DETERMINATION

BY RANDY MARKS
1/6/75



of this solution is measured to determine As present in the original solution at concentrations of 0.02 to 1.0 mg/l.

Determination of arsenic by reduction to arsine followed by atomic absorption analysis has received much recent attention and is becoming fairly widely used. Hwang and others (12) and Yamamoto and others (13, 14) have retained the zinc-$SnCl_2$-KI reduction procedure whereas Pollock and West (15) have used stannous chloride and magnesium for the reduction. Schmidt and Royer (16) and Fernandez (17) found sodium borohydride to be an effective reducing agent. The arsine generated by any of these procedures is swept by argon or nitrogen into a hydrogen-entrained air flame of an atomic absorption spectrophotometer. A detection limit in the range of 0.1 to 1 μg/ℓ is obtained by this technique.

Antimony, selenium, germanium, bismuth, and tin have also been determined by the atomic absorption analysis of their hydrides. Fernandez (17) recommends sodium borohydride as the most effective reducing agent. Detection limits are in the nanogram range.

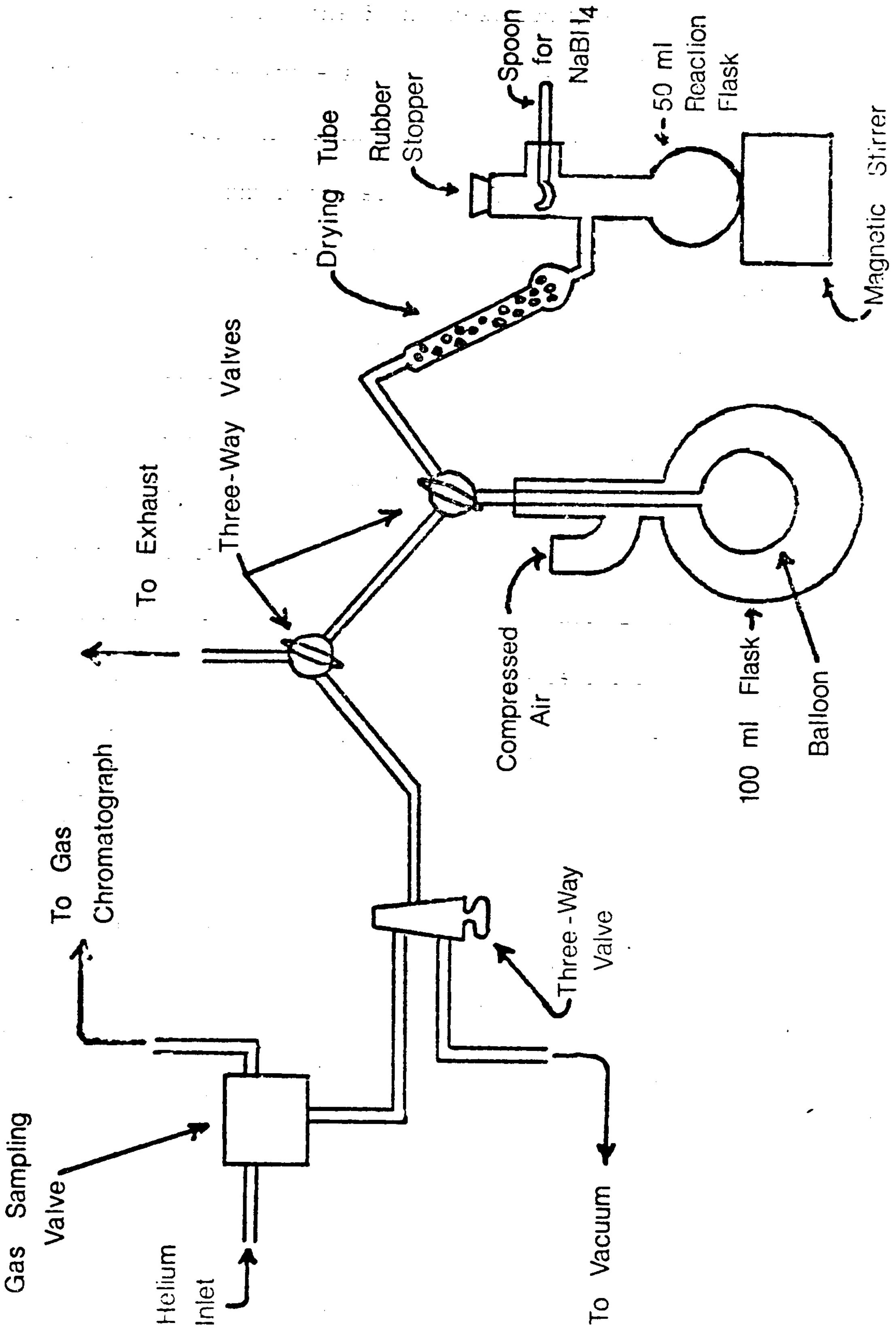
The above procedures normally permit the determination of only one element at a time. If two or more of the metalloids are to be determined, it is necessary to carry out a separate reduction for each element. Although the atomic absorption technique is relatively rapid, a method which allows the simultaneous determination of several hydrides would have a distinct advantage from the standpoint of economy of time and reagents. Use of a gas chromatograph for the simultaneous determinations is a logical choice and was investigated in our laboratory. The results of this study are reported in detail in Colorado School of Mines thesis T-1645 (18) by Robert R. Rostad. The following is a summary of this research.

