DEVELOPMENT AND EVALUATION OF A HYDRIDE TECHNIQUE
FOR As, Sb and Se DETERMINATIONS BY INDUCTIVELY
COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

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Development and evaluation of a hydride technique
for As, Sb and Se determinations by inductively
coupled plasma-atomic emission spectroscopy

by

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CHAPTER I. INTRODUCTION

Technological advances as well as environmental and biomedical concerns have generated a need for rapid and sensitive analytical determinations over wide concentration ranges of the Group IVA (Ge), Group VA (As, Sb, Bi) and the Group VIA (Se, Te) elements. Industrial uses of these elements include production of metal alloys, paints, ceramic enamels, glass, pottery, pesticides and bronzing agents (1, 2). High purity forms of all the elements either individually or as compounds are widely used as semiconductors (3, 4). In quite a different context, federal regulatory agencies are concerned with the toxicity of these elements as it relates to their occurrence levels in environmental and biomedical media. The toxicological and possibly carcinogenic aspects of Se and As have been reviewed elsewhere (5). Tellurium, antimony and germanium as well as certain of their compounds are toxic at concentrations as low as 0.1 ppm (1, 6).

The concentration levels of the elements present in the organisms and environment of a specific region depends upon its geochemical composition and socioeconomics. Persons who ingest food derived from animals which have grazed upon seleniferous plants may suffer from the toxic effects (7). Arsenic, being present in many pesticides (1), may similarly be drunk from potable water supplies. Arsenic and antimony, which are present as soluble salts in sea water (8), are

found in measureable quantities in certain marine fish tissues (9). If human consumption or inhalation of any As, Sb, or Se has occurred, these elements are usually present in urinary excretions. Because of dietary and environmental factors, wide deviations in concentration levels of those elements in urine are found (10). The concentration ranges of these elements in environmental samples may also cover several orders of magnitude. For example, selenium has been reported in water samples in the range of 0.1 to 100 $\mu\text{g/ml}$ (7).

The necessity for analytical determinations of all six elements obviously poses special problems because of the variation in the concentration ranges and matrices encountered. For these determinations, the analytical method should meet the following criteria.

1. Sufficient sensitivity or powers of detection to allow accurate determinations at the lowest probable occurrence level of the analyte.
2. Sufficient versatility to be useful for varied concentration levels and matrices.
3. Relative freedom from interference or interelement effects.
4. Capability of producing rapid analysis.
5. Instrumentation which is relatively inexpensive and does not require a highly skilled operator.
6. Minimal sample manipulation so as to reduce

contamination or loss of analyte prior to analysis.

7. Adaptability to sequential or simultaneous multi-element determination.

Three of the most sensitive multielement techniques applicable to the determination of traces of these elements are anodic stripping voltammetry (ASV), neutron activation analysis (NAA) and spark source mass spectrometry (SSMS). Although ASV is a readily available technique and provides relative detection limits in the ppb range, it is prone to interferences and requires the analyte to be in an electroactive form (11). NAA, which possesses absolute detection limits on the order of 10^{-8} to 10^{-10} gms for many elements, requires sophisticated irradiation sources and counting devices which are not readily available (12). In addition, NAA irradiation and counting periods may be long for those analytes possessing long half lives. Spark source mass spectrometry also requires more complex instrumentation than is readily available in most laboratories. Atomic absorption (AA), which is widely used for trace element determinations, experiences a variety of interferences because of the relatively low temperature and types of flames used (13-15) and is not amenable to simultaneous multielement determinations.

The inductively coupled plasma - atomic emission spectroscopy system (ICP-AES) has been shown to be superior to AA and flame emission techniques in detection power,

versatility and freedom from interferences arising in the atomization process (16, 17). The applicability of ICP-AES to a variety of sample types has been demonstrated (18). As shown by Table 1, the ICP-AES detection limits obtained with ultrasonic nebulization are well below the normative levels.

Table 1. Comparison of ICP-AES detection limits^a and normative levels

Element	Nebulization Detection Limits (µg/ml)		Normative Levels (µg/ml)	
	Pneumatic (17)	Ultrasonic (19)	Urine (20)	Blood Plasma (21)
As	0.04	0.002	0.17	0.04
Sb	0.2		0.001	0.054
Bi	0.05			
Ge	0.15			-0.03
Se	0.03	0.001	0.04	0.11
Te	0.08			-0.03

^aConcentration required to produce a net line signal that is two times greater than the standard deviation of the background scatter.

Because the lowest quantitatively determinable values (LQD), defined here as the concentrations required to give a net line signal equal to ten times the standard deviation of the background, are on the borderline of the normative levels, the determination of the analytes at concentrations even

slightly below the normative levels cannot be quantitatively performed. Thus a preconcentration of the analytes is desirable in order to alleviate the problem of marginal LQD's. If this preconcentration also separates the analytes from concomitants, then it provides a direct solution to the background and stray light problems present in ICP-AES systems (22).

The spectral background contributes a large percentage to the total measured signal in AES determinations of trace elements at concentrations near the detection limits. Stray light emission can be produced by concomitants in the sample matrix causing shifts in the spectral background in the region of the analytical lines. For example, wavelength profiles made with an ICP facility of the region surrounding the 196.0 nm Se line revealed that the far scattering radiation from the presence of 100 $\mu\text{g/ml}$ Mg (principal lines at 279.5 and 280.27 nm) and 200 $\mu\text{g/ml}$ Ca (principal lines at 393.4 and 396.8 nm) in the nebulized solutions produced signals equivalent to 0.024 $\mu\text{g/ml}$ Se and 0.009 $\mu\text{g/ml}$ Se respectively. Furthermore the signal at the Se 196.0 nm line, resulting from Ca and/or Mg concomitants in a sample, varied according to the concentration of the concomitants (23). Sufficient rejection of far scatter radiation in the 190 to 230 nm region arising from the principal Ca lines has been achieved through the use of narrow bandpass interference filters. However, the far

scatter radiation is that region arising from the principal Mg lines has not been successfully reduced by the use of interference filters (24). Therefore, other means of alleviating the problem must be explored.

Nixon has recently reviewed the various physical and chemical possibilities for effecting these separations and has described a bromide distillation procedure for isolating and concentrating As, Se, Sn and Ge (25). The ultimate LQD concentrations achievable by the Nixon procedure were still limited by the liquid co-distilled with the analyte species.

Another physical separation procedure that has been used by analysts for isolating the elements of interest from various matrices is based on the formation of gaseous hydrides. Because the gaseous compounds may be introduced directly into the plasma, this separation scheme does not entail dilution of the analytes by any solvent. Therefore relative detection limits lose their meaning and a potentially higher degree of concentration should be possible. The remainder of this thesis is an account of a study of the hydride separations combined with ICP-AES measurement of the evolved hydrides.

CHAPTER II. LITERATURE REVIEW OF HYDRIDE TECHNIQUES

The hydrides (compounds having the formula XH_n) of the IVA, VA and VIA groups of the Periodic Table are part of a greater group of covalent hydrides (hydrides of the elements in Groups III A and III B through VII A and VII B) that are distinguished from other types of hydrides by the fact that they are volatile substances. All of the IVA, VA and VIA hydrides are either gases or liquids under normal conditions (26).

As the descriptor 'covalent' implies, the chemical bonding between hydrogen and the various elements is of the electron sharing type. The degree of polarity of the bonds is dependent upon the difference in the electronegativities of the constituents. Consequently the only IVA, VA or VIA elements which form highly polar bonds are N and O. Because the covalent hydrides are not very polar, they should not be strongly attracted to one another. The temperatures at which the covalent hydrides of Groups IVA-VIA volatilize are low and depend primarily upon the molecular weight of the parent ion, so that the lighter molecules boil at lower temperatures (N and O being exceptions due to the hydrogen bonding which they undergo). Primarily because of their volatilities and ease of conversion to the hydride form, eight of the IVA-VIA covalent hydrides have become of great interest to analytical chemist seeking to determine

the parent element at trace concentration levels.

The eight hydrides are listed in Table 2 along with their melting and boiling points. Methods of arsine (AsH_3) generation for the purpose of determining arsenic have been used for over a century. However, it has only been in the last twenty-five years that the other seven hydrides have been prepared for analytical purposes, with the preparation

Table 2. Melting and boiling points of selected IVA-VIA covalent hydrides^a

Hydride	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)
GeH_4	-165	-88.5
SnH_4	-150	-52
PbH_4	?	?
AsH_3	-116.3	-55
SbH_3	-88	-17.1
BiH_3	?	22 ^b
H_2Se	-60.4	-41.5
H Te	-48.9	-2.2

^aRef. 27.

