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Guidelines on the Use and Acceptability of Oil Spill Dispersants

2nd Edition

Canada

Regulations, Codes and Protocols
Report EPS 1-EP-84-1
Environmental Protection Programs Directorate
March 1984

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GUIDELINES ON THE USE AND ACCEPTABILITY OF OIL SPILL DISPERSANTS

2nd Edition

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Environment Canada

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NOTICE

Any comments regarding the contents of these guidelines should be directed to:

Dr. F.S. Abbott
River Road Environmental Technology Centre
Environmental Protection Service
Environment Canada
Ottawa, Ontario
K1A 1C8

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S'adresser à la:

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FOREWORD

Since the publication of "Guidelines on the Use and Acceptability of Oil Spill Dispersants" in 1973 (Report EPS 1-EE-73-1) a considerable body of knowledge on the use and testing of oil spill dispersants has developed. This new information has been incorporated into the present document.

Basic policy expressed in the original guidelines has not been greatly modified. Except in extreme emergency the permission of Environment Canada or competent provincial authorities is required prior to dispersant use. Dispersants must meet stringent criteria for toxicity, effectiveness, contents and labelling. Situations where dispersants should be considered as an appropriate countermeasure have been increased and described in greater detail. Situations not amenable to the use of dispersants have been specified in detail. The procedure for placing a dispersant on Environment Canada's accepted list have also been set out. Effectiveness and toxicity testing protocols have been considerably modified in the light of new information.

A major consideration in establishing guidelines for dispersant use in Canada at present is that field experience in their application and effectiveness under conditions typical of Canadian waters is limited. Further, there is a corresponding lack of field experience concerning the impact of dispersants and dispersed oil on marine ecosystems. Although laboratory and small scale tests can provide much information, it is recognized that practical information can only be obtained through experience gained under field operating conditions. Given this situation, the On-Scene-Commander* should, in making decisions about dispersant use, take into account the considerable value of the experience gained. This is not to imply that dispersants should be used indiscriminately, but it does imply that dispersant use should be permitted when:

(i) environmental conditions indicate that dispersant use would reduce the effects of spilled oil;

(ii) dispersants can be applied using accepted techniques in defined dosages; and

(iii) the treated area will be observed and sampled to assess the effectiveness and impact of the dispersion process. This is very important.

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* In the context of these guidelines, the On-Scene-Commander is the person in charge of the cleanup operation.

In cases where the above conditions cannot be met, it may still be appropriate to apply dispersants to limited selected areas of oil to provide "treated" and "control" areas, thus permitting a scientific approach to the acquisition of information.

These guidelines will be revised in the light of experience gained under actual spill conditions. Thus, it is desirable that operators be prepared during this "learning period" to use dispersants and to document the results of field applications in order that the role of chemical dispersants as an oilspill countermeasure can be better evaluated.

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ACKNOWLEDGEMENTS

These revised guidelines are the result of the work of the Ad Hoc Committee for the Revision of the Guidelines on the Use and Acceptability of Oil Spill Dispersants chaired by Dr. F.S. Abbott, Head of Biology Section, Environmental Emergencies Technology Division, Technical Services Branch, Environmental Protection Service, Environment Canada. Members of the committee were drawn from involved government departments, academia and industry. Particular gratitude is expressed to Dr. D. Mackay who chaired the sub-committee on effectiveness testing and Dr. P. Wells who chaired the sub-committee on toxicity testing.

1 INTRODUCTION

These guidelines are provided for the information of On-Scene-Commanders*, contingency planners, operators involved in oil spill countermeasures and manufacturers of oil spill dispersants. They are intended to advise when and where dispersants should be considered for use, and the minimum requirements for acceptance of a dispersant. General criteria for making dispersant use decisions are included.

Oil spills on water can have adverse effects on aquatic life, coastal resources, and human beings. When selecting countermeasures to deal with spilled oil, the first consideration should be physical containment and removal of the oil from the water. In some situations, chemical dispersion of the oil into the water can also be an effective countermeasure. In most situations it is essential that the environmental advantages and disadvantages that may result from the use of dispersants be carefully scrutinized to ensure that a net environmental benefit will be achieved.

Dispersants are chemical formulations that promote the dispersion of oil into water. They are distinct from rig washes, bilge cleaners, etc., and they are intended for use in larger quantities. The active ingredients are surfactants that lower the interfacial tension between oil and water. With the application of mixing energy the oil breaks up into small droplets and becomes distributed into the water column as an oil-in-water dispersion. Ultimately the dispersed oil droplets are transported from the spill site and degraded by natural processes in the sea.

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* In the context of these guidelines, the On-Scene-Commander is the person in charge of the cleanup operation.

2 GUIDELINES FOR THE USE OF DISPERSANTS

2.1 Requirements

(a) The On-Scene-Commander, in consultation with appropriate agencies and personnel, will determine the priorities for protection in each spill incident and the use of dispersants is subject to these priorities.

(b) Except in the case of extreme emergency where, for example, there is an imminent threat to human life, chemical dispersants should be used only with the approval of Environment Canada. Furthermore, because of various pieces of legislation, the use of dispersants may be subject to the requirements of the provinces or territories concerned. Chemical dispersants can then be used under competent direction and in accordance with recommended techniques.

(c) Only dispersants satisfying the acceptability criteria for effectiveness and toxicity, as set forth in Sections 3 and 4 of these guidelines, may be used.

(d) All uses of chemical dispersants should be documented as outlined in these guidelines.

2.2 Conditions for Use

Dispersants may be used

(i) when their use will prevent or reduce hazard to human life or safety or reduce substantial hazard to property;

(ii) when their use will minimize the overall environmental impact of an oil spill to aquatic life or habitats, taking into account that trade-offs may be necessary.

2.3 Restrictions on Use

Dispersants generally should not be used

(i) in waters containing major fish or shellfish populations, or in waters that are key breeding, feeding, or migrating areas for aquatic life which may be damaged or reduced in market value by exposure to dispersants and/or dispersed oil;

(ii) in any waters where such use may adversely affect surface water usage, i.e., drinking water or industrial use;

(iii) where eventual dilution of the dispersed oil is limited either because the water exchange is slight or because the total volume of water is relatively small;

(iv) on natural shorelines;

(v) under conditions where the dispersant would be ineffective.

2.4 Discussion

2.4.1 Advantages/Disadvantages. Some of the advantages of dispersing oil into the water are:

(a) The removal of surface oil slicks may reduce damage to aquatic birds, sea mammals, shorelines, waterfront installations and fishing equipment.
(b) Dispersed oil in the water column is subject to subsurface currents which may carry it away from areas threatened by a floating slick.
(c) By increasing the proportion of oil that goes into dispersion in the water column, where rapid dilution may quickly reduce the concentration, dispersants can reduce the overall impact of the spill.
(d) The natural rate of biodegradation of oil may be enhanced.
(e) The cleaning of oiled surfaces or work areas may be facilitated through the application of dispersants followed by water flushing.
(f) Dispersants can eliminate the sheen which often remains on water when mechanical removal has had limited success.

Some of the disadvantages of dispersing oil into the water column are:

(a) The accelerated transfer of oil into the water column may result in localized concentrations of the oil/dispersant mixture that can be toxic to aquatic life.
(b) The dispersant itself or the oil/dispersant mixture may prove to be toxic to specific organisms in specific locations, if the particular conditions result in sufficiently high concentrations of dispersants or oil contacting such organisms.
(c) The effective use of dispersants may eliminate the possibility of future recovery of the oil by some mechanical means.

2.4.2 Decision-Making Considerations. Taking into account the above advantages/disadvantages of the effective use of oil spill dispersants, chemical dispersion is recognized as one of several tools at the disposal of those responsible for managing oil-spill countermeasures and should be used when the advantages outweigh the disadvantages. Indiscriminate and unauthorized use is dangerous and illegal.

In reaching the decision to use dispersants many difficult trade-offs must be considered. The decision tree shown in Figure 1 is offered as an aid to the On-Scene-Commander and persons advising him. Various considerations bearing on steps A and B are discussed in more detail on subsequent pages.

