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The Effect of Energy, Settling Time and Shaking Time on the Swirling Flask Dispersant Apparatus

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Abstract

The results of testing the effect of basic operational variables associated with the laboratory effectiveness test known as the 'swirling flask', are reported. It was found that most parameters for the swirling flask test were in stable regions, although some changes, such as increasing settling time, could reduce the standard deviation.

The effect of changing energy levels by changing the rotational speed from 50 to 250 rpm, in steps of 50 rpm was measured. This results in an increase in apparent effectiveness as would be expected. It was found that dispersion onsets rapidly between 100 and 150 rpm. This is consistent with previous findings that dispersion has an onset threshold of energy.

The effect of changing the settling time of 10 minutes from 5 to 80 minutes was measured. It was noted that the change in apparent effectiveness decreases slowly after 10 minutes of settling time. This indicates that mostly large, unstable droplets resurface during the initial period of time.

The amount of shaking time was measured. Only a small increase in effectiveness is observed with increased times ranging from 10 to 160 minutes. This indicates that dispersion is largely a threshold rather than a continuous process.

1.0 Introduction

This study is one of a continuing series exploring laboratory dispersant effectiveness testing (Fingas et al. 1987, 1989a, 1989b, 1995c). During the years from 1985 to 1990, Environment Canada 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 5 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

"The Effect of Energy, Settling Time and Shaking Time on the Swirling Flask Dispersant Apparatus", In Proceedings of the Twentieth Arctic Marine Dispersal Program Technical Seminar, Environment Canada, Ottawa, Ontario, pp 541-550, 1997.

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. 1989b). Tests included altering each operational 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. Examples of this were found in every known apparatus. One apparatus, for example, was setup so that the sampling port was directly in the path of large entrained particles. This resulted in large effectiveness values for oils that are less dispersible because large droplets of the oil collect at the sampling port area. Furthermore, this particular apparatus often yielded very high values because the assumption was made that the oil was homogeneously distributed throughout the water column, when in fact, lesser dispersible oils were not. Another test protocol specifies a very short settling time which yields noisy results, because at short times the rising rate is rapid and even small timing errors result in large apparent effectiveness values. The same apparatus applies energy by the rotation of a flask. Oil comes into contact with the walls to a degree far above any other apparatus. This results in loss of oil as well as an interaction between the measurement of dispersant effectiveness and surface-washing agent effectiveness. It is these types of difficulties that should be avoided in the tests.

In this paper we report a re-measurement of several effects on the swirling flask apparatus. Since the time that the test was developed several changes have been made to the test - primarily on the analytical methods. Rather than the UV methodology, which has severe limitations, a gas chromatographic method has been developed (Fingas et al. 1995b). The older measurements were encumbered with high noise levels which often obscured the phenomena being measured.

The effect of rotational speed of the vessel was varied to measure the effect of this, and to study the effect of energy on the amount of dispersion. Specific studies to measure energy had been performed. It had been found that dispersion, be it natural or chemical, was a threshold function (Fingas et al. 1995a). This means that below a certain energy there was no dispersion and above this threshold a relatively large amount of dispersion occurred. Steps to specifically measure this energy level are being taken at this time. Reports on this should be available within one year. In the earlier study of rotational energy, it had been found that the amount of dispersion did not change significantly with increasing rotational speed, but this was not very clear (Fingas et al. 1989a).

The effect of settling time was noted in the earlier studies (Fingas et al. 1989a). It was noted that the creaming or rise of droplets was exponential and was very rapid at times 5 minutes or lower. The settling time for the swirling flask was set at 10 minutes. This was done since this was about the shortest time that the rate of droplet rise was not high and also that physical handling times precluded the use of shorter periods without running into serious errors.

The third parameter examined is that of rotation time. In the original studies the time was set at 20 minutes simply because this was the shortest time that rotation could be conducted and that a uniform distribution of dispersed oil was seen in the flask for all oil types (Fingas et al. 1989a). Given that dispersion is a threshold

process, rotational time should not be a major contributor to increasing dispersion amount.

