

068 Mid-scale Testing of  
Dispersant Effectiveness

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**MID-SCALE TESTING OF DISPERSANT EFFECTIVENESS**

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## SUMMARY

The objective of this project was to develop a mid-scale test for dispersant effectiveness that incorporates all the factors believed to be important in the field use of dispersants. Such a test would permit a realistic evaluation of dispersant effectiveness prior to expensive offshore tests.

An extensive review of the published literature was undertaken to identify the essential components of the chemical dispersion process and the problems and successes that have been encountered in past effectiveness tests. The major shortfall of the many bench-scale effectiveness tests developed over the years has been their inability to model accurately dispersant application, dispersant-oil-water interaction and mixing energy. These aspects of dispersant effectiveness testing were incorporated in our design.

Field-scale dispersant application gear was used to apply dispersant to the oil-water system and mixing energy was generated by waves and wind to better simulate oceanic mixing. Sixteen tests were conducted to evaluate the potential of the experimental set-up and procedure. The effectiveness of two dispersants (Corexit 9527 and Enersperse 700) were evaluated on two oil types (fresh and weathered Alberta Sweet Mixed Blend) at two thicknesses (1 mm and 0.5 mm) and at two mixing energy levels. The dispersant-to-oil ratio used in the testing was 1:20 and the water temperature was 15°C.

Corexit 9527 dispersed from 7 to 37 % of the initial oil, Enersperse 700 from 30 to 54 %. A statistical analysis of the data indicated that dispersion efficiency was no different for the thick and thin slicks and was marginally different for the two oil types and mixing energies.

The Enersperse 700 results compare favourably with those measured during the 1985 field trial conducted by the Canadian Offshore Aerial Application Task Force (COAATF) in which Enersperse 700 dispersed between 9.5 to 41% of the initial surface oil (Gill et al. 1985). The estimated dispersion efficiency for Corexit 9527 in our tests was higher than the 1-4% efficiency measured in the offshore trial. This can be attributed to the underdosing of the oil slick in the field test program.

## RESUME

Ce projet visait à mettre au point un protocole d'essai en laboratoire à moyenne échelle qui comprendrait toutes les conditions probablement importantes dans l'utilisation des dispersants en situation réelle. Un tel protocole permettrait une évaluation réaliste des dispersants avant d'engager des essais coûteux en mer.

Un examen approfondi de toute la littérature pertinente nous a permis de cerner les aspects essentiels du processus de dispersion chimique ainsi que les difficultés et réussites enregistrées lors d'essais antérieurs. La lacune principale de ces épreuves sur banc d'essai est l'absence d'une simulation précise de l'épandage des dispersants, des interactions entre eau, pétrole et dispersant et, enfin, de l'agitation du milieu marin. Nous avons intégré dans notre protocole ces déterminants de l'efficacité des dispersants.

Les dispersants ont été appliqués avec des appareils utilisés en situation réelle et l'agitation du dispositif d'essai provenait du vent et de vagues pour mieux simuler l'action de la mer. Seize essais ont éprouvé les possibilités du dispositif et du protocole. Nous avons vérifié l'efficacité de deux dispersants (Corexit 9527 et Enersperse 700) sur deux types de pétrole ("Alberta Sweet Mixed Blend" nature et météorisé) en nappes de deux épaisseurs (0.5 et 1 mm) à deux niveaux d'agitation. Le rapport dispersant-pétrole fut toujours de 1/20 et l'eau fut maintenue à 15°C dans tous les cas.

Le Corexit 9527 a dispersé de 7 à 37% du pétrole et l'Enersperse 700 de 30 à 54%. Il n'y avait aucune différence statistiquement significative entre les taux de dispersion des nappes épaisses et minces, et une différence minime entre les deux types de pétrole et les deux niveaux d'agitation.

Les résultats obtenus avec l'Enersperse 700 se comparent avantageusement à ceux mesurés par le COAATF (Groupe canadien d'intervention en épandage aérien en mer) lors de ses essais sur le terrain en 1985, où ce produit a dispersé de 9.5 à 41% du pétrole répandu (Gill et al. 1985). L'efficacité de dispersion du Corexit 9527 mesurée dans nos essais dépasse celle de 1 à 4% obtenue lors de l'épreuve sur le terrain. Nous pouvons attribuer cette différence au sous-dosage de pétrole effectué dans les essais sur le terrain.

## **1.0 INTRODUCTION**

Ever since chemical dispersants were produced to treat offshore oil spills, many have attempted to develop a simple laboratory test with which to predict their effectiveness under actual field conditions. A number of dispersant effectiveness tests are available but several reviewers have shown these to be poor simulators of the chemical dispersion process in field situations (Wells and Harris 1979, Delvigne 1982, Lichtenthaler and Daling 1983, Nichols and Parker 1985, and Fingas 1985). Reasons for inconsistent results between the various effectiveness tests and shortcomings in testing procedures have been analysed in some detail by these reviewers.

The problem with most tests is that, in trying to keep them simple, inexpensive, and short, several key elements that are known to be crucial to the dispersion process in the field have been compromised.

The purpose of this project was to develop a mid-scale test for dispersant effectiveness that would incorporate all factors believed to be important in field applications. The result would be a more accurate simulation of the offshore dispersion process, and would permit a realistic evaluation of dispersant effectiveness prior to expensive offshore tests. Ideally, the need for such tests might actually be obviated.

## **2.0 LITERATURE REVIEW**

### **2.1 INTRODUCTION**

A quantitative comparison of results from the various, existing dispersant effectiveness tests was not performed in this study because other researchers have shown convincingly that such a comparison yields little valuable information (Nichols and Parker 1985). However, an extensive review of published literature on dispersant effectiveness testing, dating back to the 1970s, was undertaken to identify the essential components of the tests and the many problems and successes that have been encountered. This review enabled the experience of others to be used beneficially in the design of this study's mid-scale test.

### **2.2 KEY FACTORS TO CONSIDER IN THE LABORATORY SIMULATION OF THE CHEMICAL DISPERSION PROCESS**

Four main processes or events must be modelled in a laboratory test to simulate the chemical dispersion of oil:

- a) The oil is spilled and spreads and ages prior to the application of dispersant.
- b) The dispersant is applied in a spray form to the surface of the oil slick and interacts and mixes with the oil-and-water system.
- c) Natural wind and wave mixing energy (or artificial mixing by breaker boards, high-pressure water, propeller wash and so on) breaks the slick into an oil dispersion comprising a range of drop sizes.
- d) Smaller droplets are entrained into the water column; larger drops eventually re-surface and re-coalesce if the ocean's turbulence is insufficient to retain these within the water mass.

Each process is discussed under separate headings.

### **2.2.1 The Initial Form of the Oil Slick**

In a real spill situation, from the time the oil is spilled to the time dispersant is applied, many weathering processes, such as evaporation and emulsification, are at work altering the properties of both the oil and the oil slick. The distinction between the oil and the slick is important because the characteristics of each affect dispersant effectiveness in different ways.

Modelling changes in oil properties as a function of weathering, and preparing oil samples for effectiveness testing on the basis of this modelling, is a relatively simple task for two reasons. First, mathematical models are available that adequately simulate weathering processes and predict changes in oil properties as a function of spill and environmental conditions (Nadeau and Mackay 1978, Mackay et al. 1980 and 1983, Belore 1985). Secondly, laboratory methods exist to produce artificially weathered oils with properties identical to those obtained in the field after given periods of weathering (Stiver and Mackay 1982).

It is a far more difficult task to predict, and then to simulate in the laboratory, the size, shape, and pattern of the oil slick. This problem has received little attention in past tests. The general characteristics of the oil slick, i.e., its thickness, size, and distribution of oil patches, overall extent, and so on, often determine whether chemical dispersion is successful or not. For a slick composed of small patches of thick oil surrounded by large amounts of thin sheen, the application of the dispersant in an "average" concentration over the slick can result in an inefficient dispersion (Mackay 1985, Nichols and Parker 1985, Delvigne 1984). This inefficiency can only be predicted in the laboratory setting with the use of a similar patchy distribution of oil. All of the laboratory effectiveness testing to date has used uniform oil slicks and has ignored this important parameter. Small-scale tests are unable to simulate this aspect of oil slick behaviour because of the need for sizeable patches of oil to be surrounded by zones of sheen. Large and mid-scale tank tests (such as Delvigne 1984b, S.L. Ross 1985, Brown et al. 1985) may be able to address this problem to a

limited extent depending on the actual scale of the patchiness being modelled.

The importance of oil properties with regard to the effectiveness of dispersants is generally well understood. We now have the ability to predict changes in properties for oils spilled under various climatic and oceanographic conditions and so can establish the range of oil properties against which a dispersant must be effective to be practical in a specific field operation. We also have the ability to prepare weathered oil in the laboratory that simulates oil weathered under field conditions. However, our understanding of the actual surface patterns of oil on the water surface and our abilities to simulate these are limited. This limitation is important in predicting effectiveness of a chemical dispersant operation in the field and therefore needs to be investigated more fully and incorporated into any new test of effectiveness.

### **2.2.2 Dispersant Application**

Chemical dispersants have consistently been shown to be effective in both field and laboratory experiments when premixed with the oil prior to its discharge and agitation (Blackall and Sergy 1983, Delvigne 1983, Lichtenthaler and Daling 1985). On the other hand, when dispersants have been sprayed onto oil slicks in the field by vessel or aircraft application methods, the efficiencies have been generally poor. An excellent example of this was documented by Delvigne (1983) in dispersant tests in the North Sea where the dispersion rates of both pre-mixed and sprayed oil slicks were monitored under identical conditions of sea states. In many other field trials similar inefficiencies have occurred during aerial or ship-based spraying operations (Gill et al. 1985, Lichtenthaler and Daling 1983, Buckley and Humphrey 1981).

Several possible explanations have been postulated for this drastic reduction in the efficiency of dispersants when applied in a spray (especially when applied aurally).



Past field trials and theoretical analysis have indicated that a dispersant spray should contain droplets large enough that the dispersant does not drift away from the target oil slick, yet not so large that the dispersant simply penetrates the oil slick and is lost to the water phase (Aslin et al. 1981, Mackay et al. 1980). Research has indicated that to avoid these problems the dispersant should be applied in drops ranging in size from 200 to 700  $\mu\text{m}^1$  (Smedley 1980). This recognition has led to the development of spray systems capable of generating drops in this size range. Unfortunately, it has been shown that even when the drops applied are in this size range the dispersant is still not effective. Delvigne (1983) and others have suggested that the different aerial fallout rates for dispersant drops of different size may have a considerable bearing on the dispersant's effectiveness. It has been postulated that the largest of the dispersant drops hit the surface first and herds the oil into ribbons and patches (Delvigne 1984b, Fingas 1985, Belore 1985, Lichtenthaler and Daling 1985). The remaining dispersant then falls on the surface over the next several seconds but primarily hits open water and misses the oil. The end result is a greatly under-dosed oil slick. One way to correct this problem would be to develop spray systems that generate a much narrower range of dispersant drop diameters.

Another problem is that even in cases where dispersant does initially contact oil, the chemical can be lost relatively quickly to the water phase. Although dispersant formulations have a much higher affinity for oil than for water, there is such a large quantity of water in the vicinity of the dispersant that it can easily be partitioned away from the bulk oil. It has been suggested that most of the dispersant will be lost to the water phase in this way within about 15 minutes (Mackay and Hossain 1982). Clearly, if there is inadequate mixing energy to disperse the oil within at least this time, the benefits of the dispersant will be lost.

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<sup>1</sup>.  $\mu\text{m}$  represents  $\mu\text{m}$  or micrometres, and is the designation used throughout the report.

Most existing laboratory-scale tests do not provide the high water-to-oil ratio that is necessary to simulate this leaching of dispersant from the oil. One effectiveness test developed in France, however, employs a dilution technique that continuously flushes the test vessel with clean water to simulate this effect (Bocard et al. 1984b). Although this test was established to study the effects of dilution on the oil-in-water concentration for toxicity work, such a procedure might also be useful to evaluate the effects of dispersant oil/water partitioning or dispersant efficiency. However, the procedure is impractical for dispersant tests involving large tanks because of the large volumes of exchange water required.

In the past, dispersant spraying operations have used a dispersant application dosage based on the average oil thickness of the slick, and the entire slick has been treated at this dosage. However, it is known that oil slicks are usually made up of relatively small patches of thick oil surrounded by large areas of thin sheens. A uniform spraying operation therefore results in an over-dosing of the thin and an under-dosing of the thick portions of the slick with the end result being little dispersion of oil (Gill et al. 1985, Nichols and Parker 1985, Lichtenthaler and Daling 1983). A dispersing operation that concentrates on only the thick oil portions therefore has a more likely chance for success. This was demonstrated during the most recent field experiments in Norway where only the thick portions of the slick were sprayed, and the result was a relatively high dispersion efficiency (Lichtenthaler and Daling 1985).

Mackay (1985) has developed a simple computer model (which accounts for both the problems of dispersant drop size distribution and the patchiness of the target oil slick) to estimate the likely efficiency of an aerial spraying operation. The model has been applied to eight offshore field tests of dispersants and is able to predict the outcome of both the successful and unsuccessful tests. The results suggest that one of the most essential and difficult components of a successful dispersant operation is the proper application of the chemical to the oil.

Because the application phase is so important to the outcome of a field operation, any laboratory test attempting to predict the field effectiveness of a dispersant must accurately simulate the dispersant application process. Dispersant drop-size distribution, dispersant fallout timing, and oil slick patchiness and thicknesses must all be strictly controlled in the laboratory. Unfortunately, the effectiveness tests developed to date have neglected to simulate these factors properly. Pre-mixtures of dispersant and oil or dropwise addition of dispersant to uniform thicknesses of oil have been used in most tests. Certain mid-scale dispersant tests (Delvigne 1983, Belore 1985) have used more appropriate drop-size distributions but have not addressed the problem of slick patchiness. In fact, it may not be possible to study this problem in the laboratory because large surface areas are needed to produce representative thick-thin oil distributions. The best solution may be simply to focus on attempts to predict dispersant effectiveness on thick slicks only (100 um or greater) and to design the mid-scale test accordingly. Overall dispersant effectiveness in the field can then be predicted once the percentage of applied dispersant that has fallen on the thick portion of the slick is determined.

### **2.2.3 Mixing Energy to Create the Oil-in-Water Dispersion**

A major function of chemical dispersants is simply to reduce the interfacial tension between oil and water to permit the oil slick to be broken into small droplets with a minimum level of mixing energy. However, some mixing must still be available to actually break up the oil slick into droplets and to disperse the oil into the water mass. The primary source of this mixing energy in the open ocean (in the absence of artificial mixing procedures such as breaker boards, water jets, and propeller wash) are waves. The actual size and type of wave which is necessary to create natural dispersion is open for debate. Several researchers believe that significant dispersion without the addition of chemicals can only take place in the presence of breaking waves (Buist 1979, Raj 1977, Milgram 1978, Naess 1981, Delvigne 1984b).

The addition of chemical dispersants reduces the level of energy needed to generate a dispersion but the actual amount and form of energy necessary is unknown. To some extent, the amount of energy will depend on how much the dispersant is able to depress the oil-water interfacial tension (IFT). In one set of controlled small-scale laboratory tests the highest dispersion efficiency and smallest oil-drop diameters were created by dispersants that produced the lowest IFT (Lewis et al. 1985). However, the amount of energy needed to disperse an oil slick in a specific situation is undoubtedly a function of many factors and not merely the ability of the chemicals to lower oil-water interfacial tension.

MacNeill et al. (1985) studied the disappearance of chemically treated oil under low wave-energy environments in an outdoor test basin and found that effective dispersion was possible without breaking waves. Lewis et al. (1985) indicated that energy from wind-induced capillary waves is sufficient to generate a dispersion of a chemically treated oil slick. However, several offshore dispersant trials have been conducted in calm seas with little success, indicating that a minimum energy level must be available at sea to create and maintain significant dispersion (Cormack 1983, Gill et al. 1985, Bocard et al. 1984a, Lichtenthaler and Daling 1983). In most of these offshore tests an initial dispersion was observed followed by a significant resurfacing of the oil. This resurfacing may have resulted either from large oil drop sizes in the dispersion or from an insufficient background level of turbulence to maintain the dispersion.

