



## Project Summary

# Chemical Oil Spill Dispersants: Update State-of-the-Art on Mechanism of Action and Laboratory Testing for Performance

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Chemical dispersants are formulations designed to facilitate dispersion of an oil slick into small droplets that disperse to non-problematic concentrations in an underlying water column. This project had two primary objectives: (1) update information on mechanisms of action of dispersants and factors affecting their performance and (2) evaluate selected testing procedures in the laboratory for estimating performance of different dispersant agents. The first objective resulted in a report updating information on chemical dispersants, their mode of action, variables affecting dispersant performance in the field as well as the laboratory, and a discussion of a number of laboratory and rapid-screen field tests for estimating performance. Information derived in the course of preparing this report was used to select three laboratory testing procedures for evaluation of performance characteristics: the Revised Standard EPA test, the Swirling Flask test, and the IFP-Dilution test. In the laboratory, these three procedures were evaluated for their precision of results in estimating dispersant performance, costs associated with conducting a given procedure, and the ease of conducting that procedure (e.g., number of tests performed in 8 hr, skill level required of an operator, and overall complexity of the procedure). The precision of results for dispersion performance for all procedures was approximately the same (standard de-

viation of 7% to 9% in dispersion performance values). Costs to perform a procedure and ease of conducting that procedure favored the Swirling Flask test.

*This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in the two reports listed at the end of this summary (see Project Report ordering information at back).*

### Introduction

All tasks performed for this work assignment were elements of the Oil Spills Research Program that was initiated in response to the Oil Pollution Act (OPA) of 1990. The work supports the EPA workgroup concerned with revision of sub-part J (dispersant effectiveness and toxicity) of the National Contingency Plan (NCP) as required by the OPA. Primary deliverables from SAIC to EPA's Releases Control Branch/Risk Reduction Engineering Laboratory (RCB/RREL) include (1) a State-of-the-Art (SOTA) report on mechanisms of action and factors influencing dispersant performance and (2) a laboratory evaluation of candidate National Contingency Plan protocols for testing dispersant performance of candidate agents. The RCB may use information derived from the SOTA report as well as the laboratory studies as part of the work assignment to assist in evaluation of candidate tests for estimating performance of dispersant agents as



well as planning follow-on studies with chemical dispersants.

## **State-of-the-Art Report on Chemical Dispersants**

The SOTA report for chemical dispersants includes discussions of the following topics: (1) the mechanism of action of chemical dispersants for oil spills, (2) factors affecting the performance of dispersants, (3) some common laboratory methods used to measure dispersant performance, (4) aspects of the analytical measurement of dispersant performance in the laboratory, (5) a brief summary of dispersant applications and their performance in field trials and spills-of-opportunity, and (6) recommendations for future laboratory studies. The discussion of the laboratory methods includes detailed information for a number of the more commonly used tests, as well as similarities and differences among testing procedures. Differences among tests are particularly important because they may be responsible for not only significant differences in results between laboratory testing methods but also poor correlations between laboratory results and data from field tests. Four general types of laboratory testing methods are considered: (a) tank tests, (b) shake/flask tests, (c) interfacial surface tension tests, and (d) flume tests. Information is presented for general approaches used in laboratory studies, limitations inherent to the laboratory measurements, and the relevance of laboratory results to field studies or situations. Brief descriptions also are presented for a number of rapid field tests for estimating dispersant performance. Limitations inherent to measurements obtained with the latter tests are discussed.

## **General Mechanism of Action of Chemical Dispersants**

Chemical dispersants are designed to promote the break-up or dispersion of an oil slick into small droplets that distribute into a water column. The small oil droplets should not recombine or coalesce to reform surface slicks. Ideally, dispersed oil droplets will be subject to not only dilution to non-problematic concentrations in the water column but also enhanced microbial degradation as the oil-water interface increases.

