

ARSENIC IN PETROLEUM STOCKS AND CATALYSTS BY SPECTROPHOTOMETRY

UOP Method 387-62

SCOPE

This is a method for determining arsenic in petroleum stocks which contain a minimum of 5 parts per billion (ppb) of arsenic. It also provides a rapid, accurate method for determining arsenic in various types of catalysts.

OUTLINE OF METHOD

Arsenic is extracted from the liquid petroleum stock by boiling with a sulfuric acid-hydrogen peroxide mixture and is then converted to arsine. The evolved arsine is reacted with a solution of silver diethyldithiocarbamate in pyridine and the red coloration produced by this reaction is measured spectrophotometrically. Catalysts are fused with sodium peroxide before the arsine evolution and spectrophotometric determination steps.

APPARATUS

Arsine evolution apparatus as shown in the accompanying drawing. A suitable apparatus is available from Fisher Scientific Co. The apparatus consists of an evolution flask, a hydrogen sulfide scrubber and an arsine absorber. The hydrogen sulfide scrubber is filled with glass wool impregnated with lead acetate.

Balance, analytical, accurate to ± 0.1 mg

Cylinders, graduated, 100-, 500-ml

Flasks, Kjeldahl, 500-ml

Flasks, volumetric, 200-ml

Funnels, separatory, 300-ml

Peroxide bomb and assembly, obtainable from Parr Instrument Co., Moline, Illinois, or crucibles, nickel, 50-ml capacity

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Pipets, 5-, 10-, 20-, 25-ml

Spectrophotometer, Beckman Model B or equivalent

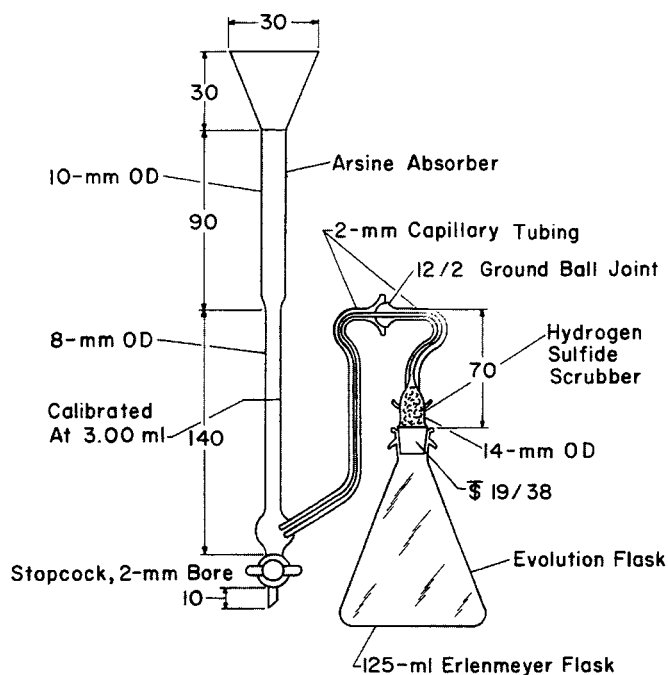
REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

Ammonium oxalate, saturated solution. Add 50 g of ammonium oxalate to 2000 ml of water.

Boiling chips, carborundum, 8-10 mesh

Hydrochloric acid, concentrated, 0.000001% arsenic or less



All Dimensions in Millimeters
Arsine Evolution Apparatus

Hydrogen peroxide, 30% solution

Hydrogen peroxide, 3% solution

Isoamyl acetate

Lead acetate solution, 10%. Dissolve 10 g of lead acetate in water and dilute to 100 ml. Saturate the glass wool used for the arsine generator with this solution; drain and dry in an oven at 105 C.

Potassium iodide, 15% solution. Dissolve 15 g of potassium iodide in water and dilute to 100 ml.

Potassium perchlorate, powdered

Pyridine

Silver diethyldithiocarbamate solution. Dissolve 1 g of silver diethyldithiocarbamate, obtainable from Fisher Scientific Co., in 200 ml of pyridine. Store in a dark brown bottle.

Sodium hydroxide, 50% solution

Sodium peroxide. Store in a Kerr jar or equivalent.

Stannous chloride solution. Dissolve 40 g of stannous chloride in 100 ml of concentrated hydrochloric acid.

Standard arsenic solution, 1 mg As/ml. Dissolve 1.320 g of arsenic trioxide in 10 ml of 50% sodium hydroxide solution and dilute to 1 liter with water.

Standard arsenic solution, 1 γ As/ml. Dilute 10 ml of the 1 mg/ml arsenic solution to 100 ml with water to make a 100 γ As/ml solution. Dilute 10 ml of the 100 γ As/ml solution to 1 liter with water.

