Round-Robin Testing of a New EPA Solidifier Effectiveness Protocol

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ABSTRACT

A new laboratory testing protocol for evaluating effectiveness of solidifiers in removing crude oil slicks on the water surface has been developed by the U.S. Environmental Protection Agency (EPA). Since an assessment of a testing protocol requires validation through an inter laboratory study with several independent research partners, a round-robin test was performed by five operators across two laboratories. The protocol was qualitatively and quantitatively evaluated to determine if it can satisfactorily differentiate product effectiveness, while still accounting for experimental and operational errors. Each operator evaluated the efficiency of six solidifier products with Arabian Light, Endicott and IFO 120 crude oils. All the experiments were carried out in triplicates and, additionally, an oil alone control sample was run for quality control purposes. The five operators were provided with all the supplies required to conduct the experiment and a detailed standard operating procedure. The results were collected and analyzed statistically to quantify repeatability and reproducibility.

The average repeatability and reproducibility standard deviations were 5.1, 2.7, and 3.3% and 11.2, 10.1, and 13.1% for Arabian Light, Endicott and IFO, respectively. The within-operator error was ≤ 5% regardless of operator and oil type. Due to the difficulty and uncertainty

associated with the separation of the solidified and un-solidified mass, the between-operator error was around 10%. The oil alone control had an average repeatability and reproducibility standard deviation of 4.8 and 6.1%, respectively. The variability among operators was also examined with *h*-statistics and the differences in operator means were found to be statistically insignificant. The variability is deemed acceptable for purposes of differentiating effective from ineffective solidifier products in the laboratory. The results from this round robin experiment will serve as an initial screening tool for the solidifier products in the market and will also help response teams determine the desirability and appropriateness of using a specific solidifier for oil spill remediation.

INTRODUCTION

Several tests have been developed to measure the effect of test conditions on oil spill countermeasures such as dispersants and bioremediation agents. Currently, the EPA requires product manufacturers to submit toxicity data for all products listed on the National Contingency Plan (NCP) Product Schedule. Dispersants and bioremediation agents must also undergo effectiveness testing in accordance with the published testing protocols developed by EPA (Haines et al., 2003; Sorial et al., 2004). Several effectiveness testing procedures for solidifiers have been described in the literature (Dahl et al., 1997; Fingas et al., 1990; Ghalambor, 1996; DeLaune et al., 1999). However, they rely on visual means to measure the effectiveness of solidifiers, and the effects of variables such as oil type and application rates have not been widely studied.

The new effectiveness test for solidifiers developed by the EPA gauged several variables at multiple levels to determine their significance to solidification and to establish optimal levels to be included in the final protocol. From a practical standpoint, the only variables that gave meaningful differences were product type, solidifier-to-oil mass ratio (SOR), and oil type. In this protocol, one operator was able to distinguish effective from mediocre and ineffective products, while maintaining a low repeatability error. The protocol involved measuring the amount of free oil remaining in the water after the solidified product was removed by using an ultraviolet–visible spectrophotometer (Sundaravadivelu et al., 2016). This protocol will provide a standard for the EPA in solidifier product evaluation prior to listing on the NCP Product Schedule. In order to determine if the protocol is repeatable and reproducible, a round robin experiment was designed. The preliminary results from this study are presented in this manuscript.

