

TRACES OF SULFUR IN LIQUEFIED PETROLEUM GASES BY THE NICKEL REDUCTION METHOD

UOP Method 381-63

SCOPE

This method is for the determination of low concentrations of sulfur in liquefied petroleum gases. The lower limit of detection ranges from 0.2 ppm sulfur in olefin-free butanes to about 20 ppm sulfur in a 100% olefin sample. The sulfur analyzed includes not only volatile compounds, but also high-boiling forms such as dissolved elemental sulfur.

OUTLINE OF METHOD

The sample is reacted with activated Raney nickel in a high-pressure glass bomb to produce nickel sulfide. Acidification of the nickel sulfide generates hydrogen sulfide which, in turn, is absorbed in a caustic-acetone solution. The absorber solution is then titrated with standard mercuric acetate, using dithizone as the indicator.

The analysis of liquefied gas samples is not straightforward because of the widely differing nature of the samples; i.e., vapor pressure and the presence or absence of olefin. Therefore, special arrangements must be made, depending on the composition of the sample, as given in the PROCEDURE.

APPARATUS

Adapter, new style special, threaded to receive metal needle valve Fischer & Porter Co., Hatboro, Pa., Cat. No. 110-957

Aerosol coupling neoprene "O" ring, for new style special adapter Fischer & Porter Co. Cat. No. 110-858

Aerosol coupling plastic part. Fischer & Porter Co. Cat. No. 110-759

Bath, constant temperature, 55 C

Bombs, glass. Aerosol compatibility tubes, 12-oz, "high-pressure" type, Fischer & Porter Co., Cat. No. 110-023. Fit with adapters, gaskets, O-rings and needle valves. Note: Hydrostatic pressure tests at UOP laboratories always have resulted in leakage and, frequently, complete rupture of the glass body at about 200 psig. *IT IS STRONGLY URGED THAT UNDER NO CIRCUMSTANCES SHOULD THIS APPARATUS BE USED ABOVE 150 PSIG; it is safer to stay below 100 psig.* It is further recommended that each laboratory hydrostatic pressure test each assembly to about 200 psig before use.

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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Buret, 25-ml

Connecting head, as shown in drawing

Cylinder, graduated, 10-ml

Needle valve, stainless steel, 1/8-inch

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

Safety shield, of appropriate size

REAGENTS

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.

Dithizone (diphenylthiocarbazone). Dissolve 0.1 g of dithizone in 100 ml of acetone. Prepare a new solution each week.

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

Isooctane, sulfur-free

Isopropyl alcohol

Mercuric acetate solution, 1 ml equivalent to 30 γ of sulfur. Dissolve 0.4045 g of oven-dried mercuric oxide (yellow powder) in 50 ml of water containing 2 ml of acetic acid and dilute to 2 l.

Mercuric acetate solution, 1 ml equivalent to 100 γ of sulfur. Dissolve 1.3 g of mercuric oxide (yellow powder) in 50 ml of water containing 2 ml of acetic acid and dilute to 2 l. Standardize the solution by titrating the hydrogen sulfide evolved from 100 to 1000 γ of precipitated sulfur dissolved in sulfur-free isooctane (see Note 1).

Raney nickel. Prepare Raney nickel by adding 0.60 ± 0.01 g of nickel-aluminum alloy (Raney nickel catalyst powder, No. 2813, available from W. R. Grace & Co., Raney Catalyst Div., S. Pittsburgh, Tenn.) to a 100-ml beaker and add 10 ml of 2.5 *N* sodium hydroxide. Swirl the beaker gently in a hood until the vigorous evolution of the hydrogen has ceased. Wash down any alloy remaining on the sides of the beaker with a minimum amount of water. Allow the reaction to continue overnight in a covered vessel, such as a large desiccator without desiccant.

