ASTM INTERNATIONAL

Designation: F3251 – 17

Standard Test Method for
Laboratory Oil Spill Dispersant Effectiveness Using the Baffled Flask[1]

1. Scope

1.1 This test method covers the procedure to determine the effectiveness of oil spill dispersants on various oils in the laboratory. This test method is not applicable to other chemical agents nor to the use of such products or dispersants in open waters.

1.2 This test method covers the use of the Baffled Flask test apparatus and does not cover other apparatuses nor are the analytical procedures described in this report directly applicable to such procedures.

1.3 The test results obtained using this test method are intended to provide baseline effectiveness values used to compare dispersants and oil types under conditions analogous to those used in the test.

1.4 The test results obtained using this test method are effectiveness values that should be cited as test values derived from this standard test. Dispersant effectiveness values do not directly relate to effectiveness at sea or in other apparatuses. Actual effectiveness at sea is dependent on sea energy, oil state, temperature, salinity, actual dispersant dosage, and amount of dispersant that interacts with the oil.

1.5 The decision to use or not use a dispersant on an oil should not be based solely on this or any other laboratory test method.

1.6 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

1.7 *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]
F2059 Test Method for Laboratory Oil Spill Dispersant Effectiveness Using the Swirling Flask

2.2 *EPA Standard:*[3]
SW-846 Method 8270D, Revision 4 Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

3. Terminology

3.1 *Definitions:*

3.1.1 *effectiveness, n*—the capability of producing a desired result – which is this case is the dispersion of oil into water.

3.1.1.1 *Discussion*—Effectiveness is given here as the percent of oil dispersed into the water column as a result of dispersant action and energy.

3.1.2 *trypsinizing, n*—the process of cell dissociation using trypsin, an enzyme which breaks down proteins, to dissociate adherent cells from the vessel in which they are being cultured.

3.1.2.1 *Discussion*—This test method uses only the vessel designed for that process (with the addition of a withdrawal tube).

4. Summary of Test Method

4.1 The dispersant is pre-mixed with oil and placed on water in a test vessel. The test vessel is agitated on a moving table shaker. At the end of the shaking period, a settling period is specified and then a sample of water taken. The oil in the water column is extracted from the water using a dichloromethane solvent and analyzed using gas chromatography.

4.2 The extract is analyzed for oil using a gas chromatograph equipped with a flame ionization detector (GC-FID). Quantification is by means of the internal standard method.

Effectiveness values are derived by comparison with a calibrated set of effectiveness values obtained at the same time and by the same method.

5. Significance and Use

5.1 A standard test is necessary to establish a baseline performance parameter so that dispersants can be compared, a given dispersant can be compared for effectiveness on different oils, and at different oil weathering stages, and batches of dispersant or oils can be checked for effectiveness changes with time or other factors. This test method provides a second test at higher mixing energy in addition to the Swirling Flask (Test Method F2059).

5.2 Dispersant effectiveness varies with oil type, sea energy, oil conditions, salinity, and many other factors. Test results from this test method form a baseline at high mixing energy, but are not to be taken as the absolute measure of performance at sea. Actual field effectiveness could be more or less than this value.

5.3 Many dispersant tests have been developed around the world. This test has been developed in recent years and provides higher mixing energies compared to other laboratory scale tests.

6. Interferences and Sources of Error

6.1 Interferences can be caused by contaminants, particularly residual oil or surfactants in solvents, on glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. 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 or similar), and acetone. Once cleaned, precautions must be taken to minimize contact of the glassware with surfactants to prevent undesired interferences.

6.2 Dispersant effectiveness is very susceptible to energy levels. Table top shakers generally start and stop slowly. Shakers that start motion rapidly and stop suddenly impart a high energy to the system and thus cause more dispersion than would be the case with a normal shaker. Furthermore, this variation would not be repeatable. The shaker table used should be observed for rapid movements or stops to ensure that it is usable for these tests. The rotational speed of the shaker should be checked with a tachometer every week before use.

6.3 The flasks used in this test are tapered and the energy level varies with the amount of fill and variation in dimensions.

6.4 The output is highly sensitive to the volume of oil, water, and extractant. All pipets and dispensers should be calibrated frequently and verified daily when in use.

6.5 The use of positive displacement pipets is mandatory for all controlled volumes of microlitre quantities. Use of volume displacement pipets will result in erroneous results due to the viscosity of the dispersants and oils, the variable viscosity of the oils to be tested (some semi-solid), and the density of dichloromethane.

6.6 The order of addition of the dispersant and oil has effects on the accuracy of results, as the dispersant may interact with the vessel walls if added first, thereby reducing the quantity available in the premix. It is therefore important to add oil to the vessel first, and add the dispersant directly to the oil. A second addition of oil is suggested simply because it is easier to control a large volume of oil than a minute volume of dispersant when attempting to achieve a specific ratio of 25:1.

