REPORTS OF FINNISH ENVIRONMENT INSTITUTE 8| 2013

Proficiency Test SYKE 9/2012

Oil hydrocarbons in water and soil

Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori and Markku Ilmakunnas

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Helsinki 2013

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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 ja kalibrointilaboratorio K054 (SFS-EN ISO/IEC 17025) sekä vertailumittausten järjestäjä Proftest SYKE PT01 (SFS-EN ISO/IEC 17043, www.finas.fi).

Tämä pätevyyskoe on toteutettu SYKEn vertailulaboratorion 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

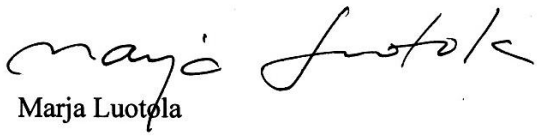
PREFACE

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector by the Ministry of the Environment according to 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. SYKE laboratories has been accredited by the Finnish Accreditation service as the testing laboratory T003 and the calibration laboratory K054 (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 the SYKE reference laboratory and it provides information about performance of the participants as well as comparability of the results at a 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 25. helmikuuta 2013 / Helsinki 10 February 2013



Marja Luotola

Laboratorionjohtaja / Chief of Laboratory

1 INTRODUCTION

In October 2012 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, ISO/IEC 17043 [1] and ISO 13528 [2] as well as IUPAC technical reports [3]. The SYKE laboratory has been accredited by the Finnish Accreditation Service as a proficiency testing provider Proftest SYKE PT01 on the field of the present PT (www.finas.fi).

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 9 495 913

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 substituete of coordinator
Markku Ilmakunnas, technical assistant, layout of the report
Sari Lanteri, technical assistant
Anne Markkanen, technical assistant
Keijo Tervonen, technical assistant
Ritva Väisänen, technical assistant

2.2 Participants

In total, 18 laboratories from Czech Republic, Denmark, Finland, Germany and Sweden participated in this PT (Appendix 1). 17 of the laboratories analysed oil hydrocarbons in water and 13 laboratories analysed oil hydrocarbons in soil. From the participant 10 used the accredited method for analysis of water and soil samples. The organizing laboratory (SYKE) had the code 19 in the result tables.

2.3 Samples and their delivery

The artificial sample A1O as well as the addition oil solution L2O for the surface water sample N2O was commercial standard solutions diluted to the final concentration. The preparation of the samples is presented in Appendix 2.

The soil sample M3O was used previously in the PT SYKE 4/2002 [7] as the sample M1. The soil sample was taken from former petrol station, which was under remediation. The soil sample was dried at the room temperature, homogenized and sieved out (fraction < 250 mm). The moisture content of the sample was less than 0.5 %. The mixed soil sample was distributed in sub samples using a rotary sample divider equipped with vibratory sample feeder.

The samples were delivered 16 October 2012. They were requested to be analysed at the latest 2 November 2012 and reported at the latest 5 November 2012. The preliminary results were sent to the participants by email 9 November 2012.

2.4 Homogeneity and stability studies

The soil sample M3O was previously used in the interlaboratory comparison 4/2002 and demonstrated then to be homogenous [7]. However, because the oil content of the sample had decreased from 345 mg/kg to 226 mg/kg, the homogeneity of the samples M3O was tested by analysing oil hydrocarbons (>C10–C40) as duplicate determinations from the four sub samples (Appendix 3). According to the homogeneity test results the samples M3O were considered to be homogenous.

The stabilities of the sample A1O and 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 by the participants after the sample receiving. The difference of these two measurements should be < 0.5 %.

2.5 Feedback from the proficiency test

Appendix 5 contains the comments sent by the participants.

2.6 Processing of the data

2.6.1 Pretesting of the data

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

The replicate results were tested using the Cochran test (C in the result sheets). In case that the result was lower than detection limit, it had not been included in the statistical handling (H in the results sheets). More detailed information of the testing and statistical treatment of the PT data is available on the internet in the guide for participating laboratories in SYKE proficiency testing schemes (www.environment.fi/syke/proftest).

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 total oil hydrocarbons (>C10−C40) in the artificial sample A1O. The expanded uncertainty of the assigned value (k = 2) was 3.2 % and the main individual resource of the uncertainty was impurity in the stock solution. The robust means of the reported results were used as the assigned value for all other measurements. The uncertainty of the assigned value was calculated using the robust standard deviation of the reported results. In the sample N2O the uncertainty of the assigned value was 14 % and in the sample M3V the uncertainties varied from 16 % to 26 %. The reliability of the assigned value was statistically tested according to the IUPAC Technical report [3]. The criterion was $u/s_p \leq 0.3$, where u is the standard uncertainty of the assigned value and s_p the standard deviation for proficiency assessment. Due to low number of the participants the criterion was not fulfilled in most cases, which indicated that the following assigned values had high uncertainty:

Sample	Measurement
N2O	>C10−C40
M3V	>C10−C21, >C21−C40, >C10−C40

After reporting of the preliminary results no changes to the assigned values have been done.

2.6.3 Standard deviation for proficiency assessment and z score

The performance evaluation was based on z score, which was calculated using the estimated standard deviation for proficiency assessment (s_p). The standard deviation for proficiency assessment was estimated on basis of the type of the sample, the concentration of the element, the results of homogeneity and stability testing, the uncertainties of the assigned values and the long-term variation in former proficiency tests. After the preliminary performance evaluation the total standard deviations were not changed.

The reliability of the target value for total deviation and correspondingly the z score were estimated by comparing the target value (s_p) with the robust standard deviation of the reported results (s_{rob}). Due to low number of the results the criterion $s_{rob} < 1.2 \cdot s_p$ was not met in the following cases:

Sample	Measurement
M3O	>C21−C40, >C10−C40

Due to this the evalution of performance is only informative for these oil fractions.

3 RESULTS AND CONCLUSIONS

3.1 Results

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

Table 1. Summary of the proficiency test SYKE 9/2012.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
>C10-C21	A1O	mg/ml	1,42	1.41	1.42	1.44	0.18	12,5	12	30	92
	M3O	mg/kg	73,4	72.51	73.45	73.00	15.83	21,5	11	40	91
>C10-C40	A1O	mg/ml	3,06	2.95	2.98	3.01	0.24	8,1	17	20	88
	M3O	mg/kg	226	203.17	226.25	220.00	65.27	28,8	13	35	62
	N2O	mg/l	0,64	0.62	0.64	0.62	0.15	23,4	17	30	71
>C21-C40	A1O	mg/ml	1,51	1.51	1.51	1.51	0.21	13,9	12	30	100
	M3O	mg/kg	161	144.05	160.79	160.00	49.75	30,9	11	40	64

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*Targ. SD%- the total standard deviation for proficiency assessment at the 95% confidence interval (=2*s_p), Accepted z-val% - the satisfactory z values.

The variation of total oil hydrocarbon results (robust standard deviation) from the synthetic sample A1O was 8 %, from the water sample N2O 23 % and from the soil sample M3O 29 % (Table 1). The deviations of the results in this PT were at the same level as in the previous similar PT in 2010, where the deviations varied from 8 % to 22 % [8].

