UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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

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Abstract.--A semi-automated method for the determination of arsenic in geological materials involves the following steps. After a manual digestion of the material in sulfuric, nitric, and perchloric acids, a hydrochloric acid solution of the sample is automatically mixed with reducing agents, acidified with additional hydrochloric acid and reacted with a sodium borohydride solution to form volatile AsH_3, arsine. The arsine is decomposed in a heated quartz tube in the optical path of an atomic absorption spectrophotometer. The absorbance peak height for arsenic is measured. Interferences that exist are minimized to the point where most geologic materials can be analyzed directly without use of the standard additions technique. The relative standard deviations (RSD) of the digestion and the instrumental procedure is <2%. The blank-limited detection limit is 0.2 µg/L As in solution with a sensitivity of 0.16 µg/L As.

INTRODUCTION

The use of hydride generation is not new in the determinaion of arsenic (for example, Holak, 1969). The semi-automated generation of arsenic and it's measurement by atomic absorption is also well established (for example: Pierce and others, 1976 and Skougstad and others, 1979). However, several modifications to these methods were found to be necessary for their application to geological materials. Large interferences were noted when trying to duplicate the method of Vijan and his co-workers (1976) and Pierce and his co-workers (1976). The described method extends the method proposed by Skougstad and others (1979) to geologic materials including soils and coals. Modifications are primarily related to reagent addition and to the sample digestion. Specifically, the addition of a secondary reducing solution minimizes interferences, especially from large ferric-ion concentrations. The addition of the sodium borohydride solution after acidification of the sample (Pierce and Brown, 1976) regulates peak shape and reduces interferences. The use of two 40-foot delay coils allows sufficient time for the arsine production reaction to reach equilibrium.

EXPERIMENTAL METHOD

Reagents

Hydrochloric Acid Solution.--Dilute "Baker Insta-Analyzed," hydrochloric acid, suitable for trace metal analysis, with an equal volume of demineralized water. The use of the "Baker Insta-Analyzed" hydrochloric acid is advised throughout this procedure to insure low arsenic blanks, 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. 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.

Arsenic Stock Solution.--(1000 μg/mL) Dissolve 1.320 g of arsenious oxide (As_2O_3) in a minimal volume of 20% potassium hydroxide. Slowly neutralize with 20% hydrochloric acid. Add 100 mL concentrated hydrochloric acid in excess. Dilute to 1.000 L with demineralized water. The working standards of 10, 30, 50, 100 μg/L are made from serial dilutions of this stock solution with 10% hydrochloric acid. The working standards are stable for at least one week.

APPARATUS

A Perkin-Elmer model 306 atomic absorption spectrophotometer equipped with a Perkin-Elmer model 056 strip chart recorder, a Gibson Minipulse II eight channel peristaltic pump with standard Technicon Tygon pump tubing, and a Technicon Auto-Analyzer II Sampler are used for the semi-automated hydride generation and detection of arsenic. The auto sampler was slightly modified. Instead of using the standard stainless steel probe, a 150 mm by 4 mm (outside diameter) glass tube is used. The sampling arm was drilled out to accept this new probe. This modification is required because of the limited life of the steel probe in 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 described by Maurice Cocchi, Water Resources, U.S. Geological Survey, Denver Central Laboratory (written communication, 1980) The quartz tube is maintained at a constant temperature of 850°C with an applied voltage of approximately 47 volts using a variable power supply. See table 1 for the instrumental parameters.

Table 1.--Instrument Parameters for the Spectrophotometer and Strip Chart Recorder

Wavelength:	193.7 nm or 197.2 nm
Slit:	0.7 nm
Background Correction:	Not used
Damping:	4 (Maximum)
Mode:	Absorbance
Light Source:	Arsenic Electrodeless Discharge lamp
Power:	8 Watts
Strip Chart	10 mv full scale response, 5 mm/min chart speed.

Sample Preparation

Weigh 1.000 g of a -80 mesh sample into a 250 mL Erlenmeyer flask. Slowly add 20 mL nitric, 10 mL sulfuric, 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 by boiling in nitric acid and rinsed with demineralized water.

