



Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration

UOP Method 163-10

Scope

This method is for determining hydrogen sulfide and mercaptan sulfur in hydrocarbons by potentiometric titration. Typical samples include gasoline, naphtha, light cycle oils and similar distillates that are liquid at ambient temperature and pressure. The lower limit of quantitation is 0.2 mass-ppm mercaptan (as sulfur) and 1.0 mass-ppm hydrogen sulfide (as sulfur).

References

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

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The liquid hydrocarbon sample is weighed into 2-propanol containing a small amount of ammonium hydroxide. The solution is titrated potentiometrically with alcoholic silver nitrate using a glass reference and silver-silver sulfide indicating electrode system. Hydrogen sulfide and mercaptan sulfur concentrations are calculated as mass-ppm. Free sulfur complicates the potentiometric curve, and instructions are given for interpreting the curve when free sulfur is present.

Apparatus

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

Balance, readability 0.1-mg

Beaker, Berzelius, tall form, 400-mL, Fisher Scientific, Cat. No. 10-310-9

Beakers, electrolytic, 250-mL, Brinkmann Instruments, Cat. No. 020212209, available from Metrohm USA, two or more required

Cleaning pad, synthetic, mildly abrasive, Scotch-Brite™, Runco Office Supply, Cat. No. MMM-96

Cylinder, graduated, 100-mL, Class B, VWR, Cat. No. 89000-270

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Desiccator, 160-mm ID, and porcelain plate, VWR, Cat. Nos. 25035-005 and 89038-068, respectively

Electrode, combination silver/glass Titrode™, 6.0430.100, Brinkmann Instruments, Cat. No. 020948507, available from Metrohm USA. The electrode should be dedicated to sulfur analysis.

Flasks, volumetric, Class A, 500-mL, VWR, Cat. No. 89090-748, two required

Pipets, volumetric transfer, Class A, 1-, 8-, and 50-mL, VWR, Cat. Nos. 89045-056, -070, and -086, respectively

Regulator, nitrogen, two-stage, high-purity, delivery pressure range 15-200 kPa (2-30 psi), Matheson Tri-Gas, Model 3121-580

Rubber bulb-type pipet filler, VWR, Cat. No. 53502-205

Titration, potentiometric, recording, ± 2000 -mV range, 1-mV resolution, capable of reducing the titration rate to a minimum in the vicinity of the endpoint, with dispenser having a volume readout of 0.00 - 99.99 mL, 0.0001 of the buret volume resolution, Metrohm Model 836 Titrand system with optional sample changer, and two 20-mL burets, Brinkmann Instruments, Metrohm USA

Automatic titration using the titrator is recommended. However, titration can be performed manually using the following equipment.

Buret, 50-mL, Class A, with PTFE stopcock, VWR, Cat. No. 89001-624

pH meter, digital, Mettler Toledo, Model S20K, VWR, Cat. No. 11238-592

Stirrer, magnetic, with stir bar, VWR, Cat. No. 12365-380

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Unqualified references to solutions mean aqueous solutions.

Ammonium hydroxide, 28.0-30.0 mass-% NH₃, Certified ACS Plus grade, Fisher Scientific, Cat. No. A669-212

Desiccant, 8-mesh, indicating, Drierite, VWR, Cat. No. 22891-028

Detergent, LiquiNox, VWR, Cat. No. 21837-005

Nitrogen, high purity, 99.99%

Paper, test, lead acetate, strips in vials, VWR, Cat. No. 60792-009

2-Propanol, Certified ACS grade, VWR, Cat. No. VW5520-3. Purge with nitrogen for 10 to 15 minutes before using.

Silver nitrate, 0.1000-N solution, VWR, Cat. No. VW3214-2

Silver nitrate, alcoholic solution, 0.0100-N. Prepare a 0.0100-N alcoholic silver nitrate solution by pipetting 50 mL of the standardized 0.1000-N solution into a 500-mL volumetric flask. Dilute to the mark with 2-propanol, cap and invert several times to mix thoroughly. This solution is stable for two months, after which a new solution is prepared.

Silver nitrate, alcoholic solution, 0.0010-N. Prepare a 0.0010-N alcoholic silver nitrate solution by pipetting 50 mL of the standardized 0.0100-N solution into a 500-mL volumetric flask. Dilute to

the mark with 2-propanol, cap and invert several times to mix thoroughly. This solution is stable for two months, after which a new solution is prepared.

