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Selenium



Method no.: ID-133SG

Method classification: Partially Validated

Sampling procedure: Collection Medium - 0.8 µm AA cellulose filter

Recommended air volume: 100 liters (minimum)

Sampling rate: 2.0 liters per minute

Summary of analytical procedure: The sample is collected on a 0.8-µm AA cellulose filter. The filters are ashed with concentrated HNO₃, 1000 ppm nickel, and HCl to destroy the organic matrix and dissolve the metal. The samples are diluted using deionized water and the samples and standards are injected into the graphite furnace to determine the sample concentration.

Detection Limit: 0.02 µg/mL

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1. Introduction

1.1. Scope

This method describes the collection and analysis of airborne selenium. It is applicable for both ceiling and time-weighted average (TWA) exposure evaluations. The analysis is based on the utilization of a graphite furnace.

- 1.2. Previous analysis of selenium was by an atomic absorption spectro-photometer (AAS). This method did not take into account the possibility of interfering complexing species such as Ni, Cu, Hg, etc. in order to dissociate these complexing species, it was necessary to develop a method in which a higher temperature, such as with the graphite furnace, was used. This proved to be a very effective and accurate method.

1.3. Uses

Selenium exhibits both photovoltaic action, where light is converted directly into electricity, and photo-conductive action, where the electrical resistance decreases with increased illumination. These properties make selenium useful in the production of photo cells and exposure meters for photographic use, as well as solar cells. Selenium is also able to convert ac electricity to dc and is extensively, used in rectifiers. Below its melting point, selenium is a p-type semiconductor, and is finding many uses in electronic and solid state applications. It is used in zerography for reproducing and copying documents, letters, etc. It is used in the manufacture of pigments, in insecticides, in rubber compounding, to remove the green (iron) tint of glass, to produce pink, ruby, and black glass glaze, to improve the machinability of copper alloys and stainless steel, to improve the grain, structure, and ductility of cast steel, to increase the depth of chill in cast iron, as a flameproofing agent for textiles and wire-cable coverings, and in chemical and ceramic manufacture. Exposures to selenium may result during the smelting and refining of ores containing selenium, in the refining of copper, silver, and gold to remove the selenium, or from the use of selenium compounds.

1.4. Physical and Chemical Properties

Selenium is a non-metallic element of the sulfur group. Selenium exists in several allotropic forms. Three are generally recognized, but as many as six have been claimed. Selenium can be found as either red in powder form, or black in vitreous form. Crystalline monoclinic selenium is a deep red; crystalline hexagonal selenium, the most stable variety, is a metallic gray. Being a member of the sulfur family, it resembles sulfur both in its various forms and in its compounds.

The physical and chemical properties of selenium are listed in Table 1.4.

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Table 1.4
Physical and Chemical Properties of Selenium

	Form I	Form II	Form III
Molecular weight	78.96 g/mole	78.96 g/mole	78.96 g/mole
Molecular formula	Se	Se	Se
color/	bluish-gray	red	red amorphous
crystalline form	met hexagonal	monoclinic prism	black vitreous
specific gravity	4.81	4.50	red 4.26
melting point (°C)	217	170-180	60-80
boiling point (°C)	634.9	634.8	634.8
Solubility (g/100 mL)			
cold water	insoluble	insoluble	insoluble
hot water	insoluble	insoluble	insoluble
H ₂ SO ₄	soluble	soluble	-----
CHCl ₃	soluble	-----	-----
alcohol	insoluble	-----	-----
CS ₂	very slightly soluble	-----	soluble
KMO ₃	-----	soluble	-----
Benzene	-----	-----	soluble

The red amorphous powder turns black upon standing and vitreous upon heating.

2. Range and Detection Limit

A lower analytical limit, 0.02 µg/mL, was selected for routine analysis.

3. Precision and Accuracy

Not determined.

4. Interferences

None known.

5. Sampling Procedure

5.1. The sample is collected on a 0.8-µm AA cellulose membrane filter using a flow rate between 1.5 and 2.0 liters per minute. Suggested minimum air volume is 100 liters. A sample blank should also be submitted. (If considerable loose dust is present in the cassette, a clean filter should be placed over the dust before sealing.)

