

TRACE SULFUR IN PETROLEUM DISTILLATES BY THE NICKEL REDUCTION METHOD

UOP Method 357-80

SCOPE

This method is for the determination of low concentrations of sulfur, ranging from 0.1 to 200 ppm, in distillate stocks free of hydrogen sulfide. It may be applied to non-olefinic materials, such as straight run naphthas, hydrogen treated stocks, reformates and aromatic hydrocarbons. It is limited to samples containing not more than 2% olefins. Oxidized sulfur forms, such as sulfonic acids, are not determined quantitatively; therefore, this method must be applied with discretion to the analysis of stocks which have been treated with sulfuric acid.

OUTLINE OF METHOD

The sample is reacted with activated Raney nickel to convert organically-bound sulfur to nickel sulfide. Acid is then added to liberate the sulfur as hydrogen sulfide. The hydrogen sulfide is absorbed in a sodium hydroxide-acetone solution and titrated with standard mercuric acetate, using dithizone as the indicator.

APPARATUS

Apparatus, as shown in the drawing

Balance, “Torsion” or equivalent, 500-g capacity; available from Sargent-Welch Scientific Co., or equivalent

Buret, 10-mL

Cylinders, graduated, 10- and 50-mL

Filter paper, Whatman 41

Flask, volumetric, 1000-mL, 2000-mL

Heating mantle, for 100-mL flask

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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Nitrogen cylinder, equipped with a pressure regulator. Arrange 2 lengths of rubber tubing to independently feed the acid reservoir and the flask respectively, as indicated on the drawing. Fit a pinchcock or a needle valve in each line to permit regulation of nitrogen flow.

Pipet, Mohr, 1-mL

Pipets, volumetric, 1-, 5- and 10-mL

Separatory funnel, 125-mL

Transformer, variable

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 are available, unless otherwise specified. References to water mean deionized or distilled water.

Acetone

Dithizone solution, dissolve 0.1 g of dithizone (diphenylthiocarbazon) in 100 mL of acetone. Prepare a new solution each week.

Dibutyl disulfide, (also identified as butyl disulfide)

Hydrochloric acid, concentrated

Hydrochloric acid solution, Dilute 1.5 volumes of concentrated hydrochloric acid with 1 volume of water.

Isooctane, pass over silica gel to remove sulfur compounds.

Isopropyl alcohol

Mercuric acetate, low-titer, equivalent to 30 $\mu\text{gS/mL}$. Prepare by dissolving 0.41 g of mercuric oxide in 50 mL of aqueous solution containing 2 mL of acetic acid; dilute to 2 L with water in a volumetric flask.

Standardize this titrant by pipeting 5 mL of sulfur standard and following the analysis of a sample as described under *PROCEDURE*.

$$\text{Low-titer mercuric acetate solution, } \mu\text{gS/mL} = \frac{CD}{E}$$

where:

C = sulfur standard, $\mu\text{gS/mL}$

D = volume of sulfur standard used, mL

E = titration volume of low-titer mercuric acetate, mL

Mercuric acetate, high-titer, equivalent to 100 $\mu\text{gS/mL}$. Dissolve 1.35 g of mercuric oxide in 50 mL of aqueous solution containing 2 mL of acetic acid. When in solution, dilute to 2 L with water in a volumetric flask. Standardize this titrant by pipetting 15 mL of the sulfur standard and follow the analysis of a sample as described under *PROCEDURE*.

$$\text{High-titer mercuric acetate solution, } \mu\text{gS/mL} = \frac{CD}{F}$$

where:

F = titration volume of high-titer mercuric acetate, mL

C and **D** are as previously defined

(Note: Granatelli found that approximately 95% recovery of the calculated added sulfur content was obtained when the complete analysis was carried out. Since the procedure is very precise, this is not an objectionable feature. However, the mercuric acetate solution must be standardized as specified above rather than by placing reliance on the molarity calculated from the weight of mercuric oxide used.)

