



Standard Test Method for Laboratory Oil Spill Dispersant Effectiveness Using The Swirling Flask¹

This standard is issued under the fixed designation F 2059; 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 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 swirling 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 effectiveness values that should be cited as test values derived from this standard test. Effectiveness values do not directly relate to effectiveness at sea or in other apparatuses. Actual effectiveness at sea is dependant on sea energy, oil state, temperature, salinity, actual dispersant dosage, and amount of dispersant that enters the oil.

1.4 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.

1.5 The decision to use or not use a dispersant on an oil should not be based solely on this or 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.*

2. Summary of Test Method

2.1 Dispersant is pre-mixed with oil, 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 pentane/dichloromethane mixture and analyzed using gas chromatography.

2.2 The extract is analyzed for oil using a gas chromatograph equipped with a flame ionization detector, (GC-FID).

Quantification is by means of comparison to an internal standard. Effectiveness values are derived by calibration at fixed effectiveness values.

3. Significance and Use

3.1 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.

3.2 Dispersant effectiveness varies with oil type, sea energy, oil conditions, salinity, and many other factors. Test results from this test method form a baseline, 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.

3.3 Many dispersant tests have been developed around the world. This test has been developed over many years using findings from world-wide testing to use standardized equipment, test procedures, and to overcome difficulties noted in other test procedures.

4. Interferences and Sources of Error

4.1 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), and acetone. Once cleaned, precautions must be taken to minimize contact of the glassware with surfactants to prevent undesired interferences.

4.2 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.

4.3 The Erlenmeyer flasks used in this test are tapered and the energy level varies with the amount of fill. The dispenser

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used to fill the vessels with water should be frequently checked by weighing the amount of water delivered.

4.4 The output is highly sensitive to the volume of oil, water, and extractant delivered. All pipets and dispensers should be calibrated on a weekly basis using water and a balance with an accuracy consistent with the weights being measured.

4.5 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.

4.6 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. The 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.

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

4.8 There are indications that the results for some premixed dispersant/oil combinations change over time. It is necessary to take precautions against this potential source of variation. The testing should be concluded as soon as possible after the premix is prepared, generally within a few hours. Results from samples stored for periods as long as a week should not be considered reliable.

4.9 Since the performance of the dispersant is affected by salinity, thorough mixing of the salt water is required. Care should also be observed to avoid evaporation from open containers of salt water. Over a period of days and weeks, the loss of water can significantly increase the salinity. An airtight closure is recommended to maintain salinity levels at 3.3 %.

4.10 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 before starting.

4.11 Extreme care should be taken when applying the oil to the surface such 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.

4.12 Water in the spout attached to the swirling flask may contain more or less oil than the water in the flask itself. Therefore, it is important to drain the contents of the spout (about 3 mL) before sampling. Oil sometimes migrates into the spout and may form a plug. This is especially true for heavy oils. It is important that the plug does not enter the sample.

4.13 The performance of the test can be verified and compared using standard oil and dispersant samples.

5. Apparatus

5.1 *Modified 120-mL Erlenmeyer Flask*, used as the test vessel. A side spout is added to enable taking the water sample

with minimal disturbance of resurfaced oil. These are illustrated in Fig. 1.

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

5.3 *Gas Chromatograph*, equipped with a flame ionization detector is used for analysis. The column is a fused silica column.

5.4 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:

5.4.1 *Fifteen Crimp Style Vials*, with aluminum/TFE-fluorocarbon seals, 12 by 32 mm,

5.4.2 *Twelve Erlenmeyer Flasks, 125 mL Glass*, modified with the addition of a drain spout attached to base,²

5.4.3 *Six Graduated Mixing Cylinders and Stoppers*, 25 mL glass,

5.4.4 *Six Separatory Funnels and Stoppers*, glass, 125 mL,
5.4.5 *Six Graduated Mixing Cylinders and Stoppers*, glass, 100 mL,

5.4.6 *Six Separatory Funnels and Stoppers*, glass, 250 mL,

5.4.7 *Six Graduated Cylinders*, glass, 50 mL,

5.4.8 *Six Dispenser or Glass Graduated Cylinders*, 5 to 25 mL,

5.4.9 *Positive Displacement Pipet*, 10 to 100 µL,

² Available from Pro Science, Inc., 770 Birchmount Road, Unit 25, Scarborough, Ontario M1K5H3.