A typical commercial chemical dispersant is a mixture of three types of chemicals: surface active agents (i.e., surfactants), solvents, and additives. Solvents are primarily present to promote the dissolution of surfactants and additives into a homogeneous dispersant mixture. Addi-

tives may be present for a number of purposes such as increasing the biodegradability of dispersed oil mixtures, improving the dissolution of the dispersant into an oil slick, and increasing the long-term stability of the dispersion. For the actual dispersion process, however, the most important components in the dispersant mixture are the surfactant molecules. These are compounds containing both oil-compatible (i.e., lipophilic or hydrophobic) and water-compatible (i.e., hydrophilic) groups. Because of this amphiphatic nature (i.e., opposing solubility tendencies), a surfactant molecule will reside at oil-water interfaces with the hydrophobic and hydrophilic groups positioned toward the oil and water phases, respectively. As such, the surfactant will reduce the oil-water interfacial surface tension. The lowering of oil-water interfacial surface tension will promote dispersion of oil droplets into the underlying water with minimal mixing energy. The oil droplets will remain dispersed in a water column if they are small enough to allow for natural water currents or Brownian motion to prevent rising to reform surface slicks.

## **Factors Affecting Chemical Dispersion of Oil and Its Measurement**

A variety of factors have major influences on the ability of chemical agents to disperse oil into water in both laboratory tests as well as actual field situations. These factors can include physical and chemical properties of an oil, the composition of a dispersant formulation, the method of applying the dispersant to an oil slick, the mixing energy available for dispersing treated oil into a water column, the dispersant-to-oil ratio, the oil-to-water ratio, temperature, and salinity. The sampling and analysis methods for evaluating dispersion performance also can influence measurement results.

Crude and refined petroleum products are complex mixtures of hydrocarbon compounds that can contain compounds in five broad categories: lower molecular weight (1) aliphatics and (2) aromatics, and higher molecular weight (3) asphaltenes, (4) resins, and (5) waxes. Interactions between the aliphatics, aromatics, asphaltenes, resins, and waxes allow for all of the compounds to be maintained in a liquid-oil state. That is, the lower molecular weight components (i.e., the aliphatics and aromatics) act as solvents for the less soluble, higher molecular weight components (i.e., the asphaltenes, resins, and waxes). In addition to inherent differences in chemical

compositions among different parent oils, oil that is released onto a water surface will undergo a variety of rapid, dynamic changes in both chemical composition and physical properties. Such changes are known as weathering and result from selective dissolution and evaporation losses of lower molecular weight components as well as photooxidation and microbial degradation of selective compounds. Complex crude oil mixtures remain as relatively stable liquid phases as long as the solvency interactions occurring in the bulk oil are maintained and thermodynamic conditions remain constant. If this equilibrium state is changed (e.g., due to weathering processes), the solvency strength of the oil may become insufficient to keep higher molecular weight components in solution and lead to their precipitation as solid particles. Accompanying changes in the physical state and chemical properties of the oil can affect the way chemical dispersants interact with the oil that has undergone such changes. Despite the preceding complexities associated with different oils, dispersant formulations are frequently designed with the intent to deal with a relatively broad range of oil types and properties.

The dispersant application method can be one of the most critical elements determining whether a particular dispersant will produce dispersion of oil or not. In field situations, dispersant is normally applied from aircraft (airplanes or helicopters) or surface vessels (boats). The dispersant is applied as relatively small droplets that descend onto a slick in a manner providing broad spatial coverage. The size of the applied dispersant droplets is important to successful application. Droplets that are too large may penetrate through an oil slick without interaction. Droplets that are too small may not reach the slick because of air or wind transport between the application source and the slick.

