

Dr. rer. nat. Matthias Koch
Dr. rer. nat. Almuth Liebich
Dr. rer. nat. Tin Win
Prof. Dr. rer. nat. Irene Nehls

**Certified Reference Materials for
the determination of mineral oil
hydrocarbons in water, soil and waste**

Impressum

Forschungsbericht 272:

**Certified Reference Materials for the determination
of mineral oil hydrocarbons in water, soil and waste**
2005

Herausgeber:

Bundesanstalt für Materialforschung und -prüfung (BAM)

Unter den Eichen 87

12205 Berlin

Telefon: +49 30 8104-0

Telefax: +49 30 8112029

E-Mail: info@bam.de

Internet: www.bam.de

Copyright © 2005 by Bundesanstalt für
Materialforschung und -prüfung (BAM)

Verlag und Vertrieb:

Wirtschaftsverlag NW

Verlag für neue Wissenschaft GmbH

27568 Bremerhaven

Telefon: +49 471 94544-0

Telefax: +49 471 94544-77/-88

Umschlag: Lutz Mittenzwei

Layout: BAM-Arbeitsgruppe Z.03

ISSN 0938-5533

ISBN 3-86509-363-9

Zusammenfassung

Das internationale Forschungsprojekt HYCREF, finanziert von der Europäischen Kommission im 5. Rahmenprogramm, beinhaltet die Entwicklung von Methoden zur Herstellung homogener und stabiler Wasser-, Boden- und Abfall-Referenzmaterialien, kontaminiert mit Mineralölkohlenwasserstoffen, sowie die Testzertifizierung des Mineralölgehalts mit Hilfe gaschromatographischer Methoden. Da Mineralölprodukte wichtige Quellen für Umweltverschmutzungen darstellen, existiert ein hoher Bedarf an zertifizierten Referenzmaterialien für ihre Bestimmung mittels der neuen gaschromatographischen Methoden (Boden: ISO/FDIS 16703, Abfall: ENpr 14039, Wasser: ISO 9377-2).

Die experimentellen Bedingungen und Ergebnisse für die Herstellung und Charakterisierung von insgesamt neun Referenzmaterialien (3 Wasser-, 3 Boden- und 3 Abfallmaterialien) werden beschrieben und diskutiert. Zu Beginn des Projektes wurden Zielwerte für die Referenzmaterialien definiert, um eindeutige Erfolgskriterien zu haben, mit denen die erreichten Ergebnisse am Ende des Projektes verglichen werden konnten. Diese Zielspezifikationen beinhalteten die maximale Unsicherheit aus den Testzertifizierungsstudien ($< 5\%$ für Boden/Abfall und $< 10\%$ für Wasser), die maximale Inhomogenität zwischen den Flaschen ($< 3\%$) und Mindestanforderungen an die Stabilität (> 5 Jahre für Boden/Abfall und > 2 Jahre für Wasser).

Die Machbarkeitsstudien zeigten, dass feste Materialien (Boden, Abfall) hinreichend homogen und stabil hergestellt werden können. Die testzertifizierten Werte der 6 Feststoffe umfassen einen weiten Mineralöl-Gehaltsbereich von etwa 200-9000 mg/kg mit erweiterten Unsicherheiten zwischen 5,7-13,1 % bei Anwendung eines Erweiterungsfaktors k ($k = 2$). Die Entwicklung von neuen Wasser-Referenzmaterialien – die so genannten „Spiking pills“ für ein offshore- und ein ländliches Abwasser stellt einen der wichtigsten innovativen Aspekte des Projektes dar. Die „Spiking pill“-Technologie erleichtert die Anwendung sowie Lagerung und verbessert die Materialstabilität verglichen mit wässrigen Materialien.

Zusätzlich zur Herstellung und Testzertifizierung von Referenzmaterialien wurden Untersuchungen der analytischen Methode für die Bestimmung von Mineralölkohlenwasserstoffe durchgeführt. Die erhaltenen Ergebnisse hinsichtlich der Methodenoptimierung (Extraktion, Probenvorbehandlung, Probenaufreinigung und Messung) wurden den entsprechenden Arbeitsgruppen von ISO/TC 190, ISO/TC 147 und CEN/TC 292 zur Verfügung gestellt und sind in die laufenden Normungsprozesse eingeflossen. Die neue Fassung der ISO/FDIS 16703 (Juli 2004) beinhaltet Verbesserungen, die auf Ergebnisse von HYCREF zurückgehen, wie z. B. die Erhöhung des Lösungsmittel-/Probe-Verhältnisses, die Entfernung von Aceton aus dem organischen Extrakt und die Anwendung der Säulentechnik anstelle der Schütteltechnik für die Probenaufreinigung.

Abstract

The international research project HYCREF, funded by the European Commission in the 5th Framework programme, aimed to develop methods to prepare homogenous and stable water-, soil- and waste reference materials contaminated with mineral oil hydrocarbons and to test certify the mineral oil content by gas chromatographic methods. As mineral oil products are important sources for environmental contaminations a high need exists for certified reference materials for their determination using the new gas chromatographic methods (soil: ISO/FDIS 16703, waste: ENpr 14039, water: ISO 9377-2).

The experimental conditions and results for preparation and characterisation of a total of nine reference materials (3 water-, 3 soil- and 3 waste materials) are described and discussed. Target values for the reference materials were defined at the beginning of the project in order to have clear quality criteria, which could be compared with the achieved results at the end of the project. These target specifications were related to the maximum uncertainty from test certification exercises (< 5 % for soil/waste and < 10 % for water), the maximum inhomogeneity between bottles (< 3 %) and minimum requirements for stability (> 5 years for soil/waste and > 2 years for water).

The feasibility studies showed that solid materials (soil, waste) could be prepared sufficiently homogenous and stable. The test certified values of the 6 solid materials comprise a wide range of mineral oil content from about 200-9000 mg/kg with expanded uncertainties between 5.7-13.1 % using a coverage factor k ($k = 2$). The development of new water reference materials – the so-called “spiking pills” for an offshore- and a land-based discharge water represents one of the most innovative aspects of the project. The spiking pill technology facilitates the application and storage and improves the material stability compared with aqueous materials.

Additional to the preparation and test certification of the reference materials investigations on the analytical method for the determination of mineral oil hydrocarbons were performed. The results obtained in relation to the optimisation of analytical method (extraction procedure, sample pre-treatment, clean-up and measurement) were provided to the respective working group of ISO/TC 190, ISO/TC 147 and CEN/TC 292 and were incorporated into the ongoing standardisation procedures. The new version of ISO/FDIS 16703 (July 2004) includes the improvements based on HYCREF results, for example the increase of the solvent/sample ratio, the removal of acetone from the organic extracts and the use of column technique instead of batch technique for clean-up.

Final Technical Report

CONTRACT N°: G6RD-CT-2002-00854-HYCREF

ACRONYM: HYCREF

TITLE: Certified Reference Materials for the determination of mineral oil hydrocarbons in water, soil and waste

PROJECT CO-ORDINATOR: BAM, Germany

PARTNERS: SINTEF, Norway
UBA, Germany
EUROFINS A/S, Denmark
SYKE, Finland
ALCONTROL, The Netherlands

REPORTING PERIOD: FROM 01/01/2003 TO 31/03/2005

PROJECT START DATE: 01/01/2003 DURATION: 27 months

Date of issue of this report: 23/05/2005



Project funded by the European Community
under the 'Competitive and Sustainable Growth'
Programme (1998-2002)

Contents

1	Executive summary	9
2	Objectives of the project	10
2.1	Mineral oil hydrocarbons in the environment and their analytical measurement	10
2.2	Certified reference materials “Mineral oil hydrocarbons” with gaschromatographic method	10
2.3	Overview of HYCREF project	10
2.4	Project work plan	11
2.5	Project partners	13
3	Scientific and technical description of the results	13
3.1	Method development (WP-2)	13
3.1.1	Comparison of GC- (FID, MS, AED) and IR-method	13
3.1.2	Comparison of ISO/DIS 16703 and Nordic Guideline TR 329	15
3.1.3	Investigations on the analytical method (GC)	16
3.1.3.1	Extraction	16
3.1.3.2	Sample treatment	17
3.1.3.3	Florisil clean-up	19
3.1.4	Pre-test study	22
3.1.5	Standard Protocols on WP-2	24
3.2	Preparation of the reference materials	24
3.2.1	Overview over the materials	24
3.2.2	Water reference materials (WP-3)	24
3.2.2.1	Soil eluate	25
3.2.2.2	Offshore pills	26
3.2.2.3	Landbased pills	27
3.2.3	Soil reference materials (WP-4)	27
3.2.3.1	Clayish soil	27
3.2.3.2	Sandy soil	27
3.2.3.3	Peat material	27
3.2.4	Waste reference materials (WP-5)	27
3.2.4.1	Off-shore marine sediment	28
3.2.4.2	Building material	28
3.2.4.3	Ni/CP-waste	28
3.2.5	Physical and chemical properties of the reference materials	28
3.3	Homogeneity and stability of the reference materials	28
3.3.1	Homogeneity	29
3.3.2	Stability	31
3.4	Test Certification Study	34
3.4.1	Introduction	34
3.4.2	Results of test certification study	34
3.5	Uncertainty budget of the reference materials	35
3.6	Assessment of the results of the feasibility study	36
4	List of deliverables	38
5	Comparison of initially planned activities and work actually accomplished	40

6	Management and co-ordination aspects	43
7	Exploitation of project results	45
8	Annex	47
	Annex A: Comparison of GC- (FID, MS, AED) and IR-method	48
	Annex B: Comparison of ISO/DIS 16703 and Nordic Guideline TR 329	55
	Annex C: Sample treatment	56
	Annex D: Results for pre-test study	57
	Annex E: Reference Materials	60
	Annex F: Interlaboratory Comparison	63
	Annex G: Standard Protocol for the determination of the hydrocarbon content in soil and waste according to ISO/FDIS 16703 and prEN 14039 (GC-method)	72
	Annex H: Standard Protocol for the determination of the hydrocarbon content index in water according to ISO 9377-2 (GC-method)	81
9	References	91

1 Executive summary

The objective of the HYCREF-project was the development of procedures and methods to prepare sufficiently homogeneous and stable soil-, water- and waste reference materials contaminated with mineral oil and to test certify the mineral oil content in these materials by means of the new gas chromatographic methods. These certified reference materials (CRM) are needed to support community policies, in particular, for the technical support to standardisation and implementation of directives (ISO 9377-2, ISO/FDIS 16703 and ENpr 14039).

The experimental conditions for preparation and characterisation of water-, soil- and waste reference materials are described in this report. Target values were set for the reference materials to fulfil a certain level of quality requirements. These target specifications were related to the maximum uncertainty from test certification exercise, the maximum inhomogeneity of the material and minimum requirements of stability. After selection and procurement a total of 9 materials (3 soil-, 3 waste- and 3 water-materials) were prepared and test certified.

The feasibility studies showed that solid materials (soil, waste) could be prepared sufficiently homogenous (inhomogeneity between bottles lower than 3%). Essential steps to reduce inhomogeneities were the preparation of sieve fractions and efficient mixing procedures. A drying step prior to sieve fractionation reduced the moisture content and consequently the probability of biodegradation. But it was also found that a material containing about 14 % water (Ni/CP-waste) did not show a significant degradation trend in short- and long-term stability studies over a period of 3 weeks and 12 months, respectively.

The development of new techniques for the preparation of suitable water reference materials represents one of the most innovative aspects of the project. There are considerable challenges related to water reference materials containing degradable non-water soluble constituents like mineral oil hydrocarbons. Procedures for preparation of a leaching water as well as for so-called "spiking pills" for an offshore and land-based discharge water were developed. It was found that aqueous reference materials are much more sensitive against degradation compared with solid materials, e.g. soils, wastes and spiking pills.

The spiking pill technology facilitates the handling and storage of such "water" samples and improves the material stability. Initial literature search revealed the potential of patents for such technologies. The project partner SINTEF (Norway) had therefore filed a description for a patent invention signed by Notarius Publicus. Such a method for making CRM could be of a more general nature and hence applicable to other types of CRM beside ones containing hydrocarbons.

The achieved results in this feasibility study project HYCREF demonstrated the ability to prepare sufficiently homogeneous and stable soil-, (water-) and waste refer-

ence materials contaminated with mineral oil and to test certify the mineral oil content in these materials by means of gas chromatographic standard methods. The test certified values of the 6 solid materials (3 soils, 3 wastes) comprise a wide range of mineral oil content from about 200 - 9000 mg/kg with expanded uncertainties between 5.7-13.1 %.

The successful results of this feasibility study project allow recommendations for a future production of CRM. A production and commercialisation of selected materials could be very useful for the lab-internal quality control. Taking into account the present lack of certified reference materials for mineral oil determination by means of gas chromatographic methods the project results gain an enormous importance for the development of reference materials.

Additional to the preparation of the reference materials a comparison study was carried out between the former widely used IR-method and the new GC-method including different GC-detection methods (FID, MS, AES). On the basis of the results of the investigations on the European and International standard methods (ENpr 14039, ISO/FDIS 16703 and ISO 9377-2) two standard protocols for the mineral oil determination in soil/waste and water were elaborated.

The determination of mineral oil hydrocarbons is a method depending procedure. Therefore, each deviation from the standard procedure may lead to non-comparable results. It was found that extraction and clean-up are the most crucial steps. For some types of solid samples the extraction efficiency depends on the extraction method. Here, higher recoveries were obtained using the shaking procedure instead of ultrasonic extraction. Extraction time and magnetic stirring speed are the crucial parameters for the analysis of water samples. Emulsions were avoided by laminar stirring. A significant influence of Florisil activity on the clean-up efficiency was determined. Variances in the water content of Florisil – caused by different pre-treatment methods – affect the Florisil-activity. Consequently, the recoveries of hydrocarbons and non-hydrocarbons decrease when Florisil is highly activated.

All project results obtained in relation to the optimisation of analytical method (extraction procedure, sample pre-treatment, clean-up and measurement) were provided to the respective working group of ISO/TC 190 "Soil quality", of ISO/TC 147 "Water quality" and of CEN/TC 292 "Characterization of wastes", and were incorporated into the ongoing standardisation procedures. The new version of ISO/FDIS 16703 (August 2003) included some improvements based on HYCREF results, for example the increase of the solvent/sample ratio (40 mL/20 mL acetone/heptane), the removal of acetone from the organic extracts (2 washing steps with 100 mL water) and the use of column clean-up instead of batch technique.

2 Objectives of the project

2.1 Mineral oil hydrocarbons in the environment and their analytical measurement

The general term “mineral oil” comprises petroleum products with complex mixtures of hydrocarbons, ranging from motor gasoline's, diesel- and heating oils, heavy fuel oils to lubricants, is also often referred to as “(total) petroleum hydrocarbons - TPH” in environmental issues.

Due to the widespread use of mineral oils with an annual EC-consumption of about 500 million tonnes, these petroleum hydrocarbons are the most common organic contaminants to be found in soil and waste, especially on former industrial- and military sites as well as on and below the grounds near petrol stations.

In the past the most widespread conventional method applied internationally by the environmental laboratories for the determination of hydrocarbons is the quantitative measurement of infrared spectroscopic absorbencies, using Freon R 113 (1,1,2-Trichloro-1,2,2-trifluoroethane) as extraction solvent [1].

Due to the significant role they play in the destruction of the earth's ozone layer it was agreed internationally in 1987 in Montreal Protocol to phase out the production as well as the use of harmful chlorofluorocarbons (CFC) including the above prescribed Freon. In the European Union the consumption of ozone depleting halocarbons was restricted by EC Regulations (3592/92 and 94/C 253/04). For the implementation of the EC Regulations regarding the restriction of the use of these CFC, laboratories involved in national and international standardisation as well as the European Commission have put a lot of effort to develop a new gas chromatographic method for mineral oil analysis to replace the IR-method, which prescribes the use of the CFC.

The ISO-standard ISO 9377-2 (mineral oil in water) [2], the draft ISO-standard ISO/FDIS 16703 (mineral oil in soil) [3] and the draft CEN standard ENpr 14039 (mineral oil in waste) [4] based on a GC-FID method using other solvents than the harmful CFC are horizontally harmonised by ISO/TC147, ISO/TC190 and CEN/TC292 for mineral oil analysis in water, soil and waste, respectively.

2.2 Certified reference materials “Mineral oil hydrocarbons” with gas chromatographic method

At present, there are no certified reference materials (CRM) available for the determination of mineral oil hydrocarbons in water, soil and waste samples by the new gas chromatographic methods. Only reference materials on the basis of the IR-method and one soil material based on Nordic GC methods are commercially available. These products are losing importance as the mineral oil content is a method-defined quantity.

An urgent need was derived from this situation for the development of CRMs basing on the gas chromatographic

determination method according to the internationally accepted analytical standards. These GC-certified reference materials are needed to support Community policies, in particular, for the technical support to standardisation and implementation of directives (ISO 9377-2, ISO/DIS 16703 and ENpr 14039).

2.3 Overview of HYCREF project

The main technological aspects of the project can be summarized as followed:

- Comparison of GC- and IR methods for mineral oil determination; optimisation of available GC-FID methods
- Selection, procurement and preparation of 9 candidate reference materials (3 for each matrix – water, soil and waste)
- Development of new techniques for preparation of homogenous and stable water reference materials
- Demonstration of homogeneity and stability of the prepared materials according to relevant BCR- and ISO-guidelines
- Interlaboratory comparisons with test batches of the prepared reference materials
- Evaluation of feasibility studies

A successful feasibility study with respect to the targeted uncertainties for test certification requires robust analytical methods for mineral oil determination in water, soil and waste. Investigations were carried out, so that the formulated standard protocols for water, soil and waste together with quality assurance requirements were provided to the participants before the start of the intercomparison. The achieved results and the optimised steps in the analytical procedure were transmitted to the responsible standardisation bodies of ISO and CEN as an input to further improvement of these analytical standards.

The main part of the project dealt with the feasibility study for the preparation and test certification of reference materials. An overall number of 9 different materials (3 water RM, 3 soil RM and 3 waste RM) were prepared. The following steps were of interest: sample selection and procurement, developing of methods to achieve homogeneous and stable samples followed by the preparation and assessments of homogeneity and stability of the candidate materials. The final step during the project stage was a test certification by means of an interlaboratory comparison with 12 participants.

For soil, three different candidate materials, a sandy soil, a clayish and a peat soil (from agriculture area) with different levels of mineral oil hydrocarbons contamination were taken into account since soil investigation is a very wide activity. This approach of three candidate materials was chosen to meet the needs and demands of the laboratories involved in soil testing, which were very much dependent upon the geographical and remediation aspect.

The choice of three waste candidate materials, a building material, a marine sediment and a residue from a physical and chemical waste treatment plant with different mineral oil hydrocarbons contamination levels was derived from a similar consideration to meet the needs of the “waste”-laboratories.

The choice of the three water candidate materials, an offshore and a land-based discharge water and a soil eluate (simulation of a ground water contamination) with different levels of mineral oil contamination were chosen to reflect the needs of the practitioners involved in a vast field of water monitoring.

The overall innovation of the project was the demonstration of the ability to produce soil-, water- and waste CRM and to certify their content of mineral oil by means of gas chromatographic methods. Until the start of the project, little work had been done and very limited experiences existed on this topic.

The preparation of sufficiently stable and homogenous aqueous CRM was the most challenging part of the project caused by the polar/non-polar repulsions between water and mineral oil. Homogeneity as well as stability of water CRM may bind considerable amount of work effort and research potential in the process of production. To be successful in this regard, investigations were done basing on two different principles:

- Preparation of a simulated ground water, water extract or leachate saturated with diesel oil, containing mostly aromatic compounds and their alkyl substituted derivatives
- Preparation of “synthetic waste waters with offshore and land-based matrices” containing real mineral oil and surfactants and other relevant and typical constituents

The project work was aimed to produce and certify reference materials with the following specification:

- Uncertainties of the mineral oil content resulting from certification exercise:
 - ≤ 5 % for soil and waste reference materials and
 - ≤ 5-10 % for water reference materials
- A sample (in)homogeneity of < 3 % for all types of CRM
- A long term stability of:
 - 5 years for soil and waste reference materials and
 - 2 years for water reference materials under optimal storage conditions

2.4 Project work plan

The project structure was focused on 6 work packages (WP) with specific tasks. Each work package represents a significant part of the project and has clearly defined objectives and verifiable deliverables. An overview over the work packages, their contents, the responsibilities, the duration as well as the expected deliverables are outlined in *Tab. 2.1*. More detailed information is given in Chapter 4 and 5 (*Tab. 4.1* and *Tab. 5.1*).

All six work packages started simultaneously in the first month of the project and finished near or at the project end (except WP-2). The activities in six separate working groups/work packages were carried out by the main partners and supervised by the project coordinator. The work packages were divided in respect to the three matrices of reference materials, which were to be produced (WP-3 water, WP-4 soil and WP-5 waste). The main efforts were focussed on the preparation and test certification of a total number of 9 reference materials (three materials of each of the three matrices water, soil and waste).

The progress in these work packages was similar; therefore, a horizontal cooperation between these working groups offers itself at each task. The WP-2 “Method development” was initiated to give support to the analyti-

Tab. 2.1
Overview of the workpackages

Work package	Work package title	Leader (Institute)	Start-months	End-months (original planed)	End-months (after project-prolongation)	Deliverable No.
WP-1	Coordination/ Management	BAM	1	24	27	D 1.1 – 1.2
WP-2	Method Development	BAM	1	9	9	D 2.1 – 2.3
WP-3	Water Reference Materilas	UBA	1	22	25	D 3.1 – 3.3
WP-4	Soil Reference Materilas	SYKE	1	22	25	D 4.1 – 4.4
WP-5	Waste Reference Materilas	BAM	1	22	25	D 5.1 – 5.3
WP-6	Technical Implementation Plan	BAM	1	24	27	D 6.1 – 6.3

cal questions of mineral oil determination (assignment of a standard protocol for all participants in the interlaboratory comparisons). The final task of WP-2 interacted with the main task of WP-3, WP-4 and WP-5 “Feasibility studies – Interlaboratory comparisons”. The interest of WP-6 (Technical Implementation Plan) was focussed on the development of a strategy for the exploitation of project results.

WP-6 was in close contact to the project partner and their results and to other interested parties outside the project.

An overview of the basic work programme carried out in the 6 work packages is presented in the following flow diagram (see Fig. 2.1) including the main objectives and tasks as well as their interactions and interrelations.

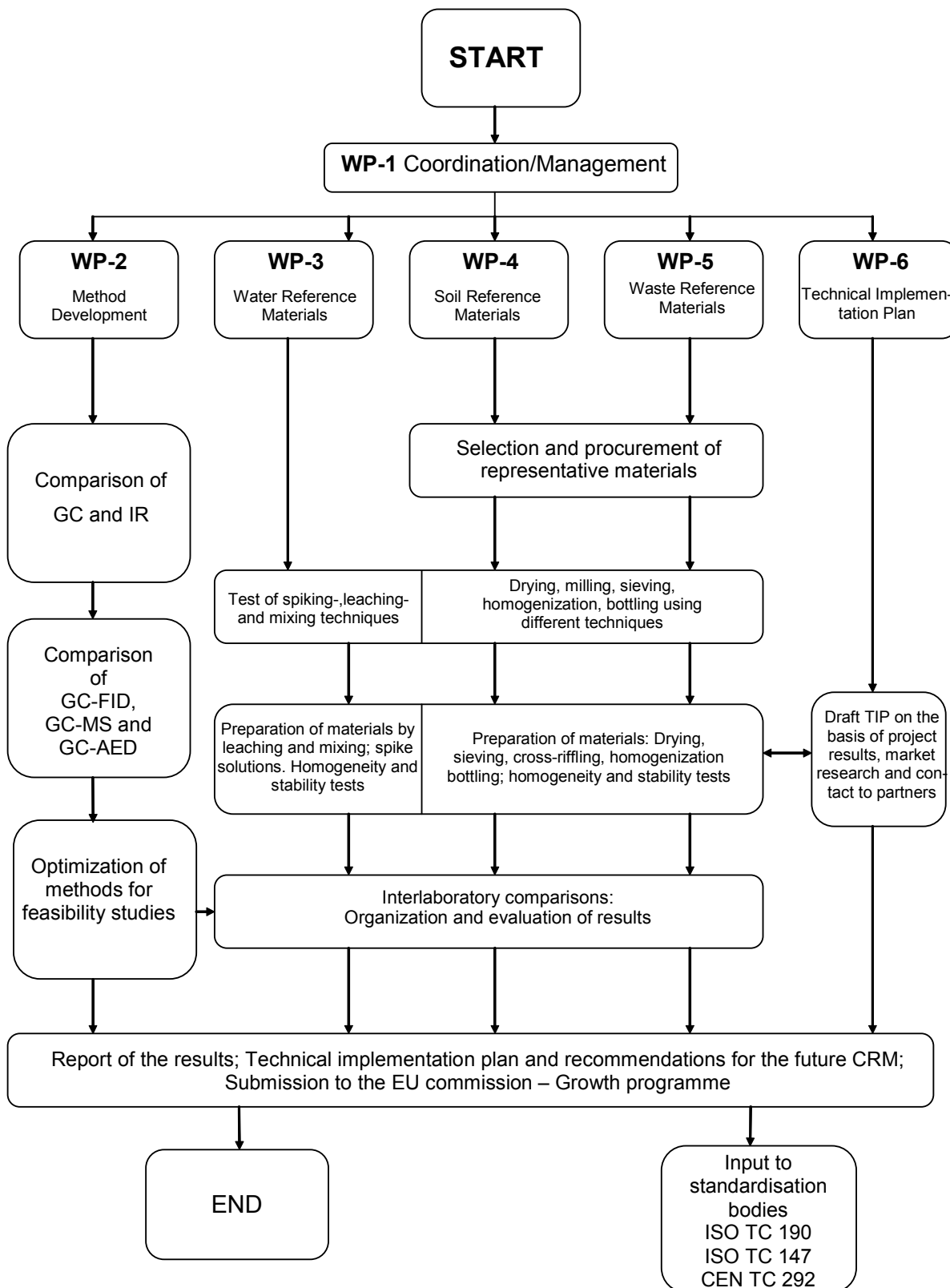


Fig. 2.1 Principle flow diagram of the work programme

2.5 Project partners

The partners of the HYCREF-project are listed in *Tab. 2.2*.

Tab. 2.2
Project partners

No.	Project role	Country	Institute
1	Coordinator	Germany	BAM-Federal Institute for Materials Research and -Testing
2	Principal contractor	Norway	Molab as c/o SINTEF Materials and Chemistry
3	Principal contractor	Germany	UBA-Federal Environmental Agency
4	Principal contractor	Denmark	EUROFINS A/S
5	Principal contractor	Finland	Finnish Environmental Institute Laboratory
6	Principal contractor	The Netherlands	ALcontrol Specials
7	Sub-contractor	Estonia	Estonian Environmental Research Centre
8	Sub-contractor	Finland	VTT-Technical Research Centre of Finland
9	Sub-contractor	Germany	Landesumweltamt Nordrhein-Westfalen
10	Sub-contractor	Germany	Landesumweltamt Brandenburg
11	Sub-contractor	Latvia	Latvian Environment, Geology and Meteorology Agency
12	Sub-contractor	Hungary	VITUKI-Environmental Protection and Water Management Research Institute

3 Scientific and technical description of the results

The following chapter contains an overview of the scientific and technical part of the project (WP-2 to WP-5).

handling problems with the GC-methods according to the standard protocols.

3.1 Method development (WP-2)

The results of this work package were needed to specify the analytical procedure used in the interlaboratory comparisons. Only methods proved as suitable were applied for the feasibility studies. Three main objectives were foreseen in the "Description of work" (Annex I of the contract):

- Comparison of GC (FID, MS, AED) and IR-methods
- Comparison of ISO/FDIS 16703 and Nordic Guideline TR 329
- Investigations on analytical methods:
 - Extraction
 - Sample treatment
 - Florisil clean-up

The results of the investigations in WP-2 were taken into account for the elaboration of the standard protocols. Two standard protocols (one for soil/waste- and one for water-analysis) were prepared based on the latest versions of the International and European standard methods (ISO/FDIS 16703, ENpr 14039 and ISO 9377-2).

In addition to the planned objectives of WP-2 a pre-test study had been conducted to detect the presence of any

3.1.1 Comparison of GC- (FID, MS, AED) and IR-method

The comparability of GC- and IR-results for the mineral oil determination was investigated. Additionally, three different types of detection methods for the GC were compared - FID, MS and AED.

Tab. 3.1 contains the concentrations of the standard solutions of 4 different mineral oils, which were measured for the comparison of GC- and IR-method. The GC-FID chromatograms are shown in Annex A, *Fig. 8.1*.

The standard solutions were prepared gravimetrically. n-Heptane was used as solvent for the GC-solutions and Freon R113 (1,1,2-Trichloro-1,2,2-trifluoroethane) for the IR-solutions. They were prepared freshly to minimize errors due to evaporation losses or other influences on the samples. The concentrations of the 16 GC-test solutions (A1-D4) were between 0.1 and 5 mg/mL. All solutions contained n-Decane (C₁₀) and n-Tetracontane (C₄₀) as RTW- (Retentions Time Window) compounds. The test solutions should not be diluted or concentrated to avoid handling errors. For the calibration the "BAM-Calibration Set" (1:1 w/w mixture of Diesel oil and Lubricating oil, mass fraction of 97 % within the range from C₁₀ to C₄₀) was used and the calibration was done according to ISO/DIS 16703.

Tab. 3.1

Standard solutions used for GC- and IR comparison measurements

Mineral oil	Solution	1	2	3	4
		0.1 mg/mL	0.5 mg/mL	1.0 mg/mL	5.0 mg/mL
Gasoline, Super unleaded, 95 octan (Elf Company)	A	a	a	a	b
Diesel oil, DK 1037, without Additives (Deutsche Shell AG)	B	a	a	a	b
Lubricating oil, HVI 50, without additives (Deutsche Shell AG)	C	a	a	a	b
1:1 (w/w) mixture of 2 white oils: RL 110 - Hydrogenated white oil from naphthenic crude without additives; Light oil of paraffines (Merck)	D	a	a	a	b

a: GC and IR measurements performed

b: Only GC measurements performed

The purity of calibration standard was taken into account for the calculation of the sample results. For IR-measurements a quartz optical cell with an optical path length of 1 cm or thinner was used. The cell could be closed to avoid the evaporation of Freon. The background (reference IR-spectrum) was detected with pure Freon R113. The IR-spectrums of the samples were recorded under identical conditions. Each IR-sample (A1-D3) was measured only once.

The results of the comparison of the GC- and the IR-method are shown in Fig. 3.1 to Fig. 3.3 for all four types of mineral oils including the standard deviations (GC-FID: 7 laboratories, IR: 3 laboratories). The data and the description of the applied methods are summarized in Tab. 8.1 to Tab. 8.4 in Annex A.

A satisfied conformity between IR-results and theoretical values (on the basis of weight) was achieved. The type of mineral oil (gasoline, diesel oil, lubricating oil and mixture of lubricating oils) had no systematic influence on the IR-results.

A quite different conclusion could be drawn from the GC-results. It was obvious that the GC-results are strongly depending on the type of mineral oil (boiling range). Gasoline (solution A) contains only a minor part of compounds within the integration range C_{10} - C_{40} (see Annex A, Fig. 8.1). Therefore, the results obtained by GC (independent of the detector-type: FID, MS, AED) using the integration rules according to the international standards (ISO/FDIS 16703, ENpr 14039, ISO 9377-2) represent the theoretical gravimetric values only for mineral oils with boiling ranges within C_{10} and C_{40} .

In addition to the low systematic errors obtained by IR-measurements it was obvious that the IR-technique is much more sensitive than the GC-technique. The lowest concentration (0.1 mg/mL) could be measured by IR without problem. Under "usual" GC-conditions a concentration of 0.1 mg/mL is near the limit of quantification. That explains the significantly higher uncertainties of the GC-FID results in Fig. 3.1.

The GC-results (FID, MS and AED) were determined by integrating the total peak area between C_{10} and C_{40} . The GC-system was calibrated using a mixture of diesel oil and lubricating oil (1:1, w/w).

The GC-MS determinations were performed using m/e 71 ($C_5H_{11}^{+}$) and the sum of m/e 67, 69 and 71 for the calculation. There are still some doubts relating to the applicability of these procedures for all different kinds of mineral oil samples. Especially high concentrations of alkyl-aromatic

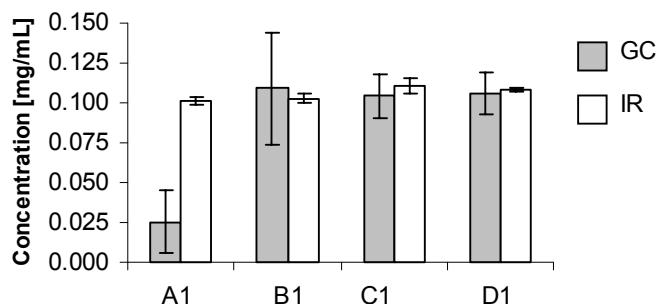


Fig. 3.1 Standard solutions of gasoline (A), diesel oil (B), lubricating oil (C) and a mixture of oils (D) with a concentration of 0.101 mg/mL

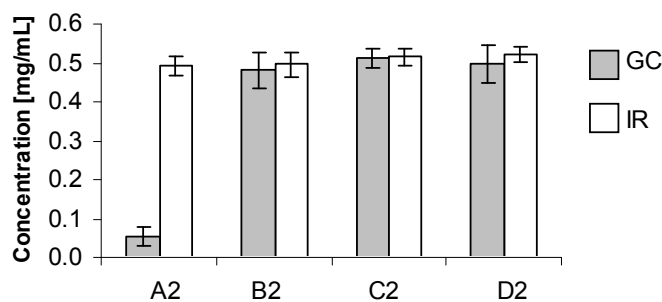


Fig. 3.2 Standard solutions of gasoline (A), diesel oil (B), lubricating oil (C) and a mixture of oils (D) with a concentration of 0.503 mg/mL

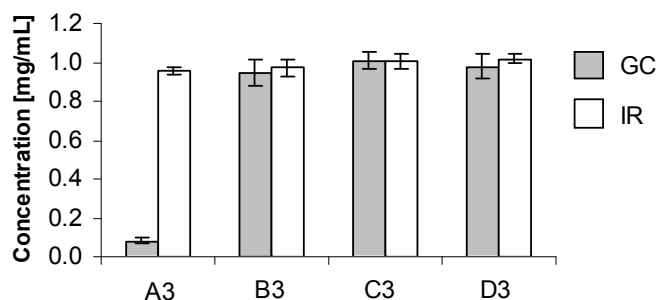


Fig. 3.3 Standard solutions of gasoline (A), diesel oil (B), lubricating oil (C) and a mixture of oils (D) with a concentration of 1.007 mg/mL

Tab. 3.2
Measured recovery in respect to the gravimetric reference value [%]

Solution ^(a)	GC-FID	GC-MS	GC-AED (496/486 nm)	IR
A	8.1	9.8	10.4	98.9
B	94.6	102.8	99.1	98.7
C	98.8	105.8	105.6	103.0
D	96.1	102.1	92.6	103.4

^(a) Solution A, B, C and D have a gravimetric mineral oil concentration of 1.0 mg/mL

compounds (m/e 91), mainly found in water samples, may lead to problems with the GC-MS method. But such a high content of alkyl-aromatic compounds is also a problem for IR-measurement since the aromatic CH-absorption band (3030 cm⁻¹) has a very weak intensity.

According to the detectable spectral emission lines of carbon and hydrogen with the AED two different sets of parameters were used: carbon – 193 nm; carbon and hydrogen – 496 and 486 nm, respectively. The carbon emission line at 193 nm is very sensitive but possesses only a limited linear calibration range.

The IR-results were determined by integrating the CH₃- and CH₂- absorption bands and using the empiric absorption coefficients stated in ISO/TR 11046.

Tab. 3.2 shows the results of different GC detection techniques and the IR-method for the 1.0 mg/mL standard solutions as example. The data for each method and the method descriptions are listed in Tab. 8.1 to Tab. 8.10 in Annex A.

No significant differences between FID, MS and AED could be observed. Taking into account the possible problems with GC-MS when high concentrations of aromatic compounds in the samples occur, FID and AED should be preferred in any case. Both techniques are related to the carbon content of the mineral oil. For solution "A" much lower recoveries are determined by all GC- methods compared to the IR method. The reason for this systematic error was described above.

The final standard protocols of WP-2 (see Annex G and Annex H) for mineral oil determination in water-, soil- and waste samples are in conformity with the latest versions of ISO/FDIS 16703, ENpr 14039 and ISO 9377-2. Only GC-

FID shall be used for measurements, as with this technique the best reproducibility in the feasibility study is expected.

3.1.2 Comparison of ISO/DIS 16703 and Nordic Guideline TR 329

The mineral oil content of the soil samples A, B and C were determined according to ISO/FDIS 16703 and Nordic Guideline TR-No. 329. Three independent determinations per soil and per method were done. The integration range for both methods was assigned from C₁₀ to C₄₀, although the Nordic Guideline prescribes C₆ to C₃₆. Sample A was the sieve fraction (< 2 mm) of a soil collected from the filters of a car washing station (water content about 7 %, pH 7.5, total carbon content 2.7 %, containing lubricating oil). Sample B was the sieve fraction (< 1 mm) of a soil contaminated with crude oil (pH 4.9, total carbon content 4.9 %). Sample C was the sieve fraction (< 1 mm) of a soil containing mineral oil with a wide boiling range and PAHs (pH 9.3, total carbon content 6.1 %).

