An Automated Vapor Generation Accessory for Atomic Absorption Analysis

Application Note

Atomic Absorption

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Introduction

Because of its extreme sensitivity for certain elements, the vapor generation technique has been widely applied in many laboratories with atomic absorption instruments and atomic emission instruments.

Early methods for the hydride determinations of arsenic and selenium employed zinc metal, but this has been almost universally replaced by sodium borohydride as the reducing agent for the production of hydride vapor [1]. Elements which can be determined at low levels by the procedure include arsenic, antimony, bismuth, selenium, tellurium and tin [2].

Vapor generation techniques which employ continuous flow technology are becoming increasingly widespread [3–9]. Other automated systems have been reported [10,11]. A variety of sample types have been analyzed including coal [3,12], soils and sediments [3,5,10], biological samples [13–16], waters [17–19] and plant materials [3,6,13,15,20].

Mercury has been measured for many years by the cold vapor method in which stannous chloride is the most commonly employed reducing agent. In the studies described here, sodium borohydride has replaced stannous chloride as the reducing agent thus simplifying the overall procedure [21].

Agilent's new vapor generation accessory features a continuous flow technique in which samples and liquid reagents are pumped and allowed to mix. The gaseous reaction products are swept into an absorption cell (heated by a flame for hydride-forming elements] located in the optical path of the atomic absorption spectrophotometer. The accessory can be readily connected to an Agilent programmable sample changer to provide automatic presentation of up to 67 samples plus up to 5 calibration standards.

Design Features

Figure 1 shows a schematic diagram of the Agilent vapor generation accessory (VGA-76). The peristaltic pump maintains a constant flow of analytical solutions. The actual flow rates are pre-determined by the diameters of the pump tubes. In the study described here, flow rates were about 8 mL per minute for the sample, 1 mL per minute for the sodium borohydride solution, and 1 mL per minute for the acid.

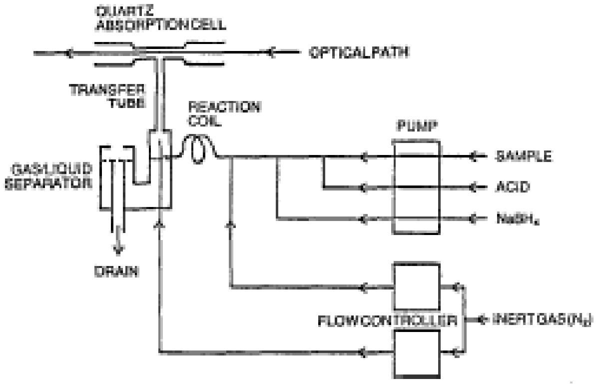


Figure 1. Schematic of vapor generation accessory.

The sample and acid are allowed to merge first before the sodium borohydride enters the stream. Nitrogen is then introduced into the liquid stream and the reaction proceeds while the mixture is flowing through the reaction coil. Vigorous evolution of hydrogen during the reaction assists the stripping of the hydride (or mercury vapor) from the liquid into the nitrogen. The gas is separated from the liquid in the separator shown in Figure 2. At this point, a second stream of nitrogen is introduced to ensure that the gas stream is not saturated with water vapor (Figure 2).

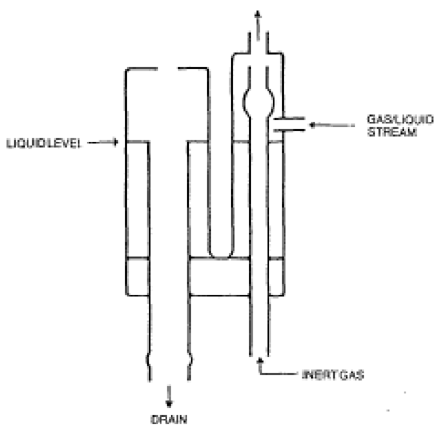


Figure 2. Gas/line separator.

