

Eija Saari

TOWARDS MINIMIZING
MEASUREMENT
UNCERTAINTY IN TOTAL
PETROLEUM HYDROCARBON
DETERMINATION BY GC-FID

FACULTY OF SCIENCE,
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF OULU

A

SCIENTIAE RERUM
NATURALIUM



ACTA UNIVERSITATIS OULUENSIS
A Scientiae Rerum Naturalium 544

EIJA SAARI

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Academic dissertation to be presented with the assent of
the Faculty of Science of the University of Oulu for public
defence in Auditorium TA105, Linnanmaa, on 18
December 2009, at 12 noon

OULUN YLIOPISTO, OULU 2009

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Acta Univ. Oul. A 544, 2009

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ISBN 978-951-42-6075-9 (Paperback)
ISBN 978-951-42-6076-6 (PDF)
<http://herkules.oulu.fi/isbn9789514260766/>
ISSN 0355-3191 (Printed)
ISSN 1796-220X (Online)
<http://herkules.oulu.fi/issn03553191/>

Cover design
Raimo Ahonen

OULU UNIVERSITY PRESS
OULU 2009

Saari, Eija, Towards minimizing measurement uncertainty in total petroleum hydrocarbon determination by GC-FID.

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Acta Univ. Oul. A 544, 2009

Oulu, Finland

Abstract

Despite tightened environmental legislation, spillages of petroleum products remain a serious problem worldwide. The environmental impacts of these spillages are always severe and reliable methods for the identification and quantitative determination of petroleum hydrocarbons in environmental samples are therefore needed. Great improvements in the definition and analysis of total petroleum hydrocarbons (TPH) were finally introduced by international organizations for standardization in 2004. This brought some coherence to the determination and, nowadays, most laboratories seem to employ ISO/DIS 16703:2004, ISO 9377-2:2000 and CEN prEN 14039:2004:E draft international standards for analysing TPH in soil. The implementation of these methods, however, usually fails because the reliability of petroleum hydrocarbon determination has proved to be poor.

This thesis describes the assessment of measurement uncertainty for TPH determination in soil. Chemometric methods were used to both estimate the main uncertainty sources and identify the most significant factors affecting these uncertainty sources. The method used for the determinations was based on gas chromatography utilizing flame ionization detection (GC-FID).

Chemometric methodology applied in estimating measurement uncertainty for TPH determination showed that the measurement uncertainty is in actual fact dominated by the analytical uncertainty. Within the specific concentration range studied, the analytical uncertainty accounted for as much as 68–80% of the measurement uncertainty. The robustness of the analytical method used for petroleum hydrocarbon determination was then studied in more detail. A two-level Plackett-Burman design and a D-optimal design were utilized to assess the main analytical uncertainty sources of the sample treatment and GC determination procedures. It was also found that the matrix-induced systematic error may also significantly reduce the reliability of petroleum hydrocarbon determination.

The results showed that strict implementation of the ISO and CEN draft standards is necessary owing to the method dependence of the analyzed parameter. Care should be taken to ensure that the methods used for petroleum hydrocarbon determination are comprehensively validated, and that routine quality control is carried out in order to ensure that the validation conclusions are applicable in the daily work.

Keywords: extraction, gas chromatography, measurement uncertainty, petroleum hydrocarbons, soil analysis

*“There is an understandable lack of enthusiasm for rousing
the sleeping dogs
of sampling when there is a fair chance of being severely
bitten”*

– Michael Thompson

Acknowledgements

The research for this thesis was carried out at the Department of Chemistry, University of Oulu, during the years 2005–2008. Financial support from the Neste Oy Foundation is gratefully acknowledged.

I wish to express sincere gratitude to my supervisor, Professor Paavo Perämäki, for allowing me to design and implement this thesis in my own way and with my own ideas. His encouraging attitude to explore the interesting field of analytical chemistry was certainly vital for the outcome of this thesis. Especially, I am indebted to his patient support in getting this thesis finished. I also express my deep gratitude to Ph. Lic Henrik Westerholm (Neste Oil Oyj, Porvoo Refinery) for having shared his expertise in the field of oil refining technology and for arousing my interest in the constructive elements of this thesis.

My specific thanks go to Päivi Joensuu (Department of Chemistry, University of Oulu) for providing me with the instrumental support, to Seppo Nikunen (Pöyry Building Services Oy) for his co-operation and to Mia Virtanen (Golder Associates Oy) for letting me carry out the primary sampling in a remediation site. I'm also indebted to PhD Risto Pöykiö and PhD Veikko Kitunen for the scientific and to PhD John Derome for the linguistic revision of the original manuscript.

And then, last but not least, I am most indebted to you, Kaisa, for your personal support and trust. It was actually your vision that encouraged me to reach for the impossible. I also wish to express my sincere gratitude to you, Marjatta. In fact, both of you deserve special thanks for providing me with the opportunity of a lifetime to do research in one of the most fascinating fields of chemistry.

Finally, my deepest gratitude goes to my husband, Tapani, and to my dear children, Tuomas, Tanja and Timi, for all the patience and understanding they have shown throughout this project. You are the most valuable thing in my life.

The inspiration for these studies matured along the intelligent and strong musical elements of the Sonata Arctica albums from *Ecliptica* to *Unia*.

Oulu, November 2009

Eija Saari

Abbreviations and definitions

ANOVA	analysis of variance
CEN	European Committee for Standardization
CITAC	international organization with the mission to improve co-operation on international traceability in analytical chemistry
ERM-CC015a	a certified reference material (mineral oil contaminated sediment, TPH 1820 ± 130 mg/kg)
EURACHEM	a network of organizations in Europe having the objective of establishing a system for the international traceability of chemical measurements and the promotion of good quality practices
FT-ICR-MS	Fourier transform ion cyclotron resonance mass spectrometry
GC-FID	gas chromatography flame ionization detection
GC-MS	gas chromatography mass spectrometry
ISO	International Organization for Standardization
MODDE	a commercial computer program for statistical experimental design
MWAE	microwave-assisted extraction
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
SPSS	a commercial statistical computer program
TPH	total petroleum hydrocarbons
Type A evaluation (top-down)	method for evaluating uncertainty by the statistical analysis of series of observations
Type B uncertainty (bottom-up)	method for evaluating uncertainty by means other than the statistical analysis of series of observations
US	ultrasonic
USEPA	U.S. Environmental Protection Agency
a	slope of a calibration line
b	intercept of a calibration line
rsd	relative standard deviation
s	standard deviation

s_e	spread of measurements around the fitted regression line
s_{ep}^2	pooled estimated variance
U_{rel}	expanded uncertainty (relative)
n	number of replicates
m	number of replicates

List of original publications

This thesis is based on the following original papers, which are referred to in the text by Roman numerals:

- I Saari E, Perämäki P, Jalonen J (2007) A comparative study of solvent extraction of total petroleum hydrocarbons in soil. *Microchim. Acta* 158: 261–268.
- II Saari E, Perämäki P, Jalonen J (2007) Effect of sample matrix on the determination of total petroleum hydrocarbons (TPH) in soil by gas chromatography-flame ionization detection. *Microchem J* 87: 113–118.
- III Saari E, Perämäki P, Jalonen J (2008) Measurement uncertainty in the determination of total petroleum hydrocarbons (TPH) in soil by GC-FID. *Chemometrics and Intelligent Laboratory Systems* 92: 3–12.
- IV Saari E, Perämäki P, Jalonen J (2008) Evaluating the impact of extraction and cleanup parameters on the yield of total petroleum hydrocarbons in soil. *Anal Bioanal Chem* 392: 1231–1240.
- V Saari E, Perämäki P, Jalonen J (in press) Evaluating the impact of GC operating settings on GC-FID performance for total petroleum hydrocarbon (TPH) determination. *Microchem J* (in press) DOI: doi:10.1016/j.microc.2009.09.004.

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1 Introduction

Oil consumption has increased steadily during recent decades along with the growing demand for energy worldwide. (1) Despite this growth in consumption the total amount of spillages has been decreasing, mainly due to tightened environmental legislation. (2) However, the release of petroleum products into the environment still remains a serious and increasingly prevalent problem. The estimated amount spilled during the period 1991–2000 was nearly 1 600 000 tonnes. The severe impacts of these spillages have created an urgent need for developing more reliable methods for the identification and quantification of petroleum products in the environment.

According to ISO, the reliability of a measurement can be expressed by stating the uncertainty of a measurement result. However, the assessment of measurement uncertainty for environmental analysis is a great challenge for environmental and analytical chemists because a comprehensive understanding is required of the performance of the whole analysis chain in order to produce valid information about the type and extent of contamination. Thus, the primary sampling stage must also be recognized as a source of uncertainty that affects the reliability of the measurement result. (3, 4)

The concepts and practices of analytical uncertainty assessment have been well described and are recognized by analytical chemists. However, the incorporation of primary sampling uncertainty means that measurement uncertainty assessment becomes a multidisciplinary subject that goes well beyond traditional analytical chemistry and incorporates chemometrics, sampling theory and national guidelines on the environmental monitoring of harmful substances. The estimation process also becomes laborious in practice because it requires comprehensive sampling strategy planning and realization, as well as a large number of replicated assays.

Despite these difficulties, measurement uncertainty assessment and minimization will become increasingly important steps in environmental studies. As a number of studies have already demonstrated, it can, depending on the analyte, be either the primary sampling or the analytical stage that contributes the largest source (50–70%) of measurement uncertainty. (5–8) Therefore, if the reliability of environmental analysis is to be improved, then the dominating sources of uncertainty have to be identified and minimized. Only then can the measurement uncertainty be efficiently reduced and appropriate assessment of the

environmental risks, as well as the selection and allocation of remediation resources, be carried out reliably.

1.1 Characteristics of petroleum products

Petroleum products are derived from crude oil by fractional distillation. In a simplified description of petroleum refining, crude oil is first distilled into different boiling range fractions which are then further treated by a range of conversion, blending and additive treatment processes. (9) A processed petroleum product is a highly complex mixture of thousands of different organic compounds including paraffinic compounds (C_nH_{2n+2}), naphthenic compounds (cycloparaffines, C_nH_{2n}), olefinic compounds (alkenes, C_nH_{2n}), aromatic and polycyclic aromatic hydrocarbons (PAH), as well as heteroatom (N, O, S) containing organic compounds. In addition, it also contains small amounts of metals (e.g. Ni, V, Fe) as well as organometallic compounds. (10) The total number of compounds belonging to these structural classes of hydrocarbons is vast. It is estimated that the number of chemically distinct constituents in crude oil lies in the range of 10 000–100 000. (11) Recent development in the area of ultrahigh resolution FT-ICR mass analysis has indicated that crude oil contains heteroatom-containing organic compounds (N, O, S) with more than 20 000 distinct elemental compositions ($C_cH_hN_nO_oS_s$). (11) The composition of diesel oil is less complex, although the number of chemically distinct compounds is still large. (12) The compositional complexity is well represented by the fact that the identification of different hydrocarbon groups of petroleum products even is difficult. (13, 14) A database was recently established for supporting the collection and distribution of the chemical and physical information related to petroleum products. (15)

Different crude oil sources usually have a unique hydrocarbon composition. Furthermore, due to differences in refining technologies and refinery operating conditions, each refining process has a distinct impact on the hydrocarbon composition of the product. (9, 16) Therefore, each petroleum product has its unique, product-specific hydrocarbon pattern known as the chemical fingerprint of the petroleum product. The potential of gas chromatography for producing information on the product-specific hydrocarbon pattern has for long been recognized by researchers in the field of petroleum hydrocarbon analysis. (17) Therefore, research related to the utilization of e.g. pattern recognition procedures for interpretation of GC data is in focus. (18) The results indicate that combining

gas chromatographic information with pattern recognition methods, such as principal component analysis, cluster analysis, discriminant analysis and genetic algorithms, simplifies the complex GC data (19–21) and makes it possible to trace the spill to its source (22), identify fuel types in complex spillage cases, and to determine the date of contaminant release into the environment. (23, 24)

Selected compound ratios, the type and composition of additives, as well as legislation relating to e.g. petroleum product quality requirements, can sometimes be utilized as indicators for differentiating contaminant types, their source and release time. (21, 23–26) In the case of complex hydrocarbon mixtures and their prolonged contact with soil, integration of various fingerprinting techniques is, however, required for the complete characterization of spillage. Although compositional variability assists in identifying spilled products and potential sources of contamination, it also makes the selection of calibration standard for quantitative determination difficult.

