

269

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Interlaboratory comparison 4/2002

Mineral oil from polluted soil and water

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Mineral oil from polluted soil and water

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CONTENT

1	INTRODUCTION	4
2	ORGANIZING THE INTERLABORATORY COMPARISON	4
2.1	Responsibilities	4
2.2	Participants	4
2.3	Sample preparation and delivery	4
2.4	Sample testing	5
2.4.1	Homogeneity study	5
2.4.2	Stability study	6
2.5	Comments sent by participants	6
2.6	Analytical methods	6
2.7	Data treatment	6
2.7.1	Testing of outliers and normality of data	6
2.7.2	Assigned value and its uncertainty	7
2.7.3	Target value for total standard deviation	7
2.7.4	Evaluation of performance	7
3	RESULTS AND PERFORMANCE	8
3.1	Results	8
3.2	Estimation of performance	10
4	SUMMARY	11
5	YHTEENVETO	12
	REFERENCES	13
	ANNEXES	
1.	Participants in the interlaboratory comparison 4/2002	14
2.	Preparation of the samples	15
3.	Results of the homogeneity study	16
4.	Results of the stability study	17
5.	Comments sent by the participants	18
6.1.	Analytical methods	19
6.2.	Results obtained by different analytical methods	22
6.3.	Results obtained by different analytical methods (the water samples V1 and V2)	23
7.	The assigned values and their uncertainties	24
8.	Results reported by the participants	25
9.	Explanations for the result sheets	26
10.	Results of each participant	28
11.	Results and measurement uncertainties reported by the participants	30
12.	Results calculated according to Robust statistics (the samples M1 and U1)	33
13.	Summary of the z scores	34
14.1.	Sample chromatograms (L1)	35
14.2.	Sample chromatograms (M1)	36
14.3.	Sample chromatogram (U1)	37
14.4.	Sample chromatogram (V1)	38
14.5.	Sample chromatogram (V2)	39
	DOCUMENTATION PAGE	40
	KUVAILOLEHTI	41

1 INTRODUCTION

The Finnish Environment Institute carried out the interlaboratory comparison test for the determination of mineral oil content in polluted soils and hydrocarbon oil index in waters in May 2002.

The interlaboratory comparison was carried out in accordance with the international guidelines, ISO/IEC Guide 43-1 (1), ILAC Requirements (2) and ISO/DIS 13528 (3).

The GC methods for the analysis of mineral oil content, ISO/DIS 16703 for the analysis of soil and EN ISO 9377-2 for the analysis of water, were recommended to be used (4, 5). Additionally, the reporting of oil fractions $C_{>10}\dots C_{23}$ and $C_{>23}\dots C_{<40}$ as well as the use of infrared spectrometric method and field method for the soil sample were voluntary.

The former SYKE interlaboratory comparison for analysis of mineral oil in soil was carried out in 2000. In 2002 SYKE organized the interlaboratory comparison for the GC analysis of mineral oil in water for the first time in Finland.

2 ORGANIZING THE INTERLABORATORY COMPARISON

2.1 Responsibilities

The responsibilities in organizing the interlaboratory comparison were as follows:

Irma Mäkinen, SYKE, coordinator

Sami Huhtala, SYKE, technical coordinator

Anna-Mari Suortti, SYKE, analytical expert (SGS Inspection Services Oy, since August 2002)

Seppo Pönni, Pirkanmaa Regional Environment Centre, preparation of the soil sample

Anne Markkanen and Riitta Vehmaa, analytical assistants.

2.2 Participants

A total of 15 laboratories from Finland, Latvia, Estonia, Norway and Sweden participated (Annex 1). The samples were distributed to 19 laboratories.

2.3 Sample preparation and delivery

Firstly, one standard solution containing a known concentration of different oils were prepared (see Table 1). Secondly, two solutions containing also a known concentration of different oils were prepared to be used as the addition solutions for preparation of water samples. These addition solutions were prepared in isopropanol according to two other similar interlaboratory comparison carried out by ITM in Sweden and by BAM in Germany (10,11). The sample preparation is presented in Annex 2. Before delivery, the sample ampoules were weighed to check the possible solvent evaporation.

Two water samples, one litre of each, were delivered. The sample V1 was municipal waste water, which was diluted (1:1) with distilled water to diminish the matrix interference. The sample V2 was lake water from the Lake Päijänne. Laboratories were asked to add precisely one milliliter (1,00 ml) of respective addition solution. Laboratories were also asked to stabilize the samples for one hour before extracting the samples.

Soil sample M1 was excavated from former petrol station, which was under remediation. To achieve homogeneity, the soil sample M1 was dried at room temperature and sieved through a 250 μm sieve. The sieved bulk material was manually mixed until the sample was sufficiently homogenous. Finally, the sample M1 was divided into 128 portions containing about 100 g of soil. This was done using a rotary sample divider equipped with a vibratory sample feeder. Moisture content of the sample was less than 1 %. The amount of organic matter, measured as ignition loss, was 0,9 % for M1.

A larger amount of the soil sample M1 was extracted at SYKE and the extract, sample U1, was divided in ampoules. The extract was not purified.

The interlaboratory comparison took place between May 28 and June 14, 2002.

The results were asked to return by June 28, 2002. Four laboratories did not return the results.

Table 1. Samples of the interlaboratory comparison 4/2002

Samples	Sample type
L1: mixture of diesel/fuel and lubricating oil (1:1)	1 synthetic solution in hexane
V1: waste water: distilled water (1:1)	1 municipal waste water (diluted 1:1) + addition of mixture of diesel/fuel and lubricating oil (2:1)
V2: lake water	1 lake water + addition of mixture of diesel/fuel and lubricating oil (1:1)
M1: soil sample	1 sandy soil sample
U1: soil extract	1 soil extract in heptane

2.4 Sample testing

2.4.1 Homogeneity study

The soil sample M1 was tested for homogeneity (Annex 3). For this purpose, ten samples of all the prepared samples were randomly selected. The samples were analysed as duplicates, and the results were estimated using one-way analysis of variance. The within-bottle standard deviation was 2 %. In general, s_{bb} was much lower than the reproducibility standard deviation of this interlaboratory comparison (s_b), 29 %, or the target total standard deviation (s_t), 35%, in which the analytical variation is included (s_{wb} %). The analytical variation was lower than 3 % and the between-bottle standard deviation (s_{bb}) was lower than 5% (Table 3).

Sample preparation of the synthetic solutions was tested by analysing the mineral oil mixtures in the ampoules L1 and V1 (Annex 3). Also the concentration of the addition solution V2 was checked. In all samples tested the recovery of the mineral oil content was between 95 % and 105 % of the calculated concentration.

2.4.2 Stability study

Stability testing of the samples was based on the analyses carried out at four times: once before the delivery and three times during the interlaboratory comparison. Stability of the samples M1 and U1 was tested. Representing the synthetic solutions, stability of the sample L1 was tested.

Stability data was tested using regression analysis (6). The standard deviation of the regression line was tested for significance with t-statistics with $n-2$ degrees of freedom, by comparing the ratio of a degradation rate and a standard deviation of the regression line. The trend of degradation was not significant (Annex 4).

2.5 Comments sent by the participants

The participants commented on their results or on their analytical methods (Annex 5).

2.6 Analytical methods

The draft standard method ISO/DIS 16703 was mainly used for the mineral oil analysis in the samples M1 and U1. The soil sample was extracted with extraction solvents as heptane/acetone, hexane/acetone, cyclohexane/acetone or hexane. One participant used an in-house method based on extraction with pentane and methanol. The extraction was carried out using ultrasonic bath or by shaking. The extraction time varied between 20 and 60 minutes.

The standard method EN ISO 9377-2 was used for analysis of mineral oil in water samples V1 and V2. Pentane, hexane or heptane was used as a extraction solvent and the volume used for the extraction varied between 5 and 50 ml. The samples were extracted either by shaking or stirring. The extraction time varied between 20 and 60 minutes.

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 ($C_{40}H_{82}$). Three participants used lower retention time window $C_{10} \dots C_{36}$ for integration. Also, some laboratories included $C_{10}H_{22}$ in the total amount of oil. Also calibration oil mixtures differed. Analytical methods for individual laboratories are presented in Annex 6.1.

Only two laboratories used IR technique and three laboratories used a hydrocarbon test kit (PetroFLAG[®], Dexsil, USA) for the measurement of the soil sample.

2.7 Data treatment

2.7.1 Testing of outliers and normality of data

The participants were requested to report three results for the soil sample M1 and one result for other samples. Measurement uncertainties were asked for all the results. Before the statistical treatment, the data was tested according to Kolmogorov-Smirnov normality test. Outliers were rejected according to the Cochran or Hampel test. The results of the samples M1 and U1 were calculated using the Robust algorithm A (3). In both cases the results of two participants were updated (Annex 12).

2.7.2 Assigned value and its uncertainty

For the liquid samples L1, V1 and V2, the calculated mineral oil content was used as the assigned value. For the analysis of the soil sample M1 and the soil extract U1 the mean value, calculated according to the Robust algorithm A, was used as the assigned value.

The assigned value was not evaluated for determination of mineral oil fractions $C_{>10} \dots C_{23}$ and $C_{>23} \dots C_{<40}$.

The uncertainty of the assigned value for samples M1 and U1 was calculated using the standard deviation based on Robust algorithm. The uncertainty was 20 % and 14 %, respectively.

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 reproducibility standard deviations and the measurement uncertainties reported by the participants. The s_{target} was 20 % (95 % confidence interval) for the analysis of the solvent sample L1. For the analysis of the water samples V1 and V2 the s_{target} was 30 % and 40 % (95 % confidence interval) respectively. In the analyses of the soil sample M1 it was 35 %, and in the analysis of the soil extract U1 it was 30 % (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:

$ z < 2$	“satisfactory” results
$2 \leq z \leq 3$	“questionable” results
$ z > 3$	“unsatisfactory” results.

The z scores are presented in Annex 10 and the summary of z scores is presented in Annex 13. Explanations to these Annexes are presented in Annex 9.

The organizing laboratory (SYKE) had the code 9 in this interlaboratory comparison.

3. RESULTS AND PERFORMANCE

3.1 Results

All of the results reported by the laboratories are presented in Annex 8. Statistically treated results for each laboratory are presented in Annex 10. The graphical presentations of the results and the uncertainty estimations are presented in Annex 11.

The results for analysis of the soil sample M1 were asked to report as triplicates. The repeatability (the within-laboratory standard deviation, s_w) of mineral oil was 7.5 % and the reproducibility (s_b) was 29 % (Table 2). Thus the ratio s_b/s_w , a measure for the robustness of the methods used, was about four. This is somewhat high, it should be between 2-3 for robust methods (7).

The participants reported the results for the mineral oil fractions $C_{>10} \dots C_{23}$ and $C_{>23} \dots C_{<40}$ also as triplicates, and the reproducibility was 71 % and 37 %, respectively.

Table 2. Results of triplicate determinations of the sample M1 (ANOVA statistics)

Analyte mg/kg	Sample	Ass. value	Mean	s_w	s_b	s_t	s_w %	s_b %	s_t %
Min.oil	M1	325	325.8	24.38	91.46	94.66	7.5	28	29
Oil. fr >10-23.	M1	125	125.7	11.33	88.13	88.85	9.0	70	71
Oil. fr >23-40	M1	194	190.6	17.80	68.15	70.44	9.3	36	37

where,

s_w = the within laboratory standard deviation

s_b = the between laboratory standard deviation

s_t = the total standard deviation.

The results of the standard solution (the sample L1) showed a good agreement between the calculated mineral oil content, the mean value and the median value of the data (Table 2). The standard deviation of the results was 21 %, which was lower than the respective standard deviation (30 %) in analysis of the synthetic solution in the former interlaboratory comparison 5/2000 (8). This is mainly due to the use of more uniform analytical methods than before. Except one laboratory, the draft international standard ISO/DIS 16703 was used. In the interlaboratory comparison organized within the framework of the 4th Pollution Load Compilation (PLC-4) of Baltic Sea monitoring, the reproducibility deviation was 26.4 % in the analysis of the synthetic solution (9, 11).

The variation in the analysis of the soil extract U1, was smaller (21 %) than the variation in the analysis of the soil sample M1 (28 %) but similar to the variation of the standard solution. This implies that the extraction step still has some pitfalls in the whole procedure.

Table 3. Summary of the interlaboratory comparison

Analyte	Sample	Unit	Ass. val	Recovery %	Mean	Med	SD	SD %	2*Targ SD %	Num of labs	Accepted z-val %
Min.oil GC	L1	mg/ml	9.12	104	9.48	9.0	1.98	21	20	15	73
	M1	mg/kg	325		325.8	321	92.3	28	35	13	77
	U1	mg/ml	0.494		0.497	0.477	0.102	21	30	12	83
	V1	mg/l	3.02	78	2.37	2.66	0.777	33	30	13	54
	V2	mg/l	0.402	81	0.327	0.38	0.118	36	40	13	62
Oil.fr >10-23	M1	mg/kg	125		125.7	117	85.42	68		9	
	U1	mg/ml	0.151		0.169	0.1505	0.069	41		8	
Oil.fr >23-40	M1	mg/kg	194		190.6	195	67.86	36		9	
	U1	mg/ml	0.298		0.295	0.318	0.099	34		8	

where,

Ass. val.