Following application of a chemical dispersant to an oil slick on water, dispersion of the oil requires input of mixing energy that results in injection of the oil as droplets into the underlying water column. The mixing energy is generally supplied by ambient wave action in field situations or mechanical agitation of test solutions in laboratory systems. Dispersion of the droplets into the water column is countered by the buoyancy of the oil droplets, which depends on the density and size of the droplets, their rise velocities as described by Stokes' Law, and natural advective processes that result in horizontal and vertical transport and dilution of the oil. In addition to mixing energy, other factors

that can affect dispersion performance of an oil include the ratios of dispersant-to-oil and oil-to-water as well as ambient temperature and salinity in the water.

Evaluation of dispersant performance in the laboratory (as well as the field) must incorporate appropriate sampling and analysis methods into a testing procedure. In the numerous studies that compare dispersion-performance values among testing procedures, agreement for results is generally poor. At least a portion of this variability is attributable to variations in the sampling approaches. For example, different laboratory testing procedures will collect test samples from reaction vessels at various times after agitation in the reaction vessel ends. A settling time (i.e., collection of samples only after agitation has stopped for some predefined period of time) may be incorporated into a testing procedure to allow larger, less stable dispersed oil droplets to return to a surface slick before smaller, more stable dispersed oil droplets are recovered in a subsurface water sample.

In addition to the preceding issues related to sampling methodology, the analytical methods chosen to quantify amounts of dispersed oil in samples also are important for dispersion measurements. The most widely used methods for quantifying amounts of dispersed oil in laboratory test samples involve extraction of a water sample with a suitable solvent and quantitation by UV-visible spectrophotometric or (less frequently) gas chromatographic methods. However, selection of the analytical wavelength(s) for spectrophotometric measurements can be important. Measurements in different laboratory testing procedures have been made at wavelengths from 340 to 620 nmeters, with wavelengths selected in part on the optical (or color) characteristics of particular oils and dispersants being tested as well as the optical characteristics of the available spectrophotometric system.

### **Laboratory Tests for Dispersant Performance**

A variety of laboratory testing methods have been used to evaluate dispersant performance. In general, laboratory tests can be placed into four categories: (1) tank tests with water volumes ranging from 1 to 150 L, (2) shake/flask tests that are conducted on a relatively smaller scale and require less sophisticated laboratory equipment, (3) interfacial surface tension tests that measure properties of the treated oil instead of dispersant performance directly, and (4) flume tests using flowing water systems with the capacity for break-

ing/nonbreaking waves to generate energy regimes that can more closely simulate real-world conditions in large water bodies (e.g., oceans and coastal bays). Each type of test uses a general approach of (1) establishing an oil slick on water, (2) applying dispersant to the slick, (3) applying energy to the oil-dispersant-water system, and (4) measuring the amount of oil dispersed into the water.

Significant differences are inherent to the various methods. For example, different methods for adding the dispersant to oil include premixing of dispersant with oil, slowly pouring dispersant onto the oil, spraying the oil surface with a fine mist of either neat dispersant or dispersant premixed with seawater, or pouring the dispersant into the water before adding the oil. Test-specific variations in the ratio of the oil-to-water volumes can affect not only the relative performance of dispersant surfactants (e.g., hydrophilic versus lipophilic) but also the magnitude of wall-effects in test containers. A variety of approaches have been used to provide mixing energy to test systems, such as circulating pumps and spray hose systems, high velocity air streams that produce small waves on the water's surface, raising and lowering of a metal hoop in the water, rotating or shaking separatory funnels, shaking flasks on a shaker table, and vertically flowing water in a test cylinder. Another variation concerns the time after mixing ends that water samples are withdrawn from the test solutions in the different procedures. In summary, the wide variety of test conditions can make comparison of results among different methods quite problematic.

Detailed descriptions of the following procedures for evaluating performance of chemical dispersants are presented in the SOTA report.

- 1) Tank tests: Mackay/Nadeau/Steelman (MNS) test, Revised Standard EPA test, oscillating hoop test, IFP-Dilution test, and flowing cylinder test.
- 2) Shake/Flask tests: rotating flask test (Labofina/Warren Spring Laboratory), swirling flask test, and Exxon dispersant effectiveness test (EXDET).
- 3) Interfacial Surface Tension tests: drop-weight test.
- 4) Flume tests: cascading weir test and Delft Hydraulics flume test.

