Use of ozone depleting substances in laboratories

Use of ozone depleting substances in laboratories

TemaNord 2003:516

Use of ozone depleting substances in laboratories

TemaNord 2003:516

ISBN 92-893-0884-2
ISSN 0908-6692
Print: Ekspressen Tryk & Kopicenter

Printed on paper approved by the Nordic Environmental Labelling.

This publication may be purchased from any of the agents listed on the last page.

Nordic Council of Ministers
Store Strandstræde 18
DK-1255 Copenhagen K
Phone (+45) 3396 0200
Fax (+45) 3396 0202

Nordic Council
Store Strandstræde 18
DK-1255 Copenhagen K
Phone (+45) 3396 0400
Fax (+45) 3311 1870

Website: www.norden.org

Nordic Environmental Co-operation

Environmental co-operation is aimed at contributing to the improvement of the environment and forestall problems in the Nordic countries as well as on the international scene. The co-operation is conducted by the Nordic Committee of Senior Officials for Environmental Affairs. The co-operation endeavours to advance joint aims for Action Plans and joint projects, exchange of information and assistance, e.g. to Eastern Europe, through the Nordic Environmental Finance Corporation (NEFCO).

The Nordic Council of Ministers

was established in 1971. It submits proposals on cooperation between the governments of the five Nordic countries to the Nordic Council, implements the Council's recommendations and reports on results, while directing the work carried out in the targeted areas. The Prime Ministers of the five Nordic countries assume overall responsibility for the cooperation measures, which are co-ordinated by the ministers for cooperation and the Nordic Cooperation committee. The composition of the Council of Ministers varies, depending on the nature of the issue to be treated.

The Nordic Council

was formed in 1952 to promote cooperation between the parliaments and governments of Denmark, Iceland, Norway and Sweden. Finland joined in 1955. At the sessions held by the Council, representatives from the Faroe Islands and Greenland form part of the Danish delegation, while Åland is represented on the Finnish delegation. The Council consists of 87 elected members – all of whom are members of parliament. The Nordic Council takes initiatives, acts in a consultative capacity and monitors cooperation measures. The Council operates via its institutions: the Plenary Assembly, the Presidium and standing committees.

Contents

Foreword

The Nordic Chemical Group under the Nordic council of Ministers has financed the project "Use of ozone depleting substances in laboratories - ODSLAB".

The Nordic Working Group on Ozone Depleting Substances, which consists of five representatives of competent authorities on ozone depleting substances, has worked as a steering group.

The practical work of the project was done by Senior Advisor, M.Sc., Mr. Miska Vaara at the Chemicals Division of the Finnish Environment Institute.

We express our deepest gratitude to laboratories for answering our questionnaire and experts for their kind help and co-operation.

Sammandrag

Projekts mål

Projektet "Use of ozone depleting substances in laboratories - ODSLAB" uppskattade användningen i Norden av ämnen som bryter ner ozonsiktet i laboratorier. Undersökningen gjordes i huvudsak med hjälp av en enkät.

Projektets viktigaste mål var att:

- finna sådana analyser och andra laboratorieändamål för vilka man använder ämnen som bryter ner ozonsiktet,
- bedöma hur stora mängder ozonnedbrytande ämnen som används,
- identifiera möjliga ersättande ämnen och metoder, speciellt för bestämning av olja i vatten,
- identifiera vad som möjligen förhindrar ersättning,
- samla information om hur ämnena hanteras efter användning,
- samla information för eventuella politiska beslut i framtiden,
- samla information åt laboratorierna om möjligheter att ersätta användningen av ämnen som bryter ner ozonsiktet och om ersättande metoder som använder andra ämnen.

Information om metoder där ozonnedbrytande ämnen används och om ersättande metoder är samlade i denna rapport. Den praktiska tillämpligheten av de ersättande metoderna bör evalueras från fall till fall.

Introduktion

Användningen av ozonnedbrytande ämnen är reglerad i de utvecklade länderna. Begränsningarna gäller inte bruk av ämnen för ändamål som är nödvändiga för hälsa och säkerhet, ifall ersättande ämnen eller metoder saknas. Användning av ozonnedbrytande ämnen för laboratorieändamål är ett sådant undantag. Montreal protokollets parter har beslutat om ett globalt undantag för användning i laboratorier till slutet av 2005.

Tillgången till ersättande metoder för enskilda laboratorieändamål evalueras kontinuerligt av en expertpanel under Montreal Protokollet. Om ersättande metoder finns, kan Montreal Protokollets parter besluta om att en viss analysmetod inte längre betraktas som ett nödvändigt ändamål. Ämnen som bryter ner ozonsiktet får inte användas vid analyser av olja, fett och total halt av oljebaserade kolväten i vatten. I några länder är användning av ämnen som bryter ner ozonsiktet redan förbjuden i laboratorier.

Några laboratorier har redan börjat jämföra nya och gamla metoder och erhållna resultat med varandra. De ersättande metoderna kan i vissa fall mäta en lite annan egenskap. Det kan därför vara nödvändigt att jämföra resultat av analyser gjorda på samma prover

med både nuvarande och ersättande metoder, speciellt eftersom proven kan innehålla så olika blandningar av kolväten.

Laboratoriers användning av ozonnedbrytande ämnen i de nordiska länder

En enkät sändes till nästan 500 laboratorier för att samla information om användning av ozonnedbrytande ämnen och om faktorer som förhindrar användning av metoder som inte förutsätter användning av sådana ämnen. Man hade uppskattat att 205 laboratorier använde ozonnedbrytande ämnen år 2001 för bestämning av olja i vatten och för 44 andra analysmetoder.

Den totala mängden av ozonnedbrytande ämnen som användes år 2001 för laboratorieändamål i de nordiska länderna var 17 400 kilogram (ODP); (ODP anger att den sammanlagda mängden är korrigerad med substansspecifika faktorer som avspeglar varje enskilt ämnes potential att nedbryta ozonsiktet). Dessutom användes återanvända och återvunna ämnen. De sammanlagda utsläppen av ämnen till atmosfären under 2001 uppskattades vara cirka 670 – 1020 kilogram (ODP). Denna mängd frigjordes från cirka 300 000 enskilda analyser.

Cirka 75 % av de ozonnedbrytande ämnena användes för att analysera olja i vatten, mestadels olja i avloppsvatten och olja i dricksvatten. Inget annat användningsändamål var så framträdande som analyser av olja i vatten. Bestämning av olja i andra medier, såsom i mark och slam, var andra ändamål för användning av ozonnedbrytande ämnen. GC-analysen ISO 9377-2 för bestämning av kolväteindex i vatten var den vanligaste av de ersättande metoder som laboratorierna redan tagit i bruk.

Enkätens resultat tyder på att de ozonnedbrytande ämnena hanteras på ett ändamålsenligt sätt efter användningen. Den mängd som används per analys har dock inte nödvändigtvis minskat så mycket som den kunde ha gjort. Förbudet att använda ozonnedbrytande ämnen vid bestämning av olja i vatten kommer att minska detta problem betydligt.

Enkäten anger att laboratoriernas användning av ozonnedbrytande ämnen år 2003 är lite mindre än 1500 kilogram (ODP). Användningen ger upphov till utsläpp av högts 100 kg (ODP) per år till atmosfären. Ersättning av ozonnedbrytande ämnen kan genomföras för de flesta användningsändamålen, men enligt enkäten kan det vara opraktiskt och dyrt.

Ersättande metoder för bestämning av olja i vatten, mark och slam utvecklas av CEN och ISO. Dessa ersättande metoder kommer möjligen att vara godkända före slutet av 2005. Ersättningen av en del metoder kommer möjligen att leda till betydande kostnader, när ny bestämningsutrustning skaffas och den nya metoden valideras, ifall bestämningen inte kan köpas från något annat laboratorium. Svårigheter med detektionsgränser och med annan prestanda kan uppstå, såsom svårigheter att utnyttja en sofistikerad metod vid kontinuerlig kvalitetskontroll eller processkontroll. Modifiering av metoder kan vara möjlig för vissa fall och prover. För några metoder, såsom för bestämning av koccidiostatika och för bestämning av metaller i mycket låga koncentrationer, finns det inte lika bra ersättande metoder. De nu existerande ersättande metoderna har detektionsgränser av en högre storleksordning.

Det finns några metoder som kan inte ersättas i slutet av år 2005. Behovet av ozonnedbrytande ämnen för dessa ändamål är cirka 100 kilogram (ODP) per år.

Summary

Outline of Project

Project "Use of ozone depleting substances in laboratories - ODSLAB" evaluated the uses of ozone depleting substances (ODS) in the Nordic countries using a questionnaire as the principal survey method.

The principal targets of the project were to:

- recognize the laboratory use purposes of ozone depleting substances
- assess the amounts of ozone depleting substances used for various use purposes
- recognize possible substitute methods, especially for oil-in-water -assays
- recognize obstacles to substitution
- gather information on the fate of the ozone depleting substances
- gather background information for future policies and especially
- give information for the laboratories on the possibilities to substitute the substances.

The recognized ODS using analysis methods and available information on substitute methods are described in this report. The practical applicability of a substitute method has to be determined case by case.

Introduction

The majority of the production and consumption of the ozone depleting substances have been prohibited in developed countries. The uses essential to human health and safety are, however, exempted from the prohibitions, provided that there are no available alternatives to these uses. Laboratory use of ozone depleting substances belongs to these essential uses, and parties have granted a global exemption to this use. The present global exemption is valid until the end of 2005.

The availability of alternative methods for individual laboratory uses are under a continuing examination by the expert panel under the Montreal Protocol. When alternatives are available for the analysis method, the Parties to the Protocol can decide, that the specific analysis method is no longer considered as essential use. The use of ozone depleting substances in oil in water –analysis was prohibited through this procedure from the beginning of 2002. In some countries it is not allowed to use the ODS for any determinations.

Some laboratories have started to compare results between old and new methods. In many cases this is necessary, because methods might measure slightly different parameters, and give a bit different results. Because samples may contain very different kind of hydrocarbon mixtures, the best way to compare methods is to do the analysis with both of the methods for each sample type concerning necessary monitored compartments or operations.

Laboratory uses of ozone depleting substances in the Nordic countries

A questionnaire was sent to almost 500 laboratories to find more information on the actual use of ozone depleting substances and the obstacles to substitution of ODS. It was estimated that 205 laboratories used ozone depleting substances for oil-in-water –assays and 44 other use purposes in the year 2001.

The total amount of new (non-recycled, non-regenerated) ODS used for laboratory purposes was estimated to be 17 400 kilograms (ODP; weight corrected by a substance specific Ozone Depleting Potential) in the Nordic countries in 2001. Additionally, it was reported that some recycled or regenerated ODS was used for laboratory purposes. Emissions from laboratory use of ODS to atmosphere were estimated to be 670 – 1020 kilograms (ODP) in the Nordic countries in 2001, resulting of more than 300 000 determinations done with the ODS.

Oil-in-water –analysis was by far the most significant laboratory use purpose. 75 % of ozone depleting substances were used for oil-in-water –assays, mostly for determinations of oil in wastewater and drinking water. The gas chromatographic determination of hydrocarbon index according to the standard ISO 9377-2 was the most general substitute method already applied by the laboratories. However, determination of oil in other medias, like in soil and sludge, are among the methods using ozone depleting substances.

On the basis of the questionnaire, it is understood that ozone depleting substances are generally treated in an appropriate way after their use. However, the amount of the substance used in individual determination has probably not been reduced as often as possible. However, the phase-out of oil-in-water will diminish significantly the problem.

Based on the questionnaire, it is estimated that the use of ozone depleting substances for laboratory and analytical purposes in the Nordic countries will be less than 1500 kilograms (ODP) in 2003 leading to emissions less than 100 kilograms (ODP)/year. The uses are summarized in Chapter 2.4. Further substitution of ODS is possible for most purposes, but based on the questionnaire information, substitution is typically understood to be impracticable or expensive.

Substitute methods for the analysis of oil in waste, soil and sludge are being prepared by the CEN and the ISO. It is possible that these methods have been approved at the end of 2005. In some cases the substitution may add the determination costs remarkably in the form of new determination equipment and validation of the new method, if the determinations cannot be purchased from elsewhere. Also problems with detection limits and other performance criteria may occur, likewise difficulties to apply a sophisticated method in round-the-clock quality or process control, and case- or sample medium specific modifications possibly has to be done. In some cases, like in the determination of coccidiostat traces (a type of veterinary medicine) and some metal analysis with extremely low detection limits, as good substitute methods are not known. The alternative methods may have detection limits higher by one order of a magnitude.

There are some use purposes in which the use of ozone depleting substances cannot be avoided after 2005. The need of ozone depleting substances for these uses is approximately 100 kilograms (ODP).

Abbreviations

1,1,1-TCE – 1,1,1-trichloroethane (methyl chloroform)
AAS – atomic absorption spectrophotometry
AED – atomic emission detector
ASTM – abbreviation for a standard, American Society of Testing Materials
ATSDR – the Agency for Toxic Substances and Disease Registry (the U.S.A.)
BOCLE – Ball-on-cylinder lubricity evaluator
BTEX – the BTEX compounds – Benzene, Toluene, Ethyl Benzene, and Xylene
BTEXN – the BTEX compounds and Naphthalene
$C_{7...10}$ – hydrocarbons having a carbon chain length of 7 - 10 carbon atoms
$C_{10...40}$ – hydrocarbons having a carbon chain length of 10 – 40 carbon atoms
Cd – Cadmium
CD – Committee Draft stage of an international standard (before DIS and FDIS stages)
CEN – The European Committee for Standardization
CFC – fully halogenated chlorofluorohydrocarbon(s), freon
CTC – Carbon tetrachloride (tetrachloromethane)
DIS – a draft international standard (before FDIS - final draft stage and approval stage)
DS – abbreviation for a Danish standard
EC – The European Communities
EC_x – quantitative equivalent carbon number index featuring equivalent boiling points for hydrocarbons. EC is based on equivalent retention times on a boiling point gas chromatographic (non-polar capillary) column normalized to n-alkanes and representing n-alkanes having the same boiling point as compound X. EC is more a physical character than an exact measure of carbon chain length.
ECD – electron capture detector
ELCD – electrolytic conductivity detector
EN – abbreviation for a European Standard
FAME – Fatty acid methyl esters
FDIS – Final Draft International Standard stage (before approval and publication as an international standard)
FID – flame ionization detector
FTIR – Fourier-transform infra-red (spectrophotometric method)
GC – gas chromatography
GPC – gel permeation chromatography
GWP – global warming potential. For example, if a compound has a GWP of 6000, 1 kilogramme has a 6000 times greater global warming impact than 1 kilogramme of carbon dioxide.
HCFC – partly halogenated chlorofluorohydrocarbon(s)
HELCOM - Baltic Marine Environment Protection Commission (Helsinki Commission)
HEM – hexane extractable Material (in the EPA Method 1664)

HPLC – High Performance Liquid Chromatography

HS-GC – (static) headspace (capillary) gas chromatography

ISO – abbreviation for an international standard (and International Standardization Organization)

IEC - International Electrotechnical Commission

IP – abbreviation for a standard method published by the Institute of Petroleum

IR – infrared (spectrometry)

ITD – ion trap detector

LL – liquid – liquid extraction, for example, extraction of hydrocarbons with hexane from water

LOD – level of detection

LOQ – limit of quantitation

MDL – minimum detection limit (U.S.EPA). A concentration of a sample that has a 50 % possibility to be detected.

ML – minimum limit (U.S.EPA). 3.18 times the MDL (for n = 7). A practical limit to minimize the possibility of false positive.

MS – mass spectrometry

MSD – mass selective detector

MTBE – Methyl tertiary-Butyl Ether

NEN – abbreviation for a Dutch standard

NIOSH - The National Institute for Occupational Safety and Health (U.S.A.)

NMR – nuclear magnetic resonance (method)

NPD - naphthalenes, phenanthrenes, dibenzothiophenes

NPM – non-polar material

NS – abbreviation for a Norwegian standard

ODP – ozone depletion potential. Different substances can deplete the stratospheric ozone layer to a different extent. The ODP of CFC-11 is defined to be 1.0. The ODPs of other compounds are calculated with respect to this reference point. If a substance's ODP is 10, it has ten times the capacity of CFC 11 per kilogramme to deplete the ozone.

ODS(s) – ozone depleting substance(s)

OEWG – Open-Ended Working Group

OIC – OSPAR Offshore Industry Committee

OIW – oil-in-water

OLF – Oljeindustriens Landsforening (The Norwegian Oil Industry Association)

Oslo Commission – the commission to administer the Convention for the Prevention of Marine Pollution by Dumping from Ships and Aircraft

OSPAR - The Oslo and Paris Commissions - OSPAR Conventions for the Protection of the Marine Environment of the North-east Atlantic

PAH – polynuclear aromatic hydrocarbons (sometimes expressed also as polycyclic aromatic hydrocarbons or polyaromatic hydrocarbons)

PARCOM – Paris Commission - a commission to administer the Convention for the Prevention of Marine Pollution from Land-based Sources

Pb – Lead

PID – photoionization detector
PLC-4 – 4th Pollution Load Compilation of the Baltic Sea Monitoring
prEN – Proposed European standard
S-316 – Tetrachlorohexafluorobutane
SC – Subcommittee
SFC – Supercritical fluid chromatography
SFR – Supercritical fluid reaction
SFS – abbreviation for a Finnish standard
SGT–HEM – Silica gel treated hexane extractable material (non-polar material)
SPE – solid phase extraction. For example, in oil-in-water –analysis, a water sample is decanted through a permeable disk (solid phase), to which oil hydrocarbons are adsorbed.
SPME – solid phase microextraction.
SS – abbreviation for a Swedish standard
STANAG – NATO Standardization Agreements
TAME – Tertiary Amyl Methyl Ether
TC – Technical Committee
TEAP – Technology and Economic Assessment Panel of the UNEP Ozone Secretariat
THC – total hydrocarbon content
TLC – thin layer chromatography
TMAH – Tetramethylammonium hydroxide
TOC – total organic carbon
TPH – total petroleum hydrocarbons
TR – Technical Report
TRPH – total recoverable petroleum hydrocarbons
TTCE – Tetrachloroethylene (perchloroethylene)
TVOC – total volatile organic carbons
UNEP – United Nations Environment Program
U.S. EPA – Environmental Protection Agency of the United States of America
UV – ultra violet (light)
VOC – volatile organic compound. Generally non polar organic compounds with boiling points approximately between –30ºC and 220ºC.
WG – Working Group

Units

kg – kilogram
l – liter
µg – microgram, 10^{-6} or $^{1}/_{1000\,000}$ grams
mg – milligram, 10^{-3} or $^{1}/_{1000}$ grams
ng – nanogram, 10^{-9} or $^{1}/_{1000\,000\,000}$ grams
ppm – parts per million
ppb – parts per billion

1 Introduction

1.1 The Montreal Protocol

1.1.1. The present requirements

The production and consumption of ozone depleting substances are controlled by the Montreal Protocol. The substances covered by the Protocol are chlorofluorocarbons (CFCs), halons, carbon tetrachloride (CTC), 1,1,1-trichloroethane (methyl chloroform, TCA), hydrobromofluorocarbons (HBFCs), hydrochlorofluorocarbons (HFCs), methyl bromide and bromochloromethane (CBM). [1, 2]

In accordance with the Protocol, the production and consumption of CFCs, halons, carbon tetrachloride, 1,1,1-trichloroethane, HBFCs and bromochloromethane have been phased out in developed countries with the exemption of essential uses. The parties to the Montreal Protocol have decided (Decision IV/25), that the use of substances controlled by the Montreal Protocol should qualify as "essential" only if:

(i) it is necessary for the health, safety or is critical for the functioning of society (encompassing cultural and intellectual aspects); and

(ii) there are no available technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environment and health

The production and consumption of a controlled substance for essential uses should be permitted only if all economically feasible steps have been taken to minimize the essential use and any associated emission of the controlled substance; and the controlled substance is not available in sufficient quantity and quality from existing stocks of banked or recycled controlled substances.

When an essential use nomination is required, the applicant should make a nomination to the national government [3]. The government reviews the application and if it meets the criteria for essential use the respective Party to the Protocol submits the nomination to the Montreal Protocol Ozone Secretariat one year before the year ozone depleting substance is to be used. The Ozone Secretariat forwards the nomination to the Technical and Economical Assessment Panel (TEAP) and its Technical Options Committees for expert review. The Panel either recommends the nomination to the Open-Ended Working Group or reports that it is unable to recommend the nomination. The Panel Report is due by 30 April of the year of the decision. The Meeting of the Parties decides whether to allow production for the essential use. The Party in possession of an essential use exemption authorizes the applicant to acquire the controlled substance according to the terms of the decision.

1.1.2. Laboratory uses as a part of the exemption

The parties decided in 1997 to authorize a global exemption for the production and consumption of CFCs, halons, carbon tetrachloride and 1,1,1-trichloroethane for laboratory and analytical purposes. The exemption was subject to the following conditions:

1) The laboratory and analytical chemicals may contain ozone depleting substances manufactured to purities of minimum 99,5 % (99,0 % for 1,1,1-trichloroethane),
2) The high purity substances and mixtures containing ODS shall be supplied only in reclosable containers or high pressure cylinders smaller than 3 liters, or in 10 ml or smaller glass ampoules, marked clearly as substances that deplete the ozone layer. The label shall also indicate that the use is restricted to laboratory use and analytical purposes, and the used or surplus substances should be collected and recycled, and if recycling is not practical, destroyed.

The laboratory uses identified to global exemption were:

- equipment calibration
- use as extraction solvents, diluents, or carriers for chemical analysis
- biochemical research
- inert solvents for chemical reactions
- as a carrier or laboratory chemical and
- other critical analytical and laboratory purposes.

For laboratory uses of other substances, like the HBFCs, a normal essential use exemption has to be applied.

The global exemption was extended until 31.12.2005. The TEAP has requested to report annually on the development and availability of laboratory procedures that can be performed without using ozone depleting substances.

In the Decision VII/11 the following uses were excluded from the global essential-use exemption, as they are not exclusive to laboratory and analytical uses and/or alternatives are available:

(a) refrigeration and air-conditioning equipment used in laboratories, including refrigerated laboratory equipment such as ultra-centrifuges
(b) cleaning, reworking, repair, or rebuilding of electronic components or assemblies
(c) preservation of publications and archives, and
(d) sterilization of materials in a laboratory.

In its report in 1998 the TEAP presented alternatives for ozone depleting substances used to extract oil and grease from water and for two other laboratory and analytical uses. The TEAP concluded, that as these specific uses have alternatives, they do no longer require the use of ozone depleting substances. [4]

Guided by the TEAP's recommendation, the Parties to the Protocol decided in 1998 to eliminate the following uses from the global exemption for laboratory uses from the end of the year 2001:

- testing of oil, grease and total petroleum hydrocarbon in water
- testing of tar in road-paving materials and
- forensic finger-printing.

The Parties also decided, that any decision taken to remove the global exemption should not prevent a Party from nominating a specific use for an exemption under the essential uses procedure set out in decision IV/25.

In some EU Member States there were difficulties to change from ODS depending oil in water –analysis to alternative methods. The European Community applied from the parties to the Montreal Protocol an emergency quota for continuing the use of ozone depleting substances for oil in water –analysis in 2002. TEAP reviewed the application and recommended to the parties the approval of the application. Among TEAPs remarks was that attention should be paid to adequate disposal of used solvent.

The European Commission published a Decision in July 2002 (2002/612/EY), where the applicant member states, The Netherlands, Spain, Sweden, Denmark and Finland were given a emergency quota of 16 tons (ODP) to be used in oil in water –analysis in 2002. The emergency exemption is not available for the year 2003.

1.2 The EC Regulation 2037/2000

Regulation 2037/2000 of the European Parliament and of the Council on substances that deplete the ozone layer implements the Montreal Protocol requirements in the Community and contains additional, stricter requirements on ozone depleting substances [5]. The same essential use exemption from the prohibitions, which is given in Montreal Protocol, exists also in the EU Regulation.

The European Union is considered as one single party to the Protocol when e.g. quotas for controlled substances, reporting of consumption, and export, and import licensing systems are carried into effect. The EU Regulation's decision making process is carried out through the Management Committee of the Regulation. The Committee consists of representatives of the Member States. The quota allocation to individual companies producing and importing ozone depleting substances is among the Committees duties.

Laboratory use quotas in the EU are allocated consistently with the Montreal Protocol global exemption for laboratory uses. The quotas can be allocated only for CFC, halon, carbon tetrachloride and 1,1,1-trichloroethane. If an European company needs e.g. HBFCs for laboratory uses, normal essential use nomination to the Montreal Protocol secretariat should be made. The quotas are given to companies, which first put the substance on the European market. The downstream distributors and final users do not need a permit from the Commission. However, there might be national permitting, notification or reporting requirements. In 2002 the overall amount of the ozone depleting substances allocated in quotas to companies for laboratory uses was 136 ODP-tons of CFCs, 3,7 ODP-tons for halons, 152 ODP-tons for carbon tetrachloride and 0,6 ODP-tons for 1,1,1-trichloroethane.

The list of the ozone depleting substances according to Directive 2037/2000 is presented in Annex 3 to this report.

1.3 National legislation in the Nordic Region

The individual Nordic Countries have implemented the respective Directives and the requirements concerning the laboratory uses of ozone depleting substances and analytical determination methods in various ways.

In Sweden, the general exemption on laboratory uses of ozone depleting substances until the end of 2002 is approved by Naturvårdsverket (the Swedish Environmental Protection Agency) in NFS 2000:2 and its amendment. In general, it is forbidden to use ozone depleting substances for any laboratory or analytical purposes after 2002. Exemptions can be provided for analysis for which there are no substitute methods available, for methods described in international and national standards, for which there are not approved alternatives, and in research and development under certain conditions. [6-8]

In Iceland, it is forbidden to import CFCs for any use purposes, including laboratory use purposes, according to the regulation nr. 586/2002. The regulation is based on the EC directive 2037/2000. [9]

On the other hand, for example, in Finland and Denmark, no further restrictions to European legislation on the use of ozone depleting substances for laboratory uses have been applied. According to the Norwegian Regulation concerning the ozone depleting substances, a general exemption exists for the use of CFC, carbon tetrachloride and 1,1,1-trichloroethane for analytical purposes until the end of 2005. The use of these substances for oil-in-water analysis is however prohibited. [10-13]

2 The situation in the Nordic Region

2.1 Legislation and Recommendations requiring the use of ozone depleting substances

2.1.1. Legislation

The most typical use purpose of ozone depleting substances is the determination of oil-in-water, especially oil-in-drinking water, for which quality criteria and determination methods are mentioned in legislation or other official guidelines. Oil is also monitored in wastewaters, surface waters, sludges and contaminated soils. For these, quality criteria and possible determination methods have been established in legislation or various official or even inofficial guidelines. In practice, the most crucial singularity in the legislation, concerning the use of ozone depleting substances, is the Danish legislation concerning the monitoring of water abstraction quality.

The Danish legislation is based on the directive 79/869/EC concerning the methods of measurement and frequencies of sampling and analysis of surface water intended for the abstraction of drinking water in the Member States, which requires the testing of dissolved or emulsified hydrocarbons when monitoring surface waters used for abstraction of drinking water. As the determination method the directive requires extraction with carbon tetrachloride followed by infra-red spectrometry or extraction with petroleum ether followed by gravimetry. The detection limit requirement for the IR method is 0,01 mg/l and 0,04 mg/l for water categories A2 and A3, respectively. The requirement of precision is 20 %, and for trueness 30 %. The directive contains requirements also for phenol and PAHs determinations. [14].

In Denmark, the total oil content quality criteria for water reaching the waterwork and leaving the waterwork is 5 or 10 µg/l, respectively. This requires a detection limit of 1 µg/l (0,001 mg/l). In addition, alkylbenzenes, benzene, MTBE, 1,2-dibromomethane, some PAHs, phenols, and for example, some pesticides are monitored in Denmark among the organic microcontaminants analysis packet including total oil.

Monitoring the total oil content in drinking water is understandably important in Denmark, since 99 % of potable water is groundwater, taken by 3000 waterworks from approximately 91 000 separate wells or boring holes possibly located at or nearby exposed or contaminated areas. Danish Miljøstyrelsen has given strict instructions on drinking water monitoring – in order to recognize possible contamination sources, including contaminated soils. The concentrations of the organic microcontaminants are determined at water intake plants in areas where contamination is possible or recognized. However, the analysis of BTXN is obligatory. [15, 16].

The later directives 80/778/EEC relating to the quality of water intended for human consumption and 98/83/EC on the quality of water intended for human consumption actually do not require the use of ozone depleting substances for quantifying oil in water. However, it is up to the member states how the directives are implemented, and

when how soon the old directives are replaced in the given time range. The directive 80/778/EEC requires the testing of hydrocarbons / mineral oils in water as mandatory. The directive states that a reference method for the determination of hydrocarbons (dissolved or in emulsion) ie. mineral oils is infra-red absorption spectrophotometry without any specific reference to a solvent. The limit value for mineral oil in water was 0,1 mg/l. The Directive 98/83/EC no longer contains a parameter for mineral oil, dispersed or dissolved hydrocarbons. However, requirements are given for benzene and, for example, some PAHs, and the performance properties of the determination methods. The directive 80/778/EEC will be repealed 3 November 2003. Directive 98/83/EEC will be repealed at the latest 22 Dec 2007 due to Water Framework Directive [17]. [18, 19]

2.1.2. Recommendations

Several HELCOM and OSPAR Recommendations mention the determination of oil content; for example, the HELCOM Recommendations 23/8 on Reduction of Discharges from Oil Refineries, 17/5 on Restriction of Discharges from the Iron and Steel Industry, and 18/2 on Offshore Activities.

One of the most crucial measures adopted by the OSPAR Commission concerning oil-in-water determinations is Recommendation 2001/1 for the Management of Produced Water from Offshore Installations [20] Recommendation 2001/1 includes further recommendations for the emissions of dispersed oil in produced water, sampling frequency, and requirements on data collection concerning different groups of aromatic hydrocarbons. The reference method given in Recommendation 2001/1for dispersed oil is an infrared method as given in Agreement 1997-16 on the Sampling and Analysis Procedure for the 40 mg/l Target Standard. An evaluation of a new reference method based on ISO 9377-2 is ongoing. Continuous monitoring of dispersed oil is possible with methods yielding equivalent results to the accepted method by calibrating the method to the satisfaction of the competent authority [20]. Recommendation 2001/1 states that Member States should achieve a 15 % reduction in oil discharges by 2006 as compared to 2000. However, a change in the reference method could result in a bigger impact than the 15 % recommended. [21]

Parcom Recommendation 89/5 concerning refineries states that the yearly average of the oil content of the effluent in wastewaters must not exceed 5 mg/l, and Parcom Recommendation 87/2 on discharges from reception facilities and oil terminals sets a standard of 15 mg/l for discharges of oily mixtures.

2.2 The questionnaire results

The questionnaire was sent to 480 laboratories in the Nordic countries. 256 answers were received. Further results of the questionnaire are presented in the Annex. The total response rate was 53 %, however, it was significantly higher than this in Finland and lower in Denmark. On the basis of the questionnaire, corrected by necessary statistical factors, it is concluded that 205 labs in the Nordic countries used approximately 17 500 kilograms (ODP) of ozone depleting substances for more than 300 000 determinations in 2001.

The quantities of ozone depleting substances used for laboratory purposes are listed in table 2.1. The table presents the amount of new (non-recycled/non-regenerated) sub-

stances needed for these purposes. The numbers marked with asterisk (*) are estimations based on the number of determinations announced for the years 2002 and 2003, and are possibly overestimations. Additionally, small amount of methyl bromide is used.

Table 2.1 **Quantities of new ozone depleting substances used for laboratory use purposes in the Nordic countries as kilograms and ODP-corrected kilograms.** Note: the total of these numbers may not match to the overall total due to rounding.

	CTC	CFC-11	CFC-113	1,1,1-TCE	Total sum
2001 (kg)	8664	4	8599	147	17414
2002 (kg)*	8413	2	8546	46	17007
2003 (kg)*	5752	0	2302	44	8098

The relationship between the quantities of ODS used for all laboratory purposes and oil-in-water determinations is visualized in the figure 2.1.

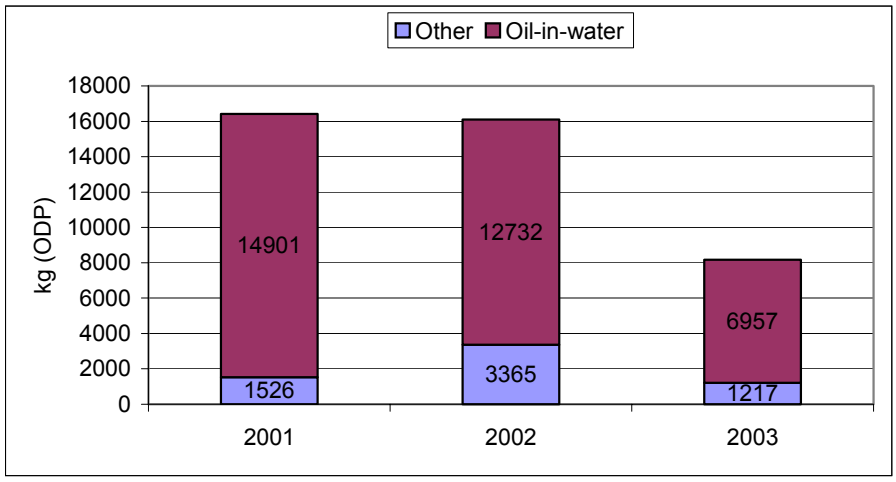

Figure 2.1 **Use of ozone depleting substances for oil-in-water determinations and other use purposes in the Nordic countries.** Note: The estimated use of ODS in 2003 is an overestimation, because information of 2001 was used if laboratory gave no information concerning years 2002 and 2003. The use of ODS for determination of oil-in-water is prohibited after year 2002.

Additionally, some recycled and regenerated ODS are used in the laboratories. Estimations on the destroyed, recycled/regenerated, and emitted ODS, calculated according to a "reasonable worst case scenario" and further detailed in the Annex, are presented in table 2.2.

Table 2.2 **Total use and the fate of the ozone depleting substances in 2001 as estimated in the "reasonable worst case" –scenario as kilograms (kg, ODP). All determinations and oil-in-water determinations specified.** *Note: The total of these numbers may not match to overall total due to rounding.

	kg	kg (ODP)	%	% (ODP)

Total use of ODS	**22028**	**19926**	**100**	**100**
Of which new ODS	(17414)	(16430)	(79)	(82)
To appropriate waste destruc-tion*	13305	13058	60	66
To recycling or regeneration*	7361	5698	34	29
As loss to air, water or sew-age*	1362	1170	6	6
Oil-in-water	**20149**	**18204**	**100**	**100**
Of which new ODS	(15761)	(14901)	(78)	(82)
To appropriate waste destruc-tion*	11996	11849	60	65
To recycling or regeneration*	6951	5336	34	29
As loss to air, water or sew-age*	1202	1019	6	6

Consultants and commercial laboratories used the most of the substances calculated as kilograms (ODP). Oil and metal industries were the next biggest users of the ODS. 75 % of ozone depleting substances were used for oil-in-water –assays, mostly for determinations of oil in wastewater and drinking water. Smaller amounts were used for other IR determinations, gravimetric determinations and other use purposes. Determinations of waste water and drinking water were the most typical sample types.

In addition to oil-in-water –analysis, ozone depleting substances are used in various other determinations. A total of 44 other than oil-in-water determination methods and use purposes were mentioned. In addition, two methods (determination of peroxide number and an additive in jet fuel) were recognized outside the questionnaire survey, the amount of ODS used in these methods not included in the figures. All these methods are used in less than 10 laboratories except the use of the substances as standards or reference materials. The possibilities to substitute the ODS in different use purposes is discussed elsewhere in this report. More information on these methods is given in the annex. The use of some of these methods has already ceased. These methods are not further discussed in this report.

The questionnaire also gave information on the obstacles to substitute the ODS with another method or substance, and information on a few possible substitute substances and methods. Additional information on the substitute methods presented in the report was collected from various other sources. Typical obstacles to substitution were the lack of a substitute method, the incompleteness of the substitution process, and costs caused by investments in instrumentation or other implementation costs. Also various other obstacles and problems caused by the substitution were recognized. More information on this subject is given in detail in the Annex.

The gas chromatographic determination of hydrocarbon index according to the standard ISO 9377-2 was the most general substitute method already applied by the laboratories.

However, determination of oil in other medias, like in soil and sludge, are among the methods using ozone depleting substances.

On the basis of the questionnaire, it is understood that ozone depleting substances are generally treated in an appropriate way after their use. However, the amount of the substance used in individual determination has probably not been reduced as often as possible. However, the phase-out of oil-in-water will diminish remarkably the problem.

Information on the quantities of the ODS used for individual determinations, laboratories' estimation on losses and various other information is presented in the Annex.

2.3 Typical determination methods using ozone depleting substances

2.3.1. Infrared spectrometric methods

SFS 3010, DS 209, NS 4753, and SS 02 81 45

A typical method used to determine oil and grease in water by using ozone depleting substances has been the infrared spectrophotometric (IR) method described in standards SFS 3010, DS 209, NS 4753 and SS 02 81 45. The smallest determinable concentration in water according to these standards is 0,1 mg/l, but in practice, a limit of detection of 0,001 mg/l is achieved in several Danish laboratories simply by using a bigger sample of water. The method or its modifications are in some cases applied to the determination of oil and grease in other sample mediums than water, e.g. like soil, sludge, and sediment.

The method determines either the total concentration of non-volatile oil and grease or the concentrations of non-volatile oil and grease separately. The total concentration of non-volatile oil and grease is understood as the concentration of organic compounds extractable with carbon tetrachloride and determinable with an infrared spectrophotometry. In practice, carbon tetrachloride has typically been replaced with CFC-113, which has a smaller ozone depletion factor (ODP). However, CFC-113 is not necessarily capable to solubilize the high molecular weight aromatics.

Oil and grease can be separated in an aluminum oxide column. Outside the Nordic countries, also other wave numbers are possibly used. Non-polar compounds pass the aluminum oxide column and can be detected by IR. Non-polar hydrocarbons, oil and mineral oil, contain CH-, CH_2- and CH_3-groups that absorb infrared light at wave numbers 2960 and 2925 cm^{-1}.

Polar compounds don't pass the column and are understood to be grease. Their concentration in oil is calculated as the difference between total concentration of (non-polar and polar) compounds and the concentration of non-polar compounds. The polar compounds include some fractions of mineral oils (aromatic hydrocarbons with big molecule size), detergents, animal and vegetable oils, grease oils, parts of lubricating oils, milk fat, glycols and many organic solvents like alcohols, ketones etc [22].

The disadvantage of the IR methods is that the response may differ very much with different hydrocarbon fractions. The response is high for the aliphatic hydrocarbons, but low for the aromatic hydrocarbons. It is possible, but difficult, to determine the aromatic

fraction by IR using other wavelengths [23]. Because of these differences in response the choice of reference standards should be made analyte specifically.

The typical solvent used in the method, carbon tetrachloride, can be purified with active carbon. The calibration sample contains, for example, n-hexadecane ($C_{16}H_{34}$), iso-octane (C_8H_{18}) and benzene (C_6H_6). According to the standard, 110 – 194 ml of carbon tetrachloride is needed for each sample. If the water and carbon tetrachloride phases do not separate, the emulsion and possibly separated phase has to be centrifuged. Emulsions are degraded with sodium sulfate, and when analyzing wastewaters and sludges, also magnesium chloride can be used. [22]

In the ranges meant in the standard, the repeatability is often better than ±2,5 % if no emulsion has occurred. Accuracy is 5 – 10 %, and it depends strongly on the comparability of the sample and the calibration standard. [22]

OSPAR IR method

OSPAR Recommendation 2001/1 defines dispersed oil as 'hydrocarbons as determined according to the reference method of analysis given in paragraph 7.2. of this recommendation'. Paragraph 7.2. refers to the IR method given in Agreement 1997-16, which provides a procedure for sampling and analysis.

According to this procedure, dispersed oils should be defined as alkanes, not including aromatic hydrocarbons [24]. In practice, the dispersed oil is actually the aliphatic part of the dispersed oil in the produced water, and dissolved aliphatic hydrocarbons in the OSPAR method are considered to be negligible. It is understood that acidification of the sample for preserving purposes may lead to conversion of certain substances from dissolved, non-extractable form to a dispersed and extractable form. Therefore the extract is treated with florisil before the analysis. [25]

ISO/TR 11046

Earlier, a method by infrared spectrometry and a gas chromatographic method were published in an ISO Technical Report ISO/TR 11046:1994. However, CFC-113 was used in the IR method [26].

2.3.2. Gravimetric methods

SFS 3009, DS 208, NS 4752, and SS 02 81 44

A typical gravimetric method is presented in the standards SFS 3009, DS 208, NS 4752, and SS 02 81 44. Substances with a boiling point under 150ºC may partly volatilize during the assay. The lowest determinable concentration is 2 mg/l. Carbon tetrachloride is used as an extraction solvent, aluminum oxide column for the separation of polar and non-polar compounds, and gravimetry for the quantitation of oil and grease compounds. In the quantitation, carbon tetrachloride is evaporated and the residues weighted. Likewise to the IR method, carbon tetrachloride has typically been replaced with CFC-113.

Like in the IR method, it is possible to determine either the total concentration of oil and grease or individual concentrations of oil and grease by using an alumina separation column. 60 – 220 ml of carbon tetrachloride is needed for each sample. The method is based on an old method of the U.S.EPA, and several in-house modifications of the method are used [27-29].

2.4 Methods probably used after 2002

The following use purposes of ozone depleting substances are likely to be used after 2002 in the Nordic countries:

- field analysis of total petroleum hydrocarbons in soil[1)]
- determination of total petroleum hydrocarbons in, for example, in soil and sludge[3)]
- determination of coccidiostats in eggs and muscles with very low detection limit[1)]
- determination of bromine index or bromine value in oils[5)]
- determination of iodine index or iodine value in oils [a)]
- clinical determination of pregnanetriole[a)]
- determination of plasticizers in plastic products [b)]
- extraction media in determination of metals in sea water with extremely low detection limit[1)]
- extraction media in determination of heavy metals in groceries[1)]
- determination of impurities in phenol[5)]
- determination of TOC in industrial processes [b)]
- liquid chromatographic separation of chlorophyll derivates [a)]
- determination of extraction compound residues in industrial processes [b)]
- gravimetric analysis of tar compounds in water [b)]
- determination oil additives and particle size distribution in oil [b)]
- determination of flavors[4)]
- water in oil analysis, especially Karl-Fischer –titring [b)]
- determination of oil in compressed air[1)]
- determination of oil in industrial gases and chemicals [b)]
- determination of humidity of gunpowder[1)]
- determination of oil, wax or paraffin compounds on metal surfaces in ammunition production[1)]
- determination of oil, wax or paraffin compounds on metal surfaces in other industries[5)]
- breathing filter test (according to an U.S. standard method) [3)]
- determination of oil mist in air (occupational hygiene) [2)]
- determination of stress-cracking in plastics [2)]
- tracers in permeability/porosity tests [a)]
- preparation of hemoglobin controls [1)]
- identification of irradiated groceries [1)]
- determination of surface coatings of fertilizers [b)]

- calibration of existing equipment [2)]
- scintillation measurements [2)]
- preparing of reference samples and standards for the analysis of ozone depleting substances in appliances and in the environment [2)]
- scaling-up and small-scale proficiency testing of new reactions and laboratory methods [2)]
- NMR analytical chemical procedures (for example, it is necessary to have a heavy solvent not containing hydrogen atoms) [2)]
- basic research where the properties of substitute substances may cause significant interference in critical phases of method or synthesis development [2)]
- determination of peroxide number in jet fuel [b)] and
- determination of additive in jet fuel [b)].

[1)] Generally the substitute methods may have not a detection limit as low and/or accuracy as good which may lead to either direct risk for health or environment or unnecessary excessive costs.

[2)] Generally the substitution of the method is impossible, requires totally new kind of technology, causes unnecessary high costs, or may cause significant and unreasonable difficulties to research, development and innovation activities, or there is no substitute method standardized or being prepared.

[3)] Generally a substitute method is under preparation or the method is required by a statute or standard.

[4)] Generally the method is used in singular or few laboratories in a relatively small scale and cannot be bought elsewhere. Substitution may cause unnecessary high costs.

[5)] Generally a substitute method may in principle exist and possible tested by the laboratory, but does not achieve detection limit or accuracy as good as needed, or is otherwise technically impracticable.

[a)] The method can probably be substituted, however, it may cause excessive costs.

[b)] Not enough information was available for the evaluation of the method in this project.

Disclaimer: Because all laboratories did not respond to the questionnaire, it is possible that further laboratory use purposes exist.

Based on the questionnaire, it is estimated that the use of ozone depleting substances for laboratory and analytical purposes in the Nordic countries will be less than 1500 kilograms (ODP) in 2003 leading to emissions less than 100 kilograms (ODP)/year.

2.5 Methods possibly used after 2005

There are few use purposes in which the use of ozone depleting substances probably cannot be avoided after the year 2005. The substitution is not possible, may cause unreasonably high economical costs or endanger the possibilities to run some basic research and development activities.

At least the following use purposes of ozone depleting substances are considered to be used after 2005 in the Nordic countries:

- the calibration of existing equipment
- the preparation and use of reference samples and standards for the analysis of ozone depleting substances in appliances and in the environment

- the scaling-up and small-scale proficiency testing of new reactions and laboratory methods
- the use in some analytical chemical procedures by NMR (it is necessary to have a solvent not containing hydrogen atoms)
- the use in scintillation equipment and
- the use in basic research where the properties of substitute substances may cause remarkable interference in critical phases of method or synthesis development.

The need of ozone depleting substances for these uses is approximately 100 kilograms (ODP).

3 Possible substitute methods for determination of TPH

3.1 General

Because a total petroleum hydrocarbon (TPH) mixture may include even hundreds of individual compounds, the properties of the mixture and the substitute determination method should be carefully considered.

An ODS using method for determination of TPH can in principle be substituted with a new solvent (and method), an indicatory TPH or hydrocarbon index method, or method(s) measuring individual fractions and substances of the TPH mixture. The three principal approaches and the possible changes caused by the substitution are described in figure 3.1.