6.7 Following dispersant addition, vigorous mixing is required to homogenize the sample. Sharp, manual strokes are suggested for light oils, while very heavy oils may require stirring with a clean glass rod or spatula.

6.8 There are indications that mixing will vary with time following preparation of the premixed dispersant/oil combinations. As a precaution it is highly recommended that the testing should be completed as soon as practical following preparation of the premix, and not stored for use at a later time.

6.9 Since the performance of the dispersant is affected by salinity, the salt water should be thoroughly mixed, stored in airtight containers, and checked with a salinity meter prior to use.

6.10 Temperature is a factor in dispersion, so it is important that all components (salt water, pre-mix, and temperature-controlled chamber) are stable at 20°C (or the chosen operating temperature) before starting.

6.11 Care should be taken when applying the oil to the surface so that mixing does not occur. The oil should gently glide across the water to form a slick. If the oil streams out into the water, the agitation can disperse the oil, increasing the amount of oil dispersed and erroneously raising the final dispersion result.

6.12 Dispersion effectiveness generally declines with increased evaporation of oil components. Care should be taken to avoid unnecessary exposure of the oil and dispersant/oil premix before and during the test procedure to protect sample integrity and minimize variability related to oil weathering. Special care should be taken to minimize the time to apply the dispersant-oil premix to all six vessels in a test run.

6.13 The procedure is time critical for the elements of mixing, settling, and sampling. Care should be taken to adhere to the times indicated in the procedure for both the mixing and settling element, as variations in energy input, and especially time allowed for droplet rise, can impact results. Since the water samples cannot be sampled simultaneously, this step must be performed as quickly as possible, to reduce the difference in settling times experienced by the samples in the test run.

6.14 Analysis of the gas chromatograph-detectable Total Petroleum Hydrocarbon (TPH) content is subject to variability in GC operation and repeatability (Test Method F2059: EPA 8270D). Therefore, it is imperative that a rigorous quality assurance program is in place to ensure the GC is functioning properly and valid results are obtained.

6.15 Care should be taken to determine the baseline in a valid and repeatable manner for both samples and calibration sets.

6.16 The accuracy and repeatability of the test can be verified and compared using standard oil and dispersant samples.

7. Apparatus

7.1 *Modified Baffled Trypsinizing Flask,* used as the test vessel. A side spout is added to a trypsinizing flask to enable sampling from the water column with minimal disturbance of the resurfaced oil. A modified 150 mL glass screw-capped trypsinizing flask with baffles (for example, Wheaton No. 355394 or equivalent) fitted with a 2-mm bore polytetrafluoroethylene (PTFE) stopcock and glass tubing, the center of which is no more than 1.3 cm from the bottom.[4] This vessel is illustrated in Fig. 1.

7.2 *Moving-Table Shaker,* with an orbital motion of 25.4 mm (1 in.) and fitted with flask holders. Ideally such shakers should be operated inside temperature-controlled chambers. If such an enclosed chamber is not used, the measurement must be conducted inside temperature-controlled rooms.

7.3 *Gas Chromatograph (GC),* equipped with a flame ionization detector is used for analysis. The column is a fused silica column.

7.4 The following is a list of other necessary supplies. Suppliers of suitable units are footnoted. Equivalent supplies are acceptable in every case. Quantities of supplies are given to conduct a full set of six samples and calibration set:

7.4.1 *Eighteen Crimp Style Vials,* with aluminum/polytetrafluoroethylene (PTFE) seals, 12 by 32 mm,

7.4.2 *Twelve Baffled Flasks,* 150-mL glass, modified as noted above.[4]

7.4.3 *Six Graduated Mixing Cylinders and Stoppers,* 25-mL glass,

7.4.4 *Six Separatory Funnels and Stoppers,* glass, 25-mL.

7.4.5 *Six Graduated Mixing Cylinders and Stoppers,* glass, 100-mL.

7.4.6 *Six Separatory Funnels and Stoppers,* glass, 250-mL.

7.4.7 *Six Graduated Cylinders,* glass, 50-mL.

7.4.8 *Six Dispenser or Glass Graduated Cylinders,* 5- to 25-mL.

7.4.9 *Positive Displacement Pipet,* variable volume 20- to 100-µL.

7.4.10 *Positive Displacement Pipet,* variable volume, 1-mL capacity.

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[4] The sole source of supply of the apparatus known to the committee at this time is Pro Science, Inc., 770 Birchmount Road, Unit 25, Scarborough, Ontario MIK5H3. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

FIG. 1 The Baffled Flask Vessel with the Addition of a Stopcock and a Withdrawal Tube

7.4.11 *Two Digital Timers,*

7.4.12 *Dispenser or Graduated Cylinders,* 20-mL and 5-mL volumes, and

7.4.13 *One Plastic Carboy*—20-L.