The assigned value

Mean

The mean value

Md

The median value

SD

The standard deviation

SD %

The standard deviation as percents

2*Targ. SD%

Acceptance level : the highest accepted deviation = the target total standard deviation (95 % confidence interval)

Num of Labs

Number of participants

Accepted z-val%

Accepted z values: the results (%), where $|z| < 2$.

In the analysis of the water samples, V1 and V2, the standard deviations were highest, 33 % and 36 %. Many of the laboratories participated in the GC analysis of mineral oil in water for the first time. The overall recovery, 78 and 81 %, was similar to recoveries in HELCOM 1999 and ITM 2001-2 proficiency tests (11,12). In the analysis of water samples, the efficiency of extraction procedure might have had an influence on the obtained mineral oil content. The results obtained by stirring technique were mainly smaller than the assigned value (Annex 6.2 and 6.3). Also, the added mineral oil might have adsorbed partly on the walls of a sample vessel during stabilization of one hour.

In the analysis of the soil sample, the standard deviation of the results, 28 %, was smaller than in the interlaboratory comparison 5/2000 (32 – 34 %), even if the mineral oil content was lower than in 5/2000 (8). According to the German study on three interlaboratory comparisons for the analysis of mineral oil in soil, a relative standard deviation of 30 % is hardly to be expected at a hydrocarbon content below 500 mg/kg (10). In this interlaboratory comparison the mineral oil content of the soil sample M1 was 325 mg/kg and thus the variation of 28 % can be regarded even lower than expected.

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 and time as well as in clean-up steps and in calibration solutions. Some laboratories (1, 7, 13 and 15) still had inaccurate calibration. This may have effected the inaccurate results for samples M1 and U1. Some laboratories (2, 4, 5) had obviously some difficulties in the extraction or in the clean-up step. In the analysis of the soil extract U1 the variation of extraction procedure was excluded.

The results of the samples M1 and U1 showed, that in some cases extraction step has been the most vulnerable step in the whole procedure. The mineral oil in soil sample contained also hydrocarbons with boiling points higher than $C_{40}H_{82}$ (see Annexes 14.2 and 14.3). The differences in integration interval in chromatograms may also have an effect on the mineral oil results.

There was variation in the reported uncertainties of the analytical methods used by the laboratories. The uncertainties were more realistic than in the former interlaboratory comparison in 5/2000, though. The uncertainty for the soil sample M1 was still overestimated in some laboratories. On the other hand, in analysis of water sample the uncertainties seemed to be underestimated in some laboratories.

The results determined either with IR procedure or the field instrument are presented in the following table. No further data treatment was done.

Table 4. The results obtained with IR or field test procedure from the soil sample M1

Laboratory	IR, mg/kg	Results of field test, mg/kg	Equipment
Lab 6	509	500	unknown
Lab 9	469	-	
Lab 13	-	1700	PetroFLAG®
Lab x ^{*)}	-	1060	PetroFLAG®

^{*)} The laboratory has only reported the results of field test.

The reporting of results for the mineral oil fractions $C_{>10} \dots C_{23}$ and $C_{>23} \dots C_{<40}$ is important in Finnish soil remediation projects. The results for these fractions seemed to be rather similar in different laboratories except for laboratories 1 and 2 (Annex 11).

3.2 Estimation of performance

In this interlaboratory comparison, 70 % of the participating laboratories reported acceptable results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval (Annex 13).

Firstly, calibration of the analytical method or the performance of the GC instrument should be checked by some participants, because only 73 % from the results of the solvent sample L1 was accepted, when the target deviation 20 % was used.

The results were most satisfactory (83 %) in analysis of mineral oil in the soil extract U1. In the analysis of the soil sample M1 77 % of the results were accepted, when the target deviation of 35 % was used. Although the participants used mainly the same draft international standard for the analysis of soil samples, the procedures are still different in different laboratories.

Finally, the water samples V1 and V2 turned to be the most critical to analyse. From the results 54 % (V1) and 62 % (V2) were accepted, when the target standard deviation was 30 % and 40 %, respectively. Many participants have little experience in using of the GC method for analysis of mineral oil in waters. In many laboratories it seems to be necessary to check the efficiency of extraction procedure in particular, because generally the results were lower than expected.

Sample preparation procedures might have had some influence on extraction efficiency particularly in case, when extraction procedure had not been strong enough.

The Finnish interlaboratory comparison for analysis of mineral oil content in polluted soil in using the GC method was carried out for the second time. These results have improved since the last comparison in 2000. The Finnish interlaboratory comparison for analysis of mineral oil content in waters in using the GC method was carried out for the first time. The ILC showed that there are still improvements to be made in some laboratories.

4 SUMMARY

The Finnish Environment Institute carried out the interlaboratory comparison test for the determination of mineral oil content from polluted soils and hydrocarbon oil index in waters in May 2002. The GC methods for the analysis of mineral oil content were recommended to be used. Additionally, the reporting of oil fractions $C_{>10} \dots C_{23}$ and $C_{>23} \dots C_{<40}$ as well as the use of infrared spectrometric method and field method for the soil sample were voluntary. A total of 15 laboratories from Finland, Latvia, Estonia, Norway and Sweden participated.

One standard solution containing a known concentration of different oils were prepared. Two solutions containing also a known concentration of different oils were prepared to be used as the addition solutions for the preparation of water samples. For this two water samples, diluted municipal waste water and lake water, were delivered. One soil sample and one soil extract were also delivered to the participating laboratories.

The draft standard method ISO/DIS 16703 was mainly used for the mineral oil analysis in the soil samples. The standard method EN ISO 9377-2 was used for analysis of mineral oil in water samples. Only two laboratories used IR technique and three laboratories used a hydrocarbon test kit for the measurement of the soil sample.

For the liquid samples the calculated mineral oil content was used as the assigned value. For the soil samples the mean value, calculated according to the Robust algorithm A, was used as the assigned value.

In this interlaboratory comparison, 70 % of the participating laboratories reported acceptable results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval. The water samples turned to be the most critical to analyse. From the results 54 % and 62 % were accepted, when the target standard deviation was 30 % and 40 %, respectively.

The Finnish interlaboratory comparison for analysis of mineral oil in polluted soil in using of the GC method was carried out for the second time. These results have some improved since the last comparison in 2000. The Finnish interlaboratory comparison for waters in using of the GC method was carried out the first time. The ILC showed that there are still improvements to be made in some laboratories.

5 YHTEENVETO

Suomen ympäristökeskus järjesti toukokuussa 2002 vertailukokeen mineraaliöljyn määrittämiseksi pilaantuneesta maasta ja vedestä. Vertailukokeessa suositeltiin käytettävän kaasukromatografisia määrittämenetelmiä. Maanäytteen öljyfraktioiden $C_{>10}\dots C_{23}$ ja $C_{>23}\dots C_{<40}$ ilmoittaminen sekä infrapunaspektrometrinen määrittämenetelmän ja kenttämenetelmien käyttö maanäytteelle olivat vapaaehtoisia. Vertailukokeeseen osallistui kaikkiaan 15 laboratoriota Suomesta, Latviasta, Virossa, Norjasta ja Ruotsista.

Vertailukokeen näytteinä oli yksi tunnetun öljypitoisuuden omaava standardiliuos, kaksi tunnetun öljypitoisuuden omaavaa lisäysliuosta vesinäytteiden valmistamista varten, kaksi vesinäytettä (yhdyksuntajätevesi ja järvivesi) sekä yksi maanäyte ja sen uute.

Maanäytteiden analysoinnissa käytettiin pääasiassa standardiliuonnoksen menetelmää ISO/DIS 16703 ja vesinäytteiden analysoinnissa standardimenetelmää EN ISO 9377-2. Vain kaksi laboratoriota käytti lisäksi IR-menetelmää ja kolme laboratoriota käytti kenttätestimenetelmää maanäytteen öljyn määrittämiseksi.

Nestemäisille näytteille käytettiin vertailuarvona laskennallista öljypitoisuutta. Maanäytteelle ja sen uuteelle vertailuarvona käytettiin keskiarvoa, joka oli laskettu robust-menettelyllä.

Tässä vertailukokeessa 70 % osallistuvien laboratorioden ilmoittamista tuloksista hyväksyttävää oli, kun z-arvojen laskennassa käytettiin 20 – 40 %:n tavoitekokonaiseskihajontoja. Vesinäytteet osoittautuivat hankalimmiksi analysoitaviksi näytteiksi. Vesinäytteiden V1 ja V2 tuloksista hyväksyttiin 54 % ja 63 %, kun tavoitekokonaiseskihajonnaksi asetettiin vastaavasti 30 % ja 40 %.

Vertailukoe mineraaliöljyn määrittämiseksi pilaantuneesta maasta järjestettiin toisen kerran Suomessa. Tulokset olivat jonkin verran parantuneet edellisestä vertailukokeesta, joka järjestettiin syksyllä 2000. Vesien osalta tämä oli ensimmäinen Suomessa järjestetty vertailukoe, missä öljymääritys pohjautui kaasukromatografiseen menetelmään.

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ANNEX 1. PARTICIPANTS IN THE INTERLABORATORY COMPARISON 4/2002

Alcontrol AB, Sweden

Dekati Measurements, Finland

Ekokem Oy Ab, Finland

Estonian Environmental Research Centre, Estonia

Fortum Oil and Gas Oy, Analytical Research, Finland

Fortum Oil and Gas Oy, Porvoon jalostamon laboratorio, Finland

Golder Associates Oy, Finland

Insinööritoimisto Paavo Ristola Oy, Finland

Juvegroup Oy, Finland

Lahden Tutkimuslaboratorio, Finland

Novalab Oy, Finland

SGS Inspection Services Oy, Finland

SIA VIDES AUDITS Laboratory, Latvia

SINTEF Applied Chemistry, Norway

SYKE, Laboratory, Finland

ANNEX 2. PREPARATION OF THE SAMPLES

The standard solution L1

Oil type	Preparation of stock solutions	Preparation of sample L1
I: Diesel/Fuel oil (BAM KS 5002)	1500.6 mg oil in 49.64 ml of hexane (Riedel 34484) => 30.23 mg/ml	15 ml I + 15 ml II in 99.50 of hexane (Riedel 34484) => 9.12 mg/ml
II: Lubricating oil (BAM KS 5003)	1500.8 mg oil in 49.64 ml of hexane (Riedel 34484) => 30.23 mg/ml	

The prepared solution was carefully mixed and sampled into a 3 ml portions. Small amber glass bottles with a teflon-lined screw cap were used. Bottles were labelled and numbered according to filling order. The weight of each bottle was recorded.

The addition solutions V1 and V2

Oil type	Preparation of stock solutions	Preparation of sample V1	Preparation of sample V2
I: Diesel/Fuel oil (BAM KS 5002)	1000.4 mg oil in 49.89 ml of iso-propanol (Rathburn 1018) => 20.05 mg/ml	10 ml I + 5 ml II in 99.65 of iso-propanol (Rathburn 1018) => 3.02 mg/ml	1 ml I + 1 ml II in 99.66 of iso-propanol (Rathburn 1018) => 0.402 mg/ml
II: Lubricating oil (BAM KS 5003)	1000.1 mg oil in 49.86 ml of iso-propanol (Rathburn 1018) => 20.06 mg/ml		
The resulting water sample concentration, when 1,00 ml was added into 1 litre of water:		3.02 mg/l	0.402 mg/l

The prepared solutions were carefully mixed and sampled into a 3 ml portions. Small amber glass bottles with a teflon-lined a screw cap were used. Bottles were labelled and numbered according to filling order. The weight of each bottle was recorded.

The soil extract U1

In total of 555 g of the soil sample M1 was extracted into 440 ml of heptane. In general, ten subsamples of approximately 55.5 g of soil were extracted with 80 ml of acetone (Merck 12) and 40 ml of heptane (Rathburn 1004) in 250 ml Pyrex bottles. The samples were extracted with one hour shaking and one hour sonication. After extraction the acetone was removed with an excess amount of water and heptanes were combined into a one litre separatory funnel where the extract was washed once more with water. The extract was dried with anhydrous sodium sulfate. The extract was carefully mixed and sampled into a 12 ml portions. Small glass bottles with a teflon-lined a screw cap were used. Bottles were labelled and numbered according to filling order. The weight of each bottle was recorded.

ANNEX 3. RESULTS OF THE HOMOGENEITY STUDY

The solvent sample L1 and the synthetic solutions V1 and V2

Preparation and distribution of the synthetic solutions L1 (the synthetic sample) and V1 (the addition solution for the water sample V1) was tested by analysing three ampoules (the first one, the middle one and the last one of the filling procedure). The results of the tested ampoules were unanimous. The concentration of the solution V2 was checked, too. The obtained mineral oil content was between 95 % and 105 % of the calculated mineral oil content in the tested subsamples of each sample.