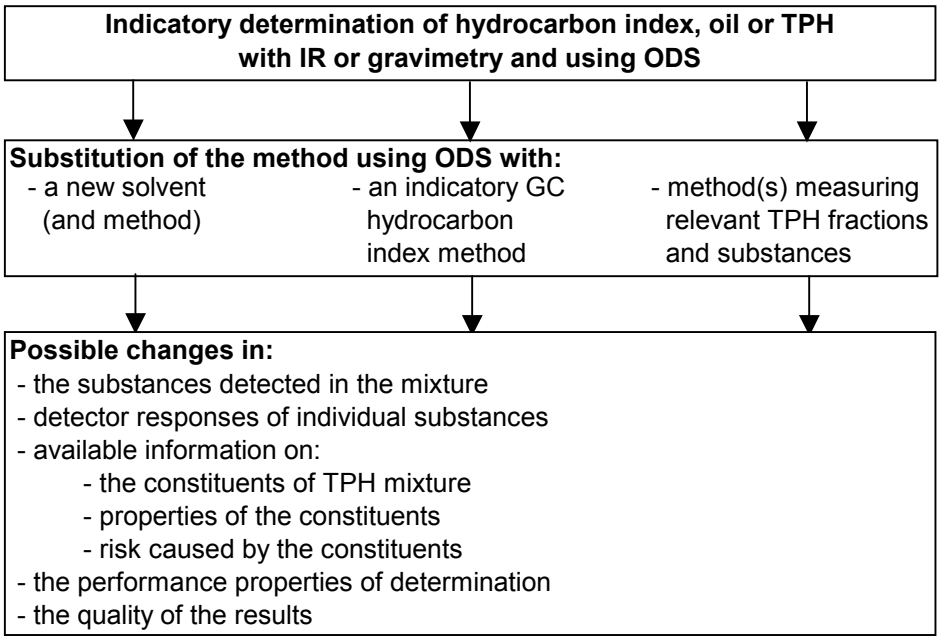

Figure 3.1. Three principal possibilities to a TPH determination method and some possible changes caused by the substitution.

More information on the properties of the TPH and validation requirements of a method is given in the Annexes.

3.2 Summary

The new method for the determination of hydrocarbon index described in standard EN-ISO 9377-2 and its national versions provides a general substitute method. Also drafts of this method and various in-house methods are applied. For offshore applications, a new method based on the standard EN-ISO 9377-2 is under preparation. However,

method EN-ISO 9377-2 is meanwhile used offshore in some countries. Also the predecessors of method EN-ISO 9377-2 described in ISO/DIS 9377-4 and ISO TC 147 (Water quality) - SC2 (Physical, chemical and biochemical methods) - N388 were used in the laboratories questioned. The EN-ISO 9377-2 has earlier replaced methods using ozone depleting substances in some countries, e.g. in Germany it replaced IR method DIN 38409-H18 at the end of 2000. [30, 31]

The most typical gravimetric substitute methods for oil-in-water –analysis applied in the laboratories are SFS 3009, DS/R 208, NS 4752, SS 02 81 44 and ISO/CD 9377-1:1998. However, the methods are very unspecific and typically have a high detection limit.

For oil in soil, method ISO/DIS 16703 Soil quality - Determination of mineral oil content by gas chromatography was a typical substitute method. Some laboratories mentioned documentation of ISO TC 190 (Soil Quality), SC3 (Chemical methods and soil characteristics), WG 6 (hydrocarbons) for the determination of some gasoline hydrocarbons in soil. For oil in waste, prEN 14039 Characterization of waste – Determination of hydrocarbon content in the range of $C_{10} – C_{40}$ by gas chromatography was applied.

Methods described in ISO TR 11046 were applied in some laboratories.

Some laboratories have substituted the ozone depleting solvent in an IR method. Few laboratories named IP 426/98 Determination of oil content of effluent water – extraction and infra-red spectrophotometric determination as a substitute method. Typically tetrachloroethylene is used with the method.

One possibility suggested is to cease the requirement to monitor the total oil content, and use other indicator substances or fractions to give a warning on contamination. It is generally understood that the BTEX substances are typical indicators of oil contamination. They are very soluble in water and very mobile compared to other hydrocarbons in gasoline, and likewise more volatile. However, some oxygenated gasoline additives are even more mobile than the BTEX, and the BTEX are not necessarily present in significant amounts in all oil products, like in lubricating oils. In general, the toxicity and mobility of the longer-chained hydrocarbons are much lower compared to the BTEX. In Denmark, it is already obligatory or possible to monitor several other indicators of oil contamination, like alkylbenzenes (sum of 1-methyl-3-ethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene), benzene, naphthalene, MTBE, 1,2-dibromomethane and some PAHs.

However, e.g. lubrication oil leaks oils from equipment, e.g. compressors used for water aeration at water abstraction and treatment plants, are typical sources of oil in drinking water in Denmark. Determination of BTEX is not necessarily sufficient to detect oil contamination. For hydrocarbons, very low detection limits are needed in order to give an early warning before hydrocarbons with very low taste thresholds enter the water distribution system.

In Sweden, the limit value concerning the water quality of surface water used for the abstraction of drinking water was 0,2 mg/l for dissolved or emulgated hydrocarbons according to the 1989 instructions. The limit value for mineral oil in drinking water was 0,010 mg/l. New instructions took effect in 2001 repealing the 1989 instructions in 2003. However, the former requirements are interpreted to be fulfilled, if the drinking water fulfills the requirements mentioned in the appendixes to the instructions given in 2001. In practice, this means fulfilling the criteria of 1,0 µg/l for benzene. In addition,

quality criteria are given, for example, for some PAHs. [32, 33] In Finland the requirement to determine mineral oils in surface water with a limit value of 0,010 mg/l has been repealed, and various TPH constituents are determined in drinking water [34].

Among other methods for the determination of TPH or its constituents, a method for recognizing possibly suitable hydrocarbon substructure by mass spectrometry in selective ion mode after a silica-gel clean up is described. However, little information on the performance properties of the method and its applicability was available.

Examples of substitute methods for the determination of TPH and some of its constituents used in the laboratories and recognized in the project are presented in table 3.1. The list is not an exhaustive presentation on available methods for the determination of TPH constituents.

Table 5.1. Substitute methods for the determination of TPH and its constituents.

COUNTRY OR ORGANIZATION	PRINCIPLE	METHOD
ISO	GC	ISO 9377-2. Water quality - Determination of hydrocarbon oil index - Part 2: Method using solvent extraction and gas chromatography.
ISO	GC	ISO/DIS 16703 Soil quality - Determination of mineral oil content by gas chromatography.
ISO	GC	ISO 15009 Soil quality - Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons - Purge-and-trap method.
ISO	GC	ISO/DIS 15680 Water quality - Determination of certain monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds - Gas-chromatographic method using purge and trap and thermal desorption.
ISO	GC	ISO 13877 Soil quality - Determination of polynuclear aromatic hydrocarbons - Method using high-performance liquid chromatography.
ISO	Gravimetry	ISO/CD 9377-1:1998. Water quality - Determination of hydrocarbon oil index - Part 1: Method using solvent extraction and gravimetry.
ISO	GC	ISO/CD 17993 Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection.
ISO	TLC	ISO/WD 7981-1 Water quality – Determination of polynuclear aromatic hydrocarbons (PAH) – Part 1: Determination of six PAH by high performance thin layer chromatography with fluorescence detection.
ISO	LC	ISO/WD 7981-2 Water quality – Determination of polynuclear aromatic hydrocarbons (PAH) – Part 1: Determination of six PAH by high performance liquid chromatography with fluorescence detection.

CEN	GC	prEN 14039 Characterization of waste – Determination of hydrocarbon content in the range of C_{10} – C_{40} by gas chromatography.
CEN	Gravimetry	prEN 14345 Characterization of waste. Determination of hydrocarbon content by gravimetry.
OSPAR/OIC	GC	A modified version of the EN-ISO 9377-2.
Nordtest	GC	NT Techn Report 329.
Finland	Gravimetry	SFS 3009. Veden öljyn ja rasvan määritys. Gravimetrinen menetelmä. Bestämning av olja och fett i vatten. Gravimetrisk metod. Determination of oil and grease in water. Gravimetric method.
Sweden	Gravimetry	SS 02 81 44. Bestämning av olja och fett I vatten. Gravimetrisk metod. Utgåva 1. (Determination of oil and grease in water. Gravimetric method.)
Norway	Gravimetry	NS 4752. Vannundersøkelse - Bestemmelse av olje og fett - Gravimetrisk metode. (Determination of oil and grease in water. Gravimetric method.)
Denmark	Gravimetry	DS 208. Vandundersøgelse. Olie og fedt. Gravimetrisk metode. (Determination of oil and grease in water. Gravimetric method.)
The Netherlands	GC	NEN 6407. Water. Gaschromatographische bepaling van het gehalte van een aantal monocyclische aromaten, naftaleen en enkele gechloreerde koolwaterstoffen met de "purge en trap" - methode en thermische desorptie. (Water. Gas chromatographic determination of a number of monocylic aromatic hydrocarbons, napthalene and several chlorinated compounds using purge and trap and thermal desorption.)
The Netherlands	GC	NEN 5733. Bodem. Bepaling van het gehalte aan minerale olie in grond en waterbodem met gaschromatografie. (Soil. Determination of mineral oil content in soil and sediments with gas chromatography)
The Netherlands	Gravimetry	NEN 6671. Afvalwater en slib. Gravimetrische bepaling van het gehalte aan petroleumether extraheerbare oliën en vetten. Soxhlet extractie. (Waste water and sludge. Gravimetric determination of petroleum ether extractable oil and fat content. Soxhlet extraction.)
The Netherlands	Gravimetry	NEN 6672. Afvalwater. Gravimetrische bepaling van het gehalte aan met petroleumether extraheerbare oliën en vetten. Directe extractie. (Waste water. Gravimetric determination of petroleum extractable oil and fat content. Direct extraction.)
The United Kingdom	IR	IP 426/98. Oil Content of Effluent Water - Extraction and Infra-red Spectrometric Method.
U.S. EPA	GC	Method 502.2 Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography With Photoionization and Electrolytic Conductivity Detectors in Series. Revision 2.1.
U.S. EPA	GC	Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry.

U.S. EPA	Gravimetry	Method 1664, Revision A: N-Hexane Extractable Material (HEM; oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM); Non-polar Material) by Extraction and Gravimetry.
U.S. EPA	Extraction	Method 3510C. Separatory Funnel Liquid-Liquid Extraction. Revision 3.
U.S. EPA	Extraction	Method 3535. Solid-phase extraction (SPE).
U.S. EPA	Extraction	Method 3540c. Soxhlet extraction. Revision 3.
U.S. EPA	Extraction	Method 3550b. Ultrasonic extraction. Revision 2.
U.S. EPA	Extraction	Method 3560. Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons.
U.S. EPA	Cleanup / separation	Method 3611B. Alumina column cleanup and separation of petroleum wastes.
U.S. EPA	Cleanup / separation	Method 3630C. Silica gel cleanup. Revision 3.
U.S. EPA	Headspace	Method 3810. Headspace.
U.S. EPA	Extraction	Method 3820. Hexadecane extraction and screening of purgeable organics.
U.S. EPA	Immunoassay	Method 4030. Soil Screening for Petroleum Hydrocarbons by Immunoassay.
U.S. EPA	GC	Method 5015C. Nonhalogenated Organics using GC/FID.
U.S. EPA	GC	Method 5021B. Aromatic and Halogenated Volatiles By Gas Chromatography using Photoionization and/or Electrolytic Conductivity Detectors.
U.S. EPA	Purge-and-Trap	Method 5030B. Purge-and-Trap for Aqueous Samples. Revision 2.
U.S. EPA	GC	Method 8015C. Nonhalogenated Organics Using GC/FID. Revision 3.
U.S. EPA	GC	Method 8021B. Aromatic and Halogenated Volatiles By Gas Chromatography Using Photoionization And/Or Electrolytic Conductivity Detectors. Revision 2.
U.S. EPA	GC	Method 8260B. Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS).
U.S.EPA	Gravimetry	Method 9071B. n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples. Revision 2.
Massachusetts	GC	Method for the determination of volatile petroleum hydrocarbons (VPH).
Massachusetts	GC	Method for the determination of extractable petroleum hydrocarbons (EPH).
ASTM	Extraction	ASTM D 5765 – 95 Standard Practice for Solvent Extraction for Total Petroleum Hydrocarbons from Soils and Sediments Using Closed Vessel Microwave Heating.

In addition to the methods listed in the table 5.1., several non-standardized methods have been evaluated in the preparation of method 9377-2. Because the evaluation proc-

ess contains general information on the applicability of various techniques, it is shortly described in this report. Also some methods applied in field or on-line, and described only in literature, are shortly presented.

3.3 Determination of oil-in-water

3.3.1. The ISO methods

ISO/DIS 9377-1

The method ISO/DIS 9377-1:1998 Water quality - Determination of hydrocarbon oil index - Part 1: Method using solvent extraction and gravimetry is under preparation, and available as a Committee Draft ISO/CD 9377-1:1998. The method includes extraction and gravimetry, and may be applied to all types of water. The extraction solvent is evaporated after the clean-up followed by a gravimetric determination of the residue. [35]

The method determines the sum of compounds extractable with a single hydrocarbon solvent or a mixture, not adsorbed on Florisil and determined by gravimetry after drying at 80ºC. The detected components are mainly non-polar, long chain or branched aliphatic, alicyclic, aromatic or alkyl substituted aromatic hydrocarbons with boiling points above 250ºC, in practice, oils and lubricants with carbon chain length at least C_{14}. Shorter hydrocarbons are partly or totally lost during the evaporation step. A Florisil clean-up is applied in order to determine petroleum hydrocarbons only. However, the determination of grease is not included in the method. The method is applicable to concentrations over 5 mg/l. Petroleum ether or other single hydrocarbon mixture with a relatively low boiling point is preferred. In case of emulsions magnesium sulfate can be used, and in case of high concentrations of surface active substances sodium chloride can be added to the sample. [35]

The ISO working group has suggested that after compilation of the ISO 9377-1 a method for total oil and grease could be established by leaving out the clean-up step. [35, 36]

ISO 9377-2

ISO 9377-2 (Water quality – Determination of hydrocarbon oil index – Part 2: Method using solvent extraction and gas chromatography), is based on solvent extraction with pentane or hexane followed by gas chromatography and typically a flame ionization detector (FID) and it is a suitable method for most oil-in-water –analysis. It is not applicable for quantitative determination of volatile mineral oils or determination of hydrocarbon index in drinking water requiring a very low detection limit. Method ISO 9377-2 is approved as an international standard, a European standard, and national standards.

Method ISO 9377-2 determines long-chain or branched aliphatic, acyclic, aromatic and alkyl-substituted aromatic hydrocarbons, unlike the old infra-red method, which determines aliphatic compounds in oil fraction. The hydrocarbon index is the sum of concentrations of compounds extractable with a hydrocarbon solvent with boiling points between 36ºC and 69ºC, which are not adsorbed to a prepared diatomaceous substance (Florisil), and which may be chromatographed with retention times between those of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$) [37]. In the method, the monoaromatic

BTEX-compounds will not be detected because the chromatography starts at C_{10}. The clean-up step removes to a large extent the polar compounds, like PAHs and partly naphthalene. The remaining aromatic compounds can be distinguished, if MS detection is used. This is not possible with the FID detector. The sample can be concentrated before injection with an evaporation apparatus. However, large-volume injections can be also used.

The reference sample consists of two specified mineral oils. It is possible to determine the boiling range of the mineral oil by comparing the gas chromatogram of the calibration mixture of n-alkanes with that of the sample extract. The boiling range gives information on the number of carbon atoms in the sample analytes in case of n-alkanes.

The method cannot be applied for the determination of grease due to the Florisil purification of the sample. Emulsions can be degraded with magnesium sulfate, and if necessary, by centrifuging. Compounds of low polarity, like halogenated hydrocarbons, and high concentrations of polar substances can interfere with the determination, likewise surface-active substances in the extraction step. [37]

Experiences on the ISO 9377-2

The present GC/FID method and old IR-method have been compared in several proficiency tests.

In a test runned by Swedish ITM, it was understood that the overall means of the samples didn't show significant difference when comparing determination of unpolar aliphatic hydrocarbons with IR and hydrocarbon oil index with GC/FID according to ISO 9377. In the test mixtures of diesel oil and lubricant oil were used as test samples, mixed with humic acids and/or coconat butter in some samples. In general, the recovery rates were about 75 % for both methods. The number of outliers was larger among the laboratories using the IR method. ISO 9377-2 method provided more information regarding the boiling point range and composition of hydrocarbons. In the determination of extractable aliphatic hydrocarbons the results were consistently higher than the reference value. This was probably caused by the vulnerability of the method to interferences (like 2-propanol not originating from the oil) due to the omission of clean up steps. It was nevertheless recommended that each laboratory should perform a side by side comparison between methods, when changing from an old method to a new one. [38]

In a German intercomparison exercise of ISO/DIS 9377-2, recoveries between 80 – 100 % were achieved. Only in the presence of surfactants, recoveries dropped down to as low as 60 %, with circa 70 % as the average. In this kind of situation a correction with water samples spiked with oil and matrix constituents should be taken into consideration, i.e. a determination of the overall recovery should be carried out during the HELCOM PLC-4 monitoring at regular intervals. Relative reproducibility standard deviations varied between 20 % and 40 % depending on the hydrocarbon concentration and the amount of interfering compounds in the sample showing acceptable accuracy. However, in this study some laboratories found exceptionally high blank values, and the recovery was only 75 % for sample having higher concentration (~2,2 mg/l) particularly in the presence of interfering substances. It was understood that the variability of the determination was due to the precision of the gas chromatographic system, because the repeatabilities were between 7 % and 16 %. The results are comparable to two earlier intercomparison tests arranged by the EC Project STM 4-CT96-2090 and the ISO/TC

147/SC2/WG 15 giving recoveries around 60 – 100 % and relative reproducibility standard deviations between 10 – 40 %, approximately. [39]

In the 20. and 21. interlaboratory comparison runned by BAM (Bundesanstalt für Materialforschung und –prüfung), the laboratories were asked to follow the method DIN 38409-H53 (a gas chromatographic method with petrol ether extraction very similar to ISO/DIS 9377-4, which was the draft version of ISO 9377-2), but unfortunately only a few laboratories made the additional work. It is understood that the results of the two methods are not comparable. The precision is quite the same, but the mean values are different. This is not very surprising, because the definition of mineral oil fraction is different in these standards [31]. There are certified reference material available by the German BAM for the calibration of the GC/FID -determination recommended for total petroleum hydrocarbons (TPH) in water (ISO 9377-2), soil (ISO/DIS 16703:2001), and waste (EN 14039:2000) [40].

In an interlaboratory comparison test carried out by the Finnish Environment Institute, the method ISO 9377-2 was used. Two water samples, diluted municipal waste water and lake water, were prepared. In the determination of the samples, the standard deviations were 33 % and 36 %. The overall recoveries were 78 and 81 %. The efficiency of the extraction procedure might have had an influence on the results. The results obtained by the stirring technique were mainly too small. It is possible that part of the oil was adsorbed on the container walls during the stabilation time. [41]

In a Danish project measuring oil in waste water, a gravimetric method and the method ISO/DIS 9377-4 were compared together. The method ISO/DIS 9377-4 gave an average recovery rate of 80 % with a detection limit between 0,02 – 0,1 mg/l. It was assumed that the GC/FID method ISO/DIS 9377-4 gave higher results than the gravimetric method on which the limit value for oil in wastewater is based on. However, in this study the wastewater may have contained oil and surfactants. [42]

The use of the instrumentation itself, (integration parameters, choice of detector, e.g. GC-FID) as well as the choice and use of reference standards are critical and are often the source of differences in results from otherwise competent laboratories. It is also essential that the extraction of the sample is performed in the sampling bottle. Container wall adhesion will otherwise be a source of error. [43]

Development of the ISO 9377-2

In the development of the ISO 9377-2 gas chromatographic method 15 existing methods were recognized and evaluated, including methods like solid phase extraction (SPE), use of supercritical CO_2 fluid, and a IR method using Potassium bromide (KBr) tablets. [44]

Supercritical fluid extraction dropped out in the evaluation due to total investment costs and the complicity of the method. Methods using halogenated solvents were abolished due to the toxicity of the halogenated solvents and their negative environmental aspects. Substituting a halogenated solvent with another one has been considered as a short-sighted alternative at least by the Swedish and Norwegian State Pollution Control Authorities. Importance of the a correlation between the old Freon-IR method and the substituting method was emphasized. Six methods were chosen to further evaluation [44].

A LL-TLC-FID –method included a liquid-liquid extraction with a hydrocarbon solvent (e.g. n-hexane), deposition of the extract on silica-rods, elution of the rods in a thin layer chromatography chamber and subsequent detection by flame ionization. The

method had a cut-off at C_{15}, and therefore the carbon window of the method ($C_{15..40}$) failed to meet the criteria of $C_{10..40}$. A LL-"3M"-IR method included a liquid-liquid extraction with a hydrocarbon solvent (like n-hexane) by deposition on a "3M" card and subsequent infrared analysis. A concentration apparatus like Kuderna Danish or rotary evaporator with controlled vacuum might be needed for the method. The application range of these methods was 1 to 1000 mg/l. [45]

Finally three standard operation procedures were chosen for an interlaboratory study [45-48]:

- a solid phase extraction using isooctane as extraction solvent followed by gas chromatography and mass spectrometry analysis (SPE-GC-MS)
- a solvent extraction followed by gas chromatography (LL-GC-FID method from NNI)
- a extraction with n-hexane as extraction solvent followed by deposition on reusable sapphire window plates, and subsequent infrared analysis (LL-IR).

Drinking water and clean groundwater samples containing low concentrations of analytes must be handled using SPME-GC-MS or SPE-GC-MS (with a concentrating step). It might be possible to achieve a carbon window $C_{5...30}$ and application range 0,001 – 5 mg/l. However, salt produces an unfavourable effect for non-volatile HCs. In the validation test a limit of detection and limit of quantitation were 0,3 mg/l and 1 mg/l, respectively, for offshore water diesel, and 5 µg/l and 15 µg/l for drinking water diesel. The validation range was 5 – 150 mg/l for offshore and 15 – 150 µg/l for drinking water diesel. The performance of the method in the range of 10 – 50 µg/l must be improved. In general, the recovery, repeatability and linearity were good for offshore water diesel samples (all recoveries within 70 %, RSD < 10 % and $r \geq 0{,}999$), but for drinking water diesel, recovery was acceptable (one value outside 70 %), linearity acceptable ($0{,}99 < r < 0{,}999$), but repeatability bad (one RSD > 15 %). [45, 47]

SPME-GC-MS is not an equilibrium based method. It is not a bulk or total extraction method, it requires separation of particulate matter prior to the extraction, and it is limited to the more water soluble hydrocarbons in "clean" water. High concentrations and two-phase hydrocarbon/water systems can be analyzed, but not correctly quantified. The SPE-GC-MS –method's application range was 0,01 – 100 mg/l. The recovery was 100±20 %, and repeatability < 10 %. Coefficient correlation between recovery and recovery with freon-IR –method was $\cong$ 1,4. Thought the SPME-GC-MS is able to detect hydrocarbons from concentrations of 0,01 mg/l, carbon window problems were recognized at the upper carbon region [44]. An alternative SPME coupled to GC-MS can be used for screening in the range of $C_{10...40}$ and quantification up to C_{12} of low levels of hydrocarbons in drinking- and groundwater. [45]

The SPE-GC-MS –method was estimated to be usable as the basis for a low level method applicable to concentrations down to 10 µg/l. The detection limit is expected to be approximately 5 µg/l, which is achieved by an increase in the volume of the water analyzed. However, the method cannot be applied to the determination of the content of volatile mineral oil ($< C_{10}$), or to the determination of polar compounds (only non-polar compounds should adsorb on the disk). Isooctane was used as an eluting solvent to remove the non-polar compounds from the disk. A calibration solution can be prepared,

for example, from crude oil ($C_{10...35}$), diesel ($C_{10...26}$) or from a mixture of n-alkanes. There are available n-alkane calibration standards for $C_{6...44}$ [46].

A screening method for in waters with hydrocarbon concentrations above 5 mg/l is possible using the same extraction and cleanup procedure as in the GC-FID –method, followed by evaporation of the extraction solvent on a sapphire window followed by IR-detection. Light hydrocarbons are lossed in the evaporation step. In the validation test, a range of 5 to 150 mg/l was used for LL-IR. Limit of detection was 1 mg/l and the limit of quantitation 5 mg/l. The LL-IR was only recommended for screening purposes and field applications. [45]

The LL-GC-FID had a repeatability equivalent to the two other methods (RSD < 10 %), a recovery > 90 %, the best comparison with Freon-IR, and when assessing robustness, the best overall performance. [44]

prEN ISO 15680

A prEN ISO 15680 rev (Water quality – Determination of certain monocyclic aromatic hydrocarbons, naphthalene and chlorinated compounds – Gas chromatographic method using purge and trap and thermal desorption) is being prepared under CEN/TC 230 Water analysis. It is partly based on the ISO 10301 standard, [49], EPA Methods 1624 [50] and 1625 [51], and BS 6920[52].

The proposed method determines certain volatile organic compounds (VOCs), like, for example, the BTEX. In this method the volatile components are purged from water with an inert gas to an adsorbent column or a cold trap. The trap is heated to desorb the components which are swept by the GC carrier gas to a capillary GC column. An electron capture detector (ECD) or an electrolytic conductivity detector can be used instead of a mass spectrometric detector (MSD) for halogenated hydrocarbons. A flame ionization detector (FID) can be used for aliphatic, aromatic and halogenated hydrocarbons in general, a photo ionization detector (PID) for aromatic compounds, and an atomic emission detector (AED) as an element specific detector. [53]

A dual column system with columns of slightly different polarity or a dual detector system can be used to reduce the risk of overlapping peaks. The analytes range from difluorodichloromethane to trichlorobenzene including all non-polar organic compounds of intermediate volatility. Detection is preferably carried out by mass spectrometry. Typically a detection limit of 10 ng/l can be achieved. The standard can be applied to drinking water, ground water, surface water, sea water and to (diluted) wastewater. The draft standard describes examples of analytes, purge-and-trap, GC and MS conditions, columns, and performance data. Also good guidance on the cleaning of glassware to avoid contamination and adsorption of analytes is given. [53]

ISO/CD 17993, ISO/WD 7981-1, and ISO/WD 7981-2

A standard draft ISO/CD 17993 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection) is being prepared. [54]

Two other methods for determination of PAHs in drinking water exist as preparatory stage working drafts: ISO/WD 7981-1 (Water quality – Determination of polynuclear aromatic hydrocarbons (PAH) – Part 1: Determination of six PAH by high performance thin layer chromatography with fluorescence detection), and ISO/WD 7981-2 (Water

quality – Determination of polynuclear aromatic hydrocarbons (PAH) – Part 1: Determination of six PAH by high performance liquid chromatography with fluorescence detection). Heavily polluted waters may also be analyzed by the methods, and the detection limit is 0,01 – 1 µg/l, depending on the sample. Work on standard methods based on GC/MS is starting. For the measurement of PAH in offshore production water, a liquid-liquid extraction and GC/MS is recommended [23].

3.3.2. The Netherlands

An IR method was used to monitor hydrocarbons in water with a quality criteria of 10 µg/l, according to the requirements of the directives 79/869/EEC and [14] 80/778/EEC [18]. After substitution of carbon tetrachloride with CFC-113, the IR method didn't work properly due to much higher adsorption of CFC-113 in the wavelength area of interest.

NEN 6407

In practice, the total hydrocarbons (TPH) parameter was abandoned and replaced by the determination of monocyclic aromatic hydrocarbons (BTEX-compounds including the three isomers of xylene), because they were considered as the most important threat for groundwater rising from contamination by petroleum hydrocarbons [36]. The determination method is a purge-and-trap –isolation followed by thermal desorption and gas chromatography described in the NEN 6407 standard [36]. The ISO/DIS 15680 [53] is based on this Dutch standard.

The method NEN 6407 can be applied for a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds [55]. A flame ionization detector (FID), or a more selective detector, like PID (photoionization detector), ECD (electron capture detector) or MSD, ITD (mass selective detector, ion capture detector) can be applied [55]. In practice, oil compounds in drinking water are measured by measuring individual BTEX compounds mostly by utilizing purge-and-trap and GC/MS or GC/FID+ECD-analysis [56]. A limit of detection of 1 – 2 ng/l for individual BTEX compounds is possible to achieve. This concentration level refers to TPH concentrations lower than the required limit value of 10 µg/l. [36]

The standard gives suggestions for a GC column, and reports on intralaboratory and interlaboratory deviations measured for various compounds in drinking water and surface water with a certain concentration level [55].

NEN 6671

The standard NEN 6671 provides a method for the gravimetric determination of petroleum ether extractable oil and fat content in wastewater and sludge after a Soxhlet extraction. The method is capable to determine concentrations of approximately 5 mg/l, but not very high concentrations of mineral oil in water. The most volatile fractions may be lost with this method. The method utilizes diatom based filtration [57].

NEN 6672

The standard NEN 6672 describes a direct extraction method for gravimetric determination of petroleum ether extractable oil and fat content in wastewater. The method does not distinguish between petroleum hydrocarbons and animal or vegetable oils, since there is no clean-up of the extract by silica, aluminum oxide or Florisil. In the method, the sample is filtered, and the filter transferred into a Soxhlet thimble. The extraction is

performed with petroleum ether with a boiling range of 40 – 60ºC for at least 4 hours. The extract is evaporated and dried at 105±3ºC to constant mass. The method has a limit of detection/determination of about 5 mg/l. [36, 57]

3.3.3. The United Kingdom

An infrared method has been maintained in the determination of oil-in-water. The method includes tetrachloroethylene extraction followed by quantification using IR. The use of carbon tetrachloride has been banned due to toxicological reasons, and the use of freons for environmental reasons. There are also plans to prohibit the use of tetrachloroethylene by environmental legislation [58].

IP 426/98

The standard method is described in the standard IP 426/98 (Oil Content of Effluent Water - Extraction and Infra-red Spectrometric Method) [59]. The method is applied over a full range of applications from drinking water quality assessment to the assessment of disposed waters from offshore oil rigs and bilge waste from ships.

Other methods

Methods using solid phase extraction (SPE) with GC/MS are not used generally, however, the detection levels achieved with the SPE/GC/MS –methods can be 5 µg/l. There may be a change in future towards the use of SPE-techniques [60]. However, it is the responsibility of the laboratory to demonstrate that SPE techniques provide equivalent data to liquid-liquid extraction methods, which may cause considerable amount of work. There will still be a demand for rapid and field testing of oil-in-water, and simple correlative methods for environments where gas chromatography is not practical [60].

3.3.4. The United States of America

In the United States, the production and import of CFC-113 and other Class I ozone depleting substances ceased at the end of 1999. However, it is allowed to recycle the existing stocks [61-63]. Oil and grease is understood to be a conventional pollutant under the Clean Water Act instead of more specific organic contaminants, since the change of the act was considered to be a lengthy and continuous operation. [61] In the analysis of drinking water, no total petroleum hydrocarbons (TPH) are determined.

EPA Method 1664 revision A

Method 1664, Revision A (N-Hexane Extractable Material (HEM; oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM); Non-polar Material) by Extraction and Gravimetry) has been approved in the Federal Register [61, 64]. The method replaces the previous EPA Method 9070. The method 1664A is approved for the analysis of non-polar material in accordance with the requirements of the Clean Water Act concerning pollution control, and Resource Conservation and Recovery Act concerning contaminated soils. The method is used mostly for determinations of wastewater.

The difference between measurements of HEM and SGT-HEM will give the amount of polar material present in the sample [61]. The concepts of HEM and SGT-HEM reflect the idea of TPH as a method-defined group parameter. The HEM fraction can contain also other substances, than hydrocarbons. For example, sulfur can be converted into

thiosulphate during acidification of a sample, and be extracted with n-hexane to be determined as HEM.

The method 1664A uses n-hexane as an extract solvent, and silica gel to absorb polar material, followed by a gravimetric determination [65]. In practice, the hexane solvent is dried in a boiling flask at 70ºC for 30-45 minutes followed by desiccation for 30 minutes. [61]

The silica gel removes theoretically polar material including aromatic compounds containing one or more benzene rings, unsaturated compounds (those containing one or more double bonds), and compounds containing atoms other than carbon and hydrogen. Polar material also includes aromatic, phenolic, and heterocyclic compounds in petroleum and petroleum products, soaps and animal fats. Non-polar material contains straight and branched chain hydrocarbons and other chemical substances in which there are no functional groups that exhibit enough polarity to be adsorbed by silica gel [65].

N-hexadecane (a major component of diesel oil) and stearic acid (the main component of animal fats) are used in the quality control despite the fact that they tend to stick on the glassware [61]. The U.S.EPA collected data on the performance between CFC-113 and n-hexane, giving identical average amounts of oil and grease but a bit bigger standard deviation for n-hexane. The minimum detection level (MDL) is 1,4 mg/l and the minimum level (ML) 5 mg/l for both HEM and SGT-HEM. [64, 65]

To break emulsions, methods like stirring, filtration through glass wool, use of solvent phase separation paper, centrifugation, use of an ultrasonic bath with ice, and addition of NaCl are suggested. Formation of emulsions may be prevented by SPE, a continuous liquid-liquid extraction and other extraction techniques, too. [64, 65]

Implementation of the EPA method 1664A

All laboratories using method 1664A have to perform an initial demonstration on the laboratory's capability to run the method 1664A. Tests for method detection limit and initial precision and recovery are provided in the method 1664A. Because n-hexane may extract more or less oil and grease depending on the properties of the discharge, the permitting authority may wish to consider establishing a conversion factor for these differences in the permit. However, the risk that the change of the extraction solvent from CFC-13 to n-hexane would lead to results that exceed the limit value is small. The U.S. EPA does not recommend a side-by-side comparison for each discharge. However, if the use of Method 1664A will cause a non-compliance with existing limit values, it is suggested to perform a side-by-side testing with Method 1664A and an approved method using CFC-113. This may be necessary also in other cases when significant differences in results between the two methods have been obtained [65]. In case of differences, EPA suggests that three replicates of each sample by both methods are analyzed on any seven days over a minimum 30-day period resulting in a total of 42 analyses. Example calculations for a side-by-side comparison with root-mean-square deviation method and development of a conversion factor are shown in the guidance material. [61]

Various extraction methods, like the mentioned solid phase extraction (SPE), are allowed to be used instead of a separatory funnel liquid-liquid extraction (LLE) technique, likewise the use of alternate concentration devices and procedures, but it's the discharger's or generator's responsibility to assure that the results produced are equivalent, and the performance criteria of the Method 1664A has to be met. An interesting

point of view is that the use of organic-free reagent water is not considered appropriate in the validation process. Many non-polar organic contaminants in aqueous sample are likely to be bound to particulate matter and extraction efficiencies are expected to be less [66]. Data demonstrating both equivalence and differences between the solid phase and the liquid phase extractions has been received by the EPA. These conclusions have been valid regardless of solvent or technique. However, based on all the results, it is likely that LLE and SPE would not produce significant differences when untreated effluents and process wastes are analyzed. In uncertain cases results obtained with liquid/liquid extraction are definitive. If possible a conversion factor between a solid phase extraction (SPE) and liquid-liquid extraction can be warranted.

Performance of the Method 1664A

The performance results of single and inter-laboratory studies give a recovery of 93 % for HEM and 89 % for SGT-HEM and a precision as relative standard deviation of 8,7 % for HEM and 13 % for SGT-HEM. A coarse estimation of 95 % confidence limits around 96 % recovery is 96 % ± 20 %. Further acceptance criterions are described in the method standard [64], and guidance in a separate document [61].

EPA Methods 502.2 and 524.2

Several organic contaminants present in petroleum substances, like the BTEX compounds can be determined with the EPA Methods 502.2 or 524.2. [67-70]

The Method 502.2 contains purge-and-trap followed by gas chromatography with photoionization detector (GC/PID) and electrolytic conductivity detector (ECD) in series. The Method gives detection limits between 0,01 – 0,02 for each of the BTEX-compounds with the PID detector. The ECD is not applicable for non-halogenated hydrocarbon compounds. Information on the columns used and retention times are available in the method tables.

The Method 524.2 includes gas chromatography with mass spectrometry (GC/MS). The method detection limits vary from approximately 0,02 – 1,6 µg/l depending on the compound, and the applicable concentration range is approximately 0,02 – 200 µg/l or 0,02 – 20 µg/l depending on the capillary column. Performance data (accuracy and precision) using cryogenic trapping option and a narrow-bore capillary column is provided in the method. Detection limits between 0,03 – 0,06 µg/l were achieved for each of the BTEX-compounds using an open split interface and an ion trap mass spectrometer.

EPA Methods 3520, 3535, 5030B, 5031, 5032, 8015C, 8021, and 8260

Several methods are available for sites impacted by petroleum hydrocarbons. Typically the BTEX is determined, like are the oxygenated additives, and total petroleum hydrocarbons in gasoline range C_4-C_{12} and/or diesel range C_{13}-C_{22}.

EPA Method 5030B provides a purge-and-trap determination procedure and is suitable for the determination of volatile organic compounds in aqueous samples and water miscible liquid samples. The gas chromatographic determinative steps are found in the Methods 8015 (GC/FID) and 8021 (GC/PID and/or GC/ECD, automated headspace). The Method 5030B in conjunction with the Method 8015C (GC/FID) is applicable for the determination of the aliphatic fraction in the light ends of total petroleum hydrocarbons. However, the Method 8015 is not accepted in all states after 2001.

The Method 5030B is also applicable to GC/MS Method 8260. In the assessment of water at petroleum hydrocarbon impacted sites, the required minimum detection limits are for the Method 8260B 1 µg/l for the BTEX, 50 – 100 µg/l for the gasoline range of TPH and 500 – 1000 µg/l for the diesel range TPH. [71-74]

The Method 8015C with purge-and-trap or direct aqueous injection is applicable to determination of the gasoline range organics corresponding for $C_{6...10}$, and the diesel range organics for $C_{10...28}$. Also injection of the concentrate from azeotropic distillation (Method 5031) or vacuum distillation (Method 5032) is possible. However, Method 8015C is not regulated under the U.S. regulations concerning contaminated soils, and other methods might be more appropriate for the determination of gasoline and diesel range organics. Ground water or surface water samples generally must be analyzed in conjunction with Methods the 5030, 5031, 5032, 3510 or 3520. [72]

For the determination of the aromatic fraction (BTEX), the use of Method 5030 and Method 8021 (GC/PID) is preferable. A total determinative analysis of gasoline fractions may be obtained using Methods 8021 in series with the Method 8015. The estimated quantitation limit of the Method 8021A for individual compounds in ground water is approximately 1 µg/l, and 0,2 – 0,5 µg/l for the BTEX using the photoionization detector (PID). [75]

Also the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) refers to the U.S. EPA Methods. According to the TPHCWG, volatile compounds in water are generally separated by EPA 5030 purge and trap method. For Headspace analysis is recommended as a screening method (EPA methods 3810, and 5021). The most common methods for extraction of water samples are EPA 3510 separatory funnel extraction, and semivolatiles, EPA 3520 continuous liquid-liquid extraction. Also solid phase extraction (EPA method 3535) can be used for extraction and concentration of semivolatile material. [76]

3.3.5. Other methods

Surface water monitoring

In some countries on-line detectors based on fluorometry, scanning fluorometry or IR reflection analysis are used to recognize oil in public water supplies. These field monitoring systems typically give a warning if oil is detected in the basin or in the water treatment processes. For example, in the UK several monitoring equipments have been installed to detect possible oil in e.g. water abstraction plants taking water from rivers. After an indicatory warning, further determinations can be done with, for example, GC/MS.

Naturally occurring fluorescent compounds can interfere with some monitoring equipment. It is understood that monitoring of aromatics instead of hydrocarbons may give a better indication of potential taste problems, since long-chain paraffins are probably odorless, tasteless and non-toxic, and very short chained hydrocarbons possibly are volatilized, whereas fuel range hydrocarbons may give taste at lower levels and aromatics at 1 µg/l level, and phenols and naphthols have taste thresholds at the ng/l level [77]. In case of groundwater, the mobility of individual hydrocarbons may define which compounds approach the water supply first.

SPE and SPME

Several articles have evaluated the possibilities to use solid phase extraction (SPE) or solid phase micro-extraction (SPME) in the determination of total petroleum hydrocarbons. The extraction methods can be applicable usable for at least some hydrocarbon fractions [78, 79]. SPE and SPME are currently used only in a few international standards, and their applicability to substitute the use of ozone depleting substances is not totally determined. The difference between SPE and SPME is emphasized.

SPE means extraction of, for example, hydrocarbons from water into, for example, solid filter disk material, followed by an extraction or direct detection of the hydrocarbons. SPE does not give information on the hydrocarbons, it typically should be calibrated with same kind of oil mixture, and adsorption of hydrocarbons on suspended solids may require e.g. dilution of the sample with pure water in order to minimize the matrix effects.

SPME is a kind of extraction/injection technology for gas chromatography. It is used for extraction of organic analyses directly from e.g. aqueous samples, or from the headspace of these samples in closed vials, onto a fused-silica fibre coated with a polymeric liquid phase. The analytes are desorbed from the fibre by heating and forwarded to the separatory column. SPME combines sampling and preconcentration in a single step, and according to various references, it has been tried to use for the determination, for example, aromatic hydrocarbons and PAHs, halogenated volatile organic compounds.

A SPME method for the determination of volatile hydrocarbons is described in a Swedish report concerning the screening and specific determination of BTEX-compounds in contaminated soils with a gas chromatograph followed by a flame ionization detector (FID) [80].

SFE

Use of supercritical fluid extraction followed by infrared determination (SFE/IR) has been described in conference materials and articles. SFE/IR gives a possibility for an on-line measurement with an interval of 15 minutes with accuracy of 81 – 100 % and precision (RSD) ranging from 3 to 17 %. The upper linear range for oils lies in the region of 70 – 130 ppm. Application of the HMSO coefficients used for IR-analysis may produce errors with samples of unknown petroleum hydrocarbons, and therefore an off-line calibration method has been created. An in-line silica gel clean up can optionally be applied. [81, 82]

In 1995, SFE was compared with Soxhlet extraction in the determination of the BTEX and TPH in soil. The recovery with SFE was understood to be better. Results with level of ng/g were reported with a 'sorbent trapping' system combined to SFE and GC/FID. [83].

Other techniques, like laser-induced fluorescence are currently investigated. No information was found on whether any of the methods like SFE/IR, fluorescence methods etc. are being standardized.

GC/MS using selective ion mode

Also methods for the determination of TPH by GC/MS in a selective ion mode (SIM) have been described. For example, Reddy and Quinn extracted TPHs and PAHs with methylene chloride (dichloromethane) and hexane, fractionated the extracts on silica-gel columns, used signal from ion m/z 57 ($C_4H_9^+$), which is a major ion in aliphatic com-

pounds, and integrated it throughout the chromatogram achieving a faster determination compared to conventional GC/FID and GC/MS analysis of TPHs and PAHs. PAHs were analyzed by using distinct quantification ions during the same run. However, the method was calibrated for the freshly spilled fuel oil and gives underestimates with weathered and/or degraded fuel oil. The minimum detection limit achieved was 16 µg/l for TPH, precision was < 10 % RSD, and relative recoveries were 90 – 110 % for ~50 – 1000 µg of TPH spiked per liter. It should be noticed, that the concentration in the blanks were 5 – 10 µg/l. [84]

Ultrasonic particle monitoring and acoustic determination

Ultrasonic particle monitoring equipment with a capability to determine particles with sizes of 1 – 100 µm, concentrations from 1 to 1000 ppm, and under certain conditions to discriminate gas bubbles, sand and oil droplets, is being developed by TNO TPD [85]. Oil droplet determination may give a good estimate of dispersable oil if no other particles, bubbles etc. are present [43]. Also a laboratory demonstration on the applicability of acoustic determination with a chemometric data treatment has been described for the determination of oil-in-water micro-pollution. [86]

3.4 Offshore

3.4.1. Development of a new method

The challenge

The IR method used to determine oil in produced water should be substituted with a method not using ozone depleting substances. Use of tetrachloroethylene as a substitute for CFCs is not preferred due to its carcinogenic properties [24]. In addition, there are several concerns with the ISO 9377-2 in the offshore use. The method ISO 9377-2 gives a different definition of oil from CFC-113 extraction and IR, the method requires skilled personnel, measures $C_{10...40}$ but not volatile hydrocarbons, there is possible loss of hydrocarbons above C_{10}, and it is laborious [25].

In a workshop held in 2001, it was understood that GC/FID with pentane extraction would give the possibility to determine short chained hydrocarbons starting from C_7 due to lower loss of volatile compounds during the concentration. However, this is less robust method due to the volatility of pentane. GC/FID with purge and trap enables the analysis of $C_{5...10}$ compounds. The disadvantage is that the analytes should be identified individually, or that the BTEX-compounds will be included in the integration of the chromatogram. GC/FID with static headspace has both advantages and disadvantages compared to GC/FID with purge and trap [24].

