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# Methods Used in the Preparation and Analysis of Orimulsion-related Samples



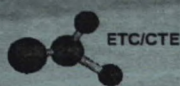
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# Methods Used in the Preparation and Analysis of Orimulsion-related Samples

by

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## Abstract

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Methods in five categories relating to the characterization or preparation of Orimulsion and related samples are reviewed. These categories are physical properties, chemical properties, bitumen preparation, aquatic toxicity studies, and test media preparation. Specific sampling and handling protocols for Orimulsion are suggested in recognition of the importance of these procedures to subsequent analysis.

In the category of physical properties, methods for water content, density, viscosity, particle size distribution, pour point, flash point, surface tension, adhesion, and total petroleum hydrocarbons are reviewed. In the chemical properties category, methods for detailed petroleum hydrocarbon analysis, volatile organic compounds, hydrocarbon groups, surfactant analysis, metals, and sulphur are reviewed. For most of the physical and chemical properties, specific methods are recommended.

Although several different methods for bitumen preparation are reviewed, the only recommendations that could be made are for better characterization of produced bitumen and additional research into the effect of preparation method on bitumen properties.

Procedures used for preparation of aquatic toxicity test media, including water-soluble fractions (WSF), oil-in-water dispersions (OWD), and water-accommodated fractions (WAF), are reviewed. These procedures need to be standardized for Orimulsion to provide effects data that are directly comparable. A standard test media preparation method is recommended based on the behavior of Orimulsion in aquatic systems and the type of exposures anticipated in the water column. This recommendation takes into consideration the guidelines being developed by the Organization for Economic Co-operation and Development (OECD) for aquatic toxicity testing of difficult substances and mixtures.

Aquatic toxicity studies are reviewed, including marine and freshwater species, plants and animals, and static and dynamic exposures. Most of these studies provide comparative toxicity data for Orimulsion and heavy fuel oil (Fuel Oil #6). Several general recommendations are made for toxicity test methods, including aspects of test design and the reporting of results.

## Resumé

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On passe en revue cinq rubriques relatives à la préparation ou à la caractérisation des échantillons d'Orimulsion et des échantillons connexes. Ce sont les propriétés physiques, les propriétés chimiques, la préparation du bitume, les études de la toxicité en milieu aquatique et la préparation des milieux d'essai. On propose des protocoles précis d'échantillonnage et de manutention de l'Orimulsion, en reconnaissance de l'importance de ces modes opératoires pour l'analyse ultérieure.

Sous la rubrique des propriétés chimiques, on passe en revue les méthodes d'analyse détaillées des hydrocarbures pétroliers, des composés organiques volatils, des groupes d'hydrocarbures, des surfactifs, des métaux et du soufre. Pour la plupart des propriétés physico-chimiques, on recommande des méthodes précises.

Bien que l'on passe en revue plusieurs méthodes de préparation du bitume, les seules recommandations que l'on ait pu faire visaient une meilleure caractérisation du bitume produit et une recherche supplémentaire sur les effets de la méthode de préparation sur les propriétés du bitume.

On passe en revue les modes opératoires de la préparation des milieux servant aux essais toxicologiques en milieu aquatique, notamment des fractions hydrosolubles, des dispersions d'huile dans l'eau et des fractions que l'on a rendues solubles dans l'eau. Ces modes opératoires ont besoin d'être normalisés pour l'Orimulsion, afin de produire des données sur les effets qui sont directement comparables. On recommande une méthode de préparation des milieux standard d'essai fondée sur le comportement de l'Orimulsion dans les milieux aquatiques et le type d'exposition prévu dans la colonne d'eau. Cette recommandation tient compte des lignes directrices élaborées par l'Organisation de coopération et de développement économiques (OCDE) pour les essais toxicologiques en milieu aquatique des substances et des mélanges difficiles.

On passe en revue les études toxicologiques en milieu aquatique employant notamment des espèces marines et dulciroles, des végétaux et des animaux et se déroulant en conditions statiques et dynamiques d'exposition. La plupart de ces études présentent des données toxicologiques comparatives sur l'Orimulsion et le mazout lourd (fioul no 6). Plusieurs recommandations générales portent sur les méthodes d'essai toxicologique, notamment sur le plan d'expérience et la communication des résultats.

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# 1. Introduction

Orimulsion, a surfactant-stabilized emulsion of approximately 70% bitumen and 30% water, is a relatively recent addition to the list of fuel oils transported by sea. Because of its unique composition, its behaviour when spilled is very different from that of conventional fuel oils. Although some properties of Orimulsion can be determined using standard methods, others cannot. In these cases, standard methods may be modified, or ad hoc methods devised. Significant differences in results can arise from the use of different sample preparation methods, as well as a variety of measurement techniques. In addition, confusion arises from the use of many alternate terms to describe the various solid and liquid phases that can be derived from Orimulsion.

To address these problems, methods used by BITOR, Environment Canada, and other agencies, in the characterization or preparation of Orimulsion-related samples, have been collected, summarized, and evaluated. Where possible, recommendations are made as to the most preferable method(s). In some cases, recommendations are made for additional method development research.

This review includes studies using both Orimulsion formulations. The chemical composition of the two formulations is relatively similar, and this is expected as the primary component of both formulations is Cerro Negro bitumen from the Orinoco Belt in eastern Venezuela. Acknowledging the similarities, based on their common primary component, natural bitumen, it is also important to note the differences between the two formulations. Table 1 identifies their principal differences, using published typical values for these parameters (Marrufo *et al.*, 1998).

Table 1. Principal Physical and Chemical Differences between Orimulsion-400 and Orimulsion-100

Parameter	Orimulsion-400	Orimulsion-100
Emulsion Additives	Alcohol ethoxylates and monoethanolamine	Nonylphenol ethoxylates
Viscosity (30°C, 100s <sup>-1</sup> ), cP	200-350	450
Magnesium (ppm)	< 20	370

## 1.1 Document Structure

The body of this report (excluding this introductory section) is divided into six parts. Because of their potential to influence all subsequent experimental or analytical procedures, the first of these is Sampling, Handling, and Storage. The remaining methods are dealt with in the following five sections: Physical Properties, Chemical Properties, Bitumen Preparation, Preparation of Aquatic Toxicity Test Media, and Aquatic Toxicity.

In each section of the report there is a brief overview, some general comments about the methods reviewed, followed by evaluations and recommendations. In sections 3, 4, and 5 (Physical Properties, Chemical Properties, Bitumen Preparation) the brief method summaries prepared during the review process are also included. Each section includes a separate list of references cited in that section.

At the end of the report, a glossary of terms relating to Orimulsion and its derivatives is presented. Frequently used acronyms are also included in the glossary.

## 2. Sampling, Handling, and Storage

---

### 2.1 Background

To understand the importance of standard procedures for the sampling, handling, and storage of Orimulsion, it is helpful to be familiar with some of the fundamentals of emulsions. Only a very brief synopsis of the subject can be given here, but there are many excellent books on emulsions including (Schramm, 1992) and (Sjöblom, 1992). A concise discussion of "Orimulsion Fundamentals" is also given in the Orimulsion quality control manual (Intevep, 1993).

Briefly, an emulsion is a heterogeneous system, consisting of at least one immiscible liquid (dispersed phase) finely dispersed in another (continuous phase) in the form of small droplets, generally ranging in diameter from 0.1 to 100  $\mu\text{m}$ . Because such systems are inherently unstable, surface active compounds (surfactants) must be added to make the emulsion stable enough for its intended use. Orimulsion is the trade name given to a bitumen-in-water emulsion stabilized by a nonionic surfactant. The bitumen is a naturally occurring petroleum hydrocarbon produced from the Orinoco Belt in Venezuela.

In spite of the presence of surface active agents, there are physical processes that can affect the physical appearance and stability of an emulsion. These processes are flocculation, creaming (sedimentation), coalescence, and inversion.

Flocculation, sometimes also referred to as aggregation or coagulation, occurs when groups of dispersed phase droplets clump together, forming loose clusters, or flocs. This produces a gradual increase in viscosity that can be reversed by applying enough energy to break up the flocs.

Creaming and sedimentation are the rising and settling, respectively, of dispersed droplets due to differences in density. These processes, which lead to the appearance of two distinct layers, one of which is richer in dispersed phase than the original emulsion, are promoted by long storage periods under static conditions. Like flocculation, creaming or sedimentation is reversible.

Coalescence is the merging of two or more droplets into a single droplet. This ultimately leads to the formerly dispersed phase becoming a second continuous phase, resulting in two separate bulk liquid phases. This is an irreversible process referred to as breaking, and may be brought about by changes in temperature or salinity, by the addition of chemicals, or by mechanical means.

Inversion is the most infrequently encountered process, and involves the interchange of dispersed and continuous phases, as when an oil-in-water emulsion becomes a water-in-oil emulsion. For this process to occur with Orimulsion requires the application of extremely high shear, and results in a water-in-bitumen emulsion having viscosities exceeding those of the bitumen itself.

As with any emulsion, Orimulsion is subject to all of the complexities associated with the above processes. Therefore, to obtain reproducible and accurate measurements of physical and chemical properties of Orimulsion requires careful attention to proper sampling, handling, and storage, using the following procedures.

---

## 2.2 Recommendations

After reviewing all the documents obtained for this project, and having considered the many deficiencies or omissions in sampling and handling procedures, the following procedures are recommended for sampling Orimulsion. These procedures are based on many years of experience primarily with crude oils, conventional fuel oils, and other oil products, but also with Orimulsion.

Only sampling from containers, up to 200 L, will be dealt with here, as this is the type of sampling likely to be encountered as the first step for most of the methods reviewed. It is recommended that prior sampling, from tanks, pipelines, tankers, or barges, be conducted in accordance with the procedures outlined in the Orimulsion quality control manual (Intevep, 1993). These sampling procedures are based on ASTM practice D 4057, *Standard Practice for Manual Sampling of Petroleum and Petroleum Products* (ASTM, 1999).

### 2.2.1 Sampling of Orimulsion from Containers (up to 200 L)

- ▶ To obtain a representative sample, the contents of any container must first be homogenized. In all cases, excessive shearing of the Orimulsion and/or the incorporation of excessive amounts of air, indicated by the presence of free bitumen and/or foam, must be avoided.
  - Large drums can be mixed by using a drum roller that rotates the drum about its long axis. To ensure complete homogenization drums should be rotated for at least 6 hours, at ambient temperatures between 15°C and 30°C.
  - Pails or cans (5 to 20 L) can be mixed by using a device that rotates or inverts the container end-over-end. This type of mixing should be used only on containers that are filled to at least 80% of their nominal capacity. To ensure complete homogenization containers should be rotated/inverted for 15 minutes to 1 hour, depending on the volume to be mixed, at ambient temperatures between 15°C and 30°C.
  - Containers up to 5 L, should be mixed by stirring. For motorized stirring, a paddle type of stirring shaft should be used rather than a propeller type, and operated at approximately 100 rpm for 15 minutes to 1 hour, depending on the volume to be mixed.
  - Volumes of 1 L or less, can be mixed manually either by inverting the container approximately 10 times, or by stirring gently but thoroughly. Vigorous shaking should be avoided.
- ▶ After homogenization sampling should occur within one hour. The taking and transferring of samples should be carried out by the most appropriate means, depending on the intended purpose of the sample, with consideration given to minimizing transfers. In many cases, it will be convenient to simply pour the Orimulsion into the receiving container, glassware, or apparatus. Clean and dry plastic, glass, or metal containers can be used.
- ▶ In some cases it may be desirable or necessary to use a syringe or pipet to deliver a small quantity of Orimulsion. Syringes should be used without needles, and should be loaded and emptied slowly to avoid excessive shearing of the Orimulsion passing through the small orifice.

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- To accurately measure quantities of Orimulsion, the glassware, pipet, or syringe should be weighed before and after delivery, and the quantity of Orimulsion calculated by difference in mass. In cases where the above methods of mixing cannot be used, or are not available, gentle stirring should be employed. For motorized stirring, a paddle type of stirring shaft should be used rather than a propeller type, and operated at approximately 100 rpm for 15 minutes to 1 hour, depending on the volume to be mixed, at ambient temperatures between 15°C and 30°C, and then sampled within 24 hours.

### 2.2.2 Storage

The material safety data sheets for Orimulsion state that it should be stored at temperatures between 5°C and 60°C (PDVSA BITOR, 1995, 1998). It is recommended that it not be stored at temperatures above 25°C for extended periods to minimize changes in the water content.

## 2.3 References

ASTM, "D 4057 Standard practice for manual sampling of petroleum and petroleum products", in *Annual Book of ASTM Standards - Section 5 Petroleum Products, Lubricants, and Fossil Fuels*, American Society for Testing and Materials, West Conshohocken, PA, 1999.

Intevep, S.A., *Characterization of Orimulsion: Quality control manual*, Bitumenes Orinoco S.A., Puerto la Cruz, Venezuela, 1993, 199 p.

Marrufo, F., W. Sarmiento, and N. Garcia-Tavel, "Redesigning a power plant fuel: Part I, Orimulsion New Generation", in *PowerGen Proceedings*, Orlando, FL, 1998.

PDVSA BITOR, *Material Safety Data Sheet*, Orimulsion, PDVSA BITOR, Caracas, Venezuela, 1995, 5 p.

PDVSA BITOR, *Material Safety Data Sheet*, Orimulsion 400, PDVSA BITOR, Caracas, Venezuela, 1998, 5 p.

Schramm, L., *Emulsions - fundamentals and applications in the petroleum industry*, American Chemical Society, Washington, DC, 1992, 428 p.

Sjöblom, J., *Emulsions - a fundamental and practical approach*, Kluwer Academic Publishers Group, Dordrecht, The Netherlands, 1992, 302 p.

### 3. Physical Properties

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This section includes nine types of methods: water content, density, viscosity, particle size distribution, pour point, flash point, surface tension, adhesion, and total petroleum hydrocarbons. A total of 37 methods, from 18 different sources, were reviewed.

#### 3.1 General Comments

In spite of their importance to the measurement of physical properties, sampling, handling, and storage of the Orimulsion were not always adequately described. Most methods also neglected to specify the number of replicate measurements made. With the exception of total petroleum hydrocarbons, physical properties were measured by relatively few different methods, and ASTM standard methods formed the basis of many of them.

#### 3.2 Evaluations and Recommendations

##### 3.2.1 Water Content

###### *Evaluation*

Water contents were determined either by distillation (BP BITOR, 1993; Intevep, 1993), in accordance with ASTM methods D 95, *Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation* (ASTM, 1999e), and D 4006, *Standard Test Method for Water in Crude Oil by Distillation* (ASTM, 1999l), or by Karl Fischer titration (Jokuty *et al.*, 1998b), as in ASTM method D 4377, *Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration* (ASTM, 1999n). The distillation method has been used for decades to reliably assay the water content of crude oils, but it has three drawbacks: a) it is time consuming; a minimum of 1.5 hours of distillation is required for each Orimulsion sample, b) results obtained by this method are negatively biased (low), probably because it is difficult to ensure that all of the water is transferred into the water trap, and c) it is a laboratory method, not adaptable to use in the field.

The Karl Fischer titration method has none of the drawbacks mentioned above. However, ASTM method D 4377 only covers the determination of water in the range from 0.02 to 2% in crude oils, and there are known interferences by mercaptan and sulphide sulphur. Nevertheless, Karl Fischer titration has been used successfully for many years to determine the water content of crude oils and water-in-oil emulsions with water contents up to 95 weight % (Jokuty *et al.*, 1999c). In implementing the use of this method, water-in-oil emulsions (50 to 80 weight % water) were tested. The sulphur content of the oil mixture used in forming the emulsions was 2.5%, comparable to Orimulsion. The water content values obtained by Karl Fischer titration differed from the calculated true values by an average of less than 4%.

###### *Recommendation*

Either of the two methods reviewed is acceptable for determining the water content of Orimulsion or bitumen derived from Orimulsion. The ASTM distillation method will probably continue to be required for assays done for certification purposes. The Karl Fischer titration method is a good choice for Orimulsion-related research, as it enables the rapid analysis of multiple samples, can be used for both Orimulsion and derived bitumen samples, and can be adapted for use in the field, if necessary (Lambert and Bobra, 1992; Lambert *et al.*, 1994).

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### 3.2.2 Density

#### *Evaluation*

Densities were measured either by using a digital density analyzer (BP BITOR, 1993; Intevep, 1993; Jokuty *et al.*, 1999b; Ostazeski *et al.*, 1997), or a pycnometer (Brown *et al.*, 1995). For the digital density analyzer, two similar ASTM methods were used: D 4052, *Standard Test Method for Density of Liquids by Digital Density Meter* (ASTM, 1999m), and D 5002, *Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer* (ASTM, 1999o). Both of these test methods are intended for samples that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C. Test method D 4052 "should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty." Its application is also restricted to viscosities below about 15,000 cSt at the test temperature. This would make it inapplicable to bitumen derived from Orimulsion. Test method D 5002 does not have these restrictions, and specifically addresses how to deal with dark and/or viscous samples.

A pycnometer is a container whose volume is precisely known, used to determine the density of a liquid by filling the container with the liquid and then weighing it. There are several different types of pycnometers, and a number of ASTM methods related to their use. The method reviewed appears to have used the type of pycnometer generally intended for determining the density or specific gravity of aqueous solutions, as described in ASTM method D 1429, *Standard Test Methods for Specific Gravity of Water and Brine* (ASTM, 1999i). The procedure followed was also similar to this test method, the scope of which covers "the determination of the specific gravity of water and brine free of separable oil". This method is not suitable for the determination of the density of either Orimulsion or bitumen because it relies on the overflow of the liquid to be measured, and then the complete removal of the excess before weighing. Due to the adhesive nature of these types of samples, this would be impossible.

The digital density analyzer produces results far more quickly than can be achieved with a pycnometer.

#### *Recommendation*

The recommended method for the determination of density of Orimulsion, or bitumen derived from Orimulsion, is ASTM method D 5002, *Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer* (ASTM, 1999o). If a digital density analyzer is not available, a pycnometer can be used as described in ASTM method D 1217, *Standard Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer* (ASTM, 1999h).

### 3.2.3 Viscosity

#### *Evaluation*

Five methods for determining the viscosity of Orimulsion or bitumen samples were reviewed. Three of the methods reviewed used the same type of concentric cylinder rotational viscometer. One of these gave too few details to be evaluated (Ostazeski *et al.*, 1997). The BITOR method (Intevep, 1993) and the Environment Canada method (Jokuty *et al.*, 1999b) are similar, but differ in a few key points. The BITOR method cautions against the use of a syringe to fill the sample cup with

Orimulsion, to avoid excessive shear on the sample as it is forced out of the syringe. As described in the previous discussion of Orimulsion handling, the careful use of a syringe body, with no needle, should be acceptable. In fact, the use of syringes is required in some types of analysis (ASTM, 1999m, 1999o).

Another difference between the BITOR and Environment Canada methods is in the thermal equilibration of the sample prior to measurement. BITOR recommends that the sample should not be allowed to thermally equilibrate in the sample cup prior to measurement, to avoid the possibility of sedimentation. As mentioned in the Orimulsion Quality Manual (Intevep, 1993), the small density difference between the bitumen and the water in Orimulsion makes sedimentation a slow process. It seems unlikely that sedimentation (or creaming) should be of concern during an interval of less than one hour, and less so at lower temperatures.

The BITOR method specifies the use of the MV1 sensor, while the Environment Canada method relies primarily on the SV1 sensor, although some measurements on Orimulsion were made with the MV2 sensor, which is very similar to the MV1. The BITOR method uses shear rates of 20 and 100 s<sup>-1</sup>, while the Environment Canada method determines viscosity at a shear rate of 100 s<sup>-1</sup> for all samples, and at shear rates of 10 and 1 s<sup>-1</sup> for samples that are markedly non-newtonian at the measurement temperature.

The choice of measurement sensor depends on a number of criteria. The most important consideration is the basic measurement range of the sensor, as defined by the instrument manufacturer. This range is dependent on shear rate. At temperatures equal to or above 15°C, neither the MV1 sensor at a shear rate of 20 s<sup>-1</sup>, nor the MV2 sensor at a shear rate of 30 s<sup>-1</sup>, has a basic measurement range suitable for the viscosity of Orimulsion at those temperatures. However, at a shear rate of 100 s<sup>-1</sup> the viscosity of Orimulsion falls within the basic measurement range of both sensors. Similarly, the SV1 sensor at shear rates of 1 to 100 s<sup>-1</sup>, is well-suited to the measurement of Orimulsion viscosities at 0°C (Jokuty *et al.*, 1999b)

Brown *et al.* (1995) used a Brookfield viscometer to measure the viscosity of Orimulsion at 25°C. With this type of instrument there is only limited control over the shear rate.

A fifth method reviewed was used only for viscosity measurements of bitumen samples derived from Orimulsion, and not for Orimulsion itself (Jokuty *et al.*, 1999a, 1999b). This method used a Haake RS100 Rheostress rheometer with a 20 mm plate/plate system. The same instrument is routinely used for the characterization of water-in-oil emulsions, and is particularly well suited to the determination of high viscosities at low shear rates.

#### *Recommendation*

To make viscosity measurements on Orimulsion, the concentric cylinder rotational viscometer is recommended. Although this type of viscometer is widely used in industry and research, there are no ASTM standard methods for its use. Regarding temperature equilibration of the sample, some research should be done to determine how Orimulsion viscosity measurements are affected by varying lengths of equilibration time in the sample cup, at various temperatures, with a variety of appropriate sensors, since the sample volume is different for each one. At temperatures equal to or above 15°C either the MV1 or MV2 sensor should be used and the viscosity measurement should be determined at a shear rate of 100 s<sup>-1</sup>. At 0°C the SV1 sensor should be used at shear rates of 1, 10,

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and  $100 \text{ s}^{-1}$ . The shear rate should be ramped up for 5 minutes, held for 5 minutes, and ramped down for 5 minutes. This allows non-newtonian behaviour to be evaluated more easily.