The soil sample M1

Homogeneity was tested as duplicate determinations from ten sample bottles. The results were calculated using one-way variance analysis.

Sample	n	Mineral oil mg/kg	Target SD % ¹⁾	S _{target}	S _{wb}	S _{wb} %	S _{wb} / S _{target}	S _{bb}	S _{bb} %	S _{bb} / S _{target}
M1	2x10	345	17.5	60.4	8.54	2.5	0.071	4.96	1.4	0.082

¹⁾ the target SD was 35 % in 95 % confidence level

The within bottle variation (including analytical variation), (s_{wb}) was 2.5 % and the between bottle variation, (s_{bb}) was 1.4 %. The within bottle and between bottle variations were compared with the accepted total standard deviation in this interlaboratory comparison, which was 35 % in analysis of the sample M1.

The set of samples was sufficiently homogenous to be used in this interlaboratory comparison.

The between bottle variations (s_{bb}) were included in the uncertainty estimation of the assigned values.

The soil extract U1

The preparation and the dividing of the soil extract U1 was tested by analysing three ampoules from the dividing procedure (the first one, the middle one and the last one). The tested subsamples were homogenous.

ANNEX 4. RESULTS OF THE STABILITY STUDY

Stability study was based on the analyses carried out four times during the analysing period of the interlaboratory comparison.

Of the synthetic solutions, only the stability of sample L1 was tested. The mineral oil content 94 – 96 % from the calculated mineral oil content was obtained during the analysing period.

Sample	$s_{y/x}$ ¹⁾	u_b ²⁾	$t_{\text{calc}} = b /u_b$	$t_{\text{crit}}(0.05)$
L1	0.093	0.0053	0.695	2.92
M1	15.15	0.762	1.028	1.81
U1	0.0033	0.0002	0.691	1.76

¹⁾ the standard deviation of the data

²⁾ the standard deviation of the slope ($y = bx + a$)

The standard deviation of the data ($s_{y/x}$) have been included in the uncertainty estimation of the assigned value even if its value was not significant.

ANNEX 5. COMMENTS SENT BY THE PARTICIPANTS

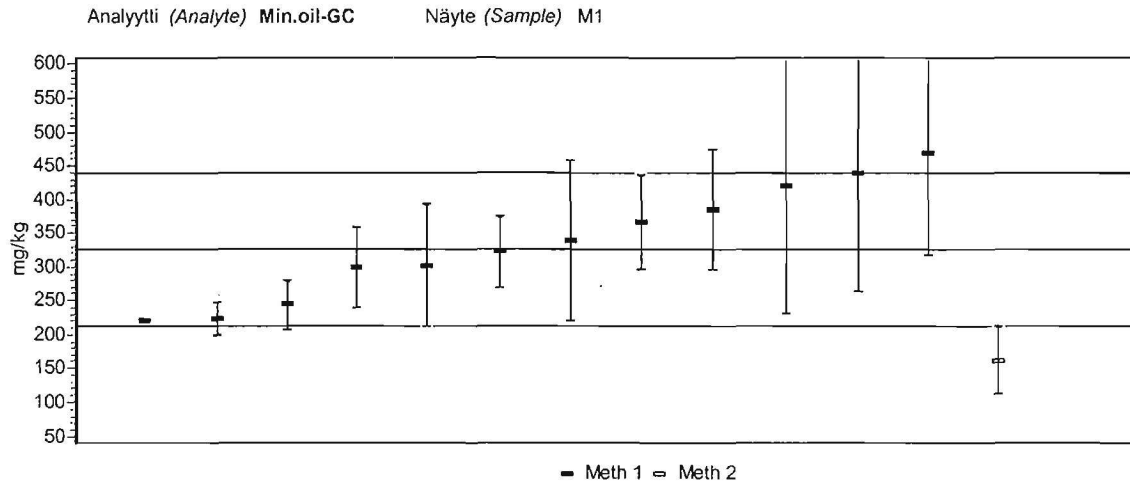
Lab	Comment	Action/SYKE
2	The laboratory used their own method for analysis of the soil sample M1 (the modification of the Nordtest guide). As integration interval in chromatograms was used the fractions C ₁₀ ...C ₁₉ and C ₂₀ ...C ₃₆ .	No action
3	Extraction procedure might have had an effect on the results of the samples V1 and V2.	No action
11	The laboratory has corrected their results later in analysis of the oil fraction C _{>10} ...C ₂₃ from the sample M1 The reported results: 151, 162 and 151 mg/ml The corrected results: 0.151, 0.162 and 0.151 mg/ml	No action
y	The laboratory did not report their results until the deadline. The results are not included to data evaluation. The results were reported 18 November 2002 and they were as follows: Hydrocarbon oil index (GC) L1 8.25 8.05 mg/l V1 2.81 3.0 mg/l V2 0.34 0.53 mg/l	No action

Lab	Soil					Water				Calibration and hydrocarbon range	GC: injection, detection and column
	Method reference Meth no.	Sample intake: M1, U1	Extraction solvent and volume	Extraction method and time	Clean up method	Method reference	Extraction solvent and volume	Extraction method and time, Meth no.	Clean up method		
1	ISO/DIS 16703, Meth 1	10 g 5 ml	Methanol: Hexane 15 ml	Ultrasonic 30 min	Florisil (1.5 g) Shaking					Purchased from gas station. $C > 10 \dots C < 40$	On column 50 °C, FID 330 °C, Precolumn (2m, 0.53mm), Analytical column (5m, 0.32mm, 1µm)
2	Own method, Meth 2	20 g 1 ml	Pentane 20ml + Methanol 20ml	Shaking 2 h	Florisil (3 g), shaking	EN ISO 9377-2	Pentane, 50 ml	Shaking 30 min, Meth 1	Florisil (2-3 g), Shaking	Diesel (Esso diesel 2000, summer quality $C_{10} \dots C_{36}$)	Split / Splitless 280 °C MSD HP5 (30m, 0.25mm, 0.25µm)
3	ISO/DIS 16703 modified, Meth 1	10 g 4 ml	Acetone 10 ml, Hexane 5 ml	Ultrasonic 1 h	Florisil (1 g), Shaking	EN ISO 9377-2, modified	Hexane, 30 ml	Shaking 1 h, Meth 1	Florisil column, (2-3 g)	Diesel / Light fuel oil, Base oil $C_{10} \dots C_{40}$	Splitless 320 °C FID 340 °C Precolumn: 2m DB-1 (15m, 0.53mm, 0.15µm)
4	CEN/TC 292 / WG 5N, Meth 1	20 g 5 ml	Heptane 10 ml	Shaking 40 min	Al ₂ O ₃ (3 g), Shaking	CEN/TC 292 /WG 5N	Heptane, 5 ml	Shaking 40 min, Meth 1	Al ₂ O ₃ (1 g), Shaking	Fuel oil, lubricating oil $C_{10} \dots C_{40}$	Split 250 °C FID 300 °C HNU NB-1 (11m, 0.32mm, 0.10µm)
5	ISO/DIS 16703, Meth 1	15 g 10 ml	Acetone 20ml + <i>n</i> -hexane 10ml	Ultrasonic 30 min	Florisil (2 g), Mini column	EN ISO 9377-2	<i>n</i> -hexane, 50 ml	Stirring 30 min, Meth 2	Florisil (2 g), Mini column	Diesel fuel +Motor oil (1:1) $C_{10} \dots C_{40}$	On column, 60 °C FID 330 °C, RTX-5 (30m, 0.53mm, 0.50µm)
6	ISO/DIS 16703, Meth 1	20 g 10 ml	Heptane 10 ml, Acetone 20 ml	Ultrasonic 30 min	Florisil (1.5 g), Stirring					Diesel and lubricating oil $C_{10} \dots C_{39}$	On column, 60 °C FID 325 °C Precolumn: HMDS (5m, 0.32mm) HP-5 (15m, 0.32mm, 1µm)

Lab	Soil					Water				Calibration and hydrocarbon range	GC: injection, detection and column
	Method reference Meth no.	Sample intake: Ml, Ul	Extraction solvent and volume	Extraction method and time	Clean up method	Method reference	Extraction solvent and volume	Extraction method and time, Meth no.	Clean up method		
7	ISO/DIS 16703, Meth 1	10 g -	Cyclo-hexane : Acetone (40:60), 20 ml	Accelerated solvent extraction 20 min	SPE-column, florisil (Seppat plus, long body)	EN ISO 9377-2	<i>n</i> -hexane 10 ml	Shaking 1 h, Meth 1	Florisil (2 g), Shaking	Soil: Diesel and Fuel oil (1:1) ("WRD"-mix) $C_{10} \dots C_{40}$ Water: BAM CRM 5004 $C_{10} \dots C_{40}$	Soil: On column FID 350 °C ZB-5 (30m, 0.25mm, 0.25µm) Water: GC-MS Split/Splitless, 200 °C DB5-MS (30m, 0.25mm, 0.25µm)
8	ISO/DIS 16703, Meth 1	20 g 2 ml	Acetone 20 ml + <i>n</i> -heptane 10 ml	Shaking 30 min	Silica-column, Isolute (0.5 g)	EN ISO 9377-2	Hexane 50 ml	Stirring 1 h, Meth 2	Silica-column, Isolute (0.5 g)	Mixture of Diesel and lubricating oil $C_{10} \dots C_{40}$	Splitless 320 °C FID 350 °C Ultra-1 (12m, 0.2mm, 0.33µm)
9	ISO/DIS 16703, Meth 1	10 g 10 ml	Acetone : Heptane (2:1), 30 ml	Ultrasonic 30 min	Florisil (2 g), Shaking	EN ISO 9377-2	Hexane, 30 ml	Stirring 30 min, Meth 2	Florisil-column (2 g)	BAM KS 5004 Diesel:lubricating oil (1:1), $C_{10} \dots C_{40}$	On column, 63 °C FID 360 °C, BPX-5 (5 m, 0.32 mm, 1 µm)
10						EN ISO 9377-2	<i>n</i> -hexane 10 + 10 ml	Stirring 1 h, Meth 2	Florisil-column (4 g)	Diesel:lubricating oil $C_{10} \dots C_{36}$	On column FID 280 °C Epsil 5Eb (25m, 0.32mm, 0.25µm)
11	ISO / TR 11046, Meth 1	12 g 10 ml	Acetone 20 ml, Hexane 10 ml	Shaking 1 h	Florisil (0.5 g) shaking	ISO 9377-4	Hexane 50 g	Shaking 1 h, Meth 1	Florisil-column (2 g)	DICK (pure diesel oil, summer quality) Basecomp 20s Pure lubricating oil, $C_{10} \dots C_{40}$	Splitless 270 °C FID 325 °C CP-SIL 5CP (15m, 0.32mm 0.25µm)
12	ISO/DIS 16703, Meth 1	40 g 2 ml	Acetone 50ml + Hexane 25ml	Ultrasonic 20 min	Florisil (4x3 g) Shaking	EN ISO 9377-2	Hexane 50 ml	Shaking 20 min, Meth 1	Florisil (2 g), Shaking	Diesel:lubricating oil (1:1) $C_{10} \dots C_{40}$	Splitless 300 °C FID 330 °C NB-1 (15m, 0.32mm, 0.1µm)

