



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

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^{ε1} NOTE—An editorial change was made to Section 6 in February 2012.

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 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 dependant on sea energy, oil state, temperature, salinity, actual dispersant dosage, and amount of dispersant that enters 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 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 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 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 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 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.

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

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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.

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

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. 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.

4.7 Following surfactant addition, vigorous mixing is required to thoroughly 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.

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 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.

4.12 A slick may form at the water surface in the spout of the swirling flask during mixing and settling. It is important this oil does not enter the water sampled for analysis. Therefore it is important to drain the contents of the spout (about 3 mL) prior to sampling, and ensure any adhering droplets do not enter the sample.

4.13 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 creaming, can impact results. Since the water samples cannot be sampled simultaneously, this step must be performed with as much careful haste as possible, to reduce the difference in settling times experienced by the samples in the test run.

4.14 Analysis of the gas chromatograph-detectable Total Petroleum Hydrocarbon (TPH) content is subject to variability in GC operation and repeatability. 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.

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

4.16 The accuracy and repeatability 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 a standard Erlenmeyer flask to enable sampling from the water column with minimal disturbance of resurfaced oil. This vessel is 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 temperature-controlled chambers. If such an enclosed chamber is not used, the measurement must be conducted inside temperature-controlled rooms.

5.3 *Gas Chromatograph (GC)*, 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 *Eighteen Crimp Style Vials*, with aluminum/PTFE (polytetrafluoroethylene) 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,

² 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 M1K5H3. 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.

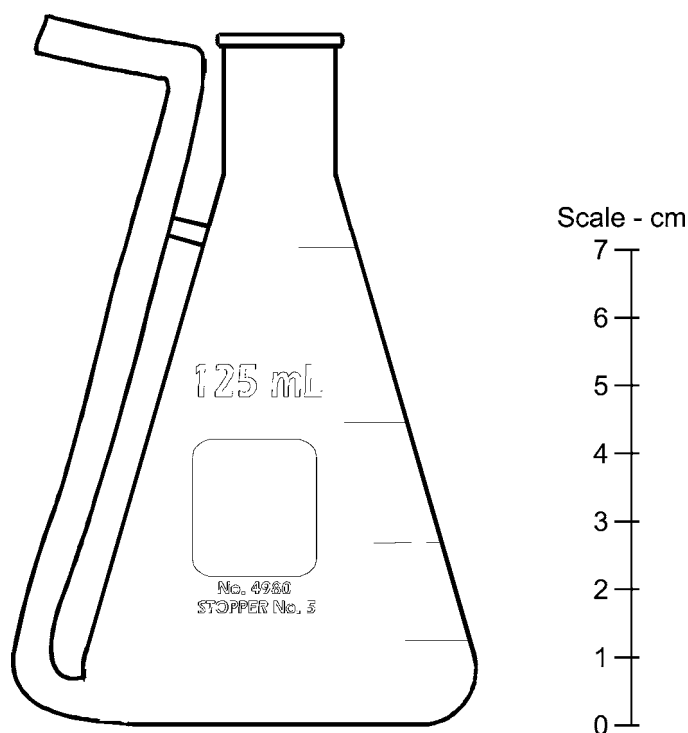


FIG. 1 Flask with Side Spout

- 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 ,
- 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 L.

6. Reagents

6.1 *Reagents*—Water purified by reverse osmosis or equivalent means is used for the test water. Dichloromethane and pentane are distilled-in-glass grades. Fine granular sodium chloride or table 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 at 20°C 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 (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.

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 stabilized 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 but can be minimized.

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 *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 a 70:30 dichloromethane:pentane solvent mixture, shaken vigorously for at least 1 min, and the extract 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/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 peak area by the following equation:

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

which simplifies to:

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

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 (Eq 3):

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

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 7.9 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 three times with 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 total baseline corrected area of the chromatogram and applying the following equations:

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

which simplifies to:

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

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:

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

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 TPH determined for each of the six samples of each dispersant/oil combination fall within the TPH range of the standards. The calibration set should be selected in 10 % effectiveness increments (10 μL), starting at no less than 10 % effectiveness (10 μL).

7.10 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 20 % increments, for example 10, 30, 50 % in one run, and 20, 40, 60 % in the other, to mitigate the impact of variations in test conditions between the two runs.

7.11 Gas Chromatograph Parameters and Sequencing—Total petroleum hydrocarbon (TPH) 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 DB-5HT 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 or comparable conditions if using hydrogen carrier gas
Injection volume	1 μL
Injector temperature	300°C
Detector temperature	320°C
Temperature program	40°C for 2 min, then 25°C/min to 325°C, hold 12 min. The total run time is 25.4 min.
Daily check	Alkane standard mixture of 20 ppm (containing 5- α -androsterane, selected alkanes, and o-Terphenyl in hexane) is measured before and following each sample set.

7.12 Cleaning Glassware—A thorough cleaning program is undertaken throughout the procedure 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 TPH from the standards and then taking the TPH of the experimental value and setting the appropriate effectiveness value.

8.2 At least six measurements of the samples and effectiveness calibration set should be taken. The standard deviation is taken and reported. A standard deviation of more than 5 (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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