

PHENOLS IN LIGHT DISTILLATES BY DIRECT TITRATION

UOP Method 729-76T

SCOPE

This method is for determining phenols and hindered phenols in petroleum fractions up to and including No. 2 distillates; e.g., gasolines, naphthas, kerosines, jet fuels, No. 1 fuels and No. 2 fuels. The procedure gives nicely defined titration curves and endpoints on samples up to No. 1 distillate, but No. 2 oils sometimes give titration curves with ill-defined endpoints. There is no way to predict this behavior, so the analyst must simply try it on the sample.

Phenols as hindered as butylhydroxytoluene (BHT) can be titrated directly using this method. Provision is included to overcome the acidity of mercaptans and thiophenols via a mild oxidation to the corresponding disulfides.

This method overlaps UOP Method 262, **PHENOLS AND THIOPHENOLS IN PETROLEUM PRODUCTS BY SPECTROPHOTOMETRY**, which can be used with accuracy on gasolines and on refinery caustic solutions.

OUTLINE OF METHOD

The sample is shaken with a copper sulfate-sodium chloride solution in the presence of air to oxidize thiophenols and alkyl mercaptans to the corresponding disulfides. This step is necessary since thiophenols are acidic enough to be titrated in *Procedure A* and mercaptans are acidic enough to be titrated in *Procedure B* and thereby either constitutes an interference. Following this sweetening step the oil is filtered and titrated by both *Procedure A* and *Procedure B*.

Procedure A, for the determination of “strong acidity”: The sample is titrated with alcoholic potassium hydroxide, using a recording titrator, to a potentiometric endpoint. The volume of titrant used is read from the chart and the acidity calculated as meq/g of sample.

Procedure B, for the determination of total acidity including phenols: The sample is titrated with tetrabutylammonium hydroxide, using a recording titrator, to a potentiometric endpoint. The total acidity is calculated as meq/g of sample.

Weak acidity is then determined by difference – i.e., total acidity minus strong acidity equals weak acidity – and calculated as phenol, wt - ppm oxygen.

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).

APPARATUS

Common to Procedures A and B

Beaker, titration, 250-ml

Cylinder, graduated, 100-ml

Filter paper, acid-free. *Do not* use acid-washed paper. Whatman No. 4 is satisfactory.

Flask, Erlenmeyer, 500-ml

Flask, volumetric, 100-ml

Funnel, separatory, 250-ml

Potentiometric titrator. Vacuum tube, automatic chart type with a 5-ml or smaller buret. A Metrohm E 336 or equivalent is satisfactory but a manual titrator *cannot be substituted*. Available from Brinkman Instrument Co., Cantiague Road, Westbury, NY 11590.

Stirrer, magnetic

Stirring bars, Teflon-coated

Exclusive to Procedure A

Electrode, combination (glass/calomel), Metrohm EA120UX or equivalent with aqueous potassium chloride electrolyte bridge. Available from Brinkman Instrument Co.

Exclusive to Procedure B

Adapter, EA857, for use with Beckman electrodes and Metrohm titrators, if needed. Available from Brinkman Instrument Co.

Electrode, Beckman probe type, combination (glass/calomel), having No. 39183 or equivalent electrode with a linen membrane. Use saturated potassium chloride in methanol as a non-aqueous solvent bridge in the outer jacket of electrode. Age the electrode by soaking it in a saturated solution of potassium chloride in methanol, refilling the outer jacket as necessary. Available from Beckman Instrument, Inc., P.O. Box 6100, Anaheim, CA 92806.

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.

Common to Procedures A and B

Benzoic acid, primary standard grade, available from the National Bureau of Standards, Office of Standard Reference Materials, Room B-311, Chemistry Bldg., Washington, DC 20234, or equivalent. Used for standardizing alcoholic potassium hydroxide and tetrabutylammonium hydroxide.

Copper-sweetening reagent. Dissolve 140 g of sodium chloride and 150 g of copper sulfate in a liter of water.