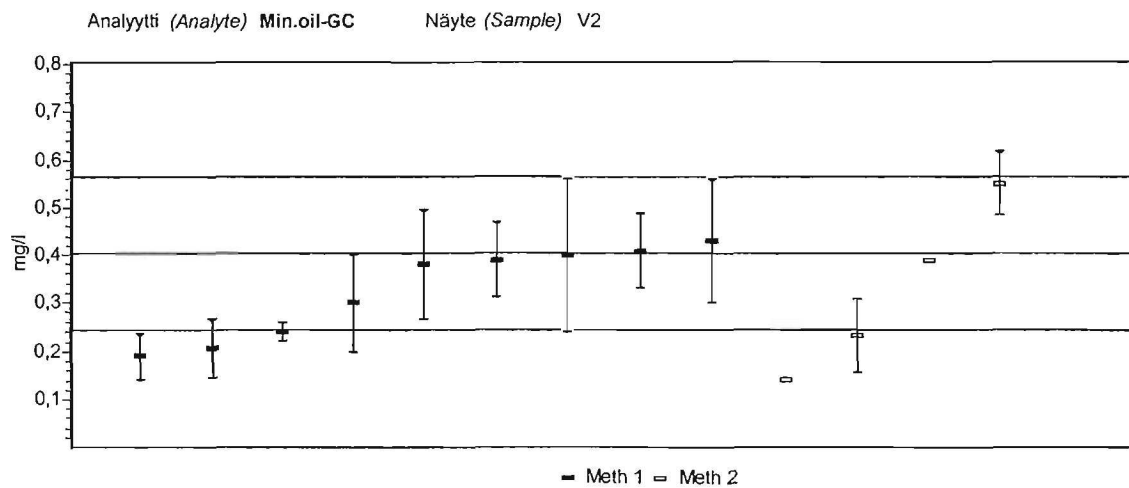
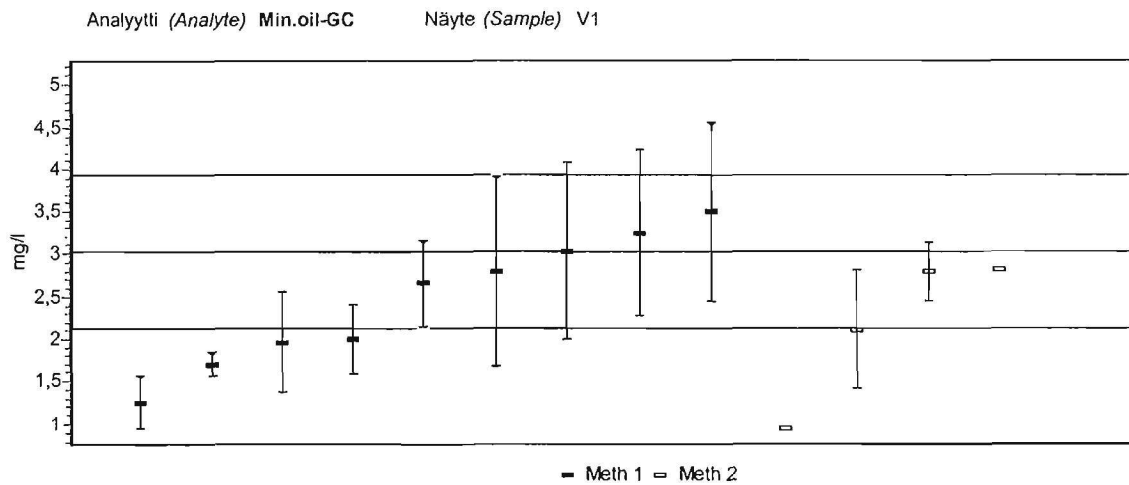
Lab	Soil					Water				Calibration and hydrocarbon range	GC: injection, detection and column
	Method reference Meth no.	Sample intake: M1, U1	Extraction solvent and volume	Extraction method and time	Clean up method	Method reference	Extraction solvent and volume	Extraction method and time, Meth no.	Clean up method		
13	ISO/DIS 16703, Meth 1	15 g 5 ml	Acetone 20 ml + <i>n</i> -heptane 10 ml	Ultrasonic 30 min	Florisil (1.5 g) shaking	EN ISO 9377-2	<i>n</i> -hexane 50 ml	Shaking 40 min, Meth 1	Florisil-column, (2 g)	Diesel:lubricating oil C ₁₀ ...C ₄₀	On column, 60 °C FID BPX-5 (25m, 0.32mm, 0.25µm)
14	ISO/DIS 16703, Meth 1	10 g 6 ml	Hexane 10 ml	Shaking 30 min	Florisil (1.5 g), Shaking	EN ISO 9377-2	Hexane 50 ml	Shaking 30 min, Meth 1	Florisil-column (2 g)	Diesel oil and lubricating oil (Fortum) C ₁₀ ...C ₄₀	On column, 50 °C FID, 360 °C BPX-5 (15m, 0.32mm, 1µm)
15						EN ISO 9377-2	<i>n</i> -hexane 50 + 10 ml	Shaking 30 min, Meth 1	Florisil-column (2 g)	VHVI: base oil / diesel oil C ₁₀ ...C ₄₀	On column, large volume inj. FID, 350 °C 5% Phenyl / 95% Dimethylpolysiloxane (15m, 0.32mm, 1µm)

ANNEX 6.2. RESULTS OBTAINED BY DIFFERENT ANALYTICAL METHODS



Meth 1: ISO/DIS 16703 or a similar method

Meth 2: A house method (pentane+methanol extraction)



Meth 1: Extraction technique - shaking

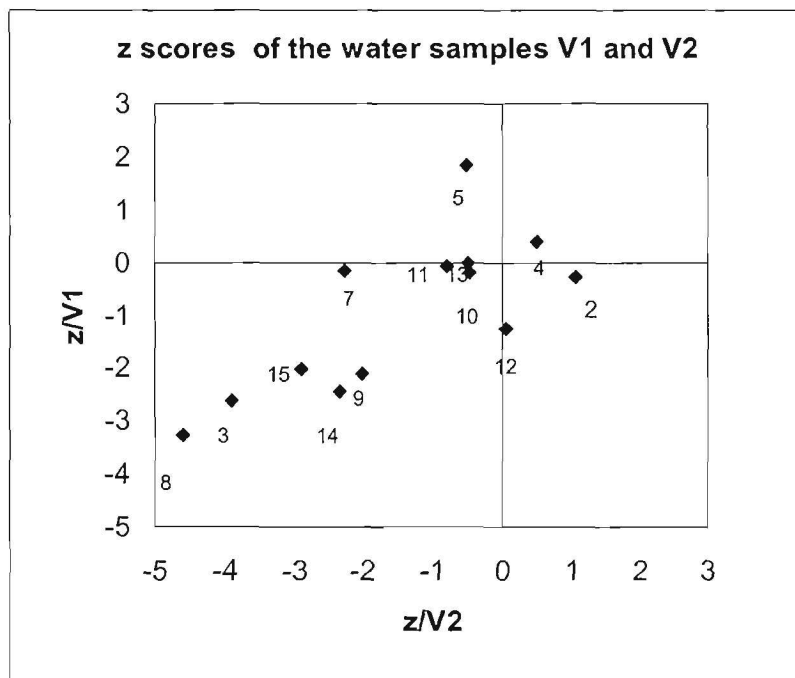
Meth 2: Extraction technique - stirring

ANNEX 6.3. RESULTS OBTAINED BY DIFFERENT ANALYTICAL METHODS (the water samples V1 and V2)

Extraction procedure:

Lab

2	shaking 30 min, pentane 50 ml
3	shaking 1 h, hexane 30 ml
4	shaking 40 min, heptane 5 ml
5	stirring 30 min, hexane 10 ml
7	shaking 1 h, hexane 10 ml
8	stirring 1 h, hexane 50 ml
9	stirring 30 min, hexane 30 ml
10	stirring 1 h, hexane 10 + 10 ml
11	shaking 1 h, hexane 50 ml
12	shaking 20 min, 50 ml (the solvent not reported)
13	shaking 40 min, hexane 50 ml
14	shaking 30 min, hexane 50 ml
15	shaking 30 min, hexane 50+10 ml



ANNEX 7. THE ASSIGNED VALUES AND THEIR UNCERTAINTIES

Assigned values

Sample	Assigned value	Estimation of the assigned value
L1	9.12 mg/ml	The calculated concentration
V1	3.02 mg/l	The calculated concentration
V2	0.402 mg/l	The calculated concentration
M1	325 mg/kg	Robust mean
U1	0.493 mg/ml	Robust mean

Uncertainties of the assigned values for the samples U1 and M1

Analyte	Sample	Assigned value	Robust-SD (=s*)	u_x	$2u_x$	$2u_x$ %
Min oil mg/kg	M1	325	98.4	32.4	64.7	20
Min oil mg/ml	U1	0.494	0.107	0.035	0.070	14

$$u_x = 1,23 \times s^*/\sqrt{p} \text{ (ISO/DIS 13528)}$$

where

s* = the Robust-standard deviation

p = the number of the results

ANNEX 8. RESULTS REPORTED BY THE PARTICIPANTS

Analyte	Sample	Unit	1			2			3			4		
Min.oil-GC	L1	mg/ml	15			10,3			8,64			8,96		
	M1	mg/kg	518	497	390	166	164	159	378	389	393	310	290	310
	U1	mg/ml	0,45						0,494			0,68		
	V1	mg/l				3,50			1,25			3,25		
	V2	mg/l				0,38			0,190			0,43		
Oil fr.>10-23	M1	mg/kg	347	345	306	94,6	93,5	97,0	107	105	105			
	U1	mg/ml	0,33						0,134					
Oil fr.>23-40	M1	mg/kg	171	152	84	71,4	70,5	62,0	257	268	272			
	U1	mg/ml	0,12						0,327					
Analyte	Sample	Unit	5			6			7			8		
Min.oil-GC	L1	mg/ml	9,013			8,48			11			8,38		
	M1	mg/kg	242	214	218	343	313	311	417	423	426	235	252	246
	U1	mg/ml	0,323			0,46			0,59			0,40		
	V1	mg/l	2,793						2,0			0,94		
	V2	mg/l	0,550						0,39			0,14		
Oil fr.>10-23	M1	mg/kg	108	68	68	126	118	117						
	U1	mg/ml	0,109			0,13								
Oil fr.>23-40	M1	mg/kg	134	146	150	217	194	195						
	U1	mg/ml	0,214			0,33								
Analyte	Sample	Unit	9			10			11			12		
Min.oil-GC	L1	mg/ml	8,74			10,59			9,09			7,80		
	M1	mg/kg	347	341	329				350	386	364	184	257	
	U1	mg/ml	0,452						0,407			0,53		
	V1	mg/l	2,11			2,81			2,66			3,04		
	V2	mg/l	0,233			0,387			0,409			0,30		
Oil fr.>10-23	M1	mg/kg	121	118	114				0,151	0,162	0,151			
	U1	mg/ml	0,141						0,163					
Oil fr.>23-40	M1	mg/kg	220	221	213				199	224	213			
	U1	mg/ml	0,309						0,244					
Analyte	Sample	Unit	13			14			15					
Min.oil-GC	L1	mg/ml	11,0			9,00			6,2					
	M1	mg/kg	430	440	450	304	296	299						
	U1	mg/ml	0,56			0,615								
	V1	mg/l	2,8			1,96			1,71					
	V2	mg/l	0,4			0,206			0,24					
Oil fr.>10-23	M1	mg/kg	150	150	140	131	128	135						
	U1	mg/ml	0,16			0,182								
Oil fr.>23-40	M1	mg/kg	280	290	310	182	177	172						
	U1	mg/ml	0,40			0,418								

ANNEX 9. 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 individual laboratory X = the reference value (<i>the assigned value</i>) 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 $\gg X$

N- non- accepted ($z < -3$), negative error, the result $\ll X$ (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, \dots, x_p .

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

$$X^* = \text{median of } x_i \quad (i = 1 \dots p)$$

$$S^* = 1.483 \text{ median of } |x_i - x^*| \quad (i = 1 \dots p)$$

The values of x^* and s^* are updated by calculating

$$\varphi = 1.5 s^*$$

For each x_i is calculated:

$$\begin{aligned}x_i^* &= x^* - \Phi && \text{if } x_i < x^* - \Phi \\x_i^* &= x^* + \Phi && \text{if } x_i > x^* + \Phi \\x_i^* &= x_i && \text{otherwise}\end{aligned}$$

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

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

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 converges.

