REPORTS OF FINNISH ENVIRONMENT INSTITUTE 8| 2011

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Helsinki 2011

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Finnish Environment Institute SYKE

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ALKUSANAT

Suomen ympäristökeskus (SYKE) on toiminut ympäristöalan kansallisena vertailulaboratoriona vuodesta 2001 lähtien. Toiminta perustuu ympäristöministeriön määräykseen, mikä on annettu ympäristönsuojelulain (86/2000) nojalla. Vertailulaboratorion tarjoamista palveluista yksi tärkeimmistä on pätevyyskokeiden ja muiden vertailumittausten järjestäminen. SYKEn laboratoriot on FINAS- akkreditointipalvelun akkreditoima testauslaboratorio T003 (SFS-EN ISO/IEC 17025) ja vertailumittausten järjestäjä Proftest SYKE PT01 (SFS-EN ISO/IEC 17043, www.finas.fi).

Tämä pätevyyskoe on toteutettu Proftest SYKEn pätevyysalueella ja se antaa tietoa osallistujien pätevyyden lisäksi tulosten vertailukelpoisuudesta myös yleisemmällä tasolla. Pätevyyskokeen onnistumisen edellytys on järjestäjän ja osallistujien välinen luottamuksellinen yhteistyö.

Parhaat kiitokset yhteistyöstä kaikille osallistujille!

PREFACE

Finnish Environment Institute (SYKE) has served as the National Reference Laboratory in the environmental sector designated by the Ministry of the Environment under the section 24 of the Environment Protection Act (86/2000) since 2001. The duties of the reference laboratory service include providing proficiency tests and other interlaboratory comparisons for analytical laboratories and other producers of environmental information. The SYKE laboratories has been accredited by the Finnish Accreditation service as the testing laboratory T003 (EN ISO/IEC 17025) and as the proficiency testing provider Proftest SYKE PT01 (EN ISO /IEC 17043, www.finas.fi).

This proficiency test has been carried out under the scope of Proftest SYKE and it provides information about performance of the participants as well as comparability of the results at more general level. The success of the proficiency test requires confidential co-operation between the provider and participants.

Thank you for your co-operation!

Helsingissä 28. helmikuuta 2011 / Helsinki 28 February 2011

Marja Luotola

Laboratorionjohtaja / Chief of Laboratory

1 INTRODUCTION

In November 2010 The Proftest SYKE carried out the proficiency test (PT) for the analysis of oil hydrocarbons in water and soil. The test was carried out in accordance with the international standards, EN ISO/IEC 17043 [1] and ISO 13528 [2] as well as IUPAC Recommendations [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as the proficiency testing provider PT01 (www.finas.fi). However, the intercomparison of the volatile oil hydrocarbons (C5–C10) did not include in the accredited scope yet.

2 ORGANIZING OF THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratories, Proftest SYKE
Hakuninmaantie 6, 00430 Helsinki, Finland
Phone: +358 20 610 123
Fax: +358 9 448 320

Subcontractor: Ramboll Analytics Oy, testing of oil hydrocarbons in water samples.

The responsibilities in organizing the PT were as follows:

Kaija Korhonen-Ylönen, coordinator
Jari Nuutinen, analytical expert and coordinator trainee
Mirja Leivuori, substitute of coordinator
Markku Ilmakunnas, technical assistant, layout of the report
Sari Lanteri, technical assistant
Anne Markkanen, technical assistant
Helena Tanttu, technical assistant
Keijo Tervonen, technical assistant
Ritva Väisänen, technical assistant

2.2 Participants

In total, 16 laboratories from Denmark, Finland, and Sweden participated in this PT (Appendix 1). Most of the laboratories analysed oil hydrocarbons in water and 9 laboratories analysed oil hydrocarbons in soil. The accredited method used 10 laboratories for oil analysis in water and 7 laboratories for oil analysis in soil. Two laboratories had been accredited their volatile oil hydrocarbons determinations. The organizing laboratory (SYKE) had the code 4 in the result tables.

2.3 Samples and their delivery

The artificial samples A1B and A1O as well as the addition solution L2O for the water sample G2O were commercial standard solutions diluted to the final concentration. The preparation of the samples is presented in Appendix 2.

The soil sample was previously used in the PT SYKE 5/2000 [7]. The soil sample taken on an oil contaminated site close to Tampere was air dried at the room temperature, homogenized and sieved out (fraction < 1 mm). The mixed soil sample was distributed in sub samples using a rotary sample divider equipped with vibratory sample feeder.

The samples were delivered 16 November 2010. They were requested to be analysed and reported at the latest 3 December 2010.

2.4 Homogeneity and stability studies

Homogeneity of the sample M3O was tested by analysing oil hydrocarbons as duplicate determinations from six sub samples (Appendix 3). According to the homogeneity test results the samples M3O were considered to be homogenous.

The stabilities of the samples A1O and A1B, as well as, the addition solution L2O were checked during the sample transport to the participants. The sample vials were weighed at SYKE before the delivering and reweighed at the participating laboratory after the receiving. The differences of these two measurements were < 0.5 %.

2.5 Feedback from the proficiency test

Appendix 5.1 contains the comments sent by the participants and Appendix 5.2 the provider´s comments to the participants.

2.6 Processing of the data

2.6.1 Testing of outliers and normality of data

Before the statistical treatment, the data was tested according to the Kolmogorov-Smirnov normality test and the possible extreme values were rejected as the outliers according to the Hampel test. Also before the robust calculation some outliers were rejected in case that the results deviated from the robust mean over 50 %.

2.6.2 Assigned value

The assigned values and their uncertainties are presented in Appendix 6. The calculated concentrations were used as the assigned values for volatile oil hydrocarbon (C5–C10) in the sample A1B and for total oil hydrocarbons (>C10–C40) in the sample A1O. The uncertainty given is the expanded combined uncertainty (k = 2) based on the combination of uncertainties associated with individual operations involved in the preparation of the sample. The main individual resource of the uncertainty was the uncertainty of the concentration in the stock solution.

The robust means of the reported results were used as the assigned value for the other determinants. The uncertainty of the assigned value was calculated using the robust standard deviation of the reported results as follows:

$$U\% = \frac{100 \times \left(\frac{2 \times 1.25 \times s_{rob}}{\sqrt{n}} \right)}{AV}$$

where:

U% = the expanded uncertainty of the assigned value (k = 2)
AV = the assigned value
s_{rob} = the robust standard deviation
n = the number of the results

The expanded uncertainty of the calculated assigned value for total oil hydrocarbons in the artificial sample A1O was 3.2 % and 2 % for volatile oil hydrocarbons in the sample A1B. When the robust mean of the results reported by the participants was used as the assigned value the uncertainties of

the assigned values varied from 7.9 % to 18 %.

After the sending of the preliminary results the provider decided to correct some of the participants' errors e.g. the unit errors and the results, which had not been entered on the appropriate line in the result sheet. Due to these corrections the assigned values changed slightly from the reported preliminary assigned values:

- >C10–C40/G2O: 0.46 mg/l, (0.482 mg/l in the preliminary results)
- >C10–C40/M3O: 553 mg/kg (524 mg/kg in the preliminary results)
- >C10–C21/M3O: 128 mg/kg (129 mg/kg in the preliminary results)
- >C21–C40/M3O: 414 mg/kg (408 mg/kg in the preliminary results)
- >C21–C40/A1O: 1.77 mg/ml (1.76 mg/ml in the preliminary results)

2.6.3 Standard deviation for proficiency assessment and z score

The performance evaluation was carried out by using the z scores (Appendix 9), which were calculated using the extimated standard deviation for proficiency assessment. The estimation of the standard deviation was based on the type of the sample, the concentration of the analyte, the results of homogeneity testing and the uncertainties of the assigned values. In the performance evaluation z scores were interpreted as follows:

$\lvert z \rvert \leq 2$	satisfactory results
$2 < \lvert z \rvert < 3$	questionable results
$\lvert z \rvert \geq 3$	unsatisfactory results

The calculated z scores with the results are presented in Appendix 7.

The reliability of the assigned value was tested according the criterion $u / s_p \leq 0.3$, where u is the standard uncertainty (U / 2) of the assigned value and s_p the standard deviation for proficiency assessment. The criterion was not fulfilled in every case, which indicated that the following assigned values had high uncertainty:

- A1O: >C10–C21
- M3O: >C10–C21

The reliability of the target standard deviation and the corresponding z score were estimated by comparing the target value (s_p) with the robust standard deviation of the reported results (s_{rob}). The criterion $s_{rob} < s_p$ was fulfilled in most cases, which indicated that the evaluation of performance was reliable for this PT.

Due to the high uncertainty of the assigned value of the fraction >C10–C21 in the sample A1O the total target value was set 30 %, when it was 20 % in the reported preliminary performance evaluation.

3 RESULTS AND CONCLUSIONS

3.1 Results

The results and the performance of each laboratory are presented in Appendix 7 and the summary of the results in Table 1. The results and their uncertainties are presented graphically in Appendix 8. Explanations for the result sheets are presented in Appendix 9. The participants were requested to report the analytical replicate results for volatile oil hydrocarbons. The results of the replicate determinations are presented in Table 2 (ANOVA statistics).

Table 1. Summary of the proficiency test 8b/2010.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2 * s_p %	Accepted z-val %
C5–C10	A1B	µg/ml	90	74.9	78.8	82.4	17.95	22.8	8	20	63
>C10–C21	A1O	mg/ml	1.67	1.67	1.67	1.71	0.37	21.9	10	30	70
	M3O	mg/kg	128	131.2	127.8	124.0	18.6	14.5	9	30	67
>C21–C40	A1O	mg/ml	1.77	1.77	1.77	1.69	0.18	10.3	10	20	80
	M3O	mg/kg	414	403.9	413.7	428.0	32.8	7.9	9	30	78
>C10–C40	A1O	mg/ml	3.62	3.34	3.33	3.46	0.41	12.4	15	20	73
	G2O	mg/l	0.46	0.48	0.46	0.47	0.09	18.4	15	30	80
	M3O	mg/kg	553	542.2	553	557	49,5	9.0	9	30	78

Table 2. Results of the replicate determinations (ANOVA statistics).

