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The Determination of Trace-Level Antimony
in Geological Materials by Semi-Automated
Hydride Generation-Atomic Absorption
Spectroscopy

By

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Abstract

A semi-automated method for the determination of antimony in geological materials involves the following steps. After a manual digestion of the sample with a mixture of concentrated sulfuric, nitric, and perchloric acids, the sample is brought to volume with 10% hydrochloric acid. The sample is then mixed in a continuous flow-automated sequence with reducing agents, further acidified with hydrochloric acid and reacted with a solution of sodium borohydride to form the gaseous hydride of antimony. The resulting gas mixture of hydrogen and hydrides is decomposed in a heated quartz tube in the optical path of an atomic absorption spectrophotometer. The amount of antimony present is proportional to the absorbance, measured by peak height. Interferences that exist are minimal and most geological materials can be analyzed directly. The relative standard deviation (RSD) of the digestion and the instrumentation is <2%. The blank-limited detection limit is 0.2 $\mu\text{g/L}$ (microgram/Liter) and the sensitivity is 0.44 $\mu\text{g/L}$ antimony.

INTRODUCTION

The determination of antimony in geological materials has always been, at best, challenging. Antimony in the subnanogram/gram concentration has in the past either been routinely done by a colorimetric method (Schnepe, 1973) or more recently, by graphite furnace-atomic absorption spectrophotometry (Aruscavage, 1977). The use of hydride generation is not new in the determination of antimony (for example, Smith, 1975 and Thompson and Thomerson, 1974). In work done by Smith (1975), antimony hydride, stibine, was manually generated and then measured by atomic absorption spectrophotometry (AAS) in an argon-hydrogen flame. In his study significant interferences from concomitant elements were noted. Fiorino and his co-workers (1976) also used AAS with the argon-hydrogen flame using a semi-automated generation of the hydrides using pneumatic controllers for the addition of reagents. Chan and Vijan (1978) and Vijan (1979) then introduced the semi-automated continuous-flow generation of hydrides and measurement by AAS of antimony in geological materials. Interference studies for the determination of antimony using hydride generation similar to those published for arsenic and selenium (Pierce and Brown, 1976; 1977) have been published by Chan and Vijan (1978) and Thompson and others (1978). The proposed method is a combination of the methods of Skougstad and others (1979), Chan and Vijan (1978), and Pierce and others (1976), along with some specific alterations which are described below. These modifications are primarily related to the method in which reagents are added to the sample, the sample digestion technique, the addition of a secondary reducing solution to help minimize interferences, especially from large ferric-ion concentrations, the addition of sodium borohydride after, instead of before, acidification with hydrochloric acid, and the use of two 40-foot delay coils to allow the reaction to reach equilibrium in the formation of stibine (SbH_3).

EXPERIMENTAL METHOD

Reagents

Hydrochloric Acid Solution: Dilute "Baker Insta-Analyzed," suitable for trace metals analysis, with an equal volume of demineralized water. The use of the "Baker Insta-Analyzed" or hydrochloric acid of similar purity is advised throughout the procedure to insure a low antimony blank, since as discussed below, the detection limit is limited by the reagent blank.

Sodium Borohydride Solution: Dissolve 40 g sodium hydroxide and 5.0 g sodium borohydride in demineralized water. Dilute to 1.00 L with demineralized water. Make fresh daily.

Potassium Iodide Solution: Dissolve 100 g potassium iodide in demineralized water. Add 1 g ascorbic acid. Dilute to 1.00 L with demineralized water.

Reducing Solution: Pour a 454 g bottle of oxalic acid into a 2 L plastic bottle. Fill with demineralized water and shake well to mix. This will form a saturated solution of oxalic acid. There should be solid oxalic acid remaining. Dissolve 200 g of hydroxylamine hydrochloride in 800 g of the saturated oxalic acid solution.

Antimony Stock Solution: (1000 $\mu\text{g/mL}$ Sb) Dissolve 2.743 g of potassium antimony tartrate hemihydrate, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$, in demineralized water. Dilute to volume with 10% hydrochloric acid. The working standards of 10, 30, 50, 100 $\mu\text{g/L}$ Sb are made from serial dilutions of this stock solution with 10% hydrochloric acid.

