ASTM INTERNATIONAL

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Standard Test Method for
Acid Number of Crude Oils and Petroleum Products by Catalytic Thermometric Titration[1]

This standard is issued under the fixed designation D8045; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of acidic components in crude oil and petroleum products including waxes, bitumen, base stocks, and asphalts that are soluble in mixtures of xylenes and propan-2-ol. It is applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9}; extremely weak acids whose dissociation constants are smaller than 10^{-9} do not interfere. The values obtained by this test method may not be numerically equivalent to other acid value measurements. The range of KOH acid numbers included in the precision statement is 0.1 mg/g to 16 mg/g.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Some specific hazards statements are given in Section 7 on Safety Precautions.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration
D974 Test Method for Acid and Base Number by Color-Indicator Titration
D1193 Specification for Reagent Water
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Terminology

3.1 For general terminology, refer to Terminology D4175.

3.2 *Definitions:*

3.2.1 *acid number, n*—the quantity of a specified base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in a specified solvent to a specified endpoint using a specified detection system.

3.2.2 *catalytic thermometric titration, n*—a method to determine the end point of a chemical reaction through the use a temperature measuring device and the addition of a chemical to enhance the detection of the endpoint.

3.2.3 *crude oil, n*—a naturally occurring hydrocarbon mixture, generally in a liquid state, which may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements.

4. Summary of Test Method

4.1 The sample and a fixed mass of paraformaldehyde are dissolved in a mixture of xylenes and propan-2-ol. The mixture is then titrated with potassium hydroxide using a constant rate of titrant addition. A plot of the temperature of the reaction mixture versus the volume of titrant is generated. An exothermic reaction between the titrant and sample occurs simultaneously with the endothermic depolymerization of paraformaldehyde. After all of the acidic material in the sample has reacted, the slope of the plot changes due to the absence of the

competitive exothermic acid-base reaction. The change in slope is the inflection point. The depolymerization of paraformaldehyde is catalytically initiated and does not consume a significant quantity of potassium hydroxide. The net change (positive or negative) in temperature prior to the consumption of the acidic sample will be dependent upon the relative magnitude of the heats of reaction and environmental influences.

5. Significance and Use

5.1 Crude oils and oil sands bitumen contain naturally occurring acidic species. Acidity of crude oil has been implicated in corrosion of distribution and process systems. The relative amount of these materials can be determined by titrating with bases. The acid number is a measure of this amount of acidic substance in the oil under the conditions of the test.

5.2 Acid number of crude and distilled petroleum fractions has been measured by Test Method D664. Test Method D664 was developed for the analysis of lubricants and biodiesel. The titration solvent used in Test Method D664 does not properly address dissolving difficult samples such as crude oil, bitumen, and high wax samples addressed in this test method. Refer to Appendix X1.

5.3 Test Method D974 is also not applicable to measuring acidity of crudes and highly colored samples because the indicator is not visible or it is difficult to discern a color change to detect the end point of the titration.

6. Interferences

6.1 Any material that reacts with potassium hydroxide will interfere and overestimate the amount of acidic material in the sample. In crude oils, bitumens, synthetic crude oils, and subsequent fractions, the constituents that may be considered to have acidic characteristics include inorganic and organic acids, particularly naphthenic acids, phenolic compounds, resins, salts of heavy metals, and acid salts of polybasic acids.

7. Safety Precautions

7.1 Wear chemical resistant gloves. Avoid excessive inhalation of organic vapors and paraformaldehyde (flammable solid) by working in a fume hood when possible. Pre-weighed paraformaldehyde packets should be substituted, if possible, to minimize potential exposures when preparing titration slurry solutions. The titrant solution is corrosive and paraformaldehyde releases small quantities of formaldehyde during depolymerization.

7.2 Consult Safety Data Sheets (SDS) for chemicals listed in this test method for further information.

8. Apparatus

8.1 *Automatic Titrator,* capable of providing a dose rate of 2 mL/min.

8.2 *Thermistor,* a device capable of measuring the temperature to 0.001 °C. The device should be immersed in the titration solvent to a depth recommended by the manufacturer and have a response time of less than 0.3 s.

8.3 *Analytical Balance,* capable of weighing to ±0.1 mg.

8.4 *Burette,* typically less than 20 mL capacity with a guard tube containing adsorbent to retard the rate of titrant reaction with atmospheric carbon dioxide.

