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Analytical Procedures for Dispersant Effectiveness Testing

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Abstract

This paper reports on studies of the analytical procedures for measuring dispersant effectiveness in the laboratory. Previous papers reported on the development of a gas chromatographic method for measuring dispersant effectiveness. This method was shown to have far greater accuracy than the old colorimetric methods. A new gas chromatographic method has been developed and tested which shows improvements in the data quality and time required for analysis.

New characteristics of the method include: correction for very low oil-in-water values, use of fewer calibration points directly around the expected value, and a different method for heavier oils with fewer resolvable chromatographic peaks. The new method is demonstrated by comparing results with older methods.

1.0 Introduction

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 done so on the basis that they were tests used by other organizations (eg. Mackay-Nadeau-Steelman tests, Warren Springs or Labofina test and the IFP test) or showed potential for further development (swirling flask and flowing column tests) (Fingas *et al.* 1987). This comparative testing showed that all five tests could produce effectiveness results of the same order-of-magnitude if: a) the oil-to-water ratio was maintained high (greater than 1:1000) and b) if the settling time was maintained at greater than 10 minutes. The following factors were not found to change results to a large degree: a) vessel shape b) mode of energy application and c) general experimental setup. The relative amount of energy applied was found to have a very large effect on the results.

Further development work was conducted on the swirling flask test (Fingas *et al.* 1989). Tests included altering each experimental parameter to measure the effect. This work was done for purely scientific reasons as well as to ensure that testing was at an optimal point. Some of the tests tried in the earlier testing showed anomalies because their operational parameters were inadvertently set at values that were critical

and variances in performing the experiment produced noisy results.

This study is one of a continuing series exploring laboratory dispersant effectiveness testing (Fingas *et al.* 1996, 1997, 1998). In this paper we report on improved methods for analysing the oil-in-water using gas chromatography. Rather than the colorimetric methodology, which has several limitations, a gas chromatographic method has been developed (Fingas *et al.* 1995). The older colorimetric measurements were encumbered with high noise levels which often obscured the phenomena being measured.

The traditional colorimetric method of measuring laboratory dispersant effectiveness is to take a small aliquot of the dispersion test water, extract the oil, usually with methylene chloride, and then measure the colour at a specific wavelength. This value is compared to a standard curve and effectiveness calculated. The preparation of the standard curve was traditionally done by injecting the appropriate amount of oil directly into the methylene chloride and measuring light absorbance. It was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some colouration in the methylene chloride, despite drying the extract. This results in inflated effectiveness values.

Experiments were conducted to investigate the problem (Fingas *et al.* 1995). Sample extracts of the methylene chloride were analysed both by the colorimetric method and by gas chromatography. Light oils have low absorbance at the typical wavelengths chosen and were found to give errors using traditional methods of analysis by as much as 300%. More typical medium oils showed errors of only a few percent, but heavy oils again show significant error because of the different wavelengths at which they absorb. Several methods of compensating for this effect were tried and found to be inadequate to compensate for this effect.

The chromatographic method and implementation for the swirling flask test that was described in a prior paper (Fingas *et al.* 1995) contained some weaknesses and these were overcome by implementing several changes (Fingas *et al.* 1998).

2.0 Experimental

The standard swirling flask method was employed as described in the Appendix to this paper. All analysis was performed only by gas chromatography. The chromatography procedure was modified using standard procedures published in the literature (Wang and Fingas, 1997, Fingas *et al.* 1998).

Six replicates were performed for each oil and dispersant combination. Only two replicates are conducted during the same batch run of six samples, providing for statistical variation between experimental runs. A 1/4 portion of the water column is collected from each sample, and the dispersed petroleum content determined by GC analysis. A standard curve is then obtained from a set of six prepared standards, each representing a percentage of the total volume of oil and dispersant used for the samples. A plot of the volume percentage against the determined mass of oil yields a linear equation of percentage versus mass. Substituting the mass of dispersed oil determined for the samples into the standard equation, corrected for the ratio of sample collected, provides a measure of the dispersant effectiveness in percentage. Any affects due to weathering or the extraction process are accounted for by subjecting the standards to the same mixing and extraction procedures as the samples. The selection of percentages to use for the standards is outlined in the procedure in

the Appendix.