To make viscosity measurements on bitumen derived from Orimulsion, the method reviewed is appropriate.

### 3.2.4 Particle Size Distribution

#### *Evaluation*

Two different types of instruments were used to measure particle size distributions in Orimulsion and Orimulsion solutions: a Malvern Particle Sizer (BP BITOR, 1993; French *et al.*, 1997; Intevp, 1993; Warren Spring Laboratory, 1989), and a Coulter Multisizer (Jokuty *et al.*, 1995, 1999b). The Malvern instrument bases its measurements on the differential scattering of light from particles of different sizes. In one of the methods using a Malvern, samples were fixed, or preserved, by the addition of a surfactant solution. Samples were then analyzed within 6 hours (French *et al.*, 1997).

The Coulter instrument determines particle size by measuring the increase in voltage as a particle passes through a small aperture between two electrodes. It is highly accurate, using software to correct for particle coincidence effects. The measurement protocol for this instrument requires dilution in an electrolyte solution. To minimize the effects of this solution, unfixed samples were measured as quickly as possible after sampling.

#### *Recommendation*

There does not appear to be any compelling reason why either of the two instruments described should not be recommended. For measurements to be made with a Malvern Particle Sizer, the BITOR method (Intevp, 1993) is very comprehensive, and includes specific instructions pertaining to Orimulsion. The BP BITOR (1993) reference includes details on a procedure and formulation for coating cell windows to reduce their susceptibility to fouling.

The use of surfactant to fix samples prior to analysis should be investigated further to determine what effects (if any) the surfactant has on the subsequent measurement of the particle size distribution, and if this technique can be applied to measurements made with the Coulter instrument.

### 3.2.5 Pour Point

#### *Evaluation*

Both BITOR (Intevp, 1993) and Environment Canada (Jokuty *et al.*, 1995, 1999a, 1999b) base their methods on ASTM method D 97, *Standard Test Method for Pour Point of Petroleum Products* (ASTM, 1999f) for the determination of the pour point of Orimulsion. One significant modification to the ASTM method is recommended by BITOR, namely, that the preliminary heating of the sample to  $50^\circ\text{C}$  be omitted as a precaution against promoting water separation.

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### Recommendation

It is recommended that ASTM method D 97 (ASTM, 1999f) be followed for the measurement of Orimulsion pour point, including the preliminary heating of the sample. Heating to the required minimum of 45°C does not exceed the maximum recommended storage temperature for Orimulsion (60°C) (PDVSA BITOR, 1995, 1998). The purpose of this step is to ensure that wax components of the oil are uniformly distributed, and omitting this step precludes direct comparison with other oils that were heated.

### 3.2.6 Flash Point

#### Evaluation

The methods reviewed cited four different ASTM methods: D 56, *Standard Test Method for Flash Point by Tag Closed Tester* (ASTM, 1999b); D 92, *Standard Test Method for Flash and Fire Points by Cleveland Open Cup* (ASTM, 1999c); D 93, *Standard Test Method for Flash Point by Pensky-Martens Closed Tester* (ASTM, 1999d) and D 3828, *Standard Test Methods for Flash Point by Setaflash closed Tested* (ASTM, 1999j).

The method specified by BITOR in their Orimulsion quality manual (Intevep, 1993) is based on ASTM method D 92. This is an open cup method, and due to difficulties encountered when heating Orimulsion to temperatures higher than 90°C (“violent bubbling/splashing of the sample, with irregular ejection of the water contained in the product”), the method is modified to determine a “flash/no flash” result at the target temperature of 85°C. The same “flash/no flash” criteria was used by BP BITOR (1993), but the method followed was ASTM method D 3828.

The method used by Environment Canada (Jokuty *et al.*, 1995, 1999a, 1999b), follows ASTM method D 56, but uses a tester that has been modified by the addition of a stirring mechanism. ASTM method D 56 covers the determination of the flash point of relatively low viscosity liquids (<5.5 cSt at 40°C or <9.5 at 25°C) with flash points up to 90°C. The addition of a stirrer assists heat distribution within samples of low thermal conductivity, improving the precision of measurements on samples outside the specified viscosity range.

ASTM method D 93 covers the determination of the flash point of higher viscosity liquids than are covered by ASTM method D 92, having flash points as high as 370°C. An unspecified modification of this method was reported to have been used with a Grabner Miniflash apparatus (Ostazeski *et al.*, 1997), but no details were given, making it impossible to evaluate.

#### Recommendation

ASTM method D 93, *Standard Test Method for Flash Point by Pensky-Martens Closed Tester* (ASTM, 1999d), is recommended for determining the flash point of Orimulsion and its derived bitumen. However, if only a “flash/no flash” determination is required, any of the above methods is adequate.

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### 3.2.7 Surface/Interfacial Tension

#### *Evaluation*

Two methods were reviewed for determining either surface tension of Orimulsion (Jokuty *et al.*, 1995, 1999b), or interfacial tension of derived bitumen and water (Brown *et al.*, 1995). The interfacial tension of Orimulsion and water cannot be determined because Orimulsion and water are miscible and do not form a stable interface. Both methods reviewed refer to ASTM method D 971, *Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method* (ASTM, 1999g), but the Environment Canada method makes use of an automatic tensiometer, while the method of Brown *et al.* (1995), uses a manual instrument. The automatic instrument is limited to samples with a maximum viscosity of 20,000 cP, hence it could not be used to measure either the surface tension or interfacial tension of bitumen derived from Orimulsion.

The manual instrument was used to measure the interfacial tension of Orimulsion-derived bitumen and distilled water (Brown *et al.*, 1995). Other physical properties were not measured, so the water content and viscosity of the bitumen samples is not known. Interfacial tension of bitumen and salt water was not measured "to avoid possible variances in seawater samples between analyses, and to limit the corrosive effects of seawater on the apparatus". However, variances in sea water samples can be minimized by using a single batch of water for all measurements, and corrosive effects on the apparatus should not be a concern, since the measurement rings are the only part of the apparatus in contact with the water, and they are made of platinum.

#### *Recommendation*

Surface tension measurements on Orimulsion can be made with either a manual or automatic ring tensiometer. Interfacial tension measurements with Orimulsion-derived bitumen (low water content) must be made with the manual instrument, and in accordance with ASTM method D 971, *Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method* (ASTM, 1999g). Extreme care must be taken with the manual tensiometer as there is a tendency, when using it with extremely viscous oils, to overshoot the correct tension.

### 3.2.8 Adhesion

#### *Evaluation*

Two fundamentally different methods for measuring adhesion were reviewed. One method, used for both Orimulsion and derived bitumen, determines adhesion by measuring the mass of sample retained, after 30 minutes, on a standard stainless steel penetrometer needle of known surface area ( $\text{g}/\text{m}^2$ ) (Jokuty *et al.*, 1998a). This method was developed by Environment Canada and has been used on a wide variety of crude oils and oil products (Jokuty *et al.*, 1999c). It has also been tested with a variety of different test surfaces, including stainless steel, glass, Teflon, plastic, wood, and ceramic (Jokuty *et al.*, 1996). It was found that the relative order of adhesiveness of different oils was independent of the type of material used for the test surface.

A different method was used to determine the adhesion of Orimulsion on coarse and fine sediments (Brown *et al.*, 1995). Sediment, Orimulsion, and sea water were mixed together for a specified time interval, and then allowed to settle for one minute. Particles that remained suspended after one

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minute were considered fine, those that settled in that time were considered coarse. The sediment fractions were solvent extracted and the concentration of hydrocarbons determined by ultraviolet-visible (UV-VIS) spectrometry. Each sediment fraction was dried and weighed, and the mass ratio of extracted hydrocarbons to sediment (mg/g) was calculated. Effects of loading rate, salinity, and mixing time were investigated, and each variable was found to have a significant effect on the results.

#### *Recommendation*

Both of the methods reviewed have their merits. If the purpose of determining an adhesion property for Orimulsion or its derived bitumen, is to obtain a relative measure of adhesiveness that can be easily compared among crude oils and other petroleum products, then the Environment Canada method is recommended. It is relatively quick and simple, and a body of data already exists for comparison.

If the purpose of making the measurement is to determine the amount of contamination to be expected for a particular sediment type, under specific loading conditions and salinities, then the type of method used by Brown *et al.* (1995) may be more suitable, provided additional method development can better establish the effects of several of the experimental parameters, including the type of sediment used, the settling time, and the multiple filtration/centrifugation steps. Also, UV-VIS spectroscopy is NOT recommended for quantitation. See the following section for recommended methods for quantitation of petroleum hydrocarbons.

### **3.2.9 Total Petroleum Hydrocarbons**

#### *Evaluation*

This category includes those methods that were used to determine the total amount of petroleum hydrocarbons in water or sediment samples resulting from Orimulsion experiments. Twelve methods were found in eleven references. These methods used either filtration (Wang and Fingas, 1996) or solvent extraction (Brown *et al.*, 1995; Esclapés *et al.*; Gassman, 1995; Jokuty *et al.*, 1995; 1999a, 1999b) to separate the hydrocarbons from the water or sediment, and a variety of methods for quantitation including gravimetry (French *et al.*, 1997; Jokuty *et al.*, 1999a, 1999b; Wang and Fingas, 1996), infrared (IR) spectrometry (Gassman, 1995; Jokuty *et al.*, 1995; Warren Spring Laboratory, 1989), ultraviolet fluorescence (UVF) spectrometry (Brown *et al.*, 1995; Washburn & Gillis Associates Ltd., 1988), ultraviolet-visible (UV-VIS) spectrometry (Brown *et al.*, 1995), and gas chromatography with flame ionization detection (GC/FID) (Ostazeski *et al.*, 1997; Wang and Fingas, 1996). A number of reference methods exist, including U.S. EPA methods (USEPA, 1983a, 1983b, 1983c), *Standard Methods for the Examination of Water and Wastewater* (APHA/AWWA/WEF, 1992a, 1992b), and an ASTM method (ASTM, 1999k). In a few of the methods reviewed one or another of these reference methods was cited, and in other cases incomplete information was provided, and one or more of the separation method, the extraction solvent, or the quantitation method could not be ascertained (Esclapés *et al.*; French *et al.*, 1997; Johnson *et al.*, 1995; Warren Spring Laboratory, 1989).

For aqueous samples, filtration and weighing can provide a relatively simple and effective method to determine dispersed bitumen. The effectiveness of such a method depends on using a suitably fine

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filter, a sensitive balance, and for low concentrations of bitumen, making corrections for blank samples.

All "total" petroleum hydrocarbon methods that use solvent extraction to separate the hydrocarbons from the sample media are limited by two factors: the ability of the solvent used to dissolve the hydrocarbons present and the ability of the quantitation method to detect the dissolved hydrocarbons. The bitumen component of Orimulsion is a very heavy oil and dissolves poorly in many of the common extraction solvents, including hexane (Brown *et al.*, 1995). In method development preparatory to the work reported by Jokuty *et al.* (1995), Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), the solvent specified in every reference method using IR quantitation (APHA/AWWA/WEF, 1992b; ASTM, 1999k; USEPA, 1983a, 1983b, 1983c) was found to be a poor solvent for Orimulsion, and carbon tetrachloride ( $\text{CCl}_4$ ) was substituted.

To further complicate matters, Freon 113 and  $\text{CCl}_4$  are controlled by measures set out in the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer (UNEP, 1997). Their import and manufacture has been banned in developed countries and is being phased out in developing countries. Although other IR-transparent solvents exist, for example perchlorethane, their ability to dissolve petroleum hydrocarbons has not been fully documented.

Of the quantitation methods listed above, gravimetry (weighing) is the simplest and most straight forward. With the use of an analytical microbalance masses in the mg range can easily be measured. Sample volume will determine the detection limit of the method.

Each of the three spectrophotometric methods (IR, UV-VIS, UVF) has its limitations. All three methods rely on the use of reference solutions of known concentrations, to which the absorbance or emission measurements of the unknown samples are compared. The absorbance/emission spectrum of the reference material should match that of the samples to be measured. Ideally, the reference solutions should be made from the same type of oil as is to be measured in the samples. This is particularly important in UV-VIS methods because crude oils, including bitumens, have no distinctive UV-VIS absorbance. Very dark oils absorb more than light-coloured oils, making this essentially a colourimetric method.

IR methods are based on absorbance near  $2950\text{ cm}^{-1}$ , a region corresponding to stretching of non-aromatic carbon-hydrogen bonds. For oils with high aromatic contents, this may not be the optimum wavelength for measurement, again highlighting the importance of matching the reference solutions to the sample solutions as closely as possible.

UVF methods are particularly well-suited to the measurement of low concentrations of soluble aromatic compounds. As only compounds that fluoresce will be detected, this should be reported as total aromatic hydrocarbons rather than total petroleum hydrocarbons.

Methods that use solvent extraction followed by GC/FID can detect smaller amounts of hydrocarbons than gravimetry, IR, or UV-VIS, but are again dependent on the solvent used and will be significantly reduced by sample cleanup techniques as described by (Wang and Fingas, 1996). The GC-determined TPH values were only 30 to 35% of gravimetrically determined values. Even when sample cleanup is not used, GC/FID values for TPH will be lower than gravimetric measurements due to retention of high molecular weight compounds in the GC inlet and column.

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### *Recommendation*

The term "total petroleum hydrocarbons", should be avoided in favour of more accurate phrases such as "total solvent extractable materials" or "recovered bitumen", in the case of gravimetric determination. That said, the preferred method for quantifying Orimulsion-derived bitumen, whether obtained from water or sediment, by filtration or solvent extraction, is gravimetry, if possible.

If the amount of recovered bitumen is too small to be determined gravimetrically, either as a result of small sample volume or low bitumen concentration, then the choice of method must take into consideration the expected concentration range of the samples. For concentrations in the range of 1 to 1000 ppm, an IR method will give acceptable results provided that a good solvent is used and that appropriate reference solutions are prepared with Orimulsion or bitumen. Supporting data should be provided for the choice of solvent. For very low (ppb) concentrations, UVF is the best choice, but again supporting data should be provided for the choice of solvent.

UV-VIS methods, although acceptable for field screening of hydrocarbon-contaminated samples (Lambert *et al.*, 1999) should be avoided in favour of the other laboratory methods discussed, due to the many difficulties encountered with the colourimetric analysis of very dark solutions.

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### 3.3 Method Summaries

#### 3.3.1 Water Content (BP BITOR, 1993; Intevep, 1993)\*

##### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*

*Characterization of Orimulsion: Quality control manual*

##### *Storage and Handling*

Storage temperature was not specified. A flat blade stirrer operating at 100 rpm for 1 hour is recommended for homogenizing the sample.

##### *Procedure*

Water contents are determined in accordance with either ASTM method D 4006, *Standard Test Method for Water in Crude Oil by Distillation* (ASTM, 1999l) or ASTM method D 95, *Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation* (ASTM, 1999e):

##### Summary of Test Method

The sample is heated under reflux conditions with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap - the water settles in the graduated section of the trap, and the solvent returns to the distillation flask.

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### 3.3.2 Water Content (Jokuty *et al.*, 1999b)\*

#### *\*Title of Source*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

#### *Procedure*

Water contents were determined by Karl Fischer titration, using a method based on ASTM method D 4377, *Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration* (ASTM, 1999n):

##### Summary of Test Method

After homogenizing the crude oil with a mixer, an aliquot of the crude, in a mixed solvent, is titrated to an electrometric-end point using Karl Fischer reagent.

A Metrohm 701 KF automatic titrator was used, and the sample was dissolved in a pre-titrated 1:1:2 volume mixture of methanol/chloroform/toluene.

Samples were run in triplicate, and the mean water content reported.

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### 3.3.3 Density (Intevp, 1993)\*

#### *\*Title of Source*

*Characterization of Orimulsion quality control manual*

#### *Storage and Handling*

Storage temperature was not specified. A flat-blade stirrer operating at 100 rpm for 1 hour is recommended for homogenizing the sample.

#### *Procedure*

The density of Orimulsion is determined in accordance with ASTM method D 4052, *Standard Test Method for Density of Liquids by Digital Density Meter* (ASTM, 1999m):

##### Summary of Test Method

Approximately 0.7 mL of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

The standard test temperature is 15°C.

#### *Source notes*

Nonhomogeneous samples (containing free bitumen) will not yield representative results. Foamy samples are not measurable as air bubbles introduce perturbations in the system restricting the oscillating tube from reaching stable vibration periods.

Extreme care must be taken during sample injection into the sample tube, as the introduction of air bubbles makes measurement impossible. The latter can be avoided if the sample injection is carried out from the lower portion of the tube at a very slow pace. ...

Digital density meters were not designed for two phase systems, although bitumen emulsions can be conveniently measured up to 70°C. Steady readings are difficult to obtain for higher temperatures.

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### 3.3.4 Density (BP BITOR, 1993; Jokuty *et al.*, 1999b)\*

#### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

Jokuty *et al.*, (1999b) report that the Orimulsion was stored between 5 and 15°C. Before sampling, the Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

#### *Procedure*

The density of fresh Orimulsion was determined in accordance with ASTM method D 5002, *Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer* (ASTM, 1999o):

##### Summary of Test Method

Approximately 0.7 mL of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

The instrument used was an Anton Paar DMA 48 densimeter. Bitumen densities were determined by the same method, but using an Anton Paar DMA 45 densimeter. Densities were determined at 0 and 15°C (Jokuty *et al.*, 1999b).

Samples were run in duplicate and the mean density reported.

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### 3.3.5 Density (Ostazeski *et al.*, 1997)\*

#### *\*Title of Source*

*The environmental behaviour of Orimulsion spilled on water*

#### *Storage and Handling*

No information given.

#### *Procedure*

The method is based on ASTM method D 4052, *Standard Test Method for Density of Liquids by Digital Density Meter* (ASTM, 1999m):

##### Summary of Test Method

Approximately 0.7 mL of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

Density of Orimulsion was determined at 0, 5, 10, 15, 20, and 25°C.

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### 3.3.6 Density (Brown *et al.*, 1995)\*

#### *\*Title of Source*

*Comparative evaluation of physical and chemical fate processes of Orimulsion and Fuel Oil No. 6 in the Tampa Bay marine environment*

#### *Storage and Handling*

No information given.

#### *Procedure*

Density was determined using precision glass pycnometers (10 mL at 20°C) and an analytical balance with a readability of 0.1 mg. The calibration constant of each pycnometer was determined with distilled water at 25°C. Oil densities were determined by filling the pycnometer vial to the indicated mark. The vial stopper was inserted, forcing all fluid in excess of the rated volumetric capacity out of the vial, through a pilot hole in the stopper. The weight of the full pycnometer was compared to the tare weight of the pycnometer to determine the apparent density of the sample. The actual density of the sample was obtained by correcting the apparent density with the calibration constant previously determined for each vial.

#### *Source notes*

The calibration constant for each vial must be recorded for each matched, and pre-labelled set of glass vials and stoppers.

#### *Reviewer's notes*

No explicit statement is made regarding the measurement temperature.

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### 3.3.7 Viscosity (Ostazeski *et al.*, 1997)\*

#### *\*Title of Source*

*The environmental behaviour of Orimulsion spilled on water*

#### *Storage and Handling*

No information given.

#### *Procedure*

The viscosity of Orimulsion was determined at 0, 5, 10, 15, 20, and 25°C using a Haake rotational viscometer, at shear rates of 10 and 100 s<sup>-1</sup>.

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### 3.3.8 Viscosity (BP BITOR, 1993; Intevp, 1993)\*

#### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*  
*Characterization of Orimulsion quality control manual*

#### *Storage and Handling*

Storage temperature was not specified.

#### *Procedure*

Viscosity measurements are made using a coaxial cylinder viscometer. The recommended measuring system is the the Haake RV20/M5 with the RC 20 Rheocontroller and the MV1 rotor.

#### *Sampling*

To ensure homogeneity only gentle stirring of the sample prior to measurement is required, unless the sample is from a large volume container, in which case the contents of the container should be homogenized by inverting the container a few times before any sampling is carried out. The Orimulsion sample should be poured or spooned into the measurement cup. Syringes should not be used, and care must be taken not to introduce air into the sample as it is placed in the cup.

#### *Sensor system/ sample volume*

The sensor system to be used is the MV1. The sample cup must be filled with the proper amount of sample, approximately 35 g for the MV1 system, although correct filling must be verified every time. Excess sample can be removed with a syringe.

#### *Sample temperature*

Temperature equilibration of the sample inside the sensor is not recommended, to avoid sedimentation of the sample or water evaporation. The preferred procedure is to immerse the sample, in a closed container, and the sensor spindle, in a thermostatic bath. The empty cup can be preheated by attaching it to the measuring head with the circulating thermal fluid in operation. Once the sample has reached the measuring temperature, it can be transferred to the sensor cup, and the measurement can be carried out after allowing the system to stabilize for a couple of minutes.

#### *Measuring program*

According to the Intevp procedure, the measuring program should consist of two shear rate ramps of 3 minutes each; first ramp, 0 to 10 s<sup>-1</sup>, second ramp, 10 s<sup>-1</sup> to 110 s<sup>-1</sup>. The results of the first ramp can be discarded. The BP BITOR procedure is similar, but the first ramp is 0 to 20 s<sup>-1</sup> and the second ramp 20 s<sup>-1</sup> to 200 s<sup>-1</sup>.

