

/ SENSITIVITY ENHANCEMENT AND INTERFERENCE STUDIES
IN ULTRA-TRACE As, Se, Sb, AND Sn DETERMINATION
BY HYDRIDE GENERATION ATOMIC ABSORPTION AND
A NEW TENAX GC/PHOTOIONIZATION SYSTEM)

by

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Chapter 1

GENERAL INTRODUCTION TO THE THESIS

In recent years, extensive exposure to arsenical herbicides, biocides, stabilizers, bactericides, antifouling agent in paints, and toxic wastes containing As, Se, and Sn from micro-electronic industries has generated serious environmental problems (1, 2). In order to effectively study the environmental impact of these elements, accurate and unusually sensitive analytical methods are necessary. Due to the poor sensitivity of direct solution methods for As, Se, Sb, and Sn determinations, hydride preconcentration techniques have evolved and proven promising. Analytical accuracy with the sensitive hydride preconcentration techniques has been the subject of considerable attention when certain transition metals and nitrogen oxides are present to lower the reaction yield (11, 16, 27, 28). This Master's thesis addresses both the sensitivity and the accuracy issue in separate sections. A general introduction to the sensitivity issue is presented below (pp. 2-9), and an introduction to the accuracy and interference issue appears on pp. 9-14.

I. Sensitivity Introduction.

In most routine atomic spectrometric methods, a sample containing As, Se, Sb, and/or Sn etc. is nebulized directly into a spray chamber leading to a hot atomization cell where atomic absorption or emission processes occur (5-7). In this method, however, the amount of sample injected is small and the corresponding signal is further reduced by severe mass transport loss due to aerodynamic discrimination against large droplets in the spray chamber. In addition, the resonance lines of some of these elements lie in the far ultraviolet region of the spectrum where flame, plasma, or atmospheric opacity can produce an extremely unfavorable signal to noise ratio. The overall detection limit of a nebulization technique is therefore far from satisfactory for metalloids such as As and Se.

In the hydride preconcentration method, volatile hydrides of the corresponding dissolved arsenic, selenium, etc. halides or oxy-anions are chemically generated in a reactor containing a reducing agent and an acidified sample. Hydride products are swept by an inert carrier gas into a separate atomic absorbance or emission detector for atomization and quantitative analysis. Covalently bonded volatile hydrides of As, Se, Sn, Sb, Ge, Te, Pb,

and Bi have been preconcentrated as gases starting from aqueous solutions of their respective halides or oxy-anions and analyzed either by atomic spectroscopy or gas chromatography (8-12).

Hydride generation methods enjoy an important benefit which can not be realized in a direct nebulization method. Namely, up to 10^4 x gas phase preconcentration can be achieved with a corresponding improvement in concentration detection limit. Tables 1.1, 1.2, and 1.3 compare concentration detection limits reported in the literature for direct nebulization and hydride generation methods for Ge, As, Se, Sn, Sb, Te, and Bi. In general, hydride generation methods provide one to three orders of magnitude better concentration detection limit than direct nebulization methods. This is simply a result of the preconcentration effect and assumes the availability of a relatively large initial sample volume, which is usually the case for an environmental or food analysis.

It should be noted that, although the enhanced sensitivity of hydride methods (Tables 1.1-1.3) is adequate for analyzing many solid foods, biological tissues, soils and environmental sediments, a sensitivity problem still remains for natural water and waste water determinations which exhibit substantially lower As and Se levels. Typical samples submitted for water quality

Table 1.1 ATOMIC ABSORPTION LIMITS (3)

Comparison of Pre-1985 Detection Limits (d.l.) (ppb) And Limits of Quantitation (L.O.Q.)* (ppb) .

	<u>Nebulization</u>		<u>Hydride</u>	
	<u>d.l.</u>	<u>L.O.Q.</u>	<u>d.l.</u>	<u>L.O.Q.</u>
Ge	20	100	4	20
As	630	3150	0.8	4
Se	230	1150	1.8	9
Sn	150	750	0.5	2.5
Sb	60	300	0.5	2.5
Te	44	220	1.5	7.5
Bi	44	220	0.2	1

* L.O.Q. = 5 x d.l. from reference 13.

Table 1.2 ATOMIC FLUORESCENCE LIMITS (3)

Comparison of Published Detection Limits (ppb) and L.O.Q. (ppb).

	<u>Nebulization</u>		<u>Hydride</u>	
	<u>d.l.</u>	<u>L.O.Q.</u>	<u>d.l.</u>	<u>L.O.Q.</u>
Ge	100	500
As	100	500	0.1	0.5
Se	40	200	0.06	0.3
Sn	50	250
Sb	50	250	0.1	0.5
Te	5	25	0.08	0.4
Bi	5	25

Table 1.3 ATOMIC EMISSION LIMITS (3)

Comparison of Published Detection Limits (ppb), and L.O.Q.'s (ppb) Reported for Inductively Coupled Plasma (ICP) and Microwave Induced Plasma (MIP) Emission Spectroscopies.

	<u>ICP/Nebulization</u>		<u>ICP/Hydride</u>		<u>MIP/Hydride</u>	
	<u>d.l.</u>	<u>L.O.Q.</u>	<u>d.l.</u>	<u>L.O.Q.</u>	<u>d.l.</u>	<u>L.O.Q.</u>
Ge	150	750	0.15	0.75
As	40	200	0.8	4	0.35	1.75
Se	30	150	0.8	4	1.25	6.25
Sn	300	1500	2	10
Sb	200	1000	1	5	0.5	2.5
Te	80	400	1	5
Bi	50	250	0.8	4

determination are in the range of 0.1-5 ppb As or Se. A sensitivity problem therefore remains in that the lower limits of quantitation (L.O.Q.) (13) for ICP emission and atomic absorption methods listed in Tables 1.1 and 1.3 are generally still too high to permit reliable quantitative analysis over the full range of 0.1-5 ppb important for assessing water quality.

Atomic fluorescence measurements can offer some additional sensitivity (see Table 1.2), but adequate atomic fluorescence instrumentation has proven generally too complex, too costly, and/or too narrowly specialized in its scope of application to warrant commercial production by an instrument manufacturer. In the field of widespread, routine environmental water quality monitoring, a sensitivity gap therefore still remains to be bridged. A more sensitive, commercially marketable instrument needs to be developed. Such a system would preferably have a L.O.Q. \leq 0.1ppb and a d.l. \leq 0.02ppb.

Once the volatile hydride has been generated, vacuum line cold entrapment techniques have been employed to further enhance the sensitivity of both atomic absorption (24, 25) and ICP (10) emission methods. However, these methods have proven too cumbersome and inconvenient to be commercially developed and marketed for routine analysis

involving large numbers of samples.

Through optimization of absorption cell design, hydride reactor design, and reaction conditions, one manufacturer has recently introduced a continuous flow atomic absorption hydride generation system exhibiting improved As, Se, etc. sensitivity and extraordinary simplicity of operation (22). The new "VGA-76" atomic absorption system by Varian Techtron (22) exhibits As and Se detection limits of 0.1ppb and 0.3ppb respectively, is fully automated, and is capable of analyzing one sample per minute. No cryogenic entrapment is employed. The atomic absorption L.O.Q.'s for this system are 0.5ppb As and 1.5ppb Se. These values are better than the atomic absorption and ICP emission data of Tables 1.1 and 1.3, but are still a bit high for some water quality (0.1-5 ppb) determinations.

One objective of this thesis project was to solve the remaining As and Se sensitivity problem by developing a simple, convenient, cost effective instrument which is a new combination involving the Varian VGA-76 continuous flow hydride generator, gas chromatography (GC) and a vacuum ultraviolet (VUV) molecular photoionization approach to replace the conventional atomic absorption detector for arsenic, selenium, etc. hydrides. This instrument makes use of cryogenic entrapment to further

preconcentrate the hydride after its generation and to facilitate suitably rapid injections onto a Tenax GC column. The new photoionization detector (PID) for GC is studied here in combination with the cryogenic entrapment variation on the VGA-76 hydride reactor employed as a sample introduction system. Possibilities for simultaneous As, Se, Sb, and Sn determination at part-per-trillion levels are explored in Chapter 3 of this thesis.

II. Introduction To Interference And Analytical Accuracy Problems With The Hydride Preconcentration.

There are two frequently used hydride generation reactions that are convenient and practical in chemical analysis: 1) excess metal/acid reduction and 2) excess NaBH_4 /acid reduction of trace aqueous arsenate, arsenite, selenite, etc.. Traces of gaseous arsine (AsH_3) and hydrogen selenide (SeH_2) along with a major amount of H_2 are liberated as a result of acid hydrolysis of the BH_4^- reagent in a polluted water sample.

Investigations using other metals such as Al(14, 15), and Mg (16) have also been reported. The metal/acid hydride generation reaction has several drawbacks. First of all, it is inherently slow, in part due to the heterogeneous reaction nature of the process. A typical

reaction time for several micrograms of analyte is 20 minutes. Secondly, prereduction of certain analytes to a favorable initial oxidation state is required prior to the actual hydride generation reaction. Thirdly, automation for the whole process is not practical with a solid reagent such as metallic zinc. Fourthly, only As, Se, Sb, and Bi hydrides have been generated this way. Finally, several transition metals have been reported to produce extremely severe inhibition of the Zn/HCl reduction (23).

The first analytical hydride generation method using $\text{NaBH}_4/\text{acid}$ was reported by Braman (4) in 1972. Since that time, several hundred more applications of that reaction have been reported. In $\text{NaBH}_4/\text{acid}$ hydride generation reactions, NaBH_4 can either be added to an aqueous sample as a solid or a solution. Major amounts of H_2 (from BH_4^- hydrolysis) and traces of AsH_3 and SeH_2 are quickly evolved with near quantitative yield from traces of aqueous arsenite, arsenate and selenite.

In addition to the relative ease of automation with a solution phase reagent, the $\text{NaBH}_4/\text{acid}$ hydride generation reaction has several advantages over metal/acid hydride generation reactions. First of all, hydride formation is much faster with NaBH_4 reagent. Typical reaction times range from 10 to 30s. Secondly, hydrides of a larger

number of elements can be generated with the BH_4^- reagent.

Although the hydride preconcentration technique has proved to be satisfactory in many applications, there are a few limitations which need to be addressed. First of all, the hydride generation technique is not universal. Only eight elements of group IVA, VA, and VIA, namely, As, Se, Sn, Sb, Te, Ge, Pb, and Bi can be readily converted into volatile, covalently bonded hydrides by the NaBH_4/HCl reaction. From the stand point of selectivity, this limitation can be regarded as an separation advantage because fewer elements forming volatile hydrides mean less spectral interference. A more complex sample matrix can therefore be tolerated before interference limits are reached, and complicated high resolution spectroscopic instrumentation with interelement correction is not required.

The second limitation is interfering chemical reactions. Hydride generation techniques suffer from chemical interference that either inhibit hydride formation in the liquid phase or degrade the hydride (in the liquid and/or gas phase) to a non-volatile product before it reaches the detector. The most prominent interferants in hydride preconcentration are Cu, Ni, Fe, and NO_x (17, 18). Interference remedies commonly used

prior to hydride generation included heating the sample on a hot plate until NO_x is gone (19), adding sulfamic acid to remove the last traces of NO_x (12, 20), chelating unwanted transition metal ions (12), and extracting the offending metal ions out of the sample matrix (21). These remedies have proven effective in some cases but not in others; especially not when copper and nitrate are simultaneously present (12). The interference remedies were developed semi-empirically. Lack of information about the nature and mechanism of the interference has made the search for effective masking agents or conditions rather slow.

An interesting development in the battle against interference occurred in some preliminary testing on this project with the new VGA-76 analyzer described earlier in the "Sensitivity Introduction" (pp. 2-9). Although the VGA-76 was designed simply to enhance the sensitivity of As, Se, etc. determination, we found that it was unusually free of metal and NO_x interferences, even without the use of masking agents or separation steps. A major focus of this thesis project was to investigate the nature of chemical interferences in the analytical hydride preconcentration, and to determine why the VGA-76 analyzer was so interference-free compared with the literature results from 1971 to present.

The unusual performance of the VGA-76 analyzer in hydride generation, the lack of data concerning the interference mechanism in the liquid phase and gas phase in hydride generation, and the quest for an economic approach to simultaneous multielemental hydride determination at the ultra-trace level collectively prompted us to undertake these investigations. The organization of studies done in this thesis is as follows. Chapter 2 is a description of the apparatus and a report on some preliminary optimizations of HCl and NaBH₄ concentration for As, Sn, and Se hydride generation using a Varian VGA-76 continuous flow hydride generation apparatus with an atomic absorption spectrometer. Chapter 3 reports the application of a VGA-76 hydride reactor in combination with gas chromatography and a photoionization detector as an unusually sensitive new approach to the simultaneous determination of As, Se, Sb, and Sn as their hydrides. Chapter 4 is a report on elucidation of the interference mechanism of copper in inhibiting SeH₂ generation. Chapter 4 also illustrates how the reaction conditions can be adjusted to effectively defeat this interference without the use of masking agents. Chapter 5 reports the nitrite, nitrate, volatile NO₂, and the combined nitrate/Cu²⁺ interferences in SeH₂ generation.

Chapter 6 summarizes the thesis results. And finally, Chapter 7 discusses possible future directions worth pursuing.

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Chapter 2

OPTIMIZATION OF As, Se, AND Sn HYDRIDE GENERATION REACTION CONDITIONS

Gaseous hydride generation techniques have been applied widely in atomic absorption spectroscopy for a variety of group IVA, VA, and VIA elements either through batch or continuous flow redox methods. The batch method of hydride generation (1-5) involves sudden addition of a NaBH_4 pellet or gradual delivery of NaBH_4 solution into a reaction vessel containing a volume of acidified aqueous sample. The continuous flow method (6-9) employs a peristaltic pump to continuously mix NaBH_4 solution with a stream of acidified water sample solution. The resulting volatile hydride product in both methods is carried by a stream of inert gas, such as N_2 , to a flame heated quartz cell where the hydride is atomized and detected by atomic absorption. The batch method produces a transient hydride signal and requires more analyst manipulation. The continuous flow method, on the other hand, generates a steady state hydride signal, allows more control over reaction conditions, and can be easily automated. This chapter is a description of the continuous flow BH_4^- reactor used throughout the thesis and a brief study

involving the optimization of the HCl and NaBH₄ concentrations in reducing aqueous As(III), Se(IV) and Sn(II) to the corresponding volatile hydrides (AsH₃, SeH₂, and SnH₄).

I. EXPERIMENTAL SECTION

1. APPARATUS. A Varian VGA-76 continuous flow BH_4^- reactor was used for hydride generation. As shown in Figure 2.1, the apparatus consists of a three channel proportioning peristaltic pump, a small bore Teflon reaction coil, a pyrex gas-liquid separator, and a flame heated quartz absorption cell. In principle, the peristaltic pump can carry more than three reagent channels. For the hydride preconcentration application in this chapter, however, only three reagent channels are required: sample, acid, and NaBH_4 channels. Channel tubings were made of polyvinyl chloride (PVC). Dimensions of the channel tubing are as follows: sample channel: 2.06mm ID X 41cm, acid channel: 0.76mm ID X 41cm, NaBH_4 channel: 0.76mm ID X 41cm.