Laboratory tests will be successful in predicting the effectiveness of dispersants at sea only if mixing mechanisms similar to those in the ocean can be reproduced in the tests. Unfortunately, little quantitative information is available on the processes and levels of oceanic mixing. Shonting and Temple (1979) performed field experiments to measure wind waves and turbulent motions in the upper boundary layer of sea and, more recently Canpolar Consultants (1985), attempted to measure mixing energies, but these studies were limited in scope and do not provide a clear picture of energy conditions as a function of sea state, winds, and so on. Considerable research in this area is necessary before it can be said

conclusively that the mixing regime produced in a given laboratory test is a good simulation of a specific sea state.

Of the existing small-scale dispersant effectiveness tests only the MNS test (Mackay and Szeto 1981) has attempted to relate the mixing energy applied in the test to oceanic conditions. Air is blown over the test basin to create wave action and surface mixing energy. The air flow rate is set such that the oxygen transfer rate at the water's surface is similar to that measured offshore. Unfortunately, despite the logic of this, the resulting mixing energy is considered to be much higher than that produced normally at sea (Rewick et al. 1982, Lewis et al. 1985).

The mid-scale effectiveness testing conducted by Delvigne (1984b) incorporated more realistic mixing energies by introducing both breaking and non-breaking waves in a large test flume. A laser-doppler system was used to characterize the turbulence in the laboratory study but the same measurements were not made in the field to directly compare the turbulence levels in the two cases. These large scale simulations of waves are the most promising method of modelling ocean turbulence but, as mentioned earlier, the actual level of turbulence first must be measured in the field and then reproduced in the laboratory to ensure accurate predictions. Other dispersant tests (shaker tests, pumped tanks, interfacial tension methods) do not even profess to simulate oceanic mixing and, therefore, are not good candidates for predicting the effectiveness of dispersants in the offshore environment.

It is perhaps worth noting that, however deficient the small-scale tests may be, they still provide an inexpensive approach for evaluating the general effects of different oil properties on the effectiveness of a dispersant under a standard (but not necessarily realistic) condition (Nichols and Parker 1985). Which of the many bench-scale tests should be used in these applications is still open to debate, although recent opinion suggests that shaker tests are useful for studying the behaviour of oil droplets once formed and that the MNS test and other surface energy systems such as

hoop tanks and weirs can be used to study the oil drop formation process (Lewis et al. 1985, Mackay 1985).

#### **2.2.4 Long-Term Dispersion of Oil in the Ocean**

The diffusion of the oil droplets, once generated, is another factor affecting dispersant effectiveness. The turbulent eddy size in the upper layer of water (resulting from wind and wave actions) and the common Langmuir circulation patterns will determine the size of oil droplets that will be suspended in the water mass or will rise to the surface due to buoyancy. It has been estimated by some researchers that oil drops in the water as large as 200  $\mu\text{m}$  will not resurface in the presence of common Langmuir circulations (Lee 1980, Lewis et al. 1985). Other researchers have indicated that an effective long-term dispersion will be achieved only if the oil drops are in the 10-50  $\mu\text{m}$  diameter range (Fingas 1985, Brown et al. 1985, Canevari 1977). The density difference between the oil drop and the surrounding water also determines whether the drop will be permanently dispersed. This density difference, along with drop size, determines the buoyant force that opposes the turbulent diffusive forces in the water.

The buoyancy of an oil droplet is easily determined but local eddy velocities resulting from ocean turbulence and larger-scale circulation patterns are not well documented and require further study before this aspect of the dispersion process can be modelled with confidence. Unfortunately, horizontal and vertical diffusion in the ocean cannot be simulated in the laboratory because of the scale of the process. Therefore, a better understanding of this process will have to be gained through field studies.

### **3.0 DISPERSANT EFFECTIVENESS TEST DESIGN**

In this section the specific parameters that should be included in a successful mid-scale dispersant effectiveness test are listed and discussed. The mid-scale work done at the Delft Hydraulics Laboratory (Delvigne 1982, 1984a, 1984b, 1985) has been drawn on heavily in this task. We feel that this work has been the most complete attempt at laboratory dispersant effectiveness testing to date and provides an excellent base upon which to make further improvements.

#### **3.1 TEST PARAMETERS**

The parameters that must be closely controlled or measured in dispersant effectiveness tests are summarized in three groups.

##### **Environmental conditions**

- \* temperature of water, oil, dispersant, and air
- \* water salinity
- \* water quality (surfactant free)
- \* surface-mixing
- \* larger-scale ocean-mixing processes (not likely scaleable in a laboratory study).

##### **Oil properties and distribution**

- \* oil thickness
- \* oil distribution
  - patchiness
  - thick to thin area ratios
- \* oil properties
  - viscosity
  - density
  - wax content

- indigenous surfactants
- \* oil aging
  - evaporation
  - emulsification
  - photo-oxidation.

### **Dispersant**

- \* type
- \* dispersant-to-oil application ratio
- \* dispersant drop-size distribution
- \* dispersant fallout timing
- \* velocity of dispersant drops on contact
- \* dispersant drop spacing and coverage
- \* dispersant loss to water column
  - direct
  - partitioning from oil.

## **3.2 CONTROL AND MEASUREMENT OF TEST PARAMETERS**

For an effectiveness test to simulate successfully a wide range of field conditions it must be able to control and vary these parameters. Various techniques have been developed by other researchers to do this which are now discussed; those that seemed most suitable for our purposes have been selected for evaluation in the initial development of our mid-scale test.

### **Environmental Conditions**

- 1) Air temperatures can easily be controlled using the laboratory's heating system (in our facility minimum temperatures are limited to the outdoor temperatures at the time of the testing).
- 2) Water temperature control (both heating and cooling) is a relatively easy task for small-scale tests but becomes more difficult and costly for systems involving large volumes of water. In our test facility,



water supply temperatures vary from +1°C to 15°C depending on the time of year. Cooling and heating can be accomplished when necessary by adding ice or hot water to the test tank.

- 3) In small tests, water salinity is generally controlled by adding "instant ocean" mixes to fresh water. Because these mixes are expensive, we use a high-grade water-softener salt to achieve the desired salinity. The salinity of the test water is determined by a simple density measurement or with specialized salinity probes.
- 4) Water quality can be maintained by emptying and cleaning the tank after each test or when the interfacial tension drops to some predetermined value. Delvigne (1984b) used the criterion that the surface tension of the water should exceed 0.064 N/m for the tank to be considered "dispersant-free", and emptied and cleaned his tank accordingly. In our case the test tank was drained, cleaned, and filled with a new supply of salt water for each individual test.
- 5) Oceanic surface mixing is difficult to simulate and measure in the laboratory. The most direct method is to produce mixing by simulated wind and wave action. Several researchers have successfully created wave action by the use of wave paddles or diverging flumes and have simulated wind action by placing a wind tunnel and fan above the water's surface. For these tests we have similarly used a paddle to generate waves at one end of the tank and have held the oil slick in the centre of the test tank by generating wind from the opposite end of the tank. A method of measuring the turbulence created by such a set-up is necessary to ensure that realistic offshore conditions are being created. Delvigne (1984b) used a sophisticated (and expensive) laser doppler anemometer (LDA) to measure local water velocities below the water surface. (As mentioned earlier, similar measurements at sea were not made so it is difficult to relate these results to actual sea conditions.) Another, less sophisticated method for measuring near-surface water turbulence has been developed by Canpolar Consultants Ltd. (1985). This device was made available for the project and was used to compare the mixing energy in the tank to that recorded at sea.

- 6) Large-scale ocean diffusion processes cannot be simulated in laboratory-scale experiments and so must be studied in field tests.

### **Oil properties and distribution**

- 1) A uniform oil thickness can be difficult to achieve over a large water surface. When the oil is simply poured onto the surface and allowed to equilibrate, oil patches or lenses surrounded by open water tend to develop as a result of surface tension effects. To create a more uniform, continuous slick we "mechanically" spread the oil lenses into each other to overcome this problem. Thickness measurements should be made in several areas of the slick to establish an average slick thickness and variations in thickness. We accomplish this by sorbing the oil from a known area of the slick and then calculating the slick thickness from the estimated volume of oil sorbed (by weight or chemical extraction and colorimetry). Electro-mechanical depth gauges have also been used to measure oil thickness (Delvigne 1984b).
- 2) Patchy oil distributions can be accomplished by pouring small slicklets of oil over the water surface, although it is not known how much control over the patchiness is possible especially in the presence of waves and wind. In any case, because of time and cost considerations we did not investigate the effects of oil patchiness on dispersant effectiveness.
- 3) Oil can be aged in the laboratory to simulate the properties of a crude oil after a given period of exposure on the open ocean (Stiver and Mackay 1982). Aging can be accomplished by bubbling air through the oil (as we have for these tests), evaporating the oil in pans placed in a calibrated wind tunnel or by a distillation process. Aging from photo-oxidation can be simulated by exposing the oil to ultra-violet lighting (Delvigne 1984b). This process was not included in our test matrix.
- 4) The competitive processes of emulsification and dispersion should be monitored during the test period. The extent of emulsification can be measured by "breaking" a known volume of emulsion and measuring the amount of water present. Significant emulsification did not take place

during our testing program so these measurements were not necessary for this study.

- 5) Important oil properties such as density and viscosity should be measured in the test. Sufficient accuracy is obtained by a variety of techniques ranging from density vials (weight of a precise volume of oil) and cross-arm viscometers, used in our testing, to sophisticated electronic devices. Wax content can be measured by precipitating the wax out of a solvent at low temperatures and by filtering out the precipitated waxes (Zagorski and Mackay 1982). Unfortunately, this technique is not very accurate. The presence of indigenous surfactants can be identified by the pendant drop apparatus but the effects of the surfactant on the dispersibility of the oil can only be determined by performing the effectiveness test.

### **Dispersant**

- 1) The dispersant-to-oil application ratio can be determined either by measuring the oil volume or oil slick thickness and area and the quantity of dispersant delivered to the surface (by placing receptor cards or pans at the surface) and then calculating the application ratio, or by sampling the oil slick after the application of dispersant and determining the quantity of dispersant in the oil analytically. For most applications the first technique is preferred because of the complexities of the analytical techniques required to detect dispersant in oil.
- 2) The dispersant drop-size distribution was measured in our test program by placing Kromecoat cards at the water surface to catch a sample of dispersant drops. The diameter of the drop stains are then related to the initial drop diameters (Smedley 1980). Another, more sophisticated technique using a Laser doppler anemometer has been reported by Delvigne (1984b) but the cost of the equipment prohibited its use in this study. Different drop-size distributions can be generated by using different nozzle types, sizes, and pressure conditions.

- 3) The uniformity of the dispersant application can be determined by measuring the dispersant application ratio at a number of locations.
- 4) Dispersant fallout as a function of drop size is difficult to simulate with a wind tunnel in place because the dispersant source must be inside the tunnel and close to the water surface.
- 5) Dispersant drop spacing and coverage can be determined from Kromecoat card analysis. Varying this parameter can be accomplished by selecting different nozzle types, sizes, flow rates, and pressures.
- 6) A suitable technique for the measurement of the amount of dispersant lost to the water column was not found in our search of the literature.

### **3.3 MEASUREMENT OF DISPERSANT EFFECTIVENESS**

The effectiveness of a dispersant is generally equated to the percentage of the surface oil slick that is dispersed into the water column over a long-term basis. This dispersion can be determined by either measuring the quantity of oil that remains on the surface or is present in the water column. Estimates of the long-term stability of the dispersion can be determined by measuring the drop size distribution of the dispersed oil.

**Surface oil measurements.** The quantity of oil remaining on the water surface has been estimated in our tests by measuring the average slick thickness (by the use of a sorption pad) and by multiplying this by the oil slick area. This technique has the obvious disadvantage of being inaccurate unless a reasonable number of thickness measurements are made. Alternatively, the surface oil could be skimmed off the water's surface and the volume measured but this does not permit several dispersion measurements to be made to determine the rate of dispersion.

**In-water oil measurements.** The general practice for determining the quantity of oil in the water column is to take grab samples of the water at various depths below the surface and to measure the quantity of oil in the samples. An estimate of the quantity of oil in the water column can then be made from the vertical oil concentration profile. Unfortunately, non-uniform oil distributions, large drops of oil in some water samples, and so on, can significantly distort the estimates of oil quantity. Because both surface and sub-surface measurement techniques have their faults we have taken both measurements during this early stage of the test development to see which technique is better suited for the test.

**Oil drop size distribution.** Dispersed oil-drop sizes can be measured in three ways. Sophisticated laser doppler systems can be used to measure the oil-drop size (Delvigne 1984b) but the cost of such systems precludes their consideration in this study. Less expensive particle-size analyzers could also be used. Examples of such devices are the Coulter Counter and the Malvern Particle Size Analyzer. The major drawbacks of these systems are first the difficulties in calibrating the systems and using them for wide drop size distributions, and secondly, their considerable cost. A photographic technique has been used successfully in our facility over the past several years. The major drawback of this method is the labour intensiveness of the data analysis (drops in each photo must be digitized manually). Drops as small as 10  $\mu\text{m}$  can be detected with the system with no practical limitations on the maximum drop size measurable.

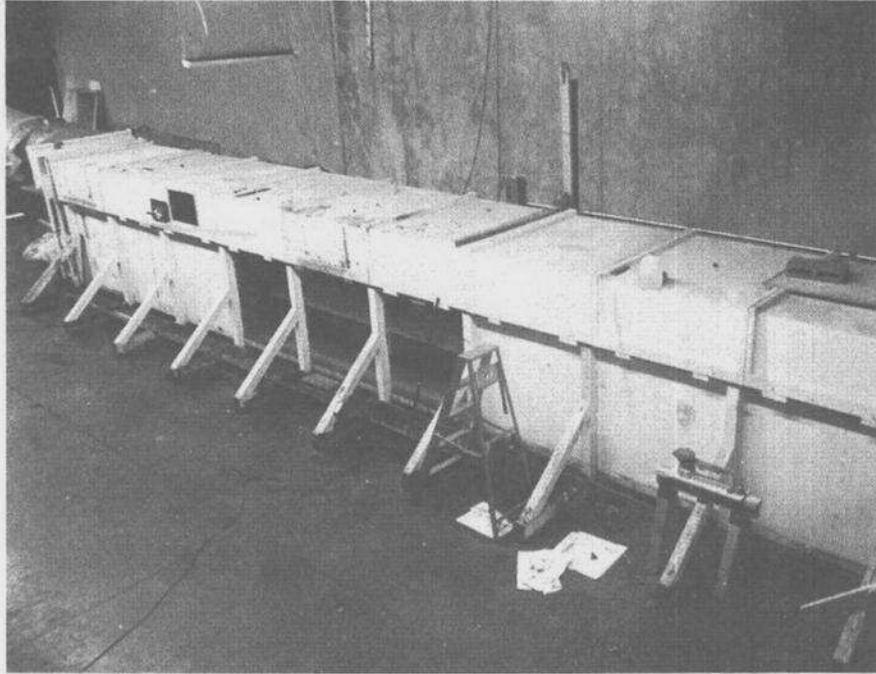
## **4.0 EXPERIMENTAL SET-UP AND DESIGN**

In this section the test apparatus, measurement techniques, and test procedure selected for use in the mid-scale test are outlined.

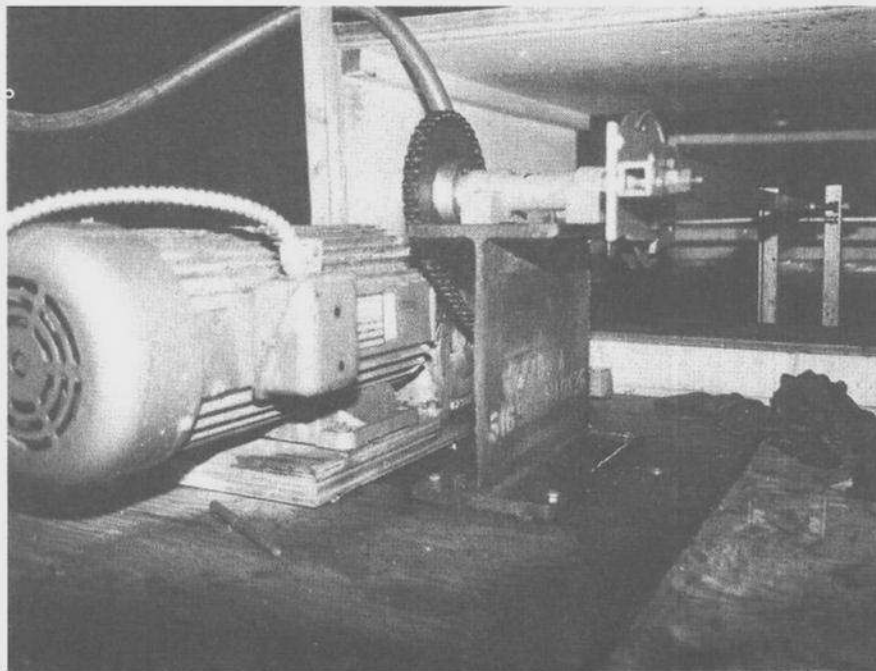
### **4.1 TEST APPARATUS**

The testing makes use of a wind-wave tank that measures 11 m x 1.2 m x 1.2 m excluding the detachable overhead wind tunnel. The tank is generally filled to the 85-cm level during tests involving wave action. The amount of water used per test is about 11,000 litres. Figure 1 shows the tank with the wind tunnel in place. The glass viewing panels, sampling access doors in the wind tunnel, and fan are all visible in the photo. The wave paddle is located at the opposite end of the tank from the fan and is driven by a 3-hp, variable-speed D.C. motor to provide a wide range of wave energy conditions (Figure 2). Control of the wind speed is attained by simply choking off the inlet side of the fan using a perforated insert (Figure 3).

