DEVELOPMENT OF A PORTABLE FIELD KIT FOR MEASURING PROPERTIES OF SPILLED OILS

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ABSTRACT

A portable kit is being developed specifically for measuring oil properties at the spill site. The kit is capable of measuring density, viscosity, flash point, water content and the chemical dispersibility of oil. This paper describes the evaluation and selection of the methods and components of the kit.

INTRODUCTION

The effectiveness of any countermeasure technique is, to a certain degree, dependent upon the physical characteristics of the spilled oil. Once oil is released into the environment, its properties are in a dynamic state due to weathering. This means that countermeasures must be adapted to deal with the changing characteristics of the oil. For example, the opportunity to use dispersants effectively is usually limited to the early stages of the spill before significant evaporation and emulsification have occurred. As well, the efficiencies of most mechanical recovery devices are limited by the rheological properties of the recovered material (Exxon, 1990). A skimmer that works well one day may become ineffective the next day because the viscosity of oil has increased beyond the capability of the equipment.
On-scene decision-makers must quickly assess the situation and then decide where to deploy the resources available. Usually the performance limits of equipment are known but not the properties of the spilled oil; at best, the properties can only be estimated. Sending samples away to be analyzed would be neither time effective nor practical. Thus, the utility of field analysis becomes evident.

The objective of this project was to develop a portable analytical kit which can be taken to the spill site and used to obtain rapid and reliable measurements of crucial oil properties. On-scene personnel can determine and monitor the properties of the oil. This information could then be readily incorporated into the operational decision-making process.

REQUIREMENTS OF THE KIT

The kit will measure the following properties:

- **Density**
  Oil density indicates the possibility of the oil sinking or being over-washed (Buist and Potter, 1987; Wilson et al., 1986).
- **Viscosity**
  Viscosity is a measure of fluidity and is normally the limiting factor for mechanical skimming and pumping equipment. Oil viscosity is also a major determinant of spreading.
- **Flash point**
  Flash point is a measurement of flammability, and is a safety factor that can influence operational decision-making.
- **Water content**
  The quantity of water in the sample indicates the degree of emulsification.
- **Dispersibility**
  A dispersibility test will show if the oil can potentially be dispersed.

In order for specific equipment and methods to be considered as part of the kit, each had to meet the criteria as described below:

- Equipment must be compatible with the limited space and weight requirements of a self-contained portable kit. The complete kit should be easily carried by no more than two persons, and can be shipped by all common forms of transportation;
- Testing can safely be performed under the demanding operational conditions expected;
- Equipment should be relatively simple to operate with little prior training and results easy to interpret;
- Results are to be within specified limits of accuracy and repeatability. Test procedures should be based upon generally accepted and standardized analytical methods;
- Definitive results are produced within hours of receipt of a sample.
EVALUATION OF EQUIPMENT AND METHODS

An extensive literature search of current methods and instruments used to analyze petroleum in the laboratory and in the field was carried out. Manufacturers were contacted and specific details regarding the equipment were obtained. Methods and apparatus that met the set criteria were selected to undergo physical testing. Any modifications to the equipment and procedures which were necessary to make the tests field-portable were instituted at this time. Laboratory tests were conducted using a variety of oils and water-in-oil emulsions. Testing was conducted under conditions which simulated the operating conditions expected at a remote spill site or on a ship at sea. The sensitivity of tests to movement and to temperature were examined. Results obtained using the field procedures were then compared with data from standard laboratory analyses.

EVALUATION OF EXISTING FIELD TESTS

Fina Oil Spill Test Kit

The Fina oil spill test kit was developed in the late 1970's by Labofina S.A. (Belgium) for the Dutch authorities Rijkswaterstaat. At the present time, it is the only portable kit available for measuring the properties of spilled oil. A Fina kit was purchased and thoroughly tested. The following is a brief summary of the evaluation.