The normal operating conditions for the VGA-76 reactor are summarized in Table 2.1. Except where otherwise mentioned, the sample is initially in 6M HCl and is further acidified with a lower flow rate of 10M HCl by the acid channel before being mixed with the 0.5% NaBH_4 channel. After liquid reagent and sample mixing, N_2 bubbling is added, and the resulting mixture is carried through a 1.32mm ID X 30.5cm Teflon reaction coil where

Figure 2.1 Schematic Diagram of VGA-76 Continuous Flow Hydride Generator.

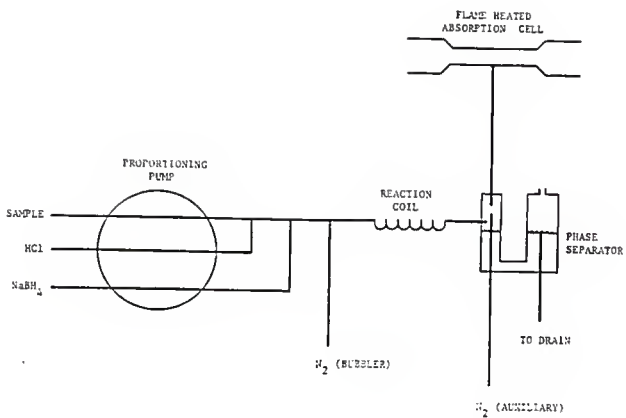


TABLE 2.1 Operating Conditions for VGA-76
Continuous Flow BH_4^- Reactor.

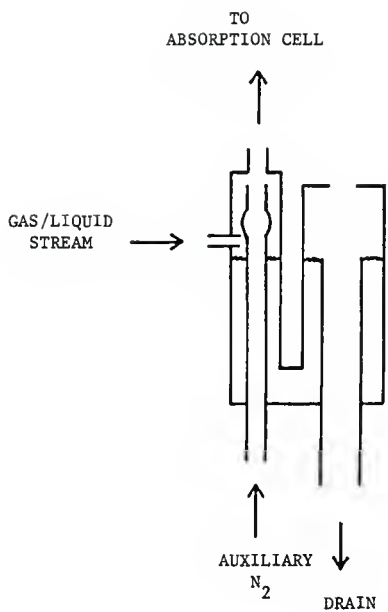
<u>CHANNEL</u>	<u>FLOW RATE</u> (mL/min)
Sample (in 6M HCl)	7
Acid (10M HCl)	1
NaBH_4 (0.5% in 0.5% KOH)	1
N_2 (bubbler)	40
N_2 (auxiliary)	40

the hydride generation reaction is completed. The resulting H_2 and analyte hydride gather into gas bubbles within the following liquid stream in the reaction coil.

The N_2 bubbler aids in degassing the volatile hydrides from solution. Products of the hydride reaction are then carried to the U-shaped pyrex gas-liquid separator (Figure 2.2) where separation of the volatile hydride and H_2 from the liquid phase is completed. A second stream of auxiliary nitrogen introduced at the outlet of the gas-liquid separator accelerates the transport of volatile analyte to the detector cell. A 3.18mm ID X 20.3cm black latex rubber tube connects the gas-liquid separator with the long path (10cm) flame heated quartz absorption cell where the volatile hydride is atomized. The quartz absorption cell is mounted on a steel bracket which suspends it in an air/acetylene flame. The cell is also optically aligned in the light path of the atomic absorption spectrophotometer to maximize the intensity of source radiation passing through the cell opening.

The detection system included a Jarrel-Ash model 850 atomic absorption spectrophotometer with premixed air/acetylene burner, H_2 continuum source background corrector, Hamamatsu (Hamamatsu Systems Inc., Waltham, MA) R106UH photomultiplier tube, Varian Techtron (Varian

Figure 2.2 Pyrex Gas/Liquid Separator.



Associates, Palo Alto, CA) Se hollow cathode lamp, As (Varian, Australia), and Sn (Varian, Ireland) hollow cathode lamps. Operational settings of the detection system are summarized in Table 2.2.

2. Reagents. A stock 1000ppm Se(IV) solution was prepared by dissolving 1.40g SeO₂ (Ventron, Danver, MA) in 1.00L de-ionized distilled water. The Se(IV) working standard was prepared by further diluting the stock solution in 6N Baker intra-analyzed grade HCl. Certified atomic absorption standards 1000ppm As (as As₂O₃ in dilute nitric acid) and 1000ppm Tin (as SnCl₂ in dilute HCl) were obtained from Fisher Scientific. Stock As(III) standard was further diluted to the desired concentration with 6N Baker intra-analyzed grade HCl. Treatment of the stock Tin solution is mentioned later in the results and discussion section. Stock 5% NaBH₄ was prepared by dissolving 5.0g Ventron analytical grade NaBH₄ in 100mL 0.5% KOH (Fisher, certified A.C.S. grade). The NaBH₄ solution is then stored at 5°C and used within a few days.

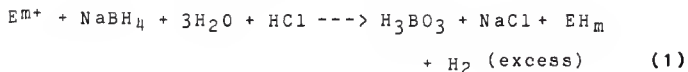
TABLE 2.2 Atomic Absorption Spectrometer Setting
for Various Hollow Cathode Lamps (HC).

<u>HC</u>	<u>WAVELENGTH</u> (A)	<u>CURRENT</u> (mA)	<u>SLIT BANDPASS</u> (A)
As	1937	10	5
Se	1961	12	15
Sn	2863	7	5

3. **PROCEDURE.** In continuous flow experiments, flow rates of NaBH_4 , acid, and sample channels were 1mL/min, 1mL/min, and 7mL/min respectively. Both bubbler and auxiliary nitrogen flow rate were 40mL/min. The steady state atomic absorption signal of the element of interest was recorded. The integration time was 5s per reading and five readings were averaged for each sample. Except where it is otherwise mentioned, the sample was first manually acidified to a level of 6M HCl and then further acidified automatically with the 10M HCl channel before being reduced by NaBH_4 . All three solutions were at room temperature. Each sample run was immediately followed by a blank run.

III. RESULTS AND DISCUSSION

The net reaction of hydride production using NaBH_4/HCl is described by Equation 1 (10):



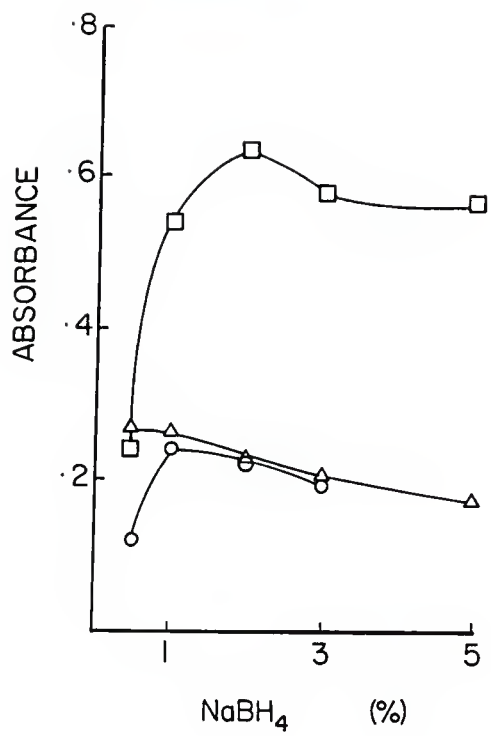
Where E is the hydride forming metalloid (eg. As(III) and Se(IV)). It should be mentioned that hydrogen gas is produced as a result of acid hydrolysis of NaBH_4 even without $\text{E}^{\text{m}+}$.

As shown in Figure 2.3, the optimal NaBH_4 concentration for single element As, Se, and Sn determinations are 2%, 0.5%, and 1% respectively. Although there is some variation in how the BH_4^- concentration effects the three elements, a reasonable response is obtained for all over the range 0.5 to 5%. For reasons of minimizing reagent contamination, quartz cell devitrification, and interference effects (to be discussed later in Chapter 4), a compromised BH_4^- concentration for later simultaneous multielement analysis was chosen to be 0.5%.

At low BH_4^- concentrations, the As and Sn conversion rates are slow. At high BH_4^- concentrations, the H_2 evolution rate (Equation 1) increases and lowers the

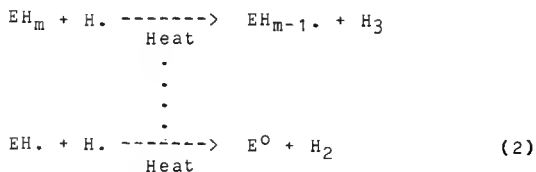
Figure 2.3 NaBH₄ Effects on As, Se, And Tin Hydrides Generation in Continuous Flow Reactor.

- □ - 10ppb As, 6M HCl
- △ - 10ppb Se, 6M HCl
- ○ - 20ppb Sn, 0.1M HCl



analyte concentration by gas phase dilution. The correlation of hydrogen production and NaBH_4 concentration is summarized in Table 2.3 and Figure 2.4. These data will be referred to again in later chapters.

Although the H_2 dilution effect alone can account for the shape of the high concentration region of Figure 2.3, several authors have noted the possible adverse effect of excessive H_2 evolution on hydride atomization in the flame heated quartz cell. Atomization in the heated quartz absorption cell also produces hydrogen according to Equation 2 (11):



Where E is the hydride forming metalloid. Clearly, large excesses of hydrogen production resulting from the acid hydrolysis of NaBH_4 could shift Equation 2 somewhat to the left (11), leading to the suppression of atomization.

We noticed that, at NaBH_4 concentrations higher than 1%, the hydride generation reaction becomes vigorous and the heated quartz absorption cell is easily devitrified. In view of the participation of a clean absorption cell

TABLE 2.3 NaBH₄ Concentration Effect on Hydrogen Generation

<u>%NaBH₄</u>	(a) <u>H₂</u> (mL/min)	(b) <u>H₂</u> (mL/min)	(c) <u>N₂</u> (mL/min)
0	0	0	81
0.5	10	10	81
1	24	21	81
2	53	48	81
3	81	75	81
5	142	120	81

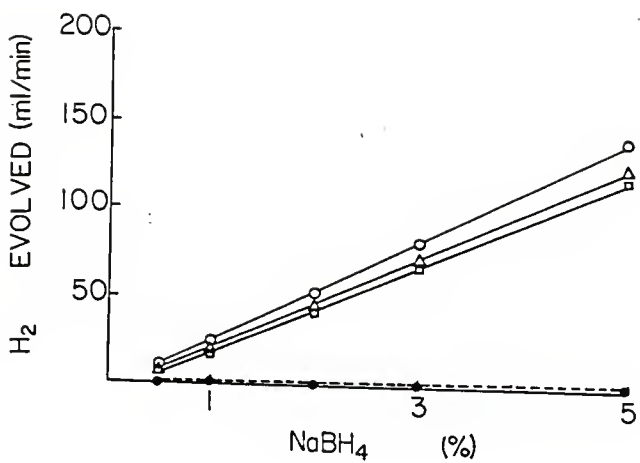
(a) 6M HCl.

(b) 2M HCl.

(c) Auxiliary N₂ 40mL/min and bubbler N₂ 41mL/min.

Figure 2.4 Effects of NaBH_4 on Hydrogen Production in Continuous Flow Hydride Reactor.

- ○ - 6M HCl, 10M HCl in acid channel
- △ - 2M HCl, 10M HCl in acid channel
- □ - water, 10M HCl in acid channel
- ● - water, water in acid channel



wall in SeH_2 atomization (12, 13), accelerated absorption cell devitrification can render the atomization of the hydride less efficient in the long run.

Figure 2.5 shows the effect of HCl concentration in the generation of As, Se, and Sn hydrides. Generally, As and Se give better hydride signals at higher HCl concentrations while the Tin hydride signal is suppressed significantly at higher HCl concentrations as a result of higher solubility of SnH_4 in a more acidic medium according to Equation 3 (14):

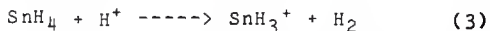
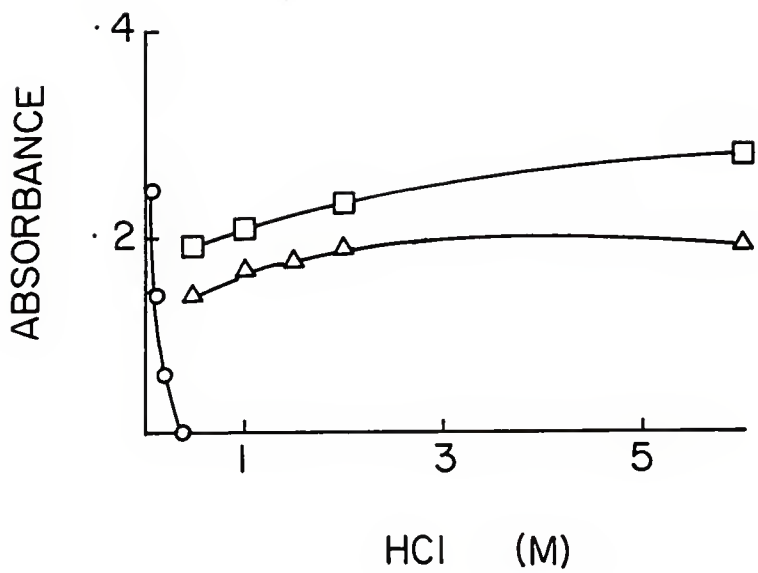


Figure 2.5 may be used to select an acidity level suited to individual single element determination. The reaction of Equation 3 and the data of Figure 2.5 indicate that some difficulty may be encountered in selecting a compromised acidity for later simultaneous multi-element determinations. These data will be important in Chapter 3 where dual reaction coils and separate acidity levels (one for Sn and another for As, Se, and Sb) are ultimately dictated for the simultaneous determination of these elements.

Figure 2.5 Effect of HCl on As, Se, and Tin Hydride Generation in Continuous Flow Reactor.

0.5% NaBH₄ in reducing agent channel.

- □ - 10ppb As
- △ - 10ppb Se
- ○ - 20ppb Sn



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Chapter 3

ULTRA-SENSITIVE, SIMULTANEOUS DETERMINATION OF As, Se, Sb, AND Sn BY HYDRIDE GENERATION GAS CHROMATOGRAPHY USING A TENAX GC COLUMN AND PHOTO-IONIZATION DETECTOR

In the previous chapters, we have demonstrated that aqueous As, Se, and Sn can be determined at part per billion levels by atomic absorption via the generation of their respective hydrides with a Varian VGA-76 continuous flow BH_4^- reactor. Since hydrides of up to nine elements can be generated simultaneously during a single $\text{NaBH}_4/\text{acid}$ reaction, it is clear that conventional single element atomic absorption detection does not make efficient use of all available information concerning a given sample, especially if that sample contains more than one hydride-forming element.