1.2 Behaviour and fate of petroleum hydrocarbons within the soil environment

The major part of soil petroleum hydrocarbon contamination is derived from the spillages related to the use and transportation of petroleum products. (1) Spillages into the soil environment usually occur through accidental surface spills or as a result of steady, slow release from leaking pipelines and underground storage tanks. (1) Due to their toxicity and multiple interactions with the environment, spilled hydrocarbons pose a threat that affects not only the land, but also the oceans, lakes, rivers and groundwater.

Following spillage into the soil, petroleum hydrocarbons become distributed among the gas, liquid and solid phases. (10) Especially the low boiling-point fraction vaporizes into the pore space in the soil. Part of the spilled petroleum products may also remain as a liquid in the pore space. The liquid fraction can then eventually dissolve in the groundwater, or float at the surface of the groundwater table and subsequently migrate over relatively long distances within the soil matrix. (10) Hydrocarbons may also become sorbed onto soil particles. (10) In such cases the migration of contaminants can be effectively retarded by increasing the organic matter content of the soil. (27) The proportion of compounds sequestered into organic matter may also increase along with of the time since contamination occurred. (27) Various mechanisms have been reported

for the diffusion and retention of hydrocarbon compounds within the soil matrix. (28–30)

The complex composition of petroleum products is further complicated by the fact that, as soon as they are released into the soil environment, the composition of the spilled product begins to change. The reactions that lead to compositional changes and to the depletion of certain hydrocarbon compounds are called collectively weathering. (10, 21, 23) Weathering can be induced by physicochemical processes such as dissolution, evaporation, photooxidation, polymerization, and adsorptive interactions between hydrocarbons and the soil. (10, 21, 31–33) Weathering is also controlled by biological factors, e.g. microbial species and strains, their activity and adaptability. (10, 34) In actual fact, the biodegradation of petroleum hydrocarbons by natural populations of microorganisms is a widely utilized remediation method for depleting hydrocarbon pollutants in the soil.

The extent and rate of weathering vary for each spill, depending on the intrinsic composition of the spilled product and environmental factors such as soil temperature, oxygen content, electron acceptor availability, nutrients, moisture and acidity. (35, 36) Furthermore, the weathering rate also depends on the type of petroleum contaminant because the susceptibility of petroleum hydrocarbons to biodegradation varies. It is known, for instance, that n-alkanes are among the most biodegradable hydrocarbons and therefore they are easily broken down and preferentially depleted from soil samples. (23, 24) The degree of branching of alkanes retards the biodegradation rate. Some compounds, such as the hopanes and steranes, are exceptionally resistant to biodegradation. (23, 24) Due to the distinctive order of compositional changes caused by biodegradation, the age of contamination can be approximated by determining the presence or the absence of selected compounds (23), and by measuring the ratios of biodegradable to less biodegradable compounds. (21, 23–25) For example, it has been suggested that the C17 / pristane ratio can be used to determine the age of diesel oil spills in the soil with a standard error of two years. This approach and its applicability have, however, remained rather controversial. (37–41)

1.3 Sampling and analysis of petroleum hydrocarbon contaminated soil

1.3.1 Why are petroleum hydrocarbons monitored?

The environmental impacts of petroleum spillages are severe. It is well known that petroleum products cause extensive damage not only to terrestrial and marine life but also to natural resources and human health. Certain petroleum residues may continue to persist indefinitely in the sedimentary record, and certain compounds formed through weathering processes may even be more toxic than their precursors. (42–44) In order to monitor and help prevent the severe impacts of spillages on ecosystem and biodiversity, petroleum hydrocarbons have to be determined in environmental samples.

Reliable monitoring methods are also required so that effective soil remediation methods for spillages can be developed, selected and targeted properly. Reliable analysis results are also required to demonstrate that the quality of remediated soil is safe for the future purpose of its use. The tightening of environmental regulations has resulted in a need for characterizing the source and time of release so that responsibility issues can be reliably decided. Unambiguous characterization is then of utmost importance because the analysis results may be used as court admissible evidence for settling legal liability and for supporting litigation against the party responsible for the spill. Also the verification of the compliance or non-compliance of oily effluents to regulatory limits requires the development of reliable measurement methods for petroleum hydrocarbon determination.

1.3.2 Methods and definitions for petroleum hydrocarbon determination in soil

At the present time no single analytical method is capable of providing comprehensive chemical information on petroleum contaminants. Non-specific methods can be used to produce information e.g. on the type and total amount of hydrocarbons present in soil, whereas specific methods are required to give detailed individual component and source-specific information on contaminants. (21, 24)

Depending mainly on the regulatory framework, a number of techniques have been used for characterizing petroleum hydrocarbon contamination in soil. (45–

61) These techniques include gravimetry, high-performance liquid chromatography, isotope ratio mass spectrometry, ultraviolet fluorescence spectroscopy, thin layer chromatography, size-exclusion chromatography, supercritical fluid chromatography and inductively coupled plasma optical emission spectroscopy. In addition, a few on-site methods based on infrared spectroscopy (62, 63), laser-induced fluorescence spectroscopy (64) and ultraviolet fluorescence spectroscopy (65) are available. Infrared spectroscopy and gas chromatography with various detection modes (FID, MS) have for long been used for the determination of petroleum hydrocarbons, although nowadays GC-FID and GC-MS have mainly replaced the former IR-based method. Instrumental and method development in the area of gas chromatography have also provided new possibilities for use in the determination of petroleum hydrocarbons. (66–70) These methods have been compared and reviewed in many papers. (71–79)

This wide range of instrumental techniques, as well as the diverging requirements about which hydrocarbon compounds are to be included in the analysis, has created a lot of confusion in the interpretation and exploitation of the results. Additionally, in the case of GC determination, variable carbon ranges from C10 to C19-C50 have been reported as TPH. (56)

Reliable sampling, pretreatment and analysis of petroleum hydrocarbon contaminated soil is already a complicated task due to the complex and variable composition of petroleum products. In addition, soil is a complex matrix whose interaction with hydrocarbon contaminants presents additional problems for the extraction and determination stages. Furthermore, as the results obtained in several national and international interlaboratory studies have shown, many laboratories have great problems in producing acceptable results in petroleum hydrocarbon analysis. (56, 57, 80) Therefore, the major sources of uncertainty in the petroleum hydrocarbon determination chain have to be identified. By locating the main sources of uncertainty and the factors affecting the measurement uncertainty, it will become possible to minimize the uncertainty related to petroleum hydrocarbon determination. This enables the reliability of petroleum hydrocarbon determination in environmental samples to be improved.

1.3.3 State of the art in petroleum hydrocarbon determination

Due to the compositional complexity of petroleum products, it is impossible to assess the extent of petroleum hydrocarbon contamination by separately

measuring the concentration of each hydrocarbon contaminant. One parameter that is currently widely used for expressing the total concentration of nonpolar petroleum hydrocarbons in soil is termed TPH. It is a non-specific, method-defined parameter which is determined by GC-FID.

According to the recent draft standards ISO/DIS 16703:2004 and CEN prEN 14039:2004:E proposed by ISO and CEN for TPH determination, the soil sample is extracted with an acetone - n-heptane mixture. (45, 46) Acetone is then removed from the extract with water. The resulting organic phase is solid phase extracted by Florisil, and the eluate analyzed by gas chromatography with flame ionization detection. The total peak area of resolved and unresolved components in the chromatogram range delimited by the retention times of *n*-decane and *n*-tetracontane is integrated (figure 1). Only semi- and non-volatile hydrocarbons are therefore included in the TPH parameter. By performing external calibration, this integrated response is related to the known TPH concentration in the calibration standards. However, due to the complexity of petroleum hydrocarbon mixtures, the selection of a calibration standard identical to the spilled hydrocarbon product is difficult. Suitable oil products for calibration are described in ISO/DIS 16703:2004 and CEN prEN 14039:2004:E. (45, 46)

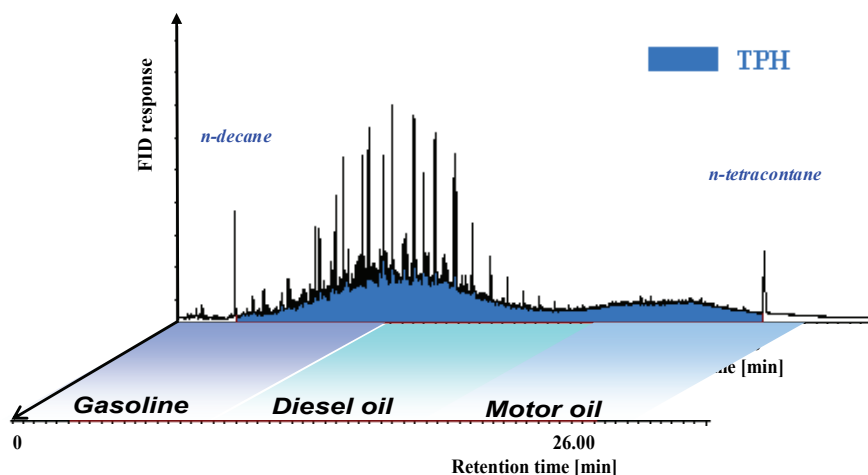


Fig. 1. Gas chromatographic determination of the parameter TPH (45, 46) and approximate description of petroleum hydrocarbon fractions determined by GC-FID. The integrated total peak area between the retention time window standards *n*-decane and *n*-tetracontane represents the sum of total petroleum hydrocarbons (TPH). Exact retention time windows for the indicated petroleum hydrocarbon fractions have not been unambiguously defined.

The advantage of gas chromatographic determination of petroleum hydrocarbons is that, in addition to the TPH concentration, it can also provide useful qualitative information about the type of contaminant (figure 1).

The major disadvantage of gas chromatographic determination is, however, that although ultimate separation temperatures are utilized, the total analysis time for a sample is too long. In the case of a standard GC system, for instance, the time required for a single separation may typically be over 20 min. The temperatures required for the determination also challenge the durability of the columns and causes column bleed, which deteriorates the analytical precision.

In addition to GC-FID, GC-MS methods have also become valuable tools for petroleum hydrocarbon analysis. By utilizing gas chromatography-mass spectrometry (GC-MS) in a selected ion monitoring mode, compound specific information on e.g. PAH's, biomarker compounds and other persistent hydrocarbons that occur at relatively low levels in petroleum products can be obtained. (24, 81) In some cases, the compound-specific information and unique compound distribution patterns are decisive for resolving forensic problems.

1.4 Sources of measurement uncertainty in TPH determination in soil

1.4.1 Primary sampling stage

It has been reported that the primary sampling stage may actually represent the largest source (50–70%) of measurement uncertainty related to the assessment of soil contamination. (3–6) This uncertainty primarily arises from the fact that the location of the individual primary sampling point cannot be properly defined. When primary sampling is repeated, the location of the true sampling point may easily vary e.g. from 1 to 5 meters. A part of the primary sampling uncertainty therefore arises from the inhomogeneous distribution of the analyte in this imprecisely defined area. (82) The sequestration, leaching and volatility of hydrocarbon compounds certainly complicate the management of the primary sampling stage and affect the quality of primary sampling. Volatility also places considerable strain on the management of the sample storage stage.

In addition to this small-scale variation, sampling uncertainty consists of factors related to e.g. the sampling strategy, sampler(s), sampling equipment, sample stability, environmental circumstances and properties of the sampling site.

(83) All these factors, too, represent various systematic and random uncertainty sources that affect the precision and accuracy of the primary sampling stage.

It is a well-known fact that the uncertainties related to the primary sampling stage cannot be compensated for afterwards by improving the quality of the analytical method in the laboratory. A composite sampling procedure has been discussed as one option to reducing inter-sample variance and, consequently, the variance of the primary sampling stage. However, this approach cannot be utilized when sampling volatile and semi-volatile petroleum hydrocarbon contaminated soil.