Apparatus and Procedure

A Beckman GC-5 gas chromatograph using a helium ionization detector was used throughout this work. Two columns in series were used for the separation of the hydrides. The first column was 12 feet of 1/8 in. -OD stainless-steel packed with 20% Dow Corning-200 on 100-200 mesh Chromosorb W (HP). The second column was 8 feet of 2 mm -ID glass tubing packed with 12% Carbowax on 100-200 mesh Chromosorb W (AW). The helium carrier-gas flow rate was 20 cc/min and the column temperature was 5°C. This temperature was maintained by putting a beaker full of dry ice in the column oven and allowing the column heater to work against the cooling effect of the dry ice. The detector output signals were recorded by a strip chart recorder having a span of 0.to 1.0 mv.

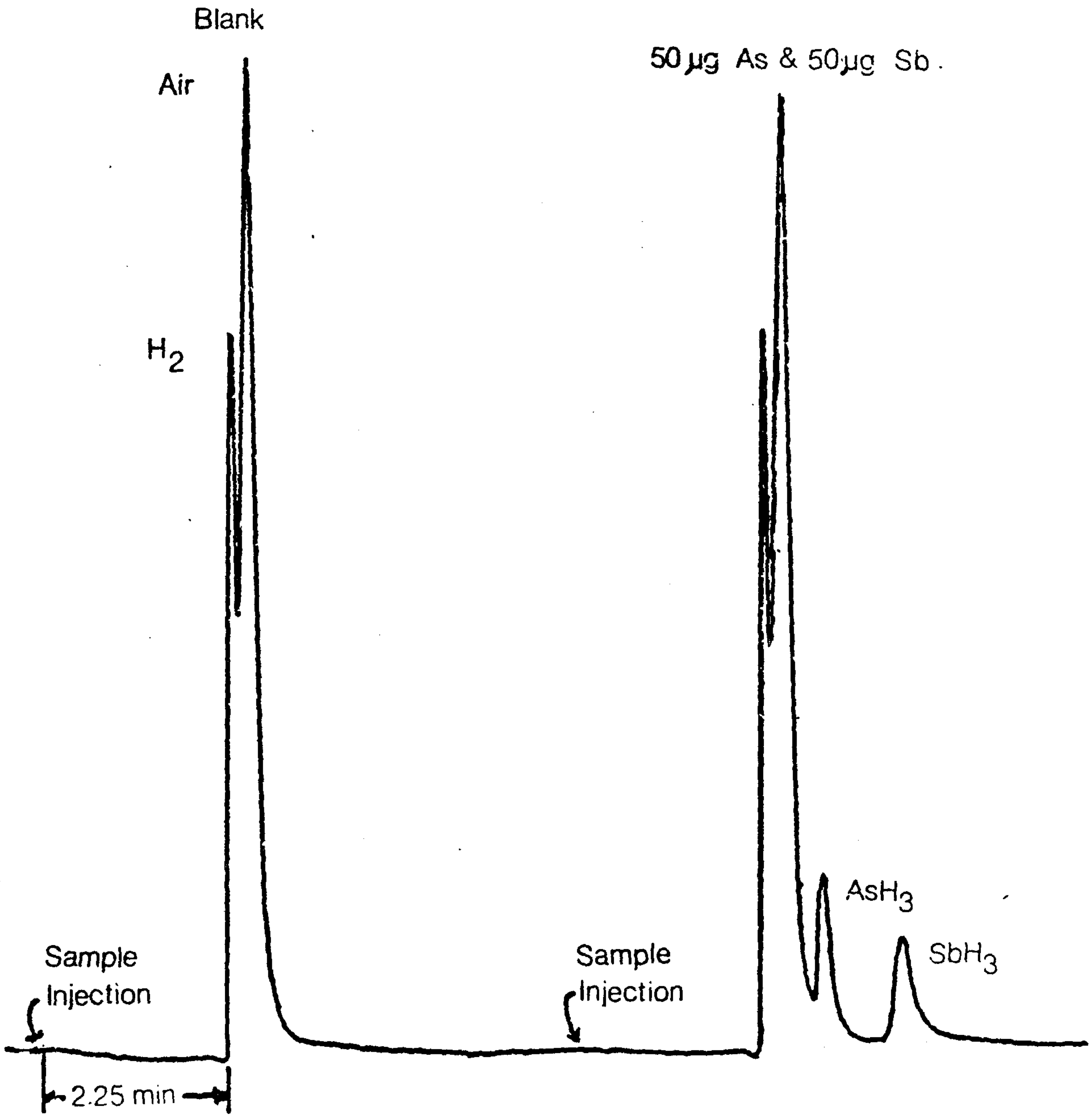
The apparatus used for generating and sampling the hydrides is shown schematically in Figure 2. In operation a 15-ml sample and 10 ml of HCl are added to the 50 ml reaction flask. This solution is cooled to room temperature and a vacuum is drawn on the reaction flask and balloon reservoir, using a water aspirator, until large bubbles just start to form in the sample. The sample is stirred vigorously with a magnetic stirrer while a sodium borohydride pellet is added. The pellet is dropped from a movable glass spoon mounted in a one-hole rubber stopper, allowing the vacuum to be maintained. The rubber stopper may be removed to put a new pellet on the spoon and also acts as a safety valve. The hydrides and hydrogen that are generated by the reaction of the sodium borohydride are passed through a drying tube filled with anhydrous calcium sulfate (Drierite) and then into the balloon. When the first 100 ml of gas is collected, that is, when the balloon just