Tab. 3.3 contains the summary of the essential steps of both methods.

The results of the comparison are shown in Fig. 3.4 to Fig. 3.6 and the data are summarized in Tab. 8.11 in Annex B.

The mineral oil content obtained by the ISO-method was always lower than the content obtained by TR-No. 329-method. That effect can be traced to the clean-up step prescribed only for the ISO-method.

Normally, an internal standard (Squalane was used as internal standard in the TR-No. 329-method) improves the precision of a method, but in the case of mineral oil hydrocarbons an internal standard is often interfered by sample

Tab. 3.3
Summary of the essential steps of ISO/DIS 16703 and TR-No. 329

Step	ISO/DIS 16703	TR-No. 329
Extraction	20 g soil, 40 mL acetone, 20 mL heptane (containing C ₁₀ and C ₄₀), sonication or shaking for 1 hour	50 g soil, 20 mL pentane containing at least 2 internal standards, 20 mL 0.05 M pyrophosphate water solution, shaking for 16 hours
Clean-up	Extract washed twice with 100 mL water to remove acetone (a phase separation can be accelerated by centrifugation), drying of heptane-extract with Na ₂ SO ₄ , clean-up 10 mL of extract over a column filled with 2 g of Florisil and 2 g of Na ₂ SO ₄	Centrifugation for separation of the phases after extraction
GC-FID	Integration between C ₁₀ and C ₄₀ , external calibration with a mixture of Diesel oil / Lubricating oil (1:1 w/w)	Integration between C ₁₀ and C ₄₀ , external calibration by use of internal standards. Calibration substance: Mixture of the n-alkanes C ₁₂ , C ₁₆ , C ₂₀ , C ₂₄ , C ₂₈ , C ₃₀ , C ₃₂ and C ₃₄

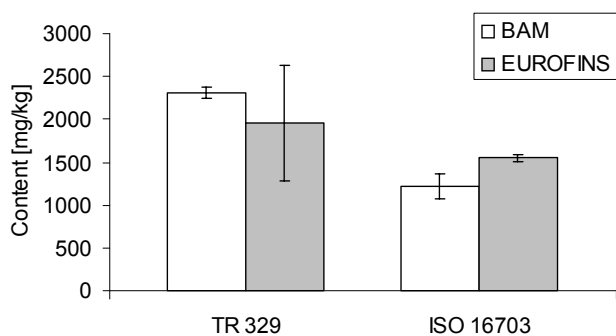


Fig. 3.4
Comparison of ISO/DIS 16703 and TR-No. 329: Sediment A

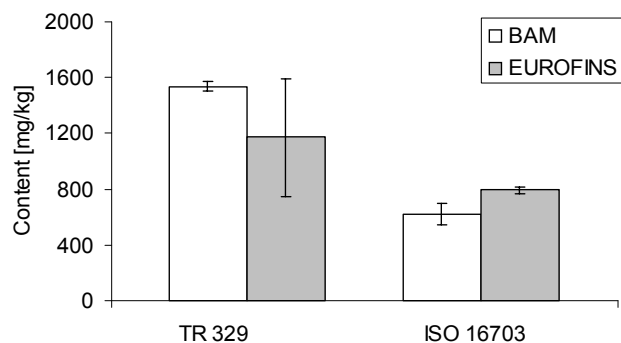


Fig. 3.5
Comparison of ISO/DIS 16703 and TR-No. 329: Sediment B

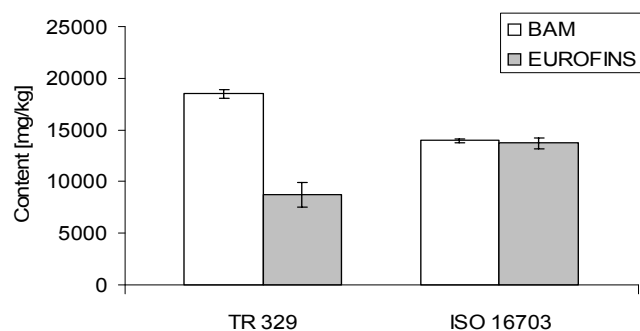


Fig. 3.6
Comparison of ISO/DIS 16703 and TR-No. 329: Sediment C

peaks. Test Soil C contained peaks in the same retention time area as the internal standard Squalane. Therefore, it was not possible to integrate this internal standard.

3.1.3 Investigations on the analytical method (GC)

3.1.3.1 Extraction

The ratio of the sample intake (g) and the solvent for the extraction (mL), prescribed in ISO/DIS 16703 and ENpr 14039, is suspected to lead to problems due to the following reasons:

- the high ratio of 20 g soil to 10 mL n-heptane could lead to an incomplete extraction recovery
- the volume of the organic phase after the extraction is not sufficient for the clean-up step

A soil highly contaminated with mineral oil and PAH (< 2 mm sieve fraction, pH 9.3, C-content 6.1 %, H-content 2.9 %, N-content 0.07 %, dry matter content 79.5 %)

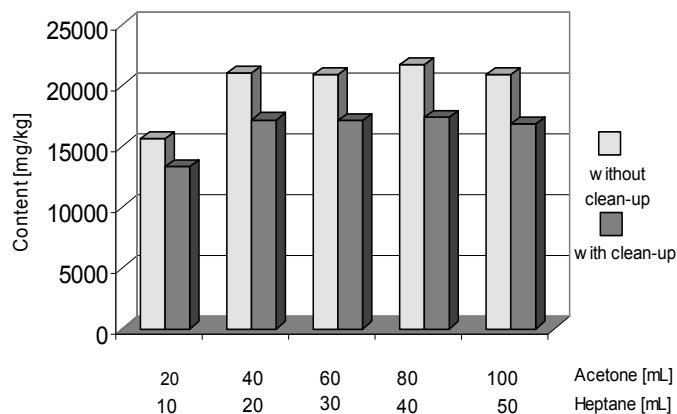


Fig. 3.7
Different extraction volumes of acetone/heptane (2:1) for the extraction of 20 g soil (n=2)

N-content 0.07 %, dry matter content 79.5 %) was used for the extraction experiments. This soil was selected due to its high mineral oil content of about 17 000 mg/kg. This way the worst case of the extraction procedure could be tested. Every extraction method was tested in duplicate. The following parameters were kept constant: sample intake (20 g), ratio of the extraction solvent acetone/heptane (2:1), ultrasonic extraction (1 hour at 40 °C), washing step (two times with water, clean-up (8 mL of extract with 1.5 g of Florisil)). The volumes of acetone and heptane were increased up to 100/50 mL (but always in the ratio 2:1). The organic extracts were analysed with and without clean-up. Fig. 3.7 shows the results obtained by the different extraction variations.

Similar results were obtained for the extraction volumes of acetone/heptane from 40/20 mL up to 100/50 mL. Both the original extracts (without clean-up) and the purified extracts (with clean-up) are comparable between this volume ranges. Only with an extraction volume of 20/10 mL of acetone/heptane, prescribed in ISO/DIS 16703 and prEN 14039, the determined mineral oil content is about 24 % lower than the content found with higher solvent volumes.

The prescribed ratio of 20 g soil and 20/10 mL of acetone/heptane is not sufficient for the complete extraction of mineral oil. The double volume of extraction solvent (40/20 mL acetone/heptane) leads to equal results as further increase of extraction solvent volumes. Therefore, the standard protocol of WP-2 prescribes for the extraction 40 mL of acetone and 20 mL of heptane for a sample intake of 20 g.

Apart from the extraction efficiency itself the volume of available extract after extraction is also of importance. A sufficient extract volume has to be obtained in order to perform the following clean-up procedure. The suggested increase of the extraction solvent volume was sufficient for all HYCREF-materials. More than 10 mL of extract were obtained, enough for performing the clean-up with exactly 10 mL. But in few cases the extraction solvent can be adsorbed by sample material so that no supernatant phase exists anymore (e.g. cable covering material). In such cases the sample intake could be reduced to e.g. 10 g or the clean-up procedure could be adapted (e.g. 5 mL of extract purified over 1 g of Florisil).

Some types of water samples tend to the formation of emulsions during their extraction with organic solvent. The prevention of the formation of an emulsion was tested by means of a bilge water sample, containing high amounts of surfactants, carbon black, salts and iron-III-oxide. The water sample was extracted with 50 mL of n-hexane according to ISO 9377-2, a strong emulsion was formed. After centrifugation only 10 mL of extract were obtained. The emulsion could be broken only by ultrasonic treatment and centrifugation.

Except the chemical composition of a water sample the stirring rate during extraction has an influence on the formation of emulsions. It could be shown that solutions should not be stirred too fast, as otherwise stronger emulsions are formed. The standard protocol (water) contains a detailed description for extraction procedures to avoid emulsions.

3.1.3.2 Sample treatment

The step "sample treatment" for soil- and waste analysis comprises the removal of acetone from the organic phase after extraction. The removal of acetone from the extract is of essential importance as the subsequent clean-up step is strongly influenced by remaining acetone. A commonly used method for the removal of acetone from non-polar extracts is the extraction (once or several times) with water. This washing method is prescribed in ISO/DIS 16703 and prEN 14039. However it is not defined how much water must be added and how often the washing step must be repeated to receive an extract free of acetone. The following investigations had been carried out to define a procedure for the sample treatment.

At first, the partition coefficient (α) of acetone in a heptane/water system was determined: The partition coefficient follows Eq. 3.1:

$$\alpha = \frac{C_{Ac}^{Hep}}{C_{Ac}^{H_2O}} \quad (3.1)$$

with:

α = partition coefficient for acetone in a heptane/water-phase system

C_{Ac}^{Hep} = acetone concentration in heptane (v/v)

$C_{Ac}^{H_2O}$ = acetone concentration in water (v/v)

If defined conditions are given, α can be expressed by means of the Eq. 3.2:

$$\alpha = \frac{\frac{V_{Ac}^{Hep}}{V_{Hep} + V_{Ac}^{Hep}}}{\frac{V_{Ac} - V_{Ac}^{Hep}}{V_{H_2O} + (V_{Ac} - V_{Ac}^{Hep})}} \quad (3.2)$$

with:

V_{Ac}^{Hep} = acetone volume in heptane

V_{Hep} = total heptane volume

V_{Ac} = total acetone volume

V_{H_2O} = total water volume

The approach of Eq. 3.2 does not consider a volume effect, which may result from mixing of acetone and non-polar solvent, e.g. n-heptane. It was found that these effects play only a minor role.

Pre-tests have shown that α is not constant for different acetone/water/heptane-ratios. Acetone tends much more to the water phase than to the heptane-phase. Under the assumption that enough heptane is present, α should depend mainly on the water/acetone-ratio.

Different defined acetone/water/heptane mixtures were prepared. The acetone concentration in the heptane phase (respective the acetone volume V_{Ac}^{Hep}) was determined by GC-FID. α could be calculated using Eq. 3.2.

Fig. 3.8 shows the obtained relation between α and the water/acetone-ratio.

The corresponding function of Fig. 3.8 can be expressed in good conformity as (Eq. 3.3):

$$\alpha = y_0 + \frac{a}{x} + \frac{b}{x^2} + \frac{c}{x^3} \quad (3.3)$$

with $\chi = \frac{V_{H_2O}}{V_{Ac}}$

and the coefficients:

$$y_0 = 0.1247 \quad a = 0.0869 \quad b = 0.0579 \quad c = -0.0093$$

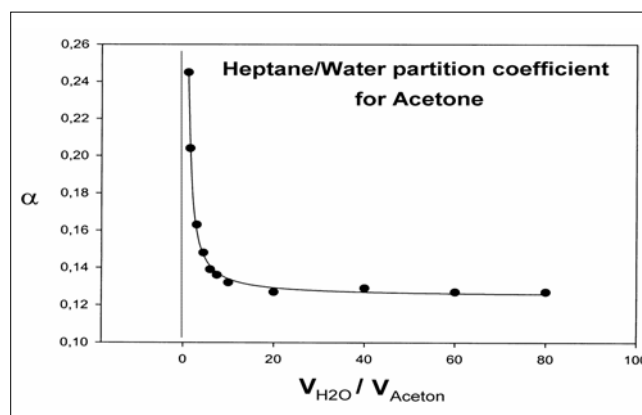


Fig. 3.8 Heptane/water partition coefficient of acetone in relation to the water/acetone-volume ratio (heptane-volume was kept constantly)

Now, α is defined and V_{Ac}^{Hep} can be calculated by Eq. 3.4 (combination of Eq. 3.2 and Eq. 3.3):

$$V_{Ac}^{Hep} = \frac{V_{H_2O} + V_{Ac}(1-\alpha) + V_{Hep} \cdot \alpha}{2 \cdot (\alpha - 1)}$$

$$-\sqrt{\left(\frac{V_{H_2O} + V_{Ac} \cdot (1-\alpha) + V_{Hep} \cdot \alpha}{2 \cdot (\alpha - 1)}\right)^2 + \frac{\alpha \cdot V_{Ac} \cdot V_{Hep}}{\alpha - 1}} \quad (3.4)$$

For the prediction of the acetone concentration in real organic soil extracts only the acetone-, heptane- and water volumes must be known.

An Excel-program was written to determine the (remaining) acetone concentration in heptane extracts. This program enables the user to predict the residue of acetone in heptane extracts after one or after several washing steps with water. This way a final target acetone concentration can be obtained using the necessary amounts of water for washing. *Tab. 3.4* shows the Excel-worksheet.

The validity of the developed method for the prediction of acetone concentrations was tested by means of 5 different soils. 20 g of each soil was extracted according to ISO/DIS 16703 with acetone/heptane (20/10 mL). For each washing step 100 mL of water were added to the extract.

The analysed acetone concentrations (by GC-FID) and the calculated acetone concentrations in the organic extract after the first and second washing step are presented in *Tab. 3.5*.

The comparison of the analysed and the calculated acetone concentrations in the organic extracts shows a very satisfactory conformity between both methods.

Furthermore, it was found in many experiments that remaining acetone concentrations of about 0.1 % can be assumed as negligible for Florisil clean-up. Taking into account that two washing steps should be performed, each washing step has to be carried out with 100 mL of water (see *Tab. 3.4*). A third washing step reduces the remaining acetone concentration to less than 0.01 %. Such low concentration is not necessary for clean-up.

An alternative procedure for the acetone removal without using centrifugation was tested. Since centrifugation of inflammable solvents requires specific safety precautions, not available in many environmental laboratories, the working groups of ISO/TC190 and CEN/TC292, which are dealing with the preparation of standards for the analysis of hydrocarbons in soil and waste, decided that centrifugation is an option for phase separation but shall not be normative. According to the alternative method the organic extract was washed twice with 100 mL of water in a separation funnel instead of the centrifugation vials. About 16 mL of organic extract can be obtained after the washing step (10 mL of the extract are necessary for the clean-up). The extraction efficiency was comparable to the original method. Both methods can therefore be applied for the sample treatment. To improve and accelerate phase separation centrifugation can be applied provided the necessary safety precautions, especially with regard to inflammable solvents are taken into account.

The developed procedure for acetone removal from heptane-extracts (two washing steps, each with 100 mL of

Tab. 3.4
Excel-worksheet for the calculation of the remaining acetone in the heptane extract after 1, 2 and 3 washing steps, respectively

	1. Washing step	2. Washing step	3. Washing step
Sample intake [g]	20.00 *	---	---
Dry matter content [%]	97.54 *	---	---
Heptane volume [mL]	20.00 *	20.00	20.00
Extract volume [mL]	----	20.99	20.02
Acetone volume [mL]	40.00 *	0.99	0.02
Water added for washing step [mL]	100 *	100 *	100 *
Original water in sample material [mL]	0.49	---	---
Total water volume [mL]	100.49	100	100
$V_{water}/V_{acetone}$	2.51	101.5	4177.3
Partition coefficient	0.168	0.126	0.125
Volume acetone in heptane phase [mL]	0.985	0.024	0.001
Vol-% acetone in heptane phase [%]	4.69 ⁺	0.120 ⁺	0.003 ⁺

* variable parameters

⁺ calculated parameters

Tab. 3.5
Analysed and calculated acetone concentrations in the heptane extracts after two washing steps with 100 mL water

Soil-No.	1. washing step acetone in heptane		2. washing step acetone in heptane	
	analysed [vol-%]	calculated [vol-%]	analysed [vol-%]	calculated [vol-%]
1	7.1	6.9	0.13	0.13
2	6.6	6.8	0.11	0.11
3	6.6	6.4	0.09	0.08
4	6.9	6.2	0.14	0.11
5	6.6	6.2	0.12	0.10

water, with or without centrifugation) replaced the existing procedure according to ISO/DIS 16703 and ENpr14039. The “new” procedure is included in the standard protocol of WP-2 for soil- and waste analysis and ISO/FDIS 16703.

3.1.3.3 Florisil clean-up

The ISO/DIS 16703 prescribes a clean-up step with Florisil using the batch technique. On the other hand the ISO 9377-2 (water) prescribes a clean-up step with Florisil using a column technique.

Preliminary results have shown that the column technique seems to be more effective than the batch technique. Therefore, both techniques cannot be used alternatively. Furthermore, a harmonisation of the clean-up steps in water-, soil- and waste analysis was aimed. The following clean-up conditions were compared and tested:

- Column- versus batch technique: PAH-mixture
- Column- versus batch technique: Stearylstearate
- Column- versus batch technique: Triglycerides
- Column- versus batch technique: 4 different contaminated soils
- Test on different column clean-up variations
- Comparison of self filled and commercial filled cartridges
- Comparison study of Florisil batches at two institutes
- Influence of Florisil-activity on clean-up recovery

Column- versus batch technique: PAH-mixture

The efficiency of both clean-up techniques was compared using selected PAH compounds. A test solution in n-heptane was prepared containing Naphthalene, Fluoranthene, Pyrene and Indeno(1,2,3-cd)pyren, each compound with a concentration of 110 µg/mL. One part of the test solution (40 mL) was purified over a glass column filled with 3 g of Florisil. To the other part of the test solution (40 mL) 3 g of Florisil were added and then shaken.

Fig. 3.9 shows the recoveries of the PAH compounds obtained after column clean-up and batch clean-up, respectively.

Tab. 3.6

Parameter for stearylstearat testing

Parameter	Column technique	Batch technique
Stearylstearate concentration	2 g/L	1 g/L
Volume of stearylstearate solution	10 mL	40 mL
Absolute amount of stearylstearate for testing	20 mg	40 mg
Florisil (150-250 µm, heated to 140°C, 16 h)	3 g	3 g

Tab. 3.7

Recovery of stearylstearate after column- and batch- clean-up

Acetone - conc. in heptane [vol-%]	Stearylstearate recovery [%]	
	Column technique	Batch technique
0.0	0.0	0.3
0.1	0.0	3.9
0.2	0.0	23
0.4	0.6	56
0.6	0.0	78
0.8	0.3	86
1.0	0.7	91

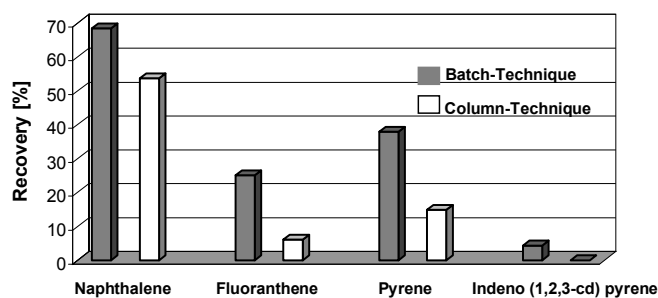


Fig. 3.9

Recovery of selected PAH after batch clean-up and column clean-up with Florisil

Both clean-up techniques were not suited to remove all PAH compounds completely. But it is obvious that the column technique is more effective than the batch technique. Except the better purification by using a column clean-up compared with the batch technique (removal of polar compounds), the column technique had an additional filtration effect on organic extracts, which often contain suspended particles.

Column- versus batch technique: Stearylstearate

Stearylstearate is the prescribed compound to test the Florisil activity according to ISO/DIS 16703, prEN 14039 and ISO 9377-2. This test is always done using an acetone free standard solution of stearylstearate in heptane or hexane. But real soil- and waste extracts contain traces of acetone (about 0.1-0.2 %, see Chapter 3.1.3.2).

The conditions presented in Tab. 3.6 were chosen to compare the column- and the batch technique regarding the removal of stearylstearate from a heptane solution. The acetone concentration in the test solutions was increased started at 0.0 % up to 1.0 %.

Tab. 3.7 contains the recoveries of stearylstearate after clean-up with column- and batch technique including the effect of acetone in the test solutions.

For the normative “test case” (0.0 % acetone in heptane) both clean-up techniques yielded an efficient removal of stearylstearate. But the stearylstearate recovery for the shaking procedure increases rapidly when the acetone

concentration increases. The column technique is more robust against this “acetone effect”.

The above described comparison test is not quite comparable because different amounts of stearylstearate have been used. But it shows the tendency that the column technique is much more effective than the batch technique.

Column- versus batch technique: Triglycerides

Three pure triglycerides (Trilaurin - $C_{39}H_{74}O_6$, Trimyristin - $C_{45}H_{86}O_6$ and Tripalmitin - $C_{51}H_{98}O_6$) were chosen for the clean-up test. These 3 compounds were selected as they are relevant for organic oils and can be analysed by GC-FID.

A test solution containing Trilaurin, Trimyristin and Tripalmitin in heptane (each 670 mg/L) was prepared. Preliminary tests have shown that the clean-up recovery of triglycerides is very low. Therefore, acetone was added to the prepared test solution to give an acetone concentration of 1 %.

One part of the test solution (40 mL) was purified over a glass column filled with 3 g of Florisil. The other part of the test solution (40 mL) was shaken after adding 3 g Florisil.

The results are given in *Tab. 3.8*.

Tab. 3.8
Recovery of triglycerides after batch- and column- clean-up

Compound	Recovery [%] batch technique	Recovery [%] column technique
Trilaurin	0.10	~ 0.01
Trimyristin	0.08	~ 0.01
Tripalmitin	0.05	~ 0.00

The clean-up results revealed that the triglycerides have a high tendency to adsorb on Florisil. No significant differences between both techniques could be observed.

Column- versus batch technique: 4 different contaminated soils

The column- and the batch- technique were compared using four different test soils, contaminated with mineral oil.

- Peat material
- Soil 1
- Soil 2
- Soil 3

The soils were extracted with acetone/heptane (2:1) by ultrasonic extraction. The extracts were washed twice with an excess of water to remove acetone.

Peat material

The extract (10 mL) of the peat material was either purified over a glass column filled with 2 g of Florisil and 2 g of Na_2SO_4 or was shaken for 10 minutes after adding 2 g of Florisil and Na_2SO_4 .

The purified extract after batch clean-up (5 minutes shaking) contained a lot of small solid particles which settled over night. Afterwards, a clear yellow solution was ob-

tained. The purified extract after column clean-up was clear and colourless, analysed by GC-FID. The chromatograms are shown in Annex C, *Fig. 8.2*.

The hydrocarbon content of the peat material calculated on the basis of the shown chromatograms strongly depends on the used clean-up technique. The difference of the hydrocarbon content after “column” and “batch” clean-up was about 53 % on the basis of the “column-value”.

Soil 1, 2 and 3

The extracts of the other soil materials (10 mL) were purified over a glass column filled with 3 g of Florisil. The other part of the soil extract (10 mL) was shaken for 10 minutes after adding 3 g of Florisil.

Fig. 3.10 to *Fig. 3.12* show the results of the clean-up experiments on the 3 different soils. The original raw extracts (without clean-up) were analysed too.

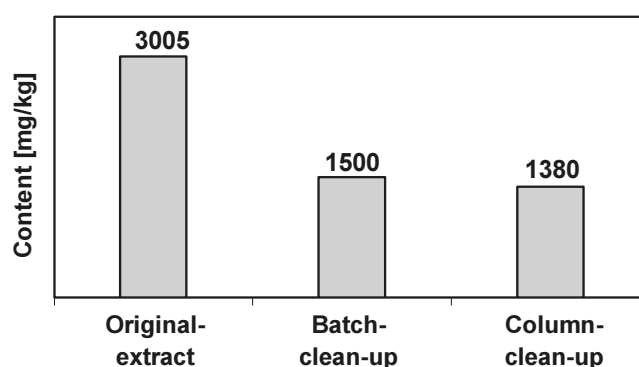


Fig. 3.10
Mineral oil content of Test soil 1 after batch- and column clean-up

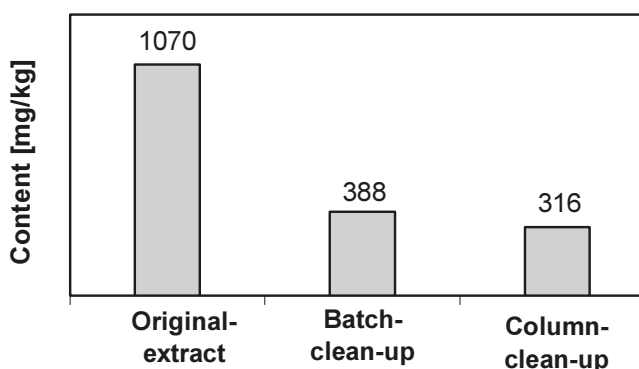


Fig. 3.11
Mineral oil content of Test soil 2 after batch- and column clean-up

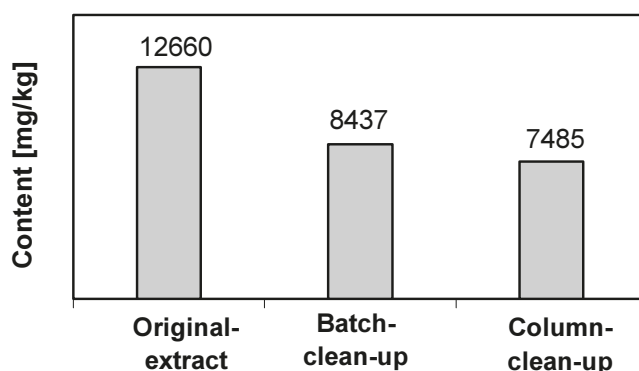


Fig. 3.12
Mineral oil content of Test soil 3 after batch- and column clean-up

The clean-up experiments of the test soils show, that the column technique is more effective than the batch technique. The difference between both techniques was about 10-20 % regarding the mineral oil content of the three tested soils.

The efficiency of the column technique to remove polar compounds is not limited on hetero-atomic substances like O-, N- or Cl-containing compounds. Also pure hydrocarbons with a tendency to adsorb on Florisil, e.g. aromatic compounds with p-electrons or alkyl aromatics give a contribution to the decrease of the "mineral oil content" if the column technique is applied.

Test on different column clean-up variations

50 g of a test-soil (highly contaminated with TPH and PAH) was extracted with 100 mL of heptane (containing C₁₀ and C₄₀) by shaking for 30 minutes. After settling of the solid material the supernatant extract (about 70 mL) was used for the subsequent clean-up experiments.

Empty glass cartridges ("Bakerbond", total volume inside: 8 mL) with a PTFE-filter were self-filled with Florisil (Merck, 0.150-0.250 mm, heated at 140 °C for 16 hours) and Na₂SO₄ (dried). The exact amount of the extract was transferred onto the columns with a pipette. The clean-up was performed without any additional pressure or vacuum on the column. The eluats were collected in a vial and analysed by GC-FID. The total peak-areas between C₁₀ and C₄₀ were integrated.

Tab. 3.9 contains the different variations used for clean-up tests and the related results being obtained.

Tab. 3.9
Column clean-up experiments on a soil extract

No.	Florisil [g]	Na ₂ SO ₄ [g]	Extract [mL]	Eluate [mL]	Recovery [%] based on the original-extract
1	1	1	5	3.0	77
2	1	2	5	2.8	77
3	2	1	5	1.7	72
4	2	1	10	6.6	75
5	2	2	5	1.5	72
6	2	2	10	6.3	74
7	3	1	5	0.2	67
8	3	1	10	5.2	70
Original-Extrakt					100

The results in Tab. 3.9 demonstrate that the selected parameters (amount of Florisil, amount of extract, ratio of Florisil/extract) are of importance for the obtained concentration of the purified extracts. The amount of Na₂SO₄ (1 g or 2 g) has no significant influence on the clean-up step.

5 mL of extract are easier to handle than 10 mL if a cartridge is used. Additionally, in the case of losses of heptane – extract during the procedure (e.g. on the solid material, emulsions during the washing steps), a remaining minimum amount of 5 mL are more probable than 10 mL of extract. On the other hand, only about 3 mL of purified extract can be expected after this clean-up procedure. That is enough to fill a GC-vial (typically 1.5 mL), but a small amount of extract is more sensitive against evaporation losses than a bigger amount.

It was shown that an adapted clean-up procedure (5 mL extract/1 g Florisil) could alternatively be used instead of the prescribed clean-up (10 mL extract/2 g Florisil). But such a modification should only be done if there is no other alternative.

Comparison of self-filled and commercially filled cartridges

Either self-filled or commercially filled columns can be taken according to ISO 9377-2 (for water), ISO/FDIS 16703 (for soil) and EN 14039 (for waste). To determine possible differences between self- and commercially filled columns the hydrocarbon recovery of BAM-CRM 5004 in n-heptane (c = 5 mg/mL) was measured for two different types of Florisil:

- Merck - Batch Florisil (150-250 µm) prepared 2 weeks before experiments, heated at 140 °C for 16 hours, cool down under nitrogen atmosphere, storage in an exsiccator over silica gel
- Baker – commercially filled cartridges with 2 g Florisil and 2 g Na₂SO₄, air tight sealed box freshly opened

The determination of the moisture content of Florisil was measured at 3 different heating temperatures (105 °C, 140 °C and 220 °C) with Karl-Fischer coulometric method (Tab. 3.10).

The hydrocarbon recovery was highly dependent on the moisture content of the used Florisil. Unfortunately, the moisture content of commercially filled cartridges cannot be reduced in contrast to batch material which can be heated. The high influence of the Florisil-water content to the hydrocarbon recovery decreases the robustness of the method significantly.

Comparison study of Florisil batches at two institutes

A direct comparison of different Florisil batch qualities at two institutes should give the answer whether the operator (and handling) or the Florisil quality is more responsible for variances. The HYCREF-partner BAM and UBA exchanged their Florisil batches and measured the recovery with the own batch and the batch from partner's institute. The results of a solution and a test soil are shown in Fig. 3.13 and Fig. 3.14.

Tab. 3.1
Hydrocarbon recovery of BAM-CRM 5004 in n-heptane (c = 5 mg/mL) for different Florisil, determined at different temperatures with Karl-Fischer-method

Florisil	Moisture content of Florisil [%]			Hydrocarbon recovery [%] of BAM-CRM 5004 in n-heptane
	105°C	140°C	220°C	
Merck – self-filled	0.65	0.82	1.03	80.7
Baker – commercially filled	1.82	2.05	2.48	93.6

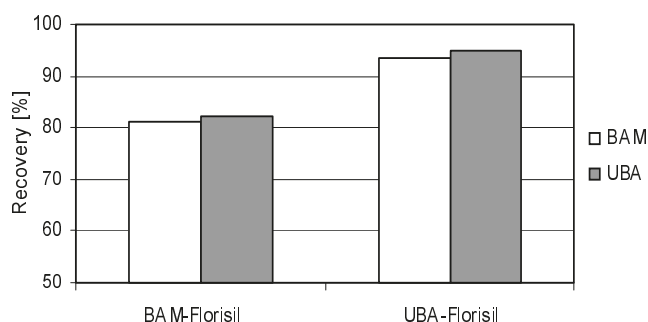


Fig. 3.13
Comparison of BAM- and UBA-Florisil batches on a test solution

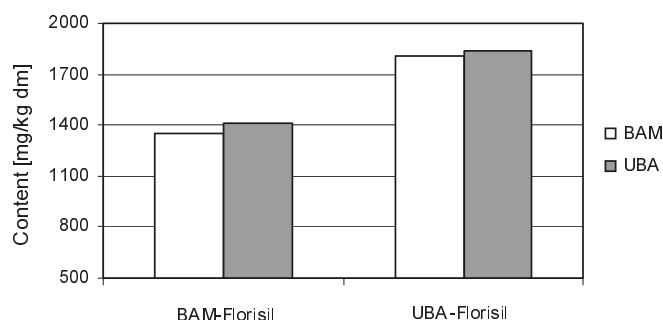


Fig. 3.14
Comparison of BAM- and UBA-Florisil batches on a test soil (filters of a car washing station)

It was clearly found that there are no significant differences in the measurement of both laboratories, but there are significant differences between the two Florisil batches. The recovery of the test solution using UBA-Florisil was about 92 % and 82 % using BAM-Florisil. The Florisil batches were activated differently: At BAM the Florisil was cooled down after heating at 140 °C under pure nitrogen in a desiccator; at UBA the Florisil was cooled down after heating at 140 °C under laboratory air. Therefore, the moisture content of these two Florisil batches may differ and could lead to non-comparable results. As lower the moisture content as lower is the clean-up recovery.

A comparison of Florisil batches from different suppliers (Baker, Promochem, Fluka, Merck) did not show any differences regarding clean-up recovery (using always the same handling procedure).

Influence of Florisil-activity on clean-up recovery

It was shown from the tests before that the Florisil-activity has a significant influence on the clean-up recovery.

The final experiment in this section was focused on the systematic investigation of the moisture content of Florisil (= Florisil activity!) on the recovery of a mineral oil standard solution during clean-up.

At first, the Florisil (Merck) was activated (heated at 140 °C for 16 hours). Afterwards, portions of Florisil were deactivated by adding water and homogenised. The following moisture contents of Florisil were obtained: 0 %, 2 %, 5 % and 10 % water.

A mineral oil standard solution in n-heptane (10 mL) was purified using Florisil with different degrees of activity. The mineral oil recovery after clean-up (on the basis of the untreated solution) is presented in Fig. 3.15.

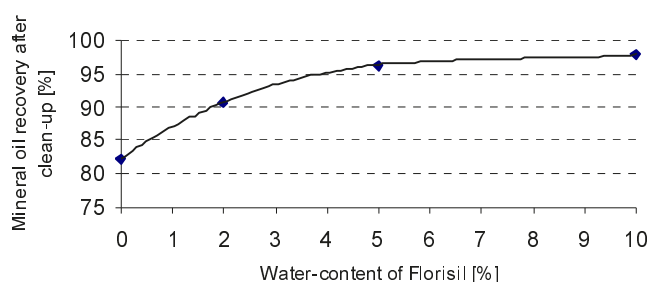


Fig. 3.15
Clean-up recovery of mineral oil using different Florisil-activities

A significant correlation was found between the moisture content of Florisil (activity) and the clean-up recovery of mineral oil. For the normative case (0 % water in Florisil) a recovery of about 82 % was obtained. This value was typical for the laboratory in which the experiments were carried out (BAM).

After deactivation of Florisil with 2 % water the recovery increases rapidly to 90 %. This result confirms the former experiments on commercial filled Florisil-columns (Baker). It was found that Florisil from the commercial filled columns had a water content of about 2 % and yielded recoveries of about 90 %.

A further deactivation of Florisil up to 10 % leads to a further increase of the clean-up recovery of the mineral oil standard up to about 98 % (Fig. 3.15).

Two conclusions can be drawn from this experiment:

- The clean-up recovery strongly depends on the water content (activity) of Florisil. This effect is more significant for low moisture contents (0-5 %).
- What does conclusion a) mean regarding a better reproducibility of the standard method ISO/FDIS 16703? It could be considered to deactivate the Florisil with e.g. 5 % water. The variety concerning mineral oil recovery would become negligible in this range of water content compared with highly activated Florisil. On the other hand, the removal of polar compounds could become incomplete caused by the lower activity of Florisil.

3.1.4 Pre-test study

Prior to the test certification study of the 9 HYCREF-materials a pre-test study was conducted to determine the presence of any handling problems with the standard protocols which based on GC-methods ISO 9377-2 (for water), ISO/FDIS 16703 (for soil) and EN 14039 (for waste). The pre-test materials, delivered to each participant, contained a standard solution (BAM CRM 5004 in n-heptane) for direct injection into the GC and one bottle of soil reference material (soil from filters of a car washing station), which should be analysed according to the standard protocol. The results including the chromatograms of the standard solution and soil sample were evaluated by BAM.

Fig. 3.16 and Tab. 3.11 present the results of the standard solution measurements intended for direct injection into the GC.