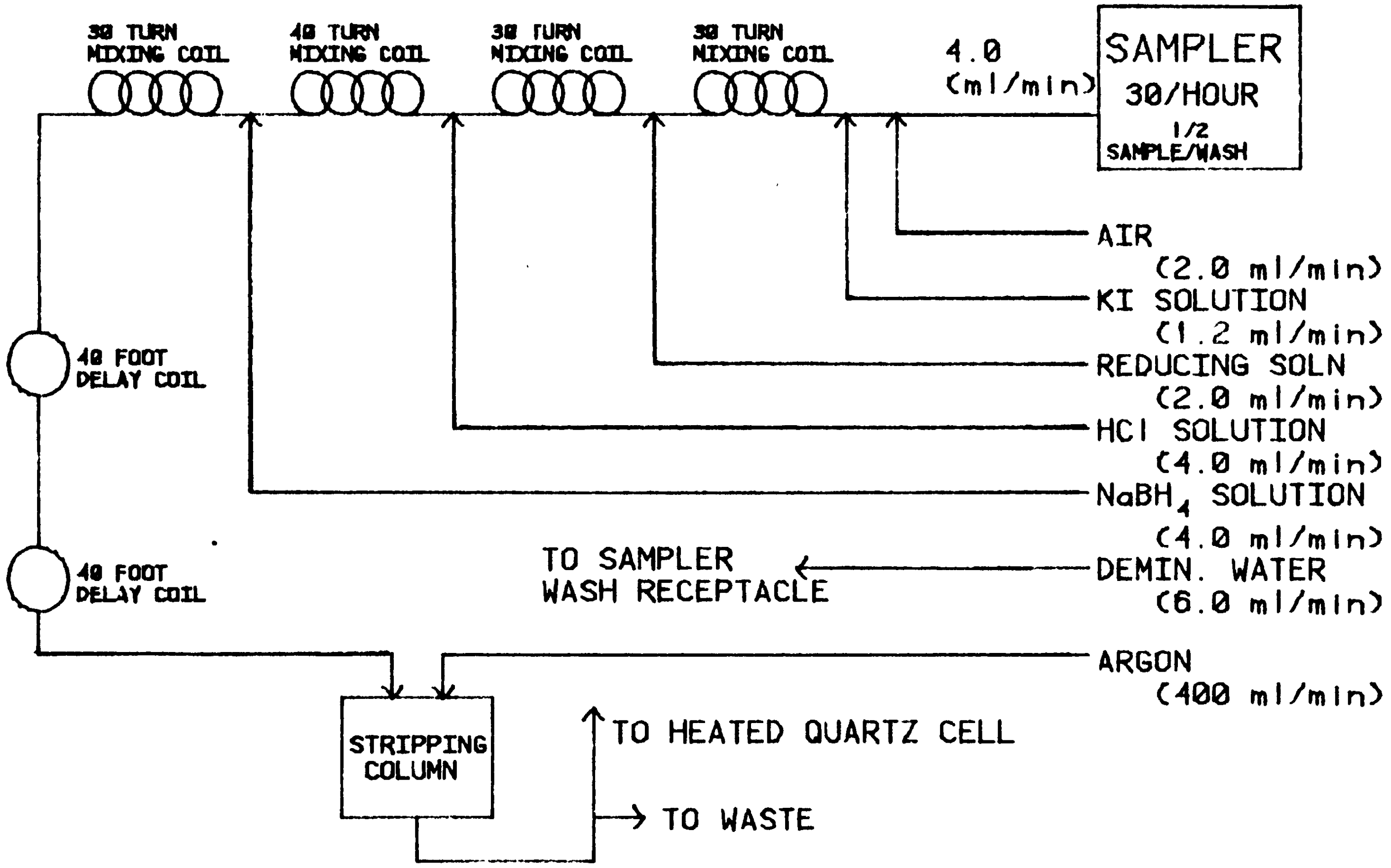
Cover with a watch glass and place on a steam bath overnight. Place the flask on a hotplate and slowly (taking at least 6 hours) bring to fumes of sulfuric acid. Keep the flask covered with its watch glass for the first 2 hours of digestion. Heating to sulfuric acid fumes may take up to 12 hours, especially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

