

## Determination of Selenium in Air

### 1. INTRODUCTION

Selenium is an air pollutant that has been generally overlooked in spite of the fact that its distribution is widespread. It is significant that selenium is considered to be an essential trace element as well as a toxin and possible carcinogen. Unfortunately, most data available on the distribution and amount of selenium present in the atmosphere are misleading because of erroneous sampling methods used. Because selenium in the air probably exists as  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_3$ , it is important that the volatility of these species are kept in mind. These, and most other selenium compounds, are so volatile that filtration by means of high-volume samplers cannot be used because the selenium is vaporized as fast as it is collected. Sampling should be done by impingement into water or an aqueous solution of  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}$  or  $\text{NaOH}$ . If the one of the latter is used, care must be taken to assure that there is no appreciable amount of selenium in the chemicals used for preparing the trapping solution.

Selenium can be determined by neutron activation (11.1), atomic absorption (11.2), gas chromatography, spectrophotometry (11.3), fluorimetry (11.4, 5), ring oven technique (11.6), or by catalytic methods (11.7). Atomic absorption and gas chromatography hold promise. Fluorometric and spectrophotometric methods, based on the reaction of selenium with 1, 2-diamino compounds to form selenoles, are sensitive and selective but require meticulous technique. The synthesis of selenoles is the basis of the ring oven method and thus may be used for field studies.

The catalytic method, based on the catalysis of the sulfide reduction of methylene blue, is very sensitive and selective. It is rapid, uncomplicated and accurate.

### 2. SCOPE AND FIELD OF APPLICATION

The method can be used for any air samples for which a sensitive, rapid and simple determination is required. It measures total selenium regardless of oxidation state. It works satisfactorily in the range of 0.1 to  $1.0\mu\text{g}$  of selenium. When present in excess of  $10\mu\text{g}$ , copper interferes seriously; however, this interference, can be eliminated as described in Section 10, Special Case.

### 3. PRINCIPLE

The determination is based on the catalytic effect of selenium in the reduction of methylene blue by sodium sulfide (11.8). Any deleterious

effect caused by polysulfide is readily overcome by the addition of sodium sulfite to form thiosulfate which, like sodium sulfite, has no interfering actions on the reduction of methylene blue. Formaldehyde is added to stabilize the blank. EDTA is used as a general masking agent for metal ions, and iron (III) has an inducing effect on the reaction. Triethanolamine is included because of its stabilizing effect on the blank, particularly in the presence of large concentrations of iron, perhaps by maintaining the higher oxidation state of iron.

#### 4. REACTIONS

The decoloration of methylene blue by excess alkali sulfides is shown by the following equation:

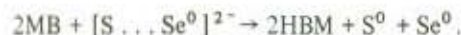


where MB represents methylene blue and HBM represents the leuco form of methylene blue.

The free sulfur is dissolved by formation of polysulfide:



When selenium is present, it is dissolved by alkali sulfides to form selenosulfides,  $[\text{S} \dots \text{Se}^0]^{2-}$ , which react with methylene blue according to the equation:



The elemental sulfur and selenium formed are redissolved by the excess of sodium sulfide with the formation of polysulfides or selenosulfides.

#### 5. REAGENTS

##### 5.1 *Stock selenium solution*

Dissolve 50mg of pure selenium metal in a minimum amount of concentrated nitric acid; boil gently to expel brown fumes and make up to 100ml with distilled water. This solution contains 0.5mg/ml of selenium. Standard working solutions are prepared by appropriate dilutions.

##### 5.2 *Alkaline sodium sulfide solution*

Dissolve 2.4g of sodium sulfide, 2.4g of sodium sulfite and 4g of sodium hydroxide in 100ml of distilled water. This solution is stable for 2 days.

### 5.3 *Conditioner solution*

Prepare 1 litre of solution containing 25g of the disodium EDTA, 0.4g of ferric chloride, and 50ml of triethanolamine; dilute to the mark with distilled water.

### 5.4 *Methylene blue solution*

Prepare a 0.05% solution in distilled water.

### 5.5 *Formaldehyde solution*

Use reagent grade (assay 36-38%).

## 6. APPARATUS

### 6.1 *Absorber*

A standard all-glass, impinger, multi-jet or fritted bubbler may be used.

### 6.2 *Air pump*

It should be capable of maintaining an air pressure differential greater than 0.5 atmosphere at the desired flow rate.

### 6.3 *Air flowmeter*

This metering device should be capable of controlling and measuring flows with an accuracy of  $\pm 2\%$ .

## 7. SAMPLING

Use a glass bubbler containing 10ml of distilled water as the trapping solution. Keeping the flow rate constant, collect approximately 30 liters of sample. Measuring the time accurately, record the actual volume of air by multiplying the flow rate by the time in minutes.

## 8. PROCEDURE

Use a ml sample or an aliquot containing 0.1 to 1.0 $\mu$ g of selenium diluted to 10ml with distilled water. Transfer this solution to a test tube and add 5ml of conditioner solution, 5ml of formaldehyde solution, and 1ml of alkaline

sulfide solution. Mix the contents of the tube well after each addition. Add 2 drops of methylene blue solution and shake briefly to ensure complete mixing. By using a stop watch, measure the time required for complete decolorization of the methylene blue. Obtain the amount of selenium present from the calibration curve. To prepare blank solutions, substitute distilled water for the sample or solutions containing selenium.

## 9. CALIBRATION CURVE

From the stock selenium solution, prepare solutions containing 0.2, 0.4, 0.6, 0.8 and 1.0 $\mu$ g of selenium. Carry out the instructions in Section 9, Procedure. Plot the reciprocal of time ( $\text{min}^{-1}$ ) versus micrograms of selenium. A linear curve is obtained.

## 10. SPECIAL CASE

If more than 10 $\mu$ g of copper are present, interference is observed. This can be eliminated by separating the copper from the selenium, by passing the solution through a 10cm column prepared by filling a 25ml buret with Dowex 50 W-X2, 50 to 100 mesh, cation exchange resin. The flow rate should be 0.5ml/min.

## 11. REFERENCES

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