

Rhodium, Metal Fume and Dust

Analyte:	Rhodium	Method No.:	S188
Matrix:	Air	Range:	0.057-0.21 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision (\overline{CV}_T):	0.079
Procedure:	Filter collection, Acid digestion, Atomic absorption,	Validation Date:	8/29/75

1. Principle of the Method

- 1.1 Sample-containing filters are wet-washed using nitric acid to destroy the organic matrix; rhodium and its compounds are then solubilized in a hydrochloric acid solution maintained at a pH of 1; potassium bisulfate is added to eliminate interferences by other common cations.
- 1.2 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrophotometer. A hollow cathode lamp for rhodium is used to provide a characteristic rhodium line at 343.5 nm. The absorbance is proportional to the rhodium concentration within a limited concentration range.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.057-0.21 mg/cu m at an atmospheric temperature and pressure of 24°C and 756 mm Hg, using a 720-liter sample. Under the conditions of sample size (720 liters), the linear working range of the method is estimated to be 0.005-0.21 mg/cu m.
- 2.2 The method may be extended to higher values by further dilution of the sample solution.

3. Interferences

Addition of 3% potassium bisulfate eliminates the interferences of other common cations, and also anions like nitrates and phosphates in the rhodium assay using an oxidizing air-acetylene flame (Reference 11.4).

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (\overline{CV}_T) for the total analytical and sampling method in the range of 0.057-0.21 mg/cu m was 0.079. This value corresponds to a 0.0079 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 1.00 ± 0.01 was determined for the collection medium; thus, no bias was introduced in the sample collection step. There may be some bias in the analytical method--the average recovery from the filters was 94.7%; the data may be adjusted by this correction factor to eliminate any bias. Thus, 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 $\pm 5\%$ 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 ultra-violet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Rhodium hollow cathode 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 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25-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 Hydrochloric acid, 6N

7.4 Potassium bisulfate, KHSO_4 . Prepare a 30% (w/v) solution in water.

7.5 Aqueous standard rhodium stock solution, 1000 $\mu\text{g}/\text{ml}$. (Commercially available)

7.6 Rhodium working standard solution, 20 $\mu\text{g}/\text{ml}$. Prepare by appropriate dilution of above solution. Prepare fresh daily.

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 rhodium, metal fume and 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.
 - 8.3.2 Wet ashing. To destroy the organic filter matrix, treat the sample in each beaker with 2 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 two more times using 2 ml of concentrated nitric acid each time. Do not allow the solution to evaporate to dryness.
 - 8.3.3 Rhodium dissolution. To ensure complete dissolution of rhodium compounds, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). This is done by adding 2 ml of 6 N aqueous HCl and evaporating to about 0.5 ml; this HCl addition and evaporation is done 3 times. Do not allow the solution to evaporate to dryness at any point.
 - 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 25-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.
 - 8.3.7 Add 2.5 ml of the 30% potassium bisulfate solution and dilute to 25 ml with distilled water.
 - 8.3.8 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 343.5 nm. The absorbance

is proportional to the analyte concentration in the sample 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 could 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.

8.3.9 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 analyte. The analyte recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery of the analyte 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 concentration expected in the sample, 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 determinations should agree within $\pm 5\%$.

For this validation study, an amount of the analyte equivalent to that present in a 720-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. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value obtained was found to be 95%.

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

$$\text{Recovery} = \frac{\text{Average Weight } (\mu\text{g}) \text{ recovered}}{\text{Weight } (\mu\text{g}) \text{ added}} \times 100$$

9. Calibration and Standards

9.1 From the 20 $\mu\text{g/ml}$ working standard solution, prepare at least 6 working standards to cover the range from 10 to 160 $\mu\text{g}/25 \text{ ml}$.

Absorbance may be a nonlinear function of rhodium concentration above 160 $\mu\text{g}/25\text{ ml}$ (Reference 11.1) so the concentration range above 160 $\mu\text{g}/25\text{ ml}$ must be adequately covered with standards. All standard solutions are made 0.2N in HCl and are stored in polyethylene bottles. Since the low concentration standards may deteriorate, the standard solutions should be made fresh each day.

9.2 Proceed as in Section 8.3.7 to 8.3.9.

9.3 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 μg per 25 ml.

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

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

where:

$$\mu\text{g sample} = \mu\text{g found in sample filter}$$

$$\mu\text{g blank} = \mu\text{g found in blank filter}$$

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

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

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

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

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 Kallmann, S. and Hobart, E.W., "Vital Parameters in the Determination of Rhodium by Atomic Absorption", Anal. Chim. Acta 51, 120-124 (1970).