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	sb / sw
C5–C10	A1B	µg/ml	90	76.6	79	3.88	10.55	11.2	5.1	14	15	2.7

Ass. val.	the assigned value
Mean	the mean value
Mean rob	the robust mean
Md	the median value
SD rob	the robust standard deviation
SD rob %	the robust standard deviation as percents
Num of Labs	the number of the participants
2 * s_p	the total standard deviation for proficiency assessment at the 95% confidence interval
Accepted z-val%	the satisfactory z values: the results (%), where $\lvert z \rvert \leq 2$.
sw	the repeatability standard error
sb	the standard error between laboratories
st	the reproducibility standard error

The variation of total oil hydrocarbon results (robust standard deviation) from the synthetic sample A1O was 12.4 %, from the ground water samples 18.4 % and from the soil samples 14.5 % (Table 1). The deviations of the results in this PT were at the same level as in the previous PT SYKE 8/2008 [8], where the deviations varied from 9.2 % to 18.6 %.

The repeatability of volatile oil hydrocarbons (within-laboratory standard deviation, s_w) was 5.1 % and the reproducibility (between-laboratory standard deviation, s_b) was 14 %, respectively The ratio s_b / s_w should be between 2 and 3 for robust methods and in this case it was 2.7 (Table 2).

3.2 Analytical methods

The analytical methods used by the participants are presented in Appendix 10.1. Method comparison was done between the applied equipment techniques and the results were coded by the coordinator as follows:

- Method 1: GC-FID
- Method 2: GC-MS

Volatile oil hydrocarbons, C5—C10

In analysing volatile oil hydrocarbons one laboratory used GC-FID and all the other Headspace-GC-MS technique. No statistical comparison between the methods could be done (Appendixes 10.1 and 10.2).

Oil hydrocarbons in water

Most laboratories determined oil hydrocarbons in water using the method, which based on the standard EN ISO 9322-2 [5] and only one laboratory used the standard method ISO 16703 [6]. The water sample was extracted with hexane, pentane or heptane. Polar substances were removed by clean-up on Florisil, Florisil/Na_2SO_4 or Al_2O_3 and the purified aliquot was analysed by GC-FID (13 laboratories) or GC-MS (2 laboratories). Statistical comparison between the applied methods could not be done, but according the graphical presentation the results produced by GC-FID do not differ systematically from the results produced by GC-MS (Appendix 10.2).

Oil hydrocarbons in soil

All laboratories used the method, which based on the standard ISO 16703 [6]. Soil sample was extracted with acetone, acetone/hexane, acetone/heptane or pentane by shaking. The extract was purified on Florisil, Florisil/Na_2SO_4 or Al_2O_3 and the aliquot was analysed using GC-FID (7 laboratories) or GC-MS (2 laboratories). Statistical comparison between the applied methods could not be done, but according the graphical presentation the results produced by GC-FID do not differ systematically from the results produced by GC-MS (Appendix 10.2).

3.3 Uncertainties of the results

Most laboratories reported the expanded uncertainties with their results (Appendix 8). In appendix 11 the reported uncertainties are grouped according to the estimation method. Most laboratories estimated uncertainties using the data of validation and internal quality control (Meth 3). The estimation method did not explain the variation between uncertainties.

Table 3. The ranges of the reported expanded uncertainties in the analysis of water and soil samples.

Compounds	Uncertainties in water analysis, %	Uncertainties in soil analysis, %
>C10–C21	-	18–40
>C21–C40	-	18–40
>C10–C40	10–42	18–40

4 EVALUATION OF PERFORMANCE

The evaluation of the participants was based on z scores, which were calculated using the estimated standard deviation for proficiency assessment. The calculated z scores are presented with the results of each participant (Appendix 7) and the summary of z scores is presented in Appendix 12.

Total oil hydrocarbons, >C10–C40

Accepting the deviation of 20 % from the assigned value of the artificial sample A1O was accepted, 73 % of the results were satisfactory. In the groundwater sample G2O and in the soil sample M3O the results were accepted to deviate 30 % from the assigned value. Then 80 % of the groundwater results and 78 % of the soil results were satisfactory , respectively. Totally, 77 % of the total oil hydrocarbons results were satisfactory. In this PT the satisfactory results were less than in the previous PT SYKE 8/2008, where 82 % of the total oil hydrocarbons results were satisfactory [8].

Fractions >C10–C21 and >C21–C40

Accepting the deviations of 30 % from the assigned values for the results of the fraction >C10–C21, 70 % of the results from the sample A1O and 67 % of results from the soil sample M3O were satisfactory. Consequently for the results of the fraction >C21–C40 the deviations of 20 % in the sample A1O and 30 % in the soil sample M3O were accepted. From the sample A1O 80 % of the results were satisfactory and from the soil sample M3O 78 % of the results were satisfactory.

Volatile oil hydrocarbons, C5–C10

For the determination of volatile oil hydrocarbons only a synthetic solution was sent. The theoretical concentration of the volatile hydrocarbons (90 µg/ml) was used as the assigned value. Accepting the deviation of 20 % from the assigned value, 63 % of the results were satisfactory. The provider asked the participant to report detailly how the quantification of the volatile hydrocarbons had been done. Because the applications of some participants were given in confidence, they are not published. According to the method descriptions all participants used different application for the calculation the concentration of the fraction C5–C10 (Appendix 10) and it is evident that the universal quantification procedure is needed. Standardization work for the determination of the fraction C5–C10 has been began at ISO/TC 190, but it takes still some years until a standard method is available.

In the draft version of the standard the quantification of the fraction C5–C10 has been descript as follows: The internal standard should be used when the aromatic compounds are measured with GC-MS. Single BTEX compounds and the sum of the peak areas of the aromatic fraction C9–C10 should be measured. The external standard should be used when the total hydrocarbon fraction is measured with GC-FID or the aliphatic hydrocarbon fraction is measured with GS-MS. Sum of the peak areas between the fraction range defining standards (e.g. after C5–C6, after C6–C8, after C8–C10) should be measured [9].

5 SUMMARY

Proftest SYKE carried out the proficiency test for the analysis of oil hydrocarbons in the groundwater and the soil samples in November 2010. In total, 16 laboratories participated in the PT. One artificial sample, one groundwater sample and one soil sample were delivered to the laboratories. In addition one standard solution for volatile oil hydrocarbons determination was delivered.

The calculated concentrations or the robust mean of the results reported by the participant were used as the assigned values for the measurand. The uncertainty of the calculated assigned values for total oil hydrocarbons was 3.2 %. Respectively, the uncertainties of the consensus assigned values (the robust mean) were from 7.5 % to 18 %.

The evaluation of the performance of the participants was carried out using z score. Accepting the deviation from 20 % to 30 % from the assigned values, 74 % of the results were satisfactory. More than a half of the participants used the accredited methods and 70 % of their results were satisfactory.

6 YHTEENVETO

Proftest SYKE järjesti pätevyyskokeen öljyhiilivetymäärityksistä marraskuussa 2010. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 16 laboratoriota.

Mittaussuureen vertailuarvona käytettiin laskennallista pitoisuutta (teoreettinen arvo) tai osallistujien raportoimien tulosten keskiarvoa (sopimusarvo). Synteettisen öljyhiilivetynäytteen A1O pitoisuus oli 3,62 mg/ml ja sen laajennettu epävarmuus oli 3,2 % (95 %:n luottamusväli).

Tuloksia arvioitiin z-arvon avulla, joka laskettiin etukäteen asetetun hajonnan tavoitearvon avulla. Tavoitehajontaa asetettaessa otettiin huomioon mittaussuureen pitoisuus, vertailuarvon mittausepävarmuus sekä näytteen homogeenisuustestin tulokset.

Kokonaisöljyhiilivetytuloksissa tulosten sallittiin poiketa vertailuarvosta synteettisessä näytteessä 20 % ja vesi- ja maanäytteessä 30 %. Tällöin synteettisen näytteessä A1O hyväksyttäviä tuloksia oli 73 %, pohjavesinäytteessä G2O 80 % ja maanäytteessä M3O 78 %. Keskimäärin kokonaisöljytuloksista oli hyväksyttäviä 77 %, mikä on vähemmän kuin edellisessä vastaavassa vertailussa SYKE PK8/2008, jolloin hyväksyttäviä tuloksia oli keskimäärin 82 % [8].

Näytteistä A1O ja M3O määritettiin myös fraktiot >C10–C21 ja >C21–C40. Näytteessä A1O >C10–C21 -tulosten sallittiin poiketa 30 % ja >C21–C40 -tulosten 20 % vertailuarvosta. Tällöin >C10–C21 -tuloksista oli hyväksyttäviä 70 % ja >C21–C40 -tuloksista 80 %. Maanäytteessä tulosten sallittiin poiketa tavoitearvosta 30 %, jolloin >C10–C21 -tuloksista oli hyväksyttäviä 67 % ja >C21–C40 -tuloksista 78 %.

Osallistujilla oli mahdollisuus määrittää myös haihtuvat öljyhiilivedyt synteettisestä näytteestä. Tavoitearvona käytettiin laskennallista pitoisuutta ja tulosten sallittiin poiketa vertailuarvosta 20 %. Tällöin hyväksyttäviä tuloksia oli 63 %. Haihtuvien öljyhiilivetyjen laskentatapa vaihteli ja yhtenäinen laskentatapa parantaisi todennäköisesti tulosten vertailtavuutta.

7 REFERENCES

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8 Korhonen, K., Sainio, P., Nuutinen, J., Markkanen, A., Tanttu, H. and Ilmakunnas, M., 2009, Proficiency Test SYKE 8 / 2008 Oil hydrocarbons and volatile organic compounds in water and soil. Reports of Finnish Environment Institute 12 / 2009. ISBN 978-952-11-3469-2 (pdf). www.environment.fi/publications.

9 ISO/TC 190/SC 3 N686. New work item proposal Soil quality – Risk-based petroleum hydrocarbons – Part 1: Determination of aliphatic and aromatic fractions of volatile petroleum hydrocarbons using gas chromatography (static headspace method).

