

# ANALYTICAL METHOD FOR THE IDENTIFICATION OF OIL SPILL DISPERSANT COMPOSITION

by  
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## ABSTRACT

*Chemical dispersants are often used to disperse spilled oils, which threaten to pollute shoreline areas. In Indonesia all dispersants produced or marketed should undergo the toxicity test with regard to certain types of fish to determine the threshold limit, LC-50. The type of surface active agent (surfactants) and the solvent used in the dispersants, which determine the dispersing quality, might be toxic to the marine species and bacteria.*

*In order to evaluate the toxic properties of the dispersants from their LC50's value, the composition of the dispersants should be understood. The key components of a dispersant are one or more surfactants that contain molecules with both water-compatible (hydrophilic) and oil compatible (lipophilic) portions. The charge type of the dispersant determines the classes of the surfactant molecule, which are anionic, cationic, nonionic and amphoteric. Early dispersant formulations were derived from engine room degreasers, which were highly toxic. In recent formulations non aromatic hydrocarbon solvents and less toxic surfactants have been used.*

*The exact details of dispersant formulations are proprietary. Nevertheless an analytical approach could be used to develop an analytical method or technique for the identification of dispersant formulation or composition. This paper describes an analytical method, which was developed using distillation technique to separate solvent from the surfactant followed by chromatographic analysis to the separated fractions. Capillary Column Gas Chromatography (GC) was used to determine the number of the components. Column Chromatography as well as Thin Layer Chromatography (TLC) were used to collect the separated fractions which are followed by the identification of the component using Fourier Transform Infrared Spectrophotometry (FTIR). The techniques have been used successfully for the composition identification of both oil and water base dispersants.*

## I. INTRODUCTION

Chemical dispersants are often used to disperse spilled oils, which threaten to pollute shoreline areas. In Indonesia the use of oil spill dispersants is controlled by the Directorate General of Oil and Gas. All dispersants produced or marketed should undergo the toxicity test. This toxicity test is conducted with regard to certain types of fish to determine the threshold limit, LC-50, of dispersants (Prasetyo, 1990).

It is generally assumed that the criteria for a good oil dispersant is adequate dispersing qualities. Dispersing the oil throughout the water column to increase its surface area should accelerate biodegradation. Not only is the oil made more readily available to microorganisms, but movement of emulsion droplets through a water column makes oxygen and nutrients more readily available to microorganisms.

On the other hand, the type of surface active agent and the solvent used in the dispersant which determine their dispersing quality might be toxic. In order to evaluate the toxic properties of the dispersants from their LC-50's value, the composition of the dispersants should be understood.

The exact details of dispersant formulations are proprietary. Nevertheless, an analytical approach could be used to develop an analytical method or technique for the identification of dispersant formulation or composition. This paper describes an analytical method, which was developed using distillation technique to separate solvent from the surfactant followed by chromatographic analysis to the separated fractions. Capillary Column Gas Chromatography (GC) was used to determine number of the components. Column Chromatography as well as Thin Layer Chromatography (TLC) were used to collect the separated fractions which are followed by the identification of the component using Fourier Transform Infrared Spectrophotometry (FTIR).

## II. DISPERSANT COMPOSITION

The key components of a dispersant are one or more surfactants that contain molecules with both water-compatible (hydrophilic) and oil compatible (lipophilic) portions. Most formulations also contain a solvent to reduce



viscosity and facilitate dispersal. The behavior of a surfactant is strongly affected by the balance between the hydrophilic and lipophilic groups in the molecule (defined as HLB, hydrophile-lipophile balance) which has range from 1 (most lipophilic) to 20 (most hydrophilic). The charge type of the dispersant determines the classes of the surfactant molecule, which are anionic, cationic, nonionic and amphoteric. *Anionic* surfactants include sulfosuccinate esters, such as dioctyl sulfosuccinate. *Cationic* surfactants are the quaternary ammonium salt, but such compounds are often toxic to many organisms and are not currently used in commercial dispersant formulations. *Nonionic* surfactants are the most common surfactants used in commercial dispersant formulations, such as sorbitan monooleate, polyethylene glycol esters of unsaturated fatty acid and ethoxylated or propoxylated fatty alcohol. *Amphoteric* surfactants contain both positively and negatively charge groups with both quaternary ammonium group and a sulfonic acid group. Such compounds, however, are not found in current commercial formulations.