The gas stream passes from the separator into the absorption cell. The short connection tube ensures that vapor is transferred rapidly to the cell from the separator. The absorption cell is located on a standard air-acetylene burner and aligned in the optical path by the burner adjusting mechanism. For the determination of the hydride-forming elements the cell is heated by a lean air-acetylene flame. Mercury is best determined with a cold cell because the analytical sensitivity is reduced when the cell is heated. Improved sensitivity for mercury is obtained by using an optional flow-through cell.

With the VGA-76 system, a continuous atomic absorption signal is produced so that integration methods (signal averaging) can be applied to the absorbance measurement. This is in contrast to earlier vapor generation techniques in which the production of transient signals required peak height or peak area measurements.

Instrumentation

Spectrophotometer	Agilent AA-975*
Sample presentation	Agilent PSC-55 for automated analyses.
Source lamps	Agilent hollow cathode lamps. HP-82905A.
Integration period	3 s
Typical delay time	about 40 s

* The VGA-76 may be fitted to any Agilent AA spectrophotometer.

Reagents and Samples

An important aspect of measurements for arsenic, selenium, antimony and tellurium by the hydride generation technique is the valence state of the element prior to the addition of sodium borohydride. Experimental studies have established practical procedures which ensure that the element of interest is present in the correct oxidation state. That is, As^{III}, Sb^{III}, Se^{IV}, Te^{IV}. Bismuth is found only in the BiIII form, the higher oxidation state being unstable.

Analytical reagent grade acids and distilled water were used for the preparation of all samples and standards. Calibration solutions were prepared by diluting 1 mg/mL B.D.H. stock solutions to provide standards of the following elements:

As^{III}	in 7 M HCl
SbI^{II}	in 7 M HCl
Se^{IV}	in 7 M HCl
Te^{VI}	in 5 M HCl
Bi^{III}	in 5 M HCl
Hg^{II}	in 0.01% $K_2Cr_2O_7$ and 0.8 M HNO_3

A stock solution of As^V was prepared by oxidizing a weighed amount of AR grade As_2O_3 with hot concentrated nitric acid, evaporating excess acid and diluting to volume.

Sn^{IV} was prepared by dissolving a weighed amount of tin in the minimum amount of aqua regia, evaporating excess and diluting in 1 M HCl. A 1000 µg/L stock solution was prepared by diluting 1 mL of 1000 mg/L tin (IV) solution to one litre with 1% tartaric acid. All subsequent dilutions were made with 1% tartaric acid.

Se^{VI} solutions were prepared by dissolving sodium selenate in water, and adding hydrochloric acid to the required level.

Te^{IV} was prepared by dissolving a weighed amount of TeO_2 in concentrated HCl and diluting the volume to 1 M HCl.

Sodium borohydride pellets (Alfa, Ventron) were dissolved in sodium hydroxide solution to provide a stock borohydride solution (0.6% w/v $NaBH_4$; 0.5% w/v NaOH). This solution was stored overnight at 5 °C and remained stable for about one week. For some experiments the sodium borohydride concentration was reduced to 0.3% w/v. A.R. grade potassium iodide was also used for some measurements.

The concentration of impurities was found to be very low in all batches of reagents used in these studies.

