Designation: F3045 – 21

Standard Test Method for Evaluation of the Type and Viscoelastic Stability of Water-in-oil Mixtures Formed from Crude Oil and Petroleum Products Mixed with Water[1]

This standard is issued under the fixed designation F3045; 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 a procedure to determine the water-in-oil emulsification tendencies and stabilities of crude oils and petroleum products in the laboratory. The results of this test method can provide oil behavior data for input into oil spill models.

1.2 This test method covers a specific method of determining emulsion tendencies and does not cover other procedures that may be applicable to determining emulsion tendencies.

1.3 The test results obtained using this test method are intended to provide baseline data for the behavior of oil and petroleum products at sea and input to oil spill models.

1.4 The test results obtained using this test method can be used directly to predict certain facets of oil spill behavior or as input to oil spill models.

1.5 The accuracy of the test method depends very much on the representative nature of the oil sample used. Certain oils can form a variety of water-in-oil types depending on their chemical contents at the moment a sample is taken. Other oils are relatively stable with respect to the type formed

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

1.7 *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.*

1.8 *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. Summary of Test Method

2.1 Oil is mixed with 33 ‰ (3.3 %) saline water for 12 h in a standard rotating apparatus. The resulting mixture is characterized after this mixing period.

2.2 The resulting mixture as created in step 2.1, is characterized by visual qualities, by measuring water content and by rheological measurements. The mixture is then classified as a stable, meso-stable, unstable emulsion or an entrained water mixture. Each of these four types of mixtures has different characteristics affecting the behavior of oil in the aquatic environment.

3. Terminology

3.1 *Definitions:*

3.1.1 *complex modulus*—One of the results of viscoelastic measurement, a measure of the resistance of a viscoelastic substance to flow under an applied dynamic stress, combining both the non-reversible (viscous) flow of the test substance and the reversible (elastic) deformation of the test substance.

3.1.2 *emulsion*—A type of colloid, specifically, a dispersion of small droplets of one immiscible liquid in another.

3.1.2.1 *meso-stable emulsions*—Emulsions that lack one or more of the compositional factors necessary to form a stable emulsion, but that are sufficiently stable to persist for short periods, typically a few hours to days.

3.1.2.2 *stable emulsions*—Emulsions that persist indefinitely, consisting of fine droplets with a rigid film interface which resists coalescence.

3.1.2.3 *unstable emulsions*—Mixtures of water and oil that resolve rapidly into two phases, usually within a few minutes to hours. There may be residual water remaining in low percentages.

3.1.2.4 *water-in-oil emulsion*—An emulsion consisting of a continuous phase of oil containing a dispersed phase of water.

3.1.3 *entrained water*—This is not an emulsion but a mechanical mixture of oil and water which has not separated due to the physical properties of the water and oil.

[1] This test method is under the jurisdiction of ASTM Committee F20 on Hazardous Substances and Oil Spill Response and is the direct responsibility of Subcommittee F20.16 on Surveillance and Tracking.

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3.1.3.1 *Discussion*—Typically, the oil and water have similar densities and the oil phase has a high viscosity.

3.1.4 *rag*—The remnant of a broken water-in-oil emulsion.

3.1.4.1 *Discussion*—Rag will not reform an emulsion. Rag is thought to consist of tightly bound asphaltenes and resins.

3.1.5 *stability index*—An index describing the stability of an emulsion.

3.1.5.1 *Discussion*—In this standard, it is calculated using data derived from rheological measurements.

3.1.6 *storage modulus*—One of the results of viscoelastic measurement, a measure of the elastic (reversible) deformation behavior of a viscoelastic substance under an applied dynamic stress.

4. Significance and Use

4.1 A standard test is necessary to establish a behavior pattern for spilled crude oils or petroleum products at different oil weathering stages.

4.2 Water-in-oil mixtures vary with oil type and oil conditions such as weathering. Results from this test method form a baseline, and usually are a measure of behavior at sea.