Apparatus

A Perkin-Elmer model 306 atomic absorption spectrophotometer equipped with a Perkin-Elmer model 056 strip chart recorder, a Gilson Minipulse 2 eight-channel peristaltic pump with standard Technicon Tygon pump tubing, and a Technicon Auto Analyzer II sampler are used for the automated, continuous-flow generation and detection of stibine. The peristaltic pump must be as pulse free as possible to prevent surging of the flow. The auto sampler was slightly modified. Instead of using the standard stainless steel sampling probe, a 150 mm by 4 mm (outside diameter) glass tube is used. The sampling arm was drilled out to accommodate the larger sample probe. This modification became very obvious after the limited life of the stainless steel probe in the highly acidic solutions. The stripping column and quartz furnace have been described by Pierce and others, (1976) and Skougstad and others, (1979). Preparation of the quartz furnace as used by Skougstad and others (1979), was done as given by Maurice Cocchi, Water Resources, U.S. Geological Survey, Denver Central Laboratory (written communication, 1980). The quartz tube furnace is maintained at a constant temperature of 850°C by an applied voltage of approximately 47 volts with a variable autotransformer. See table 1 for various instrumental parameters associated with the spectrophotometer.

Table 1.--Instrument parameters for the spectrophotometer
and strip chart recorder.

Wavelength:	217.6 nm
Slit:	0.2 nm
Background Correction:	Not used
Damping:	4 (Maximum)
Mode:	Absorbance
Light Source:	Sb Intensitron Hollow Cathode Lamp
Lamp Current:	20 ma
Strip Chart Recorder:	10 mv full scale response, 5 mm/min chart speed

Sample Preparation

Weigh 1.000 g of -80 mesh material into a 250 mL Erlenmeyer flask. Slowly add 20 mL nitric acid, 10 mL sulfuric acid, and 5 mL perchloric acids. All acids are Baker "Suitable for Mercury Determination" grade. If the sample is low (less than 10%) in organic material, such as in granites or some sandstones, the perchloric acid may be omitted. Add several boiling chips which have been cleaned in boiling nitric acid and rinsed with demineralized water.

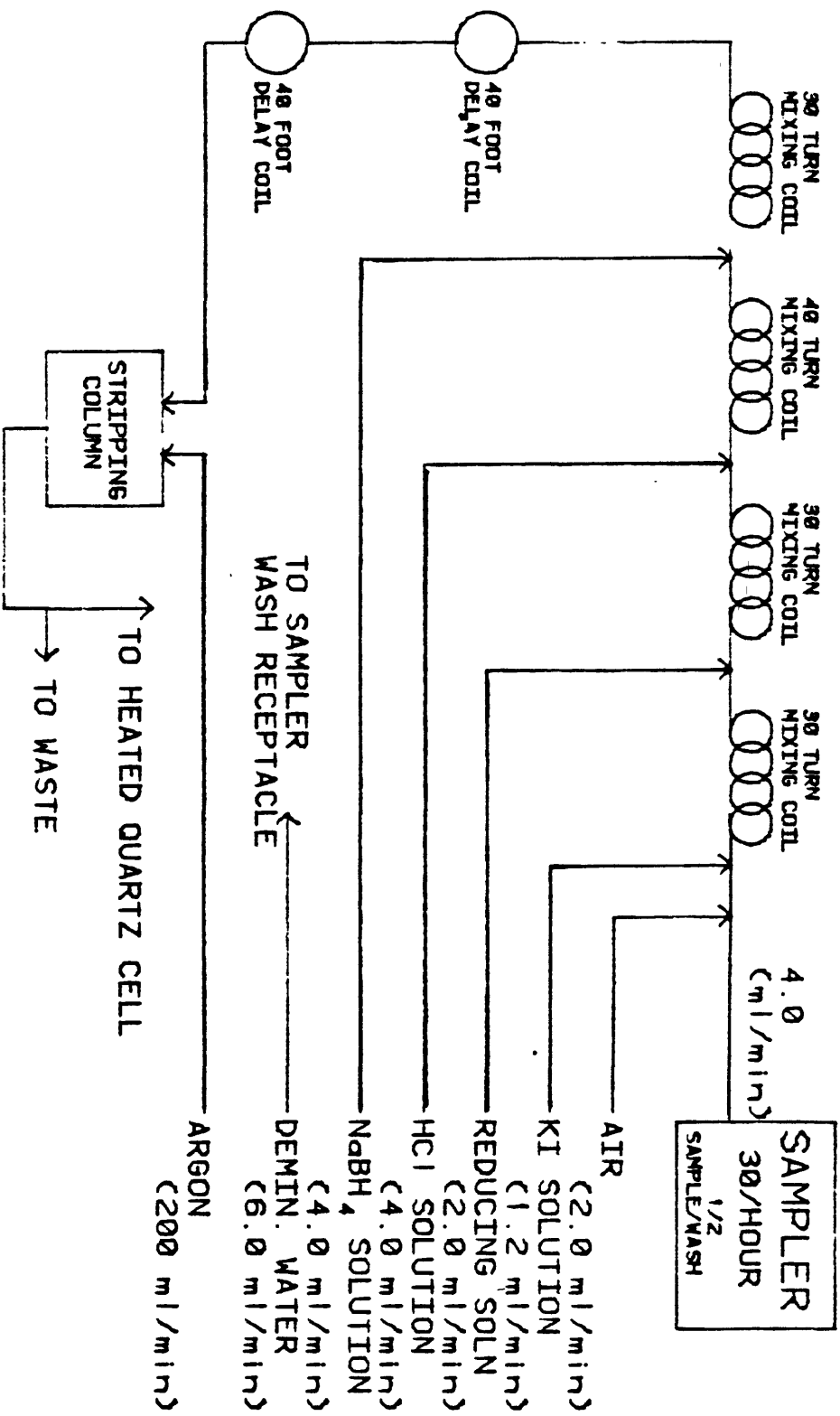
Cover with a watch glass and place on a steam bath overnight. Place the flask on a hotplate and slowly (taking at least 6 hours) raise the temperature of the sample to fumes of sulfuric acid. Keep the flask covered with its watch glass for the first 2 hours of digestion. Heating to sulfuric acid fumes may take up to 12 hours, especially for coals that are not finely ground.

