

SELENIUM COMPOUNDS (as Se)

Analyte:	Selenium	Method No.:	S190
Matrix:	Air	Range:	0.10-0.50 mg/m ³
OSHA Standard:	0.2 mg/m ³	Precision:	0.090
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	8/29/75
		Revised:	3/25/81

1. Synopsis

- 1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

The sample-containing filters are wet ashed with concentrated nitric acid to destroy the filter matrix followed by dissolution in hydrochloric acid to dissolve the selenium-containing residue. For selenium in steel dust, bulk samples should be tested to verify solubility and final solutions adjusted to contain at least 1% iron.

The solutions of samples and standards are aspirated into the flame of an atomic absorption spectrometer (AAS). An electrodeless discharge lamp is used to provide a characteristic selenium line at 196.0 nm. The absorbance is proportional to the selenium concentration.

2. Working Range, Sensitivity, and Detection Limit

- 2.1 The working range for standard selenium solution using atomic absorption spectrometry as described (argon/hydrogen flame) is 0.5-40 µg/mL; it is 4-64 µg/mL using the air/acetylene flame. This method was validated with potassium selenite aerosol over the range 0.10-0.50 mg/m³ at an atmospheric temperature and pressure of 19 °C and 762 mm Hg using a 360-L sample. The method was also tested with selenium metal fume over the range of 0.3-1.2 mg/m³ using 90-L to 250-L samples. Under the conditions of typical sample size (360 L), the linear working range of the method is estimated to be 0.03-1.4 mg/m³.

The detection limit of this method using the 25 mL final volume is 5.9 µg/sample which corresponds to 0.016 mg/m³ assuming a 360-L sample. The sensitivity is 0.6 µg/mL for 1% absorption. For selenium in steel dusts, the detection limit is 20 µg/mL, and the sensitivity is 1.2 µg/mL for 1% absorption. The method may be extended to higher values by dilution of the

sample. Measurement of lower atmospheric concentrations can be made by using smaller final solution volumes, by longer sampling times or by scale expansion to increase instrumental response.

3. Interferences

There is no known spectral line interference due to other elements. Selenium assay requires an instrument with a background corrector in order to compensate for potential interferences such as those caused by the presence of salts.

4. Precision and Accuracy

The Coefficient of Variation (\overline{CV}_T) for the total analytical sampling method in the range of 0.10–0.50 mg/m³ was 0.090 for potassium selenite, and was 0.093 for 0.16–0.31 mg/m³ selenium fume. This value corresponds to a 0.018 mg/m³ standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

- 4.2 A collection efficiency of effectively 100% for both potassium selenite aerosol and selenium fume was determined for the collection medium; thus, no bias was introduced in the sample collection step. Analytical recoveries less than 95% (Section 4.3) are accounted for by using the appropriate recovery factors (Sections 8.4 and 10.4). With these corrections made, \overline{CV}_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

Analytical recoveries for several selenium species are as follows: selenium metal, 91.8%; sodium selenate, 97.2%; selenium sulfide, 92.6%; selenium dioxide, 92.0%; potassium selenite, 92.3%; and selenium in steel (NBS SRM #339), 90.6%.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of an instrumental method.

Standards must be treated in the same manner as test samples.

6. Apparatus

Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

- 6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37 mm, three-piece cassette filter holder.
- 6.1.2 Personal sampling pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of + 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.
 - Thermometer
 - Manometer.
 - Stopwatch.
- 6.2 Mixed cellulose ester membrane filter, 37-mm in diameter having 0.8 μm pore size.
- 6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 $\text{\AA}/\text{mm}$ in the ultraviolet region. The instrument must have the burner head for an argon-air/hydrogen flame and a background corrector.
 - 6.3.1 Selenium electrodeless discharge lamp.
 - 6.3.2 Oxidant: argon-entrained air.
 - 6.3.3 Fuel: hydrogen.
 - 6.3.4 Pressure regulators: two-stage for each compressed gas cylinder used.
- 6.4 Glassware, borosilicate.
 - 125-mL Phi lips beakers with watchglass covers.
 - 6.4.2 Pipets, delivery or graduated: 1-, 5-, 10-mL and other convenient sizes for making standards.
 - 6.4.3 500-, 250-, 100-, 50-, 25-mL volumetric flasks.
- 6.5 Adjustable, thermostatically-controlled hot plate capable of reaching 140 $^{\circ}\text{C}$.

7. Reagents

- All reagents must be ACS Reagent Grade or better.
- 7.1 Distilled or deionized water.

Concentrated nitric acid.

Concentrated hydrochloric acid.

Aqua regia, 1 volume concentrated nitric acid, 3 volumes concentrated hydrochloric acid.

Aqueous standard selenium stock solution, 1000 $\mu\text{g}/\text{mL}$, commercially available.