The mean value of the analysed GC-test solution (2.92 mg/mL) was in excellent agreement with the theo

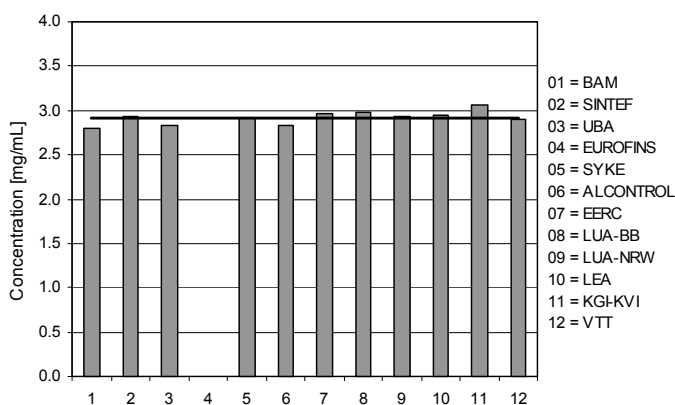


Fig. 3.16
Determination of the mineral oil hydrocarbon concentration of the GC test solution (BAM CRM 5004 in n-heptane)

retical value (2.93 mg/mL, gravimetrically prepared). The coefficient of reproducibility was 2.61 %. This study showed that the GC-performance of all laboratories was fit for purpose.

The determination of the mineral oil hydrocarbon content of the test soil was done by all laboratories according to the standard protocol. The results are outlined in Fig. 3.17 and Tab. 3.11.

An unexpected high coefficient of reproducibility of 27.7 % was obtained. Such different results could be caused by variations in the clean-up procedure.

An additional pre-test was carried out to test the clean-up recovery of each laboratory. Two clean-up test solutions were determined. The first clean-up test solution (test solution 1) was a mineral oil mixture in n-heptane. 10 mL of the solution were added to the clean-up column filled with 2 g of Florisil and 2 g of sodium sulphate and the entire eluate was collected. A portion of the purified solution was analysed by gas chromatography. The untreated solution was analysed as reference. The recovery of the hydrocarbons on the basis of the peak area of the purified and untreated solution was determined. The results are shown in Fig. 3.18 and Tab. 3.11.

Recoveries were found between 78 % and 103 % with a coefficient of reproducibility of 7.7 %. These results led to the conclusion that the clean-up recovery is strongly dependent on the way of which the Florisil was activated. Only this preparation step was done by the participants in their own laboratories.

The same tendency of the results was observed for test solution 2, a real soil extract, containing polar compounds as well as C₁₀ and C₄₀, in n-heptane. 10 mL of the solution was added to the clean-up column filled with 2 g of Florisil and 2 g of sodium sulphate. The eluate was collected. A

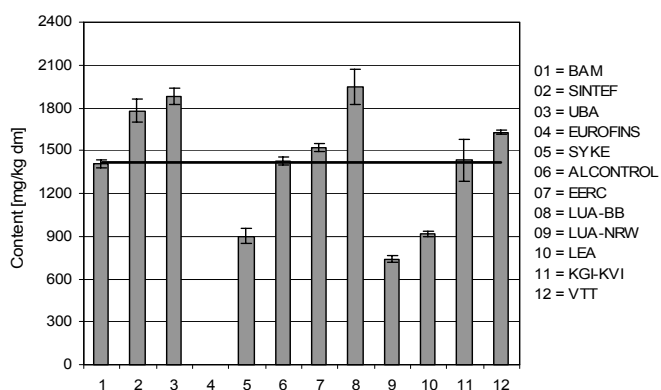


Fig. 3.17
Determination of the mineral oil hydrocarbon content of the test soil (car washing station)

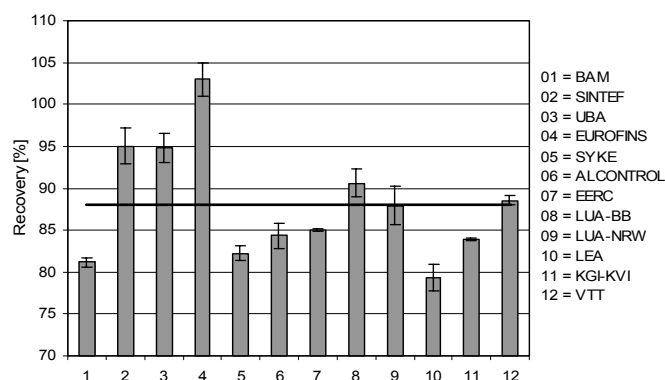


Fig. 3.18
Determination of the recovery of the test solution 1

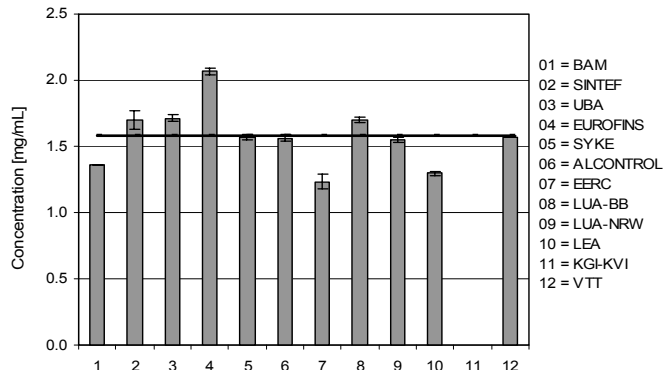


Fig. 3.19
Determination of the concentration of the mineral oil hydrocarbon of the test solution 2 (real soil extract)

portion of the purified solution was analysed by gas chromatography and the mineral oil hydrocarbon concentration (mg/mL) was calculated by means of a calibration function prepared by injecting different concentrations of BAM CRM 5004 calibration oil standard. The results are presented in Fig. 3.19 and Tab. 3.11.

Tab. 3.11
Results of pre-test measurements

	Mean of means	Coefficient of reproducibility VI	Coefficient of reproducibility VR	No. of labs
GC-test solution	2.92 mg/mL	0.08 mg/mL	2.61 %	11
Test soil	1416 mg/kg dm	392 mg/mg dm	27.7 %	11
Test solution 1	88.0 %	6.80 %	7.73 %	12
Test solution 2	1.58 mg/L	0.23 mg/L	14.44 %	11

The obtained coefficient of reproducibility (14.4 %) is relative poor taking into account that only a clean-up step and a GC-analysis was carried out. The GC-performance could be excluded to be responsible for this result (see Fig. 3.16 and Tab. 3.11).

A summary of the pre-test results is given in Tab. 3.11.

In Tab. 8.12 to Tab. 8.15 of Annex D all data of these pre-tests are summarized. Tab. 8.16 and Tab. 8.17 of Annex A contain the clean-up conditions used in the pre-test study.

After completion of this pre-test study, which was carried out in addition to the HYCREF-work plan, the test certification study was planned based on the pre-test experiences and the elaborated standard protocols.

3.1.5 Standard Protocols on WP-2

The final output of WP-2 was the elaboration of standard protocols for the determination of hydrocarbons in water-, soil- and waste samples on the basis of ISO/DIS 16703 (soil), ENpr 14039 (waste) and ISO 9377-2 (water) and on the basis of the achieved results in WP-2. Two standard protocols (one for soil/waste and one for water see Annex G and Annex H) were prepared and handed over to all participants of the ILCs and should strictly be followed.

The major changes and improvements of HYCREF standard protocols compared with the international methods are briefly summarized below (Tab. 3.12).

The improvements in Tab. 3.12 (right column) could be suggested on the basis of investigations during the HYCREF-project. On this way an added value for International standardisation bodies of ISO/TC 190 (soil), ISO/

TC 147 (water) and CEN/TC 292 (waste) will derive from the results of WP-2. Some of the achieved project results were already taken into account in the new version of ISO/FDIS 16703 (August 2003).

3.2 Preparation of the reference materials

In the following chapters the preparation and characterisation of the reference materials will be described. The challenges of the different materials will be discussed in detail. The results of the interlaboratory comparison study will be presented in the adjacent chapter.

3.2.1 Overview over the materials

The 9 selected materials, which were prepared during the project, are summarized in Tab. 3.13 together with the institutes responsible for their preparation and the origin of the materials.

3.2.2 Water reference materials (WP-3)

There are considerable challenges related to water reference materials containing degradable non-water soluble constituents. A "real" sample will normally be a 1 L bottle with a very short shelf-life even at low temperatures. Freezing of the sample would probably change the sample permanently and make it difficult to ship. The more innovative part of the project has therefore been to find new ways to produce realistic water reference materials.

Two types of water reference materials should mimic offshore produced water and land-based discharges, both containing realistic levels of hydrocarbons and contami-

Tab. 3.12
Steps, present procedure and suggestions to improve ISO/DIS 16703 and EN 14039

Step	Present method according to ISO/DIS 16703 and prEN 14039	Suggestion to improve ISO/FDIS 16703 and prEN 14039
Solvent for extraction	20 mL Acetone / 10 mL Heptane	40 mL acetone / 20 mL Heptane
Washing the extract with water	~ 35 mL ~ 60 mL	100 mL 100 mL
Clean-up	10 mL of extract ^(a) / 3 g Florisil with batch technique	Exactly 10 mL of extract with 2 g Florisil and 2 g of Na ₂ SO ₄ using column technique

^(a) The remaining part of the heptane-extract after washing the extract twice with water. This part depends on the specific conditions (type of material, centrifugation or not) and lies between 3-8 mL.

Tab. 3.13
Overview over the reference materials, the responsible institutes and the origin of the materials

Material	Responsible	Origin
Soil Eluate	UBA	Mixture of an aqueous diesel fuel extract (sample 03/I001309/1/0, Deutsche Shell GmbH, Hamburg, Germany) and an aqueous soil extract (Standard soil 2.2, batch SP 222803, Agricultural and Research Institute Speyer, Germany) containing 0.1% sodium azide
Offshore Pills ^(a)	SINTEF	SINTEF product
Landbased Pills ^(a)	SINTEF	SINTEF product
Clayish Soil	EUROFINS	Slightly contaminated clayish soil from Bioteknisk Jordrens, Kalundborg, Denmark
Sandy Soil	SYKE	Naturally contaminated soil sample from Tampere Härmälä
Peat Material	ALCONTROL	Mixture of compost and contaminated peat rich location
Marine Sediment	SINTEF	North Sea sediment
Building Material	BAM	Bricks contaminated with heating oil from a spill 1997
Ni/CP-Waste	BAM	Mixture of waste materials from Ni-galvanic factory and phys./chem. waste treatment plant

nants. It was decided to go for a “one-shot” spiking pill technology. If successful, such procedures will make it possible to make reproducible samples and to increase the CRM shelf life. Initial literature search revealed the potential of patents for such technologies. SINTEF has therefore filed a description for a potential invention signed by Notarius Publicus. Such a method for making CRMs could be of a more general nature and hence applicable to other types of CRMs beside ones containing hydrocarbons. More details are to be found in the description of TIP and exploitation plans. A patent application was made for this method. Details about the preparation procedures will therefore not be given in this report. The support material inside the pill will be referred to as “support”, the packing material as “capsule” and the finished product as “pill”.

Both offshore produced water and landbased discharges can contain different types and levels of hydrocarbons as well as different contaminants at various levels. No pill will therefore be truly relevant for the case in question. As it is believed that the spiking pills can be made with almost any ingredient compatible with the support and the capsule, it was decided to make it simple and to make two types of pills with various levels and types of hydrocarbons and not too much or many contaminant substances at this stage.

A number of different strategies were attempted before reaching the described one. These will not be discussed in this report. A lot of effort was also made on the selection and testing of the support and the capsule.

The following definitions were given to offshore discharge water pills and land-based discharge water pills for this project:

Offshore discharge water – a spiking pill containing a 50/50 mixture of diesel (BAM KS-5002) and lubrication oil (BAM KS-5003) aiming at hydrocarbon levels 15-20 mg/L (in water).

Land-based discharge – a spiking pill containing diesel (BAM KS-5002) aiming at hydrocarbon levels 7-10 mg/L (in water) and with a detergent contaminant (Miranol Ultra) at the same initial concentration as the hydrocarbon.

On this basis it was planned to prepare the following three water reference materials:

- Soil eluate
- Offshore pills
- Landbased pills

3.2.2.1 Soil eluate

3.2.2.1.1 Preparation of aqueous diesel extract

Diesel fuel (sample 03/1001309/1/0) without additives was kindly provided by Dr. Berger, Deutsche Shell GmbH, Shell Global Solutions (Germany) Hamburg. The characteristics of the material are given in *Tab. 3.14*.

1.6 L of 0.1 % sodium azide solution were placed into 2 L separatory funnel. 100 mL of diesel fuel was added with care so that no mixing occurred and kept at room temperature for 72 to 96 hours. Thereafter, approximately 1.5 L of aqueous phase were collected. This solution was used in the short-term stability study, directly. For preparation or the candidate RM the diesel extract was mixed with an aqueous soil extract.

3.2.2.1.2 Characteristics of the aqueous diesel extract

Additionally, the aqueous diesel solution was analysed by GC-MS in the full scan mode after extraction with n-hexane to get an idea on its qualitative composition. The following substance groups were identified:

- C₂- and some of the C₃-substituted benzenes elute from the GC column in front of the n-decane signal
- C₃-C₆ alkyl substituted Benzenes
- Tetrahydronaphthaline
- C₁-C₃ Alkyl-substitued Tetrahydronaphthaline
- Indane
- C₁-C₄ Alkyl-substitued Indane,
- Naphthaline
- C₁-C₃ Alkyl substituted naphthalines,
- Other condensed aromatics (e.g. Biphenyl, Acenaphthene, Fluorene)
- Dibenzofuranes
- No alkanes!!!

3.2.2.1.3 Analysis of Hydrocarbons by GC-FID

Hydrocarbon analyses of aqueous diesel extract was done according to DIN EN ISO 9377-2. The deviating from the standard extracts was dried before clean-up by adding sodium sulphate. A typical gas chromatogram of an aqueous diesel fuel extract is shown in Annex E, *Fig. 8.3*.

Tab. 3.14

Characteristics of the diesel fuel (sample 03/1001309/1/0) used for preparation of the candidate reference material

Parameter	Method	Result
Density at 15 °C [kg/m ³]	EN ISO 12185	838.6
Cloudpoint [°C]	DIN EN 23015	-15
Cold filter plugging point (CFPP) [°C]	DIN EN 116	-19
Sulfur content [%] (m/m)	DIN EN ISO 14596	0.0003
Distillation	DIN EN ISO 3405	
Start of boiling [°C]		169.6
End of boiling [°C]		363.8
Residue and losses [%] (v/v)		2.1

3.2.2.1.4 Sodium azide for chemical stabilisation and prevention of microbial degradation of hydrocarbons

From other investigations it was known that sodium azide prevents bacterial growth. Therefore, preliminary tests were done to investigate the influence of sodium azide on bacterial growth in aqueous diesel extracts stored at room temperature for 5 weeks. After a few days a slimy precipitation became visible in samples that did not contain sodium azide, which made extraction impossible and denotes that chemical stabilisation is an absolute must. Due to the toxic properties of sodium azide its amount added to the samples should be as low as possible. Hence, in a second experiment the stability of aqueous diesel extracts was tested by storing solutions containing 0.1 % and 1 % sodium azide, respectively, at 4 °C for 4 weeks. Analysis of the samples containing different concentrations of sodium azide showed no significant differences in their hydrocarbon content. Thus, a concentration of 0.1 % sodium azide was chosen for preparation of the candidate reference material.

3.2.2.1.5 Preparation of aqueous soil extract (eluate)

For the preparation of soil eluate, a loamy sand type standard soil provided by the Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer was utilised. The characteristics of this soil are given in Tab. 3.15.

110 ± 1 g of soil were placed into a 2-L-Erlenmeyer flask and 1100 mL of tap water were added. The mixture was

Tab. 3.15 Characteristics of the standard soil 2.2 (sample SP222803) used for preparation of the candidate reference material

STANDARD SOIL 2.2 (Batch SP 222803)	
Sampling date: 10.07.2003	
Parameter	Result
Organic carbon [%]	2.26 ± 0.12
Particles < 0.02 mm [%]	15.7 ± 2.6
pH (=0.1 M CaCl ₂)	6.3 ± 0.4
Cation exchange capacity [mval/100g]	11 ± 2
Soil type	Loamy sand
Particle size according to USDA	
< 0.002 mm [%]	8.0 ± 1.1
0.002 – 0.05 mm [%]	14.9 ± 2.6
0.05 – 2.0 mm [%]	77.1 ± 3.1
Water holding capacity [g/100g]	48.6 ± 4.1
Weight per volume [g/1000ml]	1148 ± 40

shaken for 24 hours using a rotary shaker. The suspension obtained was centrifuged at 10°C and 4000 g (g = 9.81 m/s²) for 30 min. The liquid phase was separated. Fine particles were removed by pressure filtration over 0.45 µm membrane filter. Then 1 g of sodium azide per litre eluate was added. The stabilised aqueous extracts were stored at 4 °C until preparation of the candidate RM.

3.2.2.1.6 Preparation of the candidate reference material "Soil eluate"

28.35 kg of aqueous diesel extract and 25 kg of soil eluate were put in each of two 60-L glass reservoirs equipped with a mechanical stirrer and discharge cock. The resulting mixtures were homogenised by mechanical stirring for 15 min. Before bottling the outlets of the reservoirs were flushed three times with one litre of the reference material. Then, from each reservoir approximately 450 mL were filled into 1 L amber glass bottles with ground glass stopper to give a final sample volume of 900 mL (Fig. 3.20). Bottles were weighed to determine exact sample mass, closed with ground glass stoppers and the stoppers fixed with metal clamps. A total of 112 samples were bottled (39 for long-term stability study, 48 for interlaboratory study and 25 as reserve).

3.2.2.2 Offshore pills

Support material (100 g) was contacted with 4 g diesel and 4 g lubricating oil. After homogenisation and drying the material was ready for encapsulation.

A total of 300 capsules were produced, 6 of them were discharged as defects. The average weight of the pills was 347 mg with a standard deviation of 1.7 %. The pill content weight was calculated to be 273 mg in average. This would give a spike concentration of 21.84 mg/L of water without losses of hydrocarbons and with the complete hydrocarbon fraction within the C₁₀-C₄₀ range. Pills with a weight differing more than two times the standard deviation from the average weight were removed from the set. The relative standard deviation of the reduced set was 1.5 %.

The weight of the pills as mentioned above is a first level of homogeneity test giving a relative standard deviation in pill weight at 1.5 %. A total of 15 pills, 5 taken randomly in each interval of 100, were selected for homogeneity testing. The results will undergo ANOVA-calculation and SoftCRM 1.2.0 – software will be used for evaluation.

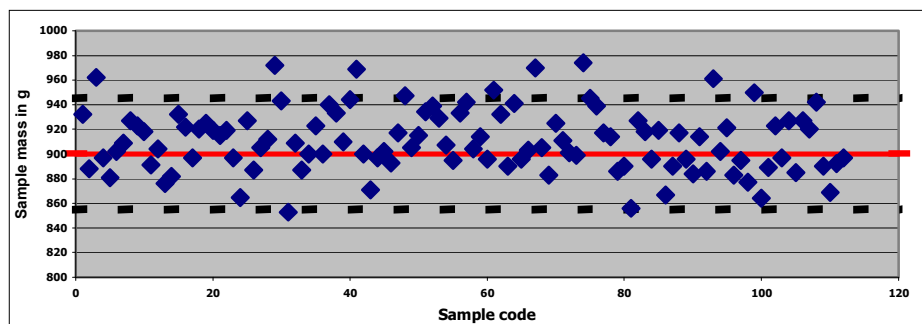


Fig. 3.20 Bottled masses (in g) of the candidate reference material "Soil eluate" (u sample mass, — Target mass, - - ± 5%)

A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.4.

3.2.2.3 Landbased pills

Support material (150 g) was contacted with 6 g diesel and 6 g Miranol Ultra. After homogenisation and drying the material was ready for encapsulation.

A total of 400 capsules were produced, 11 of them were discharged as defects. The average weight of the pills was 374 mg with a standard deviation of 1.6 %. The pill content weight was calculated to be 299.5 mg in average. This would give a spike concentration of 11.98 mg/L of water without loss of hydrocarbons and with the complete hydrocarbon fraction within the C₁₀-C₄₀ range. Pills with a weight differing more than 2 times the standard deviation from the average weight were removed from the set. The relative standard deviation of the reduced set was 1.5 %.

The weight of the pills as mentioned above is a first level of homogeneity test giving a relative standard deviation in pill weight at 1.5 %. A total of 20 pills, 5 taken randomly in each interval of 100, were selected for homogeneity testing.

A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.5.

3.2.3 Soil reference materials (WP-4)

The candidate soil reference materials were selected with respect to their environmental occurrence, to cover a wide range of matrix constitution and to contain different types and concentrations of mineral oil. On this basis it was planned to prepare the following three soil reference materials:

- Clayish soil
- Sandy soil
- Peat material

3.2.3.1 Clayish soil

A mixture of earlier experiences from similar productions, literature search and discussions with people experienced in different parts of the overall production made it possible to relatively easy set up a suggested protocol for the manufacturing process of the clayish soil.

The soil was first initially dried at 100 °C until reasonably dry, subsequently branches, stones etc. larger than approximately 25 mm were removed. The soil was then milled until approximately 99 % of the material was less than 90 µm. In connection with the milling, the material was also mixed until homogeneity could be assumed. The material was treated two times with 15 kgrey gamma radiation and put into metal containers aseptically. The dry matter content of the soil was more than 99 %.

The problems encountered were not related to the selection or production of the candidate reference materials, but were related to analytical methods. For reasons so far unknown, EUROFINs has had problems using the standard analytical protocol. The homogeneity and stability stud-

ies were done using the Danish analytical method instead of the agreed HYCREF standard protocol. A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.6.

3.2.3.2 Sandy soil

Sample preparation was done in the laboratory of Pirkanmaa Regional Environment Centre. The oil-contaminated soil was taken from Tampere Härmälä old gasoline station. While taking the soil, stones larger than 40 mm were sieved out of the 150 kg laboratory sample.

The soil was dried at room temperature and it was sieved through a 0.125 mm sieve. To achieve homogeneity, about 13 kg of sieved soil was mixed by a mechanized sample mixer. After making the soil homogenous it was distributed in sub-samples of 100 g using a rotary sample divider equipped with vibratory sample feeder with 8 exits.

A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.7.

3.2.3.3 Peat material

For the preparation of the reference material 100 kg contaminated soil was collected from a peat rich location. The percentage organic matter was 11.5 % with a mineral oil content of about 2500 mg/kg dry matter. The soil was dried at 40 °C during 6 weeks. Afterwards the soil was milled cryogenic to a particle size of less than 2 mm and sieved over a 4 mm sieve to remove particles which were not reduced in size.

It was not possible to find a location with contaminated soil consisting of 100 percent peat. Therefore 140 kg of compost was prepared with the same procedure, but the milling was done at room temperature and the drying process at 40 °C was done for one week. This delivered 46 kg of dry compost.

The compost was mixed with the soil (1:1 w/w) in portions of 10 kg. All portions were collected to give 91.2 kg mixed material.

Further preparation (sieving, homogenisation, sub-sampling) was done by the University of Wageningen. 55 kg of the material was delivered for further treatment. The material was reduced to a particle size less than 0.5 mm. The particle size was checked by sieving. 50 kg of the material was distributed over 500 sub-samples of 100 g.

A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.8.

3.2.4 Waste reference materials (WP-5)

The term "waste" comprises a wide spectrum of possible matrices with complex compositions. Hence, it is difficult to define a representative waste reference material.

However, typical areas of possible contaminations with mineral oil can be specified. Considerations were made to find out relevant waste materials. On this basis it has been planned to prepare the following three waste reference materials:

- Marine Sediment
- Building Material
- Ni/CP Waste

3.2.4.1 Off-shore marine sediment

Offshore marine sediments close to offshore oil and gas production platforms in the North Sea (and elsewhere) are contaminated with mineral oil from the drilling operations. The use of oil based drillmuds was banned in 1993. Olefinic based mud is however still used for lubrication of the drillbit.

Three different stock materials were procured to give the final waste reference material after mixing and preparation:

Stock material A: Sediment from the North Sea containing about 7 mg/kg dm THC

Stock material B: Sediment from the North Sea containing about 5000 mg/kg dm THC

Stock material C: Sediment from the North Sea containing about 40000 mg/kg dm THC (containing olefins)

A candidate reference material was first produced combining and homogenising A: 500 g, B: 10.665 g and C: 1.273 g. Based on these trials the following recipe was advised based on the available material: A: 40 kg, B: 0.8532 kg and C: 0.1018 kg. The material was sent to BAM, which had the necessary equipment for mixing and homogenising of such quantities. A procedure using a drum-hoop mixer, cross-riffling (10 exits) and two times spinning-riffling (8 and 10 exits) a total of 400 samples, each with 100 g of material were produced. 100 samples were kept by BAM for the test certification and 300 samples returned to SINTEF. A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.9.

3.2.4.2 Building material

Building materials tend to be contaminated with mineral oils as a follow of spills with heating oil (LUST – Leaking underground storage tanks) and accidents. The porous character of the building materials promotes the binding of mineral oil at the matrix.

A stock material “A” of was procured from a contaminated site in Germany (heating oil accident after a flood, 1997). A stock material “B” was procured from non-contaminated bricks. The stock materials “A” and “B” were mixed (mass ratio A:B = 3:2) to give the final reference material. This mixing procedure was necessary to have a sufficient amount (100 units of about 100 g).

The combined material (A+B) was air dried until constant conditions were obtained (about 2 weeks). Afterwards, the material was milled < 500 µm to reduce the range of particle sizes.

A pre-homogenisation was carried out by means of a drum hoop mixer for 6 hours. For the final homogenisation procedure a spinning riffler (1/10 dividing facility) was used and a so-called cross-riffling scheme was applied.

The bottling step of 100 units á 101.3 + 0.3 g of material was performed using the spinning riffler. The material was

packed in 100 mL brown glass bottles sealed with screw caps and a PTFE-inlet. All samples were stored in a freezer at –20 °C immediately after the bottling step. A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.10.

3.2.4.3 Ni/CP-waste

This candidate RM represents a mixture of real industrial waste materials from different sources. It has a considerable high moisture content compared with usual commercial CRM. Such a material will be of high importance for users as it simulates real waste samples much better than totally dried materials. One must be conscious that a poor stability of the mineral oil content might be obtained due to biodegradation.

Three different stock materials were procured to give the final waste reference material after mixing and preparation.

Stock material A: Filter cake from a nickel galvanic factory in Germany (Ni-waste), low contaminated with mineral oil

Stock material B: Residue from a chemical-physical waste treatment plant in Germany (CP-waste), highly contaminated with mineral oil

Stock material C: Inert matrix component consisting mainly of magnesium silicate, without mineral oil contamination

The stock materials A and B were milled and sieved < 500 µm. Stock material C consists of particle sizes < 250 µm. The stock-materials A, B and C were moisturized each to about 14 %. Spot-tests regarding the mineral oil content of all 3 stock materials were carried out. The ratio of A:B:C for mixture of the final RM (A:B:C ≈ 5:1:2) was chosen on the basis of the spot-tests to give a total hydrocarbon content of about 8000 mg/kg dry matter.

The homogenisation of the combined stock materials was carried out by means of a drum hoop mixer for 24 hours. Due to the low density and the high moisture content of the material a further cross-riffling of the material was not preferred. For the same reasons a manually bottling procedure was chosen to get 100 units á 93.6 + 0.3 g of material. The material was packed in 250 mL brown glass bottles sealed with screw caps and a PTFE-inlet. All samples were stored in a freezer at –20 °C immediately after the bottling step. A chromatogram of the hydrocarbon contamination is shown in Annex E, Fig. 8.11.

3.2.5 Physical and chemical properties of the reference materials

In Tab. 3.16 the physical and chemical properties of all 9 prepared reference materials are summarized.

3.3 Homogeneity and stability of the reference materials

The concepts and results of the conducted homogeneity- and stability studies of the prepared reference materials will be presented and discussed.

Tab. 3.16
Physical and chemical properties of all 9 reference materials

	TOC [%]	CHN [%]	pH (in water)	dry matter content [%]	sieve fraction
Soil Eluate	2.26 ^(a)	-	6.3 ^(a)	-	-
Offshore Pills	-	-	-	-	-
Landbased Pills	-	-	-	-	-
Clayish Soil	1.47	C: 3.014 H: 0.296 N: 0.081	6.5	99.6	< 63 µm: 92.8 % 63-125 µm: 7.1 % > 125 µm: 0.1 % 250-500 µm: 0 % > 500 µm: 0 %
Sandy Soil	0.31	C: 0.576 H: 0.242 N: 0.025	6.4	99.6	< 63 µm: 64.9 % 63-125 µm: 35.1 % > 125 µm: 0 % 250-500 µm: 0 % > 500 µm: 0 %

Tab. 3.16
continued: Physical and chemical properties of all 9 reference materials

	TOC [%]	CHN [%]	pH (in water)	dry matter content [%]	sieve fraction
Peat Material	25.06	C: 26.93 H: 3.254 N: 0.770	5.55	94.2	< 63 µm: 20.5 % 63-125 µm: 27.9 % 125-250 µm: 34.9 % 250-500 µm: 15.7 % > 500 µm: 1 %
Marine Sediment	0.20	C: 0.361 H: 0.067 N: 0.029	8.86	99.8	< 63 µm: 1 % 63-125 µm: 4 % 125-250 µm: 77 % 250-500 µm: 18 % > 500 µm: 0 %
Building Material	0.36	C: 1.07 H: 0.18 N: 0.03	9.18	99.5	< 63 µm: 67.5 % 63-125 µm: 7.5 % 125-250 µm: 11.5 % 250-500 µm: 13.5 % > 500 µm: 0 %
Ni/CP Waste	2.12	C: 2.66 H: 2.74 N: 0.12	8.25	86.4	< 63 µm: 7.7 % 63-125 µm: 46.6 % 125-250 µm: 15.6 % 250-500 µm: 30.1 % > 500 µm: 0 %

^(a) Determined in the soil, that had been used for the soil eluate

3.3.1 Homogeneity

The homogeneity studies were carried out in accordance to BCR-Guideline for Feasibility studies [5] and ISO-guide 35 [6]. The tests were evaluated using the official BCR-program SoftCRM (version 1.2.2) based on a one-way ANOVA calculation. The basic scheme of ANOVA is a separation of variances. The homogeneity study involves two uncertainty components: the repeatability of the measurement (method) and the between-sample variation. In terms of ANOVA, the samples are at the level of groups, and the repeatability of the measurement method is found within the groups [7].

The ANOVA-data were used for the determination of the uncertainty between bottles (u_{bb}) according to Eq. 3.5 and Eq. 3.6. Equation 3.6 should only be used if MS_{between} is lower or near MS_{within} .

$$u_{bb} = \sqrt{\frac{MS_{\text{between}} - MS_{\text{within}}}{n}} \quad (3.5)$$

$$u_{bb} = \sqrt{\frac{MS_{\text{within}}}{n}} \cdot \sqrt{\frac{2}{df_{\text{within}}}} \quad (3.6)$$

- u_{bb} : Uncertainty between bottles
 MS_{between} : Mean squares between bottles
 MS_{within} : Mean squares within bottles
 n : Number of replicate measurements per selected bottle
 df_{within} : Degrees of freedom of $MS_{\text{within}} = N * (n-1)$
 N : Number of selected bottles for homogeneity test

The uncertainty between bottles (u_{bb}) represents the inhomogeneity of a material (between the bottles) and contributes to the overall uncertainty of a reference material (see Chapter 3.5). The following concept, which was discussed and agreed with the consortium, gives an overview of the experiments necessary to determine the (in)homogeneity between bottles.

Between bottle homogeneity study:

- 10 bottles (of a total batch of 100 samples) are to be selected. Proposal for sampling: 1 bottle between sample-No. 001-010, 1 bottle between 021-030, 1 bottle between 031-040, etc. are randomly to be selected). A total randomly sampling scheme is possible too
- 4 independent replicate measurements per bottle (total number of analyses: $10 \times 4 = 40$)
- Analytical test-method: standard protocol for the determination of hydrocarbons in soil- and waste
- It should be ensured that only one quality/batch of chemicals (acetone, heptane, Florisil etc.) is used for the homogeneity study
- It is preferred to extract all the selected bottles once before the second/third/fourth replicates are carried out
- Suggestion for measurement: When all 40 extracts are prepared, they should be measured within one session by GC-FID in a random order. The calibration solutions shall be measured between the sample solutions
- It is also possible to analyse the first 10 extracts (one extract per selected bottle) and the calibration solutions within one GC-session; some days later the next GC-run with the second series of 10 extracts and so on

In contrast to the solid materials (soil, waste) only one replicate measurement per unit was possible for the water RM (soil eluate, spiking pills). For this reason it was necessary to determine MS_{between} and MS_{within} by two separate experiments.

For testing the homogeneity of soil eluate one batch of aqueous diesel extract was divided in eight equal portions (300 mL) which were filled in 1 L amber glass bottles. Then, approximately 600 mL of soil eluate were added to each bottle to allow for possible influence of matrix constituents on the analytical result. The resulting mixtures were homogenized by magnetic stirring and then analysed in one series.

In *Tab. 3.17* the results of the homogeneity studies of all materials are summarized.

The ANOVA evaluation revealed no significant inhomogeneities for any of the 9 materials. After this primary requirement was fulfilled the materials could be sent to the ILC-participants for test certification measurement.

Tab. 3.17

Homogeneity study of 9 reference materials

Material	Mean [mg/L] or [mg/kg] ^(a)	u_{bb} [mg/L] or [mg/kg] ^(a)	u_{bb} [%]
Soil Eluate	0.445	0.012	2.70
Offshore Pills	15.427	0.927	6.01
Landbased Pills	3.950	0.303	7.67
Clayish Soil	361.43	9.91	2.74
Sandy Soil	1634.32	47.97	2.94
Peat Material	1164.93	13.65	1.17
Marine Sediment	177.85	1.38	0.78
Building Material	1775.93	14.47	0.81
Ni/CP Waste	8728.81	28.90	0.33

^(a) The unit mg/L is valid for soil eluate and spiking pills; mg/kg is valid for soil and waste RM

The results in *Tab. 3.17* show the uncertainty between bottles u_{bb} calculated according to Eq. 3.5 and Eq. 3.6. Target specifications were set for u_{bb} (rel.) in the HYCREF project proposal (rel. $u_{\text{bb}} < 3\%$). Except for the two spiking pill materials all other reference materials have fulfilled the stated requirements.

The repeatability of the applied test method (HYCREF standard protocol) is just the square root of MS_{within} [8], equal to about 3% for soil and waste materials, except for sandy soil and clayish soil. Here, the method repeatability was between 11-14%.

Within bottle homogeneity study

The within bottle homogeneity study was carried out in order to determine the “minimum sample intake”. The following procedure to determine the “minimum sample intake” was suggested by BAM and was not obligatory for the HYCREF-consortium.

- m_0 is set to $m_0 = 20$ g sample intake (as prescribed in the standard protocol and ISO/DIS 16703)
- 6 independent replicate determinations are carried out using the standard protocol method; determine the relative standard deviation RSD (%)
- After that the sample intake is decreased in the following order:

$$\frac{m_0}{2} \rightarrow \frac{m_0}{4} \rightarrow \frac{m_0}{8} \rightarrow \frac{m_0}{16}$$

in the same way as m_0

- Prepare a diagram as shown in the following example (*Fig. 3.21*):

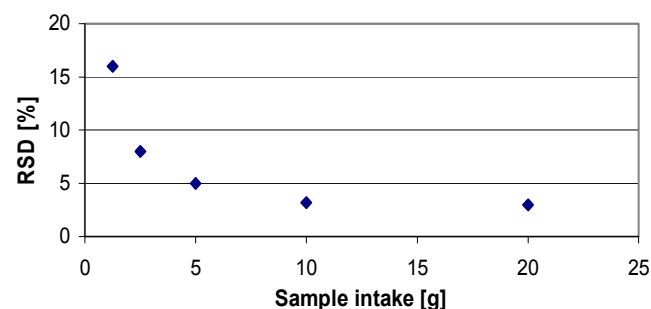


Fig. 3.21

Example of a result of “minimum sample intake” experiment

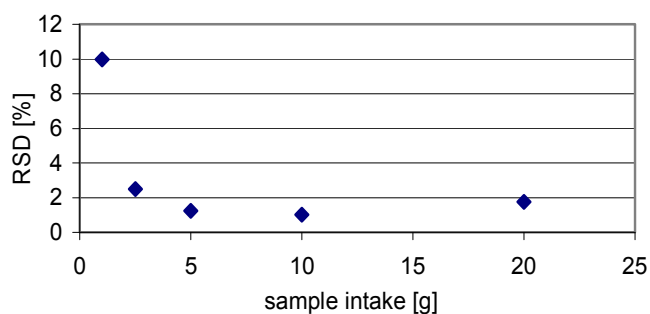


Fig. 3.22
Within-bottle homogeneity experiment for building material

- Estimate the point of a significant increase of the standard deviation from diagram
- If stable conditions were not yet obtained with the suggested scheme, additional measurements can be done for lower- or higher sample intakes

The minimum sample intake was determined for building material according to the above described scheme. Analyses were carried out with sample intakes of 1.0 g, 2.5 g, 5.0 g, 10 g and 20 g. Four replicates for each sample intake were the basis for calculating the relative standard deviation RSD of the measurements. Fig. 3.22 shows the result of the within bottle experiment for building material.

The minimum sample intake for the building material was determined to be 2.2 g with a corresponding relative standard deviation of about 3 %. A significant increase of RSD was obtained for a sample intake of 1 g (RSD ~ 10 %). This result is caused by two different effects. At first, as lower the sample intake is as higher is the inhomogeneity of a solid material. Secondly, the measurement uncertainty increases due to the high dilution of the extracts.