8.5 *Constant or Variable Speed Propeller Stirrer,* sufficient to ensure adequate mixing of the sample and titrant.

8.6 *Titration Beaker,* with sufficient volume and made of a material that does not interact with the sample, titrant or titration solvent.

8.7 *Volumetric Dispenser,* capable of consistently delivering desired volume of titration solvent.

9. Reagents

9.1 *Potassium Hydroxide Solution, Standard Alcoholic, (0.1 M)*—Add 6 g of potassium hydroxide (KOH) to approximately 1 L of propan-2-ol. Boil gently for 10 min to dissolve. Allow the solution to stand for two days and then filter the supernatant liquid through a fine sintered-glass funnel. Store the solution in a chemically resistant bottle. Dispense in a manner such that the solution is protected from atmospheric carbon dioxide (CO_2) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbents and such that it does not come into contact with cork, rubber, or saponifiable stopcock grease. Commercially prepared reagent is also suitable. Standardize frequently enough to detect concentration changes of 0.0005 mol/L by standard industry practices or by thermometric titration of known quantities of benzoic acid solution dissolved in n-heptane. See Appendix for details.

9.2 *Propan-2-ol* (anhydrous, also referred to as isopropyl alcohol, >99 % purity).

9.3 *Mixed Xylenes*—(**Warning**—Flammable.) A technical grade of hydrocarbon that includes predominantly o-xylene, m-xylene, p-xylene and lesser quantities of ethyl benzene. The boiling point range is typically 136 °C to 140 °C.

9.4 *Titration Solvent*—Add 250 mL ± 10 mL of anhydrous isopropyl alcohol to 750 mL ± 10 mL of mixed xylenes. Larger quantities of titration solvent can be prepared using volumetric ratios (25:75) of the same proportions. Commercially prepared reagent is also suitable.

9.5 *Toluene,* pre-dissolution solvent (≥99 % purity).

9.6 *Paraformaldehyde (polyoxymethylene)*—(**Warning**—Flammable solid. Harmful if inhaled. Irritant.) Terminated with hydroxyl end groups and in fine-powder form. Fine powder mesh is critical to successful and rapid analysis of the material. Too large mesh reacts slowly, resulting in erroneous results. A sample of paraformaldehyde with greater than 80 % by mass having a mesh size between 100 and 200 was found suitable. Avoid moist, aged, or oxidized reagent.

9.7 *Benzoic acid* (>99.9 % purity).

9.8 *n-heptane* (≥99 % purity).

9.9 *Water*—Type 1 deionized, or higher, as defined by Specification D1193.

9.10 *Titration Slurry with Indicator*—17 g ± 0.5 g of paraformaldehyde are added to one liter of titration solvent.

10. Sampling

10.1 Sampling is defined as all of the steps required to obtain an aliquot representative of the contents of any pipe, tank, or other system and to place the sample into a container for analysis by a laboratory or test facility. Sampling practices are covered in Practices D4057 and D4177.

10.2 The sample should be well homogenized prior to taking an aliquot for testing. Power mixing per Practice D5854 is advised for crude oils that are fluid at room temperature. Manual mixing and warming may be required for more viscous samples.

10.3 For samples that contain more than 10 % entrained water, it is advised to remove the water prior to testing using industry accepted methods. If adding toluene or other solvent to aid in water removal, be sure to correct for the solvent dilution in the hydrocarbon sample weight before analysis.

11. Preparation of Apparatus

11.1 If the burette has not been used within the last 12 h dispense sufficient titrant through the burette to remove air bubbles from the delivery tubing. Ensure that all of the components (that is, stirrer, titrant tubing, thermistor, and so forth) that are to be immersed in the titration solvent are clean and free of acidic or basic contamination.

12. Quality Control

12.1 Measure a quality control sample each day a sample(s) is tested. The quality control sample should be of similar matrix to sample tested. Control charts shall be established and maintained according to generally accepted guidelines. Practice D6299 can be used for this purpose.

13. Procedure

13.1 *Blank Determination:*

13.1.1 The blank value must be <0.1 mL. This is generally the case when high purity propan-2-ol is used. The blank value can be verified. The blank value is determined indirectly. A stable sample with a known acid number is measured using three or more different sample masses. The largest sample size must not use a volume of titrant greater than the volume of the burette.

