

Section VI

MANUAL ON OIL POLLUTION

IMO GUIDELINES FOR SAMPLING AND IDENTIFICATION OF OIL SPILLS



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Foreword

The IMO Guidelines for Sampling and Identification of Oil Spills are intended to provide guidance to governments, including those of developing countries, on the techniques, equipment and strategies for sampling oil to identify unknown sources of spilled oil. Although references are given for the laboratory methods required for analysis, the emphasis in this text is on the details of the field work required to collect the samples.

The integrity of the samples at every point from collection through shipment and analysis is important. The foundation of any chemical analysis is sampling. Sampling correctly provides a representative portion of oil that is not contaminated by other products. Storage and shipment ensure that the sample will not deteriorate before it can be analysed. For oil spills in particular, the analytical process involves comparing the chemical characteristics, or “fingerprints”, of the spilled oil and various suspected sources. Therefore, success in matching spills to sources depends on knowing locations where samples should be taken. The education of field samplers with the information in this publication will facilitate the identification of the sources of spilled oil.

This publication has been written to provide a comprehensive and detailed explanation of all aspects of the sampling process. These Guidelines, which deliberately include many different options that are currently in use, may be used in several ways. They can be provided directly to field personnel or used as a basis to prepare guidelines specifically for individual countries.

The draft of this document was developed by a working group formed of technical experts who attended the 1995 Oil Spill Research and Development Forum, which was held at IMO headquarters in London in May 1995. LCDR Kristy Plourde of the US Coast Guard Marine Safety Laboratory chaired the working group and prepared the draft, with active participation by experts from Australia, Bulgaria, the United Kingdom, Germany and Denmark.

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Contents

	<i>Page</i>
1 Introduction.....	1
2 Definitions	2
3 Acronyms and abbreviations	3
4 Supplies and equipment.....	4
5 Safety.....	7
6 Planning ahead for sample collection	7
7 Sampling procedures	8
8 Sample identification and security.....	19
9 Storing the samples.....	21
10 Requesting laboratory analysis.....	23
11 Shipping samples to the laboratory	23
12 Choosing a laboratory	29
13 Laboratory analysis.....	30
Appendix A Oil sampling and shipping checklists.....	32
Appendix B Chain-of-custody record.....	35
Appendix C Proper Shipping Names and UN Numbers for petroleum products	36
Appendix D Flashpoint ranges for typical petroleum products.....	37
Appendix E ASTM and NORDTEST standards for analysis of waterborne oil spill samples.....	38

1 INTRODUCTION

1.1 Why? Identification of the “responsible party” or source for an oil spill incident may require the laboratory analysis of oil samples. This is one part of the overall task of investigating the oil spills and suspected sources. It is possible to identify differences between one oil and another and similarities between a spilled oil and its source. Many laboratories have the ability to do the laboratory analysis and interpretation. Comparison of the spilled oil with its potential source samples can provide evidence of the source of the oil. This guide was written to help people who have the task of collecting oil samples and sending them to a laboratory. This is a very important task, as important as the analysis in the laboratory. If the tasks are not done correctly, either the laboratory will not be able to identify the source of the oil or the results will not stand up to legal examination. In either case, all the work of sampling, the laboratory analysis and the investigation may be wasted.

1.2 Who? This guide is written in the form of instructions for the “sample collector”. It is very unusual for someone to be specialized as an oil sample collector and to have no other task responsibilities. Experience is helpful; however, one purpose of this guide is to train sample collectors with no experience. Reading this guide, obtaining sampling supplies and practicing *before* a spill occurs will result in a better response in a real spill situation.

1.3 What? There are a number of different parts of the task of taking a sample from the water and sending it to a laboratory. Some involve thinking about where and how to sample; others involve the details of paperwork that are critical to establishing the legal chain of custody for the samples. It is also important to know how to store samples and how to pack and ship samples so that they arrive unbroken. This guide discusses each of these topics in detail in different chapters. This guide does not address legal requirements and only addresses general sampling procedures. Consult the legal requirements for your country to determine what evidentiary procedures are required. This includes, but is not limited to: laws and regulations pertaining to oil pollution, procedures for evidence collection and storage, witnesses required during evidence collection, number of samples required from each sampling point, limitations as to when/where samples are collected, procedures for interviewing potential defendants, reports, photographs, etc.