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

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Accepted. z-val %
>C10-C21	A1O	mg/ml	1,42	1,41	1,415	0,01398	0,1817	0,1822	0,99	13	13	30	12	92
	M3O	mg/kg	73,4	72,56	73	3,925	16,15	16,62	5,4	22	23	40	11	91
>C10-C40	A1O	mg/ml	3,06	2,95	2,997	0,05706	0,2884	0,2939	1,9	9,8	10	20	17	88
	M3O	mg/kg	226	206,7	216,3	4,554	67,2	67,35	2,2	33	33	35	13	54
	N2O	mg/l	0,64	0,6119	0,611	0,02353	0,1453	0,1472	3,8	24	24	30	17	65
>C21-C40	A1O	mg/ml	1,51	1,506	1,51	0,05809	0,1989	0,2072	3,9	13	14	30	12	100
	M3O	mg/kg	161	144,4	160	6,541	57,89	58,26	4,5	40	40	40	11	64

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

The repeatability of measurements (within-laboratory standard deviation, s_w) varied from 1.0 % to 5.4 % and the reproducibility (between-laboratory standard deviation, s_b) from 9.8 % to 40 %., The ratio s_b/s_w should be between 2 and 3 for robust methods and in this PT it varied from 3.4 to 15 (Table 2).

3.2 Analytical methods and status to the results

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

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

Oil hydrocarbons in water

Most laboratories determined oil hydrocarbons in water using the method 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. The polar substances were removed by clean-up on Florisil, Florisil/Na_2SO_4 or Al_2O_3. One laboratory purified the extract using SPE technique. The purified aliquot was analysed by GC-FID (14 laboratories) or GC-MS (3 laboratories). No statistically significant different was not observed between GC-FID and GC-MS methods.

Oil hydrocarbons in soil

Most laboratories used the method based on the standard ISO 16703 [6]. One laboratory used the method based on the standard 14039 [9]. Soil sample was extracted with acetone/hexane, acetone/heptane, acetone/pentane, hexane or pentane/sodium pyrophosphate by shaking or sonication. The extract was purified on Florisil, Florisil/Na_2SO_4 or Al_2O_3 and the aliquot was analysed using GC-FID (11 laboratories) or GC-MS (1 laboratory). Statistical comparison between the applied methods could not be done due to low number of the results, but according the graphical presentation no systematic differences between the used methods were noticed (Appendix 10.2).

3.3 Uncertainties of the results

Most laboratories reported the expanded measurement uncertainties with their results (Appendix 9). The reported uncertainties varied from 5 % to 50 % (Table 3). Most laboratories estimated uncertainties using the data of validation and internal quality control (Meth 3). The estimation method did not explain the high variation between uncertainties (Appendix 12).

Table 3. The ranges of the reported expanded uncertainties for the analysis of the oil samples

Compound	A1O %	N2O %	M3O %
>C10–C21	5−40	-	5−50
>C21–C40	5−40	-	5−37
>C10–C40	5−40	5−50	5−40

4 EVALUATION OF PERFORMANCE

The performance evaluation of the participants was based on z scores, which were calculated using the estimated standard deviation for proficiency assessment. The criteria of the performance were as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

The calculated z scores are presented with the results of each participant (Appendix 8) and the summary of z scores is presented in Appendix 10.

In total, 81 % of the results in this PT were satisfactory. About 70 % of the participants used accredited methods and 78 % their results were satisfactory. About 90 % of the results measured using non-accredited methods were satisfactory. Proftest SYKE carried out the similar proficiency test in 2010 and then 75 % of the results were satisfactory [8]. The summary of the performance evaluation is shown in Table 4.

Table 4. Summary of the performance evaluation in the proficiency test 9/2012.

Analyte / Sample	$2 \cdot s_p$	Satisfactory results, %	Remarks
>C10–C21 /A1O	30	92	Good performance. Only one unsatisfactory result
>C21–C40 /A1O	30	100	Good performance.
>C10–C40 /A1O	20	88	Mainly good performance. Two unsatisfactory results.
>C10–C40 /N2O	30	71	High uncertainty of the assigned value. Three questionable and two unsatisfactory results.
>C10–C21 /M3O	40	91	High uncertainty of the assigned value. One questionable and one unsatisfactory result.
>C21–C40 /M3O	40	64	Only informative assessment. High uncertainty of the assigned value. Four questionable results and no unsatisfactory result.
>C10–C40 /M3O	35	62	Only informative assessment. High uncertainty of the assigned value. Five questionable results and no unsatisfactory results.

5 SUMMARY

Proftest SYKE carried out the proficiency test for the analysis of oil hydrocarbons in water and soil in October 2012. In total, 18 laboratories participated in the PT. One artificial sample, surface water sample and one soil sample were delivered to the laboratories.

The calculated concentrations or the robust mean of the results reported by the participant were used as the assigned values for the measurement. 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 14 % to 23 %.

The evaluation of the performance of the participants was carried out using z score. When the deviation from 20 to 40 % from the assigned values was accepted, 81 % of the results were satisfactory. About 70 % of the participants used the accredited methods and 78 % of their results were satisfactory.

6 YHTEENVETO

Proftest SYKE järjesti pätevyyskokeen öljyhiilivetymäärityksistä lokakuussa 2012. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 18 laboratoriota, joista yksi toimitti kahdet tulokset.

Synteettisen öljynäytteen kokonaishiilipitoisuuden vertailuarvona käytettiin laskennallista pitoisuutta ja muulloin vertailuarvona käytettiin osallistujien raportoimien tulosten robustia keskiarvoa. Synteettisen öljyhiilivetynäytteen A1O vertailuarvo oli 3,06 mg/ml ja sen laajennettu epävarmuus oli 3,2 % (k = 2).

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

Kokonaisöljyhiilivetytuloksissa tulosten sallittiin poiketa vertailuarvosta synteettisessä näytteessä 20 %, vesinäytteessä 30 % ja maanäytteessä 35 %. Tällöin synteettisen näytteessä A1O hyväksyttäviä tuloksista oli 88 %, pintavesinäytteessä N2O 71 % ja maanäytteessä M3O 62 %. Keskimäärin kokonaisöljytuloksista oli hyväksyttäviä 74 %, mikä on vähemmän kuin edellisessä vastaavassa vertailussa vuonna 2010, jolloin hyväksyttäviä tuloksia oli keskimäärin 77 % [8].

Näytteistä A1O ja M3O määritettiin myös fraktiot >C10–C21 ja >C21–C40. Näytteessä A1O >C10–C21 ja >C21–C40 -tulosten sallittiin poiketa 30 % vertailuarvosta. Tällöin >C10–C21 -tuloksista oli hyväksyttäviä 92 % ja >C21–C40 -tuloksista 100 %. Maanäytteessä tulosten sallittiin poiketa tavoitearvosta 40 %, jolloin >C10–C21 -tuloksista oli hyväksyttäviä 91 % ja >C21–C40 -tuloksista 64 %.

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9 EN 14039, 2004. Characterization of waste – Determination of hydrocarbon content in the range of C10 to C40 by gas chromatography.

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Neste Oil Oyj, Naantalin laadunvarmistus, Naantali, Finland

Neste Oil Oyj, Tutkimus ja kehitys, Kulloo, Finland

Novalab Oy, Karkkila, Finland

Ramboll Finland Oy / Ramboll Analytics, Lahti, Finland

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SGS Inspection Services Oy, Kotka, Finland

Wessling GmbH, Altenberge, Germany

PREPARATION OF THE SAMPLES

Oil hydrocarbons (C10–C40)

Sample A1O

Solutions	Preparation
Diesel oil + Lubricating oil (BAM K010)	316.6 mg oil into 67,96 g (=103.13 ml) of hexane => 3.06 mg/ml

Sample N2O; L2O (the addition solution for analysis for the water sample N2O)

Solutions	Preparation
I Diesel oil (BAM-K008)	4002.7 mg oil into 29.7 g (= 45.07 ml) of hexane => 80.72 mg/ml
II Lubricating oil (BAM K009)	4001.17 mg oil in 1.6 g (=2.82 ml) of hexane + 33.17 g (=42.25 ml) of isopropanol => 80.49 mg/ml
L2O	8.0 ml I + 2.0 ml II into 100 ml of isopropanol => 8.1 mg/ml
N2O	100 µl of L2O into 1 litre of water => 0.81 mg/l

The vial L2O (3 ml) was sent to the participants. The final water sample NO2 was prepared in the participating laboratory by adding 100 µl of the addition solution L2O into the 1 litre of the water sample N2O.