1.4.2 Sample treatment procedure

Traditional instrumental methods for TPH analysis require samples in liquid form. Therefore, prior to determination the petroleum contaminants have to be extracted from the soil matrix into a suitable solvent.

The reliability of the sample treatment procedure for petroleum hydrocarbon determination has certainly suffered from the slow progress in standardization and consequent lack of uniform analytical methodology for petroleum hydrocarbon determination. In addition, the reliability has also suffered from the lack of certified reference materials for petroleum hydrocarbon determination. Furthermore, the differing instructions of the authorities have supported the use of a range of sample treatment procedures for extracting petroleum products and their compounds from a soil matrix. (50, 56, 57) Therefore, traditional Soxhlet extraction (84) is now being challenged by modern techniques such as supercritical fluid extraction (59, 61, 85–87), solid-phase microextraction (63), pressurized fluid extraction (78) ultrasonic extraction (84, 88) and microwave-assisted extraction (77, 89–92). Solvent extraction is also challenged by thermal desorption methods (66, 93). Also microwave-assisted extraction utilizing non-ionic surfactant solutions instead of traditional organic solvents has been successfully applied to the extraction of hydrocarbons from soil and sediment samples (94).

The application of different extraction methods to solid matrices has been critically reviewed in the scientific literature (95). However, the studies mainly deal with the extraction of PAHs or selected hydrocarbon compounds. Relatively little data have been published on the effect of different extraction methods on the reliability of TPH analytics. A number of interlaboratory comparisons for the analysis of mineral oil in polluted soil using GC-FID have, however, indicated

that variability in the extraction and clean-up stages does have adverse effects on the quality of the results. (56, 57, 96)

The reasons for the varying extraction recovery are multiple. First of all, the extraction recovery depends on the selection of a sub-sample for analysis. However, homogenization of the primary sample before sub-sampling has to be avoided in order to prevent the loss of hydrocarbons through evaporation. The consequent inhomogeneous distribution of contaminants certainly complicates the selection of sub-sample size for analysis and, as a result, increases the analytical uncertainty. Therefore, a sufficiently large sub-sample size has to be selected for the analysis. Otherwise the recovery will be adversely affected by the inhomogeneous distribution of hydrocarbons in the primary sample.

The extraction process itself is complicated due to the diversity of the chemical and physical properties of petroleum hydrocarbons. The differing solvent properties, as well as extraction conditions, affect not only the solubility of hydrocarbons in the solvents but also the solubility of the matrix components. Thus, many non-petroleum hydrocarbon compounds, such as naturally occurring terpenes, industrial solvents, chlorinated (PCB's, organochlorine pesticides) and oxygen-containing molecules (phthalates, triglycerides, sterols), may also be simultaneously extracted from the soil matrix.

The sorption of hydrophobic compounds on soil organic matter and mineral soil, as well as the aging of the contamination, reduces the extractability of certain hydrocarbon compounds. Weathering processes in different soil matrices change the overall composition of the spilled hydrocarbon product and alter the concentrations of the individual hydrocarbon compounds in contaminated soil. These processes may then further impact the performance of sample extraction and clean-up stages. It has also been reported that a high moisture content of the soil may reduce interaction between the nonpolar extraction solvent with the hydrated soil surfaces, consequently leading to decreased extraction recoveries. (97) The research carried out on the effect of different solvents on the extraction recoveries has, however, mainly focused on individual hydrocarbon groups (PAH's) or selected hydrocarbon compounds. (98–101) Extraction methods have also been compared, although the significance of the results remains questionable due to differences in the subsequent analytical stages utilized. (84, 97, 102, 103)

The extraction of soil samples results in extracts that contain various co-extracted substances. A clean-up stage utilizing e.g. solid-phase extraction is usually applied to remove these interfering, co-extracted substances (e.g. fulvic acids, plant fats, surfactants). A range of methods and sorbents have been used for

extract clean-up, but rather conflicting conclusions have been presented concerning the efficiency and selectivity of these adsorbents. (86, 104, 105) Ineffective extract clean-up may, however, be problematic because it easily results in a matrix-induced, chromatographic response effect during GC determination. Without effective extract clean-up, the quantification of non-petroleum based compounds subsequently results in false positive values for petroleum hydrocarbons. (106, 107) The effect of ineffective clean-up becomes even more pronounced when sampling a site with a variable soil composition. Uncontrollable matrix effects may occur if clean-up is ineffective. It has also been reported that photodegradation reactions of some hydrocarbon compounds in organic solvents during the clean-up stage may also change the composition of the original contaminant. (105, 108, 109)

The problem, therefore, is that differing sample treatment procedures involve different kinds of treatment stage, which introduce variable sources of measurement uncertainty in the result. If this measurement uncertainty is not stated, then the comparison of results becomes difficult. However, little is known about which factors or combination of factors in the sample treatment procedure has the greatest effect on the quality of TPH analyses carried out by individual laboratories. As the use of conflicting extraction methods challenges the credibility and comparability of the results, it would therefore be necessary to study which stages in the determination chain most significantly affect the reliability of TPH results.

1.4.3 Gas chromatographic determination

Gas chromatography with flame ionization detection (GC-FID) is nowadays the most common analytical technique for TPH determination. However, the slow standardization, lack of certified reference materials and differing environmental regulations have resulted in the use of a wide range of GC operating settings for TPH determination. (56, 57, 109–112) Even the latest draft standards still lack a detailed description of the gas chromatographic settings for measuring total petroleum hydrocarbons. (45, 46) Only recommendations are given, and they often seem to be overlooked by laboratories. Instead, the laboratories use proprietary GC settings for TPH determination.

Because TPH parameter is method-dependent, the adaptation of GC settings may easily lead to serious interferences which affect the total peak area between the retention times of *n*-decane and *n*-tetracontane. As a result, both the accuracy

and precision of the analysis results and the profiles of the chromatograms may become affected.

In fact, the evaluation of interlaboratory comparison and method validation data has indicated that a major part of the problems in gas chromatographic determination usually originate in the calibration and performance of the GC instrument. (57, 113) The effect of different GC settings on the performance of TPH determination has, however, not yet been thoroughly assessed.

Typical problems that occur in gas chromatographic analysis are interferences due to e.g. mass discrimination and matrix-induced chromatographic response enhancement. (114) The matrix effect in GC determination originates from the irreversible adsorption of certain sample components on the active sites (free silanol groups, metals) that are potentially present even in high quality deactivated glass injection liners. Residues of non-volatile compounds originating from previous analyses may also act as active sites in the injection liner. When a matrix-free standard solution is injected into a GC system, active sites are available for analyte absorption. This results in a reduced transfer of analytes into the chromatographic column due to their retention in the injector. The blocking of active sites on the liner by co-extracted matrix components will, however, improve the transfer of analytes from the injection port to the column. Therefore, compared to the response of analytes in a matrix-free solvent, there will be enhanced chromatographic response of analytes in the presence of matrix components. (115–118) Because the interference is not only sample- and matrix-dependent, but also partly instrument-dependent, it may cause problems in TPH determination.

Despite the fact that alternative injection systems are available, the splitless injection mode is frequently utilized for TPH determination. (114, 119) This means that there is a strong possibility that interferences caused by mass discrimination occur. Mass discrimination is promoted by thermal degradation of the analytes at the hot surfaces of the injection liner. This happens especially when there is insufficient masking of active sites in the injection liner by matrix components. Compound degradation during splitless injection subsequently leads to the situation where the hydrocarbon composition of the vaporized sample injected on the GC column does not represent the true hydrocarbon composition of the original sample. Numerous examples of mass discrimination based quantitation problems in e.g. pesticide analytics as well as in petroleum hydrocarbon analytics have been reported. (68, 120) These examples indicate

that, especially in the case of splitless injection, prevention of the thermal degradation of analytes and consequent mass discrimination becomes necessary.

Mass discrimination interference can be reduced by utilizing optional injectors or by optimizing the GC operating settings for the determination. (119, 120) Optimum operating conditions for separation and detection have been considered for other analytes. (121) However, relatively little data on mass discrimination in TPH analytics have been published in the scientific literature and, consequently, the significance of GC operating settings is not known.

The occurrence and intensity of matrix interferences in gas chromatographic analysis are often reduced by enhancing the selectivity of the extraction or purification of the extract. (122) Selected analyte protectants, which possess multiple polar groups to support interaction with the active sites in the injection liner, have also been used to counteract the matrix-induced effect. (123, 124) In addition, matrix-matched calibration has also been found to be an effective way of avoiding errors in the quantification of selected analytes. (122) However, due to the complexity of petroleum hydrocarbons as well as to the variability of the soil matrix, further improvement of e.g. extraction and clean-up stages is hardly possible. The development of effective analyte protectant(s) for use in TPH analytics may also be difficult because the volatility of the analyte protectant(s) should be similar to that of the analytes, which in this case cover a wide volatility range. The polar nature of protectant(s) may also limit their solubility in the relatively non-polar solvents used for TPH determination. Therefore, the only realistic alternative is the utilization of matrix-matched calibration standards.

The potential GC interference effects and their correction and consequent effect on the measurement uncertainty have been critically reviewed by Thompson and Ellison. (125) However, little is known about which factors or combination of factors in TPH determination by GC-FID has the greatest effect on the quality of TPH analyses produced by individual laboratories. Therefore, improvement of the accuracy and precision of the gas chromatographic determination of petroleum hydrocarbons requires the identification of the major uncertainty sources in the determination.

1.5 Assessment of measurement uncertainty for environmental analysis

According to the internationally accepted approach, the reliability of a measurement can be expressed by stating the expanded uncertainty of the

measurement result. This uncertainty then characterizes the range within which the true value lies with a specified probability. (126)

Over the past few years substantial efforts have been made to improve the methodology for estimating analytical uncertainty. The concepts and practices of analytical uncertainty assessment have been well documented, and they are recognized by analytical chemists. (127) EURACHEM/CITAC has published documents showing how the concepts of the ISO Guide (126) should be applied in chemical measurements, and how the procedures needed for the uncertainty estimation process should be integrated with existing quality assurance measures in analytical chemistry. (128–130) For the end-user of the environmental data, however, the measurand of interest is the concentration of the analyte in the primary sampling target. Thus, the individual uncertainty sources related to primary sampling have to be considered because they may strongly influence the analytical results. (83, 131, 132)

Although the contribution of primary sampling to the measurement uncertainty is required in order to completely understand the reliability of analytical results, the assessment of uncertainty associated with primary sampling has long lacked specific guidance. (132) In actual fact, it has only recently been treated by EURACHEM/CITAC. (133) Approaches have been presented in the literature for estimating the uncertainties introduced by the analytical and primary sampling stages. (83, 131, 134–137) It has been shown that the primary sampling uncertainty can be estimated by determining separately all the sources of uncertainty related to the primary sampling process. (83, 138) However, the uncertainty estimation based on this type B approach is often far too complicated and laborious for routine analyses, mainly because of the difficulty in quantifying each uncertainty component independently.

When a specific sampling design is used the measurement uncertainty can be calculated as a combination of the linear models for sampling and analysis. (139–141) In the case of nested sampling designs, statistical methods can also be used to split the total variance of the results into spatial, sampling and analytical components. (5, 142–144) However, owing to the specific characteristics (distribution, constancy of the measurement variance) of the measurement data, the assumptions of statistical methods required for the type A approach tend to present problems. The violations of these assumptions can affect the power and significance level of the test and consequently reduce the reliability of uncertainty estimate. Robust statistics and mathematical transformation of raw data can be used to reduce the problems with the assumptions of normality and

homoscedasticity. (131, 145, 146) However, their utilization requires detailed knowledge of statistical procedures. The mathematical modification of data also cause problems in the interpretation of the results and, consequently, the results may differ from the general guidelines given by EURACHEM/CITAC for reporting the expanded uncertainty of a chemical measurement. (145, III) In addition, the disadvantage of these uncertainty estimation methods is that they exclude the sampling bias from the measurement uncertainty.

