

## The Development and Application of a Modified Analytical Procedure for Laboratory Dispersant 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 which shows improvements in the data quality and time required for analysis.

New features of the method include: correction for very low oil-in-water values, use of few calibration points directly around the expected or actual value. These new features result in improved accuracy, and decreased amount of sample taking. Only about 1/3 of the calibration points are used compared to the previous test. However because calibration points are taken at specific intervals around the actual or predicted value, an improved accuracy results. The increased accuracy is particularly evidenced at low values of dispersant effectiveness.

### 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 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). In this paper we report on improved methods for analysing the oil-in-water using gas chromatography. Rather than the colorimetric methodology, which has severe limitations, a gas chromatographic method has been developed (Fingas *et al.* 1995). The older 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 colour density. 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:

1. Mathematical means for dealing with low effectiveness values were not present and negative values could possibly be assigned,
2. A new and more accurate equation was developed for calculating TPH,
3. A means of subtracting the solvent and blanks was included,
4. Several refinements to the actual chromatographic methods were needed, examples of this is the simplification of standard addition methods to avoid errors, and
5. A consistent method of preparing only fewer standards around the value of the actual run was needed. The old procedure of preparing 6 or 12 standards is excessive.

## 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).

Four replicates were performed for each experimental parameter with two being conducted during the same experimental run. Six samples are used for each run. Each experiment was conducted against two controls, a blank and an oil only experiment. This eliminates part or most of the effect of weathering during the experiment itself.

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

A new procedure was developed to minimize the number of samples. The old procedure (Fingas *et al.* 1995) recommended 12 standards. In effect, only two of these were applicable to any given oil. The same, or in fact, greater resolution can be obtained by using only 4 standards, two on either side of the expected or measured value of the measurement candidate. The values of the standards are selected by running a single sample to obtain an approximate value of TPH using similar oil standards. Two standards having values spaced 5% above this value and two below, are prepared.

### 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      **Comparison of Results from Measurement Techniques**

Oil	Dispersant	GC-TPH New Method		GC-TPH Old Method		UV-Vis Colorimetry	
		Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
ASMB	C9500	43.2	2.6	42.5	4.9	37.1	4.2
Federated	C9500	37.9	7.4	61.3	5.1	52.5	4.2
Pitas Point	C9500	90.5	3.3	72.8	7.5	44.9	6.4
Point Arguello	C9500	5.2	1.2	3.2	1.5	2.6	0.3
South Louisiana	C9500	34.0	2.0	32.8	6.1	19.3	4.0
Thevenard	C9500	74.4	5.1	88.7	6.1	>100%	
Udang	C9500	6.6	2.2	Not measured		1.1	2.9
Bunker C	C9500	6.6	2.3			0	
Hondo	C9500	8.3	1.3				
Santa Clara	C9500	2.7	0.5			0	
Sumatran Heavy	C9500	8.0	2.6			0	
Jet fuel	C9500	78.3	5.3				
Diesel (Anchorage)	C9500	69.7	6.7				
North Slope (Southern Pipeline)	C9500	42.8	4.3				

This table shows that the new methodology yields about the same results for most common oils such as ASMB, Federated, and South Louisiana, comparing the

old colorimetric and the old gas chromatographic methods. For lightly coloured oils such as Pitas Point and Thevenard Island, the value of dispersion between the colorimetric method and the gas chromatographic methods differ significantly. It had been noted in a previous paper (Fingas *et al.* 1995) that there were significant problems with the colorimetric methods and lightly-coloured oils. The colouration was not sufficient to give a strong signal versus the background. This resulted in values of dispersion ranging as high as 360%. It is interesting to note that the improved chromatographic method results in decreased values for both the lighter (in density and colour) oils used in this study. The reasons for this are not related to the previous colorimetric difficulties, but to the better calibration in the current methodology. The older calibration method appears to have had a tendency to give a higher value to less-dense oils and vice-versa.

The higher-density oils used in this study, eg. Bunker C, Santa Clara and Sumatran heavy, show that the new method does give slightly higher values for such oils. This as noted above is the result of calibration curves chosen around the actual value. In the older colorimetric method, dealing with heavy oils was difficult and they were simply assigned a value of zero if no colouration appeared in the water.

Overall, the changes in values for the new dispersant effectiveness results are not significant and the new method might be considered as an adjustment that largely increases accuracy, especially for those oils that are either very light (in density) or heavy.

It is interesting that the standard deviation is about the same for all three methods compared here. This confirms that standard deviation is not a good measure of accuracy, but is a measure of repeatability.

