Recent Results from Dispersant Testing

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Abstract

Recent results of dispersant testing are reviewed, including slight revision in the dispersant analytical procedures, testing of new products, testing of long-term stored dispersants, and a comparison of Corexit 9527 and 9500 dispersant formulations.

The procedure for the Swirling Flask Test has not altered appreciably since its inception, however the analysis of the quantity of oil dispersed has undergone significant changes. The originally-developed procedure made use of colorimetric analysis, but has since advanced to gas chromatographic analysis. With the change in analysis method, however, a host of subtle changes have been required that were not considered when first changing from colorimetry to gas chromatography. A number of minor improvements have been made to the procedure to correct and upgrade facets of the analysis.

Several new dispersant products have been tested, results of this testing will be summarized.

A test series was conducted on the dispersant Corexit 9527 that had been stored for more than 20 years in a tank truck. The tests show that the effectiveness, toxicity and colour of the product did vary somewhat between the three levels, however this might not be significant in terms of field effectiveness.

A comparison of the laboratory effectiveness of Corexit 9527 and 9500 was completed. Results show that the effectiveness of 9500 is generally greater than that of 9527, however, this is not related to the amount of effectiveness. Generally, the higher the effectiveness, the greater the effectiveness of 9500 and vice versa. Statistically, about 1/4 of the time, 9527 is more effective than 9500.

1.0 Introduction

Studies on various facets of dispersants continue at Environment Canada's laboratories. This paper reports on several smaller studies related to dispersant effectiveness. During the years from 1985 to 1990, Environment Canada and the United States Minerals Management Service endeavoured to develop new laboratory dispersant effectiveness tests that provided repeatable results with systems that have relation to the open waters where dispersants are actually used to combat oil spills. During this time, five tests were examined out of a total suite of about 20 possibilities. Initial work was done on the possible test concepts to assess potential for further study. The tests that were selected for detailed comparative testing were one so on the basis that these were tests used by other organizations (eg. Mackay-adeau-Steelman tests, Warren Springs or Labofina test and the IFP test) or showed tential for further development (swirling flask and flowing column tests) (Fingas *et* . 1987). This comparative testing showed that all five tests could produce fectiveness results of the same order-of-magnitude if: a) the oil-to-water ratio was aintained high (greater than 1:1000) and b) if the settling time was maintained at eater than 10 minutes. The following factors were not found to change results to a ge degree: a) vessel shape b) mode of energy application and c) general perimental setup. The relative amount of energy applied was found to have a very sive effect on the results.

Further development work was conducted on the swirling flask test (Fingas *et* 1989). Tests included altering each experimental parameter to measure the effect. his work was done for purely scientific reasons as well as to ensure that testing was t an optimal point. Some of the tests tried in the earlier testing showed anomalies ecause their operational parameters were inadvertently set at values that were near itical thresholds and variances in performing the experiment produced noisy results.

Recent studies of this nature focussed on improving the analytical procedures. This study is one of a continuing series exploring laboratory dispersant effectiveness esting (Fingas *et al.* 1996, 1997, 1998, 1999). New improved methods for analysing he oil-in-water using gas chromatography are given. Rather than the colorimetric ethodology, which has several limitations, a gas chromatographic method has been eveloped (Fingas *et al.* 1995a). The older colorimetric measurements were ncumbered with high noise levels which often obscured the phenomena being easured, especially for the very light oils that did not absorb in the wavelengths sed.

2.0 Analytical Methodologies

The methodology reported in a recent paper (Fingas *et al.*, 1999) was adjusted o simplify the analysis and better reflect the appropriate range of use for the method. n the original version of the swirling flask test, UV/Visible spectrophotometry was ed to quantify the oil content extracted from the oil/water dispersion. This method as capable of quantifying heavy, dark coloured oils in low concentrations, because f the high level of absorption at the applicable wavelengths. With conversion of the ethod to gas chromatography, the quantification of low concentrations of poorly esolved oils presented an obstacle. Initially, the oil content analysis continued to use lank subtraction. The error in this methodology is discussed in an earlier paper Fingas *et al.*, 1999), and was changed to comparison of resolved peaks. However, ue to the low level of resolved peaks for quantification, heavy oils continued to be nalysed by the blank subtraction method. This component of the method has now een dropped, to remove the need for a decision-making step in the analysis of the as chromatogram.

