Suomen ympäristökeskuksen moniste

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Irma Mäkinen, Pirjo Sainio and Seppo Pönni

SYKE Proficiency Test 4/2004

Mineral oil from polluted soil

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Helsinki 2004
FINNISH ENVIRONMENT INSTITUTE

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CONTENT

1 INTRODUCTION

The Finnish Environment Institute carried out the proficiency test for the determination of mineral oil from polluted soil. The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43-1 (1) and ILAC Requirements (2) and ISO/DIS 13528 (3).

For analysis of mineral oil from soil the standard dfraft, ISO/DIS 16703 for the (GC-method) is mainly used nowadays (4). Additionally, the oil fractions $C_{>10}...C_{23}$ and $C_{>23}...C_{<40}$ were asked to report.

The former SYKE proficiency test for analysis of mineral oil in soil was carried out in 2002.

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

The responsibilities in organizing the interlaboratory comparison were as follows:
Irma Mäkinen, SYKE, coordinator
Pirjo Sainio, analytical expert
Seppo Pönni, Pirkanmaa Regional Environment Centre, preparation of the soil sample

2.2 Participants

In total 14 laboratories (one Latvian, one Norwegian, one Swedish and eleven Finnish) participated in the proficiency test (Annex 1). One laboratory reported two sets of the results obtained using two different method modifications.

2.3 Sample preparation and delivery

Firstly, one standard solution containing a known concentration of different oils was prepared (see Table 1). Before delivery, the sample ampoules were weighed to check the possible solvent evaporation.

Table 1. Preparation of the synthetic sample H1

Solutions	Preparation
Mixture of diesel oil (BAM KS 5002) and lubricating oil (BAM KS 5003)	9.941 ml diesel oil (20.001 mg/ml) + 9.987 ml lubricating oil (19.977 mg/ml) in 97.6469 ml heptane (Rathburn HPLC-Grade) → 4.079 mg/ml

The soil sample was prepared in the framework of the EU/HYCREF Project "Certified Reference Materials for the determination of mineral oil hydrocarbons in water, soil and waste" (G6RD-CT-2002-00854). The oil-contaminated soil was taken from Tampere Härmälä old gasoline station (5). The soil was dried at room temperature and it was sieved through a 0.125 mm sieve. To achieve homogeneity, the soil was mixed by a mechanized sample mixer. The soil was distributed in sub samples of 100 g using a rotary sample divider equipped with vibratory sample feeder. The amount of organic carbon was 6 ± 2 g/kg. After preparation the samples were kept frozen (- 20 °C).

The samples were delivered 26 May 2004 and they were asked to analyze before 20 August 2004. The samples were asked to keep frozen until analysis.

The results were asked to return before 23 August 2004. All participating laboratories reported results.

The preliminary lists of the results were delivered during the week 37.

2.4 Sample testing

2.4.1 Sample testing method

Testing of the synthetic sample was carried out according to normal GC-programme used in hydrocarbon analyses.

In testing of the soil sample the harmonized HYCREF-protocol for determination of hydrocarbon content in waste and soil (6) was used. This protocol recommends to use acetone/heptane as a solvent and the column technique as a clean-up procedure. The volume of organic phase recommended in ISO/DIS 16703 is not sufficient in clean-up step and so the harmonized protocol recommends to use a larger volume of extraction solvents than the draft standard method does.

2.4.2 Homogeneity study

Sample preparation of the synthetic sample H1 was tested by analysing the mineral oil mixtures in three ampoules (Table 2). In all tested samples the recovery of the mineral oil content was between 98.9 % and 100.2 % of the calculated concentration.

The soil sample H2 was tested for homogeneity. For this purpose, ten samples of all the prepared samples were randomly selected. The results of duplicates were used for calculation of the within unit and between unit standard deviation using one-way analysis of variance (3). The difference between units was not statistically significant (95 % confidence interval). The within unit standard deviation was 4.5 % and the between unit standard deviation was 3.8 %. The sample was homogenous.

2.4.3 Stability study

Stability testing of the synthetic sample H1 was based on the analyses carried out at 3 times: once before the delivery, 1 time during and 1 time after the proficiency test. (Annex 3).

Stability of the soil sample H2 data was tested from the samples stored at two temperatures

(4 °C and 25 °C) and the results were compared with the results of the sampled stored at the reference temperature – 20 °C. The results were evaluated assuming linear degradation using the SoftCRM1.2.0 Software (www.eie.gr). The presence of a significant trend in the data could be hint at degradation. There was not obtained a significant trend in the stability data of the soil sample H2 stored at the temperatures 4 °C and 25 °C (Annex 3).

2.5 Comments sent by the participants

In the preliminary reporting of the results the organizer has done a printing error. The participant (lab 3) had received the corrected results immediately.

2.6 Analytical methods

The draft standard method ISO/DIS 16703 was mainly used for the mineral oil analysis. One laboratory used method based on water quality standard and another laboratory used draft standard method for waste.

The soil sample was extracted with heptane/acetone, hexane/acetone, pentane/acetone, methanol/ pentane or dichloromethane (Annex 4). The sample intake 10 – 20 g was mainly used and the extraction was carried out by sonication or by shaking. Clean-up of the extracts was carried out using the batch technique or the column technique, but the batch technique was most commonly used. Four participants did not purify their extracts at all.

The mineral oil content was measured by GC-method. Mineral oil was mainly chromatographed with retention times between those of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$). Two participants used narrower retention time window (lab 3 and lab 4: C_{10} ...C_{35}) for integration. The GC columns and the oven temperature programmes varied from one laboratory to the other (Annex 4).

Four participants used the BAM Certified Reference Material as the standard solution, which is the mixture of diesel and lubricating oil. The most of the laboratories used different kinds of mixtures of mineral oils or n-alkanes.

2.7 Data treatment

2.7.1 Testing of outliers and normality of data

The participants were requested to report three results. Measurement uncertainties were asked to report for each result, too.

Before the statistical treatment, the data was tested according to Kolmogorov-Smirnov normality test and it was normally distributed in each case. Outliers were rejected according to Hampel test. The results were calculated using the Robust algorithm A (3).

2.7.2 Assigned value and its uncertainty

For the liquid sample H1 the calculated mineral oil content was used as the assigned value (4.08 mg/ml). The robust-mean was used as the assigned value for the soil sample H2 and for the results of different oil fractions ($C_{>10}$...C_{23} and $C_{>23}$...$C_{<40}$) in each sample

The uncertainty of the assigned value for the samples H1 and H2 was calculated using the standard deviation based on Robust algorithm. The uncertainty was 5.5 % and 9.7 %, respectively (95 % confidence interval).

2.7.3 Target value for total standard deviation

The target total standard deviation (s_{target}, %) used for calculation of the z scores was estimated on basis of the mineral oil content of the samples, the results of homogeneity and stability tests, the uncertainty of the estimated uncertainties of the assigned values. In calculation the s_{target} was 10 % for the analysis of the solvent sample H1 and 15 % for analysis of the soil sample H2 (20 % and 30 %, respectively, in 95 % confidence interval).

2.7.4 Evaluation of performance

The performance evaluation was carried out by using the z scores. The z scores were calculated using the following equation:

$$z = (x_i - X)/s$$

where
x_i = the reported value of the participant
X = the assigned value
s = the target total standard deviation (s_{target}).

z scores can be interpreted as follows:

$\lvert z \rvert \leq 2$	"satisfied" results
$2 < \lvert z \rvert < 3$	"questionable" results
$\lvert z \rvert \geq 3$	"unsatisfied" results.