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

ANNEX 10. RESULTS OF EACH PARTICIPANT

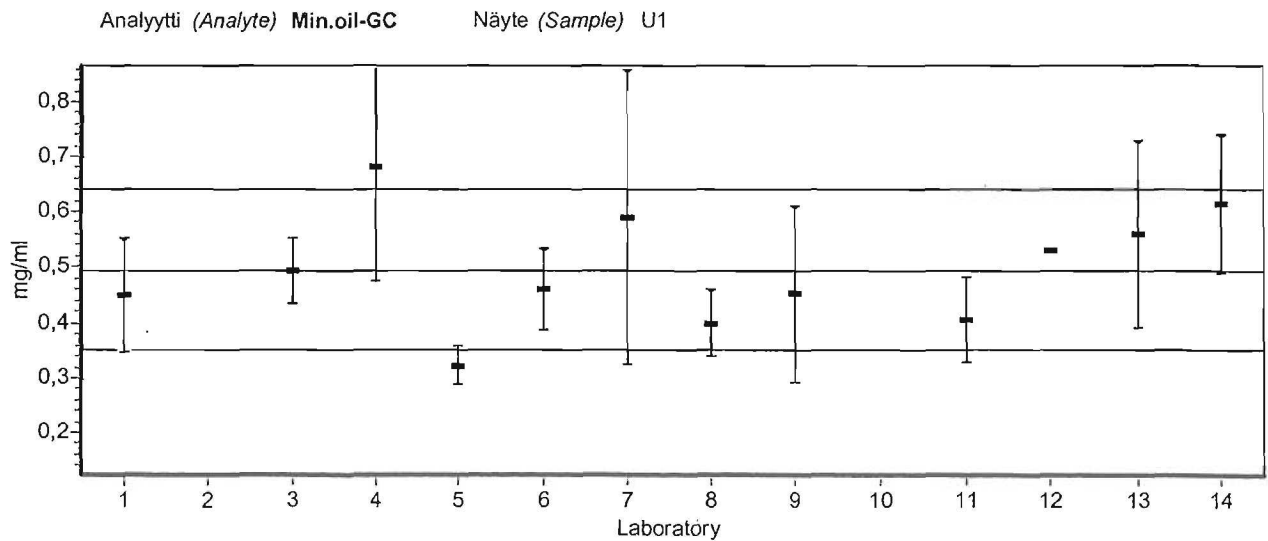
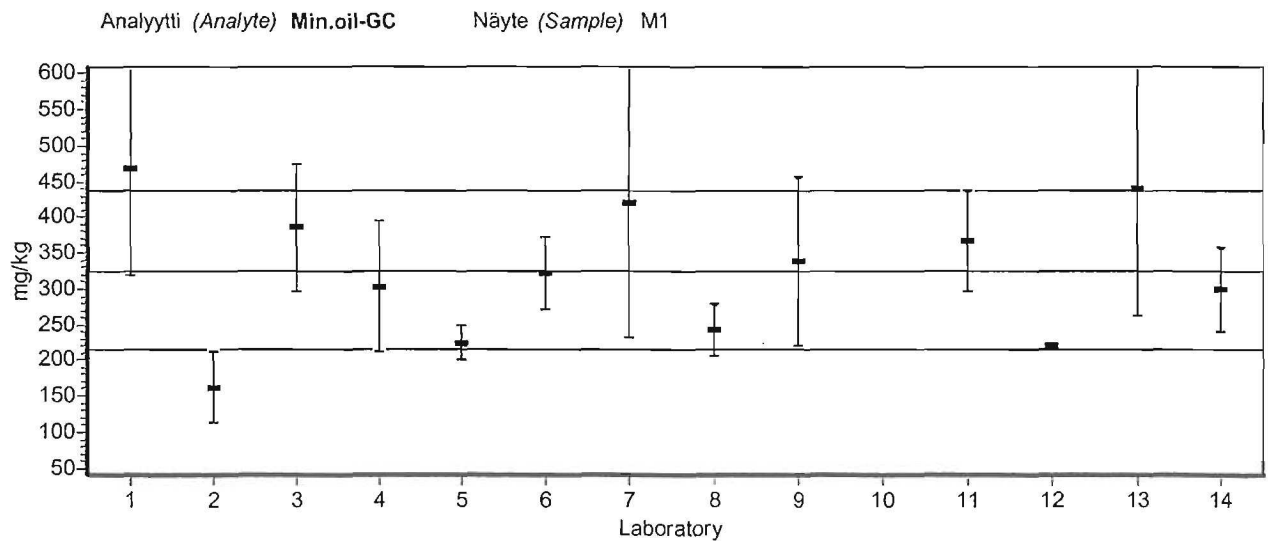
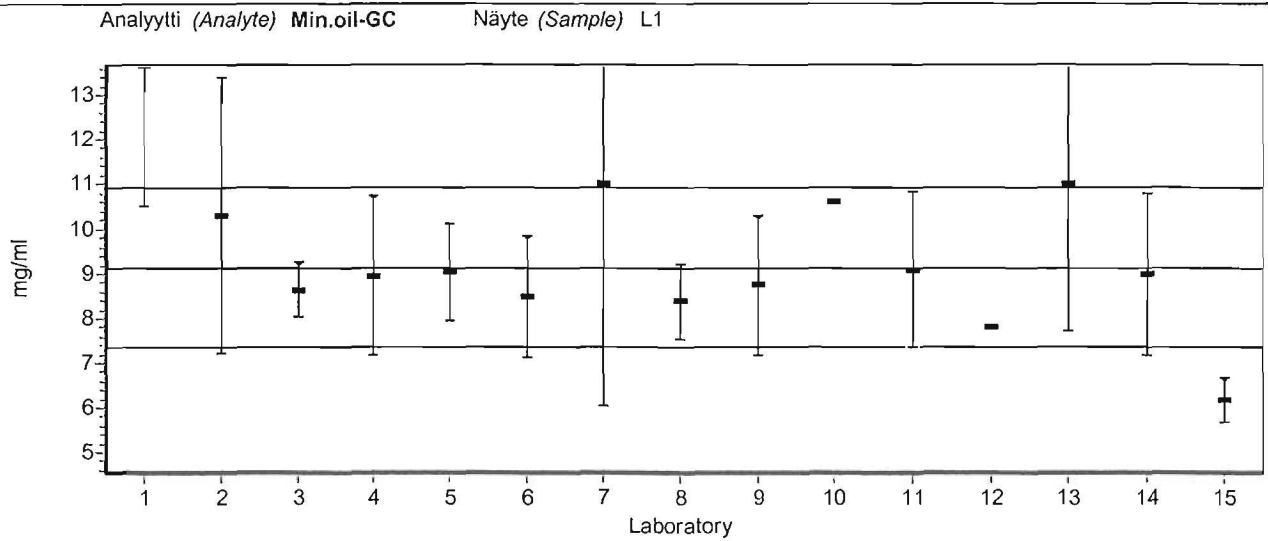
Analyte	Unit	Sample	z-Graphics					Z- value	Out/ test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl- failed	Mis- sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 1																				
Min.oil-GC	mg/ml	L1						6,447	yes	9,12	20	15	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						2,52	yes	325	35	468,3	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						-0,5938	yes	0,494	30	0,45	0,477	0,4968	0,102	20,5	12	0	0	12
Oil fr.>10-23	mg/kg	M1							yes	125		332,7	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,33	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		135,7	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,12	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 2																				
Min.oil-GC	mg/ml	L1						1,294	yes	9,12	20	10,3	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-2,848	yes	325	35	163	321	325,8	92,3	28,3	13	0	0	13
	mg/l	V1						1,06	yes	3,02	30	3,50	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-0,2736	yes	0,402	40	0,38	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		95,03	117	125,7	85,42	67,9	9	0	0	9
Oil fr.>23-40	mg/kg	M1							yes	194		67,97	195	190,6	67,86	35,6	9	0	0	9
Laboratory 3																				
Min.oil-GC	mg/ml	L1						-0,5263	yes	9,12	20	8,64	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						1,084	yes	325	35	386,7	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						0	yes	0,494	30	0,494	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-3,907	yes	3,02	30	1,25	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-2,637	yes	0,402	40	0,190	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		105,7	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,134	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		265,7	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,327	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 4																				
Min.oil-GC	mg/ml	L1						-0,1754	yes	9,12	20	8,96	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-0,381	yes	325	35	303,3	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						2,51	yes	0,494	30	0,68	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						0,5077	yes	3,02	30	3,25	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						0,3483	yes	0,402	40	0,43	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		81,33	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,109	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		143,3	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,214	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 5																				
Min.oil-GC	mg/ml	L1						-0,1173	yes	9,12	20	9,013	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-1,764	yes	325	35	224,7	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						-2,308	yes	0,494	30	0,323	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-0,5011	yes	3,02	30	2,793	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						1,841	yes	0,402	40	0,550	0,38	0,3273	0,1184	38,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		81,33	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,109	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		143,3	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,214	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 6																				
Min.oil-GC	mg/ml	L1						-0,7018	yes	9,12	20	8,48	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-0,04689	yes	325	35	322,3	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						-0,4588	yes	0,494	30	0,46	0,477	0,4968	0,102	20,5	12	0	0	12
Oil fr.>10-23	mg/kg	M1							yes	125		120,3	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,13	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		202	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,33	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 7																				
Min.oil-GC	mg/ml	L1						2,061	yes	9,12	20	11	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						1,705	yes	325	35	422	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						1,296	yes	0,494	30	0,59	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-2,252	yes	3,02	30	2,0	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-0,1493	yes	0,402	40	0,39	0,38	0,3273	0,1184	36,1	13	0	0	13
Laboratory 8																				
Min.oil-GC	mg/ml	L1						-0,8114	yes	9,12	20	8,38	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-1,418	yes	325	35	244,3	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						-1,269	yes	0,494	30	0,40	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-4,592	yes	3,02	30	0,94	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-3,259	yes	0,402	40	0,14	0,38	0,3273	0,1184	36,1	13	0	0	13

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

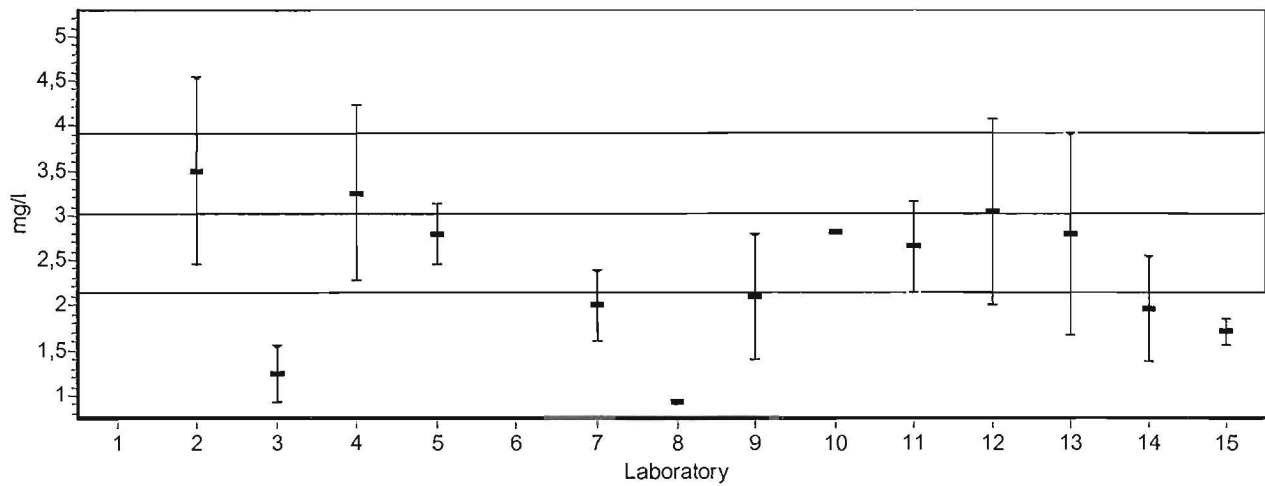
Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Passed	Outl. failed	Missing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 9																				
Min.oil-GC	mg/ml	L1						-0,4167	yes	9,12	20	8,74	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						0,2462	yes	325	35	339	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						-0,5668	yes	0,494	30	0,452	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-2,009	yes	3,02	30	2,11	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-2,102	yes	0,402	40	0,233	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		117,7	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,141	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		218	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,309	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 10																				
Min.oil-GC	mg/ml	L1						1,612	yes	9,12	20	10,59	9	9,48	1,98	20,8	15	0	0	15
	mg/l	V1						-0,4636	yes	3,02	30	2,81	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-0,1866	yes	0,402	40	0,387	0,38	0,3273	0,1184	36,1	13	0	0	13
Laboratory 11																				
Min.oil-GC	mg/ml	L1						-0,03289	yes	9,12	20	9,09	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						0,7326	yes	325	35	366,7	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						-1,174	yes	0,494	30	0,407	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-0,7947	yes	3,02	30	2,66	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						0,08706	yes	0,402	40	0,409	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		0,1547	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,163	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		212	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,244	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 12																				
Min.oil-GC	mg/ml	L1						-1,447	yes	9,12	20	7,80	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-1,837	yes	325	35	220,5	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						0,4858	yes	0,494	30	0,53	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						0,04415	yes	3,02	30	3,04	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-1,269	yes	0,402	40	0,30	0,38	0,3273	0,1184	36,1	13	0	0	13
Laboratory 13																				
Min.oil-GC	mg/ml	L1						2,061	yes	9,12	20	11,0	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						2,022	yes	325	35	440	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						0,8907	yes	0,494	30	0,56	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-0,4857	yes	3,02	30	2,8	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-0,02488	yes	0,402	40	0,4	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		146,7	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,16	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		293,3	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,40	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 14																				
Min.oil-GC	mg/ml	L1						-0,1316	yes	9,12	20	9,00	9	9,48	1,98	20,8	15	0	0	15
	mg/kg	M1						-0,4454	yes	325	35	299,7	321	325,8	92,3	28,3	13	0	0	13
	mg/ml	U1						1,633	yes	0,494	30	0,615	0,477	0,4968	0,102	20,5	12	0	0	12
	mg/l	V1						-2,34	yes	3,02	30	1,96	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-2,438	yes	0,402	40	0,206	0,38	0,3273	0,1184	36,1	13	0	0	13
Oil fr.>10-23	mg/kg	M1							yes	125		131,3	117	125,7	85,42	67,9	9	0	0	9
	mg/ml	U1							yes	0,151		0,182	0,1505	0,1686	0,06901	40,9	8	0	0	8
Oil fr.>23-40	mg/kg	M1							yes	194		177	195	190,6	67,86	35,6	9	0	0	9
	mg/ml	U1							yes	0,298		0,418	0,318	0,2953	0,09884	33,4	8	0	0	8
Laboratory 15																				
Min.oil-GC	mg/ml	L1						-3,202	yes	9,12	20	6,2	9	9,48	1,98	20,8	15	0	0	15
	mg/l	V1						-2,892	yes	3,02	30	1,71	2,66	2,371	0,7772	32,7	13	0	0	13
	mg/l	V2						-2,015	yes	0,402	40	0,24	0,38	0,3273	0,1184	36,1	13	0	0	13