In order to obtain reliable measurement uncertainty estimates for analysis, careful sampling strategy planning, as well as selection of the method for estimating the required components of sampling and analytical uncertainties, is required. However, although a predetermined sampling strategy could be helpful in assessing sampling uncertainty, its application to different contaminated sites may fail. In these cases the determination of sampling uncertainty should be driven by the characteristics of the data obtained from the contaminated site. Otherwise the expanded uncertainty becomes uncertain itself, and no benefit is gained that supports the end-use of the data. As far as primary sampling uncertainty is concerned, it should also be noted that there are large differences in European soil sampling guidelines. (147) Sampling uncertainty is also strongly affected by the environmental conditions in the soil ecosystem, and by the contaminant and its concentration distribution across the sampling target. (83) Therefore the results obtained for sampling uncertainty should be generalized only with great care.

1.6 Significance of measurement uncertainty in environmental analysis

The result of a chemical analysis is always an estimate of the exact concentration/content of the analyte in the sample/sampling target. Therefore the measurement uncertainty related to the analysis result needs to be stated so that the end-user of the chemical data can estimate the reliability of the chemical data. The end-user of the data can, for example, compare whether the result differs either from the limiting value of this characteristic quantity or from the previous measurement result. (148)

The use of measurement uncertainty in the interpretation of environmental monitoring results could reduce the risk of misinterpretations and, consequently, reduce the chance of underestimating the risks to human health or the environment. The concept of measurement uncertainty has also been found to

have significant implications for environmental risk assessment, for the identification of causes of measurement uncertainty, and for the remediation costs of contaminated areas. It has been shown that the concept of measurement uncertainty can be utilized to estimate performance for contaminated soil remediation. (149)

The significance of measurement uncertainty has also recently been recognized by the environmental authorities and, as a result, the estimation of measurement uncertainty has been accepted as an essential objective in the development of the environmental monitoring of harmful substances. (150)

2 Aims of the research

The main objective of this research was to assess the significance of different stages of the analysis chain on the uncertainty in the determination of environmentally interesting concentrations of TPH in soil. By identifying the main uncertainty sources and related factors inducing this uncertainty, it will be possible to minimize the uncertainty related to TPH determination. This will result in the generation of more reliable information about petroleum hydrocarbon contamination and the consequent fate and effects of petroleum hydrocarbons in the environment. The most important aims of this study were:

1. To compare the suitability of three different extraction methods for the determination of total petroleum hydrocarbons by GC-FID. Both qualitative and quantitative aspects were discussed. (I)
2. To investigate the presence of a matrix effect, and to evaluate the potential quantitative errors resulting from the matrix effect in the gas chromatographic analysis of petroleum hydrocarbon contaminated soil samples. (II)
3. To estimate the measurement uncertainty for the determination of total petroleum hydrocarbons in soil by GC-FID and to compare the relative contributions of sampling and analysis to measurement uncertainty. (III)
4. To study in more detail the ruggedness of the draft standard procedure CEN prEN 14039:2004:E for extracting total petroleum hydrocarbons in soil. (IV)
5. To investigate in more detail the ruggedness of the gas chromatographic method for the determination of total petroleum hydrocarbons. (V)

3 Experimental

3.1 Sample types, sampling and pre-treatment

Soil samples from three different petroleum hydrocarbon contaminated and uncontaminated areas were used in the investigations. In the comparative extraction studies (I, IV), as well as in the matrix effect investigations (II), spiked soil samples were used. Soil #1, which was used for spiking, was collected at a soil extraction area in North Ostrobothnia. The other soil type (soil #2), which was used for assessing the matrix effect (II), had a higher organic matter content and was collected at a peat extraction area in South Ostrobothnia. The soil samples (soil #3) used for assessing the measurement uncertainty in the determination of total petroleum hydrocarbons in soil by GC-FID (III) were collected from an area in South Ostrobothnia that had earlier been used for the retail sale of petroleum products. The soil was contaminated with petroleum hydrocarbon products over a period of at least twenty years. Sampling at this site was carried out below the asphalt cover that restricted the penetration and percolation of rain water into the contaminated soil. Sampling at the contaminated site was carried out in accordance with the national guidelines for the sampling of organic contaminants. (151)

Two types of soil sample were used in evaluating the ruggedness of the draft standard procedure for extracting total petroleum hydrocarbons in soil (IV). One of the samples was soil #2, described in the above. (II) The other type of soil (soil #4), which had a lower organic matter content, was sampled at the Sammallahdenmäki bronze age burial site, western Finland. Sampling at this site was carried out by the personnel of the National Board of Antiquities of Finland.

Before the spiking procedure, soil samples #1, #2 and #4, were air dried for 24 hours and sieved. The < 2 mm particle size fraction was used in all the experiments. The spiking solution was prepared by mixing equal amounts (by mass) of additive-free diesel oil (Neste Oil Oyj) and additive-free lubricating oil (Neste Oil Oyj) in acetone. No sample pretreatment was performed on the contaminated soil samples (#3) (III) in order to prevent the loss of hydrocarbons. Detailed information about the sampling sites and sample treatment, as well as the spiking procedures, are given in the original papers. (I, II, III, IV)

3.2 Sample extraction procedures

The shake extraction procedure described in CEN prEN 14039:2004:E was utilized for the extraction of soil samples. (46) In the comparative solvent extraction studies (I), closed vessel microwave-assisted extraction (I, 90), traditional Soxhlet extraction (I, 152) and ultrasonic extraction (IV) were used, as well. A brief description of the extraction methods and related parameters are given in table 1.

Table 1. Description of the extraction parameters utilized in the extraction studies.

Sample preparation procedure CEN pr EN 14039:2004:E	Paper I	Papers II, III,V	Paper IV
Subsample size for extraction	5 g	20 g	15 g, 20 g, 25 g
Extraction solvent and co-solvent added	n-heptane (20 ml) acetone (40 ml, CEN, SOX) acetone (20ml, MWAE)	n-heptane (20 ml) acetone (40 ml)	n-heptane or n-hexane (15 ml, 20 ml, 25 ml) acetone or methanol (40 ml)
Extraction	Shake (1 h, rt) MWAE (150 °C, 15 min) SOXHLET (20 h)	Shake (1 h, rt)	Shake (40 min, 60 min, 80 min, rt) US (40 min, 60 min, 80 min)
Washing and drying	water (2 × 100 ml) Na ₂ SO ₄ (2 g)	water (2 × 100 ml) Na ₂ SO ₄ (2 g)	water (2 × 50 ml, 2 × 100 ml, 2 × 150 ml)
Solid phase extraction	Florisil (2.0 g)	Florisil (2.0 g)	Florisil (0.5 g, 1.25 g, 2.0 g) Silica (0.5 g, 1.25 g, 2.0 g)

Following the procedure of CEN prEN 14039:2004:E, the sample was shaken by hand with 40 ml of acetone. After the addition of 20 ml of *n*-heptane containing 30 mg/l of *n*-decane and *n*-tetracontane, the mixture was extracted by mechanical shaking for 1 h at room temperature. Soxhlet extraction was performed according to USEPA 3540C. (109) Samples were extracted with the solvent mixture for 20 hours at 4–6 cycles per hour. Microwave-assisted extraction was carried out according to the method presented by CEM Corp. (90). The sample was weighed into the microwave extraction vessel, the solvent mixture added, and the vessels then closed. Twelve samples were extracted at the same time in the temperature controlled microwave system at 150 °C for 15 min. For ultrasonic extraction the shake extraction stage described in CEN prEN 14039:2004:E was replaced by ultrasonic extraction. The soil samples were always extracted in random order.

After the extraction stage, acetone was removed by washing the organic phase with water. The organic layer was dried with Na₂SO₄ and the solid phase extracted with Florisil or silica. The eluate was analyzed by GC-FID. More detailed information on the extraction procedures is given in the original papers. (I,IV)

3.3 Analytical equipment

The determination of TPH in the extracts was carried out by gas chromatography-flame ionization detection. The determinations were carried out using an HP Agilent 6890 gas chromatograph equipped with a FID detector, an Agilent 7673 autosampler and a low-bleed Supelco Equity™-5 capillary column (15m × 0.25 mm i.d.) with a nominal film thickness of 0.25 μm. Splitless injection method was utilized with a deactivated, splitless inlet liner with adsorbent material and taper (I-IV). In addition, deactivated, a single-taper splitless inlet liner without glass wool was used when the ruggedness of the gas chromatographic method was studied. (V) Detailed information on the instrumental settings utilized in studies I–V is presented in table 2. The method used in studies I–IV gave a complete chromatographic run within 27 min.

Table 2. GC instrumental configuration and operating settings.

	Papers I–IV	Paper V
GC operational settings		
Inlet mode	Splitless	Splitless
Inlet temperature	330 °C	260–330 °C
Injection volume	1 µl	1 µl, 2 µl, 3 µl
Split vent time	2.0 min	2.0–4.0 min
Column flow	Helium 2.0 ml/min (average velocity 50 cm/sec)	Helium 1.0 ml/min, 2.0 ml/min, 3.0 ml/min
Oven temperature program	35 °C(1.50 min) – 5 °C/min – 60 °C – 15 °C/min – 310 °C – 10 min	35 °C(1.50 min) – 5 °C/min – 60 °C – 15 °C/min – 310 °C – 10 min
FID temperature	300 °C	300–330 °C
FID gas flows	35.0 ml/min hydrogen / 350 ml/min air	35.0 ml/min hydrogen / 350 ml/min air
Instrumental configuration		
GC	Agilent 6890	
Inlet	Splitless	
Autosampler	Agilent 7673	
Detector	FID	
Column	Supelco 18523-01F Equity™-5: 15 m × 0.25 mm id., nominal film thickness 0.25 µm	
Inlet liners	Agilent Technologies, P/N 5183-4711 split/splitless inlet liner, deactivated, with taper, glass wool I–V Agilent Technologies, P/N 5181-3316 splitless inlet liner, deactivated, with taper, without glass wool V	

The suitability of the gas chromatographic system for the resolution of *n*-alkanes, as well as for the detector response, was verified according to CEN prEN 14039:2004:E. According to the standard methodology described by ISO/DIS 16703:2004 and CEN prEN 14039:2004:E, the amount of total petroleum hydrocarbons was determined as the sum parameter of resolved and unresolved components eluted from the GC capillary column between the retention times of *n*-decane and *n*-tetracontane. (45, 46) Determination of the sum parameter was based on the integrated area between the retention times of *n*-decane and *n*-tetracontane. All the integrations were corrected for column bleed.

Additional equipment used in the studies is listed in table 3.

Table 3. Additional equipment used in the studies.

Microwave oven for extraction	CEM Mars 5X (CEM Corp.)
Vessels for MW extraction	CEM Plus™ Vessels (XP-1500 Plus)
Ultrasonic bath	Bandelin, Sonorex Super RK 103H
Shaking device for CEN extraction	Griffin flask shaker
CHNS-analysis	Perkin-Elmer 2400 series II CHNS/O analyzer

3.4 Calibration and quality control

For TPH quantitation, a petroleum hydrocarbon standard solution (20 mg/ml) was prepared by mixing equal amounts (by mass) of additive-free diesel oil (DIKC, Neste Oil Oyj, Finland) and lubricating oil (CORE, Neste Oil Oyj, Finland) in n-heptane (J.T.Baker, HPLC-grade). Selected volumes of this solution were further diluted with n-heptane to give a series of working standards with TPH concentrations of 1.0, 2.0, 5.0, 10.0 and 15.0 mg/ml. Certified reference material ERM-CC015a was used to estimate the accuracy of the analytical procedure. Certified reference material ERM-CC015a is a sediment sample which has been contaminated over decades by industrial and sewage sludge. The certified TPH concentration in this reference material was 1820 ± 130 mg/kg. The presence of analytical bias was evaluated by comparing the mean value obtained for analytical replicates against the certified value.