^bRef. 26.

of plumbane being the most recent (28). In the course of this development of hydride generation as an analytical separation technique, many reducing agents and experi-

mental designs have been tested and used in conjunction with many instrumental methods. Colorimetric determination of the elements has been performed after chelation of the liberated hydride (29). These hydrides have also been generated and dissociated prior to the determination of the released free atoms in Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS) and Atomic Emission Spectroscopy (AES). The following review of hydride generation techniques and experimental designs is given as a foundation for the work performed by this author.

In the generation of hydrides, a reducing reaction of the general type shown in Equation 1 is used.

Therefore, the two factors which must be considered are the reducing agent and the effect of various acids and acidity requirements. The reducing agents that have been used include a slurry of Al-SnCl₂-HCl (30), and combinations of the following reagents Mg-TiCl₃ and Zn-TiCl₃ (31); NaBH₄-SnCl₂ (32), NaBH₄-H⁺ (33-44), and Zn-SnCl₂ (45-63). The Al slurry used by Goulden and Brooksbank (30) has two advantages; (a) a low density, and (b) suitability for pumping owing to the availability of Al as a fine powder. However, the analyte must be oxidized to its highest oxidation state prior to the reduction by the Al-SnCl₂-

HCl mixture (30). Zn in conjunction with TiCl_3 satisfactorily produces the hydrides but gives a high blank signal because of impurities in the reagents. Mg has been used in place of the Zn but the reaction time is about five minutes. A further disadvantage lies in the uniform size and weight of Mg rod that must be used to insure reproducible results. Such a rod section is difficult to introduce into the system (31). Although numerous researchers have found a combination of Zn, SnCl_2 and HCl satisfactory as a reducing agent (45-63), there are undesirable aspects inherent in its use. First, SnCl_2 is difficult to obtain in an arsenic-free form. Second, the reaction time for the Zn - SnCl_2 procedure is 2 to 3 minutes and the Zn granules must be weighed because the extent of the reduction is dependent upon the quantity of Zn present (51). Third, the size of the zinc granules or zinc powder is reported to affect the measured absorbance in atomic absorption methods (59). Finally, the hydride yield is reported to be only about 20 per cent (64).

Sodium borohydride offers several advantages over other reducing agents available. First, solutions of NaBH_4 or pellets may be employed, making it applicable to pumping systems as well as to systems with dosing stop cocks for pellet introduction. Second, NaBH_4 solutions can be stabilized for indefinite periods of time by the

addition of sodium hydroxide (65). Third, NaBH_4 pellets are stable indefinitely in dry air or in sealed containers (66). Fourth, the pellets are inexpensive, relatively easy to handle and sufficiently uniform to eliminate the need for weighing (51). Finally, a very low blank signal is obtained (51) and preoxidation of most compounds is not necessary (35). However, some NaBH_4 pellets have been reported to be contaminated with As (36). Moreover, quantitative liberation using NaBH_4 has been reported for only AsH_3 (9).

Because the nature of the acid used and the pH of the solution influences hydride formation, these two variables have been extensively investigated. Vijan and Wood found that H_2SO_4 , HCl , HNO_3 and HClO_4 all yielded similar As signals (37). Hydrobromic acid and NaBH_4 have been used for the generation of GeH_4 (44). Based on the experimental results obtained by Behard and Kerbyson, the reduction of bismuth to BiH_3 is necessarily made from either hydrochloric or sulfuric acids (67). HCl has been the acid most widely used for the generation of all the volatile hydrides.

Fernandez reported no effect on the atomic absorbance of As, Bi, Sb and Te for NaBH_4 reductions when the concentration was varied from 1 to 6N. However, this consistency of absorbance does not necessarily imply quantitative reduction but a reduction independent of acidity. Tin exhibited maximum absorbance sensitivity at

0.2N Sn. Germanium absorbance was constant over a 1 to 3 N range and diminished thereafter. Selenium exhibited maximum sensitivity in the range of 6 to 7N (51).

The experimental schemes that have been employed for the generation and analysis of volatile hydrides have fallen into two basic categories: continuous flow determinations and collection procedures. Although the specific features of the set-up used for the continuous flow procedure have differed considerably (28,33,37,49,68,70). The following general procedure has been followed. A solution of the analyte and a suitable acid were placed in the reaction vessels. The reducing agent was added via some dosing mechanism which allowed the system to remain sealed from the atmosphere. A carrier gas flowed through the system sweeping the hydride, as soon as it was evolved into the atomization source.

Collection procedures can be divided into three main categories: chemical trapping, mechanical trapping as the gas, and "freezing out" procedures. Chemical traps such as silver nitrate (71) and silver diethyldithiocarbamate dissolved in pyridine (29) have been used to capture AsH_3 for subsequent determination by colorimetric methods (29) and by atomic absorption spectrophotometry (71). However, reports of such trapping methods for any of the other elements which form analytically important covalent hydrides could not be found.

Collection chambers such as balloons have been employed to collect the evolved hydride (47,49,51,55,37,31,67,72,73). The procedure employed was the same as previously described for the continuous flow determinations except that the hydride was collected for a period of time and subsequently swept into the atomization source.

Liquid nitrogen traps have also been used to trap the hydride as it is evolved (45,60,61,73,74). The reaction was allowed to proceed for a specified period of time, called a waiting period, with a carrier gas (He) flowing through the system. The collection chamber, typically a U-tube, was then closed off at the stopcocks and sometimes detached from the system. (Feldman reported that difficulties are encountered when a trap constructed with a spiral configuration was employed (75).) The liquid nitrogen trap was removed, the atomization support gas attached at one end of the trap and the other end attached to the atomization source. As the solidified hydride warmed to room temperature, it was swept from the collection chamber into the atomization source by a carrier gas. Griffin et al. (61) used an aspirating apparatus in place of a carrier gas system; a drying tube charged with CaCl_2 or Drierite was necessary to prevent blockage of the collection chamber by condensed water vapor.

In all of the procedures discussed except the chemical trapping procedure, the choice of the carrier gas was dependent upon the gas used for the atomization source. Much of

the work reviewed herein was done using Ar as the carrier gas (46,47,51,55,60). However, helium (33) and nitrogen (45) have also been used.

Fernandez, using a balloon collection chamber, reported a substantial increase in sensitivity as opposed to continuous flow procedures (51). Equal powers of detection should be obtainable by using either procedure if signal integrations rather than peak height measurements were used. However, freeze trapping procedures should yield the best detection limits because the analyte is free from the diluting effect of the H_2 produced during the reaction.

The effect of the waiting period in collection procedures on the signal obtained has been investigated by Griffin, et al. (61) and Fernandez (51). Griffin et al. reported maximum sensitivity in the arsenic signal after a 15 minute waiting period when zinc was used as the reducing agent and a liquid nitrogen trap. The signal remained reasonably consistent up to a waiting period of 30 minutes. Fernandez, using $NaBH_4$ as the reducing agent, investigated the effect of waiting period for As, Sb, Bi, Ge, Sn, Se and Te. Only Bi and Te were reported to require careful monitoring of balloon collection times.

Variations of the hydride generation technique have been widely applied to determinations of As, Sb and Se in a variety of samples and more narrowly applied to the determination of Be, Te and Bi as summarized in Table 3.

Table 3. Applications to real samples

Element	Application	References
As	Biological samples	9, 46, 48, 52, 54, 61, 71, 72, 74
	Soil, sewage, water samples	33, 34, 59
	Air	71, 72
	Iron and steel samples	53, 57
Sb	Biological samples	9, 52
	Soil, sewage, water	30, 33-35
	Air	37
Se	Biological samples	9, 46, 52, 69, 74
	Soil, sewage, water	30, 35, 69
	Air	37
	Steel	53
Te	Air	37
Bi	Metal samples	71
	Air	37
Cc	Air	37
Sn	None	
Pb	None	

Because no practical application of the hydride generation method for determination of Sn or Pb could be found, a brief discussion of their hydrides follows.

Although tin has been determined by hydride generation techniques (51), high blank signals (69) have been reported and no practical applications could be found in the literature. SnH_4 decomposes readily at -50°C with elemental Sn, traces of O_2 , and stopcock grease serving as catalysts. However, higher concentrations of O_2 completely inhibit decomposition (76).