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

PROCEDURE

Set up the arsenic manifold configuration as shown in figure 1. For maximum sensitivity and detection use the 193.7 nm resonance line with an argon-carrier gas flow of 200 mL/min. For routine sample analysis, the 197.2 nm resonance line and an argon flow of 400 mL/min are used. This gives an effective working range of 0.1 part per million (ppm) to 10.0 ppm arsenic in sample. Serial dilutions of the sample with 10% hydrochloric acid, made by using a Lab Industries Repipet diluter, will allow the analysis of arsenic in higher sample concentrations. Standards of 0, 10, 30, 50, 100 μg/L are made by serial dilutions from the arsenic stock solution with 10% hydrochloric acid. For some undetermined reason, the first one or two signals are depressed (Skougstad and others, 1979). Therefore, the highest standard is analyzed four times, followed by the rest of the samples in triplicate or duplicate.

Figure One: Arsenic manifold



RESULTS AND DISCUSSION

Although extensive interference studies have been published on arsine formation (for example, Pierce and Brown, 1976, 1977), the common inorganic species most likely to interfere were tested in this work. Table 2 lists the tested interfering element, the concentration range tested and its effect on the arsenic absorbance signal. Some interferences are noted. These are nickel, tin, selenium, and antimony. When using the given digestion procedure, each mg/L of the interfering element would correspond to 0.01% in sample. Therefore, most interferences are not likely to be a problem for common geologic materials. For example, an interference of approximately 30% on the signal would require that the material have in it 1.0% Ni, 0.2% Sn, 0.5% Se, or 0.1% Sb.

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 its low abundance in nature (3.0 ppm in granites, 10 ppm in soils, and 6 ppm in shales; Rose and others, 1979), tin should not be a significant interferent in common geological materials.

Nickel interference will usually be insignificant because of its low abundance in most geological materials (granites, 5 ppm; shales, 68 ppm; soils 17 ppm; Rose and others, 1979). But nickel may be a problem when analyzing sulfide ores because of nickel's occurrence as pentlandite. In some sulfide bodies, nickel may occur above 1.0%. However, if the sample is a sulfide, it may also be high in arsenic, allowing for dilution of the solution, thereby, minimizing the interferences. If the arsenic is low, the method of a standard additions method will be necessary.

Table 2.--Percent Effect by Common Inorganic Species on the Absorption Signal of a 50 μg/liter Arsenic Solution

Element (All in 10% HCl)	Interfering element concentration (mg/L)/ Percent effect[1] on the arsenic signal / - no data collected					
Fe^{3+}	100/0	500/0	1000/0	5000/0	-	-
Ni^{2+}	1.0/0	5.0/0	10/0	30/0	50/-5	100/-35
Cu^{2+}	10/0	50/0	100/0	300/0	500/0	-
Sn^{2+}	0.5/0	1.0/-16	3.0/-52	5.0/-72	10/-75	-
Se^{6+}	1/0	5/0	10/-6	30/-23	50/-26	-
Sb^{3+}	1/0	5/-25	10/-35	30/-60	50/-60	-
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	-	-	-
$Cr_2O_7^{2-}$	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	-	-	-

$$*\%\text{Effect} = \left[\frac{\text{Peak Height of 50 } \mu\text{g/L As + interfering element}}{\text{Peak height of 50 } \mu\text{g/L As}} - 1\right] \times 100$$

Antimony and selenium interference will also usually be insignificant because of their relative low abundance: granites, 0.2 ppm Sb, 0.2 ppm Se; shales, 1 ppm Sb, 0.6 ppm Se, and soils, 2 ppm Sb, 0.3 ppm Se (Rose and others, 1979). If the samples have elevated concentrations of either or both selenium and antimony, arsenic should also be elevated since they are commonly associated. To minimize this interference, either sample dilution or standard addition must be used.