PARTICIPANTS IN THE PT SYKE 8b/2010

Borealis Polymers Oy, Laboratoriopalvelut, Analyyttinen ryhmä, Kulloo, Finland

Ekokem Oy Ab, Riihimäki, Finland

Eurofins Environment Sweden AB, Lidköping, Sweden

Eurofins Scientific Finland Oy, Tampere, Finland

Finnish Environment Institute, SYKE, Helsinki, Finland

Karlshamn Kraft AB, Karlshamn, Sweden

Kokemäenjoen vesistön vesiensuojelu ry, Hämeenlinna, Finland

Lab Vest I/S, Holstebro, Denmark

Lapin Vesitutkimus Oy, Rovaniemi, Finland

MetropoliLab Oy, Helsinki, Finland

Neste Oil Oyj, Laadunvarmistus, Naantali, Finland

Neste Oil Oyj, Tutkimus ja teknologia, Porvoo, Finland

Novalab Oy, Karkkila, Finland

Ramboll Analytics Oy, Lahti, Finland

Rautaruukki Oyj, Ruukki Metals, Raahe, Finland

SGS Inspection Services Oy, Hamina, Finland

PREPARATION OF THE SAMPLES

Volatile oil hydrocarbons (C5—C10)

Sample A1B

A1B was prepared by mixing individual compounds and the certified volatile petroleum hydrocarbons (VPH) mixture (AccuStandard, cat nro CCME-VPH, 1000 µg/ml in methanol).
The individual compounds were: cyclopentane, cyclohexane, methylcyclohexane, iso-propylcyclohexane and n-propylcyclohexane. Each individual stock solution was prepared by weighting methanol (10 ml) and from 0.025 to 0.042 g of the individual compound into a vial.
The CCME-VPH mixture included following compounds: 1-methyl-3-ethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, benzene, ethylbenzene, n-decane, n-heptane, n-hexane, n-octane, o-xylene, p-xylene and toluene.
The CCME-VPH mixture and the individual stock solutions were diluted with methanol, final volume was 50 ml. The theoretical concentration of the volatile oil hydrocarbons (C5-C10) was 90 µg/ml.

Oil hydrocarbons (C10–C40)

Sample A1O

Solutions	Preparation
Diesel oil + Lubricating oil (BAM K008 + BAM-K009)	360.1 mg oil in 99.5 ml of hexane => 3.62 mg/ml

Sample G2O; L2O (the addition solution for analysis of the water sample G2O)

Solutions	Preparation
I Diesel oil (BAM-K008)	873.7 mg oil in 10 ml of hexane => 87.4 mg/ml
II Lubricating oil (BAM KS-K009)	881.1 mg oil in 10.3 ml of hexane => 85.8 mg/ml
L2O	2.0 ml I + 4.0 ml II into 100 ml of isopropanol => 5.18 mg/ml
G2O	100 µl into 1 litre of water => 0.518 mg/l

The vial L2O (3 ml) was sent to the participants. The final water sample GO2 was prepared in the participating laboratory by adding 100 µl of the addition solution L2O into the 1 litre of the water sample G2O.

Sample M3O
The soil sample taken on an oil contaminated site close to Tampere was air dried at room temperature, homogenized and sieved out (fraction < 1 mm). The mixed soil sample was distributed into sub samples using a rotary sample divider equipped with vibratory sample feeder. The soil sample was used previously in the PT SYKE 5/2000 [7].

TESTING OF HOMOGENEITY

The homogeneity of the samples M3O was tested by analysing oil hydrocarbons (>C10–C40) in the six sub samples.

Analyte/sample	**Conc.** mg/kg	**s_p%**	**s_p**	**s_a**	**s_a / s_p**	**Was $s_a/s_p < 0.5$?**	**s_{bb}**	**s_{bb}^2**	**c**	**Was $s_{bb}^2 < c$?**
Oil hydrocarbons/M3O	629	15	94	14.9	0.16	yes	10.6	111	574	yes

Conc. = Concentration of C10–C40, mg/kg
s_p = target deviation for proficiency assessment, total target deviation / 2
s_p% = target deviation as percent, total target deviation / 2
s_a = analytical deviation, mean standard deviation of results in a sub sample
s_{bb} = between-sample deviation, standard deviation of results between sub samples
c = $F1 \cdot s_{all}^2 + F2 \cdot s_a^2$
where:

s_{all}^2 = $(0.3 \cdot s_p)^2$
F1 = 2.21 when the number of sub samples is 6
F2 = 1.69 when the number of sub samples is 6

Conclusion: In each case $s_a / s_p < 0.5$ and $s_{bb}^2 < c$. The samples were considered homogenous.

TESTING OF STABILITY

The samples were distributed 16 November 2010 and they were asked to analyse before 3 December 2010.

Oil hydrocarbons

Sample / Measurement	Date	Result	Unit	Calculated concentration
A1B / C5–C10	10 Nov 2010	106.0	µg/ml	90.0
	17 Nov 2010	90.0	µg/ml	
	3 Dec 2010	83.2	µg/ml	
A1O	25 Oct 2010	3.64	mg/ml	3.62
	3 Dec 2010	3.44	mg/ml	
G2O	28 Oct 2010	0.42	mg/l	0.52
	24 Nov 2010	0.64	mg/l	
M3O	13 Sep 2010	629	mg/kg	
	3 Dec 2010	631	mg/kg	

FEEDBACK FROM THE PARTICIPANTS

Lab	Comment	Action/SYKE
1	The volume of the sample A1B was not 3 ml as presented in the covering letter sent with the samples.	There was a typing error in the covering letter. Typing errors will be tried to avoid.
8	The results had been entered on inappropriate lines.	In order to improve the performance evaluation the provider exceptionally corrected the mistake of the participant.
12	The oil concentration in the sample A1O had been reported as µg/ml.	In order to improve the performance evaluation the provider made exceptionally corrected the unit mistake.
16	Due to the national legislation the participant measured the fraction C10–C35 for total oil.	The results were not included in the calculation of the assigned value.

FEEDBACK TO THE PARTICIPANTS

Lab	Comment from the provider
8, 12	In this case the provider corrected the post analytical errors, but the participant should take these analytical errors seriously as in the future.

ASSIGNED VALUES AND THEIR UNCERTAINTIES

Analyte	Sample	Assigned value	Unit	Evaluation of assigned value	Uncertainty ($U = 2\ u_c$) %
C5–C10	A1B	90	µg/ml	Calculated	2.0
>C10–C21	A1O	1.67	mg/ml	Robust mean	18
	M3O	128	mg/kg	Robust mean	12
>C21–C40	A1O	1.77	mg/ml	Robust mean	8.0
	M3O	414	mg/kg	Robust mean	6.6
>C10–C40	A1O	3.62	mg/ml	Calculated	3.2
	G2O	0.48	mg/l	Robust mean	11
	M3O	553	mg/kg	Robust mean	7.5

LIITE 7. RESULTS OF EACH LABORATORY

APPENDIX 7.

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																
>C10-C21	mg/ml	A1O		1,517	yes	1,67	30	2,05	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		0,677	yes	128	30	141	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		1,188	yes	3,62	20	4,05	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		-0,072	yes	553	30	547	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		1,299	yes	1,77	20	2,00	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		-0,129	yes	414	30	406	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		0,217	yes	0,46	30	0,475	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		-4,133	yes	90	20	52,8	79	76,65	10,85	14,1	7	1	0	8
Laboratory 2																
>C10-C40	mg/ml	A1O		0,221	yes	3,62	20	3,7	3,45	3,341	0,3771	11,2	14	1	0	15
C10-C40	mg/l	G2O		-0,145	yes	0,46	30	0,45	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 3																
>C10-C40	mg/ml	A1O		-1,215	yes	3,62	20	3,18	3,45	3,341	0,3771	11,2	14	1	0	15
C10-C40	mg/l	G2O		0,725	yes	0,46	30	0,51	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 4																
>C10-C21	mg/ml	A1O		0,319	yes	1,67	30	1,75	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		2,690	yes	128	30	179,65	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		-0,497	yes	3,62	20	3,44	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		0,935	yes	553	30	630,57	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		-0,622	yes	1,77	20	1,66	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		-0,421	yes	414	30	387,87	428	403,9	51,29	12,6	7	2	0	9
C5-C10	µg/ml	A1B		-0,756	yes	90	20	83,2	79	76,65	10,85	14,1	7	1	0	8
Laboratory 5																
>C10-C21	mg/ml	A1O		0,160	yes	1,67	30	1,71	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		-0,417	yes	128	30	120	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		-0,055	yes	3,62	20	3,6	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		0,084	yes	553	30	560	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		0,678	yes	1,77	20	1,89	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		0,419	yes	414	30	440	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		1,449	yes	0,46	30	0,56	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		-1,889	yes	90	20	73	79	76,65	10,85	14,1	7	1	0	8
Laboratory 6																
>C10-C21	mg/ml	A1O		0,160	yes	1,67	30	1,71	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		-0,208	yes	128	30	124	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		-0,442	yes	3,62	20	3,46	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		-0,181	yes	553	30	538	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		-0,170	yes	1,77	20	1,74	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		0,225	yes	414	30	428	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		0,000	yes	0,46	30	0,46	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		5,389	H	90	20	138,5	79	76,65	10,85	14,1	7	1	0	8
Laboratory 7																
>C10-C21	mg/ml	A1O		12,690	H	1,67	30	4,85	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		19,790	H	128	30	508	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		4,503	H	3,62	20	5,25	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		12,750	H	553	30	1611	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		-7,740	H	1,77	20	0,400	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		11,100	H	414	30	1103	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		4,304	yes	0,46	30	0,757	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		-0,483	yes	90	20	85,65	79	76,65	10,85	14,1	7	1	0	8
Laboratory 8																
>C10-C21	mg/ml	A1O		-0,838	yes	1,67	30	1,46	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		0,052	yes	128	30	129	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		-1,685	yes	3,62	20	3,01	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		0,048	yes	553	30	557	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		-1,243	yes	1,77	20	1,55	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		0,225	yes	414	30	428	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		2,609	yes	0,46	30	0,64	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		-1,644	yes	90	20	75,2	79	76,65	10,85	14,1	7	1	0	8

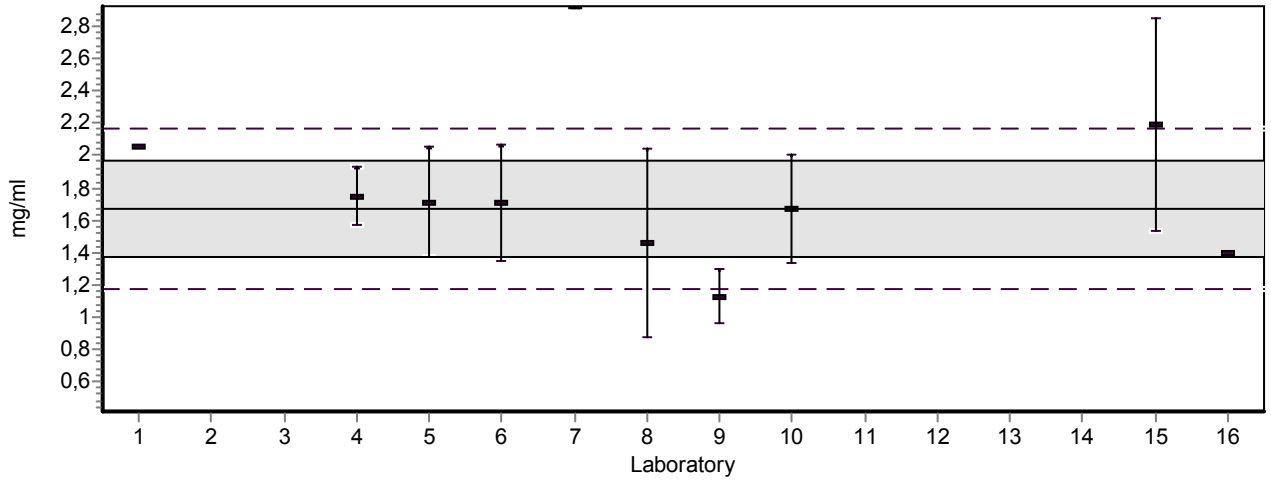
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