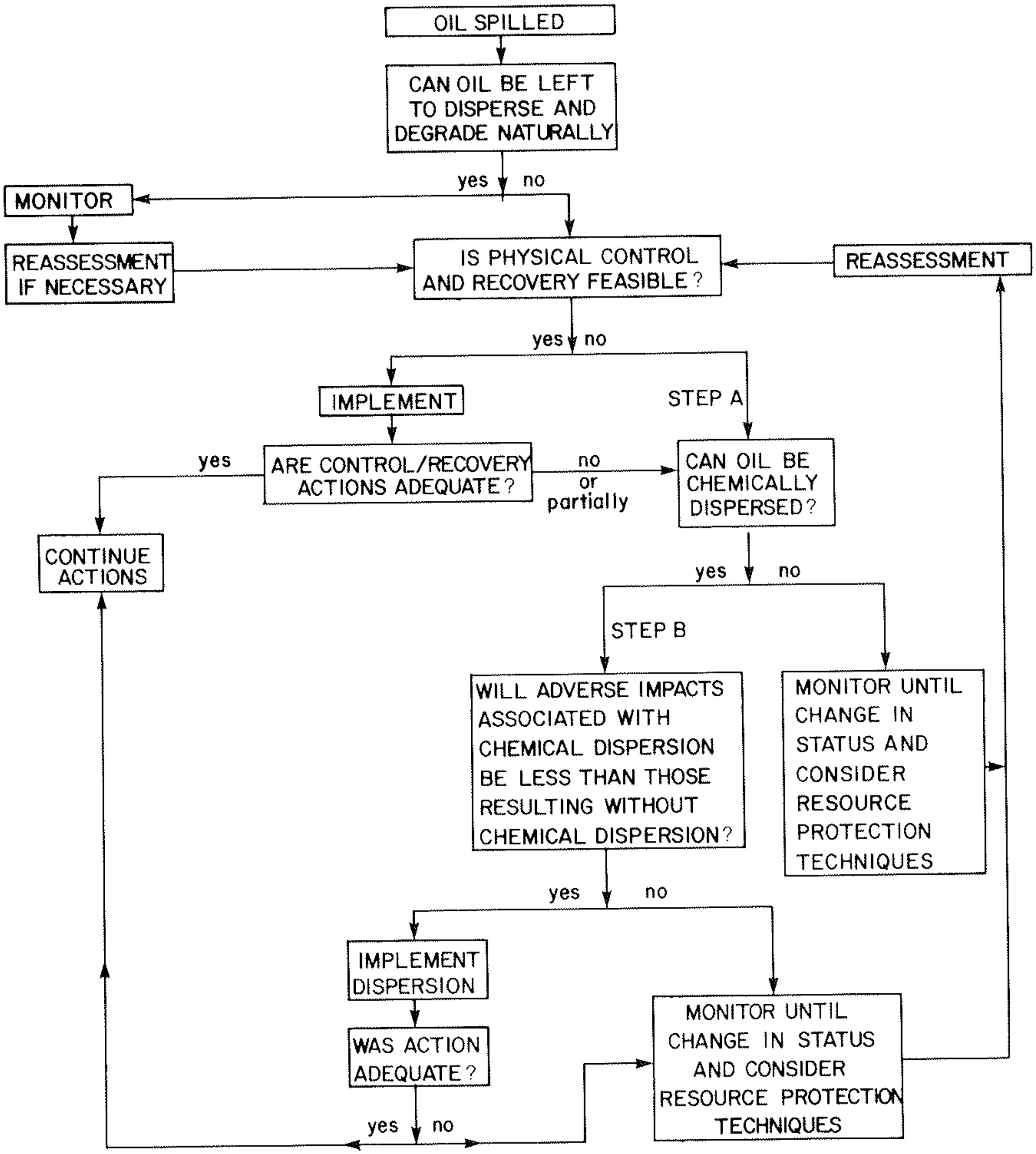

FIGURE 1 DISPERSANT USE DECISION TREE

Assuming that mechanical recovery of the oil has been eliminated as a primary countermeasure, the overriding consideration must be that the use of dispersants will result in an improvement in safety or a reduction in overall environmental impact.

Step A considerations

1) Viscosity. The effectiveness of dispersants often diminishes with increasing oil viscosity. Because the viscosity of fresh crude oils increases with the formation of water-in-oil emulsions and other weathering processes, the decision on whether to use dispersants must be made without delay. Low temperature also increases the viscosity of oil. Since 1970, most marine oil spills in Canada have been of No. 6 fuel oil, a product of such high viscosity that dispersant use is normally of little value. Less viscous refined products usually evaporate readily and disperse naturally. Modern dispersants are most appropriate with low to medium viscosity oils, preferably as soon as possible after the oil has been spilled onto the water.
2) Turbulence. While numerous dispersants in various formulations are on the market, the efficiency with which they increase the rate of oil-in-water dispersion is significantly influenced by the availability of mixing energy. This may be applied artificially through the use of a ship's propeller wash and/or breaker boards or provided naturally by wave action. Dispersants are least effective in calm water.
3) Application rate. A dispersant should be applied at the rate recommended by the manufacturer. If this rate cannot be achieved with the equipment available, the use of the dispersant must be rejected. Oil that has been insufficiently treated with dispersants may be unmanageable by other countermeasures.
4) Salinity. Dispersants currently accepted for use in Canada are formulated for seawater. Their effectiveness is decreased when applied to oil spills on fresh or brackish waters.
5) Effectiveness. Dispersant users should bear in mind that dispersants rarely if ever cause total disappearance of spilled oil from the water surface.

Step B considerations

1) Safety and human health.

   a. Fire - Spills involving volatile fluids such as fresh crude oil and some refined products present the potential for fire or explosion and any human activity in the immediate area may increase the danger to life and property. Dispersant application may promote the entry of volatile hydrocarbons into the atmosphere and appropriate precautions are necessary.

b. Work area cleansing - The use of steam with its superior cleaning action followed by oil collection using sorbents or mechanical means is recommended.

c. Water supplies - Dispersants should not be used in the vicinity of drinking or industrial water supply intakes. They are ineffective in freshwater, and even small amounts of oil or dispersant render water unusable for industrial purposes or drinking.

2) Environmental

a. Confined waters - If the water body is confined and the volume of oil is large, the capacity of the water column to dilute or degrade the dispersed oil below toxic levels in a short time may be exceeded. Dispersants should not be used under these circumstances.

b. Offshore - Oil spills occurring well out to sea with little potential for causing environmental damage or coming ashore should be left to disperse and degrade naturally. The application of dispersant over large expanses of water will affect only the rate of dispersion and is justified only under special circumstances such as the local presence of marine birds on the surface. However, where there is potential, based on trajectory models, etc. for some or all of an offshore oil spill to enter a nearshore area or affect a shoreline, consideration should be given to dispersing oil that appears to be moving towards land. It may well be that less environmental impact will result over the long term if the oil is dispersed in an open water environment, where adequate dilution and subsurface currents will readily reduce any toxic concentration much faster than if the same oil slick beached or were dispersed nearshore or in confined waters.

c. Shorelines - Where shoreline restoration is warranted by environmental or aesthetic considerations, conventional mechanical recovery is generally more efficient than dispersant use. In exposed locations natural processes of wave and ice scouring may effectively remove the oil nearly as quickly as if dispersants had been used.

d. Nearshore - Nearshore oil slicks probably present the most difficult dilemma in deciding whether to use dispersants. The decision involves particularly difficult trade-offs, and careful consideration of biological, economic and aesthetic factors. Removing oil from the water surface usually reduces the hazard posed by oil to shorelines and property, as well as the danger to biological resources utilizing the shoreline, intertidal and subtidal areas, and the water surface. Further, it reduces problems associated with cleaning up beached oil and the long-term chronic leaching of oil off beaches into a nearshore environment. These benefits must be carefully balanced against the possible transient threat to some biological resources posed by the dispersed oil. It should be recognized, however, that under certain conditions dispersants may alter the trajectory of the oil by removing it from the influence of surface currents and wind, and into the influence of subsurface currents which may prevent the oil from penetrating the nearshore or shoreline environment. Dispersant use is acceptable when their use will not cause environmental damage in nearshore waters and will mitigate the damage caused by stranding oil.

2.5 The Role of Government Agencies

In Canada the use of dispersants requires permission from Environment Canada and, in some cases, competent provincial or territorial authorities. Only dispersants on Environment Canada's accepted list are to be used. Other federal departments and services have responsibilities relative to the use of chemical dispersants in the marine environment. They, with the Environmental Protection Service (EPS), Environment Canada, provide scientific advice and recommendations concerning the use of dispersants. The role of EPS includes the coordination of inputs from involved federal and provincial agencies and the provision to the On-Scene-Commander of environmental recommendations on the use of oil spill dispersants. In each spill incident, except in extreme emergencies, the On-Scene-Commander will seek the approval of the EPS Regional Office prior to the decision to use dispersants. Appendix II is a contact list for the Environmental Protection Service across Canada.