The range of calibration standards for heavy oils also required revision. The revious version had a range of calibration standards representing from 2 to 25% ffectiveness. Often, the standards representing 2 and 5% effectiveness had no esolved petroleum hydrocarbon (RPH) content, as the combination of low oncentration and poor resolution of the measurement technique to such low levels. o eliminate this distortion to the calibration curve, the range of calibration standards

now begins at 10% effectiveness for heavy oils. As a result, the detection limit of the Swirling Flask Test is now 10%; all oils dispersing less than 10% fall below the range of calibration standards, and are reported as <10% effectiveness. The limitation in not being able to quantify effectiveness of dispersed mixtures that are below this threshold, is not considered significant, as the error and standard deviation below 10% is nearly as great.

The revised procedure is now simplified, with a single analytical method to apply to all oil types, and a detection limit of 10% dispersant effectiveness. Appendix A contains the newly revised procedures. This is also the procedure used in the following sections

3.0 Results of Testing of New Products

Several new products were tested for both dispersant effectiveness and for effectiveness as a surface washing agent. The dispersant test procedure followed that in the appendix and was implemented using the standard ASMB oil. The properties of this oil are given in Jokuty *et al.* (1999). The surface washing test results followed procedures given in the literature (Fingas *et al.*, 1995b). This test is simply a measure of the removal of Bunker C on a trough by water flushing, after the oil is treated with a ratio of 1:5 of the agent.

Test results are given in Table 1.

Table 1 shows that the products, Dasic Slickgone and Dispersit showed a moderate dispersant effectiveness and that the products, ZI-800 and ZI-808 show a high dispersant effectiveness. As surface washing agents only the Dasic Slickgone showed a moderate dispersant effectiveness and only in fresh water. This is actually an interesting result because most dispersants show little or no effectiveness as a surface washing agent.

Table 1

	Dispersant Effectiveness		Surface Washing Result			
	Average	Std. Dev.	Fresh Water		Salt Water (3.3%)	
Product	%		Average	Std. Dev.	Average	Std. Dev.
Dasic Slickgone NS	31.8	3.7	35.4	6.0	17.1	2.4
Dispersit SPC 1000	32.2	3.0	13.8	1.7	5.1	1.8
SuperDispersant 25	18.1	1.6	6.3	1.3	3.2	3.5
SX-100	0	0	9.8	3.5	5.1	1.9
Vytac DSP 2823	0	0	3.6	2.4	5.2	3.1
ZI-800	54.5	3.0	18.1	7.0	4.2	1.5
ZI-808	58.9	4.3	7.2	1.2	8.3	0.9

4.0 Storage of Dispersants over Time

One of the problems with dispersant use is that dispersants are often stored for many years and then the question of their efficacy arises. Over the years ESD has tested old stock dispersants, mostly from the Canadian Coast Guard, to assess their efficacy. The Coast Guard stock in Newfoundland is about 20 years old and is maintained in a tank trailer. Before the most recent test, the trailer had not moved for about 6 years. Sampling at three layers (top, middle and bottom; and a mixed sample) conducted to test if separation had occurred and to see if there was a loss of ectiveness. The test was dispersant effectiveness using ASMB oil, as above, and according to the standard procedure given in the appendix. Results are given in ble 2.

Table 2 Long Term Storage of Corexit 9527

	Dispersant Effectiveness %	
Layer	Average	Std. Dev.
Top	38.4	5.0
Centre	34.5	4.0
Bottom	48.3	7.3
Stirred	42.1	4.9
Average of layers	40.4	5.4

The results show that there is a small differential in effectiveness between the tom and top layers, within the standard deviation noted. This difference is about ame as when the top, centre and bottom layer effectiveness values are averaged. difference also matches the colouration differences noted in the material as denced by darker colours in the lower layer of the tank. There appears to be a ht settling of the heavier surfactants. The colouration differences, however, may due to rust or dirt particles collecting on the bottom.