Figure 2. Apparatus



fills the 100 ml flask, the three-way valves are switched to allow the rest of the generated gases to exhaust up the fume hood. When the reaction is complete (after about 30 sec.), the valves are again switched so that compressed air deflates the balloon and forces the collected gas into the 1.0 ml gas sampling valve. (Carle Instruments, Inc., micro volume valve). After the balloon has completely collapsed, the gas sampling valve is switched to inject 1.0 ml of gas into the chromatographic column. After each run, the apparatus is flushed with compressed air to remove any residual hydrides. In addition, the reaction flask is cleaned after each run by running a blank in it. A typical chromatogram is shown in Figure 3.

Figure 3. Typical Chromatogram



Column Selection

A limited number of columns were tested for separation of arsine and stibine. As will be discussed later, these were the only hydrides for which detection limits in the microgram range were obtained. The first column tested was a 12 ft., 1/8 in OD stainless steel column packed with 20% Dow Corning -200 on 100-200 mesh Chromosorb W(HP). A fairly good separation of arsine and stibine peaks was obtained at 5 ± 5°C. However, the arsine peak was not sufficiently well separated from the air peak. A 6 ft., 1/8 in. stainless steel column packed with Poropak-T, a porous polymeric material not requiring a liquid phase, was next tested. At 30°C very broad peaks were obtained which were not well resolved. Raising the temperature improved resolution, but because of the thermal instability of the hydrides, a temperature was not found at which both good resolution and good reproducibility were obtainable.

Columns packed with 3% SE-30 on Chromosorb W and 12% Carbowax -600 on Chromosorb W (AW) were found to have very poor resolution. The most effect separation obtainable from columns tested was found to result from combination of the 12 ft. 20% Dow Corning -200 column in series with an 8 ft., 2-mm ID glass column packed with 12% Carbowax -600. Many additional column packing materials and % loadings are possible and it is very probable that a more satisfactory column can be found for the hydride separations.

Column Temperature and Flow Rate

Despite the use of a drying agent in the gas stream, it was considered possible that traces of water vapor may enter the chromatograph column. To avoid possible difficulties due to formation of ice crystals, the column temperature was maintained above 0°C. A low temperature was found desirable, however, for maximum resolution. A temperature of 5°C (±5°) was therefore maintained. A helium carrier gas flow rate of 20 cm^3/min was found to be most effective in maximizing peak separations.