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

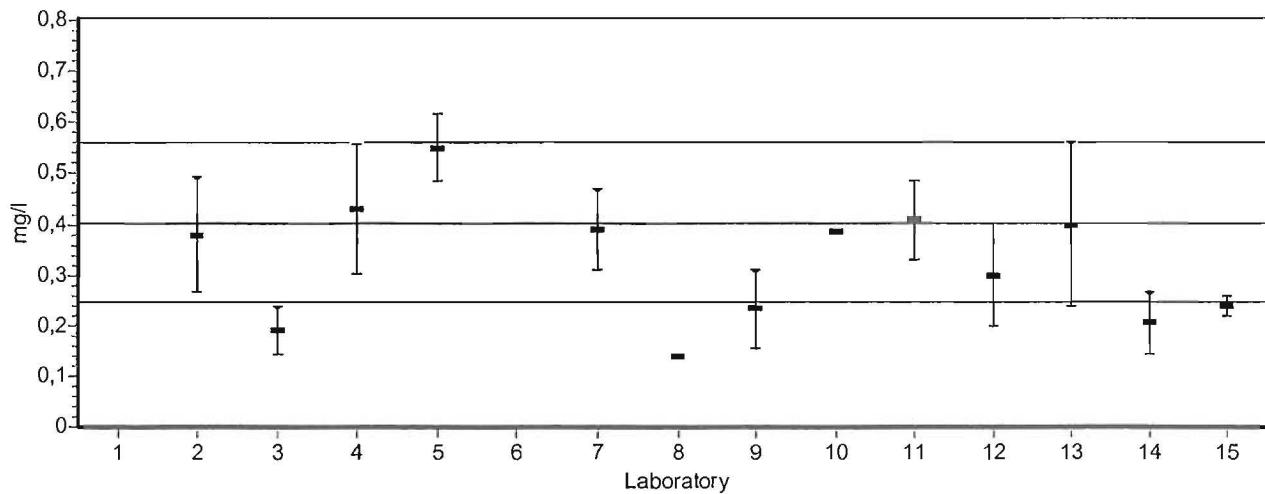
ANNEX 11. RESULTS AND MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS



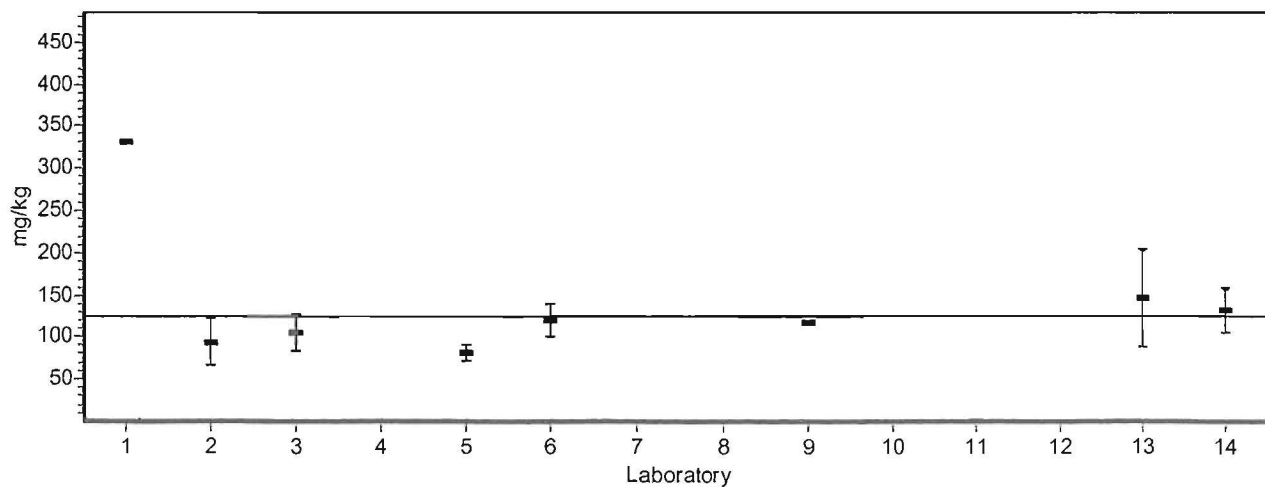
Analyttili (Analyte) Min.oil-GC Näyte (Sample) V1



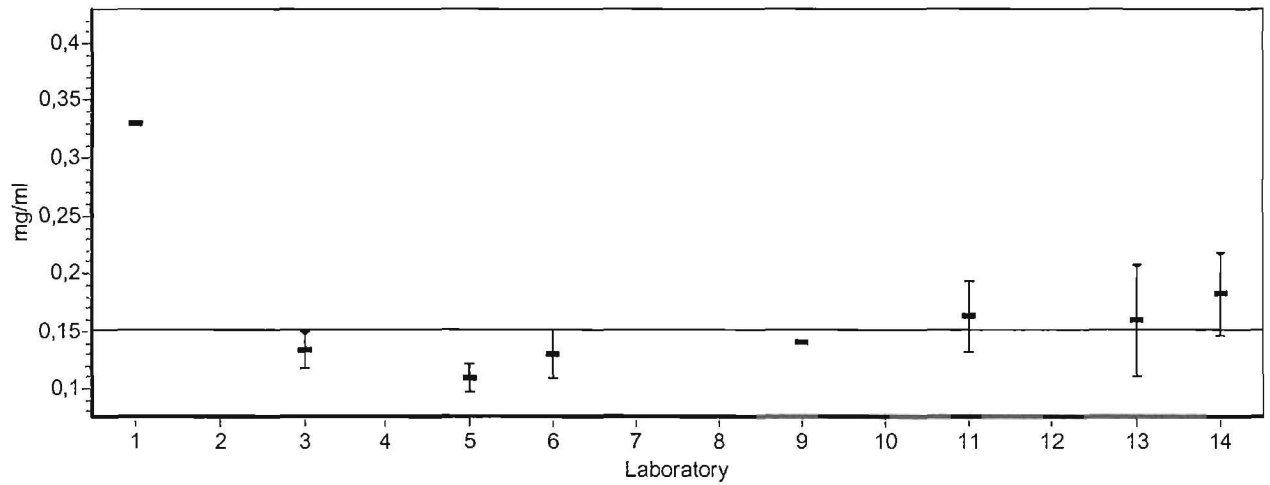
Analyttili (Analyte) Min.oil-GC Näyte (Sample) V2



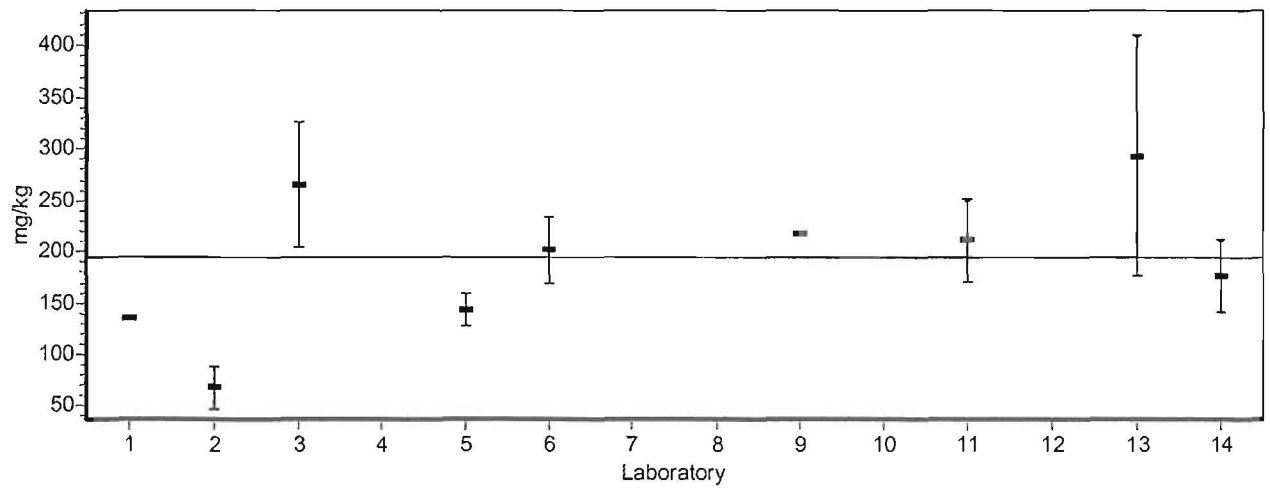
Analyttili (Analyte) Oil fr.>10-23 Näyte (Sample) M1



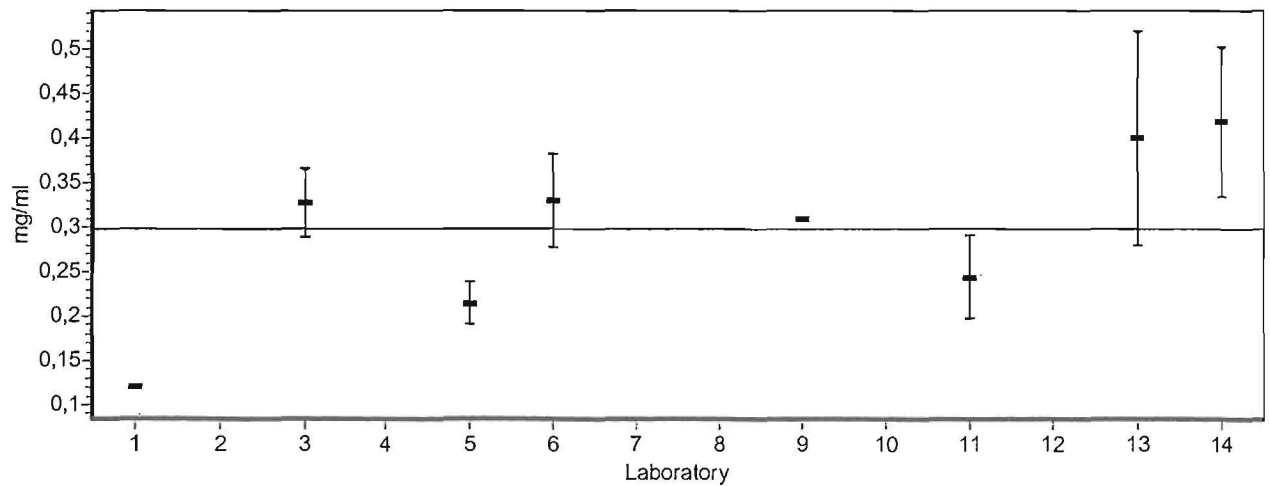
Analyytti (Analyte) Oil fr.>10-23 Näyte (Sample) U1



Analyytti (Analyte) Oil fr.>23-40 Näyte (Sample) M1



Analyytti (Analyte) Oil fr.>23-40 Näyte (Sample) U1

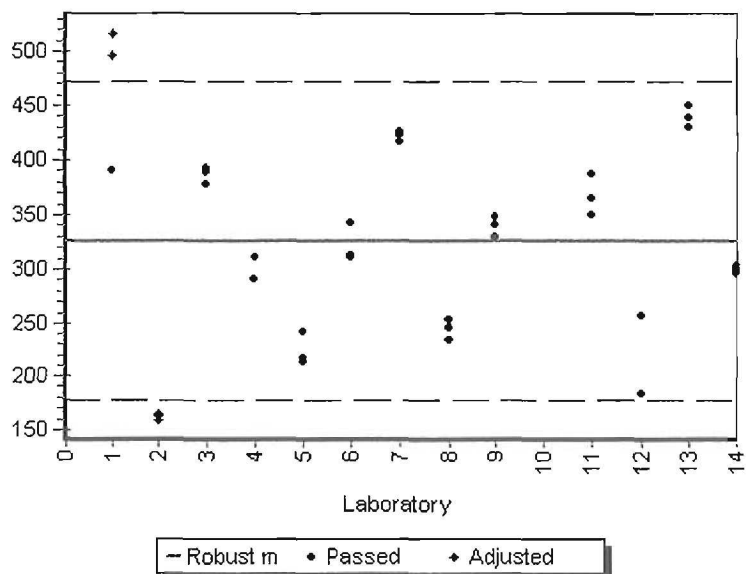


ANNEX 12. RESULTS CALCULATED ACCORDING TO ROBUST STATISTICS (the samples M1 and U1)