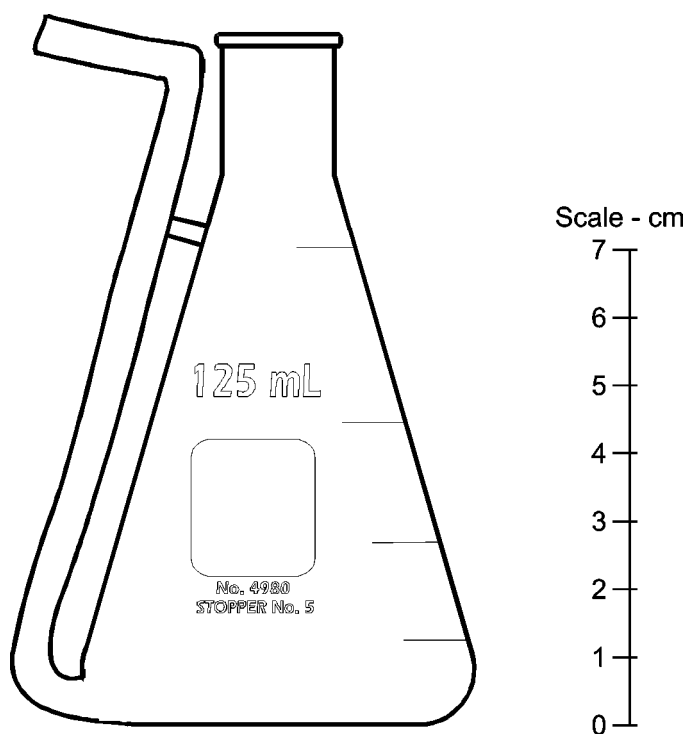


FIG. 1 Flask with Side Spout

- 5.4.10 *Positive Displacement Pipet*, variable volume, 1 mL,
- 5.4.11 *Two Digital Timers*,
- 5.4.12 *Dispenser or Graduated Cylinders*, 20 mL to 100 mL, and
- 5.4.13 *One Plastic Carboy*, 20 mL.

6. Reagents

6.1 *Reagents*—Water purified by reverse osmosis or equivalent means is used for the test water. Dichloromethane is distilled-in glass grade. Pentane is distilled-in-glass grade. Fine granular salt, non-iodized, is used for making the salt water. The chemical dispersant is used as supplied by the manufacturer. Oil is used as received.

7. Procedure

7.1 *Crude Oil and Dispersant Sample Collection and Storage*—The bulk oil is mechanically mixed for 2 to 4 h prior to obtaining a working sample. Working samples are stored in 2-L high-density polyethylene bottles with polypropylene screw closures. The working sample is mechanically shaken for 30 min 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. The dispersant is manually shaken, vigorously, prior to sampling.

7.2 *Premix Sample Preparation*—A small amount of oil is weighed into a 5-mL amber vial with TFE-fluorocarbon lined cap (approximately 1.0 mL). Approximately 100 mg of dispersant is added to the oil. Oil is added until a 1:25 ratio of dispersant to oil is achieved (approximately 2.5 mL oil is added). The sample is well mixed by manual shaking or stirring.

7.3 *Salt-Water Preparation*—Granular salt is weighed and added to water from reverse osmosis (RO) filtration to obtain a 3.3 % (w/v) solution. The water temperature is brought to 20°C before use.

7.4 *Swirling Flask Preparation*—The 120 mL of salt water is placed into a 125-mL modified Erlenmeyer 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. Extreme care should be taken when applying the oil to the surface such 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. Herding of the oil and some creeping of the mixture up the vessel wall is normal.

7.5 *Shaking of Swirling Flasks*—The flask and contents are mechanically mixed on the shaker in a temperature controlled chamber at 20°C, immediately after applying the oil to the surface of the water. A rotation speed of 150 r/min and a mixing time of 20 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.

7.6 *Sampling Collection*—After the sampling 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 plugs and 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 with 3 portions of 5 mL of a 70:30 dichloromethane:pentane solvent mixture, collected in a 25-mL graduated mixing cylinder. The final extraction volume is adjusted to 15 mL. 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.