Although the existence of PbH_4 has been confirmed by various researches (76,77), attempts to generate preparative amounts of plumbane utilizing various reductive methods have met with little success until recently (41,44,78). The decomposition temperature of plumbane is believed to be approximately -196°C which partially explains why its generation by typical methods in more than trace quantities has eluded many researchers (78). Recently, Thompson and Thomerson determined lead by a hydride method but with relatively poor efficiency of conversion (less than 5%). The acidity of the solution and the amount of NaBH_4 used were crucial to the production of the hydride. For 1 ml of sample solution in 0.2 M HCl, 1 ml of 17% m/v NaBH_4 was optimum (28).

Precise physical data for plumbane is unknown owing to the difficulties in synthesis (79). The polarity of the Pb-H bonds also may partially explain the resistance of lead

to form PbH_4 . Unsuccessful attempts to generate PbH_4 by hydrogenation of PbCl_4 in a manner analogous to the preparation of germane by Finholt et al. (80) can be explained by this polarization (81).

Even though applications of a hydride method have been studied, only a few researches have studied any of the various substances that may cause signal suppressions (37, 56, 67, 82-84). Table 4 summarizes the results that have been reported.

Smith studied the effect of various substances, six of the IVA, VA and VIA that form volatile hydrides (69). However, possible effects of pH on hydride evolution and of valency states of the analytes being determined were not included. Furthermore, only a given quantity of analyte and potential interferent (one mg) were used for all experiments. Therefore, tolerance levels of various interferents were not investigated.

Smith's results showed that all of the hydride-forming elements studied caused suppression of the signal from all the other volatile hydrides with the exception of bismuthine and hydrogen telluride on stibine and hydrogen selenide. Smith suggested that these signal suppressions were caused by compound formation in the cool argon-hydrogen flame used in AAS, which seems to be the same proposition Maruta and Sudah (83) implied for the suppression of the As signal by Se. Smith further proposed that interferences from non-hydride forming elements may be caused by preferential

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Table 4. Interelement effects .

Analyte	Concentration	Interferences	Concentration
Se	50 µg/l	NO_3^-	50 µg/l
		Hg	10 µg/l
		As	5 µg/l
As	30 ppb	Se, Co, Ni, Cr	200 µg/ml
		Pb, Fe, Cu	200 µg/ml
As	10 ppm	Co^{2+} , Ni^{2+} , Zn^{2+}	50 ppm
		Fe^{3+} , Bi^{3+} , Cd^{2+} Cu^{2+}	
Sb	25 ppm	Co^{2+} , Ni^{2+} , Fe^{3+}	50 ppm
		Bi^{3+} , Cu^{2+} , Ag^+	
As	1.0 µg/l	$\text{Cr}_2\text{O}_7^{2-}$, PO_4^{3-}	6.7 mg/l
		MnO_4^- , MoO_4^{2-}	1.6 mg/l
		VO_3^-	3.3 mg/l
		$\text{S}_2\text{O}_8^{2-}$	0.6 mg/l
		$\text{Cr}_2\text{O}_7^{2-}$	16.7 mg/l
Se	1.0 µg/l	MnO_4^- , VO_3^-	0.6 mg/l
		$\text{S}_2\text{O}_8^{2-}$	0.6 mg/l
		NO_3^-	0.6 mg/l
		MoO_4^{2-} , PO_3^{3-}	1.6 mg/l
As	0.8 µg	Se, Pb, Cr	80 µg
Bi	1 µg	As, Sb, Te, Se, Sn	100 µg

Interference Effect	Method of Observation	Reference
Suppressed formation	AAS	56
"		
"		
>10% suppression	AAS	37
10% suppression		
>10% suppression	MECA	82
"		
"		
>10% suppression		
"		
10% suppression	AAS	84
"		
"		
"		
20% suppression		
10% suppression		
50% suppression		
10% suppression		
10% suppression		
>5% suppression	AAS	83
"tolerated without significant effect"	AAS	67

reduction of the interferent which can cause a variety of problems; co-precipitation of the hydride with the interferent as also proposed by Behard and Kerbyson (67) for Bi in the presence of Cu, adsorption of the volatile hydride formed or catalytic decomposition of the hydride.

Because no published results could be found that satisfactorily described the potential interaction of the hydride forming elements during simultaneous determinations at levels encountered in many samples and because preliminary experiments performed in our laboratory showed that the effects observed cannot be entirely (if at all) explained by compound formations in the flame, a study of material interactions was undertaken in addition to the development of a hydride method compatible with the ICP system. The purposes of the secondary study were to determine the origin of the signal suppressions, to propose plausible mechanisms of the interactions and to determine the magnitude of the effects at several different levels.

CHAPTER III. EXPERIMENTAL FACILITIES

The plasma facilities used in this study have been divided into their categories; Generation, Sample Introduction, and Spectrometric Instrumentation. The principal components of the equipment are outlined in Table 5 and referenced to previous detailed descriptions. Because the development of two alternate sample introduction systems was a part of this research, only sample introduction by nebulization is described here.

Table 5. Experimental facilities employed

Plasma Generation	
Radiofrequency generator	The radiofrequency generator described in reference (85) (International Plasma Corporation Hayward, California 94544) was employed using the feedback control circuitry described in reference (86). The forward power in the transmission line was 1200 watts as measured by a Thruline Wattmeter (Model 43,2500 H element, Bird Electronic Corp., Cleveland, Ohio). The reflected power was approximately zero watts.
Impedence matching network	Variable (30-turn) vacuum capacitor coupling circuit (International Plasma Corporation, Hayward, California) as described in reference (85).
Load coil	Two-turn water cooled coil made from 5 mm O.D. copper tubing. The coil itself had a diameter of 35 mm.
Plasma torch	Concentric quartz tube configuration described in reference (16). Inner and outer tubes are clear precision quartz tubing (Wilmot Glass Company, Buena, N.J.). The torch and sample aerosol generation system are shown in figure 1.
Gas-flow rates:	
Plasma Gas (Ar):	14.5 l/min (unless otherwise stated).
Plasma Support (Ar):	Optional, used when igniting the plasma to prevent "burning" of the plasma and aerosol tubes.

Table 5. (continued)

<u>Plasma Generation</u>	
Aerosol (Ar or Ar-5% H ₂):	1.0 l/min (unless otherwise stated).
Ignition	Tesla Coil ignition with no aerosol flow and plasma gas at a flowrate of approximately 15 l/min. After plasma was formed, Tesla coil was shut off and flow rates were adjusted to operating conditions.
<u>Sample Introduction Systems</u>	
Nebulizer and Aerosol Chambers	Right-angle pneumatic nebulizer as described in Ref. (87). Aerosol chamber as described in Ref. (86). Pictured in Figure 1.
<u>Spectrometric Instrumentation</u>	
Monochromator	0.5 m Ebert mount (Jarrell-Ash Division, Fisher Scientific Co., Woltham, Mass., Model No. 82000).
Grating	1180 rulings/mm, blazed at 250 nm, first order
Slits	Fixed, 15 nm entrance, 15 nm exit, entrance slit height masked to 4mm.
Reciprocal Linear Dispersion	16nm/mm, first order
Detector	EMI 6526B photomultiplier, S-13 response (Electra Megadyen Inc.) North Hollywood, California).
Optical transfer System	Plasma emission focused by a 16 cm focal length X5 cm diameter planoconvex, fused quartz lens, with aperture limited to 3mm by an adjustable iris diaphragm concentrically mounted on the lens holder. Lens positioned at twice the focal length (2f) from

Table 5. (continued)

Spectrometric Instrumentation

the slit and plasma center for each wavelength region studied.

Amplifier

Linear picoammeter (Keithley Instrument., Cleveland, Oh., Model 417) previously described in Ref. (85).

Data Collection

System I

Recorder

X-Y recorder (Moseley Division, Hewlett-Packard, Pasadena, California, Model No. 4001A).

System II

Recorder

Speedomax H continuously adjustable Azar Recorder (Leeds and Northrup Company, Philadelphia, Pa.)

Integrator

Printing integrator (Perkin-Elmer Corporation, Norwalk, Conn., Model No. 194B).

Figure 1. Torch and sample aerosol generation system.

CHAPTER IV. DEVELOPMENT AND EVALUATION OF A HYDRIDE TECHNIQUE

Development

The major factors to be considered in adapting the hydride evolution technique to ICP-AES spectroscopy are the following: (a) selection of reducing agent; (b) reaction medium acidity; (c) design of the reaction vessel; and (d) the means of collecting and/or introducing the evolved hydrides into the plasma.