Interlaboratory comparison test 4/2002

ROBUST statistics

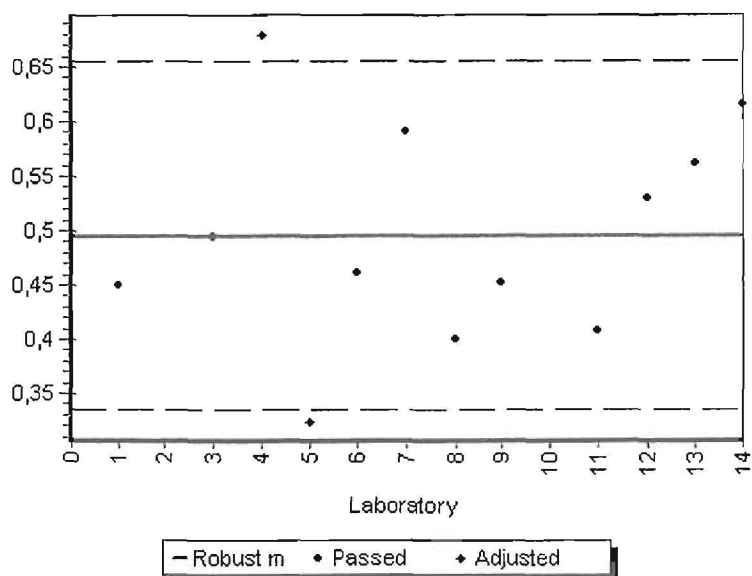
Analyte: Min.oil-GC
 Sample: M1
 Robust mean: 325
 Mean: 326
 Robust SD: 98,4 (30,3%)
 SD: 92,3 (28,3%)



Interlaboratory comparison test 4/2002

ROBUST statistics

Analyte: Min.oil-GC
 Sample: U1
 Robust mean: 0,494
 Mean: 0,497
 Robust SD: 0,107 (21,6%)
 SD: 0,102 (20,5%)



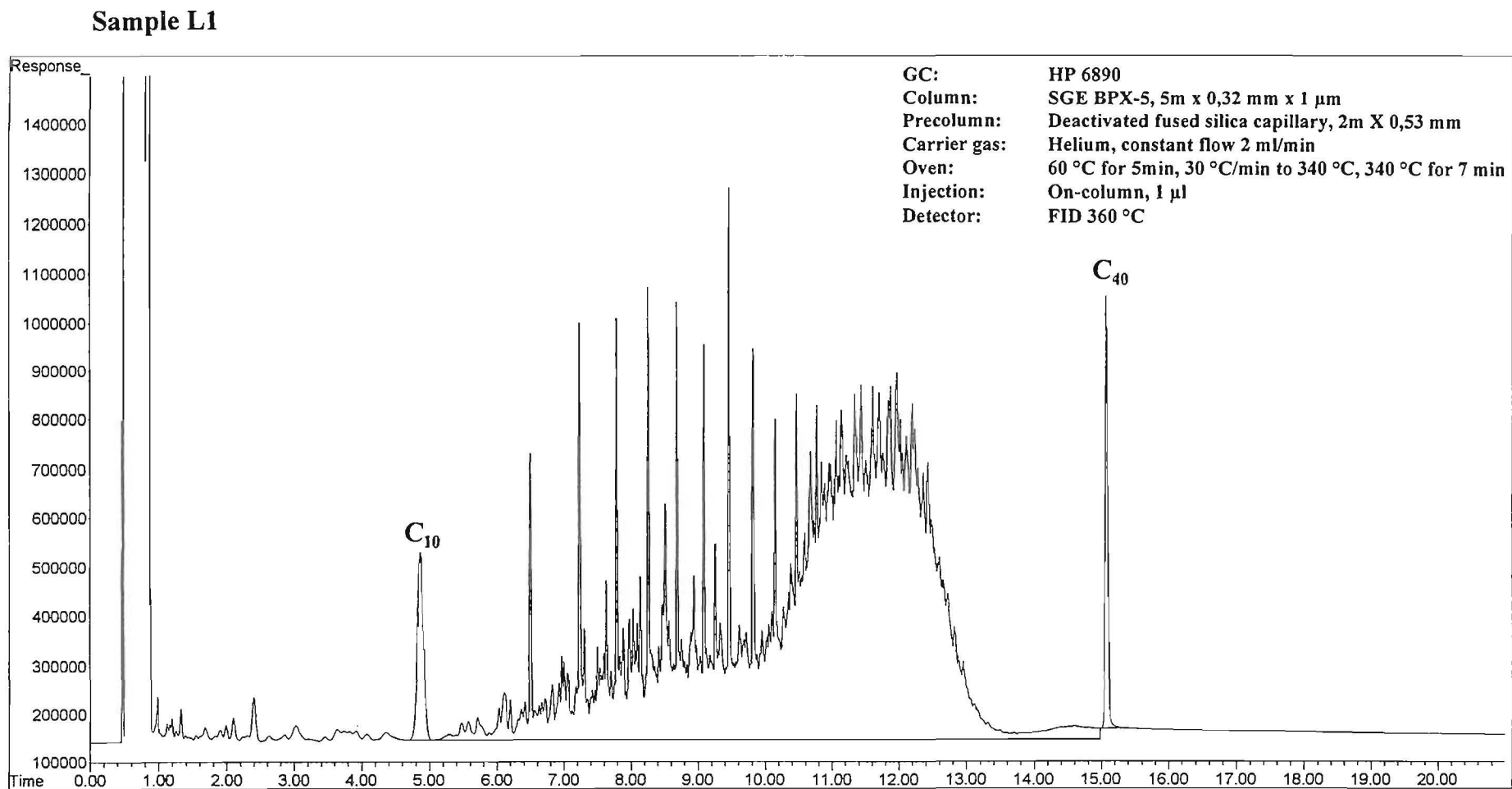
ANNEX 13. SUMMARY OF THE z SCORES

Analyte	Sample/Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	%
Min.oil-GC	L1	P	A	A	A	A	A	p	A	A	A	A	A	p	A	N	73
	M1	p	n	A	A	A	A	A	A	A	.	A	A	p	A	.	77
	U1	A	.	A	p	n	A	A	A	A	.	A	A	A	A	.	83
	V1	.	A	N	A	A	.	n	N	n	A	A	A	A	n	n	54
	V2	.	A	n	A	A	.	A	N	n	A	A	A	A	n	n	62
Oil fr.>10-23	M1
	U1
Oil fr.>23-40	M1
	U1
%		33	75	60	80	80	100	60	60	60	100	100	100	60	60	0	
Accredited		yes															

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

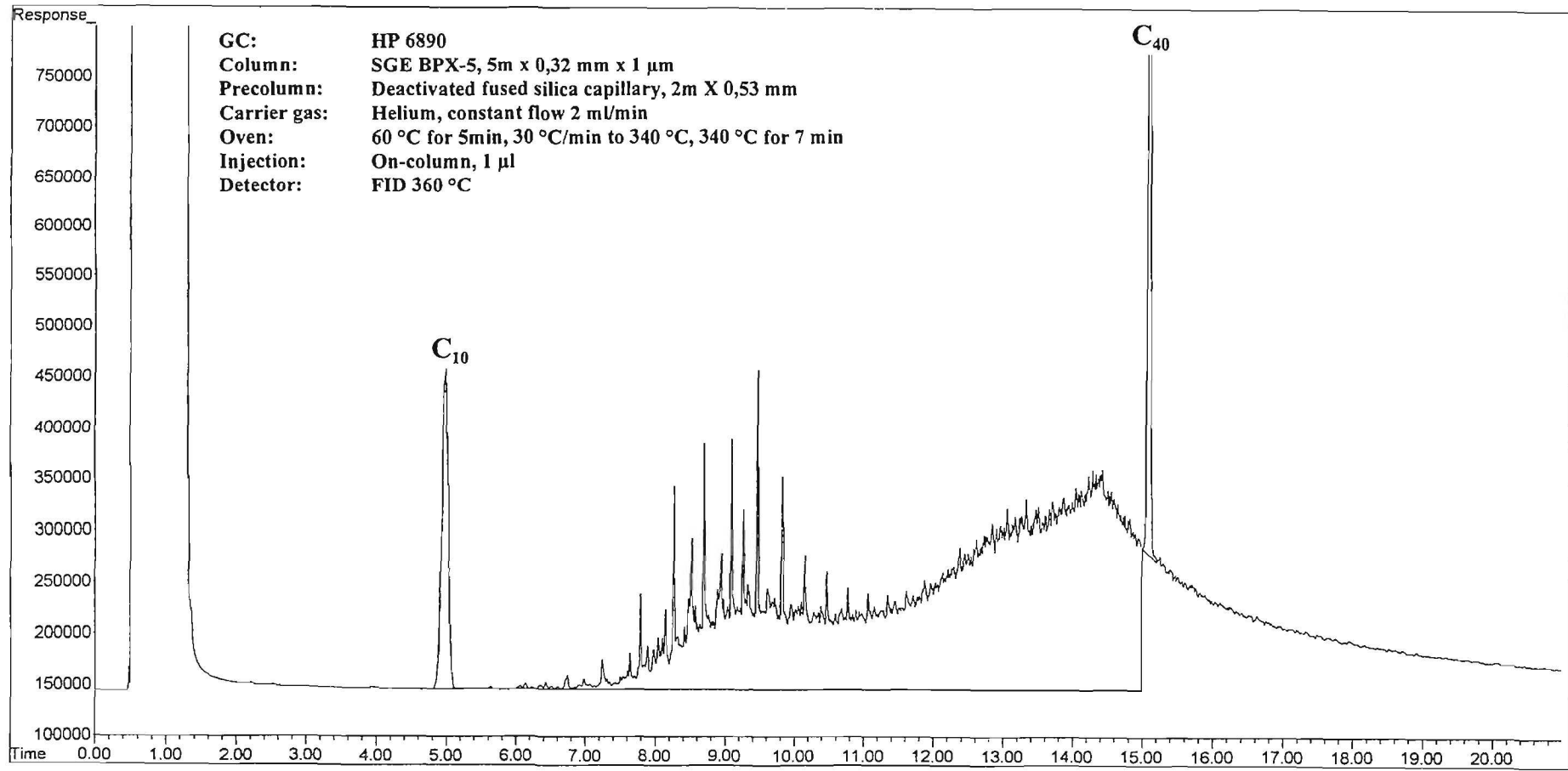
%* - percentage of accepted results

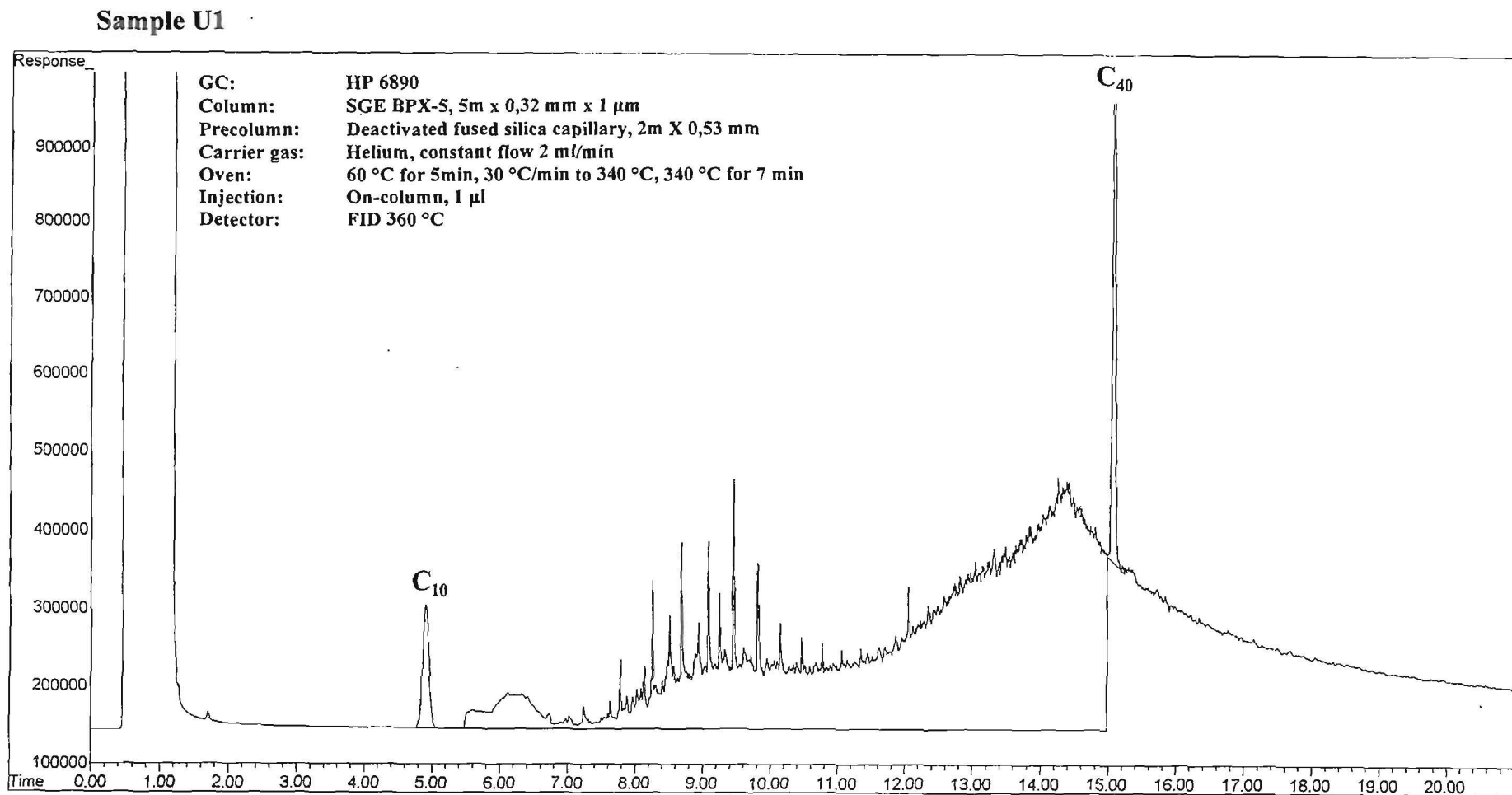
Totally accepted, % In all: 70 In accredited: 60 In non-accredited: 70