2.0 Experimental

The standard swirling flask method was employed except for the change in variables for the specific experiment (Fingas et al. 1996). All analysis, however, was performed only by gas chromatography. Four replicates were performed for each experimental parameter with two being conducted during the same experimental run. Six samples are conducted during 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.

Three oils were chosen for the experiments. The very light oil, Thevenard Island was chosen to represent a highly dispersible oil. Alberta Sweet Mixed Blend (ASMB) was chosen to represent a light crude oil of moderate dispersibility. Prudhoe Bay crude was chosen to represent a medium crude oil of lesser dispersibility.

The rotation speed was varied from 50 to 250 rpm in steps of 50 rpm. The usual rotation speed is 150 rpm. The settling time was varied from 5 to 80 minutes at double intervals (eg. 5, 10, 20, 40 and 80 minutes). The usual settling time is 10 minutes. The rotation time was varied from 10 to 160 minutes at multiples of 2 (eg. 10, 20, 40, 80, 160 minutes). The usual rotation time was 20 minutes.

The following were the supplies and apparatus employed in the standard swirling flask test:

- New Brunswick Environmental Shaker model G27 (New Brunswick Scientific, Edison, NJ)
- 12 matched semi-micro cells (Hellma Canada Ltd., Concord, ON)
- Hewlett Packard 5890 GC/FID with Chemstation software package (Hewlett Packard, Ottawa, ON) and a fused silica DB5ms column (J & W Scientific, Folsom, CA)
- 12 - 12mm x 32mm Crimp style vials with aluminium/Teflon seals (Supelco, Mississauga, ON)
- 12 - 125 mL glass, Erlenmeyer flasks, modified with the addition of a drain spout (VWR Scientific, London, ON)
- 6 - 25 mL glass, graduated mixing cylinders and stoppers
- 6 - 125 mL glass, separatory funnels and stoppers
- 5.0 mL glass pipette
- 5 µL to 100 µL positive displacement pipette (Mandel Scientific Co., Guelph, ON)
- 1 mL positive displacement pipette (Mandel Scientific Co., Guelph, ON)
- 2 - digital timers
- 20 mL to 100 mL dispenser (Brinkman Instruments Canada, Rexdale, ON)
- 2 - 25 mL glass, Erlenmeyer Flask and stopper
- 66 L plastic container and cap

Reagents and materials were as follows:

- 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, QC)

- 20 mL chemical dispersant
- 25 mL oil
- pure water (reverse-osmosis treated or equivalent)

Sample Collection and Storage

The initial oil was mechanically mixed for a minimum of 2 hours prior to obtaining a working sample. Working samples were stored in 2 L high density polyethylene bottles with polypropylene screw closures (Nalgene, Rochester, NY). For dispersant testing, an aliquot was removed as needed from the working sample and stored in a glass bottle with a plastic cap (VWR Scientific, London, ON). The working sample was manually shaken prior to removing the aliquot. When not in use, all samples were stored in a temperature controlled room at 15 °C. Handling of the samples was kept to a minimum to reduce the loss of volatile components from the oil. New consumable labware and reagents were used throughout sampling and analysis of the oils.

Procedure

The swirling flask dispersant effectiveness test was first described in Fingas et al. 1987, and subsequently several improvements have been made. A summary of the procedures used during this study have been provided in the following paragraphs.

An aliquot of 100 μ L of oil premixed with dispersant (oil:dispersant of 25:1) is added to 120 mL of artificial sea water (oil:salt water of 1:1200) in a 125 mL modified Erlenmeyer flask. The flask, termed the 'swirling flask test' vessel, was designed with a drain spout at its base to permit the collection of samples from the lower portion of the water column. The artificial salt water was a 3.3% (33 parts per thousand) by weight solution of fine granular salt in deionized water. To ensure reproducibility of results, the oil and dispersant combination were analysed using two separate runs, each containing six flasks. The flask and contents were agitated in a model G27, New Brunswick Environmental gyratory shaker with a temperature controlled chamber at 20 °C (New Brunswick, Edison, NJ). A rotation speed of 150 rpm and a mixing time of 20 minutes was normally used to agitate the samples followed by a 10 minute settling period in which the applied energy was removed. The settling time permits larger, unstable, dispersed droplets to separate out and return to the water surface (Fingas et al. 1989b). After 3 mL of the oil-in-water phase was drained to waste, a 31 mL aliquot was collected in a graduated cylinder. A 1 mL volume was used to measure the size of the dispersed droplets. The remaining 30 mL was transferred to a 125 mL separatory funnel and extracted with 3 x 5 mL of dichloromethane:pentane (70:30) solvent mixture. During extraction a web-like emulsion forms at the solvent/water interface. For this reason only 3 of the first 5 mL of the first extract was drained from the funnel. The extracts were combined in a 25 mL mixing cylinder and then the cylinder was capped. Chromatographic analysis of the total petroleum hydrocarbon (TPH) content using gas chromatograph and flame ionization detector (GC/FID) was performed on the extract.