2.6 Report of Use

Existing laboratory methods for predicting the effectiveness and toxicity of dispersants in the field are not completely satisfactory. Accordingly, detailed reports on all instances of dispersant use are required. A reporting format is shown in Table 1. These reports will be used in developing future recommendations concerning dispersants, application methods, effectiveness and possible environmental effects. Environment Canada wishes to encourage development in dispersant formulations, application and mixing methods, and evaluation procedures. The present guidelines will be revised as new knowledge and technology become available.

TABLE 1 CHECK LIST OF REQUIRED INFORMATION TO DOCUMENT DISPERSANT USE

(a) Details of the Spill
- Location
- Source and Type of Oil
- Appearance of the Oil
- Date and Time of Spill
- Estimated Amount, Slick Area and Thickness

(b) Environmental Conditions
- Air and Water Temperature
- Water Depth
- Wind, Waves and Currents
- Shoreline type and degree of exposure

(c) Dispersant Applications
- Rationale for Dispersant Use (biological, economical, aesthetic, etc.)
- Amount Used
- Application Rate
- Amount of Oil Treated
- Type of Dispersant(s)
- Application and Mixing Methods (equipment, manpower, time)
- Date and time application commenced and ceased

(d) Observations
- Visual, photographic, remote sensing, sample analysis results
- Observations on the fate of dispersed oil (spreading, disappearance, resurfacing, etc.)
- Observations hours/days after the application
- Estimated amount of oil left on the water surface
- Any observations on effects of the dispersed oil (marine birds, fish, shorelines, vegetation

(e) Were other countermeasures used? Were they successful?

Reports should be addressed to:

Regional Environmental Emergency Coordinator
Environmental Protection Service
Regional Office*

*Please refer to Appendix II for addresses of the various regional offices.

3 GUIDELINES ON ACCEPTABILITY OF DISPERSANTS

3.1 Introduction

The approach prescribed in these guidelines for acceptance of a dispersant is first to test whether the dispersant achieves a minimal level of effectiveness; a pass/fail criterion applies. Secondly, the dispersant is subject to a pass/fail criterion for toxicity. If it passes both tests the dispersant will be accepted. The sequence is set out in Figure 2.

In the event that the dispersant is very effective (thus little dispersant will be required), but fails the toxicity test, a second toxicity test may be conducted at a concentration dependent on the effectiveness. If it passes this second test it will be accepted and may be used at the correspondingly reduced application rate.

The link between effectiveness and toxicity prevents discrimination against dispersants that are highly effective but "moderately" toxic, and yet may be acceptable because relatively less dispersant is required or because its use may save a critical habitat from oil exposure. Products failing the effectiveness test are not accepted and are not tested for toxicity.

The effectiveness test is conducted using a standard oil and the submitted dispersant in the Mackay-Nadeau-Steelman apparatus under prescribed conditions which are described later. The pass/fail criterion is that 50% of the test oil must be dispersed under the prescribed conditions at an application ratio no greater than 1:10 (i.e., at a dispersant dosage of less than or equal to 10 volumes dispersant per 100 volumes of oil). The dosage required to disperse 50% of 100 volumes of oil is designated as D, i.e., D must be less than or equal to 10.

The toxicity test is conducted using fingerling rainbow trout exposed to solutions of dispersant and a reference toxicant in water for 96 hours under conditions which are described later. The first toxicity test is at a concentration of 100 mg/L dispersant. The passing criterion is that the median lethal time (LT_{50}) for the organisms exposed to dispersant must exceed 96 hours. The test is based on a maximum likely application rate of 100 L dispersant per hectare. If the dispersant is distributed uniformly in a 1 m depth of water the concentration will be 10 cm^3 per m^3 or approximately 10 mg/L*. A "factor of safety" of 10 is applied to give the criterion of 100 mg/L.

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*Assumes specific density of dispersant is 1 g/cm^3.

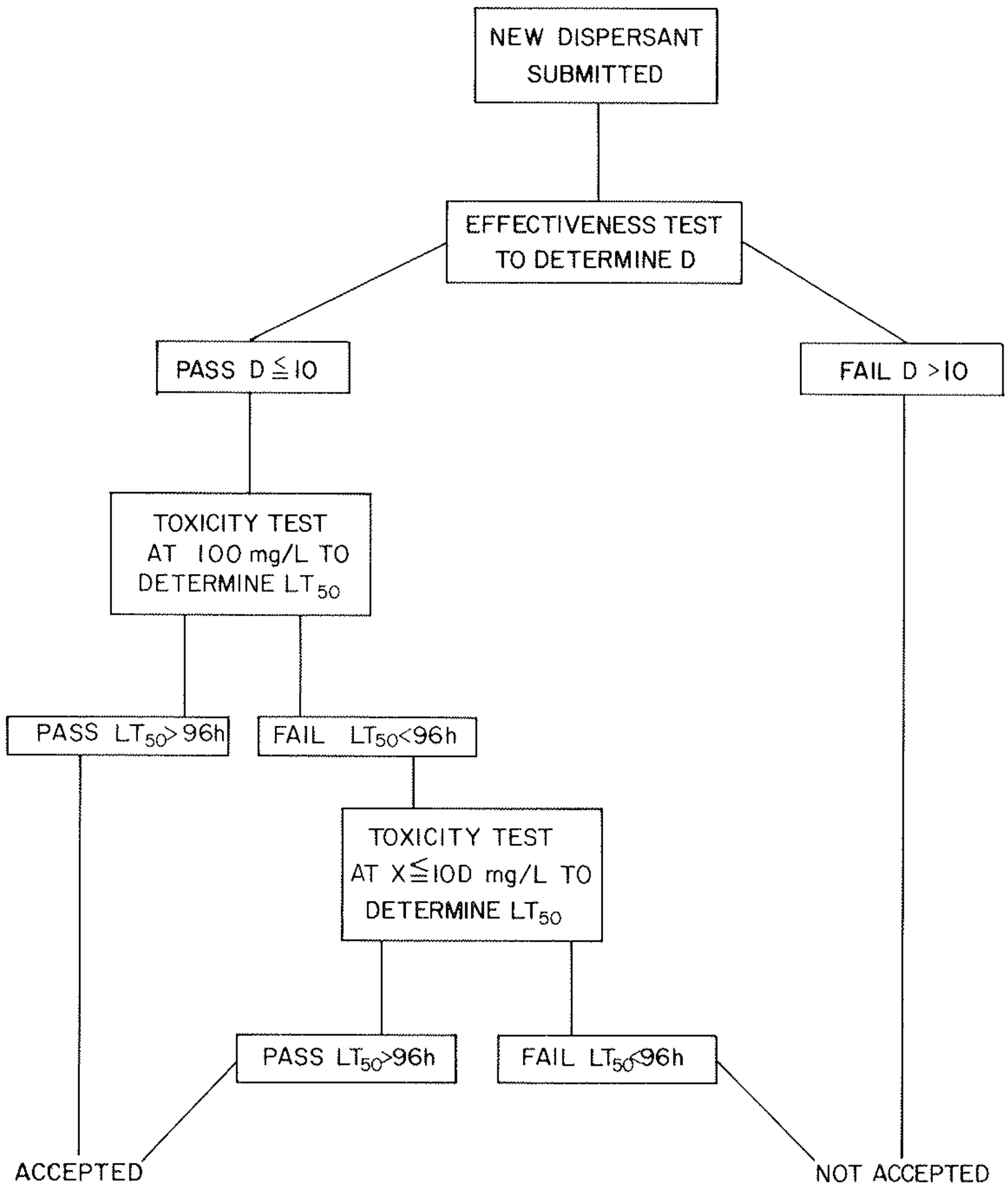

FIGURE 2 DISPERSANT TEST SEQUENCE

D is the dosage of dispersant required to disperse 50% of 100 volumes of oil in the MNS apparatus. An LT_{50} is a median lethal time at a designated concentration of test substance.

It is recognized that some new dispersants may be highly effective, i.e., D may be less than 10. Thus the application rate and dispersant concentration will be correspondingly lower. The toxicity test concentration may thus be lowered to a value of X mg/L in proportion to the reduction in D.

If, for example, D is 1, the maximum application rate becomes 10 L per hectare and the average concentration to a depth of 1 m becomes 1 mg/L. Using the same factor of safety (10), the toxicity test value X is 10 mg/L. The passing criterion at the reduced concentration is unchanged; the LT_{50} must exceed 96 hours.

In both the effectiveness and toxicity tests prescribed replication of tests must be conducted and the results obtained with the reference toxicant must fall within prescribed limits. All experimental data must be reported and data analyses must be conducted by approved methods.

For practical reasons the toxicity test is conducted on the dispersant alone with no oil present.