After dense fumes of sulfuric acid have been reached, continue heating for at least 20 minutes. Remove from the hotplate and cool. Add approximately 30 mL of demineralized water and cool. Add 10 mL of concentrated hydrochloric acid, transfer to a 100 mL volumetric flask and bring to volume with demineralized water. Reagent blanks, duplicate samples, and reference materials should be taken through this digestion procedure to verify full recovery of antimony.

PROCEDURE

Set up the antimony manifold configuration as shown in figure 1. Using the conditions given in table 1 and an argon-carrier purge gas flow of 200 mL/min, a linear working range of 0.2 to 5.0 parts per million (ppm) antimony in sample is achieved. Serial dilutions of the sample with 10% hydrochloric acid made by using a Lab Industries Repipet diluter will easily allow analysis of higher levels of antimony. Scale expansion, up to 10X, is reasonable and allows analysis of 0.02 ppm Sb in sample. The system requires conditioning by running at least two samples or standards before useful data can be collected (Skougstad and others, 1979). Therefore, the highest standard is analyzed four times, followed by the remaining standards and samples in duplicate or triplicate.

Figure One: Antimony manifold



Results and Discussion

Interference studies using the semi-automated hydride generation AAS methods have been published for antimony by Vijan (1979) and Thompson and others (1978). The inorganic species most likely to interfere were investigated using a 50 $\mu\text{g/L}$ antimony solution. Table 2 lists these elements, the concentration range tested, and their effect on the antimony absorbance signal. Some interferences are noted. Nickel, tin, selenium, and arsenic were found to interfere. When using the given digestion and dilution procedure, each mg/L of the interfering element corresponds to 0.01% of that element in sample. We can conclude from the data in table 2 that these elements are not likely to introduce a significant error for common geological materials. For example, an interference of approximately 30% would require that the material to contain 0.4% Ni, 0.04% Sn, 1% As, or more than 1% Se.

Tin usually occurs as the mineral cassiterite (SnO_2) and has a very low solubility in the digestion technique (Rose and others, 1979). Because of these facts and tin's low average natural abundance (for instance, granite, 3 ppm; soils, 10 ppm; and shales, 6 ppm; Rose and others, 1979), there should be no interference from tin.

Table 2.--Percent Effect on the Absorption Signal of a 50 $\mu\text{g/L}$ Antimony Solution by Common Inorganic Species

Element (10% HCl)	Interfering element concentration mg/L/ Percent Effect* on the antimony signal.					
Fe^{3+}	100 0	500 0	1000 0	3000 0	5000 0	**-- --
Ni^{2+}	1.0 0	5.0 0	10 0	30 -25	50 -37	100 -80
Cu^{2+}	10 0	50 0	100 0	300 0	500 0	-- --
Sn^{2+}	0.5 0	1.0 0	3.0 -26	5.0 -44	10 -66	-- --
Se^{6+}	1 0	5 0	10 0	30 0	50 0	100 -6
As^{3+}	1 0	5 0	10 0	30 0	50 0	100 -40
V^{5+}	10 0	50 0	100 0	--	--	--
Cd^{2+}	10 0	50 0	100 0	--	--	--
Zn^{2+}	10 0	50 0	100 0	--	--	--
Mn^{2+}	50 0	100 0	300 0	--	--	--
$\text{Cr}_2\text{O}_7^{2-}$	5 0	10 0	50 0	--	--	--
Pb^{2+}	10 0	50 0	100 0	--	--	--
Co^{2+}	10 0	50 0	100 0	--	--	--
Te^{6+}	1 0	5 0	10 0	--	--	--
Mo^{6+}	10 0	50 0	100 0	--	--	--
Al^{3+}	0.5 0	1.0 0	5.0 0	10 0	50 0	100 0

$$\% \text{ Effect} = \left[\frac{\text{Peak height of 50 g/L Sb} + \text{Interfering Element}}{\text{Peak Height of 50 g/L Sb}} - 1 \right] \times 100$$

**Data not collected

Nickel interference will usually be insignificant because of its low abundance in most geological materials: granite, 5 ppm; soils, 17 ppm; and shales, 68 ppm (Rose and others, 1979). But nickel may be a problem when analyzing sulfide ores or other nickel-bearing minerals. In some sulfide deposits and nickel occurrences, nickel can easily be greater than the 0.4% and would in general be soluble in the digestion procedure. To minimize this interference, either dilution of the solution or the calibration method of standard addition must be used.