Oils were chosen for the experiments from the supply in the laboratory. Properties of these oils are given in the databases published by Environment Canada (Jokuty *et al.* 1996).

The modified method specifies two procedures, one for heavier oils with few resolved peaks and one for lighter oils with an abundance of resolved chromatographic peaks. Each method will be shown to yield much more accurate results for the specific type of oil measured. The basic chromatographic method is the same, just the use of the chromatographic data varies.

3.0 Results and Discussion

The new procedure was used to measure the dispersant effectiveness of several oils which had been measured previously. Results of this comparison are given in Table 1.

Table 1 shows the results from two versions of the new method, GC-TPH resolved peaks and blank subtraction. The same chromatographs are use for each

Table 1 **Comparison of Results With Various Methods**

Oil	GC-TPH Resolved Peaks			GC-TPH Blank Subtraction			GC-TPH Old Method		UV-Vis Colorimetry	
	Average*	Std. Dev.	Mass (mg)	Average*	Std. Dev.	Mass (mg)	Average*	Std. Dev.	Average	Std. Dev.
ASMB	38.4	4.6	3.61	40.0	6.4	27.32	43.2	2.6	37.1	4.2
Belridge 2.7%	37.6	7.6	0.23	7.6	1.2	2.53				
Bunker C 8.41%	13	1.2	0.28	6.4	2.2	2.13				
Federated	37.3	5.9	4.11	37.1	2.4	22.16	37.9	7.4	52.5	4.2
Louisiana	30.6	1.6	2.17	32.4	1.5	22.16	34.0	2	19.3	4
Pitas Point	65.3	1.3	12.78	86.1	2.8	67.28	72.8	7.5	44.9	6.4
Point Arguello	11.9	1.9	0.41	8.9	1.3	3.00	3.2	1.5	2.6	0.3
Thevenard	77.3	2.1	13.41	77.2	5.1	49.15	88.7	6.1	>100	
Tapis 13.19%	69.0	2.9	21.80	77.3	3.7	46.41			>100	

(percentage refers to the percent lost by evaporation)

* *average result is the percent effectiveness of the dispersant Corexit 9500 with the particular oil*

method, but the mathematical treatments are different. The 'resolved peak' method is used in those cases where there are sufficient resolved peaks in the chromatogram to quantify the oil using only these peaks. This is the case with most light or medium crudes and diesel fuel. Heavier oils have a large 'UCM' peak or unresolved complex matter peak. Quantifying oils using the integral of all peaks is a traditional method of performing this measurement, however is less accurate in the case where there are significant resolvable peaks, because the unresolved peak is variable and because baselines for this peak are hard to establish. If there are few resolved peaks or these peaks are small in comparison to the area of the UCM, the opposite is true in terms of accuracy. This is because quantification on the basis of a small area of peaks versus a large area of UCM, is disproportionate and any small error in quantification results in a large error. Figures 1 and 2 illustrate the difference in the chromatograms of Thevenard Island crude and Bunker C which illustrates this point.

Table 1 shows the average effectiveness percent derived using the specific method and the standard deviation. For the GC-TPH methods, the mass of oil accounted for (in mg out of a total of 100 mg) in the water column accounted for by the specific method. This value is given for comparison and to illustrate the differences between methods. The 'old method' is one in which quantification was