8. Reagents

8.1 *Reagents*—Water purified by reverse osmosis or equivalent means is used for the test water. Dichloromethane is distilled-in-glass grade. Fine granular sodium chloride (or table salt, non-iodized) or reagent-grade sea salt mix (for example, SigmaAldrich or equivalent), is used for making the salt water. The chemical dispersant is used as supplied by the manufacturer. Oil is used as received.

9. Procedure

9.1 *Crude Oil Sample Storage and Preparation*—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 20°C (or the chosen operating temperature) prior to removing a sub-sample for testing. When not in use, all samples should be stored in a refrigerator at approximately 5°C.

9.2 *Dispersant Sample Storage and Preparation*—When not in use, samples should be stored in a refrigerator at 5°C in opaque or amber containers. Prior to use, the sample is equilibrated to the temperature of the test. The dispersant is then manually shaken, vigorously, prior to sampling.

9.3 *Premix Sample Preparation*—A small amount of oil (approximately 1.0 mL) is weighed into a 5-mL amber vial with PTFE-lined cap. Approximately 100 mg of dispersant is added to the oil. Oil is added until a 1:25 ratio (by weight) of dispersant to oil is achieved. The sample is well mixed by manual shaking or stirring.

9.4 *Salt-Water Preparation*—Granular salt or sea salt mix is weighed and added to purified water (reverse osmosis (RO) filtration or equivalent) to obtain a 3.3 % (w/v) solution. The water temperature is stabilized to 20°C (or the chosen operating temperature) before use.

9.5 *Baffled Flask Preparation*—The 120 mL of salt water is placed into a 125-mL Baffled Flask. The flask is inserted into the flask holders on the oscillating table of the shaker. A 100-μL volume of pre-mix solution is carefully applied onto the surface of the water using a positive displacement pipet. The tip of the pipet is placed at the water surface and the dispersant/oil mixture gently expelled. Care should be taken when applying the oil/dispersant mixture to the water surface such that premature mixing does not occur. Herding of the oil and some creeping of the mixture up the vessel wall is normal but can be minimized.

9.6 *Shaking of Baffled Flasks*—The flask and contents are mechanically mixed on the shaker in a temperature controlled chamber at 20°C (or the chosen operating temperature), immediately after applying the oil/dispersant mixture to the surface of the water. A rotation speed of 200 r/min and a mixing time of 10 min are used to agitate the samples followed by a 10-min settling period. The flasks should be removed from

the table-mounted holders prior to the settling period to limit the agitation between settling and sampling.

9.7 *Sample Collection*—After the settling time is complete, 3 mL of oil-in-water phase from the spout of the flask are drained and disposed of to remove any oil residing in the spout and to obtain a representative sample. A 30-mL aliquot of the dispersed oil in water sample is collected in a graduated cylinder and transferred to a 125-mL separatory funnel. The oil is extracted three times with 5 mL of dichloromethane, shaken vigorously for at least 1 min, and the extract poured into a 25-mL graduated mixing cylinder. Care is taken to ensure that water is not taken along with the solvent. During extraction, vigorous shaking is required to achieve full extraction. It is best to shake each separatory funnel individually to achieve consistent results. Care is taken to ensure that water is not taken along with the solvent. The final extraction volume is adjusted to 15 mL, and then a small amount of activated sodium sulfate is added to each mixing cylinder and shaken to remove any trace water.

9.8 *Sample Analysis*—Analysis consists of gas chromatographic analysis using a flame ionization detector (GC/FID) to determine the concentration of oil in solvent (Test Method F2059: EPA 8270D). A 900.0-μL portion of the 15-mL solvent extract and a 100.0-μL volume of internal standard (200 ppm 5-α-androstane in hexane) are combined in a 12 by 32 mm crimp-style vial with aluminum/PTFE seals and shaken well. Petroleum hydrocarbon content is quantified by the internal standard method, with the average hydrocarbon relative response factor (*RRF*) determined over the entire analytical range in a separate run. The petroleum content is determined by integrating the total area between C_9 and C_{40} and subtracting the average value from a set of six blank runs of solvent only; 3 at the beginning of the test set, and 3 at the end. A fixed, common baseline independent of a petroleum tail above C_{40} must be used. The calculation is completed by the following equation:

$$TPH = \frac{A_{total}}{A_{is}} \cdot \frac{1}{RRF} \cdot 20(\mu g) \cdot \frac{15}{0.9} \cdot \frac{120}{30} \qquad (1)$$

which simplifies to:

$$TPH = \frac{A_{total}}{A_{is}} \cdot \frac{1330(\mu g)}{RRF} \qquad (2)$$

where:

TPH = total petroleum hydrocarbon amount in μg,
A_{total} = integrated area for total petroleum hydrocarbons,
A_{is} = integrated area of the internal standard, and
RRF = relative response factor which in turn is given as follows: (Eq 3):

$$RRF = \frac{A}{A_{is}} \cdot \frac{C_{is}}{C} \qquad (3)$$

where:

A = area of concern,
A_{is} = area of the internal standard,
C_{is} = concentration of the internal standard, and
C = concentration of the analyte of concern.