Sample M3O

The soil sample was taken from the former petrol station, which was under remediation. The oil sample was dried at the room temperature, homogenized and sieved out (fraction < 250 mm) and moisture content was less than 0.5 %. The soil sample M3O was used previously in the PT SYKE 4/2002 as the sample M1 [7].

TESTING OF HOMOGENEITY

The soil sample M3O was previously used in the interlaboratory comparison 4/2002 and demonstrated then to be homogenous [7]. However, as the oil content of the sample had decreased (325 mg/kg →257 mg/kg), the homogeneity of the samples M3O was tested by analysing oil hydrocarbons (>C10–C40) from the four sub samples. Homogeneity testing was carried out in the beginning of February 2013, because of the disorder of the measurement equipment homogeneity testing could not be carried out before the delivery of the samples.

Analyte/sample	**Conc.** mg/kg	**s_p%**	**s_p**	**s_a**	**s_a / s_p**	**s_a/s_p < 0.5?**	**s_{bb}**	**s_{bb}^2**	**c**	**s_{bb}^2 < c?**
Oil hydrocarbons/M3O	257	17,5	45	14	0.3	yes	9.7	98	1000	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 = 2.61 when the number of sub samples is 4
F2 = 2.80 when the number of sub samples is 4

Conclusion: In each case $s_a / s_p < 0.5$ and $s_{bb}^2 < c$. The samples M3O were considered to be homogenous.

TESTING OF STABILITY

The samples were distributed 16 October 2012 and they were asked to analyse before 2 November 2012.

Criterion: D < U (U=Expanded uncertainty of the assigned value), where

For A1O: D = |Difference of the result (7 Nov) from the assigned value|
For N2O: D1 = |Difference of the result (15 Oct) from the assigned value|
D2 = |Difference of the result (2 Nov) from the assigned value|
For M3O: D1 = |Difference of the result (2 Feb 2013) from the assigned value|
D2 = |Difference of the results (7 Nov 2012) from the assigned value|

Sample / Measurement	Date	Assigned value ±U	Result	Unit	Remarks
A1O >C10-C40	7 Nov 2012	3.06 ± 0.10	2.99	mg/ml	D = 0.07 mg/ml, which is smaller than 0.1 mg/ml.
N2O >C10-C40	15 Oct 2012	0.64 ± 0,09	0.66	mg/l	D1 = 0.02 mg/l, which is smaller than 0.09 mg/l.
	2 Nov 2012		0.72	mg/l	D2 = 0.06 mg/l, which is smaller than 0.09 mg/ml.
M3O >C10-C40	7 Nov 2012	226 ± 45	218	mg/kg	D1 = 31 mg/kg, which is smaller than 45 mg/kg.
	2 Feb 2013		257[1)]	mg/kg	D2 = 8 mg/kg, which is smaller than 45 mg/kg. It is not obvious that oil content in the soil sample has been increased.

[1)] From homogeneity testing

Conclutions: All samples could be regarded as sufficient stable.

FEEDBACK FROM THE PARTICIPANTS

Lab	Comment	Action/SYKE
1, 8	The amount of the soil sample M3O was not enough for duplicate analysis.	The participants have reported the needed amount of the subsample for the measurement on the result sheet. The information will be taken into account in the planning of future PTs
3, 6	On the electrical result sheet was guided to add the method code, although no method codes were given.	On the web site the information was added to leave method column empty in the reporting step. The provider added the method codes in the data handling step .

ASSIGNED VALUES AND THEIR UNCERTAINTIES

Analyte	Sample	Assigned value	Unit	Evaluation of assigned value	Uncertainty ($U = 2\ u_c$) %	u/s_p
>C10–C21	A1O	1.42	mg/ml	Robust mean	9.1	0.3
	M3O	73.4	mg/kg	Robust mean	16	0.4
>C21–C40	A1O	1.51	mg/ml	Robust mean	8.6	0.3
	M3O	161	mg/kg	Robust mean	23	0.6
>C10–C40	A1O	3.06	mg/ml	Calculated	3.2	0.2
	N2O	0.64	mg/l	Robust mean	14	0.5
	M3O	226	mg/kg	Robust mean	20	0.6

1. >C10–C40 in the sample A1O the uncertainty was estimated on the basis of the sample preparation.

2. Other measurements – the uncertainty was estimated using the data of the 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
n = the number of the results
s_{rob} = the robust standard deviation
AV = the assigned value

TERMS IN THE RESULT TABLES

Results of each participants

Sample	the code of the sample
z-Graphics	z score - the graphical presentation
z value	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 (test for the mean value) C = Cochran test (replicate test)
Assigned value	the reference value
2* Targ SD %	the target value of total standard deviation for proficiency assessment (s_p) 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
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Outl. failed	The results not 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 data items are sorted in increasing order: $x_1, x_2, \ldots, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as follows:
x^* = median of x_i (i = 1, 2, ...,*p*)
s^* = 1,483 · median of $|x_i - x^*|$ (*i* = 1, 2, ...,*p*)
The mean x^* and s^* are updated as follows*:*
Calculate $\varphi = 1.5 \cdot s^*$. A new value is then calculated for each result x_i *(i = 1, 2 …p)*:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi \\ x_i & \text{otherwise} \end{cases}$$

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

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

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

Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons, Annex C [3].