Sample Volume

Because of the relatively poor sensitivity found in this study, it was necessary to use the maximum possible sample volume. Various sample volumes were tested by injecting air and air-hydrogen-hydride samples into the column using a gas syringe. Samples much larger than 1.0 ml were found to produce broad, unsymmetrical peaks, but 1.0 ml was satisfactory. A 1.0 ml gas sampling valve was therefore used in the remaining investigations.

Parameters Affecting Sensitivity and Resolution

Sodium borohydride reacts with an acid solution to rapidly release hydrogen gas in large excess over the amount stoichiometrically required to produce hydrides of the metals studied. This excess is essential to the complete reduction to hydrides. The hydrogen therefore constitutes the major fraction of the evolved gases. Attempts to condense the metal hydrides while allowing the hydrogen to escape met with limited success. In principle, separation of the hydrides followed by revaporization for injection into the gas chromatograph should give a considerable enhancement of sensitivity over injection of the hydrogen-hydride mixture. In practice, poor reproducibility was obtained at the microgram levels of interest. This may be due to irreversibly adsorption of hydrides on the condensation vessel.

By sampling the gases evolved on reaction of $NaBH_4$ with the acidified solution of metalloids, it was found that evolution of arsine and stibine occurred very rapidly. These hydrides can therefore be collected before complete decomposition of the $NaBH_4$, thereby increasing the hydride/hydrogen ratio in the sample. Maximum sensitivity and good reproducibility were obtained by collection of only the first 100 ml of gas evolved. Figure 4 shows the effect of chromatographic peak height on the volume of gas collected.

Because of the relatively poor separation of the arsine peak from the air peak, it is desirable to exclude air as completely as possible from the system. For this reason, a vacuum was drawn on the gas collection and sampling system before initiating the sample reduction. Exclusion of air significantly improved the reproducibility of arsine measurement.

A series of tests was carried out to evaluate the effect of acid concentration on arsine and stibine peak heights. Five to 6 <u>N</u> HCl was found to give the best sensitivity as shown in Figure 5

The oxidation state of arsenic and antimony was found to be important. $NaBH_4$ reacts rapidly with the trivalent metals, but only slowly with the pentavalent forms. A reducing agent capable of reducing As(V) and Sb(V) to the trivalent states was therefore necessary. Potassium iodide was found effective for this purpose.

Interferences

Ten milligrams or less of the following ions were found to give no measurable interference in determination of arsenic and antimony: Al^{+3}, Ba^{+2}, Cd^{+2}, Ca^{+2}, Cr^{+3}, Co^{+2}, Cu^{+2}, Fe^{+3}, Mg^{+2}, Mn^{+2}, Sr^{+2}, Li^{+}, Na^{+}, K^{+}, $NH_4{}^{+}$, Pb^{+2}, Ag^{+}, Cl^{-}, Br^{-}, I^{-}, $C_2H_3O_2{}^{-}$,

