

Application News

No. A633

Spectrophotometric Analysis

Analysis of Arsenic in High Purity Metallic Copper by Hydride Generation-Atomic Absorption Spectrometry (HG-AAS)

■ Introduction

Copper minerals may contain a certain amount of arsenic components in some cases as a result of the mineral formation process. Although arsenic (As) removal treatment is conducted in the copper (Cu) refining process when necessary, a higher sensitivity analysis method is required to control the As concentration in Cu.

One high-sensitivity As analysis method is hydride generation-atomic absorption spectrometry (HG-AAS), in which gaseous hydrides (hydride vapor) are generated and separated by reaction of target elements such as As and selenium (Se) with hydrogen generated by hydrochloric acid (HCl) and a reductant (sodium borohydride: NaBH₄). As one merit of HG-AAS, this technique offers sensitivity approximately 1,000 times higher than that of conventional flame methods and thus has the advantage of enabling quantitation from around 1 ppb in the measurement solution.

Herein we conducted a quantitative analysis of the trace amount of As contained in pure Cu by the HG method. Although Cu is generally an impediment to generation of hydrides of As, high-sensitivity measurement of As in Cu could be conducted easily by precipitation and separation of Cu in the sample preparation process.

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■ Sample Preparation

Commercially-available high-purity metallic Cu was used as the sample material. Fig. 1 shows the flow of decomposition treatment. To evaluate additional recovery performance, a sample spiked with 5 mL of a 100 ppb As(V) standard solution was also treated.

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Take 0.5 g of the sample in a beaker.  
↓← Add 4 mL of aqua regia and a small amount of water.  
↓← Spike with 5 mL of 100 ppb As(V) standard solution.  
Cover with a watch glass and heat at approximately 120 °C on a hot plate.  
↓  
Continue thermal decomposition until all solid material has been decomposed (approx. 1 h).  
↓  
Allow to cool.  
↓  
Transfer to a container and dilute to a constant volume of 50 mL with pure water.
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Fig. 1 Flowchart of Decomposition Treatment

Next, prereaction of the commercial As standard solution and thermally-decomposed Cu solution was conducted.

Here, 5 mL of the treated Cu solution was taken in a sample tube, 10 mL of concentrated hydrochloric acid, 2.5 mL of a 20 % potassium iodide solution, and 1 mL of a 10 % L-ascorbic acid solution were added as prereaction reagents, and finally the solution was diluted in the flask to 50 mL with pure water.

In prereaction treatment of the Cu solution, a white precipitate (copper (I) iodide) was formed when the solution was allowed to stand for a time after addition of the potassium iodide and L-ascorbic acid solutions. The precipitates were filtered with 5B filter paper, approximately the first 5 mL of the filtrate was discarded, and the remaining filtrate was collected in a sample tube for use as the measurement sample.

■ System Configuration and Measurement Conditions

The instrument used here was a Shimadzu AA-7000F atomic absorption spectrophotometer. An HVG-1 hydride vapor generator was used for hydride generation, and a SARF-16C atomic muffle furnace (electric cell heater) was used as the absorption cell heating method. In comparison with flame heating methods, this combination of instruments offers higher sensitivity and also has excellent stability.

Measurement was carried out by the calibration curve method. Table 1 shows the measurement conditions of AA-7000F.

Table 1 Measurement Conditions

As	
Analysis wavelength	193.7 nm
Slit width	0.7 nm
Lighting mode	BGC-D2
Lamp current	12 mA
Heating temperature	800 °C
Integration time × repetition times	5 s × 5 times
HCl concentration	5 mol/L
NaBH ₄ concentration	0.4 w/v%
Sample delivery rate ^{*1}	5 mL/min (approx.)

*1 Controlled by the rotation speed of the peristaltic pump of the HVG-1.

Measurement Results

Table 2 shows the measurement results of the As standard solution, and Fig. 2 shows the calibration curve. Table 3 shows the measurement results of the samples and the recovery rate in the additional recovery test. As was not detected in the unspiked Cu 0.1 % sample.

The recovery rate of the 1 ppm equivalent concentration (1 ppb in the measured solution) by conversion to the concentration in metallic Cu was 106 %. Fig. 3 shows the peak profiles of the As standard solution and measured samples.