In all cases the peak shapes for arsenic are similar, but with a smaller peak height when an interfering level of a given element is present. Therefore, standard addition technique using peak height measurement can be used to account for the reduction in signal introduced by these interferences.

The reported interference of the permanganate ion (Pierce and Brown, 1977) was minimized through the addition of the hydrochloric acid, because the permanganate ion is reduced by the chloride ion in an acidic solution. No organic species were tested for interferences because they will be removed in the digestion procedure. Pierce and Brown (1977) also noted an interference by the nitrate ion. The nitrate is volatized as the oxide when taking the solution to strong sulfuric-acid fumes and is therefore not present.

SENSITIVITY, PRECISION, AND ACCURACY

Figure 2 shows the absorbance signal of a 30 μg/L arsenic soluion as a function of argon-carrier gas flow. As the carrier gas flow increases, the arsenic absorbance signal decreases, due mainly to a dilution by the carrier gas.

Figure 3 shows typical tracings for aqueous arsenic solutions using the working sensitivity. The sensitivity of this method using the 193.7 nm resonance line and 200 mL/min argon carrier gas flow is 0.16 μg/L. This sensitivity is a four-fold increase over that given by Thompson and Thomerson (1974). The detection limit is blank-limited at 0.2 μg/L. The detection limit determined from noise-to-background signal is 0.05 μg/L. The 197.2 nm resonance line and an argon-carrier gas flow rate of 400 mL/min are used. Under these conditions, Beers' law is obeyed up to 100 μg/L As. However, the method is inherently sensitive enough so that maximum sensitivity is not required for analysis of most geologic materials. The average abundance of arsenic in soils is 8 ppm, shales 12 ppm, and granites 2 ppm (Rose and others, 1979). Coals will usually occur in a range of 0.5 to 50 ppm (Crock, J. G., unpublished data, 1980). Therefore, working range of 0.5 to 10 ppm in sample was chosen as a good working range for a first investigation of most geological materials.