Sodium sulfide nonahydrate, VWR, Cat. No. EM-SX0770-1

Sodium sulfide nonahydrate, 1% solution. Dissolve $1.0 \text{ g} \pm 1.0 \text{ mg}$ of sodium sulfide in 100 mL of water.

Toluene, 99.8% minimum purity, VWR, Cat. No. AA43061-K2. Purge with nitrogen for 10 to 15 minutes before using.

Water, deionized or distilled

Wipers, Kimwipes Ex-L, VWR, Cat. No. 21905-026

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of titration, and with the equipment being used.

Electrode Preparation

1. Prepare the silver electrode by cleaning the surface of the silver band on the electrode with a mild detergent. Prepare this electrode fresh daily or as required.
 - Proper electrode preparation is essential to obtain reproducible and noise-free titration curves having good distinguishable endpoints.
2. Rinse the electrode with water and wipe dry with a wiper.
3. Polish the surface of the electrode gently with a cleaning pad until the surface is smooth to the touch.
4. Rinse the electrode with water again and wipe dry with a wiper.
5. Immerse the electrode in a solution consisting of 1 mL of concentrated ammonium hydroxide, 96 mL of 2-propanol and 8 mL of 1% aqueous sodium sulfide solution. Add slowly from a buret over a period of about 10 minutes, with stirring, approximately 10 mL of 0.0100-N alcoholic silver nitrate solution. A film of silver sulfide will be deposited on the silver. Wipe off the excess silver sulfide on the electrode with a wiper.
 - The automatic titrator may be used instead of the buret, titrating a minimum of 10 mL of titrant.
 - During the titration of samples containing sulfide, the electrode will be coated with Ag₂S. It is necessary to repeat the electrode preparation when the coating begins to peel, becomes rough and uneven, or if the titration curves become noisy.
 - To remove any residue from previous titrations, it is good practice to dip and swirl the electrode in mild detergent and rinse with water at the beginning of each set of samples. This aids in keeping the titration curves noise free and reduces the chance of the appearance of false endpoints.

Titration of Sample

Mercaptans oxidize easily. It is important that samples are handled quickly in order to minimize their exposure to air. Titrate samples immediately after they are pipetted while covering the beaker with a nitrogen blanket during the analysis.

1. Prepare the titrator for operation with the proper electrode in place and with the appropriate molarity alcoholic silver nitrate solution (see Table 1) as the titrant. Set the operating parameters on the instrument to reduce the rate of titrant addition in the vicinity of the endpoints.

2. Before titrating, check the contents of the sample qualitatively for hydrogen sulfide by suspending lead acetate paper in the vapor space above the sample.
 - Moisten a piece of lead acetate paper with water and fasten one end of the paper to the stopper of a bottle containing the sample. Do not allow the paper to contact the hydrocarbon sample. Allow it to stand for about one minute.
 - If the paper turns silver-black, hydrogen sulfide is present, and the test is positive. This test is sensitive to approximately 1 mass-ppm of hydrogen sulfide. Some mercaptans will cause lead acetate paper to darken with a tan to yellow coloration. This is not to be confused with a positive hydrogen sulfide test.
 - The Doctor Test, UOP Method 41, "Doctor Test for Petroleum Distillates," may be run for confirmation if the lead acetate paper test is difficult to read.
3. Add the recommended volume of 2-propanol to the appropriate size beaker (see Table 1). Add approximately 1 mL of concentrated ammonium hydroxide.
4. Weigh a portion of the sample, to the nearest 0.1-mg, into the beaker while maintaining the solution under a nitrogen blanket. Use Table 1 as a guide in selecting the proper sample size.
 - The sample size should be selected according to Table 1 to give a titration of at least 2 mL. When the sample contains more than 500 ppm sulfur, select a sample size sufficient to give a 5- to 10-mL titration.
 - If the sample is insoluble in the 2-propanol, add enough nitrogen-purged toluene to the beaker containing isopropyl alcohol to obtain a solution.
 - Solutions containing high levels of mercaptans and low levels of hydrogen sulfide are titrated separately for the two components. A sample is titrated as above to the mercaptide endpoint, and then a larger sample is titrated only to the hydrogen sulfide endpoint. The mercaptan concentration is determined by difference between concentration determined from the total titration to the mercaptide endpoint, and the hydrogen sulfide concentration determined from the larger sample.
 - If the ratio of sulfide sulfur to mercaptan sulfur is greater than 10:1, then the mercaptan result is considered to be qualitative because the H₂S endpoint overshadows the mercaptan endpoint.