Oil remaining on the surface after the dispersion experiment was sampled with a pipette. Samples were drawn from all 12 experiments and then extracted with the 70:30 dichloromethane:pentane mixture and treated the same as the water column extracts.

A 900 μL portion of the 13 mL solvent extract and a 100 μL volume of internal standard (100 ppm 5- α -Androstane) were placed in a 12mm x 32mm crimp style vial with aluminium/Teflon seals (Supelco, Mississauga, ON) for chromatographic analysis. The resulting sample chromatograms were compared to those of the aforementioned oil-in-solvent standards to determine their respective total petroleum hydrocarbon content. In turn, the TPH concentrations of the samples and standards were used to calculate effectiveness of the dispersant. The standards represent a range of percent (%) efficiency around the expected value.

A series of 3 oil-in-solvent standards were prepared in a manner similar to the sample analysis procedure. One hundred twenty millilitres of salt water was placed in each of the 125 mL Swirling Flask Test vessels (SFT) followed by the addition of an accurate volume of oil/dispersant to the surface of the water. The progression of oil/dispersant volumes ranges from 2.0 μL to 100 μL representing 2% to 100% efficiency. For this particular experiment 3 standards around the expected percentage were prepared. As in the case of the sample analysis a 20 minute mixing time and 10 minute settling period was employed. After which the entire volume of water was extracted with 3 x 20 mL of a solvent mixture of dichloromethane/pentane. A 5 mL volume of the first extract was left in the separatory funnel due to the incomplete separation of the water and solvent layers. The extracts were combined in a cylinder to a total volume of 55 mL.

A 900 μL aliquot from the extract of each standard was combined with a 100 μL volume of internal standard (100 ppm 5- α -Androstane) in a crimp-cap vial. GC/FID analysis was performed on a 1 μL to 2 μL volume taken from the vial. The temperature program is described below. Total petroleum hydrocarbon content was 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. A calibration curve of TPH versus percent efficiency was produced. From a comparison of the calibration curve to the TPH content of the samples the percent efficiency was calculated.

Total Petroleum Hydrocarbon analysis for C_8 through C_{40} n-alkanes and pristane and phytane in 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 $^{\circ}\text{C}$
Detector temperature - 300 $^{\circ}\text{C}$
Temperature program - 50 $^{\circ}\text{C}$ for 2 minutes, then 6 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$, hold

Daily calibration - 16.7 minutes. The total run time was 60 minutes. Alkane standard mixture of 20 ppm (5- α -Androstane, Alkane mix, o-Terphenyl in hexane) was measured before and following each sample set.

- Prior to the start of the project a mechanical, hand-held tachometer (Shimpo DT-105, Japan) was used to measure the rotation speed of the New Brunswick Environmental Shaker. The speed control was adjusted as necessary to achieve a consistent setting of 150 rpm or the target rpm. As well, the interior of the sample chamber was cleaned on a bi-weekly basis.
- Positive displacement pipettes and air displacement pipettes, dedicated solely to this project, certified by the manufacturer and evaluated in the laboratory were used throughout the analysis. The positive displacement pipettes were used to prepare standards and internal standard solutions for GC analysis and add the dispersant to the oil and place the oil into the Swirling Flask Test vessel. Air displacement pipettes were used to withdraw the aliquot of the extract for chromatographic analysis.
- High purity solvents and reagents and certified standards were used throughout the analysis.
- A rigorous labware cleaning program was undertaken throughout the experiment to reduce possible cross-contamination. Labware was thoroughly rinsed with deionized water and dichloromethane between each experimental run. Once per week the labware was soaked in a Decon 75 solution (BDH Inc, Toronto, ON) for 24 hours, rinsed with deionized water followed by the solvent acetone. Glassware was dried at 180 °C while plasticware was air dried.