It was suggested to use pentane as an extracting solvent, include the window $C_{7...40}$ in the determination, subtract the TEX-compounds (toluene, ethylbenzene, and xylene), and perform the determination in combination with static headspace or purge and trap to enable the determination of $C_{5...10}$ hydrocarbons. However, there seems still to be significant differences between the proposed method and the present IR OSPAR method, especially when samples from gas and condensate installations are analyzed. [25]. Further research was recommended on possible alternative methods yielding equivalent results (cf. OSPAR Decision 2001/1, paragraph 7.1) that can be easily applied offshore

or kept available in case of non-availability of the regular analysis equipment, including SPME-GC/FID, online analysis, and handheld equipment. [24]

The workshop of 2001 gave several tasks for the countries that participated in the workshop. E.g. the countries agreed to gather data for the basis of a guidelines suggested by the Dutch. It was suggested that each country initiates a study on the comparability between the infrared and GC/FID methods. This evaluation should be combined with additional information on aromatic hydrocarbon analysis, and information should be used to verify whether total oil equals dispersed oil + BTEX. Also data on dispersed oil and phenols should be exchanged data, if these are measured in the same produced water sample. [24]

A modified ISO 9377-2 method is being prepared under the supervision of the OSPAR Offshore Industry Committee (OIC) as a new reference method. A modified method was suggested in the Draft OSPAR/OIC comparison program [87]. The modified method differs from existing in that it attempts to cover the $C_{7...40}$ –range rather than the $C_{10...40}$ as in the present ISO 9377-2 method. The lower carbon number is achieved by extracting with pentane and using large volume injection into gas chromatograph rather than concentrating the extract. N-decane ($C_{10}H_{22}$) is not used as an internal standard. A detection limit of 0,5 mg/l would be adequate for produced water. The method would possibly use large volume injection, integrate the whole gas chromatogram range $C_{7...40}$, and use higher resolution to recognize and exclude the BTEX-peaks or otherwise determine and exclude the BTEX. [21, 88]

The comparison program

The Netherlands have been requested by the OSPAR Commission to act as a lead country for carrying out a comparison program between the current OSPAR method (a 3-wave length IR analysis method using tetrachloroethylene (TTCE) as an extraction fluid), the ISO 9377-2 and a modified ISO 9377-2 method. The modified ISO 9377-2 takes into account the $C_{7...10}$ i.e. starting from n-heptane (C_7H_{16}) continuing up to C_{40} but substracting the TEX. [21, 88]

In a Quick Scan done with samples from six platforms, it was evaluated that for both dispersed oil content and total oil content, the integration over $C_{7...40}$ in the GC method for total oil gave results more comparable with the IR method, than when integrating over $C_{10..40}$. For oil platforms already $C_{10...40}$ gives a good approximation. The results obtained for total oil by integrating over $C_{7...40}$ compared poorly with the IR-method when analyzing samples from gas platforms. Ford dispersed oil comparability was good. It should be noticed that some platforms producing light crude oil may also contain relatively high contents of $C_{7...10}$ hydrocarbons. It was understood that the modified ISO 9377-2 will provide a good basis for a comparison program. However, the method is not suitable to deliver adequate results, if the method is used to evaluate the 15 % reduction target for total oil, since the results of the analysis do not provide adequate data on the total oil content. It was also understood that the current practices for the determination of oil-in-water, i.e. the application of purging, may cause difficulties to compare results obtained with separate methods [89].

In comparison studies carried out on 34 platforms, it was understood that results from 11 of the 34 platforms gave differences of more than 20 % between the methods. It was concluded that high or even very high deviations could be expected for light oils like oil condensates produced on gas / condensate platforms. In earlier Dutch studies comparing

the IR-method and the previous GC-method using pentane differences up to 370 % were shown [21]. IR results based on the CFC-113 or tetrachloroethylene extraction seemed to be equivalent for all platforms.

On that basis the OIC decided to carry out a North Sea Oil-In-Water –comparison program in OSPAR countries (the UK, Norway, Denmark, Germany and the Netherlands) on 56 platforms. Results will be available around November 2002 and reported to the OIC Meeting of OSPAR in March 2003 [88].

The future

In 2003, OSPAR/OIC will present a the proposal for a new reference method for the determination of the content of dispersed oil in produced water, and also a proposal for one or more performance standards on aromatic hydrocarbons, including appropriate reference analytical methods, and a timetable for the dates by which any such performance standard should be met [90]. Therefore, the OSPAR countries can at the earliest officially agree on a suitable CFC-free method for oil in water analysis at the meeting in March 2003 [88].

A future project on quality assurance in relation to OIC monitoring will be proposed [90]. Other OIC countries than Norway and Denmark are planning to run the modified ISO 9377-2 method only, and use the IR method with tetrachloroethylene as a temporary alternative. [91]

In the context of earlier developments, the information available has led to conclusions in the OSPAR Offshore Industry Committee, that in conjunction with the achievement of the goals and performance standards for dispersed oil in OSPAR Recommendation 2001/1, reductions of aromatic hydrocarbons in produced water would also be achieved and that there was no need for specific performances for these substances. [92]

3.4.2. Norway

NS-EN ISO 9377-2

In Norway, the method NS-EN ISO 9377-2 has been approved as the new standard method for determination of oil in produced water from January 1st, 2002. The method is implemented on several platforms in Norway with success [91]. The old infra-red spectrometric method using CFC-113 was allowed to be used until June 30th, 2002. IR method using tetrachloroethylene is not preferred, due to occupational hygienic reasons [93]. The ISO 9377-2 or a method calibrated to give equivalent results to the ISO 9377-2 must be used for the analysis of oil-in-water at offshore installations.

OLF / WG-OIW Rev 0-0896

The working group within OLF (the Norwegian Oil Industry Association) for oil in water has earlier proposed a method for determination of oil-in-water in offshore conditions. The method was called OLF / WG-OIW Rev 0-0896. This method was based on a solid phase extraction using filter disks (ø 90 mm, 3M Empore), and specific detection of the oil with GC/MS. The correlation between the standard FTIR method and the OLF method was tested on some platforms and was found to be fairly good [94, 95]. This method was, however, found to be too complicated for the offshore use.

Experiences
A comparison study of the old IR-method (NS 9803) and GC/FID (ISO 9377-2) was carried out by the Norwegian Oil Industry Association (OLF) concerning 33 platforms. In general, it was understood that relatively good correlation between the EN-ISO 9377-2 and the old IR/CFC method was achieved. [96]

The ISO 9377-2 gave somewhat lower values on an average for all 33 platforms than the Freon/IR method. The average concentration of oil-in-water was 18,1 mg/l with the Freon/IR, and 15,7 mg/l with the ISO 9377-2. The concentration of the BTEX-compounds varied between 0,2 – 41,8 mg/l at the 33 platforms in 2001, and the average was 11,0 mg/l. The concentration of non-polar volatile hydrocarbons ($nC_{4...9}$ minus the BTEX-fraction) varied between 0,4 – 14,3 mg/l, 4,7 mg/l as the average. The observed variations result probably from the fact that produced water is inhomogeneous, the methods are basically different, e.g. the definition of oil is different in the two methods. As the ISO 9377-2 was understood to become a standard method, a simple lab-instrument to be used on the platforms as an alternative to the reference standard method might be appropriate. [95]

However, in studies carried out by the UK and the NL, correlation showed to be not as good as expected. Further sampling and analysis were understood to be needed before EN-ISO 9377-2 could be accepted within the OSPAR Offshore Industry Committee. [96]

3.4.3. The United Kingdom

IP 426
In UK there is a response to analyse samples from all UK sector oil platforms by existing IP 426 and the modified ISO 9377-2 methods. Legislation has been introduced regulating the discharges of produced water from gas condensate fields. According to the legislation the oil content in the produced water is required to be analyzed by the current IR method using tetrachloroethylene (TCE) [97].

Experiences
A laboratory comparison was conducted by the United Kingdom Offshore Operators Association (UKOOA) between the newly proposed ISO 9377-2 and the current Freon/IR method using five different oils. Also the suitability of TCE was evaluated.

With method ISO 9377-2, the calibration against the actual crude oil type sample provided much higher extraction efficiency at all concentrations for all oil types. For example, for a condensate, the extraction efficiency increased from 25 – 30 % for the diesel/lube oil standard to 80 – 100 % for the sample crude standard. The IR method with TCE gave consistently higher extraction efficiencies for all sample concentrations and all oil types. Overall extraction efficiencies varied from 78 – 108 % for condensate to 92 – 108 % for crude. Values greater than 100 % reflecting the less than 100 % extraction efficiency of the back extracted standards, which were assumed to be 100 % efficient. Compared with the IR method using TCE, the ISO 9377-2 method gave substantially lower extraction efficiencies than the IR method. This is based on the calibration standards recommended in the ISO method as defined, and in addition, taking into account hydrocarbons from C_{10} upwards. The results obtained with the crude calibration standard were substantially higher. [97]

In this study, extraction efficiencies obtained with CFC-113 were 5 – 10 % lower than those with TCE as the solvent. Also the effect of Florisil treatment was evaluated. The IR analysis with triple absorbance peaks showed characteristic decrease in extraction efficiency, relative to the other standards, as oil density increases. This was due to the triple peak calculation being affected by the higher aromatic content of the condensates. [97]

3.4.4. On-line monitoring

UV fluorescence

UV fluorescence methods are very sensitive in appropriate situations. Successful quantitative studies require prior knowledge of the levels and compositions of constituent hydrocarbons being analyzed. These techniques are best suited for effluents containing an aromatic content and cannot be used for alkane-based oils and greases or vegetable oils. It is important to calibrate the instrument with an oil similar to that being monitored in the sample as responses will vary with oil type. Interfering species like nitrates and plant pigments can influence the results. [81, 98, 99].

Individual aromatic hydrocarbons may also produce very different responses, optimum excitation, and emission wavelengths. This problem can in principle be solved by using scanning fluorescence spectrometry or by creating a three-dimensional plot covering the whole relevant wavelength range [23]. Also fluorescence method combined with light scattering determination and an optimization by artificial neural network have been tried. Light scattering methods, however, react to other particles than oil droplets, too. In this method, a re-emulsification by ultrasonic techniques was used to reduce oil droplet size and improve the determination of oil droplets by size [99]. Generally, to ensure a high, stable oil response the average diameter of the oil droplets ought to be reduced [100]. Sample homogenization techniques combined with use of chemicals may help to improve the oil droplet size distribution, which leads to higher fluorescence readings and possibly better correlation to the lab methods, especially when measuring ranges above 100 ppm or the oil droplet size is definitely varying [101]. The UV-absorbance of oil-in-water has been measured also by using iso-propanol as a co-solvent to produce clear, homogenous solution [102].

Good trend in variations have been determined by BP. However, the fluorescence method cannot differentiate between dispersed oil and dissolved oil, or between coated solids and dispersed oil droplets. In another method wholly acceptable results were not achieved. The UV fluorescence detector used to measure the oil content of an n-hexane extract gave quite good results compared to an IR equipment, however, calibration was considered difficult. Due to apparent good correlation, it was possible to create a conversion graph between the methods for a specific type of oil [98].

IR light scattering

On-line IR light scatter technologies measure predominately dispersed aliphatic hydrocarbons, but not soluble or aromatic species. Systems can compensate for oily solids, but once calibrated operate only with one crude oil type. Fibre Optic Probe gave a reasonable correlation with the IR test method, but there was little relationship (i.e. accuracy or repeatability) between results from optic probe and IR test. [98] Some operators have already replaced the freon/infrared method for measuring the aliphatic

have already replaced the freon/infrared method for measuring the aliphatic oil fraction in produced water with an infrared method using pentane as solvent with satisfaction.

HATR
In Norway, oil companies are assessing a horizontal attenuated total reflection (HATR) method, and some other on-line oil in water instruments. [95].

Conclusions
As a conclusion, several methods for on-line monitoring are available or being prepared. A standard method is needed for the assessment of compliance of oil production. However, more robust on-line methods are needed for offshore conditions. These methods should be performance-based, well calibrated to give reliable results and as comparable to the standard method as possible. Statistical procedures should be established to obtain conformity between results from different oil production plants, and to assure that the result obtained with offshore on-line methods confirm the compliance with high probability of confidence.

3.4.5. Other monitored TPH parameters

The monocyclic aromatic hydrocarbons generally considered relevant in the management of produced water are the BTEX. In Denmark, also cumene is included.

Three alternative selections of most relevant PAHs are naphthalenes (alkylated and non-alkylated), the NPDs (naphthalenes, phenanthrenes, dibenzothiophenes; alkylated and non-alkylated) and the U.S.EPA list of 16 PAHs (naphthalene and phenanthrene included, dibenzothiophene not). Denmark also monitors triphenylene, perylene, 5-methylchrysene, and 7,12-dimethylbenz(a)anthracene. The PAHs are generically listed as a group on the list of chemicals for priority action in the OSPAR Strategy with regard to Hazardous Substances. Few PAHs are individually listed in the Candidate Substances List, and Naphthalene is also included in the European Union List of priority substances in the field of water policy. NPDs are considered relevant because of their loading and toxicity. Phenol and alkylated phenols are not considered as aromatic hydrocarbons in this case, however, they form a separate group in the OSPAR List of Candidate Substances, and some alkylated phenols are mentioned in the List of Chemicals for Priority Action. A separate programme might be worthwhile to initiate for the phenols. [24]

In Norway, requirements for monitoring are given in the Activities Regulations. The BTEX are monitored with GC/FID or GC/MS, headspace or purge and trap, achieving a quantitation limit of 1,0 µg/l. The NPDs and PAHs are determined, for example, with EPA methods 610 and 625 achieving a quantitation limit of 0,025 µg/l, and phenols $C_{1...9}$ with EPA Method 604 GC/MS or GLC/MS achieving the quantitation limit of 0,01 µg/l). Organic acids $C_{\leq 5}$ are determined with isotachophorese (ITP), GLC/FID or GC/MS, achieving a quantitation limit of 2 mg/l. [103-105]

3.5 Soil

3.5.1. The ISO methods

ISO/FDIS 14507
Requirements for the pretreatment of samples are established in the final draft standard ISO/FDIS 14507 (Soil quality - Pretreatment of samples for determination of organic contaminants).

ISO/DIS 16703
Method ISO/DIS (16703 Soil quality - Determination of mineral oil content by gas chromatography followed by flame ionization detector) is in draft international standard stage. The method determines the sum of all hydrocarbons extractable with acetone/n-heptane which do not adsorb on Florisil, with a boiling range of 175ºC to 525ºC, n-alkanes between $C_{10}H_{22}$ to $C_{40}H_{82}$, isoalkanes, cycloalkanes, alkyl benzenes, and alkyl naphthalenes and polynuclear aromatic compounds as mineral oil. Gasolines containing compounds $C_{<10}$ cannot be determined with this method. The method is applicable to mineral oil contents between 100 – 10 000 mg/kg. Several extraction procedures can be used, and interference of soil with higher organic content can be diminished with repeated clean-up procedure using Florisil. [106]

Experiences
So far the repeatability and reproducibility variation coefficients for the ISO/DIS 16703 have been 4,53 % and 29,39 %, respectively, in an interlaboratory trial. In practice, the repeatability of 10 – 15 % and reproducibility of 30 % are more realistic. [40]

Three proficiency rounds were run for ISO/DIS 16703:2001 by the BAM. The consensus means obtained with GC/FID are typically 10 % - 20 % (ranging 0 % and 25 %) higher than those found with IR-spectroscopy. On the contrary, coefficients of variation (CV) obtained with GC/FID are roughly twice as big as with IR. It was assumed that the applicability of the GC method for the determination of TPH in soil rapidly reaches its limit with a decreasing TPH content if a given reproducibility is aimed at. As an example it was stated that a coefficient of variation of 30 % is hardly to be expected at a hydrocarbon content below 500 mg/kg. It was assumed that the greater variability of GC is genuine and caused as additional sources of variability, i.e. chromatographic separation and integration of the TPH mixture. A certified matrix reference material was expected to be a tool for the improvement of the measurement comparability of this method. [107]

In a comparison measurements of total petroleum hydrocarbons between infrared spectrophotometry (TPH-IR) and gas chromatography (TPH-GC) typically the infrared spectrometric method gave higher results than the gas chromatographic method. Both CFC-113 and methylene chloride (dichloromethane) were used for extraction. The determination with CFC-113 and GC gave the lowest results. Interestingly, total petroleum hydrocarbon concentrations measured with the TPH-IR were higher than the actual quantities of petroleum hydrocarbon in the soil samples, possibly due to calibration with the Method 418.1 reference oil. CFC-113 did not extract fully the heavy hydrocarbon molecules found in fuel oils. [108]

ISO 9377-2
Laboratories have used the method ISO 9377-2 for soil samples, too. The method gives information also on the oil quality. The composition of the analyzed mixture has an influence on quantitation like do the aging and fractioning of oil in the samples. It is possible to analyze the composition of the hydrocarbon mixture, then create a similar stan-

dard, and calibrate the method with the standard. This gives better quantitation of the oil mixture, but takes additional time and is expensive. It is understood that the results between the old IR-method and the new GC-method vary ±50 %. It has been proposed, that this is acceptable for a general mineral oil analysis, but not for compound specific determinations. This is based on the need for a affordable, sufficiently specific and accurate method for monitoring and for the purposes of contaminated soil remediation. [109]

ISO 15009 and ISO 13877

For volatile aromatic hydrocarbons (e.g. naphthalene and halogenated hydrocarbons) a standard ISO 15009 (Soil quality - Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons - Purge-and-trap method with thermal desorption) was published in 2002. ISO 13877 (Soil quality - Determination of polynuclear aromatic hydrocarbons - Method using high-performance liquid chromatography) provides a determination method for the PAHs.

3.5.2. Nordtest

In 1996, Nordtest gave guidelines for chemical analysis of contaminated soil samples. For volatile organic compounds, EPA Methods 8270, 8240 and 8260 were recommended. Additionally, a GC/FID method using pentane and pyrophosphate water solution in extraction was described. The report included also background information on typical chemical residues in solvents, for example, traces of chloroform and tetrachloroethene in pentane.

The EPA methods 8270, 8240 and 8260 include a GC/MS and a dynamic head space (purge&trap) –GC/MS method. The detection limits vary between 0,005 – 0,2 mg/kg depending on whether the sample is a non-concentrated extract (ion trap-MS), a concentrated extract (ion trap-MS) or whether a purge & trap low level method was used. Also other detectors than MS and ion trap-MS can be applied.

Experiences

In a Nordic interlaboratory test coefficient of variation varied between 10 – 40 % depending on the compound. [110]

The Nordtest method

In the Nordtest method, pentane and pyrophosphate water solution was used as the extraction solvent. The extract was analyzed with gas chromatography followed by flame ionization detector (GC/FID). The determination of total hydrocarbons included also the determination of single components such as BTEX, and products such as oil, fuel oil and some lubricant oils corresponding to an n-alkane range of $C_{6...35}$ and a boiling point range from approximately 70ºC to 490ºC.

The detection limit for volatile components such as BTEX was 0,02 – 0,01 mg/kg. The detection limit for complex products varied depending on the product, and was e.g. 5 mg/kg for diesel oil and 25 mg/kg for fuel oil. The total content in the samples was split into three fractions, volatiles from n-C_5 (injection peak) to n-C_{10} (inclusive), calculated by the response from toluene; diesel oil from n-C_{10} to n-C_{25} (inclusive), calculated by a diesel oil standard; and heavy oil from n-C_{25} to n-C_{35} (inclusive), calculated by a fuel oil standard. It is assumed that all the components in the specified interval in a sample typi-

cally polluted with gasoline are aromatic components, alkyl benzenes. The results will therefore to some extent overestimate the content of $C_{3...4}$-alkylbenzenes. [110]

Experiences

Norwegian SFT gathered information on the analysis of total hydrocarbons and performed a ring study on 26 laboratories. According to the Nordtest report, IR spectrometry and GC/FID (n-$C_{6...35}$) were the typical determination methods. In this study, reproducibility was not understood to be as good, since the results varied approx. ± 40 % for soil samples. Variation was greater with heavy oil fractions, in this case, lubricating oils. It was comprehended that the biggest source of error arises from the instrumental part of the determination. Settings and procedures for injection, temperature programs, integration of the chromatogram, and choice of calibration standard should be optimized further. [111]

In an interlaboratory comparison carried out by the Finnish Environment Institute in 2000, the Nordtest method was used for soil analysis. The laboratories that used the Nordtest method, obtained somewhat lower results than other laboratories, probably due to different extraction solvents, different types of oil used in calibration and different clean-up procedures. The use of a mass selective detector can underestimate specifically the fraction of high boiling hydrocarbons [112].

3.5.3. The Netherlands

NEN 5733

In the Netherlands, a gas chromatographic determination by flame ionization detector (FID) according to NEN 5733 is currently used to determine 'mineral oil' in soils. The NEN 5733 method defines 'mineral oil' as the sum of all alkanes (including branched alkanes) with carbon numbers $C_{10...40}$, requiring additional analysis of aromatic and/or polynuclear aromatic hydrocarbons if their presence is expected. [113]

3.5.4. The United States of America

EPA Method 9071B

The EPA Method 9071B determines of n-hexane extractable material (HEM) in sludge, sediment, and solid samples. The method employs n-hexane as the extraction solvent in a Soxhlet extraction followed by distillation of n-hexane and weighing. [114]

The method may be used to quantify low concentrations of oil and grease. It is suitable for extracting relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, biological lipids, and related materials. It is not recommended for measuring materials that volatilize at temperatures below 85ºC. Petroleum fuels from gasoline through fuel oil may be partially lost. Some crude oils may contain materials that are not soluble in n-hexane. Non-oily extractable substance such as sulfur compounds, organic dyes, and chlorophyll may result in a positive bias. [114]

EPA Methods 3560 and 8440

U.S.EPA Method 8440 [115] is used for the IR measurement of total recoverable petroleum hydrocarbons (TRPHs) extracted with supercritical carbon dioxide from sediment, soil and sludge samples using the Method 3560 [116].

The method 8440 is not applicable to determinations of gasoline and other volatile petroleum fractions due to evaporative losses. It can detect TRPHs at concentrations of 10 mg/l in extracts i.e. 10 mg/kg in soils. Tetrachloroethylene is used in the method for the collection of TRPHs. Interfering materials are removed with silica gel. The determination is a measure of mineral oils only, and does not include the biodegradable animal greases and vegetable oils captured in oil and grease measurements. These non-mineral-oil contaminants can cause positive interferences with the IR analysis. Copper filings are added to remove elemental sulfur. Sample can be concentrated with techniques described in Method 3510, e.g. with micro Kuderna-Danish or nitrogen blowdown. [115-117]

EPA Method 8015C

EPA Method 8015C, a GC/FID determination, is applicable to gasoline range organics (GRO) with purge-and-trap or direct aqueous injection and diesel range organics (DRO) with solvent extraction. However, the performance is probably good only with concentrations of several dozens mg/kg.

EPA Methods 5021B, 8015, 8021B, and 8260B

Method 5021B, a general purpose headspace method for the analysis of VOCs, can be used to determine the BTEX in soils, sediments and solid wastes. Method detection limit varies from 0,1 to 3,4 μg/kg, and applicable concentration range is approximately 10 – 200 μg/kg. The detection is suggested to be done primarily with a EPA Method 8260B, a GC/MS method [74], but EPA Method 8015 [72], a GC/FID method, or Method 8021 [73], a GC/PID/ELCD method, can be used in conjunction as sample screening methods. For example, in California the Methods 8260B and 8021B have been used in the analytics of soils impacted by petroleum hydrocarbons. The minimum detection limits are 2 μg/kg for the BTEX-compounds, 250 – 500 μg/kg for the gasoline range, and 2500 – 5000 μg/kg for the diesel range of petroleum hydrocarbons. [72, 73, 75]

ASTM D 5765 - 95

ASTM D 5765 – 95 Standard Practice for Solvent Extraction for Total Petroleum Hydrocarbons from Soils and Sediments Using Closed Vessel Microwave Heating was reapproved in 2001. This practice consists of a solvent extraction of total petroleum hydrocarbons (TPH) from soils and sediments with acetone/hexane in a sealed microwave vessel, and analysis by gas chromatography or gravimetric measurements. [118]

3.5.5. Field

General

Various field methods has been evaluated in the United States during the last two decades on the basis of the Superfund program on contaminated soils linked to various innovative technology programs. Therefore dozens of references exist not further detailed in this report [119-138]. However, a short overview on few field methods is presented. Field test kits give rapidly information whether the soil is contaminated and possibly an estimate on the contamination level. Cheap and rapid tests are needed at remediation sites. During the excavation of contaminated masses, it is not possible to wait for hours or days for information on whether the clean soil layer has been reached or not.

Field test kits for total petroleum hydrocarbons or BTEX-compounds are typically based on immunology, UV-fluorescence or turbidity methods. It is possible to also use on-line gas chromatography, on-line gas chromatography after solid phase extraction, and on-line mass spectrometry. Other possible field test methods are IR-spectrometers for soil gas, titrimetric methods for hydrocarbons in soil and water, laser-induced fluorometers, photoionization detectors for volatile and semivolatile hydrocarbons and ion mobility spectrometry for organic gases. They can be used in orientation, field study, and remedial phase with semiquantitative results. Also mobile GC/MS –systems have been demonstrated, and analysis in less than 10 minutes is possible by non-target screening analysis [139].

Reliability of the results varies from soil to soil and between different compounds. Although many studies have demonstrated good correlations between field immunoassay and conventional laboratory analyses, in many cases the results are less consistent. Comparison with laboratory analyses is important. [110]

U.S. EPA Method 4030

The (U.S.) EPA Method 4030 is a procedure for screening soils to determine whether total petroleum hydrocarbons (TPH) are likely to be present. The method is based on an immunoassay. Depending on the product selected, it can be used to locate samples with low (< 40 – 100 ppm), medium, and high (> 1000 ppm) concentrations of contaminates, or to determine if TPH is present at concentrations above 5, 25, 100, or 500 mg/kg. The method provides an estimate of the concentration of TPH by comparison against standards, and can be used to produce multiple results within an hour from sampling.

In the Method 4030 a soil sample is extracted. An aliquot of the extract and an enzyme-TPH conjugate reagent are added to an immobilized TPH antibody. The enzyme-TPH conjugate competes with hydrocarbons present in the sample by binding to immobilized anti-TPH antibody. The test is interpreted by comparing the response produced by a sample to the response produced by a reference reaction. The lower limit of detection of the TPH compounds varies from 0,1 ppm for trimethylbenzene, via 0,5 – 300 ppm for the BTEXN-compound, and 75 – 100 ppm for gasolines and diesel oil, up to 7000 – 10 000 ppm for light lubricating oils and lithium grease. For brake fluids and chain lubricants the detection limits are even higher. The method requires the use of appropriate standards, i.e. diesel standards for diesel oil, and therefore further information on the contaminants at the site is needed.

Experiences

Using the test kit from which the actsual standard was developed, 95 % of samples containing 25 ppm or less of TPH will produce a negative result in the 10 ppm test configuration. The test is most sensitive to the small aromatic compounds e.g., ethylbenzene, xylene, and naphthalene. The action level may vary from site to site, but the test produces internally consistent results at a particular site. [140] Performance properties are based on a single laboratory study and two field trials. In the two field tests, 0 – 7 % of all results were false negatives and 10 – 17 % were false positives. Further performance properties are described in the method standard. In general, a high degree correlation was observed between the standard method and the immunoassay method. [140] However, immunoassay kits may also display strong biases. In general, test kits give less than 25 % false positives and less than 5 % false negatives [76].

3.5.6. The Nordic countries

Various practices are used in the Nordic countries for contaminated soils.

Norway

In Norway BTEX-compounds, 16 PAHs according to U.S.EPA and aliphatic hydrocarbon fractions $C_{5...10}$, $C_{>10...12}$ and $C_{>12...35}$ are determined for soils contaminated with hydrocarbons. [141, 142]

Sweden

The methods specified are typically Nordtest methods and U.S. EPA methods.

The characterization of total petroleum hydrocarbons includes determination of hydrocarbons in range $C_{6...28}$. Samples having a TPH content exceeding the action value will be determined by fractions. The fractionation to aliphatic and aromatic compounds is done with aluminum or silica column, the eluation with n-pentane (aliphatic fraction) and dichloromethane (aluminum oxide, aliphatic fraction) or dichloromethane/acetone (silica, aromatic fraction). The quantification is done by GC/FID.

Total hydrocarbons can be determined with Nordtest's method, which includes extraction with pentane/pyrophosphate followed by a GC/FID determination. Separate human toxicological limit values are given for all hydrocarbon fractions, and ecotoxicological limit values for some fractions. [143]

The Swedish Environmental Protection Agency, Naturvårdsverket and Svenska Petroleum Institutet have established determination requirements for the analysis of contaminated soils under gasoline stations. The procedure is based on the reports of TPHCWG, and groups aliphatic and aromatic hydrocarbons according to their mobility and toxicity in the environment. Limit values are represented for:

- aliphatic fractions $C_{>5...8}$, $C_{>8...10}$, $C_{>10...20}$, $C_{>12...16}$, $C_{>16...35}$
- sum aliphatic $C_{5...36}$
- the BTEX
- aromatic fractions $C_{8...10}$ and $C_{10...35}$
- five gasoline additives and
- PAHs.

Interestingly, the limit values may differ depending on whether the soil is dense or permeable.

Limit values for ground water do not have same fractioning. Limit values are available for non-polar aliphatic hydrocarbons, total extractable aromatic substances, BTEX-compounds, carcinogenic polynuclear aromatic hydrocarbons (carcinogenic PAHs), other PAHs, and four gasoline additives. [143]

For the determination of very volatile hydrocarbons in soil, gas chromatography with mass spectrometric detector (GC/MS) is recommended, with static head-space, dynamic head-space (purge and trap) or solid phase micro extraction (SPME) as a sampling method. Mass spectrometer can be used either in 'scan mode' or in 'selected ion recording' mode, and with multiple ion detection. The two methods be combined. Volatile organic compounds (VOCs) are analyzed with static head-space technique followed by

GC/MS, and heavier hydrocarbons are analyzed with GC/MS or with GC/FID by TPH-method. Pentane is needed to analyze lower fractions, and a separate sample has to be prepared for hydrocarbons $C_{5...7}$. [143]

Volatile hydrocarbons, like components of gasoline and diesel fuel, can be detected with mass spectrometry or flame ionization detector (FID) after gas chromatographic separation. However, mass spectrometry is preferred.

For aromatic and aliphatic hydrocarbons mass spectrometry is recommended. Static head space is recommended for hydrocarbons up to C_{22}. Thin layer chromatography under Nordtest is available for semivolatile hydrocarbons. Determination of TPH is understood to be suitable for semivolatile hydrocarbons. If the separation of aliphatic and aromatic hydrocarbons is not needed, the Nordtest method can be used, since it does not include a separation step.

Even further recommendations are given for determination of PAHs and gasoline additives. [143]

Because IR method SS 02 81 45, recommended for the determination of hydrocarbon compounds in water, uses ozone depleting substances, new methods, with less experience, are listed. The methods include the use of solid phase micro extraction (SPME), and use of supercritical fluid extraction (SFE).

A Swedish EGOM (extraherbart gaskromatograferbart organiskt material) method is a screening method for the determination of sum organic (both natural and antropogenic) substances in groundwater, sediment and soil. The method includes extraction with cyclohexane or acetone followed by determination with GC/FID. The method determines relatively non-polar organic substances with molecular weight up to 600 and boiling point up to approximately 400ºC. It is not suitable for compounds with low vapor pressure. [80]

Various commercial determination packets are available. Their prices vary between 150 and 300 euros. Typical detection limits are:

-	aliphatic and aromatic fractions in water (GC/MS or HS-GC/MS)	10 µg/l
-	aliphatic and aromatic fractions in soil each fraction	1 – 10 mg/kg
-	BTEX in water	0,2 – 0,5 µg/l
-	BTEX in water, individual substances	0,2 – 0,3 µg/l
-	BTEX in soil	0,05 – 0,1 mg/kg
-	volatile hydrocarbons $C_{6...10}$ in water, GC/MS-headspace/purge&trap	50 µg/l
-	volatile hydrocarbons $C_{6...10}$ in soil, GC/MS-headspace/purge&trap	20 mg/kg
-	separate aliphatic hydrocarbon fractions from $C_{6...8}$ to $C_{17...35}$, sum parameters like $C_{6...16}$, reporting limit, water	10 µg/l
-	aliphatic $C_{5...10}$ in water, GC/MS	10 µg/l
-	aliphatic $C_{10..15}$, aliphatic $C_{16...35}$, GC/FID	20 µg/l
-	screening, HS-GC/MS, water	1 – 10 µg/l

- screening, HS-GC/MS, soil 1 – 10 mg/kg
- MTBE, TAME, reporting limit 0,1 µg/l
- individual PAHs 0,1 µg/l

Finland
In Finland, when ISO 9377-2 is used in a soil remediation project, reporting of results for mineral oil fractions $C_{>10...23}$ and $C_{>23...40}$ is typically required.

In an in-house gravimetric method, the Geological Survey of Finland uses petroleum ether as an extract solvent in determination of oil and grease in soil, humus and sediment samples with Soxtec. The petroleum ether is vaporized with nitrogen, and residues are weighted. The concentrations of oil and grease can be determined individually by using an aluminum oxide column for separation. The detection limit varies between 20 – 50 mg/kg depending on the sample matrix. [144]

Experiences
A total of 15 laboratories in Finland, Sweden, Latvia, Estonia, and Norway participated in an interlaboratory comparison test carried out by the Finnish Environment Institute. One standard solution containing a known concentration of different oils was prepared. One soil sample and one soil extract were delivered. For soil samples, the draft standard method ISO/DIS 16703 was mainly used, however, two laboratories used IR technique and three laboratories a hydrocarbon test kit (PetroFLAG®, Dexsil, USA). [41]

The repeatability (the within-laboratory standard deviation) for triplicate soil sample was 7,5 % and the reproducibility was 29 %. Only one laboratory used another method than the ISO/DIS 16703. The variation in the analysis of the soil extract was 21 %, smaller than the variation in the analysis of the soil sample, 28 %, implying that the extraction step still has some pitfalls. However, the variation was smaller than in the interlaboratory comparison in 5/2000. It seems possible that some laboratories still have an inaccurate calibration, and some laboratories have difficulties in the extraction or in the clean-up step [41, 145].

3.6 Sediment

No revised international standard method for the determination of total hydrocarbons in the sediment is available. ISO/TC 190 Soil quality/SC 3 has published a technical report while waiting for the development of alternative methods. In the time of the writing the technical report, CFC-113 was typically used in the extraction followed by determination by infrared spectrometry or gas chromatography detection. [146]

NEN 5733
In the Netherlands, a gas chromatographic method exist for sediment: NEN 5733 Bodem; Bepaling van het gehalte aan minerale olie in grond en waterbodem met gaschromatografie. (Soil; Determination of mineral oil content in soil and sediments with gas chromatography).

Experiences
The GC method NEN 5733 and abandoned infrared method NEN 6675 were compared in the determination of hydrocarbons in the sediment. The results obtained by determi-

nation with gas chromatography analysis were found to be about 20 % higher compared to the IR method (range + 6 to +32 %). Causes for the differences were not found. Following modifications to improve the performance were suggested: repeated removal of co-extracted dissolved organic carbon (DOC), use of pentane instead of CFC-113 as extraction solvent, and alkaline aqueous washing (back-extraction) of extracts to remove small to medium size acidic co-extractants. However, the results thus obtained were not essentially different from those obtained with the standard method, and it was understood that the performances of the GC and IR method are comparable in applications above the determination limit of the latter method. [147]

In a Swedish study, with relatively small amount of samples, a correlation between total organic content (TOC) of sediment and some hydrocarbon fractions was noticed. GC/FID or GC/MS methods are recommended for environmental monitoring. [146]

3.7 Waste

prEN 14039 and prEN 14345

A European standard prEN 14039 for waste (Characterization of waste – Determination of hydrocarbon content in the range of C_{10} - C_{40} by gas chromatography) is under development. It is currently being proposed as an European standard. Also another proposed standard, prEN 14345 (Characterization of waste. Determination of hydrocarbon content by gravimetry.) is under development.

Leaching of mineral oil from waste has been evaluated by Dutch RIVM. A column test and serial batch test for mineral oil are intended for the investigation of the emissions of the heavy fraction $C_{18...40}$ of mineral oil. [148, 149]

4 Possible substitute methods for other determinations and purposes

4.1 General

Of the 47 determinations earlier used in the Nordic countries some have been already substituted, and some will be substituted soon. No further efforts were put to evaluate these methods. Some methods are used to determine oil in other sample mediums than water. The project tried to recognize possible substitute methods for methods using ODS still in use. Also some substitute methods already applied by the laboratories are described in this chapter, likewise comments on the substitutability of some methods. Possible substitute methods were searched from the homepages of some national and international standardization institutes, and in the EPTIS database [150]. Also contact persons of standardization committees, and representatives of some laboratories were contacted.

The list of substitute methods is not comprehensive and does not guarantee the practical applicability and performance properties of the method for each individual use purpose, sample matrix or quantitation requirement. Additional methods and draft methods can be available by various standardization organizations like ISO, CEN, ASTM, DIN, NEN, BSI, SIS, SFS, DS and NSF [151].

In some cases, for example, when the determination requires additional laboratory equipment like a centrifuge, laboratories have had difficulties to find equipment suitable to be used with flammable substitute solvents. The flammability and possible adverse health effects and the possible exposure to noxious substances are major concerns with some substitute substances.

A summary of possible substitute methods is in table 4.1. Some of these possible substitute methods use ozone depleting substances, but the method standard gives a possibility to use other solvents instead of ODS. The applicability of these possible substitute methods for specific sample types and determination cases has to be evaluated case by case. Some further information on the substitutability of methods is given in Chapters 2.4. and 2.5.

Table 4.1. Possible substitute methods.

COUNTRY OR ORGANIZATION	PRINCIPLE	METHOD
Determination of grease in wastewater		
Denmark	Gravimetry	Modification of DS/R 208.

Sweden	Gravimetry	SS 02 82 11 Vattenundersökningar - Bestämning av fetthalten (totalhalten fett, emulgerat och avskiljbart fett) i avloppsvatten från livsmedelsindustrin - Gravimetrisk metod. (Water analysis - Determination of fats in waste waters from food processing industries - Gravemetric method)
USA	Gravimetry	EPA Method 1664A.
Determination of TOC in water		
ISO		Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis).
Sweden		SS 02 81 99 Vattenundersökningar – Riktlinjer för bestämning av totalt organiskt kol (TOC) i vatten. (Guidelines for the determination of total organic carbon (TOC) in water)
Determination of oil and hydrocarbons in air		
Sweden	Gravimetry	SS 028427 Luftundersökningar - Utsläpp till luft - Bestämning av koncentration och massflöde av kolväteföreningar (aerosol- och gasform) i gaskanaler. (Air quality - Stationary source emissions - Determination of the concentration and mass flow of hydrocarbons (aerosol and gas phase) in ducts).
Various unstandardized methods	GC/FID, GC/MS, fluorescence spectrometry	Absorption of oil and hydrocarbons on various filters, sorbents, charcoal tubes, followed by extraction and determination by GC/FID, GC/MS or fluorescence spectrometry.
Testing of breathing filters		
CEN		EN 141:2000 Respiratory protective devices - Gas filters and combined filters - Requirements, testing, marking.
Determination of oil, wax or paraffin traces on surfaces and determination of surface cleanliness		
ISO		ISO 8502 Standard series (being prepared)
Nordtest		NT POLY 181 Determination of oil on surfaces (note: a sampling method, a determination method not included)
Determination of phenol impurities		
ASTM	GC	D4961-99 Standard Test Methods for Gas Chromatographic Analysis of Major Organic Impurities in Phenol Produced by the Cumene Process. (Note: also in-house modifications are used)
Determination of bromine index in oil or chemicals (note: also in-house modifications are used)		
ASTM	Electrometric titration	D1159-01 Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration.
ASTM	Coulometric titration	D1492-02 Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration.
ASTM	Electrometric titration	D5776-99 Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration.
ASTM	Electrometric titration	D2710-99 Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration.
Instrumentation suppliers		Various instrumentation specific methods.
Determination of moisture and water content in various sample types (examples of methods)		

ISO	Heating	ISO 662:1998. Animal and vegetable fats and oils - Determination of moisture and volatile matter content.
ISO	Entraiment	ISO 934:1980. Animal and vegetable fats and oils - Determination of water content - Entrainment method.
ISO	Karl Fischer	ISO 8534:1996. Animal and vegetable fats and oils - Determination of water content - Karl Fischer method.
ISO	Karl Fischer	ISO TC 34 SC 11 proposal. (being prepared)
ISO	Potentiometric Karl Fischer	ISO 6296:2000. Petroleum products - Determination of water - Potentiometric Karl Fischer titration method.
ISO	Coulometric Karl Fischer	ISO 12937:2000. Petroleum products - Determination of water - Coulometric Karl Fischer titration method.
ISO	Distillation	ISO 3733:1999 Petroleum products and bituminous materials - Determination of water - Distillation method
BS/ISO	Potentiometric Karl Fischer	Draft British Standard BS EN ISO 6296 Petroleum products - Determination of water - Potentiometric Karl Fischer titration method (ISO/DIS 6296). Draft for Public Comment.
Instrumentation suppliers		Various instrumentation specific methods.
Environmental stress cracking of plastics		
-	-	-
Determination of Iodine value in fats and edible oils (examples of methods)		
ISO		ISO 3961:1996. Animal and vegetable fats and oils - Determination of iodine value.
DGF		Iodine Value according to Hanus. Cyclohexane/glacial acetic acid method. DGF Standard Methods. Section C - Fats. C-V 11a(02)
DGF		Iodine Value. DGF Standard Methods. Section C - Fats. C-V 11 (02)
DGF		Iodine Value according to Kaufmann. Cyclohexane/glacial acetic acid method. DGF Standard Methods. Section C - Fats. C-V 11b(02)
DGF		Iodine Value according to Wijs. Cyclohexane/glacial acetic acid method. DGF Standard Methods. Section C - Fats. C-V 11d(02)
DGF		Iodine Value according to Wijs. Modified Hofmann and Green Method. DGF Standard Methods. Section C - Fats. C-V 11e(02)
Determination of phthalates in plastic foils		
-	GC/MS	Possibly modified in-house methods.
Determination of pregnanetriole		
		Radio immuno assay (RIA)
		Immunoradiometric assay (IRMA)
Determination of flavors		

	Various determination techniques	Modification of present method, change of solvents and determination method, ISO methods being prepared.
Chromatographic separation of chlorophyll derivates		
		In-house modification of present method: change of solvents and repeated extractions.
Determination of oil in compressed air		
-	-	-
Determination of metals in groceries and seawater with extremely low detection limits		
-	-	Possibly use of HRGC/HRMS in future.
Determination of coccidiostats in muscle and eggs		
		Possibly use of more sophisticated MS-methods in future.
Determination of finishing materials and lubricants applied to synthetic fibres and determination of fibre treatment chemicals		
		NMR, however, FTIR using ODS still required in calibration.
Determination of particle size and particle content in oil		
ISO	Coulter	ISO 13319:2000 Determination of particle size distributions - Electrical sensing zone method
Instrumentation suppliers	Coulter	
		ISO TC 131 SC 6 (methods being prepared, applicability uncertain)
Determination of phenol in water		
ISO	4-aminoantipyrine spectrometry	ISO 6439:1990. Water quality - Determination of phenol index - 4-Aminoantipyrine spectrometric methods after distillation.
ISO	FIA and CFA	ISO 14402. Water quality - Determination of phenol index by flow analysis (FIA and CFA)
ISO	GC/FID or GC/ECD	ISO 8165-1:1992. Water quality - Determination of selected monovalent phenols - Part 1: Gas-chromatographic method after enrichment by extraction
ISO	GC/ECD	ISO 8165-2:1999. Water quality - Determination of selected monovalent phenols - Part 2: Method by derivatization and gas chromatography
SFS/DS/NS/SIS	4-aminoantipyrine spectrometry	SFS 3011. Veden fenolien määritys. (Determination of phenolic compounds in water) (Note: Method should be consistent with DS 281, NS 4738 and SIS 02 81 28)
U.S.EPA	4-aminoantipyrine spectrometry	Method 9065. Phenolics (spectrophotometric, manual 4-AAP with distillation)
U.S.EPA	Colorimetric	Method 9066. Phenolics (colorimetric, automated 4-AAP with distillation)
U.S.EPA	MBTH spectrometric	Method 9067. Phenolics (spectrophotometric, MBTH with distillation)

4.2 Determination of grease in wastewater

In addition to the EPA method 1664A and the gravimetric methods described in the section on the determination of the hydrocarbon index, two other substitute methods were recognized.

In Denmark, the use of the gravimetric method DS/R 208 modified to use pentane is recommended for the analysis of fatty wastewater in a project measuring oil in wastewater. The method should be used only for wastewater tests, in which the majority of the extractable compounds consists of fat, e.g. from the food industry. The volatile compounds with boiling point under 140 – 150ºC are lost in the procedure. The detection limit is 2 – 5 mg/l. The limit value for oil and grease in wastewater by Miljøstyrelsen is based on this gravimetric method. When recoveries achieved by pentane, carbon tetrachloride and CFC-113 extractions were compared for oil and grease, it was measured that the recovery with CFC-113 was in average 70 % (29 % - 110 %) of the recovery achieved with carbon tetrachloride, and the recovery obtained with pentane was in average 80 % (26 – 107 %) of the recovery measured with carbon tetrachloride. The recovery rates with CFC-113, pentane, and carbon tetrachloride extractions were in average 58 %, 54 % and 65 %, respectively. [42]

In Sweden, the standard SS 02 82 11 has substituted the former method SS 02 81 44. SS 02 82 11 is a gravimetric method for determining grease in wastewaters from food industry. The practical detection limit is about 5 mg/l and the highest measurable concentrations approximately 5000 mg/l. The accuracy and precision is ±10 % with concentrations of 500 mg/l. The method determines the total grease content, emulsified grease, and separable grease. In the method the sample is left to stand for 24 hours. Separable grease flotates or sediments. A sample is taken from the middle layer. The sample is shaked with petroleum ether followed by a separation of phases. The filtrate can be filtered through a paper filter or fiberglass. Emulsion can be breaked with centrifugation. Sample flask is put into a water bath with temperature of 60ºC, and petroleum ether evaporated with nitrogen. The rest moisture is evaporated in a temperature cabinet (70ºC). The flask is cooled in a desiccator, and weighted. The separable grease content is the total grease content subtracted by the emulsified grease content. The method SS 02 82 11 has been understood to be more appropriate than the IR method SS 02 81 03 for the determination of grease in some abattoir wastewaters, which might include high concentrations of organic acids. However, losses of volatile organic compounds with boiling point under approximately 150ºC may appear with the method SS 02 82 11. [152, 153]

4.3 Determination of TOC in water

For the determination of TOC, methods ISO 10694:1995 Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis), and SS 02 81 99 Vattenundersökningar – Riktlinjer för bestämning av totalt organiskt kol (TOC) i vatten (Guidelines for the determination of total organic carbon (TOC) in water) were mentioned as substitute methods by the laboratories that responded to the questionnaire.