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 9																
>C10-C21	mg/ml	A1O		-2,156	yes	1,67	30	1,13	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		-1,198	yes	128	30	105	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		-2,210	yes	3,62	20	2,82	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		-1,832	yes	553	30	401	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		-0,396	yes	1,77	20	1,70	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		-1,900	yes	414	30	296	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		-0,768	yes	0,46	30	0,407	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		-0,194	yes	90	20	88,25	79	76,65	10,85	14,1	7	1	0	8
Laboratory 10																
>C10-C21	mg/ml	A1O		-0,004	yes	1,67	30	1,669	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		-0,417	yes	128	30	120,0	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		0,003	yes	3,62	20	3,621	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		0,108	yes	553	30	562,0	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		1,096	yes	1,77	20	1,964	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		0,443	yes	414	30	441,5	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		1,043	yes	0,46	30	0,532	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 11																
>C10-C40	mg/ml	A1O		-0,111	yes	3,62	20	3,58	3,45	3,341	0,3771	11,2	14	1	0	15
C10-C40	mg/l	G2O		0,478	yes	0,46	30	0,493	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 12																
>C10-C40	mg/ml	A1O		-0,249	yes	3,62	20	3.530	3,45	3,341	0,3771	11,2	14	1	0	15
C10-C40	mg/l	G2O		-0,464	yes	0,46	30	0,428	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 13																
C10-C40	mg/l	G2O		-0,725	yes	0,46	30	0,41	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 14																
>C10-C40	mg/ml	A1O		-2,017	yes	3,62	20	2,89	3,45	3,341	0,3771	11,2	14	1	0	15
C10-C40	mg/l	G2O		-1,739	yes	0,46	30	0,34	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 15																
>C10-C21	mg/ml	A1O		2,076	yes	1,67	30	2,19	1,71	1,674	0,3227	19,2	9	1	0	10
>C10-C40	mg/ml	A1O		-2,210	yes	3,62	20	2,82	3,45	3,341	0,3771	11,2	14	1	0	15
>C21-C40	mg/ml	A1O		-6,441	H	1,77	20	0,63	1,72	1,772	0,1609	9,1	8	2	0	10
C10-C40	mg/l	G2O		-2,754	yes	0,46	30	0,27	0,475	0,4815	0,1167	24,2	15	0	0	15
Laboratory 16																
>C10-C21	mg/ml	A1O		-1,078	yes	1,67	30	1,40	1,71	1,674	0,3227	19,2	9	1	0	10
	mg/kg	M3O		-3,646	H	128	30	58,0	124	131,2	23,94	18,2	7	2	0	9
>C10-C40	mg/ml	A1O		-1,519	yes	3,62	20	3,07	3,45	3,341	0,3771	11,2	14	1	0	15
	mg/kg	M3O		-3,014	H	553	30	303	557	542,2	69,18	12,7	7	2	0	9
>C21-C40	mg/ml	A1O		-0,565	yes	1,77	20	1,67	1,72	1,772	0,1609	9,1	8	2	0	10
	mg/kg	M3O		-2,721	H	414	30	245	428	403,9	51,29	12,6	7	2	0	9
C10-C40	mg/l	G2O		0,435	yes	0,46	30	0,490	0,475	0,4815	0,1167	24,2	15	0	0	15
C5-C10	µg/ml	A1B		-2,611	yes	90	20	66,5	79	76,65	10,85	14,1	7	1	0	8

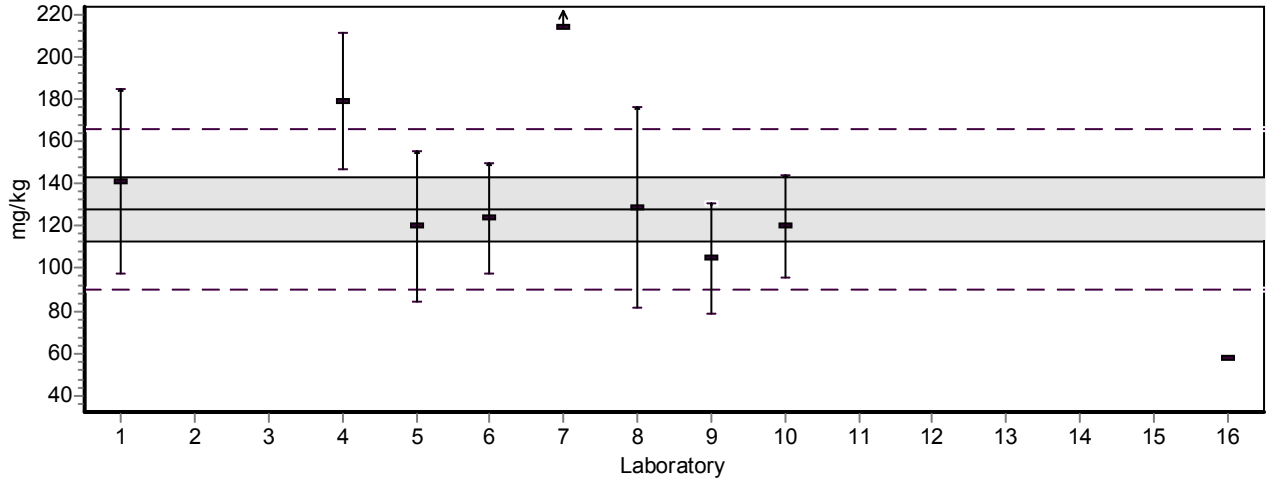
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

LIITE 8. THE RESULTS AND THEIR UNCERTAINTIES GRAPHICALLY
APPENDIX 8.

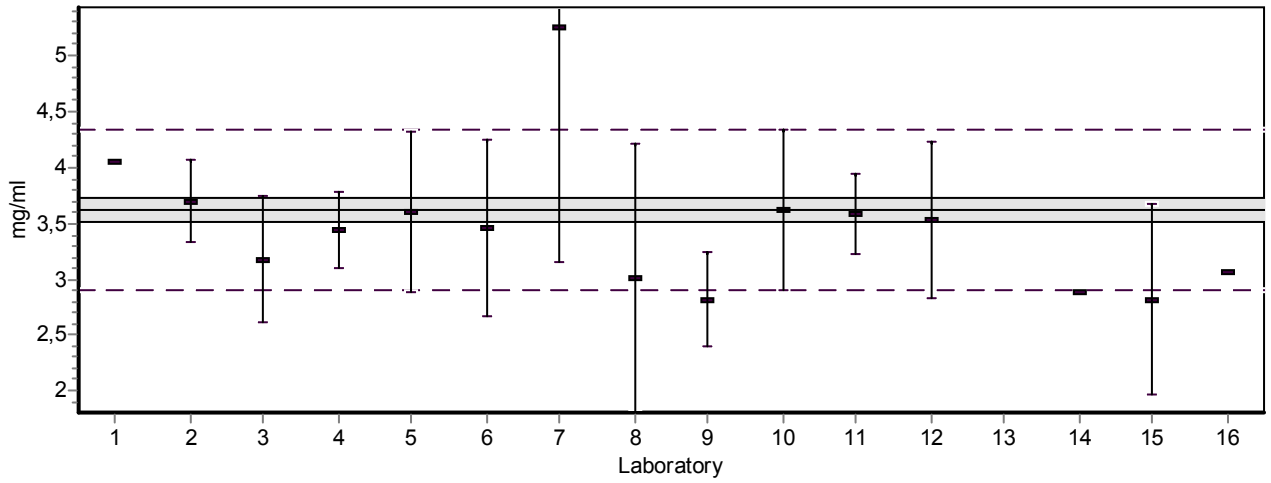
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* A1O



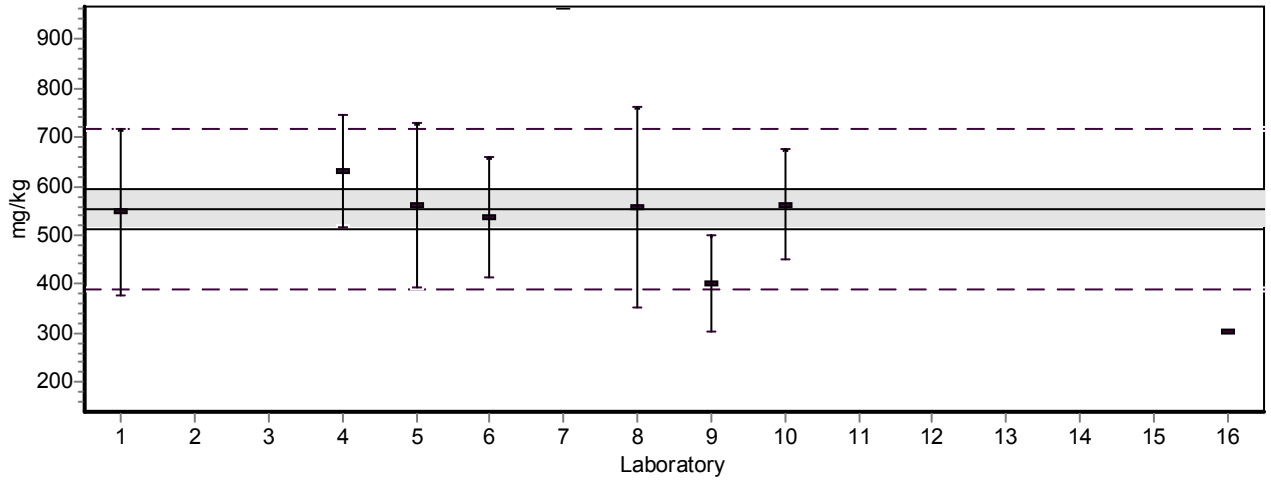
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* M3O