LIITE 8. RESULTS OF EACH LABORATORY

APPENDIX 8. *Results of each participant*

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
>C10-C21	mg/ml	A1O		-1,854	yes	1,42	30	1,025	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		-0,129	yes	73,4	40	71,5	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-3,072	yes	3,06	20	2,12	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-0,430	yes	226	35	209	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		0,495	yes	0,64	30	0,6875	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		-1,832	yes	1,51	30	1,095	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-0,745	yes	161	40	137	160	144,4	56,88	39,3	11	0	0	11
Laboratory 2																
>C10-C21	mg/ml	A1O		-0,282	yes	1,42	30	1,36	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		-0,572	yes	73,4	40	65	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		0,261	yes	3,06	20	3,14	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-0,152	yes	226	35	220	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		1,250	yes	0,64	30	0,76	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		1,192	yes	1,51	30	1,78	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-0,186	yes	161	40	155	160	144,4	56,88	39,3	11	0	0	11
Laboratory 3																
>C10-C21	mg/kg	M3O		1,635	yes	73,4	40	97,4	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/kg	M3O		1,037	yes	226	35	267	216,3	206,7	65,89	31,8	12	1	0	13
>C21-C40	mg/kg	M3O		0,248	yes	161	40	169	160	144,4	56,88	39,3	11	0	0	11
Laboratory 4																
>C10-C21	mg/ml	A1O		0,235	yes	1,42	30	1,47	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		0,620	yes	73,4	40	82,5	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-0,588	yes	3,06	20	2,88	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		2,465	yes	226	35	323,5	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		1,302	yes	0,64	30	0,765	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		-0,508	yes	1,51	30	1,395	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		2,593	yes	161	40	244,5	160	144,4	56,88	39,3	11	0	0	11
Laboratory 5																
>C10-C40	mg/ml	A1O		0,621	yes	3,06	20	3,25	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/l	N2O		2,344	C	0,64	30	0,865	0,611	0,6119	0,1446	23,6	14	3	0	17
Laboratory 6																
>C10-C21	mg/ml	A1O		0,188	yes	1,42	30	1,46	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		-2,333	yes	73,4	40	39,15	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		0,703	yes	3,06	20	3,275	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-2,971	yes	226	35	108,5	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		-0,162	yes	0,64	30	0,6245	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		1,347	yes	1,51	30	1,815	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-2,848	yes	161	40	69,3	160	144,4	56,88	39,3	11	0	0	11
Laboratory 7																
>C10-C21	mg/ml	A1O		1,197	yes	1,42	30	1,675	1,415	1,41	0,1779	12,6	11	1	0	12
>C10-C40	mg/ml	A1O		0,392	yes	3,06	20	3,18	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/l	N2O		0,042	C	0,64	30	0,644	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		-0,022	yes	1,51	30	1,505	1,51	1,506	0,203	13,4	12	0	0	12
Laboratory 8																
>C10-C21	mg/ml	A1O		1,174	yes	1,42	30	1,67	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		0,858	yes	73,4	40	86	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		0,605	yes	3,06	20	3,245	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-0,493	yes	226	35	206,5	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		-1,266	yes	0,64	30	0,5185	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		0,287	yes	1,51	30	1,575	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-1,258	yes	161	40	120,5	160	144,4	56,88	39,3	11	0	0	11
Laboratory 9																
>C10-C21	mg/ml	A1O		-0,469	yes	1,42	30	1,32	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		-0,552	yes	73,4	40	65,3	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-0,621	yes	3,06	20	2,87	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-2,351	yes	226	35	133	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		-0,573	yes	0,64	30	0,585	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		0,177	yes	1,51	30	1,55	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-2,911	yes	161	40	67,25	160	144,4	56,88	39,3	11	0	0	11

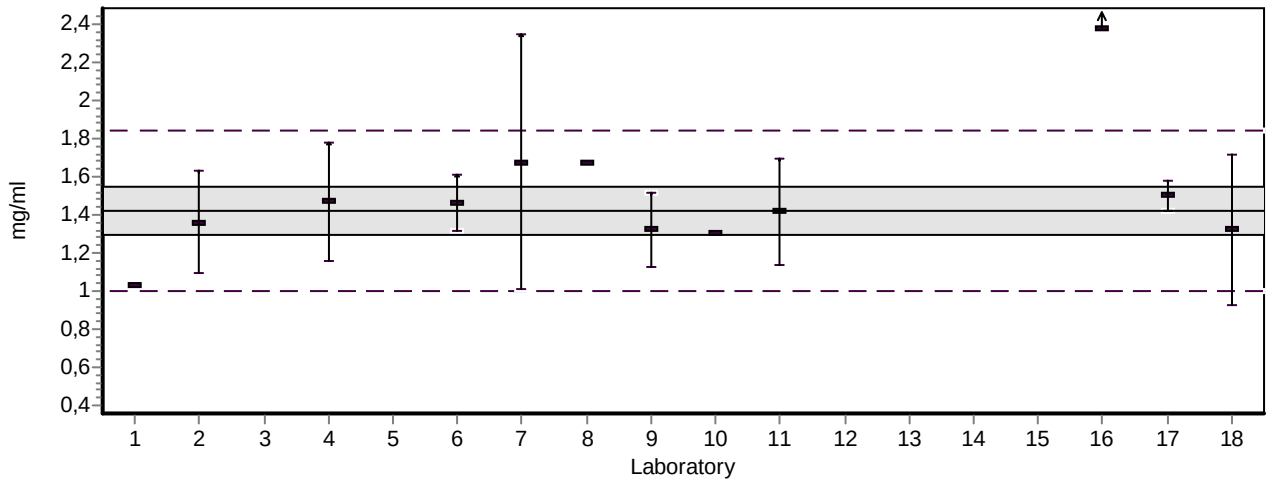
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

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 10																
>C10-C21	mg/ml	A1O		-0,563	yes	1,42	30	1,3	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		0,075	yes	73,4	40	74,5	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-0,850	yes	3,06	20	2,8	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		0,228	yes	226	35	235	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		0,833	yes	0,64	30	0,72	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		-0,044	yes	1,51	30	1,5	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-0,031	yes	161	40	160	160	144,4	56,88	39,3	11	0	0	11
Laboratory 11																
>C10-C21	mg/ml	A1O		-0,023	yes	1,42	30	1,415	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		0,841	yes	73,4	40	85,74	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-0,082	yes	3,06	20	3,035	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		1,345	C	226	35	279,2	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		-0,922	yes	0,64	30	0,5515	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		0,574	yes	1,51	30	1,64	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		1,057	yes	161	40	195,1	160	144,4	56,88	39,3	11	0	0	11
Laboratory 12																
>C10-C40	mg/l	N2O		-0,781	yes	0,64	30	0,565	0,611	0,6119	0,1446	23,6	14	3	0	17
Laboratory 13																
>C10-C40	mg/ml	A1O		-0,719	yes	3,06	20	2,84	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/l	N2O		-3,490	yes	0,64	30	0,305	0,611	0,6119	0,1446	23,6	14	3	0	17
Laboratory 14																
>C10-C40	mg/ml	A1O		0,343	yes	3,06	20	3,165	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/l	N2O		-0,089	yes	0,64	30	0,6315	0,611	0,6119	0,1446	23,6	14	3	0	17
Laboratory 15																
>C10-C40	mg/ml	A1O		-0,379	yes	3,06	20	2,944	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/l	N2O		2,615	yes	0,64	30	0,891	0,611	0,6119	0,1446	23,6	14	3	0	17
Laboratory 16																
>C10-C21	mg/ml	A1O		12,250	H	1,42	30	4,03	1,415	1,41	0,1779	12,6	11	1	0	12
>C10-C40	mg/ml	A1O		8,333	H	3,06	20	5,61	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-2,680	yes	226	35	120	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		5,833	H	0,64	30	1,2	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		0,309	yes	1,51	30	1,58	1,51	1,506	0,203	13,4	12	0	0	12
Laboratory 17																
>C10-C21	mg/ml	A1O		0,376	yes	1,42	30	1,5	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		-1,151	yes	73,4	40	56,5	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-0,850	yes	3,06	20	2,8	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-2,301	yes	226	35	135	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		-2,031	yes	0,64	30	0,445	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		-0,927	yes	1,51	30	1,3	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		-2,578	yes	161	40	78	160	144,4	56,88	39,3	11	0	0	11
Laboratory 18																
>C10-C21	mg/ml	A1O		-0,469	yes	1,42	30	1,32	1,415	1,41	0,1779	12,6	11	1	0	12
	mg/kg	M3O		0,041	yes	73,4	40	74	73	72,56	16,24	22,3	11	0	0	11
>C10-C40	mg/ml	A1O		-1,324	yes	3,06	20	2,655	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		0,923	yes	226	35	262,5	216,3	206,7	65,89	31,8	12	1	0	13
	mg/l	N2O		-0,516	yes	0,64	30	0,5905	0,611	0,6119	0,1446	23,6	14	3	0	17
>C21-C40	mg/ml	A1O		-0,773	yes	1,51	30	1,335	1,51	1,506	0,203	13,4	12	0	0	12
	mg/kg	M3O		0,870	yes	161	40	189	160	144,4	56,88	39,3	11	0	0	11
Laboratory 19																
>C10-C40	mg/ml	A1O		-0,207	yes	3,06	20	2,997	2,997	2,95	0,2893	9,8	16	1	0	17
	mg/kg	M3O		-0,201	yes	226	35	218,1	216,3	206,7	65,89	31,8	12	1	0	13