METHODS

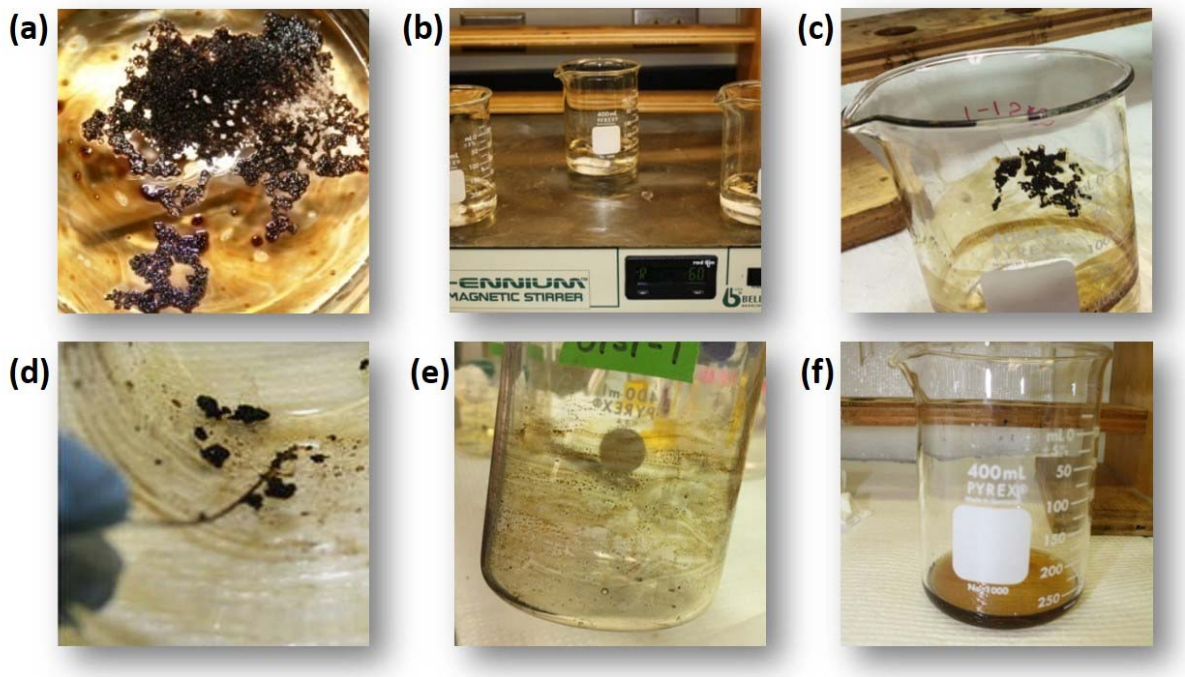
Oil Removal Efficiency

Based on results from previous studies, six solidifiers were chosen to represent three ranges of efficiency level, with the levels defined in terms of average percent oil removal as high (> 70%), intermediate (50-70%), and low (< 50%) (Sundaravadivelu et al., 2015). The products used in this study were Nochar A650 (Nochar, Inc., Indianapolis, IN, USA), Waste-Set #3200® (Environmental & Fire Technology, LLC, Grand Rapids, MI, USA), Gelco 200 (UESS, Ltd., Drayton Valley, AB), Norsorex APX® (ASTROTECH Advanced Elastomer products, Vienna, Austria), Oil Bond ® (Solidification Products International, Inc., Northford, CT) and Aqua N-Cap™ (Oil Solutions International, Amityville, NY) (referred to randomly as S1 to S6; i.e., the labels assigned should not be construed to refer to the solidifier order named above). Three oils increasing in viscosity were chosen, namely, Arabian Light, Endicott, and IFO 120.
Each solidifier was individually exposed to the oils with the following variables being fixed: temperature (22 ± 2 °C), beaker volume (400 mL), matrix (80 mL of DI water), mixing speed (60 rpm), SOR (1:4), oil volume (0.25 mL), and contact time (30 minutes).

The five operators were provided with all the supplies required to conduct the experiment and a detailed standard operating procedure, which included visual aids such as photos and videos. These instructions are summarized as follows: in a given experiment, 0.25 mL of oil was added to 80 mL of DI water in a 400 mL beaker and, subsequently, the solidifier was added at a 1:4 SOR (Fig. 1a). At the end of the contact time of 30 minute on a magnetic stir plate set at 60 rpm (Fig. 1b), the solidified mass was gently moved to the side of the beaker (Fig. 1c) and the water and remaining oil was transferred to 250-mL separatory funnels. The solidified mass (i.e.,

solidifier + solidified oil + attached unsolidified oil) on the sides of the beaker was moved around the walls of the beaker with a metal rod (Fig. 1d). Therefore, any oil that was not truly solidified into the polymer matrix remained in the beaker (Fig. 1e). The beaker was then rinsed with 20 mL dichloromethane (Fig. 1f), and was added to the separatory funnel. Liquid/liquid extraction of the samples were performed and any oil that remained unsolidified was taken into the solvent phase. All experiments were carried out in triplicate by five operators. An UV-Visible Spectrophotometer was used to analyze the dichloromethane extracts and calculate oil removal effectiveness (Srinivasan et al., 2007). The operators provided the data to EPA in a spreadsheet format for statistical analysis.