The variation in colour was measured using a Perkin-Elmer Model 552A ectrophotometer. The stirred sample was used as the reference, with changes in orbance being recorded for the other three - a positive number indicates greater orbance, and a negative number indicates lower absorbance. The wavelengths d were arbitrarily assigned, based on limits of response, covering the widest range sible. The results are in Table 3.

ble 3 Colour Variations in the Long-Term Stored Dispersant

	Relative Absorbance		
velength	Top Sample	Centre Sample	Bottom Sample
	0.008	0.012	0.125
	0.012	0.006	0.159
	-0.008	-0.001	0.049

absorbance readings for the top and centre samples indicates that there is no nificant difference between the top, centre and mixed samples. The higher dings of the bottom sample is consistent with a visually darker colour noted. re was debris in the sample, possibly rust, which may be imparting the oloration to the surrounding solution.

These data indicate that there is no significant effects as a result of the long m storage of this particular batch of Corexit 9527.

Comparison of the Effectiveness of Corexit 9527 and Corexit 9500

Several theories on the comparative effectiveness of Corexit 9527 and 9500 e been proposed. For example, some speculation was that 9500 was much more tive on heavy oils and that Corexit 9527 was more effective on certain specific

oils. Sufficient data now exist to compare these two products over a wide range of oils.

Table 4 gives the numerical summary of the test data. These data are taken from the oil properties data base (Jokuty *et al.*, 1999) and values were measured by the methods given in the appendix with the exception that the published version that was current during the year, would have been used. Figure 1 shows the same data graphically, with the best fit line through the data.