3.3.2 Stability

The stability of the materials was tested to find out both acceptable transport conditions and optimal storage conditions.

For these purposes a short-term study (3 weeks) and a long-term study (12 months) was conducted. The short-term study should simulate extreme temperature conditions during transport whereas the long-term study should detect possible (bio)degradations of the target compound under typical storage conditions.

In the recent years many efforts were made regarding the improvement of stability study-designs as well as the estimation of the contribution of short- and long-term instability to the overall uncertainty budget of reference material [9, 10, 11, 12, 13, 14, 15].

Short-term stability study

The following experimental conditions for conducting the long-term stability studies were discussed and agreed within the consortium:

- 3 sampling periods after 1, 2 and 3 weeks
- 3 storage temperatures at +22 °C (room temperature), +40 °C and +60 or +70 °C (optional)

- 1 bottle at reference temperature –20 °C (for soil eluate: +4 °C)
- Total number of needed bottles: 10 (9 bottles for measurements at 3 sampling periods and 3 storage temperatures; 1 bottle as Reference sample at –20 °C)
- 2 replicate measurements per bottle stored at higher temperatures than –20 °C; 4 replicate measurements of the “Reference sample” stored at –20 °C
- Total number of analyses: 22 = (9 x 2) + (1 x 4)
- Analytical test-method: Standard Protocol for the Determination of hydrocarbons in soil- and waste
- Measurements after 3 weeks in reference to a bottle stored at –20 °C
- Suggestion for measurement: When all 22 extracts are prepared (18 extracts of samples stored at +22 °C, +40 °C and +60/70 °C; 4 extracts of the Reference sample), they should be measured within one session by GC-FID. The 4 Reference-samples should be equally distributed over the whole sample-list. The calibration solutions should be measured between the samples

The short-term stability studies have been conducted using the advised isochronous scheme. The samples stored at 22 °C, 40 °C and 60/70 °C were measured all together after 3 weeks in reference to a sample stored at –20 °C (reference sample, for soil eluate: +4 °C). The analyses were carried out according to the HYCREF standard protocol using GC-FID.

The evaluation of the stability data is based on a trend analysis of the linear regression line using SoftCRM-programme (version 1.2.2). The linear function is a plot of the Ratio R over the time according to Eq. 3.7. The ratio R is also a function of the storage temperature (T), therefore, a linear regression line results for each storage temperature.

$$R(T) = \frac{X_T}{X_{Ref}} \quad (3.7)$$

x_T : Mineral oil content of the samples stored at higher temperatures than –20 °C

x_{Ref} : Mineral oil content of the reference sample stored at –20 °C

The first step of the trend analysis is to check whether the slope of the regression line is significantly different from zero or not. If a significant trend is detected the material can be assessed as not stable under the investigated conditions. If no significant trend is detected the second step of the trend analysis calculates the standard error of the slope (SE) automatically by SoftCRM^a. The uncertainty due to short-term stability (u_{sts}) was calculated according to Eq. 3.8

a It was found that SoftCRM-program version 1.2.2 displays the standard error of the slope on the 95 % confidences level but did not calculates SE on this level.

$$u_{sts} = u_b \cdot x_{RM} \cdot X_{Transport} \quad (3.8)$$

- u_{sts} : Uncertainty due to short-term stability [mg/kg] or [mg/L]
- u_b : Uncertainty of the slope (standard error of the slope SE) of the regression line at maximum transportation temperature [weeks⁻¹], calculated by SoftCRM
- x_{RM} : Test certified value [mg/kg] or [mg/L]
- $X_{Transport}$: Duration of transport [weeks], here 3/7 weeks (3 days) have been chosen

The transport conditions (maximum temperature, transport duration) have to be chosen in a way that u_{sts} can be assumed negligible [10]. An overview of the obtained results regarding u_{sts} is given in Tab. 3.18 and Tab. 3.19. Here, estimated transport duration of 3 days was used for calculation of u_{sts} .

Except for only three investigated cases (Soil Eluate/ 60 °C, Landbased Pills/22 °C, Peat Material/70 °C) no significant trends were detected for the materials up to 60/ 70 °C. The next step is to find out acceptable transport conditions for the materials, that means the uncertainty u_{sts} shall be as low as possible. Unfortunately, the results of the short-term stability study do not allow a clear decision regarding acceptable transport conditions. There is no significant difference between the stability results of samples stored at 22 °C and 60/70 °C! In some cases the highest temperatures led to the lowest uncertainty values (e.g. Building Material, NiCP-Waste). It is supposed that

u_{sts} is strongly influenced by the measurement uncertainty. However, nothing in the materials suggested that temperatures of about 40 °C should not be acceptable to ensure material stability for 3 days (duration of transport). Due to the nature of the contaminants (mostly high boiling mineral oils) as well as low moisture contents of the solid material a short-term stability can be expected. Consequently, the relative uncertainties of u_{sts} in the right column of Tab. 3.19 are much lower than 1 % of the test certified values. The lowest result of u_{sts} of each material in Tab. 3.19 was taken for the calculation of relative u_{sts} (%).

Long-term stability study

The following experimental conditions for conducting the long-term stability studies were discussed and agreed within the consortium:

- 4 sampling periods after 1, 3, 6 and 12 months
- 3 storage temperatures at +4 °C, +22 °C (room temperature), +40 °C (for soil eluate: +22 °C and +40 °C)
- 4 bottles at reference temperature -20 °C (for soil eluate: +4 °C)
- Total number of needed bottles: 16 (12 bottles for measurements at 4 sampling periods and 3 storage temperatures; 4 bottles as reference samples at each sampling interval)
- 2 replicate measurements per bottle stored at higher temperatures than -20 °C; 4 replicate measurements of the "Reference sample" stored at -20 °C
- Total number of analyses: 40 = (12 x 2) + (4 x 4)

Tab. 3.18
Short-term stability – uncertainty of the slope of the regression line

Material \ Storage temperature	Uncertainty of the slope u_b [weeks ⁻¹]		
	22°C	40°C	60/70°C
Soil Eluate	0.0150	0.0740	trend
Offshore Pills	0.0008	0.0246	0.0042
Landbased Pills	trend	0.0025	0.0513
Clayish Soil	0.0143	0.0250	0.0215
Sandy Soil	0.0197	0.0027	0.0220
Peat Material	0.0222	0.0066	trend
Marine Sediment	0.0185	0.0309	0.0266
Building Material	0.0326	0.0328	0.0153
Ni/CP Waste	0.0066	0.0128	0.0021

Tab. 3.19
Short-term stability (u_{sts})

Material \ Storage temperature	Uncertainty ^(a) u_{sts} [mg/L] (water) and [mg/kg] (soil, waste)			
	22°C	40°C	60/70°C	u_{sts} rel. [%]
Soil Eluate	0.003	0.013	---	0.73
Offshore Pills	0.006	0.181	0.031	0.03
Landbased Pills	---	0.005	0.093	0.12
Clayish Soil	1.314	2.297	1.975	0.61
Sandy Soil	15.900	2.179	17.757	0.12
Peat Material	12.030	3.577	---	0.28
Marine Sediment	1.553	2.594	2.233	0.79
Building Material	29.448	29.629	13.821	0.66
Ni/CP Waste	25.957	50.340	8.259	0.09

(a) $X_{Transport}$ was set to 3 days

- Analytical test-method: standard protocol for the determination of hydrocarbons in soil- and waste
- Measurements after each sampling period in reference to a bottle stored at $-20\text{ }^{\circ}\text{C}$
- It should be ensured that only one quality/batch of chemicals (acetone, heptane, Florisil etc.) is used for each series of measurements (series of measurement after 1, 3, 6 and 12 months)
- Suggestion for measurement: When all extracts of a measurement-series are prepared (6 extracts of samples stored at $+4\text{ }^{\circ}\text{C}$, $+22\text{ }^{\circ}\text{C}$ and $+40\text{ }^{\circ}\text{C}$; 4 extracts of the Reference sample), they should be measured within one session by GC-FID in the following order:
Ref/ $+4\text{ }^{\circ}\text{C}/+4\text{ }^{\circ}\text{C}/\text{Ref}/+22\text{ }^{\circ}\text{C}/+22\text{ }^{\circ}\text{C}/\text{Ref}/+40\text{ }^{\circ}\text{C}/+40\text{ }^{\circ}\text{C}/\text{Ref}$
- The calibration solutions can be measured between the samples (for example before each Ref.-sample)

The long-term stability studies have been conducted in a slight different way as the short-term studies. The samples stored at $4\text{ }^{\circ}\text{C}$, $22\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ were measured directly after each sampling period (1, 3, 6 and 12 months). Measurement drifts or measurement variances over time were reduced by evaluating the ratio R according to Eq. 3.7 by analysis of a reference sample stored at $-20\text{ }^{\circ}\text{C}$ after each sampling period together with the tempered samples (reference sample for soil eluate stored at $+4\text{ }^{\circ}\text{C}$).

The analyses were carried out according to the HYCREF standard protocol using GC-FID.

Tab. 3.20

Long-term stability – uncertainty of the slope of the regression line

Material \ Storage temperature	Uncertainty of the slope u_b [month ⁻¹]		
	4°C	22°C	40°C
Soil Eluate	trend ^a	trend	trend
Offshore Pills	0.0060	0.0053	0.0028
Landbased Pills	0.0046	0.0040	0.0059
Clayish Soil	not tested	0.0030	not evaluable
Sandy Soil	0.0112	0.0137	0.0039
Peat Material	0.0088	0.0005	0.0088
Marine Sediment	0.0087	0.0020	0.0040
Building Material	0.0031	0.0021	0.0013
Ni/CP Waste	0.0025	0.0026	0.0041

^(a) reference temperature

Tab. 3.21

Long-term stability (u_{its})

Material \ Storage temperature	Uncertainty ^(a) u_{its} [mg/L] (water) and [mg/kg] (soil, waste)			
	4°C	22°C	40°C	u_{its} rel. [%]
Soil Eluate	---	---	---	---
Offshore Pills	0.610	0.539	0.285	1.7
Landbased Pills	1.897	1.649	2.433	38.9
Clayish Soil	---	38.585	---	18.0
Sandy Soil	1261.051	1549.194	436.170	23.2
Peat Material	667.635	37.934	667.635	3.0
Marine Sediment	102.264	23.509	47.018	12.0
Building Material	392.037	265.574	164.403	7.8
Ni/CP Waste	1376.492	1431.552	2257.447	15.0

^(a) $X_{shelf-life}$ was set to 24 months for water materials including spiking pills and 60 months for soil and waste materials

The data evaluation for the long-term stability study was done in the same way as described above in chapter "Short-term stability study".

After proving the absence of a significant trend the uncertainty due to long-term stability was calculated according to Eq. 3.9 taking into account a target shelf-life X of X = 5 years (for soil and waste materials) and X = 2 years (for water materials including spiking pills).

$$u_{its} = u_b \cdot x_{RM} \cdot X_{shelf-life} \quad (3.9)$$

u_{its} : Uncertainty due to long-term stability [mg/kg] or [mg/L]

u_b : Uncertainty of the slope (standard error of the slope SE) of the regression line at selected storage temperature [months⁻¹], calculated by SoftCRM

x_{RM} : Test certified value [mg/kg] or [mg/L]

$X_{shelf-life}$: Selected shelf-life [months]; here, 60 months for soil and waste RM, 24 months for water RM including spiking pills

The chosen shelf-life of 5 years for soil and waste RM and 2 years for water RM are target values suggested in the HYCREF-project proposal (GRD1-2002-70015-HYCREF). This approach was proved and accepted by the European Commission. An overview of the obtained long-term stability results is given in Tab. 3.20 and Tab. 3.21.

A significant trend was observed for the soil eluate after 12 months at $4\text{ }^{\circ}\text{C}$ (reference temperature), $22\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ despite a chemical stabilisation using a 0.1 % solu-

tion of NaN_3 . However, a stability period of about 6 months can be achieved at 4 °C storage of the soil eluate. Unfortunately, the required shelf-life of 2 years could not be fulfilled for the soil eluate material. The main disadvantage of aqueous samples is the stability, probably caused by biodegradation. An optimisation of the NaN_3 -concentration could possibly improve the stability, what has to be investigated. The stability problem was solved by the preparation of spiking pill materials. These solid materials can be stored at -20 °C.

The general outcomes of the long-term stability studies are similar to those obtained from the short-term studies:

At first, no significant trends were detected for the materials even at 40 °C after 12 months. That was the prior necessity to estimate an uncertainty of the slope. Secondly, there is no clear correlation between u_{ITS} and the storage temperature. That means no conclusions can be drawn regarding optimal storage temperatures. At third, it is supposed that u_{ITS} is strongly influenced by the measurement uncertainty. That means that u_{ITS} do not represent the material stability (the basic intention of long-term stability study) but rather the measurement uncertainty.

The right column of *Tab. 3.21* shows the relative uncertainties of u_{ITS} (compared with the test certified value). The lowest result of u_{ITS} for each material was taken for the calculation of relative u_{ITS} (%). The broad variety in the results of very similar materials (e.g. offshore- and landbased spiking pills: 1.7 % and 38.9 %) show the insufficiency of the presented procedure for estimating the uncertainty contribution from long-term stability. Ways to increase the performance and to come to a more precise prediction for long-term stability are generally:

- prolongation of the stability study
- higher sampling frequency
- more replicate measurements
- application of an analytical method with better repeatability
- isochronous scheme

Regarding HYCREF-project the maximum duration of the long-term stability was limited to 1 year because the duration of the project was 2 years. Four sampling intervals within one year are typical for such long-term stability study. Two replicates per tempered samples and 4 replicates per reference sample can also be assessed as sufficient. The HYCREF-standard protocol was assigned as analytical method for long-term stability study. This method was also used for all other measurements (short-term stability study, homogeneity study, test certification study).

An often used procedure for predicting material stability is the *Arrhenius*-model based on kinetic data supposing a degradation reaction of first order. A linear regression of the function $\ln(k)$ (k = reaction rate) over $1/T$ (T = absolute temperature in Kelvin) delivers the activation energy of the reaction (degradation). The activation energy is used to calculate the reaction rate at a chosen storage temperature. Afterwards, the remaining mineral oil content can be calculated depending on the storage time.

Unfortunately, the *Arrhenius*-model was not applicable for some of prepared materials. That could be concluded after calculation of negative activation energy in some cases. Such results are obtained when the regression line of the function $\ln(k)$ over $1/T$ has a positive slope. That means that samples stored at 4 °C have a higher degradation over the duration of long-term stability study than samples stored at 40 °C, for example.

Despite the problems occurred, a conservative estimation of the storage temperature for solid materials should be -20 °C to ensure material stability. Due to the nature of the contaminants (mostly high boiling mineral oils) as well as low moisture contents of the solid materials a long-term stability of 5 years can be assumed under the above mentioned storage conditions. In any case, a long-term monitoring, e.g. annual measurements of the mineral oil content, is strongly recommended. This monitoring is useful for further prediction of material stability.

Experiences at BAM and Eurofins from former long-term stability studies and post certification monitoring with similar materials have shown long-term stabilities longer than 5 years, in Eurofins' experience even when stored at room temperature.

3.4 Test Certification Study

3.4.1 Introduction

Many reference materials, produced worldwide, are certified by laboratory intercomparisons, involving a large number of independent and, if possible, equally competent laboratories [1, 2].

A test certification study was carried out for the 9 prepared reference materials. All materials have been proved to be homogenous (see Chapter 3.3.1) before the inter-laboratory comparison study (ILC) was started. A total of 11 expert laboratories determined the mineral oil content of these materials according to the two standard protocols for the determination of hydrocarbons in water-, soil- and waste samples by the new gas chromatographic method (see Annex G and Annex H).

The work package leader of WP-3 (water, UBA), WP-4 (soil, SYKE) and WP-5 (waste, BAM) were responsible for the organisation and evaluation of their own part of ILC (water, soil and waste).

The ILC-test certification study was well prepared. Beside a conducted pre-test (see Chapter 3.1.4) and the successfully finished homogeneity studies, some useful instructions were elaborated: A definite time schedule for distribution and analysis of samples as well as delivery of results were agreed. Furthermore, forms for "Instruction of analysis", "Sample receipt", "Experimental conditions" and "Results" were sent to each ILC-participant (example for waste-materials see Annex F).

3.4.2 Results of test certification study

The "test certified" property value and the corresponding uncertainty due to characterisation (u_{char}) are summarized in *Tab. 3.22*. The original data of all materials and participants are listed in Annex F (Part B), *Tab. 8.18* to *Tab. 8.26*.

Tab. 3.22
Certified values and the terms of the uncertainty

Material	No. of participants of ILC	No. of accepted data sets	No. of discarded data sets	Mean of lab means \bar{x}	Uncertainty u_{char}	Relative uncertainty u_{char}
Water RM				[mg/L]		[%]
Soil Eluate	10	9	1	0.409	0.025	6.2
Offshore Pills	11	11	0	17.179	0.690	4.0
Landbased Pills	11	11	0	4.235	0.288	6.8
Soil RM				[mg/kg dm]		[%]
Clayish Soil	11	11	0	214.361	9.922	4.6
Sandy Soil	11	11	0	1883.290	72.713	3.9
Peat Material	11	11	0	1264.461	68.437	5.4
Waste RM				[mg/kg dm]		[%]
Marine Sediment	11	11	0	195.909	6.016	3.1
Building Material	11	11	0	2107.727	58.582	2.8
Ni/CP-Waste	11	11	0	9176.614	294.111	3.2

The results of the solid samples are calculated on the basis of dry matter content, which were determined by each material owner. The dry matter content was known for each ILC-participant and had to be taken into calculation.

Prior to calculation all data sets were carefully checked for technical- and statistical outliers. Data sets shall be treated as technical invalid results if the participating laboratory did not work according to the agreed HYCREF protocol. Data sets shall be treated as statistic invalid results the Single- or Double-Grubbs-Test on a significance level α of $\alpha = 0.01$ failed. Only one data set was detected as an outlier (soil eluate, technical outlier due to extremely high measurement standard deviation) and was eliminated prior to statistical evaluation. The test certified values were calculated on the basis of the mean of lab means (Eq. 3.10).

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (3.10)$$

\bar{x} : Mean of lab means (test certified value), [mg/kg dm] or [mg/L]

x_i : Individual lab mean [mg/kg dm] or [mg/L] based on 4 replicate measurements

n : Number of accepted data sets (labs) after outlier elimination

The uncertainty due to the characterisation is based on the standard deviation of the mean of lab means (Eq. 3.11) according to ISO-Guide 35 [6].

$$u_{char} = \frac{s}{\sqrt{n}} \quad (3.11)$$

u_{char} : Uncertainty due to characterisation [mg/kg dm] or [mg/L]

s : Standard deviation of the distribution of lab means [mg/kg dm] or [mg/L]

The relative uncertainty resulting from the test certification study was calculated according to Eq. 3.12:

$$u_{char}(rel) = \frac{u_{char}}{\bar{x}} \cdot 100\% \quad (3.12)$$

Target specifications were set for the contribution of uncertainty from test certification exercise (u_{char}). The maximum values of $u_{char}(rel)$ are 5 % for solid materials and 10 % for water reference materials. It can be assessed from the results in Tab. 3.22 that the stated quality demands were completely fulfilled. Only for peat material (u_{char} : 5.4 %) a slightly higher uncertainty was obtained.

3.5 Uncertainty budget of the reference materials

According to ISO-guide 35 (3rd edition) the calculation of the combined uncertainty u_{cert} is based on Eq. 3.13 taking into consideration the contributions of uncertainties from (in)homogeneity, long- and short-term stability and material characterisation in ILC.

$$u_{cert} = \sqrt{u_{bb}^2 + u_{lts}^2 + u_{sts}^2 + u_{char}^2} \quad (3.13)$$

- u_{cert} : combined uncertainty of the reference material
- u_{bb} : uncertainty due to between bottle inhomogeneity
- u_{lts} : uncertainty due to long-term stability
- u_{sts} : uncertainty due to short-term stability
- u_{char} : uncertainty due to characterisation

It was decided not to include the uncertainties of short- and long-term stability (u_{sts} and u_{lts}) in the final calculation of u_{cert} for reasons explained in Chapter 3.3.2 (stability study). The transport conditions for the materials were chosen in a way that the corresponding uncertainty u_{sts} is negligible. Regarding the long-term stability no significant decrease (slope of the regression line not significantly different from zero) was observed for the tested materials up to 40 °C for 12 months. Only one material (soil eluate) could clearly be identified as not stable over a period of 12 months. The combined uncertainty u_{cert} and the expanded uncertainty U_{cert} used for all HYCREF-materials is based on Eq. 3.14 and Eq. 3.15.

$$u_{cert} = \sqrt{u_{bb}^2 + u_{char}^2} \quad (3.14)$$

$$U_{cert} = k \cdot u_{cert} \quad (3.15)$$

- U_{cert} : expanded uncertainty
- k: coverage factor (k = 2)

The individual terms of uncertainty of each material are summarized in *Tab. 3.23* as well as the combined and expanded uncertainties calculated according to Eq. 3.14 and Eq. 3.15.

For the expanded uncertainty a coverage factor k of k = 2 was applied, representing about a half width of the 95 % confidence level. The uncertainty terms of u_{sts} and u_{lts} (not

included in calculation of u_{cert}) are taken from *Tab. 3.19* and *Tab. 3.21*.

It was found that u_{lts} would be the dominating factor of the combined uncertainty for the majority of tested material using the described procedure for calculating u_{lts} (see Chapter 3.3.2). On the other hand there are many indications that the solid materials are very stable when stored them at -20 °C. For the case that u_{lts} would be included in the calculation of the combined uncertainty u_{cert} the same materials would become useless for practical applications, e.g. lab-internal quality control, since the huge confidence intervals of the certified values do not allow any quality control!

The present certification process of the mineral oil content in a river sediment (ERM-CC015a) do not include an uncertainty contribution from long- and short-term stability study. The material was proved as stable. Additional, a long-term post certification monitoring will be done to ensure material stability and validity of the certificate.

3.6 Assessment of the results of the feasibility study

After conduction of all planned project tasks and evaluation of all project results the essential outcome of HYCREF can be focussed on the answer regarding the feasibility to prepare and to certify water-, soil- and waste reference materials contaminated with mineral oil. A summary of the test certified values of the 9 material together with their corresponding uncertainties is given in *Tab. 3.24*.

The test certified values in *Tab. 3.24* are rounded to 3 significant figures. Since the soil eluate could not fulfil the minimum requirement regarding long-term stability the given values in *Tab. 3.24* have just an informative character.

The HYCREF-project proposal and Annex I of the contract "Description of work" include target specifications and minimum requirements for the materials. A comparison of the planned and achieved specifications is summarized in *Tab. 3.25*.

Tab. 3.23
Uncertainty budget for HYCREF reference materials

Reference material	u_{bb}	u_{char}	u_{lts}	u_{sts}	Combined uncertainty u_{cert}	Expanded uncertainty $U_{cert} (k=2)$
Water RM [mg/L]						
Soil Eluate	0.012	0.025	---	0.003	0.028	0.055
Offshore Pills	0.927	0.690	0.285	0.006	1.156	2.311
Landbased Pills	0.303	0.288	1.649	0.005	0.418	0.836
Soil RM [mg/kg dm]						
Clayish Soil	9.91	9.922	38.585	1.314	14.023	28.047
Sandy Soil	47.97	72.713	436.170	2.179	87.111	174.222
Peat Material	13.65	68.437	37.934	3.577	69.785	139.570
Waste RM [mg/kg dm]						
Marine Sediment	1.38	6.016	23.509	1.553	6.172	12.344
Building Material	14.47	58.582	164.403	13.821	60.343	120.685
Ni/CP-Waste	28.90	294.111	1376.492	8.259	295.527	591.055

Tab. 3.24
Test certified values of reference materials with corresponding uncertainty

Reference Material	Test certified value	Combined uncertainty u_{cert}	Expanded uncertainty $U_{cert} (k=2)$	rel. U_{cert}
Water RM		[mg/L]		[%]
Soil Eluate	0.409	0.028	0.055	13.6
Offshore Pills	17.2	1.16	2.31	13.5
Landbased Pills	4.24	0.42	0.84	19.7
Soil RM		[mg/kg dm]		[%]
Clayish Soil	214	14	28	13.1
Sandy Soil	1880	90	170	9.3
Peat Material	1260	70	140	11.0
Waste RM		[mg/kg dm]		[%]
Marine Sediment	196	6	12	6.3
Building Material	2110	60	120	5.7
Ni/CP-Waste	9180	300	590	6.4

Tab. 3.25
Comparison between achieved and target specifications

Specification	Target value	Achieved result
Inhomogeneity between bottles (u_{bb})	$u_{bb} < 3 \%$	7 materials $u_{bb} < 3 \%$ 2 materials $u_{bb} > 3 \%$
Uncertainty contribution from test certification exercise (u_{char})	Solid RM: $u_{char} \leq 5 \%$ Water RM: $u_{char} \leq 10 \%$	Solid RM: 2.8 – 5.4 % Water RM: 4.0 – 6.8 %
Long-term stability (shelf-life X)	Solid RM: X > 5 years Water RM: X > 2 years	Solid materials (soil, waste) can be expected as stable under storage conditions at -20°C. Spiking pills are similar to solid materials. Soil eluate is not stable for 2 years under investigated conditions.

Except the two spiking pill materials all other RM revealed an inhomogeneity between bottles lower than the maximum tolerable inhomogeneity of 3 % set up in project work plan. The target specifications of uncertainty contribution from test certification exercise u_{char} for solid RM ($\leq 5 \%$) and water RM ($\leq 10 \%$) were fulfilled for all materials.

The proposed shelf-lives of 5 years for soil and waste materials and 2 years for water materials were chosen to meet practical aspects for use of such kinds of reference materials. The chosen shelf-life of a material has a direct influence on the uncertainty due to long-term stability u_{ls} (and to the combined uncertainty of the material according to Eq. 3.13). The decision not to include the uncertainty of the long-term stability u_{ls} in the calculation of material uncertainty u_{cert} was explained in detail. Nevertheless, the long-term stability is an essential part of characterisation of each reference material and has to be checked and monitored in the best way possible.

The achieved results in this feasibility study project HYCREF demonstrate the ability to prepare sufficiently homogeneous and stable soil-, (water-) and waste reference materials contaminated with mineral oil and to test certify the min-

eral oil content in these materials by means of gas chromatographic standard methods.

The experimental conditions for preparation and characterisation of these kinds of water-, soil- and waste reference materials were described in this report. It was found that aqueous reference materials are much more sensitive against degradation compared with solid materials. Therefore, the preparation of spiking pills reference materials (patent application by SINTEF) for offshore- and landbased water was a challenging and successful part of the project.

Furthermore, the preparation and test certification of the soil and waste materials was finished successfully. A further production and commercialisation of selected materials could be very useful for lab-internal quality control. They comprise a wide range of mineral oil content (about 200-9000 mg/kg) with expanded uncertainties between 5.7-13.1 %. Taking into account the present lack of certified reference materials for mineral oil determination by means of gas chromatographic methods the project results gain an enormous importance for the development of reference materials.

4 List of deliverables

Tab. 4.1:
List of deliverables completed during the project compared with planned deliverables

OVERVIEW OF DELIVERABLES				
Deliverable No.	Due date (month)	Issue date (month)	Responsible	Description of deliverable
WP-1: Coordination and Management				
-	-	4	BAM	Kick-off meeting report
-	-	8	BAM	Progress report
-	-	14	BAM	Mid-term assessment report
D 1.1	19	20	BAM	Evaluation report: Describes experiences made in ILCs and gives a harmonized guideline for ILC evaluation
-	-	27	BAM	Final project and TIP report
D 1.2	24	6, 17	BAM	Scientific publications: Presentation of the objectives and works of HYCREF - Poster at BERM-9 conference in Berlin, 17 June 2003 - Poster at Analytica conference in Munich, 11 th to 14 th May 2004 - 4 scientific publications are planned
WP-2: Method Development				
D 2.1	2	3	BAM	Preparation of 28 mineral oil standard solutions for IR and GC comparison measurement (12 IR + 16 GC-solutions).
D 2.2	7	9	BAM	Protocol of the IR and GC- (FID, MS, AED) measurements delivers a data set on comparability of these used methods for mineral oil determination.
D 2.3	9	10	BAM	Two Standard protocols (one for soil/waste and one for water) including definitions on the methods used in intercomparisons.
WP-3: Water Reference Materials				
D 3.1	7	10	UBA, SINTEF	Development of methods for the preparation of aqueous reference materials.
D 3.2	12	12	UBA, SINTEF	Preparation of three types of candidate water reference materials (an offshore- and a land-based discharge water, a leaching water) and tested for homogeneity.
D 3.3	22	(x)	UBA	Technical report on WP-3 includes all procedures and results of material preparation, homogeneity and stability study as well as evaluated results of interlaboratory comparison. Specifications for water reference materials will be set.

OVERVIEW OF DELIVERABLES (continued)				
Deliverable No.	Due date (month)	Issue date (month)	Responsible	Description of deliverable
WP-4: Soil Reference Materials				
D 4.1	6	12	SYKE	Protocol for soil sample preparation: The investigated preparation techniques will be outlined and the selected methods for preparation of candidate reference materials are described.
D 4.2	11	11	SYKE, EUROFINS, ALCON-TROL	Preparation of three types of candidate soil reference materials (a sandy soil, a peat with high content of humic material, a clayish soil) and tested for homogeneity.
D 4.3	18	(x)	SYKE	Progress report of the interlaboratory comparison. Organisation, performance, experiences and first draft of evaluation of results of the ILC will be described.
D 4.4	22	(x)	SYKE	Technical report on WP-4 includes all procedures and results of material preparation, homogeneity and stability study as well as evaluated results of interlaboratory comparison. Specifications for soil reference materials will be set.
WP-5: Waste Reference Materials				
D 5.1	6	3-10	BAM, SINTEF	Methods for preparation of waste reference materials (drying, milling, mixing, sieving, moisturizing, homogenisation, sub-sampling) and description of the method used for the preparation of candidate materials.
D 5.2	11	6-12	BAM, SINTEF	Preparation of three types of candidate waste reference materials (a contaminated building/construction material, a contaminated marine sediment, a contaminated sludge) and tested for homogeneity.
D 5.3	22	(x)	BAM	Technical report on WP-5 includes all procedures and results of material preparation, homogeneity and stability study as well as evaluated results of interlaboratory comparison. Specifications for waste reference materials will be set.
WP-6: Technical Implementation Plan				
D 6.1	4	6	BAM	Literature study and market research including a web-search on suitable CRM for determination of mineral oil in water, soil and waste materials by GC-methods.
D 6.2	12	12	BAM	Preparation of a Draft Technical Implementation Plan (TIP) containing the planned partners' strategies for exploitation of project results, the responsibilities and a time schedule.
-	-	23	BAM	Proposal for follow-up activities for certification of selected materials, this report includes the preliminary results of the feasibility study and a proposal for follow-up activities, that could be planed before the end of the project.
D 6.3	27 (24)	27	BAM	The final TIP will describe the defined strategy for exploitation of project results, the responsibilities, the assigned time schedule (very soon after the project has ended) as well as the expected economic, social and technical prospects. The main project output, which is suitable for exploitation should be the production and certification of respective water-, soil- and waste-reference materials for mineral oil determination.

(x): It was agreed within the consortium that each partner delivers their complete set of results to the co-ordinator (BAM) and to the e-Room, respectively.

All results had then been summarized in the report "Proposal for follow-up activities for certification of selected materials" and in the Final Technical Report.

5 Comparison of initially planned activities and work actually accomplished

Tab. 5.1

List of fulfilled milestones during the project compared with planned milestones

OVERVIEW OF MILESTONES					
Mile-stone No.	WP	Due date (month)	Date of fulfilment (month)	Brief description of Milestone objectives	Decision criteria for assessment
M1	1	1	1	Project work plan for all WPs is defined	Agreement of all main partners to the assigned work plan; open questions are solved before the work starts.
M2	2	2	3	The mineral oil test solutions are prepared	Solutions are prepared in sufficient purity and amount (checked by the responsible WP); save transport and storage conditions are proved.
M3	4 5	2	5	Three soil and three waste materials are selected and procured	Criteria for suitability: Representative for soil and waste materials; different types of mineral oil (and content) and matrix; contained mineral oil should mainly cover the GC-range C ₁₀ -C ₄₀ .
M4	3	7	10	Feasibility study of tested methods are finished and checked for reproducibility (including stability and conservation procedure)	Reliable data on the methods of preparation of aqueous reference materials have to be available; the predicted quality of candidate reference materials must be known and evaluated as sufficient for ILCs.
M5	2	7	9	IR and GC (FID, MS, AED) comparison measurements are completed	All required measurements have been done in a proper way (occurred problems have to be reported) and the results were summarized and ready for evaluation.
M6	2	9	10	Elaboration of two Standard protocols for mineral oil analysis which are strictly to be followed by the participants in the ILCs	Results of IR and GC comparison measurements are evaluated and conclusions for method comparability have been drawn; the standard Protocols for mineral oil analysis include definitions, which are strictly to be followed by the participants in the ILCs.
M7	4, 5	9	10	All three types of soil and waste candidate reference materials are prepared	Soil and waste candidate reference materials are prepared in a sufficient amount, bottled (at least 100 bottles á 100g per reference material) and stored at -20°C.

OVERVIEW OF MILESTONES (continued)

Mile- stone No.	WP	Due date (month)	Date of ful- filment (month)	Brief description of Milestone objectives	Decision criteria for assessment
M8	4, 5	10	9	A concept for homogeneity and stability studies for solid materials (soil, waste) is defined	Procedure for homogeneity testing shall be used by all partners (number of test samples, method for analysis, evaluation procedure: SoftCRM,). Procedure for stability testing shall be used by all partners (number of test samples, storage temperatures, method for analysis, evaluation procedure: SoftCRM).
M9	3	10	11	All three types of water candidate reference materials are prepared	Water candidate reference materials are prepared in a sufficient amount for feasibility tests (at least 100 units per reference material), packaged and stored under optimal conditions.
M10	3	11	9	A concept for homogeneity and stability studies for aqueous materials is defined	Similar to the decision criteria of M8 keeping in mind, that aqueous reference materials require individual procedures, e.g. determination of the within/between sample homogeneity, assignment of the number of test samples, method for analysis, storage temperatures.
M11	6	12	12	The mid-term assessment report and draft TIP is submitted to the commission	A continuing existence of positive and realistic perspectives for the exploitation of the results and the continuing commitment of the partners is given.
M12	1	13/14	13	The mid-term assessment report/meeting is successful	Technical and scientific results correspond to the stated objectives and milestones (M10); a successful progress of the remaining work is assessed.
			16	Pre-test study	A pre-test study had been carried out to evaluate problems still occurring during the procedure (extraction, clean-up).
M13	3 4 5	14	16	Water-, soil- and waste interlaboratory comparisons are organised; samples are sent to the participants	The organisation and logistic for the synchronous carrying out of ILCs (water, soil, waste) is guaranteed. All participants of interlaboratory comparisons are instructed on the procedure and personnel/-instrumental capacities of the members are given.

OVERVIEW OF MILESTONES (continued)					
Mile-stone No.	WP	Due date (month)	Date of fulfilment (month)	Brief description of Milestone objectives	Decision criteria for assessment
M14	3 4 5	18	18	The intercomparisons have finished, results were submitted to the ILC coordinator	Harmonised evaluation criteria for ILCs will be discussed and defined on the "Statistical evaluation meeting" soon after the end of intercomparisons (18 th month).
M15	3 4 5	22	23	Evaluations of the feasibility studies have finished; results are reported to the project coordinator	Clear description of the work done in WP-3, WP-4 and WP-5. The results are evaluated and reported in detail; conclusions, specifications and suggestions for the preparation and certification of future CRMs (water, soil, waste) will be described.
M16	1	27 (24)	27	Final project report is prepared and submitted to the commission	Criteria for successful evaluation: All project objectives and tasks were achieved and reported in time. Projects' time schedule and financial budget were not exceeded. Activities for dissemination of project results are going on.
M17	6	27 (24)	27	Technical Implementation Plan	Prospects and chances for further exploitation of results are given and the strategy for implementation is clearly described.

All initially planned activities listed in the "Description of work" were completed during the project.

An additional pre-test study was carried out before the start of the interlaboratory comparison. The aim was the evaluation of any possible sources causing problems during the procedure (sample preparation and measurement) in the different laboratories participating in the interlaboratory comparison. 4 pre-test samples were sent out to each

laboratory, 1 GC-test solution, 1 test soil and 2 clean-up test solutions. These additional investigations were of main interest, as they showed, that the pre-treatment of the Florisil before the clean-up is essential for the recovery and therefore the overall result of the hydrocarbon content. In Chapter 3.1.4 the results of the pre-test study are described.

6 Management and co-ordination aspects

On the kick-off meeting the establishment of a ProjectHotel® (eRoom) was agreed and organized by SINTEF. All HYCREF main partners and sub-contractors had access to the eRoom where all relevant information concerning the project were stored. Due to this facility the data and information transfer between the project partners was easy and fast.