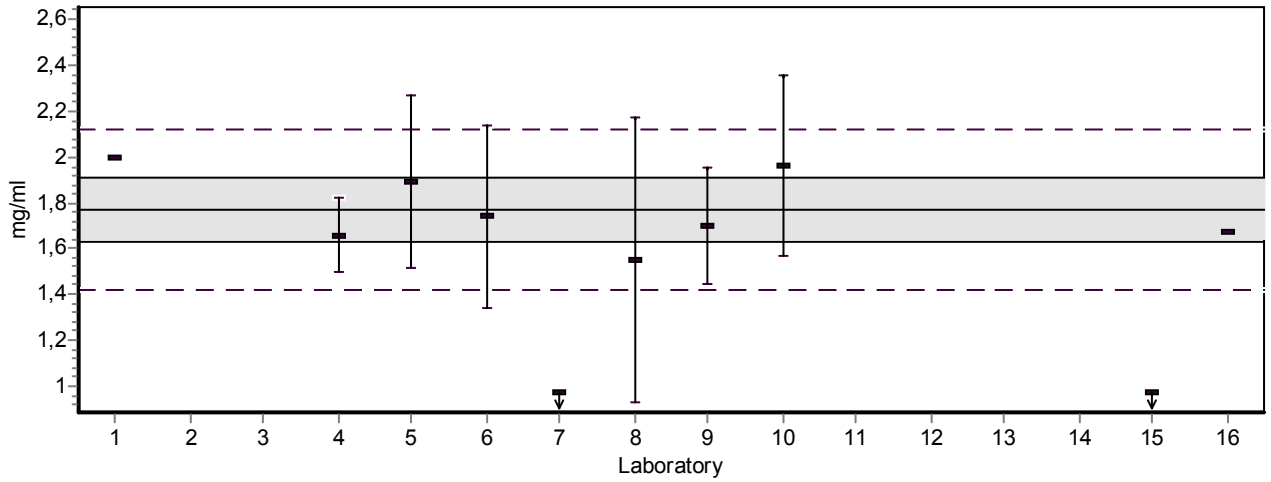
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* A1O



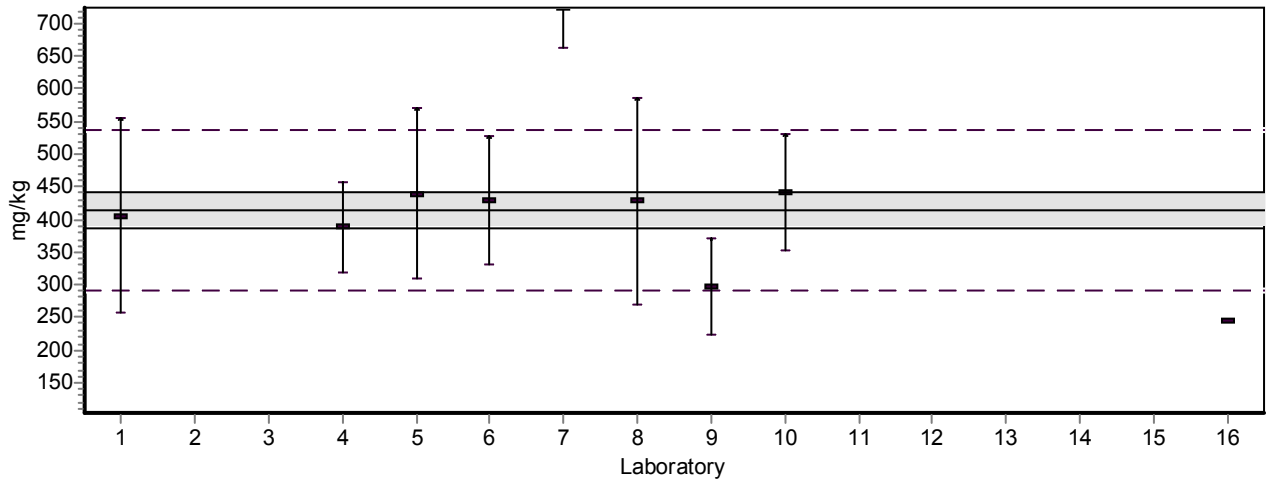
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* M3O



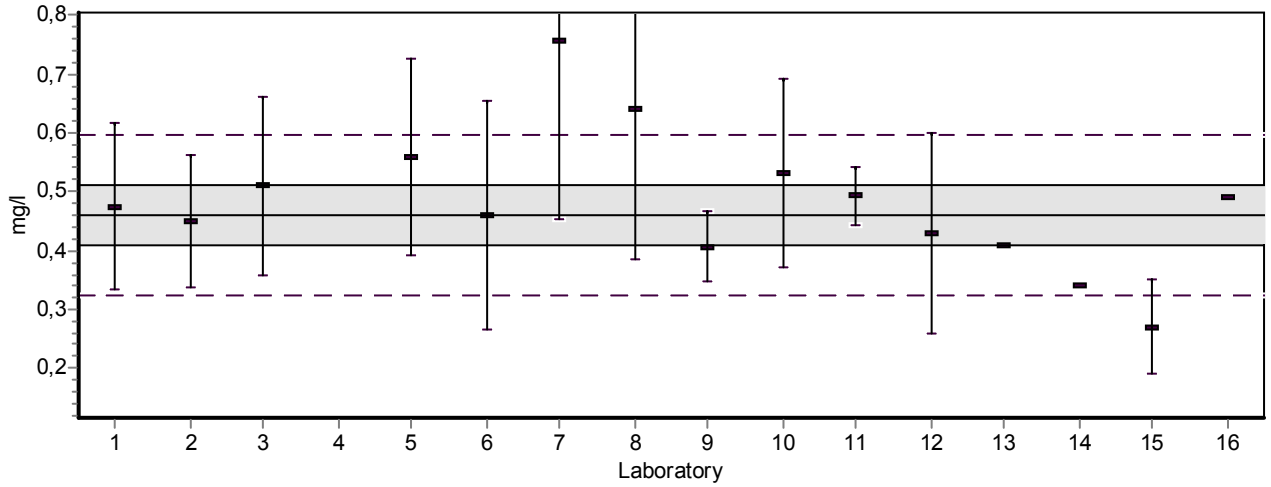
Analyytti *(Analyte)* **>C21-C40** Näyte *(Sample)* A1O



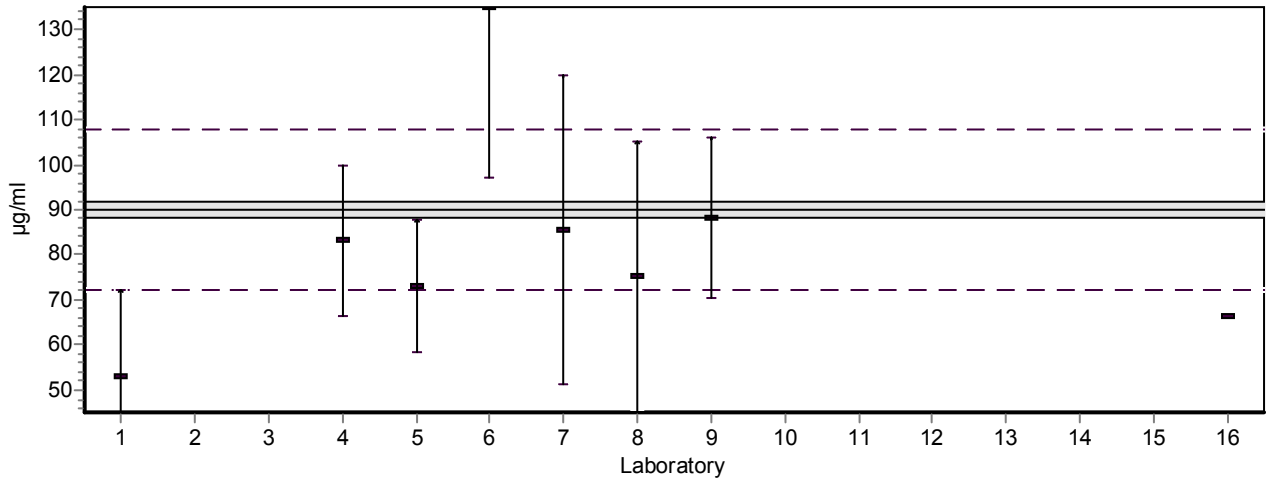
Analyytti *(Analyte)* **>C21-C40** Näyte *(Sample)* M3O



Analyytti *(Analyte)* **C10-C40** Näyte *(Sample)* G2O



Analyytti *(Analyte)* **C5-C10** Näyte *(Sample)* A1B



EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant (Appendixes 7 and 8)

Sample The code of the sample

z-Graphics z score - the graphical presentation

z score calculated as follows:
$z = (x_i - X)/s_p$, where
x_i = the result of the individual laboratory
X = the reference value (*the assigned value*)
s_p = the target value of the standard deviation for proficiency assessment

Outl test OK yes - the result passed the outlier test
H = Hampel test (a test for the mean value)
In addition, in robust statistics some results deviating from the original robust mean have been rejected

Assigned value the reference value

2* Targ SD % the target value of total standard deviation for proficiency assessment at the 95 % confidence level, equal $2 \cdot s_p$

Lab's result the result reported by the participant (the mean value of the replicates)

Md. Median

Mean Mean

Robust mean Robust mean

SD Standard deviation

SD% Standard deviation, %

SD %rob Robust 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

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than $2 \cdot s_p$ from the assigned value
q – questionable ($-3 > z < -2$), negative error, the result deviates more than $2 \cdot s_p$ from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 \cdot s_p$ from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 \cdot s_p$ from the assigned value

Robust analysis

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

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

X^* = median of x_i (i = 1, 2,…p)
$s^* = 1.483$ median of $|x_i - x^*|$ (i = 1, 2,…p)

For each x_i (i = 1, 2,…p) 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 convergences.

Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons,

Annex C ISO 13528 2005 [3].