Mercuric oxide, yellow powder

Nitrogen

Raney nickel, activated. Prepare the activated Raney nickel by placing 0.60 ± 0.1 g of nickel-aluminum alloy ("Raney catalyst", available from Sargent-Welch Scientific Co.) in a 100-mL beaker and add 10 mL of 2.5 M sodium hydroxide. Swirl the beaker gently in a hood until the vigorous evolution of hydrogen has ceased. Wash down any solids remaining on the sides of the beaker with a minimum of water. Allow the reaction to continue overnight in a covered vessel (such as a large desiccator minus desiccant).

Store the activated Raney nickel in the excess sodium hydroxide, which is in the beaker and place it in a covered vessel until ready for use. It may be stored in the desiccator for as long as a week. This is enough activated Raney nickel for the analysis of one sample. The nickel prepared in this manner from 0.6 g of the alloy is enough to reduce at least 2000 micrograms of sulfur.

Sodium hydroxide, approximately 2.5 M and 1 M

Sulfur standard. Place several grams of dibutyl disulfide into a dropping bottle. Weigh the bottle and contents to the nearest 0.1 mg. Add 60-100 mg of the disulfide to 1-liter of sulfur free isooctane. Reweigh the dropping bottle to obtain the weight of the dibutyl disulfide removed. Dilute the contents of the 1-liter flask to the mark with isooctane and mix by inverting the flask several times. Calculate the titer in $\mu\text{g/mL}$.

$$\mu\text{gS/mL (standard)} = \frac{360.5 A}{B}$$

where:

A = weight of dibutyl disulfide, mg

B = volume of isooctane, mL

Wash solution, dissolve 100 g of cadmium chloride in 250 mL of water containing 10 mL of concentrated hydrochloric acid. Dilute to 1 liter with water. Chill to below 15 C and use immediately when called for in *PROCEDURE*.

PROCEDURE

Thoroughly cleanse the reduction apparatus glassware with soap and water and then rinse at least two times with sulfur free acetone or alcohol. Dry in an oven at 110 C for one half hour or until dry. An excess of water inhibits the reduction of organic sulfur.

Test the sample for the presence of hydrogen sulfide by holding a piece of water moistened lead acetate paper in the vapor space of the sample container. If hydrogen sulfide is present the paper will darken or a silver sheen will appear. If hydrogen sulfide is not present proceed with the analysis. If hydrogen sulfide is present it must be removed as this Method is applicable for organic sulfur only. The removal of hydrogen sulfide is accomplished by the following procedure.

Add up to 60 mL of sample to a 125-mL separatory funnel. Add 10 mL of cadmium chloride wash solution (freshly prepared) to the sample and shake 1-2 minutes. Allow the layers to separate and draw off the lower layer. If the test for hydrogen sulfide was strongly positive, continue additions of the wash solution until further additions do not produce turbidity. Water wash three times, with 10 to 15 mL of water, discarding the water layers each time after shaking and letting the layers separate. Filter the sample rapidly (Whatman 41) and retain.

Decant the aqueous caustic solution from the beaker containing the activated Raney nickel just before using it. Wash the active nickel thoroughly 3 times with vigorous sprays of water. Allow the nickel to settle each time before the water is decanted, then rinse the water from the Raney nickel with 10 mL of isopropyl alcohol and discard the rinsings.

Transfer the Raney nickel to the reaction flask with 10 mL of isopropyl alcohol, rinsing down the walls of the flask with more alcohol in order to keep all of the Raney nickel submerged in the liquid. Weigh the flask containing the Raney nickel and isopropyl alcohol to the nearest 0.05 g on a Torsion balance. Add the sample (for size of sample see table below) by pipet or graduate to the flask and reweigh the flask. Rely upon accurate pipetting for samples of 5 mL or less rather than weights obtained on the Torsion balance.