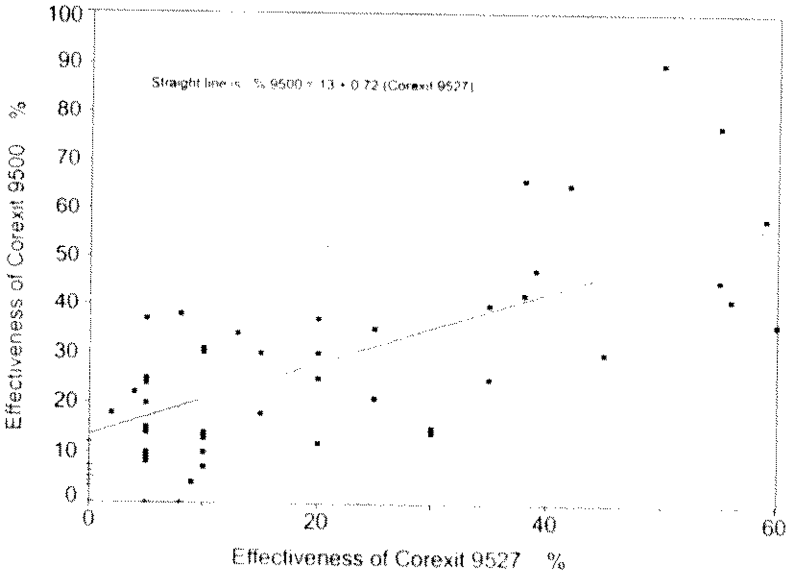

Figure 1 Comparison of the Effectiveness of Corexit 9500 and 9527

…le 4 Comparison of the Effectiveness of Corexit 9527 and 9500

ar of est	Oil Name	Evaporation % of oil	Percent Effectiveness 9500	9527
	Alberta Sweet Mixed Blend Reference #4		42	38
4	Amauligak		45	55
	Arabian Light	0	21	25
4	BCF 24		12	20
	Belridge Heavy	0	4	9
	Beta		0	0
	Bunker C Fuel Oil		7	0
4	Bunker C Light Fuel Oil		5	0
	California (API 11)		0	0
	California (API 15)		0	0
	Carpinteria	0	16	0
	Carpinteria	9	7	0
	Carpinteria	15	7	0
	Cat Cracking Feed		10	5
	Dos Cuadras	0	37	5
	Dos Cuadras	20	7	10
	Empire		41	10
4	Endicott	0	10	10
	Eugene Island Block 32		18	15
	Eugene Island Block 43		25	5
	Federated	0	37	20
	Federated	16	38	8
	Federated	28	22	4
	Federated	42	18	2
	Forties Blend		58	59
	Granite Point	0	41	56
	Green Canyon Block 109		20	5
	Green Canyon Block 65		15	5
4	Gullfaks		25	20
	Hondo	0	8	5
	Hondo	17	6	0
	Hondo	32	4	0
	Hout		18	2
	Iranian Heavy		14	10
	Lago		0	0
	Louisiana		43	13
4	Lucula		20	5
4	Main Pass Block 140		35	25
	Main Pass Block 37		30	20
	Malongo		15	5
4	Mississippi Canyon Block 194		30	15
	Oseberg		15	30
	Pitas Point	0	65	42
	Pitas Point	24	66	38
	Point Arguello Comingled	0	3	0
	Point Arguello Comingled	9	0	0
	Point Arguello Comingled	15	0	0
	Point Arguello Comingled	22	0	0
	Point Arguello Heavy	0	0	0
	Point Arguello Heavy	9	0	0
	Point Arguello Heavy	18	0	0
	Point Arguello Light	0	13	10
	Port Hueneme	0	12	0
	Port Hueneme	4	5	0
	Port Hueneme	8	0	0
	Santa Clara	0	6	0
	Santa Clara	11	4	0
	Santa Clara	22	0	8
	Ship Shoal Block 269		30	10
	Sockeye	0	24	5
	South Pass Block 60		30	45
	South Timbalier Block 130		30	10
	Statfjord		40	35
	Swanson River	0	36	60
	Takula	0	14	5
	Terra Nova (1994)		14	30
	Thevenard Island		57	55
	Trading Bay	0	47	39
	[illegible]	0	0	5

This comparison shows that generally Corexit 9500 is slightly more effective than Corexit 9527. There does not seem to be a heavy oil effect. This comparison is somewhat less effective because of the broad spectrum of data used, some of the older data may be less accurate. Furthermore, the Corexit 9527 data is older and was rounded down to steps of 5. However, the trend is still clear that the effectiveness of 9500 is higher for those oils where effectiveness is very good and only slightly more effective on the heavier, less dispersible oils. In about 1/4 of the cases, Corexit 9527 is more effective.

6.0 References

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Appendix A Swirling Flask Test Method

A.1 Summary of Test Method

Dispersant is pre-mixed with oil, placed on water in a test vessel. The test vessel is agitated on 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.

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.

A.2 Reagents and Equipment

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.

Apparatus

A modified 120 mL Erlenmeyer flask is used as the test vessel. A side spout is added to enable taking the water sample with minimal disturbance of re-surfaced oil. These are illustrated in Figure 2. Modified vessels are available from Pro Science Inc., Toronto (416-699-9901)

The shaker is a moving-table shaker with an orbital motion of 1 inch 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 should be conducted inside temperature-controlled rooms. (The New Brunswick Environmental Shaker model G27 (New Brunswick Scientific, Edison, NJ) is one enclosed shaker that meets specifications.)

Analysis is accomplished using a gas chromatograph equipped with a flame ionization detector. The Hewlett Packard 5890 GC/FID with Chemstation software package is an equivalent unit. The column is a fused silica DB5ms column (J & W Scientific, Folsom, CA or equivalent).

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

- 15 - 12mm x 32mm crimp style vials with aluminium/Teflon seals (Supelco or equivalent)
- 12 - 125 mL glass, Erlenmeyer flasks, modified with the addition of a drain spout attached to base (available from Pro Science Inc., Toronto, Ontario, phone 416-699-9901)
- 6 - 25 mL glass, graduated mixing cylinders and stoppers
- 6 - 125 mL glass, separatory funnels and stoppers
- 6 - 100 mL glass, graduated mixing cylinders and stoppers

6 - 250 mL glass, separatory funnels and stoppers
6 - 50 mL glass, graduated cylinders
6 - 5 to 25 mL dispenser or glass graduated cylinders
10μL to 100 μL positive displacement pipette (Mandel Scientific Co. or equivalent)
1 mL positive displacement pipette - variable volume (Mandel Scientific Co. or equivalent)
2 - digital timers
20 mL to 100 mL dispenser or graduated cylinders
1 - 20 L plastic carboy

3 Interferences and Sources of Error

Interferences can be caused by contaminants, particularly residual oil or factants in solvents, on glassware and other sample processing apparatus that lead discrete artifacts or elevated baselines in gas chromatograms. All glassware must thoroughly cleaned. The cleaning process includes rinsing with dichloromethane remove the oil, followed by rinsing three times each with tap water, purified water verse osmosis) and acetone. Once cleaned, precautions must be taken to minimize ntact of the glassware with surfactants to prevent undesired interferences.

