



# Project Summary

## Developing Methods for Analyzing Oil Dispersants in Seawater

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A study was conducted to develop a rapid, uncomplicated, sensitive method for measuring the concentration of surfactants that occurs in seawater when oil dispersants containing them are used for cleanup of spills. Data on the fate of surfactants in oil dispersants has been difficult to obtain because of the inadequacy of current analytical procedures, particularly under field conditions.

Seven commercial dispersants now used for oil spill cleanup were characterized colorimetrically and found to contain anionic and/or nonionic surfactants, but no cationic surfactants.

The literature was reviewed to identify suitable methods for collecting, concentrating, and isolating surfactants, and to select quantification methods thought to be appropriate for use in seawater. Based on this review, a sorbent cartridge, Waters' SEP-PAK C<sub>18</sub>,\* was chosen as the primary technique for collecting and concentrating surfactants from oil-contaminated seawater. High performance liquid chromatography (HPLC) was selected as the preferred separation technique. Two detection or quantification approaches were examined: (1) direct measurement of the surfactant by tensammetry (a polarographic technique) or by ultraviolet (UV) spectrometry; and (2) Derivation with phenyl isocyanate followed by HPLC and UV spectrometry. Though these methods are not applicable to all oil dispersants, the derivation of poly-

oxyethylated nonylphenol followed by UV measurement was encouraging and warrants further investigation.

*This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Surface-active agents (dispersants) are being used more widely around the world for the control and elimination of oil spills on the sea. When applied to a coherent spill or slick, such dispersants cause the oil to break up into fine droplets that are more readily dispersed and degraded by natural chemical or biological processes.

Although researchers have been able to study the changes in oil character and concentration during treatment, the lack of suitable analytical procedures for detecting the dispersants, particularly methods that can be used in the field, has prevented in-depth study of their behavior. Thus it has not been possible to measure dispersant concentrations in the water column or to investigate their environmental fate.

The purpose of this investigation was to define the requirements for analysis of surfactants and to develop one or more analytical procedures that would be suitable for field measurements at the relatively low concentrations found in the seawater column.

Colorimetric analytical methods are widely used at higher concentrations. They were applied in this program to

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

characterize the anionic, nonionic, or cationic nature of the surfactant ingredients of several dispersants widely used to treat oil slicks on seawater.

Combining this information with a review of pertinent literature allowed the authors to identify collection methods and analytical methods suitable for dispersants. Methods that have been used for the analysis of surfactants and dispersants, particularly in the laboratory, included colorimetric methods, gas chromatography, thin-layer chromatography, and HPLC. Of the methods known in the literature, the latter was selected by the authors as the most suitable for further evaluation. In addition, a sorbent system was also selected and evaluated as a technique for collecting and concentrating the dispersant from a seawater sample.

## Results

### Commercial Dispersant Characterization

Standard colorimetric tests were used to identify the surfactant type in each of seven commercial oil dispersants. These tests indicated that both anionic and nonionic surfactants are in use, either alone or in combination, in these seven dispersants (see Table 1). No cationic surfactants were found.

### Sample Collection and Concentration

The literature review carried out by the authors identified several sorbents for surfactants. Sorption on carbon and silica was reported to be irreversible, which would make them unsuitable for analytical purposes. Several porous resins such as Rohm & Haas XAD-2 and XAD-4 exhibit useful sorption properties, as do ion exchange resins. These materials may be preferred for larger-scale experiments. The SEP-PAK C<sub>18</sub> cartridge (Waters Associates, Inc.) was selected for evaluation because no preparation or pretreatment was required. The sorbent consists of a reverse phase liquid chromatographic packing suitable

for collecting samples from a polar solvent such as water.

Collection was evaluated with the model nonionic and anionic surfactants, PEO nonylphenol and sodium lauryl sulfate. Colorimetric tests were used to measure the residual surfactant in the cartridge eluate (methanol). Though certain components of oil interfere with the colorimetric analysis of nonionic surfactants (at 610 nm), these components were sorbed in the cartridge and not eluted by methanol. With the anionic surfactant, both seawater and oil would normally interfere with the colorimetric analysis. Fortunately, the interfering species either pass through the cartridge during the collection and concentration step or are not desorbed by methanol during the elution. Consequently, they do not interfere with the colorimetric analysis of the surfactants. Quantitative recoveries of both surfactants were achieved, even when starting with samples too dilute for direct analysis.