3.0 Results and Discussion

The results from the experiments to vary the rotational speed are given in Table 1 and shown graphically in Figure 1. Table 1 shows the effectiveness in percent along with the standard deviation. The standard deviation is very low in all cases.

Table 1. Variation of Effectiveness with Shaking Speed
Effectiveness in percent with given oil

Rotational Speed (RPM)	Prudhoe Bay	ASMB	Thevenard Island
50	0	0	0
100	3.0 \pm 1.5	1.2 \pm 1.3	2.3 \pm 1.0
150	15.6 \pm 2.6	32.1 \pm 0.9	52.2 \pm 1.6
200	25.0 \pm 3.1	42.7 \pm 2.5	66.5 \pm 3.6
250	43.0 \pm 5.3	54.0 \pm 4.2	87.2 \pm 4.5

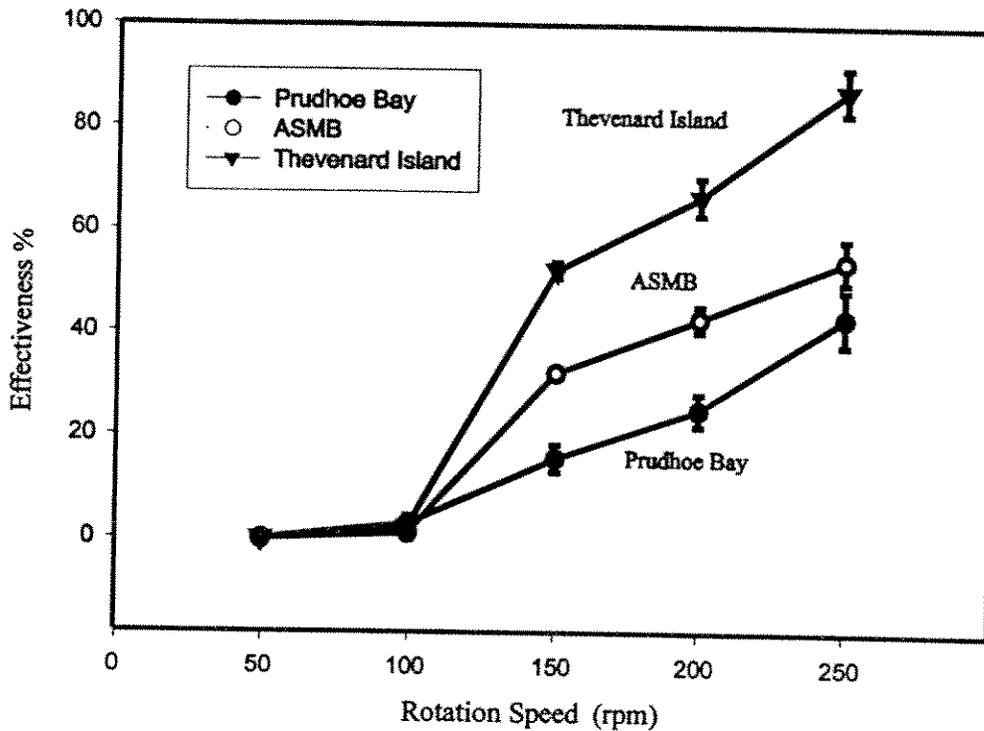


Figure 1 - Effect of Rotational Speed

The curves in Figure 1 were prepared by simple joining of the points. Figure 1 shows that the dispersion does not occur at 50 rpm and that at 100 rpm only a small amount of dispersion occurs. Dispersion rapidly onsets at energies corresponding to that occurring at the rotational speed between 100 and 150 rpm. This dispersion amount slowly increases with increasing rpm. This behaviour indicates that dispersion is a threshold process, that below a given energy level (here below that energy created in the swirling flask by an energy resulting from 100 rpm).