Table 1 summarizes features and essential procedural components in these testing methods. Strengths and limitations associated with each testing method are presented in the SOTA report.

In addition to the preceding methods, descriptions also are presented in the

SOTA report for five rapid-screen field tests for evaluating dispersant performance (the EPA field dispersant effectiveness test, the API field dispersant effectiveness test, the Mackay simple field test, the Pelletier screen test, and the Fina spill test kit\*). The detailed laboratory test methods identified in Table 1 do not readily lend themselves to onsite applications in the field. In contrast, the rapid-screen field tests have been developed to provide fast, qualitative information regarding an oil's dispersibility in field situations. These rapid-screen tests are, however, inherently limited in the scope of information that they can provide because of their necessary simplicity for use in field situations.

### **Evaluation of Laboratory Test Procedures to Assess Dispersant Performance**

Primary objectives in evaluations of laboratory testing procedures were to obtain estimates of the repeatability of measurements for dispersion performance with different testing procedures, evaluate comparability of results obtained with the procedures for selected dispersant agents and oils, and summarize the qualitative ease of conducting each testing procedure (i.e., how many individual test runs can be performed in a given period of time, the complexity of a testing procedure in relation to the required training time and skill level of an operator, and associated costs for both equipment and conduct of tests). All of these objectives have relevance to the suitability of a testing procedure for use as a routine laboratory testing method. Additional advantage could derive from identifying one or more testing procedures that could be performed in a more rapid and efficient manner than the current Revised Standard EPA protocol and that could provide results giving dispersion-performance rankings for different dispersant agents equivalent to those obtained with testing procedures used by agencies in other countries (e.g., Canada and countries of Western Europe).

### **Selection and Experimental Design for Test Procedures**

Tests selected for evaluation in the laboratory included the currently accepted Revised Standard EPA test, Environment Canada's Swirling Flask test (including three versions: premixed, 1-drop, and 2-drop dispersant additions), and the IFP-

\* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

**Table 1. Summary of Features of Laboratory Methods to Test Dispersant Performance**

Test ID	Energy Source	Energy Rating *	Water Volume (mL)	OWR †	Dispersant Application Method	DOR ‡	Settling Time (min)	Complexity Rating **
MNS	High velocity air stream	3	6000	1:600	Dropwise/premix	Variable	None	3
Revised Std. EPA	Pump	3	130,000	1:1300	Dropwise	3:100 to 1:4	None	3
Oscillating hoop	Oscillating hoop	3	35,000	1:175	Dropwise/premix	Variable	None	3
IFP-dilution\	Oscillating hoop	1-2	4000-5000	1:1000, then decrease	Dropwise	Variable	None	2
Flowing cylinder	Vertical flow of water	1	1000	1:1200, then decrease	Premix	1:25	10	2
Labofina rotating flask	Rotating vessel	3	250	1:50	Dropwise	1:25	1	1
Swirling flask	Shaker table	1-2	120	1:1200	Premix/dropwise	1:10 to 1:25	10	1
EXDET	Wrist-action shaker	1-2	250	Variable	Premix/dropwise	Variable	None	1
Drop-weight	None	0	(NA) ††	(NA)	Water-oil interaction	(NA)	(NA)	2
Cascading weir	Water passing over weirs	2-3	150,000	Variable	Spray	Variable	None	4
Dolt flume	Wave paddle	2-4	4,500,000	Variable	Spray	Variable	None	4

\*Energy Rating: 0=none; 4=highest.

† OWR = oil-to-water ratio (v:v).

‡ DOR = dispersant-to-oil ratio (v:v).

\*\*Complexity Rating: 1= lowest; 4 = highest.

†† (NA) = not applicable.