Selection of reducing agent

For reasons previously stated (p.10), NaBH_4 was chosen as the reducing agent. Because the use of NaBH_4 pellets yielded variable blank signals, a solution was used to achieve consistency. The theoretical quantity and strength of NaBH_4 solution necessary to quantitatively form the hydrides depended on the nature of the reaction involved. If all four BH_4^- hydrogens participate in hydride formation, the reaction given by Equation 2 would apply for $\text{X}=\text{As}$, Sb or Bi , and by Equation 3 for $\text{X}=\text{Se}$, Te or Ge (a).

Neither equation shows H_2 production, which was liberated at a rate of approximately 61/minute when 0.2 ml/sec of NaBH_4 was added to an acid solution. This production of $\text{H}_2(\text{g})$ must have occurred either during or after hydride formation. If $\text{H}_2(\text{g})$ production occurred during hydride formation, then

Equation 2 should be changed to Equation 4.

If a solution contained 10 mls of 6NH^+ and 0.05 ug of H_3AsO_3 , then by Equation 4, 115 mls of 2% w/v BH_4^- would be required for quantitative production of AsH_3 . However, only 2 mls of 2% w/v BH_4^- caused quantitative AsH_3 evolution. Therefore, Equations 2 and 3 must describe the hydride formation with subsequent production of $\text{H}_2(\text{g})$ according to Equation 5.

Theoretically 2 mls of 2% w/v BH_4 will reduce quantitatively 250 mg As to AsH_3 according to Equation 2. Therefore, that quantity and strength of NaBH_4 were used in this investigation unless otherwise stated.

Thermodynamic consideration of only hydride formation is misleading because the hydrides are thermodynamically unstable with respect to decomposition to their elements. (Germane is also unstable with respect to disproportionation into digermane.) Because the actual hydride evolution depends on the relative kinetics of formation, decomposition and/or disproportionation, which are unknown, and on the rate and ease of evolution, valid predictions of the quantitativity of evolution are impossible.

Reaction medium acidity

Because the evolution of As, Sb, Bi and Te has been reported to be independent of the pH of the reaction

solution (51), the acidity was chosen for optimum H_2Se evolution. At low pH values the ionization of H_2Se , which has a pK_2 value of 3.77, becomes small. Therefore, an acid normality of 6 ($\text{pH}=0$) was used even though the pH was not optimum for GeH_4 evolution. (According to Fernandez' data, the absorbance of Ge^0 , which reflected GeH_4 evolution, remained constant over the range of 1 to 3 N and decreased 20% over the range of 3.5 to 6N (51).

Design of reaction vessel

The design of the reaction flask used plays a significant role in the evolution of the hydride gases. The optimal reaction flask should have a large surface area but a limited volume. A flask meeting these requirements was constructed from a 125 ml Erlenmeyer fitted with a 24/40 outer joint as the neck and two other openings.

Hydride collection and introduction into plasma

Based on previously reported work, three methods of collecting the hydrides prior to the determination of the analyte were investigated. The first procedure, based on collection in a balloon reservoir, has been described by Manning (47) who used Zn as the reductant. During Zn reductions, $\text{H}_2(\text{g})$ is liberated at a slow rate and a balloon reservoir performs satisfactorily. However, when NaBH_4 is used, a large volume of $\text{H}_2(\text{g})$ is liberated at a fast rate creating a sufficiently sudden high stress on moderate sized balloons to

cause rupture.

If the size of the balloon reservoir is increased, the volume dilution of the analyte defeats the purpose of the procedure. Hence, this approach was abandoned.

The second collection procedure was based on the oxidation-reduction reaction of a liberated hydride in a solution, producing the analyte ions and a reduced form of the cation. The reaction of liberated AsH_3 in AgNO_3 solution, which forms As^{3+} and Ag^0 , has been used for over a century for As collection. Because similar reactions of all the hydrides of interest with some solution were feasible, this procedure was further studied for AsH_3 evolution. The maximum efficiency of collection for AsH_3 was approximately 60% for 5 mls of a solution containing 2000 ppm Ag^+ . The improvement of the efficiency would have required more effort than the method justified; therefore, this approach was abandoned.

As previously discussed (p.13) the third procedure, freeze trapping, has been widely used. For any trap design, the efficiency and reproducibility of collection and the type of signal produced upon release of the vaporized hydride from the trap are of particular interest. The efficiency of collection must be calculated from determinations of the quantity of hydride gas which is not trapped. Another important criterium for selection of a trap configuration is its ease of use. On the basis of these criteria, two trap configurations were evaluated.

The first configuration was a U-tube constructed from 9mm O.D., 5mm I.D. Pyrex tubing with an overall length of 28 cm, which was packed with glass beads to provide a suitable surface area for the condensation of the hydride gas. When the experimental set-up shown in Figure 2 was used with the U-tube trap, the extensive discoloration of the AgNO_3 solution beyond the trap signified that the collection efficiency was inadequate.

A second trap involving a spiral configuration was, therefore, evaluated. This trap, shown in Figure 3, was packed with small glass particles. The increased length of the trap and the larger condensation surface provided by the glass particles was expected to provide improved trapping efficiency.

Figure 2. Apparatus for evaluation of cold trap efficiency.

Figure 3. Diagram of spiral cold trap.

Figure 4. As peak obtained using spiral cold trap.

When a AgNO_3 solution with a tested efficiency of 29.6% was used to collect the AsH_3 which escaped the spiral cold trap, the collection efficiency for the spiral was determined to be 83.7%. Because of the boiling point of AsH_3 is lower than all the corresponding hydrides of the elements of interest except GeH_4 , the efficiency figure should be a reasonable lower limit for As, Sb, Bi, Se and Te trapping. The spiral trap repeatedly collected the same fraction of liberated hydride as measured by the AgNO_3 method.

When the spiral trap was warmed in a boiling water bath, plasma emission signals typical of those shown in Figure 4 were obtained. The variation in peak shape, which appeared to result from uneven warming throughout the trap, suggested that signal integration techniques should be used for quantitative analysis.

Further development of the collection procedures was not justifiable at this point in the investigation because direct flow methods had not been explored. However, inherent in direct flow methods is the introduction of a molecular gas (H_2) into an argon sustained plasma. When the H_2 is introduced into the argon plasma, the coupling efficiency ($\text{C.E.} = \frac{\text{forward power}}{\text{reflected power}}$) decreases because of an increased skin depth which results from the greater resistivity of H_2 . (A detailed discussion of the physics of induction-coupled plasmas is given in Ref. (88).) Because of the coupling

inefficiency exhibited by a pure argon plasma upon introduction of H_2 , an Ar-5% H_2 gas mixture was used as the aerosol gas and the impedance was matched for that gas mixture. Subsequent introduction of the H_2 by-product altered the plasma coupling to a much smaller extent.

A second problem encountered with direct flow methods was the establishment of plasma and aerosol gas flow rates compatible with the H_2 evolution rate. At a plasma gas flowrate of 20l/min and an aerosol flowrate of 1.9l/min, the plasma was stable with addition rates of the $NaBH_4$ solution to the acidified media equal to or less than 0.05 ml/sec. Because the plasma elongated in both directions under those gas flow conditions, the Ar plasma support gas (refer to p.22) was used with this method to prevent "burning" of the plasma and aerosol tubes.

The hydride generation system used is illustrated in Figure 5 and described in Table 6. In Figure 5, all of the components to the right of reaction vessel were connected to adjoining pieces with Tygon tubing. The apparatus was housed in a vented metal hood.

Table 6. Hydride generator and direct flow system

Apparatus	Description
(1) Reaction vessel	Described on page 28.
(2) Modified addition funnel	Pressure addition funnel constructed of a 24/40 outer joint and 24/40 inner joint

Table 6. (continued)

Apparatus	Description
	separated by a standard 2mm Pyrex stopcock (no. 7252) with Teflon fitting. The overall length is 18.5 cm.
(3) Dosing stopcock and carrier gas inlet (Ar-5% H ₂)	Pyrex stopcock (no. 7252) with Teflon fitting orifice bored to 3.5 mm. connection to 24/40 inner joint. 8mm O.D. x 3.5 cm. side arm for introduction of carrier gas.
(4) Drying tube	Tube filled with CaCl ₂ with glass (cotton) at both ends.
(5) Purging stopcock	Ground glass 2mm T-stopcock used to purge the air from the system before hydride generation.
(6) Gas by-pass system (Ar-5% H ₂)	Ground glass 2mm T-stopcock functioned to sustain the plasma while the reaction vessel was changed.
Plasma torch connection (not shown)	Tygon tubing was used to connect the open end of the gas by-pass stopcock to an 18/9 outer balljoint which was secured to the base of the aerosol inlet tube of the plasma torch.
(7) Carrier gas inlet (Ar-5% H ₂)	18/9 outer balljoint with glass extension used to bubble carrier gas through the reaction solution.
(8) Carrier gas control system	
Valve A	Controlled gas flow through #7
Valve B	Controlled introduction of carrier gas to generating system.