Decant the excess sodium hydroxide from the Raney nickel after activation, and wash the active nickel 3 times with 5-ml portions of water. Preserve the washed catalyst under 10 ml of isopropyl alcohol. Store the activated catalyst in a covered vessel until ready for use. It may be kept for as long as a week.

The nickel prepared in this manner from 0.6 g of the alloy is enough to reduce at least 2000 γ of sulfur.

Sodium hydroxide solutions, aqueous, approximately 2.5 *N* and 1 *N*, respectively

PROCEDURE

Analysis of liquefied petroleum gas samples must be carried out in a well-ventilated room. There must be no open flames or glowing wires. Hydrostatically test each bomb assembly to 200 psig before use.

The procedure for analyzing liquefied gas samples is not straightforward because of the widely differing nature of the samples, particularly with respect to vapor pressure and the presence or absence of olefin. The methods of analysis for the sample cases are listed below. When samples contain a combination of olefin or C₃ the analyst must use discretion in blending them with isooctane.

C₄ Samples Containing 0 to 2% Olefin

Decant the isopropyl alcohol from the beaker containing the activated Raney nickel. Transfer the Raney nickel into the glass bomb with approximately 20 ml of isopropyl alcohol, rinsing down the walls of the bomb with isopropyl alcohol in order to have all of the Raney nickel immersed in the liquid. Insert the metal adapter into the bomb and evacuate for 10 minutes. Weigh the bomb to the nearest 0.05 g on a heavy-duty, triple-beam balance.

Chill the glass bomb in an ice water bath and transfer the liquefied gas sample from the liquid phase into it (see Note 2). Pass the sample through an 8-inch length of 1/4-inch stainless steel pipe packed with clean glass wool (to filter out any scale and especially iron sulfide that may be present in the sample container). Reweigh the bomb to obtain the weight of the sample.

Take care that the glass bomb is not scratched (see Note 3). Take extreme care to avoid the presence of air in the reaction bomb; i.e., put the connecting head in place quickly without allowing air to enter.

Place the glass bomb containing the liquefied gas sample in a constant temperature bath which is set at 55 C and place the safety shield in front of the apparatus (Note 4). Allow the reaction of the nickel with the sample to take place for 30 minutes. Agitate the contents of the bomb several times during this period.

Charge the absorber with 10 ml of 1 *N* sodium hydroxide and 10 ml of acetone. Pass nitrogen through this solution while the sample is being desulfurized.

Vent the liquefied gas from the bomb after the desulfurization period, leaving the isopropyl alcohol plus the reacted Raney nickel. After the hydrocarbon has evaporated, remove the metal adapter and insert the connecting head into the bomb. Place the bomb in a beaker of water which, when heated, will reflux the contents of the bomb. Purge the bomb with nitrogen, using the tube which goes below the surface of the liquid contents.

Charge the acid reservoir with 10 ml of 1.5: 1 hydrochloric acid. Disconnect the nitrogen line from the caustic absorber and attach it to the acid reservoir by means of a glass tube inserted in a cork stopper loosely fitted into place. Flush the air from the acid reservoir with a rapid flow of nitrogen and then shut off the