Dilution test (Centre de Documentation de Recherche et d'Experimentations sur les Pollutions Accidentelles des Eaux, Plouzane, France). Test oils used in some or all portions of the laboratory study included Prudhoe Bay crude, South Louisiana crude, Alberta Sweet Mixed Blend (ASMB), Arabian crude, Bunker C, and No. 2 fuel oil. Test dispersants used in all portions of the study included Corexit 9527, Corexit CRX-8, and Enersperse 700. Common elements through tests with all of the testing procedures included the following.

- oil types: Prudhoe Bay and South Louisiana crudes
- dispersant types: Corexit 9527, Corexit CRX-8, Enersperse 700, and "no dispersant" controls
- test types: EPA-10 min, EPA-2 hr, premixed Swirling Flask, and IFP-Dilution

- analytical wavelengths: 340, 370, and 400 nmeter absorbance
- duplicate measurements for particular groups
- water temperature (not a specified variable of interest for these studies, but one that did exhibit slight variations)

### Results of Laboratory Tests

Information for the primary objectives of the laboratory study are summarized in Table 2. Estimates of precision or repeatability for dispersion-performance values (i.e., standard deviations about means) were approximately 7% to 9% for all of the testing procedures. These values should be viewed as preliminary estimates, however, because they are generated with only a limited number of oils and dispersant agents. Furthermore, final estimates

for precision associated with a given testing procedure should incorporate measurements from multiple laboratories. The nonquantitative criteria in Table 2 (i.e., number of tests that can be performed in 8 hrs; costs associated with equipment acquisition, conduct of tests, and waste disposal; and qualitative items such as necessary skill level of an operator and overall complexity of a testing procedure) favor the Swirling Flask procedure for conducting multiple tests in a relatively short period of time for the least amount of cost.

General trends for the results of dispersion performance in the laboratory tests are illustrated in Figure 1 for the two common test oils (Prudhoe Bay and South Louisiana crudes) with the four primary testing procedures (Revised Standard EPA-10 min, Revised Standard EPA-2 hr,

premixed Swirling Flask, and IFP-Dilution) and the three dispersants (Corexit 9527, Corexit CRX-8, and Enersperse 700). Dispersion for all test oils in all procedures was near zero in the absence of chemical dispersant agents. With addition of the dispersants, performance values were consistently highest with the EPA test. Similarities in relative trends for dispersion performance with the different dispersants were observed in the Revised Standard EPA and Swirling Flask procedures for Prudhoe Bay crude. Trends for dispersion performance with the different dispersants and South Louisiana crude were less comparable in the EPA and Swirling Flask procedures. Relative performance trends among dispersants in the IFP-Dilution procedure did not appear to be comparable to either the EPA or Swirling Flask tests. Statistical analyses of results showed that the major portions of differences in dispersion-performance values for the three primary testing procedures (Revised Standard EPA, premixed Swirling Flask, and IFP-Dilution) could be accounted for by differences in the oils and dispersants used in tests (i.e., at least 85% of the total variance for results with each testing procedure). Dispersion-performance values for measurements at the three analytical wavelengths (340, 370, and 400 nmeters) were negligible (i.e., <0.5% of the total variance).

## Recommendations for Laboratory Studies

Chemical dispersion of oil into water in laboratory studies involves complex interactions between many variables including the chemical and physical properties of oils and dispersants, the method of application (and its effectiveness) and mixing of a dispersant with an oil, the source and magnitude of mixing energy available to

the system, the dispersant-to-oil ratio, the oil-to-water ratio, temperature, and the salinity of the aqueous medium. Extrapolation of results from dispersion performance studies in a laboratory to field situations must take into account additional complicating variables including rapid changes that occur in properties of the oil with time (i.e., natural weathering), field application methods and logistics, ambient weather and meteorological conditions, and local sea-state or oceanographic conditions (e.g., wave heights, currents, turbulent mixing regimes, etc.). The breadth of these variables makes it unlikely that any single laboratory test will ever be completely suitable to quantify performance of chemical dispersant agents for all possible environmental scenarios. More realistically, many laboratory test results should be used to apply relative rankings to performance by various dispersant agents, including possible assignment of "pass/fail" status to individual dispersants. Scientific criteria to assign "pass/fail" status continue to be subjects for future discussion and study.