Several multi-elemental spectroscopic methods have been reported for use with volatile hydrides of As, Se, Sn, etc.. Inductively coupled plasma (ICP), direct current plasma (DCP), and microwave induced plasmas (MIP) have

been used with multichannel, photomultiplier-based, "direct reading" spectrometers (1, 3-8). A combination of high spectrometer cost, complexity of instrumental operation, and H₂ pressure incompatibility or H₂ quenching effects resulting from vigorous acid hydrolysis of the NaBH₄ reagent make ICP and MIP sources rather unattractive for ultratrace arsenic and selenium etc. determination.

Hydride generation/gas chromatography has been suggested for simultaneous, multielement hydride detection by a number of authors. GC systems with thermal conductivity detectors (TCD) (2) and flame ionization detectors (FID) (1,2) have been employed for the multi-elemental determination of hydride forming elements with limited success. The TCD detector was simply not sensitive enough for ultratrace level hydride determination. FID's also exhibit extremely poor response sensitivity to these compounds. GC-AA systems are more sensitive, but are not multielemental in nature. Use of an electron capture (EC) detector was reported for ultra-sensitive detection of organo substituted arsines but the linear dynamic range was poor and the system apparently gave no AsH₃ response. Detection of elements other than As were not reported with the EC detector (3). A GC-MS method was reported (1). This method, however, requires a major investment in capital

equipment, thus placing it beyond the budget of the majority of routine analytical laboratories. The method was also not as sensitive as expected.

Another problem has been in chromatographing compounds as reactive as SeH_2 . A GC column packing material that is inert enough not to react irreversibly with SeH_2 and still provide good separation for all of the hydrides in question has not been reported in the literature. Christian and Kadeg (1) was unable to elute SeH_2 with Porapak Q while OV-1 and silicone oil on Chromosorb W failed to retain or retard the hydrides. Skogerboe et al. (2) showed that silica gel was also ineffective in eluting SeH_2 . Caruso et al. (9, 10) was incapable of resolving Sn and Se hydrides while overlapping As and Se hydride peaks when a Chromosorb 102 column was used. The major difficulties encountered were either the column packing material irreversibly adsorbed and decomposed the hydrides, and/or SeH_2 was oxidized to form a non-volatile species either before or during the chromatographic step. An additional problem in the GC methods to date has been the thermal instability of BiH_3 at elevated column temperatures.

The purpose of this chapter is to report on a new application of a combination cryogenic trap and

temperature-jump sampling loop, a Tenax GC column operated isothermally at room temperature, and an inexpensive photoionization (PID) detector to eliminate the remaining barriers (equipment price, poor sensitivity, adverse column reactivity, and analyte thermal instability) to cost effective, reliable, simultaneous, multielement determination of elements like As, Se, Sn, and Sb at part per trillion levels by hydride generation from aqueous samples. To our knowledge, application of the PID and Tenax GC column in detecting aqueous As, Se, Sn, Sb, etc. has not been previously reported, and part-per trillion range detection limits for inorganic forms of these elements in aqueous media have not been reported in any prior analytical measurement system.

I. EXPERIMENTAL SECTION.

1. APPARATUS. The experimental setup is shown in Figure 3.1. Hydrides were generated by a Varian VGA-76 continuous flow hydride reactor. A detailed discussion of the operation of this apparatus was given in Chapter 2.

The instrumental portion of the chromatography section consists of two 4-way Alltech Teflon slider injection valves, a Perkin Elmer 990 gas chromatograph (GC), a H-Nu PI-51 photoionization detector (PID), and a Hewlett-Packard 3390A integrator, or a Cole-Parmer model 355 chart recorder.

The slider valves were pneumatically actuated with solenoid-switched, compressed air drivers operating at 100psi. The sample loop attached to this valve pair was a 5.5mL (2.83m X 1.6mm ID) Teflon tube. The PID was equipped with a 10.2eV deuterium lamp. Unless otherwise mentioned, the operating conditions of the GC system are specified in Table 3.1.

The solenoid activated slider valve, when hooked up with VGA-76 hydride reactor and Tenax GC column, allows rapid loading and injection of hydride into the column directly, without interrupting the column carrier gas flow during loading, and prevents the hydride condensed in the column from coming into contact with the oxidizing lab

Figure 3.1 Multi-elemental hydride determination setup.

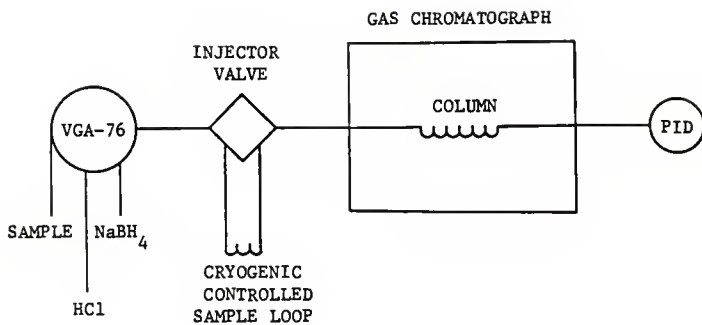


Table 3.1 Operating Conditions for Gas
Chromatograph

GC column packing	Tenax GC, 80/100 mesh
GC column dimension	1.52m X 1.6mm ID Teflon tube
Column temperature	30°C
Carrier gas	N ₂
Carrier gas flow rate	20mL/min
Injector temperature	room temperature
Solenoid switch	100psi
Detector temperature	100°C
PID lamp	10.2ev deuterium lamp
Sample loop	5.5mL X 2.83m X 1.6mm ID Teflon

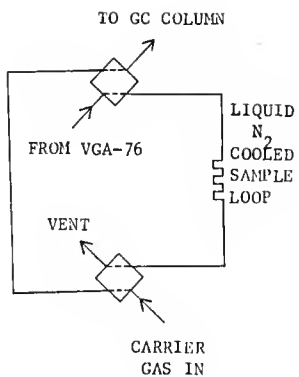
atmosphere. As shown in Figure 3.2, when solenoid A is activated, the injector is in the **LOAD** configuration. In this case, the GC carrier gas is now bypassing the sample loop and going directly to the column while analyte hydrides from the VGA-76 reactor are being condensed in the liquid nitrogen cooled sample loop. H_2 from the reactor passes through the loop uncondensed and is vented to the hood.

To inject the condensed hydrides onto the GC column, solenoid B is activated immediately followed by warming the sample loop exterior by immersing in water at room temperature. In this case, the injector system is in the **INJECT** configuration. The GC carrier gas sweeps out any volatilized effluent from the sample loop and carries it directly into the column while gases from the VGA-76 reactor are vented to the hood.

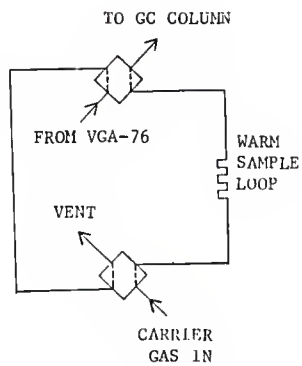
A Jarrell-Ash 850 atomic absorption spectrometer and the hollow cathode lamps described in Chapter 2 were also used in preliminary experiments to optimize the hydride generation conditions, and to confirm the elemental identity of analyte associated with the chromatographic peaks as hydrides coming out of the PID. Since the PID is virtually non-destructive, the identity of the

Figure 3.2 Alltex Slider Injector Valve and Sampling Loop.

- (a) Solenoid A actuated, "LOAD" configuration.
- (b) Solenoid B actuated, "INJECT" configuration.



(a) "LOAD"



(b) "INJECT"

chromatographic peaks were confirmed with atomic absorption by directing the PID effluent to the atomic absorption spectrophotometer.

2. REAGENTS. As was described in Chapter 2.

3. PROCEDURE.

Column Packing The Tenax GC was pre-conditioned at 200°C for two hours with air before packing into a 1.52m X 3.2mm OD X 1.6mm ID (0.8mm wall) Teflon tube. The packed column was then conditioned with N₂ (50mL/min) at room temperature for 30 minutes immediately followed by a temperature ramp from room temperature to 120°C at a rate of 3°C/min. The final column pre-conditioning temperature was maintained for not less than 6 hours before experimental work of this chapter began.

Hydride Chromatography With the sample loop at room temperature, the injector was initially set at the INJECT position. The empty sample loop was then pre-cooled with liquid nitrogen for 30s. The injector was then set to the LOAD position. Volatile hydrides were generated continuously from the VGA-76 for 2min. The power switch of the VGA-76 reagent pump was then set to OFF to stop generating the hydride. The injector remained at the LOAD

position for another 30s to allow residual hydrides in gas-liquid phase separator to condense in the sample loop completely. The injector was then switched to the INJECT configuration immediately followed by a rapid thawing of the sample loop in water at room temperature. This results in a rapid injection of any trapped hydrides onto the Tenax GC column. One minute later, the injector was reset to the LOAD position such that traces of residual moisture co-condensed with hydrides was vented to the hood. The column temperature was maintained at 30°C for 8 minutes, or until all hydrides eluted. Some additional by-products of the BH_4^- reaction (HCl vapor, CO_2 , and volatile boranes) are irreversibly trapped by the Tenax GC at 30°C. After the analytical hydride measurements are taken, these trapped by-products were desorbed by increasing the column temperature to 110°C at a rate of 24°C/min. The column temperature was kept at 110°C for about 5 minutes.

II. RESULTS AND DISCUSSION.

Injector valve and hydride trapping

Since in the absence of cryogenic entrapment, hydride generation reactions always produce a large and somewhat erratic flow of hydrogen as a result of acid hydrolysis of NaBH_4 , a noisy base line signal inevitably occurs for steady-state measurement systems such as atomic absorption or ICP emission. This type of base line noise is eliminated through the use of the cryogenic entrapment procedure described here. As hydrides are being condensed in the cooled sample loop, H_2 passes on through to the exhaust vent (see Figure 3.1) due to its greater volatility. No H_2 reaches the GC column or PID detector, so baseline noise is minimized.

The liquid nitrogen trap also provides a second stage of preconcentration of analyte in the form of condensed hydrides prior to chromatographic injection. Products of a 2 minute reaction are condensed (preconcentrated) into a single fixed injection of about 0.5s duration. The chromatographic peak intensity is proportional to both the initial analyte concentration in solution and the duration for which the continuous hydride generation reaction is allowed to proceed before injection.

Finally, the liquid nitrogen trap diminishes the large

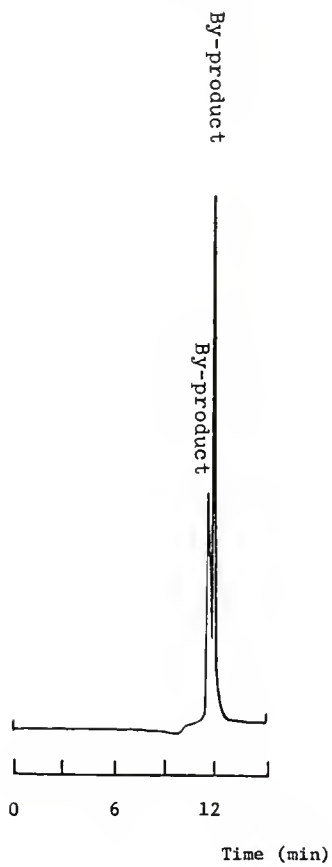
void volume inherent in gaseous sample gas chromatography. A rapid injection is therefore achieved and the chromatographic peak broadening effect is minimized.

Undesirable volatile by-products of hydride generation such as diborane, HCl and CO₂ were also trapped in the liquid nitrogen refrigerated sample loop. With several other GC columns that were tried (eg. glass beads and Chromosorb T), these interfered with the elution of analytes hydrides so that no useful data could be obtained. The Tenax GC column remedied this difficulty by irreversibly trapping the by-products at room temperature while separating and passing the analytes on to the detector. The undesired by-products are not desorbed until later when the Tenax GC column temperature is raised above 80°C (Figure 3.3). At first, this desorption (column cleanout) step was performed after each chromatogram, but it was finally ascertained that as many as 10 sample chromatograms could be run before it was necessary to thermally desorb the undesired volatile by-products.

Corrosive species such as HCl and diborane may represent an eventual threat to the column "longevity". Our columns lasted a maximum of 2 months under near-continuous daily usage with these conditions. At that point, a new column would have to be packed. Desorbed by-product signal intensities were diminished when a dry-

Figure 3.3 Blank Run.

Chromatogram of 7mL 6M HCl blank. No analyte injected. Attenuation 64, carrier gas (N₂) flow rate 18mL/min. column temperature program: initial 30°C (7.5min), final 110°C, rate 24°C/min. All peaks derived from unwanted hydride generation reaction volatile by-products.



ice/methanol cryogenic bath was used to cool the injection loop instead of liquid nitrogen. An unknown large peak, however, also eluted, probably due to the inboard permeation of CO₂ or methanol through the Teflon sample loop wall. The dry ice/methanol procedure was then abandoned in favor of the original liquid N₂ cryogenic entrapment method.

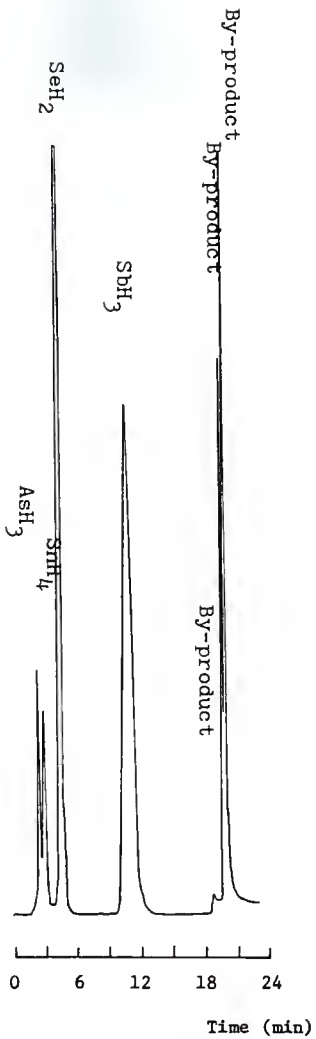
Column Packing Reactivity

Column packing material and column length considerations are important factors in gaining a good chromatogram for these hydride series. To our knowledge, Figure 3.4 illustrates the first use of a Tenax GC column and PID to separate, elute, and detect hydrides of As, Sn, Se, and Sb. It should be noted that (except for Sn) the compounds give large GC peaks and no baseline noise for part-per-billion levels.

Tenax GC is a hydrophobic polymeric material of 2,6-diphenyl phenylene oxide. When operated at room temperature, it has adequate reversible adsorptivity toward analyte hydrides but much higher (irreversible) adsorptivity toward unwanted volatile by-products of BH₃⁻ hydrolysis such as HCl vapor and diborane. Since HCl and diborane are eluted only above 80°C while hydrides of interest elute at room temperature, chromatographic

Figure 3.4 Standard Run.