Table 1
Selection of Equipment, Reagents, and Sample Volumes

<u>Expected mercaptan concentration, ppm, S</u>	<u>Beaker size, mL</u>	<u>2-Propanol, mL</u>	<u>Suggested sample mass, g</u>	<u>Normality of Titrant, N</u>
0.5-1	400	150	100	0.001
1-100	250	100	50	0.01
100-300	250	100	10	0.01
300-500	250	100	5	0.01

5. Add a stirring bar, and place the beaker in the titration apparatus. Insert the electrode and stir, covering the solution with a nitrogen blanket to prevent mercaptan oxidation. Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center. Titrate with the alcoholic silver nitrate solution, manually or automatically depending on the equipment available. Observe the respective inflections and note the corresponding volumes of titrant.
 - If the titration is to be performed manually, add the silver nitrate solution in 1-mL increments, recording the volume and emf after each addition. Near the endpoints, add the silver nitrate solution in 0.1-mL increments. Allow enough time for the titration cell to reach equilibrium before recording the volume of silver nitrate solution and the emf. The endpoints are found where the rate of change in potential with respect to the volume of added titrant is a maximum.
 - Plot the titration data as emf vs. volume of silver nitrate solution. Estimate the mid-point of each inflection by inspecting the titration curve. Alternatively, the endpoints may be determined by

examining the titration data for the emf/mL maxima, thereby obviating the task of plotting the data. This procedure can be followed by an experienced operator.

Interpretation of Titration Curves

The Figure shows titration curves that can be obtained for gasolines having different ratios of hydrogen sulfide, mercaptan and free sulfur (including polysulfides). Curve A is an example of a titration where only hydrogen sulfide is present. Curve B is an example of a titration where only mercaptan is present. Curve C is an example of a titration where both hydrogen sulfide and mercaptan are present. Curves A, B, and C are the titration curves most commonly encountered.

When free sulfur is present in the sample, it reacts with some of the mercaptan forming polysulfide, the titration of which complicates the interpretation of the titration curve. Curve D is an example of a titration where free sulfur has reacted with a portion of the mercaptan to form polysulfide and, thus, three inflections are observed: hydrogen sulfide, polysulfide and the remaining mercaptan. Curve E is an example of a titration where the free sulfur has reacted with a portion of the mercaptan to form a polysulfide but no hydrogen sulfide was present and, thus, only two inflections are observed: the first for polysulfide and the second for mercaptan.

- Disulfides do not show an inflection.

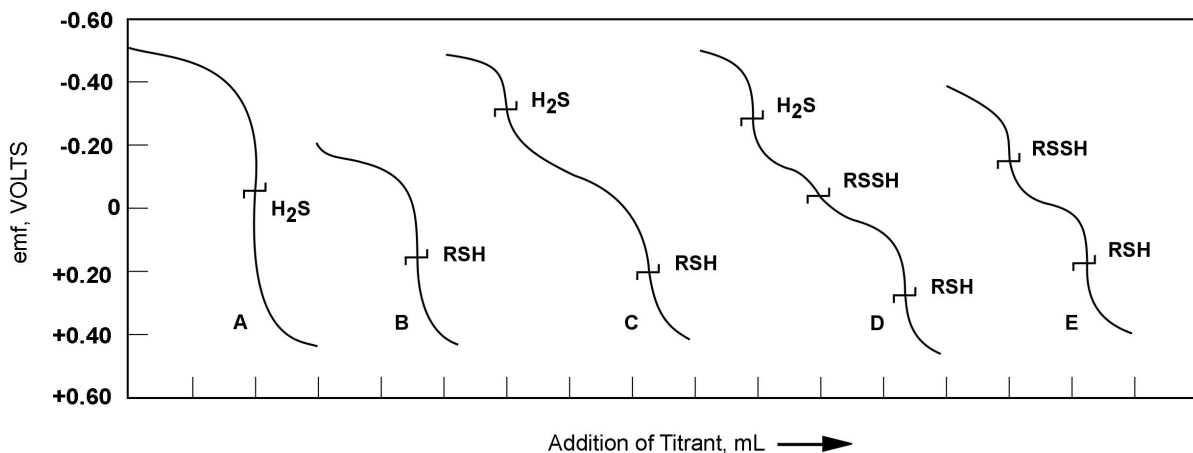


Figure
Potentiometric Titration Curves
of Sulfur Species in Gasoline

One Inflection (Curve A or B)

When the lead acetate test is positive for hydrogen sulfide and only one inflection occurs, the only species present is hydrogen sulfide (Curve A). The hydrogen sulfide content is determined from the total titration, from zero volume to the inflection point.