Discussion and Results

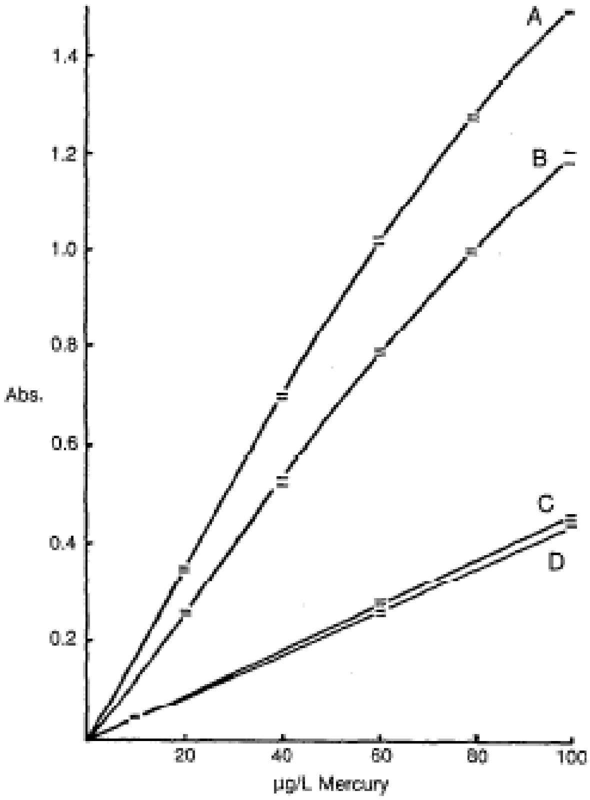
Single-element Determinations

- Before proceeding with the determination of any of these elements it was necessary to condition the apparatus by alternately presenting the highest standard and the analytical blank until consistent results were obtained for the standard.
- Calibration graphs for the elements determined are given in Figures 3 to 9. The error bars on the calibration curves represent the range of 10 measurements.

Mercury

Wavelength	253.7 nm
SBW	0.5 nm
Lamp current	4 mA
Acid channel	5 M HCl
NaBH4 channel	0.3% $NaBH_4$; 0.5% NaOH

The concentration of the added acid made little difference to the response of mercury standards prepared in distilled water. Dilute mercury solutions are unstable, and it was necessary to stabilize all solutions with 0.8 M nitric acid and 0.01% w/v potassium dichromate [22]. As indicated in Figure 3, best results were achieved with the flow-through mercury cell.



Curve	Pumped Acid	$NaBH_4$	Absorption Cell
A	5 M hydrochloric	0.3%	Flow-through
B	"	"	Quartz Atomizer (cold)
C	"	"	" " (hot)
D	"	0.6%	" " "

Figure 3. Calibration curves for mercury.

Acceptable performance was obtained with the "standard" absorption cell operated at room temperature, but the response was significantly reduced when the absorption cell was heated. When the sodium borohydride solution was used at a concentration of 0.6% rather than 0.3%, the absorbance was reduced by about 10%. This is probably due to dilution by excess hydrogen. The analytical response was severely depressed by traces of iodide in the system [23].

A detection limit of 0.1 µg/L has been found with the "standard"absorption cell and 0.05 µg/L with the flow-through cell. Typical characteristic concentration is 0.3 µg/L with the flow through cell.

Arsenic

Wavelength	193.7 nm
SBW	0.2 nm
Lamp current	10 mA

Procedure A

Acid channel	10 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH

Solutions were prepared in 1 M hydrochloric acid, and the analyte was reduced to As^{III} by the action of potassium iodide at a concentration of 1% w/v. Reduction requires about 50 minutes at room temperature or about 4 minutes at 70 °C. When the analyte was retained as As^{V} by omitting the reduction step, the analytical response was only 20% of that obtained for As^{III}. When the solution originally contains As^{III}, the reduction by potassium iodide is not required.

Procedure B

Acid channel	10 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH, 10% KI

The sodium borohydride solution for this procedure included potassium iodide at a concentration of 10% w/v so that reduction could be performed within the VGA-76 instead of using the pre-reduction method. Solutions were prepared in 7 M hydrochloric acid. The acid concentration in the acid channel was left unchanged at 10 M. Under these conditions the response for As^{V} was the same as that for As^{III}. This procedure would therefore provide a convenient solution scheme for practical analyses where other elemental determinations are required.

A calibration graph is shown in Figure 4. Typical characteristic concentration is 0.2 µg/L. The detection limit has been found to be about 0.2 µg/L.