The calculated z scores are presented in the results of each participant (Annex 7) and the summary of z scores is presented in Annex 10. Explanations to these Annexes are presented in Annex 6.

The organizing laboratory (SYKE) had the codes 8 and 10 in this proficiency test.

3. RESULTS AND PERFORMANCE

3.1 Results

All of the results reported by the laboratories are presented in Annex 5. Statistically treated results for each laboratory are presented in Annex 7. The graphical presentations of the results and the uncertainty estimations are presented in Annex 8.

The results were asked to report as triplicates. The repeatability (the within-laboratory standard deviation, s_w) of mineral oil was 3.4 % and the reproducibility (s_t) was 11 % in case of the sample H1 and 4.3 % and 17 %, respectively, in case of the sample H2 (Table 2). Thus the ratio s_t/s_w, a measure for the robustness of the methods used, was 3 (the sample H1) and 4 (the sample H2). It should be between 2 and 3 for robust methods (7).

The participants reported the results for the mineral oil fractions $C_{>10}...C_{23}$ and $C_{>23}...C_{<40}$ also as triplicates, and the reproducibility was 15 % and 22 %, respectively.

Table 2. Results of triplicate determinations (ANOVA statistics)

Analyte	Sample	Unit	Ass. val	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Accepted z-val %
Min.oil-GC	H1	mg/ml	4,08	4,018	4	0,1372	0,4491	0,4696	3,4	11	12	20	14	86
	H2	mg/kg	2254	2224	2220	95,57	369,8	381,9	4,3	17	17	30	15	93
Oil fr.>10-23	H1	mg/ml	2,38	2,379	2,48	0,07522	0,4428	0,4492	3,2	19	19		12	
	H2	mg/kg	651	640,6	667,5	28,27	93,51	97,69	4,4	15	15		12	
Oil fr.>23-40	H1	mg/ml	1,63	1,603	1,6	0,07611	0,2704	0,2809	4,7	17	18		12	
	H2	mg/kg	1606	1577	1604	60,99	348,6	353,9	3,9	22	22		12	

Ass val - assigned value, Md - median, sw - repeatability standard error, sb - standard error between laboratories, st - reproducibility standard error

The results of the standard solution (the sample H1) showed a good agreement between the calculated mineral oil content 4.08 mg/ml, the robust-mean value and the mean value of the data was 4.02 mg/ml (Table 3). The robust standard deviation of the results was 8.3 %, which was lower than the standard deviation (21 %) in the former proficiency test in 2002 (8).

Table 3. Summary of the proficiency test

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
Min.oil-GC	H1	mg/ml	4,08	4,02	4,02	4	0,34	8,3	14	20	86
	H2	mg/kg	2254	2224,26	2254,89	2220	343,65	15,2	15	30	93
Oil fr.>10-23	H1	mg/ml	2,38	2,38	2,46	2,48	0,31	12,6	12		
	H2	mg/kg	651	640,6	653,91	667,5	83,43	12,8	12		
Oil fr.>23-40	H1	mg/ml	1,63	1,6	1,63	1,61	0,3	18,6	12		
	H2	mg/kg	1606	1576,86	1604,87	1603,5	327,39	20,4	12		

where,

Ass. val.	the assigned value
Mean	the mean value
Mean rob	robust mean
Md	the median value
SD rob	the robust standard deviation
SD rob %	the robust standard deviation as percents
2*Targ. SD%	the target total standard deviation (95 % confidence interval)
Num of Labs	number of participants
Accepted z-val%	accepted z values: the results (%), where $\lvert z \rvert \leq 2$.

Although most participants used the same international standard draft method (ISO/DIS 16703) for analysis of the soil sample, the procedures of the participants differed e.g. in extraction solvent, technique in clean-up steps and in calibration solutions (Annex 4).

Table 4. The results or the mean values (mg/kg) obtained using different extraction or clean-up procedures in analysis of the soil sample H2 (the result of the lab 4,1280 mg/kg, was not taken into account in calculation)

X_{rob}	$X_{shaking}$	$X_{sonication}$	$X_{no\ clean\text{-}up}$	X_{batch}	X_{column}	X_{HYCREF}
2254	2259	2119	2507	2338	2003	1883
n=15	n=8	n=6	n=2	n=9	n=2	n=11

Extraction procedure seemed to have some effect on the results (Table 4). The mean value of the results obtained using shaking (2259 mg/kg) was slightly higher than the mean value obtained using sonication (2119 mg/kg). According to the results of the certification study carried out in the EU/HYCREF project the extraction procedure had effect on analysis of high mineral oil content (e.g. from wastes) and on analysis of material with high amount of organic matter (e.g. peat material). In particular, in these cases shaking is recommended to use in extraction.

The results of this proficiency test also shows, that the column technique seems to be more effective than the batch technique (Table 4). The similar results were obtained, when the batch technique and the column technique were compared during the EU/HYCREF project (9).

The used calibration range varied greatly from one laboratory to the other. The number of calibration points was in the most cases 6.

There was variation in the reported uncertainties of the analytical methods used by the laboratories (Annex 9). Estimation based on validation and internal quality control data was the most common procedure in calculating of the measurement uncertainty. The uncertainty was overestimated in some laboratories.

The reporting of results for the mineral oil fractions $C_{>10}...C_{23}$ and $C_{>23}...C_{<40}$ is important in Finnish soil remediation projects. The results for these fractions seemed to be rather similar in different laboratories except for laboratories 2 and 4 (Annex 8). The method of laboratory 4 is based on Nordtest method were determination is up to C_{35}.

3.2 Estimation of performance

In this proficiency test, 90 % of the participating laboratories reported satisfied results, based on the target total standard deviation 20 % (the synthetic sample) and 30 % (the soil sample) used in calculating of z scores in 95 % confidence interval (Annex 10). Only three participants had one result, which was not satisfied.

Calibration of the analytical method or the performance of the GC instrument should be checked by two participants, because their results obtained from the synthetic sample was not satisfied. Only one laboratory obtained the unsatisfied result in analysis of mineral oil from the soil sample. Although the participants used mainly the same draft international standard ISO/DIS 16703 for the analysis of soil samples, the procedures are still rather different in different laboratories, but they do not seem have much effect on results. However, the clean-up procedure showed to have some effect on the results.

The SYKE proficiency test for analysis of mineral oil content in polluted soil in using the GC method was carried out for the third time. These results have improved since the last comparison in 2002.

4 SUMMARY

The Finnish Environment Institute carried out the proficiency test for the determination of mineral oil content from polluted soil using the GC method. Additionally, the reporting of oil fractions $C_{>10}...C_{23}$ and $C_{>23}...C_{<40}$ as well. A total of 14 laboratories from Finland, Latvia, Norway and Sweden were participated. One laboratory reported the results obtained using two different method modifications.

One standard solution containing a known concentration of different oils were prepared. One soil sample was delivered to the participating laboratories.

The draft standard method ISO/DIS 16703 was mainly used for analysis of mineral oil from the soil sample. Even the participants used mainly the same draft for the analysis of soil , the procedures were still rather different in different laboratories, but they did not seem to have much effect on results. However, the clean-up procedure showed to have some effect on the results.

For the liquid synthetic sample the calculated mineral oil content was used as the assigned value. For the soil samples the robust mean value was used as the assigned value.

In this proficiency test, 90 % of the participating laboratories reported satisfied results, based on the target total standard deviation 20 % or 30 % used in calculating of z scores in 95 % confidence interval. Only three participants had reported one result, which was not satisfied.

The SYKE proficiency test for analysis of mineral oil content in polluted soil in using the GC method was carried out for the third time. These results have improved since the last comparison in 2002.