1.4 When? The best time is sooner rather than later. Petroleum oil is a complex mixture of many different chemical components. When oil is spilled, it begins to “weather”, or change, due to differences in the properties of these components. Evaporation of the lightest, most volatile, of these components is the primary process. Although the

chemist understands the weathering processes and how it affects the data, analysis is always easier with fresh oil. Another consideration is that the source of oil may change with time, especially if it is a mixture of oils within a bilge. A timely response is critical for the success of these cases.

1.5 How? The directions are accompanied by illustrations and pictures. They describe the technical procedures to be used and have been found to work. This manual has been compiled from procedures used by either NORDTEST (European analytical standard) or the US Coast Guard. There are a variety of approaches that may be useful for a given situation. Implementation of these techniques will depend on equipment and supplies that are locally available. Sampling techniques need not be restricted in concept to those described here, although legal requirements for specific countries may do so. Innovations that preserve the sample integrity, lower the cost of supplies, or increase the ease of sampling are encouraged. Suggestions for additions to this manual may be sent to the International Maritime Organization (IMO).

2 DEFINITIONS

Bilge water: a mixture including water and oil collected in the bilge of the machinery space in a ship as a result of leakage, drainage, etc.

Chain of custody: the series of actions taken in transferring a sample so that the sample cannot be tampered with or altered accidentally. The oil portion is typically a mixture of fuel oils and lubricating oils.

Enclosed space: a space which has any of the following characteristics: limited openings for entry and exit, unfavourable natural ventilation, not designed for continuous worker occupancy. It includes, but is not limited to, cargo spaces, double bottoms, fuel tanks, pump-rooms, compressor rooms, cofferdams, void spaces, duct keels, inter-barrier spaces, engine crankcases and sewage tanks.

Deck log-book: full nautical and cargo handling record of a ship's voyage, written up at the end of each watch (or duty period) by the officer in charge.

Emulsified oil: suspended mixture of two immiscible fluids (water and oil), one being dispersed in the other in the form of fine droplets.

Engine log-book: a book in which all particulars relating to the operation of the propelling and auxiliary machinery are entered by the engineers in charge.

Flashpoint: the temperature in degrees Celsius at which a product will give off enough flammable vapour to be ignited. A detailed definition of this property is contained in volume II of the International Maritime Dangerous Goods Code, class 3: Flammable Liquids.

Homogeneous: uniform throughout in composition.

Heterogeneous: any mixture or solution comprising two or more substances, whether or not they are uniformly dispersed.

Inhomogeneous: not uniform throughout in composition.

Limited quantity: as defined by International Air Transport Association (IATA) Dangerous Goods Regulations, section 2.8.

Log-book: a ship's journal or tabulated summary of the performance of the vessel, her engines and other daily events, entered by the master according to the law.

Oil record book: a book in which all operations concerning oil or oily mixtures are entered, compulsory on oil tankers of 150 grt and over, and on other ships of 400 grt and over.

Responsible party: a person or group identified as the source or cause of the oil spill.

Sample: a representative portion of an oil spill or source product which can be transported to a laboratory for identification and analysis.

Oil sheen: an extremely thin layer or film of petroleum product causing some visual evidence on the water surface.

Oil slick: a thin film of oil on water.

Slop: mixture of water and oil residues from cargo tanks in oil tankers that may contain oil/water emulsions, paraffin wax, sediments and other tank residues.

Sludge: deposits, generally from the purification of fuel and lubrication oils, consisting of mixtures including oil, paraffin wax, sediments and other tank residues.

Tank washings: tank washing water containing cargo tank residues including oil, paraffin wax, sediment and other foreign matter such as tank cleaning chemicals.

Tarballs: oil that has evaporated and possibly mixed with debris and has formed into a solid mass or solid form.

Weathering: all changes in oil composition which take place after the spillage, including evaporation, dissolution, oxidation, biological decomposition, etc.