Much has been learned about performance of dispersants and their mechanisms of action from studies conducted with the variety of laboratory testing methods shown in Table 1. Test results are, however, frequently contradictory for reasons that are probably related to test-specific characteristics. Adoption of standard experimental protocols (e.g., selection of specific reference oils and dispersants, consideration of the weathered state of test oils, use of specific oil-to-water ratios, selection or not of designated settling-times to be used in the conduct of experiments, and consideration of the natural dispersibilities of oils in a given test) might lead to closer agreement in performance results among testing methods. Further advances in testing methodologies, how-

ever, remain to be developed and refined, particularly as they relate to the environmental relevance and performance of dispersant agents. For example, approaches used to generate environmentally relevant mixing energies in laboratory studies could be improved. Continued investigation and analysis of dispersed oil droplet sizes might explain differences in energy levels and estimates of dispersion performance in different laboratory testing systems, which could lead to improved, standardized test designs. In general, laboratory experiments also have not been designed to evaluate the effects of herding of oil on dispersion results. Current testing methodologies are inadequate to investigate dispersion in thin versus thick slicks, which is important for dispersant applications at sea because slicks are usually nonuniform in thickness and distribution on the water's surface. At the same time, it is highly desirable that a laboratory testing method be simple, require equipment that is relatively easy to acquire and fabricate, require a minimum of operator training and sophistication, and allow for the conduct of a reasonably large number of tests yielding quantifiable results in an acceptably short period of time.

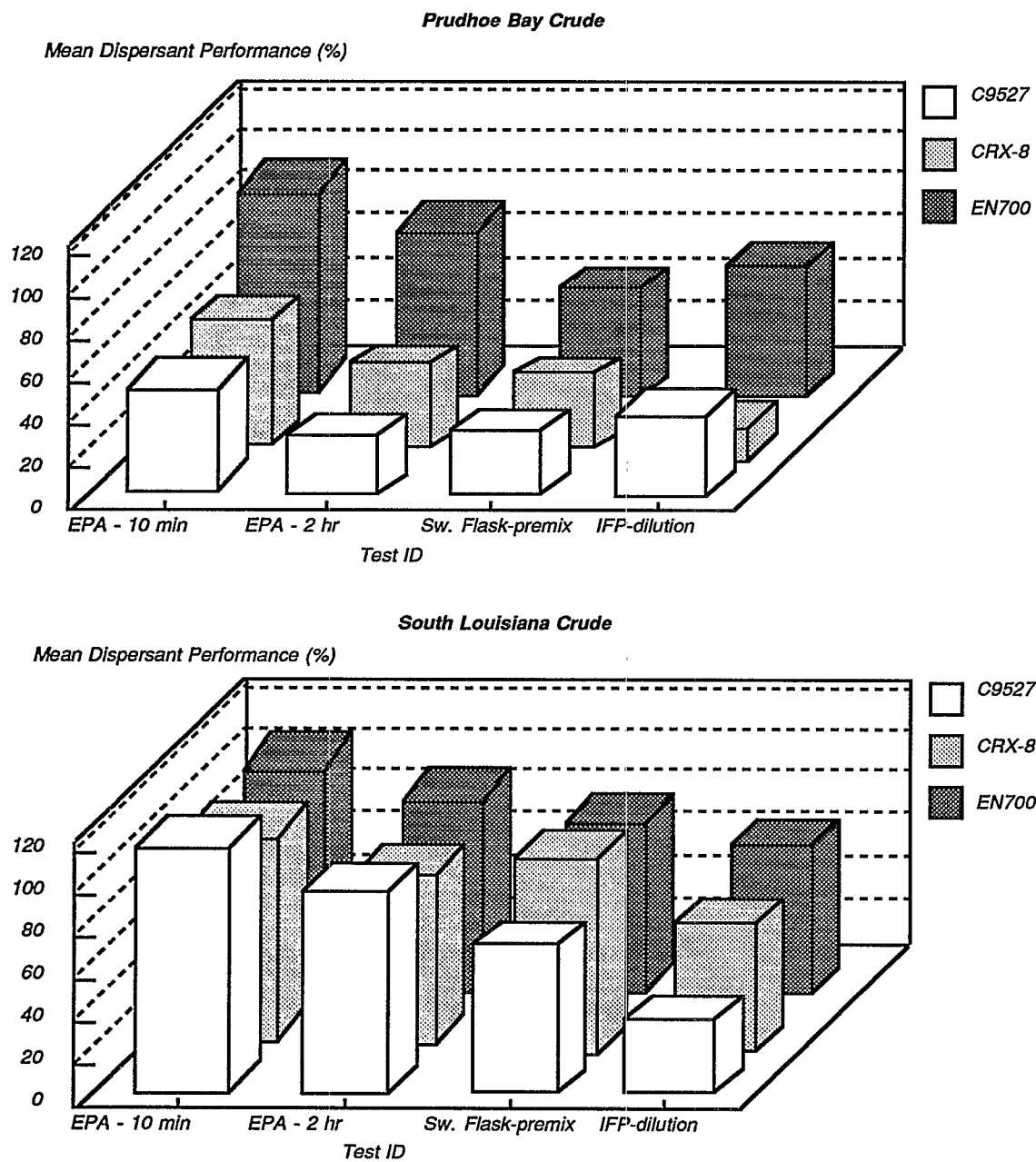
From the standpoint of using chemical dispersants for mitigating effects of oil spills in real-world situations, development and refinement of application techniques and protocols for applying dispersants in the field remain as critical needs. Successful application of chemical dispersants in field situations continues to be extremely problematic. Further studies in areas of application technologies are definitely warranted.