Table 6. (continued)

Apparatus	Description
Valve C	Control valve set so that when valve 2 was open, the path through the generator apparatus was favored over the by-pass system.

(1) Reaction Vessel	(5) Purging Stopcock
(2) Addition Funnel	(6) Gas By-Pass Stopcock
(3) Dosing Stopcock and
Carrier Gas Inlet	(7) Carrier Gas Inlet
(4) Drying Tube	(8) Carrier Gas Control
System

Figure 5. Hydride generator and direct flow system.

Operating procedures for direct flow introduction

The procedures used with the direct injection of the evolved hydrides (and hydrogen) followed the pattern outlined below. The analyte solution was added via a pipet to the reaction vessel, which contained a measured quantity of acid. Various amounts of deionized H_2O were added to the solution so that the volume and overall acidity remained constant. A Teflon stirring bar was placed in the reaction flask before the latter was attached to the system. The $NaBH_4$ solution was placed in the pressure addition funnel. For the quantitative studies, a 2 ml aliquot of 2% w/v $NaBH_4$ was used. The cap was then placed on the addition funnel and the system was deaerated for 2 minutes with an Ar-5% H_2 flow of 1.9 l/min. This aerosol gas flow was then turned off and the plasma ignited so that the toroidially shaped plasma was formed. The Ar-5% H_2 flow was again adjusted to 1.9 l/min. The impedance of the generator and load were matched by adjusting the variable capacitors in the coupling box. The reaction was then performed by either dropwise additions of the $NaBH_4$ solution (to give individual pulsed signals) or continuous additions at a rate of 0.05 ml/sec (to generate a continuous evolution signal). After the reaction was completed, the gas by-pass system was employed while the first reaction flask was replaced and a new aliquot of $NaBH_4$ was added. The system was deaerated for 1 minute before the by-pass system was closed off and the original gas flow

pattern reestablished.

Evaluation

Analytical curves

The procedure discussed above (continuous NaBH_4 addition) was used in establishing analytical calibration curves for As, Sb, Bi, Se, Te and Ge. As shown in Figure 6, the analytical curves for As, Sb, Bi, Te and Ge were linear over the range studied, whereas the Se curve behaved anomalously. The shape of the Se analytical curve suggested that beyond 5 ug incomplete conversion and/or evolution occurred. If either or both occurred, it should have been possible to measure the Se remaining in the reaction mixture.

Percent evolution

Because the ICP-AES was directly applicable to the determination of Se in solutions (if it occurred in the determinable range), it was convenient to perform direct measurement of percent evolution of Se or the other hydride forming elements. These data were obtained as follows. Ten ml of acidified solution ($\text{pH}=0$ except for Ge solutions whose pH was adjusted to ≈ 1) containing 50 ug of analyte were reacted with 10 mls of 2% w/v NaBH_4 solution in the usual manner. Any analyte remaining in the solution was subsequently determined by directly nebulizing the solution and injecting the aerosol into the plasma. The peak heights so obtained were corrected for the reaction mixture blank and background

Figure 6. Analytical curves for As, Sb, Bi, Se, Te and Ge.

contribution as described below.

Because the background signal intensities observed when the reaction solution were nebulized were somewhat greater than those observed for H₂O blanks, wavelength scans of the region surrounding the analytical lines were performed for the H₂O blank, the reaction blank, and an aqueous solution of the analyte in order to characterize the background shifts. The reaction solution exhibited a higher background than deionized H₂O at the wavelengths for As, Sb, Se, and Te; for Bi or Ge, the shift was insignificant. In addition a definite As blank was evident at the 193.7 nm As analysis line. Appropriate background and blank corrections were applied to all the data.

Table 7. Percent hydride evolution in single element matrix

Element	Percent Evolution
As (III)	100
As (V)	75-80
Sb (III)	100
Sb (V)	75-80
Bi	45
Ge	23.2
Se ^a	41.5
Te	14.2

^aThe Se sample contained 72.5 ug.

As shown in Table 7, quantitative evolution did not occur for most of the elements under the conditions studied. Germane and hydrogen telluride showed exceptionally low percent evolution. The non-quantitative evolution of H_2Te , GeH_4 and BiH_3 is most likely related to the kinetics of the decomposition reactions. For example, the $\Delta G_{\text{rx}}^\circ$ of H_2Te formation by equation 2 is -70.1 kcal/mole. The hydride decomposition reaction has a $\Delta G^\circ = -18.2$. Moreover the $\Delta G_{\text{rx}}^\circ$ of AsH_3 formation is -57 kcal/mole and the decomposition reaction has a $\Delta G^\circ = -16.5$. From strictly thermodynamic considerations, AsH_3 should be more difficult to obtain quantitatively. Therefore, one must conclude that kinetic factors are responsible for the non-quantitative evolutions of H_2Te , GeH_4 and possibly BiH_3 . (Because no thermodynamic data are available for BiH_3 , the behavior of the hydride reactions cannot be blamed entirely on kinetic factors.) In confirmation of results reported previously (9, 28, 89), the percent evolution of arsine and stibine was dependent upon their initial valence states in the sample solutions.

Vijan et al. (89) and Thompson and Thomerson (28) reported that As (V) and As (III) yielded signals (peak heights) of grossly different intensities when reduction by 1% NaBH_4 was performed and a continuous flow method was utilized for determinations. However, when 4% of NaBH_4 was used, Thompson and Thomerson (28) reported only a 10% suppression of the As (V) signal and Fiorino et al. (9) using

signal integrations reported no signal difference. In order to obtain consistent signals, prereduction of As (V) appeared to be necessary, Fiorino et al. (9) stated that prereduction was also essential to the generation of stibine.

Qualitative studies on the As (V) solutions showed that the As which remained after reaction with 2% w/v NaBH_4 was in the +3 valence state. Because there was no thermodynamic reason for the discrepant results (as shown in the appendix), it was believed that a kinetic problem was involved, i.e. the slow reduction of As (V) to As (III) by BH_4^- . Until Fiorino et al. (9) reported that As (V) signal was delayed with respect to the As (III) signal and the As (V) peak width was broader on a plot of As emission as a function of time, the kinetic factor had been completely ignored in the literature. Because solutions containing As or Sb in mixed valence states could not be analyzed with consistent results, the typical KI prereduction was utilized. Subsequent determinations showed 100% evolution for both As (III) and As(V). Although the Sb problem was not investigated further in our laboratory, Fiorino et al., reported no difference in determinations of Sb (III) and Sb (V) after prereduction with NaI (9).

The shape of the analytical curve obtained for Se and the percent evolution given in Table 2 merit special attention. Results of solutions containing 72.5 μg Se obtained from introduction of nebulization shortly after

reaction with 10 mls of 2% NaBH_4 showed that 58.5% of the Se remained in solution in some form. Determinations made four hours after the evolution reaction showed that only 48% of the Se remained. Solutions reacted with 2 mls of NaBH_4 yielded 80.6% Se remaining in solution after reactions and only 22% Se after the four-hour waiting period. The smaller values obtained after the four-hour waiting period cannot be said to be due to continued reduction because the excess NaBH_4 is destroyed by the acidic media shortly after reduction. Therefore, the smaller values must be due to the dissociation of the H_2Se with subsequent oxidation and to precipitation as Se^0 . It may be concluded that a larger percentage of H_2Se was formed than was evolved.

Because quantitative formation and evolution occurred only for As and Sb and because samples are frequently analyzed for As and Se, the remaining studies were limited to those elements except when observations on the behavior of other elements was felt to be essential.

Detection limits

The detection limits (the concentration required to produce a net line signal that is two times greater than the standard deviation of the background scatter) obtained for As, Sb and Se is best reported in absolute rather than relative terms because the volume of sample reacted can vary from 5 to 50 mls. However, for purposes of comparison, both

Table 8. Detection limits

Element	Hydride Technique Detection Limits		Ultrasonic Nebulization Detection Limits (μg/ml)
	Absolute (ng)	Relative (μg/ml)	
As	16	0.0008	0.002
Sb	20	0.0001	
Se	1.2	0.00006	0.001

absolute and relative (based on 20 ml volume) detection limits are given in Table 8 as well as selected values from Table 1. The relative detection limits obtained vary from a factor of three to an order of magnitude more than those obtained with ultrasonic nebulization.