When using the electric cell heater (SARF-16C atomic muffle furnace) as the heating method for the absorption cell of the hydride vapor generator (HVG-1) as shown schematically in Fig. 4, the limit of quantitation (LOQ) for As was 0.12 ppb.

Based on the results described above, analysis of trace amounts of As on the 1 ppm level in pure Cu can be conducted easily by using the hydride generation (HG) method after precipitation of Cu in the sample preparation process.

Table 2 Measurement Results of As Standard Solution

As			
Set concentration (ppb)	Absorbance	%RSD (n=5)	SD (n=5)
0	0.0004	332.52	0.0012
0.5	0.0521	3.92	0.0020
1	0.0992	2.91	0.0029
2	0.1951	1.60	0.0031

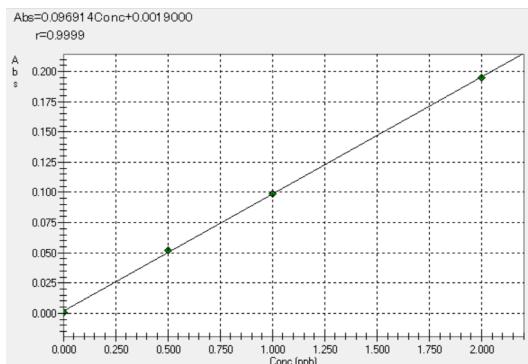


Fig. 2 Calibration Curve of As

Table 3 Measurement Results of Samples

Concentration of measured sample	As	
① Cu 0.1 % (As not spiked)	Measurement value	< 0.12 µg/L (ppb) ^{*1}
	Actual concentration ^{*2}	< 0.12 µg/g (ppm)
② Cu 0.1 % (As spiked)	Measurement value	1.06 µg/L (ppb)
	Actual concentration	1.06 µg/g (ppm)
	Recovery rate	106 %

*1 10x equivalent concentration of standard deviation of absorbance of blank ($10\sigma_{BL}$).

*2 Converted to concentration in metallic Cu.

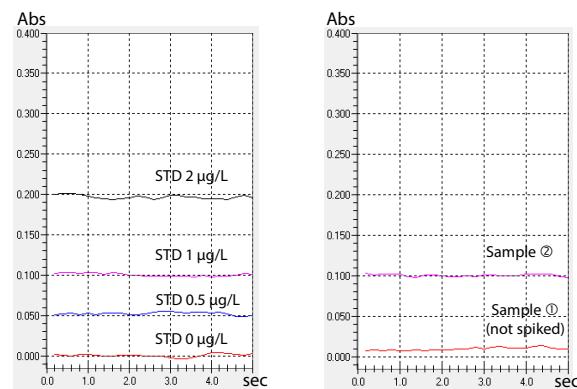


Fig. 3 Peak Profiles of (Left) As Standard Solution and (Right) Measurement Samples

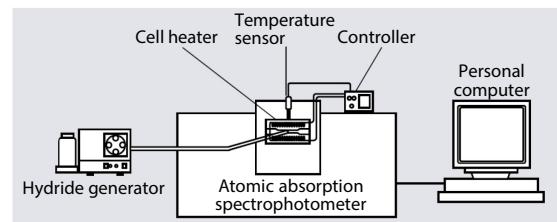


Fig. 4 Configuration of Atomic Absorption Spectrophotometer, Hydride Generator and Electric Cell Heater

Conclusion

The hydride generation-atomic absorption spectrometry method (HG-AAS) using a combination of an atomic absorption spectrophotometer, hydride vapor generator (HVG), and electric cell heater (SARF-16C atomic muffle furnace) has numerous advantages. In addition to high sensitivity and long cell life, acetylene gas and a compressor are not required because the HG-AAS method does not employ a flame. The combination of the hydride generator and electric cell heater introduced here can be used by adding the optional dedicated flame unit (AA-7000F model) or optional dedicated furnace unit (AA-7000G model + GFA: graphite furnace atomizer) to this system configuration. Use as a dedicated system for high sensitivity measurement of hydrides of As and Se is also possible by adding only the G model (without GFA).