



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 Water¹

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 Recom-*

mendations 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/>

7. Reagents³

7.1 *Reagents*—Water purified by reverse osmosis or equivalent means is used for the test water. Fine granular sodium chloride or table salt, non-iodized, is used for making the salt water. The typical brine solution of 33 ‰ (3.3 %) NaCl is prepared from salt and purified water and stored in a 20 L carboy at ambient temperatures until needed. Alternate salinities may also be prepared for testing. Reagent-grade sea salt mix (for example, SigmaAldrich or equivalent) may be substituted for preparing brine solutions. Fresh water may also be used for the test to mimic non-saline conditions.

7.1.1 *Oil*—is used as received, but is shaken for 30 minutes prior to use and is maintained at the test temperature of 15 °C or the chosen test temperature.

7.1.2 *Karl Fischer reagent*, 5 mg/mL H₂O is recommended, single component, pyridine free.

7.1.3 *Toluene*, methanol and chloroform, reagent grade, as solvent for the Karl-Fischer titration.

7.1.4 *Dichloromethane and acetone*, as clean-up solvents, and RO purified water

8. Procedure

8.1 *Crude Oil Sample Collection and Storage*—The bulk oil as received is mechanically mixed to attain homogeneity prior to obtaining a working sample. Working samples are stored in clean, airtight containers. The working sample is mechanically shaken for 30 min at 15 °C or the selected operating temperature prior to removing a sub-sample for testing. When not in use, all samples should be stored in a temperature-controlled room at 5 °C.

8.2 *Generating the water-in-oil mixture*—In summary, water-in-oil mixtures are formed in 2.2 L fluorinated vessels on an end-over-end rotary mixer (Associated Design, VA or equivalent) at a rotational speed of 55 RPM.

8.2.1 Each 2.2 L mixing vessel is filled with 600 mL of water, either salt or fresh water as selected for the test. The water should be at the test temperature at the time of addition.

8.2.2 Oil is introduced at a ratio of 1:20 oil:water by adding 30 mL of the test oil to the vessel.

8.2.3 The vessels are sealed and mounted in the rotary mixer such that the cap of each mixing vessel leads the direction of rotation to maximize the turbulence of mixing.

8.2.4 The rotary mixer and vessels are held at 15 °C or the selected operating temperature in a temperature controlled cold room for the duration of the experiment. (Note that 15 °C is the standard temperature for measuring oil properties.) If the temperature(s) of interests for a spill is different, the test should be performed at those temperatures as well. Testing at different temperatures necessitate that the entire study be performed at the new chosen temperature.

8.2.5 The vessels and their contents are allowed to stand for 4 h to thermally equilibrate.

8.2.6 The mixing is initiated using an electronic timer switch. The vessels are mixed continuously for 12 h at a rotation speed of 55 RPM.

8.2.7 After 12 h mixing, the water-in-oil mixtures are collected from the vessels and transferred to appropriately sized glass wide-mouthed jars for observation and analysis.

8.2.8 The emulsions are stored at 15 °C or the selected operating temperature for one week, followed by additional observation and analysis.

8.2.9 Each oil is tested in triplicate.

8.2.10 The visual observations, viscosity, viscoelastic properties and water content of the starting oil and the resulting water-in-oil mixture are measured for comparison as outlined in the procedures described below.

8.3 *Sampling and analysis*—A small sample is withdrawn from each wide-mouth jar for further analysis as described below. Analysis is performed twice, immediately after mixing and after one week.

8.4 *Sample Analysis for Water Content*—Water content is measured by a volumetric titrator using an appropriate Karl Fischer reagent. The solvent is 1:1:2 methanol:chloroform:toluene. A set of three measurements is made for each sample.

8.5 *Viscosity Measurement of oils*—Dynamic viscosities of the oils are measured at 15 °C using a rotational viscometer using concentric cylinder geometry. The appropriate cup and spindle combination is selected on the basis of the valid viscosity range for each type, as provided by the manufacturer. The highest suitable shear rate is selected from the manufacturer's guidance manual. The measurement protocol follows a one-minute ramp up to the target shear rate, holding for five minutes, then ramping back down to zero to evaluate thixotropy. The reported value for the oil is the average viscosity over the period of constant shear. Triplicates are performed for each sample.

8.6 *Viscoelastic Measurements of the water-in-oil mixtures*—The viscoelastic properties are determined on a rotational rheometer using plate-plate geometry. The sample stage height is set for a 2.00 mm gap to allow for larger water droplets in the sample (1/10th the gap or less). The sample is measured at 15 °C in forced oscillation mode using a stress sweep from 0.100 to 10.0 Pa at a frequency of one reciprocal second. Values of the complex modulus, storage modulus, loss modulus, and the phase shift of the strain response (tan (δ)) are obtained in the linear viscoelastic range (stress independent region of the stress response curve). Samples are measured in duplicate.