3 ACRONYMS AND ABBREVIATIONS

IMO	International Maritime Organization
IATA	International Air Transport Association
grt	gross tons
UN	United Nations
N.O.S.	not otherwise specified
ASTM	American Society for Testing and Materials
SOP	standard operating procedures
MARPOL 73/78	International Convention for the Prevention of Pollution from Ships, 1973, as amended by the Protocol of 1978 relating thereto
ISO	International Standards Organization

4 SUPPLIES AND EQUIPMENT

4.1 Obtain in advance Sampling equipment should be obtained in advance and ready for use. Consult with appropriate legal authorities to determine numbers of samples required.

4.2 Pre-clean sampling equipment Sampling equipment should be pre-cleaned to remove any oil residues (including finger oils) that may mix with the oil collected and interfere with the laboratory analysis. The use of sampling containers contaminated with oil should be avoided. Sampling equipment, if not purchased pre-cleaned, should be cleaned with a detergent wash, rinsed with distilled water, and then rinsed with solvent (like dichloromethane, hexanes, etc.). The larger the volume of oil collected, the less likely the oil-contaminated jar (or collection device) will contaminate the sample. Pre-cleaned supplies, if needed, can be wrapped in aluminium foil to prevent contamination while being stored or transported to the spill.

4.3 List of supplies and equipment Sampling equipment may include, but is not limited to, the following:

- .1** *Sample jars* for collecting samples (figure 1), glass, approximately 250 ml in size and pre-cleaned prior to use. The jar lids should be lined with Teflon[®] (TFE fluorocarbon polymer) or aluminium.
- .2** *Plastic containers* should *not* be used. Part of the plastic may mix with the oil and change the oil. However, if all you have is plastic containers or even bags, it is better to use these than nothing at all.
- .3** *Equipment for sheen collection:* TFE fluorocarbon polymer nets (figure 2) or bags (figure 3), rings and extension poles. TFE fluorocarbon polymer sheets of mesh fabric may also be used.
- .4** *Disposable gloves*, 100% nitrile medical examination gloves (figure 4). Gloves help in two ways; they keep oil from getting on your hands and keep oils from your hands from getting into the sample.
- .5** *Cardboard shipping tubes* for packing sample jars for shipment.
- .6** *Tape* for sealing sample jars and shipping tubes, approximately 2 cm wide. Also, tape for closing fibreboard box, approximately 10 cm wide.
- .7** *Fibreboard boxes* for shipping samples, approximately 25 cm × 25 cm × 25 cm.
- .8** *Sorbent material* for packing in boxes to absorb oil if jars leak.
- .9** *Greaseproof plastic bags* for lining shipping boxes, approximately 50 cm × 65 cm.