Performance of the consortium and the individual partners in terms of dedication to the project, motivation and supply of deliverables:

All HYCREF-partners were informed about their tasks in the relevant work packages, the corresponding time schedules and the conditions for reporting the results. The following items guaranteed that each partner had clearly defined tasks as well as an overview of partner's tasks within HYCREF-consortium:

- the Preparatory meeting (January 2002): first orientation and allocation of work packages between project partners had been done
- the official HYCREF-proposal (GRD1-2002-70015-HYCREF), signed by all project partners and submitted to EC (February 2002)
- the Contract Preparation Forms (CPF) and Annex I of the contract "Description of work" (October 2002), signed by all project partners
- the Kick-off meeting (January 2003) and the corresponding report: discussion of open questions and definition of the work plan
- 1st Management meeting (June 2003) and corresponding report (1st Management report): discussion and assessment of activities and achieved results, clarification of open questions, specification of the following tasks according to work plan
- Mid-term meeting (January 2004) and corresponding report (Mid-term report): report on the progress of the preparation of the reference materials, their quality (e.g. homogeneity) and the experiences on the procedures of preparation, coordination and assignment of neces-

sary steps for the following intercomparisons, summary of all results achieved in the project, assessment of realistic perspectives for exploitation of the results

- 2nd Management meeting (June 2004) and corresponding report (2nd Management report): discussion about the experiences on the performance of the interlaboratory comparisons, decision about harmonized guideline for the ILC evaluation
- Final Meeting (December 2004) and corresponding report (Final report): discussion about the overall evaluation of all achieved project results and the experiences, that had been made, decision how to define and to coordinate the exploitation of the results, the input to the standardisation bodies of ISO/TC190, ISO/TC147 and CEN/TC292 and the publication of the results
- During the entire project the co-ordinator informed the consortium (via eRoom) about planned activities, provided necessary guidelines and literature, asked for votes on prepared draft documents, helped to clarify open questions, reminded of supplying deliverables etc.

Prolongation of the project

Except for one task all planned tasks were successfully delivered during the project (see list of Deliverables and Milestones). The reason for the delay compared with the original schedule was related to the development and testing of the innovative method of making water CRM with the new spiking pill technology and all the necessary testing prior to making the final batch for the feasibility study. Just the results of the long term stability for the two water CRM (offshore and landbased spiking pills, SINTEF) were affected. Therefore a prolongation of three months for the project was applied for. The prolongation was accepted by the European Commission and the duration of the project was now 27 months (instead of 24 months). All other practical work of the project was done in full conformity with the work plan. Therefore just some modifications to the work plan had to be applied. The changes in the time schedule are listed in *Tab. 6.1*.

*Tab. 6.1
Changes in the time schedule of the project*

Deliverable No.		Original Schedule [months]	Change in Schedule [months]
D 1.2 (WP-1)	Scientific publication	24	27
D 3.3 (WP-3)	Technical report on WP-3	22	25
D 4.4 (WP-4)	Technical report on WP-4	22	25
D 5.3 (WP-5)	Technical report on WP-5	22	25
D 6.3 (TIP)	Final Tip	24	27
Milestone 16	Final Project Report	24	27
Cost statement	Additional cost statement 2005	-	27

Name and contact details of the HYCREF-Consortium

N o	Project role	Institute / Address	Contact person	Phone / Fax / Email
1	Coordinator	BAM (Federal Institute for Materials Research and Testing), Division I.2 Richard-Willstätter-Str. 11 D-12489 Berlin Germany	Matthias Koch Almuth Liebich	Phone: +49-30-8104-1124 Fax.: +49-30-8104-1127 matthias.koch@bam.de almuth.liebich@bam.de
2	Principal contractor	Molab as c/o SINTEF Materials and Chemistry P.O. box 124 Blindern Forskingsveien 1 (visiting address) N-0314 Oslo Norway	Oddvar Ringstad	Phone: +47 22067 487 Mobile: +47 982 43 946 Fax: +47 22067 331 oddvar.ringstad@molab.no
3	Principal contractor	Federal Environmental Agency Laboratory for Water Analysis, II 3.5 Bismarckplatz 1 D-14193 Berlin Germany	Peter Lepom	Phone: +49-30-8903-2689 Fax.: +49-30-8903-2965 peter.lepom@uba.de
4	Principal contractor	EUROFINS A/S Strandesplanaden 110 DK-2665 Vallensbæk Strand Denmark	Mikael Krysell	Phone: +45-7022 4230 Direct: +45-7217 8937 Fax: +45-7022 4255 mik@eurofins.dk
5	Principal contractor	Finnish Environmental Institute Laboratory Hakuninmaantie 6 FI-00430 Helsinki Finland	Pirjo Sainio, Irma Mäkinen	Phone: +358 9 40300 273 (Pirjo) Phone: +358 9 40300 839 (Irma) Fax.: +358 9 40300 890 pirjo.sainio@ymparisto.fi irma.makinen@ymparisto.fi
6	Principal contractor	ALcontrol Specials Steenhouwerstraat 15 3194 AG, Hoogvliet The Netherlands	Jaap-Willem Hutter, Theo den Ouden	Phone: +31102314778 (Jaap-Willem) Phone: +31102314847 (Theo) Fax: +31104163034 j.hutter@alcontrol.nl t.denouden@alcontrol.nl
7	Sub-contractor	Estonian Environmental Research Centre Marja 4D EE-10617 Tallin Estonia	Sibylle Mueller	Phone: +372 6112907 Fax: +372 6112901 Sibylle.mueller@klab.ee
8	Sub-contractor	Technical Research Centre of Finland (VTT) Biologinkuja 7 FIN-02150 Espoo Finland	Risto Hiukka	Phone: +358 20 722 5359 Fax: +358 20 722 7026 risto.hiukka@vtt.fi
9	Sub-contractor	Landesumweltamt NRW Auf dem Draap 25 D-40221 Düsseldorf Germany	Klaus Sielex	Phone: +49 2017995-2356 Fax.: +492017995-2425 Klaus.Sielex@lua.nrw.de
10	Sub-contractor	Landesumweltamt Brandenburg Berliner Str. 21-25 14467 Potsdam Germany	Ralf Donau	Phone: +490331 2323 224 Fax: +490331 2323 223 ralf.donau@LLB.Brandenburg.de
11	Sub-contractor	Latvian Environment Geology and Meteorology Agency Environmental Laboratory Ošu-5 LV-2015 Jūrmala Latvia	Rita Skolmeistere	Phone: +371-7754916 Fax: +371-7764162 Rita.Skolmeistere@lva.gov.lv
12	Sub-contractor	VITUKI Environmental Protection and Water Management Research Institute Kvassay Jenő út 1 H-1453 Budapest Hungary	Attila Csehi	Phone: +361-2156140 Fax: +361-2161514 vituki@vituki.hu

7 Exploitation of project results

The project results and their exploitations are summarized in *Tab. 7.1*.

Tab. 7.1
Results and exploitation

Project output / Result	Range of Applications	Expected Impact	Timing	Partner(s) responsible for exploitation
Community Added Value:				
Improvement and implementation of international/European GC-standard methods for mineral oil determination	Reliable environmental assessment of water, soil and waste by means of GC-FID	- ISO/TC 190 - ISO/TC 147 - CEN/TC 292 - National standardisation bodies	Short/ middle	- ISO/TC 190 - ISO/TC 147 - CEN/TC 292 - National standardisation bodies
Establishment of the relevant GC-standard methods across Europe	Strengthening of GC-FID method	- Laboratories involved in mineral oil analysis in water, soil and waste - Authorities	middle/ long	National standardisation bodies
Improvement of quality of mineral oil analysis	Tool for internal quality assurance	- Laboratories involved in mineral oil analysis in water, soil and waste - Authorities	middle/ long	A follow of the availability of suitable CRM
Production of water, soil and waste CRMs for mineral oil determination	Tool for internal quality assurance	- Laboratories involved in mineral oil analysis in water, soil and waste - Mineral oil industry - Organizer of PT-schemes	Next 1-2 years	HYCREF-consortium in co-operation with IRMM (for example)

Table 7.1
continued: Results and exploitation

Project output / Result	Range of Applications	Expected Impact	Timing	Partner(s) responsible for exploitation
Social / Environmental Impact:				
Technical / Economic Impact:				
Methods for the preparation of sufficient defined water, soil and waste reference materials	Detailed description to prepare qualified reference materials (water, soil, waste) for mineral oil determination	- Producer of the investigated candidate CRMs - Each Laboratory which wants to prepare own of reference materials	Short/ middle	BAM (Final technical report), HYCREF-consortium
Data on homogeneity, stability and storage conditions of the relevant materials	- Shelf-life assessment of CRM - Information on the proper use of CRMs	- Producer of the investigated candidate CRMs - Each Laboratory which wants to prepare own of reference materials	Short/ middle	BAM (Final technical report), HYCREF-consortium
Statistical data regarding the certification of the water, soil and waste RM resulting from ILCs	Improvement of data situation for further GC-certification studies	- Producer of the investigated candidate CRMs - PT-scheme organizer	Short/ middle	BAM (Final technical report), HYCREF-consortium
Data on comparability of IR/GC-methods	Assessment of IR and GC data in routine analyses	- Laboratories involved in mineral oil analysis in water, soil and waste - Authorities	short	BAM (Final technical report)
Reduce of costs for GC-analysis of mineral oils	- Costs of analysis - Costs for GC-FID equipment for mineral oil analysis	Laboratories involved in mineral oil analysis in water, soil and waste	middle	A market response on the availability of CRMs and GC-method establishment

Follow-up activities, advised by the European Commission in the frame of the Technical Implementation Plan (TIP), should focus on the preparation and certification of reference materials "Determination of Mineral oil hydrocarbons by gas chromatographic methods". These activities are justified taking into account the urgent need for such CRM. A successfully passed feasibility study is an essential and necessary presumption for the final preparation and certification of soil, waste and water materials. The results of the project demonstrate the feasibility to produce certified reference materials contaminated with mineral oil and their determination by gas chromatography.

The suggestion for follow-up activities is to produce selected types of RM, which have been proved as most promising during the project. For that purpose, material

properties, e.g. mineral oil content, constitution and origin of matrix, should be taken into consideration. No preferences could be given between low-, middle- and high contaminated materials. Each TPH-range has practical relevance in environmental analysis in Europe. A total number of about 256 units (bottles) per material could be a realistic amount for a future production. Taking into account the required units for homogeneity-, stability- and certification purposes about 170 units could be left for selling.

When mineral oil hydrocarbons in soil and waste are analysed according to the GC-standard methods a sample intake of 20 g (5-30 g) is foreseen. A sufficient number of replicate analyses will be possible when a bottle contains about 100 g.

8 Annex

Annex A: Comparison of GC- (FID, MS, AED) and IR-method

Annex B: Comparison of ISO/DIS 16703 and Nordic Guideline TR 329

Annex C: Sample Treatment

Annex D: Results for Pre-Test Study

Annex E: Reference Materials

Annex F: Interlaboratory Comparison

Annex G: Standard Protocol for the determination of the hydrocarbon content in soil and waste according to ISO/FDIS 16703 and prEN 14039 (GC-method)

Annex H: Standard Protocol for the determination of the hydrocarbon oil index in water according to ISO 9377-2 (GC-method)

Annex A Comparison of GC- (FID, MS, AED) and IR-method

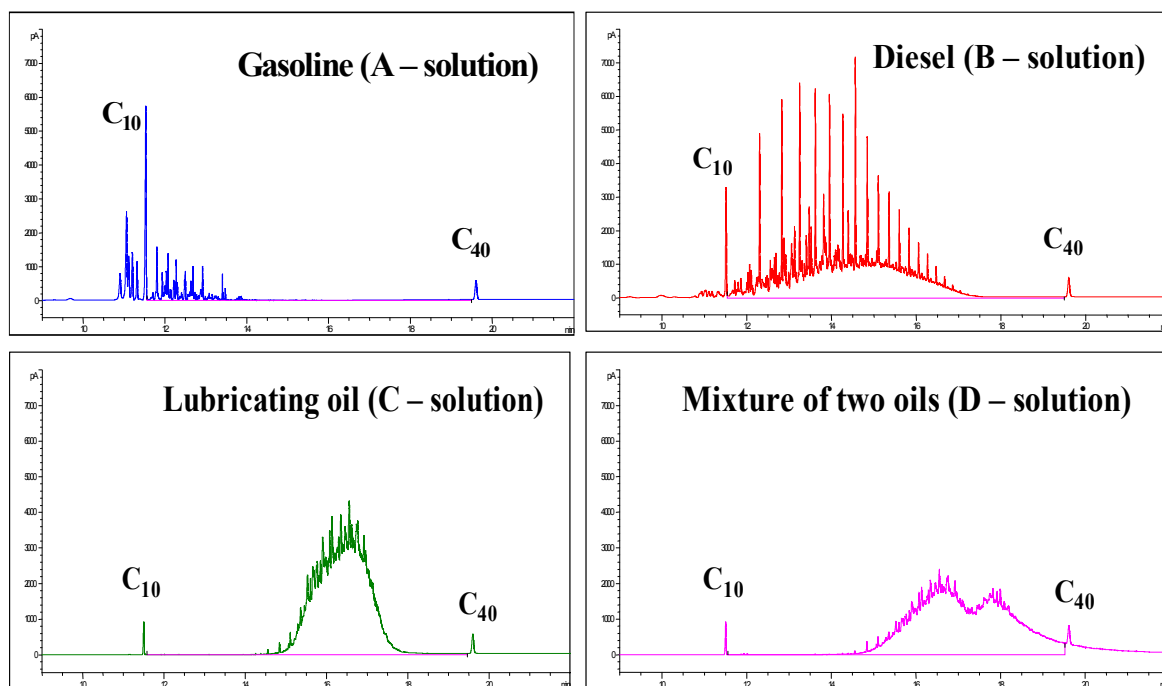


Fig. 8.1
Chromatograms (GC-FID) for the test solutions A, B, C and D

Tab. 8.1
Results of GC-FID measurements of mineral oil test solutions in mg/mL

Mineral oil sample	BAM		SINTEF		UBA		EUROFINS		SYKE		ALCONTROL		LUA-Brandenburg	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
GC-A1	(0,010)	(0,011)	< 0,060	< 0,060	<0,060	<0,060	0.055	0.054	0.011	0.011	0.018	0.021	0.017	0.016
GC-A2	0.045	0.046	< 0,060	< 0,060	<0,060	<0,060	0.089	0.095	0.048	0.040	0.028	0.035	0.063	0.059
GC-A3	0.083	0.084	0.060	0.060	0.078	0.070	0.100	0.094	0.074	0.074	0.071	0.073	0.102	0.112
GC-A4	0.391	0.390	0.340	0.350	0.423	0.441	0.428	0.402	0.380	0.372	0.473	0.471	0.475	0.466
GC-B1	0.097	0.095	0.100	0.100	0.096	0.094	0.186	0.178	0.097	0.098	0.119	0.124	0.080	0.066
GC-B2	0.472	0.476	0.460	0.460	0.468	0.473	0.516	0.520	0.483	0.484	0.553	0.564	0.419	0.403
GC-B3	0.937	0.937	0.920	0.910	0.992	0.971	1.03	1.00	0.959	0.958	1.01	1.01	0.826	0.818
GC-B4	4.69	4.69	4.61	4.62	5.03	5.15	4.99	4.98	4.84	4.81	5.33	5.28	4.68	4.59
GC-C1	0.105	0.108	0.110	0.100	0.091	0.099	0.089	0.09	0.112	0.112	0.131	0.129	0.092	0.095
GC-C2	0.510	0.510	0.490	0.490	0.503	0.489	0.528	0.528	0.535	0.533	0.541	0.542	0.496	0.467
GC-C3	1.01	1.00	0.980	0.990	0.997	1.04	1.04	1.06	1.06	1.05	0.935	0.926	0.982	1.03
GC-C4	5.08	5.07	4.97	4.97	5.26	5.22	5.31	5.28	5.22	5.23	4.68	4.72	5.14	5.08
GC-D1	0.100	0.100	0.100	0.100	0.091	0.097	0.130	0.130	0.100	0.100	0.118	0.123	0.099	0.096
GC-D2	0.481	0.482	0.460	0.460	0.475	0.481	0.553	0.576	0.497	0.499	0.569	0.567	0.434	0.458
GC-D3	0.967	0.973	0.920	0.920	0.948	0.936	1.10	1.10	1.00	0.991	1.02	1.01	0.904	0.917
GC-D4	4.77	4.77	4.65	4.66	4.61	4.57	5.08	5.15	4.98	4.96	5.15	5.14	4.27	4.28

Tab. 8.2

Description of the applied GC-FID method for the measurements of mineral oil test solutions

Method parameter	BAM	SINTEF	UBA
BAM-calibration set used for calibration	yes	yes	yes
Was the purity of the Calibration oil (mass fraction between C ₁₀ and C ₄₀) taken into account	yes	yes	yes
Range of calibration [mg/ml]	0.04 - 6 mg/mL	0.06 - 8 mg/mL	0.04 to 8.0 mg/mL
How many calibration points?	8	8	
What type of Gas chromatograph was used	Agilent 6890	Perkin Elmer Autosystem	Agilent 6890
Which GC-column was used (Type, length, ID, Film thickness)	BPX-5 (SGE, 5% Phenyl) 15 m x 0.32 mm x 1 µm	fused silica crosslinked with dimethylsilicon 12.5 m x 0.2 mm x 0.33 µm	BPX-5 (SGE) 15 m x 0.32 mm x 1 µm
Pre-column (retention gap) used	Deactivated fused silica 2.5m x 0.53 mm ID	no	no
Injection technique	on-column	splitless	splitless
Volume of injected sample [µL]	3	1	3
Manual or automatic injection	manual	automatic	automatic
Oven heating program and heating rate	50°C (10min) - 40°C/min – 360°C (10min)	50°C (2min)- 20°/min - 350°C (8min)	60°C (2min) - 20°C/min - 360°C (10 min)
Integration between C ₁₀ and C ₄₀	yes	yes	yes
Subtraction of a heptane-chromatogram before integration	no	no	yes
Problems and comments	No problems; comments: A-solutions (Gasoline) have an expected small fraction between C ₁₀ -C ₄₀ . B-solutions (Diesel) contain compounds with lower boiling points than C10 D-solutions (Oil mixture) have a measurable fraction higher than C ₄₀ .	A-solutions The samples consist of Gasoline with a boiling point range lower than C ₁₀ . The results are representing only the very small fraction of the samples with the boiling point range higher than C ₁₀ .	A-solutions: Most of the hydrocarbons Gasoline consists of eluted before C ₁₀ . Therefore, the results represent only a small fraction of the total hydrocarbon content. D-solutions contained a small fraction of hydrocarbons with carbon chain length above C ₄₀

Tab. 8.2

continued: Description of the applied GC-FID method for the measurements of mineral oil test solutions

Method parameter	EUROFINS	SYKE	ALCONTROL	LUA-Brandenburg
BAM-calibration set used for calibration	yes	yes	yes	yes
Was the purity of the Calibration oil (mass fraction between C ₁₀ and C ₄₀) taken into account	yes	yes	yes	yes
Range of calibration [mg/ml]	0.08-6.2	0.082–8.135	0-6.4	0.05-8
How many calibration points	6	8	1	10 points
What type of Gas chromatograph was used	HP 6890	HP 6890	Interscience MEGA 2	HP 5980 II
Which GC-column was used (Type, length, ID, Film thickness)	100% cyclohexyl 30 m x 0.25 mm x 0.25 µm	SGE BPX-5 5.00 m x 320 µm x 1.0 µm	DB-1 30 m x 0.32 mm x 0.1 µm	HT5 25m x 200 µm x 0,1µm
Pre-column (Retention gap) used	no	deactivated silica-column 2 m x 0.53 µm	yes	no
Injection technique	splitless	on-column	on-column	split/splitless purge after 0.3 min
Volume of injected sample [µL]	1	1	1	2
Manual or automatic injection	automatic	automatic	automatic	automatic
Oven heating program and heating rate	60°C (5min) - 8°C/min to 160°C - 20°C/min to 320°C	60 °C (5 min) - 30 °C/min - 330 °C (5 min) - 50 °C/min- 340 °C (7 min)	65°C - 25 °C/min to 315°C	60°C (1.5 min) – 15°C/min to 200°C - 10°C/min – 330°C (15 min)
Integration between C ₁₀ and C ₄₀	yes	yes	yes	according to the norm
Subtraction of a heptane-chromatogram before integration	yes	no	yes	yes
Problems and comments	Obviously problems with calibration, as we get too high values - but I have not been able of understanding why!	none	none	Inj.-temp: 280°C Det.-temp: 330°C 1.2 mL He; const. Flow

Tab. 8.3

Results of IR measurements of mineral oil test solutions

Mineral oil sample	BAM	SYKE	ALCONTROL	Grand mean [mg/mL]	SD [mg/mL]	RSD [%]	x _{ref} [mg/mL]	Recovery [%]	Average recovery [%]
IR-A1	0.104	0.100	0.099	0.101	0.002	2.4	0.100	101.4	
IR-A2	0.512	0.499	0.464	0.492	0.025	5.1	0.497	98.9	A - Solution:
IR-A3	0.968	0.968	0.931	0.956	0.021	2.2	0.995	96.1	98.8
IR-B1	0.100	0.105	0.104	0.103	0.003	2.6	0.101	102.4	
IR-B2	0.474	0.532	0.483	0.496	0.031	6.3	0.503	98.7	B - Solution:
IR-B3	0.930	1.01	0.975	0.972	0.041	4.2	1.01	96.6	99.2
IR-C1	0.116	0.109	0.107	0.111	0.005	4.4	0.100	110.6	
IR-C2	0.510	0.541	0.495	0.515	0.024	4.6	0.500	103.0	C - Solution:
IR-C3	0.998	1.05	0.971	1.00	0.04	3.7	1.00	100.4	104.7
IR-D1	0.108	0.110	0.107	0.108	0.002	1.4	0.101	107.6	
IR-D2	0.523	0.538	0.501	0.521	0.019	3.6	0.504	103.4	D - Solution:
IR-D3	1.01	1.05	0.993	1.02	0.03	2.7	1.01	101.1	104.0

All results were calculated on the basis of the equation in ISO/TR 11046 using the given empiric absorption coefficients

Grand mean: Mean of laboratory means
SD: Standard deviation of laboratory means
RSD: Relative standard deviation of laboratory means
x_{ref}: Reference value from gravimetric sample preparation
Recovery: Measurement recovery in respect to reference value
Average recovery: Mean of sample 1 - 4 of solution A, B, C and D

Tab. 8.4

Description of the applied IR-method for the measurements of mineral oil test solutions

Method parameter	BAM	SYKE	ALCONTROL
What type of IR-spectrometer was used	FTIR-Spectrometer, FTS-45A (Biorad) with DTGS-detector, He/Ne-Laser alignment, triangular apodisation	FTIR-Spectrometer, LiTa-detector, He/Ne-Laser	Perkin Elmer FTIR
Spectral range of measurement [cm^{-1}]	2700 - 3200 cm^{-1}	2500 - 3400 cm^{-1}	2800 -3200
Resolution [cm^{-1}]	2 cm^{-1} , 16 scans	4 cm^{-1} , 4 scans	1
Length of quartz optical cell(s) [cm]	1 cm quartz cell for A-1, B-1, C-1 and D-1 solution / 0.269 cm KBr-cell for all other IR-test solutions	1	1
Manual or automatic integration	manual	manual	automatic
Did you observe an aromatic CH-band at 3030 cm^{-1}	only for A-solutions (Gasoline)	yes	no
Did you calculate the mineral oil concentration by using the given Absorption coefficients acc. to ISO/TR 11046	yes	yes	yes
Was a dilution of sample necessary (in the case that the absorbance was > 1 and no thinner quartz cell was available)	no dilution but use of a thinner cell (0.269 cm KBr-cell) for conc. 0.5 and 1.0 mg/mL	samples A2, A3, B2, B3, C2, C3, D2, D3 were diluted	no
Problems and comments	none	none	none

Tab. 8.5

Results of GC-MS measurements of mineral oil test solutions

Mineral oil sample [mg/mL]	SINTEF		LUA-Brandenburg	
	1	2	1	2
GC-A1	0.005	0.011	0.019	0.016
GC-A2	0.038	0.045	0.063	0.058
GC-A3	0.078	0.091	0.107	0.116
GC-A4	0.388	0.395	0.437	0.466
GC-B1	0.085	0.095	0.098	0.092
GC-B2	0.466	0.456	0.478	0.468
GC-B3	1.00	0.930	1.12	1.08
GC-B4	5.08	4.94	4.47	4.38
GC-C1	0.085	0.085	0.122	0.109
GC-C2	0.580	0.532	0.547	0.486
GC-C3	1.14	1.10	1.06	1.01
GC-C4	4.73	4.84	4.96	5.03
GC-D1	0.093	0.089	0.113	0.099
GC-D2	0.475	0.488	0.535	0.552
GC-D3	0.930	0.910	1.20	1.12
GC-D4	4.79	4.83	4.95	5.05

Tab. 8.6
Summary of the GC-MS results (mean values of two injections)

Mineral oil sample	SINTEF	LUA	Grand mean [mg/mL]	SD [mg/mL]	RSD [%]	x_{ref} [mg/mL]	Recovery [%]	Average recovery [%]
GC-A1	0.008	0.017	0.013	0.007	52.5	0.101	12.7	
GC-A2	0.042	0.061	0.051	0.014	26.5	0.502	10.2	
GC-A3	0.085	0.112	0.098	0.019	19.5	1.00	9.8	A - Solution:
GC-A4	0.392	0.451	0.421	0.042	10.0	5.02	8.4	10.2
GC-B1	0.090	0.095	0.093	0.004	3.9	0.100	92.3	
GC-B2	0.461	0.473	0.467	0.008	1.8	0.502	93.1	
GC-B3	0.965	1.10	1.03	0.09	9.2	1.00	102.8	B - Solution:
GC-B4	5.01	4.42	4.72	0.41	8.8	5.02	94.0	95.5
GC-C1	0.085	0.115	0.100	0.022	21.5	0.102	98.3	
GC-C2	0.556	0.517	0.536	0.028	5.2	0.509	105.3	
GC-C3	1.12	1.04	1.08	0.06	5.5	1.02	105.8	C - Solution:
GC-C4	4.79	5.00	4.89	0.15	3.1	5.09	96.0	101.4
GC-D1	0.091	0.106	0.099	0.011	10.9	0.102	96.9	
GC-D2	0.482	0.544	0.513	0.044	8.6	0.509	100.7	
GC-D3	0.920	1.16	1.04	0.17	16.2	1.02	102.1	D - Solution:
GC-D4	4.81	5.00	4.90	0.13	2.7	5.09	96.3	99.0

Grand mean: Mean of laboratory means
SD: Standard deviation of laboratory means
RSD: Relative standard deviation of laboratory means
 x_{ref} : Reference value from gravimetric sample preparation
Recovery: Measurement recovery in respect to reference value
Average recovery: Mean of sample 1 - 4 of solution A, B, C and D

Tab. 8.7
Description of the applied GC-MS method for the measurements of mineral oil test solutions

Method parameter	SINTEF	LUA-Brandenburg
BAM-calibration set used for calibration	yes	yes
Was the purity of the Calibration oil (mass fraction between C_{10} and C_{40}) taken into account	yes	yes
Range of calibration [mg/ml]	0.1-6 mg/mL heptane	0.05-8 mg/mL heptane
How many calibration points	4	10 points
Internal standards used? If yes, which one	yes, hexachlorobutadiene	no
What type of Gas chromatograph was used	Varian 3400	HP 6890 Plus
Which GC-column was used (Type, length, ID, Film thickness)	J&W DB5 30 m x 0.25 mm x 0.1 μ m	HP-5MS 30m x 0.25 mm x 0.25 μ m
Pre-column (Retention gap) used?	Yes	no
Injection technique	split/splitless 1:40	split/splitless, purge after 0.8 min
Volume of injected sample [μ L]	2	2
Manuel or automatic injection	automatic	automatic
Oven heating program and heating rate	40°C (2 min) – 6°C/min to 120° - 10°C/min – 330°C (11 min)	45°C (0.5 min) – 8°C/min - 320°C (14 min)
Type of MS-Detector (e.g. Quadrupol, IonTrap)?	Finnigan ITS40 (ion trap MS)	HP 5973 (HED, Quadrupol)
MS-Mode (e.g. Scan, SIM) and Ionisation technique	scan 45-430 (EI)	sim 70.7 to 71.4 (six masses)
Which m/e was/were selected for integration	TIC of 67, 69, 71	TIC of the six masses see above
Integration between C_{10} and C_{40}	sum area	sum area according to FID-method
Problems and comments		Inj.-temp.: 280°C, const.-flow 1mL He

Tab. 8.8
Results of GC-AED measurements of mineral oil test solutions

Mineral oil sample	BAM (C: 193 nm)		BAM (C: 496 nm + H: 486 nm)	
	1	2	1	2
[mg/mL]				
GC-A1	0.014	0.015	0.047	0.046
GC-A2	0.043	0.045	0.073	0.077
GC-A3	0.086	0.085	0.105	0.103
GC-A4	0.383	0.388	0.374	0.417
GC-B1	0.102	0.102	0.129	0.129
GC-B2	0.494	0.493	0.494	0.534
GC-B3	0.964	0.973	0.948	1.04
GC-B4	4.66	4.55	4.76	4.67
GC-C1	0.103	0.100	0.135	0.142
GC-C2	0.481	0.481	0.505	0.505
GC-C3	0.943	0.931	1.02	1.13
GC-C4	3.35	3.31	4.52	5.25
GC-D1	0.089	0.090	0.119	0.134
GC-D2	0.425	0.441	0.463	0.489
GC-D3	0.828	0.861	0.907	0.979
GC-D4	4.13	4.23	4.28	4.55

Tab. 8.9
Summary of the GC-AED results (mean values of two injections)

Mineral oil sample	Mean (C: 193 nm)	x_{ref} [mg/mL]	Recovery (C: 193 nm) [%]	Average recovery [%]	Mean (C: 496 nm + H: 486 nm)	x_{ref} [mg/mL]	Recovery (C: 496 nm + H: 486 nm) [%]	Average recovery [%]
GC-A1	0.015	0.101	14.4		0.047	0.101	46.3	
GC-A2	0.044	0.502	8.8		0.075	0.502	14.9	
GC-A3	0.086	1.00	8.5	A - Solution:	0.104	1.00	10.4	A - Solution:
GC-A4	0.385	5.02	7.7	9.9	0.396	5.02	7.9	19.9
GC-B1	0.102	0.100	101.9		0.129	0.100	128.6	
GC-B2	0.493	0.502	98.3		0.514	0.502	102.5	
GC-B3	0.968	1.00	96.5	B - Solution:	0.994	1.00	99.1	B - Solution:
GC-B4	4.607	5.02	91.8	97.1	4.715	5.02	94.0	106.0
GC-C1	0.102	0.102	99.6		0.139	0.102	135.9	
GC-C2	0.481	0.509	94.4		0.505	0.509	99.1	
GC-C3	0.937	1.02	91.9	C - Solution:	1.076	1.02	105.6	C - Solution:
GC-C4	3.333	5.09	65.4	87.9	4.887	5.09	95.9	109.1
GC-D1	0.090	0.102	88.2		0.127	0.102	124.3	
GC-D2	0.433	0.509	85.0		0.476	0.509	93.5	
GC-D3	0.844	1.02	82.9	D - Solution:	0.943	1.02	92.6	D - Solution:
GC-D4	4.182	5.09	82.1	84.6	4.413	5.09	86.7	99.2

Grand mean: Mean of laboratory means
SD: Standard deviation of laboratory means
RSD: Relative standard deviation of laboratory means
 x_{ref} : Reference value from gravimetric sample preparation
Recovery: Measurement recovery in respect to reference value
Average recovery: Mean of sample 1 - 4 of solution A, B, C and D

Tab. 8.10: Description of the applied GC-AED method for the measurements of mineral oil test solutions

Method parameter	BAM (1. Series)	BAM (2. Series)
BAM-calibration set used for calibration?	yes	yes
Was the purity of the Calibration oil (mass fraction between C ₁₀ and C ₄₀) taken into account	yes	yes
Range of calibration in [mg/ml]	0.04 - 6	0.04 - 6
How many calibration points	8	8
What type of Gas chromatograph was used	Agilent 6890 N	Agilent 6890 N
Which GC-column was used (Type, length, ID, Film thickness)	HP-1 (Agilent) 25m x 0.32mm x 0.17 µm	HP-1 (Agilent) 25m x 0.32mm x 0.17 µm
Pre-column (Retention gap) used	no	no
Injection technique	splitless	splitless
Volume of injected sample in µL ?	2	2
Manual or automatic injection?	manual	manual
Oven heating program and heating rate?	50°C (8 min) - 40°C/min - 320°C (10 min)	50°C (8 min) - 40°C/min - 320°C (10 min)
AED-parameter	Microwave plasma (He plasma gas), 300°C cavity, 5 min solvent delay, 320°C transfer line	Microwave plasma (He plasma gas), 300°C cavity, 5 min solvent delay, 320°C transfer line
Which wavelengths were selected for integration	193 nm for carbon	496 nm for carbon and 486 nm for hydrogen
Integration between C ₁₀ and C ₄₀	yes	yes (sum of C and H peak areas)
Problems and comments	square calibration (very sensitive but limited linear range)	496 nm carbon- and 486 nm hydrogen emission lines are much less sensitive than the 193 nm carbon emission line.