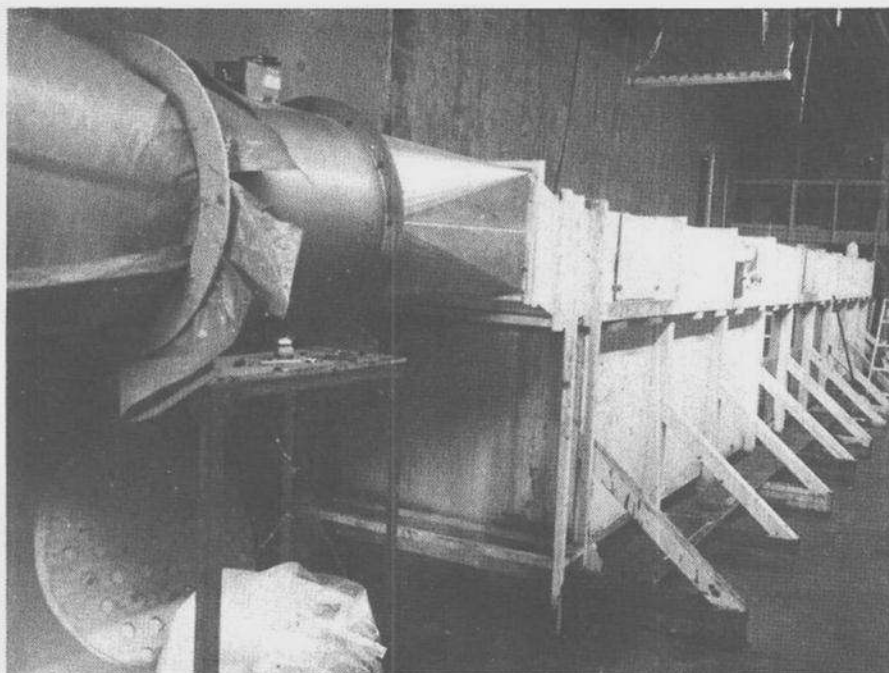
Water samples are taken from three levels in the tank through a series of tubes whose inlets are located 15 cm, 40 cm, and 65 cm below the calm water surface. One set of tubes directs water by gravity to a set of viewing cells to monitor the presence of oil in the water (Figure 4). Photographs of the oil-in-water dispersions passing through these cells are taken for subsequent determination of oil drop-size distribution. The second set of tubes is used to take water samples for subsequent oil extraction and concentration analysis.



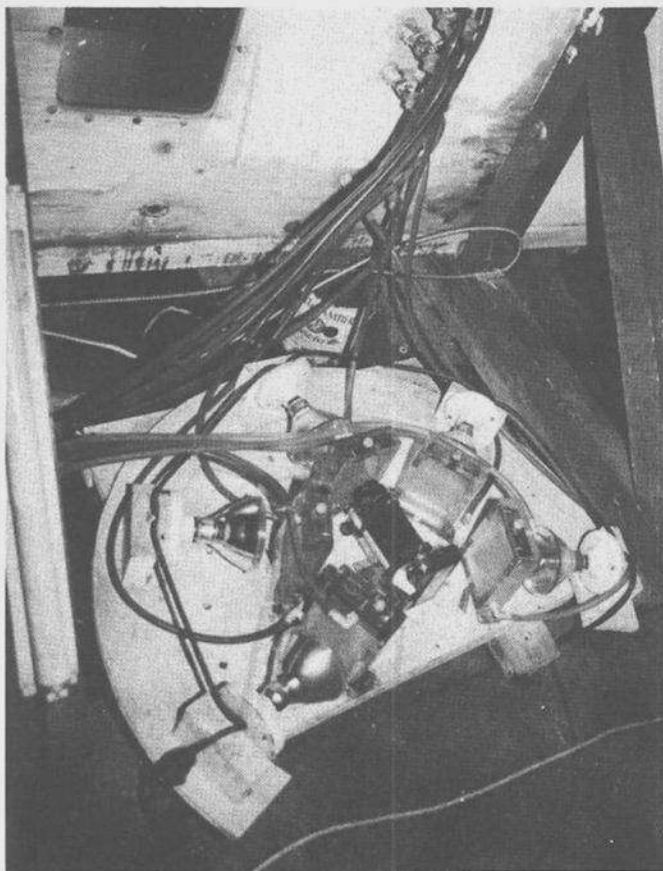
**Figure 1. Test tank.**



**Figure 2. Wave paddle and drive mechanism.**



**Figure 3. Fan and choking template.**



**Figure 4.  
Cells used in  
oil dispersion  
photography.**



Dispersant is applied to the oil-water surface by a full-size spray boom using conventional nozzles. The boom is mounted about 1 m above the calm water surface on a cart that travels on a linear bearing that extends the length of the tank. The system is pressurized by a compressed air tank that is connected via an electric valve to the dispersant reservoir and finally to the spray nozzles. The pressure vessel was charged to 100 psi and the liquid reservoir topped off with dispersant prior to each test. The forward motion of the towed cart is used to trigger the electric valve to both start and stop the spray system. The amount of dispersant applied can be varied by either replacing the nozzles on the boom or by varying the cart speed.

#### **4.2 MEASUREMENT TECHNIQUES**

The following data are collected during each test:

- \* in-water oil concentration;
- \* dispersed oil drop-size distributions;
- \* surface oil area and thickness; and
- \* oil-water interfacial tensions.

The methods used to determine each are outlined below.

Oil concentrations in the water were determined by extracting the oil in each of the grab samples with a colourless solvent (toluene). The quantity of oil in the solvent was then determined by a spectrophotometer.

Dispersed oil-drop size distributions were measured by photographing the dispersions passing through the viewing cells (see Figure 4). These photographs were taken at a known scale and were then enlarged to give a 20-times magnification. The diameters of the oil drops in these enlargements are then entered into a computer via a digitizing tablet. Computer software has been developed to determine the significant population statistics on these diameters including the volume median

oil-drop diameter (VMD). The VMD is the drop diameter where 50% of the oil volume is present in drops larger than the VMD and 50% of the oil volume is present in drops smaller than, or equal to, the VMD.

The total area of the surface slick was estimated visually as a fraction of the total water surface area and, therefore, only provides a rough quantification of the amount of oil in the surface slick. Surface oil thickness was measured by picking up a known area of the surface slick with a pre-weighed piece of oil-spill sorbent. The volume of oil recovered was determined either by weighing the oil-soaked sorbent and using the weight difference and oil density to calculate a volume or by recovering the oil from the sorbent with a solvent and determining the amount of oil present by spectrophotometry. The oil thickness is determined by dividing the oil volume recovered by the area which was sorbed. The weighing method is the simpler of the two techniques but is prone to errors from water pick-up, especially when dispersant is in the surface waters.

Oil-water interfacial tensions were measured by a duNuoy ring apparatus. In this technique a small platinum ring is drawn through the water-oil-air interfaces of a sample from the test tank. The force required to pull the ring through an interface is then used to estimate the interfacial tension. The method works well for uniform, clean, non-viscous oils but encounters problems with thicker, less homogeneous products. When the oil slick becomes thin it is also difficult to collect an oil sample large enough for use in the test.

The mixing energy levels used during the testing program were measured after the tests were completed using a device provided by Environment Canada. This turbulence probe was developed by Canpolar Consultants for ocean turbulence measurements, and is described in Appendix A.

### 4.3 TEST PROCEDURE

The major steps taken to complete a test are outlined below.

- 1) The tank is filled with salt water (32 ppt) at the required temperature.
- 2) The dispersant application gear is readied. The dispersant reservoir is filled, the air cylinder is charged to 100 psi, the cart is positioned at the end of the tank and is connected to the drive cable, and the switches used to start and stop the dispersant spray are set.
- 3) The water sampling ports are opened temporarily to clear them of air and to ready them for sampling.
- 4) The oil is placed on the water and spread to the desired coverage and thickness.
- 5) A known area of oil is picked up by an oil-spill sorbent for oil thickness estimation. A pre-test oil and water sample is taken for interfacial tension determination.
- 6) The wind and wave action is started and the wave frequency is fine-tuned to maintain the oil in the centre of the tank at the wind speed set for the test.
- 7) The dispersant is applied by the motorized boom system.
- 8) Another set of oil and water samples is taken immediately after the application of dispersant for interfacial tension analysis.
- 9) At first sight of oil in the viewing cells oil drop-size photos and water samples are taken from three depths in the tank.
- 10) The test continues for one hour with a new set of measurements taken every 15 min. Each measurement set consists of a surface oil and water sample for interfacial tension, water samples and oil drop size photos from the three sampling depths, oil thickness samples (sorbent pads), and an estimate of the area of the surface slick.
- 11) After taking the samples at one hour the test is stopped and the tank is drained and cleaned for the next test.
- 12) The in-water oil concentration and surface slick thickness samples are analysed between sampling periods. The oil-drop size photos and interfacial tension samples are analysed in batches after a number of tests are completed.

## 5.0 RESULTS

### 5.1 TEST PARAMETERS

A total of 16 different tests were completed during the experimental program. These tests were intended to investigate the ability of the test procedure to determine dispersant effectiveness as a function of oil type, dispersant type, oil thickness, and mixing energy level. The variables used in the testing program are listed below.

- \* oil type (2)                   - Fresh Alberta Sweet Mixed Blend
- aged Alberta Sweet Mixed Blend (15% loss by volume)
- \* dispersant type (2)       - Corexit 9527
- Enersperse 700
- \* oil thickness (2)         - 1 mm
- 0.5 mm
- \* energy level (2)         - high (as defined in Appendix A)
- low.

Because of time and cost constraints it was not possible to carry out a more varied test matrix. It was felt, however, that this limited series would demonstrate the potential of the test set-up and procedures.

Conditions which were kept constant during the testing are listed below.

- \* dispersant-to-oil ratio    - 1:20
- \* dispersant drop size       - 800 um VMD
- \* water salinity             - 30 ppt
- \* water temperature         - 15°C
- \* air temperature            - 20°C.

Alberta Sweet Mixed Blend crude oil and Corexit 9527 and Enersperse 700 dispersants were used in the experimentation because of their common use in effectiveness testing in Canada. These products were also used during the 1983 COAATF offshore dispersant trial (Gill et al. 1985). This allowed comparison and validation of the laboratory results with those from a field test.

## **5.2 DATA COLLECTION**

As stated, during each test data were collected on:

- \* oil-water interfacial tension;
- \* dispersed oil drop-size distributions;
- \* surface oil thickness and area; and
- \* in-water oil concentration.

In a separate set of tests the mixing energies used in the experiments were also evaluated.

Data not presented in the body of the main report are provided in Appendix B. A discussion of the general trends identified within these five data groups follows.

### **5.2.1 Mixing Energy**

The mixing energies used in the study have been measured with a turbulence probe developed by Canpolar Consultants Ltd. (1985). The technique employs a space domain measurement technique that uses a pair of fixed-velocity sensors operated in a differential mode. These sensors measure the instantaneous velocity shear in the fluid between the probes but are not sensitive to coherent water motions or to the relative motion of the sensor pair (see Appendix A).

The probe was used to measure the turbulent energy developed in the test tank at the two mixing levels used in the study. The average values recorded by the system were  $6.8 \times 10^{-4}$  Joules/kg (high energy) and  $6.3 \times 10^{-4}$  J/kg (low energy). These values can be compared to the limited data collected in the Canpolar study where the probe was deployed next to a wharf in Conception Bay during light seas and winds and with no swell. The average turbulence values measured during this program ranged from  $1 \times 10^{-5}$  J/kg up to  $8.8 \times 10^{-5}$  J/kg. Apparently the mixing energy developed in the test tank exceeded that measured during a relatively calm period at a nearshore location by an order of magnitude. Unfortunately sufficient field data are not available to enable us to estimate the type of offshore condition which the test simulated. What these measurements do tell us, however, is that the two energy levels used in the study did not differ greatly. The probe was not available at the beginning of the testing and was, therefore, not used to set the two levels of mixing energy but only to measure them after they had been established.

### **5.2.2 Oil-Water Interfacial Tension**

Oil and water samples for interfacial tension measurements were taken prior to the addition of dispersant, immediately after the dispersant application, and 15 min, 30 min, and 60 min thereafter for all but two of the tests. The results as shown in Table 1 are disappointing. In many cases the oil sample was not large enough for performing the interfacial tension test or was viscous and lumpy. The lumpy consistency of the sample resulted in an uneven force on the ring used in the duNuoy technique and, therefore, yielded questionable results. The only significant observation that can be made from these data is that a drop in interfacial tension was noted after the addition of dispersant and that this lowered interfacial tension persisted for at least the first half hour of the test.

**TABLE 1**  
**Interfacial tension measurements**  
**(mN/m)**

Oil Type	Fresh ASMB				Weathered ASMB			
	0.5 mm		1.0 mm		0.5 mm		1.0 mm	
Oil Thickness	high	low	high	low	high	low	high	low
<b>Enersperse 700</b>								
prior	3.8*				---	---	4.9	5.4*
5 min	0.0	1.0	1.3	3.0	0.0	0.0		5*
15 min	0.9	---	1.2	1.5	---	1.4	---	2.1*
30 min	---	---	1.1	1.4	---	2.4	---	---
60 min	---	---	2.2	2.0*	---	---	---	4.2*
<b>Corexit 9527</b>								
prior			---	3.4*	4.6	6.0	10.7	9.7
5 min			1.5	1.9*	3.5	2.2	1.6	2.9
15 min			1.3	2.8*	1.7	1.5	1.7	1.9
30 min			3.2*	3.1*	1.5	1.8	2.4	1.7
60 min			---	4.8*	---	3.6*	2.2	1.3

\* lumpy viscous oil

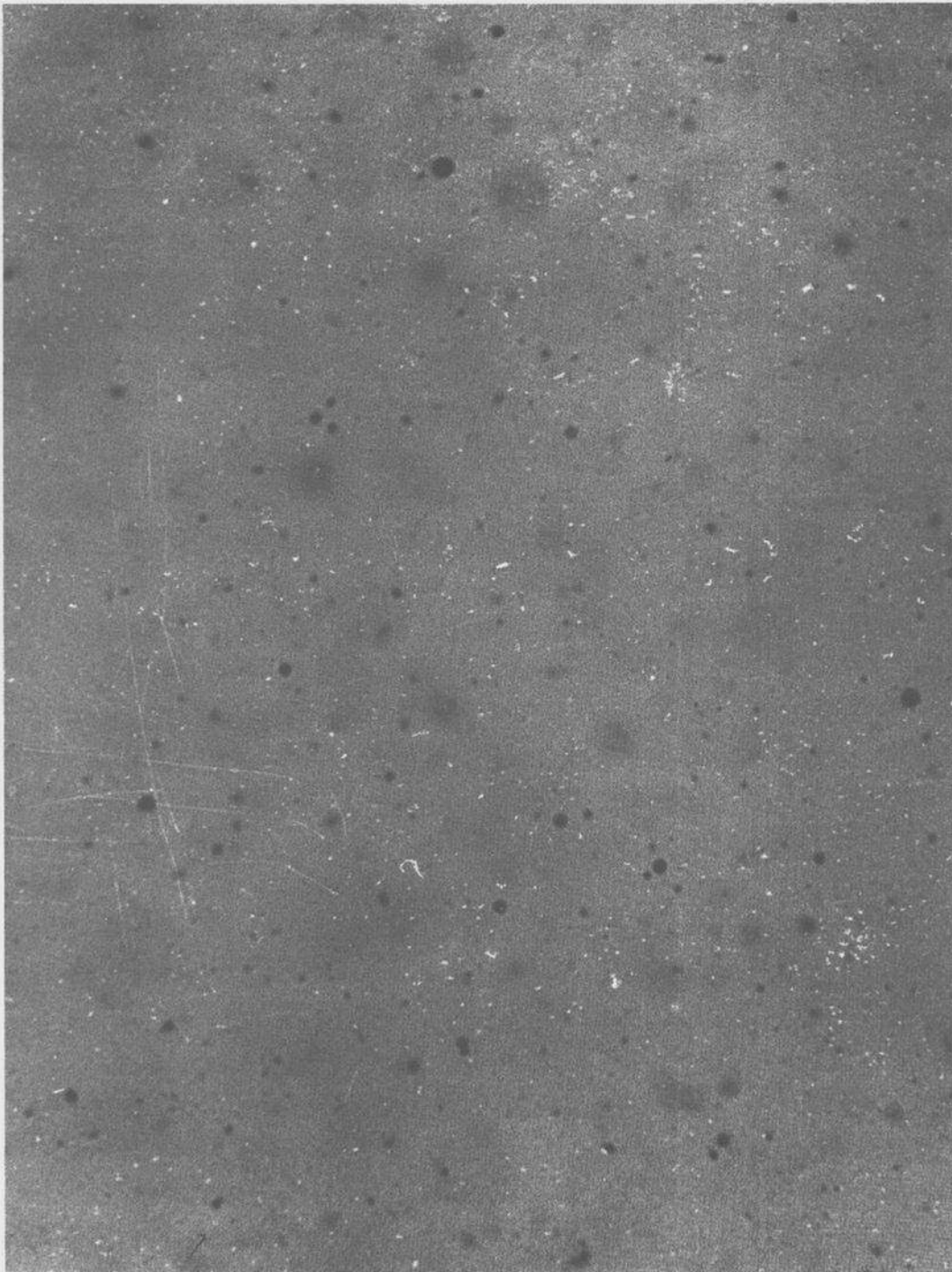
--- not enough oil in sample to analyse

Note: In a clean system the interfacial tension of fresh ASMB with salt water was measured to be 10.7 mN/m.