All reports for the work assignment were submitted in fulfillment of Contract No. 68-C8-0062 by Science Applications International Corporation under the sponsorship of the U.S. Environmental Protection Agency.

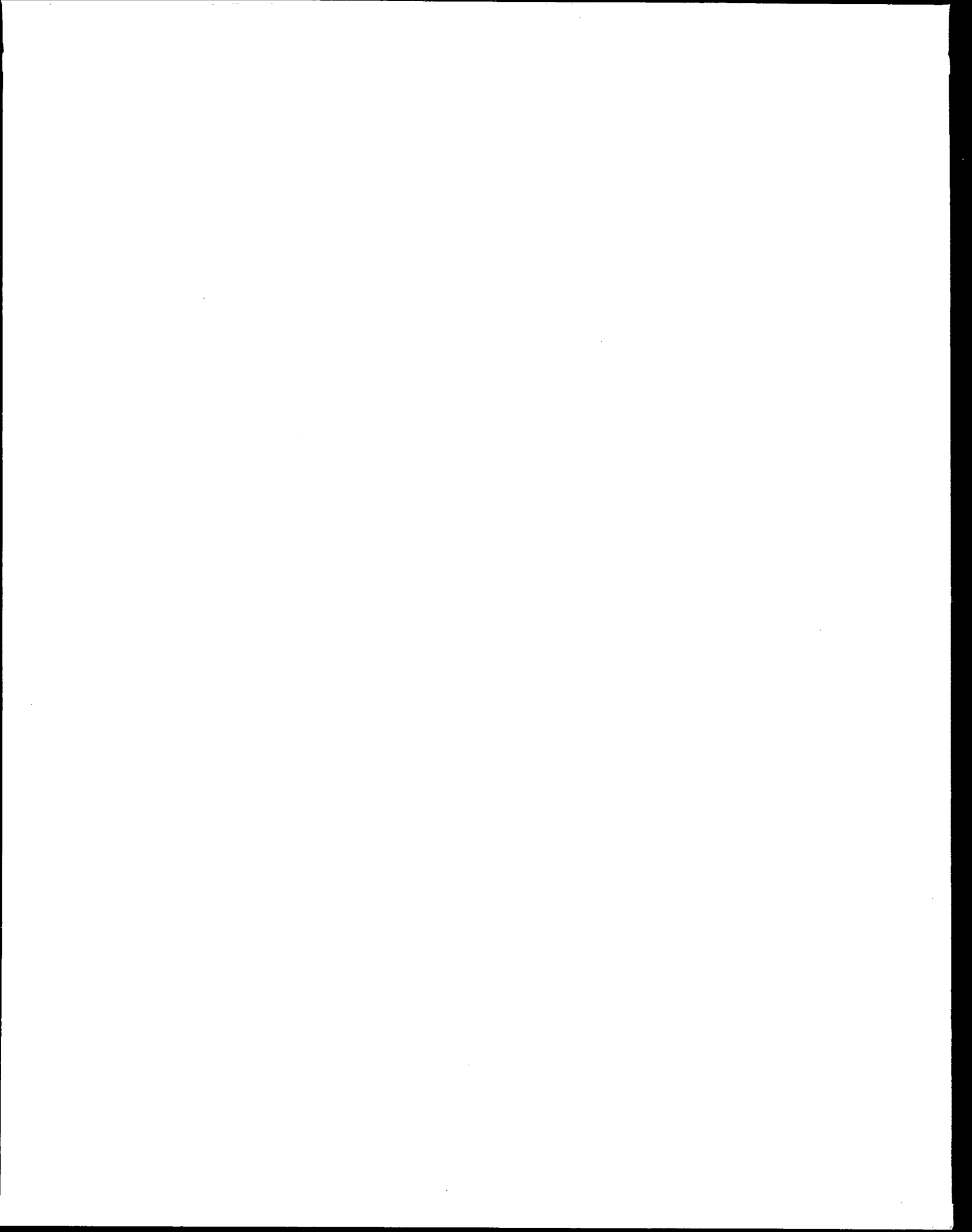
**Table 2.** Results of Test Procedures Used to Evaluate Performance of Chemical Dispersant Agents

Test Procedure	Standard Deviation for Performance	No. Tests/8 hr	Equip. Cost (\$)	Cost Run (\$)	Complexity of Procedure	Operator Skill Level
Revised Standard EPA - 10 min	<b>8.8% *</b>	2	2,280	600	High	Moderate
Revised Standard EPA - 2 hr	<b>7.2%</b>	2	2,280	600	High	Moderate
Swirling Flask (Premixed) - (2 oils)	<b>7.8%</b>	24-36	1,225	22	Low	Moderate
Swirling Flask (Premixed) - (4 oils)	<b>8.1%</b>	24-36	1,225	22	Low	Moderate
IFP-Dilution	<b>7.2%</b>	4-5	3,160	202	Moderate	Moderate

\* Bold values for standard deviations are estimates because variances among groups are heterogeneous by Bartlett's test for homogeneity.



**Figure 1.** Dispersant performance for four testing procedures with two oils and three dispersants. Values are means from replicate measurements.



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*Choudhry Sarwar is the EPA Project Officer (see below).*

*Completed reports produced in the project are the following:*

- (1) "Chemical Oil Spill Dispersants: Update State-of-the-Art on Mechanisms of Action and Factors Influencing Performance with Emphasis on Laboratory Studies. Final Report," (Order No. PB92-222 207/AS; Cost: \$19.00, subject to change)*
- (2) "Chemical Oil Spill Dispersants: Evaluation of Three Laboratory Procedures for Estimating Performance. Final Report," (Order No. PB92-222 041/AS; Cost: \$26.00, subject to change)*

*Both reports will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
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