Precision and the effect of analyte solution volume

Based on five successive determinations of reference samples containing 1 ug As, the precision obtained was $\pm 8\%$ of the mean value. The precision of the hydride technique does not compare favorable to that obtained in solution nebulization work for two reasons. First, each sample used for calibration purposes must be prepared individually, which introduces substantial chance of operator error. Secondly, the manipulations involved in evolving and transporting the gases increase the probability of both operator and random error.

The effect of analyte solution volume on the analytical curve of As was determined to be insignificant. As shown in Figure 7, the same line fits both sets of data points. The points, which were obtained from analyte solutions of 10 ml volumes, deviated on an average of 7.5% from the analytical line. Those points obtained from analyte solutions ranging in volume from 6 ml to 10 ml deviated on an average of 4.4%.

Limitations

The most severe limitation to elemental determinations by the hydride evolution technique, under the experimental

Figure 7. Effect of analyte solution volume on As analytical curve

conditions used, occurred with samples containing more than one hydride forming element. Table 9 gives the percent signal suppression produced by the presence of a second hydride-forming element in the analyte solution. The absence of any scientific evidence in the literature concerning the cause of the observed effects led to an investigation of the origin and mechanisms of the interactions.

Many researchers would agree with Smith (69) that the origin of the signal suppressions is in the atomization source. However, such a philosophy may be purely conjecture. Fleming and Ide suggested a different theory (90).

"It was expected that the majority of interferences would occur in the hydride generation cell and result in a depression or enhancement of the hydride generation or a change in the rate of hydride generation.... This possibility needs further investigation." To determine if the signal suppressions actually originated in the hydride generation cell, 12 ml of acidified solutions containing 50 μg of the principle analyte (35 μg in the case of Se) and 200 μg of the secondary analyte were reacted with 10 ml of 2% w/v NaBH_4 solution under atmospheric conditions with stirring. The solutions remaining in the reaction flasks after filtration of the precipitates were analyzed as described previously (p.39) for traces of either analyte. (Later studies showed no deviation in the percent of element found when

Table 9. Interelement effects^a

Primary Analyte	Secondary Analyte	Concentration Ratio Secondary/Primary (μg)	% Signal Suppression of Primary Analyte ^b
As	Se	100/1	34
As	Se	200/50	63
As	Te	100/1	54
As	Te	200/50	50
Sb	Se	100/1	80
Sb	Se	200/50	54
Sb	Te	100/1	80
Sb	Te	200/50	80

^aPrecipitates present in all cases.

^bAnalysis by hydride technique.

^cAnalysis by solution nebulization.

^dAnalysis by solution nebulization (Ref.17)

^eNone detected.

% Element Found In Solution ^c				Detection Limit (μg/ml) ^d	
As	Sb	Se	Te	Primary	Secondary
n.d. ^e		n.d.		0.1	0.3
n.d.			n.d.	0.1	0.2
	n.d.	4.5		0.2	0.3
	6.7		9	0.2	0.2

reactions were performed while flushing the solution with Ar-5% H_2). Those results are also shown in Table 9.

For the case of 50 μg As and 200 μg Se, Table 9 shows a 63% suppression of the As signal. Utilizing the detection limits also given in Table 9, the amount of As present must have been less than 1.0 μg because none was detected. Similarly the amount of Se present must have been less than 3.0 μg . For the case of 50 μg As and 200 μg Te, a 50% As signal suppression was observed while less than 1.0 μg As and 2.0 μg Te were found in the reaction solution. For the case of 50 μg Sb and 200 μg Se, a 54% Sb signal suppression was observed while less than 2.0 μg Sb and 9 μg Se (4.5%) were found in the reaction solution. For the case of 50 μg Sb and 200 μg Te, and 80% suppression of the Sb signal was observed while only 6.7% (3.4 μg) Sb and 9% (18 μg) Te remained in solution. In all four cases a precipitate was formed and the percent of ions remaining in solution did not account for the signal suppressions observed. Because the plasma is such a hot atomization source, the signal suppressions could not have arisen in the plasma. Therefore, the nature of the precipitates formed was investigated in more detail.

CHAPTER V. INTERELEMENT EFFECTS

Compound Formations

Theory of binary compound formations

Selenium and tellurium, being VI A elements, tend to behave in a manner analogous to sulfur. H_2Se and H_2Te , which are analogs of H_2S , are volatile, soluble in aqueous solutions (27) and ionize as very weak acids. The ionization constants and general reactivity (due to decreasing bond strengths of these hydrides) increase as the atomic weights increase so the H_2Te is extremely unstable with respect to its constituents (91).

Because of the pH dependency of H_2Se ionization mentioned previously (p. 28) and the varying texture and color of the precipitates obtained from the hydride reaction, it seemed unlikely that H_2Se ionization and subsequent precipitation as Se^0 was a tenable explanation for the Se signal suppressions.

As and Sb are known to form binary compounds with Se, Te and S having the general formulae M_2X_3 (27) and M_2Y_5 (92) where M = As or Sb, X = Se, Te or S and Y = Se or S. The sulfides of As and Sb are formed readily by precipitation from solution with $\text{H}_2\text{S}_{(g)}$ (91). The pentaselenides of As and Sb have been synthesized for analytical purposes (gravimetric determinations of As and Sb) by preparing H_2Se and bubbling it through a solution containing As or Sb ions.

The entire synthesis procedure was accomplished in an inert atmosphere (92). However, synthesis of the As or Sb triselenides or tritellurides in a similar manner has not been documented to this author's knowledge.

Relative hydride formation times

If binary compounds of Se or Te and As or Sb were indeed forming in a manner similar to the one previously described, the H_2Se and H_2Te must have been formed in the reaction solution while As and Sb were still ions. To establish if such conditions existed, the relative hydride formation times were determined. However, to insure that mixing time did not make a significant contribution to the relative formation times, the time required for complete mixing was measured first. The time required for the complete mixing of one drop of NaBH_4 with 5 ml of analyte solution under the stirring conditions used in the study was less than 0.2 seconds as measured by using one drop of KMnO_4 and visual indications of complete mixing.

The relative hydride formation times were determined by measuring the length traversed by the recorder pen from the point of its engagement (the moment the NaBH_4 droplet fell from the addition funnel) to the initial rise of the analyte signal. For a recorder chart speed of 25 sec/cm, the time required for homogenous mixing of the NaBH_4 with the reaction solution is represented by a distance less than the width of the pen line. Therefore, the length

traversed by the recorder before the initial rise was representative of the time required for formation of the hydride, its evolution from the reaction surface and transport of the hydride gas to the plasma. If the first hydride to form was considered to form instantaneously, then the distance the pen traversed in that case could be said to represent the transport time. Therefore, the relative formation and initial evolution times for the remaining hydrides could be determined.

The relative time required for the initial (surface) hydride formation and evolution was determined by reacting one drop of NaBH_4 solution with 50 ug of analyte and measuring the distance described above. To insure that the time required for transport of the surface hydride was constant, the flow rate of the Ar-5% H_2 (carrier) gas was closely monitored. The rotometer settings were directly proportional to the gas flow rates (as calibrated with the "Precision" Wet Test Meter, Precision Scientific Co., Chicago, Ill.). The general trend in initial formation time in increasing order was Ge - Sb - As = Te - Se - Bi. This trend was consistent with the necessary conditions for binary compound formations.

Proof of compound formations

To determine the chemical composition of the precipitates formed during the hydride generation reaction, a series of acidified solutions (12 milliliters volume),

which contained 50 μg of either As or Sb and 200 μg of either Se or Te, were reacted with 10 mls of 2% w/v NaBH_4 solution under normal room atmosphere. Any precipitates formed were collected on high quality, moderately retentive filter paper (Carl Schleicher and Schuell Co., No. 589) by gravitational filtration. A one inch circular section of each filter paper which contained a precipitate was carbon-coated and semi-quantitatively analyzed by an X-ray electron microprobe technique by Francis Laabs. Each sample filter was analyzed in two ways. The sample was rotated so that the electron beam scanned the sample. In that way all substances of interest present on the filter paper were determined. The sample filter was then held in a fixed position while the electron beam focused on a single particle. The X-ray emission spectra of the particles and associated numerical data were corrected for any contribution from the filter paper background by arbitrarily subtracting 95% of the signal obtained when the electron beam scanned the sample filter. The 95% figure was used because of the undesirability of subtracting 100% of the background and possibly obscuring some baseline phenomenon. At least three particles on each filter sample were examined.