Early dispersants formulations were derived from engine room degreasers and some were highly toxic. To reduce toxicity, non-aromatic hydrocarbons (or water-miscible solvents such as ethylene glycol or glycerol esters), as well as less toxic surfactant, have been used in more recent formulations. A blend of surfactants with different HLB giving a result of 12, will be more effective than a similar quantity of a single surfactant with HLB of 12. A review of the patent literature indicates that a limited number of surfactant chemicals are used in the dispersants formulations most widely available today. The exact details of dispersant formulations are proprietary but the chemical characteristics of these formulations are broadly known. Thus modern dispersant formulations containing one or more nonionic surfactants (15 - 75 %) may contain an anionic (5 - 25 %) surfactants and include one or more solvents. Nonionic surfactants which are normally used are sorbitan ester of oleic or lauric acid, ethoxylated and propoxylated fatty alcohols, and ethoxylated octylphenols, while anionic surfactants could be sodium dioctyl sulfosuccinate and sodium ditridecanoyl sulfosuccinate.

Dispersant formulation also contains solvent to dissolve solid surfactant and reduce viscosity so that the dispersant can be sprayed uniformly. The three main classes of solvents are: (1) water, (2) water-miscible hydroxy compounds, and (3) hydrocarbons. Aqueous solvents permit surfactants to be applied by reduction into a water stream. Hydrocarbon solvents enhance mixing and penetration of surfactant into more viscous oils. Examples of hydroxy-compound solvents are ethylene glycol mono-butyl ether, diethylene glycol mono-methyl ether, and diethylene glycol mono-butyl ether. An example of a hydrocarbon solvent is a low aromatic

kerosene. High boiling solvents containing branched saturated hydrocarbons are also used since they are less toxic than aromatics.

Surfactants are used for many purposes other than treating oil spills, and their degradation in the aqueous environment has been a concern since the 1950's, when synthetic alkyl benzene sulfonate (ABS) detergents were found to be resistant to biodegradation and produced persistent foam on waters receiving domestic sewage effluent. This problem was solved by replacing the ABS detergents with more readily biodegradable surfactants. The fate of solvents used in dispersant formulations might also be of concern. Hydrocarbon solvents are similar to portions of the oil being dispersed and tend to suffer a similar fate. Glycol ether solvents are likely to be more readily biodegradable than the oil being dispersed.

### III LABORATORY EXPERIMENTS

The analytical approaches used for dispersant composition identification are summarized in Figure 1 and are described in detail in the followings:

#### A. Distillation

Solvent of the dispersant was separated by distillation. The distillate and the residue were then examined by infrared spectral analysis to determine the surfactant composition and type of solvent.

#### B. Infrared Spectral Analysis

Infrared spectral analysis was performed using Fourier Transform Infrared Spectrometer, PE-1710, equipped with the Data Station enabling the comparison of the spectra through computer.

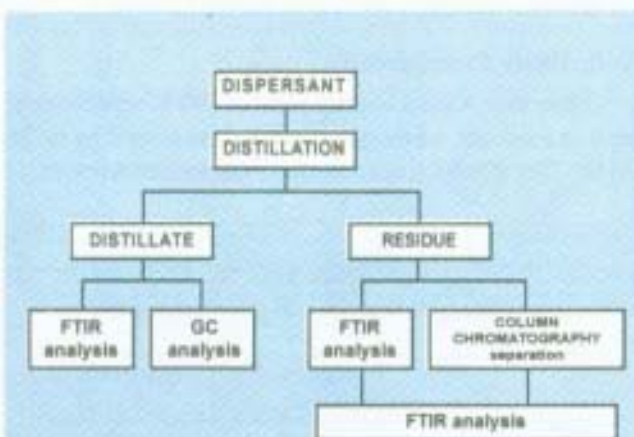


Figure 1  
An analytical approach for dispersant composition identification



### C. Gas Chromatography

Gas chromatography method was used for identifying type of the solvent after separating by distillation technique. Operating condition for gas chromatography are as follows:

Column : SPB-5 (5% diphenyl and 95% dimethyl polysiloxan) 30 M x 0.25 mm, 0.25,  $\mu\text{m}$  film

Temperature : injector 180 °C  
 detector (FID) 300 °C  
 column 45 °C for 10 minutes (initial)  
 5 °C/minute (programmed)  
 300 °C for 50 minutes (final)

Carrier gas : Nitrogen, 1.8 mL/minute.

### D. Thin Layer Chromatography (TLC)

TLC was used for separating the surface active agents in the residue. Silica gel of 1.5 cm was used and several solvent with increasing order of polarity: hexane, benzene, toluene, butanon, carbon tetra chloride, chloroform, isopropanol, ethanol and water. Detection of the spot was performed using solution of iodine in methanol.