Arsenic and selenium interferences will also usually be insignificant because of their low abundance: granites, 2 ppm As, 0.2 ppm Se; soils, 7.5 ppm As, 0.3 ppm Se; and shales, 12 ppm As, 0.6 ppm Se (Rose and others, 1979). If the material tends to be high in either or both, antimony is normally also elevated, since they are commonly associated (Rose and others, 1979). Therefore, the interference can be diluted out or the standard addition technique used.

The reported interference for arsenic by the permanganate ion (Pierce and Brown, 1977) was eliminated by the acidification of the sample prior to analysis with hydrochloric acid. The permanganate ion is reduced by the chloride ion in an acidic solution. No organic species were investigated because they all should have been removed in the digestion procedure. The nitrate interference for arsenic and antimony reported by Pierce and Brown (1977) was not investigated because all nitrate is volatilized as the oxide when taking the solution to strong sulfuric-acid fumes.

An initial test of the method described Chan and Vijan (1978) did not yield the reported sensitivity or precision. After combining the stripping column, heated quartz tube and sampler configuration from Skougstad and others (1979), Chan and Vijan's (1978) method again was tested. The sensitivity improved; however a significant interference was noted from the large ferric-ion concentrations which commonly occur in the sample solution. Further investigation of various parameters was therefore undertaken to improve sensitivity and minimized interferences, including gas-flow rate, acid content, and concentrations of reagents.

Figure 2 shows the relative absorbance signal from a 50 g/L Sb solution as a function the argon-carrier gas. The signal drops off almost linearly with increased carrier gas flow, due to dilution by the gas. The 200 mL/min was chosen for routine work.

The effect of acid content of the sample was also tested by varying the concentration of HCl from 0 to 30% in sample solution and measuring the absorbance of a solution containing 50 g/L Sb and 0, 20, and 50 mg/L Ni. The resulting relationship is shown in figure 3. The absorbance signal when nickel is present increases as the acidity of the sample increases and is still increasing even at 30% HCl. However, when no nickel is present, the absorbance reaches a plateau at 10% acid. A solution of 10% hydrochloric acid was chosen for routine sample work. Because the samples also contain between 5-10% sulfuric acid from the digestion procedure, the solution's acid content is between 20-30%.