9.9 *Calibration Standards*—A series of six oil-in-solvent standards are prepared for evaluating the efficiency of the

dispersant for each dispersant/oil combination. First is a control without added dispersant/oil representing 0 % dispersion. The remaining five calibration standards are in 20 µL increments from 20 to 100 µL to represent the volume of oil at the corresponding percentage effectiveness value, for example, 50 µL = 50 % efficiency. The dispersant/oil mixture is then accurately measured and applied to the water surface, and treated in the same manner as the samples. At this point, the entire volume of water is transferred to a 250-mL separatory funnel and extracted three times with 20 mL of dichloromethane. All oil is extracted, including the oil slick and oil on the walls of the Baffled Flask test vessel, using the volume of extraction solvent to rinse the flask of remaining oil before adding to the separatory funnel. The extracts are combined in a graduated cylinder and topped up to a total volume of 60 mL. Chromatographic analysis is then performed to determine the petroleum content by integrating the total baseline corrected area of the chromatogram and applying the following equations:

$$TPH = \frac{A_{total}}{A_{is}} \cdot \frac{1}{RRF} \cdot 20(\mu g) \cdot \frac{60}{0.9} \cdot \frac{120}{120} \qquad (4)$$

which simplifies to:

$$TPH = \frac{A_{total}}{A_{is}} \cdot \frac{1330(\mu g)}{RRF} \qquad (5)$$

where:

TPH = total petroleum hydrocarbon amount in µg,
A_{total} = total integrated area,
A_{is} = area of the internal standard, and
RRF = relative response factor which in turn is given as follows:

$$RRF = \frac{A}{A_{is}} \cdot \frac{C_{is}}{C} \qquad (6)$$

where:

A = area of concern,
A_{is} = area of the internal standard,
C_{is} = concentration of the internal standard, and
C = concentration of the analyte of concern (oil).

9.10 *Test Runs*—A test run should be limited to a set of six experimental samples and calibration standards, as the time element becomes a significant factor beyond this number. A typical run consists of three each of the test samples and the calibration standards. The calibration standards in each run should be spaced by 40 % increments, for example 0, 40, and 80 % in one run, and 20, 60, 100 % in the other, to mitigate the impact of variations in test conditions between the two runs.

9.11 *Gas Chromatograph Parameters and Sequencing*—Total petroleum hydrocarbon (TPH) analysis for C_9 through C_{40} *n*-alkanes of the dispersed oil-in-water is carried out by high resolution capillary GC/FID under the following conditions:

Column	30 M × 0.25 mm ID DB-5HT fused silica column (0.10 µm film thickness) or similar
Detector	flame ionization detector
Auto sampler	equipped with an auto sampler
Inlet	split-less
Gases,	hydrogen, 1.0 mL/min, nominal
	Make up gas, nitrogen – 45.0 mL/min
	Detector air – 400 mL/min
	Detector hydrogen – 30 mL/min or comparable conditions for effective chromatography
Injection volume	1 µL
Injector temperature	300 °C
Detector temperature	300 °C
Temperature program	40°C for 2 min, then 20°C/min to 340°C, hold 10 min
Chromatography check	Alkane standard mixture of 20 ppm (containing 5-α-androstane, selected mixture of *n*-alkanes from C_9 through C_{40}, in hexane) is measured before and following each sample set to determine the relative response factor and check instrument performance

9.12 *Cleaning Glassware*—A thorough cleaning program is undertaken throughout the procedure to reduce possible cross-contamination and accumulation of dispersants and oil on the glassware. Glassware is thoroughly rinsed with tap and purified (RO) water, and dichloromethane between each experimental run. At weekly intervals, the lab ware is soaked in an alkaline cleaning solution or equivalent for 24 h, rinsed with tap and purified (RO) water followed by the solvent acetone.

10. Calculation and Reporting

10.1 The effectiveness is calculated by creating a calibration curve of effectiveness versus TPH from the standards and then taking the TPH of the experimental value and setting the appropriate effectiveness value from the calibration curve.

10.2 At least five measurements of the samples and effectiveness calibration set are required for a valid test. The loss of more than one sample or calibration standard requires repeating the entire test. Samples and calibration standards from separate test runs should not be combined other than as described above. The standard deviation is taken and reported. A standard deviation for the test set of more than 5 (absolute value) indicates poor repeatability and the experiments should be repeated.

11. Keywords

11.1 Baffled Flask; dispersant; dispersant testing; effectiveness testing; oil spill