4.4 Determination of oil and hydrocarbons in air

An American NIOSH method utilizing ozone depleting substances and IR spectrometry is used for the determination of oil mist in air for occupational hygienic purposes . There is no ongoing work in NIOSH to try to find substitutes for the ODS [154]. However, some laboratories have modified the NIOSH method by using tetrachloroethylene instead of ODS, and have achieved good results by changing the filter disk material.

Several methods are described in the Toxicological profiles by the U.S. Agency for Toxic Substances and Disease Registry [155, 156]. For example, mineral-based crankcase oil can be collected on a membrane filter, extracted with chloroform (trichloromethane) and determined with fluorescence spectrophotometry. However, no information on the detection limit is available, and the applicability of the methods is unknown [156]. Total petroleum hydrocarbon components can be adsorbed on solid sorbents, desorbed and determined by GC/FID, or GC/MS. Separate methods are available for gasoline vapor [157]. Particulates and gases can be captured on Teflon filters and charcoal tubes, exctracted with hexane (filters) and carbon disulfide (charcoal tubes) and analyzed with GC/MS. However, methods are not necessarily standardized, and the results may depend on the method used. Because the limit value is probably based on epidemiological results and is possibly method-specific, no substitute methods can be recommended without further investigation. When using a substitute method, it should be assured that the substitute method gives results comparable to the standard method and limit values.

For the determination of contaminants in air, method SS 028427 Luftundersökningar - Utsläpp till luft - Bestämning av koncentration och massflöde av kolväteföreningar (aerosol- och gasform) i gaskanaler - Air quality - Stationary source emissions - Determination of the concentration and mass flow of hydrocarbons (aerosol and gas phase) in ducts (gravimetric method), was mentioned as a substitute method.

4.5 Testing of breathing filters

In the testing of breathing filters (personal safety equipment) a substitute European standard method EN 141:2000 exists [151]. However, ozone depleting substances have to be used since an U.S. client demands the use of an U.S. method according to 42 CFR part 84 that utilizes ozone depleting substances.

4.6 Determination of oil, wax or paraffin traces on surfaces and determination of surface cleanliness

Determination of oil, wax or paraffin traces on surfaces is used in various quality control procedures. In ammunition production the quality demands are of very high level, since even very small traces of oil may change the delay times of explosives. A gas chromatographic method is understood to be impractical.

In the determination of wax on surfaces carbon tetrachloride has been substituted with xylene extraction and an ultrasound bath, followed by a concentration step with vacuum rotation.

It is understood that infrared sensor systems for the measurement of oil film thickness don't typically reach detection limits achieved by using the ozone depleting substances. However, one laboratory has achieved very low detection limits in the determination of carbon on surfaces by using a commercial sulfur/carbon determinator.

ISO 8502 standard series gives several methods for the determination of surface cleanliness, for example, before painting. Part 6 (a method to extract soluble contaminants), and part 7 (a field method for determination of oil and grease) are under preparation. Unfortunately the work on part 7 has started over seven years ago, and no DIS has been presented [158]. Various methods are described in DIN Technical Report 28 [159]. Part 6 uses flexible cells in the form of adhesive patches designed to be filled with a solvent. However, the standard does not give test methods for the determination of a specific contaminant on the surface, or describe any performance properties [160].

The Nordtest method NT POLY 181 Determination of oil on surfaces is a field test using a sampling procedure based on the Bresle method in ISO 8502-6, and cyclohexane as the extraction solvent. Oil in the sample is brought to contact with an aqueous phase containing sulphuric acid and dipotassium dichromate. The reduction of the dichromate ion by the oil residues induces a colour change, and visual observation is used to assess the amount of oil in the sample. The colour of the aqueous phase is compared to known reference samples [161].

4.7 Determination of phenol impurities

The quality demands on product phenol are high, and determination of impurities a demanding task. A gas chromatographic method ASTM D 4961 and its in-house modifications offer alternatives for methods using ODS [162]. Various solvents have been considered to substitute the ozone depleting substances, but the use of alternatives can be impractical in a quality control.

4.8 Determination of bromine index in oil or chemicals

It is possible to use alternative solvents in potentiometric titration of bromoreactive impurities containing double and triple bonds (determination of so called 'bromine index' according to, for example, ASTM D 1159, ASTM D 1492, ASTM D 5776 and ASTM D 2710 or their modifications [163-166]) in various oil products, but the implementation typically requires some research work.

In standard ASTM D 1492 the electrolyte solution is prepared of glacial acetic acid, methanol and KBr solution. ASTM D 2710 gives the user a possibility to choose between 1,1,1-trichloroethane (an ozone depleting substance) or dichloromethane. Also mercury acetate is dissolved in the mixture.

Different methods are applicable for different kinds of oil products, bromine number and amounts of olefins in the product, especially for petroleum hydrocarbon mixtures of bromine number less than 1. [163]

For example, the method ASTM D 1159 is generally applicable for gasoline, kerosene and distillates in the gas oil range that fall in specific distillation and bromine number limits. However, the method is not satisfactory for normal alpha-olefins. The method can be used to estimate the percentage of olefins in petroleum distillates boiling up to

approximately 315ºC by using a calculation method described in the standard. Dichloromethane is temporarily being allowed as an alternative to 1,1,1-trichloroethane (an ozone depleting substance) until a permanent substitute can be identified and adopted by ASTM. A program to identify and evaluate candidate solvents is currently underway in the Subcommittee D02.04. [163]

In a Metrohm method No. 177/3 e for e.g. Titrono instruments carbon tetrachloride and 1,1,1-trichloroethane can be substituted by diethyl carbonate. Glacial acetic acid, carbon tetrachloride, methanol and H_2SO_4 for aliphatic hydrocarbons, or glacial acetic acid, 1-methyl-2-pyrrolidone, methanol and H_2SO_4 are otherwise used for samples with mainly small consumption of bromine, and glacial acetic acid, 1,1,1-trichloroethane, methanol and H_2SO_4 for samples with mainly large consumption of bromine. The method is described by an instrumentation supplier. It is an automated method for the determination of the bromine index and/or the bromine number in petroleum products. [167]

It seems that some standards, like BS 2000 : Part 129 : 1993, a British colour indicator titration method for the determination of bromine number, still mention an ozone depleting substances, like 1,1,1-trichloroethane in this case, in their text. [168]

4.9 Determination of moisture and water content

Several substitute methods are available, however, their applicability for specific use purposes has to be determined case by case. ISO 662 for the determination of moisture in animal and vegetable fats and oils involves heating the sample. The method ISO 934 uses xylene as an entrainment solvent [169-171]. More sophisticated methods, like determination by pulse nuclear magnetic resonance, have been standardized only for some materials, e.g. oilseeds.[172, 173]

Several Karl Fischer methods are available. ISO 8534 uses hydranol or alternatively pyridine as solvent. The most recent proposal by ISO TC 34 SC 11 includes stopping the use of pyridine completely [174]. For petroleum products the ISO 6296 provides a potentiometric method for the direct determination of water in petroleum products boiling below 390ºC. It covers the mass fraction range from 0,003 % (m/m) to 0,100 % (m/m). The method may be applicable also for petroleum products boiling above 390ºC, and lubricating oils, but the precision has not been established for these materials. There are various Karl Fischer reagents to be utilized in this method, and they ought to be free of ozone depleting substances [175]. Another example is ISO 12937, which gives a coulometric Karl Fischer titration method for similar petroleum hydrocarbons than in the ISO 8534. These Karl Fischer methods use xylene with other Karl Fischer reagents. [176]

A draft BS EN ISO standard (ISO/DIS 6296) is under preparation. The method is a potentiometric Karl Fischer titration method for the direct determination of water in petroleum boiling below 390ºC covering the mass fraction range 0,003 % (m/m) to 0,100 % (m/m). It is not applicable to residual fuel oils. The method uses xylene with a pyridine-containing or a pyridine-free Karl Fischer reagent, or with a Karl Fischer reagent specially formulated for ketones. [177]

Further recommendations on solvents are given for dozens of substances and products, by instrument suppliers, e.g. Metrohm. Fats, oils, tars, xanthates, dithiocarbamates and hydrocarbons are insoluble in methanol, and therefore chloroform (trichloromethane)

and trichloroethylene are typically used as mixtures with methanol [178, 179]. According to another laboratory application supplier, Mettler Toledo, mixtures of toluene can be used for the determination of humidity in waxes and tar products, and mixtures of 1-decanol, hexanol and dodecanol for oil, edible oil, gasoline, diesel oil and kerosene samples [180]. However, trichloroethylene and chloroform are volatile and harmful solvents, regulated by legislation. Their use is banned or restricted in some countries, like in Sweden, for professional use [181]. They are considered as substances with medium toxicity.[182]

For the determination of larger amounts of water in petroleum products, other methods not using ozone depleting substances are available. For example, BS 2000-74 (ISO 3733:1999) is able to determine up to 25 % of water in petroleum products and bituminous materials by distillation. In this method, the test material is heated under reflux with a water-immiscible solvent, which is co-distilled with the water in 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 still. Solvents can be aromatic, petroleum distillates or paraffinic depending on the test material. Method gives a repeatability of 0,1 ml and reproducibility of 0,2 ml for 0,0 – 1,0 ml water collected, and 0,1 ml or 2 % of the mean, and 0,2 ml or 10 % of the mean for 1,1 – 25 ml water collected, respectively [183].

4.10 Environmental stress cracking of plastics

In the determination of environmental stress cracking of plastics the solvent used is material specific. 1,1,1-trichloroethane is one solvent used in these determinations. It might be impracticable to substitute use it with any other solvent.

4.11 Determination of iodine value

The Iodine value expresses the content of compounds with unsaturated carbon-carbon double bonds. It is determined by adding a halogen, e.g. iodine to the sample. Also some carotenoids, aldehydes and ketones can react with halogens. There are several methods to determine the iodine number in animal and vegetable fats and oils, fatty acids and fatty alcohols. For some determinations a method utilizing ozone depleting substances is required by the European Pharmacopeia [184].

In the determination of the iodine value according to Hanus the sample is dissolved in cyclohexane and acetic acid and diluted with iodine monobromide solution. Potassium iodide and water are added, and the formed iodine is titrated back with sodium thiosulphate solution. The methods according to Wijs and Kauffmann slightly differ from the Hanus method. Information on the accuracy of the methods is given in the test methods. Only in the case of some oils with a high iodine value can the results deviate from one another. Cyclohexane and acetic acid have generally substituted chloroform (trichloromethane, not an ozone depleting substance) and carbon tetrachloride. Also ISO 3961:1996, which is similar to the Wijs method, uses cyclohexane and acetic acid. The modified Hofmann and Green method allows a shorter reaction time, and is recommended for samples containing hydroxy fatty acids because the substitute reactions occurring in this case using the Wijs method do not take place. [170, 185-189]

In one laboratory, chloroform had been substituted by carbon tetrachloride (an ozone depleting substance) in the determination of iodine value due to chloroform's carcinogenic properties.

4.12 Determination of phthalates

The draft standard ISO 18856 (Water quality – Determination of selected phthalates by gas chromatography/mass spectrometry) is under development.

4.13 Determination of pregnanetriole

For clinical determination of pregnanetriole, i.e. 17-hydroxyprogesterone, various immunoassay methods exist. These assays are based on RIA (radio immuno assay) or IRMA (immunoradiometric assay), and depending on the method may require use of ozone depleting substances. Alternative methods for ODS use typically diethyl petroleum ether or ethyl acetate as a solvent. The most sophisticated methods use gas or liquid chromatography and mass spectrometry.

4.14 Determination of flavors

In order to analyze flavor, methods using solid phase extraction and solid phase microextraction (SPME) and headspace gas chromatography are applied. Other determination methods possible include mass spectrometry (GC/MS), time-of-flight mass spectrometry (TOFMS), MS/MS, atmospheric pressure chemical ionization (APCI/MS), proton-transfer-reaction PTR/MS, resonance-enhanced multiphoton ionization/time-of-flight (REMPI/TOFMS), infrared spectrometry (IR) and nuclear magnetic resonance spectroscopy (NMR). For the determination of chiral properties multidimensional gas chromatography (MDGC) has been used. The extraction phase, needed in the determinations, may form a problem.

It is probable that there will be suitable substitute extraction solvents and methods, and determination techniques available for most of the flavor components, because the separation of volatile compounds is usually achieved by gas chromatography. However, in some cases several pre-separation techniques have to be used. Several methods are standardized or being standardized by the ISO. The applicability of the methods for all determination and sample types is unsure.

4.15 Chromatographic separation of chlorophyll derivates

Liquid chromatography for the separation of chlorophyll derivates is basically possible with other solvents than ODS, but the separation rate is lower, and the separation should be performed several times in order to get products of the same purity. This increases the amount the substitute chlorinated solvents used and increases the price of the final product.

4.16 Determination of oil in compressed air

In the quality control of compressed air according to the ISO 8573:2 [190], the laboratory's experience is that carbon tetrachloride cannot be substituted with any other solvent. No information was obtained whether the standard has been or will be updated.

4.17 Determination of metals in groceries and seawater

For the extraction of heavy metals from grocery and seawater samples, several alternative extraction solvents like n-heptan and methyl-iso-butylketone are available. There are also several standardized techniques for the determination of metals in the environment and food. None of these achieve as low detection limits as the freon extraction technique. Therefore they are not applicable for the determinations of metals in extremely low concentrations in groceries and seawater. These determination methods are applied only in a very few laboratories.

In the determination of metals in seawater, a high resolution gas chromatography – mass spectrometry (HRGC/HRMS) with an extremely low detection limit could be an alternative method in the future.

4.18 Determination of coccidiostats

The monitoring of coccidiostats (a type of fodder supplements having medicinal properties), like Monensin, Narasin, Salinomycin, Lasalocid and Toltrazuril, is required by the Directives 96/23/EC and 90/2377/EC. If needed, screening tests can be applied. Typical high-quality methods used in the actual determination process are high pressure liquid chromatography (HPLC) with a fluorescence detector, or LC-MS/MS with various detection techniques like APCI (Atmospheric Pressure Chemical Ionization) and ES (electrospray ionization). These methods give a possibility to analyze traces of veterinary medicines below maximum residue limits (MRL-values), which are of magnitude 4 – 25 µg/kg [191]. The use of substitute solvents, e.g. acetonitrile, has been described in the literature, but their applicability for all coccidiostats and sample matrixes is unclear [192]. The present method for coccidiostat analysis has been planned to be substituted by a more sophisticated mass spectrometric method.

4.19 Determination of finishing materials and lubricants applied to synthetic fibres and determination of fibre treatment chemicals

Typically CFC-113 (an ozone depleting substance) or perchloroethylene (tetrachloroethylene, not an ozone depleting substance) are used as solvents to extract finishing materials and lubricants from synthetic fibres before infrared spectrometric detection.

Measurement technologies using, for example, hexane are available. The weighed sample is shaken with a known volume of hexane solvent. A small sample is drawn from the test tube and deposited on an IR card. The solvent is evaporated, and the residue is measured by infrared absorption. Sample holders with recessed sapphire windows have been used in technique. The accuracy and applicability of the method is unknown [193].

In the method, the extraction solvent has to be much more volatile than the substances to be determined, e.g. the finishing materials.

In a laboratory, a NMR method is going to substitute a FTIR method previously used for the determination of fiber treatment chemicals. However, the FTIR method and an ozone depleting substance are still needed in the calibration of the substitute NMR method.

4.20 Determination of particle size and particle content

High purity of oils is extremely important for hydraulic and various other systems. For example, in insulating mineral oils formation of insoluble decay products are capable of decreasing the breakdown voltage of oil, and clogging the pores of paper insulation [194].

There might be substitute methods for the determination of the particle content and particle size distribution in oil materials. Methods for the measurement of particular contamination in oils are developed in the ISO Technical Committee 131 Fluid Power Systems SC 6 Contamination control. However, their applicability and the possibility to use them without ODS in various determinations is unclear.

Commercial equipment based on laser techniques is available. Magnetic metal particles can be separated with magnetic or electromagnetic fields. X-ray diffraction methods can determine metal particles bigger than 10 μm. Some gravimetric methods filter the oil. Other methods are available for the determination of sediment in oil. For example, BS EN ISO 3735:1999 extracts a test portion of crude petroleum or fuel oil in a refractory thimble with hot toluene until the residue reaches constant mass. The method is suitable for samples with 0,01 – 0,4 % (m/m) of sediment [195].

The electric sensing zone (Coulter) principle has been used for the determination of particles [194]. Particles as small as 0,4 μm and as large as 1200 μm in diameter can be measured with technique. For the determination of particles in oil, ammonium thiocyanate in isopropyl alcohol –electrolyte solution is suitable for the majority of oils with the Coulter counter, and methyl isobutyl ketone can be used for oils not soluble in isopropyl alcohol [196]. The Coulter method is described in the standard ISO 13319 and the subject in various ASTM standards [194, 197]. For example, the standard ISO 4406 requires the determination of the level of contamination with solid particles [198].

The applicability of these methods has to be determined separately for each use purpose.

4.21 Determination of phenol in water

Various methods exist for the determination of phenol index in water. Method established in ISO 6439:1990 (Water quality – Determination of phenol index – 4-Aminoantipyrine spectrometric methods after distillation) measures phenolic compounds with direct colorimetric method in test samples that contain more than 0,1 mg/l in the aqueous phase. With chloroform (trichloromethane) extraction, without dilution, it is possible to determine the phenol index from about 0,002 mg/l to about 0,10 mg/l. However, not all phenol compounds react with 4-aminoantipyrene and substances containing multiple phenol groups may react with several 4-aminoantipyrine molecules [199].

ISO 14402:1999 (Water quality – Determination of phenol index by flow analysis (FIA and CFA)) specifies two methods for the determination of phenol index in waters of different origin, such as ground, surface, seep and wastewaters, in mass concentrations of 0,01 mg/l to 1 mg/l (in the undiluted sample). The method 14402 is suitable for the processing of large sample series at a high analysis frequency. Clauses for the determination of the phenol index (without distillation) after extraction and (without extraction) after distillation are given [200].

Selected monovalent phenols can be determined according to ISO 8165-1:1992 (Determination of selected monovalent phenols – Part 1: Gas-chromatographic method after enrichment by extraction). The method is able to determine phenols in a concentration range from 0,1 µg/l to 1 mg/l using diethylether extraction and enrichment of the phenolic compounds. GC/FID or GC/ECD in case of polychlorinated phenols is used [201]. Other method in the standard series is ISO 8165-2:1999 (Determination of selected monovalent phenols – Part 2: Method by derivatization and gas chromatography uses extractive derivatization by means of hexane and pentafluorobenzoyl chloride followed by a gas chromatographic measurement using two capillary columns of different polarity (simultaneous splitting) and detection with electron-capture detectors (ECD). Amines and in some cases alcohols may also react in the method, and therefore it is not applicable in all cases to the examination of waste water [202].

Also national standard SFS 3011 (1976-03-26), which should be consistent with standards DS 281, NS 4738 and SIS 02 81 28, gives a method for determination of phenolic compounds in water. Method uses 4-aminoantipyrine in the presence of potassium ferricyanide to produce a coloured substance that can be measured spectrophotometrically. Chloroform (trichloromethane) is used if the sample is determined by using extraction instead of direct determination. Diethyl ether can be used instead of chloroform. [203]

Various methods are given for the determination of phenolics by the U.S.EPA. EPA method 9065 is a spectrophotometric method using reaction of phenolic materials with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH 10. Method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes. The method is capable of measuring phenolic materials that contain more than 5 – 50 µg/l [204].

EPA method 9067 is a spectrophotometric method based on the coupling of phenol with MBTH in an acid medium using ceric ammonium sulfate, i.e., ammonium hexanitratocerate (IV), as an oxidant. Method is applicable of measuring phenolic materials that contain from 50 – 1000 µg/l, or even at the 2 µg/l level. Method is applicable to samples similar to in the method 9065 [205].

EPA method 9066 can be used for the analysis of phenolic materials from 2 to 500 µg/l in ground water and of drinking, surface, and saline waters. The method is a colorimetric method based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide and 4-amino-antipyrine [206]. Chloroform can be used in concentrating extractions. A preliminary distillation may be required to remove interfering materials. A gas chromatographic method is presented in the method 8041. [207]

4.22 Determination of peroxide number in jet fuel

An UOP method is a possible substitute method [208]. In the UOP method sample reacts in a iron(II)thiocyanate solution. The result, ferric (III) ion is titrated with titanium chloride solution. Thiocyanate is used as indicator. However, the applicability of the method for jet fuel is uncertain.[209]

4.23 Determination of additive in jet fuel

Determination of tall oil fatty acid additive has strict requirements in the Nato Standardization Agreements STANAG 3747. The IR method has been substituted, because it measured also genuine acids in the fuel, like naphthenic acids, in addition to the tall oil fatty acid additive. Gel permeation chromatography (GPC), followed by determination with refractive index detector has been used as a substitute method. The GPC method is described in Nato Standardization Agreements STANAG 3390, edition 7, Annex C. However, the GPC method using methanol as mobile phase has been problematic and resulted in poor accuracy and detection limits. It is understood that the primary use of corrosion inhibitor is for lubricity improvement. Therefore the determination of corrosion inhibition has been abandoned in some places, and the GPC method has been substituted with Ball-on-Cylinder Lubricity Evaluator (BOCLE) method ASTM D 5001 . The BOCLE method measures the lubricity properties and fulfills the criteria in MIL-PRF-25017. However, the BOCLE is not suitable to measure actual amounts of additive added, however, it seems to be sufficient for quality assurance since lubricity is main purpose for the corrosion inhibitor. [210-214]

Several ISO and ASTM tests [215-217] for other sample types and a U.S. EPA gel permeation cleanup method for other substances exist, but their applicability is uncertain. The determination of longer-chained fatty acids the choice of HPLC/GPC or GC columns and operating parameters is a challenge. Typically fatty acids are methylated into esters to improve their volatility, and separated in a gas chromatograph. Esterification can be done with diatsomethane. However, it is a carcinogenic substance. Another suggestion is to use ether or ethyl acetate in extraction instead of carbon tetrachloride, use methanol with small amount of sulphuric acid in esterification , refluct the sample over night, neutralize the sample very carefully with sodium bicarbonate, and concentrate it to 1 – 2 milliliters. After this phase, it is possible to separate dimers and monomers with column chromatography to improve specificity, if needed. The solvent can be evaporated before GPC or determination with direct injection MS. If ethyl acetate is not used or it is cleaned of, determination with IR spectrometry is possible. Instead of using cuvettes, for example, a residual film can be measured. Because determination with IR does not require preparation of methyl esters, an IR determination can be tried straight after extraction with ether or ethyl acetate and evaporation of solvent. [218-220]

Use of supercritical fluid extraction/reaction (SFE/SFR) followed by capillary supercritical fluid chromatography (GC/SFC) is another possible substitute method, but the performance properties of the method are unknown. It remained unsure whether the use of other solvents, for example chloroform or tetrachloroethylene, in the IR determination is possible.

CEN/TC 19 is preparing several methods for fatty acid methyl esters (FAME) in various fuels [221]. In the painting industry, saturated and oxidized fatty acids are identified

using on-column GC/MS and Curie-point Pyrolysis-TMAH-GC/MS [222]. Various other methods for determination of fatty acids in food, feed and human body are available [221]. The applicability of these methods is uncertain.

5 Possible substitute substances

It was emphasized that various substitutes to the ozone depleting substances, are harmful or even dangerous to health or environment. This kind of properties are not presented in this report, and laboratories should take necessary precautions to minimize risks exposed by the substances. For example, n-hexane is flammable and may cause adverse effects to health. The use of some substances, e.g. tetrachloroethylene, presented in this report are not allowed in some countries, but may have been allowed in other countries, where research on true exposure and strict occupational hygienic regulations have diminished health risks into minimum. Some of the halogenated substitute compounds are suspected to have ozone depleting capabilities, but are not yet officially recognized or restricted, as such.

Extraction solvents typically applicable to substitute ODS are mentioned in the standard operation procedures, and therefore a comprehensive list on them is not gathered in this project. Some typical substitute solvents are mentioned on the whole. Volatile halogenated solvents can be used in the determination of non-volatile hydrocarbons, where the solvent is evaporated before final quantitation in infrared spectrometric determinations. If the solvent used cannot be volatilized, it must not contain carbon – hydrogen – bonds .

Hexane and **pentane** are the most typical substitute substances used in the oil-in-water determination. Both of them are typically used as substitute extraction solvents in gas chromatographic methods. The advantage of pentane is the lower loss of volatile compounds during sample concentrations, which enables the analysis of lower hydrocarbon fractions, beginning from C_7. However, in a GC/FID comparison with other extractants, it was less robust because of its volatility. [21]

Few laboratories mentioned also **heptane** as a extraction solvent for substituting ODS.

Also longer-chained hydrocarbons like **n-decane** were mentioned to be used in gas chromatographic determinations. However, this is possible only with chromatographic separation of samples not containing n-decane themselves.

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) has listed various methods to analyze TPH or TPH constituents. In addition to liquid-liquid – extraction, solvents might be applicable with some other extraction methods, which are sonication, soxhlet, solid phase extraction, super critical fluid, shaking, vortex and separatory funnel. [76]

Methanol is typically used in immunoassays for total TPH and constituent measurements and extraction with shaking or vortex. In addition, methanol is used in purge & trap concentration of BTEX and gasoline followed by a gas chromatographic analysis. [76]

Hexane, **dichloromethane** (methylene chloride), **carbon disulfide** and **ethyl acetate** are used for diesel, jet fuel, lubricating oil and miscellaneous oils in liquid-liquid extraction before a gas chromatographic determination.[76]

In ASTM D 2710 method , dichloromethane was able to substitute 1,1,1-trichloroethane. Dichloromethane was used also in the determination of surface coatings of fertilizers and in a Soxhlet extraction.

Dichloromethane can be used also as a substitute solvent in separation or extraction by shaking, vortex, soxhlet, sonication, separatory funnel, or solid phase extraction before a gravimetric determination. Dichloromethane and hexane are used in TLC (thin layer chromatography) determinations. For determinations of semivolatile constituents by gas chromatography and mass spectrometry, dichloromethane is used preceded by one of the previously mentioned extraction/separation methods. [76]

Tetrachloroethylene and **hexachlorocyclopentadiene** have been suggested as substitutes. Like carbon disulphide, unfortunately, they are problematic from a health and safety perspective.

According to an evaluation, tetrachloroethylene (TCE, perchloroethylene) was deemed as the least harmful with respect to humans even though repeated exposure to levels above the occupational exposure limit may produce adverse effects on the liver and kidneys [223].

Some laboratories have substituted ozone depleting substances with tetrachloroethylene despite of its hazardous properties for human health and environment. Tetrachloroethylene is a totally halogenated substance with no C-H –bonds. However, it is a suspected carcinogen (Carc. Cat. 3; currently under review and possibly reclassified as Carc. Cat. 2), hazardous to environment, and a very disliked compound for laboratories to use in practice. In the U.S. there has been problems with tetrachloroethylene because it degrades, and the stabilizers needed have carbon-hydrogen bonds that cause interferences in the determinations by infrared spectroscopy. The amount of stabilizers can possibly be reduced by washing the tetrachloroethylene with ionized water.

In the UK, Shell has evaluated the use of tetrachloroethylene for offshore measurements with high quality TCE product, which has the lowest IR absorbtion. It was suggested that the stabilizers are washed from tetrachloroethylene to water phase, which might cause erroneously low oil content results. It was concluded that tetrachloroethylene products stabilized with 4-methylmorpholine are unsuitable for use in the determination of oil content of water, since the oil content measurement could be reduced by ~4 ppm. Other products suffered from stabilizer leaching, but the effect was relatively small resulting in an effective reduction in oil content << 1 ppm well below the detection limit of the method. The alkyl phenol stabilized solvents can be used with a certain degree of confidence. [223].

U.S. EPA has evaluated properties of, for example, **2,2-difluoro-1,1,1-trifluoroethane** and tetrachloroethylene, but neither of these solvents produced results as close to results produced by CFC-113 as did n-hexane. [61]

Some laboratories used also **dichloroethane with carbon disulfid**e for extraction.

Trichloromethane (chloroform) was used in the determination of metals in groceries.

A few laboratories will use other totally halogenated solvents not classified as ozone depleting substances, like **polytrichlorofluoroethene**.

Also other solvents like AK-225, S-316 and Vertrel MCA are available.

Acids were used for TOC (Total Organic Carbon) analysis to make carbon dioxide to evaporate, and a TOC analysator was applied for the determination of hydrocarbons in some extraction fluids. However, the TOC analysator was applicable only for water samples.

Still other substitute substances mentioned were **ethanol** used in the analysis of free fatty acids.

Dimethylether was used in the determination of plasticizers.

Various solvents, like **xylene**, were used to analyze wax on metal surfaces.

S-316 "Flon" (tetrachlorohexafluorobutane, $C_4Cl_4F_6$) is *suspected to be an ozone depleting substance* due to its chemical formula, however, the issue is still under research [96]. S-316 is said by its manufacturer to be environmentally safe. Documentation from the manufacturer was not received during the project.

Vertrel MCA (1,1,1,2,3,4,4,5,5,5-decafluoropentane, HFC 43-10mee) is mentioned to have *a "zero" ozone depleting potential*, low toxicity, and low greenhouse gas effect. It is not transparent at the analytical wavelength used for hydrocarbon, so an aliquot of the extract is placed directly in the measurement trough and the solvent is dried [224]. Vertrel MCA is a volatile HFC solvent, however, it is a hydrocarbon which absorbs infrared and has to be evaporated before the detection. The greenhouse gas properties of this HFC compound remained unclear.

AK-225 is a volatile HCFC solvent with low ozone depletion efficiency. It is *an ozone depleting substance* similarly restricted like other ozone depleting substances. It also may slowly degrade methacrylate in laboratory equipment.

The recovery rate on various hydrocarbons may vary a lot depending on the properties of the solvent used and the properties of the sample media. In practice, results may in some cases vary a lot depending on the solvent and test method used. If significantly different results are received, it is typically suggested to do side-by-side testing with the old and the new method, and possibly use a conversion factor, if it is applicable. In case it is necessary for the results from various sites to be comparable, and the differences between the test methods are not known, it is suggested to use only one test method for all the sites, if possible.

Acknowledgements

Dr. Yang Ming, National Engineering Laboratory (NEL), United Kingdom.
Dr. John Fardon, National Laboratory Service, United Kingdom.
Dr. Ian Roberts, ITS Sunbury Technology Centre, United Kingdom.
Dr. Sean McWhinnie, Royal Society of Chemistry, United Kingdom.
Dr. Derek Woods, Laboratory for Government Chemist, United Kingdom.
Anna Baran, FOSFA International, United Kingdom.
Dr. ir. Theo Noij, Kiwa Water Research, Water Quality and Public Health, the Netherlands.
Dr. Ron Franken, RIVM, the Netherlands.
Dr. Ton van Leerdam, Kiwa Water Research, the Netherlands.
Dr. Paul C.M. Frintrop, Institute for Inland Water Management and Waste Water Treatment (RIZA), the Netherlands.
Dr. Ortwin Costenoble, NEN Energy Resources, the Netherlands.
Dr. Peter Lepom, Federal Environmental Agency, Laboratory for Water analysis, Germany.
Dr. Roland Becker, Bundesanstalt für Materialforschung und –prüfung (BAM), Germany.
Dr. Detlef Lück, Bundesanstalt für Materialforschung und –prüfung (BAM), Germany.
Dr. Christian Gertz, CUA Hagen, Germany.
Mr. Bernd Reinmüller, DIN, Germany.
Dr. Hans-Jochen Fiebig, Bundesanstalt für Getreide-, Kartoffel- und Fettforschung, Germany.
Dr. Klaus Seinsche, Wehrwissenschaftliches Institute für Werk-, Explosiv- und Betriebstoffe (WIWEB), Germany.
Dr. Frank Amoneit, Deutsche Gesellschaft für Fettwissenschaft e.V. (DGF), Germany
Dr. Nick Campbell, Atofina SA, France.
Gail Hansen, US EPA/Office of Solid Waste, the U.S.A.
Rob Davidson, Ethyl Corp., the U.S.A.
Thomas Elam, NASA Propellants management, the U.S.A.
Gene Kennedy, the U.S.A.
Valérie Hourdebaigt, Environment Canada.
Dr. Arne Kvernheim, SINTEF, Norway.
Principal Scientist Jørn Paus, Corporate Research Center, Norsk Hydro ASA, Norway.
Janne Forslund, Miljøstyrelsen, Denmark.
Dr. Göran Engström, Korrosionsinstitutet, Sweden.
Margareta Emilsson, Karlhamns AB, Sweden.
Environmental supervisor Steffen Bach, Mærsk Olie og Gas AS, Denmark.
Senior researcher Anna-Mari Suortti, Finnish Environment Institute, Laboratory, Finland
Senior researcher Kirsti Kalevi, Finnish Environment Institute, Laboratory, Finland.
Special researcher Ritva Niemi, Finnish Environment Institute, Laboratory, Finland.
Chemist Teemu Näykki, Finnish Environment Institute, Laboratory, Finland.
Chemist Kirsti Erkomaa, Finnish Environment Institute, Laboratory, Finland.

Chemist Jari Nuutinen, Finnish Environment Institute, Laboratory, Finland.
Chemist Sami Huhtala, Finnish Environment Institute, Laboratory, Finland.
Expert Susan Londesborough, Finnish Environment Institute, Chemicals Division, Finland.
Senior adviser Magnus Nyström, Finnish Environment Institute, Chemicals Division, Finland.
Senior researcher Olli Lehto, Geological Survey of Finland.
Dr. Liisa Ahola, Medix Laboratoriot, Finland.
Dr. Arto Kajamäki, Yhtyneet Laboratoriot, Finland.
Chemist Ursula Turpeinen, Helsinki and Uusimaa Hospital Group, Finland.
Occupational hygienist Sinikka Vainiotalo, Finnish Institute of Occupational Health, Finland.
Managing director Petter Hyvönen, Oy Hylab Ab, Finland.
Alpo Toivo, Fortum, Finland.
Tuula Hujanen, Fortum, Finland.
Leena Saulo, Fortum, Finland.
Lic.Phil. Ulla-Maija Lakkisto, University of Helsinki, Organic Chemistry, Finland.
Ph.D. Jorma Matikainen, University of Helsinki, Organic Chemistry, Finland.

Especially all the laboratories that responded to the questionnaire.
All the laboratories and other people who provided even further help and information.

The steering group of the project

Eliisa Irpola, Finnish Environment Institute[1)], Finland.

Mikkel Aaman Sørensen, Miljøstyrelsen[2)], Denmark.

Heiðrún Guðmundsdóttir, Umhverfisstofnun[3)], Iceland.

Anne-Margit Bull, Statens forurensninstilsyn[4)], Norway.

Maria Ujfalusi, Naturvårdsverket[5)], Sweden. (until September 2002)

Eva-Lotte Sandin, Naturvårdsverket[5)], Sweden. (from September 2002)

The steering group consists of representatives of national authorities.

[1)] Suomen ympäristökeskus / Finnish Environment Institute

Box 140 / Mechelininkatu 34a
FIN-00251 HELSINKI
FINLAND

Tel. +358 (0)9 403 000 (keskus/central)
Fax. +358 (0)9 4030 0190 (keskus/central)
Kirjaamo: kirjaamo.syke@ymparisto.fi

[2)] Miljøstyrelsen / Danish Environmental Protection Agency

Strandgade 29
DK-1410 København K
DENMARK

Tlf. +45 32 66 01 00 (central)
Fax. +45 32 66 04 79 (central)
E-post: mst@mst.dk

[3)] Umhverfisstofnun / Environment and Food Agency of Iceland

Suðurlandsbraut 24
IS-108 Reykjavik
ICELAND

Sími: +354 591 2000 (central)
Fax: +354 591 2020 (central)
E-post: ust@ust.is

[4)] Statens forurensningtilsyn (SFT) / Norwegian Pollution Control Authority

Postboks 8100 Dep / Strømveien 96
N-0032 Oslo
NORWAY

Tlf: +47 22 57 34 00 (central)
Faks: +47 22 67 67 06 (central)
E-post: postmottak@sft.no

[5)] Naturvårdsverket / Swedish Environmental Protection Agency

Blekholmsterrassen 36
S-106 48 Stockholm
SWEDEN

Tel +46 (0)8 698 10 00 (central)
Fax +46 (0)8 20 29 25 (central)
E-post: natur@naturvardsverket.se

References

1. Ozone Secretariat, United Nations Environment Programme UNEP, *Handbook for the International Treaties for the Protection of the Ozone Layer - The Vienna Convention (1985) - The Montreal Protocol (1987)*. Fifth edition (2000) ed. 2000, UNON, Kenya: Secretariat for The Vienna Convention for the Protection of the Ozone Layer & The Montreal Protocol on Substances that Deplete the Ozone Layer. 92-807-1867-3. http://www.unep.org/ozone/Handbook2000.shtml

2. CANTOX Environmental, *The Status of Class II Solvent Alternatives in Ontario. Final Report.* May 1, 2000: Prepared for: Ontario Ministry of the Environment, Air Policy & Climate Change Branch. www.ene.gov.on.ca/envision/env_reg/er/documents/2000/ra00e0031.pdf. Dec 10th, 2002.

3. The Ozone Secretariat, United Nations Environment Programme UNEP, *Handbook on Essential Use Nominations June 2001. Prepared by the Technology and Economic Assessment Panel.* 2001. ISBN 92-807-2068-6. http://www.unep.org/ozone/docs/TEAP-Essential-Use-HB-2001-final.doc

4. The Ozone Secretariat, United Nations Environment Programme UNEP, *Item 3 (g) of the provisional agenda: Update Report By The Technology And Economic Assessment Panel On Alternatives For Ozone-Depleting Substances Used To Extract Oil And Grease From Water. Twelfth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer, Ouagadougou, 11-14 December 2000. UNEP/OzL.Pro.12/INF/4, 3 November 2000.* Internet homepage. http://www.unep.org/ozone/12mop-inf4.shtml. 13 Nov 2002.

5. *Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer*. OJ L 244, 29.9.2000, pp. 1 - 24. http://europa.eu.int/eur-lex/en/consleg/main/2000/en_2000R2037_index.html.

6. *Naturvårdsverkets föreskrifter om ändring i föreskrifterna (2000:2) om avsteg från 2 § förordningen (1995:636) om ämnen som bryter ned ozonskiktet; NFS 2001:21.* NFS (2001:21). http://www.naturvardsverket.se/ -> Lag & rätt -> Naturvårdsverkets föreskrifter, NFS.

7. *Naturvårdsverkets föreskrifter om avsteg från 2 § förordningen (1995:636) om ämnen som bryter ner ozonkiktet*. NFS (2000:2). http://www.naturvardsverket.se/ -> Lag & rätt -> Naturvårdsverkets föreskrifter, NFS.

8. *Förordning (2002:187) om ämnen som bryter ned ozonskiktet*. SFS nr 2002:187. http://www.lagrummet.gov.se/.

9. Personal communication. Guðmundsdóttir, Heiðrún.

10. Miljøstyrelsen, *Oversigt over regler om ozonlagsnedbrydende stoffer*. 2002. Internet homepage. 11/11/02. www.mst.dk/transport/word/ oversigt_regulering%20ozonlagsnedbrydende%20stoffer_.doc. Dec 30, 2002.

11. *Bekendtgørelse om visse ozonlagsnedbrydende stoffer*. BEK nr 243 af 19/04/2002. http://WWW.RETSINFO.dk/DELFIN/HTML/B2001/0087105.htm.

12. *Valtioneuvoston päätös otsonikerrosta heikentävistä aineista 2.4.1998/262*. Suomen säädöskokoelma N:o 262-265, 1998, 9.4.1998, s. 979 - 984. http://www.finlex.fi/pdf/sk/98/vihko38.pdf.

13. *Forskrift om ozonreduserende stoffer*. FOR 2002-12-20 nr 1818. http://www.lovdata.no/for/sf/md/xd-20021220-1818.html.

14. *Council Directive 79/869/EEC of 9 October 1979 concerning the methods of measurement and frequencies of sampling and analysis of surface water intended for the abstraction of drinking water in the Member States*. Official Journal L, 29/10/1979, p. 44 - 53.

15. *Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg*. BEK nr 871 af 21/09/2001. http://WWW.RETSINFO.dk/DELFIN/HTML/B2001/0087105.htm.

16. Miljøstyrelsen, *Boringskontrol på vandværker*. 1997. ISBN nr. 87-7810-751-2. Vejledning fra Miljøstyrelsen. Nr. 2. http://www.mst.dk/udgiv/publikationer/1997/87-7810-751-2/pdf/87-7810-751-2.pdf.

17. *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy*. Official Journal L 327, 22/12/2000, p. 1 -73.

18. *Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption*. Official Journal L 229, 30/08/1980. P. 0011-0029.

19. 98/83/EC, *Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption*, in *Official Journal L 330, 05/12/1998, p. 32 - 54*.

20. OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, *OSPAR Recommendation 2001/1 for the Management of Produced Water from Offshore Installations*,,M.o.t.O.C. (OSPAR). Valencia: 25-29 June 2001. http://www.ospar.org (-> measures -> recommendations)

21. Leo Henriquez, State Supervision of Mines, the Netherlands. *Latest Developments With Regard To Oil-In-Water Monitoring Within The OSPAR Framework.* in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

22. Suomen standardoimisliitto - Finlands standardiseringsförbund SFS, *SFS 3010:1994. Veden öljyn ja rasvan määritys. Infrapunaspektrofotometrinen menetelmä. Bestämning av olja och fett i vatten. Infrarödspektrofotometrisk metod. Determination of oil and grease in water. Infrared spectrophotometric method.*.

23. Hansen, Nis; Dybdahl, Hans Peter. *The determination of aromatic hydrocarbons in produced water*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

24. Karman, C.C.; Scholten, M.C.Th., *Workshop report: Aromatic hydrocarbons and method of analysis for dispersed oil in produced water.* 2001. TNO-MEP. Netherlands organization for Applied Scientific Research, Environment/Energy and Process Innovation. TNO-report. TNO-MEP - R 2001/531.

25. Yang, Ming; Tulloch, Steven. *Oil-in-water monitoring - Where are we heading?* in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

26. International Organization for Standardization ISO, *ISO/TR 11046:1994(E). Soil quality - Determination of oil content - Method by infrared spectrometry and gas chromatographic method. First edition.* Geneva, Switzerland. ISO Technical Report. http://www.iso.org.

27. Suomen standardoimisliitto - Finlands standardiseringsförbund SFS, *SFS 3009. Veden öljyn ja rasvan määritys. Gravimetrinen menetelmä. Bestämning av olja och fett i vatten. Gravimetrisk metod. Determination of oil and grease in water. Gravimetric method.*.

28. Association., American Public Health, *Standard Methods for the Examination of Water and Wastewater.* 14. edition. ed. 1975, Washington. 515-516.

29. US Environmental Protection Agency. Office of Technology Transfer., *Manual of Methods for Chemical Analysis of Water and Wastes.* 1974, Washington D.C. 20460.

30. Personal communication. Lepom, Peter. July 7th 2002.

31. Personal communication. Lück, Detlef. Aug 6th, 2002.

32. *Statens livsmedelverks föreskrifter om allmänna råd om dricksvatten*. SLVFS 1989:30. http://www.lagrummet.gov.se/.

33. *Statens livsmedelverks föreskrifter om dricksvatten*. SLVFS 2001:30. http://www.lagrummet.gov.se/.

34. *Sosiaali- ja terveysministeriön asetus pienten yksiköiden talousveden laatuvaatimuksista ja valvontatutkimuksista 17.5.2001/401*. 2001Suomen säädöskokoelma 2001, N:o 400-404, 23.5.2001, s. 1150-1157.

35. International Organization for Standardization ISO, *ISO/CD 9377-1:1998. Water quality - Determination of hydrocarbon oil index - Part 1: Method using solvent extraction and gravimetry.*. 1998: Geneva, Switzerland.

36. Personal communication. Frintrop, Paul. Aug 6th, 2002.

37. International Organization for Standardization ISO, *ISO 9377-2. Water quality - Determination of hydrocarbon oil index - Part 2: Method using solvent extraction and gas chromatography.*, Geneva, Switzerland.

38. Fridström, Anders, *ITM proficiency test 2001-2. Oil in Water.* ITM. Institute för tillämpad miljöforskning. ITM rapport 93.

39. Lepom, P.; Sawal, G.; Kreßner, R.; Woitke, P., *Interlaboratory Study - Determination of Oil in water according to ISO/DIS 9377-4. Final report*. 2000, Berlin. UmweltBundesAmt (Federal Environmental Agency, Laboratory for Water Analysis, II 3.6).

40. Personal communication. Becker, Roland.

41. Mäkinen, Irma; Suortti, Anne-Mari; Huhtala, Sami; and Pönni, Seppo, *Interlaboratory comparison 4/2002. Mineral oil from polluted soil and water*. Report. Mimeograph series of the Finnish Environment Institute 269. 2002: Finnish Environment Institute. 952-11-1304-9. http://www.ymparisto.fi/eng/syke/syke.htm

42. Nielsen, Ulf; Pedersen, Bodil Mose; Jensen, Poul Erik, *Reduktion af minerals olie i spildevann*. Miljøprojekt. Vol. Nr. 609. 2001: Miljøstyrelsen. 87-7944-579-9. http://www.mst.dk/project/NyViden/2001/12190000.htm

43. Personal communication. Kvernheim, Arne.

44. Kvernheim A.L., Lund H.S., Berg B., de Pauw E., Eppe G., Chtaïb M., *Development of a new hydrocarbon index for oil-in-water.* Chemosphere, 1999. **39**(15): p. 2707-2722. http://www.elsevier.com/locate/chemosphere

45. Chemistry., SINTEF. Appliec, *Oil-in-water analysis*. Internet homepage. 8 Feb 1999. http://www.oslo.sintef.no/chem/6640/stoiw.html. 13 Nov 2002.

46. Chemistry., SINTEF. Appliec, *STOIW Method description SPE-GC-MS*. Internet homepage. 12 Dec 1998. http://www.oslo.sintef.no/chem/htmldo/6640/spegcm. 13 Nov 2002.

