The Determination of Arsenic in Non-Silicate Geological Ore Samples Using a Vapor Generation Accessory

Application Note

Atomic Absorption

Author

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Introduction

The dissolution of geological samples for analysis has been well covered and many methods using digestion and fusion have been published [1]. This study compares two digestion methods for the determination of arsenic in geological samples. One method uses a nitric acid/hydrochloric acid mixture (referred to here as aqua regia). The other method uses hydrochloric acid/hydrogen peroxide which has been used for a variety of analyses [2].

The digestion methods only work for arsenic not bound up in a silica matrix. A digest incorporating hydrofluoric acid would be required for silica matrices. The simplicity of the digestion methods described here offers potential advantages for the routine laboratory.

Agilent Technologies

Practical

All measurements were performed on an Agilent SpectrAA-40P spectrometer using a Vapor Generation Accessory (VGA-76) and a Programmable Sample Changer (PSC-56). A SpectrAA arsenic hollow cathode lamp was used. All results were printed using an Epson printer. The recommended instrument parameters were used on the spectrometer.

Milled geological samples were provided by a mining company along with an approximate indication of the expected range of arsenic concentration. The particle size was 200 mesh. A standard reference material provided by the National Bureau of Standards (Washington, D.C.), NBS SRM 1633a, was used for comparison and recovery tests.

All reagents used were analytical reagent grade (AR) or equivalent. Distilled water was used for dilutions.

A commercial aqueous stock solution (Spectrosol from BDH Ltd, Poole, England) of 1000 µg As/mL was used to prepare a working stock solution of 10 µg As/mL. Final standard solutions (typically 30, 60 and 90 ng As/mL) were made up daily from the working stock.

All final standard and sample solutions were stabilized by adding solid potassium iodide so that they were effectively 1% (w/v) KI.

Digestions were carried out in a similar manner for both of the digestion solutions.

A portion of milled sample (0.25g) was weighed out accurately into a test tube. The digestion solution (either (a) or (b) as described below) was added and the mixture allowed to stand for an hour. The mixture was then heated in a water bath (90 °C) with occasional shaking for 30 minutes or until no further reaction was observed. After cooling, distilled water (5 mL) was added, and the mixture was filtered through Whatman No.4 filter paper into a 100 mL volumetric flask. The filtrate was made up to the mark with distilled water. The white residue, presumably siliceous material, was discarded.

An appropriate aliquot (typically 1 to 5 mL) of this initial solution was pipette into another 100 mL volumetric flask. Concentrated hydrochloric acid (8 mL) and 10% (w/v) potassium iodide solution (10 mL) added as stabilizer. If the aqua regia mixture had been used, 20% (w/v) hydroxylamine hydrochloride (10 mL) was also added. The solution was then made up to the mark with distilled water.

Digestion Solutions

a. Nitric acid/hydrochloric acid (aqua regia): concentrated nitric acid (5 mL) was added with shaking to the milled sample followed by concentrated hydrochloric acid (2 mL). The mixtures were heated in a water bath until no more brown fumes evolved.

b. Hydrochloric acid/hydrogen peroxide: concentrated hydrochloric acid (5 mL) was added with shaking to the milled sample. Three portions (0.5 mL) of 30% hydrogen peroxide were cautiously added with shaking at 20 minute intervals.

Experimental

Analytical Range of Arsenic

The sensitivity of the vapor generation technique restricts the analytical range to relatively low concentration values of arsenic. There are two options available to measure higher concentrations of arsenic. The first is by appropriate dilution of the initial sample solution above. The second is by selecting one of the two analytical (or resonance) lines of arsenic. Table 1 summarizes the information.

Table 1. Valid Concentration Range, Arsenic

Range (ng/mL)	Wavelength (nm)	Slit (nm)	Current (mA)
0–50	193.7	0.5	10
0–100	197.2	1.0	10

Within these ranges calibration graphs show only slight curvature. (See Figures 1 and 2) Measurements are possible outside these ranges, but this practice is not recommended.

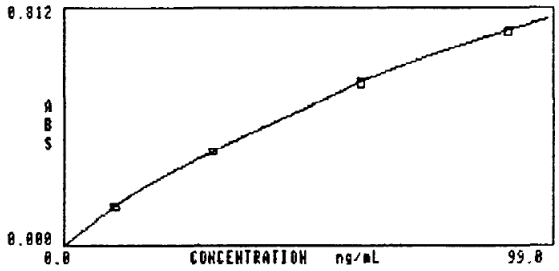

Figure 1. Calibration graph using the 1997.2 nm arsenic analytical line.

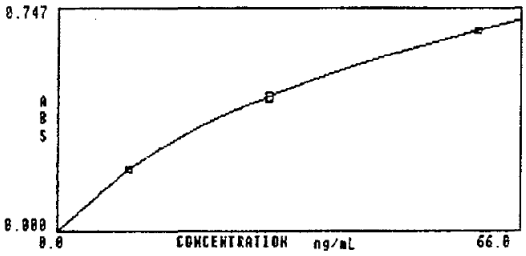

Figure 2. Calibration graph using the 1993.7 nm arsenic analytical line.

Stabilization

The borohydride reduction technique used in vapor generation AA is quantitative for the As(III) oxidation state. Low levels of As(III) are readily oxidized by air to the As(V) oxidation state. All final solutions of standards and samples must be treated with potassium iodide to reduce As(V) to As(III). If the solutions being analyzed are not pre-reduced with potassium iodide, their respective absorbance signals can show significant reductions within an hour. With stabilization, six sets of standards prepared on different days gave signals that varied within 5% of each other. Sample signals showed no significant reductions over a few days. Stabilized solutions darken with time as the iodide ion is oxidized to free iodine.

