AMERICAN SOCIETY FOR TESTING MATERIALS
1916 RACE ST., PHILADELPHIA 3, PA.

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APPROVED AS
AMERICAN STANDARD
BY THE AMERICAN STANDARDS ASSOCIATION
ASA NO.: Z11.67–1954
1955
UDC 665.5:620.1

REAFFIRMED - 1960

Standard Method of Test for

SAPONIFICATION NUMBER OF PETROLEUM PRODUCTS BY POTENTIOMETRIC TITRATION[1]

ASTM Designation: D 939 – 54

Adopted, 1950; Revised, 1952, 1954.[2]

This Standard of the American Society for Testing Materials is issued under the fixed designation D 939; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

Scope

1. (*a*) This method determines the acidic and basic constituents produced upon saponification of petroleum products under the conditions of the test, as well as those contained in them prior to saponification. The method resolves these constituents into groups having weak-acid, strong-acid, and base ionization properties, provided the dissociation constants of the more strongly acidic compounds are at least 10^3 times that of the next weaker group. It gives erroneous results with materials containing appreciable amounts of strong base. Unsaponifiable compounds whose acid or base dissociation constants in water are smaller than 10^{-9} are not detectable and do not interfere; salts react as acids if their hydrolysis constants are greater than 10^{-9}.

(*b*) The method is applicable to materials that are soluble or nearly soluble in mixtures of benzene and isopropyl alcohol. It is intended particularly for the determination of the saponification number of new and used oils, electrical oils, and greases whether compounded or not. It is useful for the identification of unmixed animal or vegetable oils and for the determination of the amount of fatty material in compounded products, provided the sample does not contain appreciable amounts of certain nonfatty compounds, such as those of sulfur, phosphorus, the halogens, nitrogen, and metals other than potassium or sodium, which consume alkali or acid under the conditions of the test.

Note 1.—A color-indicator titration method is also available in ASTM Method D 94,[3] Test for Saponification Number of Petroleum Products by Color-Indicator Titration. The two methods give comparable results when they are applied to new or slightly colored oils, or to

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[1] Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-2 on Petroleum Products and Lubricants.

[2] Prior to adoption as standard, this method was published as tentative from 1947 to 1950, being revised in 1950.

Published first as information in *Proceedings*, Am. Soc. Testing Mats., Vol. 43, p. 275 (1943).

In 1954, this method was extensively revised editorially. Sections 5(*e*), (*f*), (*g*), (*h*), (*i*), and (*j*) on buffer stock solutions were changed to conform with the solutions given in the ASTM Method D 664.

[3] 1952 Book of ASTM Standards, Part 5.

animal and vegetable oils. However, no relationship exists between results obtained by the two methods when the oil has a high inherent color or forms stable emulsions with the ethanol saponification medium used in the color-indicator method. The potentiometric method is equally applicable to colorless and colored materials, and to materials that produce colored solutions during the saponification treatment. No general relationship is known between the degree of oxidation of the oil and the saponification number as determined by either of these two methods.

Definitions and Description of Terms

2. (*a*) *Saponification Number.*—The number of milligrams of potassium hydroxide consumed by one gram of sample under the conditions of this method.

NOTE 2.—The saponification number expresses the net amount of acid or base-consuming constituents that were initially present or formed during the saponification; it includes the constituents with strong- or weak-acid characteristics that react under the conditions of the test.

(*b*) *Strong-Acid Saponification Number.*—The number of milligrams of potassium hydroxide consumed by the strong-acid constituents in one gram of sample under the conditions of this method.

NOTE 3.—The difference between the saponification number and the strong-acid saponification number expresses the amount of weak-acid constituents present or formed during the saponification.

(*c*) *Base Saponification Number.*—The number of milligrams of potassium hydroxide equivalent to the excess basic constituents present after saponifying one gram of sample under the conditions of this method.

NOTE 4.—The base saponification number expresses the net amount of constituents having basic characteristics.

(*d*) *Correct Glass Electrode Potential, cG.*—A term which expresses the relative hydrogen ion activity in the benzene–isopropyl alcohol medium in a manner similar to that in which the term pH expresses the hydrogen ion activity in aqueous solutions. The term cG is expressed in volts and ranges from zero for high concentrations of strong acid to above 0.7 for high concentrations of strong base. Its relationship to the observed cell potential, E, and the cell constant, E_{GC}, of a glass-calomel electrode system is given by the following equation:

$$cG = E - E_{GC}$$

Its relationship to pH scale reading at an absolute temperature, T, where T is in degrees Kelvin, is given by the following equation:

$$cG = 0.000198T \times \text{pH scale reading}$$

(*e*) *Cell Constant, E_{GC}.*—A term which combines all cell voltage effects that do not normally vary with variation in hydrogen ion activity during a titration. If this term is to bear a known relation to the observed cell potential, E, and the correct glass electrode potential, cG, the cell constant E_{GC} must be established as described in Section 7 (*a*) for each meter-electrode combination and must be redetermined at intervals thereafter.

Outline of Method

3. The sample, dissolved in a mixture of benzene and isopropyl alcohol, is saponified by refluxing for two hours with an excess of potassium hydroxide. The excess potassium hydroxide is then titrated potentiometrically with alcoholic hydrochloric acid, with the aid of a glass indicating electrode and a calomel reference electrode. The meter readings are plotted against the respective volumes of titrating solution and the end points are taken at the inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those obtained with nonaqueous buffer solutions and representing read-