#### 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 blank runs are assigned to zero on the effectiveness scale, thus ensuring that negative values do not occur, that calibration standards are only run at two increments above and below the actual result. The effect of this improved accuracy is to lower the effectiveness results of 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

#### Apparatus and Labware

- New Brunswick Environmental Shaker model G27 (New Brunswick, Edison, NJ)
- Hewlett Packard 5890 GC/FID with Chemstation software package (Hewlett Packard, Ottawa, ON) and a fused silica DB5ms column (J & W Scientific, Folsom, CA)
- 12mm x 32mm Crimp style vials with aluminium/Teflon seals (Supelco, Mississauga, ON)
- 125 mL glass, Erlenmeyer flasks, modified with the addition of a drain spout (VWR Scientific, London, ON)
- 25 mL glass, graduated mixing cylinders and stoppers
- 125 mL glass, separatory funnels and stoppers
- 5.0 mL glass pipette
- 5  $\mu$ L to 100  $\mu$ L positive displacement pipette (Mandel Scientific Co., Guelph, ON)
- digital timers
- 20 - 100 mL dispenser (Brinkman Instruments Canada, Rexdale, ON)
- 25 mL glass, Erlenmeyer Flask and stopper
- 20 L plastic container and cap, with drain spigot (Nalgene, Rochester, NY)
- Horiba U-10 salinity meter

#### Consumables

- Dichloromethane, distilled in glass grade (Caledon, Georgetown, ON)
- Pentane -195, distilled in glass grade (Caledon, Georgetown, ON)
- Fine granular salt (Canadian Salt Co., Pointe Claire, PQ)
- chemical dispersant
- oil
- water purified by reverse osmosis
- Disposable gloves, chemical resistant gloves and glasses

#### Crude Oil Sample Collection and Storage

The oil container, as received from the source, 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. Handling

of the samples is kept to a minimum to reduce the loss of volatile components from the oil. New consumable labware and reagents are used throughout sampling and analysis of the oils.

## Procedure

### 1. Premix sample preparation

Add about 25 mg of oil (approx. 2.5 mL) into a 5 mL amber vial with Teflon lined cap (approx. 100 mg). Weigh a suitable amount of the dispersant into the vial to obtain a 1:25.0 ratio of dispersant to oil. Mix well in an energetic shaker for at least 15 minutes.

### 2. Salt-water preparation.

Weigh out 594.0 g of granular salt on toploader balance and add to the empty 20 L carboy. Add R/O (Reverse Osmosis) water up to the previously measured 18 L mark to make a 3.3%(w/v) solution. Place on magnetic stirrer, add stirring bar and mix until salt is dissolved. Test salinity with the salinity meter and adjust if necessary. Fill 4 L bottle with salt water and add dispenser. Set dispenser to 60 mL and calibrate by dispensing into a graduated cylinder.

### 3. Swirling Flask preparation

Dispense 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  $\mu$ L 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. Up to six flasks may be used in a batch run.

### 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 during which the shaker table has been stopped. The settling time permits larger, unstable, dispersed droplets to separate out and return to the water surface. The actual time of settling is critical, as the settling is continuous, is an important parameter for this test.

### 5. Sample collection

Drain 3 mL of the oil-in-water phase to waste, eliminating the water 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. During extraction a web-like emulsion forms at the solvent/water interface. For this reason 2 mL of the extract is left in the funnel after each extraction. Thus, only 3 mL of the extract is collected in the cylinder from the first extraction, and 5 mL each for the remaining two, for a combined total of 13 mL of extract. The mixing cylinder is then capped until analyzed.

## 6. Sample analysis

Analysis consists of gas chromatographic analysis of the total petroleum hydrocarbon (TPH) content using a flame ionization detector (GC/FID) to determine the concentration of oil in solvent. A 900.0  $\mu\text{L}$  portion of the 13 mL solvent extract and a 100.0  $\mu\text{L}$  volume of internal standard (200 ppm 5- $\alpha$ -Androstane in hexane) are combined in a 12mm x 32mm Crimp style vial with aluminium/Teflon seals and shaken well. The vials are then placed on the autosampler for chromatographic analysis and the sequence programmed according to the standard GC methods outlined below. The temperature program is described below. Total petroleum hydrocarbon content is quantified by the internal standard method using the baseline corrected total area of the chromatogram and the average hydrocarbon response factor determined over the entire analytical range:

$$\text{TPH} = (\text{TPH area}) / (\text{IS area}) \times 20 \text{ (mg)} \times 15 \times 4 / 0.9 \times \text{RRF} \quad (1)$$

## 7. TPH calibration standards

A series of 4 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  $\mu\text{L}$  = 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. A 5 mL volume of the extract is left in the separatory funnel after each extraction due to the incomplete separation of the water and solvent layers. The extracts are combined in a graduated cylinder to a total volume of 55 mL. Chromatographic analysis is then performed consistent with the sample analysis (see Step 6. above). A calibration curve of TPH versus % efficiency is produced using a graphics software package (TableCurve). From a comparison of the calibration curve to the TPH content of the samples, the % efficiency is calculated.