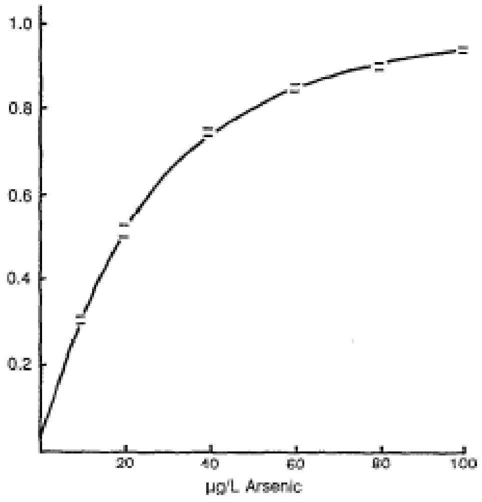


Figure 4. Calibration curve for arsenic. Standards were prepared in 7 M hydrochloric acid (from AsV stock solution). Concentrated hydrochloric acid was pumped in the acid channel, 0.6% $NaBH_4$ + 10% KI + 0.5% NaOH in the sodium borohydride channel.

Antimony

Wavelength	217.6 nm
SBW	0.2 nm
Lamp current	10 mA

Procedure A

Acid channel	10 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH

Sb^{III} solutions were prepared in 1 M hydrochloric acid. Good results were obtained at working concentrations up to 40 µg/L.

Procedure B

Acid channel	10 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH, 10% KI

As in Procedure B for arsenic, the sodium borohydride solution included potassium iodide at a concentration of 10% w/v. Solutions were prepared in 7 M hydrochloric acid. The acid concentration in the acid channel was left unchanged at 10 M. This procedure would provide a convenient solution scheme for practical analyses. A calibration graph is shown in Figure 5. Typical characteristic concentration is 0.15 µg/L.

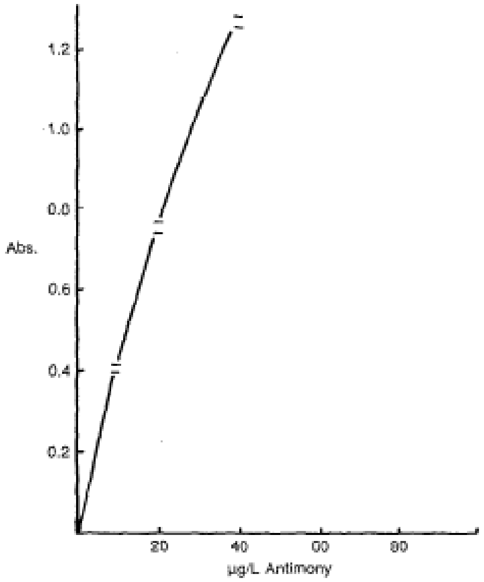


Figure 5. Calibration curve for antimony. (conditions as for arsenic).

Selnium

Wavelength	196.0 nm
SBW	1.0 nm
Lamp current	10 mA
Procedure A	
Acid channel	10 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH

Se^{VI} was quantitatively reduced to Se^{IV} by warming with concentrated hydrochloric acid. In the Se^{IV} oxidation state in 1 M hydrochloric acid, this element showed good analytical response. In the Se^{VI} oxidation state no response was detected.

Procedure B	
Acid channel	10 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH, 10% KI

The sodium borohydride solution for this procedure included potassium iodide at a concentration of 10% w/v. Solutions were prepared in 7 M hydrochloric acid.

The acid concentration in the acid channel was left unchanged at 10 M. The response for Se^{IV} was somewhat lower than that obtained by pre-reduction and preparation in 1 M hydrochloric acid. However, preparation in 7 M hydrochloric acid (including preliminary warming) would provide a convenient solution scheme for practical analyses when determining arsenic and selenium on the same sample.

Calibration curves for selenium are shown in Figure 6. Typical characteristic concentration is 0.3 µg/L. The detection limit was found to be about 0.3 µg/L.