Figure 1

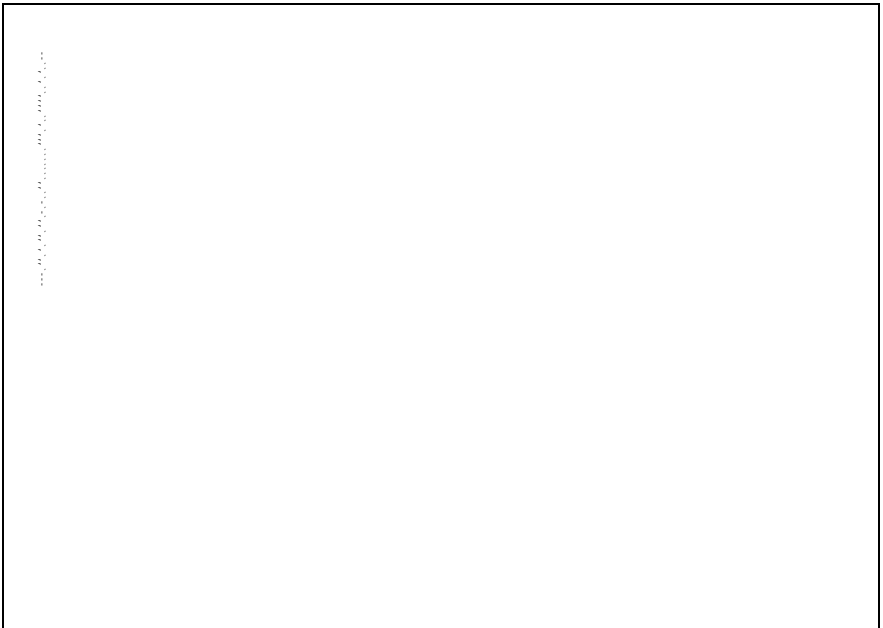


Figure 2

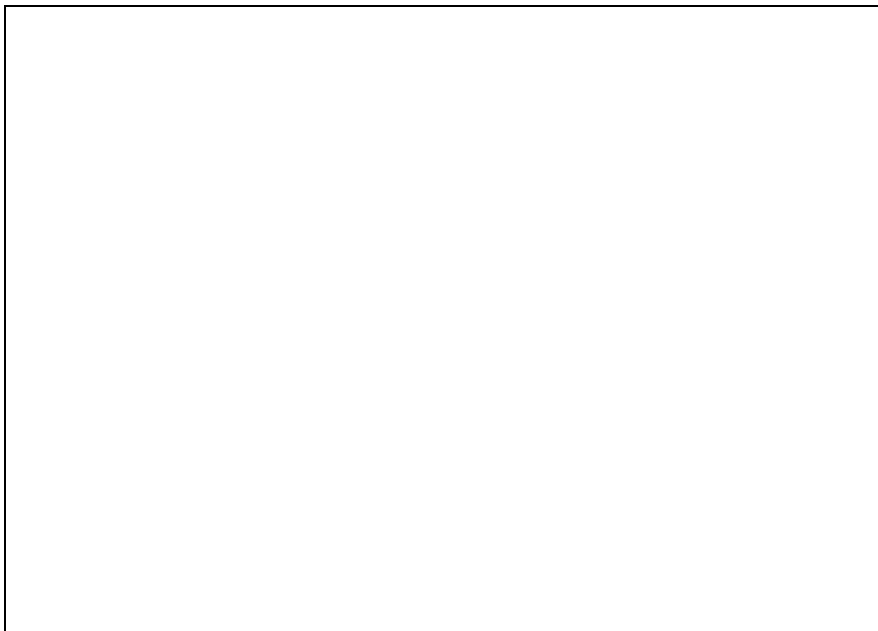


Figure 3

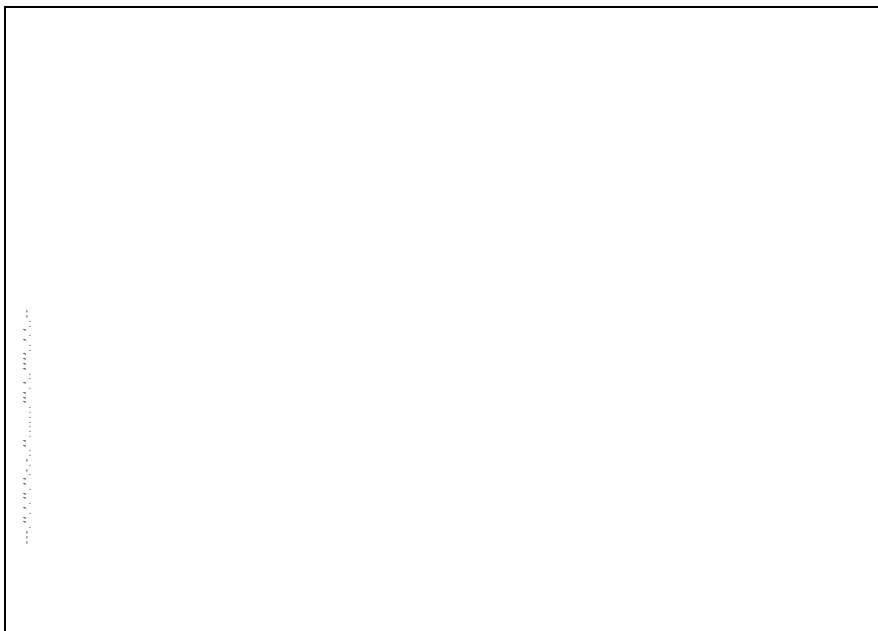


Figure 4

- .10 *Sampling log-book* to record all relevant information about the samples and spill situation.
- .11 *Chain of custody* and *sample identification labels*, white adhesive, approximately 5 cm × 10 cm, water- and oil-resistant (see figure 13).
- .12 *Shipping labels*, pressure-sensitive, approximately 10 cm × 10 cm: hazard class 3 “Flammable Liquid” label or hazard class 9 “Miscellaneous” label (see figure 17).
- .13 *Envelope*, heavy-duty, to keep paperwork clean and dry during shipment, water-vapour-proof and greaseproof.
- .14 *Towels*, absorbent cloth or paper, to clean sample jars after sample is taken.
- .15 *Twine*, string or cord for hard-to-reach sample areas, cotton, six-ply (six threads twisted together).
- .16 *Tongue depressors* or *pre-cleaned metal scoop* to aid in collecting samples of heavy oils or tar balls.
- .17 *Sampling kit case* to hold all sampling equipment ready for transport to spill location.

5 SAFETY

5.1 Think of safety first. When collecting samples from the spill, try to stay upwind of the spill.

5.2 It is important to wear clean gloves to protect your hands when collecting samples. This is true for both spill samples and suspect samples. This limits the exposure you will get to dangerous chemical compounds often found in petroleum oils (like benzene).

5.3 Collecting oil samples is often done at night or in cold weather. Staying alert is very important. If you are unsure if it is safe to collect a sample, it is probably best to wait until more information is known or until weather conditions improve.

5.4 When sampling any source, you should be accompanied by a member of the crew. It can be very dangerous taking samples from vessels and other sources, therefore persons sampling from such sources should be experienced or acquainted with the general construction of vessels and be aware of confined space entry regulations. Seek advice when in doubt. If taking samples from a ship, the sample collector should be accompanied by a member of the ship's crew at all times. The sample collector should be experienced with ships and the dangers associated with them, especially the dangers of entering confined spaces.

6 PLANNING AHEAD FOR SAMPLE COLLECTION

Planning ahead involves thinking about sampling the spilled oil and taking samples from those who are suspected of causing the spill. Take samples of the spilled oil first because the oil will change after exposure to the environment.