5 YHTEENVETO

Suomen ympäristökeskus järjesti toukokuussa 2004 pätevyyskokeen mineraaliöljyn määrittämiseksi pilaantuneesta maasta ja synteettisestä näytteestä. Pätevyyskokeessa pyydettiin käyttämään kaasukromatografisia määritysmenetelmiä. Myös öljyfraktioiden $C_{>10}...C_{23}$ ja $C_{>23}...C_{<40}$ tulokset pyydettiin ilmoittamaan. Pätevyyskokeeseen osallistui kaikkiaan 14 laboratoriota Suomesta, Latviasta, Norjasta ja Ruotsista.

Pätevyyskokeen näytteinä oli yksi tunnetun öljypitoisuuden omaava standardiliuos ja yksi maanäyte, joka oli valmistettu EU/HYCREF-hankkeessa. Hanke koski vertailumateriaalien valmistamista mineraaliöljyjen määrittämiseksi maasta, sedimentistä, jätteistä ja vesistä.

Analysoinnissa käytettiin pääasiassa standardiluonnosmenetelmää ISO/DIS 16703 eri variaatioin. Mm. ravistelutekniikka, uutteen puhdistustekniikka ja kalibrointiaineet vaihtelivat eri laboratorioissa.

Synteettiselle näytteelle käytettiin vertailuarvona laskennallista öljypitoisuutta. Maanäytteelle käytettiin vertailuarvona robusti-keskiarvoa.

Tässä pätevyyskokeessa 90 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin 20 % (synteettinen näyte) tai 30 % (maanäyte). 95 %:n luotettavuustasolla vain kolme laboratoriota raportoi tuloksen, joka ei ollut tyydyttävä.

Pätevyyskoe mineraaliöljyn määrittämiseksi pilaantuneesta maasta järjestettiin kolmannen kerran Suomessa. Tulokset olivat parantuneet edellisestä vertailukokeesta, joka järjestettiin syksyllä 2002.

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8. Mäkinen, I., Suortti, A.-M., Huhtala, S and Pönni, S., 2002. Interlaboratory comparison 4/2002 – Mineral oil from polluted soil and water. Mimeograph Series of the Finnish Environment Institute no. 269, Helsinki (in English).

9. BAM contribution to the task in WP-2 "Optimisation of methods used for ILCs" - EU/HYCREF Project G6RD-CT-2002-00854.

ANNEX 1. PARTICIPANTS IN THE INTERLABORATORY COMPARISON 4/2004

Alcontrol AB, Skara, Sweden

Analycen Oy, Tampere, Finland

Ekokem Oy Ab, Riihimäki, Finland

Eurofins A/S, Norway

Fortum Oil Oy, Porvoo, Finland

Golder Associates Oy, Helsinki, Finland

Insinööritoimisto Paavo Ristola Oy, Hollola, Finland

Nablabs Oy/Oy Juve AC, Rovaniemi, Finland

Lahden tiede- ja yrityspuisto Oy, Lahden Tutkimuslaboratorio, Lahti, Finland

Novalab Oy, Karkkila, Finland

PSV-Maa ja Vesi Oy, Oulu, Finland

SGS Inspection Services Oy, Hamina, Finland

SIA VIDES AUDITS Laboratory, Latvia

Finnish Environment Institute, Laboratory, Helsinki, Finland

ANNEX 2. HOMOGENEITY TESTING

Sample H1 – the theoretical concentration 4.08 mg/ml

4,042 (99.1 %)	4,049 (99.2 %)	4,041 (99.0 %)
4,033 (98.8 %)	4,086 (100.1 %)	4,074 (99.8 %)
4,057 (99.4 %)	4,117 (100.9 %)	4,057 (99.4 %)

Sample H2

Results of duplicates were as follows:

1660	1678	1870	1582	1562	1787	1735	1734	1691	1561	s_w = **75. 8 mg/kg (4.5 %)**
1667	1747	1807	1717	1478	1636	1802	1742	1639	1787	s_{bb} = **64.7 mg/kg (3.8 %)**

ANNEX 3. STABILITY TESTING

Sample H1

Stability of the synthetic sample H1 was tested. The mineral oil content the calculated mineral oil content was obtained during the analysing period. After receiving the sample H1 was asked to keep in cool (4 °C).

24 May 04	29 May 04	28 August 04
4,042	4,024	4,051
4,049	3,989	4,161

Sample H2

Stability study of the soil sample H2 was based on the analyses carried out three times after the preparation of the sample. As the reference temperature was used – 20 °C. Stability was tested at the temperature 4 °C and 25 °C. After receiving the sample H1 was asked to keep frozen (-20 °C).

Data for T= 4°C

Time in Months =>

Samples	January 2004	March 2004	June 2004
1	1709	1755	1808
2	1740	1782	1929
3	1784	1749	1668

Table of mean values for T= 4°

Mean	1 744.333	1 762.000	1 801.667
STDev	37.687	17.578	130.615
CV(%)	2.161	0.998	7.250

Slope of the linear regression significantly <> 0 (99%) : No
Slope of the linear regression significantly <> 0 (95%) : No
SE Slope (95%)= 1.200

Data for T= 25°C

Time in Months =>

Samples	January2004	March 2004	June 2004
1	1673	1585	1922
2	1826	1664	1633
3	1606	1536	1734

Table of mean values for T= 25°C

Mean	1 701.667	1 595.000	1 763.000
STDev	112.767	64.583	146.666
CV(%)	6.627	4.049	8.319

Slope of the linear regression significantly <> 0 (99%) : No
Slope of the linear regression significantly <> 0 (95%) : No
SE Slope (95%)= 29.901

Ratio of Means Table

R(T)=XT/Xref ± Uncertainty(T)

	January 2004	March 2 04	June 2004
R(4) ± U(4)	1.043 ± 0.047	0.989 ± 0.027	0.980 ± 0.105
R(25) ± U(25)	1.018 ± 0.079	0.896 ± 0.043	0.959 ± 0.110

Slope of the Linear Regression significantly <> 0 ?

