



A Honeywell Company

Laboratory Hydrogen Sulfide and Mercaptan Extraction

UOP Method 547-13

Scope

The purpose of this method is to remove hydrogen sulfide, and to reduce the mercaptan content, in hydrocarbons that are liquid at room temperature by extraction with sodium hydroxide under standardized conditions. The treated distillate may be processed further in a pilot plant or tested for properties other than hydrogen sulfide and mercaptan content. Such additional processing or testing is beyond the scope of this method.

The results obtained by this method can also be correlated empirically with results from a commercial extractor as a check for extractor performance. When the characteristics of a given extractor are known in terms of this test, this procedure can be used to estimate results to be expected when extracting a new stock. This type of correlation is also beyond the scope of this method.

References

ASTM Method D5191, "Vapor Pressure of Petroleum Products (Mini Method)," www.astm.org

UOP Method 41, "Doctor Test for Petroleum Distillates," www.astm.org

UOP Method 163, "Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons," www.astm.org

Outline of Method

The hydrocarbon sample is extracted under a nitrogen atmosphere with a sodium hydroxide solution in a batchwise operation. The extraction can be performed at room temperature, or at higher temperatures, to simulate commercial extractor conditions. Additional extractions of the same sample are made after draining the used sodium hydroxide and repeating with a fresh batch of sodium hydroxide. The raw and treated samples at all extraction stages are tested for hydrogen sulfide and mercaptan content. Finally, the extracted sample is water-washed to remove any residual caustic.

Apparatus

References to suppliers and catalog numbers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise.

Adapter, gas inlet, Reliance Glass, Cat. No. R-1101-100

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) 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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Bath, water, Fisher Scientific, Cat. No. 15-462-2Q

Centrifuge, general purpose, Fisher Scientific, Cat. No. 75-004-241 with rotor, Cat. No. 75-003-607, and adapter, Cat. No. 75-003-792

Chromatographic column, glass, with removable Teflon stopcock and replaceable glass tip, 300-mm long, 22-mm ID, VWR Scientific, Cat. No. 21503-123

Condenser, reflux Dewar, Reliance Glass, Cat. No. R-2909-100

Cylinders, graduated, Class B, 250-, 500-, and 2000-mL, Fisher Scientific, Cat. Nos. 08-550F, -550G, and -550J, respectively

Flask, round bottom, 2000-mL, stopcock on bottom, Teflon stopcock plug, Reliance Glass, Cat. No. R-3990T-206

Heating mantle, bottom opening for 2000-mL flask, Reliance Glass, Cat. No. R-9020-104

Marker, local supply

Pipet, Class B, 100-mL, Fisher Scientific, Cat. No. 13-650U

Pipet filler, Fisher Scientific, Cat. No. 31-681-102A

Regulator, nitrogen, two-stage high purity, 0-200 kPa (0-30 psi), Matheson Tri-Gas, Model 3121-580. Set the output pressure at not more than 35 kPa (5 psig) to avoid overpressuring the glassware.

Stirrer blade, Teflon, Reliance Glass, Cat. No. R-6040T-100

Stirrer, Fisher Scientific, Cat. No. 14-500-214

Stirrer, shaft adapter, universal joint, Reliance Glass, Cat. No. R-6118-010

Teflon sleeve, to fit the 2000-mL round bottom flask ground joints, Reliance Glass, Cat. No. R-8100-118, 3 required

Temperature controller, Fisher Scientific, Cat. No. 13-931-12

Thermometer, -20 to 110°C, Fisher Scientific, Cat. No. 15-160-20

Timer, benchtop, Fisher Scientific, Cat. No. 06-662-51

Reagents and Materials

References to suppliers and catalog numbers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise. References to water mean deionized or distilled water.