13.1.2 The volume of titrant must be ≥0.15 mL for all sample masses.

13.1.3 The sample volume in milliliters (y-axis) is plotted versus the sample mass in grams (x-axis). Using the linear equation for the best fit line (R^2 value must be 0.98 or greater), extrapolate to determine the volume of titration solvent that corresponds to a sample size of 0.0 g. See example in Fig. 1.

13.1.4 If the blank value exceeds 0.1 mL, prepare fresh titration solvent, confirm the titrant concentration and repeat the analysis. If the blank is below 0.1 mL, it is not necessary to apply a blank correction factor provided that the sample masses shown in Table 1 are used (see 13.2).

13.2 *Sample Analysis:*

13.2.1 Samples that are very viscous or solid at room temperature (that is, asphalt) shall be heated in an oven (≤120 °C) until the material flows and sample can be stirred to homogenize.

13.2.2 For samples that do not readily dissolve in the slurry, it is permissible to pre-dissolve the sample after weighing by adding in up to 10 mL of toluene or xylenes. In this case, solvent conditions shall be matched if determining the blank value.

13.2.3 Weigh the appropriate amount of sample into the titration beaker. Table 1 shows recommended initial sample size based on expected acid number value. This amount used may be adjusted to accommodate for solubility limitations and to conduct the blank determination. For unknowns, it is advised to start with a 5 g sample size, and adjust sample size as needed for subsequent measurements. The volume of titrant consumed has to be ≥0.15 mL. Titrant volume ≤0.15 mL indicates that additional sample is required, and ≥5.0 mL of titrant suggests less sample is needed.
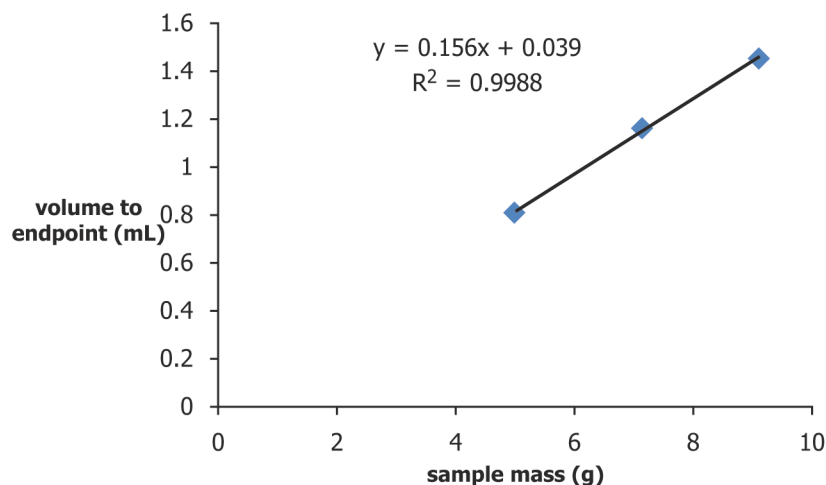
NOTE 1—The above example shows a blank calculation for a sample of crude oil with a KOH acid number of approximately 0.9 mg/g. The blank value is equal to the value of *y* when *x* is set to a value of zero (0.039 mL in this particular example). The software can be configured to calculate the equation and slope automatically.

FIG. 1 Example Blank Calculation for a Sample of Crude Oil

TABLE 1 Recommended Sample Weights

Expected Acid Number (KOH, mg/g)	Recommended Sample Mass (g) ± 10 %
0.05 to 0.99	10 to 20
1.00 to 4.99	5
5.00 to 15.00	1

13.2.4 When using less than the sample masses recommended in Table 1, due to solubility issues (that is, for asphalt, wax, and bitumen) and/or unavailability of necessary sample volume, then the blank value shall be determined for the sample and applied to the calculation of the acid number value.

13.2.5 For samples that have been heated in an oven, the beaker containing the sample and titration solvent (with pre-dissolution solvent) may be heated (≤65 °C) to ensure full solubility of the sample prior to the start of the titration. It is advised to cool the sample to room temperature before testing, provided the sample remains in solution. Analysis at slightly elevated temperatures is allowable but the rate of cooling should be minimized. Conditions shall be matched if determining the blank value. This approach can affect the precision and accuracy of the method and is not recommended for samples that can be successfully analyzed without heating.