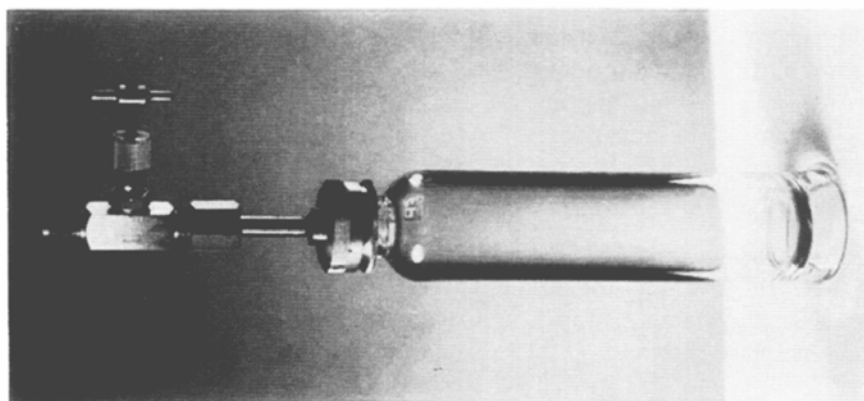


Figure 1

Assembled Fischer Porter Glass Bomb

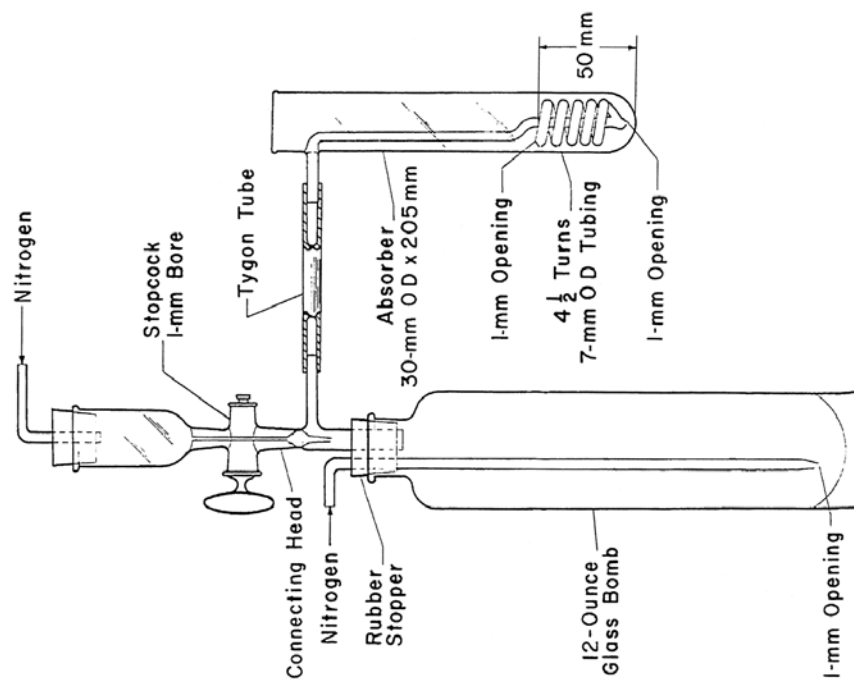


Figure 2

Titration Apparatus

flow before the stopper is put firmly into place. Connect the side - arm of the connecting head on the bomb to the side-arm of the absorber by a short piece of Tygon tubing. Add 5 drops of the dithizone solution to the liquid in the absorber.

Add the acid dropwise to the bomb while maintaining the nitrogen flow into the bomb. Add just enough of the mercuric acetate titrant to the absorber liquid to change the color from yellow to pink. For accurate analysis below 1 ppm sulfur, titrate with dilute mercuric acetate, 1 ml equivalent to 30 γ of sulfur. After the vigorous reaction of the acid with the nickel has taken place, add the remaining acid rapidly. Increase the temperature of the water to the point where the contents of the bomb just 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 mercuric acetate until the absorber solution is definitely pink and remains pink. Continue boiling the contents of the bomb for at least 30 minutes and then stop the nitrogen flow temporarily. Cool the bomb by carefully applying a cold wet cloth to the bomb's surface 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 that no absorber solution wets the horizontal portion of the delivery tube. If the absorber solution changes color from pink to yellow, add more mercuric acetate to bring the solution to a permanent endpoint. Record the volume of mercuric acetate added. The net titration for the sample is obtained by subtracting the volume used in titrating the Raney nickel blank (below).

The Raney nickel blank is determined by the following procedure: Transfer the active nickel prepared from 0.6 g of the alloy to the bomb with 10 ml of isopropyl alcohol. Rinse down the walls of the bomb with about 10 ml of isopropyl alcohol and attach the connecting head to the bomb. The procedure from this point on is the same as described for the analysis of the sample with the exception, of course, that the sample is omitted. The total volume of the mercuric acetate required to reach the endpoint is the Raney nickel catalyst blank. Run this blank each time a *new* solution of mercuric acetate is prepared.