47. Chemistry., SINTEF. Appliec, *STOIW Draft Standard Operation Procedure LL-IR. SMT4-CT96-2090, Task 2 Report.* Internet homepage. 4 June 1998. http://www.oslo.sintef.no/chem/6640/htmldo/ll3mir.html. 13 Nov 2002.

48. Chemistry., SINTEF. Appliec, *SOP of LL-GC-FID method from NNI (The Netherlands). Typed from: Document ISO/TC 147/SC 2/WG 15 N 62. May 1998 CD 9377-4.* Internet homepage. 4 Jun 1998. http://www.oslo.sintef.no/chem/6640/htmldo/llgcfi.htm. 13 Nov 2002.

49. International Organization for Standardization ISO, *ISO 10301:1997 Water quality - Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods.*.: Geneva, Switzerland.

50. U.S.EPA, *Method 1624, Revision C. Volatile organic compounds by isotope dilution GC-MS.*. June 1989.

51. U.S.EPA, *Method 1625. Semi-volatile organic compounds by isotope dilution GC-MS. Revision C.*. June 1989.

52. *BS 6920: Part 4: 1996. The GC-MS identification of water-leachable organic substances*.

53. International Organization for Standardization ISO, *ISO/DIS 15680 Water quality - Determination of certain monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds - Gas-chromatographic method using purge and trap and thermal desorption*.: Geneva, Switzerland.

54. ISO/CEN, *ISO/CD 17993 Water quality - Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection is being prepare.*

55. Normalisatie-instituut, Nederlands, *Nederlandse norm NEN 6407. Water. Gaschromatographische bepaling van het gehalte van een aantal monocyclische*

aromaten, naftaleen en enkele gechloreerde koolwaterstoffen met de "purge en trap" -methode en thermische desorptie. (Water. Gaschromatographic determination of a number of monocylic aromatic hydrocarbons, napthalene and several chlorinated compounds using purge and trap and thermal desorption.. 1997. ICS 13.060.01-40.

56. Personal communication. Noij, Theo. July 17th, 2002.

57. Normalisatie-instituut, Nederlands, *Nederlandse norm NEN 6671. Afvalwater en slib. Gravimetrische bepaling van het gehalte aan petroleumether extraheerbare oliën en vetten. Soxhlet extractie. (Waste water and sludge. Gravimetric determination of petroleum ether extractable oil and fat content. Soxhlet extraction)*. 1994. UCD 628.31:543.383.056.

58. Personal communication. Fardon, John. July 25th, 2002.

59. Petroleum, Institute of, *IP 426/98. Oil Content of Effluent Water - Extraction and Infra-red Spectrometric Method.*,,S. Methods.

60. Personal communication. Roberts., Ian. July 8th, 2002.

61. U.S.EPA, Office of Water, *Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136)*. February 2000. EPA/821-R-00-003. http://www.epa.gov/waterscience/methods/1664guide.pdf

62. *Protection of the Stratospheric Ozone: De Minimis Exemption for Laboratory Essential Uses for Calendar Year 2001*. 14760 - 14770. http://www.access.gpo.gov/su_docs/aces/aces140.html or http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=2001_register&docid=01-27383-filed.pdf.

63. *Protection of the Stratospheric Ozone: Allocation of Essential-Use Allowances for Calendar Year 2000; and Extension of the De Minimis Exemption for Essential Laboratory and Analytical Uses Through Calendar Year 2005; Final Rule*. 6352-6362. http://www.access.gpo.gov/su_docs/aces/aces140.html or http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=2002_register&docid=02-3101-filed.pdf.

64. Water., U.S.EPA. Office of, *Method 1664, Revision A: N-Hexane Extractable Material (HEM; oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM); Non-polar Material) by Extraction and Gravimetry*,, EPA-821-R-98-002. PB99-121949. February 1999. http://www.epa.gov/waterscience/methods/16640514.pdf

65. *Guidelines Establishing Test Procedures for the Analysis of Oil and Grease and Non-Polar Material Under the Clean Water Act and Resource Concervation and recovery Act; Final Rule*. 26315 - 26327. www.access.gpo.gov/su_docs/aces/aces140.html.

66. U.S.EPA, *Method 3535. Solid-phase extraction (SPE)*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3535.pdf

67. Agency., U.S. Environmental Protection, *Ground Water & Drinking Water. Approved Methods for Organic Chemicals*. Internet homepage. September 27th, 2002. http://www.epa.gov/safewater/methods/orch_tbl.html. 19 November 2002.

68. *National Primary Drinking Water Regulation: Consumer Confidence Reports; Final Rule.* 44512 - 44536. www.access.gpo.gov/su_docs/aces/aces140.html.

69. National Exposure Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio 45268. Edited by J.W. Munch (1995),, *Method 502.2 Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography With Photoionization and Electrolytic Conductivity Detectors in Series. Revision 2.1.*,,J.a.J.S.H.-M. R.W. Slater, Revision 1.0 (1986),, R. J.S. Ho - Method 502.2, Editor. 1995. http://www.ultrasci.com/Docs/500/502_2.PDF at Ultra Scientific, Inc.

70. National Exposure Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio 45268. Edited by J.W. Munch (1995),, *Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*,,J.W.E. A.Alford-Stevens, W.L. Buddle - Method 524, Rev. 1.0 (1983), R.W. Slater, Jr. -Revision 2.0 (1986), J.W. Eichelberger, and W.L. Budde - Revision 3.0 (1989), J.W. Eichelberger, J.W. Munch, and T.A. Bellar - Revision 4.0 (1992),, R. J.S. Ho - Method 502.2, Editor. 1995. http://www.ultrasci.com/Docs/500/524_2.PDF at Ultra Scientific, Ltd.

71. U.S.EPA, *Method 5030B. Purge-and-Trap for Aqueous Samples. Revision 2.*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5030b.pdf

72. U.S.EPA, *Method 8015C. Nonhalogenated Organics Using GC/FID. Revision 3.*. November 2000. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8015c.pdf

73. U.S.EPA, *Method 8021B. Aromatic and Halogenated Volatiles By Gas Chromatography Using Photoionization And/Or Electrolytic Conductivity Detectors. Revision 2.*. December 1996.
http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8021b.pdf

74. U.S.EPA, *Method 8260B. Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)*. December 1996.
http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8260b.pdf

75. U.S.EPA, *Method 5021B. Volatile organic compounds in soils and other solid matrices using equilibrium headspace analysis*. December 1996.
http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5021b.pdf

76. Weisman, Edited By: Wade, *Total Petroleum Hydrocarbon Criteria Working Group Series Volume 1: Analysis of Petroleum Hydrocarbons in Environmental Media*. March 1998: Amherst Scientific Publishers, MA, USA. ISBN 1-884-940-14-5. Available in the internet at the homepages of The Association for Environmental Health and Sciences: http://www.aehs.com/publications/catalog/tph.htm

77. Robinson, Peter. *The water industry's need for on-line oil-in-water monitors*. in *Oil Pollution Detection and Monitoring Seminar 2001*. 2001. East Kilbridge, Glasgow, Scotland. http://www.oiwclub.com.

78. Stahl, Danese C. and Tilotta, David C., *Partition infrared method for total gasoline range organics in water based on solid phase microextraction.* Environmental Science & Technology, 1999. **33**: p. 814-819.
http://pubs.acs.org/journals/esthag/index.html

79. Hennion, M.-C.; Cau-Dit-Coumes, C.; Pichon, V, *Trace analysis of polar organic pollutants in aqueous samples - Tools for rapid prediction and optimisation of the solid-phase extraction parameters.* Journal of Chromatography, A, 1998. **823**: p. 147-161. http://www.elsevier.com/locate/issn/00219673/

80. Statens Naturvårdsverket, *Förorenade områden - Analys- och testmetoder*. 1999. ISBN 91-620-4947-X (pdf). Rapport. 4947. Pdf-version available at Miljöbokhandel at http://www.environ.se.

81. Minty, Brian; Ramsey, Edward D. and Davies, Ieuan, *Development of an automated method for determining oil in water by direct aqueous supercritical fluid extraction coupled on-line with infrared spectroscopy.* Analyst, 21st November 2000. http://www.rsc.org/is/journals/current/analyst/anlcon.htm. Advance Article on the web

82. Dr. Edward D. Ramsey, Critical Solutions Technology Ltd. *A New Environmentally Clean, Rapid, Automated Method For Determining Oil/Grease In Water Using Direct Aqueous Supercritical Extraction Coupled On-Line With Infrared Spectroscopy*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

83. Yang, Y., Hawthorne, S.B., and Miller, D.J., *Comparison of sorbent and solvent trapping after supercritical fluid extraction of volatile petroleum hydrocarbons in soil.* Journal of Chromatography, A, 1995. **699**: p. 265-276. In: Förslag till riktvärden för förorenade bensinstationer. Naturvårdsverket, rapport 4889. http://www.elsevier.com/locate/issn/00219673/

84. Reddy, Christopher M. and Quinn, James G., *GC-MS analysis of total petroleum hydrocarbons and polycyclic hydrocarbons in seawater samples after the North Cape oil spill.* Marine Pollution Bulletin, 1999. **38**(2): p. 126-135. http://www.elsevier.nl/inca/publications/store/4/0/0/; article available at http://www.sciencedirect.com

85. TPD, TNO, *Projects: Ultrasonic Particle Monitoring*. 2002. Internet homepage. http://www.tpd.tno.nl/smartsite.html?id=317. Dec 29, 2002.

86. Technology, Telemark Institute of. http://www-pors.hit.no/tf/forskning/kjemomet/utrain/utrain134.htm. 23 Dec, 2002.

87. *Draft OSPAR-OIC Comparison Program*.

88. Personal communication. Henriquez, L.R. Aug 13th, 2002.

89. Ospar Convention for the Protection of the Marine Environment of the North East Atlantic. Offshore Industry Committee (OIC). *Results of a "Quick Scan" study - Comparison of OSPAR Agreement 1997-16 with GC method based on ISO 9377-2. Presented by The Netherlands.* in *Ospar Convention for the Protection of the Marine Environment of the North East Atlantic. Meeting of the Offshore Industry Committee (OIC)*. 2002. Cadiz: 11-15 February 2002.

90. Ospar Convention for the Protection of the Marine Environment of the North East Atlantic. Meeting of the Offshore Industry Committee (OIC), *Draft Work programme 2002/2003 for the Offshore Industry Committee (OIC). In: Summary Record OIC 2002. OIC 02/11/1, Annex 19.* Cadiz: 11-15 February 2002. Internet

homepage. http://www.ospar.org/eng/html/welcome.html Meetings and Documents, Summary records. 23 Dec 2002.

91. Personal communication. Øren, Hanne Marie.

92. Ospar Convention for the Protection of the Marine Environment of the North-East Atlantic, *Meeting of the Offshore Industry Committee (OIC). Agenda Item 11. OIC 02/11/1-E*. Cadiz: 11-15 February 2002. http://www.ospar.org/eng/html/welcome.html (meetings and documents, download summary records, OIC 2002, OIC 02_sr-e.doc)

93. (SFT), Statens forurensningstilsyn, *Brev til Oljeindustriens landsforening Ny standardmetode for analyse av olje i vann. Informasjon til operatørene.*. 2001. http://www.sft.no/nyheter/dokumenter/standardmetode_oljeanalyse2001.htm

94. Personal communication. Paus, Jørn. Aug 21st, 2002.

95. Paus, Jørn; Grini, Per Gerhard; Flatval, Kirsti, *Comparative study of Freon-IR (NS 9803) and GC-FID (ISO 9377-2) for analysis of oil in produced water on 33 platforms in the Norwegian sector.* 2001. OLF Working Group on OIl in Water.

96. Hardeng, Solvår, *Oil in water analysis - Status of the CFC phase out in oil in water analysis in Norway*. 2002, Statens forurensningstilsyn: Oslo.

97. Tulloch, Steven; Yang, Ming; Rusin, Jan; and Butler, Ed. *A laboratory evaluation of the current solvent extraction/IR spectrophotometry method and the pending ISO 9377-2 GC-FID method*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

98. John Ray, BP Upstream Technology Group. *Operational Experience with TTCE and Recent Evaluation of Bench Top Oil in Water Analysers*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

99. He, L.M.; Kear-Padilla, L.L.; Lieberman, S.H.; Andrews, J.M., *Online monitoring of oils in wastewater using combined ultraviolet fluorescence and light scattering with an artificial neural network*. 2000, San Diego. The Space and Naval Warfare Systems Center (SSC). Technical Report 1816. http://www.spawar.navy.mil/sti/publications/pubs/tr/1816/tr1816.pdf.

100. Niemelä, Pentti, *On-line measurement of oil contaminants in water by filter-based infrared analyzers*. 1994. Technical Research Centre of Finland (VTT). ISBN 951-38-4646-6. VTT Publications. 208.

101. Schuldt, Willy. *Effect of sample homogenization on on-line oil-in-water monitoring using UV fluorescence*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

102. Bastow, Trevor; Durnie, William H.; Jefferson, Alan and Pang, James, *Ultraviolet spectroscopy for the analysis of oil-in-water effluent using isopropanol as co-solvent.* Applied spectroscopy, 1997. **51**(3): p. 318-321.

103. *Act 29 November 1996 No. 72 relating to petroleum activities. Last amended by 28 June 2002.* http://www.npd.no/regelverk/r2002/frame_e.htm.

104. *Appendix 1 to the Activities Regulations. Requirements for Environmental Monitoring of the Petroleum Activities on the Norwegian Continental Shelf.* http://www.npd.no/regelverk/r2002/Aktivitetsforskriften_Vedlegg_1_e.htm.

105. *Regulations to Act relating to petroleum activities. Laid down by Royal Decree 27 June 1997 pursuant to Act 29 November 1996 no 72 relating to petroleum activities, section 10 - 18 and Act 10 February 1967 relating to procedure in cases concerning the public administration, section 13 c third paragraph and section 19 third paragraph. Last amended by 20 December 2002.* http://www.npd.no/regelverk/r2002/frame_e.htm.

106. International Organization for Standardization ISO, *ISO/DIS 16703 Soil quality - Determination of mineral oil content by gas chromatography*. 2001: Geneva, Switzerland. http://www.iso.org

107. Becker, Roland; Koch, Matthias; Wachholz, Sigrid; Win, Tin, *Quantification of total petrol hydrocarbons (TPH) in soil by IR-spectrometry and gas chromatography - conclusions from three proficiency testing rounds.* Accreditation and Quality Assurance, 2002. **7 (2002)**(7): p. 286-289. http://link.springer.de/link/service/journals/00769/index.htm or http://link.springer.de/link/service/journals/00769/papers/2007007/20070286.pdf

108. Nadim, Farhad; Liu, Shili; Hoag, George E; Chen, Jianping; Carley, Robert J.; and Zack, Peter, *A comparison of spectrophotometric and gas chromatographic measurements of heavy petroleum products in soil samples.* Water, Air, and Soil Pollution, 2002. **134**: p. 97-109.

109. Savolahti, Pekka. *Öljytuotteiden määritykset maa- ja vesinäytteissä.* in *Uutta ympäristötutkimuksessa ja -analytiikassa.* 2001. Fortum Oil and Gas Oy, Keilaniemi 2.-3.10.2001.

110. Karstensen, Kåre Helge, *Nordic Guidelines for Chemical Analysis of Contaminated Soil Samples.* 1996. Nordtest report. NT Techn Report 329. http://www.nordtest.org.

111. forurensningstilsyn, Statens, *Forurenset grunn - Metoder for kjemisk analyse*. SFT rapport 97:34. TA 1498/1997. 1997. ISBN 82-7655-088-6.

112. Mäkinen, Irma; Suortti, Anna-Mari; Pönni, Seppo; and Huhtala, Sami, *Proficiency test on the determination of mineral oil from polluted soils.* Accreditation and Quality Assurance, 2002. **2002**(7): p. 209-213. http://link.springer.de/link/service/journals/00769/index.htm or http://link.springer.de/link/service/journals/00769/papers/2007005/20070209.pdf

113. Franken R.O.G, Baars A.J., Crommentuijn G.H., Otte P., *A proposal for revised Intervention Values for petroleum hydrocarbons ('minerale olie') on base of fractions of petroleum hydrocarbons*. 1999. RIVM Rijksinstituut voor Volksgezondheid en Milieu. RIVM report 711701015. http://www.rivm.nl/bibliotheek/rapporten/711701015.pdf.

114. U.S.EPA, *Method 9071B. n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples. Revision 2*. April 1998. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9071b.pdf

115. U.S.EPA, *Method 8440. Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8260b.pdf

116. U.S.EPA, *Method 3560. Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3560.pdf

117. U.S.EPA, *Method 3510C. Separatory Funnel Liquid-Liquid Extraction. Revision 3*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3510c.pdf

118. ASTM International, *ASTM D 5765-95: Standard Practice for Solvent Extraction of Total Petroleum Hydrocarbons from Soils and Sediments Using Closed Vessel Microwave Heating*. 1995 (Reapproved 2001). http://www.astm.org

119. Lambert, P; Fingas, M; Goldthorp, M., *An evaluation of field total petroleum hydrocarbon (TPH) systems.* Journal of Hazardous Materials, 2001. **83**: p. 65-81.

120. Goldthorp, M.D.; Lambert, P., *Use of a portable infra-red analyzer for low-level hydrocarbon emissions.* Journal of Hazardous Materials, 2001. **83**: p. 135-152.

121. Creighton, Kathleen; Richards, Ronald, *Field Screening Technique for Total Petroleum Hydrocarbons in Soils.* Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 1997(April): p. 78-83.

122. Keller, Arturo A; Kram, mark, *Use of Laser Induced Fluorescence to Detect DNAPL and Fluorophore Mixtures In-Situ*. http://www.esm.ucsb.edu/fac_staff/fac/keller/papers/Abstract22.pdf. 23 Dec 2002.

123. Naval Command, Control and Ocean Surveillance Center, RDT&E Division, San Diego, *SCAPS-LIF Site Characterization and Analysis Penetrometer System - Laser-Induced Fluorescence*. http://www.spawar.navy.mil/sti/publications/pubs/td/2744r1/. 20 Dec 2002.

124. Robbins, Gary A., *Recommended Guidelines for Applying Field Screening Methods in Conducting Expedited Site Investigations at Underground Storage Tank Sites in Connecticut*. Department of Geology & Geophysics, University of Connecticut. http://www.sp.uconn.edu/~hydrogeo/ctfsfpdf.pdf.

125. Bujewski, Grace; Rutherford Brian, *The Rapid Optical Screening Tool (ROSTtm) Laser-Induced Fluorescence (LIF) System for Screening of Petroleum Hydrocarbons in Subsurface Soils*. National Exposure Research Laboratory, Characterization Research Division, U.S. Environmental Protection Agency, Las Vegas, Nevada. Innovative Technology Verification Report. http://www.clu-in.org/download/char/verstate/cone/rost_wrd.pdf.

126. Buerck, J.; Roth, S.; Kraemer, K.; Scholz, M., Klaas, N., *Application of a fiber-optic NIR-EFA sensor system for in situ monitoring of aromatic hydrocarbons in contaminated groundwater.* Journal of Hazardous Materials, 2001. **83**: p. 11-28.

127. CHEMetrics, Inc., and AZUR Environmental Ltd, RemediAid Total Petroleum Hydrocarbon Starter Kit, *Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil*. 2001. United States Environmental Protection Agency. Office of Research and Development EPA/600/R-01/082. http://www.epa.gov/ORD/SITE/reports/EPA600R-01082.htm.

128. Myers, Karen F.; Karn, Richard A.; Eng, Dan Y.; Konecny, Karl F.; Davis, William M., *Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Validation of the Thermal Desorption Sampler for Volatile Organic Compounds*. December 1999. US Army Corps of Engineers. Engineer Research and Development Center. Instruction Report EL-99-2. www.wes.army.mil/el/elpubs/pdf/irel99-2.pdf.

129. Coy, James D.; Bigelow, Philip L.; Buchan, Roy M.; Tessari, John D.; Parnell, James O., *Field Evaluation of a Portable Photoionization Detector for Assessing Exposure to Solvent Mixtures.* American Industrial Hygiene Association Journal, 2000. **61**(March/April): p. 268-274.

130. Strategic Environmental Research & Development Program, Dexsil Corporation, EPA NERL, TestraTech, *PetroFLAG. NETTS Project/Demonstration Summary*. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/fs_56-00_nfd.pdf.

131. Strategic Environmental Research & Development Program, Environmental Systems Corp., EPA NERL, TestraTech, *Synchronous Scanning Luminoscope. NETTS Project/Demonstration Summary*. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/fs_55-00_nfd.pdf.

132. Strategic Environmental Research & Development Program, Wilks Enterprise Inc., EPA NERL, TestraTech, *Infracal TOG/TPH Analyzer. NETTS Project/Demonstration Summary*. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/fs_54-00_nfd.pdf.

133. Strategic Environmental Research & Development Program, SiteLAB Corp., EPA NERL, TestraTech, *siteLAB Analytical Test Kit UVF-3110A. NETTS Project/Demonstration Summary*. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/fs_53-00_nfd.pdf.

134. Strategic Environmental Research & Development Program, Strategic Diagnostics Inc., EPA NERL, TestraTech, *ENSys Petro Test System. NETTS Project/Demonstration Summary*. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/fs_47-00_nfd.pdf.

135. Strategic Environmental Research & Development Program, Horiba Instruments, EPA NERL, TestraTech, *OCMA-350. NETTS Project/Demonstration Summary*. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/fs_47-00_nfd.pdf.

136. Space and Naval Warfare Systems Center, San Diego (SSC San Diego), *Site Characterization and Analysis Penetrometer System(SCAPS) Downhole Nd:YAG Laser-Based Laser Induced Fluorescence Validation. Technology Demonstration Report*. December 1997. http://enviro.nfesc.navy.mil/erb/erb_a/support/netts/char-exsitu/estcp266.pdf.

137. Energy, U.S.Department of, *Ribbon NAPL Sampler*. April 2000. Innovative Technology Summary Report. Subsurface Contaminants Focus Area and Charac-

terization, Monitoring, and Sensor Technology Crosscutting Program. DOE/EM-0522. http://apps.em.doe.gov/ost/pubs/itsrs/itsr2238.pdf.

138. Energy, U.S.Department of, *Raman Probe.* July 1999. Innovative Technology Summary Report. Tanks Focus Area and Characterization, Monitoring, and Sensor Technology Crosscutting Program. DOE/EM-0442. http://www.osti.gov/gpo/servlets/purl/354880-1D7UDk/webviewable/354880.pdf.

139. Matz, Gerhard; Schröder, Wolfgang; Kübler, Jürgen. *Field method for the detection of total petroleum hydrocarbon in water and soil samples*. in *Fifth International Symposium on Field Analytical Methods for Hazardous Wastes and Toxic Chemicals*. 1997. Las Vegas, NV, USA, Jan. 29-31, 1997. http://www.et1.tu-harburg.de/downloads_et1/umt/publikationen/kwsum.pdf.

140. U.S.EPA, *Method 4030. Soil Screening for Petroleum Hydrocarbons by Immunoassay.*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/4030.pdf

141. Aquateam - norsk vannteknologisk senter A/S, Norges Geotekniske Institutt - NGI, *Veiledning om risikovurdering av forurenset grunn*. 1999. Rapport nr: 98-086. http://www.sft.no/publikasjoner/kjemikalier/1629/ta1629.pdf.

142. *Forslag til forskrift om opprydding i forurenset grunn*. 2002.

143. Statens Naturvårdsverket, Svenska Petroleum Institutet, *Förslag till riktvärden för förorenade bensinstationer*. 1998. ISBN 91-620-4889-9 (pdf). Rapport. 4889. Pdf-version available at Miljöbokhandel at http://www.environ.se.

144. Geologian tutkimuskeskus. Kemian laboratorio, *Laboratoriopalvelujen hinnasto.* 1998.

145. Mäkinen, Irma; Suortti, Anne-Mari; Huhtala, Sami; Aallonen, Anri; and Pönni, Seppo, *Interlaboratory comparison 5/2000*. Report. Mimeograph series of the Finnish Environment Institute 223. 2001: Finnish Environment Institute. 952-11-0913-0. http://www.ymparisto.fi/eng/syke/syke.htm

146. SGU - Statens oljelager, *Bakgrundshalter av petroleumkolväten i sediment och grundvatten*. Vol. Dnr: 9030-0189/99. Februari 2000. http://www.sgu.se/verksamhet/miljo/sol/bakgrund.pdf

147. de Jong APJM, van der Heeft E, Visser T, *Vergelijking bepaling minerale olie in sediment met gaschromatografie en infraroodspectrometrie*. 1995. Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven. Rapport nr. 609021008. http://www.rivm.nl/bibliotheek/rapporten/609021008.pdf.

148. Orbons A.J., Rood G.A., van der Velde E.G., *Ontwikkeling van uitloogproeven voor minerale olie. Evalutierapport*. 1996. Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven. Rapport nr. 771402 020. http://www.rivm.nl/bibliotheek/rapporten/771402020.pdf.

149. Broekman M.H., Rood G.A., van der Velde E.G., Orbons A.J., van Gils W., *Ontwikkeling van uitloogproeven voor minerale olie. Ontwikkelingsonderzoek.* 1996. Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven. Rapport nr. 771402 019. http://www.rivm.nl/bibliotheek/rapporten/771402019.pdf.

150. *EPTIS. European Information System on Proficiency Testing Schemes.*: Federal Institute for Materials Research and Testing (BAM) Berlin. Internet-site. 04 NOV 2002. http://www.eptis.bam.de/. 5.11.2002.

151. Internet homepages of various standardization organizations. http://www.iso.org, http://www.cenorm.be, http://www.astm.org/, http://www.din.de, http://www.nen.nl, http://www.bsi-global.com, http://www.sis.se, http://www.sfs.fi, http://www.ds.dk, http://www.standard.no.

152. SIS, *SS 028211. Vattenundersökningar - Bestämning av fetthalten (totalhalten fett, emulgerat och avskiljbart fett) i avloppsvatten från livsmedelsindustrin - Gravimetrisk metod. Utgåva 1.*. 1994-05-18.

153. Statens Naturvårdsverket, *Bestämning av fetthalten i avloppsvatten - gravimetrisk metod.* Naturvårdsverkets rapport 3896. 1991. 91-620-3896-6.

154. Personal communication. Kennedy., Gene.

155. U.S.Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, *Finalized Toxicological Profiles.* Nov 4, 2002. http://www.atsdr.cdc.gov/toxpro2.html. Dec 12, 2002.

156. U.S.Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, *Toxicological profile for used mineral-based crankcase oil*. http://www.atsdr.cdc.gov/toxprofiles/tp102.html

157. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta (Georgia), USA., *Toxicological profile for total petroleum hydrocarbons.* September 1999. http://www.atsdr.cdc.gov/toxprofiles/tp123.html. 10th Dec 2002.

158. Personal communication. Reinmüller, Mr. Bernd. Thu, 05 Dec 2002.

159. Personal communication. Engström, Göran. Thu, 05 Dec 2002.

160. International Organization for Standardization ISO, *ISO 8502-6. Preparation of steel substrates before application of paints and related products - Tests for the assessment of surface cleanliness - Part 6: Extraction of soluble contaminants for analysis - The Bresle method*.: Geneva, Switzerland. http://www.iso.org

161. Nordtest, *Nordtest method NT POLY 181 Determination of amount of oil on surfaces.* 1998. http://www.nordtest.org.

162. ASTM International, *D 4961. Test method for Gas Chromatographic Analysis of Major Organic Impurities in Phenol Produced by the Cumene Process*.

163. ASTM International, *D 1159. Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration*. http://www.astm.org

164. ASTM International, *D 2710. Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration*. http://www.astm.org

165. ASTM International, *D 1492-02. Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration*. http://www.astm.org

166. ASTM International, *D 5776. Test Method for Bromine Index Aromatic of Hydrocarbons by Electrometric Titration*. http://www.astm.org

167. Metrohm, *No. 177/3 e. Automatic determinaton of the bromine index and/or the bromine number in petroleum products*, in *Application Bulletin*. http://www.metrohm.com, http://www.metrohm.com/docs/app/bulletins/bulletins_e.html

168. Standards, BSI British, *BS 2000: Part 129: 1993. Methods of test for Petroleum and its products. Part 129. Determination of bromine number - Colour indicator titration method. (Identical with IP 129/93)*. http://www.bsi-global.com

169. International Organization for Standardization ISO, *ISO 662:1998. Animal and vegetable fats and oils - Determination of moisture and volatile matter content.*.: Geneva, Switzerland. http://www.iso.org

170. International Organization for Standardization ISO, *ISO 3961:1996. Animal and vegetable fats and oils - Determination of iodine value*.

171. International Organization for Standardization ISO, *ISO 934:1980. Animal and vegetable fats and oils - Determination of water content - Entrainment method*.: Geneva, Switzerland. http://www.iso.org

172. International Organization for Standardization ISO, *ISO 10565:1998 Oilseeds - Simultaneous determination of oil and water contents - Method using pulsed nuclear magnetic resonance spectrometry*.: Geneva, Switzerland. http://www.iso.org

173. International Organization for Standardization ISO, *ISO 10632:2000 Oilseed residues - Simultaneous determination of oil and water contents - Method using pulsed nuclear magnetic resonance spectrometry*.: Geneva, Switzerland. http://www.iso.org

174. Personal communication. Fosfa, Anna Baran.

175. International Organization for Standardization ISO, *ISO 6296:2000. Petroleum products - Determination of water - Potentiometric Karl Fischer titration method*.: Geneva, Switzerland. http://www.iso.org

176. International Organization for Standardization ISO, *ISO 12937:2000. Petroleum products - Determination of water - Coulometric Karl Fischer titration method.*.: Geneva, Switzerland. http://www.iso.org

177. BSi, *Draft British Standard BS EN ISO 6296 Petroleum products - Determination of water - Potentiometric Karl Fischer titration method (ISO/DIS 6296). Draft for Public Comment.*,, Document 99/121207 DC. 24 March 1999. http://www.bsi-global.com

178. Metrohm, *No. 137/2 e. Karl Fischer water determination with the KF Coulometer*, in *Application Bulletin.* http://www.metrohm.com, http://www.metrohm.com/docs/app/bulletins/bulletins_e.html

179. Metrohm, *No. 77/2 e. Karl Fischer water determinations*, in *Application Bulletin.* http://www.metrohm.com, http://www.metrohm.com/docs/app/bulletins/bulletins_e.html

180. Toledo., Mettler, *Mettler Toledo DL31/DL38 Titrators. Application broschure 26. Fundamentals of the Volumetric Karl Fischer Titration with 10 Selected Applications*. http://www.mt.com/home/products/en/lab/wet/titration/docs/Ti1200b.PDF

181. Slunge, Daniel and Sterner, Thomas, *Implementation of Policy Instruments for Chlorinated Solvents. A Comparison of Design Standards, Bans, and Taxes to Phase Out Trichloroethylene.* Resources for the Future. http://www.rff.org/disc_papers/PDF_files/0132.pdf. Also in European Environment 11, 281-296; and Environmental Economics Unit, Sweden: EEU Reprint Series 2001:3

182. UNEP, United Nations Environment Programme, *Protecting the Ozone Layer. Volume 2. Solvents, coatings and adhesives.* 2001. http://www.uneptie.org/ozonaction/library or www.uneptie.org/ozonaction/library/ tech/vol2solvent.pdf.

183. Standards, BSI British, *BS 2000-74:2000 (ISO 3733:1999). Methods of test for petroleum and its products - BS 2000-74: Petroleum products and bituminous materials - Determination of water - Distillation method. (Identical with IP 74-2000)*. http://www.bsi-global.com

184. *Iodine Value. In: 2.5.4. European Pharmacopeia*.

185. Fettwissenschaft., DGF. Deutsche Gesellscahft für, *Iodine Value according to Hanus. Cyclohexane/glacial acetic acid method.*, in *DGF Standard Methods. Section C - Fats. C-V 11a(02)*. http://www.dgfett.de/methods/index.htm

186. Fettwissenschaft., DGF. Deutsche Gesellscahft für, *Iodine Value.*, in *DGF Standard Methods. Section C - Fats. C-V 11 (02)*. http://www.dgfett.de/methods/index.htm

187. Fettwissenschaft., DGF. Deutsche Gesellscahft für, *Iodine Value according to Kaufmann. Cyclohexane/glacial acetic acid method.*, in *DGF Standard Methods. Section C - Fats. C-V 11b(02)*. http://www.dgfett.de/methods/index.htm

188. Fettwissenschaft., DGF. Deutsche Gesellscahft für, *Iodine Value according to Wijs. Cyclohexane/glacial acetic acid method.*, in *DGF Standard Methods. Section C - Fats. C-V 11d(02)*. http://www.dgfett.de/methods/index.htm

189. Fettwissenschaft., DGF. Deutsche Gesellscahft für, *Iodine Value according to Wijs. Modified Hofmann and Green Method.*, in *DGF Standard Methods. Section C - Fats. C-V 11e(02)*. http://www.dgfett.de/methods/index.htm

190. International Organization for Standardization ISO, *ISO 8573-2:1996. Compressed air for general use - Part 2: Test methods for aerosol oil content.*.: Geneva, Switzerland.

191. Eläinlääkintä- ja elintarvikelaitos (EELA), Maa- ja metsätalousministeriö, elintarvike- ja terveysosasto (MMMELO), Elintarvikevirasto (EVI). Tekninen toteutus: Teija Pesonen, *Eläimistä saatavien elintarvikkeiden vierasainetutkimukset 2000. Results of monitoring certain substances and residues thereof in live animals and animal products in Finland 2000.* 2001, Helsinki. http://www.eela.fi/1tiedotus/raportit/Vieraine2000.pdf

192. Shu-Chu Su, Pi-Chiou Chang and Shin-Shou Chou, *An Analytical Method for Lasalocid Residues in Livestock Products.* Journal of Food and Drug Analysis, 1998. **6**(2): p. 495 - 504. http://www.nlfd.gov.tw/jfda/content/62/6204.html

193. Wilks Enterprise, Inc, *Infracal® TOG/TPH Analyzer. IR Platform Model HATR-T, Cuvette Model CVH, IR Card Model CH - User's Guide.* 1999. Rev. 3.1, February 1999. http://www.wilksir.com/manuals.htm. 4th Dec 2002.

194. Lobeiras, Andres and Sabau John. *Counting and Sizing Particles in Insulating Mineral Oils*. in *6th World Congress of Chemical Engineering*. Melbourne 2001.

195. Standards, BSI British, *BS EN ISO 3735:1999, BS 2000-53:1999. Crude petroleum and fuel oils - Determination of sediment - Extraction method. (Identical with IP53/1999)*. http://www.bsi-global.com

196. *Application note. Determination of Size and Concentration of Particles in OIls Using the Beckman CoulterÔ MultisizerÔ 3 COULTER COUNTERÒ.*

197. International Organization for Standardization ISO, *ISO 13319:2000 Determination of particle size distributions - Electrical sensing zone method.*: Geneva, Switzerland. http://www.iso.org

198. International Organization for Standardization ISO, *ISO 4406:1999 Hydraulic fluid power - Fluids - Method for coding the level of contamination by solid particles*.: Geneva, Switzerland. http://www.iso.org

199. International Organization for Standardization ISO, *ISO 6439:1990. Water quality - Determination of phenol index - 4-Aminoantipyrine spectrometric methods after distillation.*. 1990: Geneva, Switzerland. http://www.iso.org

200. International Organization for Standardization ISO, *ISO 14402. Water quality - Determination of phenol index by flow analysis (FIA and CFA)*. 1999: Geneva, Switzerland. http://www.iso.org

201. International Organization for Standardization ISO, *ISO 8165-1:1992. Water quality - Determination of selected monovalent phenols - Part 1: Gas-chromatographic method after enrichment by extraction*. 1992: Geneva, Switzerland. http://www.iso.org

202. International Organization for Standardization ISO, *ISO 8165-2:1999. Water quality - Determination of selected monovalent phenols - Part 2: Method by derivatization and gas chromatography*. 1999: Geneva, Switzerland. http://www.iso.org

203. Suomen standardoimisliitto - Finlands standardiseringsförbund SFS, *SFS 3011. Veden fenolien määritys. Determination of phenolic compounds in water.*. http://www.sfs.fi

204. U.S.EPA, *Method 9065. Phenolics (spectrophotometric, manual 4-AAP with distillation)*. September 1986. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9065.pdf

205. U.S.EPA, *Method 9067. Phenolics (spectrophotometric, MBTH with distillation)*. September 1986. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9067.pdf

206. U.S.EPA, *Method 9066. Phenolics (colorimetric, automated 4-AAP with distillation)*. September 1986. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/9066.pdf

207. U.S.EPA, *Method 8041. Phenols by gas chromatography*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8041.pdf

208. UOP. http://www.astm.org

209. Personal communication. Hujanen, Tuula. Feb 2nd, 2003.

210. *Performance specification. Inhibitor, corrosion/lubricity improver, fuel soluble. MIL-PRF-25017F*. 1997. http://www.desc.dla.mil/DCM/Files/qpl25017.pdf

211. Defence, Ministry of, *Fuel Soluble Lubricity Improving Additives for Aviation Turbine Fuels.*, in *NATO Code: S-1747. Joint Service Designation: AL-61*. 2001. http://www.dstan.mod.uk/data/68/251/00000200.pdf

212. ASTM International, *ASTM D 5001-90a(2000)e1. Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE)*. 1990/2000. http://www.astm.org

213. Personal communication. Matulevicius, Edward. Feb 28th, 2003.

214. Personal communication. Seinsche, Klaus. Feb 27th, 2003.

215. International Organization for Standardization ISO. http://www.iso.org

216. U.S.EPA, *Method 3640A. Gel-permeation cleanup.*. September 1994. [http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3640a.pdf

217. ASTM International. http://www.astm.org

218. Personal communication. Matikainen, Jorma. Feb 28th, 2003.

219. Personal communication. Huhtala, Sami. Feb 21st, 2003.

220. Personal communication. Lakkisto, Ulla-Maija. Feb 25th, 2003.

221. http://www.dgfett.de/methods/index.htm. Feb 27th, 2003.

222. *MOLART. A multidisciplinary NWO PRIORITEIT on Molecular Aspects of Ageing in Painted Works of Art. Progress Report 1995 - 1998.*, ed. E.b.L.J.H.a. J.J.Boon. 1998: FOM Institute AMOLF. http://www.amolf.nl/research/biomacromolecular_mass_spectrometry/molart/progress_report98.pdf

223. Alan Devlin, Shell UK. *Issues Surrounding the Use of Tetrachloroethylene In Oil-in-Water Analysis*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

224. Anderson, Graham. *Vertrel MCA, an alternative solvent for oil-in-water monitoring*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

225. Caudle, Dan. *Sources of error in oil in water measurements and their impact on comparing oil in water monitors*. in *Oil-in-Water Monitoring Workshop*. 22nd & 23rd May 2002. The Aberdeen Marriot Hotel, Dyce, Aberdeen: NEL. http://www.nel.uk.

226. Utvik, Toril I. Røe, *Chemical characterisation of produced water from four offshore oil production platforms in the North Sea.* Chemosphere, 1999. **39**(15): p. 2593-2606. Article available at http://www.sciencedirect.com

227. Potter, Thomas L; Simmons, Kathleen E, *Total Petroleum Hydrocarbon Criteria Working Group Series Volume 2: Composition of Petroleum Mixtures*. May 1998: Amherst Scientific Publishers, MA, USA. ISBN 1-884-940-19-6. Available in the internet at the homepages of The Association for Environmental Health and Sciences: http://www.aehs.com/publications/catalog/tph.htm

228. Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG), Toxicology Technical Action Group, *Selection of representative TPH fractions based on fate and transport considerations. TPHCWG Series 3.* 1997a. Amherst Scientific Publishers, Amherst (MA) USA.

229. Gustafson, John B; Tell, Joan Griffith; Orem, Doug, *Total Petroleum Hydrocarbon Criteria Working Group Series Volume 3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations.* July 1997: Amherst Scientific Publishers, MA, USA. ISBN 1-884-940-12-9. Available in the internet at the homepages of The Association for Environmental Health and Sciences: http://www.aehs.com/publications/catalog/tph.htm

230. U.S.EPA, *Method 3611B. Alumina column cleanup and separation of petroleum wastes*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3611b.pdf

231. U.S.EPA, *Method 3630C. Silica gel cleanup. Revision 3*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3630c.pdf

232. U.S.EPA, *Method 3810. Headspace*. September 1986. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3810.pdf

233. U.S.EPA, *Method 3540c. Soxhlet extraction. Revision 3*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3540c.pdf

234. U.S.EPA, *Method 3550b. Ultrasonic extraction. Revision 2*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3550b.pdf

235. U.S.EPA, *Method 3545. Pressurized Fluid Extraction. Revision 0*. December 1996. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3545.pdf

236. Massachusetts Department of Environmental Protection, Division of Environmental Analysis, Office of Research and Standards, Bureau of Waste Site Cleanup, *Method for the determination of extractable petroleum hydrocarbons (EPH)*. January 1998. http://www.state.ma.us/dep/bwsc/vph_eph.htm

237. Massachusetts Department of Environmental Protection, Division of Environmental Analysis, Office of Research and Standards, Bureau of Waste Site Cleanup, *Method for the determination of volatile petroleum hydrocarbons (VPH)*. January 1998. http://www.state.ma.us/dep/bwsc/vph_eph.htm

238. Commonwealth of Massachusetts, Executive Office of Environmental Affairs, Department of Environmental Protection. (MADEP), *Characterizing Risks Posed by Petroleum Contaminated Sites: Implemenation of the MADEP VPH/EPH Approach. Final Policy, October 31, 2002. Policy #WSC-02-411*. 2002. http://www.state.ma.us/dep/bwsc/vph_eph.htm

239. U.S.EPA, *Method 3820. Hexadecane extraction and screening of purgeable organics.*. September 1986. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3820.pdf

240. CCME, Canadian Council of Ministers of the Environment, *Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method. Publication No. 1310*. 2001. 1-896997-01-5. http://www.ccme.ca/assets/pdf/final_phc_method_rvsd_e.pdf Addendum available at: http://www.ccme.ca/assets/pdf/phc_method_addendum_1.pdf

241. Research & Productivity Council RPC, *Environmental Analytical Statement of Qualifications.*. 2002. http://www.environmentlab.com

242. Baars AJ, Theelen RMC, Janssen PJCM, Hesse JM, van Apeldoorn ME, Meijerink MCM, Verdam L, Zeilmaker MJ, *Re-evaluation of human-toxicological maximum permissible risk levels*. 2001. Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven. Rapport nr. 711701025. http://www.rivm.nl/bibliotheek/rapporten/771701025.pdf.

243. Personal communication. Franken, Ron. 13 Dec 2002.

244. Verbruggen EMJ, Posthumus R, and van Wezel AP, *Ecotoxicological Serious Risk Concentrations for soil, sediment and (ground)water: updated proposals for first series of compounds*. 2001. Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven. Rapport nr. 711701020. http://www.rivm.nl/bibliotheek/rapporten/771701020.pdf.

245. Lijzen JPA, Baars AJ, Otte PF, Rikken MGJ, Swartjes FA, Vergruggen EMJ and van Wezel AP, *Technical evaluation of the Intervention Values for Soil/sediment and Groundwater*. 2001. Rijksinstituut voor Volksgezondheid en Milieu (RIVM), Bilthoven. Rapport nr. 711701023. http://www.rivm.nl/bibliotheek/rapporten/771701023.pdf.

246. Faksness, Liv-Guri; Weiss, Hermann M.; Daling, Per S., *Revision of the Nordtest Methodology for Oil Spill Identification*. 2002. SINTEF Applied Chemistry. ISBN 82-14-02680-6. SINTEF Report STF 66 A02028 / NT Techn Report 498. http://www.nordtest.org/register/techn/tlibrary/tec498.pdf.

247. Vorhees, Donna J; Weisman, Wade H; Gustafson, John B, *Total Petroleum Hydrocarbon Criteria Working Group Series Volume 5: Human Health Risk-Based Evaluation of Petroleum Release Sites: Implementing the Working Group Approach*. 1999: Amherst Scientific Publishers, MA, USA. ISBN 1-884-940-12-9. Available in the internet at the homepages of The Association for Environmental Health and Sciences: http://www.aehs.com/publications/catalog/tph.htm

248. Edvards DA, Andriot MD, Amoruso MA, Tummey AC, Bevan CJ, Tveit A, Hayes LA, Youngren SH and Nakles DV, *Total Petroleum Hydrocarbon Criteria Working Group Series Volume 4: Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons.* 1997: Amherst Scientific Publishers, MA, USA. ISBN 1-884-940-13-7. Available in the internet at the homepages of The Association for Environmental Health and Sciences: http://www.aehs.com/publications/catalog/tph.htm

249. The Ministry of Housing, Spatial Planning and the Environment. Directorate-General for Environmental Protection., *Environmental Quality Standards in the Netherlands. A review of environmental quality standards and their policy framework in the Netherlands. 1999*. 2001: Kluwer, Alpen aan den Rijn. ISBN 90 14 08189 8.

250. International Organization for Standardization ISO, *ISO 8402. Quality management and quality assurance - Vocabulary.*. 1994: Geneva, Switzerland.

251. International Organization for Standardization ISO, *ISO 5725-1:1994/Cor 1:1998. Accuracy (Trueness and Precision) of Measurement Methods and Results - Part 1: General Principles and Definitions, Technical Corrigendum 1*.: Geneva, Switzerland.

252. International Organization for Standardization, Geneva, Switzerland., *International vocabulary of basic and general terms in metrology (VIM)*. Second edition ed. 1993.

253. *Guide to the Expression of Uncertainty in Measurement (GUM)*, ed. BIPM/IEC/IFCC/ISO/IUPAC/IUPAP/OIML. 1993/1995: International Organization for Standardization, Geneva, Switzerland.

254. ISO/IEC, International Organization for Standardization and the International Electrotechnical Commission, Geneva, Switzerland., *ISO/IEC 17025:1999. General Requirements for the Competence of Testing and Calibration Laboratories*.