Figure Two

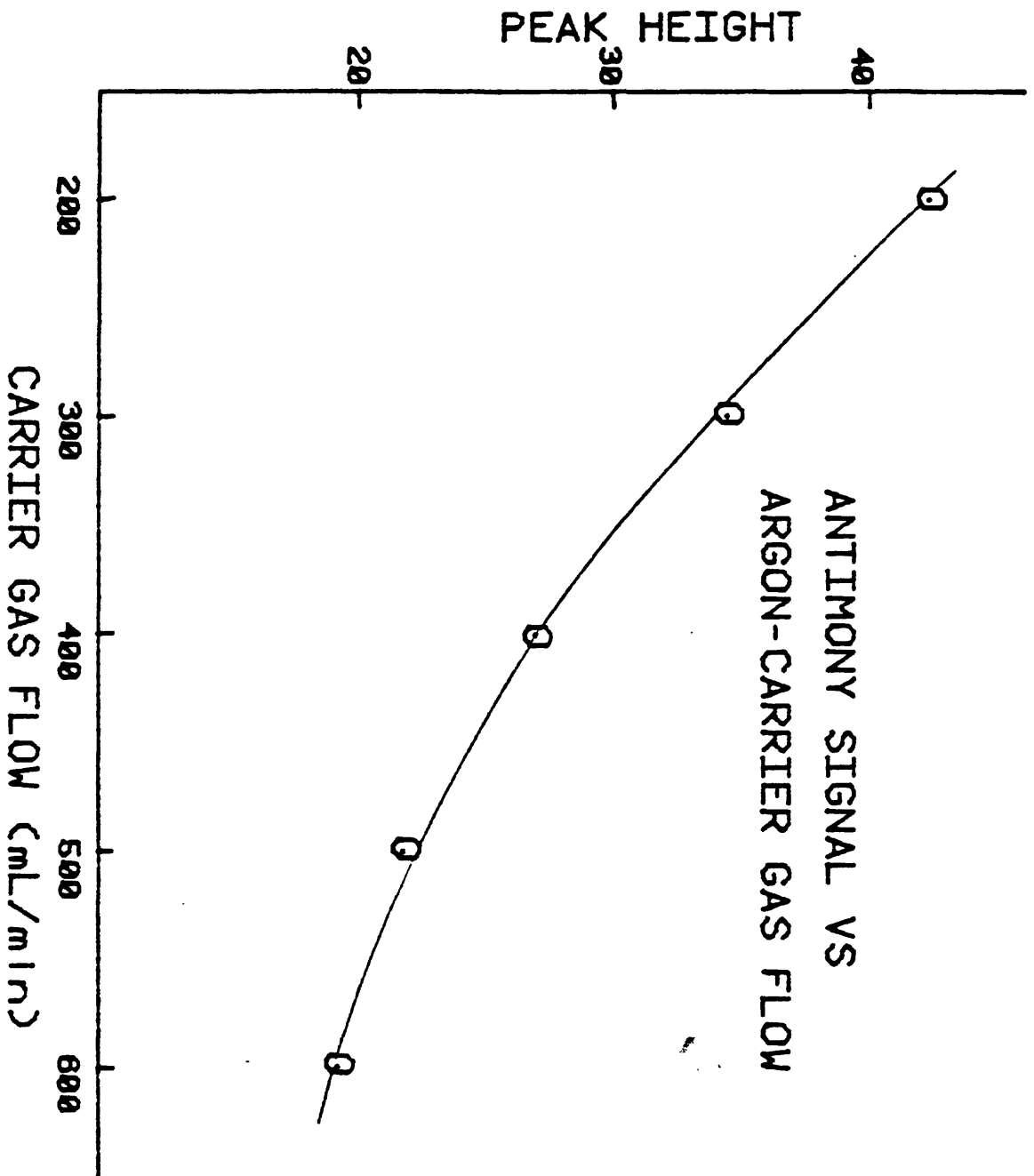