C₄ Samples Containing More than 2% Olefin

Determine the olefin content of the sample to be analyzed by a gas liquid chromatography analysis. It is mandatory that the exact analysis be obtained since a 2% olefinic concentration will give results 15% below the true value. Estimate the amount of sample required to produce an olefin content of 1% or less when blended with isooctane (see Note 5). Prepare a stock blend of isooctane and the sample by the following procedure:

Determine the weight of the empty glass bomb and to it add approximately 180 g of isooctane. Place the metal adapter into position and evacuate the bomb. Determine the weight of the isooctane present in the bomb. Chill the bomb in ice water and transfer (in the case of approximate 100% olefin sample) 40 g of sample to the glass bomb by passing it through an 8-inch length of 1/4-inch stainless steel pipe packed with clean glass wool. Mix the blended sample thoroughly. Place the glass bomb with the isooctane-sample blend in a container with dry ice.

Prepare a second glass bomb which is to be used for the actual analysis by the following procedure:

Decant the liquid from the beaker containing the activated Raney nickel. Transfer the Raney nickel into the glass bomb with approximately 20 ml of isopropyl alcohol. Rinse down the walls of the bomb with alcohol in order to have all of the Raney nickel immersed in the liquid. Determine the weight of the bomb plus the isopropyl alcohol and catalyst.

Add 50 g of sulfur-free isooctane to the bomb and chill the bomb and its contents in ice water. Transfer an aliquot of the stock blend to the analysis bomb, using a pipet which has been chilled in dry ice. Choose the aliquot so that the blend analyzed will contain 0.4 g or less of olefin in 50 g of isooctane. Purge the glass bomb with nitrogen and place the metal adapter in position. Determine the weight of the aliquot of the stock blend added.

Place the glass bomb in a constant temperature bath set at 55 C (see Note 4) and allow the desulfurization to take place for 30 minutes. Agitate the contents of the bomb several times during the 30 minutes.

Charge the absorber with 10 ml of 1 *N* sodium hydroxide and 10 ml of acetone and pass nitrogen through this solution during the time that the sample is being desulfurized.

Vent the light hydrocarbons from the bomb after the desulfurization period, leaving the isopropyl alcohol, isooctane and the reacted Raney nickel. Quickly insert the connecting head into the glass bomb and purge nitrogen through the bomb by means of the tube which goes below the liquid surface. Place the bomb in a beaker of water which, when heated, will reflux the contents of the bomb.

Take special care to avoid the presence of air in the reaction bomb and when the hydrogen sulfide is being evolved.

Charge the acid reservoir with 10 ml of 1.5 to 1 hydrochloric acid after the desulfurization is completed. Disconnect the nitrogen line from the caustic absorber and attach it to the acid reservoir by means of a glass tube inserted in a cork stopper loosely placed in position. Flush the air out of the acid reservoir with a rapid flow of nitrogen and then shut off the flow of nitrogen before the stopper is put firmly into place. Connect the side-arm from the connecting head on the glass bomb to the side arm of the absorber with a short piece of Tygon tubing. Add 5 drops of dithizone solution to the liquid in the absorber.

Add the acid dropwise to the bomb while maintaining the nitrogen flow into the bomb. Add just enough of the mercuric acetate titrant (30 γ S/ml) to the absorber liquid to change the color from yellow to pink. From this point on, carry out the analysis of the sample in the same manner specified under *C₄ Samples Containing 0 to 2% Olefin*.

Determine the sulfur content of the isooctane used for blending by analysing it by the same procedure used for the sample. Subtract the total micrograms of sulfur present in the isooctane from the total micrograms of sulfur calculated from the net titration.