### E. Column Chromatography

Glass column having 1 cm internal diameter containing  $\pm 40$  gram silica was used for separating the residue. According to the TLC results, elution for water base dispersant (dispersant A) was a mixture of butanon-water 9:1, while for oil-base dispersant (dispersant B) was isopropanol. The eluates were then evaporated and the residues were examined by FTIR.

## IV. RESULTS AND DISCUSSIONS

Distillation process of the dispersants resulted distillates and residues having properties as shown in Table 1.

### A. Distillate Examination

Dispersant A has a boiling point of 100 °C representing water as a solvent, while dispersant B shows a boiling range of 180 - 295 °C which need further examination for solvent

**Table 1**  
Distillates and residues of the dispersants

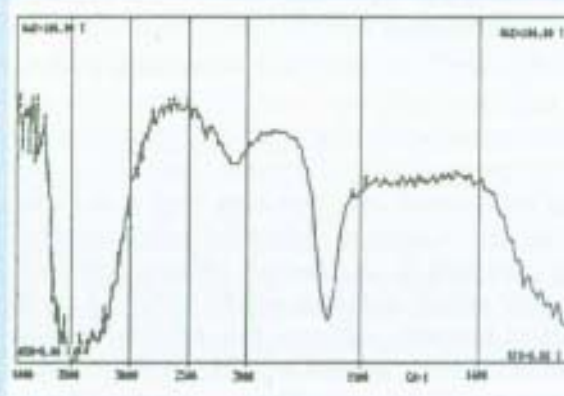
	Dispersant A (water-base)	Dispersant B (oil-base)
Distillate colour	discolour	yellow
Residues colour	yellow	yellowish-brown
Initial boiling point, °C	100	180
Final boiling point, °C	100	295

identification. This could be done either by infrared or gas chromatography analysis.

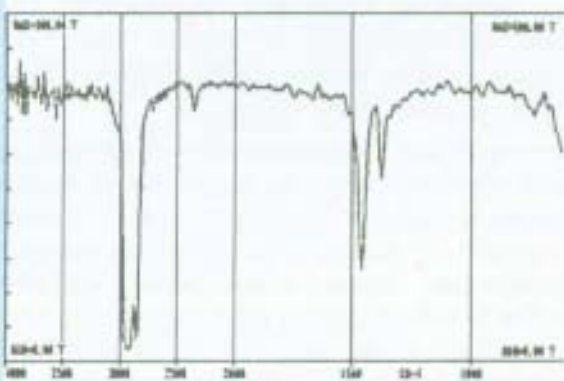
Infrared analysis of the solvent of dispersant A shows an OH-group which exhibit at 3300  $\text{cm}^{-1}$  and inter molecular hydrogen bonding at  $\sim 1650$   $\text{cm}^{-1}$  (cf. Figure 2).

Infrared spectra showing such absorption bands indicate the existence of water and this is confirmed with its boiling point. Absorption bands of the dispersant B molecular groups of methyl  $-\text{CH}_3$  and methylene  $-\text{CH}_2-$  at 2952  $\text{cm}^{-1}$ , 1458  $\text{cm}^{-1}$  and 1373  $\text{cm}^{-1}$  (cf. Figure 3)

Such absorption bands indicate strongly the presence of hydrocarbon solvent, which can be examined further using gas chromatography method to classify the hydrocarbon components. Figure 4 shows a chromatogram of the distillate of dispersant B, which shows normal alkane peaks having atom carbons ranging from  $\text{C}_9$  to  $\text{C}_{23}$ . These