The data from varying the settling time are given in Table 2 and shown graphically in Figure 2. The curves in figure 2 were prepared by simple joining of the points.

Table 2. Variation of Effectiveness with Settling Time

Settling Time (minute)	Effectiveness in percent with given oil		
	Prudhoe Bay	ASMB	Thevenard Island
5	21.6 ± 1.7	43.1 ± 4.4	59.9 ± 3.8
10	15.6 ± 2.6	32.1 ± 0.9	52.2 ± 1.6
20	14.2 ± 2.0	28.8 ± 1.9	49.8 ± 2.3
40	8.8 ± 1.5	21.1 ± 1.7	26.0 ± 2.9
80	8.5 ± 1.2	19.8 ± 3.3	23.5 ± 3.8

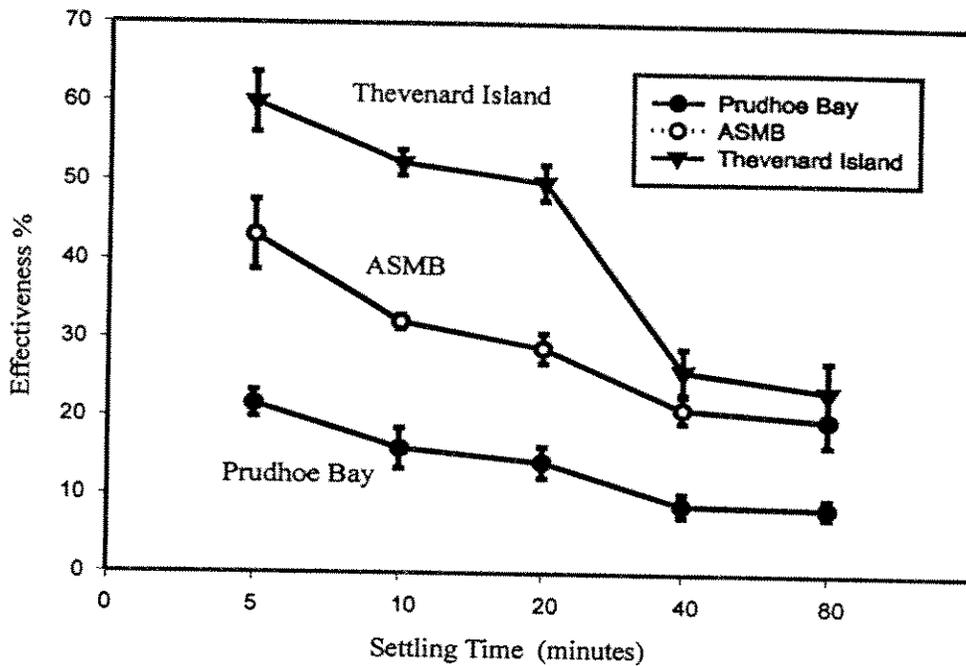


Figure 2 Effect of Settling Time

Figure 2 shows that dispersion amount as represented by the effectiveness decreases rapidly with time. The rate of change of effectiveness is particularly sharp at 5 minutes. The decrease after 80 minutes is expected to be small. The time of 10 minutes chosen represents the first time that the rate is relatively small and may be a satisfactory point for laboratory testing. Running 6 samples simultaneously entails a few minutes of sampling so that the sampling time error is still significant at 10 minutes and unacceptable at 5 minutes. A more optimal time might be 20 minutes.

Table 3 lists the results of varying the shaking time and Figure 3 illustrates the results.

Table 3 Variation of Effectiveness with Shaking Time
Effectiveness in percent with given oil

Shaking Time (minute)	Prudhoe Bay	ASMB	Thevenard Island
10	16.5 ± 2.1	28.3 ± 4.4	38.8 ± 6.1
20	15.6 ± 2.6	32.1 ± 0.9	42.1 ± 1.5
40	16.1 ± 2.2	30.5 ± 4.2	41.6 ± 6.8
80	17.4 ± 4.0	31.0 ± 6.1	38.8 ± 0.9
160	16.3 ± 1.2	30.2 ± 4.6	43.7 ± 2.4