Selenium working standard solution, 100 $\mu\text{g}/\text{mL}$. Prepare fresh daily by appropriate dilution of the stock standard solution with 0.1 N nitric acid.

Iron solution, 1%. Dissolve 48.3 g ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in sufficient distilled or deionized water to make 1 L of solution.

8. Procedure

Cleaning of Equipment

- 8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.
- 8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, aqua regia, and then rinsed with tap water and distilled water, in that order, and then dried.
- 8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, aqua regia and water rinses are adequate.

Collection and Shipping of Samples

- 8.2.1 Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.2.2 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

- 8.2.3 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.
- 8.2.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.
- 8.2.5 A sample size of 360-600 L is recommended. Sample at a flow rate of 1.5-2.0 Lpm. The flow rate should be known with an accuracy of $\pm 5\%$.
- 8.2.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.
- 8.2.7 Terminate the sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.
- 8.2.8 Carefully record the sample identity and all relevant sampling data.
- 8.2.9 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.
- 8.2.10 The cassettes in which the samples are collected should be shipped in a suitable container designed to prevent damage in transit.

8.3 Analysis of Samples

- 8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of tweezers and transfer the filter to a 125-mL Phillips beaker.
- 8.3.2 Digestion of samples. Treat the filter in the beaker with 1 mL of concentrated nitric acid. Heat at 140 °C until the filter is just dissolved. Add 1 mL of concentrated hydrochloric acid and continue heating for one minute. Allow to cool.

8.3.3 Quantitatively transfer the flask contents into a 25-mL volumetric flask. Rinse the digestion flask at least twice with distilled water and make to volume with distilled water.

NOTE: For steel dust samples, use 1% iron solution instead of distilled water in this step.

8.3.4 Aspirate the solutions into an argon-air/hydrogen flame and record the absorbance at 196.0 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low selenium concentrations are found in the sample, scale expansion can be used to increase instrument response.

NOTE: The sensitivity in the argon-air/hydrogen flame may be suppressed 90% or more by high concentrations of iron. Therefore, in the case of small amounts of selenium in steel dust samples, use a lean air/acetylene flame.

NOTE: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.5 Appropriate filter blanks must be analyzed by the same procedure used for the samples.

8.4 Determination of Sample Recovery

8.4.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the true value.

8.4.2 Procedure for determining recovery. Use known amounts of the bulk sample for this determination. A known amount of the analyte, present in the bulk sample, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered and analyzed as described in Section 8.3. Determinations should agree within $\pm 5\%$.

For this study, amounts of analytes not exceeding 300 μg were deposited on six filters for each species. A parallel blank filter was also treated in

the same manner except no sample was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value over all species (Section 4.3) was found to be 93%.

$$\text{Recovery} = \frac{\text{Average weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}}$$

9. Calibration and Standardization

9.1 From the selenium working standard solution, prepare at least six standards by adding 10–200 μg Se to separate 125-mL Phillips beakers containing blank filters. Digest these standards by the sample procedure used for samples beginning at Section 8.3.2.

9.1.1 Alternatively, a standard addition calibration procedure may be employed.

9.2 Proceed as in Section 8.3.3.

Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in $\mu\text{g}/25 \text{ mL}$. It is advisable to run a set of standards both before and after the analysis of a series of samples to ensure that conditions have not changed.

10. Calculations

10.1 Read the weight in μg corresponding to the total absorbance from the standard curve. No volume corrections are needed because the standard curve is based on $\mu\text{g}/25 \text{ mL}$.

Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where: $\mu\text{g sample} = \mu\text{g found in sample filter.}$
 $\mu\text{g blank} = \mu\text{g found in blank filter.}$

Divide the total weight by the recovery to obtain the corrected $\mu\text{g}/\text{sample}$.

$$\text{Corrected } \mu\text{g}/\text{sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

Determine the volume of air sampled at ambient conditions in liters based on the appropriate information such as flow rate in Lpm multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is as follows:

$$\text{Corrected Volume} = f \times t \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{1/2}$$

where: f = flow rate sampled.
t = sampling time.
P₁ = pressure during calibration of sampling pump (mm Hg).
P₂ = pressure of air sampled (mm Hg).
T₁ = temperature during calibration of sampling pump (°K)
T₂ = temperature of air sampled (°K).

The concentration of the analyte in the air sampled can be expressed in mg/m³ (μg/L = mg/m³).

$$\text{mg/m}^3 = \frac{\text{Corrected } \mu\text{g (Section 10.3)}}{\text{Air volume sampled (L)}}$$

11. References

Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Heavy Metal Aerosols: Collection and Dissolution Efficiencies, NIOSH Contract 210-79-0058, W. F. Gutknect, M. D. Ranade, P. M. Grohse, A. Damle, D. O'Neal, Research Triangle Institute, Research Triangle Park, North Carolina 27709, March, 1981.