### **5.2.3 Dispersed Oil-Drop Size Distributions**

During every sampling period in each test, photographs were taken of the oil-in-water dispersions at all sampling depths. An example of such a photograph is included as Figure 5. The oil-drop diameters in these photos were then digitized and stored on computer files for analysis. For each photograph the oil-drop size distributions were evaluated (Table 2). This is the result of the analysis carried out on the data collected from Figure 5. The volume median diameters calculated for each test at each sampling depth (averaged from three data sets collected over the entire test period) are summarized in Table 3. The volume median drop diameters ranged from 60 to 100  $\mu\text{m}$ . As would be expected the oil drop diameters were largest at the water surface and decreased in size with depth. The larger drops are more buoyant and therefore are not driven to as great a depth. In most cases the higher mixing energy gave a slightly smaller volume median drop diameter. The difference is small likely because the two energy levels used were not drastically different. The oil drops generated in the tests using Enersperse 700 were generally smaller than those measured for the Corexit 9527 tests. The oil-drop diameters generated with the weathered oil were consistently smaller than for the fresh oil. The reason for this is not clear.





**Figure 5. Example photograph of oil-in-water dispersion**

**TABLE 2**

**Example of oil drop size distribution statistics  
generated by computer program**

Date of Run [D/M/Y]: 02/05/86  
 Type of Mixing System: wind/wave tank - high energy  
 Dispersant to Oil Ratio: 1:20  
 Track Speed [m/s]: .00

**GENERAL OIL DROP SIZE INFO (MICRONS)**

Maximum Drop Size: 152.6  
 Minimum Drop Size: 9.0  
 Ave Drop Size (D10): 43.4  
 Vol Mean Dia (D30): 57.3  
 Sauter Mn Dia (D32): 75.1  
 Volume Median Dia: 91.6

**OIL DROP SIZE DISTRIBUTIONS**

<b>RANGE</b>	<b># OF DROPS</b>	<b>% OF DROPS</b>	<b>% LESS THAN</b>	<b>VOL %</b>	<b>% VOL LESS</b>
0. - 10.	1	.5	.5	.00	.00
10. - 20.	17	8.1	8.6	.20	.20
20. - 30.	50	23.9	32.5	1.91	2.11
30. - 40.	51	24.4	56.9	5.49	7.60
40. - 50.	26	12.4	69.4	5.70	13.30
50. - 60.	29	13.9	83.3	12.03	25.33
60. - 70.	8	3.8	87.1	5.73	31.06
70. - 80.	9	4.3	91.4	9.76	40.82
80. - 90.	5	2.4	93.8	7.87	48.68
90. - 100.	6	2.9	96.7	13.09	61.78
100. - 110.	1	.5	97.1	2.87	64.65
110. - 120.	1	.5	97.6	3.80	68.45
120. - 130.	3	1.4	99.0	15.24	83.69
130. - 140.	0	.0	99.0	.00	83.69
140. - 150.	1	.5	99.5	7.28	90.97
150. - 160.	1	.5	100.0	9.03	100.00

Total # drops - 209 Total Oil Volume (ML) = .00002060

**TABLE 3**  
**Dispersed oil-drop sizes:**  
**average volume median drop diameters**  
**(microns)**

Oil Type	Fresh ASMB				Weathered ASMB			
	0.5 mm		1.0 mm		0.5 mm		1.0 mm	
Oil Thickness	high	low	high	low	high	low	high	low
Energy Level	high	low	high	low	high	low	high	low
Enersperse 700								
overall	78	79	77	100	68	68	62	74
top	97	90	82	112	80	87	71	86
middle	76	76	81	94	61	66	58	72
bottom	68	69	67	84	66	45	51	60
Corexit 9527								
overall	82	105	91	81	---	90	---	---
top	111	102	102	101	---	96	---	---
middle	66	108	99	79	---	105	---	---
bottom	66	105	73	61	---	76	---	---

--- data not collected.

#### **5.2.4 Surface Oil Slick Thickness and Area**

Three samples of surface oil-slick thickness were taken prior to the addition of dispersant and about 15 minutes after the dispersant was applied. The amount of oil sorbed by each sampling disk was estimated by weight and by chemical extraction and colorimetric analysis. The oil thicknesses estimated from the three samples were then averaged to provide an estimate of the average oil-slick thickness. At the time that each surface sample series was taken a visual estimate of the oil coverage and overall slick extent was made. This estimate of oiled area has been multiplied by the average thickness to estimate the volume of surface oil present at the time of sampling. The results, summarized in Table 4, are disappointing. The greatest error in the procedure was undoubtedly the determination of the total oiled area by a simple visual estimate. The patchiness of the oil slick also made it difficult to estimate average thickness by using only three samples. If estimates of surface oil quantity are to be used in future tests a more accurate method of determining the total oiled area will be required. This perhaps could be achieved by taking and analysing photographs of the surface area. To accomplish this it would be necessary to replace the existing wind tunnel with a transparent material.

#### **5.2.5 In-Water Oil Concentrations**

Dispersed oil concentrations versus time for the three sampling depths have been plotted for all tests and are included in Appendix B. Figure 6 has been derived from these plots and illustrates the general behaviour of the dispersion process that occurred during the testing. For most of the tests the upper sampling location recorded a high initial oil concentration but this quickly dropped off as oil diffused both to greater depth and laterally within the tank. Diffusion to greater depths is illustrated by comparing the times at which maximum oil concentrations occurred at the three sampling depths and noting the lag time that exists between peaks at successively deeper sampling points.

**TABLE 4**  
**Surface oil volumes estimated by slick**  
**thickness and areas**  
**(litres)**

Oil Type	Fresh ASMB				Weathered ASMB			
	2 litres		4 litres		2 litres		4 litres	
Initial Oil Volume	high	low	high	low	high	low	high	low
Enersperse 700								
prior	2.6a	---	---	---	1.0	1.4	2.3	3.2
to application	1.0b	1.2	1.7	---	1.8	.8	1.8	2.3
15 min after								
	2.4	---	---	---	.18	1.4	.08	.5
	1.5	---	---	---	.13	1.2	.05	.3
Corexit 9527								
prior	3.0	9.6	---	---	2.5	2.5	3.0	6.2
	---	---	---	2.2	2.0	1.9	2.0	4.3
15 min after								
	---	---	---	---	1.8	2.0	2.3	5.1
	---	---	---	---	1.3	1.8	1.9	4.6

a) top# - uses oil thickness determined by extraction  
b) bottom # - uses oil thickness determined by weight  
--- missing data.

Note: Slick thickness and areas used in volume calculations are presented in Appendix B.

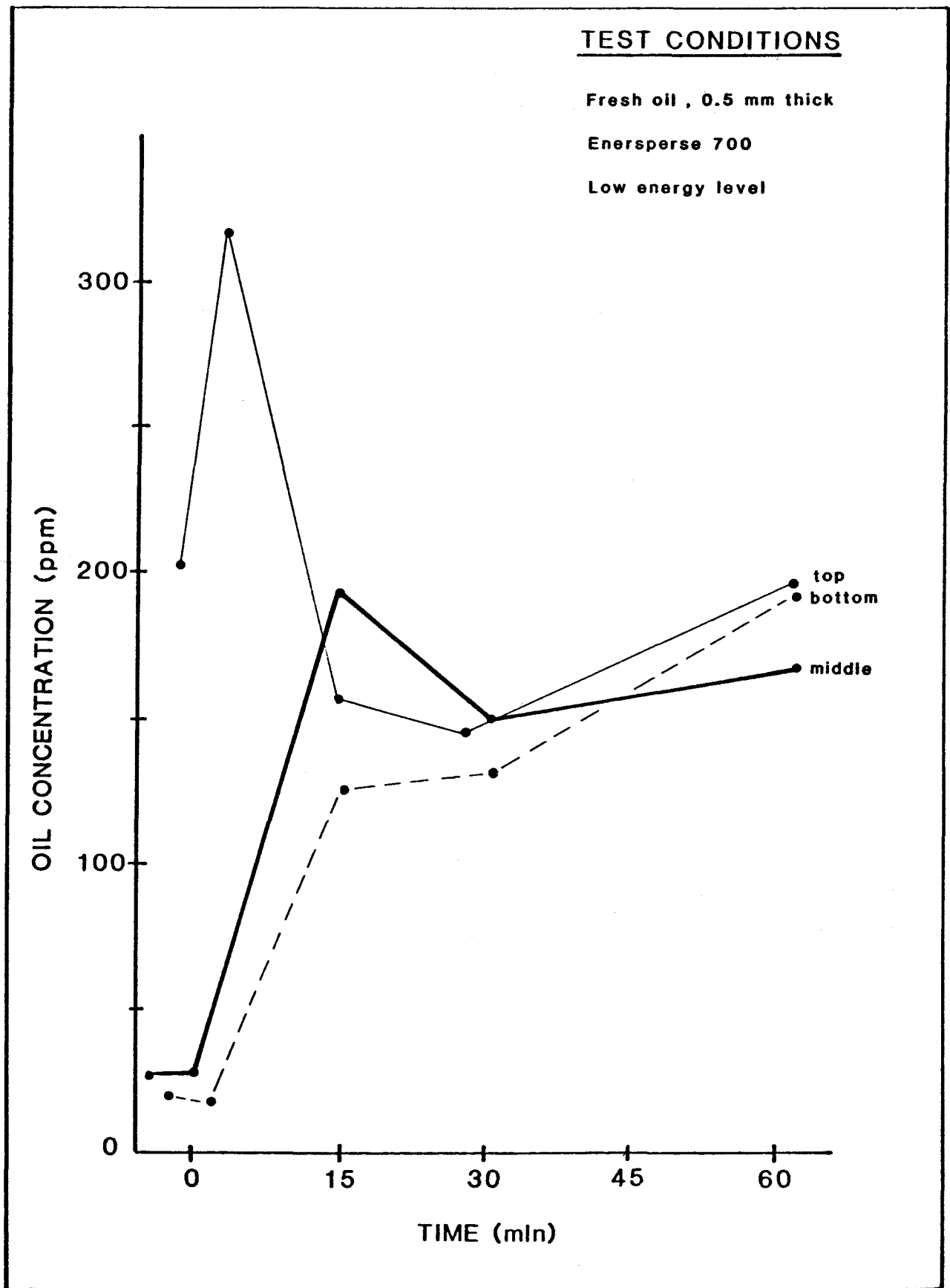


Figure 6 Example plot of oil concentration vs time

Lateral diffusion of oil to each end of the tank also takes place as the oil moves deeper, which further reduces the measured oil concentrations. This lateral diffusion and dilution occurs because the initial oil slick is confined to the central third of the tank and, therefore, any dispersed oil also originates in the centre of the tank. The lateral diffusion rate was determined by dumping pre-mixed oil and dispersant into the centre of the tank and by measuring the oil concentration at the centre and at each end of the tank over time. The results of this indicate that lateral diffusion is quite rapid in that uniform concentration throughout the tank was achieved in less than 15 minutes (Figure 7).

For many of the experiments the oil concentrations throughout the tank became fairly uniform after 15 to 20 minutes but continued to increase steadily over the remainder of the test. Because of this slow but steady dispersion most of the experiments resulted in very high overall dispersion efficiencies (50-100%) over the full one hour duration of the test. It is likely that this ultimate, high degree of dispersion results from the fact that, unlike field conditions, this system is a closed one in which the dispersant is always present in the water in sufficient concentrations to maintain a low interfacial tension between the oil and the water.

Based on measured oil/water partitioning coefficients for dispersants including Corexit 9527 (Mackay and Hossain 1982), and the quantities of oil and water used in the test, the equilibrium concentration of the dispersant in the oil can be calculated to be about 1:500 which in pre-mixed dispersant/oil systems is adequate to disperse oil over the long term. This was verified in a smaller test tank system (hoop tank) in which dispersant was added to the water rather than to the oil and the long-term dispersion efficiency measured. It was found that the dispersant was as effective in this test as when applied directly to the oil. Another hoop-tank experiment was then carried out to evaluate the effect of drawing off the oil and dispersant which disperses in the upper water layer and replacing it with uncontaminated water. This dilution test resulted in a significantly reduced dispersion of oil over the test duration. These series of smaller scale tests

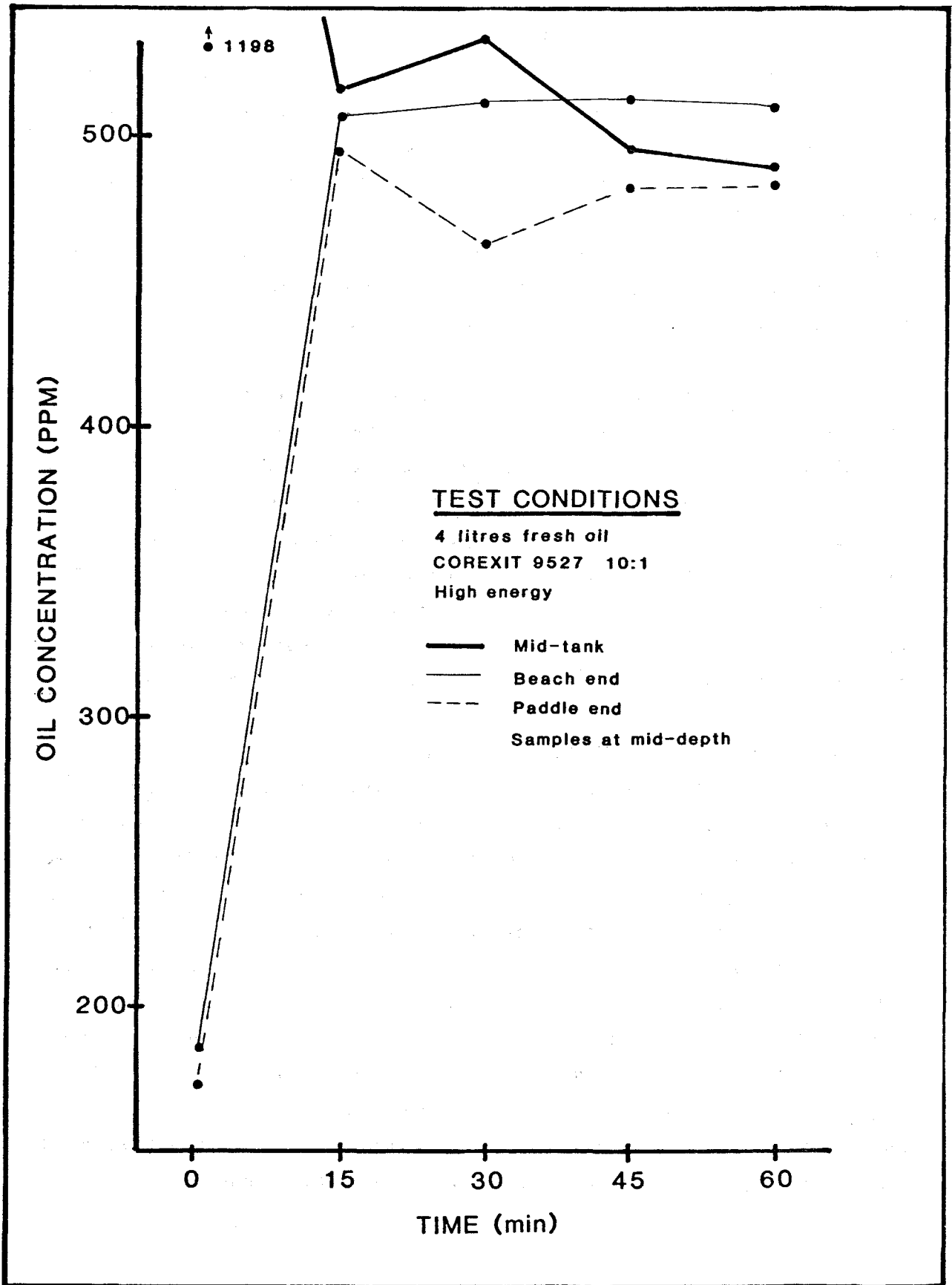


Figure 7 Progression of dispersed oil cloud originating at tank centre



demonstrated that closed system tests suffer from a dispersant loading in the water which would not be present in an ocean environment. As a result dispersant effectiveness is over-estimated if the test duration is excessive. In our mid-scale test we believed that the dispersion efficiencies measured at the 15-min point are most indicative of the likely efficiencies of the dispersant in a field application.