Bottle, glass, 125-mL, Fisher Scientific, Cat. No. 02-911-784

Bottle, glass, 1.9-L, Fisher Scientific, Cat. No. 02-991-895

Bottle, polypropylene, 2-L, Fisher Scientific, Cat. No. 02-924A

Centrifuge tubes, 250-mL, polypropylene, Fisher Scientific, Cat. No. 05-538-53

Cotton, absorbent, Fisher Scientific, Cat. No. 07-886

Dry ice, crushed, local supply

Ice, water, local supply

Isopar M, Fisher Scientific, Cat. No. NC9872259

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Sodium hydroxide, 50% mass/mass, Fisher Scientific, Cat. No. SS410-4

Sodium hydroxide, 15% mass/mass. Add, slowly, 300 g of the 50% sodium hydroxide to a 2-L polypropylene bottle containing 700 g of water while cooling on wet ice. Invert several times to mix thoroughly.

Stoppers, to fit sample transfer apparatus, Figure 2, and sample containers

Tubing, Teflon, Nalgene, 25 feet, 6.4-mm OD, Fisher Scientific, Cat. No. 14-176-179

Water, deionized or distilled

Procedure

The analyst is expected to be familiar with general laboratory practices and the equipment being used. Dispose of all reagents, materials, and samples in an environmentally safe manner according to local regulations.

In both *Procedures A and B*, a minimum of four extractions is recommended. However, more extractions may be done at the direction of the customer. All of the following operations (*Procedures A and B*) must be performed in a properly operating fume hood.

A. Extraction at Room Temperature

1. Set up the apparatus as shown in Figure 1. Use Teflon sleeves to seal the ground glass joints. Mark the flask at 1.6 L, liquid volume.
2. Fill approximately two thirds of the condenser with dry ice. Slowly add approximately 50 mL of Isopar M to the condenser. Do not exceed the condenser capacity.
3. Purge the empty flask with a flow of nitrogen for 2 to 5 minutes.
 - This will remove air from the flask.
 - Ensure that the outlet pressure of the nitrogen regulator does not exceed 35 kPa (5 psig) to prevent overpressuring any glassware in the event of a blockage.
4. Reduce the nitrogen to a gentle flow for the following operations.
5. Transfer approximately 1.6 L of the sample into the flask through the condenser joint (remove condenser first). Ensure an air-free transfer of the sample, see Figure 2.
 - If light hydrocarbons are present, the sample should be chilled prior to the transfer step. Once transferred, the sample should be allowed to reach room temperature before extraction with the sodium hydroxide.
6. Add, by graduated cylinder, 160 mL of 15% sodium hydroxide solution to the flask containing the sample through the nitrogen inlet.
 - Do not stop the nitrogen purge, simply loosen the connection and add the sodium hydroxide solution slowly.
7. Turn the stirrer on and stir at full speed for ten minutes.
 - The stirrer should achieve a strong vortex without excessive splashing.
8. Allow the mixture to settle until there is a distinct phase separation.
9. Open the stopcock at the bottom of the flask. Drain and discard the caustic layer.

10. Remove, by pipet, 100 mL of the hydrocarbon layer for the doctor test (UOP Method 41, "Doctor Test for Petroleum Distillates") and mercaptan sulfur determination (UOP Method 163, "Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons"). Transfer to a nitrogen purged sample bottle.
 - If the 100-mL hydrocarbon sample is turbid, it may be necessary to centrifuge the sample to remove entrained caustic prior to performing UOP Method 163.
11. Repeat the extraction three more times (or as many times as requested) with a fresh batch of caustic followed by separation and analysis as described in Steps 6 through 10. Maintain a constant ratio of sodium hydroxide to sample during all extractions. For example, since 100 mL of the hydrocarbon sample were removed after the first extraction, the amount of sodium hydroxide to be used for the second extraction should be 150 mL.
12. After the final caustic extraction, wash the hydrocarbon layer by adding 400 mL of water to the flask containing the hydrocarbon sample.
13. Turn the stirrer on and stir for five minutes.
 - The stirrer should achieve a strong vortex without excessive splashing.
14. Allow the mixture to settle until there is a distinct phase separation.
15. Open the stopcock at the bottom of the flask. Drain and discard the aqueous layer.
16. Purge the chromatographic column packed with 90 mm of the absorbent cotton with nitrogen. Filter the hydrocarbon layer using the chromatographic column packed with 90 mm of the absorbent cotton. Collect the sample in a nitrogen purged glass bottle.
 - If the sample contains light hydrocarbons, the nitrogen purged glass bottle should be placed in a wet ice bath to collect the filtered sample.
 - To ensure that there has been adequate protection against air oxidation of mercaptans, determine the total sulfur on the raw distillate sample and on the sample after the final stage of washing. If the total sulfur depletion does not correspond with the disappearance of the hydrogen sulfide and mercaptan sulfur, repeat the extraction, ensuring that air is excluded.
 - The sample is now ready for inspection tests or further processing.