7.7 *Sample Analysis*—Analysis consists of gas chromatographic analysis using a flame ionization detector (GC/FID) to determine the concentration of oil in solvent. 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/TFE-fluorocarbon 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 resolved peak area by the following equation:

$$RPH = A_{\text{total}}/A_{\text{is}} \times 1/RRF \times 20 (\mu\text{g}) \times 15/0.9 \times 120/30 \quad (1)$$

which simplifies to:

$$RPH = A_{\text{total}}/A_{\text{is}} \times 1330/RRF(\mu\text{g}) \quad (2)$$

where:

RPH = resolved petroleum hydrocarbon amount in μg,

*A*_{total} = total area of resolved peaks in counts,

*A*_{is} = area of the internal standard, and

RRF = relative response factor which in turn is given as follows:

$$RRF = A/A_{\text{is}} \times C_{\text{is}}/C \quad (3)$$

where:

A = the area, and

C = the concentration of the compound of interest.

7.8 *Calibration Standards*—A series of six oil-in-solvent standards are prepared for evaluating the efficiency of the dispersant for each dispersant/oil combination. The volume of premixed dispersant/oil solution for each standard is selected to represent a percentage efficiency of the dispersed oil, for example, 50 μL = 50 % efficiency (see 7.10 for method of choosing calibration standard volumes). The dispersant/oil mixture is then accurately measured and applied to the water surface, and treated in the same manner as the samples (see 7.4 and 7.5). At this point, the entire volume of water is transferred to a 250-mL separatory funnel and extracted with 3 portions of 20 mL of a solvent mixture of 70:30 dichloromethane:pentane. All oil is extracted, including the oil slick and oil on the walls of the swirling 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 resolved peak area by the following equations:

$$RPH = A_{\text{total}}/A_{\text{is}} \times 1/RRF \times 20 (\mu\text{g}) \times 60/0.9 \times 120/120 \quad (4)$$

which simplifies to:

$$RPH = A_{\text{total}}/A_{\text{is}} \times 1330/RRF (\mu\text{g}) \quad (5)$$

where:

RPH = resolved 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:

$$RRF = A/A_{\text{is}} \times C_{\text{is}}/C \quad (6)$$

where:

A = area, and

C = concentration of the compound of interest.

7.9 Selecting the Volume Range of the Calibration Standards—The volumes of the six calibration standards are chosen such that the RPH determined for each of the six samples of each dispersant/oil combination fall within the RPH range of the standards. The following guide is used to determine the range of standards for each type of oil being dispersed:

Heavy Oil – 10, 15, 20, 25, 30, 35 %

Medium Oil – 10, 20, 30, 40, 50, 60 %

Light Oil – 30, 40, 50, 60, 70, 80 %

7.10 Gas Chromatograph Parameters and Sequencing—Resolved petroleum hydrocarbon (RPH) analysis for C_8 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 \times 0.25 mm ID HP-5 fused silica column (0.10 μm film thickness)
Detector	flame ionization detector

Autosampler	equipped with an autosampler
Inlet	splitless
Gases, carrier	helium, 1.6 mL/min, nominal
	Make up helium – 28.4 mL/min
	Detector air – 400 mL/min
	Detector hydrogen – 30 mL/min
Injection volume	1 μL
Injector temperature	290°C
Detector temperature	320°C
Temperature program	50°C for 1 min, then 15°C/min to 310°C, hold 5 min.
	The total run time is 23.33 min.
Daily calibration	Alkane standard mixture of 20 ppm (containing a 5- α -androstane, selected alkanes, and α -Terphenyl in hexane) is measured before and following each sample set.

7.11 Cleaning Glassware—A rigorous cleaning program is undertaken throughout the experiment to reduce possible cross-contamination and accumulation of surfactants 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. Glassware is dried at 180°C while plastic ware is air dried.

8. Calculation and Reporting

8.1 The percentage of dispersion is calculated by creating a calibration curve of effectiveness versus RPH from the standards and then taking the RPH of the experimental value and setting the appropriate effectiveness value.

8.2 At least six measurements of the RPH and effectiveness should be measured. The standard deviation is taken and reported. A standard deviation of more than 10 (absolute value) indicates poor repeatability and the experiments should be repeated.

9. Keywords

9.1 dispersant; dispersant testing; effectiveness testing; oil spill; swirling flask

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