When the lead acetate test is negative, the only species present is mercaptan (Curve B). The mercaptan content is determined from the total titration, from zero volume to the inflection point.

Two Inflections (Curve C or E)

When there are two inflections and the lead acetate test is positive, the first inflection is hydrogen sulfide, and the second inflection is mercaptan (Curve C). The hydrogen sulfide content is determined from the volume of titrant from zero volume to the first inflection point. The mercaptan

content is determined from the volume of titrant used from the first inflection point to the second inflection point.

When the lead acetate test is negative, and the absence of H₂S is confirmed by UOP Method 41, Doctor Test, disregard the first inflection point. The mercaptan content is determined from the total titration, from zero volume to the second inflection point (Curve E).

Three Inflections (Curve D)

When there are three inflections, and the lead acetate test is positive, the first inflection point is hydrogen sulfide. Disregard the second inflection point. The mercaptan content is determined from the volume of titrant from the first inflection point to the third inflection point.

Three inflections are not normally seen when the lead acetate test is negative. Verify the sulfur types in the sample using UOP Method 41, Doctor Test, and check the equipment for proper operation.

Calculations

Calculate the concentration of hydrogen sulfide and mercaptan, as sulfur, using Equations 1 and 2, respectively. Report the results to the nearest 1 mass-ppm unless the 0.001-N titration solution was used and the result is less than 1 mass-ppm. Then report to the nearest 0.1 mass-ppm.

$$\text{Hydrogen sulfide, as S, mass-ppm} = 10^3 \frac{16AN}{W} \quad (1)$$

$$\text{Mercaptan, as S, mass-ppm} = 10^3 \frac{32(B - A)N}{W} \quad (2)$$

where:

A = volume of silver nitrate solution used to reach the sulfide ion endpoint, mL

B = volume of silver nitrate solution used to reach the mercaptide ion endpoint, mL

N = normality of the alcoholic silver nitrate solution, moles/L

W = mass of sample, g

16 = molecular weight of sulfur divided by 2, the number of reactive hydrogen sites in hydrogen sulfide

32 = molecular weight of sulfur divided by 1, the number of reactive hydrogen sites in mercaptan

10³ = factor to convert L to mL and g/g to µg/g

Notes

1. Whenever there is a question regarding the identity of an inflection point, it is advisable to verify the sulfur types in the sample using the lead acetate paper or the Doctor Test.
2. Hydrogen cyanide, if present, titrates with two inflection points and may cause confusion in the interpretation of the titration curves. Generally, the mercaptan inflection is observed between the two cyanide inflections.
3. Some recording titrators will produce a small inflection that occurs a few seconds after the titration is begun. This has been attributed to electrode conditioning and is not to be interpreted as a hydrogen sulfide inflection point. To distinguish between this phenomenon and a true hydrogen sulfide inflection point, repeat the titration with twice the sample volume. If the inflection is due to hydrogen sulfide, the titration volume will double.

Precision

Precision statements were determined using UOP Method 999, from precision data obtained using a Brinkmann Metrohm Model 751GPD Titrino titrator with an automatic sample changer.

Repeatability and Intermediate Precision

A nested design was carried out for determining mercaptan in two samples with two analysts in one laboratory. The two analysts carried out tests on the two samples on two separate days, performing two tests on each sample each day. The total number of tests at each concentration was eight. In addition, one analyst in one laboratory performed eight replicate analyses on each of two low-level mercaptan samples. The precision data are summarized in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

Table 2
Repeatability and Intermediate Precision, mass-ppm

<u>Component</u>	<u>Mean Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Mercaptan	5	0.23	1.0	0.25	0.9
Mercaptan	303	1.4	5.4	1.7	6.7
Mercaptan	0.6	0.023	0.08		
Mercaptan	1.0	0.026	0.09		

The data in Table 2 are a short term estimate of repeatability and site precision. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long term intermediate precision.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time and labor requirements are identical, 0.3 hour.

Suggested Suppliers

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

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Metrohm USA, 6555 Pelican Creek Circle, Riverview, FL 33578 (813-316-4700)
www.metrohmusa.com

Runco Office Supply, 1655 Elmhurst Road, Elk Grove Village, IL 60007 (847-437-4300)
www.runcoonline.com

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