8.7 *Data recording of the measurements*—The visual observations and the data on the water content and the viscoelastic measurements are recorded for the water-in-oil mixtures on the test day following the 12-h mixing and again after one week. The water content and viscosity measurements are taken of the starting oil. All values are recorded to 3-significant-figure accuracy. For the viscoelastic measurements, it is necessary to record the complex modulus (mPa), storage modulus (mPa). Viscosity modulus (mPa) and tan delta (V/E). The water content is measured as recorded as percentage water in oil by weight. Three oil samples are taken for the tests, the water

³ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

content and viscosity are measured in triplicate and the viscoelastic measurements are taken in duplicate.

8.8 Calibration Standards and Methods:

8.8.1 The mixing apparatus is verified daily with a tachometer to ensure a rotational rate of 55 RPM \pm 2 RPM.

8.8.2 The salinity of the salt solution is verified using a water quality meter (SensIon 745 or equivalent), 3.3.0 % \pm 0.1 PSU.

8.8.3 The rheometer calibration is checked with certified viscosity standards. If the rheometer reading is out of the manufacturer's specification (\pm 5 % mPa.s of certified value), the instrument is to be serviced by certified technicians.

8.8.4 The Karl-Fischer titrant is calibrated following each addition to the titrant reservoir following the manufacturer's protocol using purified water. The relative standard deviation is acceptable if less than 1 %.

8.8.5 The Karl-Fischer titration apparatus is checked daily using purified Type 1 water (Ultrapure water as defined by laboratory water standards) in Sample Mode. A response of 100 % \pm 1 % water (by weight) is acceptable.

8.9 *Cleaning Labware*—A thorough cleaning program is undertaken throughout the procedure to reduce possible cross-contamination and accumulation of contaminants on the labware. Labware is thoroughly cleaned with DCM and rinsed with tap and purified (RO) water, between each experimental run and allowed to dry. Rheometer spindles are cleaned with DCM and acetone.

9. Calculation and Reporting

9.1 The values of viscosity, water content and the values from the viscoelastic measurements are evaluated. The measurements, and repeatabilities are summarized in **Table 1**. Three oil samples are taken for the tests, the water content and viscosity or the starting oil are measured in triplicate. The viscoelastic measurements on the resulting mixture are taken in duplicate.

9.1.1 The values for the replicate sets within each measurement on the oil and on the resulting mixtures should agree within the percentage specified:

Water content - \pm 2 %

Viscosity - \pm 5 %

Viscoelasticity measurements - \pm 15 %

A sample measurement is valid if it is within the specified tolerance compared with the average values of other individual measurements.

Water content - \pm 5 %

Viscoelasticity measurements - \pm 30 %

9.2 The stability is calculated using:

$$Stability = \ln \left[\left(\frac{\frac{complex\ modulus}{starting\ oil\ viscosity} \times \frac{storage\ modulus}{starting\ oil\ viscosity}}{10000} \right)^2 \right] \quad (1)$$

where:

complex and storage modulus = mPa

Starting oil viscosity = mPa.s, and

ln = is the natural logarithm

9.3 The data taken are compared to values in **Table 2** to classify the oil type.

9.4 Data reports should include the data in three significant figures, and the average of these three points. Presentation of data should also be made in accordance with **Table 2** showing how the oil was classified as either one of the four water-in-oil mixtures. To capture oil changes due to weathering, it is advised to perform this test with several (three is suggested) weathered samples of the oil in addition to the fresh oil.

10. Keywords

10.1 emulsions; emulsion stability; water-in-oil emulsions; water-in-oil mixtures; oil spills; entrained water

TABLE 1 Measurement Table

Target	Measurement	Timing	Repetitions	Target
Starting oil	Viscosity	before mixing	3	\pm 5 %
	Water content	before mixing	3	\pm 2 %
Mixing experiment Water-in-oil Mixture		after mixing	3	
	Viscoelastic Measurement (Complex Modulus and Storage Modulus)		2	\pm 15 %
	Water content		3	\pm 2 %
		after one week		
	Viscoelastic Measurement (Complex Modulus and Storage Modulus)		2	\pm 15 %
	Water content		3	\pm 2 %
	Comparison between 3 mixing runs			
	Water content			\pm 5 %
	Viscoelastic Measurement			\pm 15 %