Annex B: Comparison of ISO/DIS 16703 and Nordic Guideline TR 329

Tab. 8.11

Results of the mineral oil determination of 3 soils according to ISO/DIS 16703 and TR 329

	BAM		EUROFINS A/S	
	TR 329	ISO/DIS 16703	TR 329	ISO/DIS 16703
Soil A [mg/kg]				
A1	2354	1148	1570	1555
A2	2244	1113	2730	1509
A3	2341	1378	1577	1584
Mean Soil A [mg/kg]	2313	1213	1959	1549
SD Soil A [mg/kg]	60	144	668	38
RSD Soil A [%]	2.6	11.9	34.1	2.5
Soil B [mg/kg]				
B1	1575	547	1487	794
B2	1510	619	1328	765
B3	1529	697	696	817
Mean Soil B [mg/kg]	1538	621	1170	792
SD Soil B [mg/kg]	33	75	419	26
RSD Soil B [%]	2.2	12.1	35.8	3.3
Soil C [mg/kg]				
C1	18214	13981	9535	13938
C2	18347	13737	9357	14078
C3	18933	14129	7304	13119
Mean Soil C [mg/kg]	18498	13949	8732	13712
SD Soil C [mg/kg]	383	198	1240	518
RSD Soil C [%]	2.1	1.4	14.2	3.8

Annex C Sample treatment

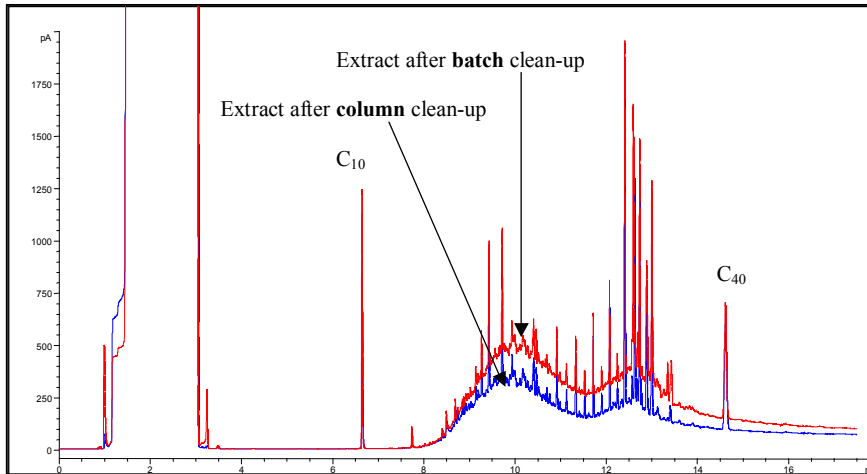


Fig. 8.2
GC-FID chromatograms of peat material extracts after batch- and column clean-up

Annex D

Results for pre-test study

Tab. 8.12
Results of GC-test solution

Institute	Hydrocarbon concentration [mg/mL]		Lab mean [mg/mL]
	1	2	
Theoretical value	2.93		
BAM	2.79	2.81	2.80
SINTEF	2.92	2.93	2.93
UBA	2.85	2.82	2.84
EUROFINS	-	-	-
SYKE	2.92	2.91	2.92
ALCONTROL	2.85	2.82	2.83
EERC	2.96	2.98	2.97
LUA-Brandenburg	2.98	2.98	2.98
LUA-NRW	2.94	2.92	2.93
LEA	2.97	2.92	2.95
KGI-KVI	3.05	3.09	3.07
VTT	2.90	2.89	2.90

Tab. 8.13
Results of test soil

Institute	Bottle-No.	Hydrocarbon content [mg/kg dm]				Lab mean	SD	RSD [%]
		1	2	3	4 (not obligatory)			
BAM	013	1407	1437	1373	1415	1408	26.6	1.9
SINTEF	003	1700	1860	1780		1780	80.0	4.5
UBA	010	1860	1830	1940		1877	56.9	3.0
EUROFINS	012	-	-	-		-	-	-
SYKE	002	876	873	957		902	47.7	5.3
ALCONTROL	011	1417	1399	1461		1426	31.9	2.2
EERC	001	1530	1550	1490		1523	30.6	2.0
LUA-Brandenburg	009	2088	1883	1874		1948	120.9	6.2
LUA-NRW	006	744	717	764		742	23.6	3.2
LEA	004	934	914	896		915	19.0	2.1
KGI-KVI	005	1525	1511	1267		1434	145.1	10.1
VTT	008	1630	1610	1640		1627	15.3	0.9

Tab. 8.14
Clean-up test-solution 1

Institute	Hydrocarbon recovery [%]					RSD [%]
	1	2	3	Lab mean	SD	
BAM	81.18	80.63	81.71	81.18	0.54	0.67
SINTEF	95.34	96.95	92.84	95.05	2.07	2.18
UBA	93.6	96.10		94.85	1.77	1.86
EUROFINS	103.00	101.00	105.00	103.00	2.00	1.94
SYKE	81.40	82.04	83.14	82.19	0.88	1.07
ALCONTROL	86.00	84.00	83.00	84.33	1.53	1.81
EERC	85.00	85.20	84.80	85.00	0.20	0.24
LUA-Brandenburg	89.04	92.42	90.39	90.62	1.70	1.88
LUA-NRW	86.10	90.50	87.20	87.93	2.29	2.60
LEA	81.00	79.00	78.00	79.33	1.53	1.93
KGI-KVI	83.90	83.80	84.00	83.90	0.10	0.12
VTT	88.90	88.00	88.80	88.57	0.49	0.56

Tab. 8.15
Clean-up test-solution 2

Institute	Hydrocarbon concentration [mg/mL]					RSD (%)
	1	2	3	Lab mean	SD	
BAM	1.36	1.36	1.36	1.36	0.00	0.16
SINTEF	1.78	1.69	1.64	1.70	0.07	4.17
UBA	1.70	1.73		1.72	0.02	1.24
EUROFINS	2.08	2.04	2.08	2.07	0.02	1.12
SYKE	1.55	1.59	1.57	1.57	0.02	1.22
ALCONTROL	1.57	1.58	1.53	1.56	0.02	1.59
EERC	1.30	1.20	1.20	1.23	0.06	4.68
LUA-Brandenburg	1.72	1.68	1.70	1.70	0.02	1.18
LUA-NRW	1.55	1.53	1.57	1.55	0.02	1.29
LEA	1.30	1.31	1.28	1.30	0.02	1.18
KGI-KVI	-	-	-	-	-	-
VTT	1.57	1.58	1.57	1.57	0.01	0.37

Tab. 8.16

Florisol used for clean-up test solutions and test soil

No.	Institute	Florisol supplier	Florisol particle size [μm]	Self filled or commercial filled column used?	1. Florisol activated? 2. How?	When was the Florisol activated?	Storage of activated Florisol	Florisol covered with 2g of Na_2SO_4 ?
1	BAM	Merck	150 - 250	self filled glass columns (10mm ID) with PTFE-frits	1.) yes 2.) 140°C, 16 h	about 1 week before use	exsiccator over silica gel	yes
2	SINTEF	---	---	commercial filled: Macherey-Nagel, Chromabond, Na_2SO_4 , 6 mL / 2000 / 2000 mg Cat.no: 730 249G	---	---	---	yes
3	UBA	MERCK	150-250	glass columns, ID 6 mm, self-filled, glass wool	1. yes 2. 140°C, 16 h	3 weeks before use	exsiccator over silica gel	yes
4	EUROFINS	SIGMA	60 - 100	self filled glass columns 10mm ID	1. yes 2. 110°C, 12 h	2 weeks before use	exsiccator over silica gel	yes
5	SYKE	FLUKA	150-250	self filled glass columns with glass frits	1. yes 2. 140°C, 16 h	2 days before use	exsiccator over silica gel	yes
6	ALCONTROL	Merck	150 - 250	self filled glass columns	1. yes 2. 140 °C, 16 h	about 1 day before use	exsiccator over silica gel	yes
7	EERC	Baker	140 - 250	self filled glass columns (10mm ID) with glass wool	1. yes 2. 140°C, 16 h	2 days before use	exsiccator over silica gel	no
8	LUA-BB	Baker	150 - 250	self filled glass columns (10mm ID) with PTFE-frits	1. yes 2. 140°C, 16 h	about 4 weeks before use	exsiccator over silica gel	yes
9	LUA-NRW	Merck	150-250	self filled glass columns (8mm ID) with glass wool plug	1. yes 2. 140°C, 16 h	1 day before use	exsiccator over silica gel	yes
10	LEA	ACROS	150-250	self filled glass columns (10mm ID) with PTFE-frits	1. yes 2. 140°C, 16 hours	2 days before use	exsiccator over silica gel	yes
11	KGI-KVI							
12	VTT	Fluka	150 - 250	self filled glass columns (10 mm ID)	1. yes 2. 140°C, 16 h	3.2.2004	exsiccator over silica gel	yes

Tab. 8.17

Clean-up conditions used for clean-up test solutions and test soil

No.	Institute	Column rinsed with solvent before clean-up?	10 mL of solution 1 and 2 used for clean-up?	Clean-up under additional pressure, vacuum or atmospheric pressure?	Column rinsed with solvent after clean-up?
1	BAM	no	yes	atmospheric pressure	no
2	SINTEF	no	yes	vacuum	no
3	UBA	no	yes	atmospheric pressure	no
4	EUROFINS	rinsed with heptane before use	yes	atmospheric pressure	column rinsed with solvent, results corrected accordingly
5	SYKE	no	yes	atmospheric pressure	no
6	ALCONTROL	no	yes	atmospheric pressure	no
7	EERC	no	yes	atmospheric pressure	no
8	LUA-BB	no	yes	atmospheric pressure	no
9	LUA-NRW	no	yes	atmospheric pressure	no
10	LEA	no	yes	atmospheric pressure	no
11	KGI-KVI				
12	VTT	no	yes	atmospheric pressure	no

Annex E Reference Materials

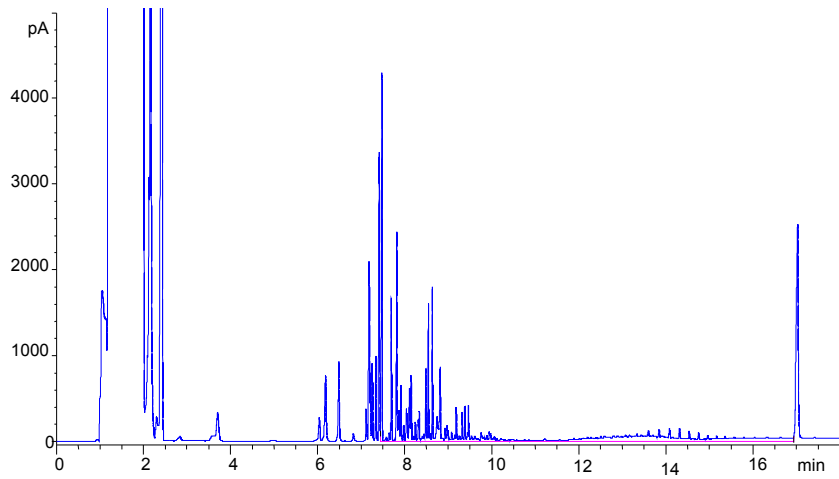


Fig. 8.3
Chromatogram of the hydrocarbon contamination in the Soil Eluate

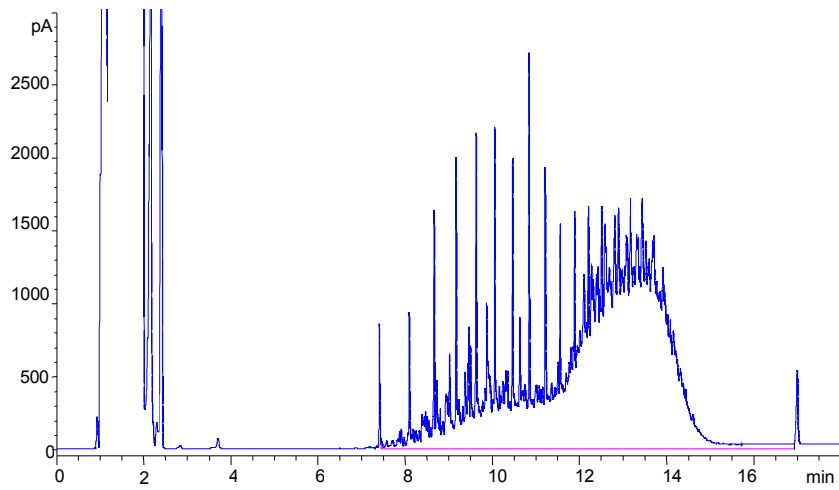


Fig. 8.4
Chromatogram of the hydrocarbon contamination in the Offshore Pills

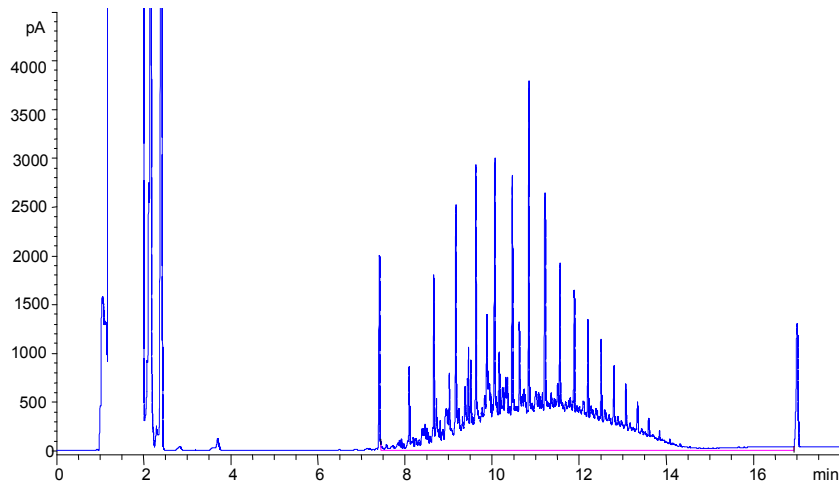


Fig. 8.5
Chromatogram of the hydrocarbon contamination in the Landbased Pills

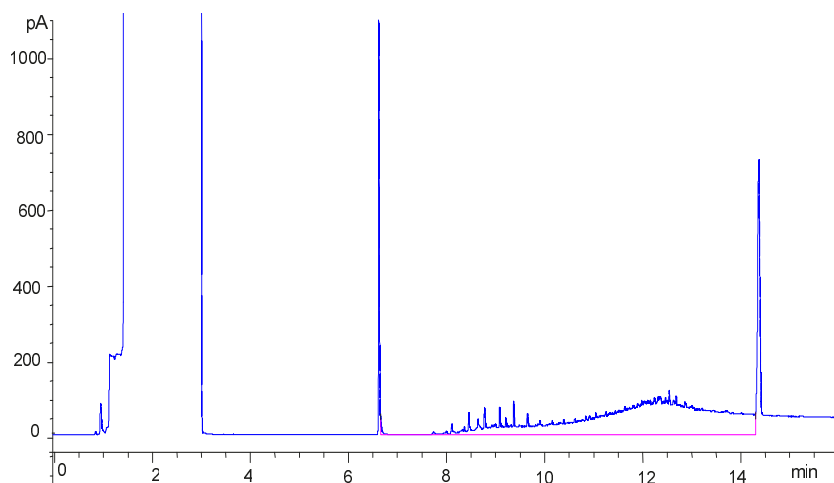


Fig. 8.6
Chromatogram of the hydrocarbon contamination in the Clayish Soil

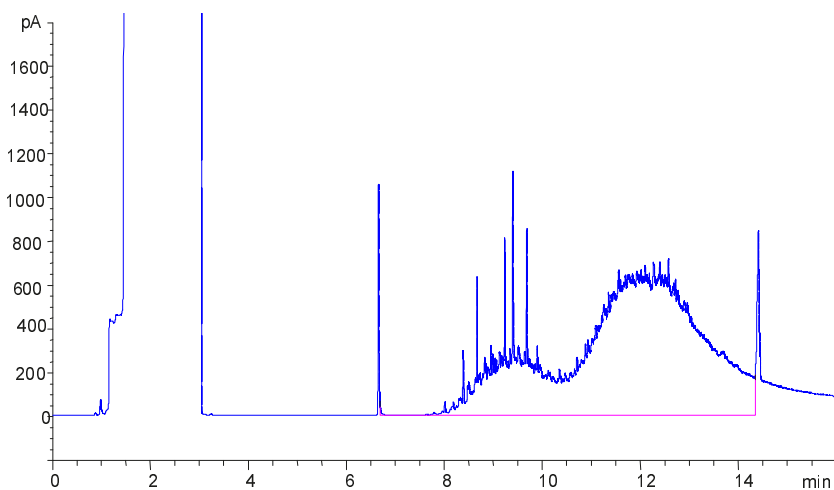


Fig. 8.7
Chromatogram of the hydrocarbon contamination in the Sandy Soil

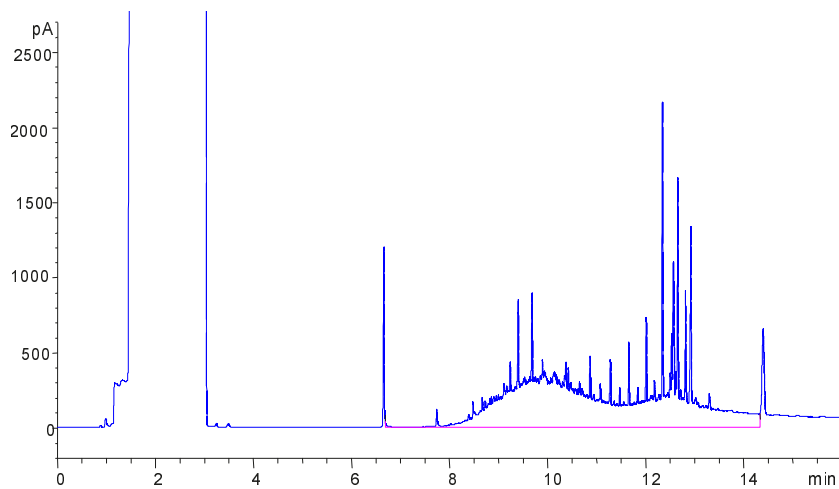


Fig. 8.8
Chromatogram of the hydrocarbon contamination in the Peat Material

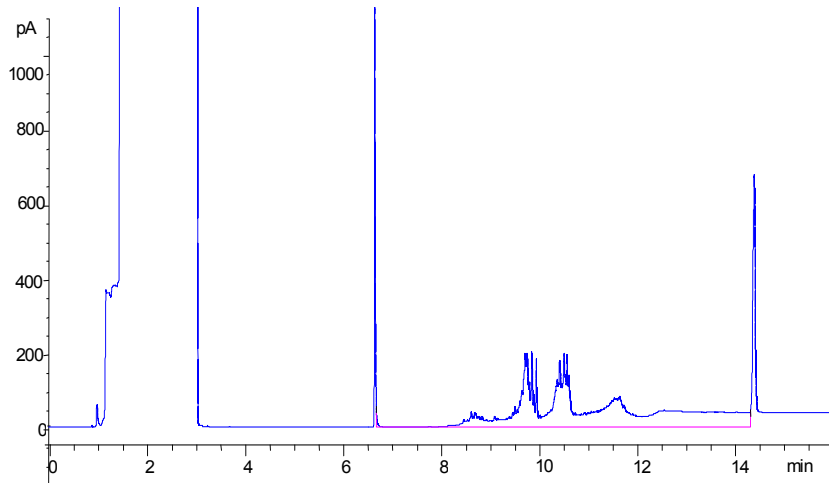


Fig. 8.9
Chromatogram of the hydrocarbon contamination in the Marine Sediment

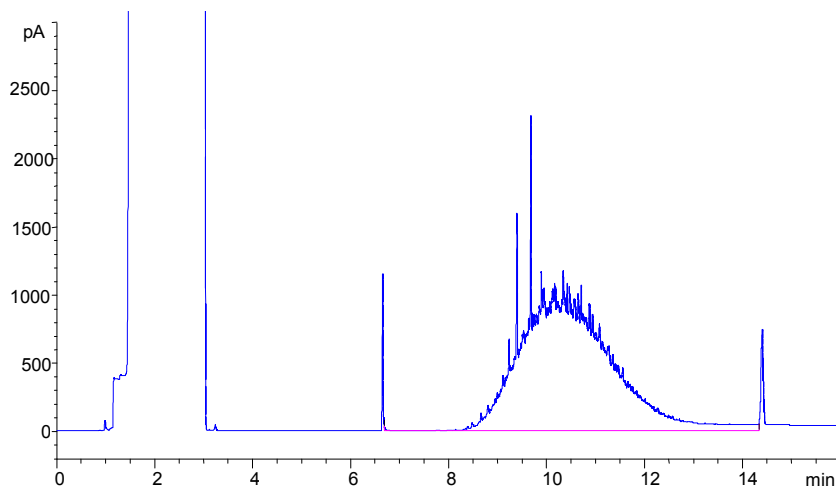


Fig. 8.10
Chromatogram of the hydrocarbon contamination in the Building Material

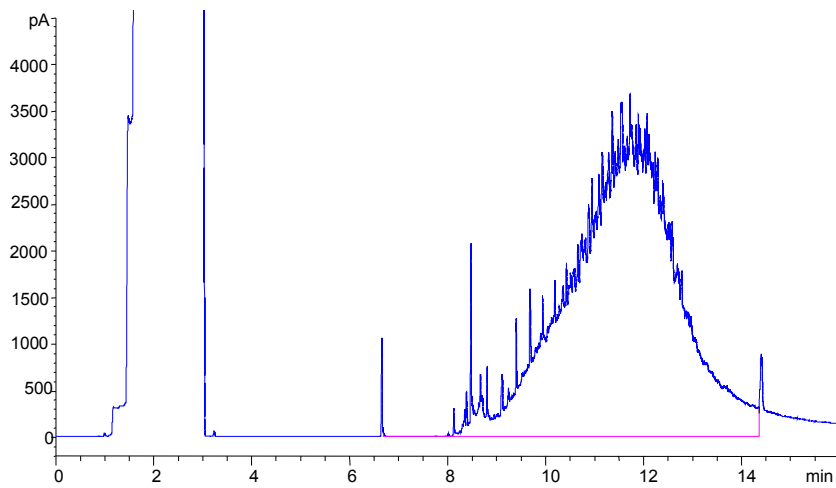


Fig. 8.11
Chromatogram of the hydrocarbon contamination in the Ni/CP-Waste

Annex F Interlaboratory Comparison

Part A: Forms sent to all participants (example for waste materials)

Part B: Results for 9 materials

Annex F Part A: Forms sent to all participants (example for waste materials)

Instructions for analysis

1) Test soil and GC-Test solution

Prior to the analysis of the three Waste Reference Materials the **Test soil** and the **GC - test solution** have to be analysed as agreed at HYCREF mid-term meeting.

The **Test soil** constitutes of an air dried (d_m : 98,0 %) and sieved (< 500 μm) material from the filters of a car washing station. The bottle contains **130 + 1 g** of material. Please analyse the Test soil sample according to “**HYCREF Standard Protocol for soil and waste**” available in eRoom. Please determine **three** independent replicates with a sample intake of **20 g** of material.

The **GC – test solution** contains a mineral oil mixture, n-decane (C_{10}) and n-tetracontane (C_{40}) as RTW-(Retentions Time Window) compounds, dissolved in n-heptane.

The GC - Test solution shall be analysed **directly by GC-FID** without any dilution or concentration steps to avoid handling errors. The GC - Test solution shall be injected **twice**. For calibration and integration please refer to chapter **6.8** and **10.3** of HYCREF Standard Protocol for soil and waste.

The results of the Test soil and the GC – Test solution are to report by using the Excel-file “**Results of Test soil and GC – Test solution.xls**” available in eRoom. Please send the completed Excel-file to Matthias Koch by email (matthias.koch@bam.de) until **02 March 2004**.

Please also send a typical **GC–chromatogram** of the Test soil sample and the GC-test solution with the drawn integration marks (either by email or in a printed version).

2) Waste Reference Materials

You have received 3 types of waste reference materials (2 bottles of each material), which will be tested in the Interlaboratory comparison study.

Please analyse the materials according to “**HYCREF Standard Protocol for soil and waste**” available in eRoom. Please determine **four** independent replicates per material with a sample intake of **20 g** of material. It doesn't matter whether the 4 sample intakes will be drawn only from **one bottle** or from **both bottles** (e.g. 2 sample intakes per bottle) because the materials have been tested as **homogenous**.

The results and the experimental conditions of the analyses of the 3 waste materials are to report by using the Excel-files:

- “**Results of Waste Reference Materials.xls**” and
- “Experimental conditions.doc”

available in eRoom. Please send the completed Excel-files to Matthias Koch by email (matthias.koch@bam.de) until **24 May 2004**.

Please also send a typical **GC–chromatogram** of each of the tested waste reference materials with the drawn integration marks and a chromatogram of a calibration solution (either by email or in a printed version).

Important information

After extraction of **Waste-samples** and **Test-soil** (acc. to chapter **10.2** of HYCREF Standard Protocol) please let the solid material settle for about **1 hour** before transferring the supernatant into a separatory funnel. The tendency of a subsequent formation of an emulsion during the washing step decreases as much as possible of solid particles have been removed.

Please use the provided BAM-Calibration oil mixture **CRM 5004** (1:1 w/w mixture of Diesel oil and Lubricating oil) for GC-FID calibration.

The calibration oil mixture CRM 5004 has a total mass fraction of **97,05 %** within the C_{10} - C_{40} integration range (2,95 % are out of this boiling range). **The mass fraction (purity) of 97,05 % has to be taken into account for the calculation of all results.**

Please do not present your results in eRoom !!!

Confirmation of sample receipt

Return to:

Fax: 0049-30-8104-5990

Dr. Matthias Koch
BAM-I.22 "Trace Analysis of organic compounds"
Bundesanstalt für Materialforschung und-prüfung (BAM)
Federal Institute for Materials Research and Testing
Richard-Willstätter-Str. 11, 12489 Berlin, Germany

E-mail: matthias.koch@bam.de

Name of the laboratory:

Date of receipt:

Contents:

2 bottles of Offshore sediment	[] Yes / No	[]	ID-No. of bottles:
2 bottles of Building material	[] Yes / No	[]	ID-No. of bottles:
2 bottles of Ni/CP-waste	[] Yes / No	[]	ID-No. of bottles:
1 bottle of Test Soil	[] Yes / No	[]	
1 GC -Test solution	[] Yes / No	[]	Weight after receipt:
1 Hydrocarbon calibration set	[] Yes / No	[]	
1 Confirmation of sample receipt	[] Yes / No	[]	
1 Instructions for analysis	[] Yes / No	[]	

Any remarks:

Date:

Signature:

Experimental conditions

Please specify your experimental conditions. Please describe any modification and deviation from **HYCREF Standard Protocol** in the respective step as others. **Please send a typical GC-chromatogram of each of the tested Waste Reference Materials with the drawn integration marks.**

Sample intake:

Waste Sample	Bottle-No.	Sample intake (g)			
		1. Replicate	2. Replicate	3. Replicate	4. Replicate
Offshore sediment					
Building Material					
Ni/CP-Waste					

Sample treatment:

Step	HYCREF Standard Protocol	Yes (✓)	Others (describe)	Comments and conditions if appropriate (e.g. time, temperature, pressure)
Extraction solvent	40 mL acetone + 20 mL heptane (including n-decane and n-tetracontane)			
Extraction method	- Shaking - Sonication			
Separation of liquid extract and solid material after extraction	- Settling - Centrifugation			
Removal of acetone from extract	Thoroughly skaking twice with 100 mL of water			
Florisil / Na ₂ SO ₄ - column	- Self prepared acc. to Standard Protocol - Commercially available cartridge			
Ratio of Florisil / Na ₂ SO ₄ / extract	- 2g / 2g / 10mL - 1g / 1g / 5mL			
Clean-up performance	- with vacuum - with pressure - without vacuum / pressure			Appr. Flow rate (mL/min):

GC conditions:

	Description	Comments
Injection mode : - on-column, PTV, others - manuell, automatic		
Injection volume (µL)		
GC- capillary column: Type Length (m) ID (mm) Film thickness (µm)		
Pre-column used? Type Length (m) ID (mm) Coated?		
Oven temperature program:		
FID Detector temperature (°C)		
Carrier gas: Carrier gas flow (mL/min)		

Calibration, Integration, Calculation:

	Description	Comments
BAM-standard (CRM 5004) used for Hydrocarbon calibration?		
Calibration range: From (mg/mL) to (mg/mL) Number of calibration points		
Purity of calibration oil (mass fraction between C ₁₀ and C ₄₀ = 97,05 %) taken into account?		
Limit of determination of your GC-FID-system for hydrocarbons in solution (mg/mL)		
Integration between n-decane and n-tetracontane?		
Solvent chromatogram subtracted prior to integration of the other chromatograms (acc. to HYCREF-Protocol 10.3.6)?		
Procedural blank (HYCREF-Protocol 10.1) subtracted from sample? <i>The procedural blank shall be determined but not subtracted from sample value (10.3.7)!</i>		

Recoveries:

	Value
Volume of heptane extract (mL) obtained after phase separation and washing twice with water	
Recovery (%) of stearyl stearate (acc. to HYCREF-Protocol 10.4.1)	
Recovery (%) of the hydrocarbon standard solution (acc. to HYCREF-Protocol 10.4.2)	

Dates:

	Date
Date of sample arrival in laboratory	
Date of sample analysis (extraction, clean-up)	
Date of sample measurement (GC-FID)	
Date of result submission to ILC-organizer	

Any other comments:

Date:

Organisation:

Signature:

Form for results for waste reference materials

HYCREF - Test Certification Study (Waste Reference Materials)

Please, insert the name of your laboratory:

Name of the Laboratory

Please, use the comma "," instead of point "." as decimal separator.
Express the hydrocarbon content in **mg/kg dm**, to **3 significant figures**.

		Hydrocarbon content (mg/kg dm)					
Waste sample	Dry matter content dm (%)	Value 1	Value 2	Value 3	Value 4	Procedural blank*)	Comments
Offshore sediment	99.8						
Building material	99.5						
Ni/CP-waste	86.4						

*) The Procedural blank (PB) has to be expressed in the same dimension as the sample value. For the calculation of PB the "Sample intake" and the "Dry matter content" must be set to the same values as for the real sample.

Date:	Signature:
--------------	-------------------

Annex F

Part B: Results for 9 materials

Tab. 8.18

Soil eluate; original data of interlaboratory comparison in mg/L

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	0.510	0.081	0.493	0.524	0.413	0.608
SINTEF	0.400	0.028	0.397	0.436	0.396	0.369
UBA	0.465	0.033	0.494	0.444	0.430	0.492
SYKE	0.279	0.105	0.359	0.380	0.202	0.175
ALCONTROL	0.380	0.039	0.435	0.381	0.356	0.349
EERC	-	-	-	-	-	-
LUA-BB	0.330	0.038	0.300	0.300	0.380	0.340
LUA-NRW	0.393	0.099	0.378	0.479	0.457	0.259
LEA	0.420	0.071	0.380	0.420	0.520	0.360
KGI-KVI	0.519	0.582	0.030	1.280	0.666	0.101
VTT	0.501	0.044	0.542	0.522	0.500	0.441

Tab. 8.19

Offshore pills; original data of interlaboratory comparison in mg/L

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
BAM	16.950	1.799	18.400	14.400	17.000	18.000		
SINTEF	18.525	1.204	18.900	18.000	20.000	17.200		
UBA	19.100	1.173	17.700	19.600	20.300	19.900	18.000	
SYKE	15.800	1.669	15.500	17.700	13.700	16.300		
ALCONTROL	18.225	0.359	17.900	18.000	18.300	18.700		
EERC	17.020	0.976	16.400	15.700	17.400	17.400	18.200	
LUA BB	18.110	0.240	18.480	18.070	18.200	18.010	18.150	17.750
LUA-NRW	19.900	1.080	18.500	19.600	20.700	20.800		
LEA	14.025	0.960	12.600	14.600	14.300	14.600		
KGI-KVI	12.417	0.861	11.300	11.400	12.800	12.600	13.100	13.300
VTT	18.900	0.455	19.500	18.800	18.400	18.900		

Tab. 8.20

Landbased pills; original data of interlaboratory comparison in mg/L

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
BAM	4.308	0.531	4.380	3.670	4.220	4.960		
SINTEF	3.668	0.870	4.500	2.770	4.320	3.080		
UBA	4.618	0.203	4.390	4.790	4.800	4.700	4.410	
SYKE	3.285	1.089	2.140	3.970	2.600	4.430		
ALCONTROL	5.100	0.082	5.100	5.100	5.200	5.000		
EERC	4.423	0.167	4.250	4.280	4.410	4.720	4.420	4.460
LUA-BB	4.395	0.098	4.510	4.420	4.370	4.450	4.400	4.220
LUA-NRW	5.528	0.275	5.860	5.640	5.260	5.350		
LEA	4.008	0.403	4.500	4.110	3.880	3.540		
KGI-KVI	2.130	0.117	2.110	2.130	2.240	1.920	2.240	2.140
VTT	5.120	0.216	5.060	5.440	4.970	5.010		

Tab. 8.21

Clayish soil; original data of interlaboratory comparison in mg/kg dm

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	219.000	28.343	196.000	193.000	242.000	245.000
SINTEF	203.250	7.136	196.000	201.000	213.000	203.000
UBA	235.500	7.416	239.000	225.000	242.000	236.000
SYKE	202.750	1.893	204.000	204.000	200.000	203.000
ALCONTROL	232.000	10.456	218.000	230.000	240.000	240.000
EERC	245.250	27.354	284.000	227.000	245.000	225.000
LUA-BB	233.725	7.077	236.800	242.100	226.400	229.600
LUA-NRW	213.000	4.690	219.000	211.000	208.000	214.000
LEA	133.000	7.616	139.000	125.000	140.000	128.000
KGI-KVI	250.000	20.849	252.000	266.000	220.000	262.000
VTT	190.500	8.544	200.000	188.000	180.000	194.000

Tab. 8.22
Sandy soil; original data of interlaboratory comparison in mg/kg dm

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	1935.000	231.012	1740.000	1730.000	2130.000	2140.000
SINTEF	2092.500	26.300	2080.000	2130.000	2070.000	2090.000
UBA	1947.500	49.917	1980.000	2000.000	1910.000	1900.000
SYKE	1940.000	138.323	1860.000	1800.000	2110.000	1990.000
ALCONTROL	1950.000	49.666	1900.000	1920.000	2010.000	1970.000
EERC	2017.500	118.145	1990.000	2060.000	1870.000	2150.000
LUA-BB	1525.693	15.943	1506.930	1536.370	1541.220	1518.250
LUA-NRW	2002.500	54.391	1960.000	2080.000	2000.000	1970.000
LEA	1317.500	57.373	1240.000	1370.000	1310.000	1350.000
KGI-KVI	2090.500	210.457	2277.000	2267.000	1886.000	1932.000
VTT	1897.500	17.078	1880.000	1890.000	1900.000	1920.000

Tab. 8.23
Sandy soil; original data of interlaboratory comparison in mg/kg dm

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	1335.000	197.400	1160.000	1170.000	1530.000	1480.000
SINTEF	1382.500	22.174	1390.000	1400.000	1390.000	1350.000
UBA	1540.000	147.648	590.000	1470.000	1720.000	1380.000
SYKE	1073.750	110.858	1020.000	955.000	1210.000	1110.000
ALCONTROL	1272.500	67.020	1360.000	1280.000	1200.000	1250.000
EERC	1612.500	106.575	1510.000	1570.000	1760.000	1610.000
LUA-BB	1185.150	20.868	1176.900	1216.000	1177.800	1169.900
LUA-NRW	1296.667	55.076	1360.000	1260.000	1270.000	
LEA	794.750	38.353	845.000	752.000	787.000	795.000
KGI-KVI	1088.750	30.026	1132.000	1083.000	1077.000	1063.000
VTT	1327.500	156.072	1450.000	1360.000	1400.000	1100.000

Tab. 8.24
Marine sediment; original data of interlaboratory comparison in mg/kg dm

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	193.250	12.633	183.000	184.000	210.000	196.000
SINTEF	157.000	5.354	157.000	156.000	164.000	151.000
UBA	205.000	10.739	216.000	210.000	203.000	191.000
SYKE	188.500	8.386	197.000	191.000	189.000	177.000
ALCONTROL	194.250	8.016	202.000	196.000	196.000	183.000
EERC	179.000	5.477	186.000	177.000	173.000	180.000
LUA-BB	233.500	6.245	227.000	236.000	241.000	230.000
LUA-NRW	189.750	11.087	180.000	182.000	193.000	204.000
LEA	201.750	7.544	193.000	207.000	209.000	198.000
KGI-KVI	193.750	13.889	199.000	173.000	202.000	201.000
VTT	219.250	15.108	198.000	231.000	219.000	229.000

Tab. 8.25
Building material; original data of interlaboratory comparison in mg/kg dm

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	2182.500	448.730	1820.000	1780.000	2660.000	2470000
SINTEF	2262.500	45.735	2270.000	2210.000	2250.000	2.320.000
UBA	2317.500	58.523	2340.000	2230.000	2350.000	2350.000
SYKE	1757.500	41.130	1810.000	1770.000	1730.000	1720.000
ALCONTROL	1957.500	38.622	1960.000	1920.000	2010.000	1940.000
EERC	2137.500	230.705	2480.000	2030.000	1980.000	2060.000
LUA-BB	2040.000	24.495	2050.000	2070.000	2020.000	2020.000
LUA-NRW	2402.500	79.320	2510.000	2320.000	2400.000	2380.000
LEA	1862.500	49.917	1900.000	1810.000	1910.000	1830.000
KGI-KVI	2082.500	116.154	2060.000	2070.000	1960.000	2240.000
VTT	2182.500	83.815	2060.000	2210.000	2250.000	2210.000

Tab. 8.26

Ni/CP waste; original data of interlaboratory comparison in mg/kg dm

Lab	Mean	SD	Sample #1	Sample #2	Sample #3	Sample #4
BAM	8970.000	525.040	8610.000	8430.000	9440.000	9400.000
SINTEF	10425.000	50.000	10400.000	10400.000	10400.000	10500.000
UBA	9592.500	59.090	9600.000	9650.000	9610.000	9510.000
SYKE	9220.250	89.414	9188.000	9329.000	9246.000	9118.000
ALCONTROL	9225.000	194.165	9070.000	9090.000	9490.000	9250.000
EERC	10350.000	173205	10100.000	10400.000	10400.000	10500.000
LUA-BB	7722.500	187.861	7730.000	7950.000	7490.000	7720.000
LUA-NRW	9935.000	221.133	9920.000	9960.000	9660.000	10200.000
LEA	7262.500	454.350	6826.000	6915.000	7636.000	7673.000
KGI-KVI	9112.500	374.021	8930.000	8700.000	9270.000	9550.000
VTT	9127.500	151.959	9030.000	8970.000	9290.000	9220.000

Annex G: Standard Protocol

for the determination of the hydrocarbon content in soil and waste according to ISO/DIS 16703 and prEN 14039 (GC-method)

1 Introduction

Hydrocarbons are important constituents of many types of waste and contaminated soils. They have been determined up to now mainly by infrared spectroscopy after extraction with halogenated solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane or tetrachloromethane. The objective of the new standards is to provide analytical methods for the determination of hydrocarbon content by capillary gas chromatography avoiding the use of such solvents.

The user of these standards should be aware that the results obtained with the new methods might not be comparable with those obtained when using infrared spectroscopy.

2 Scope

This Standard Protocol specifies a method for the quantitative determination of the hydrocarbon content (C_{10} - C_{40}) in soil and solid waste samples by gas chromatography. The method is applicable to hydrocarbon extract concentrations between 0.1 and 10 mg/mL (the corresponding hydrocarbon content depends on the dry matter content of the sample – the scope is between 100 and 10000 mg/kg for absolutely dry samples).

3 Normative References

ISO/DIS 16703

Soil quality – Determination of hydrocarbon content in the range of C_{10} to C_{40} by gas chromatography.

prEN 14039

Characterisation of waste – Determination of hydrocarbon content in the range of C_{10} to C_{40} by gas chromatography.

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.

4 Definitions

For the purpose of these International and European Standards, the following definition applies:

Hydrocarbon content by gas chromatography

The sum of compounds extractable with acetone/n-heptane (2+1) which do not adsorb on Florisil and can be chromatographed on a non-polar capillary column with retention times between those of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$).

NOTE 1 - Substances that comply with that definition are mainly long chain or branched aliphatic, alicyclic, polycyclic- or alkyl substituted aromatic hydrocarbons.

NOTE 2 - This definition differs from that given in prEN 14345 Characterisation of waste – Gravimetric determination of hydrocarbon content.

5 Principle

A known amount of the homogenised soil- or waste sample is extracted by mechanical shaking or sonication with acetone/n-heptane. The extract is separated and washed twice with water. Polar compounds are removed from the n-heptane extract by adsorption chromatography on Florisil. An aliquot of the purified extract is analysed by capillary gas chromatography with flame ionisation detection.