Fig. 1. Experimental procedure



Statistical Analysis

Oil removal efficiency results were analyzed to quantify the closeness of agreement for a given sample analyzed by an independent operator and the average values obtained by several operators while measuring the same item. The repeatability and reproducibility deviation was used to represent the maximum anticipated differences between any two measurements by the same analyst (S_r) or any two analysts (S_R), which were calculated with Eqn. 1 and Eqn. 2, respectively.

$$s_r = \sqrt{\frac{\sum s_i^2}{i}} \qquad \text{(Eqn. 1)}$$

where,

s_i = standard deviation of each operator

i = total number of operators

$$s_R = max \left\{ \quad s_r \quad \middle| \quad \sqrt{s^2 + \left(1 - \frac{1}{j}\right) s_r^2} \quad \right\} \qquad \text{(Eqn. 2)}$$

where,

s = Standard deviation amongst all operators

i = total number of operators

j = total number of measurements per operator

Furthermore, the data was investigated for consistency by examining the *h*-statistic for each product (solidifier 1 to 6 by operator 1 to 5). The *h*-statistics is a dimensionless quantity given by Eqn. 3, which describes the deviation of each operator from the group mean for any given product. The critical value of *h* was calculated using Eqn. 4 and it depends on the number

of independent operator (p) and the number of replicates for any given operator. If all standardized operator means (h_i) fell within the critical value ($\pm h_{crit}$), it was then concluded that the operator means were statistically similar.

$$h_i = \frac{x_i - x}{s} \quad \text{(Eqn. 3)}$$

where,

x_i = mean for operator i

x = mean for all operators

s = standard deviation amongst all operators

$$h_{crit} = \frac{(p-1)*t}{\sqrt{p(t^2+(p-2))}} \quad \text{(Eqn. 4)}$$

where,

p = degree of freedom

t = Student's t value [$t_{(\alpha=0.995,\ p = 0.005,\ df = p-2)}$]

RESULTS AND DISCUSSION

The two components of precision in a measurement system includes repeatability and reproducibility (Taylor and Kuyatt, 1994). While repeatability is "within operator" error, usually traced to the nature of the test itself, reproducibility is "between operator" error, and is usually traced to differences among the operators who obtain different measurements while using the same protocol (ISO Guide 5725-1, 1994). Repeatability and reproducibility standard deviations were computed as described in the ASTM standard for conducting an inter-laboratory study to evaluate the precision of a protocol (ASTM Standard E691, 1999). The computed values of the

repeatability standard deviation (S_r as per Eqn. 1), the reproducibility standard deviation (S_R as per Eqn. 2), and the oil removal efficiencies for each oil and solidifier type are listed in Table 1.

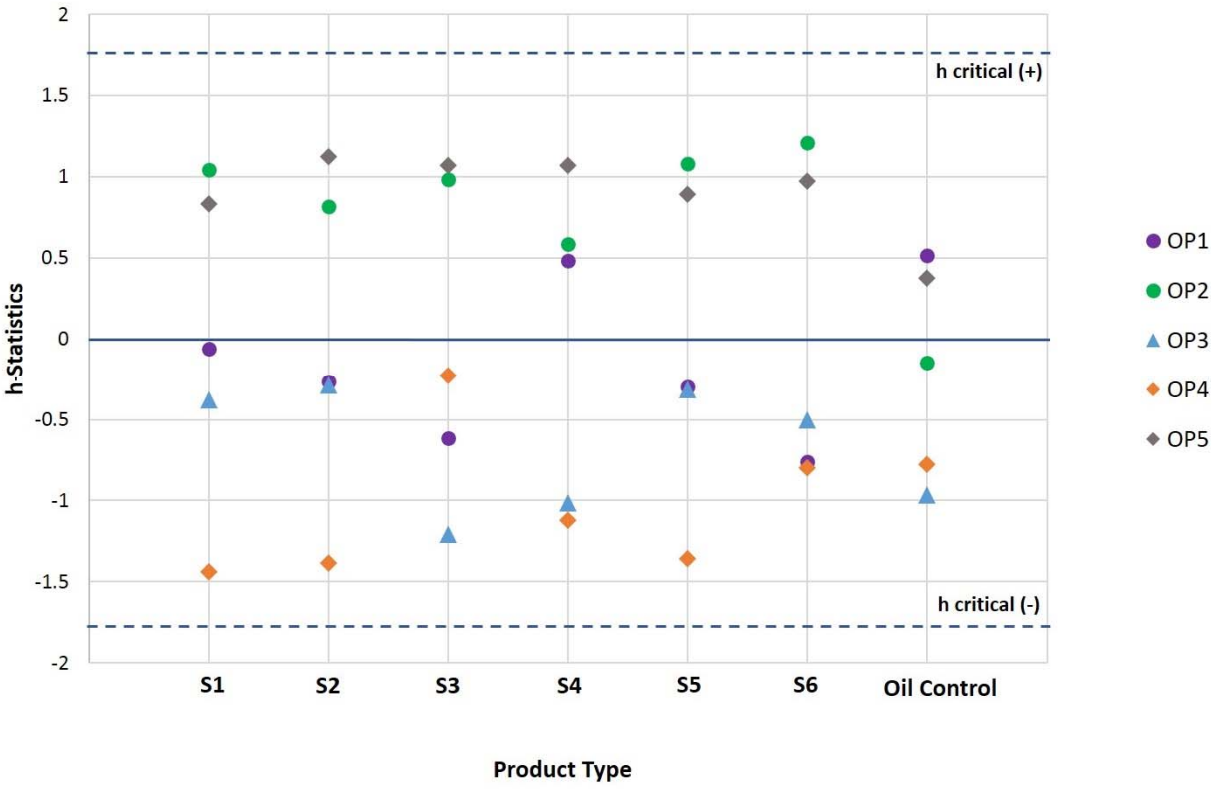
Table 1. Solidifier effectiveness, repeatability standard deviation, and reproducibility standard deviation for three oils