3.5 Experimental design and statistical analysis

In the comparative study on the solvent extraction of TPH in soil, homogeneity of the variances was tested using the Bartlett's test (I), and the statistical significance of the extraction method on the recovery results was tested with a single-factor analysis of variance (ANOVA) (I). In the matrix effect study (II), comparison of the slopes of the regression lines was performed by means of a *t*-test. The equality of residual variances was tested using the F-test. The statistical significance of the analytical bias (III, IV) was tested using the two-way Student's *t*-test. The equality of variances was tested using the F-test and the uncertainty of the difference between the certified value and the analysis result was calculated by using a pooled estimate of the standard deviation. In the assessment of measurement uncertainty for TPH determination (III), the total variance of the experimental results was broken down into geochemical, sampling and analytical variation using classical ANOVA (type I SS). The normality of the experimental

data (III,IV) was evaluated using the Kolmogorov-Smirnov test of normality. The measurement uncertainty for TPH determination was also assessed using the linear precision modelling method presented by Lee and Ramsay. (141) SPSS 14.0 for Windows was used for the statistical evaluation of the experimental data, and MODDE 7.0 software was used for the experimental design. (IV,V) The effects of 11 factors on the extraction recovery of TPHs in soil samples were investigated using a two-level Plackett-Burman design. A D-optimal design was elaborated to investigate in more detail the ruggedness of the gas chromatographic method for TPH determination. (V, 153) Because the optimization of the GC operating conditions resulted in a multiple response problem, a desirability function was constructed. (154)

4 Results and discussion

4.1 TPH concentrations in the contaminated site

The TPH concentrations were compared against both the recommended maximum value (900 mg/kg, representing fractions C10–C21 + C21–C40 in total) and the threshold value (3000 mg/kg, representing fractions C10–C21 + C21–C40 in total) for mineral oil in soil in Finland. The results indicated that the TPH concentrations in most cases exceeded the recommended maximum value for mineral oil in soil (Figure 2). Some sampling areas appeared to be highly contaminated because the TPH concentrations exceeded the threshold value for mineral oil in soil. This indicates a potential environmental and health risk, and the possible need to reduce the risk by decreasing the TPH concentration in the site. However, the above-mentioned SAMASE values are currently being replaced due to a decision by the Finnish Council of State in 2007. The current values are given in table 4.

Table 4. Threshold and guideline values in Finland based on the decision of the Council of State in 2007.

Mineral oil carbon range	Threshold value mg/kg	Lower guideline value mg/kg	Higher guideline value mg/kg
C10–C21		300	1000
C21–C40		600	2000
C10–C40	300		

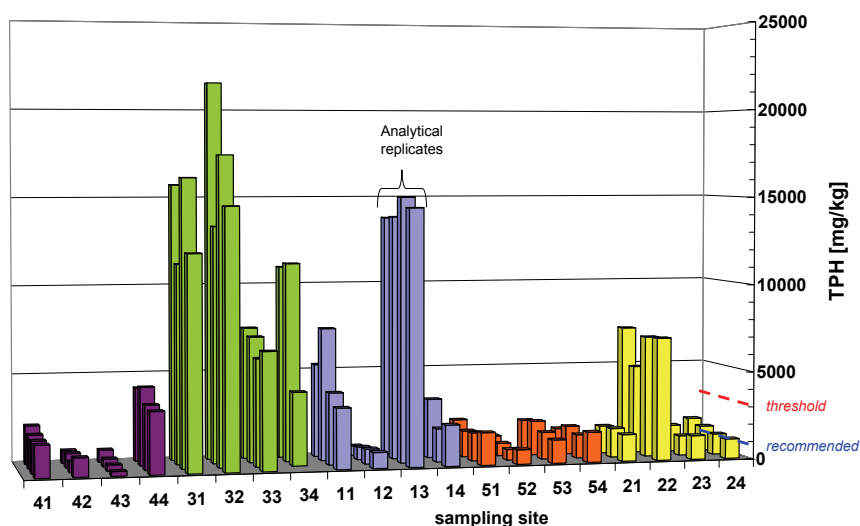


Fig. 2. Analytical results obtained for the contaminated site.

4.2 Estimation of measurement uncertainty for TPH determination in soil (III)

Measurement uncertainty for the analysis of petroleum hydrocarbon contaminated soil was estimated in order to establish the comparability of the results. The accuracy of the CEN prEN 14039:2004:E procedure used for the determination proved to be sufficient by extracting and analysing certified reference material ERM-CC015a samples at random positions among the samples. The mean measured concentration (2075 ± 185 mg/kg, $n = 3$, $U_{rel} = 9\%$) was in good agreement with the certified concentration (1820 ± 216 mg/kg, $m = 11$, $U_{rel} = 12\%$). Hence analytical bias was found to be absent, and its contribution as an additional uncertainty component to the measurement uncertainty not taken into account.

As a balanced design of replicate samples and analyses (figure 3) was utilized for sampling, two different methods could be used for estimating the measurement uncertainty due to sampling and analysis of petroleum hydrocarbons in soil.

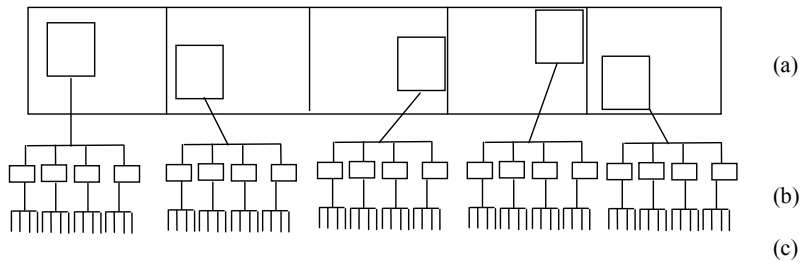


Fig. 3. Hierarchical sampling and analysis design (a) primary sampling locations, n = 5, (b) primary samples, n = 20, (c) laboratory samples, n = 80.

Although the use of ANOVA for type A evaluation of measurement uncertainty has been successfully applied in other contamination cases, its applicability was challenged in this study by the log-normality and heteroscedasticity of the raw data. Figure 4 summarizes the expanded uncertainties obtained using ANOVA both for individual sampling points and for the whole sampling area.

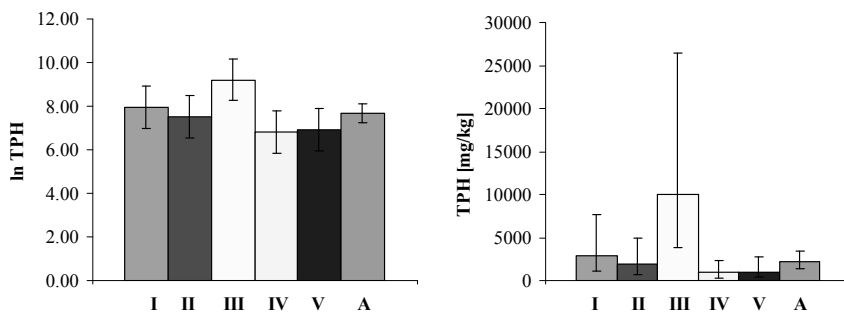


Fig. 4. Mean values and corresponding expanded uncertainties for individual sampling points (I-V) and for the whole sampling area (A): (a) log-transformed population, (b) original population.

However, further interpretation of the results suffered from the mathematical transformation used to overcome the discrepancy between the raw data and the ANOVA assumptions. Firstly, back-transformation of ANOVA results ends up in a geometric mean with an asymmetric confidence interval around the geometric mean. Secondly, because the additivity of estimated variance components is lost with back-transformation, no comparison can be made of the relative contributions of analytical and sampling uncertainties for the measurement uncertainty.

The measurement uncertainty was also estimated from the calculated linear precision equations for sampling and analysis. Linear precision modelling showed a statistically significant precision change for sampling and analysis along with increasing TPH concentration. Consequently, the measurement uncertainty was calculated as a combination of the analytical and sampling precision equations. Figure 5 summarizes the expanded uncertainty values obtained with linear measurement precision modelling and classical ANOVA.

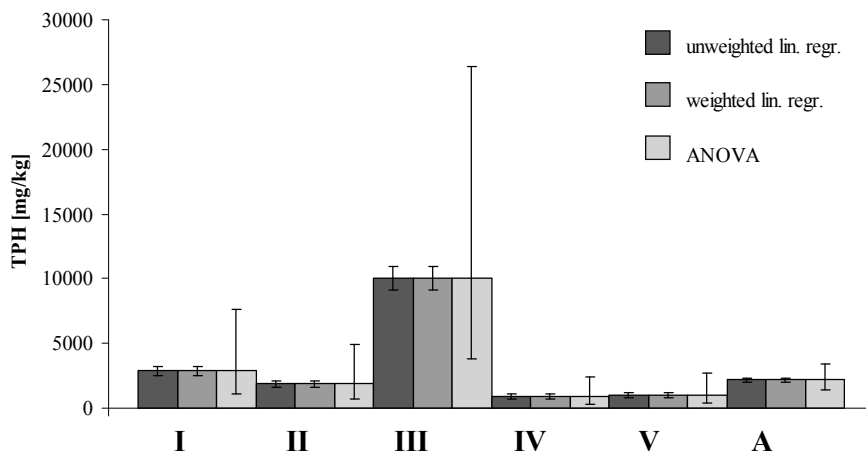


Fig. 5. Comparison of the expanded uncertainties at the geometric means of individual sampling points (I–V) and at the geometric mean of the whole sampling area (A).

Comparison of the uncertainty values to those obtained with ANOVA revealed that ANOVA overestimated the expanded uncertainty at both low and high TPH concentrations. This discrepancy may be due to fact that ANOVA assumes a constant value for measurement precision, which was not valid in this study.

According to the linear precision modelling, the relative expanded uncertainty for TPH determination was moderate, ranging from 21% at a TPH concentration of 895 mg/kg to 9% at a concentration of 10 019 mg/kg. However, when the relative contributions of the sampling and analytical uncertainty components were compared, it was found that the main part of the measurement uncertainty originated from the analytical uncertainty. Within the concentration range studied here, the analytical uncertainty comprised as much as 68% - 80% of the measurement uncertainty (Figure 6). The result indicated that, if the

measurement uncertainty is to be improved, then the variance of analytical stage has to be reduced.

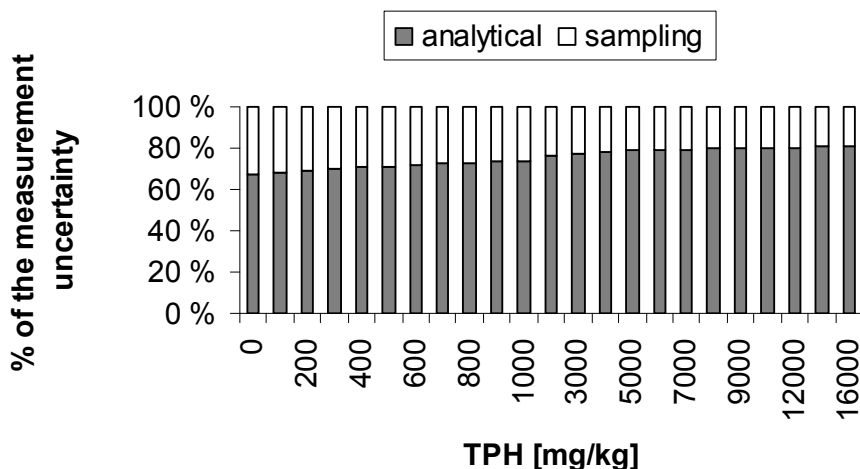


Fig. 6. Relative size of the uncertainties in the analytical and sampling stages.

One potential reason for the unexpectedly large proportion of analytical uncertainty may be the fact that the inhomogeneous distribution of contaminants increases the variance of subsampling for analysis. When an extensive area is sampled, the change in matrix may also reduce the repeatability and accuracy of the extraction, clean-up and GC determination stages. Furthermore, the petroleum hydrocarbon composition of the calibration standard may be clearly distinct from that of the petroleum product extracted from the sample. The last one point is, however, always a problem especially with older contamination sites with highly degraded and variable hydrocarbon products. The significance of uncertainty sources related to these stages were investigated in this study. The influence of sample matrix on the uncertainty of TPH determination was also evaluated.

4.3 Factors affecting the analytical uncertainty

4.3.1 The effect of extraction method (I)

Measurement uncertainty for TPH determination was found to be dominated by analytical uncertainty. Consequently, the uncertainty of the analytical stage should be the main reduction target in order to minimize measurement uncertainty.