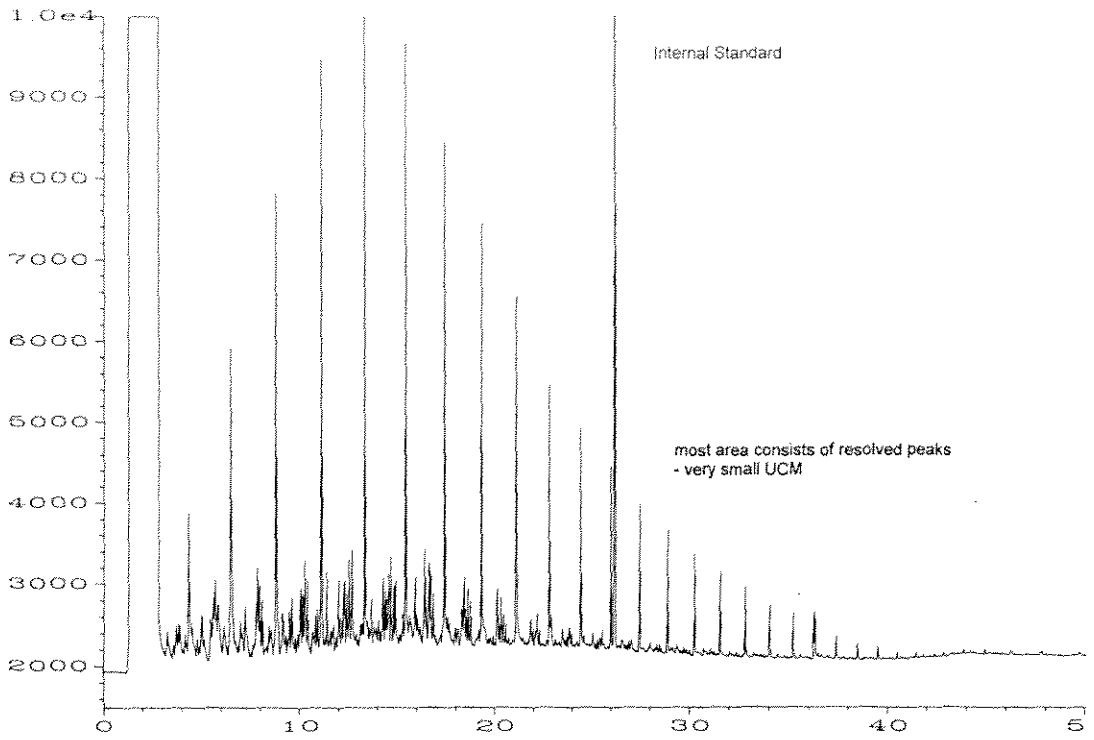

Figure 1 - Chromatogram of Thevenard Island Oil

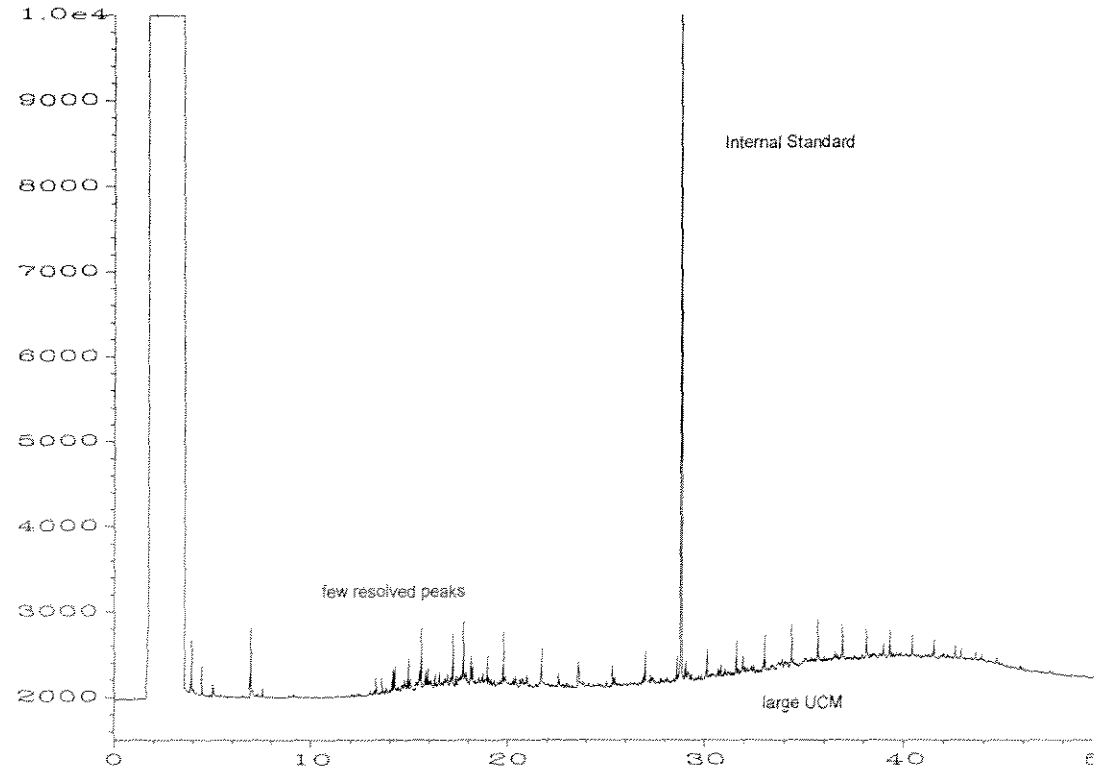

Figure 2 - Chromatogram of Bunker C

done on the basis of total integration (similar to 'blank subtraction method') with a number of minor changes. The UV-Vis method use colorimetry to quantify the oil. Several comparison of this method with gas chromatographic methods have been made (Fingas *et al.* 1995).

Data in Table 1 illustrate several points. Medium crude oils such as ASMB are measured relatively similar by all four methods. Heavy oils such as Belridge and Bunker C, are best analyzed by the blank subtraction method because their resolved peak areas are too small in comparison to the unresolved peak area. This can be seen by comparing the mass of oil accounted for in the resolved peak area. This peak area is 0.23 and 0.28 mg for Belridge and Bunker respectively. These values represent a small fraction of mass compared to that of the blank subtraction method (2.53 and 2.13 mg). In the case of heavy oils, the resolved peak method over calculates effectiveness by as much as 5 times as in the case of Belridge.

Very light oils such as Pitas Point and Thevenard are best measured using the resolved peak method; the blank subtraction method yields slightly higher results. It is important to note that the older UV-vis method often yields very high results for these light oils, usually over 100%.

An examination of the effectiveness values achieved from the UV-Vis methods shows these to be anomalous except for light to medium crudes such as ASMB. Past studies have shown this method to be very flawed (Fingas *et al.* 1995). The primary reason for this is the inconsistent coloration of oil dispersion in water, the basis of the method.

It is interesting that the standard deviation is about the same for all four methods compared here.

4.0 Conclusions

A modified chromatographic method for the measurement of laboratory dispersant effectiveness was presented and tested on several oils. Results were compared with older methodologies. Several problems had been noted with the older methodologies, and these have been corrected by ensuring that the nature of the oil is taken into account. Oils which have a large chromatographic areas in resolved peaks are analyzed using this as a basis. Oils which have large chromatographic unresolved peaks are best analysis using a blank subtraction method. The effect of this improved accuracy is to lower the effectiveness results of very light oils (in density) and increase the results of dense oils. These results are only slightly changed. Dispersability for light and medium crude oils does not change significantly.