	a = 99%	a = 95%	SE Slope (95
R(4)	No	No	0.(
R(25)	No	No	0.(

ANNEX 4.1 ANALYTICAL METHODS

Experimental conditions - intake, treatment and GC-conditions

Lab	g	Extr.solvent	Extr.method	Separation	Acet/rem.	Clean-up	Ratio of Florisil	Clean-up perform.	Injection and volume	GC-column	m/mm/μm	Pre-col.
1	~10	hexane (10 ml) acetone (20 ml)	Shaking	Centrifug.	$NaCl/H_3PO_4$	Batch	2g/16 ml	no vacuum	1μl/on-col.	SP-SIL8-5	9/0.25/0.25	No
2	~20	hexane (10 ml) acetone (20 ml)	Sonication	Setting	Water	Column	2g	no vacuum	1μl/on-col.	RTX-5	30/0.53/0.50	No
3	~10	dichlorometane (20 ml)	Shaking	Centrifug.		No			1μl/split/splitless	Restd-5	30/0.25/0.50	No
4		methanol+pentane	Shaking+ Sonication			No						
5	~20	heptane (10 ml) acetone (20 ml)	Sonication	Centrifug.	Water	Batch	1.5g/0.3g/10ml	shaking	0.2μl/on-col.	HP-5	15/0.32/1.0	HMDS 5/0.53
6	~10	hexane (5ml) acetone (10 ml)	Sonication	Centrifug.	Water	Batch	1.5g/0.5g/5ml	shaking	2μl/splitless	DB-1	15/0.35/0.15	HP retention 1.5/0.53
7		heptane (10 ml) acetone (20 ml)	Shaking	Centrifug.	Water	Batch	2g:1		2/splitt	Agilent	12/0.32/0.25	
8	~10	heptane (10 ml) acetone (20 ml)	Sonication	Centrifug.	Water	Batch	1.5g/0.5g/10ml	no vacuum	1μl/on-col.	SGE BPX-5	5/0.32/1	Silica 2/0.53
9	~25	pentane (20 ml) acetone (20 ml)	Shaking			No						
10	~10	heptane (20 ml) acetone (40 ml)	Sonication	Centrifug.	Water	Column	2g/2g/10ml	no vacuum	1μl/on-col.	SGE BPX-5	5/0.32/1	Silica 2/0.53
11	~15	hexane (10 ml) acetone (20 ml)	Shaking	Centrifug.		No			2μl/autom.	DB-5	30/0.32/0.25	
12	~20	hexane (25ml) acetone (50 ml)	Sonication	Decant.	Water	Batch			2μl/splitless	NB-1	15/0.32/0.1	
13	~20	hexane (10 ml) acetone (20 ml)	Shaking	Centrifug.	Water	Batch	1.5g/0.5g/10ml	shaking	1μl/splitless	CP-SIL 5CB	15/0.32/0.25	
14		hexane+acetone	Shaking	Centrifug.		Batch	1.5-3/0.5	vacuum	autom/on-col.	SGE BPX-5	15/0.32/1	SGE Silica 2
15		heptane (10 ml) acetone (20 ml)	Shaking	Centrifug.		Batch	3/1		0.5/om-col	Methyl-silicone	30/0.32/0.25	Yes

ANNEX 4.2 ANALYTICAL METHODS

Experimental conditions- GC-conditions, calibration, limit of determination, integration and guide for analysis

Lab	Oven-T °C/min	FID-T °C	Gas ml/min	Standard	No.of points/ Cal.range mg/ml	Purity of cal. oil taken into account	L of D mg/ml	Intergration	Solvent chr	Reference
1	60°/10,15°/1 to 27°/5, 514.5°/1 to 290°/23	300	N_2 1.3	BAM CRM 5004	6/0.05-2.0	No	0.1	Yes		EN ISO 9377-2
2	60°/2,30°/1 to 320°/10	330	He 20 psi	Diesel+Motor	6/1-10		0.2	Yes	Yes	ISO/DIS 16703, 2001
3	40°/2,10°/1 to 200°/10, 6°/1 to 310°/8	325		n-alkanes	0-20	No		Yes	No	Nordtest report 329, 1996 measurement: until C_{35}
4										Nordtest method measurement: until C_{35}
5	60°/1,20°/1 to 320°/15	325	He 4		6/0.1-2.4	No	0.05	Yes	No	ISO/DIS 16703
6	40°/4, 50o/1 to 325°/10	340	He	Gas oil+ Base oil	7/0.3-8	Yes	0.1	Yes	Yes	ISO/DIS 16703
7	60°/1, 20°/1 to 300°/8	300	He 2	Different oils	6/0-2		0.05	Yes		CEN Draft
8	60°/5,30°/1 to 330°/5, 50o/1 to 340°/7	360	He 2	BAM CRM 5004	11/0.05-9.56	Yes	0.05	Yes	No	ISO/CD 16703
9				n-alkanes						
10	60°/5,30°/1 to 330°/5, 50o/1 to 340°/7	360	He 2	BAM CRM 5004	8/0.10-9.87	Yes	0.05	Yes	No	EU/HYCREF-Protocol
11	40°,20°/1 to 320°/15	350		BAM CRM 5004	9/0.05-8.0		0.05			ISO/DIS 16703
12	50°/4, 15°/1 to 320°/10	330	He 1.2	BAM CRM 5004	6/0.17-1.02		0.1			ISO Draft
13	50°/5, 15°/1 to 300°/13	325	He 1	Diesel+Lubr.	7/0-2		0.01	Yes	Yes	ISO Draft
14	50°/1, 20°/1 to 340°/19.5	360	He	Diesel+Lubr.	6/0.2-1.2		0.03	Yes	Yes	ISO/DIS 16703
15	60°/2, 10°/1 to 300°	300	He 1.5	Diesel+Lubr.	6/0.32-32		0.2		Yes	ISO/DIS 16703

ANNEX 5. RESULTS REPORTED BY THE LABORATORIES AND THEIR CLEAN UP TECHNIQUES

Analyte	Sample	Unit	1				2				3				4			
Min.oil-GC	H1	mg/ml	3,23	2,93	3,04	3	3,9596	3,9871	4,0131	3	5,222	4,874	5,051	3	3,309	3,459	3,822	3
	H2	mg/kg	2565	2705	2527	2	2054	2083	1903	1	1969,6	2038,0	2058,9	3	1286	1150	1403	3
Oil fr.>10-23	H1	mg/ml					1,2609	1,2575	1,2574	3	2,950	2,846	2,898	3	2,111	2,197	2,374	3
	H2	mg/kg					529	527	479	1	697,7	706,0	735,8	3	478	454	545	3
Oil fr.>23-40	H1	mg/ml					2,5987	2,7296	2,7557	3	2,272	2,033	2,153	3	1,198	1,263	1,449	3
	H2	mg/kg					1525	1556	1424	1	1272,0	1332,1	1363,0	3	808	696	829	3
Analyte	Sample	Unit	5				6				7				8			
Min.oil-GC	H1	mg/ml	4,31	4,34	4,40	3	3,77	3,76	3,76	3	3,79	3,65	3,76	3	4,02	4,05	4,16	3
	H2	mg/kg	2140	2000	2170	2	2460	2510	2530	2	2220	2160	2210	2	2190	2300	2250	2
Oil fr.>10-23	H1	mg/ml	2,60	2,62	2,66	3	2,48	2,48	2,47	3	2,44	2,33	2,30	3				
	H2	mg/kg	663	591	613	2	728	744	754	2	710	700	650	2				
Oil fr.>23-40	H1	mg/ml	1,70	1,72	1,74	3	1,29	1,28	1,29	3	1,35	1,32	1,46	3				
	H2	mg/kg	1480	1410	1560	2	1730	1760	1770	2	1510	1460	1560	2				
Analyte	Sample	Unit	9				10				11				12			
Min.oil-GC	H1	mg/ml	4,120	3,920	3,970	3					4,06	4,00	4,14	3	3,90	3,90	4,43	3
	H2	mg/kg	2770	2800	2670	3	1965	1989	2023	1	2260	2510	2030	3	1780	1890	1900	2
Oil fr.>10-23	H1	mg/ml	2,510	2,460	2,480	3					1,87	1,88	1,92	3	2,56	2,53	2,87	3
	H2	mg/kg	699	715	706	3					514	496	457	3	576	640	640	2
Oil fr.>23-40	H1	mg/ml	1,610	1,460	1,490	3					1,98	2,02	1,94	3	1,34	1,37	1,56	3
	H2	mg/kg	2070	2090	1960	3					1890	1960	1790	3	1200	1250	1260	2
Analyte	Sample	Unit	13				14				15							
Min.oil-GC	H1	mg/ml	4,15	4,12	4,28	3	3,83	3,91	4,00	3	4,43	4,52	4,42	3				
	H2	mg/kg	2490	2340	2300	2	2623	2522	2467	2	2580	2610	2690	2				
Oil fr.>10-23	H1	mg/ml	2,64	2,60	2,68	3	2,23	2,27	2,30	3	2,75	2,81	2,75	3				
	H2	mg/kg	701	672	651	2	707	673	660	2	740	750	760	2				
Oil fr.>23-40	H1	mg/ml	1,51	1,52	1,60	3	1,60	1,63	1,68	3	1,69	1,71	1,67	3				
	H2	mg/kg	1786	1665	1647	2	1899	1832	1793	2	1840	1860	1930	2				