Dispersed oil quantities were estimated for each test at 5, 15, and 60 min after dispersant application. This estimate was accomplished by plotting the dispersed oil concentrations versus water depth for each of the sampling times, by calculating the areas under these curves, and finally by multiplying this value by the areal extent of the dispersed cloud at the time of measurement. For the initial dispersion calculation (about 5 min into the test) the areal extent was assumed to be one-third of the tank surface or the initial slick coverage. For the 15-min estimate two-thirds of the tank was assumed to be filled with dispersed oil at the concentration profile measured in the centre of the tank. For the one-hour estimate of dispersion efficiency it was assumed that the dispersed oil cloud was uniform throughout the entire tank volume. The results of this analysis are presented in Table 5. It should be re-emphasized that the dispersant efficiency measured at the 15-min point in the experiments is likely the most indicative of the efficiency that would result from a field application of the dispersant.

The effect of the test parameters (oil thickness, oil age, mixing energy, and dispersant type) can now be discussed based on the results of this table. There appears to be very little difference in dispersion efficiency for the two thicknesses studied. The fresh oil was dispersed slightly better than the weathered oil. The high-energy tests generally resulted in higher levels of dispersion but in many cases these were only marginal differences. The experiments with Enersperse 700 resulted in a slightly higher dispersal efficiency than that resulting from the Corexit 9527 experiments. To investigate these trends further a statistical comparison of

**TABLE 5**  
**Estimates of dispersion efficiency using**  
**dispersed oil concentrations**  
**(%)**

<b>Oil Type</b>	<b>Fresh ASMB</b>				<b>Weathered ASMB</b>			
	<b>0.5 mm</b>		<b>1.0 mm</b>		<b>0.5 mm</b>		<b>1.0 mm</b>	
<b>Oil Thickness</b>	<b>0.5 mm</b>	<b>1.0 mm</b>	<b>0.5 mm</b>	<b>1.0 mm</b>	<b>0.5 mm</b>	<b>1.0 mm</b>	<b>0.5 mm</b>	<b>1.0 mm</b>
<b>Energy Level</b>	<b>high</b>	<b>low</b>	<b>high</b>	<b>low</b>	<b>high</b>	<b>low</b>	<b>high</b>	<b>low</b>
<u>Enersperse 700</u>								
5 min	27	23	11	30	16	7.5	15	7
15 min	67	62	38	46	61	19	36	41
60 min	138*	107	56	75	96	28	116*	65
<u>Corexit</u>								
5 min	5	21	17	15	12	5	6	2
15 min	30	28	44	27	33	9.3	17	45
60 min	90	50	126*	34	51	90	85	70

\* Reasons for these data anomalies are unknown.

means was undertaken to determine if there was any statistically valid difference in dispersant effectiveness for the above comparisons (Guttman et al. 1971; Spiegel 1961). The following hypotheses were tested in this analysis:

- 1) Ho:  $\mu_{\text{thick}} = \mu_{\text{thin}}$  (i.e., the mean dispersant efficiency measured for the thick oil tests is statistically the same as the mean dispersant efficiency for the thin oil tests.
- 2) Ho:  $\mu_{\text{fresh}} = \mu_{\text{weathered}}$
- 3) Ho:  $\mu_{\text{high energy}} = \mu_{\text{low energy}}$
- 4) Ho:  $\mu_{\text{Enersperse 700}} = \mu_{\text{Corexit 9527}}$

For these analyses all the data in Table 5 were used in the following formulae for a student's t distribution where:

$$t = \frac{X_1 - X_2}{\sigma \sqrt{1/N_1 + 1/N_2}}$$

and

$$\sigma = \sqrt{\frac{N_1 S_1^2 + N_2 S_2^2}{N_1 + N_2 - 2}}$$

$X_1$  - mean of sample size  $N_1$  from 1st series of tests

$X_2$  - mean of sample size  $N_2$  from 2nd series of tests

t - t statistic

$\sigma$  - estimated by  $S = \sqrt{N/(N-1)}$ .

The results of the analysis are shown in Table 6. The null hypothesis assumes that there is no difference between the tested conditions. When t measured is greater than the t statistic at the desired confidence level the null hypothesis is disproven and the means are considered different. These results indicate that without question (i.e., >99.5% probability) the Enersperse 700 tests resulted in higher dispersion efficiencies than the Corexit 9527. The thick and thin slick dispersion results are essentially the

**TABLE 6****Results of statistical comparison of means**

	<b>Hypothesis</b>	<b>t measured</b>	<b>Rejection Level</b>
1)	Ho: $\mu_{\text{thick}} = \mu_{\text{thin}}$	0.3662	$t_{65} = 0.390$
2)	Ho: $\mu_{\text{fresh}} = \mu_{\text{weathered}}$	1.11	$t_{85} = 1.059$
3)	Ho: $\mu_{\text{high}} = \mu_{\text{low}}$	1.396	$t_{90} = 1.318$
4)	Ho: $\mu_{\text{Enersperse 700}} =$ $\mu_{\text{Corexit 9527}}$	7.567	$t_{995} = 2.707$

same because the null hypothesis can be accepted only at the 65% confidence level. The two remaining comparisons, fresh versus weathered and high energy versus low energy, are not as definitive, but the null hypothesis for these two parameters can be accepted at the 95% and 90% level respectively. Although normal practice is to use a 95% or higher confidence level before rejecting the tested hypotheses, we know from other test programs that these parameters do affect dispersion efficiency. For this reason we are reasonably confident in assuming that the data are indeed unique and that the small differences result from the small differences in mixing energy levels and weathered states used for this testing program.

Because the thick and thin slick results are essentially from the same population these results can be averaged to simplify the presentation of the final results. We also believe that the dispersion efficiencies measured at the 15-min point in the test are the most realistic measures of dispersant efficiency and, therefore, are of primary interest. The data in Table 5 can thus be reduced to the values shown in Table 7. The overall average value is included in the table as a distillation of all of the data (i.e., assumes that all of the null hypothesis of Table 6 except for dispersant type are valid). The average results have been compared to the data collected during the 1983 COAATF dispersant trial (Gill et al. 1985) in which both Enersperse 700 and Corexit 9527 were used. As seen in the Table 7, the laboratory results for Enersperse 700 compare favourably to the offshore test results. The Corexit 9527 test results show a higher dispersion efficiency than was measured in the field. This can be attributed to the under-dosing of the oil slick in the field study. Although the database is a limited one from which to make conclusions, this mid-scale test appears to have realistically predicted the effectiveness of these two dispersants on Alberta Sweet Mixed Blend crude oil.

**TABLE 7**  
**Measured dispersion efficiencies**  
**(% at 15 minutes)**

Oil Type	Fresh ASMB		Weathered ASMB		Overall Average	*1985 COAATF Results
	high energy	low energy	high energy	low energy		
Enersperse						
700	52	54	48	30	46	41
Corexit						
9527	37	28	25	7	24	3.75

\* Gill et al. 1985.

## **6.0 CONCLUSIONS AND RECOMMENDATIONS**

### **6.1 TEST DESIGN**

The equipment and procedures used during the test program generally worked well and allowed two personnel to conduct each test without difficulty. The following modifications to the test procedure and equipment are recommended to improve the test design.

- 1) This test should be shortened to 15 min because dispersion after this time likely results from the presence of dispersant in the water rather than from dispersant in the oil. In an ocean environment dispersant quickly diffuses away from the upper water layers and no longer affects the dispersion of oil. If this laboratory test lasts longer than 15 min, unrealistically high dispersion efficiencies will likely result. A longer test could be used if the tank's water were continually diluted with dispersant-free water but this would be difficult with the large tank volume used in the study.
- 2) Water samples, for oil concentration measurement, should be taken at more locations in the tank to provide more accurate oil mass balance and dispersion efficiency determinations.
- 3) The fan used for the wind tunnel should be controlled by a variable-speed motor to permit the generation of a wider range of wind speeds. Because the wind is used to hold the oil in the centre of the tank (by opposing the movement due to waves) a wider range of wind speeds would also allow the tests to be carried out over a wider range of wave energies.

### **6.2 TEST MEASUREMENT METHODS**

The techniques used to measure oil concentration in the water column and dispersed oil-drop size distribution provided the most consistent and useful data collected during the study.

The determination of surface oil quantities by sorbent sampling and oiled area estimation was inaccurate, primarily, because of poor area estimates.

Interfacial tension measurements were reasonable when the oil was relatively fresh and fluid and when enough oil could be sampled from the tank. If the oil sample was too small or too viscous or lumpy the device used to measure the interfacial tension (duNuoy ring apparatus) gave questionable results. An inexpensive method is needed to determine the concentration of dispersant in both the oil and the water over the duration of the test. This information would improve our understanding of the interaction of the dispersant, oil, and water and the overall chemical dispersion process.

The turbulence probe used to measure the mixing level in the tank performed as expected but similar measurements have not been made in actual ocean environments over a wide enough range of sea states to enable us to compare the mixing levels in our tests to those under actual field conditions. The probe should be used to establish the mixing generated during the range of sea states considered acceptable for dispersant application.

### **6.3 DISPERSANT EFFECTIVENESS**

The averaged estimate of percentage of oil dispersed by Enersperse 700 in our tests compares favourably with those measured during the 1985 COAATF dispersant trials (46% (test) vs 95 to 41% (field) for Enersperse 700. The estimated dispersion efficiency for Corexit 9527 in our tests was higher than that measured in the offshore trial (24% vs 1 to 3.75%). This may be due to the small quantity of dispersant applied in the field test (Gill et al. 1985).



Dispersant effectiveness was the same for the two oil thicknesses used in the study (0.5 mm and 1.0 mm). There were only slight differences in effectiveness for the different mixing energies and for the two oil types (fresh and weathered) used in the testing. These findings may result from insufficient differences in the test parameters to affect the dispersant's performance.

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**APPENDICES**

## **APPENDIX A: TURBULENCE PROBE**

The following information has been adapted from Canpolar 1985.

### **THE SHEAR PROBE**

Conventional turbulence measurement techniques based on the measurement of velocity fluctuations followed by time domain analysis are not usable in situations which include a free liquid boundary subject to significant wave motions of similar frequency. The periodic motion component of regular waves is non-turbulent but is often more energetic than the turbulent motions and obscures the velocity information of interest. This can be largely overcome by turning to a space domain measurement and analysis system. A pair of fixed velocity sensors operated in a differential mode will indicate the instantaneous velocity shear in the fluid between the probes but will be insensitive to coherent motions of the water or relative motion of the sensor pair (including wave induced motions).

### **EXPERIMENTAL METHODS**

A shear probe based on the electrochemical anemometer was designed and built to provide this space domain measurement system.

Briefly: Five sensor probes were constructed with dimensions of 1 mm diameter x 8 mm length and were positioned at intervals of 5 mm, 10 mm, 20 mm, and 40 mm. The sensors project about 20 mm forward from a urethane pharing located on a 1 metre bar connecting a surface float to a damping plate. The entire assembly is designed to follow waves with periods greater than 1 second and to orient the sensors into any prevailing current so as to avoid the measurement of turbulence introduced by the suspension system.

The sensors are connected by a cable to a portable electronics package. The readout is designed to display the instantaneous velocity measured at any one probe or to display a turbulence factor based on a

differential measurement of velocity incoherence between any two selected probes. The turbulence factor is derived by filtering the incoming signals to remove differential signals below 0.1 Hz and to remove d.c. offset. The difference signal is multiplied by a factor of 50 and the resulting signal analysed for its true RMS signal strength using a 100 second integration time.

$$V_T = [(50(S_1 - S_2))^2]^{1/2} \quad (1)$$

The speed measured by an individual probe can be calculated from

$$S = (V_{pi}(0.98)t/k^1A)^{2.5} \quad (2)$$

S = speed in cm/sec.

$V_{pi}$  = instantaneous voltage out put from a single probe

t = time from reset in minutes

A = surface area of the probe  $mm^2$  (A = 15  $mm^2$ )

$k^1$  = 0.0175

in practice  $k^1A = k = 0.28$

The actual turbulent energy will be calculated from

$$E_T = 1/2 mv^2 \quad (3)$$

Where

m = mass in kg

v = velocity in m/sec

$E_T$  = turbulent energy in joules/kg

Combining (1), (2), and (3)

$$E_T = 2.93 \times 10^{-2} ((V_{Px} + V_T/100)^{2.5} - (V_{Py} - V_T/100)^{2.5})^2 \quad (4)$$