Recoveries

A recovery study was carried out by adding an aqueous equivalent of the expected arsenic level in the NBS standard during the digestion step. Recoveries ranged between 90% and 107% for both types of digest.

Calculations

Concentrations of the analyte element in solution are typically measured as ng/mL or µg/L, (parts per billion by solution) and usually must be converted to a final answer in µg/g (parts per million by mass) of the original solid.

If,

Initial mass	=	0.25 g
Initial volume	=	100 mL
Aliquot taken	=	V mL (diluted to 100 mL)
Measured concentration	=	C ng/mL

then the solid concentration can be expressed as:

Concentration in the solid (equation (1))	=	$\frac{10000 \times C\ \mu g}{1000 \times 0.25 \times V\ g}$ $(10 \times C)/(0.25 \times V)\ \mu g/g$

Weight/Volume Correction

Calculations involving equation (1) will be complicated by the fact that the mass weighed out will not be exactly 0.25 g and a mass correction factor must be calculated. While volume correction is not as common, its factor can be used to include constants.

The necessary factors for this calculation are defined as shown below:

Mass correction factor	=	$\frac{\text{nominal mass}}{\text{actual mass}}$
Volume correction factor	=	$\frac{\text{actual volume}}{\text{nominal volume}}$

Equation (1) can now be generalized to:

$$\text{Concentration in the solid} = \frac{10 \times C \times \text{mass correction factor}}{0.25 \times V}\ (\mu g/g)$$

$$\text{or,} = \frac{40 \times C \times \text{mass correction factor}}{V}\ (\mu g/g)$$

The value 40/V can be incorporated into a volume correction factor so equation (1) can be finally reduced to:

Solid concentration (µg/g)	=	C × volume correction factor × mass correction factor

where,

Nominal mass	=	0.25 g
Actual mass	=	Recorded mass weighed out
Nominal volume	=	Aliquot used (V mL)
Actual volume	=	40 mL

The SpectrAA Utilities (Version 6) and Report Manager (85-100700-00) contain programs which can automatically make these adjustments.

Results

Calibration

Typical results for each of the two wavelengths are compared in Table 2.

Table 2. Comparison of the Two Wavelengths of AS

As concentration (ng/mL)	Wavelength 193.77(nm)	197.2(nm)
10	0.205 (0.8%)	0.133 (2.7%)
30	0.452 (1.6%)	0.320 (1.0%)
60	0.679 (0.5%)	0.560 (1.8%)
90		0.738 (1.0%)
Measurement time	1 s	
Replicates	3	
% RSD in brackets		

The respective calibration curves are shown in Figures 1 and 2.

Samples

Typical sample values, including the NBS SRM 1633a values are summarized in Table 3. The concentration column has two values. The first column is the concentration (ng/mL) as measured in the final aqueous solution.

The second column is the weight and volume corrected value which yields the original concentration (µg/g) in the solid. The expected values are accurate for the NBS standard reference material only. The sample values were approximate values as determined by the donor company using a different method.

Each sample has two duplicates. The first was determined using the aqua regia digest, the second by the hydrochloric acid/hydrogen peroxide digest.

Discussion

The values obtained for the NBS standard reference material by the two digestion methods are in agreement, and both lie within the expected concentration range.

The expected concentration for the samples was supplied as a rough approximation only, (as the results show). However, the closeness of the NBS result gives confidence in the two methods described.

Table 3. Comparison of Sample Values

Samples	Digest*	Mean abs	%RSD	Measured concentration (ng/mL)	(µg/g)	Expected concentration µg/g
MMC#01	AR	0.021	8.8	1.4	56	–
	HH	0.022	5.1	1.4	55	–
MMC#04	AR	0.059	2.9	4.1	161	–
	HH	0.049	3.1	3.4	135	
MMC#06	AR	0.601	1.2	47.6	1894	~ 2300
	HH	0.613	0.5	49.6	1942	
MMC#07	AR	0.598	0.5	47.3	1867	~ 2300
	HH	0.560	0.3	42.9	1705	
MMC#08	AR	0.465	0.4	32.9	1304	~ 1600
	HH	0.422	0.3	29.1	1139	
MMC#12	AR	0.450	0.7	31.4	1231	~ 1550
	HH	0.362	1.0	25.0	994	
NBS 1633a	AR	0.066	1.5	4.0	159	145 ± 15
	HH	0.066	1.5	4.0	158	
Measurement time	1 s					
Replicates	3					
193.7 nm analytical line used						

*AR = aqua regia. HH = hydrochloric acid/hydrogen peroxide

Conclusion

The aqua regia digest appears to give the more consistent results for these particular samples. It is also a slightly simpler and quicker digest. It does require the use of an additional reagent, hydroxylamine hydrochloride. However the limited shelf life of 30% hydrogen peroxide may also need to be considered.

The use of the 197.2 nm analytical line of arsenic is recommended as it covers a wider analytical range and produces a more linear calibration graph over that range.

Neither digestion method can extract arsenic from within a silica matrix. The dissolution of silicates requires the use of reagents such as hydrofluoric acid. However the simplicity of the method offers advantages for the routine laboratory.

References

1. R. Bock, “A Handbook of Decomposition Methods in Analytical Chemistry”, International Textbook Co., 1979
2. R. M. O’Leary and J. G. Viets, At. Spectrosc, 1986, 7, 4 - 8

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