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- 5.2. The sample cassettes are plugged, sealed with OSHA tape, labeled, and sent to the laboratory for analysis.
- 5.3. No storage problems are normally anticipated. Vibration or jolting of samples should be kept to a minimum to avoid dislodging of dust from the filter.

6. Analytical Procedure

6.1. Apparatus

Atomic absorption spectrophotometer equipped with graphite furnace, argon purge system, and deuterium arc background corrector.

Chart recorder.

Glassware.

AA filters (0.8- μm , cellulose membrane filters 37-mm diam)

2-or 3-piece filter cassettes Personal sampling pump (capable of sampling between 1.0 and 2.0 liters per minute)

6.2. Reagents

HCl, reagent grade

HNO₃, reagent grade

A certified aqueous standard such as "SPEX" 1,000 ppm standard. 1,000 ppm Ni solution, prepared as follows:

Dissolve 5.0 g Ni(NO₃)₂·6H₂O in 100 mL H₂O, add 5 mL KNO₃, dilute to 1 L.

Diluting solution: Twenty AA filters are ashed with 100 mL concentrate MNO₃ and 100 mL of 1,000 ppm Ni solution to a volume of 20 - 40 mL, diluted to 500 mL with deionized water and 2 mL HCl.

6.3. Standards Preparation

Standards are prepared to match the matrix of the samples (filter content acid and nickel concentration) as closely as possible according to the dilution scheme of Table 6.3.1.

The 0.2, 1, 2, 5, 10 and 20 ppm "stock solutions" are made by serial dilution of the 1,000 ppm As stock (with deionized water) as follows in Table 6.3.1.

Table 6.3.1
Stock Solutions

Stock Solution	Standard Solution Used	mL Used	Final Volume
10 ppm	1000 ppm	10 mL	1000 mL
1.0 ppm	10 ppm	100 mL	1000 mL

The diluted stock solutions should be prepared just before using them to prepare the working standards as outlined in Table 6.3.2. When preparing the working standards from the stock solutions, all dilutions are made with the diluting solution.

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Table 6.3.2
 Working Standard Solutions

STD (ppm)	mL Stock Used	Stock Concentration (ppm)	Final Volume
0.02	2	1	100 mL
0.05	5	1	100 mL
0.1	10	1	100 mL
0.2	20	1	100 mL
0.5	5	1	100 mL
1.0	10	10	100 mL
2.0	20	10	100 mL

6.4. Sample Preparation

Note: All glassware must be rinsed with 1:1 HNO₃ and deionized water prior to use. Phillips beakers used for the digestion are refluxed with 1:1 nitric acid and rinsed with deionized water before use. Place filter in 125 mL Phillips beaker, add 5 mL of 1000 ppm Ni solution and 5 µL concentrated HNO₃ and ash to approximately 1-2 mL volume. After sample has cooled, add 2 drops HCl and swirl contents (no additional heating is done). Quantitatively transfer sample to 25 mL volume flask, dilute to volume with deionized water, and mix. Additional dilutions for samples over 2 ppm Se are made with the diluting solution.

6.5. Sample Analysis

The analysis for selenium is performed using a graphite furnace. Instrumental parameters are as follows:

Wavelength = 196.0 nm	Dry	= 90T, 40H, 150F
Slit 4	Char	= 900T, 502, 30H, 100F
Injection volume = 10 µL	Atomize	= 2650T, 0R, 8H, 15F
	Chart	= Range 10
	EDL Power	= 6 1/2 watts
	(STDS prepared same as As)	

The 2.0 ppm standard should give a near full scale deflection using these conditions. The entire series of standards should be run at the beginning and the end of the analysis. A standard should be run after every fourth or fifth sample in the sample range.

6.6. Calculations

A linear regression of standard ppm vs standard peak height is performed using the OSHA Automatic AA program. The sample results are calculated based on sample peak heights; a function of sample absorption.

$$\frac{mg}{m^3} = \frac{(ppm\ Se^*)(sample\ volume)(dilution\ factor)}{(air\ volume, liters)}$$

*blank corrected