13.2.6 Add titration solvent, typically 30 mL, to the titration beaker and place the thermistor and titrant delivery line into the sample. Stir the contents for a minimum of 30 s as rapidly as possible without exposing the thermistor to a vortex and causing sample or solvent loss. The sample shall be fully dissolved before titrating. Increase mixing time as needed to completely dissolve the sample. Samples shall stay in solution throughout the titration.

13.2.7 *Manual Paraformaldehyde Addition*—Add 0.50 g ± 0.10 g of paraformaldehyde per 30 mL of titration solvent to the beaker and start the titration. It is permissible to pause the stirring temporarily for the addition of the paraformaldehyde powder.

13.2.8 *Automated Paraformaldehyde Addition*—Use of automated delivery systems for the paraformaldehyde addition is permitted if precision and accuracy are not degraded. Such systems may dose solvent with the paraformaldehyde for automated delivery such that the same amount of paraformaldehyde is added as in 13.2.7. The solution should be well mixed and undergoing constant stirring during delivery. Follow manufacturer's recommendation.

13.2.9 Titrate the dissolved mixture with 0.1 M KOH at a suggested rate of 2 mL∕min. Ensure that a minimum volume of ≥0.15 mL titrant is used.

13.3 *End Point Detection:*

13.3.1 A change in the slope of the plot of temperature versus volume indicates the endpoint of the titration (Fig. 2). The net change (positive or negative) in temperature may vary from laboratory to laboratory due to the types of samples and environmental effects. The use of software to calculate the second derivative facilitates the determination of the endpoint.

13.3.2 After completion of the titration, *verify that all of the sample remains solubilized in the titration solvent*. If this is not the case, the titration is invalid. Rinse all of the components that were immersed in the titration solvent with toluene or some other suitable nonacidic solvent. Immersing the probe in solvent with stirring may aid in removal of any visible material not removed by solvent rinse. A dip rinse in xylene with stirring has proven to be sufficient for cleaning.

13.4 It is advised that the KOH burette be flushed with Type 1 water if the burette is to be idle for an extended period of time to prevent salt deposits from forming.

14. Calculation

14.1 Calculate the acid number using Eq 1:

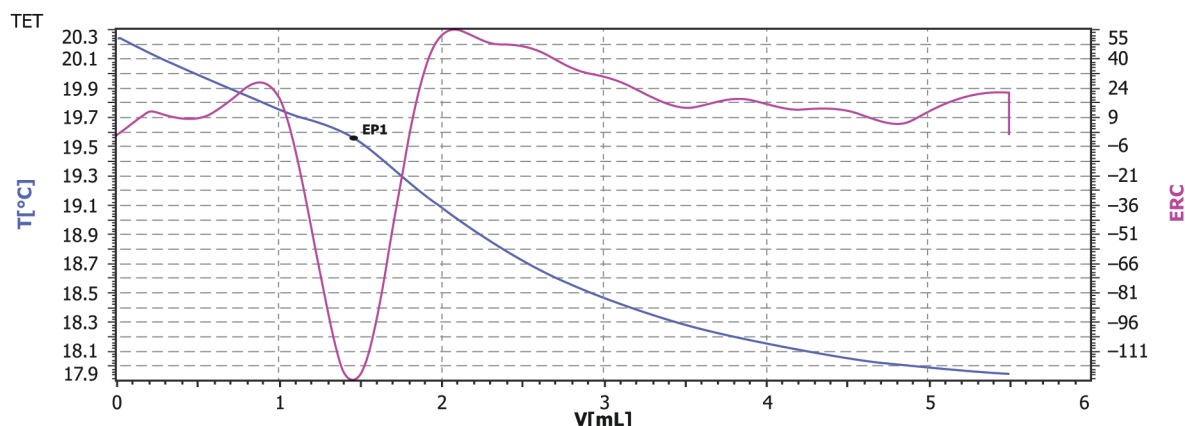$$(\text{KOH acid number, mg/g}) = \frac{(A)(M)(56.11)}{W} \qquad (1)$$

where:
A = volume of titrant at the end point, mL,
M = titrant concentration, mol/L, and
W = sample mass, g.

14.1.1 The constant value of 56.11 is the molar mass of potassium hydroxide in grams per mole. Two unit conversions negate each other (grams to milligrams and liters to milliliters).

TET = Thermometric Endpoint Detection
ERC = Endpoint Recognition Criteria

FIG. 2 Example Titration Curve