Clean-up methods:

1 column technique
2 batch technique
3 no clean-up

ANNEX 6. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant (Annex 10):

Analyte	Min.oil-GC
Unit	mg/kg or mg/ml
Sample	The code of the sample
z-Graphics	z score - the graphical presentation
z-value	z-score, calculated as follows: $z = (x_i - X)/s$, where x_i = the result of the invidual laboratory X = the reference value (the assigned value) s = the target value for the total standard deviation (s_{target}).
Outl test OK	yes - the result passed the outlier test
Assigned value	the reference value
2* Targ SD %	the target total standard deviation (95 % confidence interval).
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores (Annex 13):

A - accepted ($-2 \leq z \leq 2$)
p - questionable ($2 < z \leq 3$), positive error, the result > X
n - questionable ($-3 \leq z < -2$), negative error, the result < X
P - non- accepted ($z > 3$), positive error, the result >>> X
N - non- accepted ($z < -3$), negative error, the result <<< X (X = the reference value)

Robust analysis (Calculation of the assigned value for the samples M1 and U1, Annex 7)

The items of data is sorted into increasing order, $x_1, x_2, \ldots, x_i, \ldots, x_p$.

Initial values for x^* and s^* are calculated as:

$X^* =$ median of x_i $(i = 1 \ldots p)$
$S^* = 1.483$ median of $| x_i - x^* |$ $(i = 1 \ldots p)$

The values of x^* and s^* are updated by calculating
$\varphi = 1.5\, s^*$

For each x_i is calculated:

$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$
$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$
$x_i^* = x_i$ otherwise

The new values of x^* and s^* are calculated from:

$$X^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergenes.

Ref: Statistical methods for use in proficiency testing by interlaboratory comparisons, Annex C (ISO/DIS 13528, Draft 2002-02-18)

ANNEX 7. RESULT OF EACH PARTICIPANT

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
Min.oil-GC	mg/ml	H1		-2,484	yes	4,08	20	3,067	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		1,020	yes	2254	30	2599	2220	2224	373,7	16,8	15	0	0	15
Laboratory 2																
Min.oil-GC	mg/ml	H1		-0,229	yes	4,08	20	3,987	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-0,712	yes	2254	30	2013	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		1,259	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		511,7	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			H	1,63		2,695	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1502	1604	1577	344	21,8	12	0	0	12
Laboratory 3																
Min.oil-GC	mg/ml	H1		2,375	yes	4,08	20	5,049	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-0,686	yes	2254	30	2022	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,898	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		713,2	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		2,153	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1322	1604	1577	344	21,8	12	0	0	12
Laboratory 4																
Min.oil-GC	mg/ml	H1		-1,348	yes	4,08	20	3,53	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-2,882	yes	2254	30	1280	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,227	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		492,3	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,303	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		777,7	1604	1577	344	21,8	12	0	0	12
Laboratory 5																
Min.oil-GC	mg/ml	H1		0,662	yes	4,08	20	4,35	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-0,446	yes	2254	30	2103	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,627	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		622,3	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,72	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1483	1604	1577	344	21,8	12	0	0	12
Laboratory 6																
Min.oil-GC	mg/ml	H1		-0,776	yes	4,08	20	3,763	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		0,728	yes	2254	30	2500	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,477	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		742	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,287	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1753	1604	1577	344	21,8	12	0	0	12
Laboratory 7																
Min.oil-GC	mg/ml	H1		-0,850	yes	4,08	20	3,733	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-0,170	yes	2254	30	2197	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,357	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		686,7	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,377	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1510	1604	1577	344	21,8	12	0	0	12
Laboratory 8																
Min.oil-GC	mg/ml	H1		-0,008	yes	4,08	20	4,077	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-0,022	yes	2254	30	2247	2220	2224	373,7	16,8	15	0	0	15
Laboratory 9																
Min.oil-GC	mg/ml	H1		-0,188	yes	4,08	20	4,003	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		1,457	yes	2254	30	2747	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,483	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		706,7	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,52	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		2040	1604	1577	344	21,8	12	0	0	12
Laboratory 10																
Min.oil-GC	mg/kg	H2		-0,774	yes	2254	30	1992	2220	2224	373,7	16,8	15	0	0	15

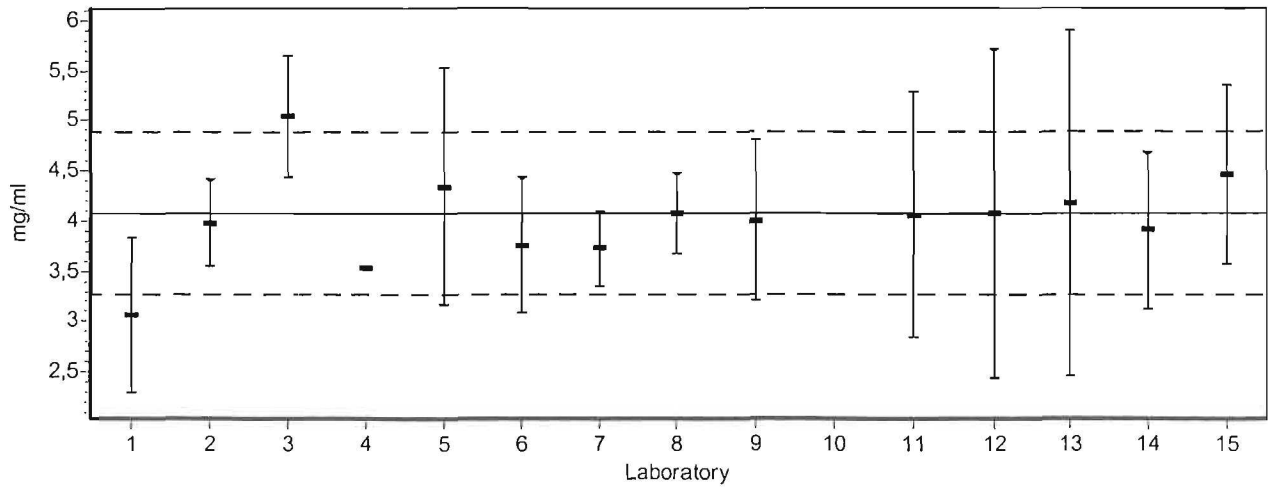
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 11																
Min.oil-GC	mg/ml	H1		-0,033	yes	4,08	20	4,067	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		0,037	yes	2254	30	2267	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		1,89	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		489	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,98	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1880	1604	1577	344	21,8	12	0	0	12
Laboratory 12																
Min.oil-GC	mg/ml	H1		-0,008	yes	4,08	20	4,077	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		-1,175	yes	2254	30	1857	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,653	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		618,7	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,423	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1237	1604	1577	344	21,8	12	0	0	12
Laboratory 13																
Min.oil-GC	mg/ml	H1		0,253	yes	4,08	20	4,183	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		0,363	yes	2254	30	2377	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,64	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		674,7	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,543	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1699	1604	1577	344	21,8	12	0	0	12
Laboratory 14																
Min.oil-GC	mg/ml	H1		-0,409	yes	4,08	20	3,913	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		0,838	yes	2254	30	2537	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,267	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		680	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,637	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1841	1604	1577	344	21,8	12	0	0	12
Laboratory 15																
Min.oil-GC	mg/ml	H1		0,923	yes	4,08	20	4,457	4	4,018	0,459	11,4	14	0	0	14
	mg/kg	H2		1,102	yes	2254	30	2627	2220	2224	373,7	16,8	15	0	0	15
Oil fr.>10-23	mg/ml	H1			yes	2,38		2,77	2,48	2,379	0,4365	18,3	12	0	0	12
	mg/kg	H2			yes	651		750	667,5	640,6	95,1	14,8	12	0	0	12
Oil fr.>23-40	mg/ml	H1			yes	1,63		1,69	1,6	1,603	0,2727	17,0	11	1	0	12
	mg/kg	H2			yes	1606		1877	1604	1577	344	21,8	12	0	0	12