ANALYTICAL METHODS

Sample A1B, Volatile oil hydrocarbons

Lab	Injection	Equipment	Reference
1	Headspace	GC-MS	In house method
4	Headspace	GC-MS	In house method
5	Headspace	GC-MS	In house method
6	Headspace	GC-MS	In house method
7	Headspace	GC-MS	EN ISO 15680
8	Headspace	GC-MS	In house method
9	Headspace	GC-MS	In house method
16	?	GC-FID	In house method

Water – G2O, Oil hydrocarbons

Lab	Solvent	Extraction	Purification	Injection	Equipment	Reference
1	n-Pentane	Shaking, 900 ml / 40 min	Florisil/Na_2SO_4	Split, 3 ml	GC-FID	EN ISO 9377
2	n-Pentane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	Solvent vent, 50 µl	GC-FID	EN ISO 9377-2
3	n-Hexane	Shaking, 50 ml / 30 min	Florisil	Split, 20 µl	GC-FID	EN ISO 9377-2
5	Heptane	Shaking, 10 ml / 40 min	Al_2O_3	Split, 2 µl	GC-FID	ISO 16703
6	n-Hexane	Shaking, 25 ml / 1 h + 25 ml / 30 min	Florisil	Splitless, 2 µl	GC-FID	EN ISO 9377-2
7	n-Hexane	Shaking, 40 ml / 30 min + 40 ml / 30 min	Florisil/Na_2SO_4	Splitless, 1 µl	GC-MS	EN ISO 9377-2
8	n-Hexane	Shaking, 50 ml / 20 min	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID	EN ISO 9377-2
9	n-Hexane	Shaking, 20 ml / 10 min	Florisil/Na_2SO_4	Splitless, 0.5 µl	GC-MS	EN ISO 9377-2
10	n-Hexane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	On column, 2 µl	GC-FID	EN ISO 9377-2
11	Heptane	Shaking, / 30 min	Florisil	Splitless, 1 µl	GC-FID	?
12	n-Hexane	Shaking,	Florisil/Na_2SO_4	On column, 1 µl	GC-FID	EN ISO 9377-2
13	n-Pentane	Shaking	Florisil/Na_2SO_4	LVI	GC-FID	EN ISO 9377-2
14	n-Pentane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	PTV, 20 µl	GC-FID	EN ISO 9377-2
15	n-Hexane	Shaking, 50 ml	Florisil/Na_2SO_4	Split, 2 µl	GC-FID	EN ISO 9377-2
16	n-Pentane	Shaking, 2.5 ml / 1 h	?	?	GC-FID	EN ISO 9377-2

PTV Programming temperature injector
LVI Large volume injector

ANALYTICAL METHODS

Soil – M3O

Lab	Solvent	Extraction	Purification	Sampling / Injection	Equipment	Reference
1	Acetone/heptane	Shaking, 20 g	Florisil/Na_2SO_4	Split, 3 µl	GC-FID	ISO 16703
4	Acetone/hexane	Shaking, 10 g	Florisil/Na_2SO_4	On column, 1 µl	GC-FID	ISO 16703
5	Acetone	Shaking, 15 g / 40 min	Al_2O_3	Split, 2 µl	GC-FID	ISO 16703
6	Acetone/hexane	Sonication, 10 g / 30 min	Florisil	Splitless, 2 µl	GC-FID	ISO 16703
7	Acetone/hexane	Shaking, 20 g / 1 h	Florisil/Na_2SO_4	Splitless	GC-MS	ISO 16703
8	Acetone/hexane	Shaking, 20 g / 1 h	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID	ISO 16703
9	Acetone/hexane	Shaking, / 1 h	Florisil/Na_2SO_4	Splitless, 0.1 µl	GC-MS	ISO 16703
10	Acetone/hexane	Shaking, 20 g / 30 min	Florisil/Na_2SO_4	On column, 2 µl	GC-FID	ISO 16703
16	Pentane	Shaking, 10 g / 16 h	?	?	GC-FID	?

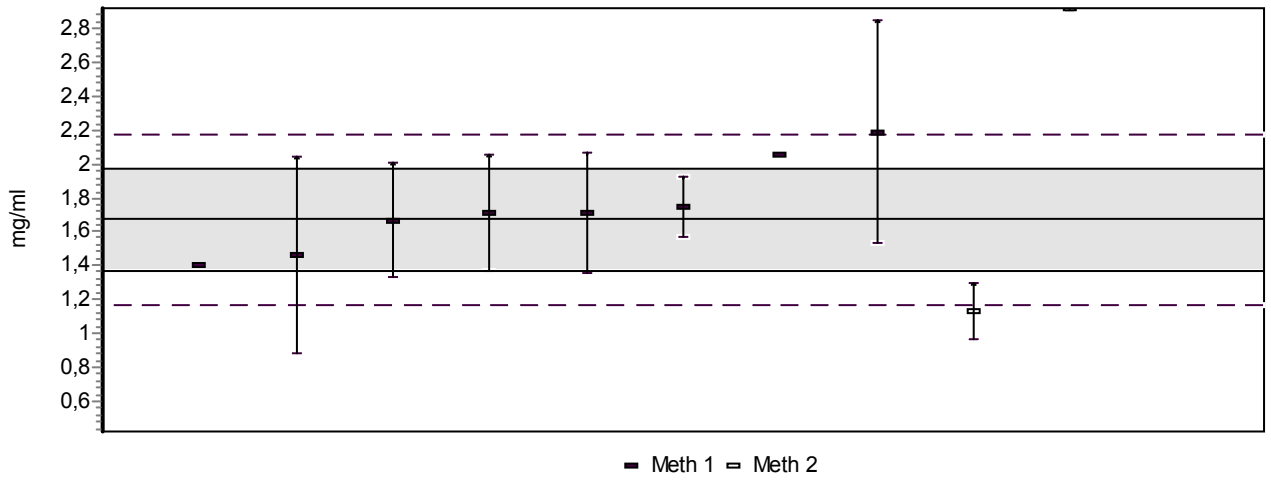
RESULTS GROUPED ACCORDING TO THE METHODS

Method 1 GC-FID

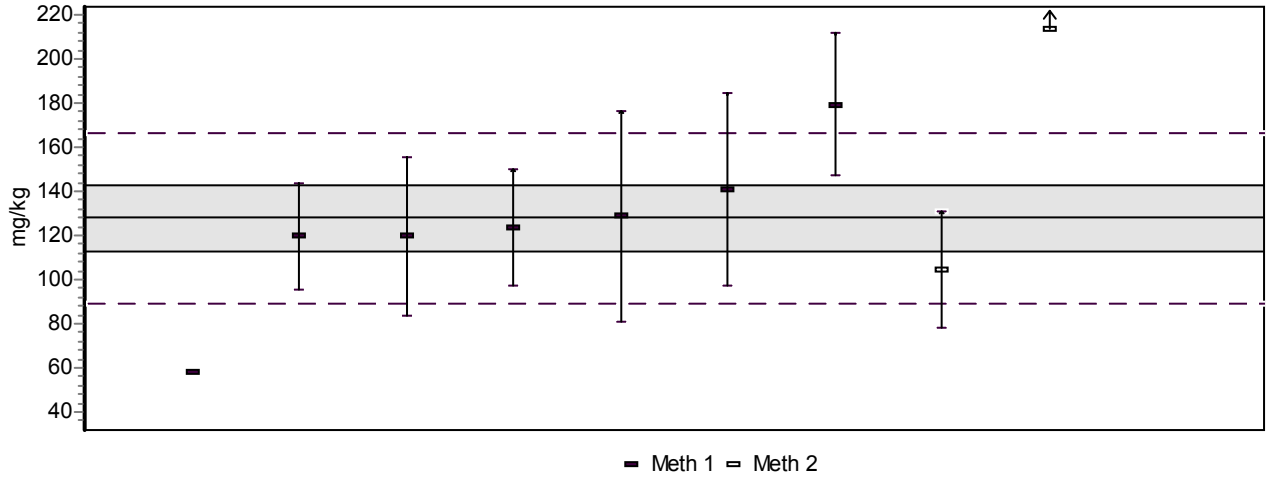
Method 2 GC-MS

LIITE 10.2.
APPENDIX 10.2.

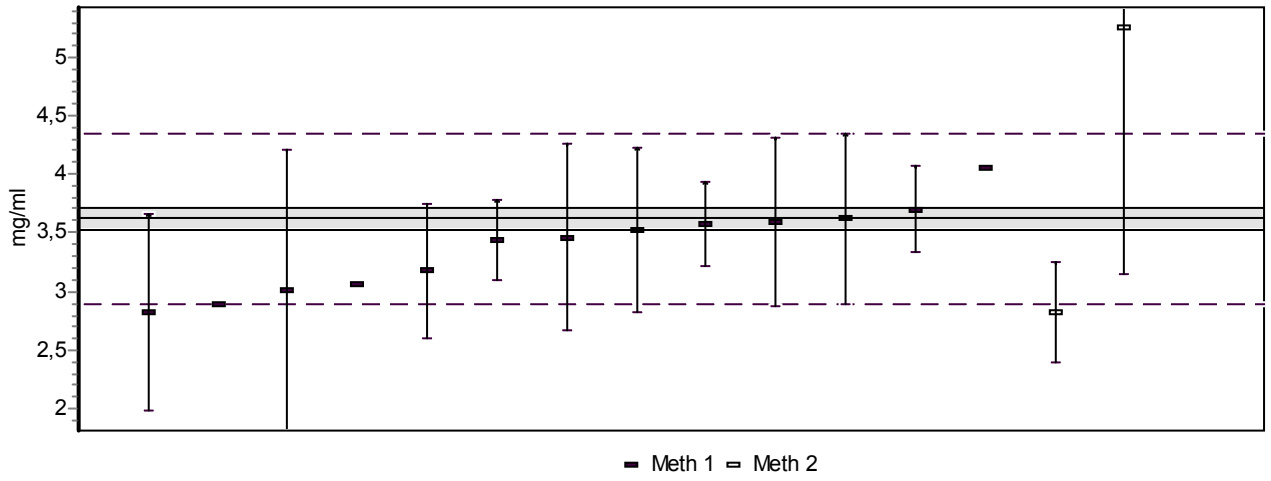
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* A1O



