Designation: D8045 – 17 (Reapproved 2023)

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

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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.