4.3 This test has been developed over many years using standardized equipment, test procedures, and to overcome difficulties noted in other test procedures.

4.4 This test should be performed at the temperatures and degrees of weathering corresponding to the spill conditions of interest.

5. Interferences and Sources of Error

5.1 Interferences can be caused by contaminants, such as residual oil or surfactants on labware, and other sample handling supplies and apparatus that lead to irregular results. Surfactants in particular will influence results, as small amounts will disrupt the stability of a water-in-oil emulsion. All glassware must be thoroughly cleaned. The cleaning process includes rinsing with dichloromethane to remove the oil, followed by rinsing three times each with tap water, purified water (reverse osmosis), and acetone. Once cleaned, precautions must be taken to minimize contact of the labware with contaminants to prevent interferences.

5.2 Emulsion formation is somewhat susceptible to energy levels. The rotational speed of the shaker should be verified with a tachometer before each use. The specified direction of rotation should be followed (vessel cap leads rotation on start-up).

5.3 The specified fill volumes of the test vessels must be observed as the energy level varies with the amount of fill.

5.4 Temperature is a factor in emulsification, so it is important that all components (salt water, oil, and temperature controlled chamber) are stable at 15° C or the selected test temperature, before starting.

5.5 The handling of the samples after the mixtures are formed is important. Care must be taken to take a representative sample. Excess water should be avoided when sampling.

5.6 Since the test results may be affected by salinity, thorough mixing of the salt water is required. Salinity should be verified using a salinity meter before use.

5.7 Oil recovered for a source, especially crude oil fields, vary with production conditions and over time. Oil samples should be considered as indicative of the oil source at a moment within a range of variability and are not necessarily representative of all oil recovered from the source. Some oils are near the threshold of two different water-in-oil types. Depending on the actual conditions under which the oil was sampled, different results may occur. Other oils are not as sensitive.

5.8 Additives introduced in the production and transport of oils can change their emulsification behavior. Some oils have added asphaltene suspenders or emulsion inhibitors. These may significantly alter the outcome of this test. Information on the oil treatment should be obtained before making the test.

6. Apparatus

6.1 2.2-litre fluorinated HDPE wide-mouth bottles, approximately 24 cm in height and 6 cm in radius (Nalgene or equivalent), used as the test vessel. These vessels match the shaker as described below.

6.2 Variable speed end-over-end rotary mixer capable of maintaining 55 RPM, with a radius of rotation of 15 cm (7.5 cm from center of vessel) (Associated Design or equivalent).[2]

6.3 *Automated Karl Fischer titration analyser,* This device is used to measure the water content of the resulting water-in-oil mixture.

6.4 *Rheometer,* capable of functioning in forced-oscillation mode with parallel plate geometry. This device is used to measure the rheological properties of the resulting water-in-oil mixture.

6.5 Circulating bath with a range from 0 to 25 °C (±0.1).

6.6 *Salinometer or water quality meter,* SensIon 745 or equivalent with a sensitivity of ±0.1 PSU (practical salinity unit).

6.7 Oil-mixing devices including a shaker for mixing the small samples prior to use and devices to mix the oil contained in drums.

6.8 The following is a list of other necessary supplies. Equivalent supplies are acceptable.

6.8.1 Disposable 30- and 1-mL plastic syringes,

6.8.2 20-L plastic or glass carboy, stirring plate and stir bar.

6.8.3 Spatulas, scoops and wide-mouth bottles for sample handling and storage,

6.8.4 Electronic timer switch.

[2] These devices are described in EPA standards for use in extraction tests: EPA Method 1310 Extraction Procedure (EP) Toxicity Test Method And Structural Integrity Test, EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP), and EPA 1312 Synthetic Precipitation Leaching Procedure (SPLP). Environmental Protection Agency 1200 Pennsylvania Avenue, N.W. Washington, DC 20460. http://www3.epa.gov/