An interesting observation is that the standard deviation of the new method is within about 10% of the value. The standard deviation of the older, and sometimes very inaccurate methods, was about the same. This confirms that standard deviation is an indicator of repeatability and not accuracy.

5.0 References

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Appendix

Detailed Methodology for The Swirling Flask Test and Gas Chromatographic Analysis

Crude Oil Sample Collection and Storage

The oil container 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 (Nalgene, Rochester, NY). For dispersant testing, an aliquot is removed as needed from the working sample and stored in a 40 mL glass vial with teflon lining (VWR Scientific, London, ON). The working sample is shaken 30 minutes prior to removing the aliquot. When not in use all samples are stored in a temperature controlled room at 5 °C.

Procedure

1. Premix sample preparation

Weigh a small amount of oil into a 5 mL amber vial with Teflon lined cap (approx. 1.0 mL). Add approximately 100 mg of dispersant into the oil. Add oil until a 1:25.0 ratio of dispersant to oil is achieved (approx. 2.5 mL). Mix well with manual shaking.

2. Salt-water preparation.

Weigh out granular salt and add to water from reverse osmosis (RO) filtration, or equivalent, to obtain a 3.3%(w/v) solution.

3. Swirling Flask preparation

Measure 120 mL of salt water into a 125 mL modified Erlenmeyer flask. Insert the flask into the flask holders on the oscillating table of the shaker. Using a positive displacement pipette, carefully apply 100 µL of pre-mix solution onto the surface of the water by touching the tip of the pipette to the surface and gently expelling the oil/surfactant mixture.

4. Shaking of Swirling Flasks

The flask and contents are mechanically mixed on the shaker with the temperature controlled chamber at 20 °C. A rotation speed of 150 RPM and a mixing time of 20 minutes is used to agitate the samples followed by a 10 minute settling period.