Because the analytical uncertainty is undoubtedly affected by both the accuracy and precision of the extraction stage, the performance characteristics of the CEN prEN 14039:2004:E draft standard method were compared to those obtained with Soxhlet extraction and microwave-assisted extraction.

The efficiencies of the three extraction methods were studied by analysing samples prepared by adding known amounts of petroleum hydrocarbons to the soil matrix. In addition, the petroleum hydrocarbon mixture used for soil spiking was also extracted.

The TPH recoveries obtained for the petroleum hydrocarbon mixture were acceptable (Table 5). The best recovery and repeatability values ($99\% \pm 3\%$) were obtained with microwave-assisted extraction, which indicated that petroleum hydrocarbons can be completely recovered by this method. However, there was a statistically significant difference between the extraction performances of the different methods. The recoveries obtained with CEN prEN 14039:2004:E and Soxhlet extraction were significantly lower than the recovery obtained with microwave-assisted extraction. The result indicated that the sophisticated microwave-assisted extraction system gives a higher recovery with good precision within a shorter time scale than conventional extraction methods. One reason for the good recovery may be that the closed vessel system prevents the loss of volatile hydrocarbon compounds during extraction.

Table 5. Recoveries obtained for a standard oil mixture (std oil) with different extraction methods. Sample treatment, excluding extraction, was performed according to CEN prEN 14039:2004:E.

Sample	Extraction method	Target value (mg/l)	Obtained results; n = 3			
			Average s (mg/l) \pm (mg/l)	rsd (%)	Recovery s (%) \pm (%)	rsd (%)
Std oil	CEN shake	1870	1500 \pm 161	11	80 \pm 9	11
	Soxhlet	1730	1250 \pm 65	5	72 \pm 4	5
	MW-assisted	1930	1920 \pm 57	3	99 \pm 3	3

The results obtained for spiked soil samples were found to be different. The average TPH recoveries obtained with microwave-assisted and Soxhlet extractions were relatively good, whereas the efficiency of the CEN prEN 14039:2004:E shake extraction was poorer (Table 6). On the other hand, the precision of the CEN prEN 14039:2004:E method (6%) was the best of the three methods. In the case of the soil samples, however, there were no significant

differences between the TPH recoveries obtained with the individual extraction methods. Further analysis of the recovery results indicated that the differences between the methods were actually obscured by the variation attributable to the heterogeneous distribution of the analytes in the spiked soil sample.

When the overall profiles of the gas chromatograms, as well as the individual peak heights and peak areas of certain hydrocarbon compounds were compared, a distinct difference between the extraction methods was found. The chromatograms presented in figure 7 indicated that the overall GC profile obtained from non-spiked soil using the microwave-assisted extraction method clearly differs from that obtained using the CEN-shake extraction method.

Table 6. The results obtained for spiked soil samples and for non-spiked soil samples with different extraction methods. Sample treatment, excluding extraction, was done according to CEN prEN 14039:2004:E.

Sample	Extraction method	Target value (mg/g)	Obtained results; n = 3			
			Average s (mg/g) ± (mg/g)	rsd (%)	Recovery [*] s (%) ± (%)	rsd (%)
Spiked soil	CEN shake	6.75	6.4 ± 0.3	6	78 ± 4	6
	Soxhlet	6.75	7.4 ± 1.3	20	102 ± 20	20
	MW-assisted	6.75	7.9 ± 3.0	44	103 ± 45	44
Non- spiked soil	CEN shake	–	1.1 ± 0.6	58	–	–
	Soxhlet	–	0.6 ± 0.1	24	–	–
	MW-assisted	–	1.0 ± 0.2	22	–	–

^{*}The blank value was subtracted

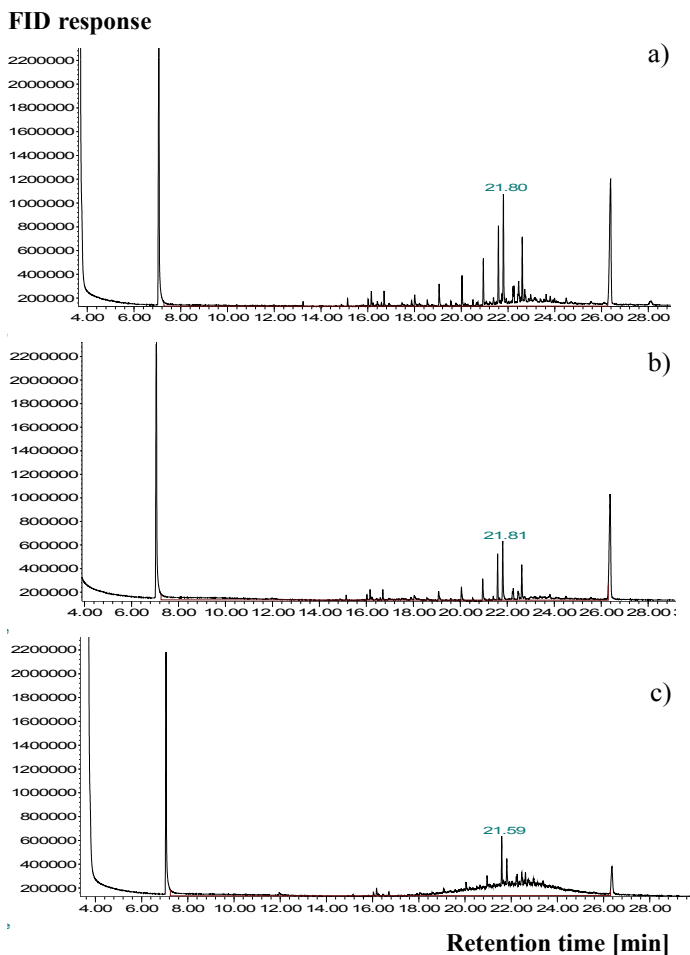


Fig. 7. GC chromatograms obtained for non-spiked soil with the different extraction procedures. The chromatograms are at the same scale. a = microwave-assisted extraction, b = Soxhlet-extraction, c = CEN prEN 14039:2004:E shake extraction.

The same was the case with Soxhlet –extraction, although the difference was not so evident. Of course the variation in the profile of the GC trace in the chromatogram may be caused either by the heterogeneous distribution of the contaminants in the soil samples or by diverging TPH concentrations in the sample. However, the same trend was observed in the chromatogram profiles for standard oil mixtures and for the spiked soil samples, as well (figure 8).

Because the composition of the standard oil mixtures was considered to be very homogeneous, it was assumed that the differences in the overall profile of the gas chromatogram resulted from the difference between the extraction methods. The clearest differences in the GC traces appeared to be in the peak height of the middle-distillate region compounds. This distinctive variation, caused by the extraction method, demonstrated that care should be taken when using chromatograms obtained after the application of different extraction methods on petroleum contaminated samples in fingerprinting or age-dating studies. Otherwise misleading conclusions concerning the age of the spillage could be drawn.

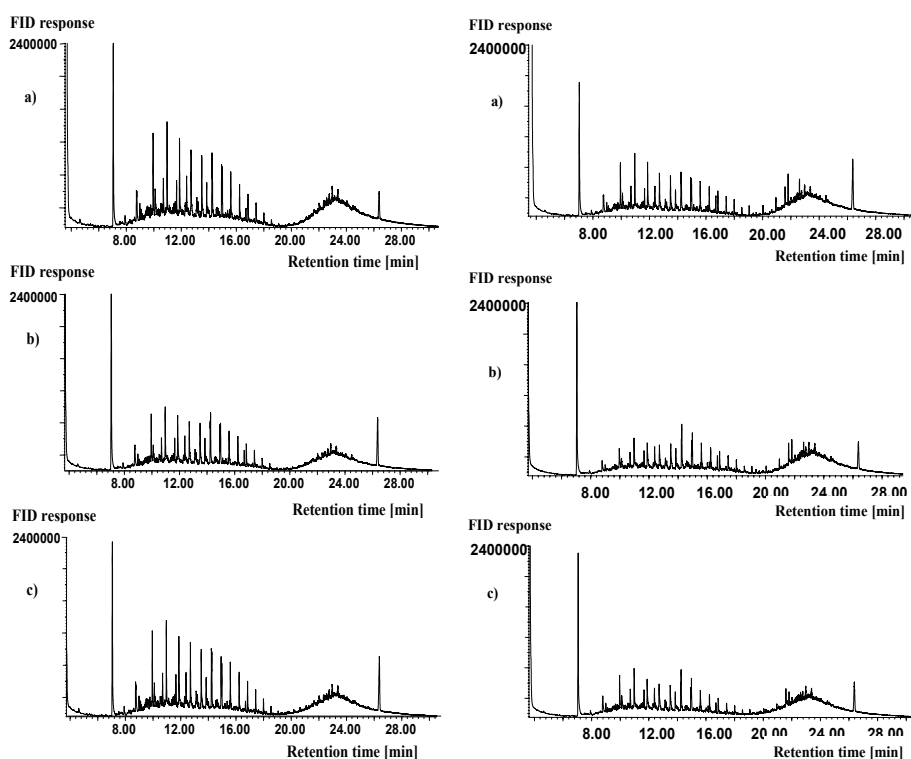


Fig. 8. GC chromatograms obtained for standard oil mixtures (left column) and for spiked soil samples (right column) with the different extraction procedures. The chromatograms are at the same scale. a = microwave-assisted extraction, b = Soxhlet-extraction, c = CEN prEN 14039:2004:E shake-extraction.

4.3.2 Matrix effects in GC determination (II)

The effect of a matrix-induced chromatographic response appears to be a commonly encountered problem in gas chromatographic analysis. Because its occurrence is not only dependent on the sample matrix, but also partly on the instrument used, it may also reduce the accuracy and precision of the gas chromatographic determination of TPH in soil samples. (115) In this study, the presence of a matrix effect and its consequent effect on quantitative determination of TPH by GC-FID was investigated. Two types of soil with three different TPH levels were selected for the evaluation. The occurrence of the relative systematic error resulting from the matrix effect was investigated by comparing the slopes of the matrix-matched calibration lines with that of a pure solvent calibration line (table 7).

Table 7. Statistical comparison of the slopes of matrix-matched calibration and conventional calibration.

Soil sample	TPH [mg/kg]	Slope						
		a ± 95% CI	s _e ²	F-test	F crit	s _{ep} ²	t-test	t crit
Conventional calibration		8.94E+08 ± 1.54E+07	3.24E+16					
Multiple standard addition method								
Soil #1	10 000	1.06E+09 ± 1.68E+07	1.13E+16	2.87	15.44	2.19E+16	6.30	2.45
Soil #1	2 500	1.07E+09 ± 1.90E+07	1.45E+16	2.23	15.44	2.35E+16	6.24	2.45
Soil #1	–	1.01E+09 ± 1.20E+07	5.78E+15	5.61	15.44	1.91E+16	4.84	2.45
Soil #2	10 000	1.03E+09 ± 1.12E+07	2.53E+15	12.80	39.17	2.05E+16	3.92	2.57
Soil #2	2 500	1.06E+09 ± 1.60E+07	1.03E+16	3.15	15.44	2.14E+16	6.21	2.45
Soil #2	–	1.02E+09 ± 1.73E+07	1.21E+16	2.68	15.44	2.23E+16	4.75	2.45

As the results indicate, the slopes of the conventional calibration line and the standard addition line were significantly different at the 5% probability level. Hence, there was significant enhancement of the response when matrix components were present. The same was true for both types of soil at each of the TPH level studied. The results confirmed that enhancement of the matrix-induced chromatographic response may result in a proportional systematic error in TPH determination by GC-FID. Due to the matrix effect, too high TPH concentrations were obtained when using external calibration with a standard oil diluted in an extracting solvent. Consequently, the results confirmed that the presence of a

matrix effect may prevent the accurate determination of TPH concentration in soil by GC-FID.