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

The Erlenmeyer flasks used in this test are tapered and the energy level varies h the amount of fill. The dispenser used to fill the vessels with water should be quently checked by weighing the amount of water delivered.

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

The use of positive displacement pipettes is mandatory for all controlled umes of microlitre quantities. Use of volume displacement pipettes will result in neous results due to the viscosity of the dispersants and oils, the variable osity of the oils to be tested (some semi-solid) and the density of hloromethane.

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

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

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 after the premix is prepared as possible, generally within a few hours. Results from samples stored for periods as long as a week should not be considered reliable.

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%.

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.

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.

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 forms plug. This is especially true for heavy oils. It is important that the plug does not enter the sample.

The performance of the test can be verified and compared using standard oil and dispersant samples. These are available at no charge, but in limited quantities, from the Emergencies Science Division, Environment Canada, Ottawa, Ontario, phone: 613-998-9622.

A.4 Procedures

A.4.1 Crude Oil and Dispersant Sample Collection and Storage

The bulk oil is mechanically mixed for 24 hours 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 minutes 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.

A.4.2 Premix Sample Preparation

A small amount of oil is weighed into a 5 mL amber vial with Teflon lined cap (approx. 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 (approx. 2.5 mL oil is added). The sample is well mixed by manual shaking or stirring.

A.4.3 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.

A.4.4 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 µL volume of pre-mix solution is carefully applied onto the surface of the water ne a positive displacement pipette. The tip of the pipette is applied to the water ace and the dispersant/oil mixture gently expelled. Extreme care should be taken hen applying the oil to the surface such that mixing does not occur. The oil should ntly glide across the water to form a slick. If the oil streams out into the water, the tation can disperse the oil, increasing the amount of oil dispersed and erroneously ing the final dispersion result. Herding of the oil and some creeping of the mixture the vessel wall is normal.

5 Shaking of Swirling Flasks

The flask and contents are mechanically mixed on the shaker in a temperature ntrolled chamber at 20°C, immediately after applying the oil to the surface of the ter. A rotation speed of 150 RPM and a mixing time of 20 minutes are used to itate the samples followed by a 10 minute settling period. The flasks should be moved from the table-mounted holders prior to the settling period to limit the tation between settling and sampling.

6 Sample Collection

After the settling time is complete, 3 mL of the oil-in-water phase from the out of the flask are drained to waste to dispose of any oil plugs and obtain a presentative sample. A 30 mL aliquot of the dispersed oil in water sample is llected in a graduated cylinder and transferred to a 125 mL separatory funnel. The l is extracted with 3 portions of 5 mL of a 70:30 dichloromethane:pentane solvent ixture, collected in a 25 mL graduated mixing cylinder. The final extraction volume adjusted to 15 mL. Care is taken to ensure that water is not taken along with the lvent. During extraction, vigorous shaking is required to achieve full extraction. It best to shake each separatory funnel individually to achieve consistent results.

7 Sample Analysis

Analysis consists of gas chromatographic analysis using a flame ionization tector (GC/FID) to determine the concentration of oil in solvent. A 900.0 µL ation of the 15 mL solvent extract and a 100.0 µL volume of internal standard (200 m 5-α-Androstane in hexane) are combined in a 12mm x 32mm crimp-style vial th aluminum/Teflon seals and shaken well. Petroleum hydrocarbon content is antified by the internal standard method, with the average hydrocarbon relative ponse factor (RRF) determined over the entire analytical range in a separate run. e petroleum content is determined by integrating the resolved peak area by the lowing equation

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

which simplifies to:

$$RPH = A_{total}/A_{is}\ X\ 1330/RRF(\mu g) \qquad (2)$$

Where

RPH is the Resolved Petroleum Hydrocarbon amount in µg
A_{total} is the total area of resolved peaks in counts
A_{is} is the area of the internal standard
RRF is the Relative Response Factor which in turn is given by
$RRF = A/A_{is}\ X\ C_{is}/C$, where A is the area, C is the concentration of the compound of interest.