5. Sample collection

Drain 3 mL of the oil-in-water phase to waste, eliminating any oil from the spout of the flask. Collect a 30 mL aliquot in a graduated cylinder and transfer to a 125 mL separatory funnel. Extract with 3 x 5 mL of a 70:30 dichloromethane:pentane solvent mixture, collected in a 25 mL graduated mixing cylinder and topped up to 15 mL.

6. 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 12mm x 32mm Crimp style vial with

aluminium/Teflon seals and shaken well. Total 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:

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

which simplifies to:

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

Where:

RPH is the Resolved Petroleum Hydrocarbon amount in µg

A_{total} is the total area of resolved peaks in counts or, in the case of heavy oils, 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 $RRF = A/A_{is} \text{ X } C_{is}/C$, where A is the area, C is the concentration of the compound of interest.

7. TPH 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 8. 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. above). At this point, the entire volume of water is transferred to a 250 mL separatory funnel and extracted with 3 x 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 consistent with the sample analysis (see Step 6. above). A calibration curve of RPH versus % efficiency is produced using a graphics software package. The calibration curve is used to the determine the RPH content of the samples, the % efficiency is calculated. For oils with a high ratio of unresolved complex matter, generally the heavy oils and products, the total area is integrated. RPH is calculated as:

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

which simplifies to:

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

Where:

RPH is the Resolved Petroleum Hydrocarbon amount in µg

A_{total} is the total area of resolved peaks in counts or, in the case of heavy oils, 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 $RRF = A/A_{is} \times C_{is}/C$, where A is the area, C is the concentration of the compound of interest.

8. 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 TPH range of the standards. The following guide is used to determine the range of standards for each type of oil being dispersed:

Heavy Oil - 2, 5, 10, 15, 20, 25%
Medium Oil - 10, 20, 30, 40, 50, 60%
Light Oil - 30, 40, 50, 60, 70, 80%

9. Gas chromatograph parameters and sequencing

Total Petroleum Hydrocarbon analysis for C_8 through C_{40} n-alkanes and pristane and phytane 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
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 (5-a-Androstane, Alkane mix, o-Terphenyl in hexane) is measured before and following each sample set.

Notes on the Method

Labware and Supplies

Surfactants are very interactive substances, and as a consequence their behaviour is often unpredictable. This can lead to problems of carryover if the labware is cleaned meticulously. The cleaning process uses a surfactant solution "Decon 75" after 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.

The use of positive displacement pipettes is a must for all controlled volumes of microlitre quantities. Use of volume displacement pipettes 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.

Premix Sample Preparation

The order of addition of the dispersant and oil may have implications to the actual ratio, 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.

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.

There are indications that the results for some premixed dispersant/oil combination change over time. This has not been confirmed, however it is sensible to take precautions against this potential source of variation. For this reason, 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.

Salt Water Preparation

The storage of salt water has an impact on the salinity of the working water samples. There have been incidents when a large sample of salt water (20 litres) was left to stand for several days, resulting in stratification of the salinity. Since the performance of the dispersant is affected by salinity, mixing prior to obtaining the working samples is suggested.

Care should also be observed regarding the evaporation of an open container 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 saline levels at 3.3%.

Swirling Flask Preparation

Temperature is a factor in dispersion, so it is important that all components (salt water, pre-mix and temperature controlled chamber) be 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.

Light oils will generally "herd" to the vessel walls, and may climb a short distance. This is unavoidable, and expected. The "swirling" effect during mixing should overwash the oil and not affect results, unless the glassware is not properly cleaned.

Shaking of Swirling Flasks/Sample Collection

Timing should be strictly adhered to, as the dispersion is a dynamic process, and seemingly insignificant variations can have significant impact on results. This is especially true for the settling time. Performing batch runs of six samples already limits the precision of the timing for each individual sample due to the time required to sample from the other five, and should be completed as quickly and efficiently as possible.

Volumes are important, as the quantity of oil determined is calculated based on the assumption that the proper volumes were used. This is true for the sample of dispersed oil-in-water, and the volume of oil-in-dichloromethane extract. Special care needs to be taken with the 15 mL samples, as a relatively low volume is used.

During extraction, vigorous shaking is required to achieve full extraction. It is best to shake each separatory funnel individually to achieve consistent results.