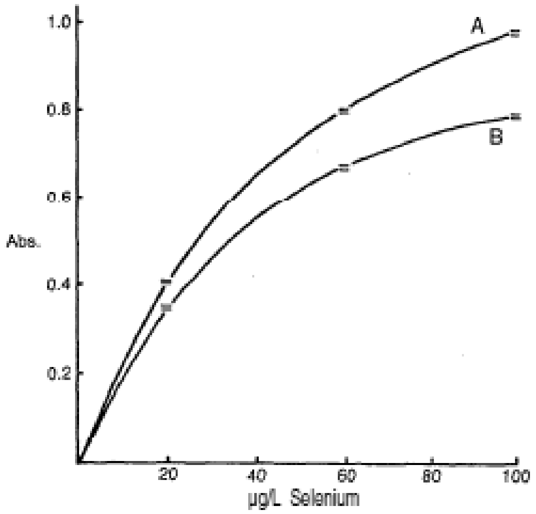


Figure 6. Calibration curves for selenium.
(A) Se^{IV} standards prepared in 7 M hydrochloric acid, concentrated hydrochloric acid pumped in the acid channel, 0.6% $NaBH_4$ in 0.5% NaOH in the sodium borohydride channel.
(B) Conditions as for arsenic.

Tellurium

Wavelength	214.3 nm
SBW	0.2 nm
Lamp current	10 mA
Procedure A	
Acid channel	5 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH

Te^{IV} in 1 M hydrochloric acid gave good results. The Te^{VI} oxidation state gave no response under these conditions. The response for Te^{IV} decreased as the hydrochloric acid concentration increased, either in the sample or in the pumped channel. As with selenium, tellurium may be reduced from the higher oxidation state by warming in 7 M hydrochloric acid. Typical characteristic concentration is 0.15 µg/L. The presence of iodide caused a severe suppression of the analytical response. The calibration shown in Figure 7 was obtained using 0.2 nm SBW and a lamp current of 10 mA; increased curvature was evident at larger spectral band widths.

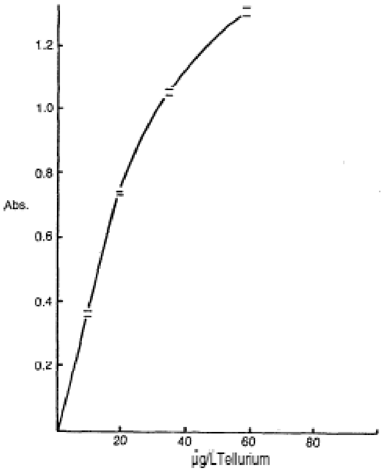


Figure 7. Calibration curve for tellurium. Te^{IV} standards prepared in 1 M HCl, 5 M HCl pumped in the acid channel, 0.6% $NaBH_4$ + 0.5% NaOH pumped in the sodium borohydride channel.

Bismuth

Wavelength	223.1 nm
SBW	0.2 nm
Lamp current	10 mA
Procedure A	
Acid channel	5 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH

Good results were obtained for this element with solutions prepared in 1 M hydrochloric acid as illustrated by Figure 8.

Higher acid concentrations depressed the analytical signal. The presence of iodide caused severe suppression of the analytical response. Typical characteristic concentration is 0.2 µg/L.

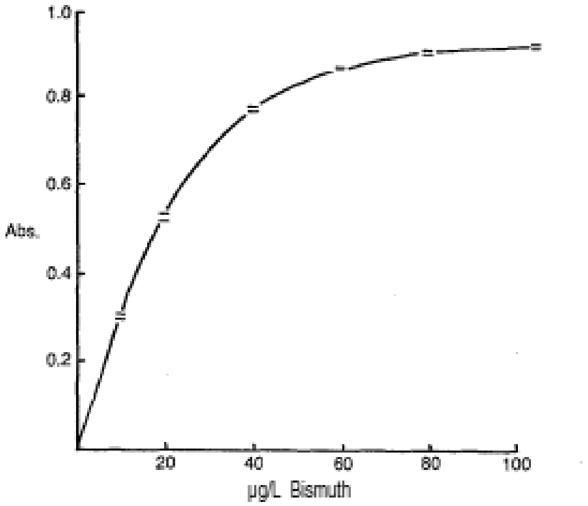


Figure 8. Calibration curve for bismuth. Conditions the same as tellurium.