**Figure 2**  
Infrared spectra of the distillate of dispersant A



**Figure 3**  
Infrared spectra of the distillate of dispersant B

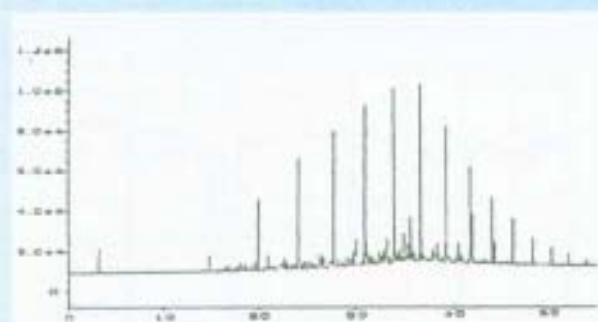


Figure 4  
Chromatogram of the distillate of dispersant B

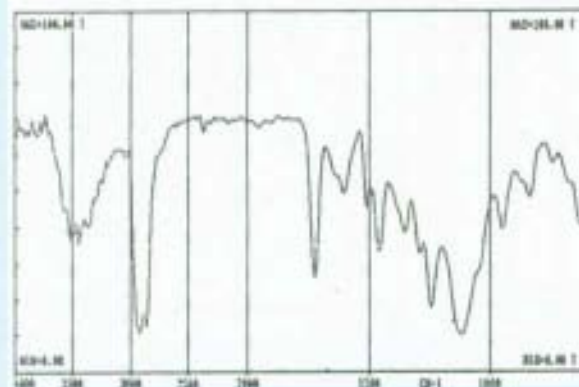


Figure 5  
Infrared spectra of the residue of dispersant A

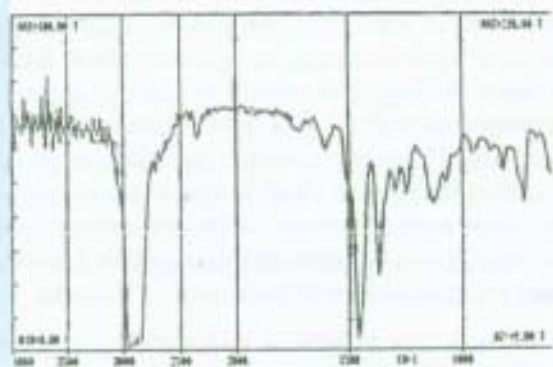


Figure 6  
Infrared spectra of the residue of dispersant B

alkanes correspond to kerosene fraction and are confirmed with its boiling range of the distillate.

### B. Residue Examination

Infrared spectral analysis of the residues are presented in Figure 5 and Figure 6 for dispersant A and dispersant B respectively. Thin layer chromatography (TLC) analysis of the residues show a complex mixture for dispersant A, while there is less components for dispersant B (cf. Figure 7). The residue of dispersant A was estimated contains a mixture of polymers having small differences of molecular weights regarding that the spots were close to each other. The long spot at the beginning was probably a mixture of polymers having similar degree of polarity. The residue of dispersant B which shows several spots could be assumed as a mixture of several components. This mixture could be identified using infrared spectral analysis after treating through chromatography column. Figure 8 and Figure 9 represent the infrared spectra of the separated fractions of dispersant A and dispersant B, respectively.

Several chromatographic fractions were collected and analyzed by FTIR. For dispersant A there was one fraction, i.e. second fraction (cf. Figure 8a) which shows a different infrared spectra comparing to the other fractions. All other fractions, except those mentioned above have similar infrared spectra (cf. Figure 8b). The second fraction of dis-