6.1 Spill samples Sample different parts of the spilled oil as soon as possible. The oil may spread out on the water. If this happens, it can be hard to collect a sample. The number of samples taken depends on the size and location of the spill. For large spills, take at least three samples of the oil from different places, or one sample from each locality if the spill is widely dispersed. For small spills, do your best to take one or two samples.

6.2 Suspect samples Samples should be collected from anyone who may have spilled the oil. This means all facilities or vessels in the area of the spilled oil at the time of the spill. On a vessel, you may need to take samples from different places like the fuel tank, day tank, cargo tank, waste oil or slop tanks and the bilge. Read and be familiar with the guidelines in section 7.6. Be prepared to take samples from each tank and the bilge if you cannot see where the spill came from. Do not try to determine the oil type by just looking at its colour. For example, just because a spilled oil is black does not mean that it came from a bilge. It may be a weathered fuel oil. This is a common error made by samplers. After deciding who the suspects are and which tanks, etc., to sample, investigators must document (1) which suspects were sampled and (2) why any possible suspects were not sampled. Note that factors such as wind and water flow direction might eliminate a vessel or facility from being a suspect. In general, however, all possible suspects should be sampled.

6.3 Reference samples (blanks or clean water samples) This sample is taken to show what the water was like before the oil spill. The sample should be taken upstream and away from the spill area. However, because spilled oil, especially a light oil, spreads rapidly, a very thin layer of oil on the surface of the water may not be visible to the unaided eye. A reference sample can also be collected from other background environments (beach, etc.) whenever relevant, in order to determine whether the spilled oil has been contaminated by an earlier spill or other organic material. If there is a limited volume of oil in the spill, a reference sample should be taken. Close harbour areas tend to have higher background levels and therefore reference samples should be taken in these areas.

7 SAMPLING PROCEDURES

7.1 Main types of samples The following main types of oil or oily mixture may occur at spill sites and suspected sources:

- oil, oily water, heavily emulsified oil, tarballs or lumps on the water surface
- mixtures of oil and sorbents or other materials which are soaked with oil
- mixtures of oil and foreign materials on beaches