### Detection and Separation Methods

As noted earlier, HPLC was selected as the most appropriate technique for separating the surfactant from the samples after they had been collected and isolated from a seawater-oil matrix by the sorbent cartridge technique. The two specific techniques evaluated for detection and quantification were tensammetry (a modified polarographic procedure) after HPLC and derivation coupled with a second HPLC separation and UV detection of the derivatives.

An extensive evaluation of the tensammetric procedure was carried out using two different HPLC columns, Waters'  $\mu$  Bondapak C<sub>18</sub> (reverse phase) and Whatman's Partisil-10 SAX, a strong anion exchange resin, and various solvent systems. However, it was impossible to produce a system that allowed (1) separation of both ionic and nonionic surfactants, (2) sufficient electrolyte to dissolve in the solvent for the needed moderate-to-low cell resist-

ance, and (3) sufficient differences in cell current for quantification at levels lower than those measurable by other techniques such as UV spectrometry.

Nonionic surfactants such as ethoxylated alcohols can be derived with phenyl isocyanate to yield urethanes with UV absorption levels not attainable with the original aliphatic surfactants. This approach was applied to two of the commercial nonionic dispersants, Corexit 9527 and Conco K, as well as to a standard, polyethoxylated nonylphenol. After derivation, the surfactant was separated by HPLC and measured by UV spectrometry. Both the POE nonylphenol and Corexit 9527 produced strong responses at the test level of 2500 ppm. The method is described more fully in the report. Unfortunately, the project schedule did not allow for the continued development and evaluation of this procedure.

## Conclusions

Colorimetric analysis of several commercial dispersants indicated that anionic and nonionic surfactants are used either alone or in combination. No cationic surfactants were found in the dispersants tested.

Both anionic and nonionic surfactants can be successfully collected and concentrated on SEP-PAK C<sub>18</sub> (Waters Associates, Inc.). This procedure also separates the surfactants from potentially interfering constituents.

Tensammetric (polarographic) detection of surfactants could not be developed into a suitable analytical technique, possibly because of the complexity of the technique and its limited sensitivity.

Derivation of certain surfactants in oil dispersants, specifically nonionized surfactants such as polyethoxylated nonylphenol, followed by HPLC and detection and quantification by UV spectrometry, appears to be a promising technique.

## Recommendations

Additional effort is required in several areas to refine and validate both the collection (SEP-PAK) and the HPLC quantification procedure. Specific recommendations include the following:

1. The effectiveness of the SEP-PAK cartridge should be evaluated with other oils and dispersants.
2. Other sorbents such as Rohm & Haas XAD resins should be evaluated as alternative adsorbents

Table 1. Oil Dispersant Types

Name of Dispersant	Manufacturer	Surfactant Type
Corexit 9527	Exxon Chemical Co.	Anionic, nonionic
Gold Crew	Ara Chemical Co.	Anionic, nonionic
Sea Master, NS 555	Whale Chemical Co.	Nonionic
BP 1100X	BP North America	Nonionic
Conco K	Continental Chemical Co.	Nonionic
Nokomis 3 Mi-Dee Formula 50	Nokomis International	Anionic, nonionic
AP	Atlantic-Pacific	Anionic

that could be used for larger-scale experiments.

3. More extensive testing of the derivation process and the HPLC separation method is clearly required. Application of the method to other nonionic surfactants must be established.

4. Analytical methods for anionic surfactants still must be sought.

The full report was submitted in fulfillment of Grant No. R-807059-01 by SRI International under the sponsorship of the U.S. Environmental Protection Agency.

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*The complete report, entitled "Developing Methods for Analyzing Oil Dispersants in Seawater," (Order No. PB 84-238 328; Cost: \$8.50, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

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