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### *Reporting results*

The viscosity is reported at 20 s<sup>-1</sup> and/or 100 s<sup>-1</sup>.

### *Source notes (Intevp, 1993)*

At present, the Orimulsion apparent viscosity is analysed for shear rates of 20 and 100 s<sup>-1</sup>, at 30°C. However, it has been found that the repeatability of the experimental viscosity measurement tends to decrease for decreasing shear rates. For this reason, it is highly convenient to report viscosity values at the higher shear rates, since the repeatability is greatly enhanced.

### *Precision*

Provided the sample is homogeneous, the relative standard deviations, calculated for 10 viscosity measurements of Orimulsion, under repeatability conditions in more than one experimental session, are:

RSD = 7.0 % @ 30°C and 20 s<sup>-1</sup>

RSD = 4.8 % @ 30°C and 100 s<sup>-1</sup>

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### 3.3.9 Viscosity (Jokuty *et al.*, 1995, 1999b)\*

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

#### *Procedure*

##### *Fresh Orimulsion*

Dynamic viscosity measurements were made on Orimulsion samples using a Haake RV20 Rotovisco with the M5 measuring system, Haake RC20 Rheocontroller, and SV1 and MV2 sensors. Measurements were made at 0, 15, 20, 30, and 40°C.

An aliquot of Orimulsion was obtained using a disposable syringe body (no needle). The excess was wiped from the outside of the syringe and the sample cup was carefully filled. For all measurements made with the MV2 sensor, samples were allowed to equilibrate for approximately five minutes at all temperatures. Measurements with the SV1 sensor were made after 45 minutes of equilibration at 0°C, and 30 minutes at 15 or 20°C. All samples were measured initially at a single shear rate of 100 s<sup>-1</sup>. At 0°C samples displaying significant non-newtonian behaviour were also measured at shear rates of 10 and 1 s<sup>-1</sup>. In all cases, the shear rate was ramped up 5 minutes, held 5 minutes, and ramped down 5 minutes. Most samples were run in duplicate and the mean viscosity is reported. In some cases, to conserve both sample and time, measurements were made only once.

##### *Bitumen*

For bitumen samples derived from the evaporation of Orimulsion, the Haake RS100 Rheostress rheometer was used. A 20 mm plate/plate system was chosen, to allow measurement of the highest possible viscosity values. The bitumen was warmed to room temperature, then sampled with a spatula, scooping the bitumen onto the 20 mm base plate. The base plate was then raised to the rotary plate leaving a gap of 2 mm. The excess Orimulsion was removed from the base plate. The sample was allowed to equilibrate for 30 minutes before measurement. Viscosity was measured using a controlled shear rate from 0.1 to 10 s<sup>-1</sup>, at 0 and 15°C, with logarithmic distribution. Duplicate measurements were taken at each shear rate, and the mean viscosity is reported.

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### 3.3.10 Viscosity (Brown *et al.*, 1995)\*

#### *\*Title of Source*

*Comparative evaluation of physical and chemical fate processes of Orimulsion and Fuel Oil No. 6 in the Tampa Bay marine environment*

#### *Procedure*

The viscosity of Orimulsion was determined with a Brookfield LVDV-II+ digital viscometer equipped with a model TC-500 Brookfield refrigerated bath/circulator. The viscometer was equipped with a small sample adapter, which required only 8 mL of sample. Viscosity readings were recorded at 25°C. The instrument was operated in strict accordance with the manufacturer's operating instructions.

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### 3.3.11 Particle Size Distribution (French *et al.*, 1997)\*

#### *\*Title of Source*

*Validation of an Orimulsion spill fate model using observations from test spills*

#### *Storage and Handling*

No information given.

#### *Procedure*

Particle size samples were fixed immediately in the field by adding 30 mL of a 25% surfactant (nonylphenol ethoxylate) solution to 500 mL of sample. A Malvern Particle Sizer was used to measure particle size distributions. Measurements were made within 6 hours of sampling.

#### *Source notes*

Preliminary tests before the trial were performed to determine the amount of surfactant needed to fix the size distribution. Recounting of samples several weeks later showed no significant changes in particle size distributions.

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### 3.3.12 Particle Size Distribution (BP BITOR, 1993; Intevep, 1993; Warren Spring Laboratory, 1989)\*

#### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*

*Characterization of Orimulsion quality control manual*

*Observations of the behaviour of Orimulsion released into the sea and in a test tank*

#### *Storage and Handling*

Storage temperature was not specified. A flat blade stirrer operating at 100 rpm for 1 hour is recommended for homogenizing the sample.

#### *Procedure*

A Malvern Particle Sizer is used to measure particle size distributions. The details below are taken from Intevep (1993).

A given volume of homogeneous sample is dispersed in 50 mL of a solution containing 1 g/L sodium pyrophosphate and 80 g/L of a non-ionic surfactant. For Orimulsion, the sample volume is "about half a spatula (flat tip, 4 mm wide, 100 mm long)". Before carrying out the measurement the following instrument parameters must be verified: absolute cleanliness of cell windows, pipes, and receiver lens; correct position of flow cell and detector; and optimum laser alignment. Before pouring the dispersed sample into the ultrasonic tank, its stability must be checked. The combined procedures of sample addition, sample concentration checking, measurement, and calculation should not last more than three minutes. The following measurement steps are carried out, in order:

Background measurement: The type B Alarm option will warn the operator about an unacceptable background level (i.e. cell windows not clean or air bubbles present).

Addition of the sample to the ultrasonic tank: This must be done at low stirrer and sample pump speeds (dial 3 and 4, respectively). Do not use ultrasonic stirring.

Sample concentration check: Although the recommended values for obscuration index are 0.10 to 0.30, it is advisable to work in the range of 0.15 to 0.20.

Check for air bubbles by observing the graphs of %volume vs. droplet size or light intensity vs. ring number. If the curves show strong oscillations for the higher droplet sizes of the distribution, or for the smaller rings, this should be taken as evidence of air bubbles.

Measurement: After the measurement routine the log diff or % residual values must be checked. Log diff values of 4 to 5 or % residual values of 0.1 to 1, are indicative of good data-fitting.

Once the measurement procedure has been completed, the operator must select the statistical parameters to report. At least two parameters are necessary to characterize the sample: a population average and a term of broadness. The median ( $D(v,0.5)$ ) or mean volume diameter ( $D(4,3)$ ) can be

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used to represent the population average. The span may be used to represent the broadness of the distribution. Span is defined as:

$$span = \frac{D(v,0.9) - D(v,0.1)}{D(v,0.5)}$$

where  $D(v,0.9)$  and  $D(v,0.1)$  are the droplet diameters such that 90% and 10%, respectively of the total dispersed phase is in droplets of smaller diameters.

#### *Source notes*

The 100 mm focal length receiver lens is adequate for Orimulsion use. However, samples with extreme distribution values surpassing the lens range limits, should be measured with the 300 mm lens.

A thorough description of terms and criteria for liquid drop size analysis is presented in ASTM standard practice E-799, *Standard Practice for Determining Data Criteria and Processing for Liquid Drop Size Analysis* (ASTM, 1999p).

#### *Reviewer's notes*

A Malvern Particle Sizer was also used in a study done by the Warren Spring Laboratory (Warren Spring Laboratory, 1989), but no details of the method were given.

The BP BITOR (1993) reference includes details on a procedure and formulation for coating cell windows to reduce their susceptibility to fouling.

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### 3.3.13 Particle Size Distribution (Jokuty *et al.*, 1995, 1999a)\*

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

#### *Procedure*

Particle size distribution was determined using a Coulter Counter Multisizer with AccuComp software. The Coulter Counter determines particle size by measuring the increase in voltage as a particle passes through a small aperture between two electrodes. The particles are suspended in an electrolytic solution that is drawn by vacuum suction through a small aperture separating two electrodes under applied current. As a particle passes through the aperture, there is an increase in resistance between the electrodes that results in a voltage pulse. The magnitude of the voltage pulse is proportional to the volume of the particle passing through the aperture. The voltage pulses are scaled and counted by the AccuComp<sup>R</sup> software package, which can then mathematically manipulate the data to provide particle size distribution information. The mean volume diameter [D(4,3)] is reported.

#### *Source notes*

When comparing results for different types of water, it must be noted that the limitations of the instrument were such that particles larger than 45 micrometres could not be measured, and plugging of the orifice that the particles pass through (70 micrometre diameter), determined the maximum time interval for which a distribution could be measured properly. (Jokuty *et al.*, 1998b)

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### 3.3.14 Pour Point (Intevep, 1993)\*

#### *\*Title of Source*

*Characterization of Orimulsion quality control manual*

#### *Storage and Handling*

Storage temperature was not specified. A flat blade stirrer operating at 100 rpm for 1 hour is recommended for homogenizing the sample.

#### *Procedure*

With the exception that preliminary heating is not recommended since it promotes water separation, the pour point is determined according to ASTM method D 97, *Standard Test Method for Pour Point of Petroleum Products* (ASTM, 1999f):

##### Summary of Test Method

After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the oil is observed is recorded as the pour point.

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### 3.3.15 Pour Point (Jokuty *et al.*, 1995, 1999b)\*

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

#### *Procedure*

The Orimulsion was poured into test jars meeting the specifications of ASTM method D 97, *Standard Test Method for Pour Point of Petroleum Products* (ASTM, 1999f). The test jars were fitted with stoppers and ASTM-designated thermometers, and warmed in a water bath to 50°C. The samples were removed from the bath and allowed to cool to room temperature. For additional cooling, the samples were moved sequentially to a cold room maintained at 5°C, and a freezer at -25°C. While cooling, the sample was checked periodically as per ASTM method D-97, but not necessarily at multiples of 3°C. When the pour point was reached, 3°C was added to the temperature recorded from the thermometer, as specified in the ASTM method. This value is reported as the pour point. Samples were run in duplicate and the mean pour point reported.

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### 3.3.16 Flash Point (BP BITOR, 1993)\*

#### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*

#### *Procedure*

The flash point of fresh Orimulsion is determined by method A as given in ASTM method D 3828, *Standard Test Methods for Flash Point by Setaflash Closed Tester* (ASTM, 1999j):

#### Summary of Test Method

A portion of sample is introduced by a syringe into the cup of the selected apparatus that is set and maintained at the specified temperature. After a specific time a test flame is applied and observation is made as to whether or not a flash occurred.

#### *Source notes*

... the flash point of the bitumen used to manufacture Orimulsion is typically ca 120°C.

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### 3.3.17 Flash Point (Intevp, 1993)\*

#### *\*Title of Source*

*Characterization of Orimulsion quality control manual*

#### *Storage and Handling*

Storage temperature was not specified. A flat blade stirrer operating at 100 rpm for 1 hour is recommended for homogenizing the sample.

#### *Procedure*

The flash point of fresh Orimulsion is determined by a method based on ASTM method D 92, *Standard Test Method for Flash and Fire Points by Cleveland Open Cup* (ASTM, 1999c):

##### Summary of Test Method

The test cup is filled to a specified level with the sample. The temperature of the sample is increased rapidly at first and then at a slow constant rate as the flash point is approached. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point.

The cup is filled with homogenized Orimulsion at room temperature. The sample is heated so that the rate of temperature increase is approximately 14 to 17°C/minute, until the temperature of the sample reaches 70 to 75°C. The rate of heating is reduced to 5 to 6°C/minute until the sample reaches the target temperature of 85°C. The test flame is applied following the instructions given in ASTM method D92 and the sample is observed for a flash or no flash at 85°C. The result is reported as flash point higher (>) or lower (<) than the target temperature, 85°C.

#### *Source notes*

Experimentally, the heating of Orimulsion at temperatures higher than 90°C produces a violent bubbling/splashing of the sample, with irregular ejection of the water contained in the product. If at this point, a test flame is applied to the product, no flashing will be seen, because the water evaporation can extinguish the test flame. Therefore, the flash point value of Orimulsion should not be measured using the same criterion applied to crude oils and other petroleum products.

For these reasons, the aim of this test is to determine a flash/no flash result at the target temperature of 85°C, reporting the value as flash point  $\geq 85^{\circ}\text{C}$ .

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### 3.3.18 Flash Point (Jokuty *et al.*, 1995, 1999b)\*

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, it was removed from cold storage and shaken on a reciprocating shaker for 30 minutes.

#### *Procedure*

The method used was based on ASTM method D 56, *Standard Test Method for Flash Point by Tag Closed Tester* (ASTM, 1999b):

##### Summary of Test Method

The sample is placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. A small flame of specified size is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

The instrument used was a SUR BERLIN TAG 2 automatic flash point tester, modified by adding a stirring mechanism. The stirrer aids in producing more uniform heat transfer to oils that exceed the design viscosity, and in no way interferes with the test mechanism. Samples were run in duplicate and the mean flash point reported.

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### 3.3.19 Flash Point (Ostazeski *et al.*, 1997)\*

#### *\*Title of Source*

*The environmental behaviour of Orimulsion spilled on water*

#### *Storage and Handling*

No information given.

#### *Procedure*

The flash point of fresh Orimulsion was determined with a Grabner Miniflash apparatus following a method based on ASTM method D 93, *Standard Test Method for Flash Point by Pensky-Martens Closed Tester* (ASTM, 1999d):

##### Summary of Test Method

The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

The sample was incrementally heated from ambient temperature and a spark source was engaged at regular intervals. Samples were run in duplicate and the mean flash point reported.

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### 3.3.20 Surface/Interfacial Tension (Jokuty *et al.*, 1995, 1999b)\*

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*  
*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

#### *Procedure*

Surface tension was measured using a Kruss K10ST automatic Du Nuoy ring tensiometer. The instrument was operated according to the manufacturers instructions, with one modification - ordinary 100-mL Pyrex beakers were used instead of the special sample containers supplied by Kruss. The beakers were prepared for use by rinsing with dichloromethane, followed by soaking and washing with a commercial cleaner (Decon 75), and thorough rinsing with water purified by reverse osmosis. The beakers were then oven-dried at 160°C, cooled to room temperature, and stored at the desired measurement temperature. Samples were run in duplicate and the mean surface tension reported.

Calculation of the surface tension was done as described in ASTM method D 971, *Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method* (ASTM, 1999g):

#### Summary of Test Method

Interfacial tension is determined by measuring the force necessary to detach a planar ring of platinum wire from the surface of the liquid of higher surface tension, that is, upward from the water-oil interface. To calculate the interfacial tension, the force so measured is corrected by an empirically determined factor which depends upon the force applied, the densities of both oil and water, and dimensions of the ring. Measurements are made under rigidly standardized nonequilibrium conditions in which the measurement is completed within 1 min after formation of the interface.

#### *Source notes*

Oil-sea water interfacial tension could not be measured because the Orimulsion layer did not form a clean interface with the water, but instead partially dispersed into the water layer. Oil-fresh water interfacial tension could not be measured because Orimulsion is denser than fresh water and sinks.

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### 3.3.21 Surface/Interfacial Tension (Brown *et al.*, 1995)\*

#### *\*Title of Source*

*Comparative evaluation of physical and chemical fate processes of Orimulsion and Fuel Oil No. 6 in the Tampa Bay marine environment*

#### *Storage and Handling*

No information given.

#### *Procedure*

Interfacial tension measurements are made using a Fisher Scientific du Nouy ring apparatus (Surface Tensiomat model 21), in accordance with ASTM method D 971, *Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method* (ASTM, 1999g):

##### Summary of Test Method

Interfacial tension is determined by measuring the force necessary to detach a planar ring of platinum wire from the surface of the liquid of higher surface tension, that is, upward from the water-oil interface. To calculate the interfacial tension, the force so measured is corrected by an empirically determined factor which depends upon the force applied, the densities of both oil and water, and dimensions of the ring. Measurements are made under rigidly standardized nonequilibrium conditions in which the measurement is completed within 1 min after formation of the interface.

The apparatus is checked just prior to each oil sample analysis by measuring the interfacial tension of hexane-distilled water (51.1 dynes/cm).

#### *Source notes*

All interfacial tension readings will be determined in distilled water, to avoid possible variances in seawater samples between analyses, and to limit the corrosive effects of seawater on the apparatus.

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### 3.3.22 Adhesion (Jokuty *et al.*, 1998a)\*

#### *\*Title of Source*

*Bitumen adhesion as a function of time*

#### *Storage and Handling*

The Orimulsion was stored at 15°C. Before sampling, it was removed from cold storage and shaken on a reciprocating shaker for 30 minutes (Jokuty *et al.*, 1998a; Jokuty *et al.*, 1999b).

#### *Procedure*

This method requires the use of an analytical pan balance capable of weighing to 0.0001 g, with provision for weighing from below the pan, and a standard penetrometer needle as described in ASTM method D 5, *Standard Test Method for Penetration of Bituminous Materials* (ASTM, 1999a) adapted for hanging below the balance. Adhesion measurements were made according to the following protocol.

The balance was prepared for measurement by hanging a penetrometer needle, for which the surface area of the stainless steel section had been calculated, from the balance hook and allowing the weight to stabilize. The weight of the clean needle was recorded. The sample to be evaluated was placed in an appropriate vessel and elevated, using a lab jack, until the top of the stainless steel needle met the top of the oil. The needle was left in the oil for 30 seconds, and then the vessel was lowered, allowing the needle to hang undisturbed. After 30 minutes the weight of the needle plus oil was recorded. The needle was cleaned with dichloromethane and allowed to dry before the measurement was repeated. Five measurements were made on each sample. The oil adhesion was calculated as the weight of oil remaining on the needle divided by the needle's surface area. The mean value  $\pm$  one standard deviation was reported.

#### *Reviewer's notes*

This method was developed by the Emergencies Science Division of Environment Canada. The stainless steel penetrometer needle was chosen as the standard test surface because it is an easily obtained piece of equipment, with well-defined specifications. Other materials have been investigated (Jokuty *et al.*, 1996), and correlations with various physical properties have been measured. It was found that the relative order of adhesiveness of different oils was independent of the type of material used for the test surface; for a variety of oils, from light to heavy, adhesion values measured using different surface materials fell within half an order of magnitude; in general, for both fresh and evaporated oils, there are a limited number of good correlations of adhesion with other oil properties, in particular asphaltene content, viscosity, and density.

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### 3.3.23 Adhesion (on Coarse and Fine Sediments) (Brown *et al.*, 1995)\*

#### *\*Title of Source*

*Comparative evaluation of physical and chemical fate processes of Orimulsion and Fuel Oil No. 6 in the Tampa Bay marine environment*

#### *Storage and Handling*

No information given.

#### *Procedure*

Adhesion experiments were conducted in batch mode at  $20 \pm 2^\circ\text{C}$ , as follows:

##### *Batch procedure*

- 1) Weigh bottle A and add sediment
- 2) Prepare a solution of Orimulsion (about 10 g oil/L sea water).
- 3) Add 100 mL of Orimulsion solution to bottle A, and then fill the bottle with sea water, to completely eliminate the head space.
- 4) Rotate these bottles for the specified time period, then stop the rotation and let sediments settle for one minute.
- 5) Transfer the supernatant solution to bottle B and centrifuge for 4 minutes at 10 rpm.
- 6) Use a pipette to carefully take out the supernatant of (5) and add sea water to resuspend the fine particles, then centrifuge again.
- 7) Repeat step (6) twice.
- 9) Filter the solution, discard the filtrate, and replace the collection vessel.
- 10) Use 30 mL dichloromethane to wash the fine particles, until the eluate is colourless.
- 11) Determine the filtrate concentration by UV-VIS spectrometry.
- 12) Weigh the filter paper with fine sediments when they are dry.
- 13) Gently wash the sediments in bottle A twice with standard sea water.
- 14) Transfer an aliquot of sediments from bottle A to weighed beaker, and use 100 mL dichloromethane to extract the total petroleum hydrocarbons (TPH) from these sediments (coarse sediments).
- 15) Determine TPH concentration by UV-VIS.
- 16) Weigh the coarse sediments after extraction.
- 17) Calculate the amount of Orimulsion attached to the coarse and fine sediments.

Replication was completed in triplicate. Experiments were performed at salinities of 23.0, 11.5, 5.7, and 0.7 ppt. Two sediment loading rates were used: 5 and 20 grams in 140 mL of solution (35,710 and 142,860 mg/L). Approximately 14.3 g/L of Orimulsion in sea water was mixed with the sediment for periods extending up to 2 hours. Coarse sediment fractions were defined as the material that settled to the bottom of quiescent test containers within one minute. The finer fraction was equated to material that remained in suspension after one minute of quiescent settling. It was determined that this fraction comprised 0.14% w/w of the total sediment added. At indicated times, samples of both sediment fractions (i.e., fine and coarse, were separated for hydrocarbon extraction with methylene chloride and analysis by UV-visible spectrometry. Concentration values were estimated with respect to calibrated Orimulsion standards.

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### 3.3.24 Total Petroleum Hydrocarbons (Wang and Fingas, 1996)\*

#### *\*Title of Source*

*Separation and characterization of petroleum hydrocarbons and surfactant in Orimulsion dispersion samples*

#### *Procedure*

##### *Gravimetric*

Orimulsion dispersion samples (1 L, in glass jars) were vigorously shaken for five minutes. In most cases a 10.0 mL aliquot of sample, from the mid-depth of the bottle, was transferred to a filter funnel using a disposable pipet. For samples with obviously low oil concentrations, 200 mL of sample was transferred. Samples were filtered by vacuum through Supelco Nylon 66 0.45- $\mu$ m membranes. The recovered oil was completely transferred to a beaker using dichloromethane, and dried by passing the solution through anhydrous sodium sulphate. The dried solutions were concentrated by rotary evaporation, solvent-exchanged to hexane, and made up to an appropriate volume. Aliquots of the concentrated oil-in-hexane solutions were blown down to dry residues with nitrogen, and weighed on a microbalance to obtain total solvent-extractable materials (TSEM).