Suggested Sample Size for Analysis

<u>Sulfur, ppm</u>	<u>Sample Size, mL</u>	<u>Concentration of Titrant, $\mu\text{gS/mL}$</u>
0-1	50	30
1-10	50	100
10-20	20	100
20-100	5	100
100-200	2	100

Rinse the walls of the flask with about 5 mL of isopropyl alcohol to ensure contact of the entire sample with the Raney nickel. Place the flask in the heating mantle, lubricate the connecting-head with stopcock grease and install it on the flask. Charge the absorber with 10 mL of 1M sodium hydroxide, 10 mL of acetone, and 5 drops of dithizone solution. Assemble and connect the apparatus as indicated in the drawing. Set the nitrogen pressure regulator for 2-5 psig and allow the nitrogen to flow through the reaction vessel and on into the absorber at a rate of one bubble every 1 or 2 seconds. Turn on the heater and allow the reactants to warm to a temperature at which no sample will be lost as a result of distillation during the sulfur reduction step (i.e., use a temperature which is just short of inducing boiling). Allow the sulfur reduction to proceed for 30 minutes, agitating the contents of the flask several times during this period.

Charge the acid reservoir of the connecting-head with 10 mL of 1.5:1 hydrochloric acid after the desulfurization is completed. Attach a nitrogen line loosely to the acid reservoir using a glass tube inserted in a neoprene stopper. Flush the air from the acid reservoir with a rapid flow of nitrogen and then reduce the rate of flow of the nitrogen and put the stopper firmly into place.

Add the acid *dropwise* to the reaction flask while maintaining the nitrogen flow through the reaction flask and into the absorber. Add just enough of the appropriate mercuric acetate titrant to the absorber liquid to change the color of the solution from yellow to pink. After the vigorous reaction of the acid with the nickel has taken place, the remaining acid can be added rapidly. Maintain the nitrogen flow through the flask and reservoir. Increase the temperature to the point where the contents of the flask just barely reflux.

As the evolved hydrogen sulfide begins to be absorbed in the caustic solution, the color of the solution will change from pink back to yellow. Titrate with the mercuric acetate solution until the absorber solution is definitely pink and remains that color. Continue boiling the reaction flask contents for at least 30 minutes and then stop the nitrogen flow temporarily. Cool the reaction flask by applying a cold, wet cloth above the heating mantle, so that the absorber solution is sucked up into the delivery tube. When the liquid approaches the side-arm, turn on the nitrogen to force the liquid back into the absorber. Repeat this operation several times, being careful not to allow any absorber solution to wet the horizontal portion of the delivery tube. If the absorber solution changes color from the pink to the yellow following this operation, titrate further with mercuric acetate to bring the solution to a permanent endpoint. Record the total volume of mercuric acetate titrant used. Obtain the net titration volume for the sample by subtracting the titration volume determined for the Raney nickel blank.

Determine a blank titration for each new batch of Raney nickel by the following procedure: Transfer the active nickel prepared from 0.6 g of the alloy to the reaction flask with 10 mL of isopropyl alcohol. Rinse down the walls of the flask with about 5 mL of isopropyl alcohol and attach the greased connecting-head. From this point on follow the procedure as described for the analysis of the sample with the exception that the sample is omitted. The total volume of the mercuric acetate required to reach the endpoint is the Raney nickel catalyst blank. The blank should amount to 0.1 to 0.2 mL of the 100- μ gS titrant or 0.3-0.6 mL of the 30- μ gS titrant. This amounts to 17-34 ppm sulfur in the Raney nickel alloy.

CALCULATIONS

$$\text{Sulfur, ppm} = \frac{AT}{W}$$

where:

A = net volume of mercuric acetate solution used in titration, mL

T = titer of the mercuric acetate solution, μ gS/mL

W = weight of sample, g

PRECISION

Duplicate results should be considered suspect if they differ by more than the following amounts:

Level of S, ppm	Allowable Difference ppm, S
1	0.3
10	0.6
50	2
250	6