The criteria for acceptance have been designed to ensure that dispersants used in Canadian waters meet standards of effectiveness and toxicity. It is recognized that exceptional situations may arise in which modified acceptance criteria are appropriate. Environment Canada will consider such approvals on an individual basis, taking into account all relevant information supplied by the applicant.

Quantities of the standard oil may be obtained from Environment Canada. The reference toxicant is dodecyl sodium sulphate and may be obtained from scientific supply houses. Fingerling rainbow trout are widely available.

3.2 Effectiveness Testing Protocol

The Mackay-Nadeau-Steelman test is described in detail in a report by Mackay and Szeto (1981). The test apparatus and procedure is generally as described in that report but some minor changes have been made.

Apparatus. The glass vessel shown in Figure 3 is available from scientific supply houses and is approximately 310 mm in external diameter by 310 mm high. The walls are 5 mm thick. It is located in a temperature controlled bath containing 30-40 litres of water.

A lid is provided consisting of a 12.7 mm (0.5 inch) thick plexiglas sheet as detailed in Figure 4. The plexiglas lid is fitted with a 2 mm thick soft rubber gasket to seal it against the glass vessel. Four locating blocks are glued to the lid to ensure reproducible location on the vessel. The lid is drilled to accept: (i) a thermometer, (ii) a port for addition of oil and dispersant (closed by a rubber bung when not in use), (iii) a

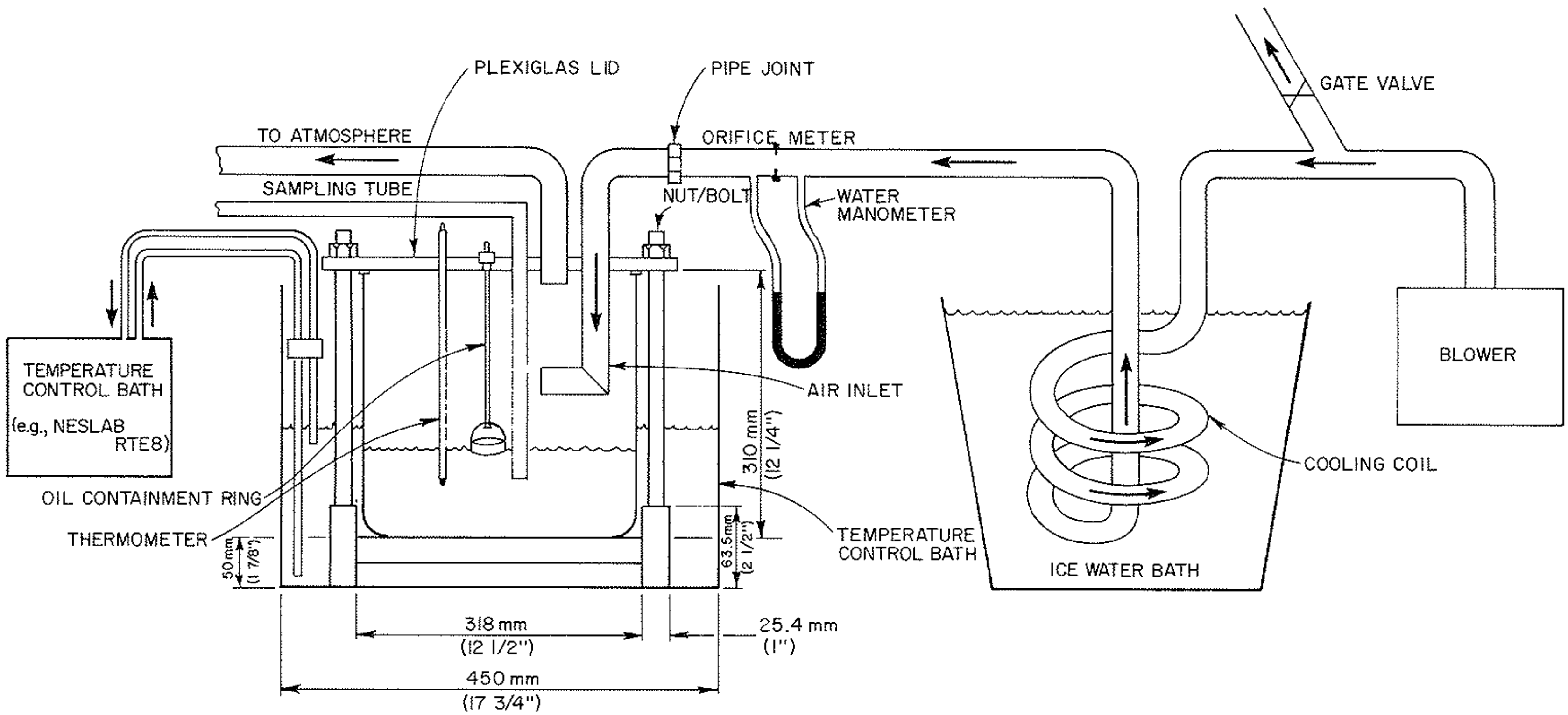

FIGURE 3 GENERAL ARRANGEMENT OF TESTING APPARATUS

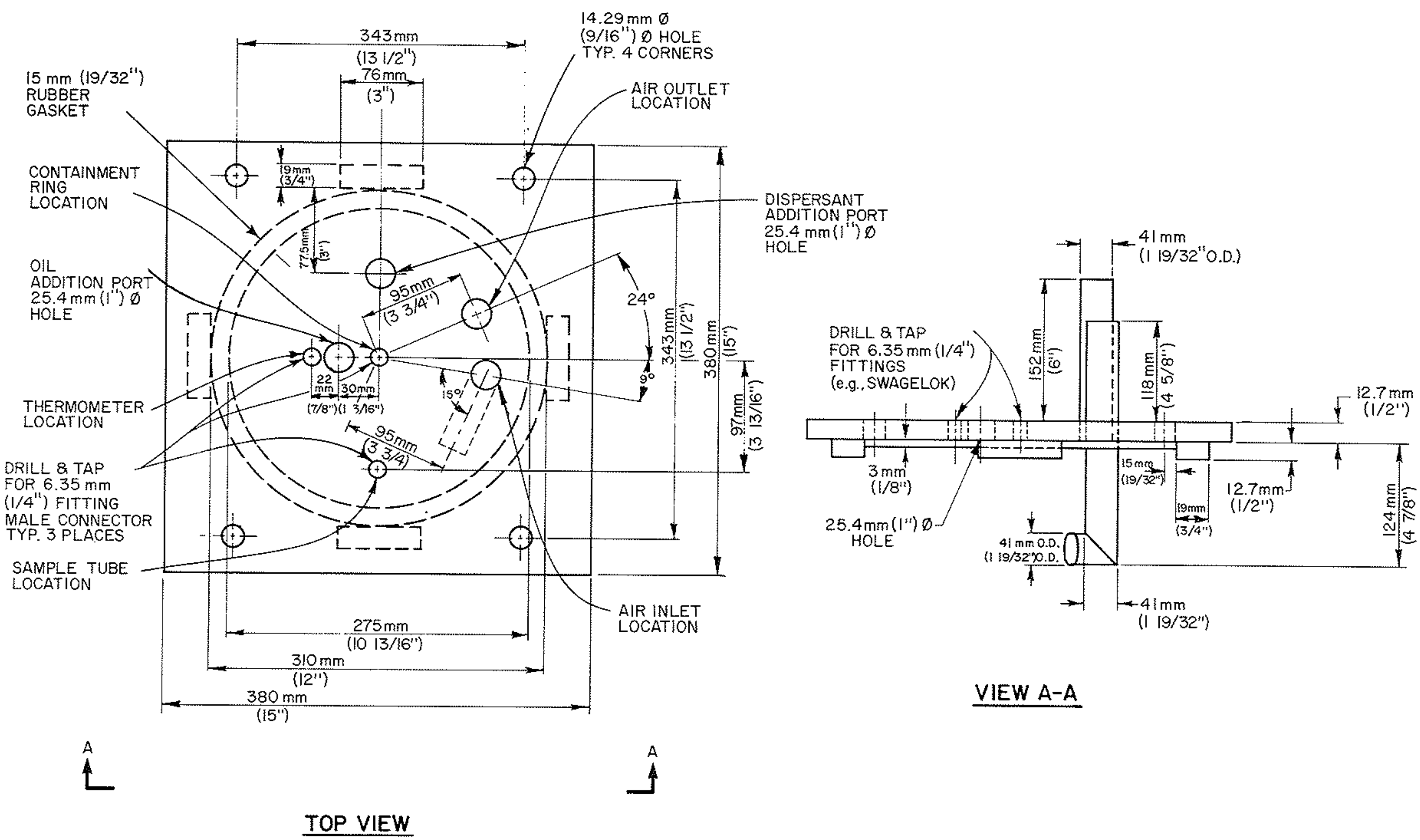

FIGURE 4 DETAILED SCHEMATIC OF PLEXIGLAS LID

fitting to support the containment ring rod, and (iv) an identical fitting to support the glass sampling tube, and inlet and outlet pipes. The lid is drilled to accept 6.35 mm (1/4 inch) fittings (e.g., "Swagelok" fittings). The air flow in and out is provided as shown, with details of the copper tubes as illustrated in Figure 5. The sharp 90° bend in the air inlet pipe was selected because it is more easily specified than a continuous, curved bend. These tubes are a push fit into the plexiglas lid. Epoxy cement may be used to locate them permanently. It is important that the angle and location of the inlet tube be exactly as shown.