Figure Two

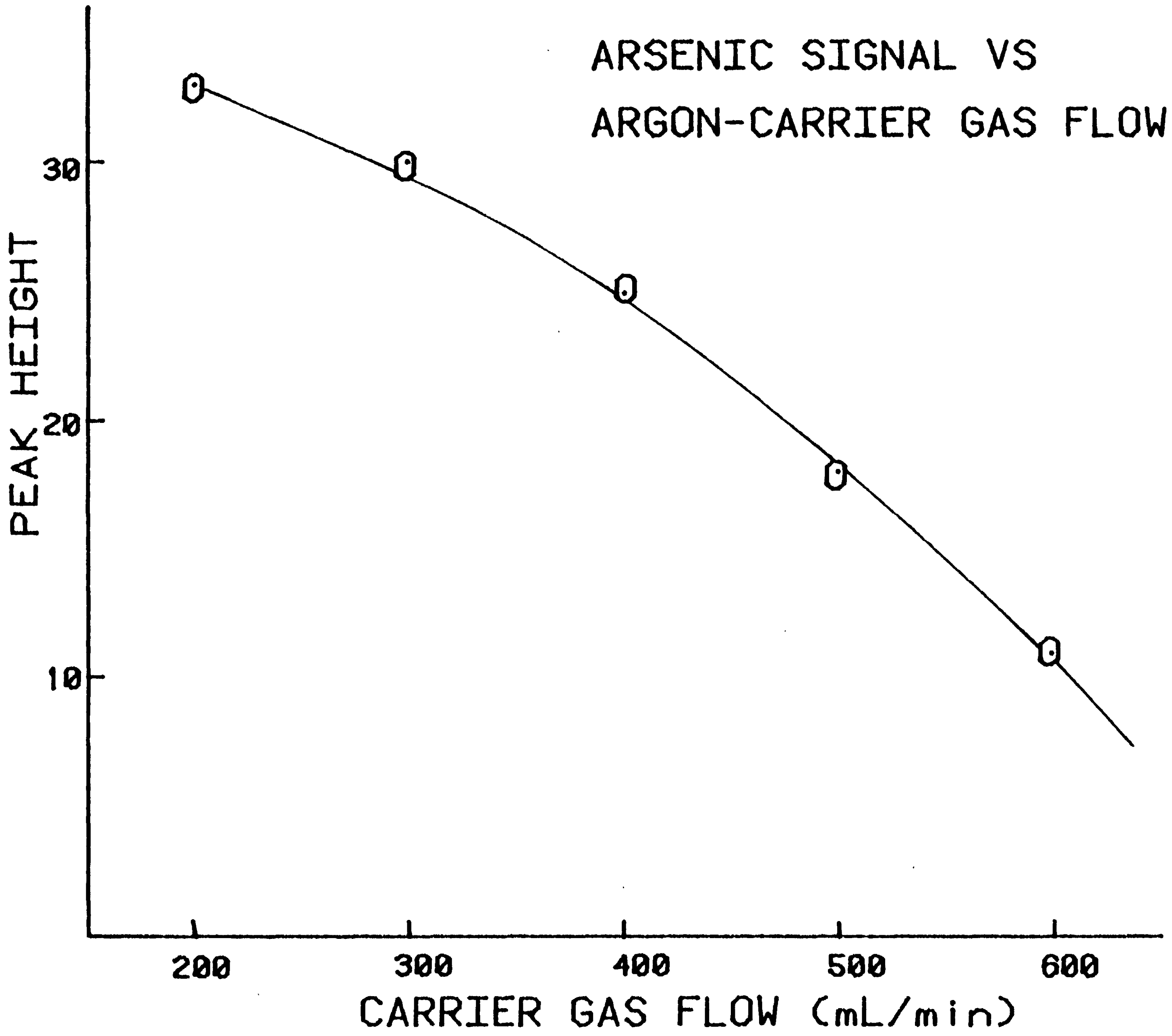
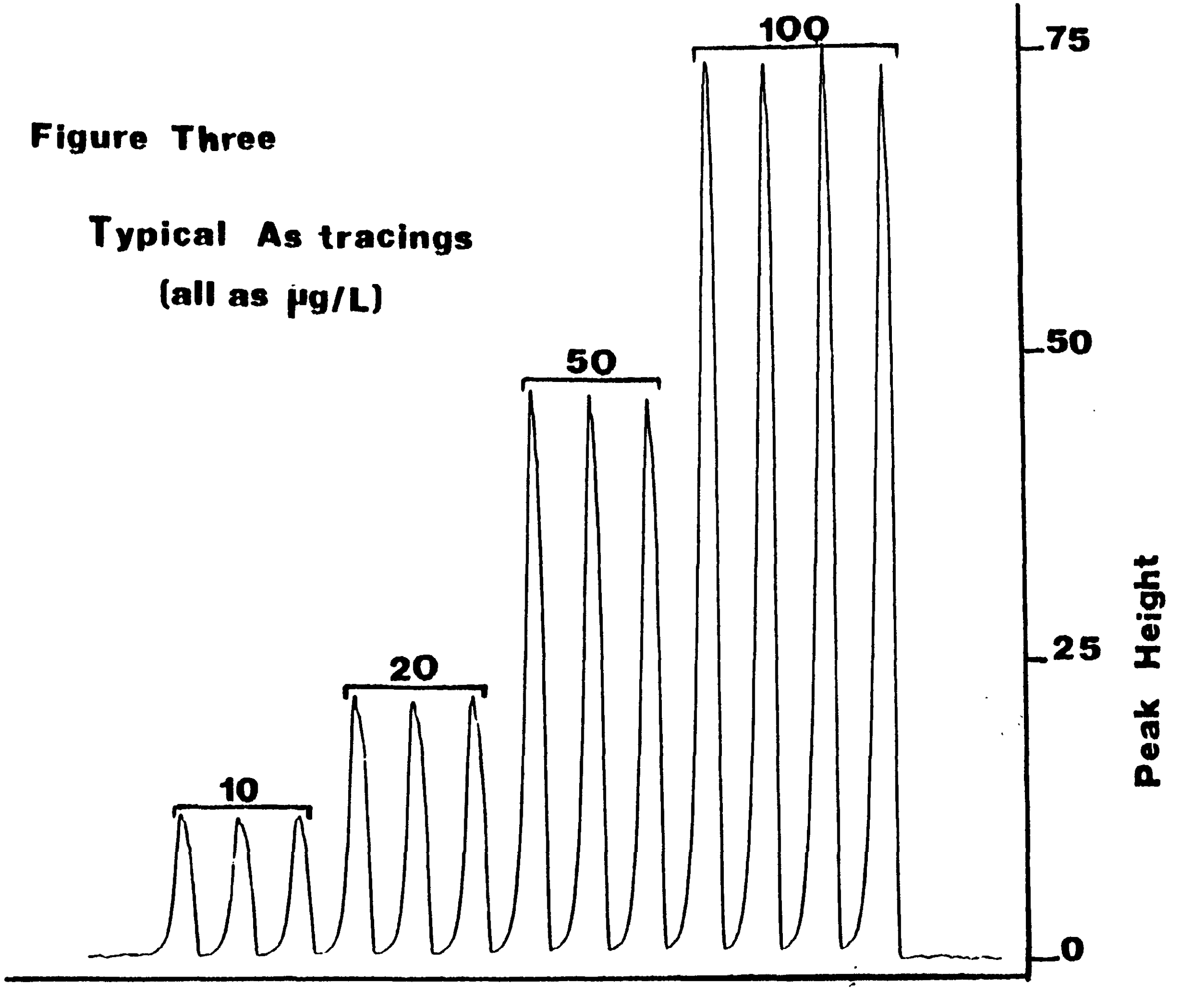