Chromatogram derived from BH_4^- reduction of 14mL 6M HCl sample containing 5ppb As(III), 1ppm Sn(II), 300ppb Se(IV), and 400ppb Sb(III). Order of elution: AsH_3 , SnH_4 , SeH_2 , and SbH_3 . Attenuation 64, carrier gas (N_2) flow rate 21mL/min. Column temperature program: initial 30°C (15.9min), final 110°C, rate 24°C/min.



interference from the by-products is therefore not a concern. The low water affinity of Tenax GC is desirable because moisture is an unavoidable product in this reactor system.

Column lengths of 1.22m, 1.52m, 1.83m, and 2.13m were tested. The 1.52m Tenax GC column proved to be the most effective column length that gives good resolution and narrow chromatographic peaks at reasonable retention time and gas pressures compatible with this particular injector valve system.

Effects of Column Treatment on Tenax GC Adsorptivity

The Tenax GC column exhibits different hydride adsorptivities under different pre-conditionings before packing. When Tenax GC was pre-conditioned at 200°C in air for two hours and then packed into the column and conditioned as described in the procedure prior to actual analysis, relatively good hydride separations were obtained (see Figure 3.4). If the Tenax GC was simply packed without preheating in the air into the Teflon column before conditioning under a N₂ atmosphere as described in the procedure prior to actual analysis, we were not able to effectively separate hydrides of As, Se, and Sn. The retention times of SnH₄ and SeH₂ were significantly shortened such that they overlapped with the

AsH₃ peak. In addition, the retention time of SbH₃ was noticeably shortened.

The adsorptivity of Tenax GC appears to be related to the morphology and the extent of surface oxidation of the material. Polymeric column materials such as Tenax GC undergo some morphological changes at different temperatures as evidenced by the variable magnitude of shrinkage after pre-conditioning at different temperatures and variable hydride desorption rates found for different preconditioning temperatures.

The degree of air oxidation of the Tenax GC material at high temperature appears to play a major role in the column adsorptivity toward hydrides. Tenax GC changed to a light brown color after long hours of air exposure at high temperature (eg. 200°C). The color change of Tenax GC was not noticeable at reasonably high temperature under N₂ atmosphere, however. It is possible that further investigation into the effect of air oxidation of Tenax GC could improve the AsH₃/SnH₄ separation beyond that observed in Figure 3.4, but the preconditioning of Tenax GC as described in the procedure was maintained for the present.

Chromatographic Results

A typical chromatogram for a sample containing trace As, Se, Sn, and Sb as their hydrides is shown in Figure 3.4. The order of elution of the hydrides appears to follow ranking of the boiling point of the hydrides (see Table 3.2). The higher the boiling point, the slower the hydride is eluted.

Figure 3.4 shows that all of the elements tried here exhibited a fantastic response sensitivity to the PID detector, except Sn. Upon closer examination, it was found that SnH_4 actually exhibits good response sensitivity. We were simply not getting a high yield of SnH_4 from the BH_4^- reduction of Sn(II) in the original aqueous solution. The key to this problem may be found in the HCl incompatibility of Sn with As, Se, and Sb as suggested earlier in Chapter 2 (see Figure 2.3 page 31).

From Figure 2.3, Tin hydride generation from 6M HCl is clearly orders of magnitude less efficient than As, Se, and Sb hydride evolution at this acidity. This is why in Figure 3.4, a much higher concentration (eg. 1ppm) of Tin was required to generate a good hydride signal.

Table 3.2 Comparison of Boiling Points of
Selected Hydrides (11)

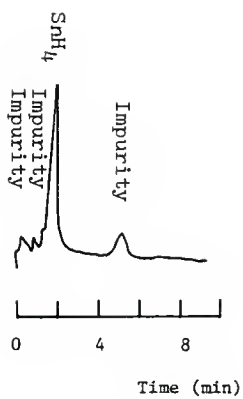
<u>Hydrides</u>	<u>Boiling Points (°C)</u>
AsH ₃	-55
SnH ₄	-52
SeH ₂	-41.5
SbH ₃	-17.1
GeH ₄	-88.5
TeH ₂	-2.2
BiH ₃	-22

Tin Signal Improvements

When Tin was dissolved in 0.1M HCl, a much improved Tin hydride signal was obtained for as little as 10ppb (see Figure 3.5). The HCl incompatibility of Tin and other metalloids could be defeated easily by eliminating preliminary acidification with 6M HCl, programming the pH of the acid channel during the run and running the acid channel at a higher flow rate. Alternatively, a five-channel peristaltic pump system could be used instead of the "normal" three-channel system. With a five channel system, two separate aliquots of sample containing As, Se, Sn, and Sb would be dissolved in 0.1M HCl. One of these aliquots can be further acidified to 6M HCl. In one Teflon reaction coil, Tin hydride can initially be generated from 0.1M HCl as in the regular three channel system (with omission of the 10M HCl acid channel). The other Teflon reaction coil would be operated in parallel with the first and the aliquot of sample in 6M HCl would be further acidified by the normal 10M HCl acid channel at its normal flow rate. Two separate parallel NaBH₄ channels would be needed (one for each parallel reaction coil). Effluent from the two reaction coils would empty into the same gas liquid separator via two separate entry ports. AsH₃, SnH₄, SeH₂, and SbH₃ would mix only as gases, and would exit the

Figure 3.5 Chromatogram of SnH₄:

Derived from 14mL 0.1M HCl sample containing 10ppb Sn(II).
Reagent channels: 1% NaBH₄ and 0.5M HCl. Attenuation 0.5;
carrier gas (N₂) flow rate 30mL/min, column at 40°C.



would exit the gas-liquid separator together.

Detection Limits

Detection limits are defined as "the concentration required to produce a signal equivalent to twice the standard deviation of the baseline." For 2 minutes of hydride generation, and a typical 14mL sample, detection limits obtained for As, Se, Sn, and Sb are summarized in Tables 3.3 and 3.4. As, Se, and Sb hydrides were evolved from 6M HCl while Sn hydride was evolved separately from 0.1M HCl with 0.5M HCl in the acid channel.

Clearly, the absolute weight detection limits of the PID are about 3 orders of magnitude improved and the concentration detection limits are 2 to 5 orders of magnitude better than other detectors for inorganic As, Se, Sn, and Sb cited in the literature to date. The unusually low concentration detection limits of this new hydride generation/Tenax GC/PID method of analysis will therefore permit reliable quantitative analysis of Se, As, and Sn in natural water and waste water samples in the range of 0.1-10 ppb on a routine basis with little or no baseline noise!

In principle, there is no limit as to how long the hydride can be generated and condensed in the sample loop, so even better concentration sensitivity is theoretically

Table 3.3 Absolute Detection Limits (ng).

Comparison of selected hydride detection limits (ng) of PID (a), AA (12), MS (1), TCD (2), molecular emission (ME) (13) detectors used in gas chromatography

<u>Hydrides</u>	<u>PID</u>	<u>AA</u>	<u>MS</u>	<u>TCD</u>	<u>ME</u>
AsH ₃	.025	60	10	100	200
SeH ₂	.025	100	---	---	---
SnH ₄	.050	100	50	---	---
SbH ₃	2.8	---	100	1000	1000

Note: (2) S/N = 2.

(13) S/N = 2.

Table 3.4 Concentration Detection Limits (ppb).

Comparison of selected hydride detection limits (ppb) of PID (a), AA (12), MS (1), TCD (2), and molecular emission (ME) (13) detectors used in gas chromatography

	(a)	(b)	(c)	(d)	(e)
<u>Hydrides</u>	<u>PID</u>	<u>AA</u>	<u>MS</u>	<u>TCD</u>	<u>ME</u>
AsH ₃	.002	3	2	1	200
SeH ₂	.002	5	---	---	---
SnH ₄	.004	5	10000	---	---
SbH ₃	.2	---	20000	10	1000

Note: (2) S/N = 2.

(13) S/N = 2.

(a) Results from this work, based on 14mL sample.

(b) Based on 20mL sample.

(c) Based on 5mL sample.

(d) Based on 100mL sample.

(e) Based on 1mL sample.

possible where large sample volumes are available for this preconcentration method. In practice, we were able to condense at a 1ppb level of the hydride for a maximum of about 4 minutes without building up too much ice in the sample loop as a result of co-condensation of CO_2 , HCl , B_2H_6 , and traces of water vapor among other unidentified volatile products. The concentration detection limits listed in Table 3.4 are lowered even further when the hydride is generated and condensed beyond two minutes, but the absolute weight detection limits shown in Table 3.3 are not affected.

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Chapter 4

IDENTIFICATION AND BLOCKING OF THE COPPER INTERFERENCE MECHANISM IN SeH_2 EVOLUTION

The gaseous hydride pre-concentration technique is widely used in the routine analysis of selected elements of group IVA, VA, and VIA in aqueous solution because of its enhanced concentration sensitivity and relative freedom from spectral interference. One disadvantage is that under some experimental conditions, selenium, arsenic, etc. hydride preconcentration methods suffer from severe interference by selected transition metals such as copper and nickel (1-18).

Several attempts to mask transition metal interferences have been reported for selenium and arsenic determination by hydride generation atomic absorption and emission spectroscopy, or even electrochemistry. Kirkbright and Taddia (1) used thiosemicarbazide and 1,10-phenanthroline to mask the effect of copper. Dennis, Moyers, and Wilson report preliminary extraction of the offending metals with 8-quinolinol immobilized on glass beads (25), and Viets, O'Leary, and Clark have extracted copper with 10% (V/V) Aliquat 336-isobutyl methyl ketone (18) prior to SeH_2

evolution. Copper has been coprecipitated with lanthanum (15, 21-24) or ferric hydroxides (20, 21), masked (along with nickel) by BH_3CN^- which simultaneously served as a primary selenium reductant (2), and has been removed by cation exchange (e.g. Chelex 100 (6)).

Over the past 10 years, a number of copper interference mechanisms have been suggested, but not verified. In the last few years, the process of elimination has refuted a number of incorrect or unimportant mechanisms (e.g. reagent depletion, viscosity effects, ionic copper and selenium redox effects, etc.) (3, 5, 9, 12) and gradually convinced several authors that reduced copper (Cu^0 produced by preliminary reaction of Cu^{++} with BH_4^-) is the most likely interferant in H_2Se and AsH_3 evolution from aqueous media (5, 9, 10). This was concluded by several authors who observed the following indirect evidence: 1.) the depression of H_2Se or AsH_3 evolution by added Cu^{++} is generally accompanied by formation of an orange precipitate (probably Cu^0) in suspension, and 2.) successful masking agents for the Cu^{++} interference on Se determination also prevents the orange precipitate formation in BH_4^- reactions (1, 2, 15, 20-24). The masking agents have presumably complexed Cu^{++} , thereby preventing or slowing its BH_4^- reduction to Cu^0 . Several authors have assumed that H_2Se and AsH_3 adsorb or chemisorb onto

Cu^0 (3, 5, 9, 10, 12), but no direct, conclusive evidence for this has been reported in an analytically useful hydride preconcentration system for ultra-trace level determinations of selenite, arsenite, etc. in aqueous media.

Earlier data at much higher concentrations from those reported in the literature of inorganic and physical chemistry indicate that adsorption and chemisorption of milligram amounts of H_2Se and AsH_3 gases can occur onto metallic surfaces (gram quantities) such as Cu^0 (19). This information, together with the aforementioned observation of orange precipitates and masking agent effects in ultra-trace analytical systems, collectively suggests the following mechanism for copper interference in the analytical hydride preconcentration of selenium and arsenic from aqueous media: BH_4^- probably first rapidly reduces microgram amounts of Cu^{++} to Cu^0 (a finely divided solid in suspension). On a slower time scale, BH_4^- is likely to reduce picogram to nanogram amounts of selenite and arsenite to H_2Se and AsH_3 in solution (without probable interference from copper as yet). Once the hydrides are produced, the suspended microgram quantities of Cu^0 precipitate are then likely to immobilize picogram to nanogram amounts of AsH_3 or H_2Se by adsorption or

chemisorption before they can be degassed from solution. If the analyte hydrides become immobilized on a Cu^0 precipitate surface, they would not be able to reach the detector via the gas stream.

Evidence for this interference scenario in ultra-trace analytical systems has been acknowledged by several authors (3, 5, 9, 10) and is intuitively convincing, but it remains indirect in nature. The inorganic and physical chemistry experiments mentioned above (19) lend support, but great care must be taken in extrapolating mechanism deduced from high concentration experiments (milligram and gram quantities) to the ultra-trace range of concentration relevant to analytical measurements.

The purpose of this chapter is to provide evidence of a more direct nature and in a more relevant concentration region for BH_4^- reduction of Cu^{2+} to Cu^0 and subsequent immobilization of H_2Se by gas-solid adsorption onto Cu^0 as the principal mechanism of Cu^{++} interference in ultra-trace, aqueous, ionic selenium determination by the analytical hydride preconcentration method.

In previous analytical systems, the Cu^0 has formed in suspension (within relatively large pyrex reactor vessels containing a substantial aqueous solution volume) and has not been directly examined for conclusive evidence of H_2Se adsorption. In the present experiment, a small bore,

Teflon tubing reactor replaced the large solution volume, and any Cu^0 that formed was quickly deposited on the Teflon tubing wall. This facilitated some unique phase separation experiments and allowed a more direct study of the interaction of H_2Se with Cu^0 (independent of Cu^{++} and independent of how the H_2Se is produced). In this system, the microgram levels of Cu^0 produced by the BH_4^- reaction may be recovered for analysis or for further experiments. An investigation into the kinetic aspects of the copper interference is presented in this chapter in order to identify simple, effective means of eliminating the interference (without use of masking agents) through a judicious choice of more selective reaction conditions such as acidity and especially BH_4^- concentration.

EXPERIMENTAL SECTION

1. APPARATUS. The VGA-76 continuous flow hydride generator and the Jarrel-Ash 850 atomic absorption spectrometer setup for selenium detection was as described in the Chapter 2. Gaseous SeH_2 effluent from the BH_4^- reactor (VGA-76) was transported to the atomic absorption detector via one of three possible pathways: 1.) normally; ie. direct introduction of SeH_2 through a latex tube leading to the detector (see Figure 2.1 of Chapter 2, p. 21); 2.) bubbling of SeH_2 through 4mL of another solution (eg. Cu^{2+}) immediately prior to the detector (Figure 4.1); 3.) passing SeH_2 gas through an empty Cu^0 plated secondary Teflon tube reaction coil immediately prior to the detector (Figure 4.2). No liquids are present in the secondary reaction coil, only SeH_2 gas, some H_2 , and some N_2 . Cu^0 plating of the secondary reaction coil was initially carried out using the configuration of Figure 4.3 (prior to use in Figure 4.2).