Many of the test methods used in this kit are based upon empirical estimation and not upon generally accepted analytical methods. Measurements therefore require subjective interpretation by the operator. Consequently, the precision and accuracy depend upon the operator, the working environment, and the physical characteristics of the sample. Several tests involve difficult, time-consuming manipulations, and require relatively large amounts of oil. Little or no provision is made for cleaning the equipment; thus, performing repeat measurements is difficult. The kit and consumable supplies used for the tests are not readily available in North America.

Although the Fina kit can measure 11 properties, the methods used do not generally follow standardized procedures. Since the development of the Fina kit, there have been significant advances in analytical instrumentation. Modern instruments are more accurate, user friendly, and conform to standardized methods. Many of these instruments can be made field portable.

Field Dispersant Effectiveness Tests

A previous study by Ross (Ross, 1988) examined four different field tests for determining dispersant effectiveness (Pelletier Screen Test, Fina Spill Test Kit, Mackay Simple Field Test, and EPA’s Field Dispersant Effectiveness Test). All tests were designed to provide quick, qualitative results. The EPA’s Field Dispersant Effectiveness Test (FDET) is commercially available (Sunshine Technology Corporation - West Hartford, Connecticut) and the Fina Test is part
of the Fina Oil Spill Test Kit. The other test kits must be assembled by the user. Ross found that the portable tests, although simple to perform, had deficiencies. The most serious problem was the lack of correlation between the results of the field tests and accepted laboratory tests. Ross developed a test (the S.L.Ross Field Test) which overcame most of the deficiencies of the earlier field tests. It provided quantitative results of effectiveness which correlated with the Warren Spring Laboratory Rotating Flask Test.

METHODS AND EQUIPMENT SELECTED FOR KIT

Procedures were chosen for the five physical measurements, as well as for collecting and preparing oil samples. For most of the tests, numerous methods and apparatus were evaluated, this work is not described here.

Sample Collection and Preparation

Equipment is provided in the kit to collect oil samples from both an oiled beach and from the water surface. Beach samples are collected in a container using a scoop. A Teflon/polypropylene net on a telescopic extension pole is used to gather oil floating on the water surface.

Debris in the sample, such as beach material and flora, could potentially damage the more sensitive instruments included in the kit, as well as affect the measurements. It is therefore important to remove any interfering material from the samples. This must be done in such a way as not to alter the properties of the oil. A self-contained filter press is provided with the kit (Fann Model MB Filter Press, Baroid Testing Equipment - Houston, Texas). This filter press is extremely rugged and portable. It is designed to be used by the drilling industry for on-site filtration tests of drilling mud. Carbon dioxide from small, disposable gas cartridges is used to provide pressure which forces the sample through a filter medium. A specially designed polyester mesh filter of 105 micron size is provided with the kit.

Density

An Anton Paar DMA35 density meter (Anton Paar K.G. - Austria) is used to measure density. This hand-held instrument is battery-powered and provides digital readings in grams per milliliter (± 0.001 g/mL) within seconds. It has an operational temperature range of 0 to 40°C and requires only 2 mL of sample. The density meter uses the mechanical oscillator technique, which determines density from the change in vibrational frequency. The procedure is similar to ASTM D4052-86 "Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter."
Viscosity

Viscosity measurements are performed using a Bohlin Visco 88 BV viscometer (Bohlin Reologi Inc. - Sweden). This variable speed rotational viscometer is fully portable and battery-powered. It can be operated as a hand-held instrument and provides a direct reading of viscosity in Pascal-seconds (1 Pascal-second = 1000 centipoise). Samples with viscosities from 0.006 to 350 Pa-s (6 to 350,000 cP) can be measured.

The Visco 88 provides many features that are normally found only in larger, more expensive laboratory viscometers, and it is the only rotational viscometer that is battery operated. The viscometer's built-in software gives it the capability to generate different types of rheological data. These can be used to characterize the non-Newtonian flow behaviour of samples, such as water-in-oil mousse. Direct readings from the instrument can be used to generate rheological flow curves (shear rate versus shear stress, and viscosity versus shear rate). The flow curves can then be used to calculate yield points and apparent viscosities. The viscometer can interface with a computer to increase the operating and data analysis capabilities.