Tin

Wavelength	286.3 nm
SBW	0.2 nm
Lamp current	7 mA
Procedure A	
Acid channel	5 M HCl
$NaBH_4$ channel	0.6% $NaBH_4$; 0.5% NaOH

Use of the 286.3 nm resonance line was found to be essential for achieving good sensitivity and dynamic range. The non-resonance 235.5 nm line commonly used in flame or furnace AA gave very poor sensitivity and the 224.6 nm line showed little increase in response above 0.3 absorbance units.

Response for tin was found to depend critically on the acid concentration in the samples. Good results were obtained with solutions prepared in 1% tartaric acid. In the preparation of standards all dilutions (from the 1000 mg/L stock down) were made in 1% tartaric acid. When the stock was diluted to an intermediate stage in 1 M hydrochloric acid, the variations in acidity in the final tin solutions gave erroneous results.

A calibration curve is shown in Figure 9. Typical characteristic concentration is 0.4 µg/L.

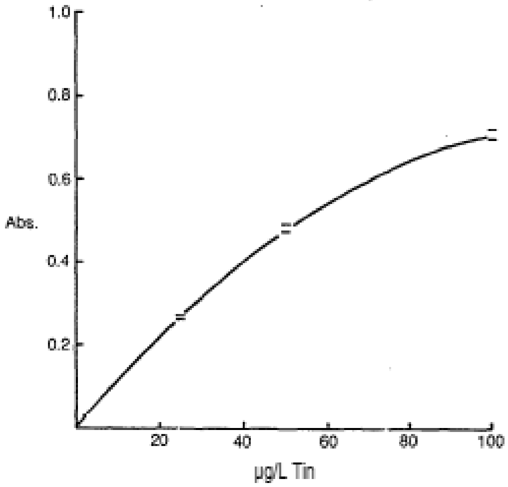


Figure 9. Calibration curve for tin. Samples in 1% tartaric acid, 0.5 M HCl pumped in acid channel, 0.6% $NaBH_4$ + 0.5% NaOH pumped insodium borohydride channel.

Lead

It has been established that to determine lead by vapor generation the pH of the solution must be maintained within a narrow range, certain reagents (such as tartaric acid) are essential, and oxidizing agents such as potassium dichromate or hydrogen peroxide must be used [2,9,17,24]. These procedures were followed for this study.

The study established that the sodium borohydride concentration is critical in obtaining a satisfactory response for lead and it is unlikely that useful analytical signals can be obtained at sodium borohydride concentrations lower than about 5% w/v. Operation of the system at such concentrations causes rapid devitrification of the absorption cell.

The VGA-76 is not recommended for the determination of lead.

A Simplified Analytical Scheme for Sequential Elemental Analysis

While the determination of any one of the hydride forming elements, or mercury, is relatively straightforward, the measurement of a given sample for several elements in an automated mode presents a number of challenges. For example, it is necessary to have the element present in the correct oxidation state prior to the formation of the hydride (or mercury vapor), and some chemical pre-treatment has often been required. The various oxidation states that may be found in real samples and the one preferred or necessary for quantitative analytical measurement are listed in Table 1. An objective of this study has been to devise a suitable scheme whereby a number of elements can be determined in the one solution in order to provide the capability for sequential elemental analysis.

Table 1. Oxidation States

Preferred	Alternates	Successful pre-treatment/comments	References
As^{III}	As^{V}	Reduction with KI — (heating may be required)	2,3,5,19
Sb^{III}	Sb^{V}	Reduction with KI — spontaneous	12,19,25
Bi^{III}	Bi^{V}	Bi^{V} is unstable	19
Se^{IV}	Se^{VI}	Reduction with 6-7 M HCl (heating may be required)	2,4,5,7,2,15,19
Te^{IV}	Te^{VI}	Reduction with 6-7 M HCl (heating may be required)	12,19
Sn^{IV}	Sn^{II}	Maintain correct pH for hydride formation	12,24
Hg^{II}	—	Ensure Hg^{II} is stabilized in solution	22

In order to provide a simple analytical scheme for determinations of As, Sb, Se, Bi and Te, our studies have shown that samples should be prepared in 7 M hydrochloric acid. For mercury determinations the procedure is sufficiently different to require a separate analytical scheme. (Refer to single element determinations.)