Potassium chloride, reagent grade

Exclusive to Procedure A

Buffer, nonaqueous, basic. Accurately weigh 2.78 ± 0.01 g of *m*-nitrophenol and transfer it to a 100-ml volumetric flask containing 10 ml of isopropyl alcohol. While continuously stirring, add 10 ml of 0.1 *N* alcoholic potassium hydroxide solution and 5 ml of water. Dilute to the mark with isopropyl alcohol and mix well.

Note: This buffer is used only to secure a workable setting on the titrator (for standardizing the potassium hydroxide or titrating the sample in Procedure A) in the following manner. Add 10 ml of buffer solution to a mixture of 50 ml of benzene and 50 ml of isopropyl alcohol in a titration beaker. Place on the titrator and set the meter at pH 9.0 with the buffer solution in place against the electrodes. As the operator becomes more familiar with the method, this buffer step may be eliminated.

Electrolyte bridge solution, saturated solution of potassium chloride

Isopropyl alcohol

Phenolphthalein, 1% alcoholic solution

Potassium hydroxide, alcoholic solution, 0.100 *N*. Obtainable from Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219. Standardize to 0.0001 *N* against benzoic acid. Protect the solution against contamination by carbon dioxide by storing in a container equipped with a drying tube containing Drierite or Ascarite. To standardize, weigh between 0.5 and 0.6 g of dry benzoic acid to the nearest 0.1 mg into a clean, dry 100-ml volumetric flask. Dissolve and dilute to the mark with a 10% solution of isopropyl alcohol in carbon dioxide-free water. Pipet a 10-ml aliquot into 100 ml of the 10% isopropyl alcohol and titrate to the endpoint potentiometrically. Determine a possible solvent blank by titrating 100 ml of the 10% solvent. Calculate the normality of the potassium hydroxide as:

$$\text{Normality of KOH, } N_1 = \frac{A}{1.2212 B}$$

where:

A = total weight of benzoic acid in 100-ml of stock solution, g

B = volume of potassium hydroxide used in titrating (blank corrected), ml

Exclusive to Procedure B

Benzene

Electrolyte bridge solution, methanol saturated with potassium chloride

Methanol, in wash bottles. Use to wet the electrode junction between titrations and as nonaqueous electrolyte solvent.

Pyridine

Tetrabutylammonium hydroxide, 0.03 molar. Dilute 3 ml of 1.0 molar methanol solution of tetrabutylammonium hydroxide (TBAH) to 100 ml with benzene. Standardize daily to 0.0001 *N* against benzoic acid. The 1.0 molar methanol solution of tetrabutylammonium hydroxide is available from Southwestern Analytical Chemicals, P.O. Box 485, Austin, TX 78767. To standardize, weigh between 0.1 and 0.15 g of dry benzoic acid to the nearest 0.1 mg into a clean, dry 100-ml volumetric flask. Dilute to volume with benzene and mix well. Pipet 10 ml of the benzoic acid solution into a titration beaker containing 100 ml of titration solvent. Titrate to the first potentiometric endpoint. Determine a possible solvent blank by titrating 100 ml of the titration solvent. Calculate the normality as:

$$\text{Normality of TBAH, } N_2 = \frac{C}{1.2212 D}$$

where:

C = total weight of benzoic acid in 100 ml of stock solution, g

D = volume of TBAH used in titrating to the first endpoint (blank corrected), ml

Titration solvent. Mix equal volumes of benzene and pyridine.

PROCEDURE

Determine the density of the hydrocarbon sample by any convenient means.

Measure approximately 150 ml of the hydrocarbon sample into a 500 - ml Erlenmeyer flask (see Note 1). Add 100 ml of the copper-sweetening reagent, stopper and shake for 30 minutes. Transfer the mixture to a separatory funnel. Let the layers separate, discard the aqueous layer and filter the now copper-sweetened hydrocarbon (see Note 2) through filter paper (see Note 3).