Obtain the net titration for the blended sample by subtracting the Raney nickel blank from the total of titrant used. Determine the Raney nickel blank by the same procedure given under *C₄ Samples Containing 0 to 2% Olefin*. The only difference is that the blank is determined using mercuric acetate equivalent to 30 γ S/ml instead of the more concentrated solution.

C₃ Samples

Determine the propane content of the sample to be analyzed. This is mandatory for safety reasons because of the high vapor pressure which would develop if propane were analyzed by itself. Calculate the amount of sample which, when mixed with isooctane, will produce a blend containing 5% or less propane (see Note 5).

Prepare a stock blend of isooctane and the sample by the following procedure:

Determine the weight of the empty glass bomb and add about 180 g of isooctane. Place the metal adapter into position and evacuate the bomb. Determine the weight of the isooctane present in the bomb. Chill the bomb in ice water. Add 30 g of sample (if near 100% propane) to the glass bomb by passing the sample through an 8-inch length of 1/4-inch stainless steel pipe packed with clean glass wool. Mix the blended sample thoroughly. Place the glass bomb with the isooctane - sample blend in a container with dry ice.

Prepare a second glass bomb, which is to be used for the actual analysis, by the following procedure:

Decant the isopropyl alcohol from the beaker containing the activated Raney nickel. Transfer the Raney nickel into the glass bomb with approximately 20 ml of isopropyl alcohol. Rinse down the walls of the bomb with it in order to have all of the Raney nickel immersed in the liquid. Determine the weight of the bomb plus the catalyst.

Add 50 g of isooctane to the bomb. Chill the bomb and its contents in ice water. Transfer 20 g of the stock blend to the bomb, using a pipet chilled in dry ice. Blanket the contents of the bomb with nitrogen and place the metal adapter in position (see Note 4).

Place the glass bomb in a constant temperature bath set at 55 C and allow the desulfurization to take place for 30 minutes. Agitate the contents of the bomb several times during the 30 minutes. Analyze the contents of the bomb in the same manner specified under *C₄ Samples Containing More than 2% Olefin*.

CALCULATIONS

Direct Analysis

$$\text{Sulfur, ppm S} = \frac{A \times T}{W_1}$$

where:

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

T = titer of the mercuric acetate solution, γ S/ml

W₁ = sample weight, g

Analyses Involving Blending

$$\text{Sulfur, ppm S} = \frac{(A \times T) - (B)}{W_2}$$

where:

B = sulfur present in the isooctane used, γ in the blend which was reacted with Raney nickel

W₂ = weight of original sample present in the blend reacted with the Raney nickel, g

A and **T** are as defined above

NOTES AND PRECAUTIONS

1. Granatelli (see Reference) 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 objectionable. However, the mercuric acetate solution must be standardized as specified above rather than relying on the normality calculated from the weight of mercuric oxide used.

2. Be certain that the sample is withdrawn from the liquid phase in the sample storage container, *not* from the gas phase.
3. Take care not to scratch the glass bomb, thereby avoiding strains which may develop and tend to weaken the glass.
4. Place a safety shield in front of the apparatus when desulfurizing the sample.
5. Procedures listed in the method are for extreme cases. When samples, which contain olefin in addition to C₃, are to be analyzed the analyst must use his discretion as to the method of blending the sample.

PRECISION

The following data should be used for judging the acceptability of results:

<u>Type of Sample</u>	<u>Lower Limit of Detection, ppm S</u>	<u>Range, ppm S</u>	<u>Repeatability, ppm S</u>
C₄, 0-2% Olefin	0.2	0.2-10	0.2
		10-100	1
		100-500	4
C₄, 100% Olefin	20	20-500	30
C₃	2	2-500	5

It is believed that when liquefied gases contain olefin concentrations of less than 100%, the lower limit of detection and the repeatability will decrease correspondingly. However, no experimental work has been done to confirm this.

REFERENCE

Granatelli, L., *Anal. Chem.*, **31**, 434 (1959)