Table 10. Variability of precipitate composition

Atmosphere	Element Ratio	Number of Particles Analyzed	Mean	S.D.	Range
				Atomic Ratios	
Air	Se/As	8	14.78	-0.98	13.5-15.7
Air	Te/Sb	9	8.34	-2.88	7.3 -10.5
Ar-5%H ₂	Se/Sb	8	2.43	-0.78	1.5 - 3.6

An atomic ratio of the elements measurable in each particle was computed. The data obtained on precipitates formed when the reactions were performed under atmospheric conditions are given in Table 10. This table shows a consistency in the precipitate composition for Se-As and Te-Sb samples. A Te-As sample for which data are not given in the table varied over a range of atomic ratios of 41-100. These results did not confirm the presence of either tri- or penta-selenides or tellurides but rather indicated the formation of other compounds perhaps containing oxygen or chlorine. Because the results obtained under air atmosphere yielded no useful information, the hydride reaction was performed under an Ar - 5%H₂ atmosphere for a mixture containing 50 μ g Sb and 200 μ g Se, which was selected because no identifiable Sb-Se precipitate was formed under air atmosphere. The results of the microprobe analysis of the precipitate obtained are also given in Table 10. The microprobe X-ray spectrum of this precipi-

Figure 8. X-ray Spectrum of precipitate from Sb-Se mixture. (Reaction performed in Ar-5% H_2 atmosphere).

tate is shown in Figure 8. The results yielded some evidence to support the formation of a most likely binary compound having a formula $\text{SbSe}_{2.43}$. However, the determination of the exact formulation and quantitative yield figures were beyond the scope of this investigation. It is sufficient to recognize that the analytes were being immobilized by the formation of compounds between the analyte and concomitants. The difference in precipitates obtained in two different gas atmospheres further indicated that the reaction atmosphere was a fundamental variant in the nature of the side reaction which occurred.

The analytical curves for As and Sb with 100 μg Te as the concomitant, which are shown in Figures 9 and 10 confirmed the formation of telluride compounds under $\text{Ar-5\%H}_2$ atmosphere during the hydride reaction. In Figure 9, the relative intensity observed for 1 μg Sb represents a number which is 82% less than the value obtained for 1 μg Sb when only Sb was present in the reaction mixture. Similarly the slope from 0-5 μg represents a 82% reduction of the slope of the pure Sb analytical curve. Therefore 82% of the Sb must have been forming the precipitate. If Te was considered to have a 14.2% conversion efficiency to H_2Te and 100% of the H_2Te reacted to form the precipitate, the point at which the change in slope occurred (5 μg Sb) represents an atomic ratio of Te/Sb of 3.3. Figure 10 shows a similar case for As. The slope of the As curve from 0-4.2 μg

Figure 9. Interference curve for Sb with 100 μg Te present in reaction solution.

Figure 10. Interference curve for As with 100ug Te present in reaction solution.

represents a 93.5% reduction of the slope of a pure As analytical curve; that is, 93.5% of the As reacted to form the precipitate. Considering the Te to behave as previously described, the atomic ratio of Te/As at the point of the change in the slope (4.2 μg As) is 2.1. In both figures, the second slope (from 5-10 μg Sb and from 4.2-10 μg As) represents an excess of analyte above the concentration required to form a precipitate.

Based on the experimental evidence presented herein, it can be concluded that the signal suppressions reported in Table 9 for Sb-Se, As-Te, Sb-Te and very probably As-Se mixtures were due to the formation and precipitation of some compound of the analyte and the concomitant during the reaction process. Previously such signal suppressions had been blamed most frequently on compound formations in the flame (69). The first obvious implication of this study is that simultaneous, multi-elemental determination of these hydride forming elements over wide concentration ranges cannot be successfully completed even utilizing high temperature excitation sources such as the inductively coupled plasma. The second implication is that single element determinations over the ranges studied here, which were performed utilizing hydride generation, must be free of the interfering elements before valid data can be obtained.

Other Significant Observations

Characteristic evolution patterns

Acidified solutions of the analytes reacted with 2% w/v NaBH_4 solution added one drop at a time yielded signal patterns specific to the analyte or pairs of analytes. The characteristic evolution patterns for AsH_3 , SbH_3 , H_2Se and H_2Te are shown in Figures 11-14. Each figure represents the evolution of the hydride from one reaction solution. Each peak represents the signal resulting from the addition of one drop of NaBH_4 . The As and Sb curves displayed nearly complete evolution of the hydride with the addition of the first three drops of NaBH_4 , whereas the evolution patterns for H_2Se and H_2Te consisted of many successive peaks. In all cases one drop ($\sim 0.05 - 0.2$ mls) of NaBH_4 theoretically provided an excess of reagent for the formation of the respective hydrides, assuming that the hydride reaction indeed produces quantitative conversion. Furthermore, the assumptions that these data may reflect kinetically inhibited H_2Se and H_2Te formation and/or evolution upon addition of the first drop of NaBH_4 would be in direct contradiction to the data presented previously (p. 43). Because mixing occurred too swiftly and conditions were carefully controlled to minimize transport effects, the patterns

Figure 11. Characteristic evolution pattern for AsH_3 .

Figure 12. Characteristic evolution pattern for SbH_3 .

Se (200 μ g)
Se 196.1 Line

Figure 13. Characteristic evolution pattern for H_2Se .

Figure 14. Characteristic evolution pattern for H_2Te .

evidently reflect only the evolution properties of the hydrides under the reaction conditions.

Synergistic behavior

The characteristic evolution patterns changed when more than one element was present in a solution. The evolution behavior exhibited by H_2Se and H_2Te when As or Sb were present in a solution mixture suggested that the hydrides of Se and Te were acting in a manner synergistic to the VA (As or Sb) hydrides. For example, Figure 15 shows that the evolution of H_2Se which does occur in the presence of 50 μg Sb appears to be essentially complete after the addition of 4 drops of NaBH_4 solution, whereas in the absence of Sb, appreciable H_2Se evolution occurs even after the 14th drop as shown in Figure 13. As Figure 16 shows for the case of H_2Se evolution in the presence of 50 μg As, the evolution behavior of H_2Se is basically similar to the case of H_2Se in the presence of 50 μg Sb, although significant H_2Se evolution still occurred after the addition of 10 drops of NaBH_4 reagent. The peaks shown in Figure 16 are larger than those shown in Figure 13. The significant point is that H_2Se evolution in the presence of 50 μg of As or Sb was transformed into a pattern that more closely resembled the AsH_3 and SbH_3 patterns shown in Figures 11 and 12.

Perhaps the best example of this synergistic effect was the evolution behavior of H_2Te in the presence of 50 μg

Figure 15. H_2Se evolution pattern with 50 μ g Sb present.

Figure 16. H_2Se evolution pattern with $50\mu\text{g}$ As present.

Figure 17. H_2Te evolution pattern with 50 μ g Sb present.

Sb. Figure 17 shows that the H_2Te evolution which does occur is essentially complete after the addition of one drop of NaBH_4 whereas Figure 14 shows repeated increments of H_2Te evolution. The H_2Te evolution in the presence of 50 μg of Sb more closely resembled the SbH_3 pattern shown in Figure 12 than the H_2Te pattern of Figure 14.

These phenomena were not the typical type of synergisms in which the element present in a lesser quantity exhibited the behavior of the element present in greater quantities. For example, Figure 18 shows that the evolution pattern exhibited by 50 μg Sb in the presence of 200 μg of Se or Te is basically similar to the pattern exhibited by 50 μg Sb when present alone in the solution mixture (see Figure 12). However because of the precipitates being formed, the presence of Se and Te did cause considerable Sb signal suppression. When the respective concentrations differed by two orders of magnitude, the typical synergistic effects were observed. As shown in Figure 19, the behavior of 1 μg Sb in the presence of 100 μg of Se is similar to the evolution pattern when Se alone is present in solution (see Figure 13).

The synergistic effects observed could arise in a number of ways, two of which will be considered here. First the synergistic behavior may reflect changes in the solubility of the gas. In the case of covalent substances, solubility does not necessarily imply ionization of the

Figure 18. SbH_3 evolution pattern in presence of 200 μg Se and 200 μg Te.