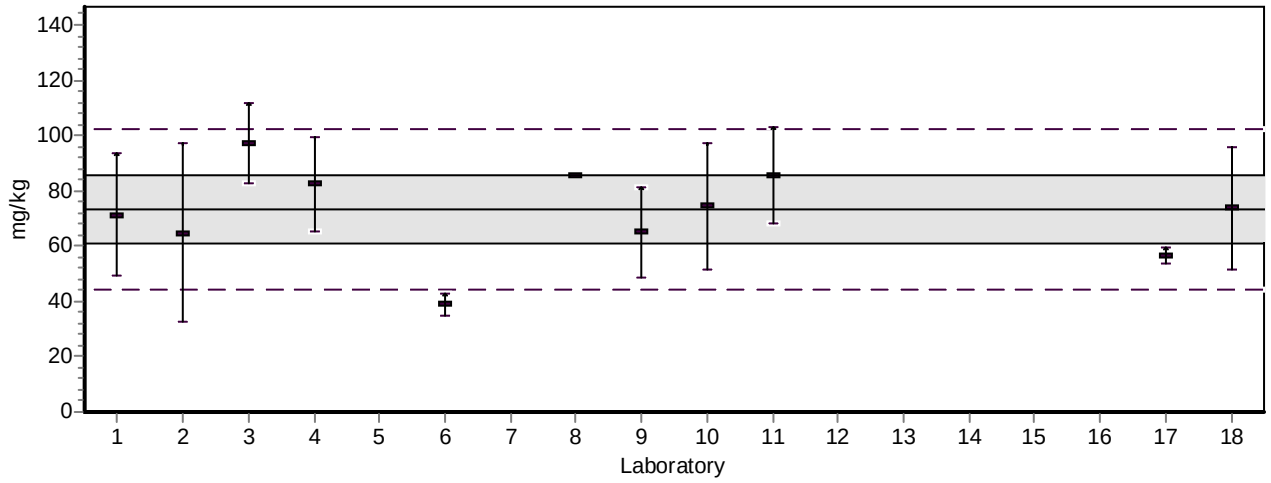
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

LIITE 9. RESULTS AND THEIR UNCERTAINTIES
APPENDIX 9.

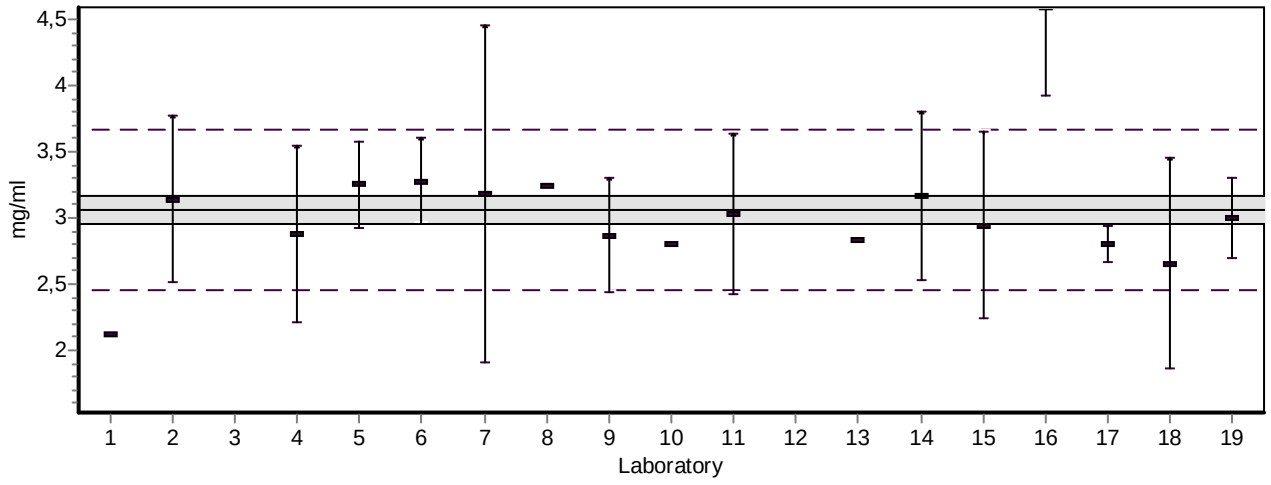
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* A1O



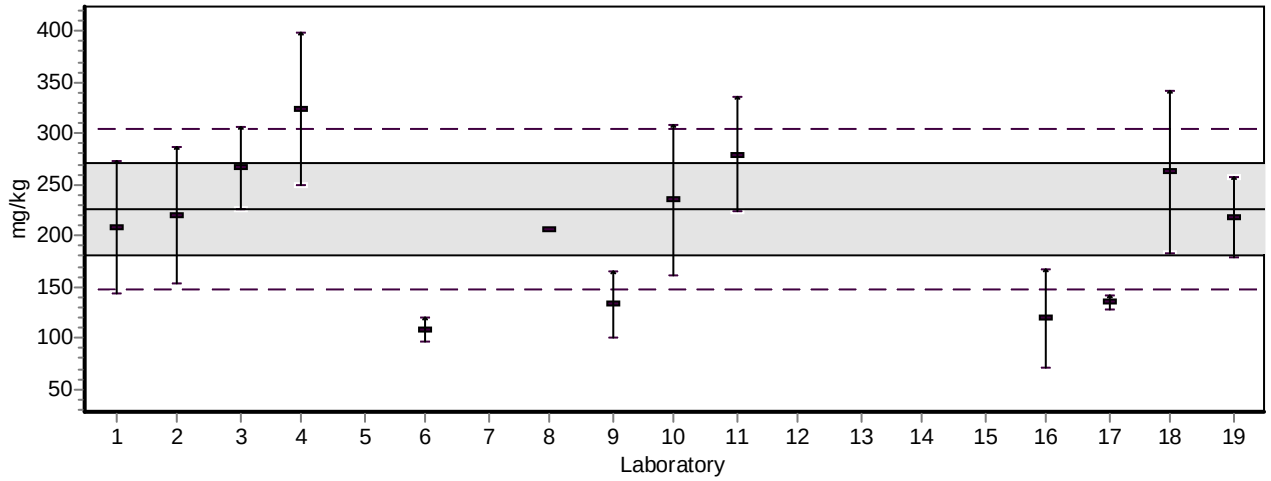
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* M3O



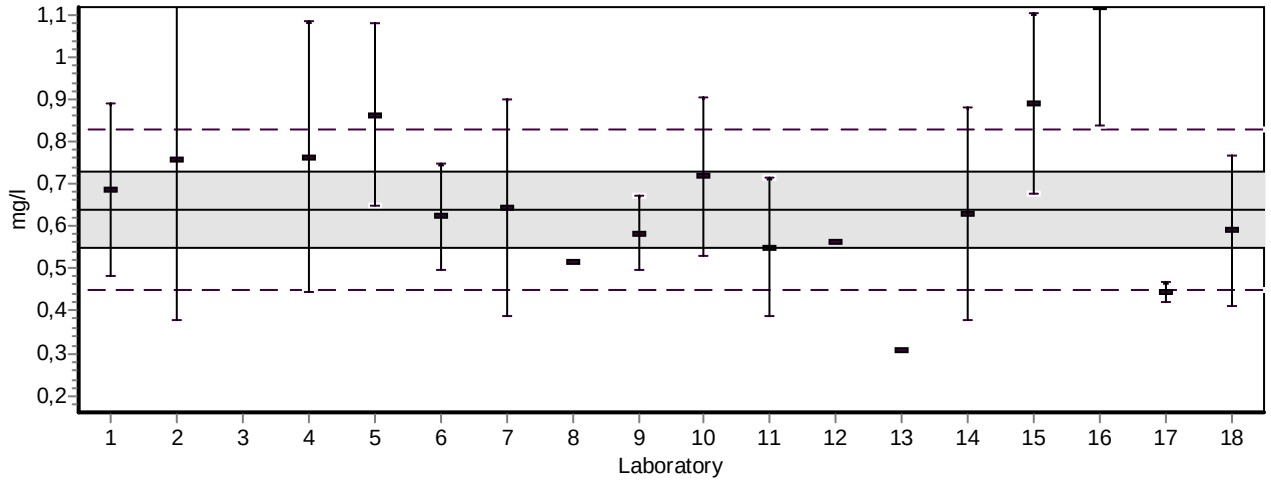
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* A1O