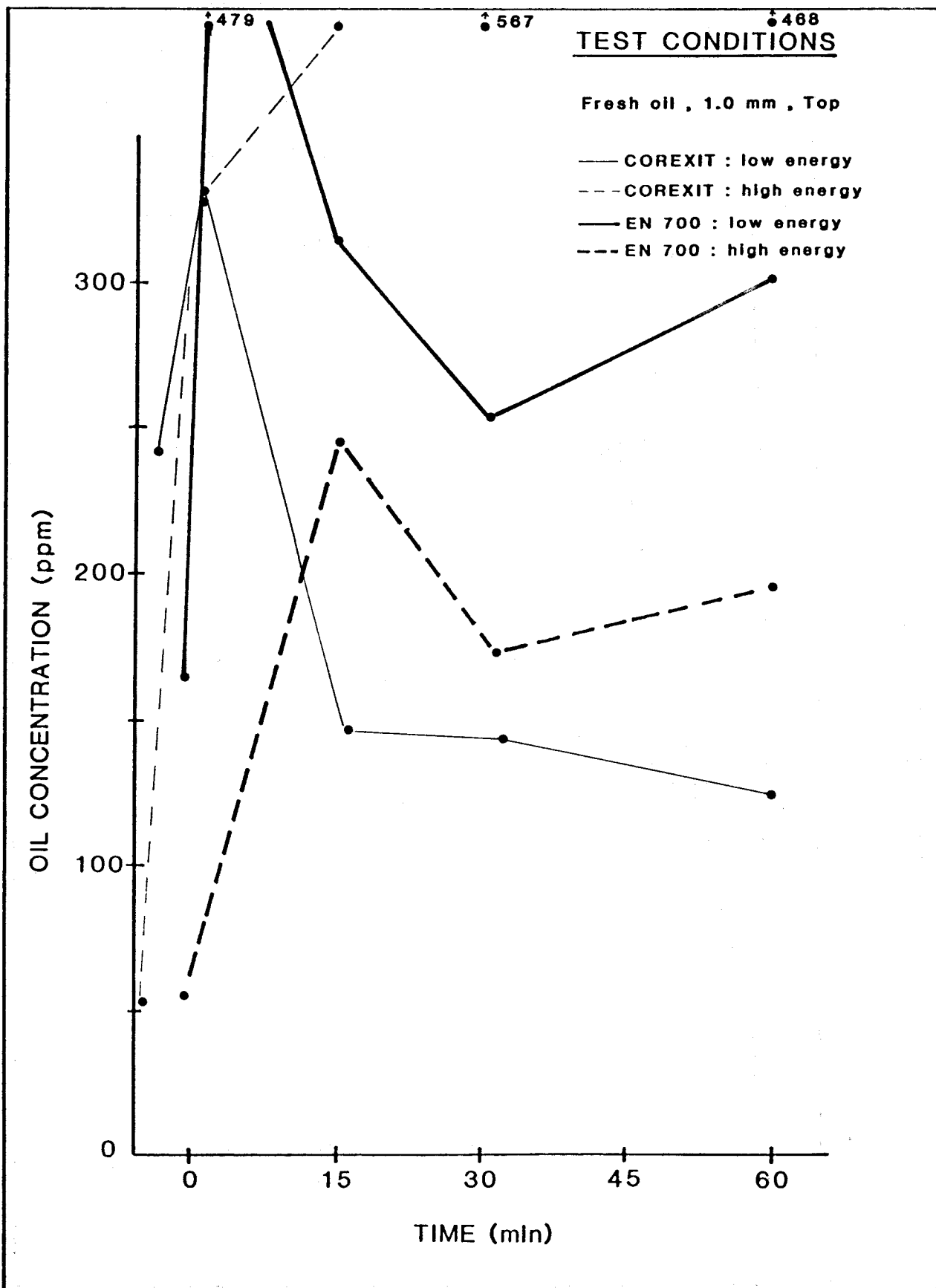
## **APPENDIX B: STUDY DATA**

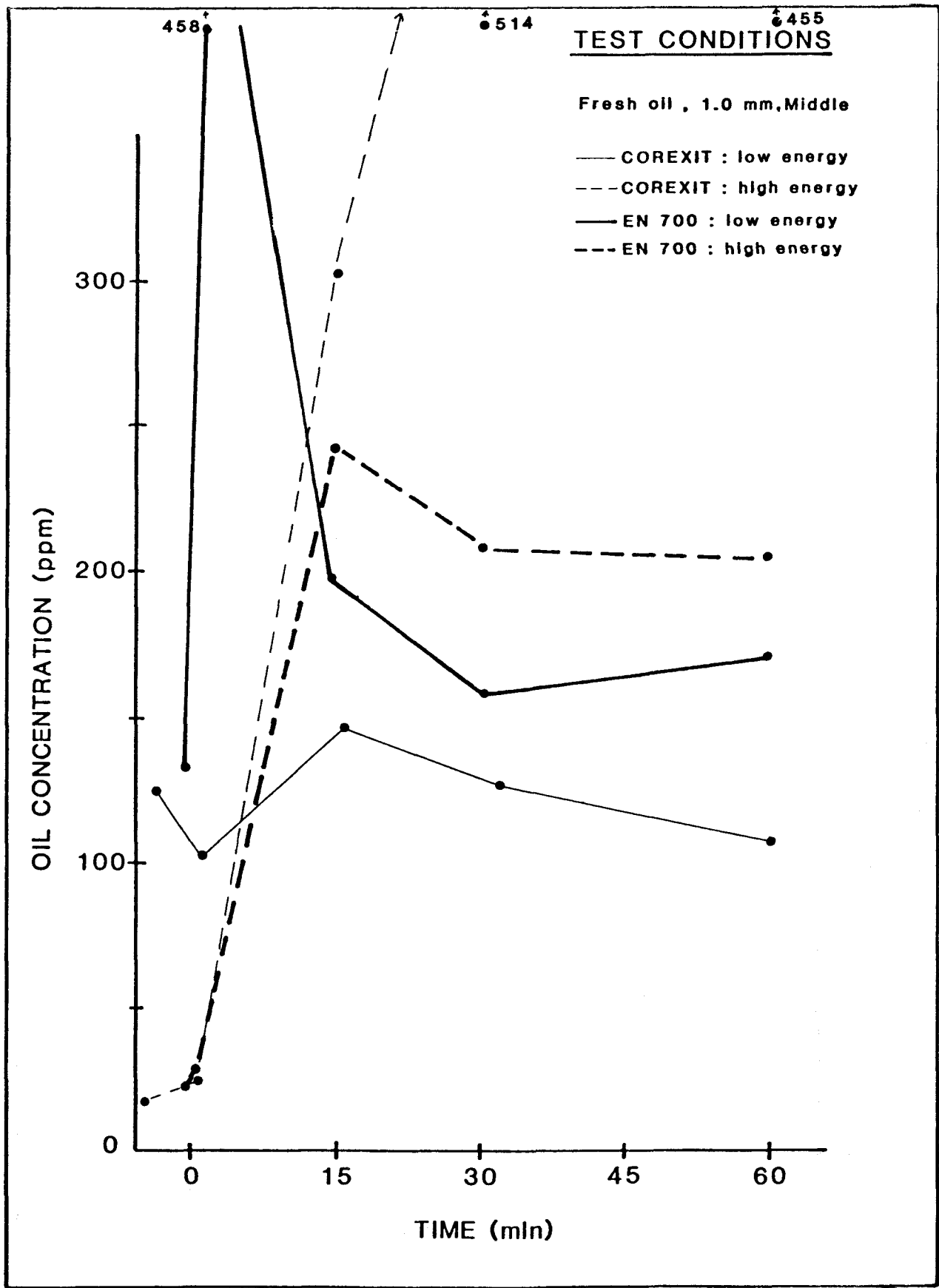
- 1) Oil concentration measurements
- 2) Oil slick thickness and area
- 3) Turbulence measurements



## 1) Oil Concentration Measurements

The oil concentrations measured during the test program are presented in the following graphs. The test conditions are noted on each plot. A separate graph is provided for each sampling depth.

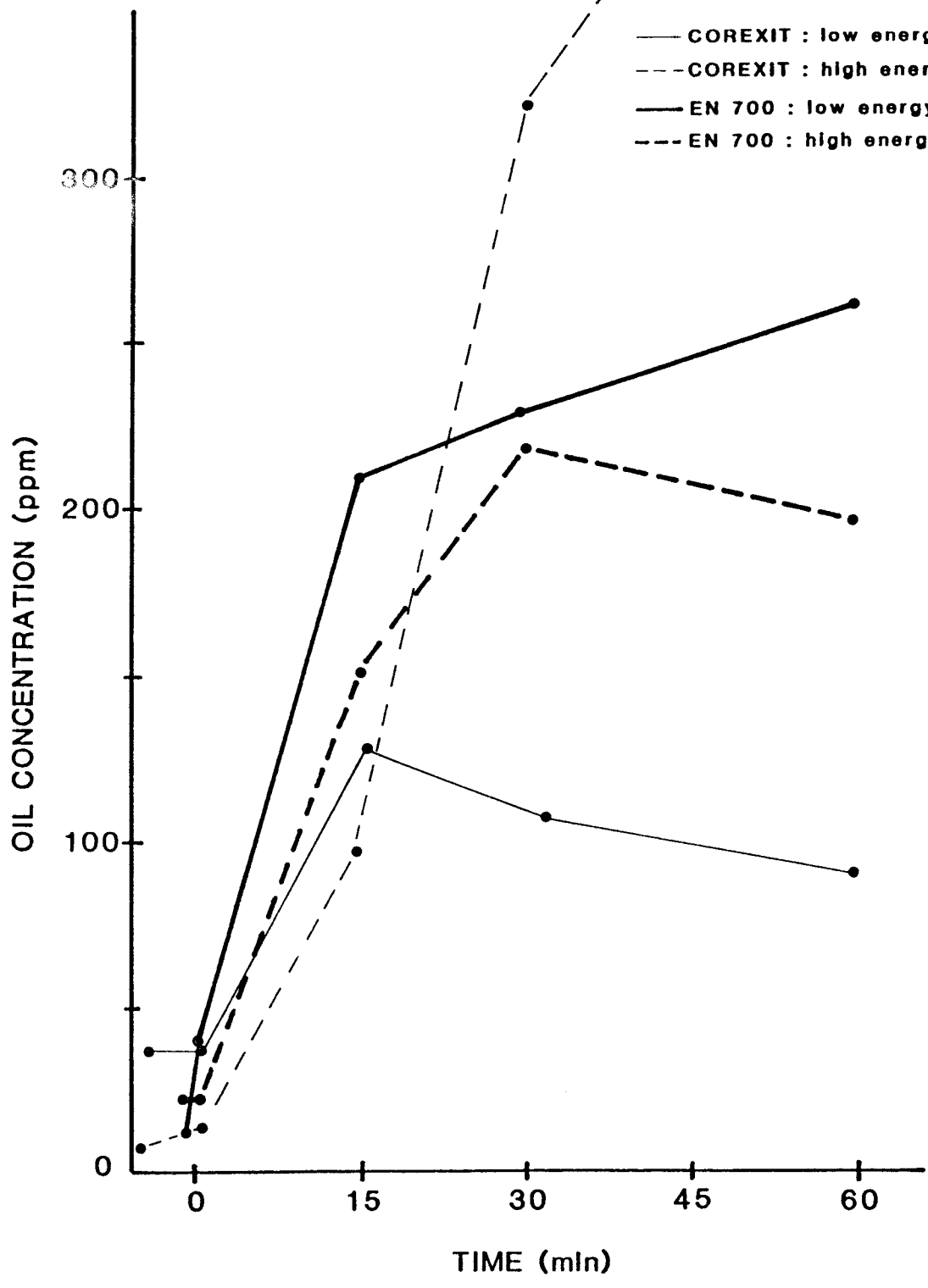


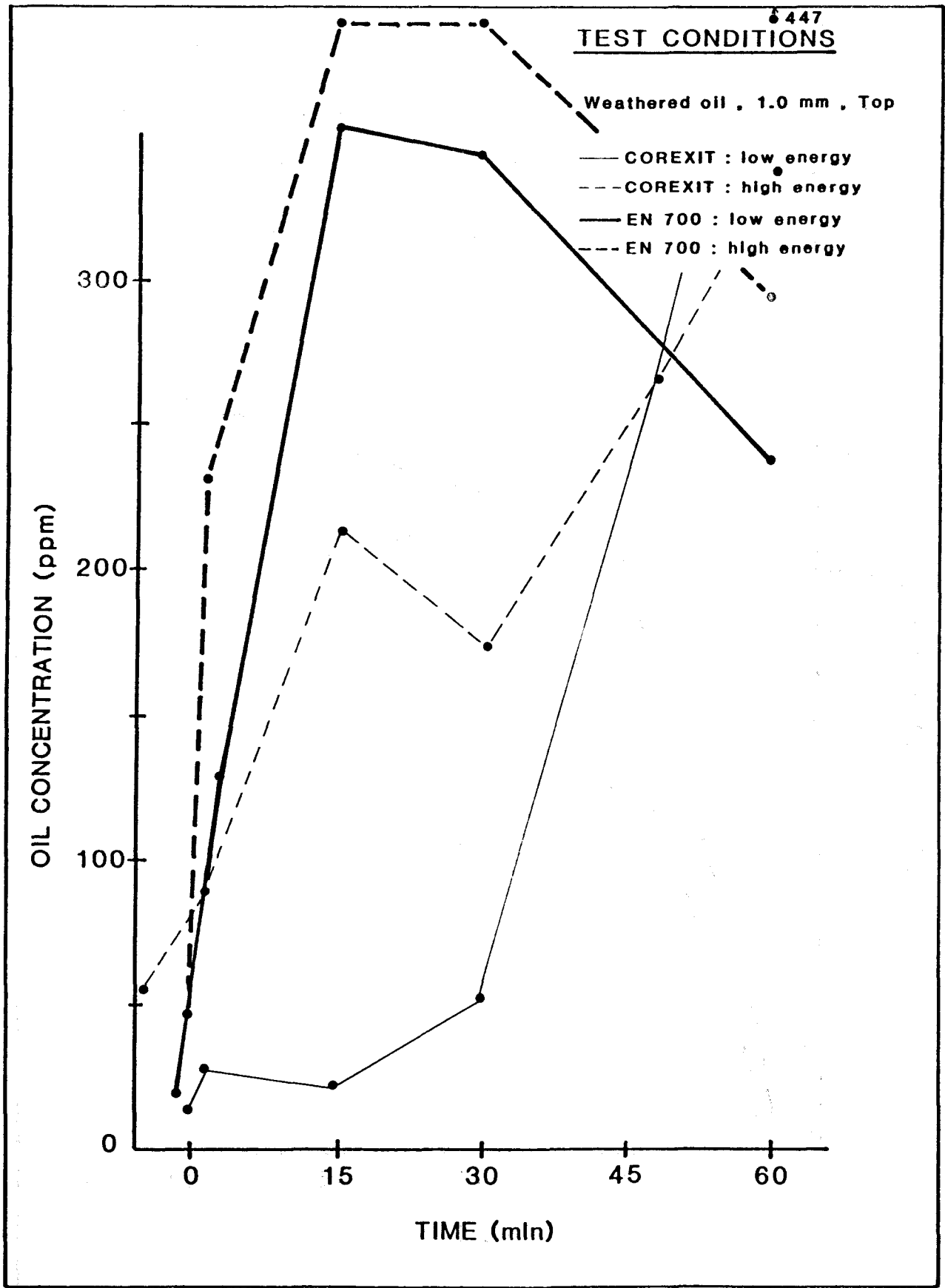


TEST CONDITIONS

Fresh oil , 1.0mm , Bottom

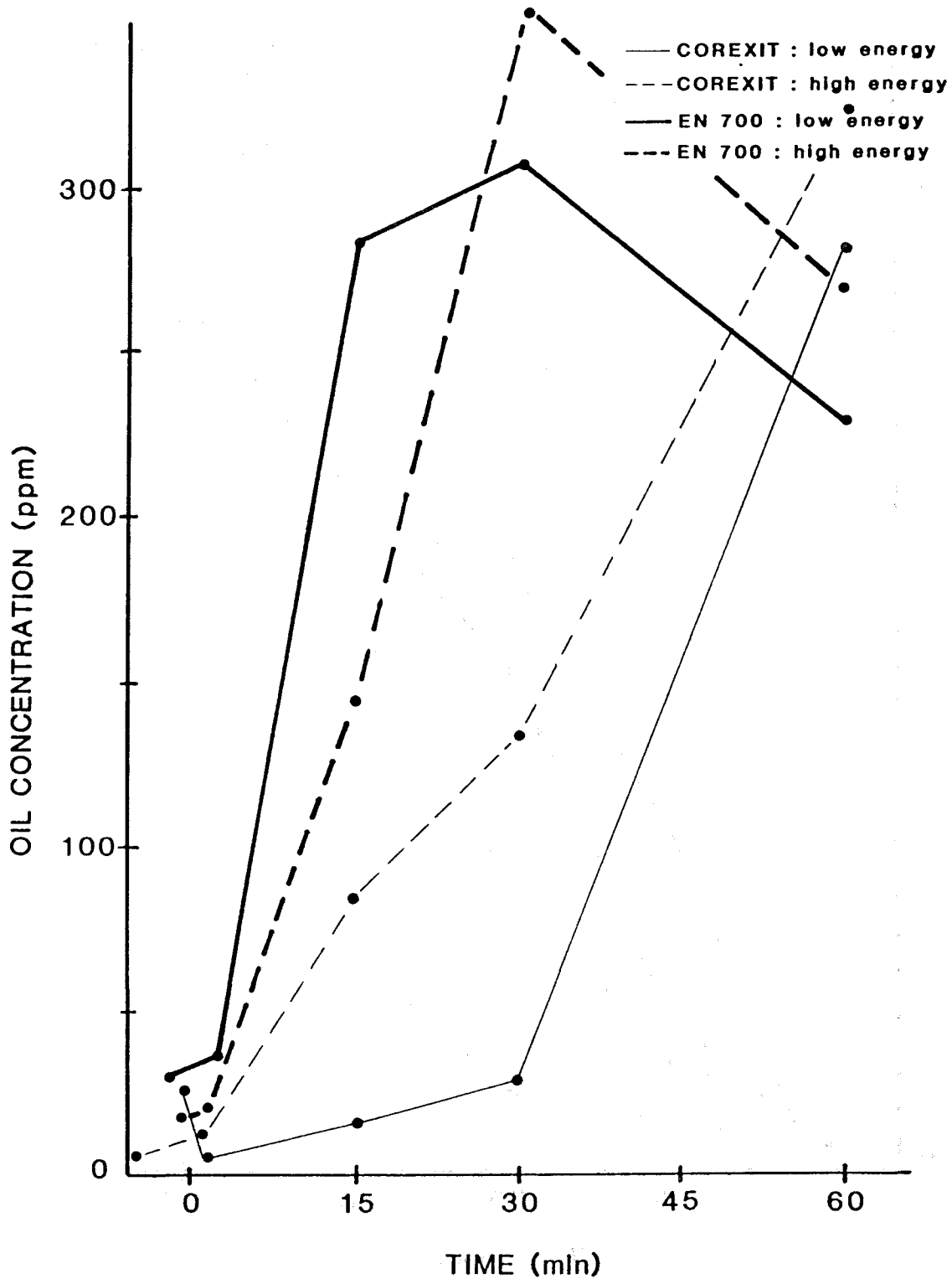
- COREXIT : low energy
- - - COREXIT : high energy
- EN 700 : low energy
- - - EN 700 : high energy