A separate detection system for monitoring Cu^0 production in the BH_4^- reactor via its disappearance from the flowing Cu^{2+} solution stream emerging from the VGA-76 primary reaction coil included a Jarrell-Ash 810 atomic absorption spectrophotometer and copper hollow cathode lamp (Varian Associates, Palo Alto, CA). The primary

Figure 4.1 Apparatus for Selectively Observing the Separate Effect of Cu^{2+} on SeH_2 Liberation.

SeH_2 was produced in the absence of copper and then bubbled through a flask containing 4mL of 20ppm Cu^{2+} dissolved in 6M or 2M HCl while SeH_2 signal was being monitored. Cu^{2+} was the only form of copper to which the SeH_2 was exposed. No Cu^0 was produced or present anywhere in this configuration.

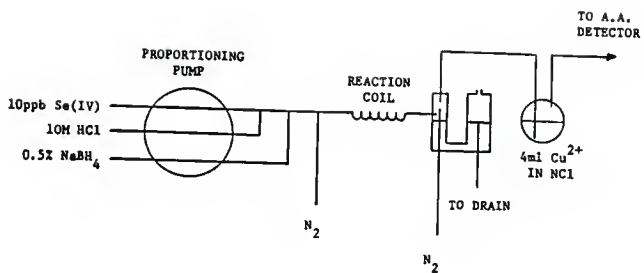
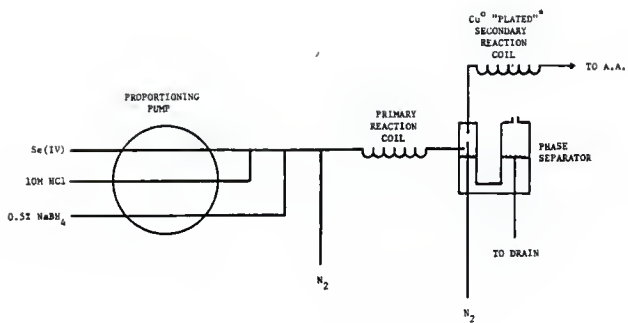
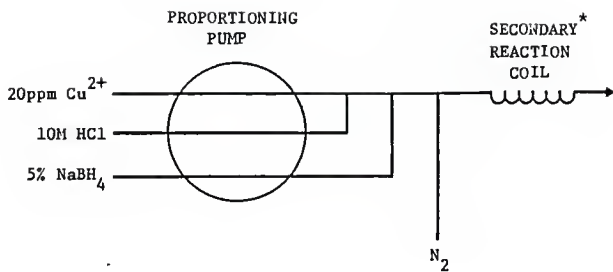


Figure 4.2 SeH_2 being generated in a clean primary reaction coil and passed through Cu^0 "plated" secondary Teflon reaction coil prior to signal monitoring by AA.



* Prior Plating Performed as in Figure 4.3.

Figure 4.3 Configuration for Preliminary Plating Cu^0 onto Secondary Teflon Reaction Coil (of Figure 4.2).

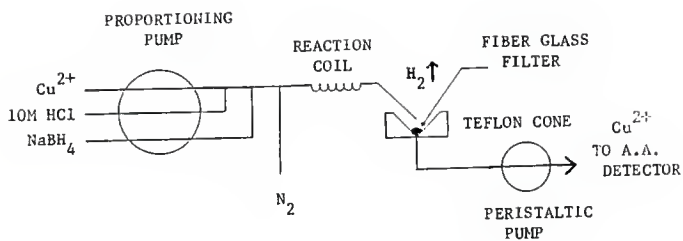


* Being Plated with Cu^0

gas/liquid separator was omitted in this configuration. A high solids nebulizer with wide bore 1.9mm ID sample tubing (26, 27) and air/acetylene flame was used to atomize the remaining Cu^{2+} and a secondary Teflon cone, gas liquid separator (Figure 4.4) was used to eliminate noise from vigorous hydrogen bubbling (due to BH_4^- hydrolysis). With this separator, the liquid solution was passed on to the nebulizer and A.A. detector, and the gas was expelled to the atmosphere. The atomic absorption detection wavelength was set at 324.8nm in order to monitor Cu^{2+} remaining in the solution emerging from the primary BH_4^- reaction coil.

Figure 4.4 Apparatus for CuO Production Monitoring.

Cu²⁺ dissolved in 6M HCl was delivered at the VGA-76 sample channel at a rate of 7mL/min. The resulting liquid stream was being pump to the A.A. at a rate of 7mL/min via a Teflon cone with a pledge of fiber glass filter to filter out any Cu⁰ particle not plating in the reaction coil. Most of the H₂ produced from acid hydrolysis of BH₄⁻ escaped to the atmosphere, only a small amount of H₂ reached to the A.A. detector.



2. REAGENTS. Stock 1000ppm Cu^{2+} solution was prepared by dissolving an appropriate amount of Baker & Adamson $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in deionized distilled water. High purity Instra-Analyzed HCl was diluted as needed with distilled deionized water. All other solutions were prepared as described in the previous chapter.

3. PROCEDURE. Except where noted, samples are typically made in 6M HCl prior to introduction into the VGA-76 sample channel at 7mL/min. Except where noted in the text or Figures, the VGA-76 system manifold was connected such that the selenium sample or Cu^{2+} sample (in 6M HCl) was acidified further with 1mL/min of 10M HCl before the addition of NaBH_4 (in 0.5% KOH) solution. This is the normal operation mode for the VGA-76 reactor. Each sample run was immediately followed by a blank run of 6M HCl. The experiment was conducted at room temperature.

When copper or selenium was studied as a function of NaBH_4 concentration, either the selenium or copper signal was recorded as the effluents emerged from the VGA-76 system. For copper atomic absorption, the primary pyrex gas/liquid separator was bypassed and the VGA-76 effluent was taken directly from the exit of the Teflon reaction coil. Figure 4.4 shows that reactor effluent was deposited

into an open-air Teflon funnel where the majority of the hydrogen, which is a product of the acid hydrolysis of NaBH_4 , escaped to the atmosphere. A "Rabbit" peristaltic pump immediately delivered the solution from the bottom of this Teflon funnel to a high solids flame A. A. nebulizer utilizing 1.9mm ID sample tubing (26, 27) at a rate approximately equal to the rate of the solution coming out of the VGA-76 system. The atomic absorption signal of copper was then recorded. The elimination of hydrogen gas with this apparatus and the use of a large bore nebulizer tubing (1.9mm ID) effectively cut down the flame flicker noise due to hydrogen gas bubbles in the nebulizer solution tubing.

The orange Cu^0 was deposited on the wall of the VGA-76 Teflon reaction coil and did not reach the A.A. nebulizer. It's presence on the reaction tubing wall was deduced by its orange color and was noted quantitatively by a decrease in the copper A.A. signal indicative of dissolved Cu^{2+} emerging from the reactor. The orange precipitate observed on the inside walls of the reactor tubing was immediately dissolved in a minimum volume of 5D% HNO_3 , typically 1mL or less, and then heated on a hot plate for 30 minutes to remove all nitrogen oxide fumes before making up to volume with 6M HCl. A selenium standard given the same HNO_3 treatment yielded little or no selenium

signal loss. Any selenium sample containing a high copper concentration from this experimental phase was further diluted with 6M HCl to bring the copper content below the effective interference level before a selenium hydride atomic absorption experiment was conducted.

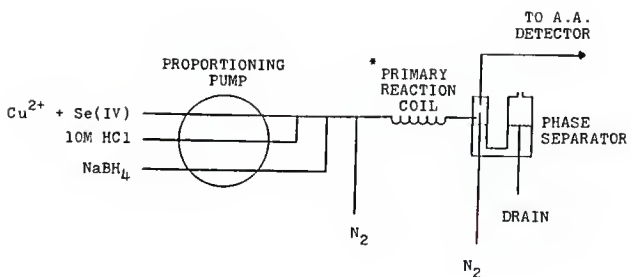
II. RESULTS AND DISCUSSION

A. Effect of BH_4^- Concentration.

Using the normal configuration of Figure 2.1, p. 21 and Figure 4.5, the copper interference on SeH_2 evolution was observed as a function of BH_4^- concentration. The results are given in Figure 4.6. It can be clearly seen that, contrary to the untested presuppositions of numerous authors (4, 28, 29), larger BH_4^- concentrations do not lead to less copper interference. In fact, the data show that use of normal BH_4^- levels of 3 to 5% can be extremely detrimental, and are the reason most everyone in this field has been plagued with copper interference since the early 1970's. Figure 4.6 shows that it is clearly advantageous to utilize BH_4^- concentrations at or below 1%, where the copper interference can be avoided altogether.

The superior performance of the **more dilute** BH_4^- reagent solutions is clear evidence that the copper is most certainly not competing with Se (IV) for the BH_4^- reductant, and copper is most certainly not interfering by depleting the reductant concentration as a number of authors have suggested (4, 28, 29).

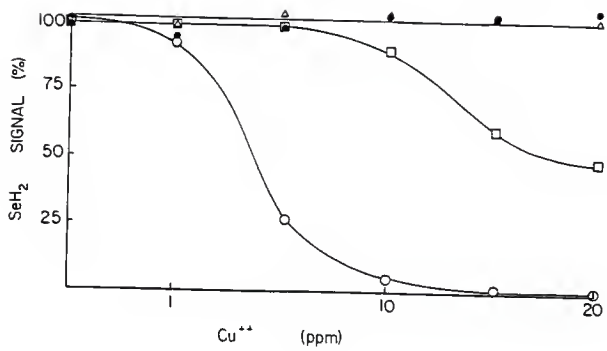
Figure 4.5 Configuration for Evaluation of BH_4^- Concentration on The Overall Copper Interference.



* No prior Cu^0 plated

Figure 4.6 Influences of NaBH_4 in Copper Interference of SeH_2 in A Continuous Flow Reactor.

- ● - 0.5% NaBH_4 (reducing agent channel), Se(IV) in 6M HCl, 10M HCl (acid channel).
- △ - 1% NaBH_4 (reducing agent channel), Se(IV) in 6M HCl, 10M HCl (acid channel).
- □ - 5% NaBH_4 (reducing agent channel), Se(IV) in 6M HCl, 10M HCl (acid channel).
- ○ - 5% NaBH_4 (reducing agent channel), Se(IV) in 2M HCl, 10M HCl (acid channel).



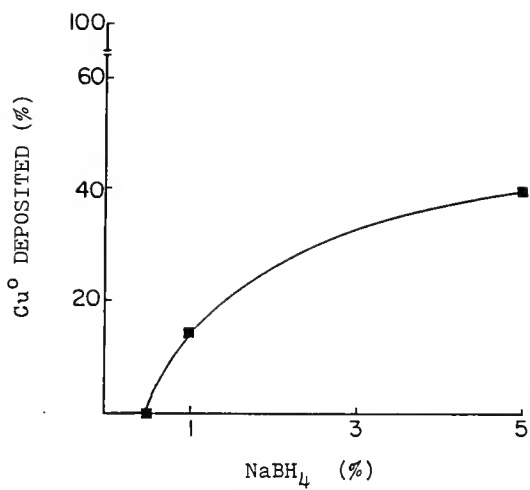
B. Production of Cu^0 .

The real culprit in copper interference is proposed to be Cu^0 produced by BH_4^- reduction of Cu^{++} . The first test of this hypothesis was conducted as a measurement of the rate or yield of Cu^0 that can be produced under real experimental analytical conditions. At first, Cu^0 production was visually noticed as an orange precipitate coated on the inside of the translucent Teflon tubing of the primary reactor coil employed to generate some of the data of Figure 4.6. No Cu^0 was visually detected for 0.5% or 1% BH_4^- concentrations, but the Teflon reactor turned noticeably orange when the concentration was raised to 5%.

It was next decided to get some quantitative measure of the Cu^0 yield. This was accomplished with the apparatus of Figure 4.4. The deposition of Cu^0 in the small bore, primary Teflon tube reactor was measured by the disappearance of Cu^{++} from the reactor effluent. This was noted by the decrease in the atomic absorption signal for copper in the reactor effluent and was studied as a function of BH_4^- concentration. The results for Cu^0 production from a 20 ppm Cu^{++} sample solution are plotted in Figure 4.7. Similar behavior (fewer milligrams of Cu^0 , but a similar percentage conversion) was observed for the 5 and 10 ppm Cu^{++} sample solutions.

Figure 4.7 NaBH₄ Concentration Effect on Cu⁰ Production in The Absence of Se(IV) in Continuous Flow Hydride Generator.

0.5% NaBH₄ in the reducing agent channel and 10M HCl in the acid channel. sample channel contained 20ppm Cu²⁺ dissolved in 6M HCl.



The data of Figure 4.7 show that major amounts of Cu^0 are produced with 5% BH_4^- . This was the condition under which major copper interference on SeH_2 evolution was noted earlier in Figure 4.6. Figure 4.7 also shows that for a BH_4^- concentration of 0.5%, no measureable Cu^0 is produced. This was the case for which no copper interference on SeH_2 evolution was noted earlier in Figure 4.6, and it strongly suggests that Cu^0 is the culprit.

C. SeH_2 Adsorption.

The next step was to rinse the reactor thoroughly with deionized water and then to dissolve some of the residual Cu^0 plating off of the Teflon tube reactor wall from the earlier 5% BH_4^- experiments shown in Figure 4.6 and assay the resulting solution by atomic absorption. This was done with 50% HNO_3 and extreme dilution as anXhwKpnd at the end of the procedure section of this Chapter. The assay revealed significant amounts of selenium had been retained by the Cu^0 . In fact, all of the missing selenium hydride in the earlier copper interference studies of Figure 4.6 could be easily accounted for in this section where it was recovered from the Cu^0 precipitate (plated onto the Teflon reactor wall).

To determine whether the immobilized selenium was the result of SeH_2 adsorption onto the Cu^0 film or whether it

was a simple CuSe precipitate ($K_{sp} = 10^{-48.1}$ (30)), or for that matter even some precipitate of Se (IV), the following experiments were conducted. A precipitate of cupric selenide (CuSe) was initially thought implausible because of the protonation effect on the solubility of ions like Se^{2-} in acid media. However, some quick conditional solubility calculations showed that this possibility could not be immediately ruled out. The equilibrium calculations were inconclusive because any protonated Se^{2-} was subject to removal from the system as the volatile hydride. The instantaneous solution concentration of SeH_2 was impossible to estimate, so a worst case condition was the only thing that could be calculated. This calculation indicated that a cupric selenide precipitate was possible, even in 6M HCl, so an experiment was devised to test the relative contribution of this source to the copper interference on SeH_2 evolution.

