

Rhodium, Soluble Salts

Analyte:	Rhodium	Method No.:	S189
Matrix:	Air	Range:	0.0004-0.0018 mg/cu m
OSHA Standard:	0.001 mg/cu m	Precision (\overline{CV}_T):	0.069
Procedure:	Filter collection, Acid digestion, AA/high temperature graphite atomizer	Validation Date:	8/29/75

1. Principle of the Method

- 1.1 Sample-containing filters are wet-ashed using nitric acid and perchloric acid to destroy the organic matrix; rhodium and its compounds are then solubilized in an acid solution maintained at a pH of 1.
- 1.2 The solutions of samples and standards are analyzed by flameless atomic absorption spectroscopy in a heated graphite atomizer.
- 1.3 The area of the resulting absorption peak at 369.5 nm is determined and compared with areas of absorption peaks obtained from injection of standards.
- 1.4 The samples must be carefully interspersed between calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.0004-0.0018 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 370-liter sample. Under the conditions of sample size (370 liters), the linear working range of the method is estimated to be 0.0002-0.003 mg/cu m when the total sample collected is diluted to 25 ml and a 50-microliter aliquot is analyzed.
- 2.2 The lower limit of detection for a 50-microliter sample aliquot is 0.003 micrograms per ml.

3. Interferences

There are no known interferences to the rhodium assay using the high temperature graphite accessory.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.0004-0.0018 mg/cu m was 0.069. This value corresponds to a 0.000069 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 $99.6 \pm 0.9\%$ 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 105%; the data may be adjusted by this correction factor to eliminate any bias. 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 tedious and requires a high degree of technical skill.

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 direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and deuterium background corrector accessory. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 369.5 nm wavelength.

- 6.4 The rhodium radiation source may be either an electrodeless discharge lamp or a hollow cathode lamp. The former is recommended because it is a brighter source.
- 6.5 An electronic integrator, or some other suitable method for measuring peak areas.
- 6.6 Eppendorf automatic pipettor with disposable plastic pipets for accurately injecting 50-microliter sample aliquots into the graphite furnace tube.
- 6.7 Glassware, borosilicate:
 - 6.7.1 125-ml Phillips beakers with watchglass covers
 - 6.7.2 Pipets, delivery or graduated, 1, 5, 10 ml
 - 6.7.3 25-ml volumetric flasks
- 6.8 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 Perchloric acid
- 7.4 Nitric Acid - Perchloric Acid Mixture (2 parts HNO_3 + 1 part HClO_4)
- 7.5 Rhodium Standards
 - 7.5.1 Rhodium standard stock solution, 1000 $\mu\text{g}/\text{ml}$, (Commercially available from reliable suppliers such as Fisher Scientific).
 - 7.5.2 Dilute rhodium stock solution, 1 $\mu\text{g}/\text{ml}$. Prepare by appropriate (preferably sequential) dilution of above solution. Prepare fresh daily in 0.01M nitric acid.
 - 7.5.3 Working standards. Prepare by diluting 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, and 1.2 ml of the dilute rhodium stock solution (Section 7.5.2) to 25 ml with 0.01 M nitric acid. These solutions contain rhodium in the concentration range of 0.004 to 0.048 $\mu\text{g}/\text{ml}$. Prepare solutions 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 soluble salts, 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 samples submit a 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. Submit one blank for every ten samples.
- 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 and digestion. 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 once more using 2 ml of concentrated nitric acid. Cool beaker and contents and add 3 ml of $\text{HNO}_3\text{-HClO}_4$ mixture and continue evaporating to fumes to effect complete digestion of filter. Do not allow to evaporate to dryness at any point.

- 8.3.3 Cool solutions and add 10 ml of distilled (or deionized) water to each one.
- 8.3.4 Quantitatively transfer the clear solutions into a 25-ml volumetric flask.
- 8.3.5 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 and dilute to 25 ml.

8.3.6 Spectrophotometric measurements.

1. The instrumental parameters for source power, background corrector, and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying and atomization should be established in accordance with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of rhodium during these steps.
2. Inject a 50-microliter aliquot of the sample solution into the graphite tube using an automatic pipettor with disposable plastic tips.
3. A minimum of duplicate analyses per sample should be done.
4. To obtain reliable results, samples must be frequently alternated with standards which give responses close to that of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate, and reinject standard in duplicate, ...etc.

NOTE: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak areas, it must be rejected and replaced because results so obtained are not reliable.

- 8.3.7 Measurement of Area. The area of the absorption peak is measured by some suitable form of area measurement such as a planimeter or an electronic integrator. Note that peak height measurements will give neither precise nor reliable results.

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 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 370-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 105%.

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 Prepare a series of working standards containing 0.1 to 1.2 micrograms of rhodium in 25 ml of 0.01 M nitric acid. These standards should be prepared fresh each time. Refer to Section 7.5.3.

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

10. Calculations

10.1 Determine the weight in micrograms corresponding to the absorbance area of the sample by using the appropriate response factor for the sample.

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 $\mu\text{g/sample}$

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

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m ($\mu\text{g per liter} = \text{mg/cu m}$).

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

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.