Sucrose, powdered

Sulfuric acid, concentrated, 0.000001% arsenic or less

Sulfuric acid, 1:1 solution. Mix equal volumes of concentrated sulfuric acid with water.

Zinc, 20-mesh, 0.000001% arsenic or less, e.g., Baker's Reagent Grade. This zinc should be "pickled" before use as follows: Pour 1 lb of 20-mesh zinc into a 600-ml beaker and cover with water to a depth of 1 inch. Add 15 ml of concentrated hydrochloric acid. Stir until the surface of the zinc becomes uniformly bright. Pour off the acid, then wash the zinc with water by decantation and stirring until the zinc is free of acid. It is good practice to leave the porcelain measuring spoon in the beaker to prevent contamination. Cover the beaker with a watch glass.

CALIBRATION

Transfer aliquots of the standard 1 γ As/ml solution containing 1, 2, 3, 4, 5, 6, 8, and 10 γ of arsenic to separate evolution flasks. Add 12 ml of 1:1 sulfuric acid to each flask, and to an empty flask, and dilute each with water to 50 ± 5 ml. Cool and to each flask add 2 ml of potassium iodide solution. Then with swirling, add 5-6 drops of stannous chloride solution and allow the mixtures to stand for 10-15 minutes

Place an evolution flask in an ice bath, attach the hydrogen sulfide scrubber to the absorber, and add 3.0 ml of silver diethyldithiocarbamate solution to the absorber. Add 5.0 ± 0.1 g of zinc to the evolution flask and immediately attach the hydrogen sulfide scrubber to the evolution flask. When the reaction slows down (10-15 minutes), remove the apparatus from the ice bath and allow the reaction to continue for an additional 30 minutes. Remove the evolution flask from the absorber and carefully dilute the solution in the absorber to the 3.0-ml mark with pyridine. (Some pyridine has been lost through evaporation.) Pass a gentle stream of air through the absorber to mix the solution and drain the solution into a 1-cm spectrophotometer cell. Repeat this procedure for each aliquot taken. Measure the respective absorbances of the aliquots at 540 m μ , using the reagent blank solution as the reference liquid. Plot the absorbances vs. micrograms of arsenic.

In general, concentrations of sulfuric and other reagents in the calibration are the same as for the respective types of samples analyzed.

PROCEDURE

Liquid Petroleum Stocks

Determine the specific gravity of the sample is not already known.

Add 15 ml of concentrated sulfuric acid and 20 ml of 30% hydrogen peroxide to a 500-ml Kjeldahl flask containing 2 or 3 boiling chips and cool to 0-5 C. Add up to 300 ml of sample containing 1-10 γ of arsenic to the flask. Shake the mixture vigorously and then reflux the sample for 30 minutes with occasional shaking.

Cool the mixture, transfer it to a separatory funnel, and drain the acid layer back into the Kjeldahl flask. Wash the hydrocarbon layer once with 10 ml of water and drain the water into the Kjeldahl flask. With samples that do not char easily and when sample volumes of 20 ml or less are to be run, the separation may be eliminated and the organic layer merely boiled away.

Heat the solution to the point where sulfuric acid fumes are evolved, adding hydrogen peroxide or nitric acid when necessary to destroy the organic matter. If the solution darkens during the digestion process add nitric acid or hydrogen peroxide immediately to prevent loss of arsenic.

When all the organic matter is destroyed, add 15 ml of saturated ammonium oxalate solution and heat to the point of evolution of sulfuric acid fumes.

Cool the solution and wash it into a 100-ml volumetric flask. Pipet an aliquot containing 1-10 γ of arsenic from the 100-ml volumetric flask into an evolution flask. Adjust the acid content of the aliquot to the equivalent of 6 ± 1 ml of concentrated sulfuric acid, then adjust the total volume to 50 ± 5 ml with water. Cool, add 2 ml of 15% potassium iodide solution and, with swirling, add 5 or 6 drops of stannous chloride solution. Allow the mixture to stand 10-15 minutes. Place the evolution flask in an ice bath, attach the hydrogen sulfide scrubber to the absorber and add 3.0 ml of silver diethyldithiocarbamate solution to the absorber. Add 5.0 ± 0.1 g of zinc to the evolution flask and immediately attach the hydrogen sulfide scrubber and absorber to the evolution flask. When the reaction slows down (10-15 minutes), remove the apparatus from the ice bath. Allow the reaction to continue for an additional 30 minutes. Then detach the adsorber and dilute the solution to exactly the 3.0-ml mark with pyridine. Read the absorbance of the colored solution as described under *CALIBRATION*. Determine the micrograms of arsenic in the sample from the calibration curve.

It is advisable to run 2 or 3 aliquots (1-10 γ) of the standard arsenic solution along with the sample to check points on the previously established calibration curve.