255. OECD, Organisation for Economic Co-operation and Development., *OECD Series on Principles of Good Laboratory Practice and Compliance Monitoring.* Internet-site. http://www.oecd.org/EN/document/0,,EN-document-526-14-no-24-6553-0,00.html. 5.11.2002.

256. International Organization for Standardization ISO, *ISO 9001:1994 Quality systems -- Model for quality assurance in design, development, production, installation and servicing*.: Geneva, Switzerland.

257. International Organization for Standardization ISO, *ISO 9001:2000 Quality management systems -- Requirements.*

258. International Organization for Standardization ISO, *ISO 5725-2:1994/Cor 1:2002. Accuracy (Trueness and Precision) of Measurement Methods and Results - Part 2: Basic Method for the Determination of Repeatability and Reproducibility of a Standard Measurement Method*.: Geneva, Switzerland.

259. International Organization for Standardization ISO, *ISO/IEC Guide 43-1:1997. Proficiency testing by interlaboratory comparisons - Part 1: Development and operation of proficiency testing schemes.*, Geneva, Switzerland.

260. International Organization for Standardization ISO, *ISO/IEC Guide 43-2:1997. Proficiency testing by interlaboratory comparisons -- Part 2: Selection and use of proficiency testing schemes by laboratory accreditation bodies.*

261. International Organization for Standardization ISO, *ISO 5479:1997. Statistical interpretation of data - Tests for departure from the normal distribution*.: Geneva, Switzerland.

262. International Organization for Standardization ISO, *ISO 5725-3:1994/Cor 1:2001. Accuracy (trueness and precision) of measurement methods and results - Part 3: Intermediate measures of the precision of a standard measurement method*.: Geneva, Switzerland.

263. International Organization for Standardization ISO, *ISO 5725-4:1994. Accuracy (trueness and precision) of measurement methods and results - Part 4: Basic methods for the determination of the trueness of a standard measurement method*.: Geneva, Switzerland.

264. International Organization for Standardization ISO, *ISO 5725-5:1998. Accuracy (trueness and precision) of measurement methods and results - Part 5: Alternative methods for the determination of the precision of a standard measurement method*.: Geneva, Switzerland.

265. International Organization for Standardization ISO, *ISO 5725-6:1994/Cor 1: 2001. Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values*.: Geneva, Switzerland.

266. International Organization for Standardization ISO, *ISO 1095:1996. Linear calibration using reference materials*.: Geneva, Switzerland.

267. International Organization for Standardization ISO, *ISO 11843-1:1997. Capability of detection - Part 1: Terms and definitions*.: Geneva, Switzerland.

268. International Organization for Standardization ISO, *ISO 11843-2:2000. Capability of detection - Part 2: Methodology in the linear calibration case*.: Geneva, Switzerland.

269. International Organization for Standardization ISO, *ISO 5667-3, Water quality - Sampling - Part 3: Guidance on the preservation and handling of samples*.: Geneva, Switzerland.

270. International Organization for Standardization ISO, *ISO 8466-2:2001. Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 2: Calibration strategy for non-linear second-order calibration functions.*.: Geneva, Switzerland.

271. International Organization for Standardization ISO, *ISO 8466-1, Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function*.: Geneva, Switzerland.

Annex 1. The questionnaire results

1 General information

A sample of 483 laboratories in the Nordic countries was collected on the basis of them being known users of ozone depleting substances or working in a analysis branch expected to use the substances ("probable users"). The latter laboratories were recognized from laboratory catalogs or lists of accreditation organs. Contact information was not found for 3 laboratories, and the questionnaire was sent to 480 laboratories. The questionnaire form was in English, Swedish and Finnish. The form was also downloadable at the project Internet-homepage so it was possible to fulfil it by computer and send it by email. If no answer was received, a reminder letter, telefax or email message was sent to most of the laboratories. The questionnaire form and the accompanying letter is attached to this report (Annex 2). 256 answers were received. The response rates are presented in table 1.1.

Table 1.1 The response rates.

	Number of laboratories	Response rate
Total number of laboratories recognized:	483	
Questionnaire was sent to:	480	
Total number of answers:	256	53 %
Denmark:		25 %
Norway:		45 %
Sweden:		60 %
Finland:		71 %
Iceland:		100 %

The response rate in Denmark was unfortunately quite low. There are few large users of the substances in Denmark, and this may cause significant statistical uncertainty in the Danish figures. Few answers arrived late. They were rejected from the survey because most of the results were already calculated. It is estimated that this does not have an influence on the overall figures despite of the fact that small quantities of methyl bromide is used in organic synthesis development and research are not presented in the figures. However, the obstacles to substitution are presented in this report whether the answer was late or not.

The laboratories were asked whether they use or have used, have adopted or intend to adopt substitute substances or methods, or if they have never used the substances. Based on the response rates, an estimation on the number of laboratories using the substances was done. The figures are presented in table 1.2. A couple of laboratories actually used other solvents than ozone depleting substances, which is corrected in the figures.

Table 1.2 Number of laboratories using ODS in 2001.

	Number of laboratories
1. Uses or has used ODSs:	203
2. Has adopted or intend to adopt substitute substances or methods:	66
3. *Both 1 and 2*	63
4. *1 or 2*	217

Later in this report, all the figures describe the sum use of ozone depleting substances in all the Nordic countries, and they are corrected by response rates and possibly other statistical factors, if not otherwise determined. If the absolute number of answers or laboratories is presented, the number is mentioned separately.

2 The quantities of the ozone depleting substances used for laboratory purposes

The quantities of ozone depleting substances used for laboratory purposes are listed in table **2.1**. The table represents the amount of new substances needed for these purposes. The numbers marked with asterisk (*) are estimations based on the number of determinations announced for the years 2002 and 2003. Many laboratories mentioned only the number of determinations for the year 2001, or mentioned a number of determinations using the ozone depleting substances despite of the ban to use them for oil-in-water determinations. In case of no other information on the substitution or ceasing the use of ozone depleting substances was given, it was estimated that the number of determinations will stay the same (a "business as usual" –assumption). Due to these reasons the estimations on the use of ozone depleting substances in 2002 and 2003 are possibly overestimations and, additionally, may include also use of regenerated substances.

Table 2.1 Quantities of new ozone depleting substances used for laboratory use purposes in the Nordic countries as kilograms and ODP-corrected kilograms. Note: the total of these numbers may not match to the overall total due to rounding.

	CTC	CFC-11	CFC-113	1,1,1-TCE	Total sum
2001 (kg)	8664	4	8599	147	17414
2002 (kg)*	8413	2	8546	46	17007
2003 (kg)*	5752	0	2302	44	8098
2001 (ODP)	9530	4	6879	15	16427
2002 (ODP)*	9254	2	6837	5	16097
2003 (ODP)*	6328	0	1842	4	8174

The quantities used for oil-in-water determinations are presented in table2.2. The figures marked with an asterisk (*) are estimations similar to in table 2.1.

Table 2.2 Quantities of new ozone depleting substances used foroil-in-water determinations as kilograms and ODP-corrected kilograms. Note: the total of these numbers may not match to the overall total due to rounding.

	CTC	CFC-11	CFC-113	1,1,1-TCE	Total sum
2001 (kg)	7849	4	7818	91	15761
2002 (kg)*	7710	2	5310	2	13024
2003 (kg)*	5120	0	1657	2	6778
2001 (ODP)	8634	4	6254	9	14901
2002 (ODP)*	8482	2	4248	<1	12732
2003 (ODP)*	5632	0	1325	<1	6957

The relationship between the quantities of ozone depleting substances used for all laboratory purposes and oil-in-water determinations is better visualized in the figure 2.1.

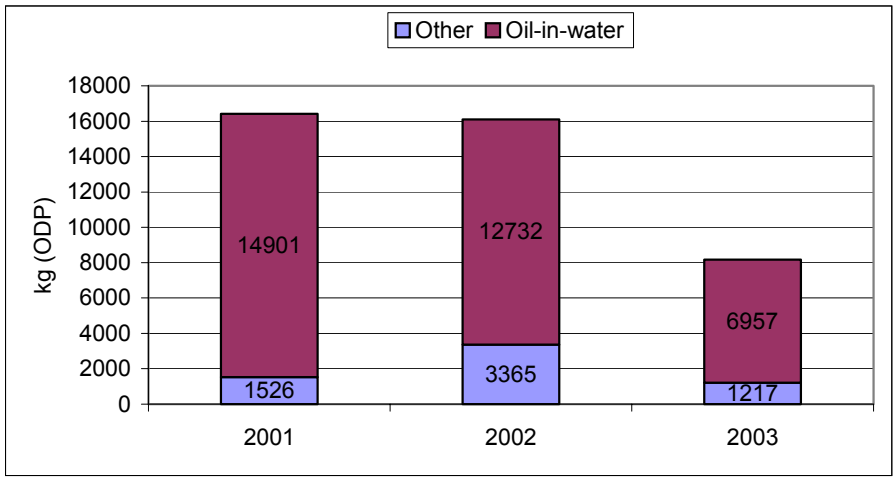

Figure 2.1 **Use of ozone depleting substances for oil-in-water determinations and other use purposes in the Nordic countries.**

The ozone depleting potentials (ODP) factors are presented in table 2.3.

Table 2.3 **The ozone depletion potential factors (ODP factors).**

	CTC	CFC-11	CFC-113	1,1,1-TCE
ODP	1,1	1,0	0,8	0,1

The number of individual determinations in which the ozone depleting substances are used is presented in figure 2.2.

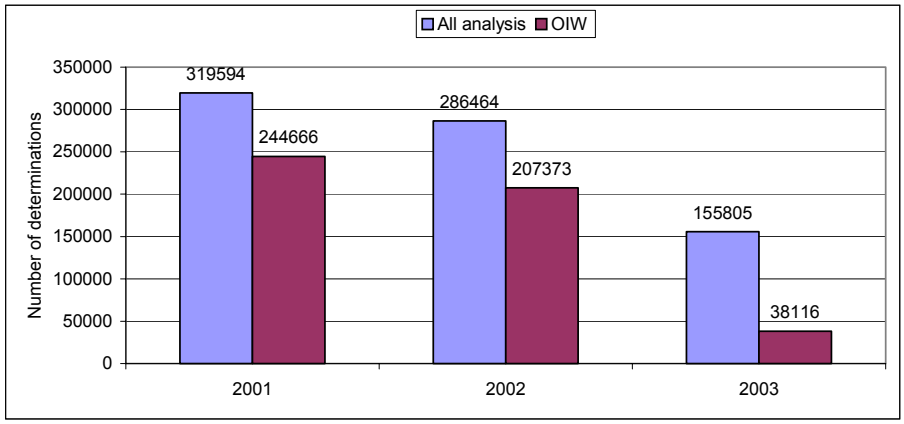

Figure 2.2 **Estimated number of determinations using the ozone depleting substances in 2001 – 2003. All determinations and determinations of oil-in-water specified.**

3 The use of the ozone depleting substances according to industrial branch

The number of laboratories using ozone depleting substances in various branches is presented in the figure 3.1. Research and education includes universities, schools and most research institutes. Oil industry includes oil production and refineries. If the number of laboratories in a branch was less than five, they have been included in the group "Other". This group includes, for example, electric and electronic industry, waste management and recycling, military products and personal safety, forest and packaging industry, energy production, glass industry, plastics industry, textile industry, and trading of chemicals.

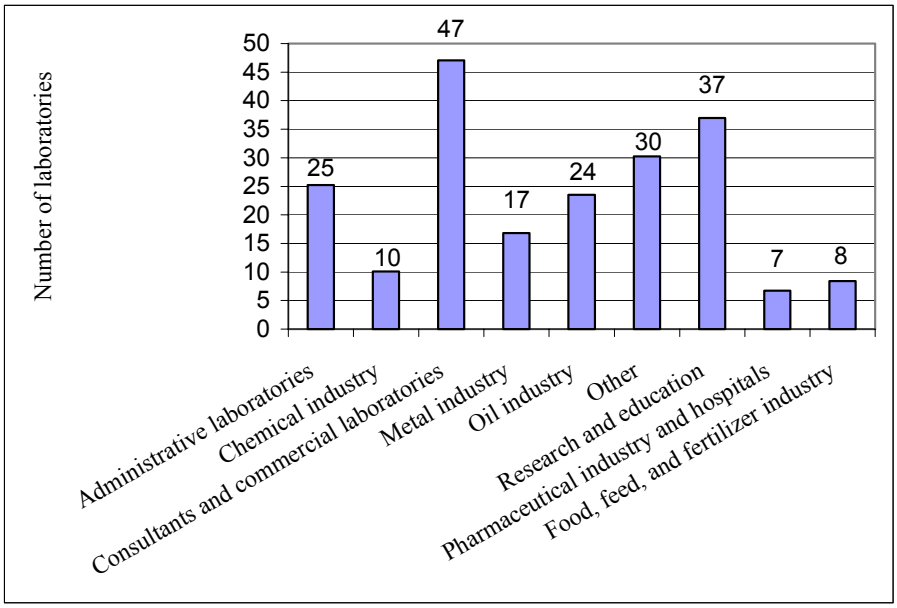

Figure 3.1 Number of laboratories using ozone depleting substances in various branches in 2001.

The quantities of ozone depleting substances used in the various branches for all use purposes, oil-in-water determinations, and other use purposes than determination of oil-in-water are presented in figures 3.2 – 3.4.

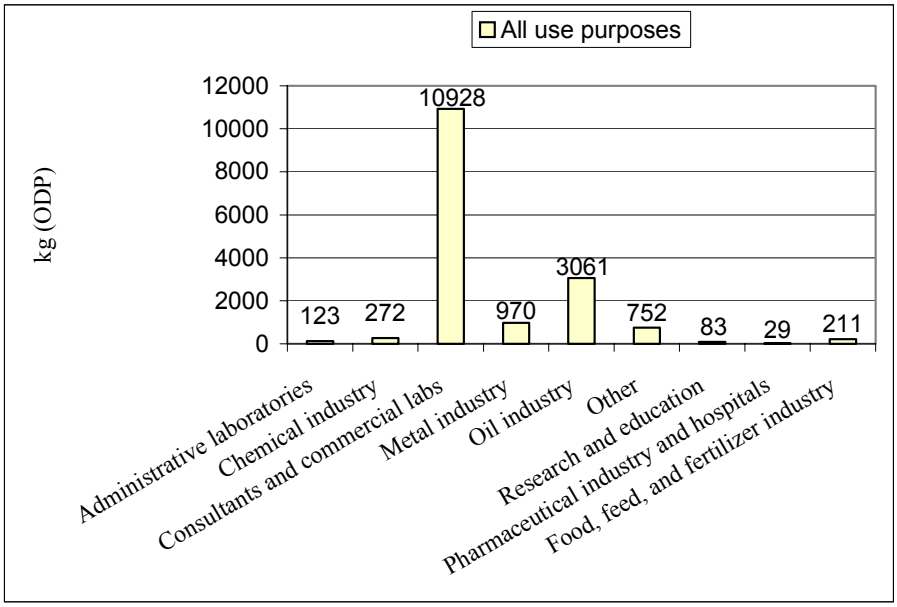

Figure 3.2 Quantities of ozone depleting substances used in various branches for all use purposes as kilograms (ODP) in 2001. Note: the total of these numbers may not match to overall total due to rounding.

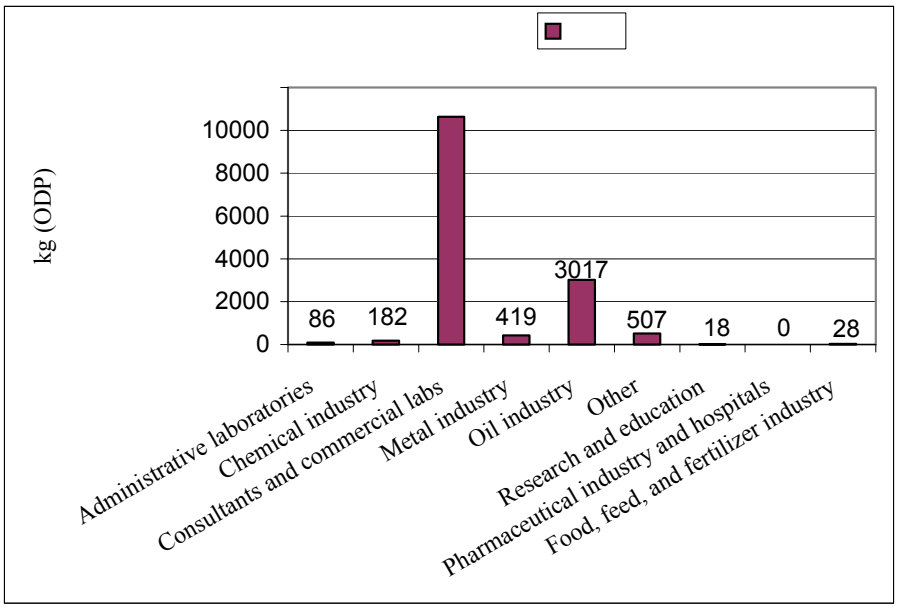

Figure 3.3 Quantities of ozone depleting substances used in various branches for oil-in-water determinations in 2001. Note: the total of these numbers may not match to the overall total due to rounding.

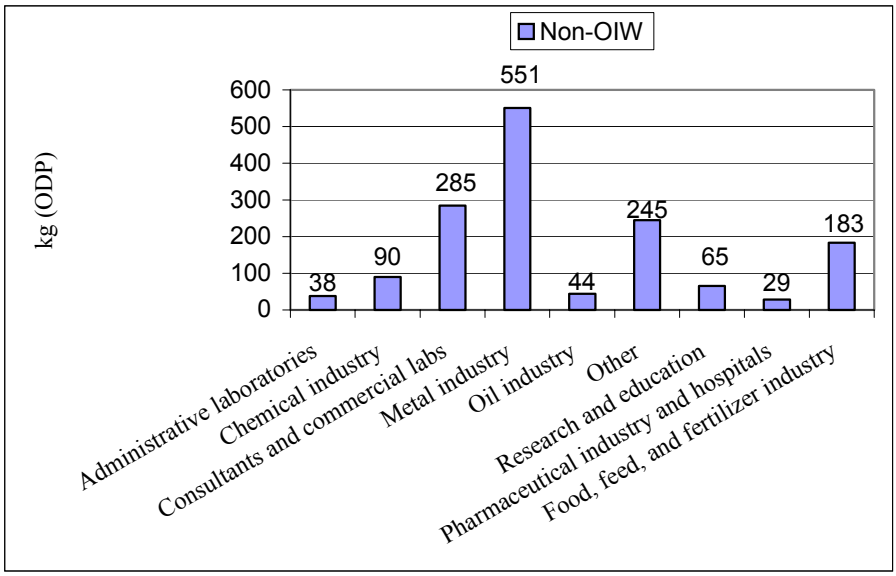

Figure 3.4 Quantities of ozone depleting substances used in various branches for other use purposes than determination of oil-in-water in 2001. Note: the total of these numbers may not match to the overall total due to rounding.

It can easily be seen that commercial laboratories and the oil industry are the most significant users of the ozone depleting substances. Despite of the large number of laboratories using the substances, the absolute quantity of the substances is low, for example, in the branch "research and education".

4 Use of the ozone depleting substances according to the determination method

The use of the ozone depleting substance for determinations done by infrared spectrometry, gravimetry, or with any other determination method or for any other use purpose was estimated. The results are presented in figure 4.1. It can easily be seen that the use of substances in infrared spectrometry for oil-in-water determinations is the most significant use of the substances. Gravimetry is used for determination of oil-in-water, determination of oil-and-grease-in-water, and other determinations.

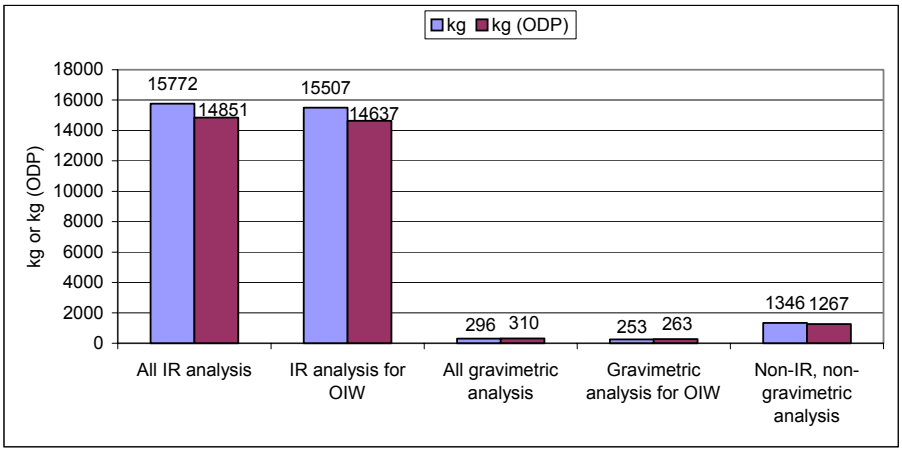

Figure 4.1. Use of ozone depleting substances for infrared (IR), gravimetric and other determinations in 2001. All determinations and determinations of oil-in-water specified. Note: the total of these numbers may not match to overall total due to rounding.

The infrared determination methods mentioned in the answers were:

- SFS 3010. Veden öljyn ja rasvan määritys. Infrapuna-spektrofotometrinen menetelmä
- DS/R 209. Vandundersøgelse. Olie og fedt. Infrarød spektrofotometrisk metode/Determination of oil and grease in water - Infrared spectrophotometric method
- NS 9803. Vannundersøkelse. Bestemmelse av olje I vann – Infrarødspektrofotometrisk metode
- SS 02 81 45. Bestämning av olja och fett i vatten. Infrarödspektrofotometrisk metod
- SM 503 B (1985) (Infrared spectrometric method, total petroleum hydrocarbons, oil and grase; Standard Methods 503B, 16th Edition) or (US) EPA 600 Method 418.1
- SS 02 81 03 Vattenundersökningar - Bestämning av fetthalt i avloppsvatten från livsmedelsindustrin - Infrarödspektrofotometrisk metod - Determination of fat in wastewater from food processing industries - Infrared spectrophotometric method
- any (laboratories' own) modifications of these methods.

The gravimetric determination methods mentioned in the answers were:

- SFS 3009. Veden öljyn ja rasvan määritys. Gravimetrinen menetelmä. (Finnish)
- DS/R 208. Vandundersøgelse. Olie og fedt. Gravimetrisk metode/Determination of oil and grease in water - Gravimetric method (Danish)
- NS 4752. Vannundersøkelse - Bestemmelse av olje og fett - Gravimetrisk metode/Water analysis - Determination of oil and grease - Gravimetric method (Norwegian)
- NS 9804. Vannundersøkelse - Bestemmelse av fett i avløpsvann fra næringsmiddelindustrien - Infrarødspektrofotometrisk metode/Water analysis - Determination of fat in wastewater from food processing industries - Infrared spectrophotometric method (Norwegian)
- SS 08 82 11 Vattenundersökningar - Bestämning av fetthalten (totalhalten fett, emulgerat och avskiljbart fett) i avloppsvatten från livsmedelsindustrin - Gravimetrisk metod (Swedish)
- extraction with Soxhlet and gravimetric determination of oil or grease

- any modifications of these methods.

44 other determination methods or use purposes than determination of oil-in-water by infrared spectrometry or gravimetry were mentioned. In addition, two methods (determination of peroxide number and an additive in jet fuel) were recognized outside the questionnaire survey, the amount of ODS used in these methods not included in the figures. All these methods or use purposes are used in less than 10 laboratories except for the use of the ozone depleting substances as standards or reference materials.

Other use purposes for the ozone depleting substances were:

- for cleaning of equipment (for example, vacuum pumps)
- for calibration of equipment
- as a standard or reference or preparing standard and reference samples and
- for scintillation analysis
- for identification of irradiated groceries
- for other cleaning or solvent use
- in preparing of hemoglobin controls
- for chromatographic separation of chlorophyll derivates
- in synthesis
- for testing of personal safety equipment
- in NMR (nuclear magnetic resonance) spectrometry
- in field kits for soil and water analysis
- as tracers in permeability and porosity tests and as leak tracers

Other determination methods were:

- phenols in water (SFS 3011, SS 02 81 28)
- oil in pipes (SPRJ råd 6.1)
- hydrocarbons in soil
- plasticizers in folios
- oil additives
- Pb and Cd in groceries (AAS)
- stress-cracking in plastics
- tar in water (gravimetric)
- particle size distribution and total solids content in oil
- oil in metal shells
- cleanness of aluminum pipes
- wax in steel products
- flavours
- humidity in gunpowder
- paraffines
- wax removal
- metals in seawater (very low LOD)

- coatings in fertilizers
- coccidiostats in eggs and muscles
- air samples (GC-analysis)
- water in oils, fats and vegetable oils, Karl-Fischer titration
- TOC (total organics content or total organic carbon) in water, pipes, extraction process fluids
- oil mist in air (occupational hygiene)
- oil in compressed air
- fiber treatment chemicals
- pregnanetriol
- bromine index or bromine value in oil or chemicals (with e.g. ASTM D 1159, ASTM D 2710)
- iodine index or iodine value, edible oil analysis
- structures in polymer samples with NMR
- organic compounds in mineral products
- kerosene and extract chemicals in process waters
- determination of peroxide number in jet fuel (ASTM D 3703-99)* and
- determination of tall oil fatty acid additive in jet fuel*.

* not included in the questionnaire result figures.

Product parameters are determined for compressed air, industrial gases, ammoniac, fertilizers, cement material samples etc.

The quantities of the ozone depleting substances used for field applications, offshore, and in continuous or on-line determinations and number of individual determinations in 2001 are presented in figure 4.3. Significant uncertainties include in the figure, since the number of answers per question was low.

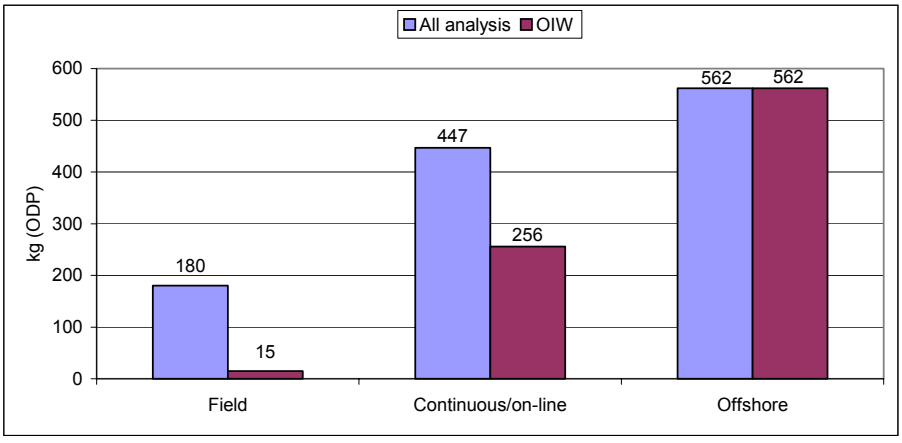

Figure 4.2 Use of ozone depleting substances for field applications, continuous or on-line methods and offshore activities as kilograms (ODP) in 2001.

The field applications include determinations of phenol impurities, determinations of hydrocarbons in soil, calibration of scintillation measurement equipment, and determinations of oil-in-water. Continuous and on-line methods are used for determinations of

industrial gases, bromine index in oil and chemical products, kerosene and extraction chemicals in mineral industry, and oil-in-water. Determinations done offshore are merely oil-in-water -analysis.

5 The use of the ozone depleting substances according to sample type

If classified by the sample type or media, determinations of water, like wastewater, drinking water, surface, recipient, and ground waters, is clearly the most significant use purpose of the ozone depleting substances. Smaller amounts of the substances are used for determinations of soil, waste, sludge, various products, and other use purposes. Among the determination of products, like oil, wood, minerals, plastics, textiles, chemicals, and pipes, no distinctive media arose.

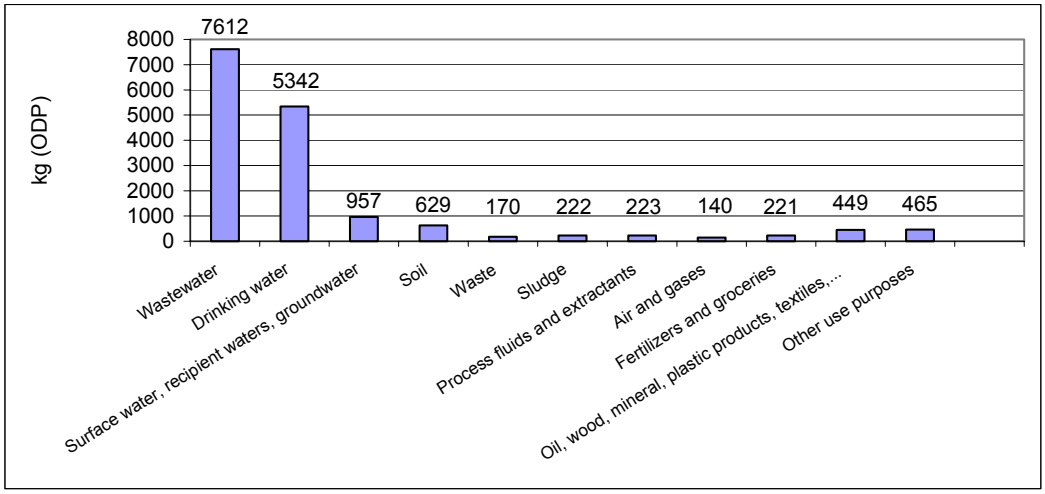

Figure 5.1 The use of the ozone depleting substances classified by the sample type in 2001. Note: the total of these numbers may not match to overall total due to rounding.

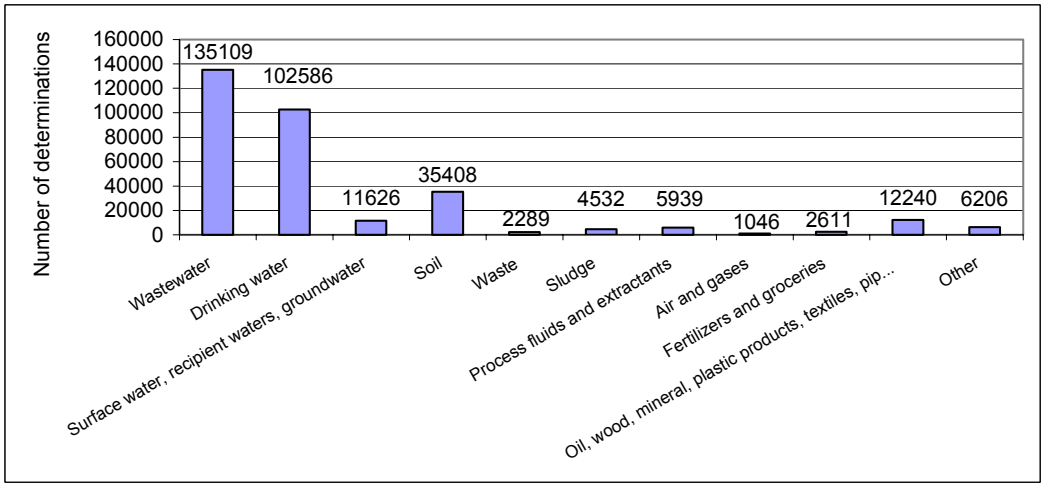

Figure 5.2 Quantity of individual determinations classified by the sample type in 2001. Note: the total of these numbers may not match to overall total due to rounding.

6 The amount of the ozone depleting substances used for an individual determination

An important way to decrease the use and emissions of ozone depleting substances is to reduce the amount of the substance used in an individual determination. 99 laboratories gave information on the volume of the substance used in an individual determination concerning a total of 120 method cases.

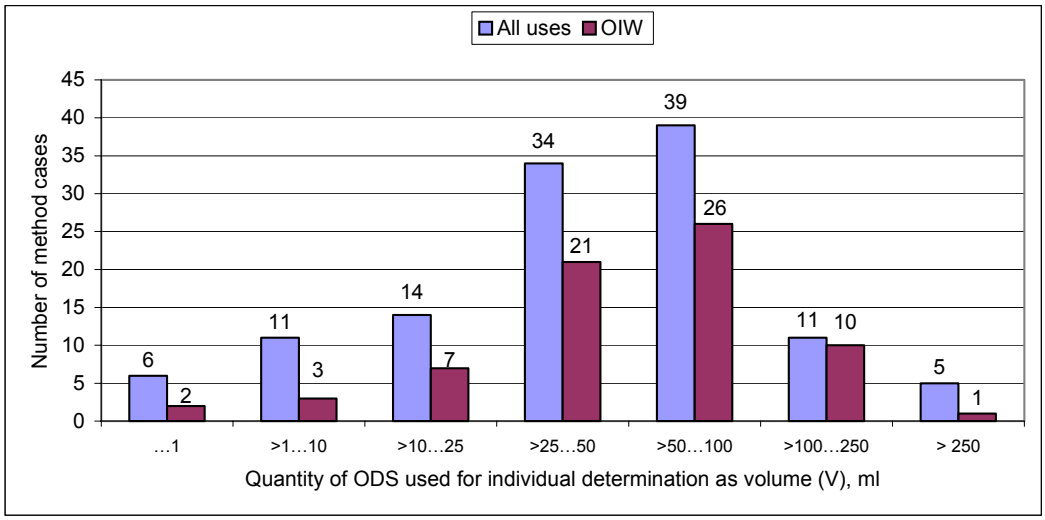

Figure 6.1 The volume of an ozone depleting substance used in an individual determination in 2001 as milliliters (ml). All determinations and determinations of oil-in-water specified. (n = 120)

The smallest volumes were needed when the substances were used as standards or references, in scintillation analysis, and in determinations of oil additives, bromine index, and polymer structure. The biggest volumes were used in extraction with Soxhlet equipment, and for a rare use purpose, the chromatographic separation of chlorophyll derivates. The total use of the substances classified by the volume is presented in figure 6.2., and the quantity of determinations in figure 6.3.

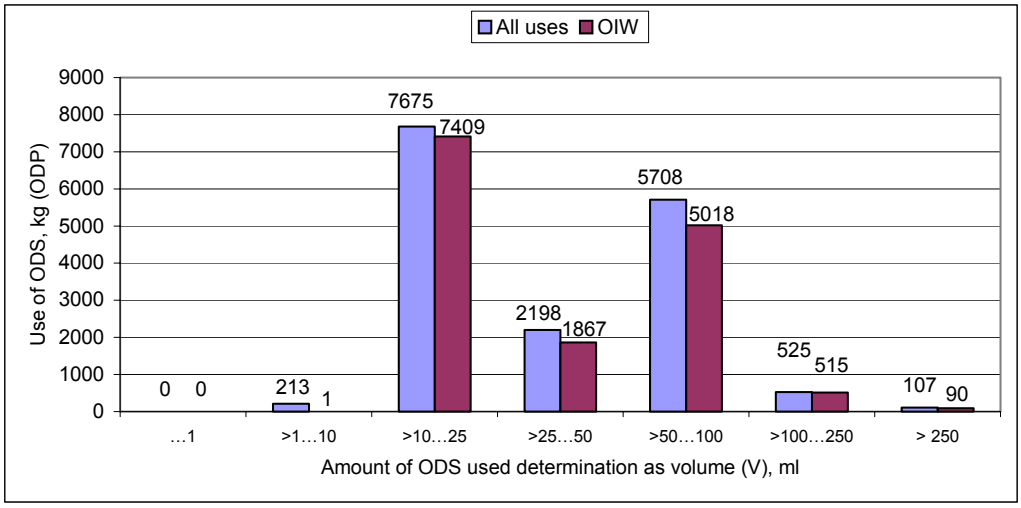

Figure 6.2 Amount of ozone depleting substances used in 2001 as kilograms (kg, ODP) classified by the volume used in individual determinations. All determinations and determinations of oil-in-water specified. Note: the total of these numbers may not match to overall total due to rounding.

Most of the substances are used in determinations in which >10 - 25 ml or >50 - 100 ml of substance is needed. This is easily explained by the total number of individual determinations done in these volume classes.

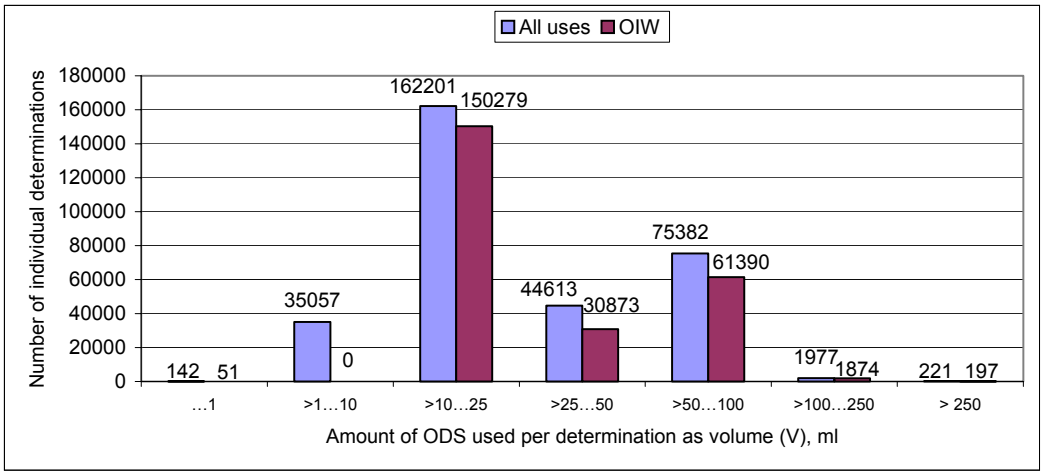

Figure 6.3 Quantity of determinations classified by the volume of ozone depleting substance used in an individual determination in 2001. All determinations and determinations of oil-in-water specified. Note: the total of these numbers may not match to overall total due to rounding.

The result suggest that reducing the volume of an ozone depleting substance used for an individual determination has been applied quite well, but not comprehensively. However, the accuracy of the method and recoveries may severely suffer, for example, due to the decreased quantity of extraction solvent used in the determination, and therefore good experience on each determination method and sample type is a prerequisite to decrease the volume of the substance used.

7 The quantities of the ozone depleting substances used in individual laboratories

It was estimated how much ozone depleting substances are used in an individual laboratory. However, because a laboratory may use the substances for one or more use purpose, it is more practical to count each use purpose in each laboratory as an individual case, named as "number of cases" in figures 7.1. and 7.2. Quantitative information on 128 determination methods or other use purposes was received from 110 laboratories.

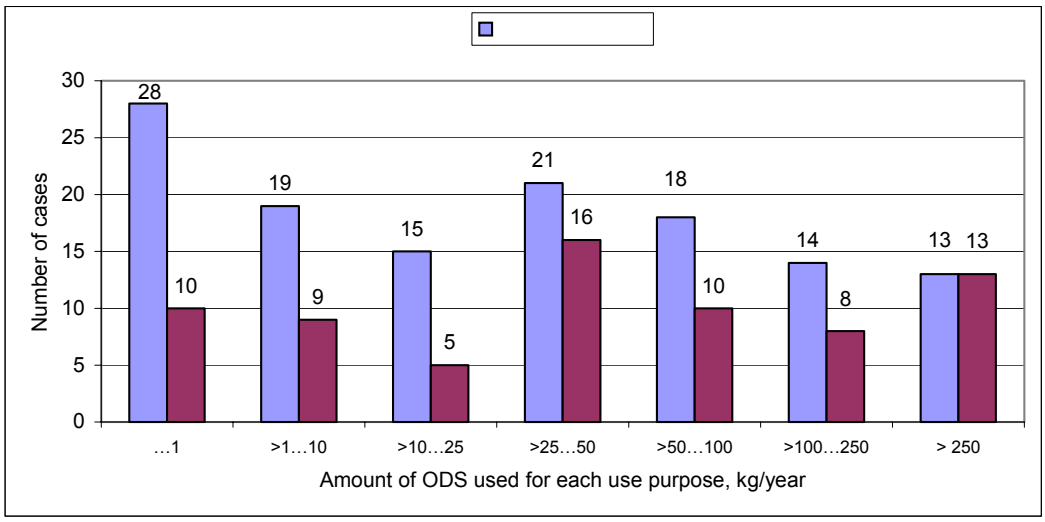

Figure 7.1 Number of use purposes classified by the quantity of ozone depleting substances used for the purpose in an individual laboratory in 2001. All determinations and determinations of oil-in-water specified. (n=110)

There are several use purposes for which only relatively small quantities of the ozone depleting substances are used. It is suggested that substitution is easy in some cases, e.g. when it is not economically viable to buy a gas chromatograph to substitute determination of oil-in-water by infrared spectrometry, the determinations can easily be bought from a commercial laboratory. However, this is not true for all use purposes.

The absolute amount of the ozone depleting substances used in each size class was estimated as presented in figure 7.2.

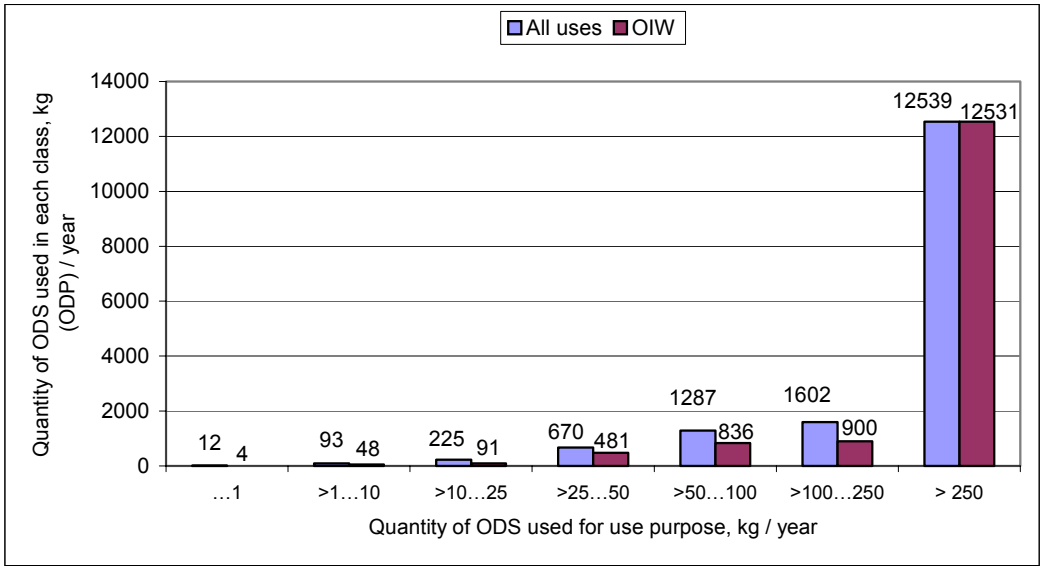

Figure 7.2 Quantities of the ozone depleting substances used in each size class in 2001 as kilograms (kg, ODP). All determinations and determination of oil-in-water specified. Note: the total of these numbers may not match to overall total due to rounding.

It can easily be seen that most of ozone depleting substances were used in the biggest laboratories. Also most of the individual determinations are done in these laboratories.

8 The after-use fate of the ozone depleting substances

The laboratories were asked whether the ozone depleting substances are recycled or regenerated, delivered to an appropriate waste treatment/thermal destruction plant, or lost to air, water or sewage. 93 laboratories gave an estimation of the fate of the substances concerning 110 use purposes. 58 laboratories estimated that no losses take place. 18 laboratories answered that in 20 use purposes the substances are recycled or regenerated after use. The estimations of losses as percents of the amounts of substance used for each use purpose are presented in figure 8.1.

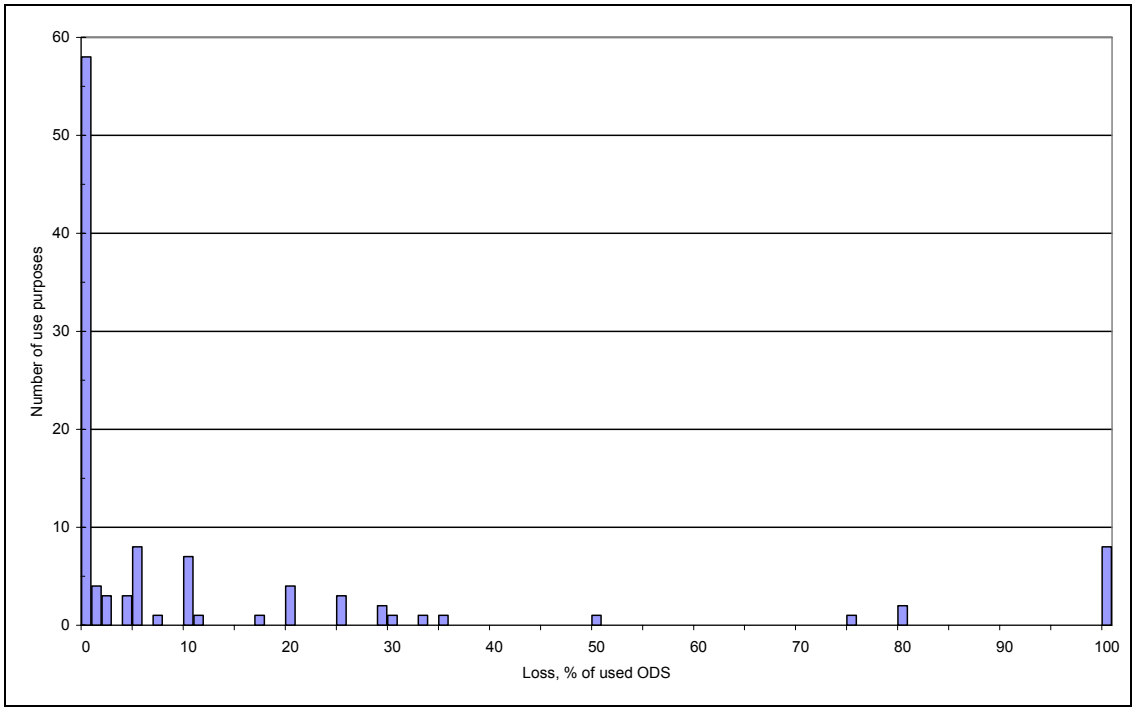

Figure 8.1 Number of use purposes classified by the percent of ozone depleting substance lost into air, water or sewage.