$$\text{TPH} = (\text{TPH area}) / (\text{IS area}) \times 20 \text{ (ppm)} \times 60 \times 4 / 0.9 \times \text{RRF} \quad (2)$$

## 8. Selecting the volume range of the calibration standards

The volumes of the four calibration standards are chosen such that the TPH determined for each of the four samples of each dispersant/oil combination fall within the TPH range of the standards. Since there are several factors influencing TPH determination (GC response flux, density of sample, evaporation of sample, solvent evaporation from the internal standard and vial samples, and volume addition errors of the dispersant/oil, extract and internal standard) efficiency of the test procedure is less than 100%. Therefore, a direct correlation cannot be used to select the volume of the standard, ie. a TPH range of 15 - 20 mg for the four samples does not necessarily

allow the selection of a range of standards from 15 to 20  $\mu\text{L}$ . Since the resulting values for the samples are below 100% recovery, then the lowest mass from the samples can be used as the low end of the scale for the calibration standards. It is then a simple matter of scaling up sufficiently by 5 or 10  $\mu\text{L}$  increments to have all four sample points fall within the chosen range. As an example, if the TPH mass of the set of samples is determined to be 23, 30, 27 and 28 mg, then the calibration standards would be chosen as 20, 25, 30 and 40  $\mu\text{L}$ . Any value below 5  $\mu\text{L}$  would automatically become 2, 5, 10 and 15  $\mu\text{L}$ . One important point is that the linear regression of the resulting calibration curve should still pass through the origin of a TPH vs.%Efficiency graph.

#### 9. Batch testing

Since running a single sample at a time is inefficient, up to six samples and/or standards may be performed at one time. For statistical reasons, four samples and four standards are performed for each dispersant/oil combination. The samples must be performed as two sets of pairs, with only one pair in a given batch of six. The standards are to be performed as a set of four in a single batch.

#### 10. Calibration and maintenance of equipment

A description of the instrumentation and experimental parameters follows, as well as a maintenance and calibration schedule for the equipment to ensure reproducibility and accuracy of results.

- Prior to the start of a measurement program, a mechanical, hand-held tachometer (Shimpo DT-105, Japan) is used to measure the rotation speed of the New Brunswick Environmental Shaker. The speed control is adjusted as necessary to achieve a consistent setting of 150 RPM. As well, the interior of the sample chamber is cleaned on a bi-weekly basis.
- The buildup of salt deposits on the dispenser used to add the salt water to the SFT (Swirling Flask Test) vessel affects the mechanics of the apparatus. Over time it will result in a decrease in the accuracy of the volume of water delivered. As such each time the reagent bottle is replenished with salt water the dispenser is thoroughly cleaned with R/O water. To confirm that the dispensette delivered the specified volume of salt water the ensuing test is performed. Two, 60 mL volumes of salt water are dispensed into an appropriate graduated cylinder and the volume on the cylinder read. Adjustments to the setting of volume control are made as necessary. Delivery volume is typically  $120 \text{ mL} \pm 1 \text{ mL}$ .
- Positive displacement pipettes dedicated solely to this project, certified by the manufacturer and evaluated in the laboratory, are used throughout the analysis. The positive displacement pipettes are used to add the dispersant to the oil and place the oil into the Swirling Flask Test vessel, as well as to withdraw the aliquot of the extract for chromatographic analysis.
- High purity solvents and reagents and certified standards are used throughout the analysis.
- A rigorous labware cleaning program is undertaken throughout to reduce

possible cross-contamination. Labware is thoroughly rinsed with R/O water and dichloromethane between each experimental run. On the last working day of the week the labware is soaked in a Decon 75 solution (BDH Inc, Toronto, ON) for 24 hours, rinsed with R/O water and then with acetone. Glassware is dried at 180 °C while plasticware is air dried.

#### 11. Gas chromatograph parameters and sequencing

Total Petroleum Hydrocarbon analysis for C<sub>8</sub> through C<sub>40</sub> 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:

- Instrument - Hewlett Packard 5890 (Hewlett Packard, Ottawa, ON)
- Column - 30 M x 0.32 mm ID DB-5 fused silica column (0.25 µm film thickness), (J & W Scientific, Folsom, CA)
- Detector - flame ionization detector
- Autosampler - Hewlett Packard 7673
- Inlet - Splitless
- Gases - Carrier - helium, 2.5 mL/min, nominal  
Make up - helium, 27.5 mL/min  
Detector air - 400 mL/min  
Detector hydrogen - 30 mL/min
- Injection volume - 1 µL
- Injector temperature - 290 °C
- Detector temperature - 300 °C
- Temperature program - 50 °C for 2 minutes, then 6 °C/min to 300 °C, hold 16.7 minutes. The total run time is 60 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.