1. Bismuth and Tellurium

Use the following procedure:

Pumped channel	Reagents
Acid	Distilled water
$NaBH_4$ solution	0.6% $NaBH_4$ in 0.5% NaOH
Samples	7 M hydrochloric acid

There is a severe suppression effect of iodine/iodide on the determination of bismuth and tellurium, and therefore all glassware and pumping tubes need to be thoroughly clean and free from iodine/iodide for these elements. Bismuth and tellurium would normally be analyzed first, before changing the methodology for arsenic, antimony and selenium.

To remove traces of iodine/iodide, the gas/liquid separator and absorption cell must be removed and washed with dilute sodium hydroxide, then dilute hydrochloric acid and finally distilled water and air dried. Tubing should also be thoroughly washed and dried before attempting to determine any of these elements.

Standards should be prepared in 7 M hydrochloric acid, and may contain all the elements to be analyzed. If the samples are of a complex nature, a standard additions calibration procedure must be adopted.

The VGA-76 should be started and allowed to run for one minute to ensure that the pumping lines have been purged with the reagent solutions. Distilled water is pumped through the sample tube. Before proceeding with each set of analyses, the equipment should be conditioned as described under single element determination.

2. Arsenic, Antimony and Selenium

Use the following procedure:

Pumped channel	Reagents
Acid	Concentrated hydrochloric acid
$NaBH_4$ solution	0.6% $NaBH_4$ in 0.5% NaOH and 10% KI
Samples	7 M hydrochloric acid

The samples are prepared in 7 M hydrochloric acid. A known volume of the sample should be heated at about 70 °C for 30 minutes. This will ensure any Se^{VI} or Te^{VI} present is reduced to Se^{IV} and Te^{IV} respectively. The sample should then be cooled and made up to the correct volume to ensure accuracy of the determination. Allow the VGA-76 to be conditioned in the manner earlier described before proceeding with the analysis.

Standards should be prepared in 7 M hydrochloric acid, and may contain all the elements to be analyzed. If the samples are of a complex nature, a standard additions calibration procedure must be adopted.

The mean results for the analysis of EPA water pollution quality control samples using standards prepared in 7 M hydrochloric acid are given in Table 2. Mercury was analyzed directly in the sample, and the standards were stabilized with 0.01% w/v potassium dichromate in 5% nitric acid.

Table 2. EPA Water Pollution Quality Control Samples

Element	Sample	True value (µg/L)	Found (µg/L)
As	4	22	21
	5	60	55
	6	300	330
Se	4	6	7.2
	5	30	27
	6	50	48
Hg	4	0.75	0.67
	5	3.5	3.5
	6	8.0	7.9

These results confirm the accuracy of the technique. Precision of the VGA-76 (expressed as % RSD) was found to be about 10% at absorbance up to 0.008, 5% up to 0.02 A, 1% or better at 0.1 A.

The sample is consumed at the rate of about 8 mL/minute and the precision is excellent, requiring only about 3 replicate measurements of 3 second integrations. Allowing for a 40 second rinse time initially, the amount of sample consumed per determination is about 7 mL. With a 10 second rinse time between samples, one complete measurement may be carried out in about one minute.

Summary

This paper describes the analytical performance of a new continuous flow device in which the sample and acid solutions are mixed before reacting with the borohydride solution in a reaction coil. The hydride formed is transported by a stream of nitrogen from a gas/liquid phase separator into a quartz absorption cell heated by an air-acetylene flame. Conventional AA measurement follows.

Mercury has been determined (along with the other hydride forming elements) through the sodium borohydride reaction rather than with the more commonly used stannous chloride reduction. Typical working ranges are up to 50–100 µg/L for As, Sb, Bi, Se, Te, Sn, Hg. Detection limits for the important elements arsenic, selenium and mercury are less than 0.5 µg/L. Precision of the measurements is typically in the range 0.5–1.5 %RSD.

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