The total peak area between the retention time window standards n-decane and n-tetracontane is measured and the amount of hydrocarbons in the sample is quantified against an external standard consisting of equal amounts of two different types of mineral oil.

NOTE - Instead of heptane, other non-polar solvent (e.g. petroleum ether, cyclohexane, n-hexane) can be used, however its suitability for the extraction of hydrocarbons from soil and waste has to be proven. It should be kept in mind that volatile solvents, e.g. petroleum ether, can easily evaporate, what leads to a concentration of the extracts.

6 Reagents

In general, all reagents shall be at least reagent grade and suitable for their specific purposes.

6.1 Acetone, $(CH_3)_2CO$

6.2 n-Heptane, C_7H_{16}

6.3 Florisil for preparation of clean-up column,

particle size 150 μm to 250 μm (mesh 60 to 100), heated for at least 16 h at 140°C and stored in a desiccator over a molecular sieve. Alternatively, commercially available Florisil cartridges containing 2 g of Florisil and 2 g of sodium sulphate are also applicable.

NOTE - Florisil is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of these International and European Standards and does not constitute an endorsement by ISO and GEN of this product. Equivalent products may be used if it can be shown to lead to comparable results.

6.4 Anhydrous sodium sulphate, Na_2SO_4 , heated for at least 2 h at 550 °C

6.5 Test solution

of n-octadecanoic acid octadecyl ester (stearyl stearate), $C_{36}H_{72}O_2$. Dissolve about 100 mg of n-octadecanoic acid octadecyl ester in 100 mL n-heptane [6.2].

6.6 Retention time window (RTW)

standard solution containing n-tetracontane and n-decane:

Weigh (30 ± 1) mg of n-tetracontane into an 1 L volumetric flask, dissolve completely in an appropriate volume of n-heptane [6.2], add 30 μ L of n-decane (about 21 mg), mix well, fill up to volume with n-heptane and homogenise. This solution shall be used for all dilution steps of the hydrocarbon standard [6.7] and be stored at room temperature.

NOTE - n-tetracontane is only moderately soluble in n-heptane. Slight warm up and/or sonication accelerates the dissolution process.

6.7 Hydrocarbon standard solution for calibration

Mix approximately equal masses of two different types of mineral oil. Weigh accurately this mixture and dissolve in the RTW standard solution to give a total hydrocarbon concentration of about 10 g/L.

Preparation of the calibration solutions can be done by diluting an aliquot of this standard solution [6.8] with the RTW standard solution.

The first oil type should show discrete peaks in the gas chromatogram as can be seen in Annex G1, *Figure G.1* (left part of the chromatogram). A suitable oil of this type is a diesel fuel without any additives. The second type should have a boiling range higher than the first one and should show a "hump" in the gas chromatogram, as can be seen in Annex G1, in *Figure G.1* (right part of the chromatogram). A suitable oil of this type is a lubricating oil without any additives.

NOTE - General purpose hydrocarbon standards for calibration can be obtained from many commercial organisations. Calibration standards specific to these International and European Standards can be purchased from Bundesanstalt für Materialforschung und -prüfung, Fachgruppe I.2, Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany.

This information is given for the convenience of users of these International and European Standards and does not constitute an endorsement by ISO or CEN of this product.

6.8 Control solution

Prepare an independent control solution according to [6.7] with a hydrocarbon concentration of about in the middle of the working range.

Note – This solution is used to perform the GC-repeatability test [10.3.2], the validity check of the calibration function [10.3.4] and the hydrocarbon recovery test [10.4.2].

6.9 System performance standard solution

Prepare a mixture of equal amounts, on a mass basis, of the n-alkanes with even carbon numbers from C_{10} to C_{40} , dissolved in n-heptane [6.2], to give concentrations of about 50 mg/L of each n-alkane. Store this solution at room temperature.

NOTE 1 - This solution is used to verify the suitability of the gas chromatographic system for the resolution of n-alkanes as well as for the detector response.

NOTE 2 - This solution is used to give information of the retention times of the n-alkanes to characterise the hydrocarbons in the samples.

6.10 Preparation of the clean-up column

A plug of pre-washed glass wool or a PTFE frit is pushed down into the column [8.9]. Then, successively 2 g of Florisil [6.3] and 2 g of sodium sulphate [6.4] are added. The column shall be prepared immediately before use.

7 Hazards

Anyone dealing with waste and sludge analysis has to be aware of the typical risks of that kind of material irrespective of the parameter to be determined. Waste and sludge samples may contain hazardous and inflammable substances. They may contain pathogens and be liable to biological action. Consequently it is recommended that these samples should be handled with special care. The gases which may be produced by microbiological activity are potentially inflammable and will pressurise sealed bottles. Exploding bottles are likely to result in infectious shrapnel and/or pathogenic aerosols. National regulations should be followed with respect to all hazards associated with this method.

8 Equipment

8.1 Standard laboratory glassware, which shall be heated or rinsed with acetone [6.1] and dried before use.

8.2 Devices for extraction:

Mechanical shaker or ultrasonic bath

8.3 Gas chromatograph, equipped with a non-discriminating injection system

(preferably on-column or programmable temperature vapourisation injection), a capillary column and a flame ionisation detector (FID).

NOTE - The use of a large volume injection system can improve the limit of detection considerably

8.4 Capillary column,

fused silica column with suitable stationary phase and dimensions, e.g.

stationary phase: non-polar, e.g. immobilised 100 % dimethyl polysiloxane, 95 %-dimethyl-5 %-diphenyl polysiloxane, modified siloxane polymer, etc.

length: at least 5 m;
internal diameter: 0.1 mm to 0.32 mm;
film thickness: 0.1 μ m to 1.0 μ m.

The column should give a baseline separation of the n-alkanes with even carbon numbers when the system performance standard solution [6.9] is run.

NOTE 1 - Thermally stable low bleed columns should be preferred.

NOTE 2 - The use of a pre-column, e.g. wide-bore (0.53 mm I.D.) deactivated fused silica of at least 2 m of length that suits to the analytical column and connected to it using zero-volume connector is recommended.

8.5 Data system,

capable of integrating the total peak area between C_{10} and C_{40} and re-integrating after defining a new baseline according to 10.3.6.

8.6 Glass extraction vessel,

at least 100 mL, with ground glass stopper or screw caps incorporating a septum coated with polytetrafluoroethylene (PTFE).

8.7 Glass tube,

25 mL, with ground glass stopper or screw caps incorporating a septum coated with polytetrafluoroethylene (PTFE).

8.8 Separatory funnel,

at least 250 mL, with a ground glass stopper

8.9 Chromatography column for clean-up,

glass columns of about 10 mm I.D. shall be used. The upper part of the column should be widened to use as solvent reservoir and the lower part to be narrowed to form a tip.

9 Sample conservation and pre-treatment

The samples shall be kept sealed in darkness at a temperature of about 4°C and extracted within a period of one week. If this is not possible samples shall be stored at -18 °C or lower. Before analysis the sealed samples shall be homogenised by slightly shaking for about one minute. If samples with a very small particle size or low density are to analyse the bottles should not be open just after shaking to avoid contaminating dust.

The extracts shall be kept sealed at room temperature and analysed within 3 days. The storage of extracts at lower temperatures (e.g. in a fridge) can lead to a crystallisation of n-tetracontane (and other compounds).

10 Procedure**10.1 Procedural blank**

With each series of samples a procedural blank determination has to be carried out according to [10.2.] using all reagents in identical amounts but without a sample. Procedural blank values shall not exceed 10 % of the lowest sample value. If the procedural blank values do not fulfil this requirement every step in the procedure shall be checked to find the reason for these high procedural blanks. Eliminate the source of impurities and repeat the procedural blank.

NOTE 1 – The 10 % rule for the procedural blank is limited by the limit of determination. Only values higher than the limit of determination can be quantified.

Note 2 - A “negative procedural blank” (if the peak area of the procedural blank is lower than the intercept of the calibration function) could be caused either by impurities of n-heptane, which adsorb on Florisil or by a high uncertainty of the intercept of the calibration function.

10.2 Extraction and clean-up

Weigh accurately about 20 g of the homogenised sample into a glass extraction vessel [8.6], add (40 ± 1) mL of

acetone [6.1] After short shaking by hand add (20 ± 0.1) mL of the RTW standard solution [6.6]. Extract the sample by shaking or sonication for one hour. After settling of the solid material transfer as much as possible of the supernatant into a separatory funnel [8.8]. To remove the acetone wash the organic phase twice by shaking thoroughly (5 minutes) with 100 mL of water. Collect the organic layer in a glass tube [8.7]. Add sufficient amount of sodium sulphate so that no lumps are formed anymore. Transfer 10 mL of the extract to a clean-up column filled with Florisil [6.10]. Do not pre-wash the column with organic solvent. Collect the entire eluate. Transfer an aliquot of the purified extract to a GC-vial and analyse by gas chromatography.

NOTE 1 - If appropriate, test portions of 5 to 30 g can be used (e.g. smaller test portion should be used if samples adsorb the major portion of the extraction solvent added, sample intake should be increased if high sensitivity is required)

NOTE 2 - Alternative extraction procedures e.g. accelerated solvent extraction (ASE) can be used provided they give comparable extraction performances.

NOTE 3 - To improve and accelerate phase separation centrifugation can be applied provided the necessary safety precautions, especially with regard to inflammable solvents, are taken into account.

NOTE 4 - Alternatively, commercially available Florisil cartridges containing 2 g of Florisil and 2 g of sodium sulphate are also applicable.

NOTE 5 - Only if less than 10 mL of extract are obtained after drying with sodium sulphate, the clean-up procedure can be modified as follows: Transfer 5 mL of the extract to a clean-up column filled with 1 g of Florisil and 1 g of sodium sulphate.

10.3 Determination by gas chromatography**10.3.1 Test of the performance of the gas chromatographic system**

Use a capillary column with one of the specified stationary phases [8.4] for gas chromatographic analysis. Adjust the gas chromatograph [8.3] to provide an optimal separation. The n-alkanes in the system performance standard solution [6.9] shall be baseline separated. The relative response of the n-tetracontane (C_{40}) shall be at least 0.8, with respect to n-eicosane (C_{20}). For an example of gas chromatographic conditions see Annex G1.

10.3.2 Repeatability Test

Record a gas chromatogram by injection of an appropriate volume of n-heptane. Inject the same volume of the control solution [6.8] three times and record the chromatogram for each injection. Correct the chromatograms of the control solution by subtracting the chromatogram of n-heptane and integrate the corrected chromatograms [10.3.6]; calculate the mean of the measured peak areas and the corresponding standard deviation. The relative standard deviation shall not exceed 5 %.

10.3.3 Calibration

Before the method is used for the first time, or when the operating conditions are changed, a basic calibration ac-

ording to ISO 8466-1 including the determination of the limit of detection and limit of determination shall be carried out. A calibration shall be done by analysing a minimum of five dilutions of the hydrocarbon standard solution [6.7] which cover the working range. Calculate a calibration function by linear regression analysis of the corrected peak areas [10.3.6]. From the calculated regression line the current sensitivity of the method is determined.

10.3.4 Validity check of the calibration function

The validity of the calibration function shall be checked within each batch of samples by analysis of one independent control solution [6.8]. The calibration check identifies problems of calibration before real samples are run. Check whether the result is within + 10 % of the reference value of the control solution. If this is the case the actual calibration function is assumed to be valid. If not, a new calibration according to 10.3.3 shall be performed.

NOTE 1 - It is good analytical practice to perform both a calibration check and Analytical Quality Control using an independent solution [6.8] randomly placed during the analysis of the batch of samples. This independent solution can perform both functions.

Note 2 - Alternatively, control charts can be used to check the validity of the calibration function. In this case the ordinary rules for the interpretation of control charts (ISO 8258) shall be considered.

10.3.5 Measurement

Analyse n-heptane [6.2], procedural blanks [10.1], sample extracts [10.2], calibration standards [6.7], control solutions [6.8] and system performance standard solutions [6.10] under identical gas chromatographic conditions. n-Heptane shall be analysed in each sample batch.

NOTE - If samples are to measure, which contain hydrocarbons in a high boiling range or are highly contaminated, a subsequent GC-run by injecting n-heptane is recommended to demonstrate the absence of impurities in the GC-system.

10.3.6 Integration

Correct the chromatograms of procedural blanks [10.1], sample extracts [10.2], calibration standards [6.7], control solutions [6.8] and system performance standard solutions [6.9] for column bleeding by subtracting the chromatogram of n-heptane [6.2] prior to integration.

Integrate the total area of the resulting chromatograms between the n-decane C_{10} and n-tetracontane C_{40} peaks. Start integration at the retention time just after the end of the n-decane-peak at the signal level in front of the solvent peak. End the integration of the total area at the retention time just before the beginning of the n-tetracontane peak at the same signal level (see Annex G1).

The presence of peaks on the tail of the solvent peak with retention times less than that of n-decane indicates that the sample contains low boiling volatile hydrocarbons. This should be mentioned in the test report.

A non-horizontal baseline at the end of the chromatogram (retention time greater than that of n-tetracontane), with a signal level greater than the column bleed, indicates that the sample contains high-boiling hydrocarbons with more

than 40 carbon atoms. This should be mentioned in the test report. It should be ensured that these compounds elute completely from the column. Otherwise they can cause interferences with the subsequent sample analysis.

NOTE 1 - If the data system is capable to perform the integration procedure according to 10.3.6 without a prior baseline correction by subtraction of an n-heptane chromatogram, it is not necessary to correct the chromatograms of procedural blanks [10.1], sample extracts [10.2], calibration standards [6.7], control solutions [6.8] and system performance standard solutions [6.9]. But all integrations have to be done using only one selected procedure.

NOTE 2 - All chromatograms should be checked visually for correct integration. The start and stop times of the integration should be visible on the chromatogram.

NOTE 3 - The range of the carbon numbers of n-alkanes present in the sample is determined by comparing the gas chromatogram of the sample extract with that of the system performance standard solution [6.9]. The corresponding boiling range can be derived from Annex G2.

NOTE 4 - Peak shape and signal intensity of n-decane and n-tetracontane are sensitive to changes in the surface properties of the injector and/or the pre-column due to contamination by sample constituents. Therefore, they can be used as a good indication for replacing pre-column and/or liner.

10.3.7 Calculation

The hydrocarbon content of the sample is calculated using Equation 1.

$$HC = \frac{c \cdot V \cdot 100\%}{m \cdot d_m} \quad (\text{Eq. 1})$$

where

- HC is the hydrocarbon content of the sample, in milligrams per kilogram dry matter [mg/kg dm]
- c is the hydrocarbon concentration of the extract calculated from the function, in milligrams per millilitre [mg/mL]
- V is the volume of the n-heptane used for extraction, in millilitres [mL], usually 20 mL
- m is the mass of the sample taken for analysis, in kilograms [kg]
- d_m is the dry matter content of the analysed sample, in percent [%]

Calculate the procedural blank in the same way as the sample. Do not subtract the procedural blank value from the sample value but report the procedural blank in addition to the sample value. Please be aware that only values higher the limit of determination can be quantified.

10.3.8 Expression of results

Express the hydrocarbon content in soil and waste, in milligrams per kilogram dry matter, to three significant figures. Examples:

hydrocarbon content	5370 mg/kg dm
hydrocarbon content	435 mg/kg dm

10.4 Quality control

10.4.1 Suitability check of the clean-up procedure

The clean-up efficiency of each batch of Florisil shall be checked (if Florisil cartridges are used their suitability for the clean-up procedure shall be checked in the same way) by the following procedure:

Add 10 mL of the n-octadecanoic acid octadecyl ester solution [6.5] to the clean-up column [6.10] filled with 2 g of Florisil and 2 g of sodium sulphate and collect the entire eluate. Analyse a portion of the resulting solution by gas chromatography. Analyse an 1+19 dilution of the untreated n-octadecanoic acid octadecyl ester test solution [6.5] as reference. Determine the recovery of the n-octadecanoic acid octadecyl ester after clean-up on the base of the peak area in respect to the untreated n-octadecanoic acid octadecyl ester (Equation 2).

$$R_{oo} = \frac{A_{foo}}{A_{uoo}} \times 5 \quad (\text{Eq. 2})$$

where

R_{oo} is the recovery of n-octadecanoic acid octadecyl ester after clean-up on the Florisil column, in percent [%]

A_{foo} is the peak area of n-octadecanoic acid octadecyl ester after clean-up on the Florisil column

A_{uoo} is the peak area of the (1+19) dilution of untreated n-octadecanoic acid octadecyl ester

The recovery shall not exceed 5 %. If the recovery of n-octadecanoic acid octadecyl ester is above 5 % activate the Florisil according to [6.3] and repeat the test.

10.4.2 Recovery of the Control Solution

The recovery of hydrocarbons using the Control Solution [6.8] shall be checked with each batch of Florisil (if Florisil cartridges are used recovery shall be checked in the same way) by the following procedure:

Add 10 mL of the Control Solution [6.8] to the clean-up column [6.10] filled with 2 g of Florisil and 2 g of sodium sulphate and collect the entire eluate. Analyse a portion of the purified solution by gas chromatography. Analyse the untreated Control Solution [6.9] as reference. Determine the recovery of the hydrocarbons on the base of the peak area of the purified and untreated Control Solution (Equation 3).

$$R_{HC} = \frac{A_{thc}}{A_{uhc}} \times 100 \quad (\text{Eq. 3})$$

where

R_{HC} is the hydrocarbon recovery of the Control Solution, expressed in percent [%]

A_{thc} is the peak area of the Control Solution after clean-up on the Florisil column

A_{uhc} is the peak area of untreated Control Solution

The recovery should be more than 80 %.

11 Test report

The test report shall contain at least the following information:

- The date of sample arrival in the lab and the date of commencement of the analysis;
- a reference to the used method (extraction: shaking or sonication or other; clean-up, analytical conditions);
- a complete identification of the sample;
- the results of the determination, the units the results are given in;
- statement on the uncertainty of the results;
- any details not specified in this protocol or which are optional, as well as any other factor that might have affected the results;
- a reference to the occurrence of low ($< C_{10}$) and/or high boiling ($> C_{40}$) compounds in the chromatogram.

Annex G1 (informative)

Examples of gas chromatograms of hydrocarbon standard, soil and waste samples.

Fig. G.1 shows the gas chromatogram of the calibration mixture of mineral oil consisting of equal parts of a diesel fuel and a lubricating oil. *Fig. G.2* shows the same gas chromatogram after correction for the column bleed and integration. The total peak area between n-decane (C_{10}) and n-tetracontane (C_{40}) used for quantification is indicated as hatched area.

The *Fig. G.3* and *G.4* show integrated gas chromatograms corrected for the column bleed of contaminated soil and waste samples, respectively.

Fig. G.5 shows the gas chromatogram of the system performance standard solution containing n-alkanes with even carbon numbers from C_{10} to C_{40} .

The chromatograms have been recorded under the following conditions:

Injection technique: on-column

Injection volume: 2 μ L

Column: fused silica capillary column

Column length: 12 m
 Internal diameter: 0.25 mm
 Liquid phase: BPX-5
 Film thickness: 1.0 μ m
 Pre-column: deactivated fused silica capillary, 2 m x 0.53 mm
 Carrier gas: Helium
 Pressure: 150 kPa
 Detector: Flame ionisation detector
 Detector temperature: 360 $^{\circ}$ C
 Oven temperature: 80 $^{\circ}$ C for 1 min
 20 $^{\circ}$ C/min to 360 $^{\circ}$ C
 300 $^{\circ}$ C for 10 min
 360 $^{\circ}$ C for 15 min

These chromatographic conditions are only an example!

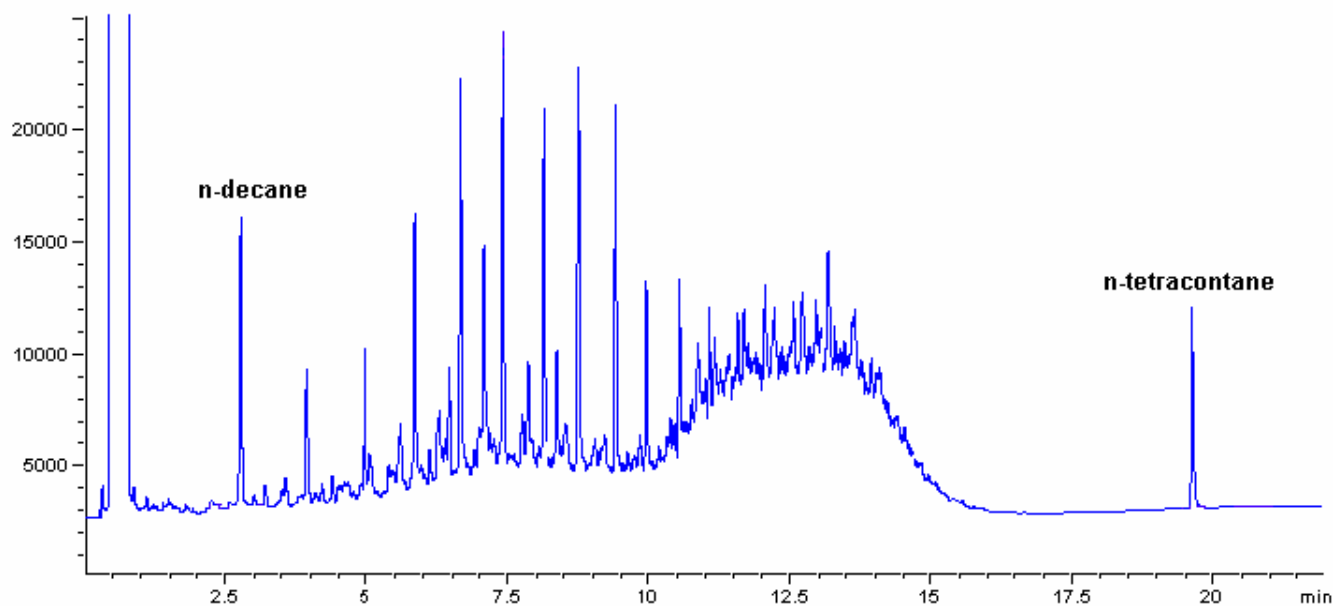


Fig. G.1
 Gas chromatogram of the hydrocarbon standard solution (6.8) consisting of equal parts of diesel fuel and lubricating oil

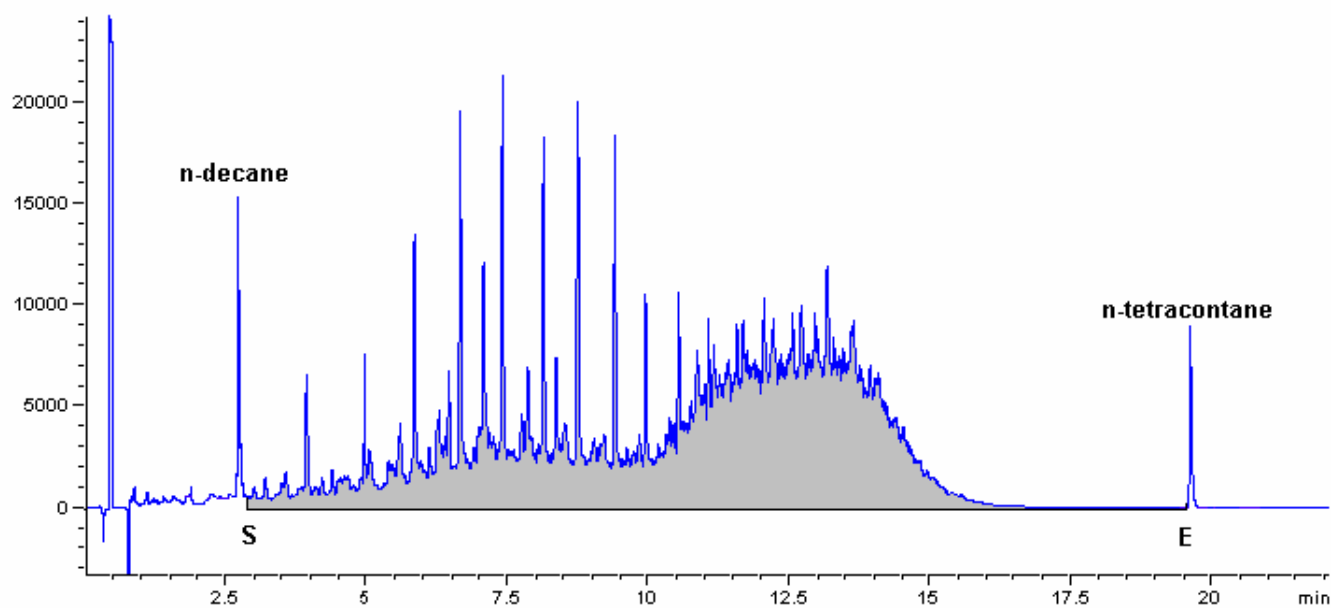


Fig. G.2
Integrated gas chromatogram of the hydrocarbon standard solution (6.8) corrected for the "column bleed"

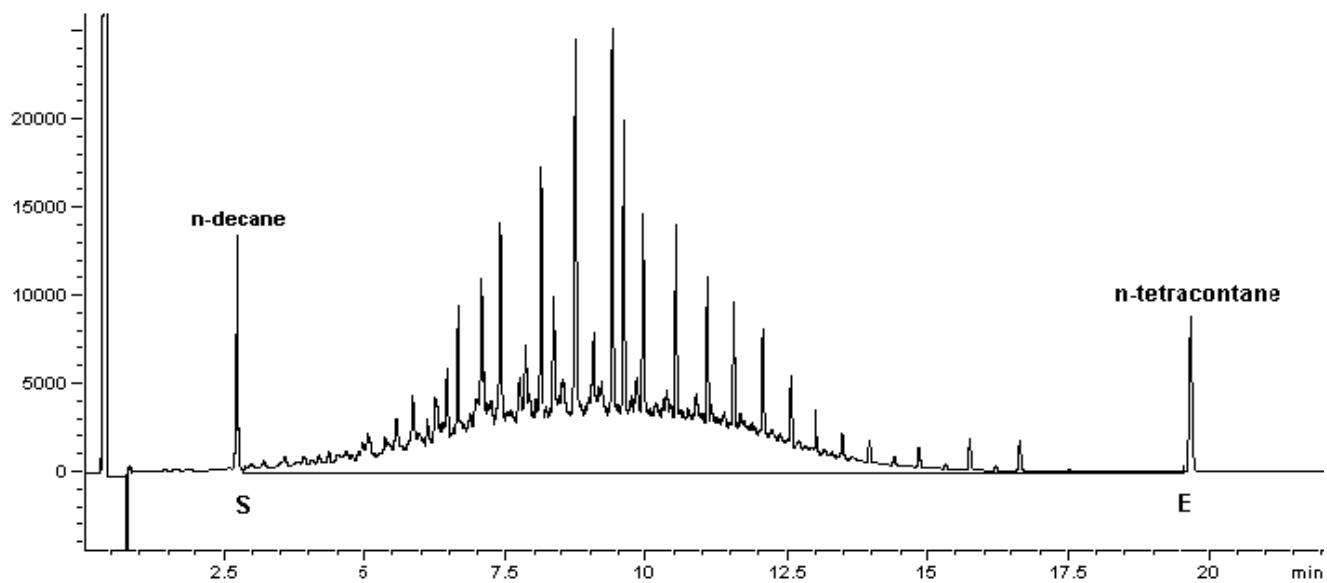


Fig. G.3
Integrated gas chromatogram of a contaminated soil sample corrected for the "column bleed"

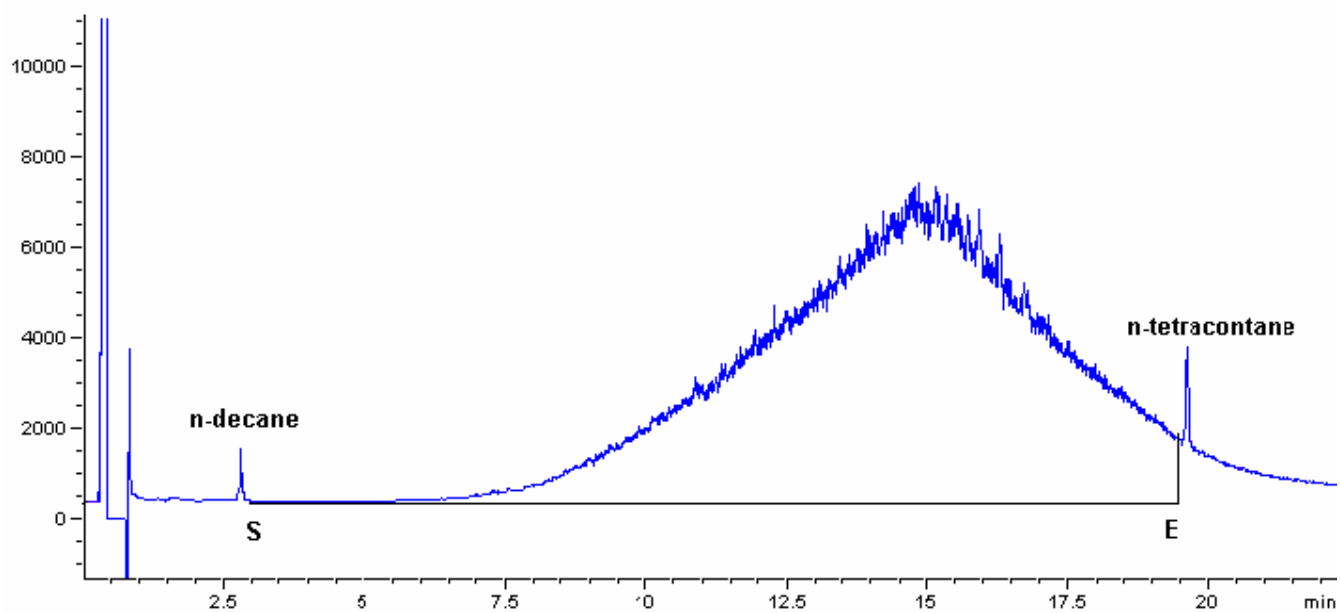


Fig. G.4
Integrated gas chromatogram of a highly contaminated waste sample corrected for the "column bleed"

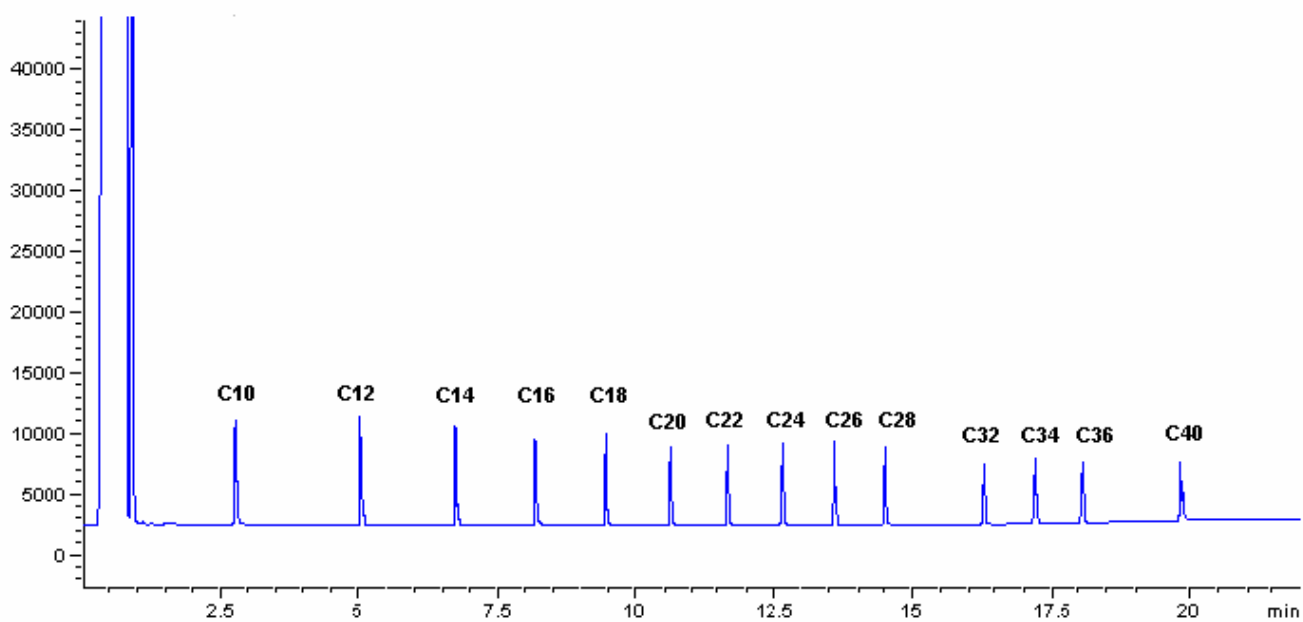


Fig. G.5
Gas chromatogram of a system performance standard solution containing *n*-alkanes with even carbon numbers from C_{10} to C_{40}

Annex G2 (informative)

Determination of the boiling range of mineral oil from the gas chromatogram

Using the data from *Table G.1* the approximate boiling range of the hydrocarbons in the sample can be estimated by comparison of the peak pattern of the sample chromatogram and that of the n-alkane mixture.

Table G.1
Boiling points of the n-alkanes with from 6 to 44 carbon atoms

Number of carbon atoms	boiling point in °C
6	69
7	98
8	126
9	151
10	175
11	196
12	216
13	235
14	253
15	271
16	287
17	302
18	317
19	331
20	344
21	356
22	369
23	380
24	391
25	402
26	412
27	422
28	432
29	441
30	450
31	459
32	468
34	483
35	491
36	498
37	505
38	512
39	518
40	525
41	531
42	537
43	543
44	548

Annex H: Standard Protocol for the determination of the hydrocarbon oil index in water according to ISO 9377 Part 2 (GC-method)

1 Scope

This Standard Protocol specifies a method for the determination of the hydrocarbon content ($C_{10} - C_{40}$) in waters by means of gas chromatography. The method is suitable for surface water, waste water and water from sewage treatment plants and allows the determination of a hydrocarbon oil index in concentrations above 0.1 mg/L.

The method is not applicable to the quantitative determination of the content of volatile mineral oil. However, on the basis of the peak pattern of the gas chromatogram, some qualitative information on the composition of the mineral oil contamination can be derived.

NOTE 1 - The mass concentration of animal and vegetable fat should not exceed 150 mg/L, because at higher values the adsorption capacity of the clean-up column packing may not be sufficient.

NOTE 2 - In case of highly polluted waste water, especially if containing a high amount of surfactants, a loss in recovery may occur.

2 Normative References

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 9377.

ISO 5667-3: 1994, Water quality – Sampling – Part 3: Guidance on the preservation and handling of samples.

ISO 8466-1: 1990, Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.

3 Terms and Definitions

For the purposes of this part of ISO 9377, the following term and definition applies.

Hydrocarbon oil index by GC-FID

The sum of concentrations of compounds extractable with a hydrocarbon compound or mixture, boiling point/range between 36 °C and 69 °C, which do not adsorb on Florisil and which can be chromatographed on a non-polar capillary column with retention times between those of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$).

NOTE - Substances complying with this definition are mainly long chain or branched aliphatic, alicyclic, polycyclic- or alkyl substituted aromatic hydrocarbons.

4 Interferences

Compounds of low polarity (e.g. halogenated hydrocarbons) and high concentrations of polar substances can interfere with the determination. Surface active substances interfere with the extraction step.

5 Principle

The water sample is extracted with an extracting agent. Polar substances are removed by clean up on Florisil. A purified aliquot is analysed by capillary gas chromatography using a non-polar column and a flame ionization detector (FID). The total peak area between n-decane and n-tetracontane is measured. The concentration of mineral oil is quantified against an external standard consisting of two specified mineral oils, and the hydrocarbon oil index is calculated.

It is absolutely essential that the test described in this part of ISO 9377 to be carried out by suitably qualified staff.

6 Reagents

All reagents shall be reagent grade and suitable for their specific purpose.

6.1 Water for the preparation of solutions

Distilled water, or water from a generator of purified water capable of removing organic traces, for example using activated carbon, shall be used.

6.2 Extracting agent,

n-hexane, C_6H_{14}

6.3 Sodium sulfate,

anhydrous, Na_2SO_4 , heated for at least 2 h at 550°C

6.4 Magnesium sulfate heptahydrate,

$MgSO_4 \cdot 7 H_2O$

6.5 Mineral acid,

e.g. hydrochloric acid, $c(HCl) = 12 \text{ mol/L}$ ($\rho = 1.19 \text{ g/mL}$)

6.6 Acetone,

$(CH_3)_2CO$

6.7 Florisil

for preparation of clean-up column, particle size 150 μm to 250 μm (mesh 60 to 100), heated for at least 16 h at 140 °C and stored in a desiccator over a molecular sieve. Alternatively, commercially available Florisil cartridges containing 2 g of Florisil and 2 g of sodium sulphate are also applicable.

NOTE - Florisil is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of this Standard and does not constitute an endorsement of this product. Equivalent products may be used if it can be shown to lead to comparable results.

6.8 Mixture of mineral oils

6.8.1 Standard mixture

Weigh approximately equal amounts of two different types (type A and type B, both containing no additives) of min-

eral oil and add enough extraction solvent stock solution (6.11.1) to give a total hydrocarbon concentration of about 10 g/L.