Despite various potential approaches for compensating for the matrix effect, few of them are actually applicable to TPH determination in soil (II). The standard addition method is often used as a means of correcting matrix interference effects that result in relative systematic errors. However, when the standard addition line was studied in more detail, there was a clear deviation from linearity over the extrapolated region. Figure 9 presents the observed percentage enhancement of the FID response due to the presence of a constant concentration of interfering matrix. The percentage enhancement of the FID response due to the presence of an interfering matrix was calculated as $[100 \times (A - B)/B]$, where A = the matrix standard response, and B = the fitted response (external calibration). The percentage suppression of the FID response compared to the response estimated from the regression line calculated from the measured calibration data was calculated as $[100 \times (C - D)/D]$, where C = the solvent standard response, and D = the fitted response (external calibration).

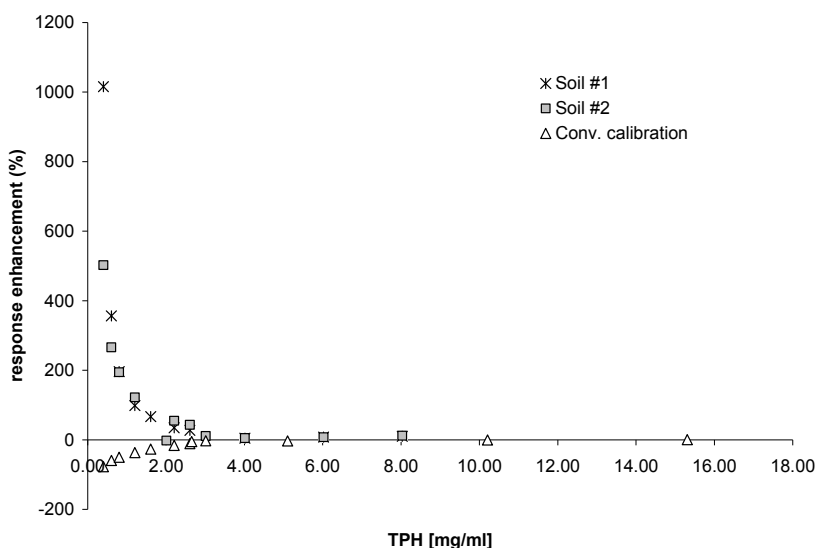


Fig. 9. Percentage enhancement of the FID response due to the presence of an interfering matrix in sample extracts (♦ Soil #1 ■ Soil #2) and percentage suppression of the FID response compared to the response estimated from the regression line calculated from the measured calibration data (▲ External calibration). For the calculation of suppression and enhancement values please refer to the text.

It was also evident that, over the extrapolated region, the percentage change in the FID response due to the interfering matrix was neither constant nor directly proportional to the TPH concentration.

Greater enhancement of the response was encountered at lower analyte concentrations. The magnitude of the matrix effect diminished at TPH concentrations higher than about 3 mg/ml and, as a consequence, the dependence of the response was linear. Because the CEN prEN 14039:2004:E procedure was used for sample preparation in this study, this concentration corresponds to a mineral oil concentration in soil of 3000 mg/kg. Consequently, it can be concluded that the range over which a linear response can be expected must be established when using matrix-matched calibration or the method of standard additions. Otherwise too high TPH concentrations will be obtained.

The shape of the external calibration line within the low TPH concentration region (< 3 mg/ml) was also studied. A slight deviation from linearity was detected. At lower analyte concentrations the FID response was suppressed due to the adsorption of certain analytes on the liner during injection. The calculated percentage suppression of the FID response compared to the response estimated from the regression line calculated from the measured calibration data is presented in figure 9. As a result of this suppression, the results obtained using the linear least squares regression line were underestimates of the actual TPH concentration of the sample. At higher TPH concentrations, the contribution of adsorptive effects diminishes and linear dependence of the response will be attained. It should be noted that this deviation from linearity occurs over a TPH concentration range that is important in environmental monitoring. For instance, at the recommended maximum value for mineral oil in soil (900 mg/kg in Finland), the results appear to be 30% lower than the target value. Therefore, matrix effect may increase the probability of underestimating the risk posed to human health or to the environment.

4.3.3 The effects of extraction and clean-up parameters (IV)

A two-level Plackett-Burman design was utilized to determine the effect of CEN prEN 14039:2004:E extraction method parameters on the extraction recovery of TPH in soil. The effects of 11 different method parameters, including both quantitative and qualitative factors, were investigated. The analytical methods used by the individual laboratories in an interlaboratory comparison were utilized in selecting the values for the upper and lower levels of the quantitative factors, as

well as for the levels of the qualitative factors. (57) The factors and their levels are summarized in table 8.

Table 8. The factors and their levels used in the Plackett-Burman design.

Factor	Unit	Type	Nominal level (0) [*]	Low level (-1)	High level (+1)	
F1	Sample mass	g	quantitative	20	15	25
F2	Soil type	-	qualitative	-	Soil #1	Soil#2
F3	Co-solvent type	-	qualitative	Acetone	Acetone	Methanol
F4	Extraction method	-	qualitative	Shake	Ultrasonic	Shake
F5	Water volume	ml	quantitative	100	50	150
F6	Adsorbent	-	qualitative	Florisil	Silica	Florisil
F7	Adsorbent mass	g	quantitative	1.25	0.5	2.0
F8	Extraction time	min	quantitative	60	40	80
F9	Extraction solvent volume	ml	quantitative	20 ± 0.1	15	25
F10	TPH level	mg/kg	quantitative	-	1000	5000
F11	Solvent type	-	qualitative	n-heptane	n-heptane	n-hexane

*tolerance reported if stated in CEN prEN 14039:2004 (E) and ISO/FDIS 16703:2004

The factor levels used were selected in such a way that, for all the quantitative factors except for adsorbent mass, the nominal level (0) of the factor represented the level of the factor as it is specified in the ISO/DIS 16703:2004 and CEN prEN 14039:2004:E draft standards. (45, 46) Due to practical reasons, the nominal level (0) of the adsorbent mass was selected to be lower than that specified in the draft standard. The upper level (+1) then matched that of the draft standard specification. Because a complete factorial design at two levels for eleven factors would have required a total of 2048 experiments, a Plackett-Burman design involving a total of 16 experiments was generated instead. The 16 experiments were carried out in duplicate. The calculated TPH recoveries were used as the response in the experimental design.

The studies on the certified reference material (III, IV) allowed us to conclude that quantitative TPH recoveries can be obtained by using an n-heptane - acetone solvent mixture and the Florisil clean-up procedure, as recommended in the ISO/DIS 16703:2004 and CEN prEN 14039:2004:E draft standards. However, adaptation of the draft standards was found to affect the validity of the analytical results. Variations in factor levels within the experimental region resulted in a TPH recovery higher than 200% or lower than 70%. The exact significance of this factor effect, and consequently the need for optimization, depends greatly on the

permissible variation in TPH recovery. Because there was no change in the standard deviation with changes in concentration, it was concluded that the presence of analytical bias cannot be demonstrated over a TPH recovery range of 84–116%. This was then accepted as a permissible variation in TPH recovery.

The factorial experiment revealed the statistically significant main effects on TPH recovery (Figure 10). The plot displays the change in the predicted values of the response, when the factor varies from a low to a high level, all other factors in the design being set at their average values. As can be seen from figure 10, the factors with a statistically significant effect on TPH recovery were the solvent and co-solvent used for extraction, the extraction time, adsorbent and its mass and sample TPH concentration.

The selection of extracting solvent had an especially strong influence on TPH recovery. n-heptane was found to be the preferred solvent for extracting TPH in soil, because using n-hexane as the solvent resulted in too high TPH recoveries. Thus, the results indicate that n-heptane should not be replaced by n-hexane. The effects of co-solvent, extraction time, adsorbent type and its mass and sample TPH concentration were moderate.

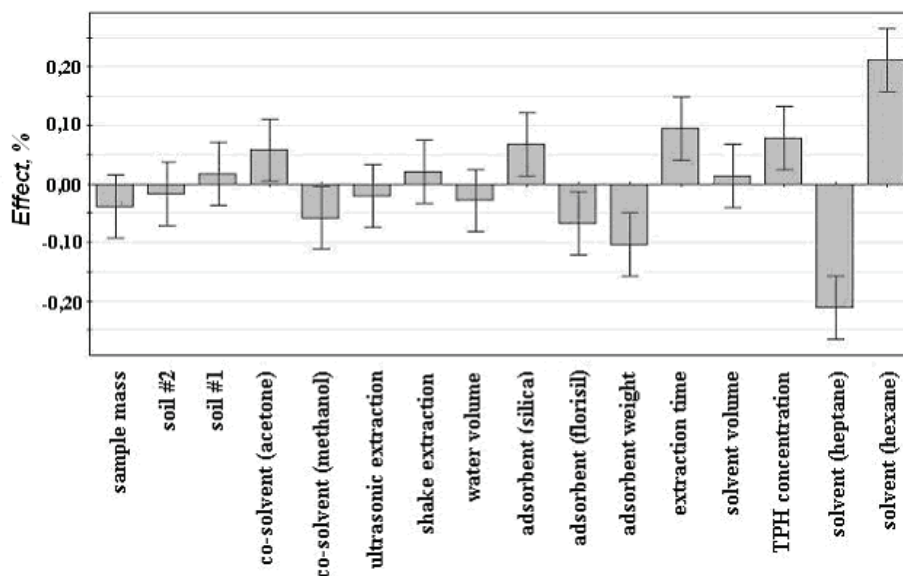


Fig. 10. Main effect plot for TPH recovery. The 95% confidence interval is shown for each effect.

When the influence of different co-solvents was studied, using acetone as a co-solvent and nominal levels for the other factors resulted in good TPH recoveries irrespective of the sample TPH concentration. Although a slight decrease in TPH recovery was observed with decreasing TPH concentrations, this variation was insignificant. It was assumed that the slight decrease in recovery probably resulted from the fact that a small part of the TPH is strongly adsorbed and is therefore non-extractable.

In contrast, when methanol was substituted for acetone, the decrease in recovery with decreasing TPH concentration eventually resulted in too low TPH recovery values at a TPH concentration close to the recommended maximum value for mineral oil in soil. (IV) Slightly better recoveries, especially at low TPH concentrations, were again obtained by optimizing the extraction time and mass of the adsorbent. With decreasing sample TPH concentration and methanol as co-solvent, longer extraction times were actually needed for quantitative TPH recovery. It is therefore evident that adaptation of the draft standards with respect to the significant factors especially, easily leads to erroneous TPH values. Acetone was found to be a slightly more effective co-solvent than methanol. This supported the earlier observations on the outstanding ability of acetone to remove entrained compounds. This is probably due to its ability to swell the soil matrix, which consequently enhances the diffusion of analytes and matrix components from the matrix into the solvent. The role of co-solvent seemed to be especially significant at low TPH concentrations, where the strongly adsorbed fraction of the hydrocarbons has to be removed from the soil matrix into the solvent.

The ISO/DIS 16703:2004 and CEN prEN 14039:2004:E draft standards consider Florisil to be applicable for extract clean-up. When the efficiencies of Florisil and silica were compared, both the type of adsorbent and its weight were found to have a significant influence on TPH recovery. By using nominal amounts of Florisil, good TPH recoveries could be obtained irrespective of the sample TPH concentration. When silica was substituted for Florisil, the increase in TPH recovery with increasing TPH concentration eventually resulted in too high TPH recovery values at high TPH concentrations. It was also found that, with increasing sample TPH concentration, a larger amount of silica was needed for quantitative TPH recovery. This clearly indicated the presence of an interfering agent, which was a consequence of the inefficient clean-up stage. Florisil was, therefore, found to be a more efficient adsorbent for the clean-up procedure. Consequently, the replacement of Florisil by silica should not be considered without careful method optimization.

As a whole this approach allowed us to conclude that the adaptation of draft standards certainly affects the validity of the analytical results.

4.3.4 The effect of GC operating settings (V)

The performance criterion proposed by ISO and CEN draft standards ISO/FDIS 16703:2004 and CEN prEN 14039:2004:E states that the response of *n*-C40 with respect to *n*-C20 shall be at least 0.8. If this criterion is not fulfilled during TPH determination by GC-FID, the validity of the results will be affected by mass discrimination. A D-optimal design was therefore utilized to study the effects of six different GC operating settings on this performance criterion. One qualitative factor (liner design) and five quantitative factors (inlet temperature, injection volume, split vent time, column flow and detector temperature) were selected as variables in the D-optimal design. The settings of these design variables were selected both from the analytical methods used by individual laboratories in an interlaboratory comparison and from the literature. The factors, as well as the levels of these factors, are summarized in table 9.