Water Content

Determining the water content of a stable mousse, even under laboratory conditions, can be extremely difficult. Evaluation of existing methods which could be adapted for field use showed that only the volumetric Karl Fischer titration technique would analyze viscous emulsions reliably and consistently. The instrument that was chosen was a Metrohm 701 Karl Fischer Titrator (Metrohm Limited - Switzerland). This automated system can measure water content of any substance from 0 to 100%. Analysis takes only a few minutes and repeat measurements are easily performed. The instrument is self-cleaning and will display the calculated water content. The instrument has been equipped with a DC/AC inverter, thus allowing it to operate using 120 volt AC or a gel cell (12 volt car battery).

The test procedure is analogous to the protocols for API MPMS (chapter 10.7), ASTM D4377-88 and IP 356/87 - "Standard Test Method for Water in Crude Oils (Karl Fischer) Titration." A 100 microliter sample is injected into the titration vessel containing a solvent mixture (1:1:2, methanol:chloroform:toluene) which dissolves the emulsion. The free water is then automatically titrated to an electrometric end point with Karl Fischer reagent. The water content is displayed on the screen as a weight percent value.

Flash Point

The Setaflash Model 13740 (Stanhope/Seta - England) is a portable unit powered either by a 120 volt AC source or a 12 volt battery. It has a measuring range of 0 to 100°C. The test will be conducted as a flash/no flash procedure at two selected temperatures: the prevailing environmental temperature and 60°C. The procedure is based on ASTM D3828-87 and IP 303/80 "Standard
Dispersibility

The use of dispersants remains an attractive countermeasure option for dealing with large oil spills. At this time there are a variety of tests for measuring dispersant effectiveness. Unfortunately, different tests can yield very different values. It should be recognized that no test, not even an elaborate laboratory test, can fully simulate oceanographic conditions. Nevertheless, many recent advances have been made in understanding the variables that affect dispersant effectiveness. After reviewing the existing field tests (Pelletier Screen Test, Fina Spill Test Kit, Mackay Simple Field Test, EPA’s Field Dispersant Effectiveness Test, and S.L. Ross Field Test), it was concluded that it was possible to draw upon all findings and develop a procedure that would avoid most of the artifacts and deficiencies of existing tests. This portable test will allow on-scene personnel to examine the relative effectiveness of a dispersant on an actual sample of the spilled oil using indigenous water and prevailing environmental temperatures.

The test selected was designed in such a way as to allow the operator to make a quick qualitative observation of dispersant effectiveness, and to obtain a quantitative value of effectiveness. The difficulties associated with using visual methods were pointed out by Ross (Ross, 1988) in his evaluation of field dispersant effectiveness tests. A major problem is that the colour of the oil affects the amount of oil perceived to be dispersed. If two oils of different colours were equally dispersed, the darker oil appears to be more dispersed. Therefore, assigning any kind of numerical value to effectiveness based on the appearance of the water containing the dispersed oil can be erroneous, if calibration standards are not prepared for comparison. These standards must use the same oil, water and dispersant that will be used during the sample test. A visual inspection will show, at least qualitatively, if the dispersant has had any effect. This can be done by comparing the results from a dispersant-treated oil against a non-treated oil. The non-treated oil will show the oil’s natural dispersibility and thus act as a control. In order to obtain a valid measure of effectiveness, the amount of oil dispersed into the water must be analyzed using appropriate techniques.

During the development of this test, numerous methods were examined. Different vessels were tested and different modes of mixing energy were studied. The test method described here was chosen because it can be performed easily and rapidly, the results are relatively insensitive to minor variations in mixing energy due to the human operator, and the values are repeatable and comparable to laboratory effectiveness tests. The test takes into account factors not considered by the previous field tests. Recent findings (Daling, 1988; Fingas et al., 1989; Fingas and Kolakowski, 1990; Nes, 1984) have shown the importance of certain variables on dispersant effectiveness testing. These variables are: the water-to-oil ratio; the length of settling time between the cessation of mixing energy and the withdrawal of a water sample; the extent to which the oil naturally disperses; and the manner in which the
standards are prepared. Each of these factors has been shown to have a significant effect upon dispersibility. It has been demonstrated that when the protocols of various existing laboratory tests are adjusted in such a way that these conditions are taken into account, the different tests yield comparable results (Fingas et al., 1989). None of the previous field tests account for these recent findings in their protocols.