Using the apparatus of Figure 4.1, a small amount of SeH_2 was generated in a clean primary reactor with no copper present in any form. After passing the gas-liquid separator, the SeH_2 was bubbled through a solution containing only acidified Cu^{++} . No Cu^0 was present anywhere in the system, and no reducing agent was present

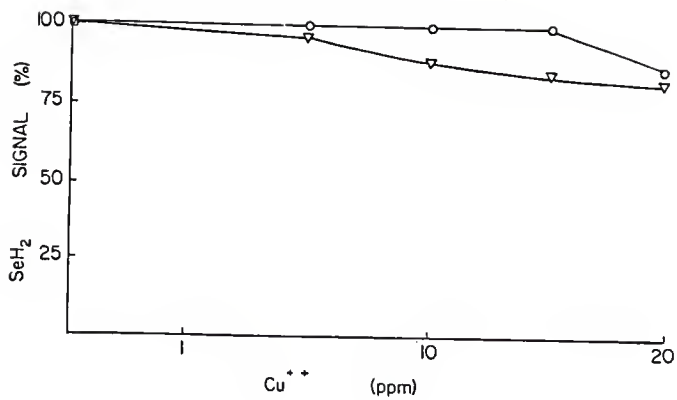
in the Cu^{++} bubble chamber. Any SeH_2 effluent which "survived" the Cu^{++} bubble chamber was detected by AA. If a cupric selenide precipitate were formed, it would have been retained as a solid by the Cu^{++} bubble chamber and would have shown up as a decrease in the AA detector signal (a decrease over the experimental control which included a 6M HCl bubble chamber with no Cu^{++} added). This experiment was conducted at bubble chamber acidities of both 6M and 2M HCl. The results are given in Figure 4.8 for a variety of Cu^{++} concentrations in the auxiliary bubbler.

A minor effect can be seen at the highest Cu^{++} concentration tested, and at the lowest acidity, indicating that minor amounts of cupric selenide could be forming under extreme conditions. However, these data generally show that CuSe precipitation cannot account for the major copper interference effects seen earlier in Figure 4.6, where less than 10% of the selenium signal was recovered in some cases.

The possibility of Se (IV) reacting with Cu^0 was eliminated using the apparatus of Figure 4.9 which incorporates **no reducing agent** in the experiment, but utilizes a primary Teflon reaction coil previously plated with Cu^0 (and then rinsed with deionized water) prior to

Figure 4.8 Selective Observation of Cu^{2+} Effects on SeH_2 Generation in a Continuous Flow Reactor.

SeH_2 was bubbled through a flask (see Fig. 4.1) containing 4mL of Cu^{2+} in 6M HCl (~ \bigcirc -) and 2M HCl (~ \triangle -).



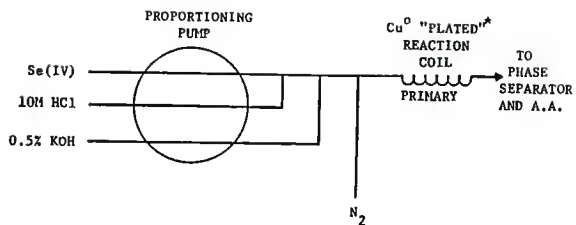
the present experiment. After passing substantial volumes of Se (IV) through the system, the Cu^0 film was dissolved from the reactor wall with 50% nitric acid, diluted extensively, and assayed for immobilized selenium as described at the end of the procedure. No detectable selenium could be found immobilized on the Cu^0 film.

The next set of experiments studied the adsorption of SeH_2 onto a pre-deposited Cu^0 film. In the first test, the system was modified slightly as in Figure 4.10. The only difference from the previous experiment in which no Se (IV) was immobilized (as in Figure 4.9), was that, this time, some reducing agent (BH_4^-) was added to convert the Se (IV) to SeH_2 before exposing it to the pre-deposited Cu^0 film in the Teflon reactor coil. This time 40% of the SeH_2 signal was suppressed.

At this point it seemed clear that, as several authors have speculated (3, 5, 9, 10, 12), nanogram to picogram amounts of SeH_2 can indeed become immobilized on a Cu^0 film of microgram proportions. The Se of Figure 4.10 passed through the Cu^0 plated Teflon reactor coil as a dispersion of gas bubbles and liquid solution. The next question to answer was whether the interfering adsorption reaction occurred before or after the SeH_2 analyte was degassed from solution. This was investigated using the

**Figure 4.9 Selective Observation of Cu⁰ Effects in The
Absence of NaBH₄.**

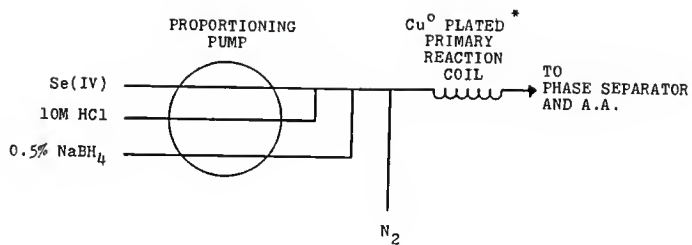
Se(IV) was being passed through Cu⁰ plated primary Teflon reaction coil (prior Cu⁰ plating performed as in Fig. 4.3) in the absence of NaBH₄.



* Prior Plating Performed as in Figure 4.3

Figure 4.10 Selective Observation of Cu⁰ Effects on SeH₂ Generation in The Presence of NaBH₄ in a Continuous Flow Reactor.

SeH₂ was generated under "normal" VGA-76 operation conditions and passed through a Cu⁰ "plated" primary Teflon reaction coil (prior Cu⁰ plating performed as in Fig. 4.3). The resulting SeH₂ signal was being monitored by an A.A. detector.



* Prior plating performed as in Fig. 4.3

apparatus of Figure 4.2, where SeH_2 only comes into contact with Cu^0 after it has been generated and degassed from solution. The interaction of SeH_2 and Cu^0 in this case occurs without any BH_4^- or Cu^{++} present in the secondary reactor. Any SeH_2 effluent "surviving" the secondary Cu^0 plated reaction coil of Figure 4.2 was monitored on-line by atomic absorption spectrometer.

The results were as follows. At first, major suppression of the SeH_2 signal (37%) was induced by the Cu^0 film (as compared with an experimental control with no copper present). This clearly indicates that Cu^0 can adsorb ultra-trace levels of SeH_2 , thereby producing a major interference effect. It should be noted that as more and more SeH_2 was passed over the Cu^0 film (beyond the SeH_2 exposure typical of an analysis), the surface eventually passivated and no further signal loss was observed. The Cu^0 film was next dissolved in 50% nitric acid, diluted as in the procedure section, and assayed for selenium content. 72% of the original missing selenium was recovered by analysis of the dissolved Cu^0 film, indicating a clear adsorption mechanism.

The adsorption of SeH_2 onto Cu^0 also appears to be accompanied by some sort of surface degradation, because re-dissolution of the Cu^0 film in HCl is not accompanied by SeH_2 release or re-evolution. The Se is easily

redissolved, but more reducing agent must be added (BH_4^-) before it will degas from solution again as SeH_2 . A surface degradation reaction has been suggested by Saleh (19).

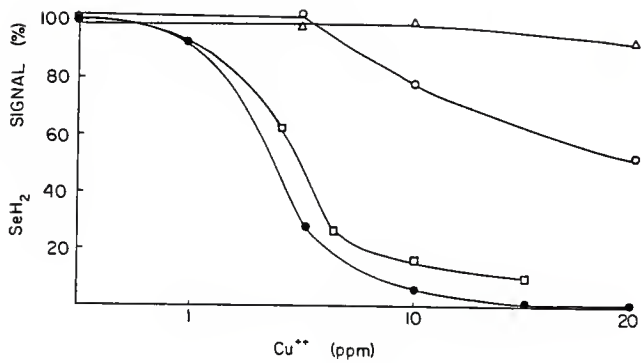
D. Acidity Effect.

In addition to the dramatic effect of BH_4^- concentration seen earlier in Figure 4.6, the standard configuration of Figure 2.1, p. 21, and Figure 4.5 (except that the acidity was varied at constant BH_4^- concentration), was used to investigate the role of HCl molarity in controlling the copper interference. The results are given in Figure 4.11. It is clear from curves 4.11A and 4.11B that higher acidity (eg. 6M HCl) is desirable in minimizing the copper interference. Lower acidity (eg. 2.7M HCl) leads to more copper interference.

It was assumed the improvement of 6M HCl over 2M HCl in minimizing the copper interference was either due to the increased solubility of Cu^0 , or that less Cu^0 was produced as a result of a lowered effective instantaneous BH_4^- concentration (due to faster reagent hydrolysis in 6M acid). The latter was ruled out from data of Chapter 2 (Figure 2.4, p. 35) which showed very little difference in hydrolysis rate (H_2 evolution) between the 6M and 2M acid levels.

Figure 4.11 Influence of HCl in Copper Interference on SeH_2 Generation.

- (A) - \triangle - VGA-76, final HCl and NaBH_4 concentrations were 5.8M and 0.056% respectively (Se(IV) dissolved in 6M HCl, acid channel was 10M HCl, and reducing agent channel was 0.5% NaBH_4).
- (B) - \circ - VGA-76, final HCl and NaBH_4 concentrations were 2.7M and 0.056% respectively (Se(IV) dissolved in 2M HCl, acid channel was 10M HCl, and reducing agent channel was 0.5% NaBH_4).
- (C) - \bullet - VGA-76, final HCl and NaBH_4 concentrations were 2.7M and 0.5% respectively (Se(IV) dissolved in 2M HCl, acid channel was 10M HCl, and reducing agent channel was 5% NaBH_4).
- (D) - \square - Batch reactor, final HCl and NaBH_4 concentrations were 2.7M and 0.56% respectively.



E. Combined Acidity And BH_4^- Concentration Effect.

The earlier data of Figure 4.6 were all taken at high acidity. The acidity data in curves A and B of Figure 4.4 were all taken at low BH_4^- concentration. The combination of high BH_4^- and low acidity produced the worst copper interference of all as seen in curves C and D of Figure 4.11. Regardless of whether a batch or continuous flow reactor is employed, catastrophic copper interference levels are encountered at commonly employed NaBH_4 levels of 5% and modest acidity of 2.7M HCl or less. In this case, 10ppm or more of copper in a sample almost completely obliterates all selenium signal response.

Curve A of Figure 4.11 shows that all such copper interferences may be avoided by use of a low BH_4^- concentration (0.5%) and a high acidity level (6M HCl).

CONCLUSION

It appears that almost everyone (except F. D. Pierce and Brown (4)) has been adding too much borohydride reagent in the analytical hydride preconcentration. The excess reagent has simply resulted in the production of an undesirable Cu^0 precipitate from Cu^{2+} in the samples (even for trace amounts) which has been responsible for SeH_2

responsible for SeH_2 immobilization via a degradative adsorption mechanism. The results of our copper interference mechanism studies are summarized in Table 4.1. The copper interference does not occur until after the Se (IV) has been successfully reduced to SeH_2 , and probably not until the SeH_2 has degassed from solution. The interference is simply a gas-solid adsorption reaction which may be avoided by preventing the formation of any solid Cu^0 precipitate in the first place. This is easily accomplished by lowering the BH_4^- concentration to a point (0.5%) where SeH_2 is still evolved, but where no measurable Cu^0 production occurs; the copper remains as Cu^{++} and does not interfere.

Figures 4.6 and 4.11 indicate that if the BH_4^- concentration is lowered to 0.5% and the acidity is kept at 6M HCl or higher, ultra-trace level selenium determinations in aqueous media may be performed without fear of copper interference from most any natural water or other environmental sample. The copper levels studied here are environmentally significant and the conclusions drawn would apply in most real analyses. An exception might perhaps be a copper ore sample or a metallurgical analysis where the copper level exceeds the limits studied here.

Since Cu^0 has been implicated as a catalyst in the BH_4^- conversion of nitrate to nitrite with subsequent

Table 4.1 Results of Copper Interference Studies.

<u>Species Involved</u>		<u>Interference</u>
Se(IV)	Cu ²⁺	NO
Se(IV)	Cu ⁰	NO
SeH ₂	Cu ²⁺	WEAK
SeH ₂	Cu ⁰	STRONG

interference by nitrite and its volatile disproportionation products (NO, NO₂, etc.) on SeH₂ evolution (2), the results of the present chapter on the copper interference will also be of considerable interest in the next chapter on nitric acid and nitrogen oxide interferences.

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Chapter 5

NO_3^- , NO_2^- , and VOLATILE NO_x INTERFERENCES IN SeH_2 EVOLUTION

A number of authors have reported severe interference with the analytical hydride preconcentration when solid samples were prepared by dissolution in hot nitric acid (1-11). Previous studies from this laboratory have shown the so-called "nitric acid" or "nitrate" interference to actually be due to reduced nitrogen oxides such as nitrite or its acidic disproportionation products, NO and NO_2 which can immobilize SeH_2 by oxidizing it to a nonvolatile product (12). The reduced nitrogen oxides are formed as by-products of the nitric acid oxidation of solid samples.

In at least one case, interference was shown to occur after the SeH_2 had been generated, degassed from solution, and transported downstream to a drying agent used with a cryogenic entrapment scheme. In that instance, acidified nitrite from the sample had disproportionated to NO and NO_2 which degassed from the solution along with the SeH_2 . These compounds traveled together downstream to a conc. sulfuric acid drying trap where the volatile nitrogen oxides became dissolved as NO^+ which, as a powerful oxidant, lingered to oxidatively interfere with and immobilize the SeH_2 analyte for that sample and for any

subsequent samples to follow (12).

The interference by reduced nitrogen oxides has been so severe that steps are normally taken to remove all traces of nitrite from the sample by extensive boiling prior to Se (IV) reduction with BH_4^- . Some questions may arise about potential loss of volatile selenium compounds upon sample boiling, but this simple procedure at least removes all interfering nitrogen oxides except nitrate. Residual nitrate, **by itself**, was shown to give minimal interference, so the boiling procedure was assumed by a number of authors to be reliable.

Additional testing by other students from this lab, however, showed that when the residual nitrate (after boiling) was present **together with traces of Cu^{++}** , an unusually severe interference was generated (12). The Cu^{++} was being rapidly reduced by 5% BH_4^- in 2.7M HCl (the lesson of Chapter 4 had not yet been learned) to yield Cu^0 which acted as a catalyst for the subsequent excess BH_4^- reduction of nitrate to nitrite (a far more severe interferant). Since this occurred **after the boiling step**, a previously unrecognized source of nitrite was being catalytically produced "in situ" and gave rise to a serious new class of interference (12). To make matters worse, the copper catalysis effect occurred at far lower

copper levels (e.g. as little as 0.5 ppm Cu) than were known to produce a direct metal interference (such as the one encountered above 5 ppm Cu in Chapter 4). The catalytic effect of low level copper on nitrate to nitrite conversions was far worse than the individual components (Cu^{++} or nitrate) could produce when taken separately, and it could not be circumvented by the standard boiling technique (12). The only reliable solution to this problem was to perform a pH adjustment after boiling and to exhaustively remove all traces of Cu^{++} (the catalyst precursor) by extraction prior to Se (IV) reduction. This procedure was quite tedious, but it was the only alternative.