##### *GC/MS analysis*

For samples where TSEM was too low for the method above, 1 L of sample was successively extracted three times with 50 mL portions of dichloromethane using a liquid-liquid extraction technique in a separatory funnel. The extract was then concentrated, solvent-exchanged to hexane, and fractionated for GC analysis (Wang *et al.*, 1994a, 1994b):

A microcolumn fractionation technique was used for sample cleanup and fractionation of the concentrated oil extracts. Aliquots of extracts containing approximately 20 mg of TSEM were applied to 3-g silica gel columns, preconditioned with 12 mL of hexane. Half of the hexane fraction (F1) and half of the 50% benzene:hexane fraction (F2) were combined (F3) and used for the determination of total petroleum hydrocarbons. The fractions were concentrated under a stream of nitrogen, spiked with surrogates and internal standards, and adjusted to accurate pre-injection volumes for GC analysis.

Analysis for total petroleum hydrocarbons was performed on a Hewlett-Packard (HP) 5890 gas chromatograph (GC) equipped with a flame-ionization detector (FID) and an HP 7673 autosampler. A 30-m, 0.32-mm i.d., 0.25- $\mu$ m film thickness DB-5 capillary column was used. The carrier gas was helium (2.5 mL/min). The injector and detector temperatures were 290°C and 300°C respectively. The temperature program was initial temperature 50°C for 2 minutes, increased to 300°C at 6 °C/min, and held for 16 minutes. A 1- $\mu$ L volume was injected in the splitless mode with a 1-minute purge-off.

#### *Source notes*

*Gravimetric:* After filtration, the filtrate was clear and colourless.

*GC/MS:* "The TPHs (saturates plus aromatics) are only 30-35% of the total weight of TSEM, indicating a relatively high portion (~60-70%) of resins and asphaltenes in Orimulsion."

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### 3.3.25 Total Petroleum Hydrocarbons (Brown *et al.*, 1995)\*

#### *\*Title of Source*

*Comparative evaluation of physical and chemical fate processes of Orimulsion and Fuel Oil No. 6 in the Tampa Bay marine environment*

#### *Procedure*

##### *Dissolved hydrocarbons*

Fourteen mL of aqueous sample is transferred to a 140-mL centrifuge bottle, and diluted to volume. The solution is centrifuged for 15 minutes. Fifty mL of the centrifuged solution is vacuum filtered through a 0.45- $\mu$ m filter. The filtrate is transferred to a separatory funnel. The filtration flask is rinsed with methylene chloride and the washing is also transferred to the funnel. The aqueous sample solution is sequentially extracted with three 20-mL portions of methylene chloride. The combined extracts are transferred to a 100-mL volumetric flask and diluted to volume with solvent. Twenty mL of this solution is transferred to a vial and closed with no head space. The vials are labelled and refrigerated until analysed by UV-fluorescence spectrometry.

#### *Source notes*

This procedure was adapted from "Determination of Petroleum Hydrocarbons in Sediments", United Nations Environment Program (UNEP), Reference Methods for Marine Pollution Studies No. 20.

With this procedure concentrations of total aromatic hydrocarbons can be determined in sediment samples. The UNEP method was adapted for the analysis of TPH extracts from water samples. The liquid-liquid Methylene Chloride extracts (EPA # 3510A) were concentrated and analyzed by UV-fluorescence directly. The UNEP suggested reference compound, Crysene [sic], was used for calibration purposes. Data obtained by this method correspond to the total aromatic fraction of the extracted TPH, and are semi-quantitative in nature. This method was selected due to its high sensitivity.

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### 3.3.26 Total Petroleum Hydrocarbons (Esclapés *et al.*, )\*

#### *\*Title of Source*

*Toxicity of Orimulsion and Fuel Oil No. 6 to Mysidopsis babia, Menidia beryllina and Cyprinodon dearborni*

#### *Procedure*

Total hydrocarbons were determined by "Oil and Grease Analysis, through UV-visible Method".

#### *Reviewer's notes*

No other details given.

The reference cited for the above method is *Standard Methods for the Examination of Water and Wastewater* (APHA/AWWA/WPCF, 1976). This edition was not available for checking the method described, but a more recent edition (APHA/AWWA/WPCF, 1992b) contains only gravimetric and infrared methods for oil and grease.

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### 3.3.27 Total Petroleum Hydrocarbons (Gassman, 1995)\*

#### *\*Title of Source*

*Comparison of Orimulsion and Fuel Oil No. 6 on selected fish species inhabiting Tampa Bay*

#### *Procedure*

Samples were analyzed for total recoverable petroleum hydrocarbons (TRPH) by EPA method 418.1.

#### *Source notes*

Samples were stored in the refrigerator for no more than 7 days prior to extraction and analysis.

#### *Reviewer's notes*

No other details given.

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### 3.3.28 Total Petroleum Hydrocarbons (Jokuty *et al.*, 1995)\*

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

#### *Procedure*

Each 10-mL sample was extracted in the following manner. The sample was expelled from the syringe into a 60-mL separatory funnel. Three drops of 6 M hydrochloric acid were added to ensure that the sample was at a pH of 2 or less. 15 mL of carbon tetrachloride ( $\text{CCl}_4$ ) was poured into a 20-mL beaker. The syringe was rinsed, first by drawing up approximately 10 mL of the  $\text{CCl}_4$  and expelling it into the separatory funnel. The syringe was then pulled apart. The plunger was rinsed in the remaining 5 mL of  $\text{CCl}_4$  and this was then poured through the syringe body into the separatory funnel. After this procedure, no bitumen could be seen adhering to the syringe. An additional 15 mL  $\text{CCl}_4$  was added to the separatory funnel (30 mL total). The contents of the funnel were mixed manually by using 15 wrist rotations at a rate of approximately one per second. The two layers were allowed to separate for one minute. The bottom ( $\text{CCl}_4$ ) layer was then drawn off, through a fluted filter paper containing approximately 0.5 g sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), into a 100-mL volumetric flask. The aqueous layer was then extracted with two more 3-mL portions of  $\text{CCl}_4$ , which were also drawn off into the 100-mL volumetric flask. The extract was then brought to volume with the addition of  $\text{CCl}_4$ .

The total hydrocarbon content of each extract was determined using a Buck Scientific total hydrocarbon analyzer, Model HC404. This instrument measures infrared absorbance at  $2924\text{ cm}^{-1}$ . An Orimulsion working curve was established by preparing a  $1000\text{ }\mu\text{g bitumen/mL}$  stock solution from which solutions of  $500\text{ }\mu\text{g/mL}$ ,  $100\text{ }\mu\text{g/mL}$ ,  $50\text{ }\mu\text{g/mL}$ , and  $10\text{ }\mu\text{g/mL}$  were made. The instrument was operated according to the manufacturers instructions and a linear relationship was established between absorbance and concentration. Method blanks were also analyzed and the absorbance of the blank was subtracted from the sample absorbances before calculating the sample concentrations.

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### 3.3.29 Total Petroleum Hydrocarbons (Jokuty *et al.*, 1999a, 1999b)\*

#### *\*Title of Source*

*The dynamics of Orimulsion spills in salt, fresh, and brackish water*  
*Orimulsion-400: A comparative study*

#### *Procedure*

60 mL water samples were extracted with three 25-mL portions of dichloromethane. The solvent was then evaporated, the bitumen weighed, and the concentration calculated as parts-per-million of bitumen in water.

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### 3.3.30 Total Petroleum Hydrocarbons (French *et al.*, 1997)\*

#### *\*Title of Source*

*Validation of an Orimulsion spill fate model using observations from test spills*

#### *Procedure*

Total hydrocarbons were determined by gravimetric methods.

#### *Source notes*

The detection limit was 40 mg/L (40 ppm).

#### *Reviewer's notes*

No other details given.

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### 3.3.31 Total Petroleum Hydrocarbons (Warren Spring Laboratory, 1989)\*

#### *\*Title of Source*

*Observations of the behaviour of Orimulsion released into the sea and in a test tank*

#### *Procedure*

Oil contents were measured with a Miran-1A Infrared Analyser.

#### *Reviewer's notes*

No other details given.

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### 3.3.32 Total Petroleum Hydrocarbons (Washburn & Gillis Associates Ltd., 1988)\*

#### *\*Title of Source*

*Orimulsion (TM) - Toxicity Tests Final Report*

#### *Procedure*

Aqueous samples were dissolved in hexane and analyzed by fluorescence spectroscopy at a wavelength of 360 nm. Calibration curves of known concentrations of Orimulsion in spectrophotometric grade hexane were used to determine the concentration of the experimental solutions.

#### *Source notes*

The Orimulsion immediately adhered to the sample bottles upon collection. All samples were analyzed within two weeks after collection.

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### 3.3.33 Total Petroleum Hydrocarbons (Ostazeski *et al.*, 1997)\*

#### *\*Title of Source*

*The environmental behaviour of Orimulsion spilled on water*

#### *Procedure*

Analysis of Orimulsion for total petroleum hydrocarbons (TPH) was performed following methods that are modifications of EPA method 8100. The total gas chromatographic hydrocarbon signature of Orimulsion was determined using a Hewlett-Packard 5890 Series II capillary gas chromatograph equipped with flame ionization detection (GC/FID). A 3  $\mu$ L aliquot of a 5 mg/mL dichloromethane dilution of the oil was injected using splitless techniques onto a 30-m DB-5 capillary column (0.32-mm i.d., 0.25  $\mu$ m film thickness). The oven was programmed from 35°C to 320°C at 6°C/min. Prior to sample analysis, a 6 point calibration curve for *n*-C<sub>8</sub> to *n*-C<sub>40</sub> *n*-alkanes, pristane, and phytane was used to demonstrate instrument calibration and performance.

Total petroleum hydrocarbons, (resolved plus unresolved TPH) were quantified by the method of internal standards using the baseline corrected total area of the chromatogram and the average hydrocarbon response factor of the individual C<sub>8</sub> to C<sub>40</sub> *n*-alkanes. 5 $\alpha$ -androstane was used as the internal standard.

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### 3.3.34 Total Petroleum Hydrocarbons (Johnson *et al.*, 1995)\*

#### *\*Title of Source*

*Acute toxicity test of Orimulsion and Fuel Oil No. 6 using standard test species*

#### *Procedure*

Samples were analyzed for total recoverable petroleum hydrocarbons (TRPH).

#### *Reviewer's notes*

No other details given.

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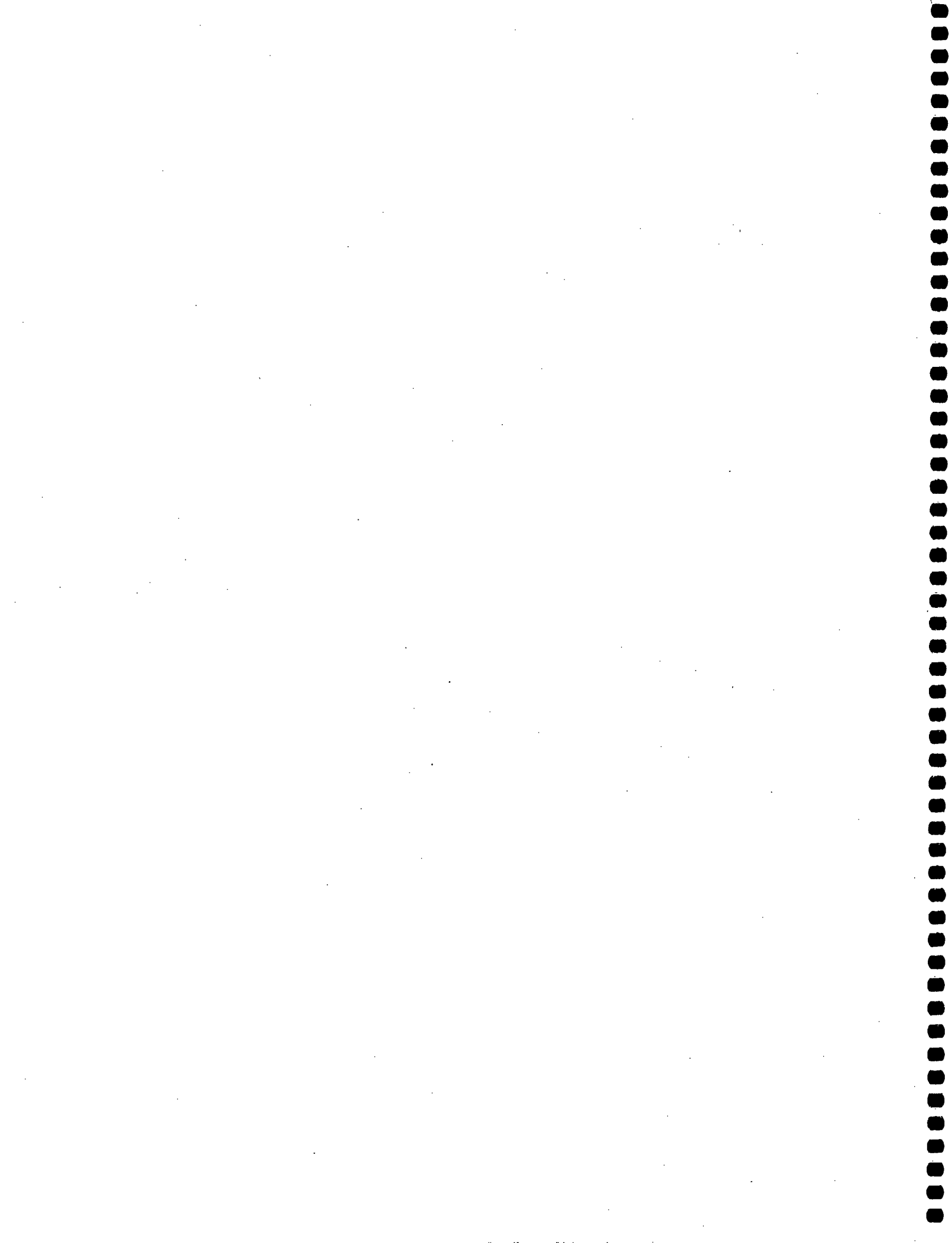
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## 4. Chemical Properties

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This section covers methods in 6 different categories: detailed petroleum hydrocarbon analysis, volatile organic compounds, hydrocarbon groups, surfactant analysis, metals, and sulphur. A total of 20 methods, from 10 different sources, were reviewed.

### 4.1 General Comments

Unlike the methods for physical properties, many of the chemical properties methods reviewed did not cite reference methods. In some cases method development was either the primary purpose of the work, or a necessary step to acquire the desired data.

### 4.2 Evaluations and Recommendations

#### 4.2.1 Detailed Petroleum Hydrocarbon Analysis

##### *Evaluation*

This section includes methods that were used to determine a wide variety of analytes including *n*-alkanes, isoprenoid hydrocarbons, unsubstituted and alkyl homologues of polycyclic aromatic hydrocarbons (PAHs), and dibenzothiophenes. (Ostazeski *et al.*, 1997; Potter *et al.*, 1997; Wang and Fingas, 1996).

Solvent extraction with dichloromethane was used in all of the methods, but beyond that there were major differences in sample preparation procedures. Ostazeski *et al.* (1997) analyzed a dilution of the extracted oil without further processing. Wang and Fingas (1996) used a silica microcolumn technique for sample cleanup and fractionation of the concentrated extracts into saturates and aromatics. Potter *et al.* (1997) extracted filtered, aqueous samples first at neutral pH and then after acidification. The acid and neutral extracts were combined, dried, and then separated into paraffinic, aromatic, and polar fractions on neutral alumina. Such cleanup and fractionation techniques can have significant effects on analyte recovery, as discussed in section 3.2.9.

In the methods reviewed, alkanes and isoprenoid hydrocarbons were determined by GC/FID while PAHs and dibenzothiophenes were determined by gas chromatography/mass spectrometry (GC/MS). These GC/FID and GC/MS methods were modifications of EPA methods 8100, *Polynuclear Aromatic Hydrocarbons* and 8270, *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)* respectively (USEPA, 1980a, 1980c). Ostazeski *et al.* (1997) quantitated the alkylated PAH homologues using the response factors of the parent PAH standards, while Wang and Fingas (1996) determined relative response factors for alkylated PAHs directly. This technique should result in more accurate quantitation of alkylated PAHs. In spite of this difference, the results of the two methods were similar.

##### *Recommendation*

The referenced EPA methods, 8100 and 8270, are good starting points for detailed hydrocarbon analysis of Orimulsion and related samples. Further method development research with Orimulsion or bitumen is required to determine the relative merits of the different sample preparation techniques.

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#### 4.2.2 Volatile Organic Compounds

##### *Evaluation*

Volatile organic compounds (VOCs) were measured in three of the studies reviewed. Benzene, toluene, ethylbenzene, xylenes (BTEX), and C<sub>3</sub>-substituted benzenes were determined directly by GC/MS (Jokuty *et al.*, 1999). This method has been demonstrated to be rapid, reliable, and effective (Wang *et al.*, 1995). VOCs were also determined by purge-and-trap GC/MS (Potter *et al.*, 1997), with analytical conditions cited as equivalent to EPA method 8260, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)* (USEPA, 1980b). The results obtained by this method were in agreement with those obtained by the direct determination method. A third source referred to the analysis of samples for "purgeable" aromatics, but gave no details of the analytical method (Johnson *et al.*, 1995).

##### *Recommendation*

Both the method of Wang *et al.* and EPA method 8260 (USEPA, 1980b) are suitable for the determination of VOCs in Orimulsion and related samples.

#### 4.2.3 Surfactant Analysis

##### *Evaluation*

Two methods were reviewed relating to Orimulsion surfactant analysis (Potter *et al.*, 1997; Wang and Fingas, 1996). The methods used were similar. Both methods used filtration to remove bitumen particles prior to analysis by high-performance liquid chromatography (HPLC) with acetonitrile/water mixtures as the mobile phase.

##### *Recommendation*

Although both of the methods reviewed are suitable for Orimulsion surfactant analysis, additional research to determine the effect (if any) of the different acetonitrile/water ratios used, could be useful.

#### 4.2.4 Hydrocarbon Groups

##### *Evaluation*

The hydrocarbon groups determined in Orimulsion were saturates, aromatics, resins, and asphaltenes. Two different methods were reviewed. The Environment Canada method uses *n*-pentane to precipitate asphaltenes followed by open column chromatography on silica to separate the saturates, aromatics, and resins. Each group is then determined by gravimetry and corrections are made for loss of volatile saturates and aromatics, although in the case of Orimulsion, these are absent (Jokuty *et al.*, 1995). The sample analyzed was residual bitumen from the nearly complete evaporation of water from Orimulsion. A very good mass balance was obtained.

(Ostazeski *et al.*, 1997) determined asphaltenes gravimetrically after precipitation from *n*-pentane (soft asphaltenes), or *n*-heptane (hard asphaltenes). Saturates, aromatics, and resins were determined by

thin-layer chromatography with flame ionization detection (TLC/FID) using an Iatroscan instrument. The ability of the detector to completely ionize the higher molecular weight components of the bitumen have not been clearly demonstrated, and it is not possible to directly calculate a mass balance.

#### *Recommendation*

Because hydrocarbon groups are essentially defined by the methods used to produce them, the results of the two methods reviewed are expected to be somewhat different. Nevertheless, the Environment Canada method of hydrocarbon group analysis is recommended for Orimulsion, until it can be demonstrated that the flame ionization detection used in the Iatroscan method can adequately detect the resin fraction.

### 4.2.5 Sulphur

#### *Evaluation*

Four different methods were reviewed for the determination of sulphur in Orimulsion.

In the quality manual used by Bitor Europe, (BP BITOR, 1993), it is recommended that sulphur content of Orimulsion be determined by any one of three methods: ASTM method D 129, *Standard Test Method for Sulfur in Petroleum Products (General Bomb Method)* (ASTM, 1999a); ASTM method D 1552, *Standard Test Method for Sulfur in Petroleum Products (High-Temperature Method)* (ASTM, 1999b); or IP method 242, *Sulphur in Petroleum Products, Flask Combustion Method* (IP). ASTM method D1552 is also specified in the Orimulsion Quality Manual (Intevep, 1993). It is noted in this particular method that nitrogen contents in excess of 0.1% can interfere with the sulphur measurement. The nitrogen content of Cerro Negro bitumen is 0.64% (IIT Research Institute, 1989).

The method used by Environment Canada (Jokuty *et al.*, 1999) is based on ASTM method D 4294, *Test Method for Sulfur in Petroleum Products by Energy-dispersive X-ray Fluorescence Spectroscopy* (ASTM, 1999d). Orimulsion should not produce any of the possible interferences noted in this method.

#### *Recommendation*

Until it can be demonstrated that the nitrogen content of Orimulsion does not affect sulphur measurement by ASTM method D 1552, this method is not recommended. As satisfactory results seem to have been obtained by each of the other methods, any of them may be used, the final choice to be determined by availability of equipment. A comparative study of these three methods would be useful.

### 4.2.6 Metals

#### *Evaluation*

Metals in Orimulsion were determined either by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Jokuty *et al.*, 1995; Kamiura *et al.*, 1996) or by flame atomic absorption spectroscopy (FAAS) (BP BITOR, 1993; Intevep, 1993; Platteau and Carillo, 1995). ICP-AES was also used to determine metals in Orimulsion water-soluble fractions (Potter *et al.*, 1997).