B. Extraction Above Room Temperature

When this method is used to compare results with a commercial extractor, the temperature of the contents of the flask should be adjusted to approximately the same temperature that prevails in the commercial extractor. This procedure was found satisfactory, when extracting at 37°C, a light straight-run gasoline having an initial boiling point of 41°C and a Reid vapor pressure of 68 kPa. This procedure is not used for extracting pentane or lighter fractions. The customer designates the number of extractions to be performed and the temperature.

1. Set up the apparatus as described in *Procedure A*, Steps 1 through 4, and place a heating mantle under the flask shown in Figure 1.
2. Add the hydrocarbon sample as described in *Procedure A*, Step 5, and heat to the requested temperature while stirring slowly. Check the temperature periodically until it levels off at the desired temperature.
 - The sample should be chilled prior to Step 2 if light hydrocarbons are present.
 - A thermometer can be used to check temperature by loosening the gas inlet and inserting the thermometer.
3. Measure 160 mL of the sodium hydroxide solution into a 250 mL graduated cylinder. Immerse the graduated cylinder containing the sodium hydroxide in a hot water bath and allow it to warm to a few degrees above the extraction temperature.

- This allows for heat loss when measuring the caustic solution.
4. Add the warm sodium hydroxide solution to the flask containing the sample through the nitrogen inlet and repeat *Procedure A*, Steps 7 through 16.
 - Do not stop the nitrogen purge, simply loosen the connection and add the sodium hydroxide solution slowly.

Precision

Based on a limited number of replicate extractions made on several sour gasolines, which did not require chilling or special handling, the mercaptan sulfur values on duplicate sample extractions, at each stage of sodium hydroxide washing should not differ by more than the following:

Table Mercaptan Sulfur by UOP Method 163, mass-ppm	
<u>Range</u>	<u>Allowable Difference</u>
1-10	1.0
10-50	1.5
50-100	3.0
100-1000	3 to 15

Based on the mean range for 18 pairs, representing seven stages of extraction, the estimated standard deviation was calculated to be 0.29 mass-ppm (average over the range).

Time for Analysis

The elapsed time for the extraction will vary according to the ease of separating the aqueous-hydrocarbon emulsion. The labor requirement for a three stage extraction is four hours.

Suggested Suppliers

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700,
www.mathesontrigas.com

Reliance Glass Division, Wilmad/Lab Glass, 1455 Elmhurst Rd., Elk Grove Village, IL 60007,
USA, 1-847-228-2851, www.lab-glass.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