Figure 4. Peak Height vs Solution Volume

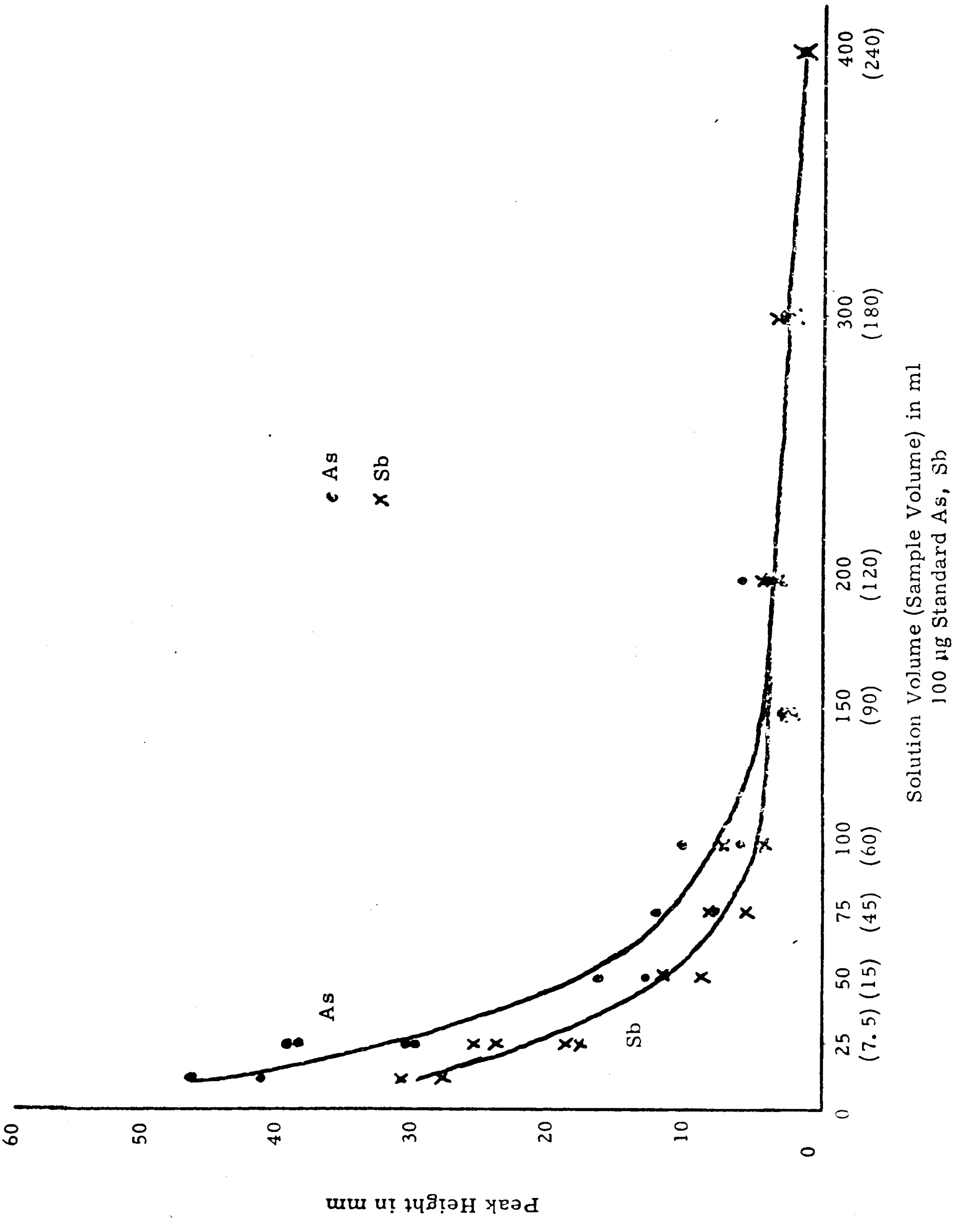
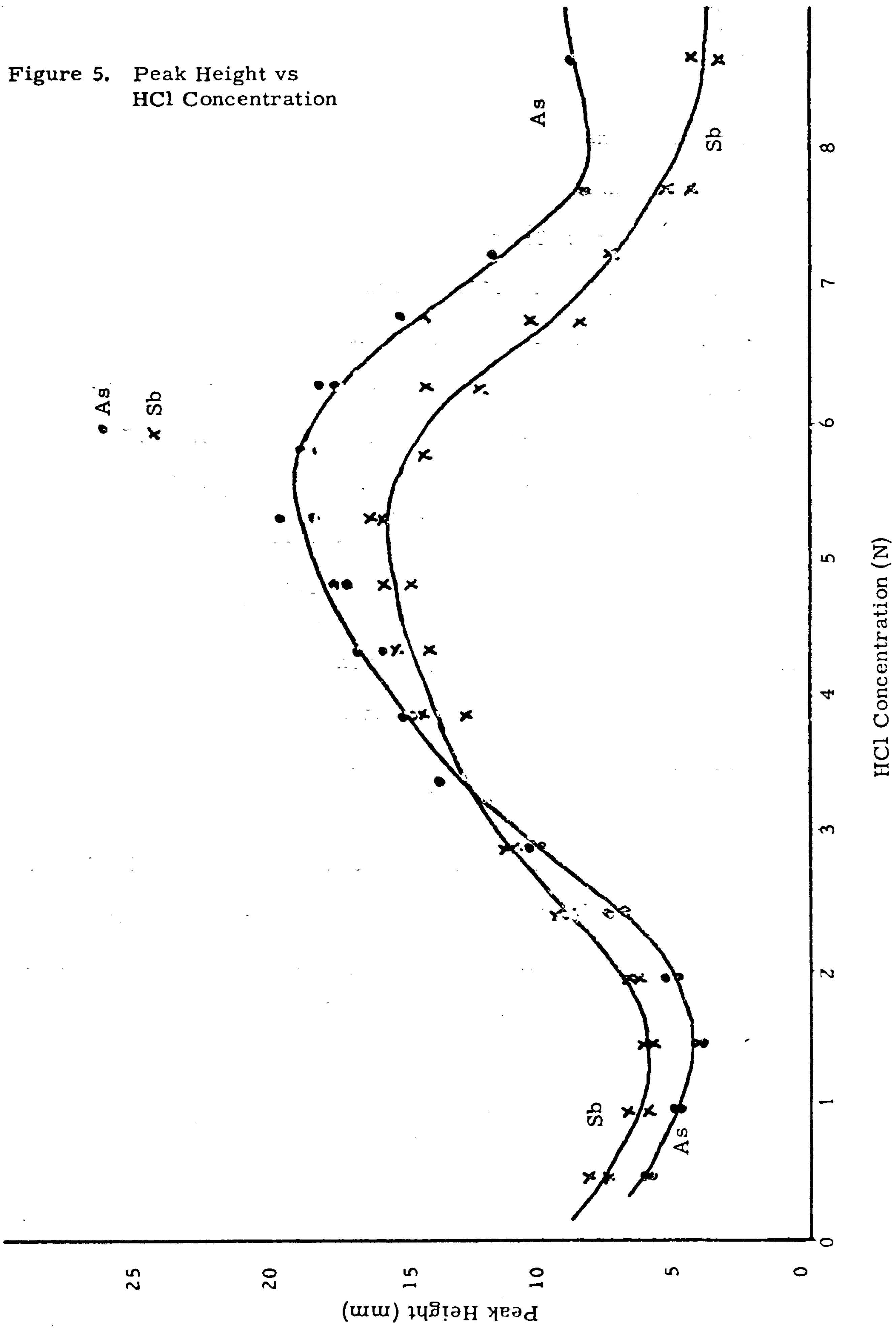