Type A should show discrete peaks in the gas chromatogram as can be seen in Annex H1, Figure H1 (left part of the chromatogram). A suitable oil of this type is diesel fuel without any additives. Type B should have a boiling range higher than that of type A and should have unresolved signals ("hump") in the gas chromatogram, as can be seen in Annex H1, Figure H1 (right part of the chromatogram). A suitable oil of this type is a lubricating oil without any additives.

NOTE - General purpose hydrocarbon standards for calibration can be obtained from many commercial organisations. Calibration standards specific to this Standard Protocol can be purchased from Bundesanstalt für Materialforschung und -prüfung, Fachgruppe I.2, Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany.

This information is given for the convenience of users of this Standard Protocol and does not constitute an endorsement of this product.

6.8.2 Calibration mixture

Prepare at least five different calibration solutions by diluting aliquots of standard mixture (6.8.1) with the extraction solvent stock solution (6.11.1). Store the calibration mixture tightly sealed.

6.8.3 Quality Control (QC) standard

Prepare an independent control solution according to 6.8.1 in acetone (6.6) with a hydrocarbon concentration of about in the middle of the working range (e.g. 1 mg/mL).

NOTE – This solution is used to perform the procedural recovery test (9.2).

6.9 System performance standard solution

Prepare a mixture of equal amounts, on a mass basis, of the n-alkanes with even carbon numbers from C_{10} to C_{40} , dissolved in extracting agent (6.2), to give concentrations of about 50 mg/L of each n-alkane. Store this solution at room temperature.

NOTE 1 - This solution is used to verify the suitability of the gas chromatographic system for the resolution of n-alkanes as well as for the detector response.

NOTE 2 - This solution is used to give information of the retention times of the n-alkanes to characterise the hydrocarbons in the samples.

6.10 Reference compounds

6.10.1 n-Decane, $C_{10}H_{22}$

6.10.2 n-Tetracontane, $C_{40}H_{82}$

6.10.3 n-Eicosane, $C_{20}H_{42}$

6.11 Extraction solvent with reference compounds

6.11.1 Extraction solvent stock solution

Weigh (20+1) mg of n-tetracontane (6.10.2) into an 1 L volumetric flask, dissolve completely in an appropriate volume of extracting agent (6.2), add 20 μ L of n-decane (6.10.1) (about 14 mg), mix well, fill up to volume with extracting agent and homogenise. Store this solution tightly sealed at room temperature.

NOTE - n-tetracontane is only moderately soluble in the extracting agent. Slight warm up and/or sonication accelerates the dissolution process.

6.11.2 Extraction solvent standard solution

Immediately prior to use, dilute the extraction solvent stock solution (6.11.1) with tenfold extracting agent (6.2).

NOTE – This solution is used for sample extraction.

6.12 Test solution of stearyl stearate, ($C_{36}H_{72}O_2$)

Dissolve 200 mg of stearyl stearate (n-octadecanoic acid octadecyl ester) in 100 mL of extracting agent (6.2). Store this solution tightly sealed at room temperature.

NOTE - This solution is used to check the efficiency of the clean up procedure.

6.13 Preparation of the clean-up column

A plug of pre-washed glass wool or a PTFE frit is pushed down into the column (7.7). Then, successively 2 g of Florisil (6.7) and 2 g of sodium sulphate (6.3) are added. The column shall be prepared immediately before use.

NOTE - Alternatively, commercially available Florisil cartridges containing 2 g of Florisil covered with 2 g of sodium sulphate are also applicable.

7 Apparatus and equipment

7.1 Standard laboratory glassware

Clean all glassware by the usual procedures for this type of analysis. If necessary, rinse the glassware with extracting agent (6.2).

7.2 Gas chromatograph,

equipped with a non-discriminating injection system (preferably on-column or programmable temperature vaporisation injection), a capillary column and a flame ionisation detector (FID).

NOTE - The use of a large volume injection system can improve the limit of detection considerably.

7.3 Column for gas chromatography,

fused silica, with one of the following stationary phases and typical dimensions:

Stationary phase: non-polar, e.g. immobilized 100 % dimethyl polysiloxane, 95 % dimethyl-5 %-diphenyl polysiloxane, modified siloxane polymer, etc.

length: 5 m to 30 m

internal diameter: 0.25 mm to 0.53 mm

Film thickness: 0.25 μ m to 1.2 μ m

NOTE 1 - Thermally stable low bleed columns should be preferred.

NOTE 2 - The use of a pre-column, e.g. wide-bore (0.53 mm I.D.) deactivated fused silica of at least 2 m of length that suits to the analytical column and connected to it using zero-volume connector is recommended.

7.4 Data system,

suitable for integrating the total area of the gas chromatogram between C_{10} and C_{40} and suitable for re-integrating after defining a new base line according to (9.7.5).

7.5 Sampling bottles,

glass, with ground glass stopper, capacity 250 mL and 1000 mL, or with screw cap, lined with PTFE (polytetrafluoroethene). The sampling bottle shall allow direct extraction from the bottle.

7.6 Microseparator,

example see Annex H3, or other suitable device for phase separation.

7.7 Chromatography column for clean-up,

glass columns of about 10 mm to 22 mm I.D. shall be used. The upper part of the column should be widened to use as solvent reservoir and the lower part to be narrowed to form a tip.

7.8 Kuderna Danish apparatus,

with a 250 mL flask or other suitable concentration apparatus, e.g. a rotary evaporator with controlled vacuum.

7.9 Magnetic stirrer with bar,

length suitable to ensure thorough mixing.

8 Sample conservation

The samples shall be kept sealed in darkness at about 4 °C and extracted within 4 days after arrival.

NOTE - If formation of emulsions or a concentration of animal and vegetable oil > 150 mg/L are expected, it is advisable to withdraw additionally a smaller sample volume in a 250 mL sampling bottle.

9 Procedure

9.1 Procedural blank

With each series of samples a procedural blank determination has to be carried out according to 9.3 using all reagents and glassware in the same way as for the samples but without a sample.

Procedural blank values shall not exceed 10 % of the lowest sample value. If the procedural blank values do not fulfil this requirement every step in the procedure shall be checked to find the reason for these high procedural blanks. Eliminate the source of impurities and repeat the procedural blank.

NOTE 1 – The 10 % rule for the procedural blank is limited by the limit of determination. Only values higher than the limit of determination can be quantified

NOTE 2 - A “negative procedural blank” (if the peak area of the procedural blank is lower than the intercept of the calibration function) could be caused either by impurities of extracting agent, which adsorb on Florisil or by a high uncertainty of the intercept of the calibration function.

9.2 Determination of the recovery

Determine the recovery at regular intervals, preferably in each series of samples, using 900 mL of water (6.1) to which 1 mL of the QC standard (6.8.3) has been added. Perform the test starting with 9.3 and calculate the recovery. Ensure that the recovery is between 80 % and 110 %.

9.3 Extraction procedure

Cool the sample to about 10 °C, if necessary, to prevent losses of the extracting agent by volatilization.

Weigh the filled sample bottle prior to extraction (m_1) to an accuracy of 1 g. The sample volume should be about 900 mL. Acidify the sample to pH 2 by adding mineral acid (6.5). Add about 80 g of magnesium sulphate (6.4) per 900 mL of sample to avoid emulsions.

Add 50 mL of extraction solvent standard solution (6.11.2) and a magnetic stirrer bar, close the bottle and stir vigorously for 30 minutes on the magnetic stirrer (7.9). Let phases separate for approximately 30 min. Remove the stopper and replace it by the microseparator (7.6). Add enough water (6.1) to allow withdrawal of the organic extract layer from the microseparator. Collect the organic phase in e.g. an 100 mL Erlenmeyer flask. Add anhydrous sodium sulphate as far as lumps are not formed any longer. Then, transfer the clear extract to the clean up column (7.7). Wash the sodium sulphate thrice with small volumes of the extraction solvent and transfer the washings to the Florisil column (7.7) as well. Proceed according to 9.4.

Leave the empty sample bottle to drain for 5 minutes. Close the bottle with the previously used cap and determine its mass (m_2) to an accuracy of 1 g.

NOTE 1 – Alternatively, extraction by shaking for 30 minutes is also applicable.

NOTE 2 - In the case of strong emulsions centrifugation can be applied to improve and accelerate phase separa-

tion provided the necessary safety precautions, especially with regard to inflammable solvents, are taken into account. Ultrasonic treatment can also be applied for improving phase separation.

9.4 Clean up procedure

Pre-rinse the clean-up column (7.7) filled with 2 g of Florisil and 2 g of Na_2SO_4 with 10 mL of extracting agent (6.2) to prevent the formation of channels and to remove interfering compounds possibly adsorbed on Florisil and/or sodium sulphate. Discard the eluted extracting agent.

Transfer the entire organic phase (see 9.3) to the clean-up column. Take care to avoid the transfer of water as this will incrust the surface of the sodium sulphate. It is recommended to transfer the organic layer in several steps using a pipette, or, when using the microseparator (7.6) to position the meniscus below the cock.

Let the organic extract phase run through the column; rinse the column with 10 mL of extracting agent (6.2); collect the entire eluate in a suitable concentration apparatus (7.8).

9.5 Concentration

Using the evaporation apparatus (7.8), concentrate the extract to a volume of approximately 6 mL. Concentrate the extract further to slightly less than 1 mL using a gentle flow of nitrogen. Make up to a volume of 1 mL with extracting agent (6.2) or calculate the exact volume of the concentrated extract by weighing using the density of the extracting agent. Transfer an aliquot of the final extract to a GC-vial and analyse by gas chromatography.

NOTE - Concentration of the extract to 1 mL may be omitted if a high hydrocarbon oil index is expected or if a large quantity, e.g. 100 μL , of the partially or non-concentrated extract is injected by means of the so-called "large volume injection system".

When using a large volume injection, it is necessary to bring the extract to a known volume, e.g. 50 mL or 100 mL after treatment with Florisil. In this case the concentration of the calibration solution (6.8) and the system performance solution (6.9) should be correspondingly lower.

9.6 Suitability testing of Florisil

Check the suitability of Florisil at regular intervals and each time a new batch of dried Florisil is used, as follows:

Perform the clean up procedure (9.4) with 10 mL of the stearyl stearate solution (6.12), then add extracting agent (6.2) to a volume of 25 mL. Transfer an aliquot of the purified solution to a GC-vial and analyse by gas chromatography (9.7).

Dilute 0.5 mL of stearyl stearate solution with extracting agent (6.2) to 25 mL and analyse by gas chromatography. Calculate the ratio of the peak areas for stearyl stearate in the treated and in the untreated solution. This ratio should be less than 1 (that corresponds to a stearyl stearate recovery of less than 5 %). If not, activate the Florisil according to 6.7.

Perform the clean up procedure (9.4) with 10 mL of a 2 mg/mL calibration solution of mineral oils (6.8), then add

extracting solvent standard solution (6.11.2) to a volume of 25 mL. Transfer an aliquot of the purified solution into a GC-vial and analyse by gas chromatography. Dilute 10 mL of a 2 mg/mL calibration solution of mineral oils (6.8) with extracting solvent standard solution (6.11.2) to 25 mL and analyse by gas chromatography. Determine the mineral oil recovery on the basis of the peak area between C_{10} to C_{40} in the treated (with Florisil) and untreated calibration solution. The mineral oil recovery should be at least 80 %.

9.7 Determination by gas chromatography

9.7.1 Adjusting the gas chromatograph

Select a capillary column with one of the specified stationary phases (see 7.3) for gas chromatographic analysis. Adjust the gas chromatograph to provide an optimal separation. The peaks in the gas chromatogram of the standard mixture of *n*-alkanes (6.9) shall be baseline-separated. The relative response (peak area) of *n*-tetracontane ($C_{40}H_{82}$) compared with *n*-eicosane ($C_{20}H_{42}$) should be at least 0.8. If not, the discrimination of the injection system is too high and the injection system shall be optimised or replaced.

9.7.2 Repeatability Test

Record a gas chromatogram by injection of an appropriate volume of extracting agent. Inject the same volume of a calibration solution three times and record the chromatogram for each injection. The concentration of this calibration solution shall lie between 40 % and 80 % of the working range. Correct the chromatograms of the calibration solution by subtracting the chromatogram of solvent and integrate the corrected chromatograms according to 9.7.5; calculate the mean of the measured peak areas and the corresponding standard deviation. The relative standard deviation shall not exceed 5 %.

9.7.3 Calibration

9.7.3.1 General

For calibration a distinction is made between initial calibration, working calibration and checking of the validity of the calibration curve. Initial calibration determines the working range and the linearity of the calibration function according to ISO 8466-1. Perform this calibration when the apparatus is used for the first time.

In the next step establish the final working range and perform the routine calibration. Carry out this calibration after maintenance (e.g. replacement of the capillary column), after repair of the gas chromatographic systems, and in case the system has not been in use for a longer period of time, or if the validity criteria cannot be met. Check the validity of the initial calibration with each series of samples to be analysed.

9.7.3.2 Initial calibration

Establish the preliminary working range by analysing at least five calibration mixture solutions (6.8.2). Test for linearity according to ISO 8466-1.

9.7.3.3 Routine calibration

After examining the final working range analyse a minimum of five calibration mixture solutions (6.8.2). Calculate

a calibration function by linear regression analysis of the corrected peak areas. The actual sensitivity of the method may be estimated from the calculated regression function.

9.7.3.4 Validity check of the calibration function

Check the validity of the calibration function from the routine calibration with each batch of samples by analysis of one standard solution after every ten samples. The concentration of this standard solution shall lie between 40 % and 80 % of the working range. Make sure that the individual results do not deviate by more than 10 % of the working calibration line. If this is the case the actual calibration function is assumed to be valid. If not, re-calibrate according to 9.7.3.3.

For large batches of samples the number of analyses of the standard solution may be reduced, provided that at least 3 measurements are obtained for calculating the mean result.

NOTE - Alternatively, control charts can be used to check the validity of the calibration function. In this case the ordinary rules for the interpretation of control charts (ISO 8258) shall be considered.

9.7.4 Measurement

Measure the concentrated purified sample extracts (9.5), the calibration solutions (6.8.2), the procedural blank (9.1) and the extracting agent (6.2) under identical gas chromatographic conditions. Extracting agent shall be analysed in each sample batch.

NOTE 1 - The sample extracts shall be kept sealed at room temperature and analysed within 3 days. The storage of extracts at lower temperatures (e.g. in a refrigerator) can lead to a crystallisation of n-tetracontane (and other compounds).

NOTE 2 - An increase in 'column bleeding' may indicate contamination of the injection system or the column.

NOTE 3 - If samples are to measure, which contain hydrocarbons in a high boiling range or are highly contaminated, a subsequent GC-run by injecting n-heptane is recommended to demonstrate the absence of impurities in the GC-system.

9.7.5 Integration parameters

Correct all chromatograms for column bleeding by subtracting the chromatogram of extracting agent (6.2) prior to integration.

Integrate the total area of the resulting gas chromatograms between the n-decane (C₁₀H₂₂) and n-tetracontane (C₄₀H₈₂) peaks. Start the integration just after the n-decane peak at the signal level in front of the solvent peak. End the integration just before the beginning of the n-tetracontane peak on the same signal level (see Annex H1). All chromatograms should be checked visually for correct integration. The start and stop times of the integration should be visible on the chromatogram.

The presence of peaks between solvent peak and n-decane indicates that the sample probably contains low-boil-

ing, volatile hydrocarbons. This should be mentioned in the test report.

Discrete peaks or an increased level of the baseline at the end of the chromatogram (retention time greater than the of n-tetracontane) indicate that the sample probably contains hydrocarbons with a high boiling point. This should be mentioned in the test report.

NOTE 1 - If the data system is capable to perform the integration procedure without a prior baseline correction by subtraction of a solvent chromatogram, it is not necessary to correct the chromatograms of procedural blanks (9.1), sample extracts (9.5), calibration standards (6.8.2) and QC-solutions of recovery test (9.2). But all integrations have to be done using only one selected procedure.

NOTE 2 - The range of the carbon numbers of n-alkanes present in the sample is determined by comparing the gas chromatogram of the sample extract with that of n-alkane standard solution (6.9). The corresponding boiling range can be derived from Annex H2.

NOTE 3 - Peak shape and signal intensity of n-decane and n-tetracontane are sensitive to changes in the surface properties of the injector and/or the pre-column due to contamination by sample constituents. Therefore, they can be used as a good indication for replacing pre-column and/or liner.

9.8 Calculation

Calculate the hydrocarbon oil index of the sample using Equation 1:

$$\rho = \frac{c \cdot f \cdot V}{(m_1 - m_2)} \quad (\text{Eq. 1})$$

where:

ρ is the hydrocarbon oil index, in milligrams per litre [mg/L]

c is the hydrocarbon concentration of extract calculated from calibration function, in milligrams per millilitre [mg/mL]

f is any dilution factor of the sample extract

V is the volume of the final extract, in millilitres [mL]

m_1 is the mass of the filled sampling bottle in grams [g]

m_2 is the mass of the empty sample bottle in grams [g]

Calculate the procedural blank in the same way as the sample. Do not subtract the procedural blank value from the sample value but report the procedural blank in addition to the sample value. Please be aware that only values higher the limit of determination can be quantified.

9.9 Expression of results

Express the concentration of mineral oil in water as hydrocarbon oil index, in milligrams per litre, to three significant figures. Examples:

Hydrocarbon oil index	15.1 mg/L
Hydrocarbon oil index	2.95 mg/L
Hydrocarbon oil index	0.526 mg/L

10 Test report

The test report shall contain at least the following information:

- a) The date of sample arrival in the lab and the date of commencement of the analysis;
- b) a reference to the used method (extraction method; clean-up, analytical conditions);
- c) a complete identification of the sample;
- d) the hydrocarbon oil index, in milligrams per litre;
- e) statement of the uncertainty of the results;
- f) any peculiarities observed during the test;
- g) any details not specified in this protocol or which are optional, as well as any other factor that might have affected the results;
- h) a reference to the occurrence of low ($< C_{10}$) and/or high boiling ($> C_{40}$) compounds in the chromatogram

Annex H1 (informative)

Examples of gas chromatograms

Figure H.1 shows the gas chromatogram of the calibration mixture of mineral oil consisting of equal parts of a diesel fuel and a lubricating oil. Figure H.2 shows the same gas chromatogram after correction for the column bleed and integration. The total peak area between n-decane (C_{10}) and n-tetracontane (C_{40}) used for quantification is indicated as hatched area.

The Figures H.3 and H.4 show integrated gas chromatograms corrected for the column bleed of contaminated soil and waste samples, respectively.

Figure H.5 shows the gas chromatogram of the system performance standard solution containing n-alkanes with even carbon numbers from C_{10} to C_{40} .

The chromatograms have been recorded under the following conditions:

Injection technique: on-column

Injection volume:	2 μ L
Column:	fused silica capillary column
Column length:	12 m
Internal diameter:	0.25 mm
Liquid phase:	BPX-5
Film thickness:	1.0 μ m
Pre-column:	deactivated fused silica capillary, 2 m x 0.53 mm
Carrier gas:	Helium
Pressure:	150 kPa
Detector:	Flame ionisation detector
Detector temperature:	360 $^{\circ}$ C
Oven temperature:	80 $^{\circ}$ C for 1 min 20 $^{\circ}$ C/min to 360 $^{\circ}$ C

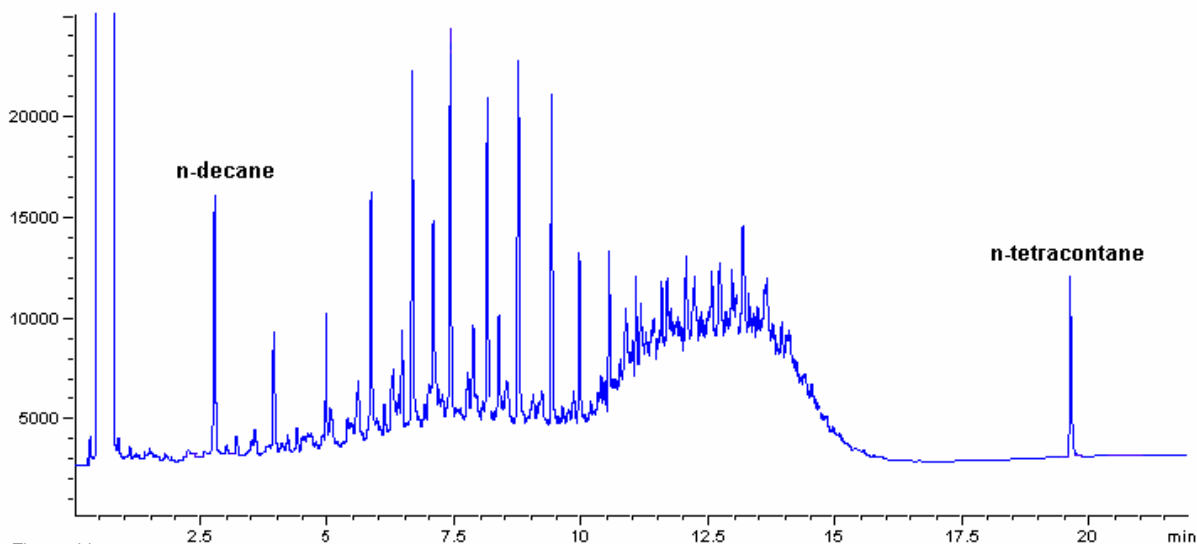


Figure H.1
Gas chromatogram of the hydrocarbon standard solution (6.8) consisting of equal parts of diesel fuel and lubricating oil

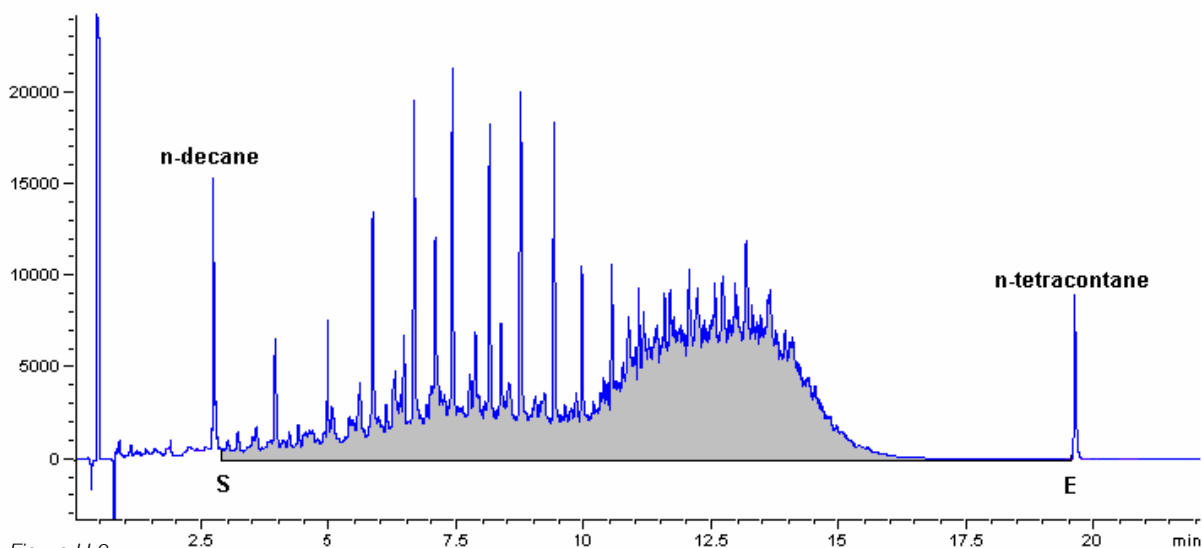


Figure H.2
Integrated gas chromatogram of the hydrocarbon standard solution (6.8) corrected for the "column bleed"

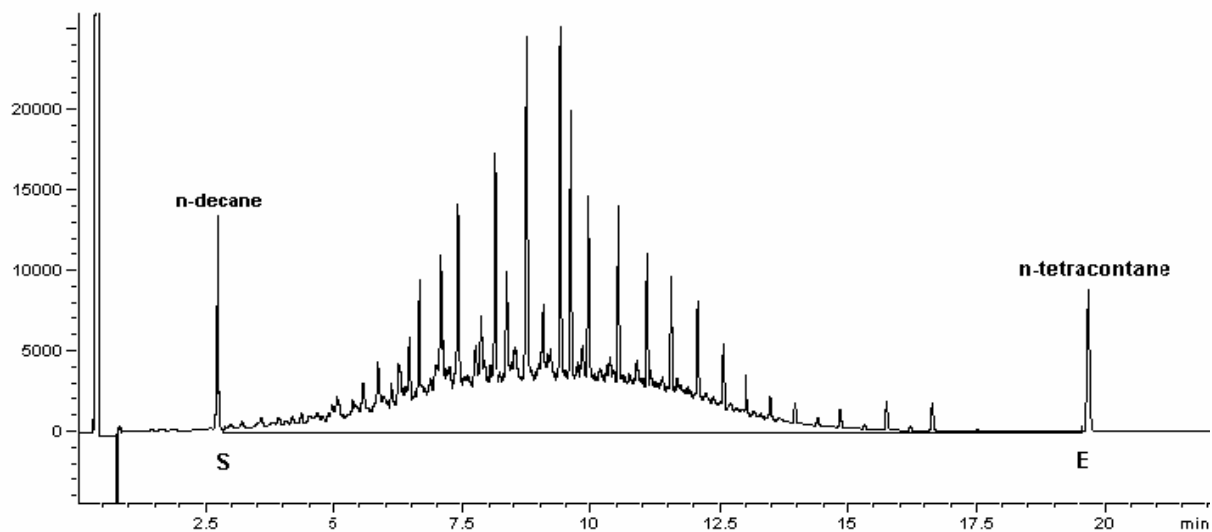


Figure H.3
 Integrated gas chromatogram of a contaminated soil sample corrected for the "column bleed"

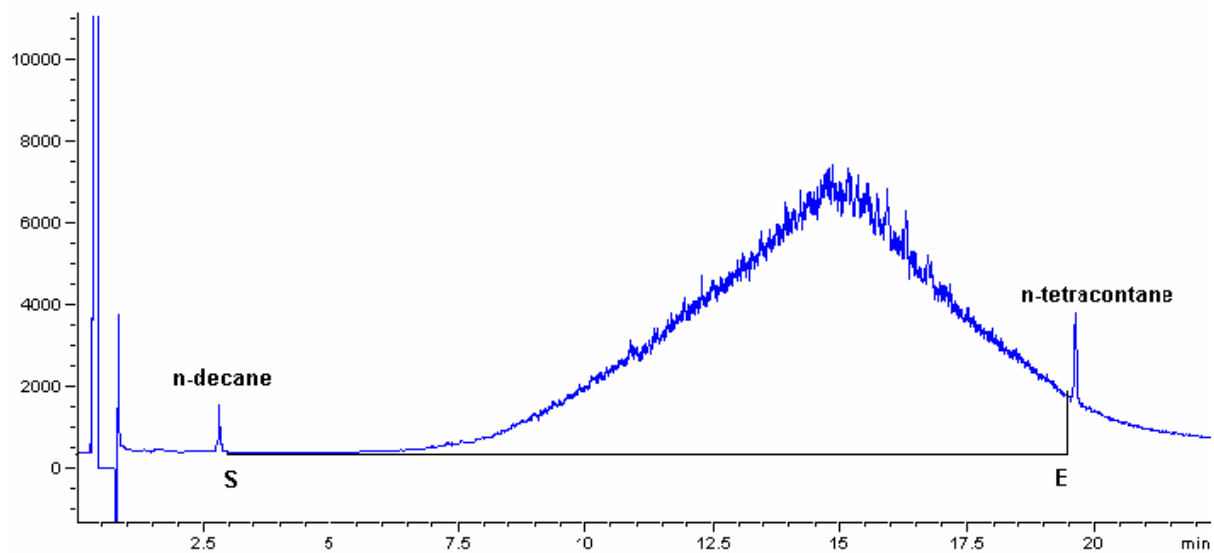


Figure H.4
 Integrated gas chromatogram of a highly contaminated waste sample corrected for the "column bleed"

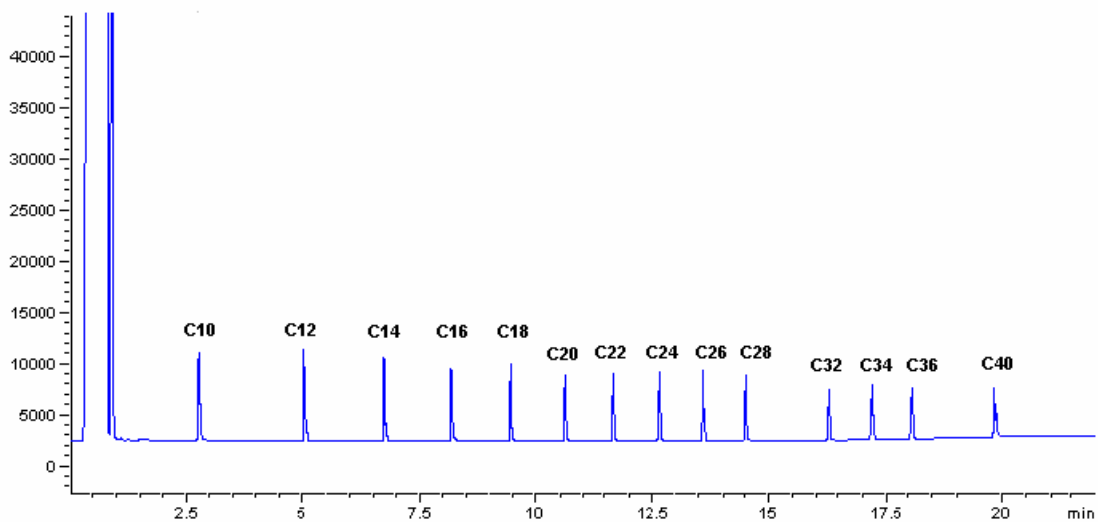


Figure H.5
 Gas chromatogram of a system performance standard solution containing n-alkanes with even carbon numbers from C₁₀ to C₄₀

Annex H2 (informative)

Determination of the boiling range of mineral oil from the gas chromatogram

Using the data from Table H.1 the approximate boiling range of the hydrocarbons in the sample can be estimated by comparison of the peak pattern of the sample chromatogram and that of the n-alkane mixture.

Table H.1

Boiling points of the n-alkanes with from 6 to 44 carbon atoms

Number of carbon atoms	boiling point in °C
6	69
7	98
8	126
9	151
10	175
11	196
12	216
13	235
14	253
15	271
16	287
17	302
18	317
19	331
20	344
21	356
22	369
23	380
24	391
25	402
26	412
27	422
28	432
29	441
30	450
31	459
32	468
34	483
35	491
36	498
37	505
38	512
39	518
40	525
41	531
42	537
43	543
44	548

Annex H3 (informative)

Example of a microseparator

Figure H.6 shows an example of a microseparator separation of the organic extraction phase from sample according to (7.6) of the Standard Proto
 Dimensions in millimeter

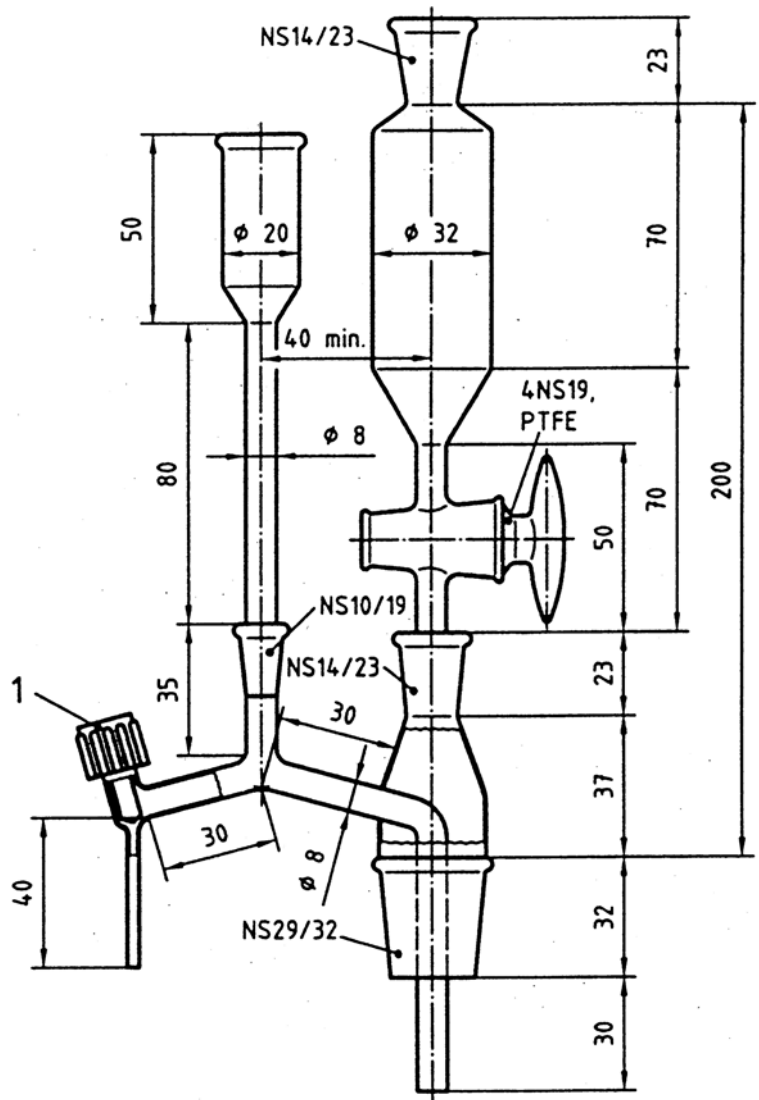


Figure H.6
 Example of a microseparator

9 References

- 1 ISO/TR 11046: Soil quality – Determination of mineral oil content – Method by infrared spectrometry and gas chromatographic method. ISO/TC 190/SC 3, 1994
- 2 ISO 9377-2: Water quality - Determination of hydrocarbon oil index: Method using solvent extraction and gas chromatography. ISO/TC 147/SC 2/WG 15, 2000
- 3 ISO/FDIS 16703: Soil Quality - Determination of hydrocarbon content in the range of C₁₀ to C₄₀ by gas chromatography. ISO/TC 190/SC 3, 2003
- 4 ENpr 14039: Determination of hydrocarbon content by GC in the range of C₁₀-C₄₀. Characterisation of waste. CEN/TC 292, 2000
- 5 EC/BCR GUIDELINES for Feasibility Studies on Certified Reference Materials, EUR 20574 EN, 2002
- 6 ISO Guide 35 (3rd edition): Certification of reference materials – General and statistical principles. ISO/REMCO WG 1, 2003
- 7 van der Veen AMH, Pauwels J (2000) *Accred Qual Assur* 5:464-469
- 8 van der Veen AMH, Linsinger T, Pauwels J (2001) *Accred Qual Assur* 6:26-30
- 9 Linsinger TPJ, van der Veen AMH, Gawlik BM, Pauwels J, Lamberty A (2004) *Accred Qual Assur* 9:464-472
- 10 Linsinger TPJ, Pauwels J, Schimmel H, Lamberty A, van der Veen AMH, Schumann G, Siekmann L (2000) *Fresenius J Anal Chem* 368:589-594
- 11 Linsinger TPJ, Pauwels J, van der Veen AMH, Schimmel H, Lamberty A (2001) *Accred Qual Assur* 6:20-25
- 12 Linsinger TPJ, Pauwels J, Lamberty A, Schimmel HG, van der Veen AMH, Siekmann L (2001) *Fresenius J Anal Chem* 370:183-188
- 13 Lamberty A, Schimmel H, Pauwels J (1998) *Fresenius J Anal Chem* 360:359-361
- 14 van der Veen AMH, Linsinger TPJ, Lamberty A, Pauwels J (2001) *Accred Qual Assur* 6:257-263
- 15 Pauwels J, Lamberty A, Schimmel H (1998) *Fresenius J Anal Chem* 361:395-399
- 16 Pauwels J, Lamberty A, Schimmel H (1998) *Accred Qual Assur* 3:180-184
- 17 Guidelines for the production and certification of BCR reference materials (1997) – document BCR/01/97, European Commission, Dg XII-5-C (SMT Programme)

List of abbreviations

AED	Atom-Emission-Detector	FDIS	Final Draft International Standard
ASE™	Accelerated Solvent Extraction	m/e	Mass-Charge-Ratio
BCR	Bureau Communautaire de Référence	MS	Mass Spectrometry
CEN	European Committee for Standardisation	n	Number of independent measurements
CFCs	Chlorofluorocarbons	pH	Logarithm of the Reciprocal of the Hydrogenion Concentration
CRM	Certified Reference Material	PAH	Polycyclic Aromatic Hydrocarbon
dm	Dry Matter Content	RM	Reference Material
EC	European Commission	RSD	Relative Standard Deviation
EN	European Standardisation	RTW	Retention Time Window
ENpr	Draft European Standard	SD	Standard Deviation
FID	Flame-Ionisation-Detector	TC	Total Carbon
Florisil	Florisil®	TIC	Total Inorganic Carbon
GC	Gas Chromatography	TOC	Total Organic Carbon
ILC	Interlaboratory Comparison	TPH	(Total) Petroleum Hydrocarbons
IR	Infrared Spectroscopy	WP	Work Package
ISO	International Organization for Standardization		
DIS	Draft International Standard		