ARSENIC SIGNAL VS
ARGON-CARRIER GAS FLOW
PEAK HEIGHT
30
20
10
200
300
400
500
600
CARRIER GAS FLOW (mL/min)

Figure Three

Typical As tracings (all as µg/L)



To define precision and accuracy, seven 50 µg/L aqueous arsenic solutions, seven 50 µg/L arsenic solutions carried through the digestion, and seven samples of NBS standard coal #1635 spiked prior to digestion with 1 µg arsenic, were each analyzed seven times.

The average relative standard deviation (RSD) for the arsenic aqueous solutions not taken through the digestion procedure was 1.15% and the RSD for the digested aqueous standards was 1.11%. There was complete recovery of arsenic in both the digested 50 µg/L arsenic aqueous solutions and the coal spike. The certified value of NBS #1635 is 0.42 ppm arsenic and 0.4 ppm was determined in all cases. See table 3 for the analysis of some reference materials for arsenic. The low results for SY-2 and SY-3 may be caused by incomplete digestion of the arsenic-bearing phase.

Table 3.--Arsenic Content of Some Standard Reference Materials.

Standard	Arsenic content This Work	 Reported	Source
S01 (soil)	2.3	1.9 ± 0.3	1
S02 (soil)	1.1	1.2 ± 0.2	1
S03 (soil)	3.0	2.6 ± 0.2	1
S04 (soil)	6.6	7.1 ± 0.7	1
NBS 1635	0.4	0.42	2
NBS 1632a (coal)	9.5	9.3 ± 1.0	2
NBS 1633a (coal fly ash)	135	145 ±15	2
NBS Orchard Leaves	9.7	10 ± 2	2
MAG	7.7	<5	3
SGR	61	75	3
RMG-1	0.2	<5	3
SCo-1	11	11 ± 3	3
BHVO-1	0.2	<5	3
AGV-1	0.8	0.8	1
DTS-1	<0.1	0.03	1
MRG-1	0.6	0.7	1
GSP-1	0.2	0.1	1
W-1	1.9	1.9	1
SY2	14	18	1
SY3	14	20	1
PCC-1	<0.1	0.05	1

Source
1) Abby, 1980

2) National Bureau of Standards, Certificate of Analysis for Standard Reference Materials.

3) Fabbi and Espos, 1976.

CONCLUSION

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

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