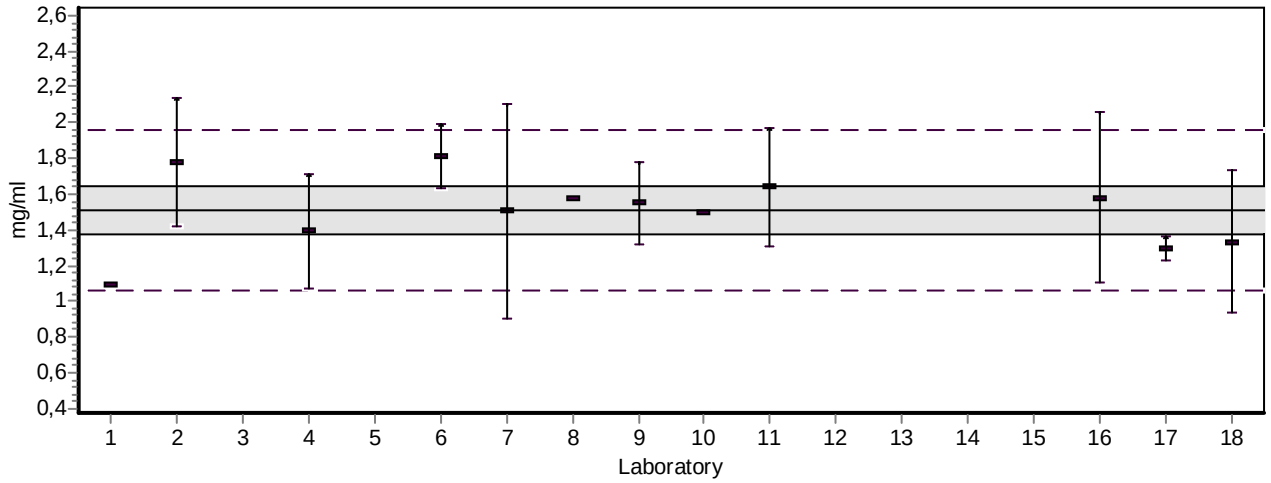
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* M3O



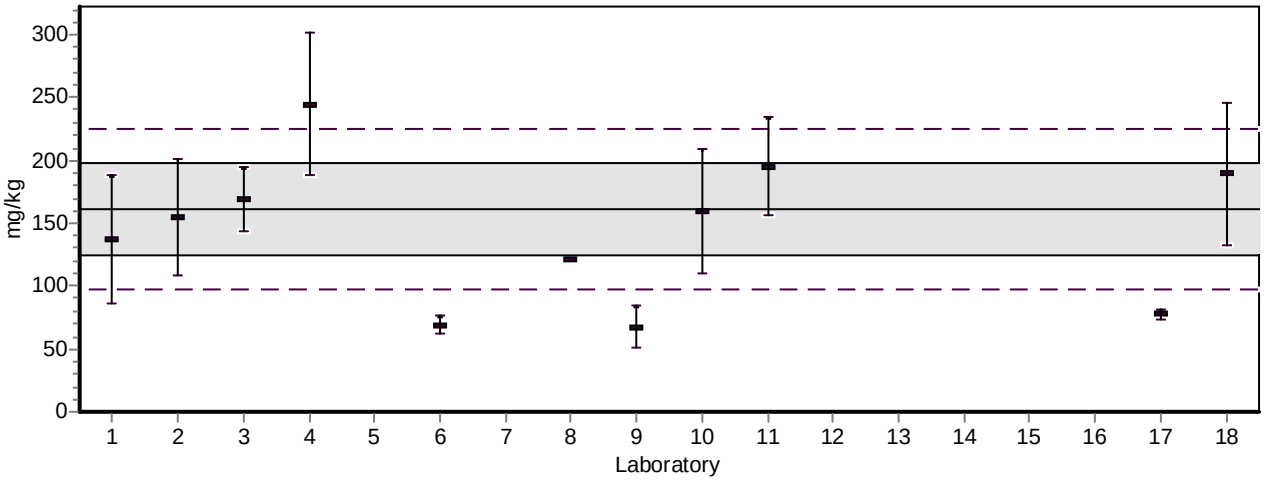
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* N2O



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



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



LIITE 10. SUMMARY OF THE z SCORES

APPENDIX 10.

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	%
>C10-C21	A1O	S	S	.	S	.	S	S	S	S	S	S	.	.	.	.	U	S	S	.	92
	M3O	S	S	S	S	.	q	.	S	S	S	S	.	.	.	.	.	S	S	.	91
>C10-C40	A1O	u	S	.	S	S	S	S	S	S	S	S	.	S	S	S	U	S	S	S	88
	M3O	S	S	S	Q	.	q	.	S	q	S	S	.	.	.	.	q	q	S	S	62
	N2O	S	S	.	S	Q	S	S	S	S	S	S	S	u	S	Q	U	q	S	.	71
>C21-C40	A1O	S	S	.	S	.	S	S	S	S	S	S	.	.	.	.	S	S	S	.	100
	M3O	S	S	S	Q	.	q	.	S	q	S	S	.	.	.	.	.	q	S	.	64
% Accredited		86 yes	100 yes	100 yes	71 yes	50 yes	57 yes	100 yes	100	71 yes	100 yes	100	100	50	100	50	20 yes	57 yes	100 yes	100 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: 81 In accredited: 78 In non-accredited: 90

ANALYTICAL METHODS

Water – N2O, Oil hydrocarbons

Lab	Solvent	Extraction	Purification	Injection	Equipment	Reference
1	n-Pentane	Shaking, 50 ml / 40 min	Florisil/Na_2SO_4	Splitless, 3 ml	GC-FID	EN ISO 9377-2 modified
2	Heptane	Shaking, 4 ml / 40 min	Al_2O_3	Split, 2 µl	GC-FID	ISO 16703 modified
4	n-Hexane	Stirring, 30 ml / 60 min	Florisil/Na_2SO_4	PTV, 5 µl	GC-FID	EN ISO 9377-2
5	n-Pentane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	PTV, 50 µl	GC-FID	EN ISO 9377-2
6	n-Pentane	Shaking, x ml / 2 h	-	Splitless, 1 µl	GC-FID	-
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	Stirring x ml / 30 min	Al_2O_3	Split, 2 µl	GC-FID	EN ISO 9377-2
9	n-Hexane	Shaking	Florisil/Na_2SO_4	Splitless, 0.5 µl	GC-MS	EN ISO 9377-2 modified
10	n-Hexane	Shaking, 50 ml / 20 min	Florisil/Na_2SO_4	Spitless, 1 µl	GC-FID	EN ISO 9377-2
11	n-Hexane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	On column, 2 µl	GC-FID	EN ISO 9377-2
12	n-Pentane	SPE equipment	SPE	Split, 30 µl	GC-FID	EN ISO 9377-2
13	n-Pentane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	PTV, 20 µl	GC-FID	EN ISO 9377-2
14	n-Hexane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	On column, 1 µl	GC-FID	EN ISO 9377-2
15	Heptane	Shaking	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID	EN ISO 9377-2
16	n-Hexane	Stirring	Florisil/Na_2SO_4	Split	GC-MS	-
17	Iso-Hexsane	Shaking	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID	EN ISO 9377-2
18	n-Hexane	Shaking	Florisil	On column, 2 µl	GC-FID	EN ISO 9377-2