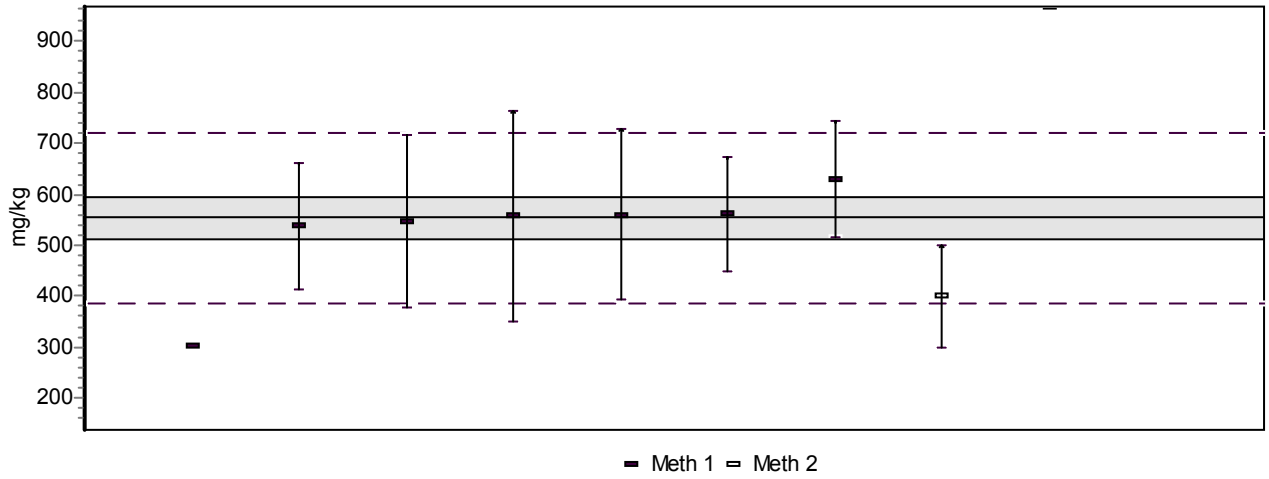
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* M3O



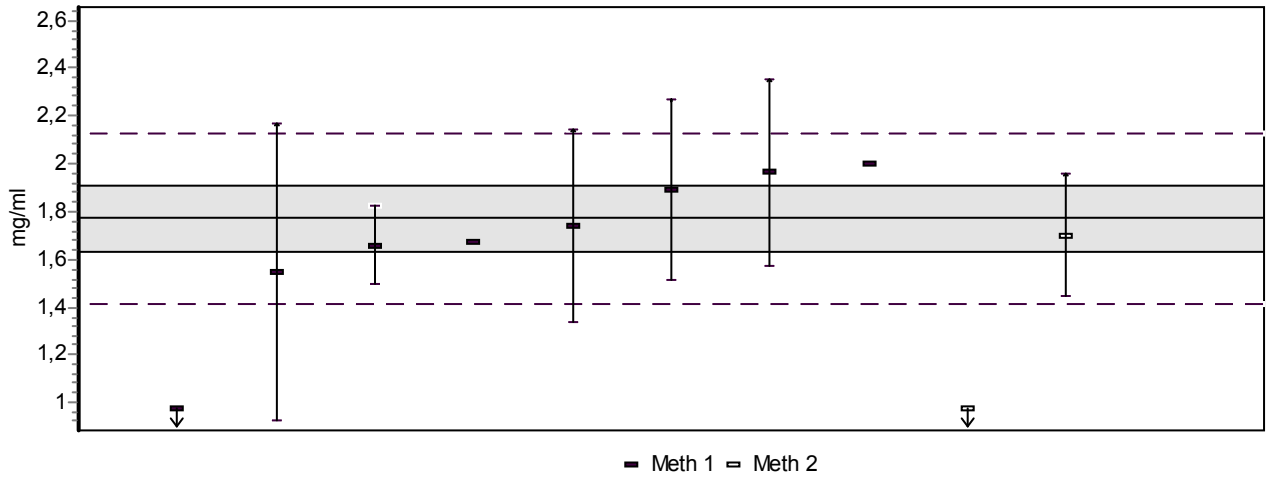
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* A1O



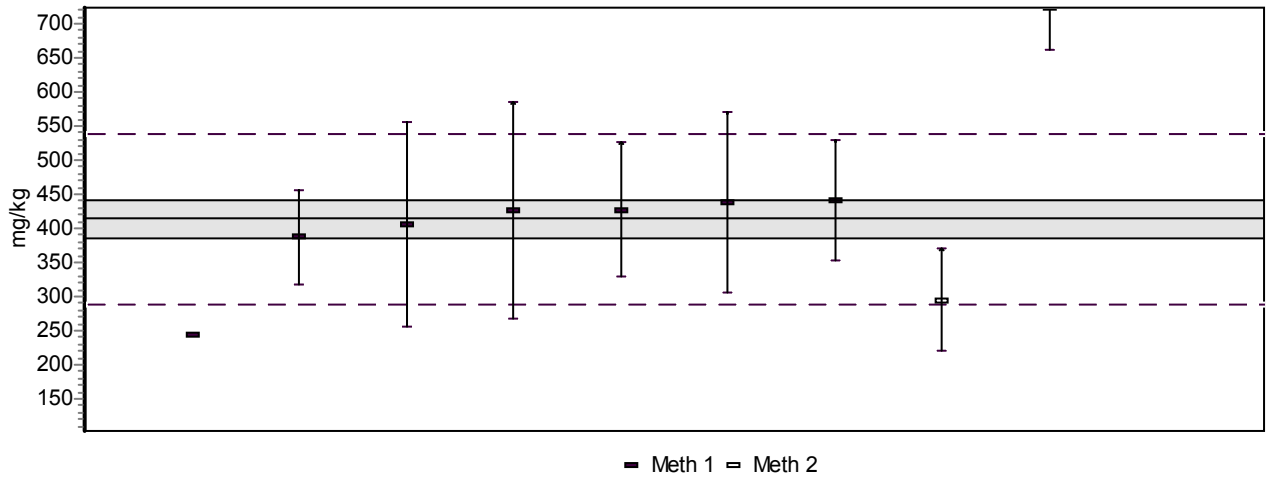
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* M3O



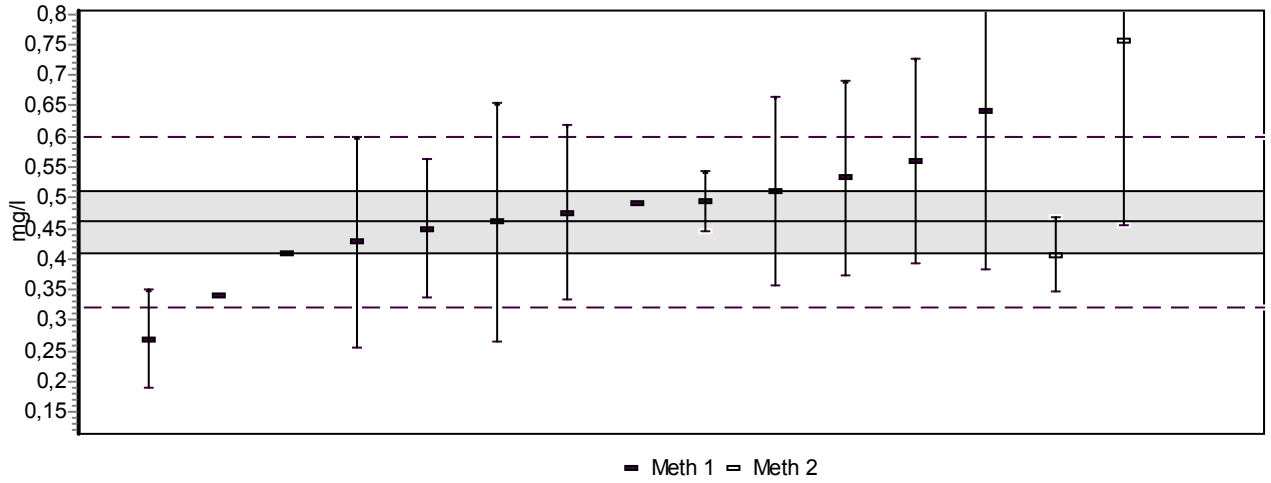
Analyytti *(Analyte)* **>C21-C40** Näyte *(Sample)* A1O



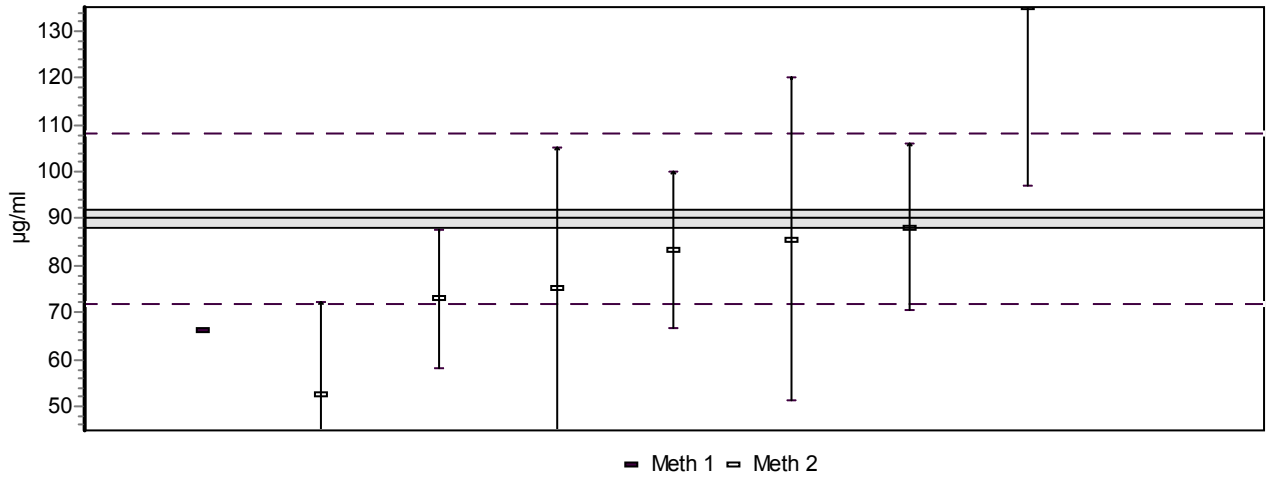
Analyytti *(Analyte)* **>C21-C40** Näyte *(Sample)* M3O



Analyytti *(Analyte)* **C10-C40** Näyte *(Sample)* G2O



Analyytti *(Analyte)* **C5-C10** Näyte *(Sample)* A1B



MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS

For evaluation of the measurement uncertainty the participants have used the procedures as follows:

In the figures the procedures have been presented using the same code number.