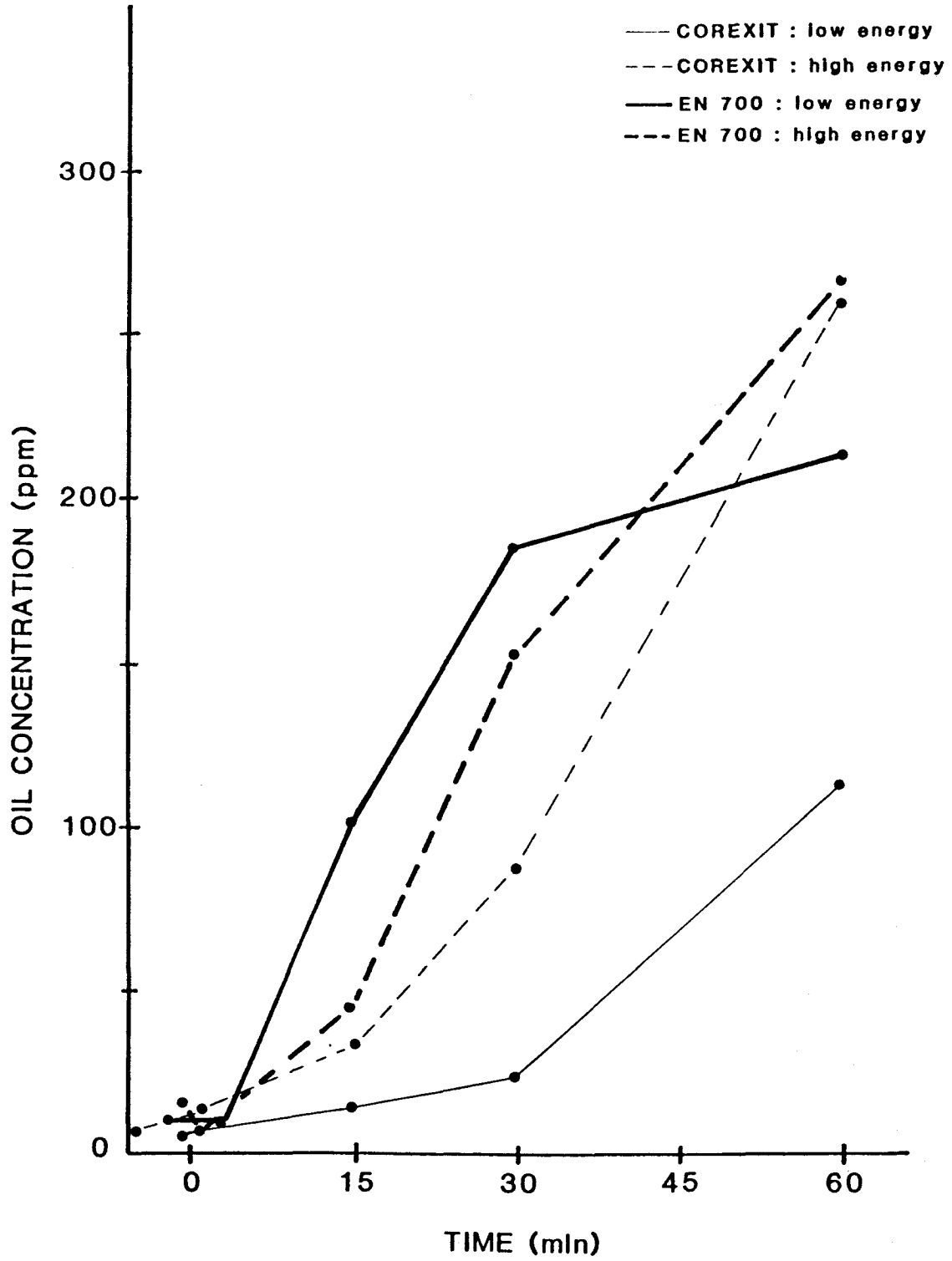
# TEST CONDITIONS

Weathered oil , 1.0 mm , Middle



### TEST CONDITIONS

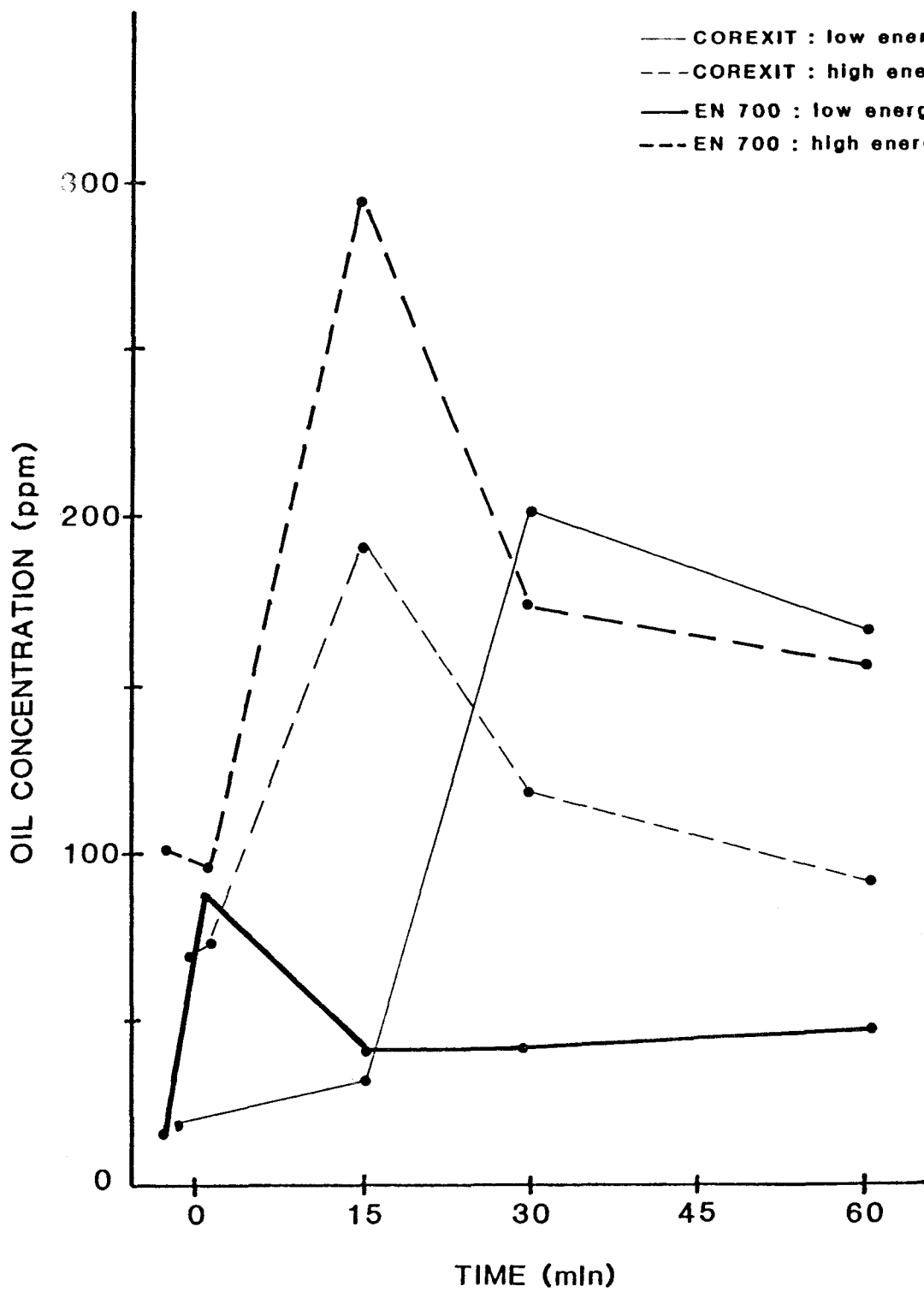
Weathered oil , 1.0 mm , Bottom



### TEST CONDITIONS

Weathered oil , 0.5 mm , Top

- COREXIT : low energy
- - - COREXIT : high energy
- EN 700 : low energy
- - - EN 700 : high energy

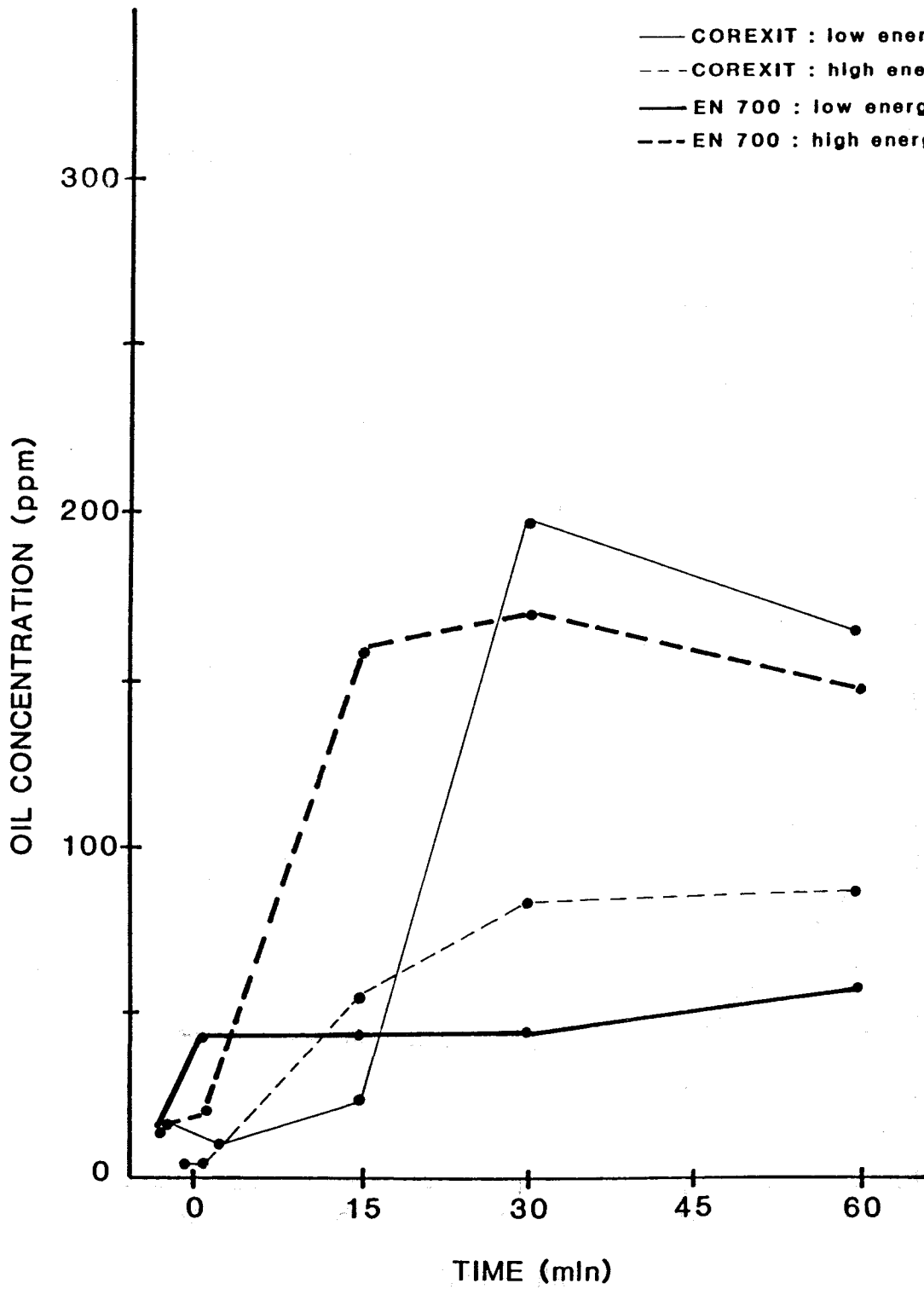




TEST CONDITIONS

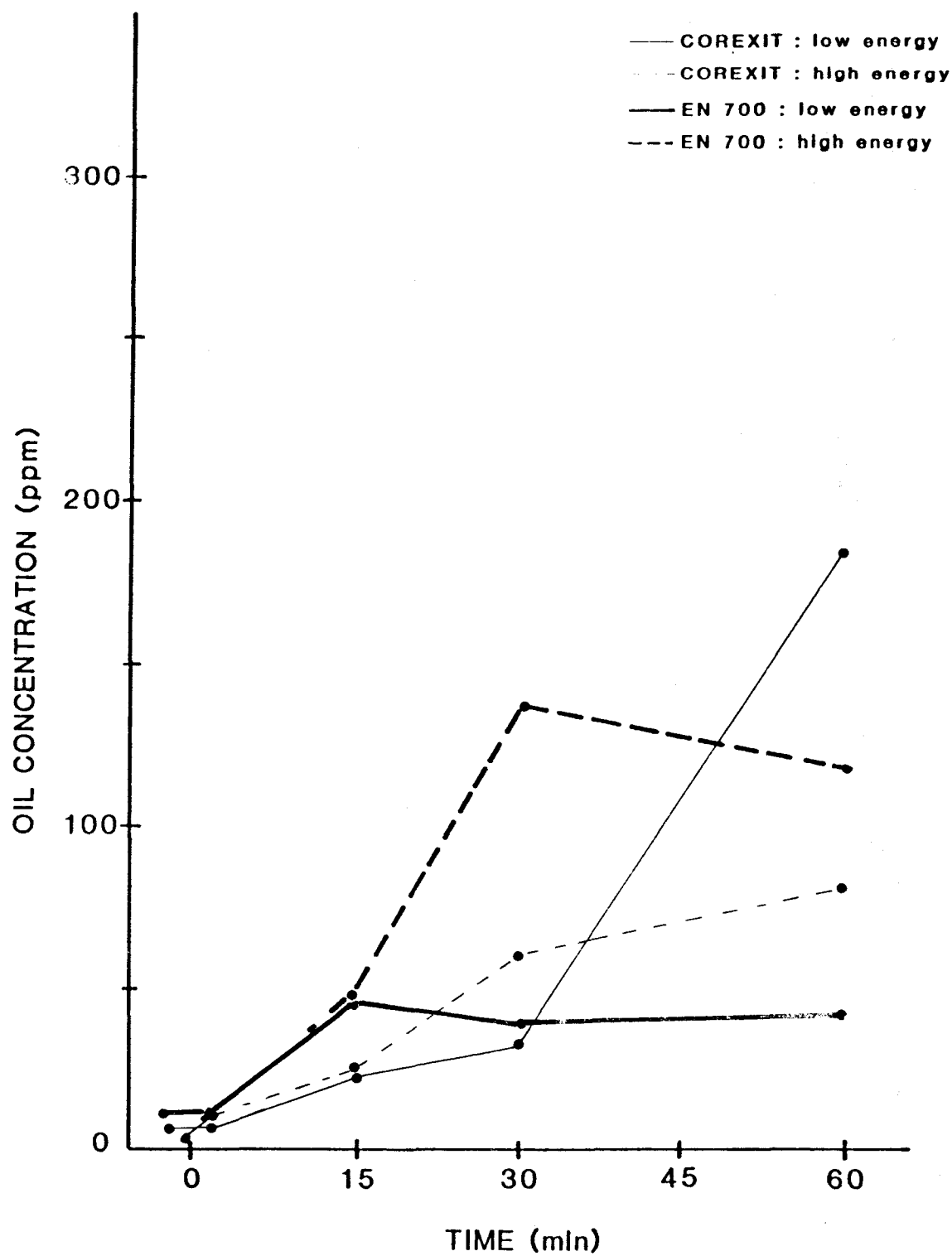
Weathered oil , 0.5 mm , Middle

- COREXIT : low energy
- - - COREXIT : high energy
- EN 700 : low energy
- - - EN 700 : high energy