The purpose of the work of this chapter was to study interference by nitrogen oxides in more detail to learn more about how the interference is produced and what the factors are which control its severity. The influence of BH_4^- concentration, acidity level, and reactor design on the various types of nitrogen oxide interference were investigated. Both continuous flow and batch reactors were evaluated, and a simpler overall procedure was finally developed to circumvent nitrogen oxide interference in all of its forms. The goal was to circumvent even the copper catalyzed nitrate interference without having to employ tedious extraction techniques.

I. EXPERIMENTAL SECTION

1. APPARATUS. There are two physical approaches to chemically generate volatile SeH_2 for atomic absorption determination: batch and continuous flow methods. In the batch method, NaBH_4 solution is gradually delivered to a fixed volume, static reservoir of acidified Se(IV) sample, typically 50mL. The resulting hydride is rapidly swept away by a carrier gas bubbling through the reservoir and is collected in a cryogenic trap. Once the reaction is complete, the trap temperature is jumped and atomization of the thawed hydride produces a transient atomic absorption detector signal. The batch hydride generator of this study and its operating conditions have been described previously (12).

In the continuous flow hydride generation method, a proportioning peristaltic pump is employed to continuously mix a stream of acidified sample with a stream of NaBH_4 solution as described in Chapters 2 and 4. The resulting hydride is degassed from the liquid phase by N_2 bubbling and is accelerated toward the detector by an additional auxiliary N_2 flow (see Figure 2.1, pp. 21). A steady-state atomic absorption detector signal is therefore produced. Both methods achieve significant hydride preconcentration factors and exhibit a separation effect of the selenium

from the aqueous sample matrix constituents.

A Jarrell-Ash 850 atomic absorption spectrometer was used as the hydride detector. The spectrometer and hollow cathode lamp settings were described in Chapters 2 and 4.

2. REAGENTS. NO_2^- standards were prepared fresh daily from KNO_2 (Mallinckrodt, analytical reagent) in deaerated water and kept stoppered under N_2 . NO_3^- standards were prepared from Mallinckrodt KNO_3 . Other necessary reagents were described in Chapters 2 and 4.

3. PROCEDURES. The batch reactor method was as described in Fry et al. (12). The final NaBH_4 concentration was 0.5% for all nitrite and nitrate studies. Unless otherwise mentioned, the concentrations of HCl and NaBH_4 were 2.7M and 5%, respectively for the batch reactor, and 6M and 0.5%, respectively for the VGA-76 continuous flow reactor.

II. RESULTS AND DISCUSSION.

Effect of BH_4^- Concentration.

Figure 5.1 shows that, unlike the copper interference of Chapter 4, BH_4^- concentration has almost no effect on the nitrite interference in a continuous reactor.

Acidity Effect.

Figure 5.2 shows that the acidity level has some effect on the nitrite interference. The lower acidity (2M HCl) produces less nitrite interference than the higher acidity (6M HCl). This is probably due to increased volatile NO_x formation as a result of accelerated acidic disproportionation of nitrite in 6M HCl. This is supported by the visual observation of a rapid formation of brown solution color and brown NO_2 fumes which are liberated more vigorously from 6M acid than from 2M acid.

Gas Phase Reactions.

To determine whether the nitrite interference was due to inhibition of the Se (IV) reduction, or whether interference occurred after SeH_2 was produced and degassed from solution, the apparatus configuration of Figure 5.3 was utilized to study the direct gas phase reaction of NO_x and SeH_2 .

Figure 5.1 Effect of NaBH₄ Concentration

Sample dissolved in 6M HCl, acid channel was 10M HCl.

- ○ - 0.5% NaBH₄
- △ - 1% NaBH₄
- □ - 5% NaBH₄

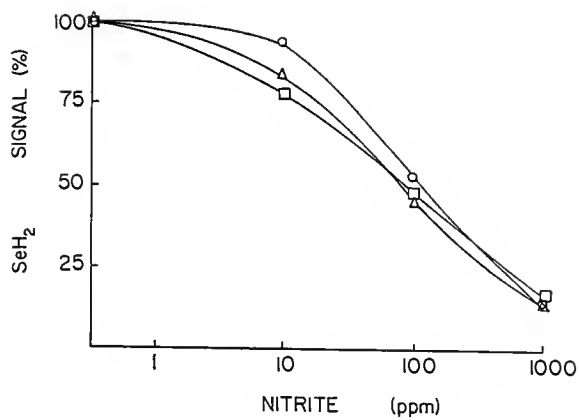


Figure 5.2 Influence of Acidity Level in Nitrite Interference of SeH_2 Determination.

Acid channel was 10M HCl, reducing agent channel was 0.5% NaBH_4 .

- ○ - Se(IV) dissolved in 2M HCl

- △ - Se(IV) dissolved in 6M HCl

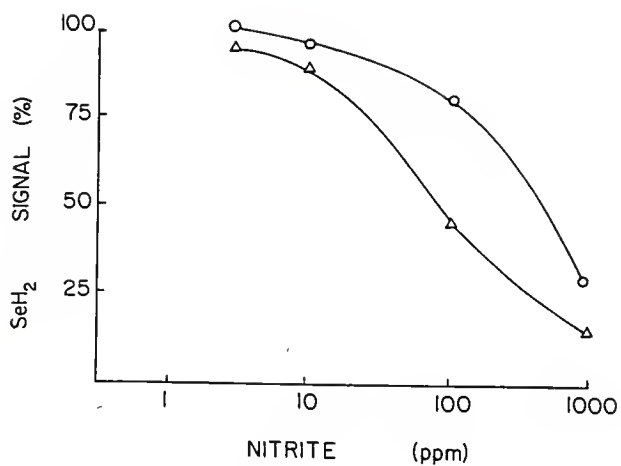
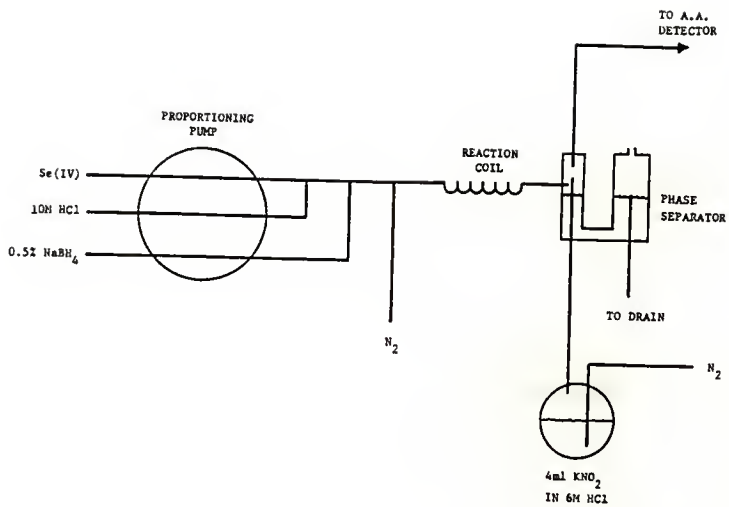


Figure 5.3 Experimental Setup for NO_x Effect in SeH₂ Determination.

Volatile NO_x, which was generated from 4mL of 1000ppm KNO₂ dissolved in 6M HCl, was swept by N₂ to the phase separator to react with clean SeH₂ while the SeH₂ signal was being monitored.



In this experiment (see Fig. 5.3), SeH_2 was generated separately (no nitrite in the sample). NO_x was added in the gas liquid separator after SeH_2 was degassed from solution. NO_x was produced with a stream of N_2 which bubbled through a flask containing 4mL of 1000ppm KNO_2 dissolved in 6M HCl. Brown NO_2 fumes and colorless NO resulted from the acidic disproportionation of nitrite. The NO_x was constantly swept to the gas liquid separator for reaction with the incoming gaseous SeH_2 directly before going to the absorption cell. The consequent SeH_2 signal was monitored with the atomic absorption spectrometer.

As a result of the NO_x reaction in the gas phase experiment, more than 90% of the SeH_2 signal was suppressed initially. As the NO_x supply from the KNO_2 reservoir was gradually exhausted by degassing, more than 80% of the SeH_2 signal response sensitivity was eventually recovered. These experiments show that most of the nitrite interference in the continuous flow reactor can be accounted for by a gas phase reaction. NO and NO_2 are powerful oxidants which are probably converting SeH_2 to a non-volatile oxidation state. In fact, orange deposits were observed on the Teflon tubing leading from the gas liquid separator to the A.A. detector. These orange deposits were possibly Se^0 .

Effect of Reactor Type.

Figure 5.4 shows the interference of nitrite (as KNO_2) on SeH_2 evolution with relatively concentrated BH_4^- (5%). Data are given for the batch type reactor and the VGA-76 continuous reactor under otherwise identical conditions. At high nitrite levels, severe interference is encountered with both reactors, but the effect is noticeably worse with the batch reactor.

The only things we could observe that might account for the difference in reactor type were: 1.) the length of path and corresponding time for gas phase reaction of NO_x and SeH_2 between the reaction vessel and the detector, 2.) the depth of solution through which SeH_2 bubbles must travel to escape into the gas stream, 3.) the available reactor and tubing wall surface area for condensation of nonvolatile oxidized Se following gas phase reactions of SeH_2 and NO_x , and 4.) availability of additional potential NO_x collection and reaction sites (e.g. sulfuric acid trap and liquid N_2 cryogenic trap (see Figure 5.5)) in the batch reactor. All of the above differences are less favorable for the batch reactor, and could account for the increased nitrite interference seen in Figure 5.4 for this type of reactor.

Figure 5.4 Comparison of Nitrite Interference in Batch and Continuous Flow SeH_2 Generation.

- \square - Batch reactor, final HCl and NaBH_4 concentrations were 2.7M and 0.56% respectively.
- \triangle - VGA-76 reactor, final HCl and NaBH_4 concentrations were 2.7M and 0.56% respectively (10M HCl in acid channel, and 5% NaBH_4 in the reducing agent channel, and Se(IV) in 6M HCl).

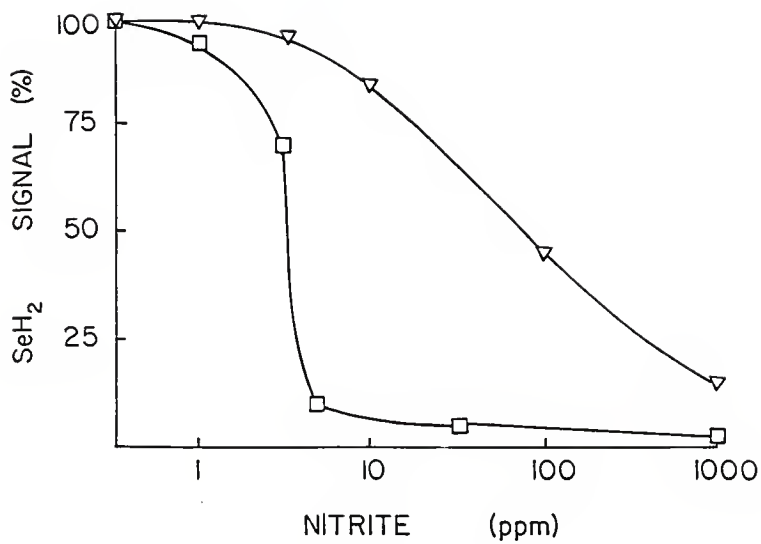
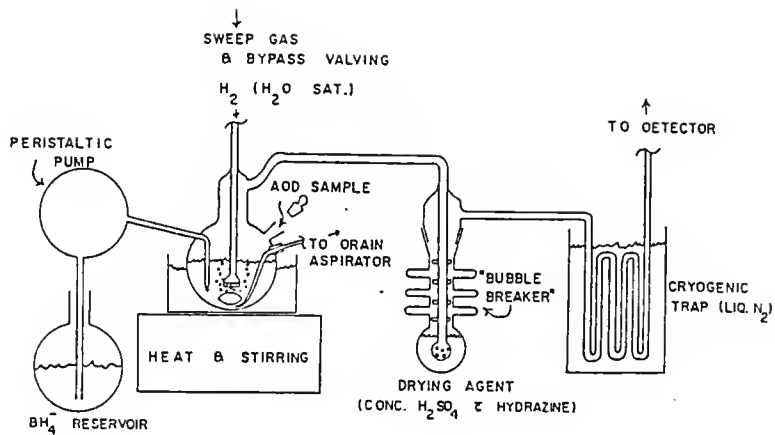


Figure 5.5 Batch Hydride Generator.



One of these possibilities was examined further to see if it could account for the difference in reactor type. The experimental setup is as shown in Figure 5.6. According to this Figure, the 25.4cm Teflon tube carrying the clean SeH_2 from the gas-liquid separator was submerged 1.9cm below the liquid surface of a 4mL reservoir of KNO_2 (auxiliary bubble chamber). To separate the interference of aqueous nitrite from that of NO_x , one experiment was performed with the KNO_2 reservoir as a neutral water solution of nitrite. And a second experiment was performed with the KNO_2 reservoir as a 6M HCl solution of KNO_2 . One of the advantages of this experimental setup is that the interaction of SeH_2 and aqueous nitrite may be observed independent of NO_x and NaBH_4 while the SeH_2 signal is being monitored.

The results of these two experiments are shown in Figure 5.7. The figure shows that aqueous nitrite can interfere after the production but before the degassing of SeH_2 . This may occur in addition to downstream NO_x reactions noted earlier from the experiments of Figure 5.3, or it may even account for most all of the observed interference for continuous type reactors (the aqueous nitrite curve of Figure 5.7 is almost identical to the real analytical interference curves seen earlier in Figure 5.1).

Figure 5.6 Apparatus for Studying Liquid Level Effect of Nitrite Interference on SeH_2 Generation.

SeH_2 was generated and bubbled through a flask containing 4mL of KNO_2 dissolved in 6M HCl and in water while SeH_2 signal was being monitored.

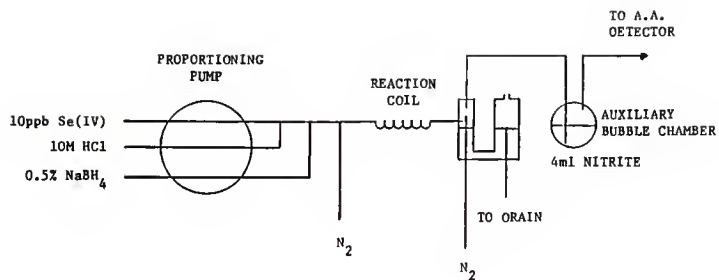
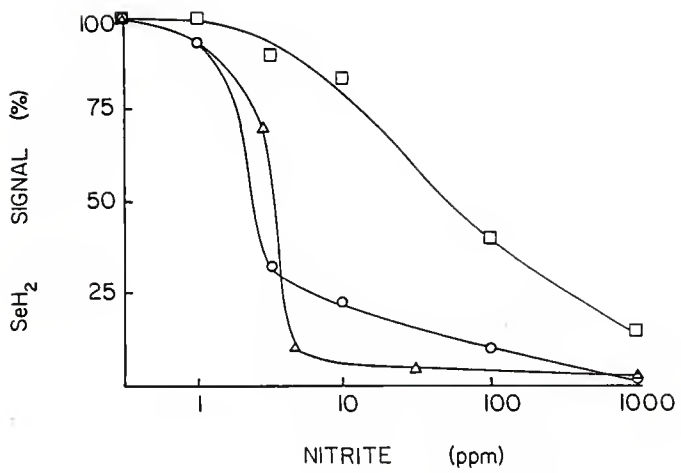


Figure 5.7 Comparison of Nitrite Interferences in SeH_2 Generation of Batch and Continuous Flow Reactors.