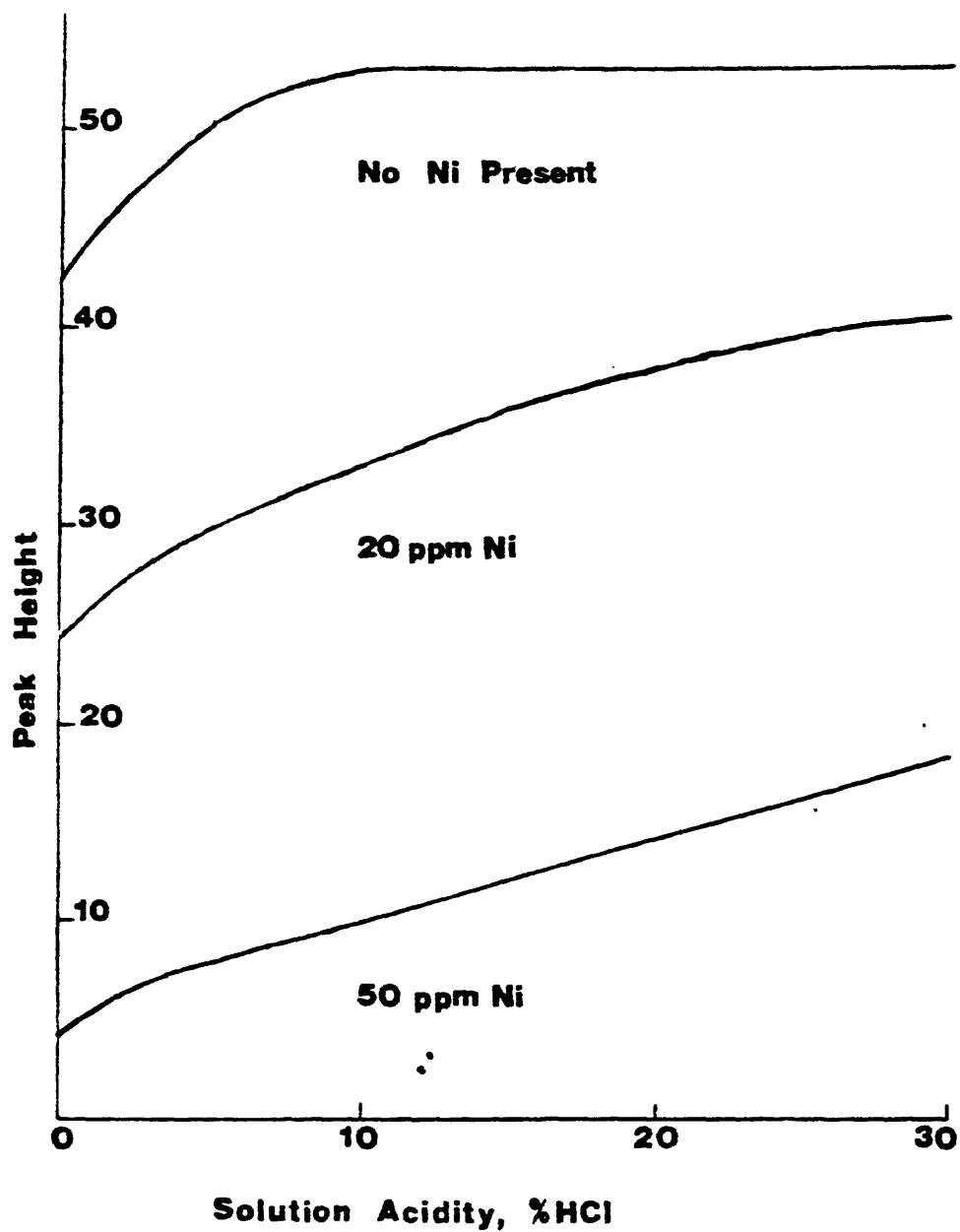


