Analyte:	Tellurium Hexafluoride	Method No.:	S187
Matrix:	Air	Range:	0.094-0.37 mg/cu m
OSHA Standard:	0.02 ppm (0.2 mg/cu m)	Precision ($\overline{CV}_T$):	0.054
Procedure:	Adsorption on charcoal, desorption with 0.01 N sodium hydroxide, atomic absorption	Validation Date:	8/29/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the tellurium hexafluoride vapors present; a filter is placed before the charcoal tube to trap the particulate tellurium compounds.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 0.01 N sodium hydroxide.

1.3 The desorbed sample is analyzed by atomic absorption spectroscopy using an air-acetylene flame and a tellurium electrodeless discharge lamp.

1.4 The area of the resulting absorption peak at 214.3 nm is determined and compared with areas of absorption peaks obtained from injection of standards.

1.5 In order to minimize errors due to variations in flame response, the samples must be carefully interspersed between calibration standards which give about the same response as the samples.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.094-0.373 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 390-liter sample. Under the conditions of sample size (390 liters), the probable useful range of this method is 0.04-0.6 mg/cu m. This method is capable of measuring smaller amounts if the desorption efficiency is adequate and by using scale expansion to increase instrumental response.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the

air. The first section of the charcoal tube was found to hold at least 0.29 mg of analyte when a test atmosphere containing 0.63 mg/cu m of analyte in air was sampled at 1.1 liters per minute for 420 minues; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, tellurium hexafluoride vapors may not be trapped efficiently.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 Other tellurium compounds which exist as vapors will interfere with the analysis. It is expected that interference from particulate tellurium compounds may be eliminated by putting a filter cassette before the charcoal tube.

3.4 Zinc, which has a absorption line at 213.9 nm, could be a potential interfering element.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.094-0.373 mg/cu m was 0.054. This value corresponds to a 0.011 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 100% was determined for the collection medium; thus no bias was introduced in the sample collection step. Likewise, any bias due to analytical method recovery has been accounted for by the use of the desorption efficiency factor. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal; other than zinc, there are no known spectral line interferences for the tellurium assay. The tubes are analyzed by means of an instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A personal sampling pump calibrated with a representative filter and charcoal tube in line and whose flow can be determined within +5% at the recommended flow rate. (Reference 11.2)

6.2 Charcoal tubes: glass tube with both ends flame-sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tellurium electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: purified acetylene.

6.3.4 Pressure regulators, two-stage, for each compressed gas tank used.

6.4 Volumetric flasks: 10-ml and other convenient sizes for making standards.

6.5 Pipets: Assorted sizes for making standards.

6.6 Assorted glassware.

7. Reagents

All chemicals must be ACS reagent grade or better.

7.1 Tellurium hexafluoride, gas for determining desorption efficiency.

7.2 Sodium hydroxide, 0.01 N.

7.3 Distilled water.

7.4 Tellurium standards

7.4.1 Tellurium standard stock solution, 1000 ppm. Stock solutions may be purchased from reliable suppliers.

7.4.2 Dilute tellurium stock solution (20 µg/ml). Dilute 2.0 ml of the 1000 ppm standard to 100 ml with 0.01 N sodium hydroxide. Prepare fresh daily.

7.4.3 Working standards. Prepare by diluting 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the dilute tellurium stock solution (Section 7.4.2) to 10 ml with 0.01 N sodium hydroxide. These solutions contain 10, 20, 40, 60, 80 and 100 µg/10 ml as tellurium. Multiply by 1.893 to obtain tellurium hexafluoride equivalent.

8. Procedure

8.1 Cleaning of Equipment. All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is cleaned with hot, concentrated nitric acid and thoroughly rinsed with tap water followed by distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter and charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 Connect a filter cassette holder to the front section of the charcoal tube to separate particulate tellurium compounds.

8.3.3 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.4 The charcoal tube should be placed in a vertical position during sampling to minimize channeling through the charcoal.

8.3.5 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.6 A sample size of 400 liters is recommended. Sample at a rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.7 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.8 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.9 One tube for every 10 samples submitted should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.10 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize the tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 10-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to a second 10-ml stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of samples. Prior to analysis, 10.0 ml of sodium hydroxide is pipetted into each sample container. Desorption should be done for 60 minutes. Tests indicate that this desorption period is adequate provided the samples are occasionally agitated by manual shaking during that period.

8.4.3 Spectrometric measurements. Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 214.3 nm. The sample concentration is proportional to the measured absorbance. Use scale expansion when necessary for low sample concentrations. Follow instrument manufacturer's recommendations for specific operating parameters.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. A standard charcoal tube from the same batch as that used for the samples should be used. Break both ends of the tube and using a gas-tight syringe slowly add known aliquots of tellurium hexafluoride gas to the front 100 mg section of the tube. Remove the 50-mg backup section immediately after spiking and analyze this backup section to test for completeness of addition to the front section. There should be no tellurium hexafluoride in the backup section. The amount of analyte to be added is equivalent to that present in a 400-liter sample at 0.5, 1 and 2X OSHA standard level. A gas mixture of tellurium hexafluoride in air at 1:5 dilution (20%) can be used by adding 20, 40 and 80 µl aliquots to the charcoal tube.

The desorption efficiency should be determined at least in duplicate for each of these three test levels. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.5 to correct for adsorption losses.

9. Calibration and Standards

9.1 Prepare a series of working standards containing 10-100 µg of tellurium in 10 ml of 0.01 N sodium hydroxide. These standards should be prepared fresh each day. Refer to Section 7.4.

9.2 To determine the response factor, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbance readings during any given day.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance of the sample by using the appropriate response factor determined from the response of the calibration standard.

10.2 Convert micrograms tellurium to micrograms tellurium hexafluoride using molecular weight ratio, 241.59/127.6 = 1.893.

10.3 Corrections for the blank must be made for each sample.

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

where:

μg sample = μg found in front section of sample tube
μg blank = μg found in front section of blank tube

10.4 Add the amount present in the front and backup sections of the sample tube to determine the total weight in the sample.

10.5 Divide the total weight in μg found by the desorption efficiency as discussed in Section 8.5.

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to μg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.5)}}{\text{Air Volume Sampled (Liters)}}$$

10.7 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

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

11.2 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.