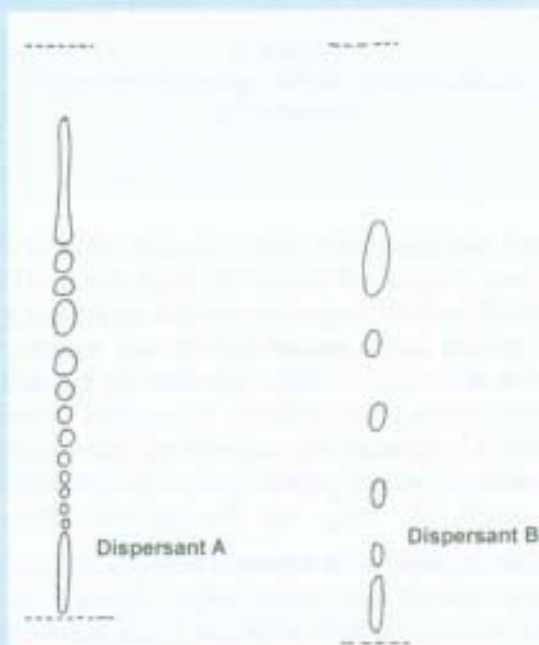


Figure 7  
Thin layer chromatography of the residues



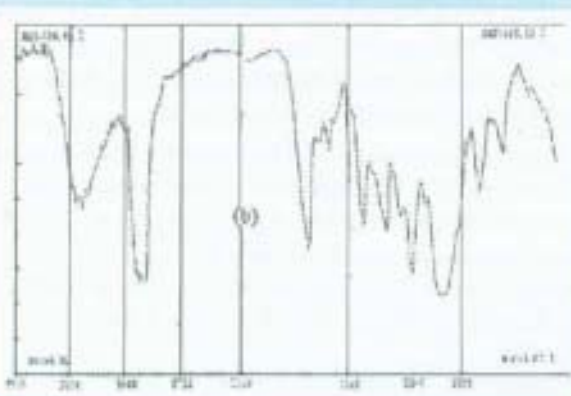
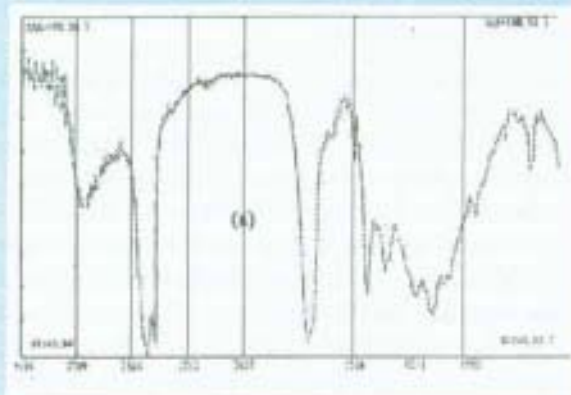


Figure 8  
Infrared spectra of the separated fraction of  
dispersant A

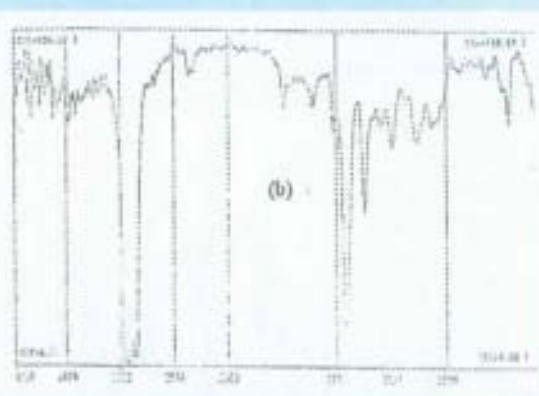
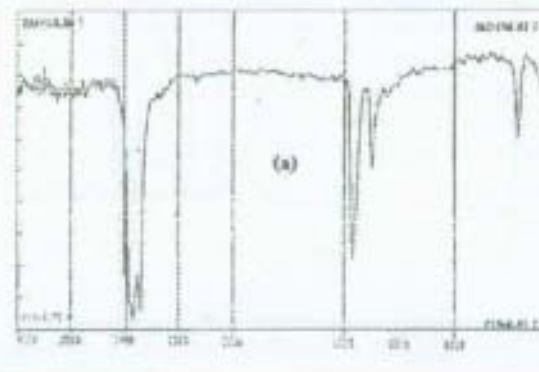


Figure 9.  
Infrared spectra of the separated fraction of  
dispersant B

persant A was identified as castor oil, while all other fractions were ethoxylated castor oil. Both castor oil and ethoxylated castor oil are used as non-ionic surfactants. Castor oil spectra in the second fraction was probably an indication of the residual castor oil which did not undergo complete process of ethoxilation. Hydrophilic groups of dispersant A is represented by carboxyl and hydroxyl groups of the molecule, while lyophobic groups are represented by long chain of  $\text{CH}_2$ - of the polyoxyethylene.

Infrared spectra of the separated fractions of dispersant B do not show different wavenumbers to each other (cf. Figure 9b), except for the first fraction, which shows similar spectra to the solvent (Figure 9a). The infrared spectra were dominated by the  $\text{CH}_2$ - and  $-\text{CH}_2$ - groups indicating a long chain of methylene. There is also an indication of hydroxyl group representing a long chain of alcohol compounds. Such compounds have been used as detergents and surfactants.

## V. CONCLUSION

The analytical approaches used in this experiment for identification of surfactant compounds in the dispersant utilize distillation technique to separate solvent from the dispersants. Boiling point as well as infrared spectra and chromatography analysis of the solvent indicate type of the solvent, which normally is water, polyethylene glycol or hydrocarbon compounds. Identification of the residue needs further separation techniques which are either thin layer chromatography or column chromatography followed by infrared spectral analysis of the separated fractions.

Although this analytical approach uses only two analytical methods, infrared spectrometry and gas chromatography, the techniques have been used successfully for the composition identification of both oil and water based dispersants. More detail separation and more positive

identification could be achieved by using sophisticated techniques such as high performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry system (GC-MS). These techniques need more attention and will be used in next experimentation.

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