An orifice plate (detailed in Figure 5) is used to indicate the air flow rate by pressure drop across a water manometer. This orifice plate differs from that specified in previous reports; it has a standard configuration and a smaller orifice diameter which magnifies the pressure drop by a factor of approximately six.

The oil and dispersant are introduced onto the water surface in a containment ring which prevents the oil from spreading over the water surface and enables the dispersant to be added more reproducibly to the oil. The ring is detailed in Figure 5 and is made of glass sawn from a 70-mm internal diameter tube with a wall thickness of 2 mm. Two holes are drilled halfway between the top and the bottom of the ring to permit the support to be connected with small bolts and nuts. A 6.35-mm (1/4-inch) diameter stainless steel rod supports the ring. Its vertical location is adjustable and it can be locked in place by tightening the fitting. Glass was selected as the containment ring material because the amount of oil adhering to it can be easily seen.

Water sampling is performed through a 6.35-mm (1/4-inch) outside diameter glass tube which is located as shown in Figure 3. The sampling tube is 300 mm long with the inlet located 45 mm below the mean water surface when sampling. A 60 mm long piece of plastic (e.g., Tygon) tubing is connected to the outflow end of the sampling tube to allow another 500 mm long, 6.35-mm (1/4-inch) outside diameter glass tube to be connected. The outflow of this second piece of glass tubing is positioned below the inlet opening of the 300 mm long sampling tube in order to provide a siphon. The outlet of the 500 mm long glass tube is equipped with a stopcock.

Air flow is provided by a blower. A blower that can deliver 10-15 m^3/minute with a back pressure of 30 cm of water is adequate. Some blowers are cooled by the air flow; thus the air emitted may be several degrees warmer than desired. A cooler should be installed in front of the orifice meter and may consist of a coil of copper tubing immersed in an ice-water bath. Air flow is controlled upstream of the cooler. The temperature of the air entering the vessel should be measured and adjusted to within

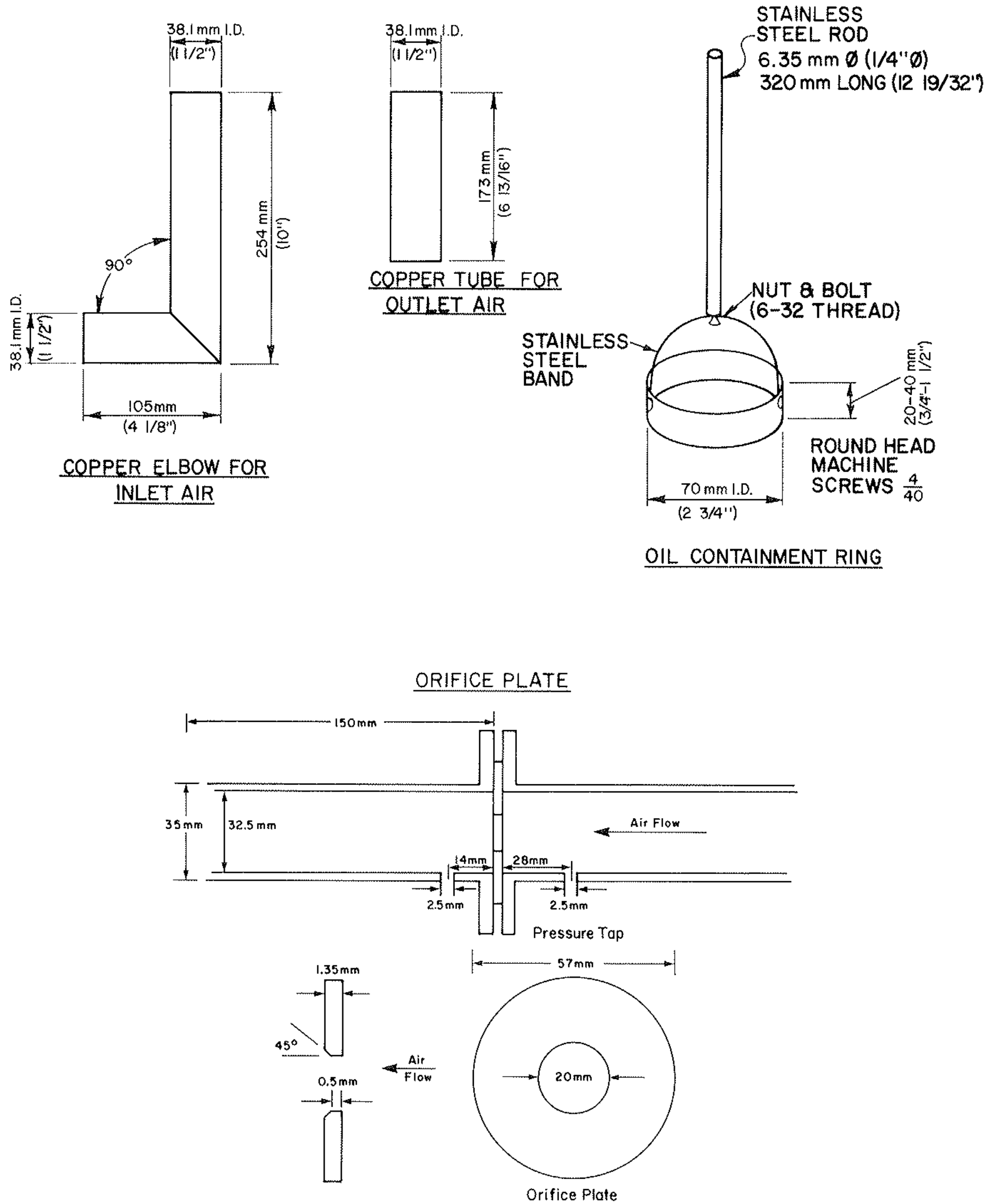

FIGURE 5 DETAILS OF AIR INLET TUBE, AIR OUTLET TUBE, OIL CONTAINMENT RING, AND ORIFICE PLATE

about 1°C of the desired water temperature. Water temperature must be maintained in the range of 0°C to 2°C for the duration of the test.

Dispersant and Oil Addition Techniques. The dispersant and the oil are at 20°C prior to application. The standard test oil is added by a standard 10-mL pipette. Digital pipettes (e.g., Brinkman continuously variable digital pipettes) are used to add the undiluted dispersant to simulate "neat" application by aircraft. Two digital pipette sizes are recommended: (1) a 10-100 µL and (2) a 100-1000 µL. The pipettes or syringes must be calibrated for each oil and dispersant. The oil and dispersant amounts delivered must be measured by weighing before and after delivery, and the volumes estimated from the known liquid densities.

If the manufacturer recommends that the dispersant be added in solution or suspension in seawater (as occurs often when applied from boats), the dispersant delivery system should be modified. The dispersant solution may be pipetted directly onto the oil surface as above, or a spray system may be used. Figure 6 shows a suitable system which consists of two plastic 10-mL syringes bolted back-to-back with one fitted with a plastic nozzle of the type used for spraying plants. The water-dispersant mixture is prepared, drawn into the lower syringe, and delivered by applying pressure to the upper syringe. Some trial and error adjustment of the nozzle is necessary to obtain a spray of the desired dimension. Some dispersants are not fully miscible with water; the syringe should be shaken or inverted frequently to ensure mixing. The results should be reported as volume of dispersant added, not volume of solution.

Test Conditions

Volume of oil	10 mL
Temperature	0-2°C
Turbulence	20 cm water pressure drop
Salinity	33‰

Synthetic Seawater Recipe

NaCl	22.70 g
$MgCl_2 \cdot 6H_2O$	9.88 (46.9% anhydrous salt, i.e., 4.63 g)
Na_2SO_4	3.78 g
$CaCl_2$	1.06 g
KCl	0.64 g
$NaHCO_3$	0.19 g
	38.25 g (33.00 g anhydrous salt)

Make up to 1L with distilled water.