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The ICP-AES methods used a variety of different sample preparation techniques including conventional nitric acid digestion (Potter *et al.*, 1997), pretreatment with yeast, followed by nitric acid digestion (Kamiura *et al.*, 1996), and microwave digestion with nitric acid (Fingas *et al.*, 1995). The microwave digestion procedure is much faster than the conventional procedure. The FAAS method used dehydration of Orimulsion followed by dry ashing (Platteau and Carillo, 1995). Results were compared with those from an unspecified dispersive X-ray fluorescence method and found to be in good agreement.

#### *Recommendation*

All of the methods reviewed have been found to produce reliable and comparable results. Therefore the choice of method for determination of metals in Orimulsion should be based on instrument availability. The microwave digestion method is recommended as an effective and rapid alternative to conventional wet ashing procedures.

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## 4.3 Method Summaries

### 4.3.1 Detailed Petroleum Hydrocarbon Analysis (Ostazeski *et al.*, 1997)\*

#### *\*Title of Source*

*The environmental behaviour of Orimulsion spilled on water*

#### *Procedure*

##### *GC/FID analysis*

Analysis of Orimulsion for C<sub>8</sub> to C<sub>40</sub> *n*-alkanes and isoprenoid hydrocarbons was performed following methods that are modifications of EPA Method 8100. The total gas chromatographic hydrocarbon signature of Orimulsion was determined using a Hewlett-Packard 5890 Series II capillary gas chromatograph equipped with flame ionization detection (GC/FID). A 3 µL aliquot of a 5 mg/mL dichloromethane diution of the oil was injected using splitless techniques onto a 30-m DB-5 capillary column (0.32-mm i.d., 0.25 µm film thickness). The oven was programmed from 35°C to 320°C at 6°C/min. Prior to sample analysis, a 6 point calibration curve for *n*-C<sub>8</sub> to *n*-C<sub>40</sub> *n*-alkanes, pristane, and phytane was used to demonstrate instrument calibration and performance.

Alkanes were quantified by the method of internal standards using the baseline corrected total area of the chromatogram and the average hydrocarbon response factor of the individual C<sub>8</sub> to C<sub>40</sub> *n*-alkanes. 5α-androstane was used as the internal standard.

##### *GC/MS analysis*

Analysis of Orimulsion for C0 through C4 alkyl homologues of 2-, 3-, 4-, 5-, and 6-ring polynuclear aromatic hydrocarbons (PAHs), and dibenzothiophenes was performed following methods that are modifications of EPA Method 8270. All sample extracts were analyzed using a Hewlett-Packard 5890 gas chromatograph equipped with a 5970 mass selective detector (GC/MS) operating in the selected ion-monitoring (SIM) mode. A 2 µL aliquot of the sample was injected using splitless techniques onto a 30-m DB-5-MS capillary column (0.25-mm i.d., 0.25-µm film thickness). Prior to sample analysis, the GC/MS was tuned with a perfluorotributylamine (PFTBA), and a minimum of a 5-point initial calibration consisting of parent and alkylated PAH compounds was established to demonstrate the linear range of the analysis.

Individual components were quantified by the method of internal standards using response factors generated for the each component relative to the response facotrs obtained for the internal standards acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, and benzo[a]pyrene-d<sub>12</sub>. The alkyl homologues were then quantified using the baseline integration of each level of alkylation and the response factor of the respective parent PAH compound.

#### *Source notes*

The method described achieves near-baseline separation of the petroleum-specific PAH compounds.

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#### 4.3.2 Detailed Petroleum Hydrocarbon Analysis (Potter *et al.*, 1997)\*

##### *\*Title of Source*

*Chemical characterization of the water soluble fraction of Orimulsion-in-water dispersion*

##### *Procedure*

##### *Sample preparation*

The aqueous phase of Orimulsion was prepared in two ways.

- 1) Orimulsion was frozen at  $-20^{\circ}\text{C}$ , then thawed. The free-flowing liquid was decanted, centrifuged at 10,000 g. The supernatant was filtered through 0.45- $\mu\text{m}$  Teflon membrane filters. The bitumen was then re-equilibrated with a volume of distilled-deionized water equal to the liquid volume drained from the thawed Orimulsion and shaken for 1 hour on a wrist action shaker. The mixture was frozen and the free-flowing liquid processed as described above.
- 2) Orimulsion was diluted with distilled-deionized water or sea water, with slow stirring using a Teflon-coated stir bar in a glass beaker. Dilutions of 1:9, 1:99, and 1:999 were used. After the Orimulsion was completely mixed with the water, aliquots were vacuum filtered sequentially through glass fiber filters, 1  $\mu\text{m}$  nominal pore size, and 0.45- $\mu\text{m}$  Teflon membranes. Filtrates were frozen at  $-20^{\circ}\text{C}$  until analysis.

##### *Extractable hydrocarbon analysis*

100-mL aliquots of each filtrate were spiked with a surrogate standard mixture consisting of approximately 50  $\mu\text{g}$  each naphthalene- $\text{d}_8$ , perylene- $\text{d}_{12}$ , and phenol- $\text{d}_6$ . This was followed by sequential extraction with three 25-mL portions of dichloromethane at neutral pH and after acidification with hydrochloric acid to pH 2. The acid and neutral extracts were combined, dried with anhydrous sodium sulphate and separated into paraffinic, aromatic, and polar fractions on neutral alumina. The alumina column was sequentially with hexane, dichloromethane, and methanol. The extracts were concentrated under nitrogen and then analyzed using a Hewlett Packard model 5989 GC/MS system. Anthracene- $\text{d}_{10}$  was used as an internal standard.

##### *Source notes*

Reference analytical procedures were USEPA Methods 8270 (GC/MS), 3510 (separatory funnel extraction) and 3611 (chromatography on alumina).

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### 4.3.3 Detailed Petroleum Hydrocarbon Analysis (Wang and Fingas, 1996)\*

#### *\*Title of Source*

*Separation and characterization of petroleum hydrocarbons and surfactant in Orimulsion dispersion samples*

#### *Procedure*

##### *Sample preparation*

Orimulsion dispersion samples (1 L, in glass jars) were vigorously shaken for five minutes. In most cases a 10.0 mL aliquot of sample, from the mid-depth of the bottle, was transferred to a filter funnel using a disposable pipet. For samples with obviously low oil concentrations, 200 mL of sample was transferred. Samples were filtered by vacuum through Supelco Nylon 66 0.45- $\mu$ m membranes. The recovered oil was completely transferred to a beaker using dichloromethane, and dried by passing the solution through anhydrous sodium sulphate. The dried solutions were concentrated by rotary evaporation, solvent-exchanged to hexane, and made up to an appropriate volume.

For samples where TSEM was too low for the method above, 1 L of sample was successively extracted three times with 50 mL portions of dichloromethane using a liquid-liquid extraction technique in a separatory funnel. The extract was then concentrated, and solvent-exchanged to hexane, and made up to an appropriate volume.

A microcolumn fractionation technique was used for sample cleanup and fractionation of the concentrated oil extracts (Wang *et al.*, 1994a; Wang *et al.*, 1994b). Aliquots of extracts containing approximately 20 mg of TSEM were applied to 3-g silica gel columns, preconditioned with 12 mL of hexane. Half of the hexane fraction (F1) was used for analysis of saturates and biomarker compounds. Half of the 50% benzene:hexane fraction (F2) was used for analysis of target polycyclic aromatic hydrocarbons (PAH) and alkylated PAH homologues. The fractions were concentrated under a stream of nitrogen, spiked with surrogates and internal standards, and adjusted to accurate pre-injection volumes for GC analysis.

##### *GC/FID analysis*

Analysis for *n*-alkane distribution hydrocarbons was performed on a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a flame-ionization detector and an HP 7673 autosampler. A 30-m, 0.32-mm i.d., 0.25- $\mu$ m film thickness DB-5 capillary column was used. The carrier gas was helium (2.5 mL/min). The injector and detector temperatures were 290°C and 300°C respectively. The temperature program was initial temperature 50°C for 2 minutes, increased to 300°C at 6°C/min, and held for 16 minutes. A 1- $\mu$ L volume was injected in the splitless mode with a 1-minute purge-off.

##### *GC/MS analysis*

Analyses of target PAHs and biomarker compounds were performed on an HP 5890 GC equipped with an HP 5972 mass selective detector (MSD). The MSD was operated in the scan and selected ion monitoring (SIM) modes for identification of components and in the SIM mode for quantitation of target compounds. A 30-m, 0.25-mm i.d., 0.25- $\mu$ m film thickness HP-5 capillary column was used. The carrier gas was helium (1.0 mL/min). The injector and detector temperatures were 290°C and 300°C respectively. The temperature program for target PAHs was initial temperature 90°C for 1 minute, increased to 160°C at 25°C/min and then to 290°C at 8°C/min, and held for 15 minutes. The temperature program for alkylated PAHs and biomarker compounds was initial temperature 50°C for 2 minutes, increased to 300°C at 6°C/min, and held for 16 minutes. A 1- $\mu$ L volume was injected in the splitless mode with a 1-minute purge-off.

#### *Source notes*

The ratios of UCM/TPH [unresolved complex mixture/total (resolved) petroleum hydrocarbons] are exclusively higher than 98% for all samples including the source Orimulsion samples, and no GC-resolved *n*-alkane peaks including isoprenoids such as pristane and phytane were detected. Only when higher sensitivity GC/MS ... is used to analyze F1 could very small peaks of *n*-alkanes from C<sub>11</sub> to C<sub>15</sub> be distinguished.

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#### 4.3.4 Volatile Organic Compounds (Jokuty *et al.*, 1999)\*

##### *\*Title of Source*

*Orimulsion-400: A comparative study*

##### *Storage and Handling*

The Orimulsion was stored at 15°C. Before sampling, it was removed from cold storage and shaken on a reciprocating shaker for 30 minutes.

##### *Procedure*

Approximately 0.2 g of oil is made up to 10.00 mL in n-pentane. To 0.100 mL of this solution is added 0.200 mL of 10 ppm d10-ethylbenzene as internal standard, and 0.700 mL of n-pentane. Benzene, toluene, ethylbenzene, xylenes (BTEx), and C<sub>3</sub>-substituted benzenes are determined directly from a 1.0 µL injection volume, using gas chromatography with mass spectrometric detection (GC/MSD) (Wang *et al.*, 1995).

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#### 4.3.5 Volatile Organic Compounds (Potter *et al.*, 1997)\*

##### *\*Title of Source*

*Chemical characterization of the water soluble fraction of Orimulsion-in-water dispersion*

##### *Storage and Handling*

No information given.

##### *Procedure*

###### *Sample preparation*

The aqueous phase of Orimulsion was prepared in two ways.

1) Orimulsion was frozen at -20°C, then thawed. The free-flowing liquid was decanted, centrifuged at 10,000 g. The supernatant was filtered through 0.45 µm Teflon membrane filters. The bitumen was then re-equilibrated with a volume of distilled-deionized water equal to the liquid volume drained from the thawed Orimulsion and shaken for 1 hour on a wrist action shaker. The mixture was frozen and the free-flowing liquid processed as described above.

2) Orimulsion was diluted with distilled-deionized water or sea water, with slow stirring using a Teflon-coated stir bar in a glass beaker. After the Orimulsion was completely mixed with the water, aliquots were syringe filtered sequentially through glass fiber filters, 1 µm nominal pore size, and 0.45 µm Teflon membranes. Filtrates were frozen at -20°C until analysis.

###### *Volatile hydrocarbon analysis*

Samples were analyzed by purge-and-trap GC/MS using a Hewlett-Packard model 5971 GC/MS system.

##### *Source notes*

Analytical conditions were equivalent to USEPA Method 8260.

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#### 4.3.6 Volatile Organic Compounds (Johnson *et al.*, 1995)\*

##### *\*Title of Source*

*Acute toxicity test of Orimulsion and Fuel Oil No. 6 using standard test species*

##### *Storage and Handling*

No information given.

##### *Procedure*

Samples were analyzed for purgeable aromatics (benzene, toluene, ethylbenzene, and xylenes).

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#### 4.3.7 Surfactant Analysis (Potter *et al.*, 1997)\*

##### *\*Title of Source*

*Chemical characterization of the water soluble fraction of Orimulsion-in-water dispersion*

##### *Storage and Handling*

No information given.

##### *Procedure*

###### *Sample preparation*

The aqueous phase of Orimulsion was prepared in two ways.

1) Orimulsion was frozen at -20°C, then thawed. The free-flowing liquid was decanted, centrifuged at 10,000 g. The supernatant was filtered through 0.45-µm Teflon membrane filters. The bitumen was then re-equilibrated with a volume of distilled-deionized water equal to the liquid volume drained from the thawed Orimulsion and shaken for 1 hour on a wrist action shaker. The mixture was frozen and the free-flowing liquid processed as described above.

2) Orimulsion was diluted with distilled-deionized water or sea water, with slow stirring using a Teflon-coated stir bar in a glass beaker. Dilutions of 1:9, 1:99, and 1:999 were used. After the Orimulsion was completely mixed with the water, aliquots were vacuum filtered sequentially through glass fiber filters, 1 µm nominal pore size, and 0.45-µm Teflon membranes. Filtrates were frozen at -20°C until analysis.

Methanol extracts of samples were prepared for analysis by solid-phase extraction on LC-18 cartridges.

##### *HPLC analysis*

Each sample was analyzed for total nonylphenol ethoxylate (NPE). In addition, the frozen extract and the 1:9 dilutions in fresh and sea water were tested for the NPE metabolites nonylphenol (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenoxy acetic acid (NP1EC), and nonylphenoxy ethoxy acetic acid (NP2EC). A Lichrosphere RC18 column (5 µm particle size, 3 mm i.d., 250 mm) was used with acetonitrile/aqueous 0.14% aqueous NaClO<sub>4</sub> gradient. Well resolved peaks were obtained for NP1EC, NP2EC, total NPE (less NP1EO and NP2EO). A fourth peak representing the sum of the concentrations of NP1EO, NP2EO and NP was obtained. An NP1EC analytical standard was synthesized using 4-nonylphenol and chloroacetic acid. Intan-100, the surfactant used in the formulation of Orimulsion, was used as the reference standard for total NPE. Reference samples of NP1EO and NP2EC were also used.

Another series of analyses were performed on the methanol extracts in which the NPE oligomers were separated. The separation was reverse phase and isocratic. The mobile phase was 95/5 acetonitrile/distilled deionized water. A Waters Resolve CN column was used in Radial-Pak format.

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A series of mixed NPE standards (POE 1-2, POE 4, POE 8, POE 12, POE 15, POE 20) was used to assign an effective EO number to HPLC peaks.

*Source notes*

Reference analytical procedures were USEPA Methods 8270 (GC/MS), 3510 (separatory funnel extraction) and 3611 (chromatography on alumina).

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#### 4.3.8 Surfactant Analysis (Wang and Fingas, 1996)\*

##### *\*Title of Source*

*Separation and characterization of petroleum hydrocarbons and surfactant in Orimulsion dispersion samples*

##### *Storage and Handling*

The dispersion samples were stored at 4°C prior to analysis.

##### *Procedure*

###### *Sample preparation*

Orimulsion dispersion samples (1 L, in glass jars) were vigorously shaken for five minutes. In most cases a 10.0 mL aliquot of sample, from the mid-depth of the bottle, was transferred to a filter funnel using a disposable pipet. For samples with obviously low oil concentrations, 200 mL of sample was transferred. Samples were filtered by vacuum through Supelco Nylon 66 0.45- $\mu$ m membranes. The filtrate was used for surfactant analysis by high-performance liquid chromatography (HPLC).

###### *Analysis*

Surfactant analysis was performed with a Shimadzu system, including a variable wavelength ultraviolet-visible (UV-VIS) detector. The chromatographic separation was carried out isocratically in the reversed-phase mode with a 150-mm, 4.6-mm i.d. stainless C1 TMS column (particle size 5  $\mu$ m). The mobile phase used was a mixture of HPLC-grade methanol and deionized water (60:40 v/v). The column effluent was monitored at 220 nm (deuterium lamp, flow cell volume 8  $\mu$ L). The flow rate was maintained at 1.0 mL/min, and the column was maintained at ambient temperature ( $22 \pm 1^\circ\text{C}$ ). The injection system was a Rheodyne Model 7125 sample injector equipped with a 20- $\mu$ L sampling loop.

###### *Source notes*

Because of the lack of single-ethylene oxide (EO) number nonylphenol standards, the identification of the Orimulsion surfactant oligomer peaks was based on comparison of the retention times with those of reference materials nonylphenol (EO = 0), Igepal CO-210 (its major component is ethoxylated nonylphenol (EO = 1), and polyethoxylated nonylphenol (average EO = 20) and on the well-accepted assumption that the oligomer peaks differ from one another by one EO unit.

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#### 4.3.9 Hydrocarbon Groups (Jokuty *et al.*, 1995, 1999)\*

##### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

*Orimulsion-400: A comparative study*

##### *Storage and Handling*

The Orimulsion was stored at 5 to 15°C. Before sampling, it was removed from cold storage and shaken on a reciprocating shaker for 30 minutes.

##### *Procedure*

Asphaltenes are precipitated from n-pentane according to ASTM method D 2007, *Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum Derived Oils by the Clay-Gel Absorption Chromatographic Method* (ASTM, 1999c). The deasphalted oil (maltenes) (0.4 to 0.5 g) is placed on an open glass column (400 mm x 19 mm I.D. x 22 mm O.D., fritted, with stopcock) packed with 30 g silica and topped with 1.5 cm anhydrous sodium sulphate. The sample is eluted sequentially with 100 mL hexane, 100 mL hexane/benzene (1:1), 100 mL methanol, and 100 mL methylene chloride. The saturates are collected from the hexane, the aromatics from the hexane/benzene, and the resins are recovered from the combined methanol and methylene chloride fractions. Solvents are recovered by rotary evaporation and each hydrocarbon group is determined by weighing.

If the oil used has an initial boiling point (IBP) above 250°C (determined by simulated distillation), a good mass balance can be obtained (>95%). However, most fresh crude oils will have an IBP below 250°C, and the loss of light ends during solvent recovery results in a poor mass balance. By making the reasonable assumptions that a) resin and asphaltene contents are not affected by evaporative losses, and b) the lost aromatics can be equated to the BTEx + C<sub>3</sub>-benzenes content, it is possible to calculate the correct distribution of hydrocarbon groups.

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#### 4.3.10 Hydrocarbon Groups (Ostazeski *et al.*, 1997)\*

##### *\*Title of Source*

*The environmental behaviour of Orimulsion spilled on water*

##### *Storage and Handling*

No information given.

##### *Procedure*

Soft asphaltenes are precipitated from n-pentane, filtered, and determined gravimetrically with a microbalance.

Hard asphaltenes are precipitated from n-heptane, purified by soxhlet extraction, filtered, and determined gravimetrically with a microbalance.

Saturates, aromatics, and resins are determined by thin-layer chromatography with flame ionization detection (Iatroscan). Approximately 20 µg of oil are spotted onto a silica rod, and the saturated, aromatic and resin fractions of the oil are separated by development of the rods in a series of increasingly polar solvents (n-hexane, toluene, dichloromethane:methanol). The relative distribution of each fraction on each rod is then determined by flame ionization detection.

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#### 4.3.11 Sulphur (BP BITOR, 1993; Intevep, 1993)\*

##### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*  
*Characterization of Orimulsion quality control manual*

##### *Storage and Handling*

Storage temperature was not specified. A flat blade stirrer operating at 100 rpm for 4 hours is recommended for homogenizing the sample.

##### *Procedure*

Sulphur contents were determined according to ASTM method D 1552 - *Standard Test Method for Sulfur in Petroleum Products (High-Temperature Method)* (ASTM, 1999b).

##### *Source notes*

Stir the sample for about four hours before subsampling for analysis. Longer stirring periods give better precision in this determination.

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#### 4.3.12 Sulphur (Jokuty *et al.*, 1995, 1999)\*

##### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*  
*Orimulsion-400: A comparative study*

##### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

##### *Procedure*

Sulphur contents were determined using a Horiba MESA 200 sulphur and chlorine analyzer. Duplicate samples were run twice, and the mean of the four measurements is reported. The method used is ASTM method D 4294 - *Standard Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy* (ASTM, 1999d).

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#### 4.3.13 Metals (Jokuty *et al.*, 1995)\*

##### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

##### *Storage and Handling*

The Orimulsion was stored between 5 and 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes.

##### **Procedure**

##### *Sample preparation*

Two 0.2 g samples of Orimulsion were digested with 10 mL of nitric acid in 100-mL, closed-cup Teflon vessels using a CEM model MDS 2000 microwave oven. The digestion parameters were 10 minutes at 50% power, 190 minutes at 60% power. The digestion vessels remained in the oven following the digestion period, until the pressure dropped below 40 psi, at which time they were vented manually, transferred to 50-mL volumetrics flasks, and diluted to volume with deionized/distilled water. The samples were filtered through Whatman #41 ashless paper into clean amber glass vials with Teflon-lined caps.

##### *Analysis*

Metal content was determined using an ARL 3410 ICP-AE spectrometer controlled by a computer and Plasma Vision 10 software package. Eleven metals were determined. Additional details of the method, including instrument parameters can be found in (Fingas *et al.*, 1995).

##### **Reviewer's notes**

Additional details of the method, including instrument parameters can be found in (Fingas *et al.*, 1995).

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#### 4.3.14 Metals (Kamiura *et al.*, 1996)\*

##### *\*Title of Source*

*Pretreatment by yeast of nickel and vanadium in bitumen-in-water emulsion by inductively coupled plasma atomic emission spectrometry*

##### *Storage and Handling*

No information given.