Figure 5. Peak Height vs HCl Concentration



NO_3^-, SO_4^{-2}, PO_4^{-3}.

A positive interference was detectable for 5 mg or more of Sn^{+4} and 10 mg or more of F^-. Negative interferences were detectable for 10 µg or more of $Cr_2O_7^{-2}$, 100 µg or more of Bi^{+3}, Hg^{+2}, and Se^{+4}, 1 mg or more of Ni^{+2} and 10 mg or more of Ge^{+4} and Te^{+4}. The Sn^{+4} interference may be due to As impurity in the Sn, but appears to be due to evolution of a small amount of SnH_4 which comes off the column with AsH_3. The negative interferences are probably due to a decrease in the rate of formation of AsH_3 and SbH_3.

Reproducibility and Detection Limit

Reproducibility was tested primarily by comparing the peak heights of 50 µg standard samples run on different days over a period of a month and determining the relative standard deviation of the peak heights. In addition, a smaller amount of data was compared using a different weight of standard arsenic and antimony. The results are shown below.

Element	Wt. (µg)	Average Peak Height (mm)	Peak Height Range (mm)	Number of Determinations	Relative Standard Deviation
As	50	18.9	16-21	40	7.4%
	150	48.9	47.5-50	4	2.3%
Sb	50	14.0	12-16	40	8.2%
	150	38.9	37-39.5	4	3.2%

The data for the 150 µg samples were all taken on the same day and show the relative standard deviation obtainable over a relatively short period of time.

A practical detection limit of 8 ug was found for both arsenic and antimony. This would be a concentration of 0.5 mg/l for the

15 ml sample volume used in most of this work. A lower detection limit is probably possible with better instrumentation than was available for this work.

Detection of Hydrides

Although Fernandez (17) has reported satisfactory atomic absorption analyses for a variety of elements when reduced to their hydrides with $NaBH_4$, only arsenic and antimony were detectable to a significant extent in this gas chromatographic study. Efforts were made to detect the hydrides of Bi, Se, Te, and Sn in the present study, but satisfactory results were not obtained. Al_2Se_3 was synthesized to test for H_2Se sensitivity. The Al_2Se_3 will react with water to produce hydrogen selenide and it therefore provides a certain source of this hydride. In analysis of H_2Se prepared in this way, three peaks were observed in the chromatogram. A large amount of Al_2Se_3 is required, however, so the sensitivity for the evolved gases is very unsatisfactory. The explanation for three peaks rather than one has not yet been adequately established.