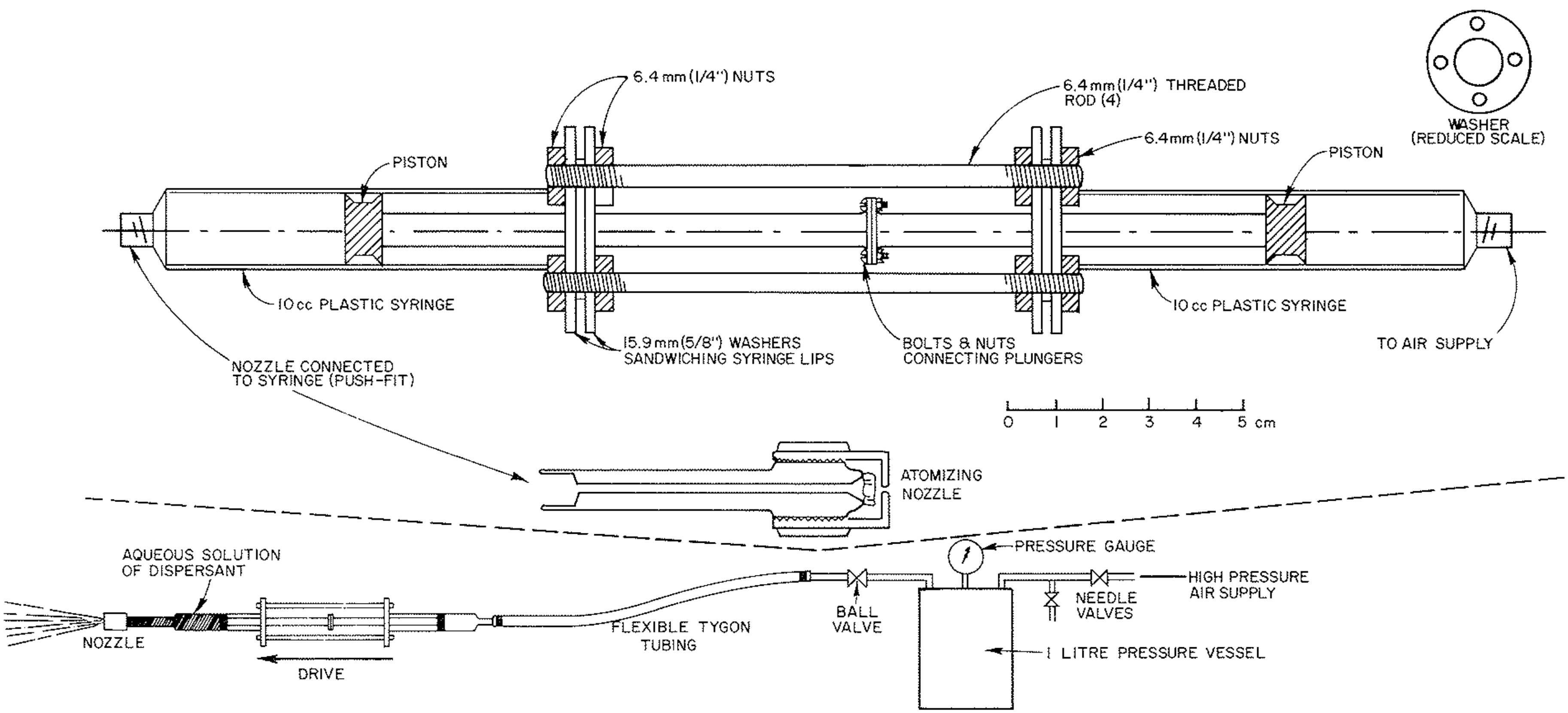

FIGURE 6 AIR SUPPLY SYRINGE-NOZZLE SYSTEM

Test Procedure. Natural seawater or synthetic seawater (6.0 litres) of desired salinity and temperature is added to the clean vessel. The lid is fitted and the containment ring lowered until it is half immersed in the water. The sampling tube is also immersed in the water. The air flow is then turned on and regulated to produce a pressure drop across the orifice plate that corresponds to the desired turbulence or energy level. The system is then allowed to equilibrate until a steady wave motion develops. This may be hastened by operating at a higher air flow rate for a short period and then decreasing the air flow rate down to the desired level. Some oils and dispersants contain compounds that tend to cause wave damping. The amplitude of the waves prior to oil addition, after oil addition and after dispersant addition should be measured approximately by observation using a scale glued to the outside of the vessel wall. The wave amplitude (crest to bottom) should not fall below 3.5 cm. If this occurs a higher air flow rate should be selected until a 3.5-cm amplitude is maintained. Oil is then added to the water surface inside the containment ring, care being taken to ensure that no oil escapes over or under the ring. The dispersant is then added in drops to the oil surface from the pipette, or from the spray nozzle, care being taken to distribute the dispersant drops over the oil surface from a height of approximately 10 mm.

Delivery should take place over a period of 10 to 30 seconds. One minute after starting the dispersant delivery procedure, to allow the dispersant to penetrate into the oil, the containment ring is lifted and the air flow continued for an additional 10 minutes. About 30 seconds after lifting the containment ring, the ring is dipped several times into the water to dislodge adhering oil. The ring is then raised to its maximum extent and clamped into position.

After 10 minutes of agitation (after lifting the containment ring) suction is applied to the sample tube and a 500-mL sample of water and oil mixture is siphoned through the sample tube into a 1 000-mL separatory funnel while the air is still flowing. Prior to taking any sample, about 50 mL of fluid (more than two volumes of the sampling system) is allowed to flow through the sampling system to ensure that a representative sample is obtained. The sampling procedure should take about one minute. After this sample has been taken, the air flow is stopped. The apparatus is then dismantled and cleaned.

Analysis is accomplished by extracting the oil from the 500-mL water sample with three 20- to 40-mL aliquots of spectro-grade methylene chloride. This solvent is selected because of its high extraction efficiency and relatively low mammalian toxicity.

The extract is filtered and diluted to a total volume of either 100 or 200 mL. A suitable UV-visible spectrophotometer is used for analyzing the extract. The absorbance of the extract at a selected wavelength is recorded. The concentration of the test oil in the extract is then determined from a calibration curve prepared by adding known amounts of the oil to methylene chloride. A dispersant blank correction is used to minimize the contribution of the dispersant in the oil analysis. An oil blank (i.e., the amount of oil dispersed without the addition of dispersant) is also performed. The volume percentage of the oil dispersed in the water can then be calculated.

The test program should contain a sufficient number of experiments to locate the effectiveness-dosage curve with the required precision and to obtain an estimate of confidence interval. The results should be presented as the measured volumes of test dispersant (D) required to disperse 100 volumes of oil with an effectiveness of 50%. This quantity is normally obtained by conducting four experiments, in duplicate, spanning the effectiveness range 30-70% as illustrated in Figure 7, in order to obtain a regression line. The 95% confidence interval in dosage necessary to achieve 50% dispersion is also reported.

3.3 Toxicity Testing Protocol

A primary objective of the toxicity test, in combination with the effectiveness test, is to identify dispersants that have a relatively low acute toxicity to aquatic organisms. Existing data on the acute toxicity of conventional dispersants, together with practical considerations, suggest that the rainbow trout is a suitable organism for the test (Doe and Wells, 1978; Wells and Moyse, 1981).

The rainbow trout test is a modified version of the freshwater rainbow trout toxicity test described in Anon. (1973) and Sprague (1973), and prescribed for routine use by Environment Canada (Anon. 1980). The test is simple and scientifically credible. It has a pass-fail "acceptability" criterion based on a one-concentration exposure. It is a practical acute toxicity test which allows comparisons with past Canadian results and produces reliable comparative rankings of dispersants. Rainbow trout are cultured widely, easily obtained, well documented and are an accepted reference test fish (A.P.H.A., 1980; Wells and Moyse, 1981).