##### *Procedure*

A 0.2 to 2.0 g sample of Orimulsion was weighed into a conical beaker. Approximately 80 mg (dry cell weight) of the yeast *Debaryomyces melissophilus* IFO 1900, dispersed in 30 mL of distilled water, was added to the vessel. The contents were shaken for three days at room temperature. Then 50 mL of concentrated nitric acid (HNO<sub>3</sub>) was added twice, and the contents were heated on a hotplate for three days to dissolve the bitumen-in-water emulsion until the solution became clear. The solution was evaporated to dryness and the residue was dissolved in 50 mL of 0.1 N HNO<sub>3</sub>. The resulting solution was transferred to a 100-mL volumetric flask, and diluted to a constant volume with distilled water. A blank sample (without oil) was treated in the same way. The samples were analyzed immediately by ICP-AES using analytical wavelengths of 231.60 nm for Ni(II) and 311.07 nm for V(II).

##### *Reviewer's notes*

Other information given by the authors includes detailed ICP-AES operating conditions for the Shimadzu ICP-1000 II, and cultivation of the microorganisms.

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#### 4.3.15 Metals (BP BITOR, 1993; Intevp, 1993; Platteau and Carillo, 1995)\*

##### *\*Title of Source*

*Orimulsion: Analysis and characterisation manual*

*Characterization of Orimulsion quality control manual*

*Determination of metallic elements in crude oil-water emulsions by flame AAS*

##### *Procedure*

The method is based on an *in situ* dehydration process followed by dry ashing of the sample in the presence of a retaining agent for volatile porphyrinic compounds. The elements are determined by flame atomic absorption spectroscopy (FAAS), using aqueous solutions for calibration of the instrument, with addition of ionization suppressor for some elements (V, Mg, and Na).

##### *Reviewer's notes*

(Platteau and Carillo, 1995) have provided a very detailed description of the experimental procedures used including instrumental parameters, preparation of reagents and solutions, cleaning of glassware, sample preparation, and metals determination.

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#### 4.3.16 Metals (Potter *et al.*, 1997)\*

##### *\*Title of Source*

*Chemical characterization of the water soluble fraction of Orimulsion-in-water dispersion*

##### *Storage and Handling*

No information given.

##### *Procedure*

The aqueous phase of Orimulsion was prepared in two ways.

- 1) Orimulsion was frozen at -20°C, then thawed. The free-flowing liquid was decanted and centrifuged at 10,000 g. The supernatant was filtered through 0.45 µm Teflon membrane filters. The bitumen was then re-equilibrated with a volume of distilled-deionized water equal to the liquid volume drained from the thawed Orimulsion, and shaken for 1 hour on a wrist action shaker. The mixture was frozen and the free-flowing liquid processed as described above.
- 2) Orimulsion was diluted with distilled-deionized water or sea water, with slow stirring using a Teflon-coated stir bar in a glass beaker. After the Orimulsion was completely mixed with the water, aliquots were vacuum filtered sequentially through glass fibre filters, 1 µm nominal pore size, and 0.45-µm Teflon membranes. Filtrates were frozen at -20°C until analysis.

Extracts were tested by ICP for vanadium, nickel, and magnesium after digestion in nitric acid.

##### *Source notes*

The reference EPA Methods were 6010 (ICP) and 3005 (acid digestion).

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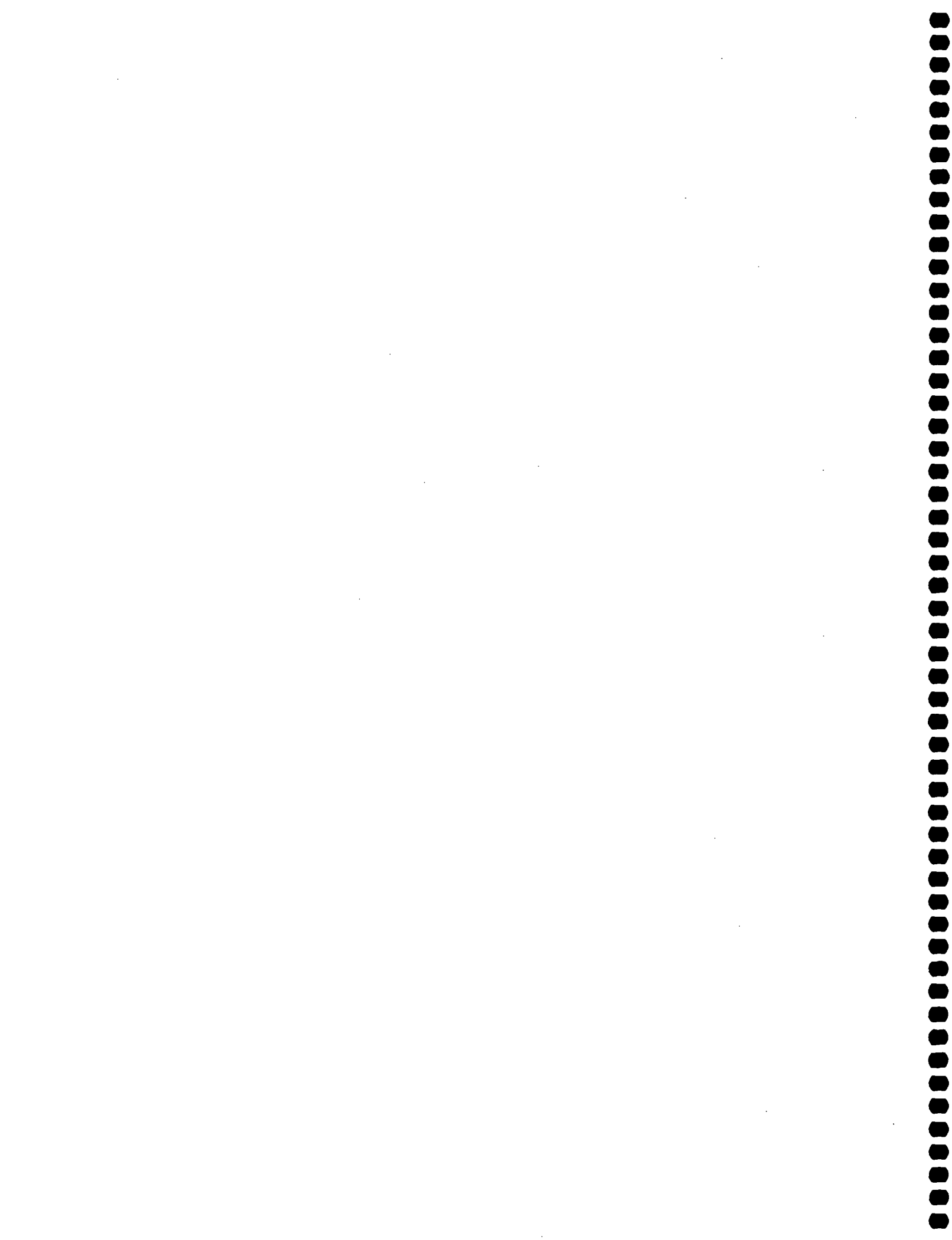
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## 5. Bitumen Preparation

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Six methods, from eight studies, were reviewed. Six different methods were used to produce bitumen for a number of purposes, including the determination of physical and chemical properties, penetration and retention potential in different sediment types, and the ability of recovery and cleaning processes to cope with bitumen from an Orimulsion spill.

### 5.1 General Comments

In only half of the studies reviewed was the characterization of the bitumen the primary reason for undertaking its preparation, and in two studies the prepared bitumen underwent no testing at all.

### 5.2 Evaluations and Recommendations

#### *Evaluation*

Four studies produced bitumen specifically for determination of physical and/or chemical properties (Brown *et al.*, 1995; Jokuty *et al.*, 1995, 1998a, 1999a). Three different methods were used. Brown *et al.* (1995) placed Orimulsion and sea water in 4-L batch reactors and exposed them to outdoor, atmospheric weathering for 14 days. This method produced insufficient bitumen for the determination of physical properties, but enough for chemical analysis. An Orimulsion:water ratio of 1:33 was used, although it had been observed that at dilutions of 1:50 or less Orimulsion retained its dispersive properties over long periods of time. Continuous moderate levels of mechanical stirring may have enhanced the separation of bitumen in this method, but the fate of the surfactant was not determined and remains uncertain.

Jokuty *et al.* used two different methods to produce bitumen. Large-scale rotary evaporation of Orimulsion at 60°C (Jokuty *et al.*, 1995) or 80°C (Jokuty *et al.*, 1999a) for 48 hours, produced bitumen with low residual water content, in sufficient quantities for the determination of physical and chemical properties. Bitumen produced by this method retains the surfactant. A second method, intended to produce bitumen specifically for the determination of adhesion as a function of time, used a relatively high (1:50) ratio of Orimulsion to water (Jokuty *et al.*, 1998a). This resulted in incomplete separation of the bitumen from the water. The fate of the surfactant was not determined and remains uncertain. The amount of bitumen produced by this method was only marginally sufficient for the desired analysis.

In two studies bitumen was produced by similar procedures, but for different purposes. Bitumen was produced by mixing Orimulsion and sea water together and recirculating the mixture with a centrifugal pump. Equal volumes of Orimulsion and water were used to produce bitumen for the determination of penetration and retention potential in different sediment types (Harper and Kory, 1997). The bitumen produced by this method was described as "highly viscous" and "ropey", but was not otherwise characterized. One part Orimulsion was combined with eight parts water in spill trials designed to test the ability of recovery and cleaning processes to cope with bitumen from an Orimulsion spill (Clement *et al.*, 1997). No characterization of the bitumen was made.

In tests made to assess the effectiveness of various chemical agents on the removal of Orimulsion from solid surfaces (Guénette *et al.*, 1998), the bitumen used was derived from one of the experiments described by Jokuty *et al.* (1999a). The bitumen was produced from an experiment in which Orimulsion and brackish water (salinity 2%) in a 1:1000 bitumen:water ratio, were subjected

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to continuous moderate agitation for 48 hours. The bitumen was recovered by scraping the side of the tank in the subsurface agitation zone. Bitumen produced by this method is expected to be essentially surfactant-free as a result of the high dilution ratio and extended mixing time.

### *Recommendation*

No single method can be recommended for the preparation of bitumen from Orimulsion. Further research is required to determine the effect of different methods of preparation on the characteristics of the bitumen produced. It is recommended, however, that as research into the fate and effects of Orimulsion spills continues, that whenever bitumen is produced it should be characterized as thoroughly as possible. Given the variety of purposes for which bitumen is produced, at a minimum this characterization should include the measurement of water content, and if possible viscosity. Confirmation of at least the presence or absence of detectable surfactant would also be highly desirable.

An additional recommendation is made regarding bitumen terminology as it relates to Orimulsion. A number of authors have attempted to use a single set of terms in referring to Orimulsion and its derivatives (Harper and Kory, 1997; Guénette *et al.*, 1998; Owens and Sergy, 1999). Based in large part on the work of these authors, it is suggested that the following terminology be used:

Orimulsion	The original product; an oil-in-water emulsion consisting of approximately 70% bitumen, 30% water, and a small amount of stabilizing surfactant.
Dispersed bitumen	A dispersion of bitumen in water resulting from an Orimulsion spill or intentional dilution of Orimulsion with water.
Coalesced bitumen	A black, highly viscous, sticky, tar-like semi-solid that is formed by the coalescence of dispersed bitumen, or directly from the breaking of the Orimulsion emulsion.
Weathered bitumen	Coalesced bitumen that has been exposed to weathering processes such as occur during shoreline stranding.

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## 5.3 Method Summaries

### 5.3.1 Bitumen Preparation (Brown *et al.*, 1995)\*

#### *\*Title of Source*

*Comparative evaluation of physical and chemical fate processes of Orimulsion and Fuel Oil No. 6 in the Tampa Bay marine environment*

#### *Storage and Handling*

No information given.

#### *Procedure*

Batch mode experiments were conducted outdoors in 4,000-mL Erlenmeyer flasks. Each flask initially contained 3,500 mL of sea water treated with sodium azide to retard biodegradation, and approximately 30 g/L of Orimulsion. Samples were run in triplicate. Exposure was at moderate levels of continuous mechanical mixing (stir bar), at a continuous air flow rate, and subject to a daily temperature range of  $24 \pm 3^\circ\text{C}$ , moderated by a circulating water bath. Samples were exposed for 0.5 hours, 6 hours, 1 day, 7 days, and 14 days.

#### *Source notes*

... a very limited amount of material was available to measure changes of physical properties with time; the small amount of retrieved sample was readily sufficient, however, to determine changes in Orimulsion's chemical composition...

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### 5.3.2 Bitumen Preparation (Jokuty *et al.*, 1995, 1999a)

#### *\*Title of Source*

*Orimulsion: physical properties, chemical composition, dispersibility, and toxicity*

*Orimulsion-400: A comparative study*

#### *Storage and Handling*

The Orimulsion was stored at 5 to 15°C. Before sampling, it was removed from cold storage and shaken on a reciprocating shaker for 30 minutes.

#### *Procedure*

Orimulsion was subjected to the standard Emergencies Science Division protocol for bulk evaporation. This procedure consists of rotary evaporation at ambient pressure over a water bath at 80°C, for a total of 48 hours. For details refer to Jokuty *et al.* (1999b).

#### *Source notes*

In Jokuty *et al.* (1995) a water bath at 60°C was used.

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### 5.3.3 Bitumen Preparation (Jokuty *et al.*, 1998a)\*

#### *\*Title of Source*

*Bitumen adhesion as a function of time*

#### *Storage and Handling*

The Orimulsion was stored at 15°C. Before sampling, it was removed from cold storage and shaken on a reciprocating shaker for 30 minutes.

#### *Procedure*

A 20-L cylindrical glass vessel (30 cm o.d.) was filled with 10 L of 3.3% salt water. 200 mL of Orimulsion was measured into a 250-mL graduated cylinder, and then added to the salt water. A magnetic stirrer set at a very low rate was used to stir the water while the Orimulsion was added (30 seconds). The stirrer was then turned off and the vessel was allowed to stand undisturbed, at room temperature (15 to 20°C) for the desired time interval (1, 2, 4, 8, or 16 days). At the end of the time interval the bitumen layer was removed, using a spatula, and placed into a suitable container for the adhesion measurement.

#### *Source notes*

The relatively high ratio of bitumen to water (1:50) in these experiments did not allow for complete separation of the bitumen from the water. The bitumen layers that were removed were black and/or brown, but still very fluid, indicating a high water content.

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#### 5.3.4 Bitumen Preparation (Harper and Kory, 1997)\*

##### *\*Title of Source*

*Orimulsion Shoreline Studies Program - Sediment interaction experiments*

##### *Storage and Handling*

No information given.

##### *Procedure*

The bitumen was produced by placing equal volumes of Orimulsion and artificial sea water (salinity 32 ppt) in a container and recirculating the mixture through a high-speed, centrifugal pump for five to ten minutes.

##### *Source notes*

The bitumen produced was "highly viscous" and "ropey".

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### 5.3.5 Bitumen Preparation (Clement *et al.*, 1997)\*

#### *\*Title of Source*

*Trials of recovery and cleanup techniques on bitumen derived from Orimulsion*

#### *Storage and Handling*

No information given.

#### *Procedure*

The bitumen was prepared by pouring 1 m<sup>3</sup> of Orimulsion into about 8 m<sup>3</sup> of sea water in a tank. Bitumen was produced by extensive pumping inside the tank with a Desmi 210 screw pump, and surface churning with a centrifugal pump.

#### *Source notes*

...the combined action [of the two pumps] destabilized the Orimulsion in the form of a foam that rapidly collapsed into a thick layer of bitumen at the surface.

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### 5.3.6 Bitumen Preparation (Guénette *et al.*, 1998)\*

#### *\*Title of Source*

*Removal of stranded bitumen from intertidal sediments using chemical agents - Phase I Screening of chemical agents*

#### *Storage and Handling*

Orimulsion was stored at 15°C. Before sampling, Orimulsion was removed from cold storage and shaken on a reciprocating shaker for at least 30 minutes (Jokuty *et al.*, 1998b).

#### *Procedure*

The bitumen used in this study was a by-product of another study. It was obtained following a dispersion test using the "oscillating hoop" apparatus (Jokuty *et al.*, 1998b). The apparatus consists of a cylindrical tank 90 centimetres in diameter and 106 cm in height, and a vertically oscillating, flat, stainless steel hoop, 4.5 cm wide and 78 cm in diameter. The hoop was adjusted to oscillate below the surface of the water, between 6 and 18 cm from the surface, at a rate of 60 cycles per minute.

For each test, the tank was filled with approximately 400 L of water. Salt was added as appropriate to obtain the desired salinity, nominally 0%, 2.0%, and 3.3%. The temperature of the water was between 17 and 21°C for all tests. A bitumen-to-water mass ratio of approximately 1:1000 was used. For all runs the Orimulsion was added with the hoop in motion, and timing of the run began as soon as Orimulsion was released into the water. Agitation was continued for 12 to 48 hours.

The bitumen used by Guénette *et al.* (1998) was derived from a 48-hour experiment with Orimulsion-400 in brackish water (salinity 2.0%). The bitumen was collected after the test, by scraping the side of the tank.

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## 6. Preparation of Aquatic Toxicity Test Media

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This section covers methods for three types of test media preparation: oil-in-water dispersions (OWD), water-accomodated fractions (WAF), and water-soluble fractions (WSF).

### 6.1 Background

Experimental Orimulsion spills in aquatic systems have shown that the bitumen particles and the water phase of the fuel quickly disperse in the water column. Unlike most floating fuels, a surface slick, and accompanying plume of dissolved hydrocarbons do not form.

For aquatic toxicity testing, Orimulsion may be defined as a multi-component mixture. The Organization for Economic Co-operation and Development (OECD) *Revised Draft Guidance Document on Aquatic Toxicity Testing of Difficult Substances and Mixtures* (OECD, 2000) defines multi-component mixtures as those comprising a complex mix of individual substances with different solubilities and physico-chemical properties. The OECD recommends a product-specific approach in media preparation for aquatic toxicity tests for multi-component mixtures that are not fully soluble in water.

The OECD recommends the use of a water-accomodated fraction (WAF) to evaluate the toxicity of multi-component mixtures. The term WAF is used for aqueous media containing the dissolved fraction and the stable dispersion of particles in a multi-component mixture. Aquatic toxicity testing using the WAF represents exposures that closely mimic environmental conditions following a spill of emulsified fuels such as Orimulsion.

In the past, the environmental toxicity of Orimulsion has been evaluated through testing of WAF, oil-in-water dispersion (OWD), and water-soluble fraction (WSF). An OWD is prepared through direct addition of the fuel to the aqueous media, mixing, and immediate use of the test solution (Anderson *et al.*, 1974). A WAF is prepared in a similar manner, except that the test medium is mixed for a longer period of time prior to use. The terms OWD and WAF have been used interchangeably in the literature. The difference between a WAF and an OWD is simply the length of time that the test media is mixed to allow dissolution of substances into the aqueous media.

A WSF contains dissolved compounds from the test oil, with little or no particulate oil matter present. For Orimulsion, the use of a WSF is not ecologically relevant, as the spilled fuel in the environment would always include both the dissolved fraction and the bitumen particles.

Aquatic toxicity tests using OWD and WSF have been widely used for floating oils (i.e., Fuel Oil #6). Emulsified fuels behave differently in the environment, and the media preparation used for these toxicity studies should reflect the environmental exposure of aquatic organisms to this type of fuels.

### 6.2 Evaluations and Recommendations

Table 2 summarizes Orimulsion media preparation methods used in previous aquatic toxicity studies. Orimulsion WSFs have also been used for chemical characterization of this fuel, and these studies were reviewed by Jokuty *et al.* (1999).