Table 9. Factors and their levels used in the D-optimal design.

Factor	Unit	Type	Low level (-1)	High level (+1)
F1 Injection temperature	°C	quantitative	260	330
F2 Split vent time	min	quantitative	2	4
F3 Injection volume	µl	quantitative	1	3
F4 FID temperature	°C	quantitative	300	330
F5 Column flow	ml/min	quantitative	2	3
F6 Inlet liner design	–	qualitative	with ads	no ads

A D-optimal design was then generated: RSM design, quadratic model with potential cubic terms, total runs 406. The best subset of experiments from the candidate set was selected on the basis of the G efficiency. In conclusion, a D-optimal design with 42 runs including three centre points was generated (G efficiency 60.6, condition number 14.6). The design matrix based on the G efficiency for the D-optimal design is presented in table 10.

Table 10. The design matrix based on G efficiency for D-optimal design.

Exp No	F1	F2	F3	F4	F5	F6
1	1	1	-1	1	-1	with ads
2	-1	1	1	1	-1	with ads
3	1	1	-1	-1	1	with ads
4	-1	1	1	-1	1	with ads
6	-1	-1	1	1	1	with ads
7	1	1	1	1	1	with ads
8	-1	-1	-1	-1	-0.4	with ads
9	-1	-1	-1	0.333	-1	with ads
10	-1	-1	1	-0.333	-1	with ads
11	-1	-1	0	-1	1	with ads
12	-1	1	0	-1	-1	with ads
13	1	-1	-1	1	0.4	with ads
14	1	-1	0	-1	1	with ads
15	1	-1	0	1	-1	with ads
16	1	1	1	0.333	-1	with ads
17	1	0.3	-1	-1	-1	with ads
18	0.343	-1	1	-1	-1	with ads
19	0	0	0	0	0	with ads
20	1	-1	-1	-1	-1	no ads
21	1	1	1	-1	-1	no ads
22	1	-1	1	1	-1	no ads
23	-1	-1	-1	1	1	no ads
24	-1	1	1	1	1	no ads
25	-1	-1	1	1	-0.4	no ads
26	-1	-1	0	-1	-1	no ads
27	-1	1	-1	-0.333	-1	no ads
28	-1	-0.3	-1	-1	1	no ads
29	-1	0.3	-1	1	-1	no ads
30	-1	0.3	1	-1	-1	no ads
31	1	-1	-1	0.333	1	no ads
32	1	-1	1	-1	0.4	no ads
33	1	1	-1	1	0.4	no ads
34	1	1	0	-1	1	no ads
35	1	-0.3	1	1	1	no ads
36	-0.343	-1	-1	1	-1	no ads
37	-0.343	-1	1	-1	1	no ads
38	-0.343	1	-1	-1	1	no ads
39	0.343	1	1	1	-1	no ads
40	0	0	0	0	0	no ads
41	0	0	0	0	0	no ads
42	0	0	0	0	0	no ads

The performance of the GC system was then tested by analysing aliquots of an n-heptane solution containing 30 mg/l of n-decane, n-eicosane and n-tetracontane according to the experimental design. For the evaluation, a desirability function (154) was constructed from three responses; 1) peak area for n-eicosane, 2) peak area for n-tetracontane, and 3) the peak area ratio (n-tetracontane / n-eicosane). This was required because the acceptable response ratio could be obtained, even though the GC operating conditions resulted in detrimental peak broadening and too low a signal-to-noise ratio. The experiment indicated the main effects and the statistical significances of factors for the response (Figure 11).

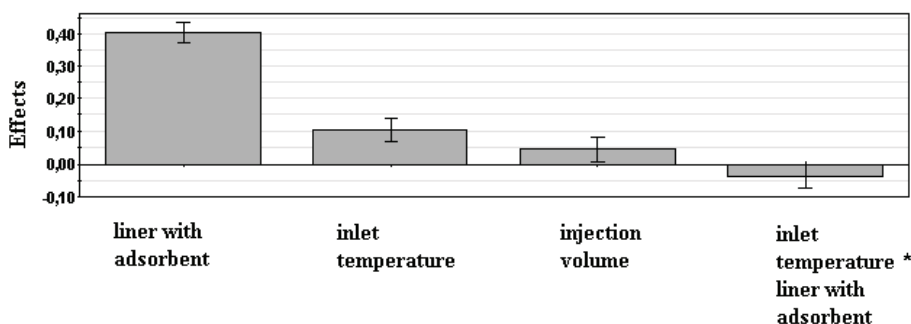


Fig. 11. Main effect plot for TPH recovery. The 95% confidence interval is shown for each effect.

This approach allowed us to conclude that the operating settings of the gas chromatographic system do have a significant influence on the *n*-C20 and *n*-C40 peak areas and on the proposed GC performance criteria. (V) The use of splitless injection with a non-optimal combination of GC system and operating settings easily result in the mass discrimination of high-boiling compounds. In particular, the combination of liner design, inlet temperature and injection volume require optimization. Liner design was expected to be significant, because literature surveys have indicated that the use of an adsorbent material inside the liner facilitates the vaporization of less volatile, high-boiling compounds. This consequently minimizes mass discrimination. Furthermore, the inlet temperature requires optimization in order to ensure that there will be enough thermal energy in the inlet liner to be absorbed by the high-boiling hydrocarbon compounds. (114) Only then can the interference caused by mass discrimination during sample vapour injection on the column be minimized.

An increase in injection volume resulted in a higher signal-to-noise ratio and sensitivity. As a result, this assisted in distinguishing the analyte peaks from the background. The results also indicated that, with a constant injection volume, higher peak areas and acceptable values for the response ratio can be more easily obtained with increasing inlet temperature. This was suggested to be a consequence of more efficient volatilization of n-C40, which then results in a larger peak area and response ratio. The measurement method was, however, robust with respect to small changes in the split vent time, column flow and detector temperature.

The results obtained in this study showed that, because the variation in GC splitless injection settings clearly affects the accuracy of TPH results, the splitless injection settings presuppose careful optimization. If no further specifications concerning the GC operating conditions are to be given, then it should be required that, especially when adapted methods are used for TPH analysis, the measurement uncertainty be stated together with the analysis result. This not only supports the credibility of analytical services, but also prevents the data end-users from drawing misleading conclusions concerning the environmental risks and potential need for remediation.

5 Conclusions

The CEN prEN 14039:2004E method, as utilized in this investigation, was found to be effective for the determination of the TPH concentration in contaminated soil samples. The presence of analytical bias could not be demonstrated, and the relative standard deviation obtained for certified reference material (ERM-CC015) was adequate, being 9%. However, the attempt to estimate the measurement uncertainty due to primary sampling and the analysis of petroleum hydrocarbons in soil indicated that, although it would be easier to follow a predetermined methodology for the assessment of measurement uncertainty, the determination of primary sampling and analytical uncertainty components should always be driven by the statistical characteristics of the data obtained. Otherwise the expanded uncertainty becomes uncertain itself, and no advantage is gained to support the end-use of the data.

The utilization of a proper measurement uncertainty estimation methodology revealed that there was a statistically significant precision change for sampling and analysis along with changes in the TPH concentration. The expanded relative uncertainty for TPH determination ranged from 21% at a TPH concentration of 895 mg/kg to 9% at a concentration of 10 019 mg/kg. The most significant finding was, however, that within the concentration range studied here 68–80% of the measurement uncertainty resulted from the analytical uncertainty. This demonstrated that, owing to its high relative contribution to the measurement uncertainty, the analytical stage should be the target of reduction in variance if the measurement uncertainty is to be improved. As far as the numerical values obtained for the measurement uncertainty are concerned, it should be understood that not all European countries have similar soil sampling guidelines and, consequently, great care should be taken in generalizing about the measurement uncertainty values.

Adaptation of the sample extraction and clean-up parameters was found to be one of the most significant factors affecting the analytical uncertainty. The results obtained showed that, due to the method dependence of the TPH parameter, strict implementation of the ISO and CEN draft standards ISO/DIS 16703:2004 and CEN prEN 14039:2004:E is necessary. Of the parameters investigated, the extracting solvent had the strongest influence on TPH recovery. The effects of co-solvent, extraction time, adsorbent type and its mass and sample TPH concentration were found to be more moderate, but still statistically significant.

Adaptation of the operating settings of the gas chromatographic system was also found to have a significant influence on the proposed GC performance criteria and, consequently, on the quality of TPH determination. In the case of splitless injection, the results were found to be seriously affected by the interference caused by the mass discrimination of high-boiling compounds. Avoidance of this mass discrimination interference required proper optimization of liner design, inlet temperature and injection volume. The measurement method, however, was robust with respect to small changes in split vent time, column flow and flame ionization detector temperature. The results demonstrated that adaptation of the draft standards by laboratories with respect to the significant factors of extraction, clean-up and GC determination stages certainly leads to erroneous TPH values. Therefore, adaptation clearly undermines the credibility of the data produced by laboratories and creates confusion for the end-users of the data.

Comparison of the extraction methods used for TPH determination indicated that the analytical uncertainty cannot be successfully reduced by replacing the CEN prEN 14039:2004:E shake extraction method by Soxhlet or microwave-assisted extraction. In the case of TPH-contaminated soil samples, there were no significant differences between the TPH recoveries obtained with the different extraction methods. The differences between the methods were obscured by the variation created by the heterogeneous distribution of the analytes in the spiked soil sample. In the case of synthetic solvent samples, however, there was a statistically significant difference between the extraction performances of the different methods. The best recovery and repeatability values ($99\% \pm 3\%$) were obtained with microwave-assisted extraction.

The matrix-induced chromatographic response effect was found to have a significant effect on the TPH determination by GC-FID. Due to the matrix effect there was a relative systematic error. As a result, too high TPH concentrations are obtained when conventional solvent calibration is used. Avoidance of the matrix effect by using standard addition method was not successful because there was a clear deviation from linearity over the extrapolated region. Thus, it is obvious that, when using matrix-matched calibration or the method of standard additions for the minimization of the matrix effect, the range over which a linear response can be expected has to be established. However, due to the variability in soil composition the effect of the matrix on TPH determination requires further study.

The results of this study showed that TPH concentrations can be reliably determined in contaminated soil samples by GC-FID. However, the results also

demonstrated that the analytical results are strongly dependent on the analytical methods chosen and, as a result, strict implementation of the ISO and CEN draft standards ISO/DIS 16703:2004 and CEN prEN 14039:2004:E is essential. If adapted methods are used, care should be taken to ensure that the methods used for TPH determination are comprehensively validated, and that routine quality control is carried out in order to ensure that the validation conclusions are applicable to daily work. At the moment, however, the validity of the method does not have to be presented. Therefore, this study will hopefully stimulate the authorities to require that, especially when adapted methods are used for TPH analysis, the measurement uncertainty is given together with the analysis result. This not only supports the credibility of the analytical services, but also prevents the data end-users from drawing misleading conclusions concerning the environmental risks and potential need for remediation.

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Original publications

- I Saari E, Perämäki P & Jalonen J (2007) A comparative study of solvent extraction of total petroleum hydrocarbons in soil. *Microchim. Acta* 158: 261–268.
- II Saari E, Perämäki P & Jalonen J (2007) Effect of sample matrix on the determination of total petroleum hydrocarbons (TPH) in soil by gas chromatography-flame ionization detection. *Microchem J* 87: 113–118.
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- V Saari E, Perämäki P & Jalonen J (in press) Evaluating the impact of GC operating settings on GC-FID performance for total petroleum hydrocarbon (TPH) determination. *Microchem J* (in press) DOI: doi:10.1016/j.microc.2009.09.004.

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ISBN 978-951-42-6075-9 (Paperback)

ISBN 978-951-42-6076-6 (PDF)

ISSN 0355-3191 (Print)

ISSN 1796-220X (Online)