- \triangle - Batch reactor, nitrite added to reaction flask. Final HCl and NaBH_4 concentrations were 2.7M HCl and 0.56% respectively. as bad (see Fig. 5.4).
- \circ - VGA-76, clean SeH_2 bubbled through a flask containing 4mL nitrite dissolved in 6M HCl.
- \square - VGA-76, clean SeH_2 bubbled through a flask containing 4mL nitrite dissolved in water.



The data of Figure 5.7 for the acidified nitrite reservoir (continuous reactor) are much more severely depressed. In this case, the interference is nearly as bad as for the batch reactor. This suggests that the bubbling or degassing of SeH_2 from deep below the liquid level of a large volume reservoir such as the auxiliary bubble chamber (Fig. 5.6) or the primary reaction vessel of a batch reactor (Fig. 5.5) may account for the original differences observed in reactor type for nitrite interference. The continuous reactor is normally operated without any large solution reservoirs; all SeH_2 bubbles are generated near the liquid surface in the small bore Teflon tube reactor, hence the nitrite interference is not as bad (see Fig. 5.4).

No matter what experimental conditions are employed or which reactor type is used, the data of this chapter have shown that nitrite still interferes to some extent. It will therefore still be necessary to boil any samples prior to Se (IV) reduction with BH_4^- . This simple procedure will entirely eliminate all of the nitrite and its direct interference effects seen thus far in Chapter 5. The only remaining source to be considered is nitrite indirectly generated "in situ" from the copper catalyzed reduction of residual nitrate (12). This source of nitrite cannot be removed by boiling and is studied below.

Direct Nitrate Interference.

Although Figure 5.8 suggests that SeH_2 is relatively unaffected by nitrate in both reactors, the batch reactor exhibits more nitrate interference than the VGA-76 continuous flow reactor. While 40% SeH_2 signal suppression was observed with the batch reactor at 1000ppm nitrate, no loss of SeH_2 signal at the same nitrate concentration was observed with the continuous flow reactor in either 2M or 6M HCl samples. The unusual nitrate tolerance of the continuous flow reactor apparently is not a direct result of HCl concentration variation. No attempt was made in evaluating the NaBH_4 concentration effect in nitrate interference.

Copper Catalyzed Reduction of Nitrate to Nitrite.

This type of catalysis in a batch reactor is documented in reference 12 and results from the initial 5% BH_4^- reduction of as little as 0.5 ppm Cu^{++} to Cu^0 in 2.7M HCl. The Cu^0 then acts as a catalyst for the excess BH_4^- reduction of nitrate to nitrite (in spite of any earlier boiling of the sample) which then severely interferes with SeH_2 detection (see curve C in Figure 5.9).

The cure for this type of catalytic interference is to simply prevent production of the active form of the

Figure 5.8 Comparison of Nitrate Interferences in Batch and Continuous Flow SeH_2 Generation.

- ○ - Batch reactor, final HCl and NaBH_4 concentrations were 2.7M and 0.56% respectively.
- □ - VGA-76, final HCl and NaBH_4 concentrations were 2.7M and 0.056% respectively (Se(IV) dissolved in 2M HCl, acid channel was 10M HCl, and reducing agent channel was 0.5% NaBH_4).
- △ - VGA-76, final HCl and NaBH_4 concentrations were 5.8M and 0.056% respectively (Se(IV) dissolved in 6M HCl, acid channel was 10M HCl, and reducing agent channel was 0.5% NaBH_4).

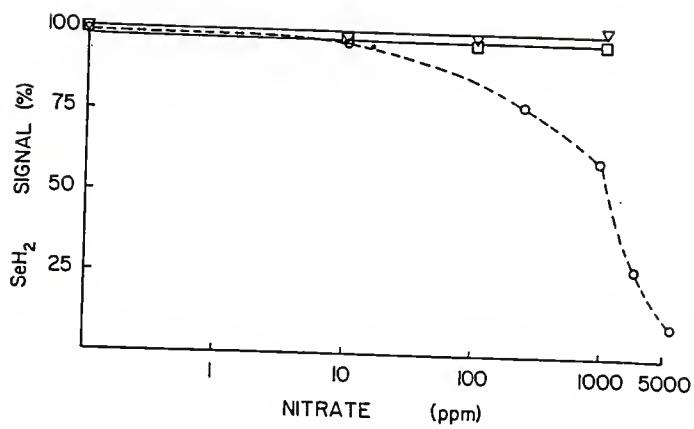
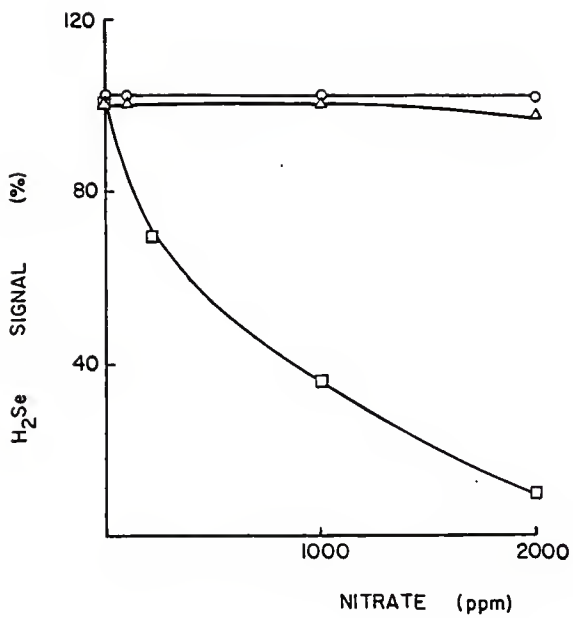


Figure 5.9 Comparison of The Combined Interferences of Cu^{2+} and Nitrate in Batch and Continuous Flow SeH_2 Generations.

- (A) - \square - Batch reactor, final HCl and NaBH_4 concentrations were 2.7M and 0.56% respectively, Se(IV) sample contained 0.5ppm Cu^{2+} .
- (B) - \circ - VGA-76, final HCl and NaBH_4 concentrations were 2.7M and 0.056% respectively (Se(IV) dissolving in 2M HCl, acid channel was 10M HCl, and reducing agent channel was 0.056%), Se(IV) contained 5ppm Cu^{2+} .
- (C) - \triangle - VGA-76, final HCl and NaBH_4 concentrations were 5.8M and 0.056% respectively (Se(IV) dissolved in 6M HCl, acid channel was 10M HCl, and reducing agent channel was 0.056%), Se(IV) contained 5ppm Cu^{2+} .



catalyst (Cu^0). Chapter 4 suggests a very easy way to accomplish this, namely to lower the BH_4^- concentration to the level of 0.5%. When this is done in the VGA-76 continuous reactor, curves A and B of Figure 5.9 show that no significant nitrate interference is encountered, even at the highest nitrate levels studied and even for much higher levels of Cu^{++} added (e.g. 5 ppm). This makes sense, because nitrate itself is known not to interfere, and no Cu^0 is formed at these BH_4^- levels. The copper remains as Cu^{++} , no catalyst is therefore present, and the nitrate cannot be converted to nitrite (the active interfering form).

A combination of the reaction conditions of curves A and B in Figure 5.9 (low BH_4^- concentration in a continuous reactor), and boiling the sample to remove any nitrite or NO_x produced in solid sample dissolution is finally sufficient to eliminate all significant interference from nitrogen oxides in all forms. Samples may therefore be analyzed with confidence and reliability regardless of whether atomic absorption, emission, or gas chromatography detectors are employed with the analytical hydride preconcentration.

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Chapter 6

Summary and Conclusion

I. Sensitivity Enhancement Studies

The use of a cryogenic entrapment variation on the continuous flow hydride generation technique results in further preconcentration and facilitates rapid injections into a gas chromatograph which can be used for multi-element hydride analysis. BH_4^- reaction by-products (HCl , H_2O , CO_2 , and borane vapors) normally overlap the hydride analytes elution and obliterate any PID response to As, Se, Sn, and Sb using GC columns such as Chromosorb T, and glass beads. Tenax GC as a polymeric column packing material, however performs the separation effectively. At room temperature, it irreversibly traps the unwanted by-products of BH_4^- hydrolysis and passes the desired traces of AsH_3 , SeH_2 , SnH_4 , and SbH_3 analytes into the PID detector one at a time.

The separated hydrides are detected by a photoionization detector with absolute detection limits of 25pg for As and Se, 50pg for Sn, and 2800pg for Sb. The corresponding concentration detection limits are 0.02ppb As, 0.02ppb Se, 0.04ppb Sn, and 0.2ppb Sb. These detection

limits represents 2 or more orders of magnitude improvement over other detectors cited in Tables 3.2 (p. 65) and 3.3 (p. 70) and more than one order of magnitude improvement over the hydride generation ICP emission method (see Table 1.3). These detection limit improvements will finally allow for reliable quantitative determination of As and Se content at baseline levels in natural water and waste water samples.

II. Interference and Analytical Accuracy Investigations

Copper and nitrite can both produce severe interference with a hydride generation procedure if the experimental conditions are poorly chosen. Direct nitrite interference is simply avoided by boiling the sample prior to BH_4^- reduction. Copper indirectly (catalytic) produces nitrite interference and is avoided by raising the acidity (eg. 6M HCl) and lowering the BH_4^- concentration to 0.5% where copper remains as Cu^{2+} and is not reduced to Cu^0 .

It was the metallic copper (Cu^0) that suppressed the selenium hydride signal at higher BH_4^- and lower acidity. The interference was occurring after the formation of selenium hydride. Cu^0 precipitate adsorbed SeH_2 and prevented its transport to the detector. Higher NaBH_4 concentrations speed up the production of Cu^0 from Cu^{2+} thereby making the interference worse! The interference

can be eliminated entirely by raising the HCl concentration and lowering the BH_4^- concentration to prevent Cu^0 from accumulating in the reactor manifold tubing. Additional HCl helps by increasing the solubility of copper.

As a result of these studies, a new hydride-generation/GC-PID instrument has been developed, and interference-free determination of As, Se, Sb, and Tin may now be performed in aqueous media on a simultaneous multielement basis at several orders of magnitude lower concentration than was previously possible. The previously troublesome direct copper interference mechanism has been identified and circumvented as well as the copper catalyzed nitrate interference.

Chapter 7

Recommendation for Future Studies

A longer GC column is recommended to improve the baseline separation of AsH_3 and SnH_4 . To cope with the corresponding increase in back pressure, a higher pressure GC system is recommended.

While the instrumental setup of Figure 5.2 proved to be effective for the multi-hydride analysis, there is room for improvement. A conceivable setup that I propose features direct cryo-focusing hydride from the VGA-76 reactor onto a small inlet section of the Tenax GC column. Several advantages become obvious with this arrangement. First, sample loop is eliminated, therefore, reduces the potential hydride degeneration from thawing and from hydride transportation. Secondly, direct cryo-focusing takes full advantage of the thermal adsorbability/desorbability of Tenax GC. Since Tenax GC adsorbs hydrides strongly below 10°C , an ice water cryogenic bath is probably sufficient to concentrate the incoming hydride onto the Tenax GC for latter thermal desorption. The injection would be more rapid and the peak broadening effect resulting from the slow thawing and transportation of the hydride through a long sample loop

would be reduced. Equal importantly, the whole operation is simplified and more cost effective.

Two of the desired features a GC column packing material for the application of hydride separation are short column and low adsorptivity of the hydride reaction products. Although tenax GC was able to thermally desorbed CO_2 , B_2H_6 , and HCl at about 85°C , the adsorption of corrosive and reactive species such as diborane and HCl represents a thread to longevity of the column and is potential interferent. Haye-Sep, a porous polymeric divinyl benzene recently marketed by Alltech Associates, was reported to perform far superior than Porapak Q for gas sample regarding to retention time reproducibility, resolution per column length, and stability(1). No application of Haye-Sep in hydride separation has been reported. Since Porapak Q has been used to separate hydrides (2), the applicability of Haye-Sep in hydride separation might be warranted.

Capillary column represents the ultimate chromatographic sensitivity and resolution obtainable. The application of a DB-5 capillary column in organo Tin hydride separation has been reported (3). The incorporation of this capillary column into our VGA-76---GC---PID system may improve the chromatographic

resolution. It could be added in combination with a Tenax GC trap to remove BH_4^- reaction by-products.

Direct coupling of hydride generators to ICP's or MIP's lead to unregulated pressure surges from H_2 evolution. The attachment of the cold trap sampling variation developed here for the VGA-76 reactor should facilitate adaptation to ICP and MIP systems.

Additional Tenax GC-PID studies are recommended to determine applicability to Hg and organo substitute As, Se, Sn, and Hg compounds. Some ionization potentials listed in Table 7.1 indicates that these compounds should be detectable with our 10.2ev PID lamp.

Table 7.1 Ionization Potentials (ev) of Hg⁰ and Selected Hydrides.

<u>Hydrides</u>	<u>Ionization Potentials (ev)</u>	<u>References</u>
AsH ₃	10.03	4
SeH ₂	9.88	5
SnH ₄	9.2	6
SbH ₃	9.58	7
PbH ₄	-----	---
TeH ₂	9.138	8
BiH ₃	-----	---
GeH ₄	12.3	7
SiH ₄	12.2	7
CH ₃ AsH ₂	9.7	7
(CH ₃) ₂ AsH	9.0	7
Hg ⁰	10.43	7

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SENSITIVITY ENHANCEMENT AND INTERFERENCE STUDIES
IN ULTRA-TRACE As, Se, Sb, AND Sn DETERMINATION
BY HYDRIDE GENERATION ATOMIC ABSORPTION AND
A NEW TENAX GC/PHOTOIONIZATION SYSTEM

by

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Abstract

Data are given concerning to the effects of NaBH_4 and HCl in As, Se, Sn, and Sb hydrides generation in commercial continuous flow hydride generator. The design of a ultra-sensitive, simultaneous multielemental hydride determination instrument featuring a continuous flow hydride generator, a gas chromatograph, and a photoionization detector is presented. The studies utilizing this instrument to simultaneously determine As, Se, Sb, and Sn are reported. Results of the investigation about the copper interference in selenium hydride evolution are presented. Results of the studies of NO_x interference in selenium hydride generation are reported.