The spill kit procedure entails adding 200 µL of oil (premixed with dispersant at a dispersant-to-oil ratio of 1:25) to 240 mL of seawater contained in a 250 mL Teflon separatory funnel. The funnel is hand-rotated at 30 rpm for two minutes and then allowed to settle for 30 minutes. A 30 mL water sample is drained into a 125 mL separatory funnel where it is extracted with 15 mL of solvent. The same procedure is used for determining natural dispersibility, except that dispersant is not added. A set of standards is made up by adding 5 µL, 15 µL, and 25 µL of oil (premixed with dispersant) to 30 mL of water. The entire volume of each standard is then extracted using 15 mL of solvent. The standards represent 20%, 60% and 100% dispersion respectively. Dichloromethane is the solvent that is presently specified, but the use of other solvents is being examined.

An estimate of the amount of oil that has been dispersed can be obtained by comparing the colour of the solvent from the test runs (both the natural and chemical dispersibility) to the colours of the standard solvents. An accurate determination of effectiveness can be made spectrophotometrically. The kit contains a hand-held, battery-powered Mini Spectronic 20 spectrophotometer (Milton-Roy Ltd., Rochester, New York). The operator will use scaled graph paper to plot the transmittance values of the standards versus percent oil dispersed in order to obtain a calibration curve. The percentage of the test oil dispersed can be read directly from the graph.
RESULTS

The instruments and standard methods used for the laboratory analyses are listed in Table I. Table II illustrates that the results obtained for density, viscosity, flash point, and water content using the field kit instruments are in good agreement with measurements from standard laboratory methods. It can also be seen from Figure 1 that the Bohlin viscometer provides an accurate rheological characterization of a water-in-oil mousse that exhibits non-Newtonian flow behaviour.

<table>
<thead>
<tr>
<th>Test</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density - Anton Paar DMA 45 digital density meter</td>
<td>ASTM D4052 - 86</td>
</tr>
<tr>
<td>Viscosity - Haake RV20 rotational viscometer</td>
<td>DIN 53018</td>
</tr>
<tr>
<td>Flash Point - Pensky-Martens Closed Tester</td>
<td>ASTM D93 - 85</td>
</tr>
<tr>
<td>Water Content - Photovolt Coulometric Karl Fischer</td>
<td>ASTM D1533 - 88 Method B</td>
</tr>
</tbody>
</table>
Table II: Comparison of Test Kit Results and Laboratory Results

<table>
<thead>
<tr>
<th>Test</th>
<th>Sample</th>
<th>Test Kit Result</th>
<th>Lab Result</th>
<th>Absolute Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/ml)</td>
<td>ASMB Crude</td>
<td>0.840(15°C)</td>
<td>0.8458(15°C)</td>
<td>0.0058</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.847(0°C)</td>
<td>0.8514(0°C)</td>
<td>0.0044</td>
</tr>
<tr>
<td></td>
<td>Norman Wells Crude</td>
<td>0.866(15°C)</td>
<td>0.8674(15°C)</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>Endicott Crude</td>
<td>0.915(15°C)</td>
<td>0.9154(15°C)</td>
<td>0.0004</td>
</tr>
<tr>
<td></td>
<td>Emulsion</td>
<td>1.003(15°C)</td>
<td>1.0010(15°C)</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.005(0°C)</td>
<td>1.0041(0°C)</td>
<td>0.0009</td>
</tr>
<tr>
<td>Viscosity (Pa-s)</td>
<td>Standard</td>
<td>1.049</td>
<td>1.0007</td>
<td>0.0483</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>Jet Fuel A1</td>
<td>44</td>
<td>42***</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>ASMB</td>
<td>6</td>
<td>7**</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Mousse Mix Oil**</td>
<td>72</td>
<td>71</td>
<td>1</td>
</tr>
<tr>
<td>Water Content (%)</td>
<td>Emulsion</td>
<td>69.31</td>
<td>69.00</td>
<td>0.31</td>
</tr>
</tbody>
</table>