	ALC			END			IFO		
	AVG	**S_r**	**S_R**	**AVG**	**S_r**	**S_R**	**AVG**	**S_r**	**S_R**
S1	65.9	6.7	13.5	64.8	2.8	10.0	62.7	3.2	12.9
S2	67.5	4.9	11.8	66.9	2.8	15.2	65.5	3.5	14.3
S3	72.9	3.7	5.7	77.9	2.7	7.5	74.0	3.1	9.8
S4	32.5	7.8	8.9	28.0	2.9	10.8	39.3	3.1	14.7
S5	63.1	7.1	16.0	59.5	2.7	12.8	57.7	4.6	14.3
S6	77.9	2.7	11.3	78.6	1.4	3.5	67.7	3.4	11.9
OIL	4.2	3.1	5.4	-1.8	3.4	5.2	1.6	2.4	6.7

The average repeatability and reproducibility standard deviation amongst all operators and oils were 6.9 and 11.8%, respectively. Since the reproducibility standard deviation includes the repeatability standard deviation (Eqn. 2), the former is always greater. The average repeatability standard deviation for each of the oils was 5.1, 2.7 and 3.3%, respectively. The repeatability (within-operator error) comprised mostly of the inherent error in the method, while quantifying a product's ability to solidify oil and did not significantly vary based on operator, solidifier, or oil type. The average reproducibility standard deviation for each of the oils was 11.2, 10.1, and 13.1%, respectively. The heavier IFO oil was difficult to work with due to its increased viscosity and hence the observed larger variations amongst operators. Furthermore, the removal of the unsolidified oil from the solidified mass as seen in Fig. 1d introduced some variation between the operators. Products S3 and S6 were the best performing, irrespective of oil type, while S4 was the least effective. In general, the best performing products had lower S_r and S_R values. The negative control set up with oil alone yielded oil removal efficiencies close to 0% and the S_r and S_R values were significantly lower than the treatments with solidifier present. To

determine if data from the three oils could be pooled for purposes of reporting, solidifier effectiveness for each of the oils and operators was analyzed. The results for the 3 oils were statistically equivalent ($p = 0.562$). Therefore, for all future analyses, the data from the 3 oils were pooled, thus yielding 9 total replicates (instead of 3).

Fig. 2. Between-operator variability based on *h*-statistics



When using the 6 products (S1 to 6), the differences amongst the 5 operators (OP1 to 5) were analyzed with *h*-statistics by using Eqn. 3 and Eqn.4 (ISO Guide 98-3, 2008). The results are presented in Fig. 2. In this graphical investigation, the interpretation of the result is as follows: for a given solidifier, say S1, the pooled effectiveness value (3 oils × 3 replicates = 9 replicates) was 63.8 ± 3.9 % for OP1. The mean of all measurements by all 5 operators was 64.5

± 10.2 %. In this instance, the operator mean is very close to the grand mean. Furthermore, all the other operators are also well within the critical value (± h_{crit}). The level of variation amongst the operators was similar for the products with higher efficiency (such as S6) and lower efficiency (S4). The protocol does not exhibit any bias for either the highly efficient or the inefficient products. The controls (oil alone samples) fit more closely with the grand mean and had lower S_r and S_R values as seen in Table 1. The *h*-statistics showed that there is evidence of operator effect for all solidifiers. The effectiveness values for OP2 and OP5 were always higher than that of OP3 and OP4, while OP1 was closed to the grand mean. Regardless of product effectiveness or operator effect, the *h*-statistics for all the operators fell within the critical value which in turn signifies that the differences between the operators are statistically insignificant. The results from this preliminary study will be incorporated in developing pass-fail decision rules for solidifier manufacturers prior to having their products listed on the NCP Product Schedule.

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