A.4.8 Calibration Standards

A series of 6 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, eg. 50 µL = 50% efficiency (see Step 4.10 below 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 Step 4.4 and 4.5 above). 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:

$$RPH = A_{total}/A_{is}\ X\ 1/RRF\ X\ 20\ (\mu g)\ X\ 60/0.9\ X\ 120/120 \qquad (3)$$

which simplifies to:

$$RPH = A_{total}/A_{is}\ X\ 1330/RRF\ (\mu g) \qquad (4)$$

Where:

RPH is the Resolved Petroleum Hydrocarbon amount in µg
A_{total} is the total integrated area
A_{is} is the area of the internal standard
RRF is the Relative Response Factor which in turn is given by
$RRF = A/A_{is}\ X\ C_{is}/C$, where A is the area, C is the concentration of the compound of interest.

A.4.9 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%

A.4.10 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 x 0.25 mm ID HP-5 fused silica column (0.10 µm film thickness)
Detector -	flame ionization detector
Autosampler -	Hewlett Packard 7673 or equivalent
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 minute, then 15 °C/min to 310 °C, hold 5 minutes. The total run time is 23.33 minutes.
Daily calibration - Alkane standard mixture of 20 ppm (containing 5-α-Androstane, selected alkanes, and o-Terphenyl in hexane) is measured before and following each sample set.

Cleaning Glassware

A rigorous cleaning program is undertaken throughout the experiment to
possible cross-contamination and accumulation of surfactants on the
are. Glassware is thoroughly rinsed with tap and purified (RO) water and
romethane between each experimental run. At weekly intervals, the lab ware is
l in a Decon 75 (BDH Inc., or equivalent) solution or equivalent for 24 hours,
with tap and purified (RO) water followed by the solvent acetone. Glassware
d at 180 °C while plastic ware is air dried.

Calculation and Reporting

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

At least six measurements of the RPH and effectiveness should be measured.
andard deviation is determined and reported. A standard deviation of more
(absolute value) indicates poor reproducability and the experiments should be
ed.

Low RPH values that fall below the range of the lowest calibration value
be reported as less than the value of that calibration standard. This last
ation standard is also the detection limit of the test.

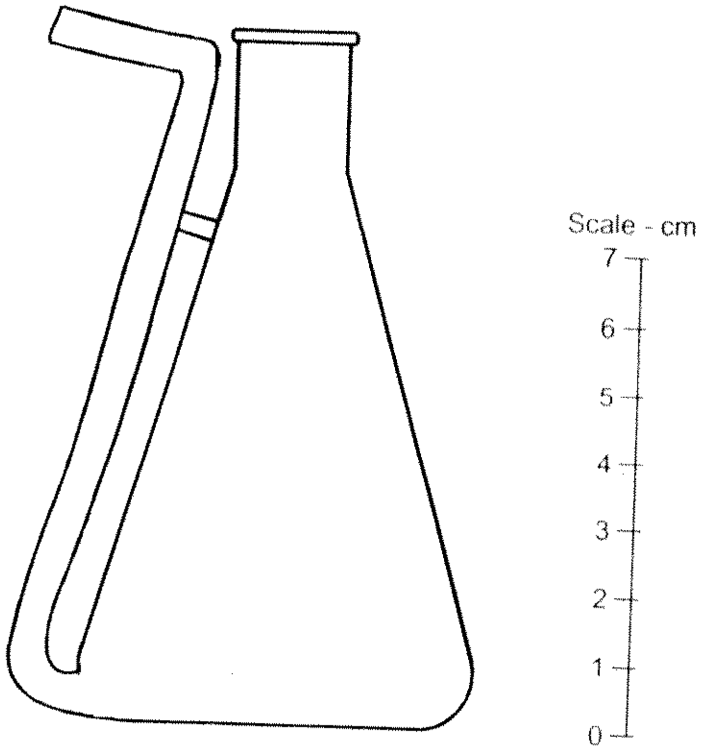

Figure 2 - The Swirling Flask Vessel