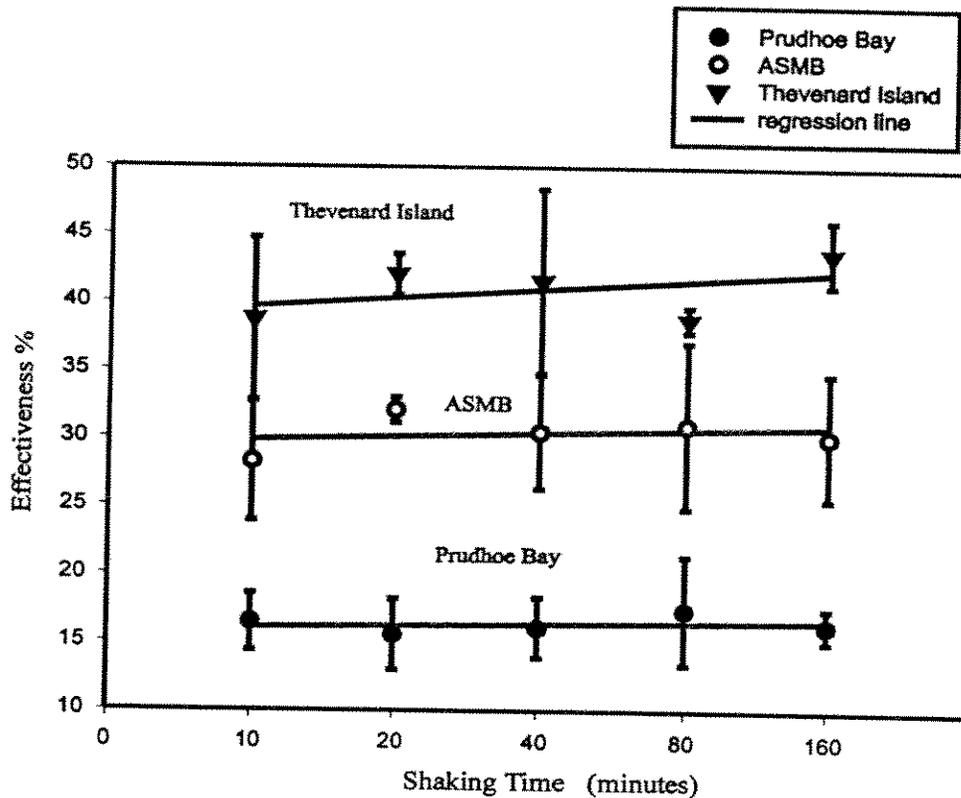


Figure 3 Effect of Agitation Time

Figure 3 shows that the dispersion amount does not change significantly with increasing shaking time. This indicates that the dispersion is a threshold process. This implies that the dispersion largely occurs at the time at which the energy threshold is reached and then little dispersion occurs afterward. This is consistent with past findings on energy relationships (Fingas et al. 1995b)

4.0 Conclusions

The studies on rotational speed for the swirling flask apparatus show that the onset of dispersion occurs between 100 and 150 rpm. The rapid onset is indicative of a threshold process for dispersion. This threshold process has been observed in previous studies. The dispersion amount increases with increasing rotational energy as would be expected and as shown by earlier studies directly toward energy-dispersion studies. The 150 rpm now specified for the swirling flask test is at a region of relatively little changes.

Dispersion amount was found to decrease rapidly (perhaps exponentially) with settling time. The change at the 5-minute time was large and at the 80-minute point of time was small. The 10-minute time specified for the swirling flask test might be changed to 20 minutes, although this would only marginally improve the standard deviation. The concern over settling time involves 3 factors, first the large, unstable droplets cream to the surface very rapidly after the absence of turbulent energy, as they would at sea. Secondly, the point at time at which the dispersion is sampled should not be critical so that a small error in timing does not change the

dispersion amount significantly. Finally, with multiple samples run at the same time, not all samples are taken at precisely the specified time. The resulting error decreases as settling time increases.

The rotational time or time that energy is applied does not change the amount of dispersion significantly. A small upward trend is observed, as might be expected. The little amount of change with increasing rotational time is consistent with a threshold process that has been proposed for oil spill dispersion.

5.0 References

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