Table 2. Summary of Media Preparation Methods for Aquatic Toxicity Studies Using Orimulsion

Source	Media Type	Preparation
Brey <i>et al.</i> , 1993 (PDVSA-Intevep, Venezuela)	WSF	1 part Orimulsion : 9 parts water -magnetic stirrer, 20 hours; settled for 4 hours -filtered, glass fiber (pore size not specified) -used within 24 hours
Esclapés, <i>et al.</i> , 1995 (PDVSA-Intevep, Venezuela)	WSF	1 part Orimulsion : 9 parts water -covered, shaken, 20 hours; settled for 2 hours -vacuum filtered, 1 micron
	OWD	1 part Orimulsion : 1,000 parts water -sealed with plastic, circular shaker, 5 minutes; settled for 20 min.
Fishman <i>et al.</i> , 1995 (University of Miami, USA)	OWD	1 part Orimulsion : 100 parts water -stirred for 15 minutes; settled for 1 hour
Gassman, 1995 (University of Miami, USA)	WSF	1 part Orimulsion : 9 parts water -magnetic stirrer (vortex 25% of depth), 20 hours; settled for 2 hours -vacuum filtered, 1 micron -used within 2 hours
	OWD	1 part Orimulsion : 1,000 parts water -5 minutes, magnetic stirrer (gently); no settling; used within 1 hour
Johnson <i>et al.</i> , 1995 (Golder Associates Inc., USA)	WSF	1 part Orimulsion : 9 parts water -shaker table (vigorous), 20 hours; settled for 2 hours -pressure filtered, 1 micron -used within 1 hour
	OWD	1 part Orimulsion : 1,000 parts water -magnetic stirrer, platform shaker, top-mounted stirrer -covered mixing for 5-15 minutes; no settling; used immediately
Jokuty <i>et al.</i> , 1995 (Environment Canada)	OWD	1 Orimulsion : 40 water (26.66 g : 1,000 ml) -stirred 2 to 3 days; settled for 3 hours, or added directly to test chambers, stirred, aerated for 30 minutes
	WSF	OWD filtered through a 1 micron pore size membrane
Bjornestad <i>et al.</i> , 1998 (VKI, Institute for the Water Environment, Denmark)	WAF	1 g Orimulsion : 500 ml water -ultrasonification for 5 minutes -stirred for 20-22 hours; settled for 2 hours
Armsworthy <i>et al.</i> , 1999 (Department of Fisheries and Oceans, Canada)	OWD	Did not specify details of stock solution preparation -flow-through exposure pumped from stocks
Golder Associates Geoanalysis, s.r.l., 1999 (Italy)	OWD	1 part Orimulsion : 1,000 parts water -stirred gently by hand, 2 minutes; covered, settled for 1 hour
Jokuty <i>et al.</i> , 1999 (Environment Canada)	OWD	11.8 g Orimulsion : 1,000 ml water, or 10.25 g Orimulsion : 1,000 ml water Method 1 (Microtox): mixing time not specified Method 2 (rainbow trout): direct mixing in test chamber
	WAF	1 part Orimulsion : 40 parts water (26.66 g : 1,000 ml) -covered, magnetic stirrer, 33.5 hours; settled for 30 minutes to 4 hours
	WSF	OWD and WAF filtered to 1 micron
PDVSA-Intevep, 1999	WSF	1 part Orimulsion : 100 parts water -shaker table, 16 hours -centrifuged at 12,000 rpm., 15 minutes at 4°C -filtered, 1 micron
Johnson <i>et al.</i> , 2000 (Golder Associates Inc., USA)	OWD	1 part Orimulsion : 1,000 parts water -stirred gently by hand, 2 minutes; covered, settled for 1 hour

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### 6.2.1 Evaluations

#### OWD

Ten studies were reviewed that used OWD for aquatic exposures. The following is a summary of the type of studies reviewed:

- A series of tests conducted by PDVSA-Intevep, the research center for Petroleos de Venezuela, on Orimulsion-100 (Esclapés *et al.*, 1995);
- Three studies, using a series of estuarine species, prepared as part of a regional comparative risk assessment for Orimulsion-100 and Fuel Oil #6 (Gassman, 1995; Johnson *et al.*, 1995; Fishman *et al.*, 1995);
- Two reports prepared by Environment Canada based on their research on the two formulations of Orimulsion (Jokuty *et al.*, 1995, 1999);
- A series of studies on both formulations using sea scallops by Canada's Department of Fisheries and Oceans (Armsworthy *et al.*, 1999);
- A series of studies conducted on Orimulsion-400 using standard and Mediterranean species (Golder Associates Geoanalysis, 1999);
- Toxicity tests were conducted by the German Hygiene Institute (Schrammeck, 1998);
- Multiple aquatic toxicity studies, using both formulations, are described in a manuscript being prepared for publication (Johnson *et al.*, 2000).

Most of the above studies prepared the OWD by placing 1 part Orimulsion in 1,000 parts dilution water; the equivalent stock concentration of 1,000 ppm. The only exceptions were Jokuty *et al.* (1995, 1999), using different ratios of fuel-to-water in order to achieve the selected stock concentrations. The Orimulsion and water mixtures were then mixed (stirred or shaken) gently for 2 to 15 minutes at room temperature. Jokuty *et al.* (1995) mixed the Orimulsion stocks for 2 to 3 days or, depending on the species tested, added the fuel directly to the test chambers, stirred, and then aerated for 30 minutes. Based on the definitions offered earlier in this paper, the stocks mixed for 2 to 3 days can be considered WAFs.

In most cases the mixing chambers were covered, and the mixtures were used in tests immediately (Johnson *et al.*, 1995) or allowed to settle for up to 3 hours (Jokuty *et al.*, 1995). The OWD were then diluted to the series of test concentrations needed to assess acute and sublethal effects. In two cases, the fuel was added directly to each test chamber (Jokuty *et al.*, 1995, 1999). Armsworthy *et al.* (1999) used flow-through conditions and pumped each stock directly into each test chamber.

#### WAF

WAF were used in two laboratories, Environment Canada and VKI, the Danish Institute for the Water Environment.

Environment Canada (Jokuty *et al.*, 1995, 1999) prepared the WAF by stirring the mixture from 33.5 hours to 3 days; the WAF was then allowed to settle for a period of 30 minutes to 4 hours. Danish studies (Bjornestad *et al.*, 1998), based on previous UK guidance documents for testing difficult substances, used ultrasonification of the Orimulsion and water mixture for 5 minutes, followed by stirring for 20 to 22 hours. The WAF was then allowed to settle for 2 hours prior to use in tests.

Studies have also been conducted using the WSF of Orimulsion and are included in Table 2 (Brey and Feragotto, 1993; Esclapés *et al.*, 1995; Gassman, 1995; Johnson *et al.*, 1995; Jokuty *et al.*, 1995, 1999; PDVSA-Intevep, 1999). These studies are not discussed in detail in this method review paper because this type of exposure, a dissolved water phase of Orimulsion without bitumen particles, will not occur in the environment under any plausible spill conditions. Methods using a filtered WAF or a WSF are relevant for oils that generate a plume of dissolved hydrocarbons below the surface slick. Orimulsion does not form a surface slick, with accompanying dissolved plume, thus the evaluation of Orimulsion filtered fractions is not ecologically relevant or representative of the environmental behavior and exposure of dispersed Orimulsion.

## 6.2.2 Recommendations

In order to standardize media preparation methods for Orimulsion, the following procedures and terminology are proposed. An OWD is recommended for aquatic toxicity tests using Orimulsion. An OWD also fits the definition of a WAF for this particular emulsified fuel. If the term WAF is used for Orimulsion in order to reflect method harmonization with OECD (2000), procedures should clearly state whether the test concentrations were mixed for an extended period of time, and the period of water accommodation. It is important to note that testing an OWD is a more conservative evaluation of Orimulsion effects, as hours of mixing required for the preparation of a WAF can enhance the evaporation of the small amount of volatile hydrocarbons present in Orimulsion. An Orimulsion spill that has weathered in the environment could be represented through a WAF.

### *Oil-in-water Dispersion Method*

The OWD should be prepared by direct addition of Orimulsion into the aqueous media (salt or freshwater). The OWD should be mixed gently by hand using a glass rod for 5 minutes. A range of concentrations should be prepared by serial dilution of a single OWD stock. The test organisms should be added to each test chamber within 1 hour of test concentration preparation.

Toxicity tests using an OWD can be conducted under static conditions (OWD is prepared once, at test initiation), static-renewal conditions (OWD is prepared every 2 or 3 days and the test organisms are transferred to the new OWD), or under dynamic (flow-through) conditions (freshly prepared OWD are slowly pumped into each test chamber for the duration of the test). The type of test exposure should be determined based on the species tested and the objective of the study.

### *Chemical Analysis of Test Concentrations*

The OWD of an emulsified fuel represents a complex mixture of substances, thus a single analysis does not quantify the exposure to aquatic organisms. It is recommended that for emulsified fuels, such as Orimulsion, test results be reported as nominal concentrations or loading rates (reflecting the amount of fuel added) (OECD, 2000).

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### *Need for Accommodation Period*

Previous studies (Battelle, 1998; Potter *et al.*, 1997; Wang and Fingas, 1996) have shown that the bitumen in Orimulsion is highly weathered and that PAH and BTEX concentrations in aqueous dilutions of the fuel are extremely low. Brown *et al.*, (1995) also demonstrated that significant dissolution of components from the bitumen particles do not appear to occur following dilution of Orimulsion in aqueous media. This is expected based on the fact that 30% of the fuel is water, and that the majority of components able to dissolve in water may have already done so through the fuel manufacturing and shipping process. Based on this characteristic particular to Orimulsion, mixing for an extended period of time to accommodate the water phase is not necessary, and extended periods of mixing could volatilize the small concentration of dissolved hydrocarbons present in the initial dilution of the fuel.

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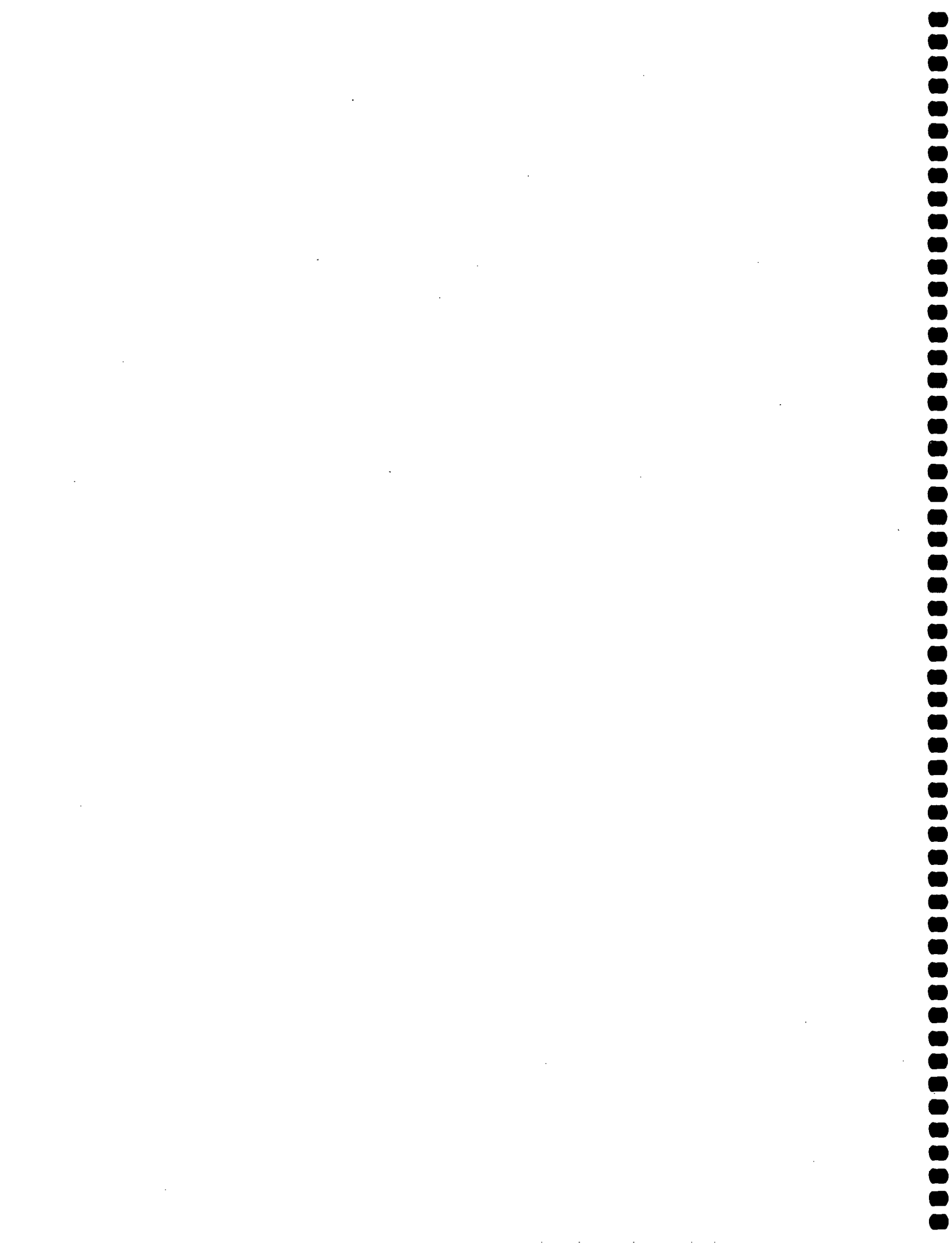
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## 7. Aquatic Toxicity

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Numerous aquatic toxicity tests have been conducted using both Orimulsion formulations by laboratories in the United States, Canada, Italy, Denmark, Germany, United Kingdom, and Venezuela to evaluate their environmental toxicity to aquatic organisms, ranging from bacteria to fish. Only Orimulsion-400 studies were reviewed, as this is the only formulation presently used worldwide. These studies are described in the following sections and the data are summarized in Table 3.

### 7.1 Bacterial Studies

#### 7.1.1 Microtox

Environment Canada (Jokuty *et al.*, 1999) conducted a series of bacterial studies on Orimulsion-400 using two protocols: the Microtox Basic protocol and the Microtox 100% protocol. Both protocols involved exposing the bacterium, *Vibrio fischeri*, for 15 minutes to test concentrations of Orimulsion-400. Unfiltered and filtered OWD were tested. The Microtox analyzer records the light output from the bacteria, a decrease in light output is interpreted as a toxic response. An  $EC_{50}$  (median effective concentration - calculated concentration which causes 50% decrease in light output or bioluminescence) was estimated using the Microtox software. The  $EC_{50}$  was calculated based on nominal concentrations of Orimulsion-400 and measured concentrations as TSEM (total solvent extractable materials).

Golder Associates Geoanalysis also conducted Microtox studies using Orimulsion-400 OWD in support of projects in Italy (Golder Associates, 1999). The OWD was prepared by placing 1 part Orimulsion-400 in 1,000 parts water. The mixture was stirred gently by hand with a glass rod for a period of two minutes at room temperature. The mixing chamber was covered after stirring and left undisturbed for one hour. The OWD was siphoned from the bottom of the mixing chamber into another container for use in the preparation of test dilutions. Test results were reported as nominal concentrations. Three sets of tests were conducted using Orimulsion-400; parallel Fuel Oil #6 tests were also conducted.

OWD effect concentrations reported by Jokuty *et al.*, (1999) and Golder Associates (1999) were very similar.

#### 7.1.2 Activated Sludge

An activated sludge study was conducted by Bjornestad *et al.* (Bjornestad *et al.*, 1998). Unspecified microorganisms, in activated sludge, were exposed for 3 hours to concentrations of Orimulsion-400 WAF. The WAF was prepared by adding 1 gram of Orimulsion-400 to 0.5 L of seawater. This mixture was treated with ultrasonification for 5 minutes, followed by stirring for 20 to 22 hours. The suspension was then allowed to settle for 2 hours and the WAF was siphoned and used as the stock solution. The endpoint was measured in terms of inhibition of nitrification. The No Observed Effect Concentration (NOEC) based on nitrification inhibition was reported based on nominal concentrations.

**Table 3. A Summary of Orimulsion-400 Toxicity Test Results**

Test Organism	Test Type	Media Type	Nominal Conc'n Results (mg/L) <sup>a</sup>	Measured Conc'n Results (mg/L)	Source*
<b>ALGAE/BACTERIA</b>					
Bacterium (Microtox) ( <i>Vibrio fischeri</i> )	15-minute basic	OWD <sup>b</sup> unfiltered	EC <sub>50</sub> =2,800 (95% C.L.=1,850-4,220)	EC <sub>50</sub> =2,060 <sup>c</sup>	1
			EC <sub>50</sub> =2,579 ± 247		2
Activated Sludge	3-hour inhibition of nitrification	WAF <sup>d</sup>	EC <sub>50</sub> >1,600		3
Algae ( <i>Skeletonema costatum</i> )	72-hour growth and reproduction	WAF	EC <sub>50</sub> =500 NOEC=200		3
Algae ( <i>Scenedesmus subspicatus</i> )	72-hour growth	OWD	EC <sub>50</sub> >100		4
Algae ( <i>Selenastrum capricornutum</i> )	72-hour growth and reproduction	OWD	EC <sub>50</sub> >1,000		2
<b>INVERTEBRATES</b>					
Rotifer ( <i>Brachionus plicatilis</i> )	24-hour acute	OWD	LC <sub>50</sub> =653 ± 67		2
Water flea ( <i>Daphnia magna</i> )	48-hour acute	WAF unfiltered	LC <sub>50</sub> =19.3% = 4,850 EC <sub>50</sub> =0.56% = 140	LC <sub>50</sub> = 488 <sup>c</sup> EC <sub>50</sub> = 14.2 <sup>c</sup>	15
	48-hour acute	OWD	LC <sub>50</sub> =169		
	48-hour acute	OWD	EC <sub>50</sub> =100		4
	48-hour acute	WAF filtered	Not acutely toxic		1
	24-hour acute	OWD	LC <sub>50</sub> =603 ± 300		2
	48-hour acute	OWD	LC <sub>50</sub> =464 ± 276		2
Anostracs ( <i>Artemia salina</i> )	24-hour acute	OWD	LC <sub>50</sub> >1,000		2
Anostracs ( <i>Thamnocephalus platyurus</i> )	24-hour acute	OWD	LC <sub>50</sub> >1,000		2
Mysids ( <i>Mysidopsis bahia</i> )	96-hour acute	OWD	LC <sub>50</sub> =42.7 (1997) LC <sub>50</sub> =24.6 (1998)		6
	96-hour acute	WSF <sup>d</sup> filtered	LC <sub>50</sub> =7,070 (1997) LC <sub>50</sub> = 15,246 (1998)	LC <sub>50</sub> = 2,113 <sup>c</sup>	6
Copepod ( <i>Acartia tonsa</i> )	48-hour acute	WAF	LC <sub>50</sub> = 650		3
Amphipod ( <i>Corophium volutator</i> )	22-day life-cycle	WAF	LOEC=10		3
	10-day acute	WAF	LC <sub>50</sub> >500 mg/kg <sup>f</sup> NOEC=500 mg/kg <sup>f</sup>		3
	10-day acute	OWD	LC <sub>50</sub> =601 (95% C.L.=541-667)		2
	28-day chronic	OWD	LC <sub>50</sub> =293 (95% C.L.=261-328)		2
Sea urchin ( <i>Lytechinus pictus</i> )	20-minute fertilization	WAF unfiltered	IC <sub>50</sub> =21.5%=5,730	IC <sub>50</sub> = 21.5% = 21.1 <sup>c</sup>	1
Sea urchin ( <i>Paracentrotus lividus</i> )	Fertilization	OWD	EC <sub>50</sub> =296.2		2
	Embryo dev.	OWD	EC <sub>50</sub> >500		2

**Table 3. A Summary of Orimulsion-400 Toxicity Test Results (continued)**

Test Organism	Test Type	Media Type	Nominal Conc'n Results (mg/L) <sup>a</sup>	Measured Conc'n Results (mg/L)	Source*
<b>FISH</b>					
Threespine stickleback ( <i>Gasterosteus aculeatus</i> )	96-hour acute	OWD	LC <sub>50</sub> =3,200	LC <sub>50</sub> = 1,330 <sup>c</sup>	1
Rainbow trout ( <i>Oncorhynchus mykiss</i> )	96-hour acute	OWD	LC <sub>50</sub> =301 <sup>1</sup>	LC <sub>50</sub> = 192 <sup>c</sup>	1
Zebra fish ( <i>Brachidanio rerio</i> )	96-hour acute	OWD	LC <sub>50</sub> =215		7
Inland Silverside ( <i>Menidia beryllina</i> )	96-hour acute	OWD	LC <sub>50</sub> =200 (1997) LC <sub>50</sub> =114 (1998)		6
	96-hour acute	WSF filtered	LC <sub>50</sub> =12,800	LC <sub>50</sub> = 3,368 <sup>e</sup>	6
Turbot ( <i>Scophthalmus maximus</i> )	96-hour acute	WAF	LC <sub>50</sub> =1,000-2,000 NOEC=500		3
Sheepshead minnows ( <i>Cyprinodon dearborni</i> )	96-hour acute	OWD	LC <sub>50</sub> >1,000		5
Chub ( <i>Leuciscus idus</i> )	48-hour acute	OWD	LC <sub>50</sub> =1920		4
Marine guppy ( <i>Poecilia spphenops</i> )	96-hour acute	OWD	LC <sub>50</sub> >1,000		7

<sup>a</sup> Nominal concentration as milligrams of added fuel per liter of water (mg/L), unless noted otherwise.

<sup>b</sup> OWD = oil-in-water dispersion.

<sup>c</sup> Measured concentration based on TSEM (total solvent extractable materials).

<sup>d</sup> WSF or WAF = water soluble fraction or water accommodated fraction.

<sup>e</sup> Measured concentration based on total recoverable hydrocarbons method developed by Battelle (USCG, 1997).

<sup>f</sup> Nominal concentration as milligrams of added fuel per kilogram of dry sediment (mg/kg).

\*Sources

<sup>1</sup> Jokuty *et al.* (1999)

<sup>2</sup> Golder Associates (1999)

<sup>3</sup> Bjornstead *et al.* (1998)

<sup>4</sup> Schrammeck (1998)

<sup>5</sup> Esclapés *et al.* (1997)

<sup>6</sup> Johnson *et al.* (2000)

<sup>7</sup> Esclapés *et al.* (1998)

## 7.2 Algal Studies

Bjornestad *et al.* (1998) exposed a marine micro alga, *Skeletonema costatum*, to a series of Orimulsion-400 WAF concentrations (WAF was prepared as described for the activated sludge test). After 72 hours, growth of the algae were measured.

Golder Associates (1999) conducted algal tests using the freshwater micro alga, *Selenastrum capricornutum*, and found no quantifiable response to Orimulsion-400 up to 1,000 ppm (OWD), the highest concentration tested (three separate tests were conducted). Parallel Fuel Oil # 6 tests were also conducted on this algal species.

The German Hygiene Institute (Schrammeck, 1998) conducted 72-hour tests with the green alga *Scenedesmus subspicatus* according to OECD Guideline 201. Cell multiplication inhibition was evaluated.

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## 7.3 Aquatic Invertebrates

### 7.3.1 Rotifer - *Brachionus plicatilis*

Golder Associates (1999) conducted 24-hour exposures of the freshwater rotifer (*B. plicatilis*) using OWD (prepared as described for the Microtox test). Three separate tests were conducted using Orimulsion and Fuel Oil #6.