* Alberta Sweet Mix Blend Crude Oil.
** this oil is a mixture of 50% Bunker C and 50% Alberta Sweet Mix Blend. The oil has been artificially weathered by air stripping; 7.7% by weight of the oil was evaporated off.
*** Data taken from Bobra and Callaghan (Bobra and Callaghan, 1990).
Figure 1: Viscosity versus Shear Rate Graph
Water-in-Oil Emulsion at 15 degrees Celsius

- Bohlin Visco88 BV
- Hooke RV20
The dispersibility values for four oils as determined by the Portable Field Kit Test are presented in Table III, along with results obtained from the Warren Spring Laboratory Rotating Flask Test and the Swirling Flask Test. Procedures for the WSL Test and the Swirling Flask Test were taken from Martinelli (Martinelli, 1984) and Fingas et al. (Fingas et al., 1989). Tests were conducted at room temperature using oil pre-mixed with Corexit 9527 at a dispersant-to-oil ratio of 1:25. For all tests, an oil-to-water ratio of 1:1200 was used and the settling period was 30 minutes. All three tests rank the oils in the same order of dispersibility; Bunker C was the least dispersed and Alberta Sweet Mix Blend was the most dispersed. The results obtained using the Portable Field Kit Test are comparable with the other tests; the effectiveness values from the Portable Field Kit are in-between those of the Swirling Flask Test and those of the WSL Test.

Table III: Dispersibility Results

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Oil</th>
<th>Dispersibility %</th>
<th>No. of Data Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSL* Rotating Flask Test</td>
<td>Alberta Sweet Mix Blend</td>
<td>57% ± 10%</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Norman Wells</td>
<td>54% ± 4%</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Endicott</td>
<td>36% ± 10%</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Bunker C</td>
<td>7% ± 5%</td>
<td>9</td>
</tr>
<tr>
<td>Portable Field Kit Test*</td>
<td>Alberta Sweet Mix Blend</td>
<td>53% ± 12%</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Norman Wells</td>
<td>31% ± 10%</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Endicott</td>
<td>8% ± 3%</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Bunker C</td>
<td>3% ± 3%</td>
<td>5</td>
</tr>
<tr>
<td>Swirling Flask Test</td>
<td>Alberta Sweet Mix Blend</td>
<td>20% ± 4%</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Norman Wells</td>
<td>20% ± 2%</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Endicott</td>
<td>3% ± 3%</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Bunker C</td>
<td>1% ± 1%</td>
<td>8</td>
</tr>
</tbody>
</table>

* Warren Spring Laboratory
** data include runs where the rpm was varied slightly and the size of the separatory funnel was altered.

NOTE: All dispersibility results were measured after a 30 minute settling time. The dispersibility results are written as the arithmetic mean plus/minus the standard deviation.
SUMMARY

Individual test components of a portable field kit have been selected and have undergone testing in the laboratory under simulated field conditions. The test methods were selected on the basis of portability, simplicity, safety, ruggedness, and reliability. A step-by-step manual is being compiled which provides detailed operation and maintenance procedures. A storage/transportation container is being designed that will hold all instruments and peripheral equipment. Besides protecting the kit during transportation, the container will also serve as a "lab station" which can easily be secured for aboard-ship operation where the tests can readily be performed.

Although refinements to the procedures are still being performed, the equipment is presently in a ready-to-go state. Should a spill-of-opportunity occur, the kit and an operator can be provided. The performance of the kit under field conditions will be assessed and appropriate improvements made.

ACKNOWLEDGEMENTS

This project was funded by Environment Canada, the U.S. Minerals Management Service, and the American Petroleum Institute.

REFERENCES