Figure 19. SbH_3 evolution in the presence of $100\mu\text{g}$ Se.

compound but solvation. When a gas is solvated, weak covalent bonds form which prevent evolution from the solution and affect the solubility of that gas. As Table 11 shows, the solubilities of the gases increase in the following order $\text{SbH}_3 < \text{AsH}_3 < \text{H}_2\text{Se} < \text{H}_2\text{Te}$. The least soluble gas SbH_3 exhibits a single signal evolution pattern (see Figure 12). The more soluble gases H_2Se and H_2Te exhibit multiple signal evolution patterns (Figures 13 and 14). If the environment of the solvated substance is changed from a solution to a gas, increased evolution may occur. For example, if SbH_3 were desolvating some of the H_2Se , then increased H_2Se evolution would occur upon the addition of the first drop of NaBH_4 . As shown in Figure 15, H_2Se did behave as if it were being desolvated by SbH_3 . Therefore, the solubility model would seem to satisfactorily explain the synergistic effects observed.

A second model which might be invoked to explain the observed phenomena is one of "secondary" reductions. A secondary reduction will be defined here as the generation of one hydride by the action of a second hydride. For example, in a solution containing Sb and Te, 14.2% of the Te should form H_2Te and evolve as the hydride leaving 85.8% of the Te in solution in some form. (Disregard the precipitate formation for the moment.) SbH_3 is also formed by the action of NaBH_4 . Now consider SbH_3 as a reducing agent. Equation 5a describes the oxidation of SbH_3 to Sb^0 . Note

Table 11. Solubility data

Species	Solubility	Temperature
AsH_3^{a}	51.3 gms/100 mls H_2O	20°C
AsH_3^{a}	40.5 gms/100 mls H_2O	25°C
SbH_3^{b}	8.7 gms/100 mls H_2O	22°C
$\text{H}_2\text{Se}^{\text{c}}$	999 gms/100 mls H_2O	22.5°C
$\text{H}_2\text{Te}^{\text{b}}$	"Very Soluble"	

^aRef. 93.^bRef. 27.^cRef. 94.

that SbH_3 is a stronger reducing agent than NaBH_4 (Equation 5b).

Equation 6 describes a similar secondary reduction of Te^{+4} by SbH_3 . Similarly AsH_3 might reduce Te ions according

to Equation 7. Similar equations can be written for the

reduction of Se ions, by AsH_3 and SbH_3 . The secondary reduction model would seemingly explain the synergisms observed in Figures 15-17. However if secondary reductions were the correct explanation, one would not expect either the Se and Te signal suppressions which were observed or the formation of precipitates which contained two hydride forming elements.

The synergistic effects noted here could be used to aid the evolution of H_2Se and H_2Te if a means of controlling the compound formations were found. One similar example will be given in Chapter VII.

CHAPTER VI. SUMMARY

In Chapter I, seven criteria for the development of a suitable analytical method for the determination of As, Sb and Se were cited. Criterion one is satisfied by the data in Table 8, page 45. Criteria four through six are also satisfied to a high degree by the hydride evolution-ICP technique, but criteria two, three and seven are not. Of the latter three, the interelemental interaction caused by the simultaneous presence of group VA and VI A analytes in the sample is the most significant. With reference to these interelement effects, the results reported in this thesis have provided the following insights into the nature of the interactions.

- I. There is a definite difference in the initial formation times of the hydrides. The general trend in increasing order was $\text{Ge} \prec \text{Sb} \prec \text{As} \approx \text{Te} \prec \text{Se} \prec \text{Bi}$. This trend was consistent with the necessary conditions for binary compound formation.
- II. The precipitates formed showed a consistency of composition although a determination of the exact formulation was not performed.
- III. The signal suppressions reported in Table 9 were due to the formation and precipitation of some compound of the analyte and the concomitant during the reaction process.

IV. The hydrides of As, Sb, Se and Te evolve in a characteristic fashion which may be altered by the presence of certain concomitants in the reaction solution.

CHAPTER VII. SUGGESTIONS FOR FUTURE WORK

To alleviate the problem of signal suppressions, the most obvious approach is to provide environmental conditions giving; (a) greater % evolution of the respective hydrides; (b) elimination of the undesirable precipitation side reactions. Two papers just published offer several suggestions. McDaniel, Shendrikar, Reiszner and West (95) have proposed a hydride evolution technique for selenium determinations which yields a 90% efficiency of H_2Se evolution. They reported a study of potentially interfering ions including Sb^{+3} and HAsO_4^{2-} with the result that the presence of Sb^{+3} and HAsO_4^{2-} in the reaction solution did not cause an interference of more than 5%. McDaniel et al. concluded that "the increased efficiency of the procedure...may account for the reduction of interference"(95). A second paper by Fleming and Ide (90) suggested that various acid media and other reagent additions may improve the signals obtained. The most notable improvement was observed for Pb. A tartaric acid and $\text{K}_2\text{Cr}_2\text{O}_7$ solution increased a 10 ug Pb absorbance from nearly zero to almost 9.4 absorbance units (90). It seems possible that the interferences reported in this thesis can be minimized by new hydride techniques such as the one proposed by McDaniel et al. in the future. Certainly work along the lines proposed by McDaniel et al. (95) and Fleming and

Ide (90) promises a brighter future for the hydride technique.

Another subject worthy of further study is the secondary reduction theorized in Chapter V. Although there was insufficient evidence to tie the synergistic effects observed to such a theory, some data suggest such reductions might indeed be factual for some reaction mixtures. For example, BiH_3 possessed an evolution efficiency of 45% and presumably the same conversion efficiency because it exhibited no difficulty in evolution. As shown in Figure 20, that fraction of the Bi which evolves as BiH_3 does so upon the addition of one drop of 2% w/v NaBH_4 and subsequent additions do not produce further signals. It is worthwhile to note that concentrated Bi solutions proceed through an observable gray state (possibly a metallic state) during the reaction process when 100 μg As were added to 1 μg Bi in a solution mixture, a 100% enhancement of the Bi signal was observed. Similarly when 100 μg Ge were added a 73% enhancement was observed. However, 100 μg Sb did not produce similar results. Because of the evolution properties of BiH_3 , it is unlikely that As or Ge has desolvated the gas. Therefore, consider the possibility of a secondary reduction.

The potential for Equation 8 is unknown. However, because NaBH_4 which has a potential of 0.48 v reduces Bi^{+3} to BiH_3 , the potential for Equation 8 must be less than 0.48 v. Similarly the potential for Equation 9 is unknown. It is

Figure 20. Characteristic evolution pattern for BiH₃.

It is entirely possible that AsH_3 might reduce Bi^{+3} by Equation 10 or possibly Equation 11 if there is indeed a metallic intermediate.

Similar equations could be written for the use of Sb and possibly Ge, to determine if secondary reductions do contribute to or cause the Bi signal enhancements, further study is needed.

The synergistic effects reported in Chapter V might also prove useful if the compound formations can be controlled. During this investigation, one potentially useful combination of elements was discovered. A qualitatively reproducible enhancement of a 50 μg Se signal was produced by the presence of 200 μg Bi in the reaction mixture. As Figure 21 shows, the effect of Bi on H_2Se evolution is similar to the case for H_2Se in the presence of As. Although significant H_2Se evolution still occurred after the addition of 9 drops of NaBH_4 , the peaks shown in Figure 21 more closely resemble the BiH_3 peaks of Figure 20 than the H_2Se peaks of Figure 13. The fact that enhancements were observed and precipitates were not formed clearly shows the potential usefulness of

Se(200 μ g) + Bi(50 μ g) Mixture
Se 196.1 Line

Figure 21. H_2Se evolution pattern with 50 μ g Bi present.

this combination if the enhancements can be quantitatively controlled.

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APPENDIX: THERMODYNAMIC CONSIDERATION OF THE VALENCE STATE PROBLEM

Strictly from the thermodynamic considerations, the reduction of As(+5) to As(-3) by reaction with BH_4^- could be a one step process. (The protonated species were chosen for these considerations based on calculations of the solution equilibrium conditions before reduction).

However, the discrepancy in the results obtained suggests a multi-step mechanism of reaction. The following mechanism may seem probable.

However, calculations show that Step 3 alone will not occur spontaneously using BH_4^- as the reducing agent. (G 0)

Therefore, the reduction of As^{+3} to As^{-3} must occur as a single step (Step 2a) and the reduction of As^{+5} to As^{-3} as two steps (Step 1 and Step 2a).

Step 1 is thermodynamically favorable whether the reducing agent employed is BH_4^- or I^- .

Step 1 with BH_4^- as the reducing agent

Step 1 with I^- as the reducing agent

Since step 1 is the rate determining step, reduction of As^{+5} with BH_4^- results in incomplete conversion to the hydride.

When I^- is used to reduce the As^{+5} to As^{+3} prior to reduction to the hydride by BH_4^- , no discrepancy occurs. Similar considerations can be used to illustrate the Sb^{+5} reduction problem.