The obligatory trout toxicity test examines dispersants alone. It is well recognized that the inclusion of standardized tests using oils, alone and with dispersants, would provide information on the change in toxicity of the hydrocarbons as a result of dispersant application. However, such tests are complicated to conduct and become

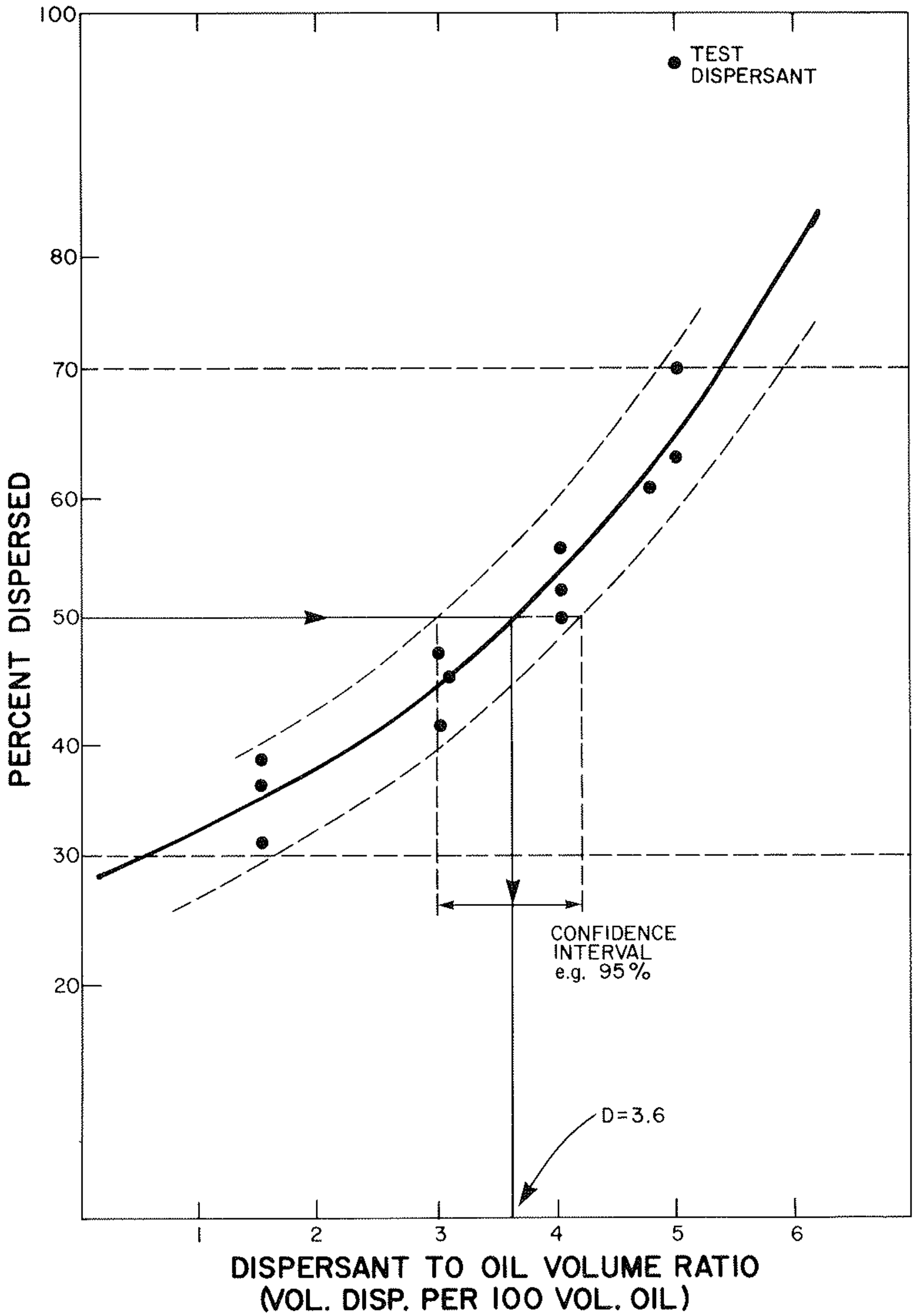

FIGURE 7 ILLUSTRATION OF EFFECTIVENESS RESULTS

subject to misinterpretation. By comparison, the identification of low-toxicity dispersants can be accomplished through a simple "screening" toxicity test on the dispersant alone.

The toxicities of biodegradation products of dispersants, oil and dispersed oil are not addressed in this protocol. Chronic sublethal toxicities associated with these materials and their breakdown products, alone or in combination with hydrocarbons, are not addressed by the toxicity test.

Because this is a single-concentration test an LT_{50} (median lethal time) at a specific concentration is derived. The test concentration of dispersant is either 100 mg/L or X mg/L, each replicated five times, and run for 96 h at 15°C. Controls include a freshwater control and a reference toxicant, each replicated five times. The test concentration for the reference toxicant, dodecyl sodium sulphate, is 80% of the lowest recorded four-day LC_{50}, i.e., 3.4 mg/L (Pessah et al., 1976). The LT_{50} (median lethal time) in the dispersant treatment must be greater than 96 hours for the dispersant to pass the test. The LT_{50} for the reference material must be four days or greater and survival must be 90% or greater in the control water for the toxicity test to be considered valid. The LT_{50}s are calculated by graphical procedures as in Litchfield (1949). All LT_{50}s must be reported.

Test conditions for the procedure are as follows, adopted directly from Anon. (1980):

(1) Rainbow trout (Salmo gairdneri Richardson) are to be used as the test species.

(2) Only healthy stocks of acclimated fish are to be used.

(3) Individual fish are to weigh between 2 and 10 g and the length of the largest fish should not be more than twice the length of the smallest in the same vessel.

(4) Twenty-five test fish, five in each of five tanks, are to be exposed to the dispersant for up to 96 hours. An equal number of freshwater control and reference toxicant fish are to be exposed to their respective media for the same time period. The test can be terminated when more than 50% of the fish exposed to the dispersant are dead.

(5) The test is rendered invalid and can be terminated if less than 90% of the fish in the control water survive for 96 h. The test must not be terminated before 96 h if mortalities occur in the reference treatments.

(6) For every one gram of fish, there will be at least 1.0 litre of treatment or control water for every 24 hours that the fish are exposed.

(7) The minimum water depth in any test vessel will be 15 cm.

(8) The water used to make up each test solution should be at the saturation level for dissolved oxygen. Dissolved oxygen levels should not fall below 7 mg/L during the test. Aeration should be avoided to prevent stripping the tested products of fractions which may be toxic. If levels drop below 70% saturation, indicating an appreciable oxygen demand by the dispersant or hyperactivity of the fish, gentle aeration at 5.0 - 7.5 cc air/min/L test solution should be started. Note of this aeration should be made in the final report on the dispersant.

(9) The test should be conducted at 15 ± 1°C.

(10) The total numbers of live and dead fish should be observed several times each day up to 96 hours, preferably following a logarithmic time scale. Dead fish should be removed upon observation.

A dispersant passes this standard test for acute lethality to fish if more than 50% of the fish survive the 96 hours of exposure to the dispersant, either at 100 mg/L or at X mg/L, under the standard conditions. The LT_{50} must be greater than 96 hours. A dispersant fails the standard test for acute lethality to fish if 50% or fewer of the test fish survive 96 hours of exposure to the dispersant under the standard conditions. The LT_{50}s in all of the control treatments must be greater than 96 h, as verification of fish health and repeatability of the test.

The following explanatory notes clarify the test methods described above; they should not be construed as eliminating the need for applying sound judgment in the conduct of the tests. The procedure and conditions are very similar to those described in Standard Methods for Examination of Water and Waste Water, 15th edition (A.P.H.A., 1980). The most important elements of the procedure for testing lethality using rainbow trout are described.

(i) Procurement of Fish Stocks. Stocks of healthy trout for use in these tests can be obtained from approved fish hatcheries. Procurement and shipment of disease-free fish must be approved by the Federal Department of Fisheries and Oceans.

(ii) Holding and Acclimation of Fish. Fish should be acclimated to the laboratory conditions over a period of at least three weeks prior to testing. The purpose of acclimation is to determine that fish are healthy and to allow them to adjust to the holding conditions. The following describes a number of conditions that are known to be important.

(iii) Water Quality. Characteristics of the freshwater such as hardness, pH, alkalinity, heavy metals, turbidity, chlorine, etc., are very important since they influence survival and health of fish and should be monitored. Chlorine, in particular, is lethal to fish in concentrations as low as 10 $\mu g/L$ and occasionally lower, necessitating the dechlorination of municipal tap waters before conducting the tests. For dechlorination, activated carbon (bone charcoal) filters are suggested. Even after contact with the carbon, residual chlorine and chloramines can remain, particularly during periods of high chlorination of tap water. In most locations these conditions occur following heavy rains or spring and fall turnover of lakes. These problems can be overcome by the use of ultraviolet irradiation subsequent to activated carbon filtering (Armstrong and Scott, 1974). Ultraviolet irradiation offers the added advantage of reducing bacterial levels.