To estimate the emission of the ozone depleting substances to atmosphere from laboratory uses two scenarios were calculated. It is assumed in both scenarios that losses to air, water or sewage are finally totally emitted into atmosphere.

In the first scenario, estimated "as announced", if no information on the losses was given, a country specific rate for waste treatment, recycling/regeneration and loss to air, sewage or water was used. A country specific factor was needed due to differences in the recycling/regeneration rate between the countries. It was noticed that the substances are recycled or regenerated in the greatest ratio in Norway, where the substances are used in, for example, for determinations of produced water at offshore oil production plants. For example, in Denmark, the determination of oil in drinking water is a significant use of the substances, and the detection limit requirements, and therefore the requirements for the purity of the substances are different. However, typically relatively small amounts of ozone depleting substances were used for an individual determination in Denmark. This scenario may produce an underestimation of the emissions, since many laboratories assumed that absolutely no losses took place.

In the second, "reasonable worse case" scenario, it was presumed that at least some losses took place in every laboratory. A country specific loss rate was calculated on the basis of those laboratories assuming non-zero losses. This loss rate replaced all zero loss assumptions. It is understood that this scenario does not necessarily lead to a significant overestimation on the losses.

Since some laboratories recycled or regenerated the substances, the quantity of new substances needed is smaller than the amount actually used. Therefore "total use" was calculated using various methods. Typically a laboratory knew the number of determinations done, and the amount of substance used for one determination. It is easy to calculate the total consumption, for example, 100 determinations times 100 ml per determination leads to 10 liters, and the laboratory has bought 5 liters of new substance, and in addition, used recycled substance. Some uncertainty in the results occur due to the fact that some laboratories have estimated their use of the substances with the same method not calculating the amounts needed for blank and standard samples, rinsing sample bottles, cuvettes etc.

The estimation on the "total use" and fate of the ozone depleting substances in 2001 is presented in table and the fate of ozone depleting substances as estimated in the "as announced" and "reasonable worst case" scenarios are given in tables 8.1 and 8.2.

	kg	kg (ODP)	%	% (ODP)
Total use of ODS	**22028**	**19926**	**100**	**100**
Of which new ODS	(17414)	(16430)	(79)	(82)
To appropriate waste destruction*	13688	13425	62	67
To recycling or regeneration*	7382	5697	34	29
As loss to air, water or sewage*	958	805	4	4
Oil-in-water	**20149**	**18204**	**100**	**100**
Of which new ODS	(15761)	(14901)	(78)	(82)
To appropriate waste destruction*	12355	12195	61	67
To recycling or regeneration*	6974	5336	35	29
As loss to air, water or sewage*	820	673	4	4

Table 8.1 Total use and the fate of the ozone depleting substances in 2001 as estimated in the "as announced" –scenario as kilograms (kg, ODP). All determinations and determinations of oil-in-water specified. *Note: The total of these numbers may not match to overall total due to rounding.

	kg	kg (ODP)	%	% (ODP)
Total use of ODS	**22028**	**19926**	**100**	**100**
Of which new ODS	(17414)	(16430)	(79)	(82)
To appropriate waste destruction*	13305	13058	60	66
To recycling or regeneration*	7361	5698	34	29
As loss to air, water or sewage*	1362	1170	6	6
Oil-in-water	**20149**	**18204**	**100**	**100**
Of which new ODS	(15761)	(14901)	(78)	(82)
To appropriate waste destruction*	11996	11849	60	65
To recycling or regeneration*	6951	5336	34	29
As loss to air, water or sewage*	1202	1019	6	6

Table 8.2 Total use and the fate of the ozone depleting substances in 2001 as estimated in the "reasonable worst case" –scenario as kilograms (kg, ODP). All determinations and determinations of oil-in-water specified. *Note: The total of these numbers may not match to overall total due to rounding.

On the basis of the scenarios, it is estimated that the emissions of the substances into atmosphere from laboratory use purposes were 670 – 1020 kg (ODP) in the Nordic countries in the year 2001. The estimation is relatively low compared to a figure presented in literature, which presumed that the recoveries of extraction solvents can be as low as 60 %, and 85 % at the maximum. [225].

The recycling ratio is smaller when expressed as kilograms (ODP) due to the use of CFC-113 with smaller ODP-factor by big users recycling the substances. There is no one explanation for why the ozone depleting substances are not recycled or regenerated more. One explanation is the high quality demands for laboratory chemicals, that is, the reuse is possibly avoided in the fear of contamination.

An estimation of losses classified by the quantity of the substances used for individual use purposes was done for both scenarios as presented in figures 8.3 and 8.4.

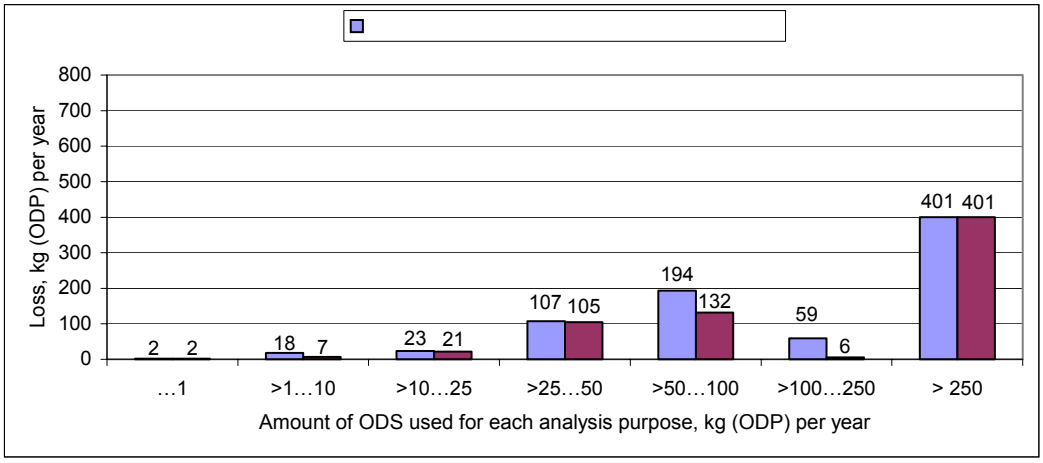

Figure 8.2 Loss of the ozone depleting substances as kilograms (kg, ODP) classified by the quantity of the substances used for individual use purposes - "as announced" -scenario. All determinations

and determinations of oil-in-water specified. Note: The total of these numbers may not match to overall total due to rounding.

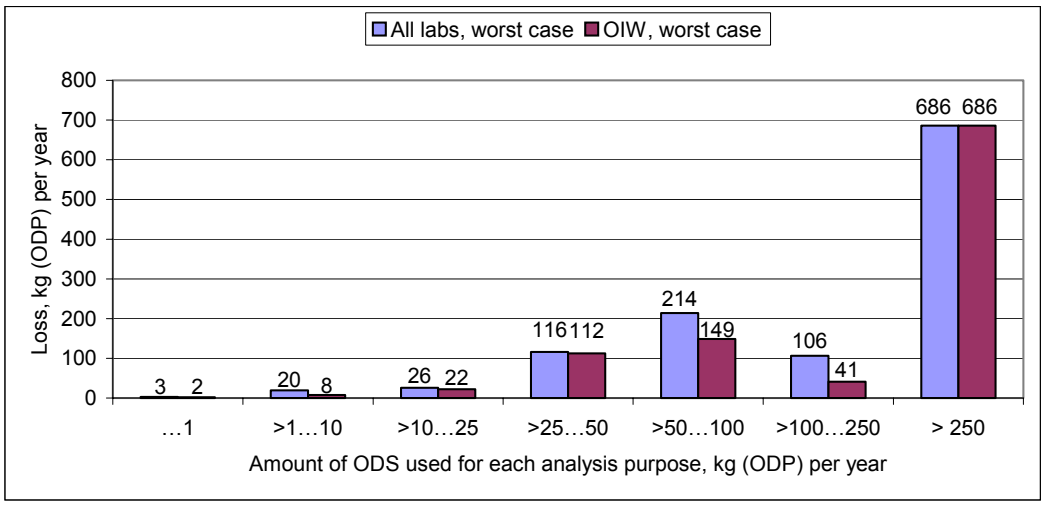

Figure 8.3 **Loss of the ozone depleting substances as kilograms (kg, ODP) classified by the quantity of the substances used for individual use purposes - "reasonable worst case" -scenario. All determinations and determinations of oil-in-water specified.** Note: The total of these numbers may not match to overall total due to rounding.

According to the "as announced" –scenario, the losses compared to the amount of ODS used, as presented in figure 7.2., are generally smaller in the laboratories using the greatest amounts of ODS. In the "reasonable worst case" –scenario the losses increase in the laboratories using the greatest amounts of ODS, but in general, the losses are still relatively smaller than in the smaller laboratories.

9 Detection limits

Detection limit was understood as one of the most important performance properties of a method. It is emphasized that a good detection limit of a substitute method does not mean that the method is applicable and suitable. However, it was used as an important parameter to describe the requirements to substitute methods.

Detection limit of 0,1 mg/kg was typical for determinations in soil, waste, and sludge samples. For soil and sludge analysis, detection limits were higher especially for gravimetric determinations. Detection limit of 10 mg/kg was typical, and limits varied up to 150 mg/kg for determinations of fertilizer coatings. A typical detection limit for organic compounds in mineral products and hydrocarbons in soil was 1 mg/kg.

The most typical detection limit for oil-in-water analysis using ozone depleting substances was 0,1 mg/l. Methods with the detection limit of 0,1 mg/l were used also for various wastewater and drinking analysis. Detection limit of 1 mg/l was used for the determination of kerosene and extract chemicals in process waters. Detection limit of 1 mg/l was achieved also in gravimetric determination of oil-in-water -analysis. Detection limit of 2 mg/l was used for determination of particles in oil and gravimetric oil in wastewater analysis, but also for some infrared determinations of oil in wastewater. A

higher detection limit, 5 mg/l, was used in oil, grease and tar in wastewater analysis, and in oil additives analysis.

Lower detection limits were needed for some measurements. Detection limits from 0,01 mg/l to 0,05 mg/l were achieved in phenol in wastewater and oil in wastewater analysis, and limits between 0,001 mg/l and 0,01 mg/l were achieved in the analysis of oil-in-wastewater, especially in determinations of oil-in-drinking water, oil mist in air for occupational health purposes and oil in compressed air. Detection limits even below 0,001 mg/l were achieved in determination of metals in seawater. A detection limit of 0,001…0,01 mg/kg was achieved in determination of coccidiostats in eggs and muscles. Very low detection limits are required also in some oil on metal surfaces –analysis (0,001 mg/m^2), and in permeability and porosity testing.

10 Obstacles to substituting the ozone depleting substance or the method using an ozone depleting substance

95 laboratories gave information on the reasons why an ozone depleting substance or a method using ozone depleting substances has not been substituted. The reasons are presented in table 10.1.

Number of laboratories	All answers	Oil-in-water
No substitute method is known.	47	13
Development of substitute method is not completed.	38	24
Detection limit of substitute method is deficient.	13	7
Accuracy (like repeatability or reproducibility) of substitute method is inadequate.	8	4
Substitution causes investments in instrumentation or other implementation costs.	20	15
Determination method is strictly determined in monitoring program or environmental license.	10	7
Determination method is required on the basis of a PARCOM or HELCOM decision or recommendation.	1	1
Other, please specify?	20	9

Table 10.1 Obstacles to substitution of methods using ozone depleting substances. (n = 95)

For some analysis methods or use purposes several obstacles were mentioned. In some cases, many methods were announced to be in use, but it was not specified which methods the obstacles presented concerned.

No substitute method was known for the following methods or use purposes (number of answers in parentheses):

- determination of oil and grease in wastewater or surface water (13)
- determination of oil and grease in drinking water (5)
- determination of oil and grease in soil (4)
- determination of bromine index (3)
- research of various chemical synthesis (4)
- conservation of art[1)] (2)
- determination of oil and grease in sludge (2)

- determination of iodine index (2)
- determination of rest oil in metal products (2)
- metals in water with a very low detection limit (2)
- analysis of oil on complex metal surfaces (1)
- determination of phenol impurities (1)
- determination of oil in industrial gases (1)
- field determination of hydrocarbons in soil (1)
- determination of oil additives (1)
- preparation of hemoglobin controls (1)
- determination of organic compounds in mineral products (1)
- chromatographic separation of chlorophyll derivates (1)
- determination of flavours (1)
- determination of wax in steel products (1)
- NMR (nuclear magnetic resonance) analysis (1)
- determination of oil and grease in industrial gases (1)
- determination of grease in food industry wastewater (1)
- Karl-Fischer titring: water in fats and vegetable oils (1)
- determination of stress-cracking in plastics (1)
- permeability and porosity detection (1)
- identification of irradiated groceries (1) (need to use a heavy non-polar solvent)

[1)] Illegal use of ozone depleting substances. User and importer notified.

A substitute method was under development, but not completed, for the determination of (number of answers in parentheses):

- oil and grease in wastewater, surface water or recipients (23)
- oil and grease in soil (6)
- oil and grease in sludge (6)
- oil and grease in drinking water (3)
- oil in metal products (2)
- surface coatings of fertilizers (2)
- oil and grease in waste (2)
- oil product (1)
- fiber treatment compounds (1)
- organic compounds in mineral products (1)
- freon extraction of metals in seawater (1)
- permeability and porosity (1)
- plasticizers in a plastic product (1)

- TOC in waste and soil (1) and
- for Karl-Fischer –titration (2) and
- for research of various chemical synthesis.

Detection limit when using the substitute was deficient for the determination of (number of answers in parentheses):

- oil and grease in wastewater or surface water (5)
- oil and grease in drinking water (5)
- oil and grease in soil (2)
- oil and grease in sludge (2)
- metals in water with a very low detection limit (2)
- compressed air analysis (1)
- coccidiostats in eggs and muscle (1) and
- polymer structures with NMR (1).

Accuracy of the substitute method was inadequate for the determination of (number of answers in parentheses):

- oil and grease in wastewater or surface water (4)
- oil and grease in soil (4)
- oil and grease in drinking water (3)
- oil and grease in sludge (2)
- oil and grease in waste (1)
- oil product (1)
- surface coatings of fertilizers (1)
- polymer structures with NMR (1) and
- freon extraction of metals in seawater (1).

Investments in instrumentation or other implementation costs were obstacles to the substitution of the method used for the determination of (number of answers in parentheses):

- oil and grease in wastewater or surface water (12)
- oil and grease or hydrocarbons in soil (5)
- oil and grease in sludge (4)
- oil and grease in drinking water (2)
- organic compounds in mineral products (1)
- rest oil in metal products (1)
- analysis of oil on complex metal surfaces (1)
- oil mist in air (1) and
- Karl-Fischer –titration (2).

Monitoring program or environmental license strictly determined the method used for the determination of (number of answers in parentheses):

- oil in wastewater (3) (in one answer: ISO 9377-2 is not good enough for analysis aliphatic and aromatic hydrocarbons and nonpolar aliphatic hydrocarbons)
- oil in drinking water (3) (national environmental protection agency requires the use of IR-method [with low detection limit])
- oil and grease in soil (1)
- oil and grease in sludge (1)
- grease in food industry wastewater (1) and
- phenol in industrial wastewater (1).

Other obstacles to the substitution were:

- poor comparability between results (oil in soil, water and waste; TOC)
- needs to measure grease in oil (analysis of grease in water, soil and sludge)
- there is no as good solvent available as carbon tetrachloride (oil in water and soil, gravimetric method)
- in some cases cannot be replaced with any other solvent (chromatographic separation of chlorophyll derivates)
- substitute method is slow (oil in soil, waste)
- substitute solvent contains too much disturbing impurities (oil in compressed air)
- gravimetric method is not suitable for use purpose (oil analysis of industrial gases)
- method is a pharmacopean standard (iodine value of groceries)
- difficulties to substitute in all cases (synthesis)
- rinsing of sample bottles is required by standard (determination of oil-in-water)
- method is the only allowed test protocol in the U.S.A. (testing of personal safety equipment)
- there are no available centrifuges suitable for use with solvents needed in substitute method (oil in soil and waste)
- old and new method are used concurrently to evaluate accuracy of the new method
- there is no suitable method to be used in a small laboratory (analysis of Pb and Cd from groceries by AAS)
- amount of substance needed is extremely small (calibration of scintillation equipment)
- there is a need to buy a direct measuring instrument with FID-detector (analysis of oil in air)
- new GC-method measures only $C_{10...40}$ –fraction (analysis of oil industry wastewater)
- new analysis method is arguable and not accepted by all (analysis of oil in wastewater and slam)

The ozone depleting substances were also used as necessary and unreplaceable standards for various organic analytics, for example, in determination of volatile organic carbons in water, air, waste and contaminated soil. Couple respondents mentioned that the substances are used for teaching purposes in small quantities: as a reagence for determination of organic compounds and as a solvent for determination of oil-in-water

with IR. One laboratory mentioned problems with emulsions in their samples, and difficulties to separate light and heavy hydrocarbons in a GC-analysis. Concerning TOC analysis, it was mentioned that the results achieved with different techniques are not comparable, because they measure separate fractions of organic carbons.

10 Substitute methods and phase of substitution

51 laboratories gave at least some information on a substitute substance or method concerning 53 method cases. In 12 cases the present method will be used with the ozone depleting substance substituted. However, most of the laboratories have substituted or will substitute both the substance and the method.

The use of most typical substitute substances is presented in figure 10.1.

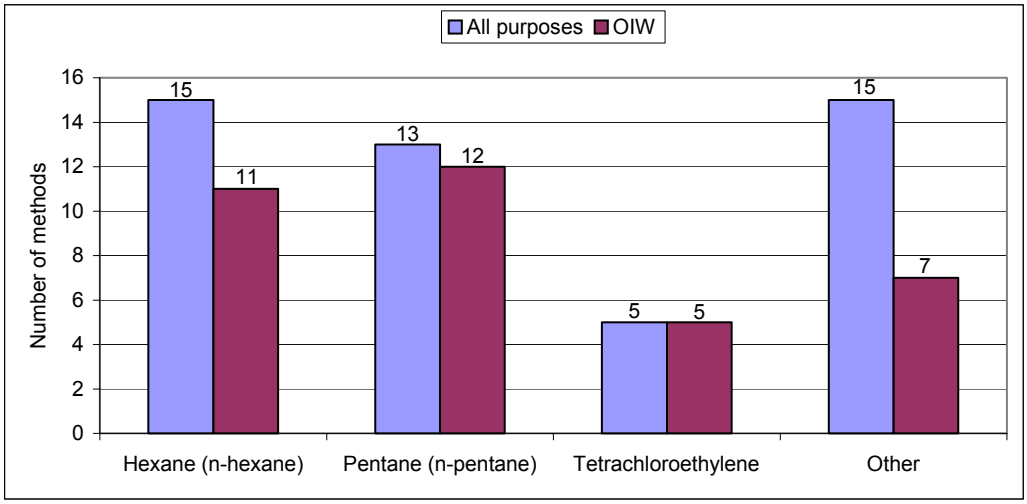

Figure 10.1 The number of method cases in which substitute substances are used. All determinations and determinations of oil-in-water specified. (n=51)

41 laboratories gave information on 48 substitute method cases. The new EN-ISO 9377-2 (or its national versions) was the most typical substitute method. Some laboratories also used old, new or even draft gravimetric methods.

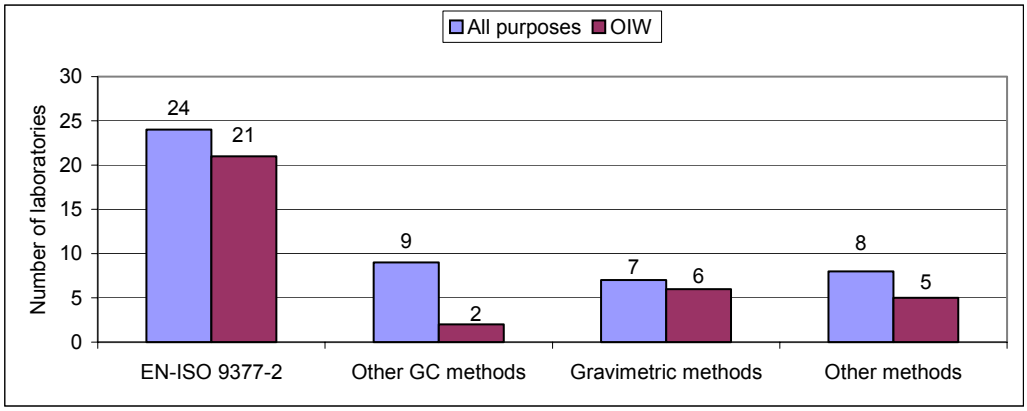

Figure 10.2 The substitute methods. All determinations and determinations of oil-in-water specified. (n=41)

The detection limits of substitute methods varied from 0,1 mg/l to 50 mg/l depending on the substitute method or substance, and sample type. No answer mentioned a detection limit below 0,1 mg/l, however, only quite few laboratories gave any information on the detection limit.

Information on the situation of substitution was received concerning 46 method cases.

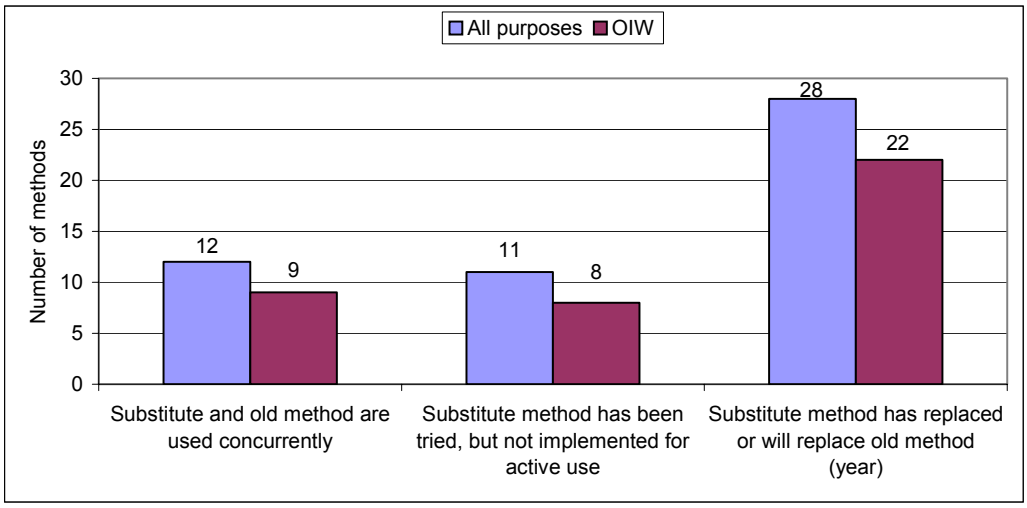

Figure 10.3 Situation of substitution. All determinations and determinations of oil-in-water specified. (n=46)

19 laboratories gave information on their participation in method development or validation.

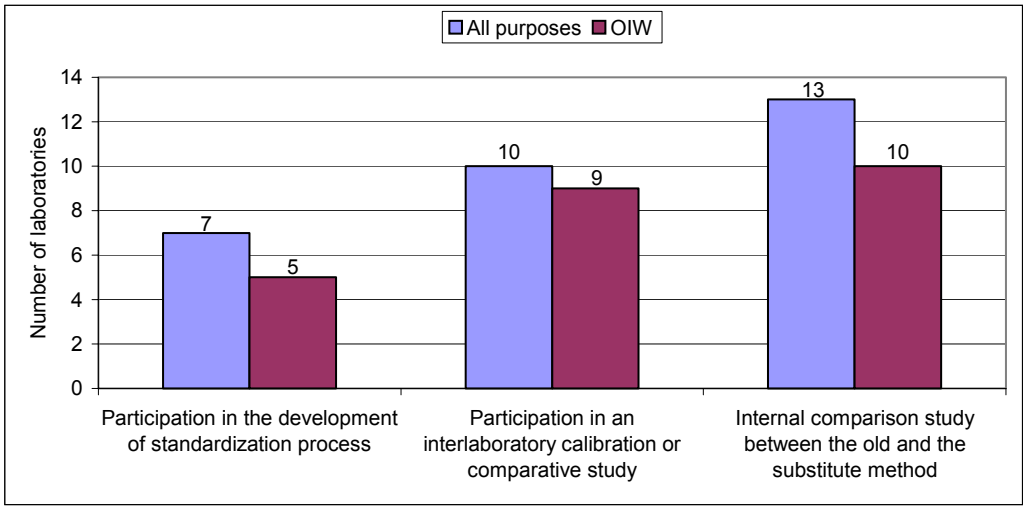

Figure 10.4 Laboratories' participation in method development or standardization process, interlaboratory calibrations or comparatives studies, and internal comparison studies. All determinations and determinations of oil-in-water specified. (n=19)

Additionally, few labs mentioned that they haven't yet started the comparison of the present and the substitute method. Some smaller laboratories announced that they have already quitted or are going to quit using IR-method and will start to buy the determinations from other laboratories.

11 Economical consequences of the substitution

It is difficult to estimate economical and other consequences of substitution, because the laboratories have very different kind of needs and possibilities to substitute a method. At least the following issues influence the possibility to substitute a method:

- availability, applicability and suitability of a substitute method in the laboratory and for the sample types
- comparability of the results between the present and substitute methods

- possibility to use existing equipment with or without modifications
- costs of substitute equipment, cost and time needed to qualificate the substitute method
- costs between the present and the substitute method
- time needed for an individual determination and delays of the results with the substitute method
- possibilities to buy analysis from another lab.

The performance properties of a substitute method have to be assessed for each sample media. In some cases, existing equipment, like a gas chromatograph, can be used as a substitute equipment, however, a new injection equipment, separation column and/or detector is possibly needed. In small laboratories, it is probably not economically reasonable to buy a new gas chromatograph unless is is necessary to run the determination, for example, in the very vicinity of an industrial process, or the determination is not available in commercial laboratories. In the biggest laboratories, several gas chromatographs might be needed to run large amounts of samples. Calibration and qualification of the substitute method adds application costs.

A coarse estimation on the substitution costs of oil-in-water determinations was calculated based on the information given by the laboratories. If the information was not available, a subjective case-by-case evaluation was done. The estimation is only trend-setting and describes only the order of magnitude of probable substitution costs. It was estimated that 35 laboratories, of which 30 are running oil-in-water determinations, will change to a gas chromatographic method in oil-in-water determinations, and 25 laboratories probably have a gas chromatograph of their own. A new column or detector is possibly needed. 10 laboratories will continue with an infrared method with a substitute substance, and 5 laboratories will substitute to a gravimetric method. 15 laboratories, of which 13 running oil-in-water determinations, will cease the determinations. 3 laboratories are going to use a totally different kind of method. In practice, the numbers should be doubled to cover the all laboratories in the Nordic countries. It is also unsure how many offshore production plants have a gas chromatograph of their own, or whether the determinations are done in onshore laboratories.

For example, Norway has 33 offshore determination points. A typical gas chromatograph with a FID costs approximately 40 000 euros. Additional equipment like autosamplers add to the price. A typical determination of oil-in-water requires at least 20 minutes, some less volatile or slightly polaric hydrocarbons might need a longer purge time to improve the recovery rate. If a new column for GC costs around 500 euros, and a new detector for GC approximately 6000 euros. Equipment for gravimetric determinations are assumed to already exist in the laboratories. Other substitution costs are not included. Further, it is assumed that no less than 30 new GCs are needed, not including the possible offshore use, and need for on-line determinations offshore. The equipment costs for 30 new GCs are 1,2 million euros. Because the GC can be used in various other methods, it is assumed that many laboratories would have bought a GC anyway during the next 5 – 10 years. An assumption was made that half of the laboratories would have bought a GC in any case, and five years was chosen as a typical lifetime for a GC. During the next ten years, substitution of ozone depleting substances in determination of oil-in-water will lead to a reduction of 6700 – 10200 kg (ODP) of emissions, costing 0,6 million euros. The costs per reduced emission ton is therefore estimated to be 60 000 – 90 000 euros.

On the other hand, estimating that 5 % of the used substance is emitted, and 50 ml of substance with a density of 1,4 is used in an individual determination, approximately

286 000 determinations are done per an emitted ton (ODP), and substitution costs per an individual determination are less than one euro. This is not quite true, because an average laboratory runs approximately 1000 determinations in one year, and a GC with a price of 40 000 euros will lead to equipment costs of 4 euros per determination during next 10 years. Some of the GCs will probably be used for the determination of BTEX in drinking water. In these cases, a bench scale GC with a PID or MSD is needed. A typical instrument of this kind costs almost 100 000 euros even without purge-and-trap or head space injection included in the price. Some savings or additional costs can be added or reduced by work and solvent prices depending on the case and sample type.

A typical price of a determination by IR is 75 – 100 euros, even less, by gravimetry around 75 – 125 euros, and for example, determination of the BTEX with GC/FID between 100 – 140 euros, sometimes including also determination of MTBE, TAME and TVOCs. Determination packets of various petroleum components by GC/FID and GC/MS cost around 150 – 320 euros depending on the fractions to be determined, and prices of aromatic hydrocarbons and volatile mineral oils approximately 80 euros. As a comparison, price of determination of PAHs by GC/FID in water costs around 160 euros.

Annex 2. The questionnaire form

SYKE

Date 22.8.2002

Number SYKE-2202-P-157-041

ORGANIZATION
Department
Person

Postal address
City
Country

Subject LABORATORY USES OF OZONE DEPLETING SUBSTANCES

Detta följebrev och bifogade frågeformulär finns även på Internet på engelska, finska och **svenska** http://www.ymparisto.fi/ympsuo/kemik/ODSLAB.htm (fil format: Microsoft® Word 97). Frågeformuläret kan returneras per e-post.

Saatekirje ja kyselylomake ovat saatavissa myös Internetissä englanniksi, ruotsiksi ja **suomeksi** http://www.ymparisto.fi/ympsuo/kemik/ODSLAB.htm (tiedostotyyppi: Microsoft® Word 97).

Kyselylomakkeen voi palauttaa sähköpostitse.

Dear Sir / Madam,

Finnish Environment Institute (SYKE) executes an inquiry on the use of ozone depleting substances (ODS) for analysis and laboratory purposes in the Nordic countries.

Aim of the inquiry

Project ODSLAB – Laboratory Uses of Ozone Depleting Substances collects information on the use of ozone depleting substances (ODS) in laboratories. Information collected and produced in the project is used to recognize the needs for ODS use, evaluate the possibilities to substitute ODS with less harmful compounds, and to assess measures taken in ODS abatement.

Current issues concerning the use of ozone depleting substances in laboratories

Use of ozone depleting substances (like carbon tetrachloride, 1,1,1-trichloroethane, CFC-compounds) for analytical purposes is regulated by the Montreal Protocol. The Parties to the Protocol decided in their 11th meeting to prohibite the use of ODS in **Testing of oil, grease and total petroleum hydrocarbons in water**, **Forensic fingerprinting** and **Testing of tar in road-paving materials** after 2001. An emergency exemption quota was granted to European Union for the testing of oil, grease and total petroleum hydrocarbons in water for 2002.

Finnish Environment Institute	Postal address	Box 140, FIN-00251 Helsinki	Tel. +358 9 403 000	Email	kirjaamo.syke@ymparisto.fi
	Visiting address	Mechelininkatu 34 a	Fax. +358 9 4030 0190	Internet	www.environment.fi/syke
Finlands miljöcentral	Postadress	PB 140, FIN-00251 Helsingfors	Tfn. +358 9 4030 00	e-post	kirjaamo.syke@ymparisto.fi
	Besöksadress	Mechelingatan 34 aFax +358 9 4030 0190		Internet	www.miljo.fi/syke

Financier of the project and publication of results

The project is financed by the The Nordic Chemical Group (NKG) under the Nordic Council of Ministers. The project is commissioned and guided by Nordic competent authorities for ozone deplesting substances. A summary report will be published in TemaNord –series in 2003. Individual replies are comprehended as confidential. Summary information concerning a nation or all the Nordic countries will be published in such a manner that no information on an individual laboratory can be deduced. **A copy of the summary report in electric form will be send to all who have responded to the questionnaire and given their contact information.**

Additional information

For additional information on the project, please contact Senior Expert, Mr. Miska Vaara, +358 9 4030 0576, email miska.vaara@environment.fi, or Senior Advisor, Mrs. Eliisa Irpola, tel. +358 9 4030 0525, email eliisa.irpola@environment.fi.

Deadline for returning the questionary form

Please send the completed questionary **to Finnish Environment Institute at the latest Friday, 6th of September 2002**. **The questionnaire can also be returned by email to Mr. Miska Vaara**, miska.vaara@environment.fi. The questionary form is available as a Microsoft® Word file at http://www.ymparisto.fi/ympsuo/kemik/ODSLAB.htm.

Finnish Environment Institute

The Finnish Environment Institute (SYKE) is the national environmental research and development centre of the environmental administration. SYKE is also the national competent authority in the implementation of Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer.

Thank You very much for Your co-operation.

With kind regards,

Jukka Malm	*Miska Vaara*
Mr. Jukka Malm	Mr. Miska Vaara
Division Manager	Senior Expert, chemical risk management

Enclosures

Questionary form

Return envelope (no stamp required)

Finnish Environment Institute
Chemicals Division

QUESTIONNAIRE ON THE LABORATORY USES OF OZONE DEPLETING SUBSTANCES

GENERAL INFORMATION

CONTACT INFORMATION OF THE RESPONDENT

COMPANY OR ORGANISATION	PLACE OF BUSINESS OR DEPARTMENT
POSTAL ADDRESS	COUNTRY
POSTAL CODE AND CITY	TELEPHONE NUMBER FOR CONTACT PERSON
CONTACT PERSON	EMAIL ADDRESS FOR CONTACT PERSON

1. ARE OZONE DEPLETING SUBSTANCES* USED OR HAVE THEY BEEN USED FOR ANY LABORATORY OR ANALYTICAL PURPOSES** IN YOUR ACTIVITIES?

☐ Yes, we use or we have used these substances for laboratory or analytical purposes**.
Please respond to the questions in chapter 2.

☐ We have adopted or intend to adopt substitute substances or methods.
Please respond to the questions in chapter 3.

☐ No, we have never used ozone depleting substances in our activities.
The questionnaire is completed. Thank you for your respond! You can give feedback on the other side of this sheet or directly to our contact persons.

* **DEFINITION.** Ozone depleting substances are carbon tetrachloride (CTC), 1,1,1-trichloroethane, fully halogenated chlorofluorohydrocarbons (CFCs, freons), halons, partly halogenated chlorofluorohydrocarbons (HCFCs), methyl bromide and partly halogenated bromofluorohydrocarbons as represented in annex to Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer.

****DEFINITION.** Typical laboratory and analytical uses include: equipment calibration, extraction solvents, diluents, carriers for specific chemical analyses; inducing chemical-specific health effects for biochemical research, as a carrier for laboratory chemicals, in reagent use; and for other critical purposes in research and development where substitutes are not readily available, or where standards set by national and international agencies require specific use of the controlled substances. Use of ozone depleting substances in refridgerators and general air conditioning are not laboratory and analytical uses mentioned in this inquiry.

INSTRUCTIONS. In order to get specific information, please complete an individual sheet for each type of analysis or other use purpose under titles 2 and 3 whenever possible and applicable. Please take additional copies of the questionnaire if needed.

Contact persons:
Mrs. Eliisa Irpola
Mr. Miska Vaara

Postal Address:
Finnish Environment Institute
Chemicals Division
Box 140
FIN-00251 HELSINKI
FINLAND

Telephone: +358 9 403 000

Telefax: +358 9 4030 0591

Email:
eliisa.irpola@environment.fi
miska.vaara@environment.fi

Please take a copy of the questionary form or part of it if needed.
Questionary form downloadable as a Microsoft® Word file at:
http://www.ymparisto.fi/ympsuo/kemik/ODSLAB.htm

FEEDBACK

1. PLEASE GIVE US FEEDBACK AND ANY OTHER COMMENTS

2. FOR WHAT ANALYTICAL OR LABORATORY PURPOSES OZONE DEPLETING SUBSTANCE ARE USED OR HAVE BEEN USED?

INSTRUCTIONS. PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH ANALYSIS METHOD AND OTHER USE OF SUBSTANCE. Please take additional copies of the questionnaire if needed. Amounts of after use treatment can be written as percentage values, volumes or weights. If only the total consumption or total amount of waste of a given substance is known, please mark these only on the first sheet.

2.1. ANALYSIS OR OTHER USE PATTERN IN WHICH OZONE DEPLETING SUBSTANCE IS USED

☐ Oil-in-water analysis, please specify:
- ☐ DS 209. Vandundersøgelse. Olie og fedt. Infrarød spektrofotometrisk metode.
- ☐ NS 9803 Vannundersøkelse - Bestemmelse av olje i vann - Infrarødspektrofotometrisk metode.
- ☐ SS 02 81 45. Bestämning av olja och fett I vatten. Infraröd spektrofotometrisk metod.
- ☐ Other oil-in-water analysis method, please specify?

☐ Any other determination or use, please specify?

2.2. USE OF METHOD IN FIELD APPLICATIONS OR OFFSHORE ACTIVITIES, CONTINUOSLY OR ON-LINE

☐ Method is used in field applications

☐ Method is continuous or used on-line

☐ Method is used in offshore activity

Principle of method (example: UVF):

Instrument (name of manufacturer and device):

2.3. NAME OF OZONE DEPLETING SUBSTANCE USED IN METHOD

(EXAMPLE: "CFC-11")

2.4. AMOUNT OF SUBSTANCE USED FOR ONE DETERMINATION, AVERAGE (EXAMPLE: "100 ml")

2.5. PURPOSE OF OZONE DEPLETING SUBSTANCE IN METHOD

☐ Extraction solvent

☐ Other, please specify?

2.6. DETECTION LIMIT (EXAMPLE: "0,1 mg/l", IF APPLICABLE)

☐ Detection limit mentioned in the standard:

☐ Laboratory's detection limit for the method is:

2.7. NUMBER OF DETERMINATIONS YEARLY

determinations in 2001

determinations in 2002

determinations in 2003

Method has not been used or will not be used after year:

2.8. NUMBER OF SAMPLE TYPES IN YEAR 2001 (NUMBER OF DETERMATIONS OR PERCENTAGE VALUES, APPRX.)

☐ Wastewater or effluent analysis . ☐ Soil analysis .

☐ Waste analysis . ☐ Drinking water analysis .

☐ Sludge analysis . ☐ Oil product analysis .

☐ Other, please specify? , .

☐ Other, please specify? , .

2.9. AMOUNT OF SUBSTANCE USED IN THE YEAR 2001

(EXAMPLE. "10 KG")

Amount of substance used for this purpose:

2.10. TREATMENT AFTER USE IN THE YEAR 2001

(AS AMOUNTS "12 KG" OR PERCENTAGE VALUES "10 %")

- to appropriate thermal/waste destruction:
- to recycling or regeneration:
- as loss or wastage to air, water or sewage:

PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH USE OF SUBSTANCE. COPY SHEET IF NECESSARY.

Please turn the page!

OTHER INFORMATION ON THE ANALYSIS METHOD OR OTHER USE PURPOSE

We are interested to receive any information on obstacles that impede or delay the substitution of ozone depleting substances in your activity, and on (other) necessities to use ozone depleting substance for the analysis method or other use purpose. Some possible reasons are listed as examples, but we kindly ask You for a more detailed description on the case, technical problems, deficiencies in methods or legislation, or any other reasons that impede the substitution of ozone depleting substances.

2.11. OBSTACLES TO SUBSTITUTING THE METHOD OR OZONE DEPLETING SUBSTANCE IN THE USE PURPOSE

- ☐ No substitute method is known.
- ☐ Development of substitute method is not completed.
- ☐ Detection limit of substitute method is deficient.
- ☐ Accuracy (like repeatability and reproducibility) of substitute method is inadequate.
- ☐ Substitution causes investments in instrumentation or other implementation costs
- ☐ Determination method is strictly determined in monitoring program or environmental licence.
- ☐ Determination method is required on the basis of a PARCOM or HELCOM decision or recommendation.
- ☐ Other, please specify?

2.12. DETAILED DESCRIPTION OF OBSTACLE (IF NEEDED)

2.13. INFORMATION ON LABORATORY'S MEASURES FOR EMISSION ABATEMENT (IF NEEDED)

(EX. EXAMPLE REDUCTIONING QUANTITIES USED PER DETERMINATION)

2.15. LABORATORY IS NOT AWARE OF THE EXACT REASON WHY USE OF A SPECIFIC METHOD IS REQUIRED. IT MIGHT BE USEFUL TO CONTACT AN OTHER ORGANISATION FOR FURTHER INFORMATION

(WHICH ORGANISATION? PLEASE MENTION CONTACT PERSON, ORGANISATION AND A POSSIBLE REASON)

2.16. OTHER INFORMATION ON THE USE PURPOSE (IF NEEDED)

PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH USE OF SUBSTANCE. COPY SHEET IF NECESSARY.

If no substitute methods have been implemented or are going to be implemented, the questionnaire is completed. Thank you for your respond!

If substitute methods are used are going to be used, please continue to chapter 3.

3. WHAT SUBSTITUTE SUBSTANCES AND METHODS HAVE BEEN OR ARE GOING TO BE IMPLEMENTED

With the help of questions in chapter 3 we try to recognize analytical procedures that substitute methods using ozone depleting substances, and receive experiences on substitute methods. PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH ANALYSIS METHOD AND OTHER USE OF SUBSTANCE. Please take copies of sheet if needed.

A) FOR THE DETERMINATION OF HYDROCARBON INDEX, OIL AND GREASE, OR TOTAL PETROLEUM HYDROCARBONS (TPH)?

3.1. SUBSTITUTE STANDARD OR WORKING METHOD

- ☐ DS/R 208. Vandundersøgelse. Olie og fedt. Gravimetrisk metode
  NS 4752. Vannundersøkelse – Bestemmelse av olje og fett - Gravimetrisk metode.
  SS 02 81 44. Bestämning av olja och fett I vatten. Gravimetrisk metod.
- ☐ ISO/CD 9377-1:1998. Water quality – Determination of hydrocarbon oil index – Part 1: Method using solvent extraction and gravimetry.
- ☐ ISO/DIS 16703 Soil quality – Determination of mineral oil content by gas chromatography
- ☐ ISO 9377-2. Water quality – Determination of hydrocarbon oil index – Part 2: Method using solvent extraction and gas chromatography.
  SS-EN ISO 9377-2 Vattenundersökningar - Bestämning av oljeindex - Del 2: Gaskromatografisk metod efter vätskeextraktion
  DS-EN ISO 9377-2 Vandundersøgelse - Mineralolie (hydrocarbon olieindeks) - Del 2: Væskeekstraktion og gaskromatografi. NS-EN ISO 9377-2 Vannundersøkelse - Bestemmelse av olje i vann - Del 2: Metode basert på løsemiddelekstraksjon og gasskromatografi .
- ☐ prEN 14039 Characterization of waste - Determination of hydrocarbon content in the range of C10 - C40 by gas chromatography
- ☐ Modification of ISO 9377-2 for offshore purposes (analysis of $C_{7..10}$ –fraction): name or code of method, directive or standard operation procedure?
- ☐ Scanning fluorometry: name or code of method, directive or standard operation procedure?
- ☐ SPE-GC/MS (Solid Phase Extraction with Gas Chromatography/Mass Spectrometry): name or code of method, directive or standard operation procedure?
- ☐ U.S.EPA Method 1664 (Rev. A): N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry.
- ☐ Other, please specify?

PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH USE OF SUBSTANCE. COPY SHEET IF NECESSARY.

B) FOR ANY OTHER ANALYSIS METHOD OR USE PURPOSE?

3.2. SUBSTITUTE METHOD OR OTHER USE PURPOSE

(STANDARD, WORKING METHOD OR OTHER DESCRIPTION ON THE USE PURPOSE)

PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH USE OF SUBSTANCE. COPY SHEET IF NECESSARY.

Please turn the page!

SUBSTITUTE METHOD – PAGE 2

3.3. DATE OF IMPLEMENTATION

☐ Both substitute (new), and ozone depleting (old) methods are used concurrently.

☐ Substitute method has been tried, but it has not been implemented for active use.

☐ Substitute method has totally replaced the old method, year:

will totally replace the old method, year: .

3.4. NAME OF NEW, SUBSTITUTE SUBSTANCE (IF APPLICABLE, EXAMPLE: "HEXANE")

Substitute, replacing substance is:

3.5. USE OF SUBSTANCE IN FIELD APPLICATIONS OR OFFSHORE ACTIVITIES

☐ Method is used in field applications ☐ Method is continuous or used on-line

☐ Method is used in offshore activity

Principle of method (example: UVF)**:**

Instrument (name of manufacturer and device):

3.6. PURPOSE OF SUBSTITUTE SUBSTANCE IN METHOD

☐ Extraction solvent

☐ Other, please specify?

3.7. NUMBER OF DETERMINATIONS YEARLY

determinations in 2001

determinations in 2002

determinations in 2003

3.8. DETECTION LIMIT (EXAMPLE: "0,1 mg/l")

☐ Detection limit is the one mentioned in the standard. Detection limit is:

☐ Laboratory's detection limit for the method is:

3.9. DISTRIBUTION OF DETERMINATIONS BETWEEN SAMPLE TYPES IN YEAR 2001
(NUMBER OF DETERMINATIONS OR PERCENTAGE VALUES, APPROXIMATELY)

☐ Wastewater or effluent analysis . ☐ Soil analysis .

☐ Waste analysis . ☐ Drinking water analysis .

☐ Sludge analysis . ☐ Oil product analysis .

☐ Other, please specify? , .

☐ Other, please specify? , .

3.10. LABORATORY'S PARTICIPATION IN METHOD DEVELOPMENT AND VALIDATION

☐ Laboratory has participated in the development or standardization process of the substituting method.

☐ Laboratory has participated in an interlaboratory calibration or comparative study.

☐ Laboratory has done an internal comparison study between the old and the substitute method.

PLEASE COMPLETE AN INDIVIDUAL SHEET FOR EACH USE OF SUBSTANCE. COPY SHEET IF NECESSARY.

Questionnaire is completed. Thank you for your respond!