PTV Programming temperature injector
LVI Large volume injector
SPE solid phase extraction

ANALYTICAL METHODS

Soil – M3O

Lab	Solvent	Extraction	Purification	Sampling / Injection	Equipment	Reference
1	Acetone / Heptane	Shaking	Florisil/Na_2SO_4	Splitless, 3 µl	GC-FID	ISO 16703 modified
2	Acetone / Heptane	Shaking, 15 g /40 min	Al_2O_3	Split, 2 µl	GC-FID	ISO 16703 modified
3	Acetone / Pentane	Shaking, 14 g / 12 h		Split, 1 µl	GC-FID	-
4	Acetone / Hexane	Sonication, 7 g	Florisil/Na_2SO_4	Splitless, 2 µl	GC-FID	ISO 16703
6	Pentane / Sodium pyrophosphate	Shaking, 14 g / 16 h		Splitless 1 µl	GC-FID	-
8	Hexane	Shaking, / 30 min		Split, 2 µl	GC-FID	ISO 16703
9	Acetone / Hexane	Shaking, 10 g / 1 h	Florisil/Na_2SO_4	Splitless, 0.1 µl	GC-MS	ISO 16703 modified
10	Acetone / Hexane	Shaking, 5 g /	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID	ISO 16703
11	Acetone / Hexane	Shaking, 5-15 g /30 min	Florisil/Na_2SO_4	On column, 2 µl	GC-FID	ISO 16703
16	-	-	-	-	-	-
17	Acetone / Hexane	Shaking, 5 g / 1 h	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID	ISO 16703
18	Acetone / Hexane	Shaking, / 30 min	Florisil	On column, 2 µl	GC-FID	EN 14039
19	Acetone / Hexane	Shaking	Florisil/Na_2SO_4	On-column, 1µl	GC-FID	ISO 16703 modified

RESULTS GROUPED ACCORDING TO THE METHODS

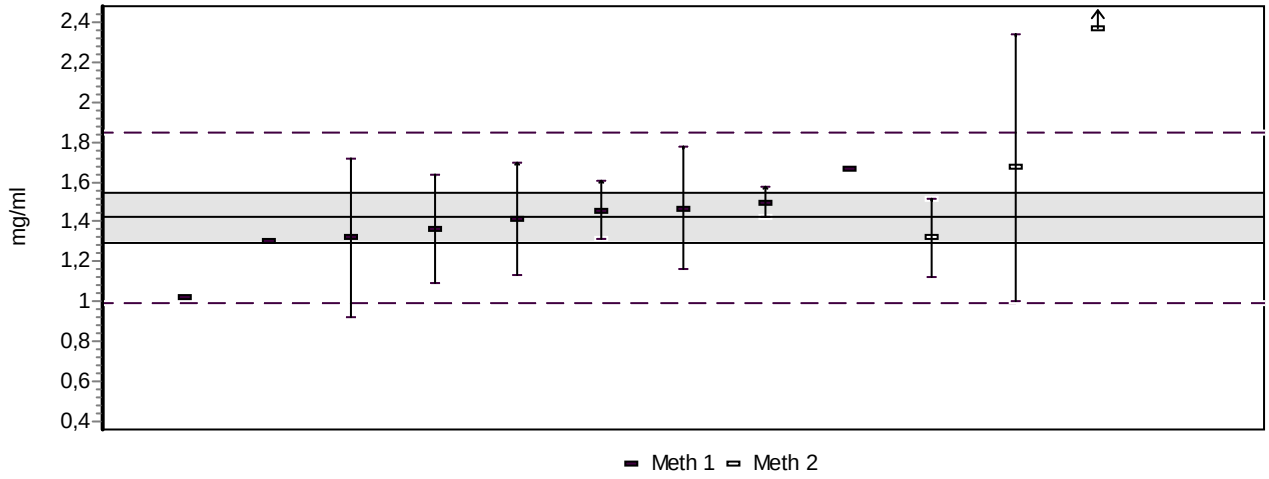
Method 1 GC-FID

Method 2 GC-MS

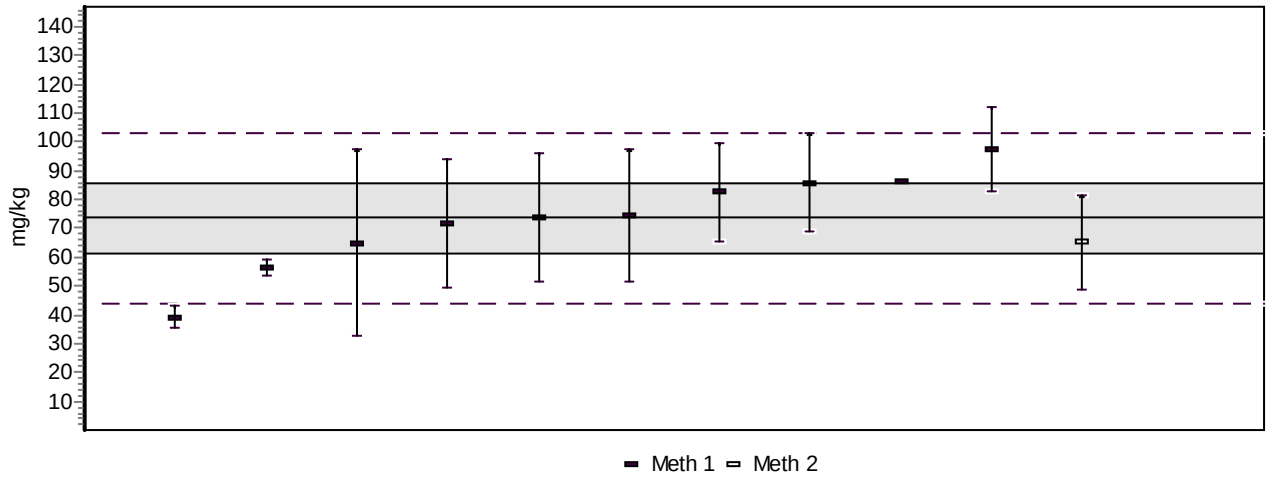
Method 3 Not specified

LIITE 11.2.
APPENDIX 11.2.