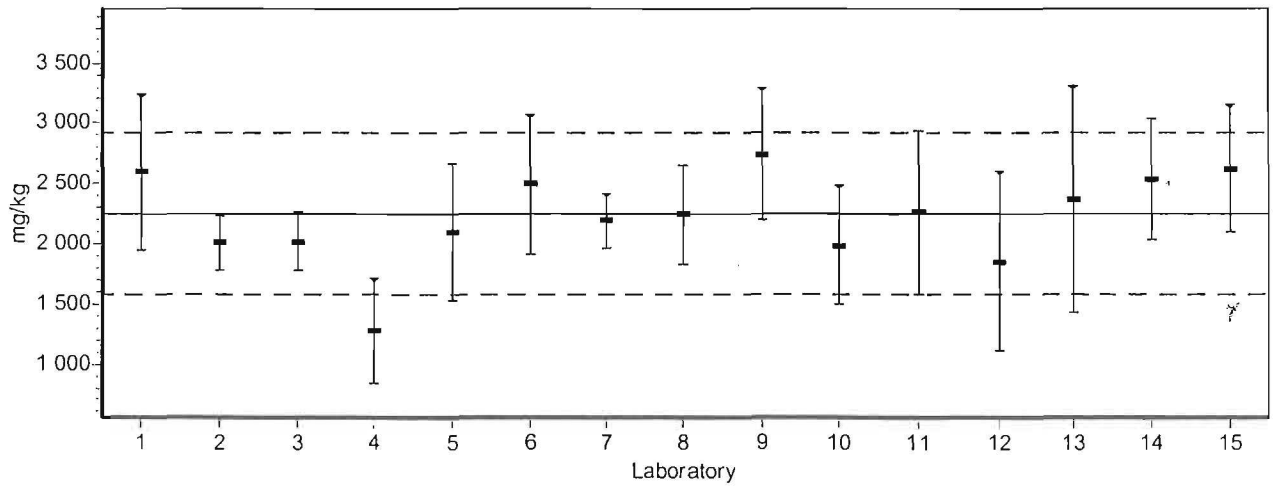
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

ANNEX 8. RESULTS AND MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS

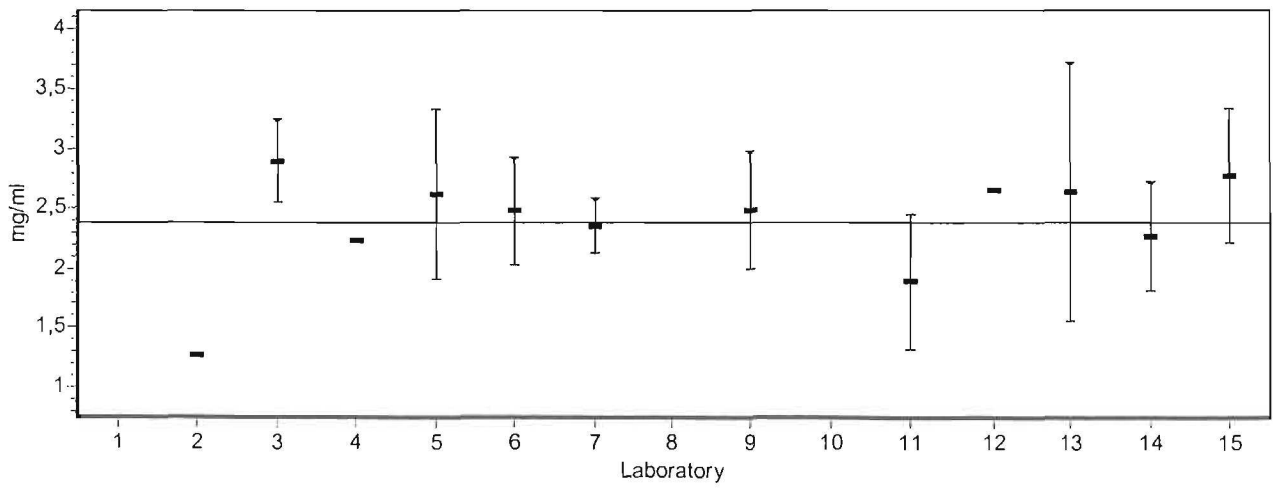
Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* H1



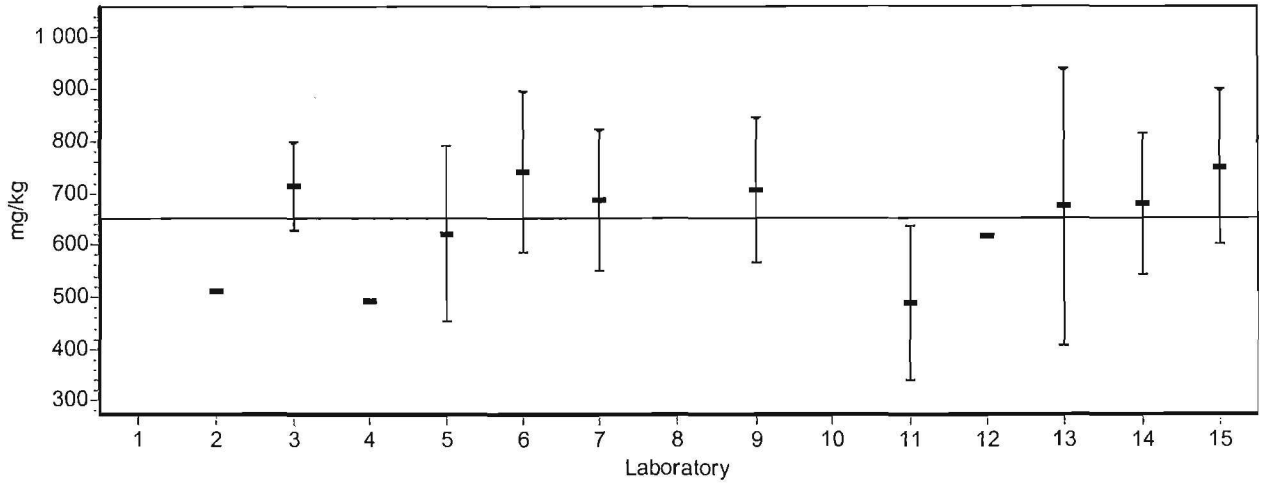
Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* H2