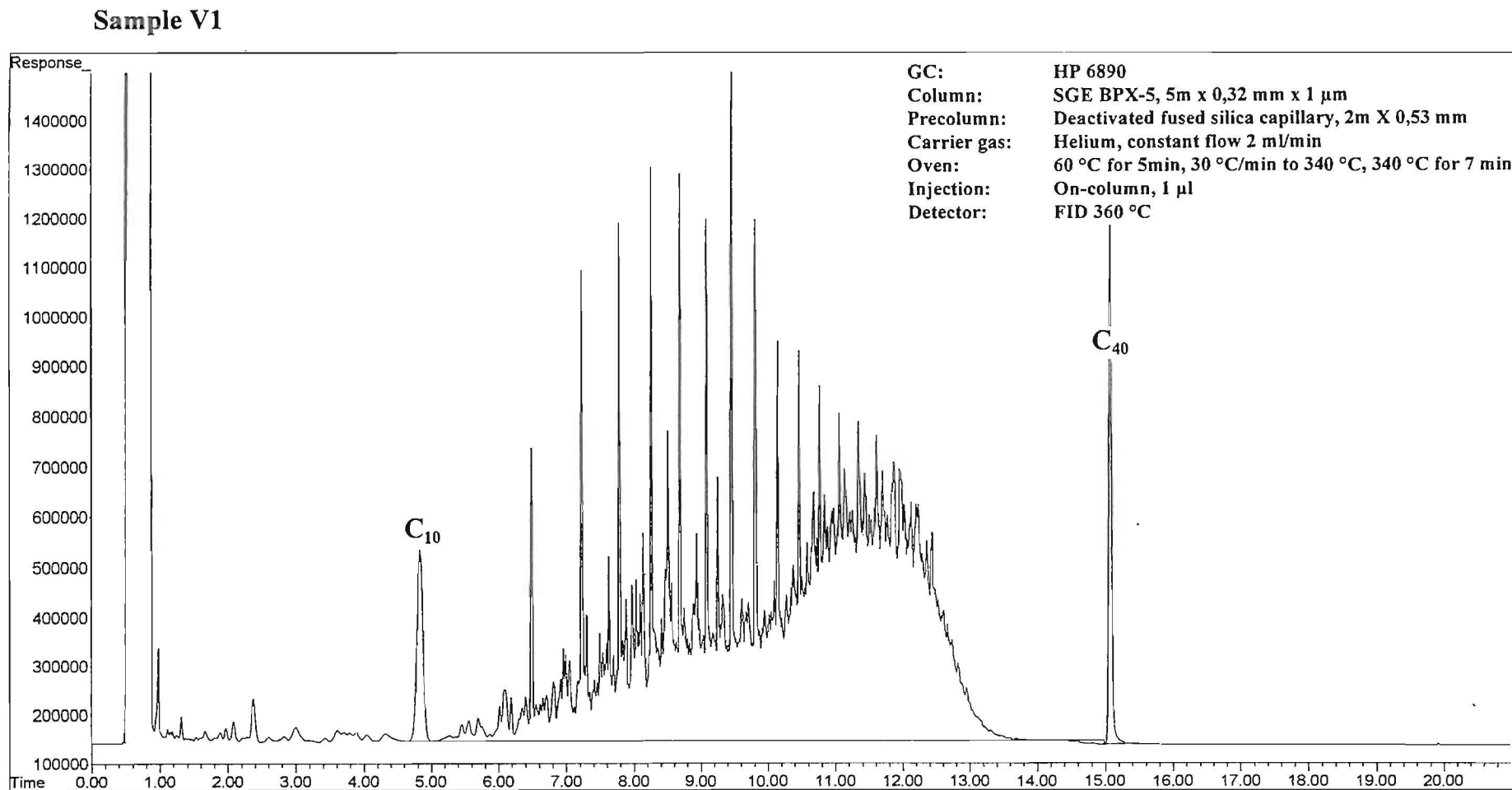
ANNEX 14.2. SAMPLE CHROMATOGRAMS (M1)

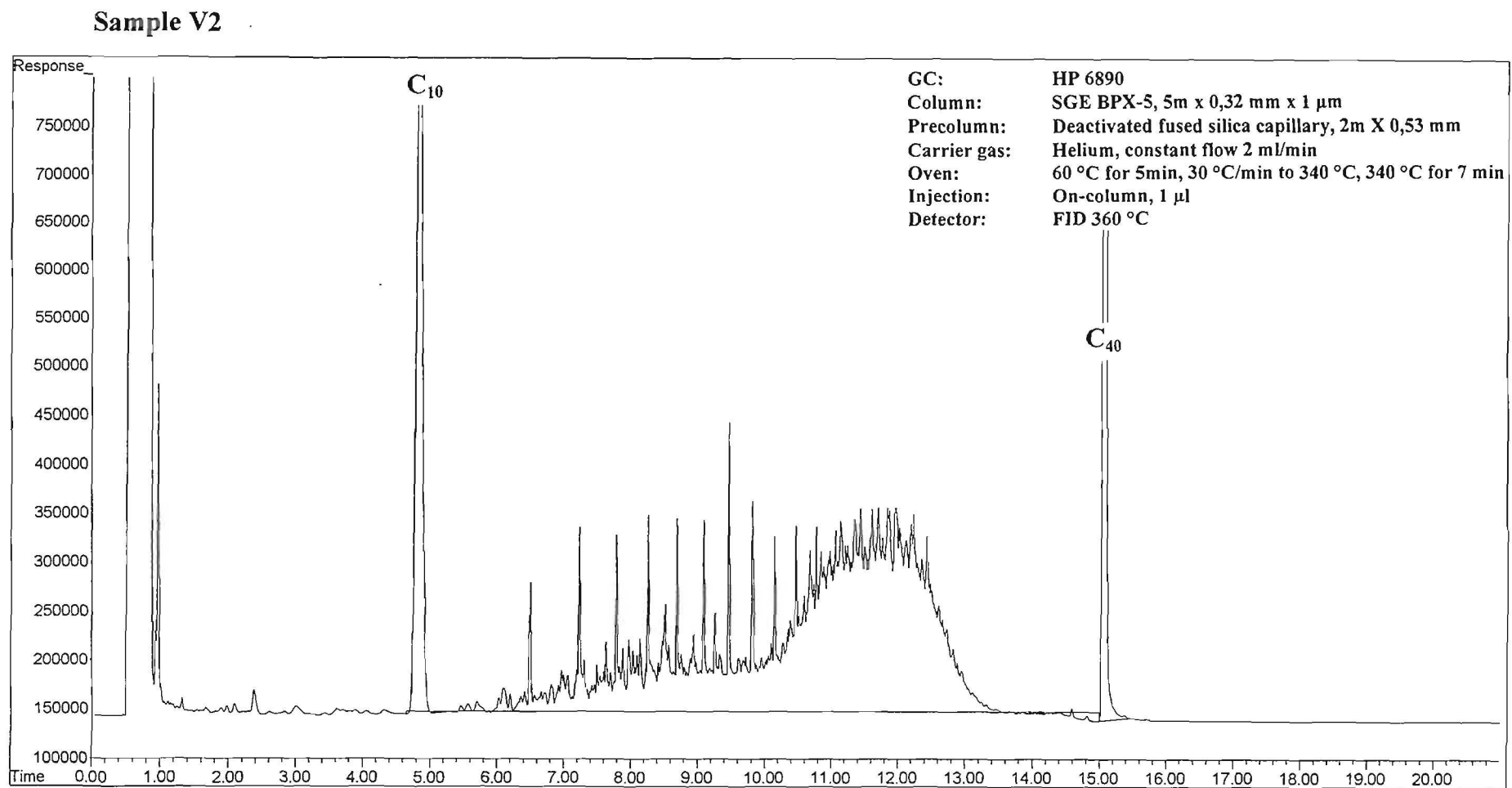
Sample M1





ANNEX 14.4. SAMPLE CHROMATOGRAMS (VI)





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Irma Mäkinen, Anna-Mari Suortti, Sami Huhtala and Seppo Pönni

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Interlaboratory Comparison 4/2002

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Report

Commissioned by

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Abstract

The Finnish Environment Institute carried out the interlaboratory comparison test for the determination of mineral oil content from polluted soils and hydrocarbon oil index in waters in May 2002. The GC methods for the analysis of mineral oil content were recommended to be used. Additionally, the reporting of oil fractions $C_{>10}\dots C_{23}$ and $C_{>23}\dots C_{<40}$ as well as the use of infrared spectrometric method and field method for the soil sample were voluntary. A total of 15 laboratories from Finland, Latvia, Estonia, Norway and Sweden participated.

One standard solution containing a known concentration of different oils were prepared. Two water samples, diluted municipal waste water and lake water, were delivered. One soil sample and one soil extract were also delivered to the participating laboratories.

The draft standard method ISO/DIS 16703 was mainly used for the mineral oil analysis in the soil samples. The standard method EN ISO 9377-2 was used for analysis of mineral oil in water samples. Only two laboratories used IR technique and three laboratories used a hydrocarbon test kit for the measurement of the soil sample.

In this interlaboratory comparison, 70 % of the reported results was regarded to be acceptable, when the target total standard deviation 20 - 40 % was used in calculations of z scores in 95 % confidence interval. The water samples turned out to be the most critical to analyse. From the results 54 % and 62 % were accepted, when the target standard deviation was 30 % and 40 %, respectively.

The Finnish interlaboratory comparison for analysis of mineral oil in polluted soil in using of the GC method was carried out for the second time. These results have some improved since the last comparison in 2000. The Finnish interlaboratory comparison for waters in using of the GC method was carried out the first time. The ILC showed that there are still improvements to be made in some laboratories.

Keywords

water analyses, water and environmental laboratories, interlaboratory comparison, performance testing, intercalibration

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Tekijä(t) (toimielimestä: nimi, puheenjohtaja, sihteeri)
Irma Mäkinen, Anna-Mari Suortti, Sami Huhtala, Seppo Pönni

Julkaisun nimi (myös ruotsinkielinen)
Laboratorioiden välinen vertailukoe 4/2002

Julkaisun laji
Raportti

Toimeksiantaja

Toimielimen asettamispm

Julkaisun osat

Tiivistelmä

Suomen ympäristökeskus järjesti toukokuussa 2002 vertailukokeen mineraaliöljyn määrittämiseksi pilaantuneesta maasta ja vedestä. Vertailukokeessa suositeltiin käytettävän kaasukromatografisia määrittämenetelmiä. Maanäytteen öljyfraktioiden $C_{>10}...C_{23}$ ja $C_{>23}...C_{<40}$ ilmoittaminen sekä infrapunaspektometrisen määrittämenetelmän ja kenttämenetelmien käyttö maanäytteelle olivat vapaaehtoisia. Vertailukokeeseen osallistui kaikkiaan 15 laboratoriota Suomesta, Latviasta, Virosta, Norjasta ja Ruotsista.

Vertailukokeen näytteinä oli yksi tunnetun öljypitoisuuden omaava standardiliuos, kaksi vesinäytettä sekä yksi maanäyte ja sen uute.

Maanäytteiden analysoinnissa käytettiin pääasiassa standardiluonnosmenetelmää ISO/DIS 16703 ja vesinäytteiden analysoinnissa standardimenetelmää EN ISO 9377-2. Vain kaksi laboratoriota käytti lisäksi IR-menetelmää ja kolme laboratoriota käytti kenttätestimenetelmää maanäytteen öljyn määrittämiseksi.

Tässä vertailukokeessa 70 % tuloksista oli hyväksyttäviä, kun z-arvojen laskennassa käytettiin 20 – 40 %:n tavoitekokonaiskeskihajontoja. Vesinäytteet osoittautuivat hankalimmiksi analysoitaviksi näytteiksi. Vesinäytteiden V1 ja V2 tuloksista hyväksyttiin 54 % ja 63 %, kun tavoitekokonaiskeskihajonnaksi asetettiin vastaavasti 30 % ja 40 %.

Vertailukoe mineraaliöljyn määrittämiseksi pilaantuneesta maasta järjestettiin toisen kerran Suomessa. Tulokset olivat jonkin verran parantuneet edellisestä vertailukokeesta, joka järjestettiin syksyllä 2000. Vesien osalta tämä oli ensimmäinen Suomessa järjestetty vertailukoe, missä öljymääritys pohjautui kaasukromatografiseen menetelmään.

Asiasanat (avainsanat)

vesianalyysi, vesi- ja ympäristölaboratoriot, vertailukoe, interkalibrointi, pätevyystesti

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