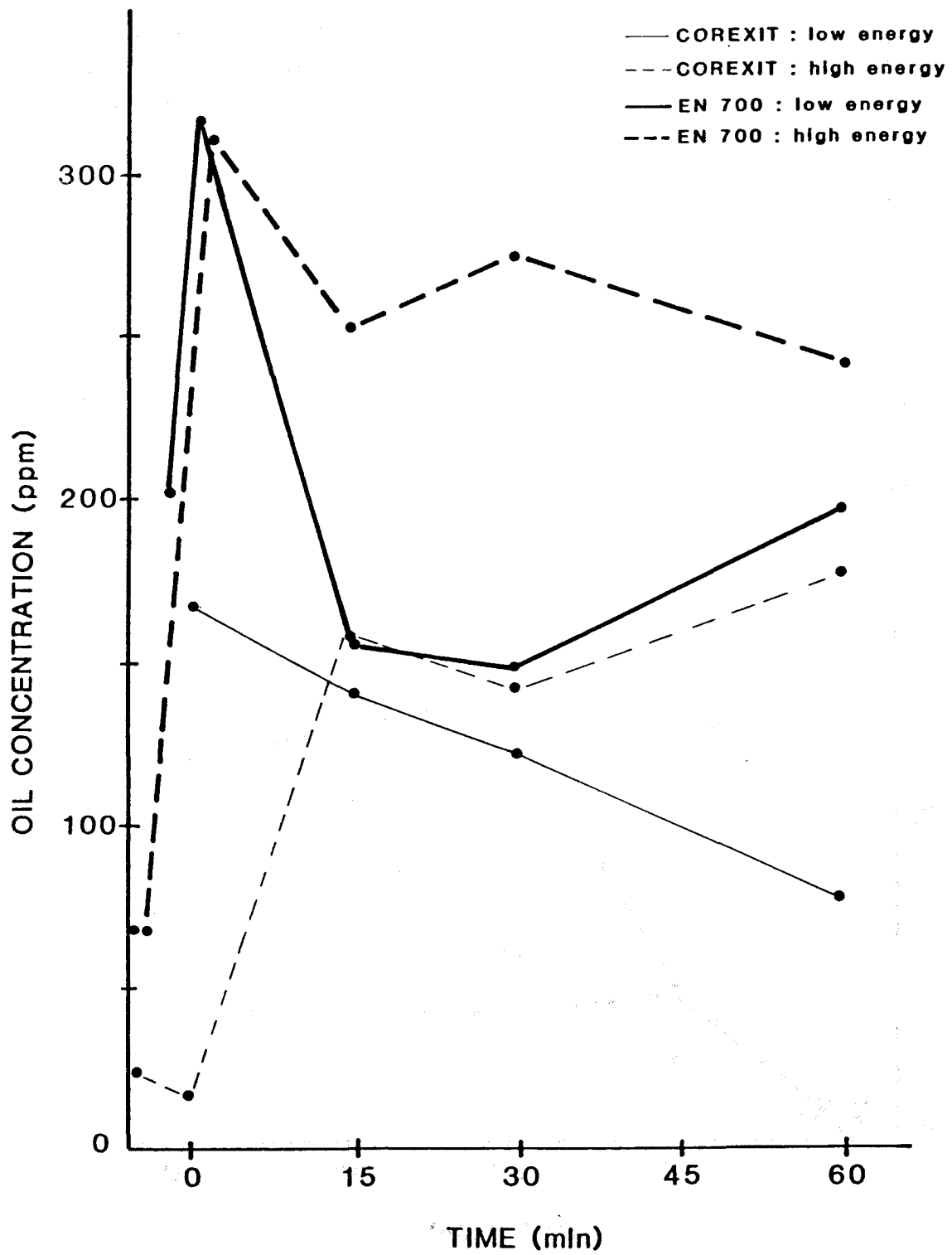
### TEST CONDITIONS

Weathered oil , 0.5 mm , Bottom



### TEST CONDITIONS

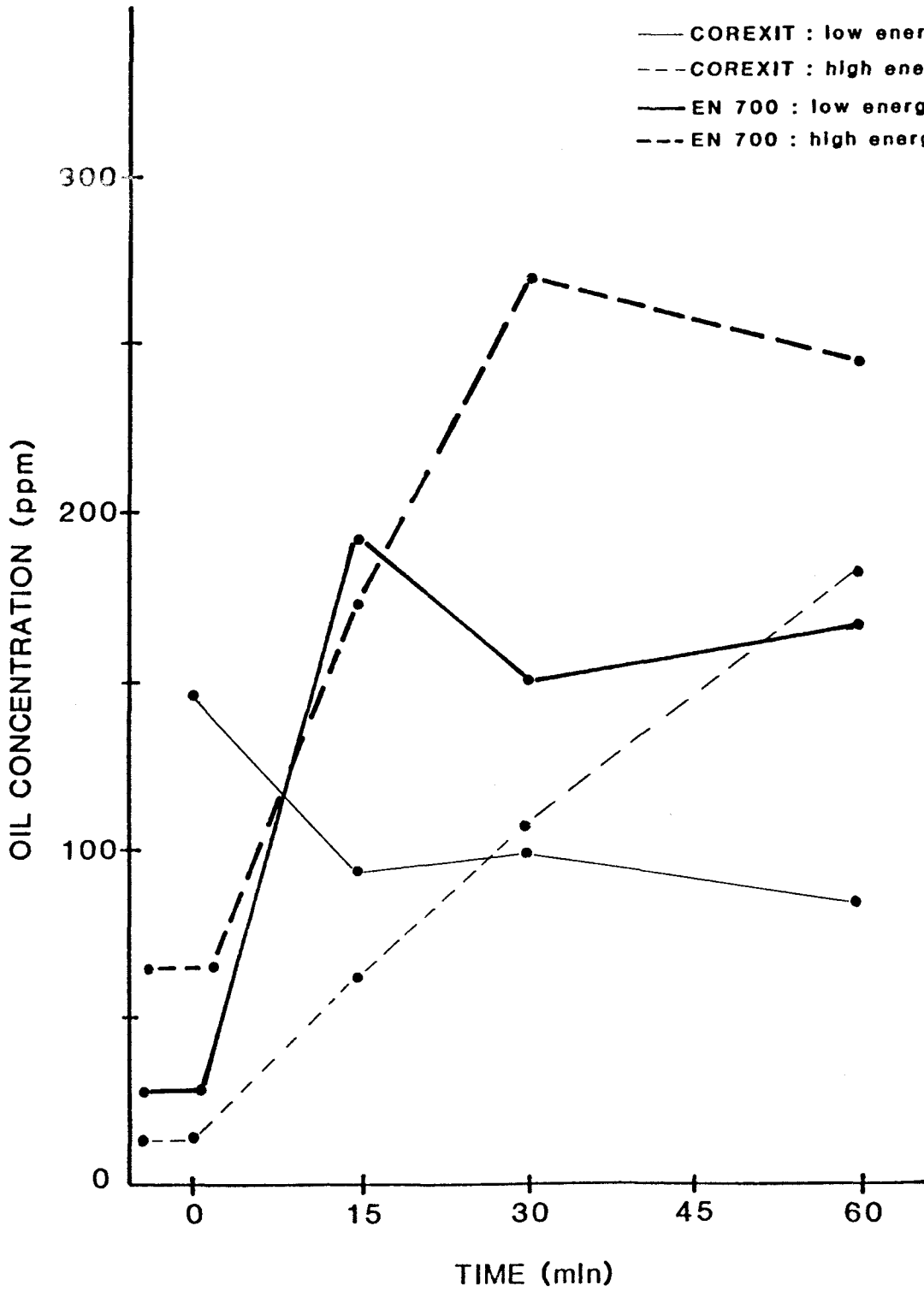
Fresh oil ; 0.5 mm ; Top



### TEST CONDITIONS

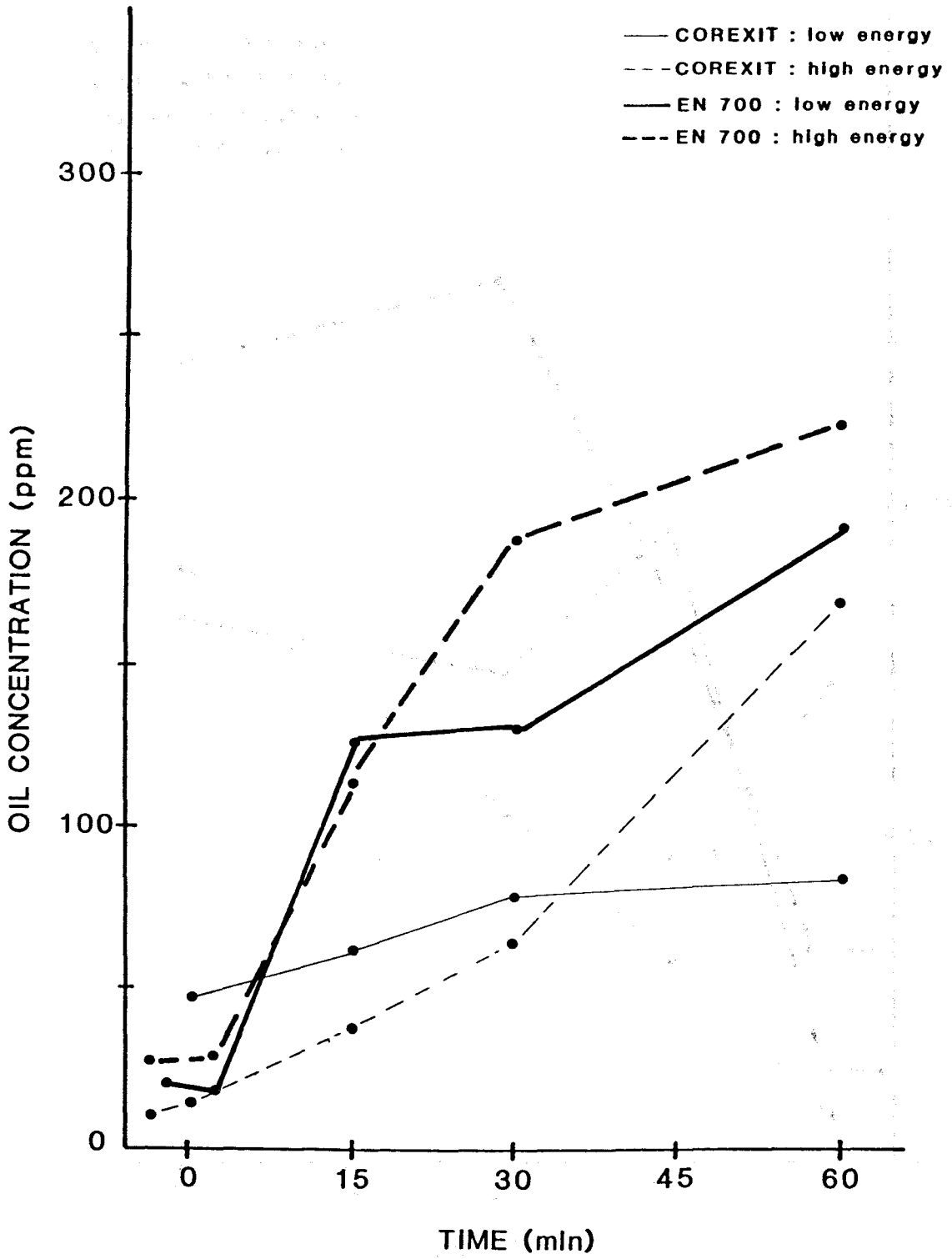
Fresh oil , 0.5 mm , Middle

- COREXIT : low energy
- - - COREXIT : high energy
- EN 700 : low energy
- - - EN 700 : high energy



TEST CONDITIONS

Fresh oil , 0.5 mm , Bottom



## **2) Oil Slick Thickness and Areas**

Estimates of oil slick thicknesses and areas made during the test program are summarized in the following table.

Oil Thickness and Surface Slick Area Estimates - Raw Data

Run	Time of Sample (meas. from disp. applic.)	Slick Area Estimate (m <sup>2</sup> )	Thickness by Extraction (microns)	Surface Oil Vol. (by extraction) (litres)	Thickness by Weight (microns)	Surface Oil Volume (by weight) (litres)
1	not measured					
2	-9	4.4	679	3.0	----	----
3	not measured					
4	-11	4.4	2182	7.6	----	----
5	-10	4.4	----	----	500	2.2
6	not measured					
7	-3	4.4	----	----	378	1.7
8	-2	4.4	----	----	281	1.2
	15	4.4	----	----	311	1.4
9	-4	5.1	517	2.6	193	1.0
	15	4.4	546	2.4	336	1.5
10	-3	2.9	484	1.4	285	.8
	22	2.2	627	1.4	469	1.2
11	-3	5.9	314	1.8	179	1.0
	15	0.7	251	0.2	181	0.1
12	-2	3.7	857	3.2	632	2.3
	15	1.5	314	0.5	198	0.3
13	-1	2.9	800	2.3	610	1.8
	18	.3	301	0.08	188	0.05
14	-2	3.7	677	2.5	490	1.8
	15	2.9	694	2.0	579	1.8
16	3	2.9	808	2.4	678	1.3
	17	2.9	623	1.8	446	2.0
17	-6	4.4	681	3.0	460	2.0
	19	2.2	1038	2.3	866	1.9
18	-1	4.4	1400	6.2	971	4.3
	16	5.9	809	5.1	704	4.1

### **3) Turbulence Measurements**

The values recorded by Canpolar's turbulence probe to measure the mixing energies used during the testing are presented in the following tables.



### High Energy

	<b>Probe Pair</b>	<b>V<sub>P<sub>o</sub></sub></b>	<b>V<sub>T<sub>o</sub></sub></b>	<b>V<sub>P</sub></b>	<b>V<sub>T</sub></b>	<b>E<sub>T</sub> x 10<sup>-4</sup></b>
<b>1</b>	<b>1-4</b>	<b>1.0</b>	<b>4.0</b>	<b>.81</b>	<b>3.4</b>	<b>11.7</b>
<b>2</b>	<b>2-4</b>	<b>.91</b>	<b>3.5</b>	<b>.68</b>	<b>1.8</b>	<b>6.8</b>
<b>3</b>	<b>1-3</b>	<b>.83</b>	<b>2.9</b>	<b>.68</b>	<b>1.8</b>	<b>3.5</b>
<b>4</b>	<b>2-4</b>	<b>.80</b>	<b>3.8</b>	<b>.62</b>	<b>2.1</b>	<b>5.4</b>
<b>5</b>	<b>2-5</b>	<b>.97</b>	<b>3.8</b>	<b>.77</b>	<b>2.3</b>	<b>9.7</b>
<b>6</b>	<b>1-2</b>	<b>1.0</b>	<b>3.4</b>	<b>.83</b>	<b>2.2</b>	<b>9.0</b>
<b>7</b>	<b>2-3</b>	<b>.90</b>	<b>3.1</b>	<b>.70</b>	<b>1.5</b>	<b>5.1</b>
<b>8</b>	<b>3-5</b>	<b>.84</b>	<b>3.8</b>	<b>.69</b>	<b>1.7</b>	<b>6.3</b>
<b>9</b>	<b>4-5</b>	<b>.80</b>	<b>3.2</b>	<b>.63</b>	<b>1.6</b>	<b>3.8</b>
<b>10</b>	<b>2-5</b>	<b>1.0</b>	<b>3.7</b>	<b>.76</b>	<b>2.1</b>	<b>10.0</b>
<b>11</b>	<b>3-4</b>	<b>.88</b>	<b>2.6</b>	<b>.69</b>	<b>1.5</b>	<b><u>3.4</u></b>
					<b>Average</b>	<b>6.8</b>

Low Energy

	Probe Pair	$V_{P_0}$	$V_{T_0}$	$V_P$	$V_T$	$E_T$ $\times 10^{-4}$
1	1-4	1.0	4.0	.78	2.6	11.7
2	2-4	.83	3.3	.67	1.9	4.6
3	1-3	.82	3.6	.65	2.2	5.2
4	2-4	.78	3.4	.61	1.7	4.0
5	2-5	1.0	3.3	.72	1.7	8.0
6	1-2	1.0	4.1	.73	2.6	12.3
7	2-3	.90	2.7	.67	1.2	3.9
8	3-5	.82	3.7	.64	1.3	5.5
9	4-5	.79	3.3	.61	1.5	3.9
10	2-5	1.0	3.3	.74	1.3	8.0
11	3-4	.87	2.3	.68	1.1	<u>2.6</u>
					<b>Average</b>	<b>6.3</b>