In subsequent studies of interferences in the arsenic-antimony analyses, it was found that the hydrides of Ge, Sn, and S could also be detected, but only at very high concentrations of these elements in solution. The sensitivity was not sufficiently high to warrant detailed investigation in the present study. Since arsenic and antimony were the only elements for which a reasonably low detection limit was obtained, the remainder of this report is confined to analysis of these two elements.

Analysis of Natural Waters

The detection limit of 0.5 mg/l for both arsenic and antimony is not sufficiently low for most natural waters. Some acid mine drainages, however, do have high enough arsenic concentrations to be measured by this method. Two natural streams waters were also spiked with arsenic and antimony to determine if interferences occured. Results of these tests are summarized below.

Water Sample	As Added (mg/l)	As Found (mg/l)	Sb Added (mg/l)	Sb Found (mg/l)
Clear Creek	0	<8, <8	0	<8, <8
Clear Creek	3.33	3.4, 3.1	3.33	3.4, 3.1
S. Platte	0	<8, <8	0	<8, <8
" "	3.33	3.3, 3.4	3.3	3.2, 3.3

Water Sample	As Found by AAS (mg/l)	As Found by GLC (mg/l)	Sb Found (mg/l)
Argo Tunnel	.10	< 0.5	<0.5
Quartz Hill	.95	0.7	< 0.5
TW8		0.5	<0.5
TW17	7.8	4.9	<0.5
TW 22	< .003	<0.5	<0.5
TW 30	0.22	< 0.5	<0.5
TW36	0.11	<0.5	<0.5

Summary and Conclusions

Gas chromatography and anodic stripping voltammetry have been investigated as methods for simultaneous multielement analysis of trace metals and metalloids in natural waters. Atomic absorption spectrophotometry is commonly used for analysis of most of the elements of particular interest in this study and therefore it is with this technique that comparisons must be made. The value of the GC and ASV techniques as alternative methods is dependent on a) speed, b) sensitivity, c) accuracy and precision, d) cost, and e) ease of operation.

The gas chromatographic method studied was based on reduction of metalloids to hydrides in a manner similar to the technique now gaining acceptance for the atomic absorption analysis of arsenic, antimony, and selenium. Although the GC separation of As and Sb proved possible, the technique was disappointing from the standpoints of sensitivity, ease of operation, and versatility. Although Fernandez (17) has reported successful AAS analysis of many hydride-forming elements, a similar reduction technique was found to produce only AsH_3 and SbH_3 in sufficient amounts to be detectable below 1 mg/l in the GC analysis. Other hydrides could be detected at much higher levels, but were not studied in detail because of the very poor sensitivity. Even for As and Sb the detection limit is about two orders of magnitude greater than is desirable for water analyses. Furthermore, the technique was found to be somewhat cumbersome in operation. It is likely that somewhat better sensitivity and resolution can be obtained with more sophisticated equipment than was available to the present investigators, but the likelihood of obtaining reproducible results in the ug/l concentration range does not appear particularly good.

Anodic stripping voltammetry proved to be a much more satisfactory method of high sensitivity multielement analysis. Cd, Cu, Hg, Mn, and Pb were successfully determined at concentrations as low as 1 ug/l. (The lower detection limit for Mn was not determined because of its relatively high abundance in natural waters.) The method is fairly rapid, but does not afford a distinct advantage over atomic absorption in this respect. The primary advantage of ASV over AAS is the low detection limits which may be obtained without preconcentration of samples. Complexation with ammonium pyrolidene dithiocarbamate followed by extraction into methylisobutyl ketone is quite widely used to concentrate metals in water for atomic absorption analysis. This method is applicable to determination of a large number of metals in natural waters. Although the technique is relatively rapid, it significantly adds to the time required for AAS analyses. In both the ASV and AAS methods, considerable care must be exercised to avoid contamination. The problem is particularly acute in the case of lead where adsorption on glassware may be significant and where impurities in reagents may present difficulty.

Although ASV has a distanct advantage where very low detection limits are required, it was the experience of the present investigators that it is a more difficult technique than AAS to master. Reproducibility of electrode behavior was found to be somewhat difficult to maintain and extensive monitoring using reference standards or the standard addition technique is desirable. In the hands of a careful worker, good accuracy and precision are obtainable. Since the added sensitivity of ASV is not usually required for water analyses, it appears to have no clear cut advantage over atomic absorption for use in this project.

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