### 7.3.2 Waterflea - *Daphnia magna*

Jokuty *et al.* (1999) conducted 48-hour acute tests using the waterflea, *Daphnia magna*. The WAF stock was prepared by mixing Orimulsion-400 and freshwater (1:40 oil-to-water ratio). The mixture was stirred for 33.5 hours and then it was allowed to settle for 30 hours. The WAF was then removed from the bottom of the mixing chamber; a portion of this stock was used for an unfiltered WAF *D. magna* acute test. Ten less than 24-hour-old neonates were distributed to each of the 200-ml glass beakers. The test temperature and photoperiod were  $20 \pm 1^\circ\text{C}$  and 16 hours of light, respectively. At test termination (48 hours), the *D. magna* were observed for immobility and death. Based on nominal concentrations, the  $\text{EC}_{50}$  (for immobilization) and  $\text{LC}_{50}$  (i.e., concentration that kills 50% of the test animals) were estimated based on nominal and measured concentrations as TSEM. A second test was conducted by Jokuty *et al.* (1999) using the filtered WAF. No acute toxicity was measured in this test.

Studies were also conducted by PDVSA-Intevep to evaluate acute effects on *D. magna* (Esclapés *et al.*, 1997). In this assay, organisms were exposed to the OWD using Orimulsion-400. The OWD was prepared by mixing the fuel and water in a 1:1,000 ratio. The preparation was shaken for 20 minutes at 250 cycles per minute on a shaker platform. The OWD was allowed to settle for 20 minutes before using the dispersion for testing purposes. The 48-hour OWD  $\text{LC}_{50}$  was estimated based on nominal concentrations.

Schrammeck (1998) reported results of one *Daphnia* 48-hour test using the OWD of Orimulsion according to OECD Guideline 202. The test results were based on the effect on mobility of the daphnids.

Golder Associates (1999) conducted OWD tests using *D. magna*, three 48-hour tests were conducted. The OWD were prepared as described for the Microtox test. Parallel Fuel Oil # 6 tests were also conducted.

Test results based on mortality reported by Esclapés *et al.*, (1997) and Golder Associates (1999) were similar; mortality results reported by Jokuty *et al.*, (1999) showed significantly reduced mortality, as compared to the other *D. magna* data available. Jokuty *et al.*, (1999) accommodated the Orimulsion fraction for an extended period of time prior to testing, and this may have reduced the toxicity of the WAF. Results based on effects (immobilization,  $\text{EC}_{50}$ ) were also similar between Jokuty *et al.*, (1999) and Schrammeck (1998).

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### 7.3.3 Anostracs - *Thamnocephalus platyurus* and *Artemia salina*

Golder Associates (1999) conducted 24-hour OWD using 2 species of anostracs, these tests were conducted in triplicate. These species were not sensitive to the OWD of Orimulsion-400, up to the highest concentration tested. Parallel tests were also conducted using Fuel Oil #6.

### 7.3.4 Mysids - *Mysidopsis bahia*

Effects of Orimulsion-400 on *Mysidopsis bahia* were evaluated by Johnson *et al.* (2000). Mysids ( $\leq 24$  hours old) were exposed to both the OWD and the WSF of Orimulsion-400 in 450-ml glass dishes for 96 hours. Ten mysids were used per replicate, two replicates per test concentration. The tests were conducted at a temperature of  $25 \pm 2^\circ\text{C}$ , a photoperiod of 16 hours of light, and a salinity of  $20 \pm 2$  parts per thousand. The OWD was prepared by mixing Orimulsion-400 and seawater; this stock emulsion was then used for testing. The 96-hour OWD  $\text{LC}_{50}$ s were estimated for two samples, one received in 1997 and one received in 1998. Test results were reported using nominal concentrations, and the two samples showed similar effects on this estuarine mysid.

The WSF was prepared by mixing 1 part Orimulsion-400 and 9 parts saltwater. The mixture was then stirred gently by hand for a period of 2 minutes at room temperature, the chamber was then covered and left undisturbed for 20 hours. The WSF was siphoned and filtered through a 1.5 micron pore size filter. The 96-hour  $\text{LC}_{50}$  was estimated based on measured Total Recoverable Petroleum Hydrocarbons (TRPH) using a method developed by Battelle (United States Coast Guard, 1997).

### 7.3.5 Copepods - *Acartia tonsa*

The acute toxic effects of Orimulsion-400 WAF on a copepod, *Acartia tonsa*, were evaluated by Bjornestad *et al.* (1998). The copepods were exposed for 48 hours to a series of test concentrations of Orimulsion-400 WAF (prepared as described for the activated sludge test). The 48-hour  $\text{LC}_{50}$  was estimated based on nominal concentrations.

A chronic (life-cycle) toxicity study using *Acartia tonsa* was also conducted by Bjornestad *et al.* (1998). The copepods were exposed to Orimulsion-400 (WAF) for 22 days. The endpoints were larval and adult growth, egg production, egg hatching, and development time for larvae. The lowest-observed-effect concentration (LOEC) in this test was based on the most sensitive endpoint (egg production).

### 7.3.6 Amphipod - *Corophium volutator*

A 10-day acute toxicity study was conducted by Bjornestad *et al.* (1998) to evaluate the effects of Orimulsion-400 on a sediment-dwelling amphipod (*Corophium volutator*). The amphipods were exposed for 10 days to sediments dosed with Orimulsion-400. The NOEC was determined to be the highest Orimulsion-400 concentration tested.

Golder Associates (1999) conducted water column OWD exposures of Orimulsion-400 using the Mediterranean species *C. orientale* (including uncontaminated sediments in test chambers) and determined a 10-day acute  $\text{LC}_{50}$  and a 28-day chronic value based on nominal concentrations. Three separate tests were conducted using Orimulsion-400 and Fuel Oil #6.

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### 7.3.7 Sea Urchin - *Lytechinus pictus* and *Paracentrotus lividus*

A 20-minute sea urchin fertilization study was conducted by Jokuty *et al.* (1999). The species used was *Lytechinus pictus* and testing was performed at  $20 \pm 1^\circ\text{C}$ . Orimulsion-400 WAF, prepared as described for the *D. magna* test, was used. Sperm were exposed to WAF test solutions for 10 minutes, then eggs were added and the exposure continued for an additional 10 minutes. At test termination, formalin was added to the test vessels. The percent fertilization was determined from 100 exposed eggs in each test vessel. The  $\text{IC}_{50}$  (i.e., concentration that inhibits 50 percent of fertilization) was estimated based on nominal concentrations and measured concentrations as TSEM.

Golder Associates (1999), using a different sea urchin species for the tests conducted in Italy, found that the sea urchin *Paracentrotus lividus* were more sensitive to the OWD than *L. pictus* was to the WAF. This difference may be due to the species difference or the preparation method of the Orimulsion; *L. pictus* sperm were exposed to a WAF that was accommodated for a longer period of time. Effects on embryo development were also evaluated by Golder Associates (1999), and no effects were observed in any of the test concentrations tested.

### 7.3.8 Sea Scallops - *Placopecten magellanicus*

Experiments were conducted by Canada's Department of Fisheries and Oceans (Armsworthy *et al.*, 1999) to evaluate the lethal and sublethal effects of two formulations of Orimulsion to a commercially important benthic species, the sea scallop. This study showed that *P. magellanicus* survivorship and somatic and reproductive tissue weight were unaffected by the addition of up to 1 mg per liter of Orimulsion. The lack of detrimental biological effects was attributed to the highly weathered nature of bitumen in the Orimulsion.

## 7.4 Fish

### 7.4.1 Threespine Stickleback - *Gasterosteus aculeatus*

Jokuty *et al.*, (1999) evaluated the acute toxicity of Orimulsion-400 OWD to threespine stickleback. The fish (0.17-0.18 g wet weight) were exposed to a series of concentrations of the freshly prepared OWD. The 96-hour acute test was performed at  $10 \pm 1^\circ\text{C}$  with a photoperiod of 16 hours of light. The 96-hour  $\text{LC}_{50}$  was determined based on nominal concentrations of Orimulsion-400 OWD and measured concentrations as TSEM.

### 7.4.2 Rainbow Trout - *Oncorhynchus mykiss*

Jokuty *et al.*, (1999) evaluated the acute toxicity of Orimulsion-400 OWD to rainbow trout; the fingerlings were 0.2 to 0.5 g (wet weight) each. The 96-hour acute test was performed at  $15 \pm 1^\circ\text{C}$  with a photoperiod of 16 hours of light per day. The 96-hour  $\text{LC}_{50}$  was determined based on nominal and measured concentrations as TSEM.

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#### 7.4.3 Zebra Fish - *Brachidanio rerio*

Acute toxicity of Orimulsion-400 OWD on zebra fish was evaluated by Esclapés (1998). The OWD was prepared by mixing Orimulsion-400 and freshwater, and from this stock emulsion exposure test concentrations were obtained for the assay. The 96-hour  $LC_{50}$  was determined based on nominal concentrations.

#### 7.4.4 Inland Silverside - *Menidia beryllina*

Effects of Orimulsion-400 on inland silverside were evaluated by Johnson *et al.* (2000). Test fish were 12-13 days old, had a standard length of 9-13 mm, and a wet weight range of 0.0043-0.0143 g. The fish were exposed to both OWD and WSF of Orimulsion-400 in 450-ml glass dishes for 96 hours. The OWD and WSF test concentrations were prepared as described for the mysid test. Ten fish were used per replicate, and two replicates per test concentration. The tests were conducted at a temperature of  $25 \pm 2^{\circ}\text{C}$ , a photoperiod of 16 hours of light/day, and a salinity of  $20 \pm 3$  parts per thousand. The OWD  $LC_{50}$ s were estimated based on nominal concentration using an Orimulsion-400 sample collected in 1997 and one collected in 1998. The WSF  $LC_{50}$ s were estimated based on TRPH (United States Coast Guard, 1997).

#### 7.4.5 Turbot - *Scophthalmus maximus*

The acute toxicity of Orimulsion-400 WAF on turbot, *Scophthalmus maximus*, was evaluated by Bjørnstad *et al.*, (1998). The fish were exposed to a series of test concentrations of the WAF for 96 hours (WAF was prepared as described for the activated sludge test). The 96-hour  $LC_{50}$  was estimated based on nominal concentrations. Although no mortality occurred at 1,000 mg/L, signs of toxicity (swimming behavior, pigmentation changes) were observed at this test concentration.

#### 7.4.6 Sheepshead minnows - *Cyprinodon dearborni*

The acute toxicity of Orimulsion-400 OWD using sheepshead minnows was evaluated by Esclapés *et al.* (1997). The OWD was prepared by directly mixing the fuel and seawater. No mortality was observed at any concentration tested, including 1,000 mg/L nominal Orimulsion-400 after 96 hours.

#### 7.4.7 Chub - *Leuciscus idus*

The German Hygiene Institute tested this fish using the OWD of Orimulsion.

#### 7.4.8 Marine guppy - *Poecilia spheonops*

The acute toxicity of Orimulsion-400 OWD on this species was evaluated by Esclapés (1998). Individuals were exposed to a series of test concentrations of the OWD for 96 hours. No toxic effects were observed in any test concentration, including 1,000 mg/L nominal Orimulsion-400 concentration.

## 7.5 Recommendations

Figure 1 summarizes the set of acute toxicological data for Orimulsion-400. This curve shows a cumulative distribution of species arrayed in rank order by the species-specific effect values. Thus, for Orimulsion-400 the mysid shrimp is shown as the lowest ranked species in terms of its  $LC_{50}$  value, whereas the highest  $LC_{50}$  value estimated was for the fish *Gasterosteus aculeatus*. In other words, based on all studies evaluated the mysid shrimp was the most sensitive species to this fuel, and *Gasterosteus* was the least sensitive. The distribution of species sensitivities to Orimulsion-400 is consistent with species sensitivities estimated for the original formulation. This figure includes the most conservative values available for each species tested. The results summarized in Table 3 and Figure 1 can be used as a guide to the selection of test species for future toxicity studies.

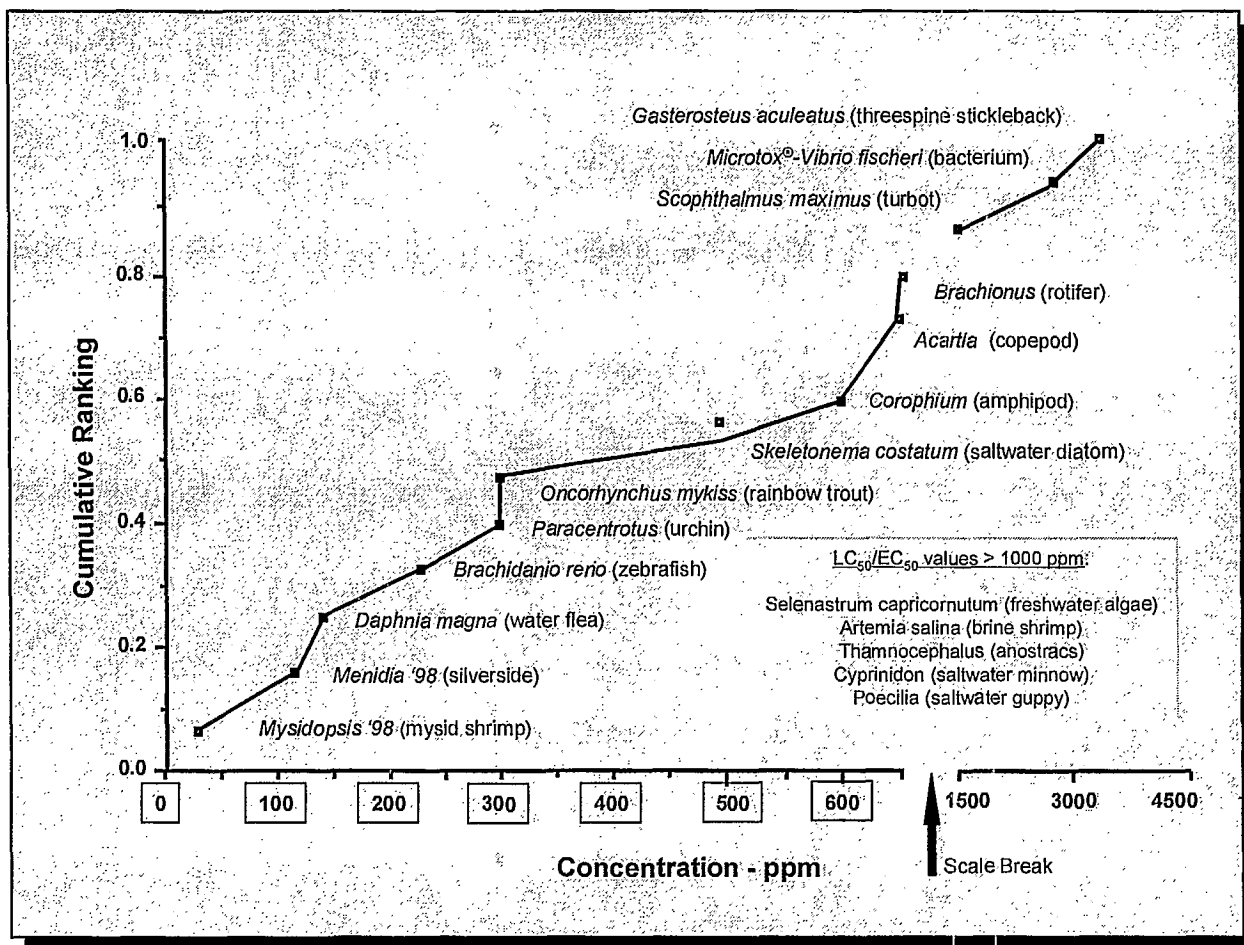


Figure 1. Cumulative Distribution of Orimulsion-400 Acute Toxicity Data

Based on the numerous studies conducted worldwide using Orimulsion products, it is apparent that aquatic toxicity methods have been widely standardized based on the consistency of the results obtained. It is recommended that standard aquatic effects methods should continue to be used as they provide consistent benchmark data for effects comparisons. Methods recommended include those promulgated by ASTM, Environment Canada, OECD, and EPA. A large number of marine and estuarine species have been tested providing a robust aquatic toxicity database. A significant number of studies have been conducted using freshwater studies, and at this time an evaluation of additional freshwater species is being initiated jointly by Environment Canada and Golder

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Corporation. Acute toxicity tests using spiked sediments are also planned as part of the additional aquatic toxicity studies to be conducted this year.

The media preparation method used for the aquatic toxicity tests seems to be the most critical aspect affecting the effects data and the interpretation of results. An Orimulsion OWD (similar to the WAF for Orimulsion) should be used for all water column exposures. A range of concentrations should be prepared by serial dilution of a single OWD stock. Effect concentrations should be reported based on nominal concentrations (loading rates), as recommended by the OECD (2000) for multi-component mixtures. Analysis of any one parameter, or use of any one method, can not quantify all of the components in emulsified fuels such as Orimulsion.

It is important to note that direct comparisons of acute or sublethal effect levels (*e.g.*,  $LC_{50}$ ,  $EC_{50}$ ) of Orimulsion and other fuels are not appropriate, as the effect concentrations may be based on different analytical methods reflecting different fractions of each fuel. The behavior of emulsified fuels in aquatic systems can be very different than the behavior of floating fuels; this difference in partitioning in the environment directly affects the exposure to aquatic organisms. Aquatic toxicity studies should be designed to evaluate exposures similar to those anticipated in the environment, this will facilitate the assessment of potential effects and the response to accidental spills of Orimulsion in the aquatic environment. When making exposure comparisons among fuels, all fuel exposure pathways should be noted, including the effects of oil slicks for floating oils.

Data developed using the nominal Orimulsion concentrations reflect water column exposures for this dispersed fuel. Use of the dissolved fraction of floating fuels represents the dissolved hydrocarbon plume that forms below a slick, also representing water column exposures.

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## 7.6 References

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## 8. Glossary

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ASTM	American Society for Testing and Materials
BITOR	PDVSA BITOR is a Commercial Unit of PDVSA's Exploration and Production division of Petróleo y Gas, which is a subsidiary of Petróleos de Venezuela, S.A. PDVSA BITOR is responsible for the exploitation and emulsification of natural bitumen, as well as the supply and marketing of Orimulsion.
bitumen	a heavy, almost solid form of petroleum occurring in natural deposits
breaking	an irreversible process in which the formerly dispersed phase of an emulsion becomes a second continuous phase, resulting in two separate bulk liquid phases
BTEX	benzene, toluene, ethylbenzene, and xylenes
coalesced bitumen	a black, highly viscous, sticky, tar-like semi-solid that is formed by the coalescence of dispersed bitumen, or directly from the breaking of the Orimulsion emulsion
coalescence	the merging of two or more droplets into a single droplet
creaming	the rising of dispersed droplets due to differences in density
dispersed bitumen	a dispersion of bitumen in water resulting from an Orimulsion spill or intentional dilution of Orimulsion with water
EC50	median effective concentration
emulsion	a heterogeneous system, consisting of at least one immiscible liquid (dispersed phase) finely dispersed in another (continuous phase) in the form of small droplets
EPA	Environmental Protection Agency
FAAS	fluorescence atomic absorption spectrometry
flocculation	occurs when groups of dispersed phase droplets clump together, forming loose clusters, or flocs
GC/MS	gas chromatography/mass spectrometry
GC/FID	gas chromatography/flame ionization detection
HPLC	high performance (pressure) liquid chromatography
IC50	median inhibition concentration
ICP-AES	inductively coupled plasma-atomic emission spectrometer

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<b>Intevep</b>	This PDVSA subsidiary is a research and technology development company which provides its services on technology to the oil and petrochemical industry.
<b>inversion</b>	the interchange of dispersed and continuous phases, as when an oil-in-water emulsion becomes a water-in-oil emulsion
<b>IR</b>	infrared
<b>LC50</b>	median lethal concentration
<b>LOEC</b>	lowest observed effect concentration
<b>NOEC</b>	no observed effect concentration
<b>OECD</b>	Organization for Economic Co-operation and Development
<b>Orimulsion</b>	Orimulsion® is the brand name given to a fossil fuel produced from natural bitumen mixed with water - approximately 70% bitumen, 30% water, and a small amount of stabilizing surfactant.
<b>OWD</b>	oil-in-water dispersion
<b>PAH</b>	polycyclic aromatic hydrocarbon
<b>PDVSA</b>	Petróleos de Venezuela, S.A.; PDVSA is owned by the Republic of Venezuela, and is charged with the development of the petroleum, petrochemical, and coal industry.
<b>sedimentation</b>	the settling of dispersed droplets due to differences in density
<b>surfactant</b>	surface active agents; chemicals that modify the nature of surfaces often by reducing the surface tension of water. Surfactants are widely used as wetting agents, detergents, emulsifiers, dispersants, penetrants, and antifoaming agents.
<b>TLC/FID</b>	thin layer chromatography/flame ionization detection
<b>TPH</b>	total petroleum hydrocarbons
<b>TRPH</b>	total resolvable petroleum hydrocarbons
<b>TSEM</b>	total solvent extractable material
<b>UV-VIS</b>	ultraviolet-visible
<b>UVF</b>	ultraviolet fluorescence
<b>VOC</b>	volatile organic compound

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**WAF**      water-accommodated fraction - Aqueous media containing the dissolved fraction from the test oil and the stable dispersion of particles, in a multi-component mixture.

**weathered bitumen**      coalesced bitumen that has been exposed to weathering processes such as occur during shoreline stranding.

**WSF**      water-soluble fraction - Aqueous media containing the dissolved fraction from the test oil, with little or no particulate oil matter present.

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