1. Using the variation of the results in X chart (for the artificial samples)

2. Using the variation of the results in X chart and the variation of the replicates (r%- or R- chart for real samples)

3. Using the data obtained in method validation and IQC, see e.g. NORDTEST TR 537[1)]

4. Using the data obtained in the analysis of CRM (besides IQC data). see e.g.NORDTEST TR 537[1)]

5. Using the IQC data and the results obtained in proficiency tests. see e.g. NORDTEST TR 537[1)]

6. Using the "modelling approach" (GUM Guide or EURACHEM Guide Quantifying Uncertainty in Analytical Measurements[2)]

7. Other procedure

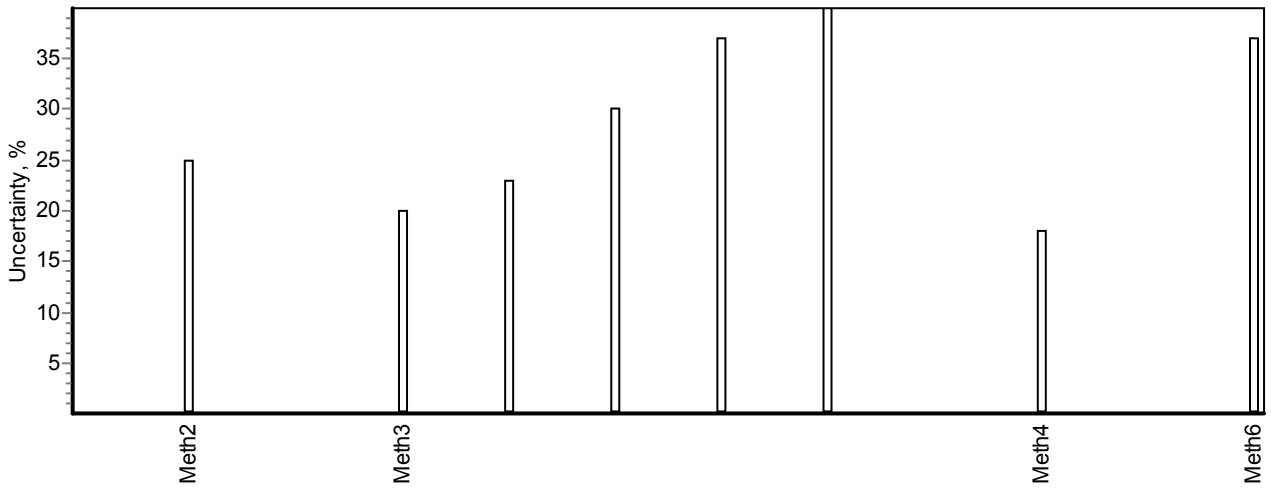
8. No uncertainty estimation

IQC = internal quality control

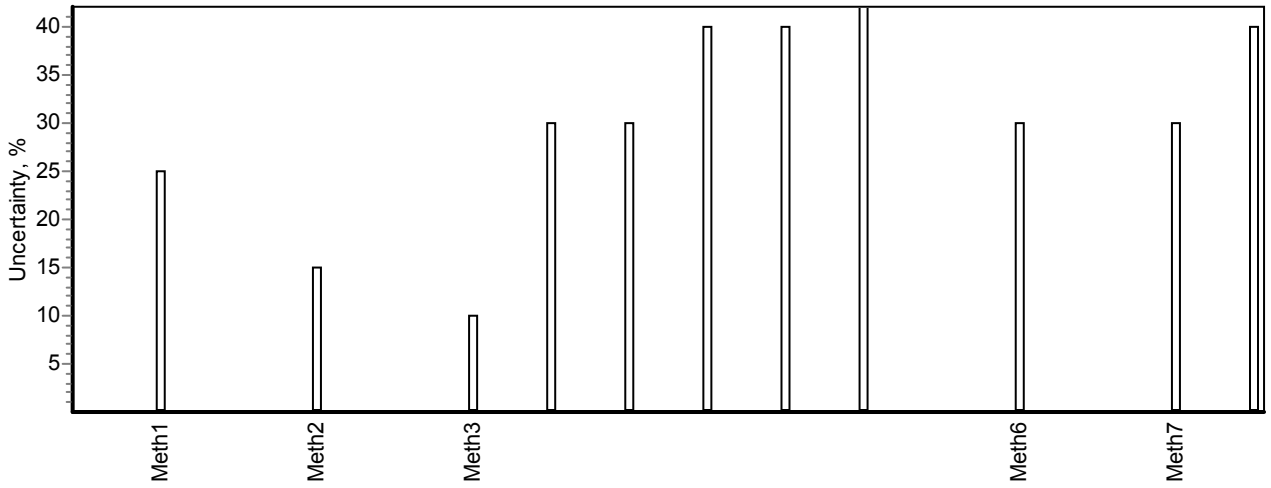
[1)] http://www.nordicinnovation.net
[2)] http://www.eurachem.org

LIITE 11.
APPENDIX 11.

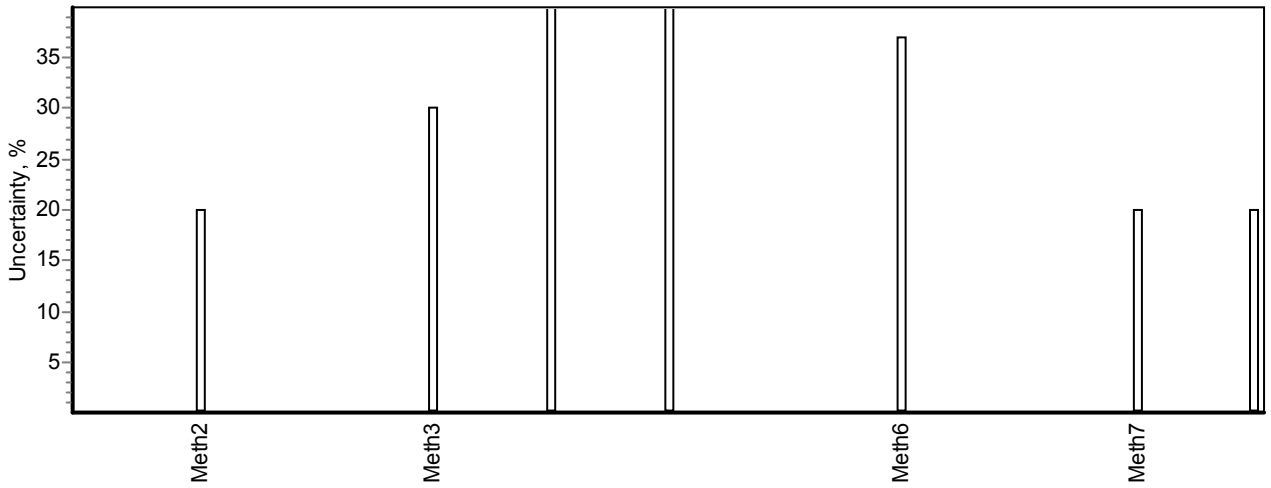
Analyytti *(Analyte)* **>C21-C40** Näyte *(Sample)* M3O



Analyytti *(Analyte)* **C10-C40** Näyte *(Sample)* G2O



Analyytti *(Analyte)* **C5-C10** Näyte *(Sample)* A1B



LIITE 12. SUMMARY OF THE z SCORES

APPENDIX 12.

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	%
>C10-C21	A1O	S	.	.	S	S	S	U	S	q	S	.	.	.	.	Q	S	70
	M3O	S	.	.	Q	S	S	U	S	S	S	.	.	.	.	.	u	67
>C10-C40	A1O	S	S	S	S	S	S	U	S	q	S	S	S	.	q	q	S	73
	M3O	S	.	.	S	S	S	U	S	S	S	.	.	.	.	.	u	78
>C21-C40	A1O	S	.	.	S	S	S	u	S	S	S	.	.	.	.	u	S	80
	M3O	S	.	.	S	S	S	U	S	S	S	.	.	.	.	.	q	78
C10-C40	G2O	S	S	S	.	S	S	U	Q	S	S	S	S	S	S	q	S	80
C5-C10	A1B	u	.	.	S	S	U	S	S	S	.	.	.	.	.	.	q	62
%		88	100	100	86	100	88	12	88	75	100	100	100	100	50	0	50	
Accredited		yes	yes	yes	yes	yes	yes	yes	yes	yes						yes	yes	

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), u - unsatisfactory ($z \leq -3$)

%* - percentage of satisfactory results

Totally satisfactory, % In all: 74 In accredited: 70 In non-accredited: 93

Documentation page

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Author(s)	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori and Markku Ilmakunnas	
Title of publication	Proficiency Test SYKE 8b/2010 Oil hydrocarbons in water and soil.	
Parts of publication/ other project publications	The publication is available only on the internet www.ymparisto.fi/julkaisut.	
Abstract	The Finnish Environment Institute carried out the proficiency test for analysis of oil hydrocarbons from water and soil in November 2010. One artificial sample and one groundwater sample and one soil sample for the determination of total oil hydrocarbons were distributed. In addition a synthetic sample for the analysis of volatile oil hydrocarbons was available. In total, 16 laboratories participated in the PT. Either the calculated concentration or the robust mean value was chosen to be the assigned value for the measurand. The performance of the participants was evaluated by using z scores. In this proficiency test 74 % of the results were satisfactory when the deviation of 20–30 % from the assigned value was accepted.	
Keywords	water analysis, soil analysis, oil hydrocarbons, proficiency test, intercomparison	
Publication series and number	Suomen ympäristökeskuksen raportteja 8 / 2011	
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Project name and number, if any		
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Julkaisun nimi	Proficiency Test SYKE 8b/2010 Oil hydrocarbons in water and soil.	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä. www.ymparisto.fi/julkaisut	
Tiivistelmä	Suomen ympäristökeskus järjesti pätevyyskokeen öljyhiilivetyjen määrityksistä vesi- ja maanäytteistä marraskuussa 2010. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 16 laboratorioita. Mittaussuureen vertailuarvona käytettiin laskennallista arvoa tai osallistujien tulosten robustia keskiarvoa. Pätevyyden arvioimisessa käytettiin z-arvoa ja sitä laskettaessa tulokselle sallittiin 20–30 %:n poikkeama vertailuarvosta. Kokonaisuudessaan hyväksyttäviä tuloksia oli 74 %.	
Asiasanat	vesianalyysi, maa-analyysi, öljyhiilivedyt, pätevyyskoe, vertailumittaus	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 8 / 2011	
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Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under november 2010 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av olja kolväte föreningar i grundvatten och i förorenad jord. Proven sändes ut till 16 laboratorier. Som referensvärde av analytens koncentration användes det teoretiska värdet eller robust medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 74 % av alla resultaten tillfredsställande, när 20–30 % totalavvikelsen från referensvärdet accepterades.	
Nyckelord	vattenanalyser, jordanalyser, olja kolväte, provningsjämförelse, interkalibrering	
Publikationsserie och nummer	Suomen ympäristökeskuksen raportteja 8 / 2011	
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