Catalysts

Weigh 0.1-0.6 g of finely ground catalyst to the nearest 0.1 mg into a peroxide bomb. Add 0.5 g of potassium perchlorate, 0.7 g of powdered sucrose and 12 g of sodium peroxide and mix with care. Fuse and fire the mixture in the usual way and allow the bomb to cool.

If a peroxide bomb is not available, the finely ground sample may be weighed (not more than 0.6 g) into a 50-ml nickel crucible. Add 3.0 ± 0.2 g of sodium peroxide to the crucible and mix well. Cover the crucible contents with an additional 1.0 g of sodium peroxide. Fuse in a muffle furnace at 525 ± 15 C for one-half hour. Remove the crucible from the furnace and cool it to room temperature.

In either instance, leach the melt in 50-100 ml of water and gently boil the alkaline solution for 10 minutes to decompose the excess peroxide. Cool and filter the solution into a 200-ml volumetric flask and dilute to volume with water. If the catalyst contains platinum, filter it into a separatory funnel. Complete according to one of the following procedures.

A. Procedure for Cobalt Oxide-Molybdena-Alumina Catalysts. Transfer an aliquot of 25 ml or less of the above solution (containing no more than 10 γ of arsenic) to an evolution flask. Adjust the volume to 25 ml with water. Acidify with 1:1 sulfuric acid until the precipitate of aluminum hydroxide formed just redissolves, then add 12 ml more. Adjust the volume to about 50 ml with water, then add 2.0 ml of 15% potassium iodide solution and 5 or 6 drops of stannous chloride solution. Complete the arsine generation and reading of the absorbance of the colored solution as described above for petroleum stocks.

B. Procedure for Chromium-Bearing Catalysts. Proceed as described for cobalt oxide-molybdena-alumina catalyst to the adjustment of the volume to about 50 ml. Then add dropwise, with swirling, 3% hydrogen peroxide until 1 drop no longer gives the bluish purple tinge of perchromic acid. Add 2.0 ml of 15% potassium iodide solution and 5 or 6 drops of stannous chloride solution. Complete the arsine generation and read the absorbances of the colored solutions as described for petroleum stocks.

C. Procedure for Platinum-Bearing Catalysts. Acidify the solution in the separatory funnel with 1:1 sulfuric acid until the aluminum hydroxide just redissolves. Add 8 ml of concentrated hydrochloric acid and cool. Add 1 ml of stannous chloride solution and dilute with water to about 90 ml. Extract with three 15-ml portions of isoamyl acetate, draining off the isoamyl acetate layer each time. Finally, drain the aqueous layer into a 200-ml volumetric flask and dilute to volume with water. Transfer an aliquot of 25 ml or less (containing not more than 10 γ of arsenic) to an evolution flask. Add 12 ml of 1:1 sulfuric acid and adjust the volume to about 50 ml. Add 2.0 ml of 15% potassium iodide solution and 5 or 6 drops of stannous chloride solution. Complete the arsine generation and read the absorbances of the colored solutions as described for petroleum stocks.

CALCULATIONS

Calculate the arsenic content of petroleum stocks as follows:

$$\text{Arsenic, ppb} = \frac{1000 \text{ GD}}{\text{VS}}$$

where:

$$\text{D} = \text{dilution factor} = \frac{\text{A}}{\text{B}}$$

where:

A = volume to which sample was diluted, ml

B = volume of aliquot taken for analysis, ml

G = concentration of arsenic read from the calibration curve, γ

S = specific gravity of the sample

V = volume of sample taken for analysis, ml

Calculate the arsenic content of catalysts as follows:

$$\text{Arsenic, wt-\%} = \frac{\text{GD}}{10,000 \text{ W}}$$

where:

W = weight of sample taken for analysis, g

D and **G** are as defined above

REMARKS AND PRECAUTIONS

To avoid contamination, reserve the reagents and apparatus for this method only.

If desired, 1 ml of isopropyl alcohol may be added to the arsenic generating flask to slow down the evolution rate.

Stibine is the only likely interference in the color development as it also forms a red color with the silver diethyldithiocarbamate reagent. The sensitivity for antimony at 540 mμ is about 8% that of arsenic.

After the generation of arsine has been completed, always pass a gentle stream of air through the absorber to mix the colored solution *before draining* it into the 1-cm spectrophotometer cell.

PRECISION

<u>Sample Type</u>	<u>Repeatability</u>
Liquid Petroleum Stocks	
5-20 ppb As	± 10%
Over 20 ppb As	± 5%
Catalysts	± 3%

REFERENCE

Liederman, D., Bowen, J. E., and Milner, O. I., *Anal. Chem.* **31** 2052 (1959)