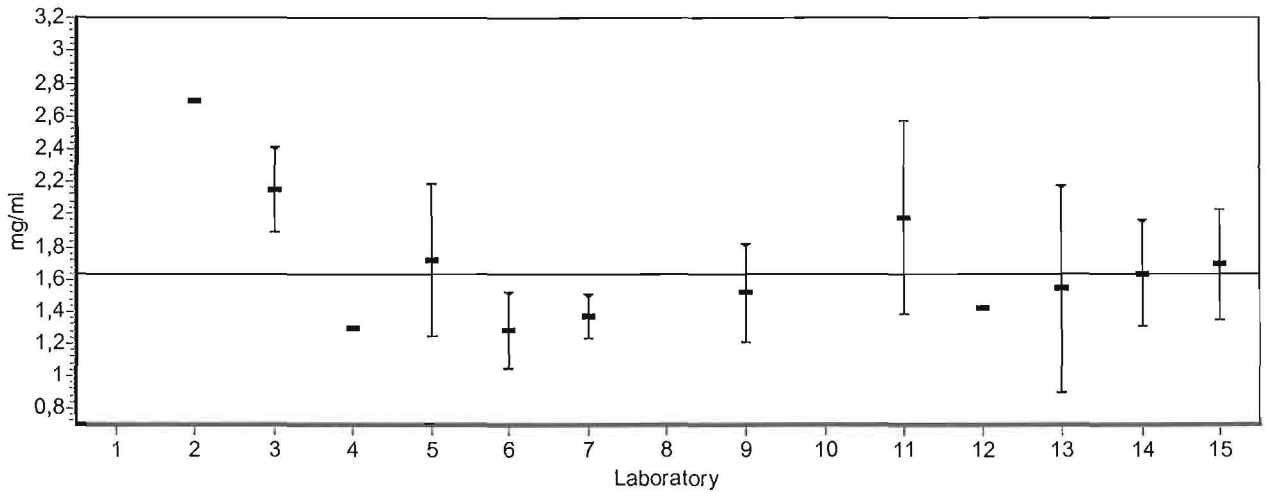
Analyytti *(Analyte)* **Oil fr.>10-23** Näyte *(Sample)* H1



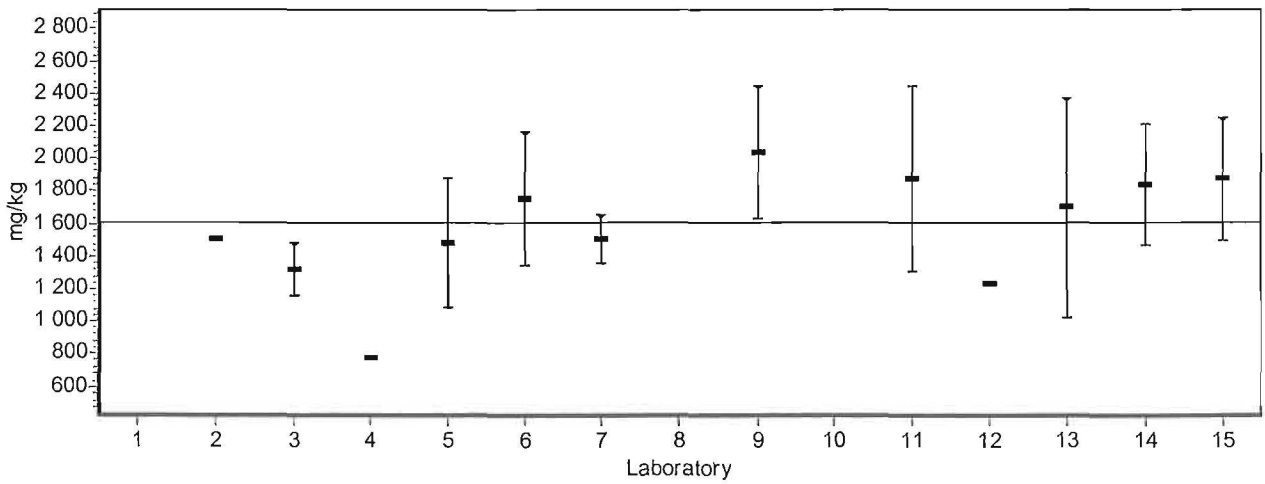
Analyytti *(Analyte)* **Oil fr.>10-23** Näyte *(Sample)* H2



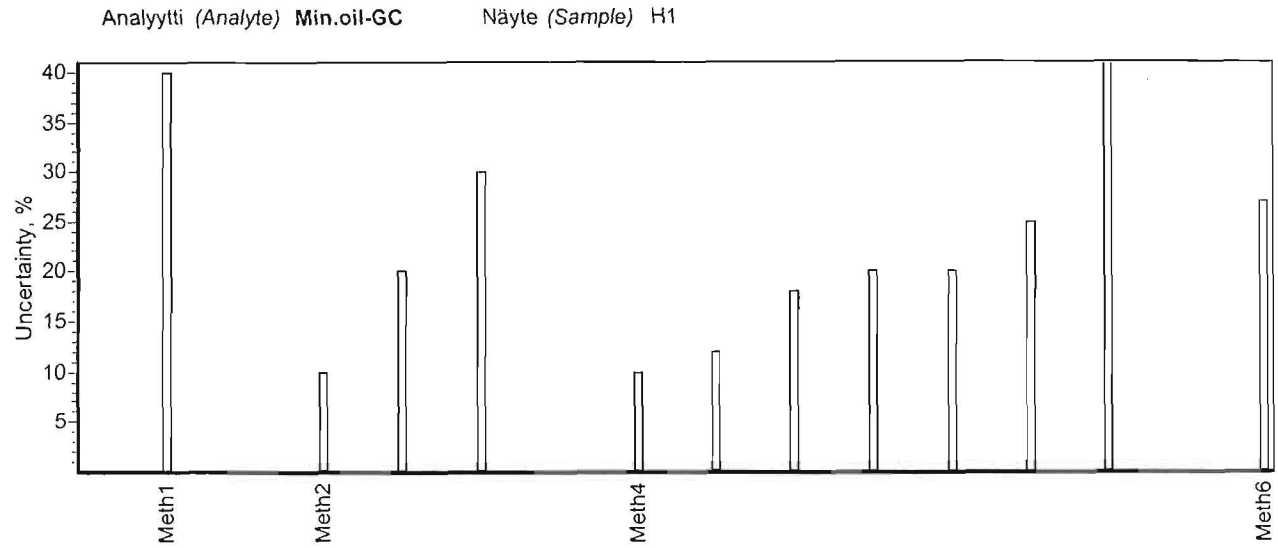
Analyytti *(Analyte)* **Oil fr.>23-40** Näyte *(Sample)* H1

