Titanium Dioxide

Analyte: Titanium Dioxide		Method No.: S385
Matrix: Air		Range: 8.1-29.5 mg/cu m
OSHA Standard: 15 mg/cu m		Precision ($\overline{CV}_T$): 0.112
Procedure: Filter collection Acid digestion Atomic absorption		Validation Date: 10/24/75

1. Principle of the Method

1.1 Sample-containing filters are wet-ashed using nitric acid to destroy the organic matrix.

1.2 The titanium dioxide is solubilized by further heating with sulfuric acid and ammonium sulfate.

1.3 The solutions of samples and standards are aspirated into the nitrous oxide-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for titanium is used to provide a characteristic titanium line at 364.3 nm. The absorbance is proportional to the titanium concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 8.1-29.5 mg/cu m at an atmospheric temperature and pressure of 23°C and 767 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters), the linear working range of the method is estimated to be 2-30 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

Ammonium fluoride strongly enhances the titanium absorbance (Reference 11.4). If fluorides are known to be present, an excess of ammonium fluoride should be deliberately added to the sample solutions and standard solutions.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.1-29.5 mg/cu m was 0.112 This value corresponds to a 1.7 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 11.3.

4.2 A collection efficiency of 100% was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was also no bias in the analytical method—the average recovery from the filters was 97%. 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

The method is simple.

6. Apparatus

6.1 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 3-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 filter holder and filter in the line.

6.1.3 Thermometer

6.1.4 Manometer

6.1.5 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

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 have the burner head for a nitrous oxide-acetylene flame.

6.3.1 Titanium hollow cathode lamp

6.3.2 Nitrous oxide

6.3.3 Fuel: purified acetylene

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

6.4 Glassware, borosilicate: Use glassware only if fluorides are absent.

  6.4.1 125-ml Phillips 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 50-ml volumetric flasks

6.5 Adjustable thermostatically-controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Nitric acid, 0.1N

7.4 Concentrated sulfuric acid

7.5 Sulfuric acid/ammonium sulfate mixture. Dissolve 40 g of ammonium sulfate in 100 ml of sulfuric acid.

7.6 Aqueous standard titanium stock solution, 500 µg/ml as titanium. Dissolve 0.4170 g of dried, analytical reagent grade titanium dioxide in 25 ml of the sulfuric acid/ammonium sulfate mixture. Dilute to 500 ml with water in a volumetric flask. A commercially available titanium stock solution (1000 µg/ml) may also be used.

8. Procedure

8.1 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, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect titanium dioxide dust, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.2 Blank. 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 for the samples except that no air is drawn through it. Label this as a blank.

8.2.3 Shipping. The filter cassettes 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 Millipore filter tweezers and transfer filter to a 125-ml Phillips beaker. Rinse the inner portion of the cassette holder with distilled water and transfer rinsings to Phillips beaker.

NOTE: If the outer surface of the cassette filter holder is heavily coated with dust, carefully swab the outer surface with moistened paper towel before opening the cassette so as to minimize sample contamination. Discard the paper towel.

8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 3 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and the volume is reduced to about one-half milliliter. Repeat this process once more using 3 ml of concentrated nitric acid. Do not allow the solution to evaporate to dryness. Cool solution.

8.3.3 Titanium dioxide dissolution. To ensure complete dissolution of titanium dioxide, add 8 ml of the sulfuric acid/ammonium sulfate mixture and continue heating on a high temperature hot plate (400°C) until all the remaining solids completely dissolve. This heating cycle will require approximately 60 minutes. To avoid "bumping" during the dissolution process, add a couple of glass beads. Do not allow the solution to evaporate to dryness at any point. If fluorides are present, some loss of titanium due to formation of titanium tetrafluoride may occur.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 50-ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 5 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute to volume.

NOTE: If fluorides are known to be present, add 5 ml of 1N ammonium fluoride before diluting to volume.

8.3.7 Aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 364.3 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.6 than is necessary to effect a quantitative transfer.

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

8.3.8 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. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then recovered from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within +5%.

For this validation study, an amount of the analyte equivalent to that present in a 100-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly by adding weighed amounts of titanium dioxide. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.3. The average recovery value obtained was found to be 97%.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) Recovered}}{\text{Weight (mg) Added}}$$

9. Calibration and Standards

9.1 From the standard titanium stock solution, prepare at least six working standards to cover the titanium concentration range from 0.2 to 3.0 mg/ml. Add 8 ml of the sulfuric acid/ammonium sulfate mixture to each of these working standard solutions and dilute to 50 ml with 0.1N nitric acid. Prepare these working standards fresh daily.

9.2 Proceed as in Section 8.3.7.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in mg/50 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 mg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 50 ml. Note that the data will be in mg of titanium. Convert to titanium dioxide by multiplying with the molecular weight ratio, 79.89/47.9 = 1.667.

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

mg = mg sample - mg blank

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the recovery to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.4 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1971.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

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

11.4 Bond, A.M. "Use of Ammonium Fluoride in Determination of Zirconium and Other Elements by Atomic Absorption Spectrometry in the Nitrous Oxide-Acetylene Flame", Anal. Chem. 42, 932 (1970).