Figure Three

**50 $\mu\text{g/L}$ Sb Signal With Varying Solution
Acidity And Ni Concentration**

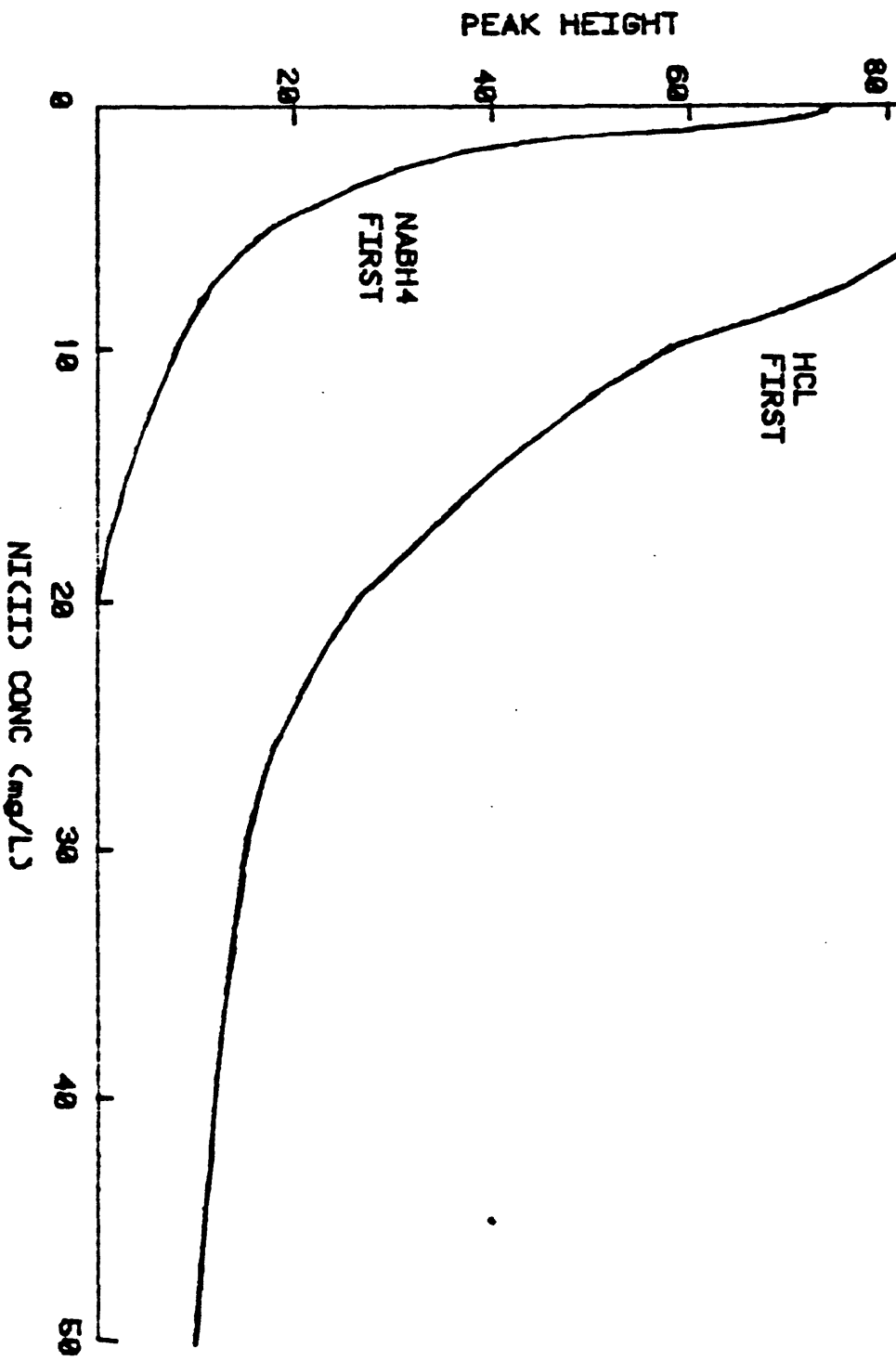


Various acid stock feeds added prior to the sodium borohydride solution were also tested. No difference was observed between 50% hydrochloric acid or sulfuric acid. Because the manual method described by Pierce and Brown (1977) suggests that the higher the solution's acid content before the addition of the borohydride solution, the more likely the complete evolution of arsine, 50% hydrochloric acid was chosen as the stock feed. Sulfuric acid as the acid stock feed is avoided because of its detrimental effects on regular Tygon and Technicon-Acidflex pump tubing.

Pierce and Brown (1977) suggested that the sample be acidified first and then reacted with the sodium borohydride acid to help minimized interferences. The study shown in figure 4 confirms this. When adding the sodium borohydride solution first, the nickel interference is greatly enhanced. When the sodium borohydride is added first, the peak height was depressed and the peak was saddle-shaped. This is caused by surges in the system when the sample solution is mixed with the sodium borohydride solution. The varying amounts of hydrogen formed by alternating the acidified sample solution and the water rinse, when reacted with the sodium borohydride, caused the system to pulse or surge, thus yielding the saddle-shaped absorbance peaks. When the sample and water rinse are first acidified, then reacted with the sodium borohydride solution the peaks became very regular, lost the depression from the surging and the nickel interference was decreased. (See figure 4.)

Figure Four

NICIID EFFECT ON THE SB SIGNAL:
ADDING THE HCL OR NABH4 FIRST



Instead of the 0.5% sodium borohydride solution, a 2.0% solution was tested. The signal was reduced by 50% and was much broader and irregular. There was increased background noise resulting in an irregular baseline. This was attributed to the noticeably larger amount of hydrogen produced which burnt at the ends of the quartz tube.

Several investigations were conducted to reduce the interference caused by high ferric-ion concentrations. An additional 40-foot delay coil positioned after the addition of sodium borohydride helped reduce the interference slightly. The suppression of the antimony signal caused by 5000 mg/L ferric ion was eliminated by the addition of a 20% (weight/volume) hydroxylamine hydrochloride/saturated oxalic acid solution, as a secondary reducing agent, after the addition of the potassium iodide solution.

PRECISION, SENSITIVITY, AND ACCURACY

Figure 5 shows the typical tracings for antimony solutions taken through the digestion procedure and analyzed in triplicate under the conditions given in table 1. Using standards of 10, 25, and 50 $\mu\text{g/L}$ antimony results in an effective working range of 0.2 to 5.0 ppm antimony in sample. This is satisfactory for most common geological materials, i.e., soils average 2 ppm; shales, 2 ppm, and granites, 0.2 ppm (Rose, and others, 1979).

The average relative standard deviation (RSD) for seven 50 $\mu\text{g/L}$ antimony aqueous solutions, each analyzed seven times, is 1.31%. The RSD for seven 50 $\mu\text{g/L}$ antimony aqueous solutions taken through the digestion procedure each analyzed seven times is 1.40%. The sensitivity of this method using the given instrumental conditions and manifold configuration is 0.44 $\mu\text{g/L}$ Sb. The detection limit is blank limited at 0.2 $\mu\text{g/L}$ Sb. The detection limit determined from the signal-to-background ratio is 0.1 $\mu\text{g/L}$ Sb. See table 3 for the analysis of reference materials for their antimony content. The low results for AGV-1, SGR, GSP-1, PCC-1 and W-1 may be caused by incomplete digestion of the antimony-bearing phase.

Figure Five
Typical Sb tracings
(all as $\mu\text{g/L}$)