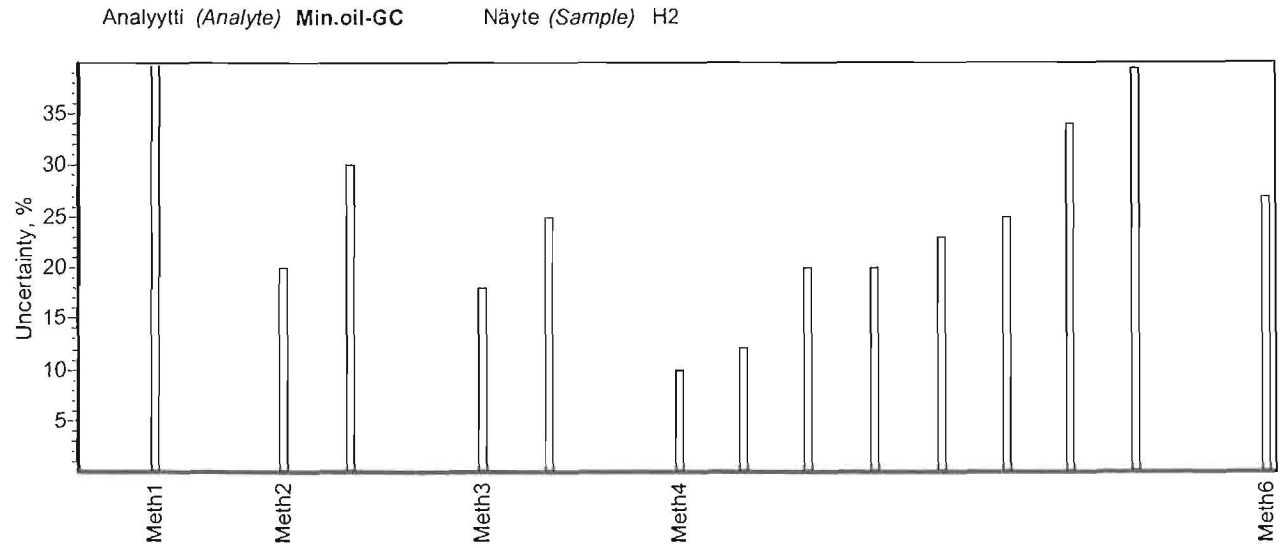


Analyytti *(Analyte)* **Oil fr.>23-40** Näyte *(Sample)* H2



ANNEX 9. ESTIMATION OF MEASUREMENT UNCERTAINTIES





Meth 1: using the variation of the results in X chart (for artificial samples)
Meth 2: using the variation of the results in X chart and the variation of the replicates (r %- or R-chart)
Meth 3: using the variation of the data obtained in analysis of CRM
Meth 4: using the data obtained in method validation (and IQC)
Meth 6: adapting the EURACHEM- Guide "Quantifying Uncertainty in Analytical measurements"

ANNEX 10. SUMMARY OF THE Z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	%
Min.oil-GC	H1	n	A	p	A	A	A	A	A	A	.	A	A	A	A	A	86
	H2	A	A	A	n	A	A	A	A	A	A	A	A	A	A	A	93
Oil fr.>10-23	H1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	H2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Oil fr.>23-40	H1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	H2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
% Accredited		50	100 yes	50 yes	50 yes	100	100 yes	100 yes	100 yes	100 yes	100	100	100	100 yes	100	100	

A - accepted (-2 ≤ Z ≤ 2), p - questionable (2 < Z ≤ 3), n - questionable (-3 ≤ Z < -2), P - non-accepted (Z > 3), N - non-accepted (Z < -3),

%* - percentage of accepted results

Totally accepted, % In all: 90 In accredited: 88 In non-accredited: 92

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Joulukuu 2004
Tekijä(t)	Irma Mäkinen, Pirjo Sainio ja Seppo Pönni	
Julkaisun nimi	SYKE Proficiency Test 4/2004 (mineral oil from soil) SYKEn pätevyyskoe 4/2004 (mineraaliöljyt maasta)	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Suomen ympäristökeskus järjesti toukokuussa 2004 pätevyyskokeen mineraaliöljyn määrittämiseksi pilaantuneesta maasta ja synteettisestä näytteestä. kaasukromatografisella menetelmällä. Pätevyyskokeeseen osallistui kaikkiaan 14 laboratoriota Suomesta, Latviasta, Norjasta ja Ruotsista. Pätevyyskokeen näytteinä oli yksi tunnetun öljypitoisuuden omaava standardiliuos ja yksi maanäyte, joka oli valmistettu EU/HYCREF-hankkeessa. Analysoinnissa käytettiin pääasiassa standardiluonnosmenetelmää ISO/DIS 16703 eri variaatioin. Mm. ravistelutekniikka, uutteen puhdistustekniikka ja kalibrointiaineet vaihtelivat eri laboratorioissa. Synteettiselle näytteelle käytettiin vertailuarvona laskennallista öljypitoisuutta. Maanäytteelle käytettiin vertailuarvona robusti-keskiarvoa. Tässä pätevyyskokeessa 90 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin 20 % (synteettinen näyte) tai 30 % (maanäyte) 95 % merkitsevyystasolla. Pätevyyskoe mineraaliöljyn määrittämiseksi pilaantuneesta maasta järjestettiin kolmannen kerran Suomessa. Tulokset olivat parantuneet edellisestä vertailukokeesta, joka järjestettiin syksyllä 2002.	
Asiasanat	maanäytteet, mineraaliöljyt, hiilivedyt, ympäristölaboratoriot, pätevyyskoe, vertailukoe	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen moniste 314	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
	ISSN 1455-0792	ISBN 952-11-1906-3
	Sivuja 29	Kieli englanti
	Luottamuksellisuus Julkinen	Hinta
Julkaisun myynti/ jakaja	Suomen ympäristökeskus, asiakaspalvelu sähköpostiosoite: neuvonta.syke@ymparisto.fi puh. (09) 4030 0119, telefax (09) 4030 0190	
Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2004	
Muut tiedot		

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date December 2004
Author(s)	Irma Mäkinen, Pirjo Sainio and Seppo Pönni	
Title of publication	SYKE Proficiency test 242004 (mineral oil from soil)	
Parts of publication/ other project publications		
Abstract	The Finnish Environment Institute carried out the proficiency test for the determination of mineral oil content from polluted soil using the GC method. A total of 14 laboratories from Finland, Latvia, Norway and Sweden were participated. One standard solution containing a known concentration of different oils were prepared. One soil sample was delivered to the participating laboratories. The sample was prepared in the framework of the EU/HYCREF project. The draft standard method ISO/DIS 16703 was mainly used for analysis of mineral from the soil sample. Even the participants used mainly the same draft for the analysis of soil samples, the procedures were still rather different in different laboratories, but they did not seem to have much effect on results. However, the clean-up procedure showed to have some effect on the results. For the liquid synthetic sample the calculated mineral oil content was used as the assigned value. For the soil sample the robust mean value was used as the assigned value. In this proficiency test, 90 % of the participating laboratories reported satisfied results, based on the target total standard deviations of 20% or 30 % (95 % confidence interval). The SYKE proficiency test for analysis of mineral oil from polluted soil in using the GC method was carried out for the third time. The results have improved since the last comparison in 2002.	
Keywords	soil analysis, mineral oil, hydrocarbons, environmental laboratories, proficiency test, interlaboratory comparisons	
Publication series and number	Suomen ympäristökeskuksen moniste 314	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
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Other information		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum December 2004
Författare	Irma Mäkinen, Pirjo Sainio, Sami Huhtala och Seppo Pönni	
Publikationens titel	SYKE Provningsjämförelse 4/2004 (mineralolja i jord)	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	Under Mars 2004 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av mineralolja med GC i ett syntetiskt prov och ett jordprov. Jordprovet framställdes i ett EU/HYCREF –projekt. Proven sändes ut till 14 laboratorier i Finland, Lettland, Sverige och Norge. Huvudsakligen hade laboratorierna använt en analysmetod som baserar sig på internationella standardförslaget ISO/DIS 16703. Skillnaderna i metoderna använda av deltagarna hade ringa inverkan på resultaten. Resultaten värderades med hjälp av z-värden. Beräkningen av z-värdena baserade sig på totalstandardavvikelser, som sattes till 20 % eller 30 % (95 % sannolikhetsnivå). Det teoretiska värdet eller robust-medelvärdet användes som referensvärde (*the assigned value*). I provningsjämförelsen var 90 % av resultaten nöjaktiga. Jämförelsen genomfördes för tredje gången. Resultaten förbättrades sedan den senaste jämförelsen 2002.	
Nyckelord	jordanalyser, mineral olja, hydrocarbons, provningsjämförelse, miljölaboratorier	
Publikationsserie och nummer	Suomen ympäristökeskuksen moniste 314	
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