Annex 3. List of the ozone depleting substances

The following substances are comprehended as ozone depleting according to the Annex I of the Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer:

Group	Substance	Ozone-depleting potential
Group I	$CFCl_3$ (CFC-11)	1,0
	CF_2Cl_2 (CFC-12)	1,0
	$C_2F_3Cl_3$ (CFC-113)	0,8
	$C_2F_4Cl_2$ (CFC-114)	1,0
	C_2F_5Cl (CFC-115)	0,6
Group II	CF_3Cl (CFC-13)	1,0
	C_2FCl_5 (CFC-111)	1,0
	$C_2F_2Cl_4$ (CFC-112)	1,0
	C_3FCl_7 (CFC-211)	1,0
	$C_3F_2Cl_6$ (CFC-212)	1,0
	$C_3F_3Cl_5$ (CFC-213)	1,0
	$C_3F_4Cl_4$ (CFC-214)	1,0
	$C_3F_5Cl_3$ (CFC-215)	1,0
	$C_3F_6Cl_2$ (CFC-216)	1,0
	C_3F_7Cl (CFC-217)	1,0
Group III	CF_2BrCl (halon-1211)	3,0
	CF_3Br (halon-1301)	10,0
	$C_2F_4Br_2$ (halon-2402)	6,0
Group IV	CCl_4 (carbon tetrachloride)	1,1
Group V	$C_2H_3Cl_3$ (2) (1,1,1-trichloroethane)	0,1
Group VI	CH_3Br (methyl bromide)	0,6
Group VII	$CHFBr_2$	1,00
	CHF_2Br	0,74
	CH_2FBr	0,73
	C_2HFBr_4	0,8
	$C_2HF_2Br_3$	1,8
	$C_2HF_3Br_2$	1,6
	C_2HF_4Br	1,2
	$C_2H_2FBr_3$	1,1
	$C_2H_2F_2Br_2$	1,5

	$C_2H_2F_3Br$	1,6
	$C_2H_3FBr_2$	1,7
	$C_2H_3F_2Br$	1,1
	C_2H_4FBr	0,1
	C_3HFBr_6	1,5
	$C_3HF_2Br_5$	1,9
	$C_3HF_3Br_4$	1,8
	$C_3HF_4Br_3$	2,2
	$C_3HF_5Br_2$	2,0
	C_3HF_6Br	3,3
	$C_3H_2FBr_5$	1,9
	$C_3H_2F_2Br_4$	2,1
	$C_3H_2F_3Br_3$	5,6
	$C_3H_2F_4Br_2$	7,5
	$C_3H_2F_5Br$	1,4
	$C_3H_3FBr_4$	1,9
	$C_3H_3F_2Br_3$	3,1
	$C_3H_3F_3Br_2$	2,5
	$C_3H_3F_4Br$	4,4
	$C_3H_4FBr_3$	0,3
	$C_3H_4F_2Br_2$	1,0
	$C_3H_4F_3Br$	0,8
	$C_3H_5FBr_2$	0,4
	$C_3H_5F_2Br$	0,8
	C_3H_6FBr	0,7
Group VIII	$CHFCl_2$ (HCFC-21) [3]	0,040
	CHF_2Cl (HCFC-22) [3]	0,055
	CH_2FCl (HCFC-31)	0,020
	C_2HFCl_4 (HCFC-121)	0,040
	$C_2HF_2Cl_3$ (HCFC-122)	0,080
	$C_2HF_3Cl_2$ (HCFC-123) [3]	0,020
	C_2HF_4Cl (HCFC-124) [3]	0,022
	$C_2H_2FCl_3$ (HCFC-131)	0,050
	$C_2H_2F_2Cl_2$ (HCFC-132)	0,050
	$C_2H_2F_3Cl$ (HCFC-133)	0,060
	$C_2H_3FCl_2$ (HCFC-141)	0,070
	CH_3CFCl_2 (HCFC-141b) [3]	0,110
	$C_2H_3F_2Cl$ (HCFC-142)	0,070
	CH_3CF_2Cl (HCFC-142b) [3]	0,065
	C_2H_4FCl (HCFC-151)	0,005
	C_3HFCl_6 (HCFC-221)	0,070
	$C_3HF_2Cl_5$ (HCFC-222)	0,090
	$C_3HF_3Cl_4$ (HCFC-223)	0,080
	$C_3HF_4Cl_3$ (HCFC-224)	0,090
	$C_3HF_5Cl_2$ (HCFC-225)	0,070
	$CF_3CF_2CHCl_2$ (HCFC-225ca) [3]	0,025
	CF_2ClCF_2CHClF (HCFC-225cb) [3]	0,033
	C_3HF_6Cl (HCFC-226)	0,100

$C_3H_2FCl_5$ (HCFC-231)	0,090
$C_3H_2F_2Cl_4$ (HCFC-232)	0,100
$C_3H_2F_3Cl_3$ (HCFC-233)	0,230
$C_3H_2F_4Cl_2$ (HCFC-234)	0,280
$C_3H_2F_5Cl$ (HCFC-235)	0,520
$C_3H_3FCl_4$ (HCFC-241)	0,090
$C_3H_3F_2Cl_3$ (HCFC-242)	0,130
$C_3H_3F_3Cl_2$ (HCFC-243)	0,120
$C_3H_3F_4Cl$ (HCFC-244)	0,140
$C_3H_4FCl_3$ (HCFC-251)	0,010
$C_3H_4F_2Cl_2$ (HCFC-252)	0,040
$C_3H_4F_3Cl$ (HCFC-253)	0,030
$C_3H_5FCl_2$ (HCFC-261)	0,020
$C_3H_5F_2Cl$ (HCFC-262)	0,020
C_3H_6FCl (HCFC-271)	0,030

(1) These ozone-depleting potentials are estimates based on existing knowledge and will be reviewed and revised periodically in the light of decisions taken by the Parties.

(2) This formula does not refer to 1,1,2-trichloroethane.

(3) Identifies the most commercially viable substance as prescribed in the Protocol.

In the Annex II of the Regulation, bromochloromethane is defined as a new substance. The production, release for free circulation in the Community and inward processing, placing on the market and use of new substances in Annex II are prohibited. This prohibition does not apply to new substances if they are used as feedstock. The Commission shall, as appropriate, make proposals to include in Annex II any substances that are not controlled substances but that are found by the Scientific Assessment Panel under the Protocol to have a significant ozone-depleting potential, including on possible exemptions from paragraph 1.

Annex 4. Properties of total petroleum hydrocarbons (TPH)

1 Introduction

IR-determination of total petroleum hydrocarbons or its fractions has been the most significant use purpose of the ozone depleting substances in laboratories during last years. In most of the cases, the presently used infrared spectrometric method can be easily substituted with a gas chromatographic method determining hydrocarbon index, which provides a generally simple indicatory method for various use purposes.

A petroleum hydrocarbon mixture may contain several hundreds of individual substances varying according to the original source of oil, distillation fraction, type of emission, and weathering of the mixture in the environment. Therefore, due to the complexity of mixtures covered by term "total petroleum hydrocarbons" it is quite understandable that two different methods measuring "oil" will always give different results at least for some samples. However, it is difficult to find other ways to define oil in other ways as by an analytical determination. Rather than having one possibly less robust method covering all possible definitions, a set of methods used alone or in combinations allows determinations related to the relevant environmental standards in each case [43].

Compared to present methods offering a possibility to determine separate hydrocarbon fractions and toxicologically most relevant individual substances, the old infrared spectrometric method had various restrictions. The general trend is to base the risk assessment on determination of various oil fractions and specific contaminants posing hazards (like the BTEXN, PAHs, oxygenated gasoline additives and specified aromatic and aliphatic fractions) – not on one index not necessarily determining more than one type of substances in the hydrocarbon mixture.

In other words, the extraction rate, detector response, and losses during the determination of individual substances present in total petroleum hydrocarbons may vary method by method, and mixture by mixture. Instead of measuring a general hydrocarbon index by IR or other detection method, present detection equipment allow further analysis of TPH constituents needed to assess the real environmental behaviour and toxicological properties of a TPH contamination. Therefore, in addition to determination of the hydrocarbon index with substitute methods, determination of individual TPH fractions and some of its major substances is rehearsed in this report.

2 Composition of some petroleum hydrocarbon mixtures

2.1 General

Total petroleum hydrocarbons (TPHs) originate from crude oils. TPHs are mainly carbon and hydrogen, but may also contain oxygen, sulfur and nitrogen, also in heterocyclic compounds. Petroleum crude oils can be broadly divided into paraffinic, asphaltic and mixed crude oils. Paraffinic crude oils are composed of aliphatic hydrocarbons (paraffins), paraffin wax (longer chain aliphatics) and high grade oils. Naphtha is the lightest part of the paraffinic fraction, followed by kerosene fractions.

Asphaltic crude oils contain larger concentrations of cycloaliphatics and high viscosity lubricating oils. Petroleum solvents are products of crude oil distillation and classified according to the boiling point range. Lubricants, greases and waxes are high boiling point fractions of crude oils. The heaviest, solid fraction are the residuals or bitumen. In other words, general classes of TPH include (in order of increasing carbon number) petroleum-derived gasses, liquefied gases, solvents, white spirits ($C_{9...11}$), kerosenes ($C_{10...16}$), jet fuels, diesel, automotive and railroad fuels, fuel and lubricating oils, bitumen compounds and waxes. [113]

The composition of oil may vary depending on the product and source. For example, the composition of polynuclear aromatic hydrocarbons in crude oil may differ from the priority pollutant PAHs of U.S.EPA, since polynuclear aromatic hydrocarbons in crude oil are mostly alkylated [23]. Characteristics of principal refinery streams have been gathered and documented by, for example, Franken et al from various CONCAWE reports [113].

2.2 Produced water

In water, oil can be present in three forms.

Dispersed oil means that oil is in form of small droplets. Both aliphatic and aromatic hydrocarbons can be present in the dispersed oil. [25]

Most soluble parts are typically mostly dissolved. The dissolved hydrocarbons are dominated by the volatile aromatic fraction of the oil: compounds such as BTEX-compounds, some of the PAHs, and phenols [226] [25]. The PAHs are dominated by naphthalene, phenanthrene and dibenzothiophene (NPD) and their $C_{1...3}$ alkyl homologues, but also heavier components like chrysene and benzo(a)pyrene are reported [226]. Phenols may be alkylated up to C_7, and organic acids are dominated by $C_{1...6}$ acids.

Free oil is floating on the surface of water or in the form of large droplets that will settle out quickly.

Since the dissolved parts are predominately the aromatics, phenols and carboxylic acids, these are not included in the IR quantification of the OSPAR analysis method, and the measured oil is therefore referred as the dispersed oil [25]. It is usually understood that the aromatic hydrocarbons carry most of the toxicity of the produced water at offshore oil produced plants, the phenols as another important substance group. There is not nec-

essarily a correlation between the total hydrocarbon content and the content of the aromatic compounds.

2.3 Gasoline

Gasoline includes approximately 200 hydrocarbons, mainly naphthahydrocarbons with $C_{4...12}$. Half of them are aliphatic and half aromatic hydrocarbons. Toluene and xylene dominate the aromatic hydrocarbons.

Petrol range organics (PRO) are defined as the total volatile hydrocarbon content in the carbon range $C_{4...10}$ including aliphatic alkanes and mono-aromatic hydrocarbons.

The diesel range organics (DRO) as defined as the non-volatile or extractable hydrocarbon content typically in the carbon range $C_{10...40}$ including aliphatic, aromatic and heterocyclic compounds. The fractionation may emphasize hydrocarbons $C_{10...22}$, whereas winter diesel contains relatively more fraction $C_{10...16}$, and light burning fuel $C_{12...22}$. If classified by the structure, diesel contains aliphatic hydrocarbons 75 – 85 %, monoaromatics 15 – 20 %, diaromatics 5 – 6 % and small amounts of polynuclear aromatic hydrocarbons. [146]

2.4 Gasoline additives

Small amounts of benzene, tetraethyl lead and tetramethyl lead, dichloroethane and dibromomethane have been used in leaded gasoline. [146] The typical oxygenated additives are methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME). Also alcohols are used in some gasolines. Various minor additives are better presented elsewhere.

2.5 Jet fuel

In jet fuel JP4 both aliphatic and aromatic hydrocarbons are included. Approximately 10 % (w) are $C_{5..6}$, 60 % of $C_{6...10}$ and 30 % of $C_{10...14}$ hydrocarbons.

3 Total petroleum hydrocarbons in the environment

3.1 Fate of TPHs in the environment

Aromatic hydrocarbons are more soluble in water than aliphatic hydrocarbons. The BTEX-compounds are the most soluble aromatic hydrocarbons, and benzene is more soluble than other BTEX-compounds.

In general, the volatility of aliphatic hydrocarbons is greater than the volatility of aromatic hydrocarbons. The trend in volatility by compound class is: alkenes = alkanes > aromatics = cycloalkanes.

The solubility in water and volatility decreases with increasing molecule weight, i.e. when the length of the carbon chain increases. In general, biodegradation is more rapid under aerobic conditions.

Trends in degradation rates according to structure are: n-alkanes, especially in the range $C_{10...25}$ are degraded easily; isoalkanes are degraded more slowly; alkenes degrade more slowly than alkanes; BTEXs are metabolized when present in concentrations not toxic to the microorganisms; PAHs degrade more slowly than the monoaromatics; and degradation of higher molecular weight cycloalkanes may be very slow. Branched hydrocarbons typically degrade slower than straight-chained hydrocarbons.

Typically the BTEX are considered as the most soluble and mobile hydrocarbons and therefore as a good indicator for contamination by petroleum hydrocarbons. Sometimes also naphthalene is monitored (BTEXN). The behavior of the BTEX-compounds in surface waters differ from groundwater, however, small concentrations of BTEX-compounds have been determined in river water, for example, in the Netherlands. Despite of their volatility, the water solubility of the BTEX is high, and the Henry's law's constant related to the volatility from water is not so high. Therefore the BTEX compounds are understood to remain in sufficient amounts in water. [36]

There are major qualitative and quantitative differences between fresh and weathered petroleum fuel mixtures. The trend is toward depletion of the more water soluble, more volatile and more easily biodegradable compounds. The overall environment hazard posed by weathered petroleum mixtures may be less than that posed by fresh mixtures [227]. However, the mobility of hydrocarbons may increase the risk of exposure somewhere else, and some hazardous hydrocarbons, like PAHs can be relatively or very persistent in the environment.

3.2 TPH in contaminated soils

Total petroleum hydrocarbons (TPH) is a major criteria when contamination of soil is assessed. Despite of the fact that the determination of TPH is a very good indicatory method, it is not able to describe exactly all possible risks. It is on the method, whether the achieved result can be calibrated with a specific hydrocarbon mixture (product) producing a good estimate on the true risk or not. For example, the same TPH level may include carcinogenic substances in one site, while no carcinogenics exist in another site. Therefore a valid correlation between TPH and risk would have to be site- and time-specific, related to a single spill, and, even then, the correlation might not be the same around the periphery of a plume where the rate of compositional change accelerates [76].

As TPH is not necessarily an accurate measurement of petroleum-derived hydrocarbon concentration, additional approaches have been taken. A general trend is to recognize the risks by determination of risk-specific components and various hydrocarbon fractions. In this kind of approach, typically specific compounds, like BTEX-compounds, compound groups, like PAHs, and various aliphatic and aromatic oil fractions are determinated depending on the type of the contamination and the purpose of the determination. In some cases, also determination of very soluble and movable oxygenated gasoline additives may be necessary. The fractionation of TPH is understood critical in the North American assessments of contaminated soils based on risk based corrective actions.

However, TPH provides an inexpensive tool to be used when determining if there is a problem, assessing the severity of the contamination, and following the process of a remediation effort. Further information on the analysis of TPH concentration, petroleum

group type concentration and individual petroleum constituent concentrations is evaluated in the material of the Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG). [76]

4 The Total Petroleum Hydrocarbons Criteria Working Group approach

4.1 The fractionation principle

Fractionation of petroleum hydrocarbons, mainly for the purposes of soil analysis, is evaluated by ATSDR, Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG) and RIVM [113, 157, 228].

The TPHCWG has considered the importance of exposure potential as the overlying theme. The fate and transport of a chemical or mixture defines the exposure route and concentrations at receptors. It is understood that requirements usually focusing on total petroleum hydrocarbon standards ranging from tens to thousands of milligrams of TPH per kilogram of soil are not based on a scientific assessment of human health risk.

TPHCWG's work summarizes the methods used to delineate TPH into equivalent carbon number fractions based on fate and transport considerations. The fractions defined in the study were, as ranges of equivalent carbon numbers, ECs:

- aliphatic $EC_{5...6}$, $EC_{>6...8}$, $EC_{>8...10}$, $EC_{>10...12}$, $EC_{>12...16}$, and $EC_{>16...35}$,
- aromatic benzene ($EC_{6,5}$), toluene ($EC_{7,6}$), and
- aromatic $EC_{>8...10}$, $EC_{>10...12}$, $EC_{>12...16}$, $EC_{>16...21}$, and $EC_{>21...35}$.

Benzene and toluene are identified as separate fractions for convenience, because benzene is likely to be evaluated as a carcinogen in addition to the noncancer evaluation described in the report. [229]

4.2 Methods defined by the TPHCWG

The TPHCWG analytical methodology, also referred in the Toxicological profile for total petroleum hydrocarbons, is based on a n-pentane solvent extraction, and separation of the extract to aliphatic and aromatic petroleum-derived fractions. The group-type separation is based on SW-846 EPA Method 3611, Alumina Column Cleanup and Separation of Petroleum Wastes, and SW-EPA Method 3630, Silica Gel Cleanup. [230, 231]. The aliphatic and aromatic fractions are analyzed separately with gas chromatography, and quantified by summing the signals within a series of specified carbon ranges. The gas chromatograph is equipped with a boiling point column (non-polar capillary column).

EPA Method 5035, purge and trap, specifies a methanol extraction, which is usually done by mechanical shaking of the soil with methanol. Headspace analysis, EPA Methods 3810 [232] and 5021 [75], works well for volatiles in soils. EPA Method SW-846 3540 [233], a Soxhlet extraction, is used for semivolatiles. Sonication extraction, EPA Method SW-846 3550 [234], can also be used for semivolatiles, and supercritical fluid extraction, EPA Method 3545 [235] provides an accelerated Solvent Extraction, in

which methylene chloride (dichloromethane) is heated and pressurized. Various concentration techniques to purge and trap method are available. [76]

4.3 U.S. ATSDR

The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) focuses on the assessment of the health effects of petroleum hydrocarbon transport fractions, as suggested by the TPHCWG. [157]

In the approach, specific carcinogenic compounds that have EPA cancer risk estimates are assessed, namely, benzene and benzo(a)pyrene. EPA relative potency factors are used for various other PAHs.

Noncarcinogenic effects have been evaluated for:

- aliphatic fractions $EC_{5...8}$, $EC_{>8...16}$, and $EC_{>16...>35}$, and
- aromatic fractions $EC_{5...9}$, $EC_{>9...16}$, and $EC_{16...35}$.

4.4 Massachusetts

Massachusetts has adopted a similar approach to the TPH Criteria Working Group.

In Massachusetts the analytical methodology has been used for evaluating the TPH parameter in human health risk assessment. The hydrocarbons are divided into fractions of interest determined with volatile petroleum hydrocarbon method (VPH) and extractable petroleum hydrocarbon method (EPH). The fractions of interest are the:

- the aliphatics $C_{5...8}$ (VPH), $C_{9...12}$ (VPH), $C_{9...18}$ (EPH), and $C_{19...36}$ (EPH), and

- the aromatics $C_{9...10}$ (VPH) and $C_{11..22}$ (EPH).

17 PAHs, BTEX, MtBE, and Naphthalene are determined if needed. Fractions are determined by GC methods, which are modifications of the former EPA SW-846 method series. The VPH method is a purge and trap-GC/PID/FID. The EPH is a solvent extraction/fractionation GC/FID method. Both methods are suitable for the analysis of waters, soils, and sediments. For the extractable petroleum hydrocarbons (EPH) the protocol involves a methylene chloride (dichloromethane) extraction followed by Kuderna-Danish concentration. After solvent exchange to hexane, a silica gel cartridge and two eluants (hexane followed by methylene chloride) are used to separate the extract into the aliphatic and aromatic fractions. [76]

The quantitation in the VPH method is based on comparing the PID and FID detector responses (detectors in series) of a sample. The PID is used for detection of the volatile petroleum hydrocarbons (VPH) analytes and the $C_{9...10}$ aromatic fraction, and target analytes BTEXN and MTBE. The FID is used to determine the collective concentration of aliphatic hydrocarbons within the $C_{5...8}$ and $C_{9...12}$ ranges in the VPH method, aliphatic $C_{9...18}$ and $C_{19...36}$, and aromatic $C_{11..22}$ ranges in the EPH method, optionally also individual concentrations of target PAH analytes in the EPH method.

The reporting limits are approximately:

- analytes in soil 2 – 10 mg/kg
- analytes in water 50 – 100 µg/l

- target analytes (BTEXN, MTBE) in soil 0,1 – 0,2 mg/kg
- target analytes (BTEXN, MTBE) in water 1 – 10 µg/l
- target PAH analytes in soil 0,5 – 1,0 mg/kg
- target PAH analytes in water 1 – 5
- target PAH analytes in soil 0,5 – 1,0 mg/kg
- target PAH analytes in water 1 – 5 g/l.

In Round-Robin tests the relative standard deviation typically varies between 20 – 52 % for separate fractions. [236-238]

There might be some overlaps with pi-bonded aliphatics and aromatics and determination of some aliphatic compounds as aromatics with PID, but it is understood that this is not a major problem. However, some products like kerosene and Jet Fuel A might produce significant overquantitation of the aromatic fraction. In practice, the naphthalenes have leached into the aliphatic fraction. If the PAH concentration exceeds the remediation limits, a confirmatory GC/MS or other suitable analysis is recommended. [238]

A draft GC/MS method to determine air-phase petroleum hydrocarbons (APH) for aliphatic fractions $C_{5...8}$ and $C_{9...12}$, and aromatic $C_{9...10}$ is on public comments. The method can be used to determine the BTEX-compounds, MtBE, naphthalene, 2-methylnaphthalene and 1,3-butadiene, too. A GC/MS modification is also used to determine both VPH and EPH. The methods are performance-based, modifications are permissible, and the environmental agency has a certification program. [238]

Drinking water tests are done according to appropriate U.S.EPA "500" series. For TPH, also U.S. EPA Method 1664 modified U.S. EPA Method 8100 (a unresolved GC/FID method for determination of PAHs) and modified U.S. EPA Method 8015 (a purge-and-trap or headspace GC/FID method) are used. [238] A solvent-exchange/silica-gel-fractionation process is optional to obtain the total petroleum hydrocarbon (TPH) concentration. This method provides a cost-effective analytical screening value despite of the fact that it provides little information on the chemistry or toxicity of the petroleum mixture: for the price of one EPH test it may be possible to perform 4 - 10 field screening analyses. It is also recommended to screen the samples prior to analysis with EPA Methods 3810 (headspace method) or 3820 (hexadecane extraction and screening method) [232, 239].

4.5 Canada

In Canada, a reference method for petroleum hydrocarbon in soil determines four fractions:

- $EC_{6...10 - BTEX}$ (F1-range $EC_{6...10}$ excluding the BTEX-compounds)
- $EC_{10...16 - napth}$ (F2 range $EC_{10...16}$ excluding naphthalene)
- $EC_{16...34 - PAH}$ (F3 range $EC_{10...16}$ excluding named PAH compounds), and
- $nEC_{34...50}$ either by GC (F4) or by gravimetric heavy hydrocarbons (F4G).

The F4G fraction is determined only if hydrocarbons heavier than EC_{50} are present.

The method is performance based, and any method performing as well or better can be used in the determination. The BTEX is to be analyzed at any site where volatile hydrocarbons are suspected, and PAHs if they may be present. Determination by GC/MS is recommended for the BTEX and PAHs. For the F1 fraction, methanol extraction and purging followed by GC/FID is used. For other fractions, a hexane-acetone extraction in a Soxhlet apparatus followed by sodium sulphate drying and silica gel treatment for removal of polar compounds followed by GC/FID determination is applied. [240]

The method detection limits vary between 3,9 and 29 mg/kg for individual fractions. Soil samples containing high organic content or remediated with manure may give higher than expected values. In the first case, it is recommended that the extract be analyzed by GC/MS. An uncontaminated control can be used in both cases. Crude and partially weathered or degraded compounds can contain significant amounts of polar compounds removed in the silica gel cleanup. [240]

For example, a laboratory in Canada using a GC/MS for PAHs, purge-and-trap/GC-MS for TPH $_{Purgeables}$ and microextraction/GC/FID for TPH $_{Extractables}$ achieves detection limits in water:

- BTEX 0,1 µg/l
- TPH $C_{6...24}$ 2,5 µg/l
- TPH $C_{24...32}$ 40 µg/l
- PAHs 0,01 µg/l

Aromatic and aliphatic fractions are determined by fractionation with a silica gel column followed by chromatography with detection limits varying between 100 and 200 µg/l. [241]

4.6 The Netherlands

A Dutch intervention value 'Total Petroleum Hydrocarbons – TPH' was revised using ecotoxicological and human toxicological data with respect to TPH fractions in 1999. Serious soil contamination concentrations were compiled by Franken et al. for TPH fractions [113]:

- aliphatic $EC_{5...6}$, $EC_{>6...8}$, $EC_{>8...10}$, $EC_{>10...12}$, $EC_{>12...16}$ and $EC_{16...21}$and
- aromatic $EC_{5...7}$, $EC_{>7...8}$, $EC_{>8..10}$, $EC_{>10...12}$, $EC_{>12...16}$, $EC_{>16...21}$ and $EC_{>21...35}$.

Mainly in connection with the work of the Total Petroleum Hydrocarbon Criteria Working Group, human toxicological data were used to calculate the potential human risk for TPH fractions. No HC_{50} levels and Intervention Values were calculated for ecotoxicological values due to scarce sound terrestrial data. [113]

The report recommends to distinguish the TPH fractions in the range $C_{5...40}$ reviewed and replace the earlier Dutch method characterizing fractions in the range $C_{10...40}$ and possibly underestimating the (non-carcinogenic) human-toxicological risk of TPH from light fuels, like petrol, even diesel and fuel oil, the carbon range of which are typically $C_{4...10}$ for petrol, $C_{8...20}$ for diesel, and $C_{8...20}$ for fuel oil. The advantage of the fraction approach (or 'hydrocarbon block method') is that results from freshly added oil in laboratory experiments are directly comparable with aged concentrations in the field.

Properties of various aliphatic and aromatic hydrocarbon fractions and their intervention values for soil and groundwater based on a Dutch human-toxicological and ecotoxicological serious soil contamination concentrations are proposed by Franken et al [113]. It should be recognized that direct human exposure to contaminants in groundwater has not been considered in the first steps of the risk assessment, because it is unlikely in the Netherlands. In the final step the intervention value has been corrected, if it has exceeded the maximum permissible risk (MPR_{human}) for a human, resulting a value exactly equal to the MPR_{human}. [113]

If the proposal for intervention values for TPH fractions is adopted, the Dutch intervention value for mineral oil could lapse. It is recommended to consider concentration addition for TPH fractions if and only if no fraction–specific serious soil contamination concentration value (SCC) is exceeded. An overall site-specific contamination index is calculated as a sum of all measured concentrations in fraction *i* divided by the serious contamination concentration of the fraction *i*. [113]

Besides the determination of the TPH fractions, the BTEX and/or PAH analysis should be maintained to consider the carcinogenic risk of TPH in the case of soil contamination with mixtures of petroleum hydrocarbon products, because the BTEX and PAH are not considered in the serious soil contamination risk assessment of mineral oils. The first steps, the 'indicator approach' including assessment the hazard of (human) carcinogenic compounds (such as BTEX and certain PAHS), and secondly, if possible and applicable, the 'whole product approach' is applied assessing possibly the hydrocarbon product (like gasoline or jet fuel) before the 'surrogate approach' including the fraction-specific mixtures described in the report [113].

It has to be noticed that new human-toxicological maximum permissible risk (MPR) values have been established in 2001. There is no MPR value for total petroleum hydrocarbons. However, new MPR values are available for [242]:

- BTEX
- PAHs
- aliphatics $EC_{>5..8}$, $EC_{>8...16}$, $EC_{>16...35}$, and $EC_{>35}$, and
- aromatics $EC_{>5....9}$, $EC_{>9...16}$, and $EC_{>16...35}$.

The TDI-values (tolerable daily intakes) for these fractions vary from 30 to 20000 µg/kg bw/day, and between 0,5 and 500 µg/kg bw/day for PAHs.

Ecotoxicological risks with respect to hydrocarbon fractions are currently evaluated by the RIVM. The report is expected to be available in 2003. [243] However, ecotoxicological Serious Risk Concentrations have been updated in 2001 for the BTEX and various PAHs [244]. The intervention values have been technically evaluated in 2001, inter alia, for BTEX-compounds, PAHs, and mineral oil. [245]

No official standard method is available for the fractionated analysis of TPH, but a GC/FID method based on NEN 5733 extended with a procedure to distinguish aliphatic and aromatic fraction can be used. [243]

Additionally, in cases of contaminated soil, gasoline additives like tetraethyl lead (TEL), tetramethyl lead (TML) and rapidly-moving oxygenates tert-amyl methyl ether (TAME) and methyl tert-butyl ether (MTBE) can be determined, too.

5 Further information

This report doesn't handle further determinations of produced water, like particle concentration, size and shape measurements, or monitoring of other parameters than the hydrocarbon index. Further information is available, for example, in the proceedings of the Oil-in-water Monitoring Workshops. Neither does this report handle fingerprint properties of oil, for which further discussion and updated standard operation procedures are presented by the Nordtest [246].

Further properties of total petroleum hydrocarbons are presented, for example, in the material of Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) [76, 227, 229, 247, 248].

U.S. Agency for Toxic Substances and Disease Registry has produced several Toxicological profiles on various hydrocarbons and hydrocarbon mixtures, like BTEX-compounds, naphthalene, hydraulic fluids, mineral-based crankcase oil, total petroleum hydrocarbons, automotive gasoline, fuel oils, jet fuels JP-4, JP-5, JP-7, and JP-8, Otto Fuel II, and various polynuclear aromatic hydrocarbons. Toxicological profiles also contain information on suitable analysis methods, detectors used in the method, sample detection limits and percent recoveries, however, most of the profiles are several years old, and do not necessarily describe the most sophisticated and/or practical present methods. [155]

ANNEX 5. Environmental properties of some selected hydrocarbons

	Benzene	Toluene	Ethylbenzene	Xylenes	Naphthalene	Styrene	Mineral oil	PAH sum[7]	MTBE	TAME
CAS-No	71-43-2	108-88-3	100-41-4	95-47-6 108-38-3 106-42-3	91-20-3	100-42-5			1634-04-4	994-05-8
Boiling temperature, ºC	80,1[15]	110,6[14]			217,9-218[13]	145 – 146[16]			55,2 – 55,3[12]	86[19]
Density at 20ºC, g/cm^3	0,879[15] (25ºC)	0,8669 [14]			1,175 [13] (25ºC)	0,9059			0,741[12]	0,77[19]
Vapor pressure at 20ºC, Pa	9970 [15]	3000 [14]			7,2	663 [16]			27000[12]	9000[19]
Log K_{ow}	2,13 [15]	2,65 [14]			0,59 [13]	2,95			1,06[12] (25ºC)	1,55[19]
Water solubility, mg/l	1800 [15]	515 [14]			30	300 [16]			42 000[12] (20ºC)	11 000[19]
Henry's law constant, Pa m^3/mol	432,6 [15]	537 [14]			44,86 [13]	279			43,8[12]	90[19]
log K_p[11] l/kg	0,97	1,15	1,3	1,87	2,37	2,02				1,47[19]
K_{oc}	134,1 [15]	177 [14]			1250 [13]	520 – 555			9,1[12]	22,7[19]
Biodegradability in water (aerobic)	Readily biodegradable [15]	Readily biodegradable			Inherently biodegradable [13]	Readily biodegradable			Not readily biodegradable [12]	Inherently biodegradable, not fulfilling criteria [19]
BCF	13 [15]	90 [14]			427 [13]	12			1,5 [12]	4,14[19]
Half-life in surface water, d	0,029 – 68,2 [15]	30			0,3 - 30	5 – 30 (75)[16]				150[19]
Target value for ground water, µg/l[1]	0,2 [13,4,17]	7[17]	4[4,17]	0,2 [3,417]	0,01[4,17]	6[4,17]	50[4,17]	0,2[17]	9200 [4,18,20]	[21]
Target value for surface water, µg/l[1]	2[5,17]	7[17]	4[5] [17]	4[5] [17]	0,01[5] [17]	6[5] [17]	200[6] [17]			
MPC for surface water, µg/l [10]	240[4,5,17]		370 [4,5,17]	380[4,5, 17]	1,2[4,5, 17]	570 [4,5,17]				
WHO standard for the production of drinking water, µg/l[2]	10	700	300	500		20				
EC standard for drinking water[2], µg/l	1						10	0,1[8]		
U.S.EPA Maximum Contaminant Level in drinking water [11]	5	1000	700	10000		100				

[1)] Target and MPC values for ground water and surface water are Dutch examples. For further information and calculation basis for organic matter dependence of the values, see reference. [249]

[2)] The WHO and EC standards for drinking water are from Environmental quality standards in the Netherlands. [249]

[3)] Detection limit.

[4)] Dissolved.

[5)] Total.

[6)] Several Water Supply Resolution classes for intake point quality standards varying between 50 – 1000 µg/l.

[7)] 10 PAH according to VROM: naphthalene, anthracene, phenantrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indenopyrene. Note: various individual PAH-compounds have limit values of their own.

[8)] Sum of four PAHs: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene. Note: various individual PAH-compounds have limit values of their own.

[9)] Also Water Supply Resolution class for intake point quality standard exists.

[10)] MPC is a maximum permissible concentration, which is a scientifically derived value for a substance, which specifies the concentration at which no harmful effect is to be expected in the ecosystem and the humans. The MPC is derived based on an (eco)toxicological risk assessment.

[10)] K_p is partition coefficient suspended matter-water.

[11)] National Primary Drinking Water Regulations in July 2002

[12)] European Union Risk Assessment Report

[13)] Draft European Union Risk Assessment Report, October 2001, last update 15-Feb-2002

[14)] Draft European Union Risk Assessment Report, October 2001, last update 18-June-2001

[15)] Draft European Union Risk Assessment Report, May 2002, last update 21-Aug-2002

[16)] Draft European Union Risk Assessment Report, November 1999

[17)] A new MPR (maximum permissible risk value) has been established in 2001.[242]

[18)] Indicative level serious pollution

[19)] Draft European Union Risk Assessment Report, 11-Feb-2003

[20)] Taste detection threshold 0,134 mg/l (Risk Assessment Report), overall results 0,0025 – 0,190 mg/l.

[21)] Taste detection threshold 0,128 mg/l (Draft European Union Risk Assessment Report)

Previously mentioned values may differ from national limit values presented elsewhere. Further information is available also in the reports of RIVM, ATSDR, MADEP and Total Petroleum Hydrocarbons Working Group. [113, 157, 228, 238, 242, 244, 245]

ANNEX 6. Some environmental properties of selected hydrocarbon fractions

	Aliphatics						
		EC 5-6	EC >6-8	EC >8-10	EC >10-12	EC >12-16	EC >16
Vapour pressure, atm[6)]		0,35	0,063	0,0063	0,00063	0,000076	0,0000011
Solubility, mg/l[6)]		36	5,4	0,43	0,034	0,00076	0,0000025
Henry's law constant, cm^3/cm^3 [6)]		47	50	55	60	69	85
Log K_{oc} [6)]		2,9	3,6	4,5	5,4	6,7	8,8
ECOTOX SCC		-	-	-	-	-	-
HUMTOX SRC soil, mg/kg [1)]		35	109	28	152	55000	>100000
HUMTOX SRC Groundwater, µg/l [2)]		613	444	15[3)]	10[3)]	0,59[3)]	0,001[3)]
	Aromatics						
	EC 5-7	EC >7-10	EC >8-10	EC >10-12	EC >12-16	EC >16-21	EC >21-35
Vapour pressure, atm[6)]	0,11	0,035	0,0063	0,00063	0,000048	0,0000011	0,00000000044
Solubility, mg/l[6)]	220	130	65	25	5,8	0,65	0,0066
Henry's law constant, cm^3/cm^3 [6)]	1,5	0,86	0,39	0,13	0,028	0,0025	0,000017
Log K_{oc} [6)]	3	3,1	3,2	3,4	3,7	4,2	5,1
ECOTOX SCC		-	-	-	-	-	-
HUMTOX SRC soil, mg/kg [1)]			59	317	5900	17500	19200
HUMTOX SRC Groundwater, µg/l [2)]			640	2170	5810	543	6,6[3)]

[1)] SRC is a newly evaluated Dutch Serious Risk Concentration for soil [245]

[2)] Proposal for Intervention Value groundwater conc. [113]

[3)] Detection limit is exceeded, or attention has to be given to detection limit ("mineral oil")

[4)] For the aliphatic fraction EC >16-21 a daily intake of 150 mg a day does not result in human risk. A daily intake of 150 mg soil is a default assumption in the CSOIL model to calculate the human toxicological serious soil contamination. [113]

[5)] Since benzene (EC = 6,5) and toluene (EC = 7,5) are the only representatives of these groups, both will be measured individually; therefore these fractions could be skipped. [113]

[6)] Sources: Total Petroleum Hydrocarbons Criteria Working Group and ATSDR. [157, 228]

[7)] Note: New human-toxicological MPR (maximum permissible risk) values lying in the background of the HUMTOX SCC values have been established in 2001 for aliphatics $EC_{>5..8}$, $EC_{>8...16}$, $EC_{>16...35}$, and $EC_{>35}$, and aromatics $EC_{>5..9}$, $EC_{>9...16}$, and $EC_{>16...35}$. [242]

Previously mentioned values may differ from national limit values presented elsewhere. Further information is available also in the reports of RIVM, ATSDR, MADEP and Total Petroleum Hydrocarbons Working Group. [113, 157, 228, 238, 242, 244, 245]

Annex 7. General performance requirements to a substitute method

The performance properties of a substitute method must typically meet various criteria. These criteria can be strictly described in a statute or recommendation, or, in many applications, determined by the laboratory itself, however, according to typically unconditional requirements concerning the environment, health, safety or product quality. Since many requirements for a determination method are performance based, the performance criteria may create a major obstacle to substitution. Or on the other hand, if several methods fulfilling the criteria are available, the substitution is relatively easy. To understand some principles concerning the performance properties of a determination method and requirements on performance, some principal definitions and procedures are summarized in this report.

In general, a determination method has various method-specific properties. The properties are assessed in a validation process. Typically an analysis laboratory must be accreditated before it is allowed to run determinations concerning environment, health, safety and/or product quality. Accreditated methods don't necessarily have to be international or national standards, in-house methods are allowed, but they should be validated i.e. their performance properties must fulfil the necessary criteria. In an international standardization process a candidate method goes through a systematic evaluation process. A laboratory can typically run a simplified validation process for not standardized methods, and has to evaluate the performance of a standardized method, too. Since the terms may vary, several explanations for some terms are used.

Validation is confirmation of a method by examination and provision of objective evidence that the particular requirements for a specified intended use are fulfilled [250]. In a method-evaluating proficiency test a method is evaluated in several laboratories analyzing a test sample sent to the laboratories using the test under evaluation (interlaboratory testing). Later proficiency testing or interlaboratory calibrations can routinely be used for laboratory's quality checking.

The validation process includes evaluation of:

- trueness and precision
- specificity (and selectivity)
- linearity
- limit of detection
- limit of quantitation
- sensitivity
- ruggedness/robustness
- measurement uncertainty

Accuracy is the closeness of agreement between an observed value and the true value [251]. It is the uncertainty of an observed value, including both precision and trueness, or precision and bias. Trueness is the closeness of agreement between the arithmetic mean of a large number of test results and the true or accepted reference value [251]. Bias is actually, by definition, the difference between the expectation of the test results and an accepted reference value [251].

Precision is the closeness of agreement between independent test results obtained under stipulated conditions [251], or the closeness of agreement among the measured values at a setpoint, the closeness of results of multiple analyses to each other. It is often expressed as a standard deviation. For example, the HELCOM PLC-4 work requires that the standard deviation within replicate determinations must not exceed 10 % for standard solutions, 20 % for hydrocarbon concentrations in the middle of the working range, and 30 % for hydrocarbon concentrations near the determination limit. [39]

Repeatability and reproducibility are consolidated to precision. Repeatability is the closeness of agreement among a number of measured values at a setpoint, under the same operating conditions, or by the exact definition, precision under repeatability conditions [251]: conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time [251]. Reproducibility is by definition precision under reproducibility controls [251]: conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment [251]. In other words, it is the closeness of agreement among repeated measured values at a setpoint, within the specified reference operating conditions, made over a specified period of time, approached from both directions. It measures the method's ability to perform a routine analysis and deliver the same results using a particular method irrespective of laboratory, equipment and operator changes. Reproducibility refers to the results of collaborative studies between laboratories. It is expressed as relative standard deviation.

Specificity is the ability of the method to measure only what it is intended to measure. It assures that the signal assigned to an analyte is only due to that particular analyte, not other components that may be expected to be present in the sample matrix. Specificity and selectivity assure the reliability of method in the presence of interferences.

Linearity is the closeness to which three or more measurements approximate a straight line over a specified range.

Limit of detection is the smallest concentration of a substance or an amount of analyte that an analytical method can reliably distinguish from zero. It is, for example, a point at which a measured value is larger than the uncertainty associated with it, i.e., the lowest concentration or amount of analyte that can be detected, not quantitated. The signal-to-noise –ratio should be, for example, higher than 3. Limit of quantitation is the smallest concentration of a substance or an amount of analyte that an analytical method can measure with a specified degree of confidence. The signal-to-noise –ratio can be, for example, higher than 10.

Robustness describes the method's susceptibility to variation and errors, or the method's capacity to remain unaffected by small deliberate variations in method parameters. Ruggedness is the degree of reproducibility of the results obtained under a variety of conditions.

Uncertainty of measurement is defined as the parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand [252]. In practice, it contains standard uncertainty, combined standard uncertainty, and expanded uncertainty. [253]

Standard uncertainty is the uncertainty of the result of a measurement expressed as a standard deviation.

Combined standard uncertainty is the standard uncertainty of a result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the term being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities.

Expanded uncertainty is the quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand.

Coverage factor is defined as the numerical factor (k) used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty; k = 2 for an approximate level of confidence of 95%.

The measurement uncertainty can be estimated by listing all of the possible errors in the form of standard deviations (Budget model). The combined standard uncertainty is then calculated as the square root of the sum of squares of the individual error components. The other way is to use the experimental data i.e. validation data, internal quality control results, proficiency testing results etc. for the estimation combined standard uncertainty.

Sometimes terms sensitivity, practicability or suitability, range and resolution are also consolidated to validation terms. Practicability or suitability describes the factual possibility to take the method in practice in respect to economical, technical and timing aspects. For example, a method requiring very expensive and fragile equipment and very experienced staff is not practical for field use or occasional determinations. Sensitivity describes the gradient of the response curve, i.e. the change in instrument response that corresponds to a change in analyte concentration or amount of analyte. Range is the interval between the upper and lower levels that have been demonstrated to be determined with precision, accuracy and linearity using the method as written. It is the range of analyte concentrations or amounts of analyte over which the method may be used. Within this range a linear response range may exist. In this range the signal response has been determined to be linear with respect to the analyte concentration. Resolution describes the method's or measuring system's ability to react on small changes in the quantity of analyte to be determined.

Since a substitute method might have a different kind of sampling, extraction, purification, concentration or detection/determination principle, it may, in practice, measure a similar kind of parameter, but not be exactly equivalent to the present method. For example, also sensitivity may differ significantly. In this kind of cases the limit values and performance requirements have to be determined again, or if possible, create a correlation curve between the present method and the substitute method based on representative samples and appropriate statistical evaluation. Sometimes authorities provide a calibration procedure in a substitution process or in the comparison of a stationary and a field method. It should be remembered that various interferences are possible, for example due to low recovery rates with a new extraction solvent with a sample media, evaporation or degradation of volatile compounds or dissimilar separation of compounds in the sample pretreatment, or for example, similar retention times in a separation column or similar signal from a detector.

The use of the instrumentation itself, e.g. the choice of integration parameters using GC-FID as well as the choice and use of reference standards is often critical, and can be

often a source of different results from otherwise competent laboratories. It is also essential that the extraction of oil is performed in the sampling bottle. Container wall adhesion will otherwise be a large source of variations between laboratory. [43]

Accreditation can be granted according to GLP, ISO 9000 series, or ISO/IEC 17025 [254-257], which is better linked to the ISO 9001 and ISO 9002 standards, and a revision of the international ISO/IEC guide 25:1990 and the European standard EN 45001:1994, actually replacing the latter. The ISO/IEC 17025 gives a validation procedure for methods used in a laboratory by using reference standards, comparison of the results obtained with other methods, proficiency testing and systematic review on the factors affecting the results. More information on the validation of a method and proficiency tests is available in material and standards provided by the ISO, CEN and IEC [251, 258-268]. The most crucial standards in determining the accuracy of a test method are ISO 5725-1 and ISO 5725-2.[251, 258] For water quality analysis there are many further normative documents to be recognized in standard development.[269-271]

For on-line determination methods, ongoing standardization proceeds in working groups WG 2 On-line sensors/analyzers and WG 3 Field methods under ISO/TC 147 Water quality. A final draft for water quality measurements on-line is prepared under the ISO as ISO/FDIS 15839 Water quality – On-line sensors/analyzing equipment for water – Specifications and performance tests. For field measurements a draft standard ISO/CD 17381 Water quality – Field methods for the analysis of water – Guidelines for the appropriate use of portable Ready-to-use test kit methods is being prepared.

It will also be possible to define performance using certified reference materials. A new project with the aim of defining methods to produce relevant certified material is now underway with support from the EU Commission and will be finished early 2005. Actual materials for water analysis will be available at the earliest later that year. With such performance standards any method can be used as long as the targets are met using the reference materials. The actual definition of hydrocarbons and matrixes are essential to such reference material use.[43]

Index of methods