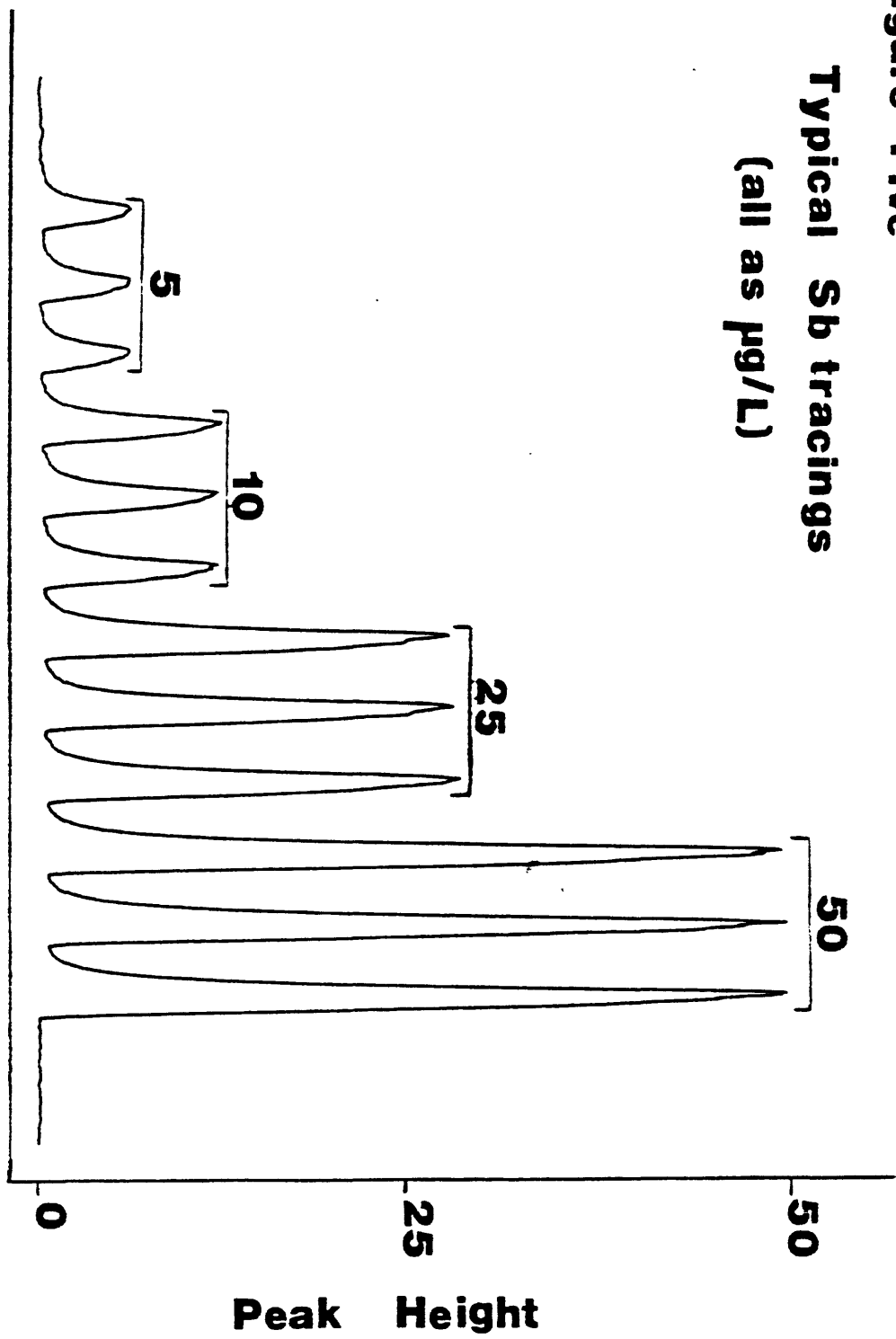


Table 3.--Antimony content of some standard reference materials.

Standard	<u>Antimony Concentration</u>		Source
	This Work	Reported	
S01 (soil)	0.1	0.2	1
S02 (soil)	0.1	0.1	1
S03 (soil)	0.3	0.3	1
S04 (soil)	0.5	0.3	1
1632a (coal)	0.6	0.6	2
1633a (coal fly ash)	6.2	7.	2
NBS Orchard Leaves	3.1	2.9	2
NBS 1635 (coal)	0.2	--	--
MAG	0.5	0.9	3
SGR	2.3	3.7	3
RMG	0.7	1.3	3
SCo	1.3	2.5	3
BHVO	0.1	0.2	3
MRG	0.3	0.4	3
AGV-1	1.3	4.3	1
DTS-1	0.3	0.5	1
BCR-1	0.3	0.6	1
GSP-1	2.0	3.1	1
PCC-1	0.4	1.4	1
W-1	0.2	1.0	1
SY2	0.3	0.2	1
SY3	0.3	0.3	1

- 1) Abby, 1980
- 2) National Bureau of Standards, Certificate of Analysis for Reference Materials.
- 3) Schwarz and Rowe, 1976.

Conclusion

The formation of stibine and measurement of antimony by atomic absorption spectroscopy proves to be a quick, very sensitive, precise, and accurate method for the determination of antimony in geological materials. While direct analysis can be used for most samples, the method of standard addition may be required for mineralized samples. The use of automation with a continuous-flow chemistry lends itself to rapid analysis even when the method of standard additions is required.

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