(iv) Holding Facilities. The acclimation tanks and accessories should be made of non-leaching materials, such as glass, porcelain, fibreglass, stainless steel, polyethylene, acrylic, polypropylene, or fibreglass-reinforced polyester. The acclimation tanks should be located away from any physical or chemical disturbances. A constant flow of water through the holding tanks is necessary during acclimation. To prevent overcrowding there should be at least one litre of water for every 10 g of fish in the holding tank (Sprague, 1973). At least 1.4 L of new water should enter the tank every day, for every gram of fish in the tank.

(v) Photoperiod. The photoperiod should be a constant sequence of 14 hours of fluorescent light and 10 hours of darkness. Light intensity at the surface of the fish tanks should be 20 to 30 lux. Ideally, lights should be turned on or off gradually over at least 15 minutes, since abrupt changes in intensity startle and stress fish.

(vi) Aeration in Holding Tanks. Supplementary aeration should be provided if necessary to keep the dissolved oxygen concentration greater than 7 mg/L during acclimation. Supersaturation must be avoided. Glass-filtered, oil-free compressed air is commonly used.

(vii) Cleaning of Holding Tanks. Holding tanks should be kept clean. Designs for tanks which are partially self-cleaning are available. However, periodic siphoning of settled material is usually necessary. Tanks should also be disinfected with an iodophore disinfectant between batches of fish to minimize the occurrence of disease.

(viii) Temperature. Since the temperature of the holding water used during the transfer of fish from the hatchery to the laboratory may be outside the acceptable limits for the test (15 ±1°C), it may be necessary to gradually change the temperature. The temperature may be changed at a rate not exceeding 2°C per day until the desired temperature for acclimation is achieved. The fish should be held at this temperature for the remainder of the three-week acclimation period before being used in a toxicity test.

(ix) Feeding. Feeding the fish twice each day is customary. Very small fish (up to 5 cm fork length) may require additional feedings of small quantities of food every day. Fish should be fed with food containing 30% to 40% protein with some vegetable substances. Many commercial preparations are available. The fish should be fed an amount of food that can be consumed in about 10 minutes, approximately 4% of the wet weight of the fish per day.

(x) Disease Detection and Control. Daily inspection of fish in holding tanks is an essential part of the detection of disease, as "healthy" vs. "unhealthy" conditions should be recognized. The "Handbook of Trout and Salmon Diseases" (Roberts and Shephard, 1974) is a good basic guide to diagnosing and treating disease.

(xi) Test Vessels. Test vessels should be constructed of glass or be polyethylene lined. Liners must be rinsed with dilution water prior to use and should be used only once.

(xii) Definition and Sources of Control Water. Control freshwater is the liquid that is:

(a) used to acclimate the test fish,
(b) used in the control part of the test, and
(c) used to dilute the dispersant and reference toxicant.

Control water used for the above purposes should be taken from the same source. While respecting the criteria described in item (iii) Water Quality, control water may be dechlorinated tap water, spring, lake, or well water which can be supplied with consistent quality.

(xiii) Control Test. A test using control water should be conducted at the same time and under identical conditions as the dispersant sample. The toxicity test is declared invalid if less than 90% of the control fish survive in the control vessels.

(xiv) Start of Test. Prior to commencing the test, the test vessels and accompanying tubing should be cleaned and rinsed with control water. Temperature and dissolved oxygen levels should be checked in the test vessels and the fish randomly introduced. Once all the fish have been introduced, the test commences.

(xv) Randomization. Some form of randomization of fish into test vessels should be employed when transferring them from the acclimation tank.

(xvi) Observations of Mortality. The fish in the test vessels should be observed at approximately 1/2, 1, 2, 4, 8, 24, 48, 72 and 96 hours after commencement of the test. The number of dead fish should be recorded and dead fish removed. Fish are considered dead when, upon a mild mechanical prodding, there are no visible respiratory or other movements.

(xvii) Other Observations. Measurements should be made of the aeration rate, flow rates, temperature, pH, and dissolved oxygen content of the water containing the dispersant, the control water, and the water containing the reference materials. These checks should be made at least daily.

4 PROCEDURE FOR ACCEPTANCE

4.1 Prohibited Ingredients

(a) The dispersant shall not contain polyaromatic hydrocarbons, chlorinated hydrocarbons, nor heavy metals in concentrations greater than:

Total polyaromatic hydrocarbons: 3%

Total chlorinated hydrocarbons: 0.05 mg/L

Heavy metals: 0.05 mg/L

(b) The dispersant shall be non-corrosive to the storage containers and shall not contain any caustic alkali or free mineral acid.

4.2 Acceptance Procedure

(a) Persons wishing to have dispersants placed on the list of accepted dispersants should contact:

Environmental Emergencies Technology Division
River Road Environmental Technology Centre
Environmental Protection Service
Environment Canada
Ottawa, Ontario K1A 1C8

Phone: (613) 998-9622

A 25-litre sample of the product should be forwarded to the Centre or to an address designated by the Centre.

(b) The following requirements must be observed.

(i) The dispersant submitted for acceptance must be homogenous, not separated into layers.

(ii) The name or the contents of the dispersant material may not be changed after acceptance. If either is changed the dispersant must be resubmitted for testing. If batch differences occur they will be considered changes in formulation.

4.3 Labelling Instructions

A copy of the proposed label for the product submitted for acceptance must accompany the sample sent to the Centre. The label must show the contents and the following critical properties:

- Flash point,
- First aid instructions.

4.4 Submission Data

In addition to the data required for the label, the following data must accompany the sample:

- Solubility in water
- Vapour pressure
- Boiling point
- Melting point
- Human health hazards (e.g., LD_{50} oral, rat)
- The results of effectiveness and toxicity tests set out in the format shown in Appendix I.

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APPENDIX I

A. Effectiveness Test Results Form

1. Agency and individual performing test and date.

2. Identification of product and test oil.

3. Test conditions (temperature, salinity, pressure drop, duration, etc.)

4. Test results for product (attach separately if desired).

Volume Dispersant	D	% Oil Dispersed	Comments

5. Summary test results.

   Estimated D to achieve 50% dispersion

   ______________ (with error limits)

B. Toxicity Test Results Form

1. Agency and individual performing test and date.

2. Identification of product, reference toxicant and source of fish.

3. Test conditions (temperature, DO, pH, fish weights and lengths, means and ranges).

4. Summary test results (attach more detailed results).

   LT_{50} of product at 100 mg/L (with confidence limits and slope).

   LT_{50} of product at X mg/L (with confidence limits and slope, define X).

   LT_{50} of reference toxicant at 3.4 mg/L (with confidence limits and slope).

   LT_{50} of control with confidence limits and slope.

APPENDIX II - LIST OF CONTACTS

ENVIRONMENTAL PROTECTION SERVICE
REGIONAL ENVIRONMENTAL EMERGENCY COORDINATORS

		JURISDICTION
Regional Environmental Emergency Coordinator Atlantic Region Environmental Protection Service Environment Canada 5th Floor, Queen's Square 45 Alderney Drive, Dartmouth, Nova Scotia B2Y 2N6	Area Code 902 Emergency: 426-6200* Office: 426-2576/6317 TELEX: 019-21565 (EPS DRT)	Nova Scotia New Brunswick Prince Edward Island Newfoundland
Regional Environmental Emergency Coordinator Quebec Region Environmental Protection Service Environment Canada 1550 Maisonneuve Blvd. Montreal, Quebec H3G 1N2	Area Code 514 Emergency: 283-2333* Office: 283-2345/6418 TELEX: 055-60234 (DOE SP RQ MTL)	Quebec
Regional Environmental Emergency Coordinator Ontario Region Environmental Protection Service Environment Canada Arthur Meighen Building 7th Floor 25 St. Clair Avenue East Toronto, Ontario M4T 1M2	Area Code 416 Emergency: 966-5840* Office: 966-5840* TELEX: 062-3601 (DOE EPS TOR)	Ontario
Regional Environmental Emergency Coordinator Environmental Conservation Branch Western and Northern Region Environmental Protection Service Environment Canada 8th Floor 9942-108 Street Edmonton, Alberta T5K 2J5	Area Code 403 Emergency: 420-2580* Office: 420-2580* TELEX: 037-2099 (DOE EPS EDM)	Alberta Saskatchewan Manitoba Northwest Territories
Regional Environmental Emergency Coordinator Pacific and Yukon Region Environmental Protection Service Environment Canada Kapilano 100 - Park Royal West Vancouver, British Columbia V7T 1A2	Area Code 604 Emergency: 666-6100* Office: 666-1370/6711 TELEX: 04-54476 (EPSPACIFIC VCR)	British Columbia Yukon Territory

*24-hour service