Procedure A. Determination of Strong Acidity

Measure 100 ml of copper-sweetened hydrocarbon (see Note 1) into the graduated cylinder and transfer it to the titration beaker. Add 100 ml of isopropyl alcohol measured in the same graduated cylinder as the sample, 3 ml of water, and a stirring bar. Following the manufacture's instructions for the titrator used, adjust the delivery of titrant to the lowest possible rate – no more than 0.25 ml per minute. Titrate with 0.1 *N* alcoholic potassium hydroxide while stirring moderately. Add a few drops of phenolphthalein indicator to make sure there are no unexpected breaks, as the last straight portion of the titration curve is used as the endpoint. (On some samples the potentiometric endpoint may occur as much as 1.0 pH units after the phenolphthalein color change.) Read the volume of titrant used to the nearest 0.002 ml. Wash the electrode well with water after each titration and dry with a clean paper towel.

Titrate 100 ml of isopropyl alcohol and 5 ml of water in the same manner as for the sample to obtain a solvent blank.

Procedure B. Determination of Total Acidity

Measure 5 to 15 ml of copper-sweetened hydrocarbon into a 250-ml titration beaker and add 100 ml of titration solvent. Do *not* add phenolphthalein. Wet the linen membrane of the electrode with methanol and remove the excess by touching it to a soft tissue.

Place the beaker on the titrator and immerse the electrode and delivery tip. Using a stirring bar, stir gently. Using a range of 0 → 1500 mv (full scale) titrate slowly (0.2 ml/minute) with TBAH until the break at 940 to 1020 mv is obtained. The break or equivalence point is usually heralded by the development of a yellow (or sometimes amber) color. This development is usually complete when the break is obtained. Consider the titration complete at about 1050 mv.

Titrate 100 ml of titration solvent in the same manner to obtain the solvent blank.

CALCULATIONS

For Procedure A

$$\text{Strong acidity, meq/g} = \frac{(V_1 - B_1) N_1}{SG}$$

where:

- B₁** = blank titration for 100 ml of isopropyl alcohol, ml
- G** = density of sample, g/ml
- N₁** = normality of potassium hydroxide titrant, meq/ml
- S** = volume of copper-sweetened sample used for titration, ml
- V₁** = volume of titrant used, ml

For Procedure B

$$\text{Total acidity, meq/g} = \frac{(V_2 - B_2) N_2}{SG}$$

where:

- B₂** = blank titration for 100 ml of titration solvent, ml
- G** = density of sample, g/ml
- N₂** = normality of TBAH titrant, meq/ml
- S** = volume of copper-sweetened sample used for titration, ml
- V₂** = volume of titrant used, ml

For Phenols

$$\text{Phenols, as oxygen, wt-ppm} = 16,000 (X - Y)$$

where:

X = “total acidity” from Procedure B, meq/g

Y = “strong acidity” from Procedure A, meq/g

NOTES AND PRECAUTIONS

1. Because of the possibility of contamination from acid-washed beakers or acid fumes, it is strongly recommended that samples be run in duplicate.
2. Take care to exclude any sweetening reagent from the hydrocarbon sample, since an increased acidity would result.
3. Do *not* use acid-washed filter paper.
4. Proper use and maintenance of the electrode is essential in *Procedure B*; careful attention to details is necessary.
5. The millivolt range for the phenol break is given only as a general guide. In some cases the break may occur at a lower (but never higher) potential.
6. None of the usual acid-base indicators can be added since these will titrate in this system.
7. Rinse the electrode thoroughly with methanol between titrations and wipe with a soft tissue. Wet the linen membrane of the electrode with methanol just prior to the next titration.
8. If, at the start of a titration, erratic behavior of the recording pen occurs, the membrane has probably dried out. Stop the titration and repeat on a fresh sample. Wet the membrane with methanol just prior to the next titration.
9. As with all combination electrodes, always maintain the electrolyte level in the electrode at least one inch above the level of the liquid in the titration beaker. Uncover the filling hole during the titration.
10. When not in use store the electrode in a saturated solution of potassium chloride in methanol.

PRECISION

Based on 4 replicate determinations, duplicate determinations, will probably not differ by more than 5 ppm at the 40-ppm level.

TIME FOR ANALYSIS

A single determination requires 2.0 man-hours. The total elapsed time for a single determination is 2.5 hours.

REFERENCES

Buell, B. E., *Anal. Chem.* **39**, 762 (1967)

Cundiff, R. H., and Markunas, P. C., *Anal. Chem.* **28**, 792 (1956)

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