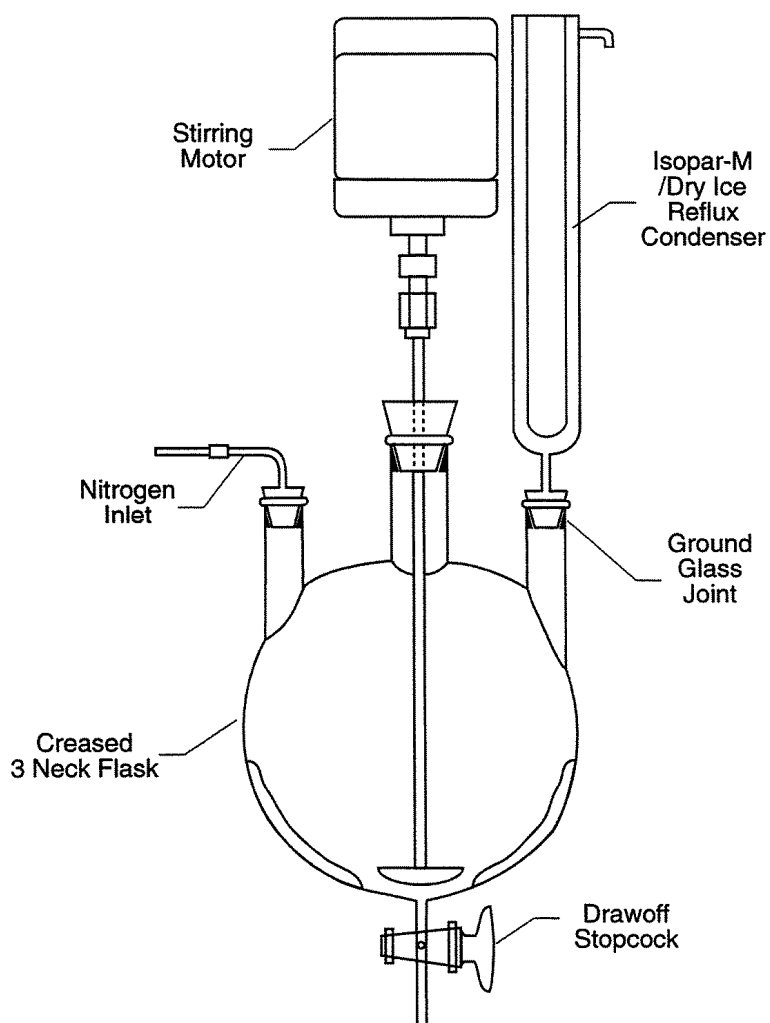


Figure 1
Stirred Contactor

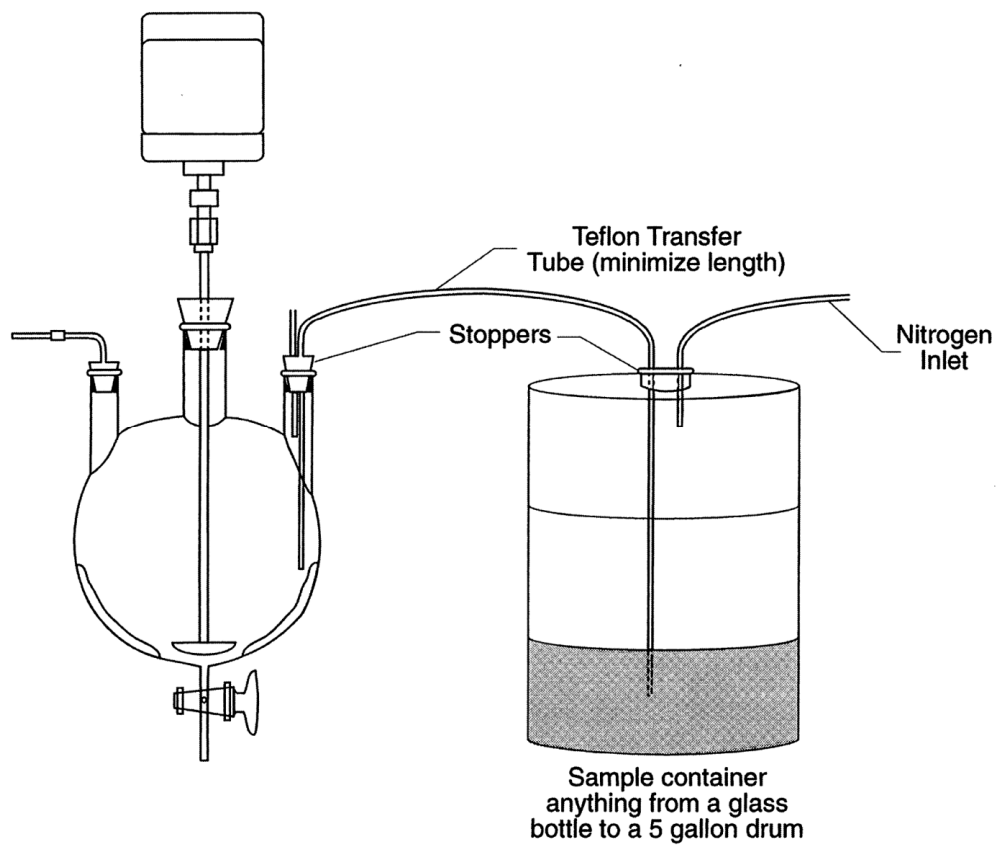


Figure 2
Air-Free Sample Transfer Apparatus