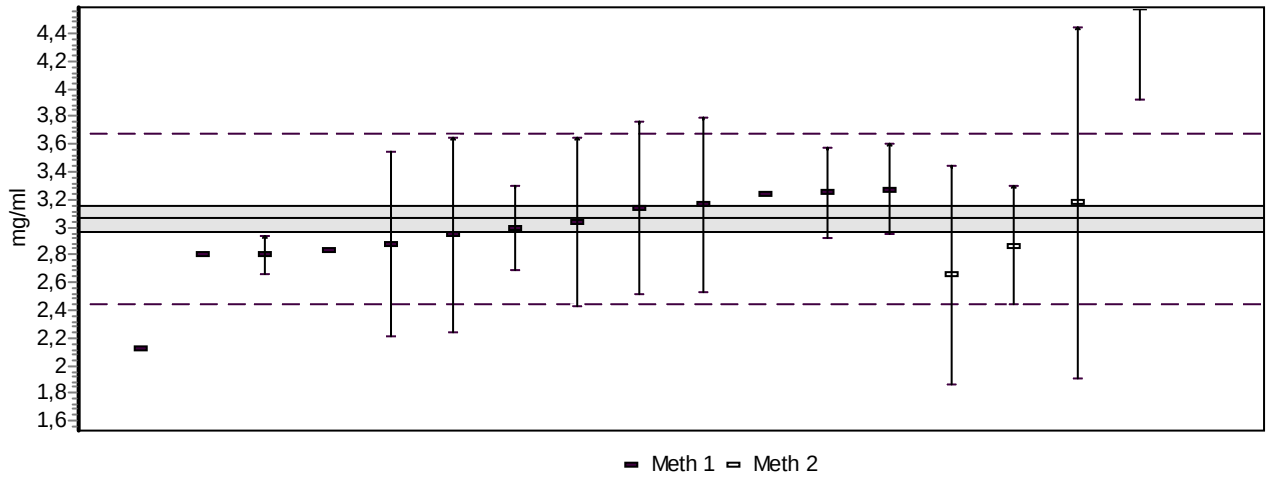
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* A1O



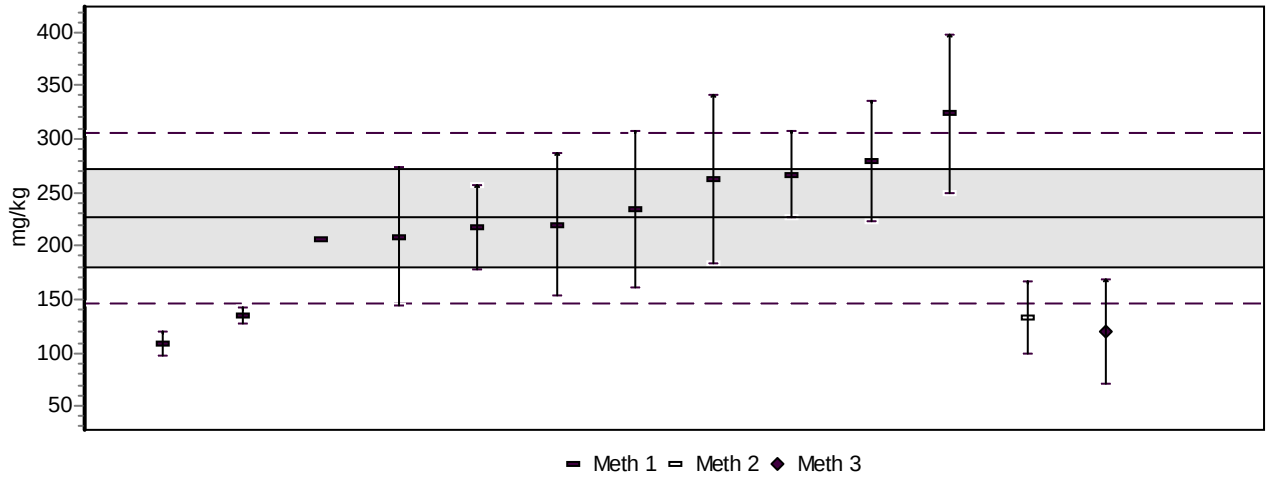
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* M3O



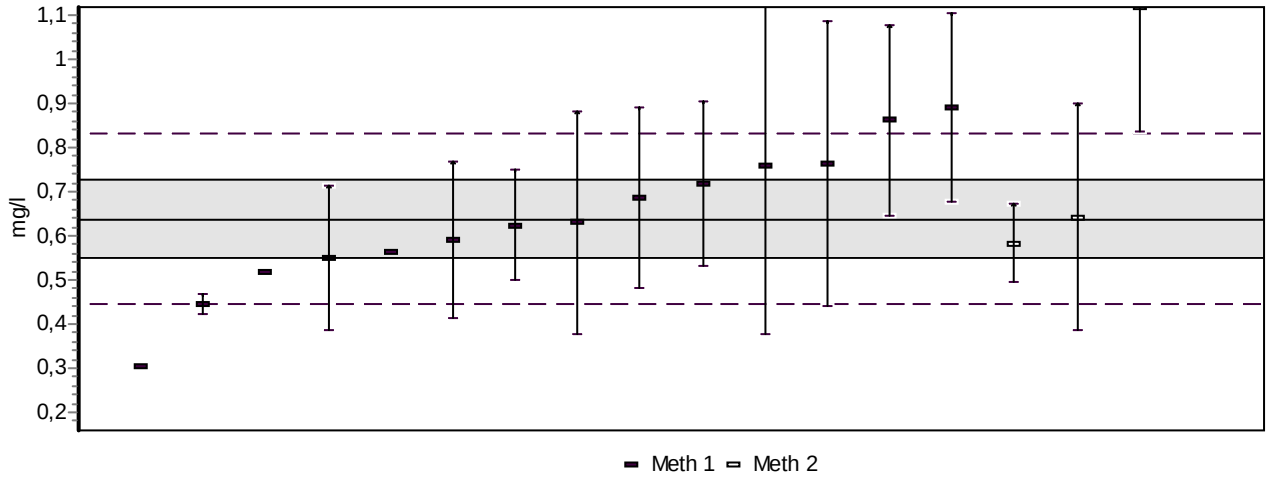
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* A1O



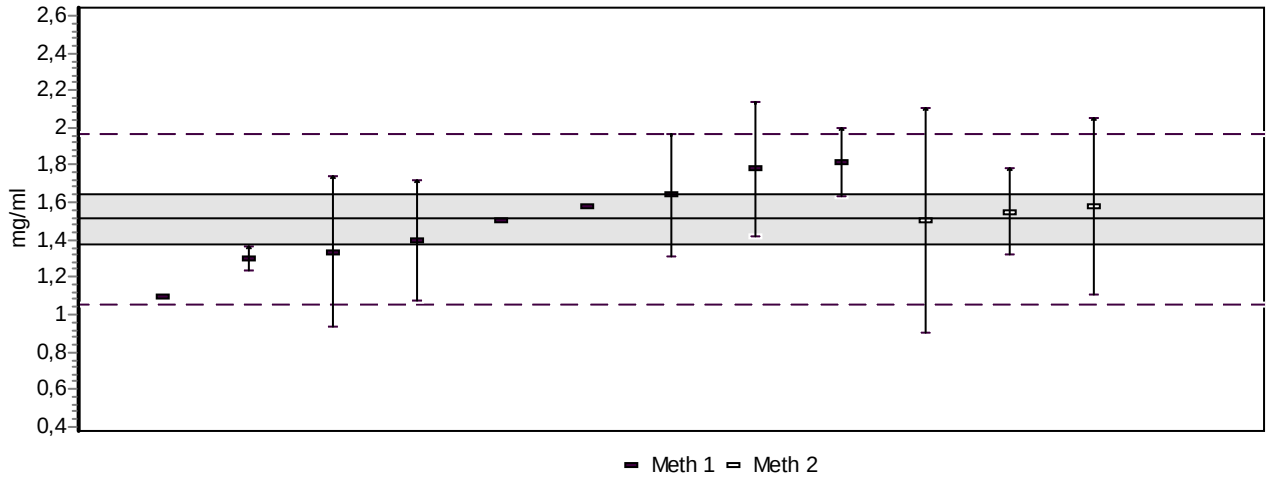
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* M3O



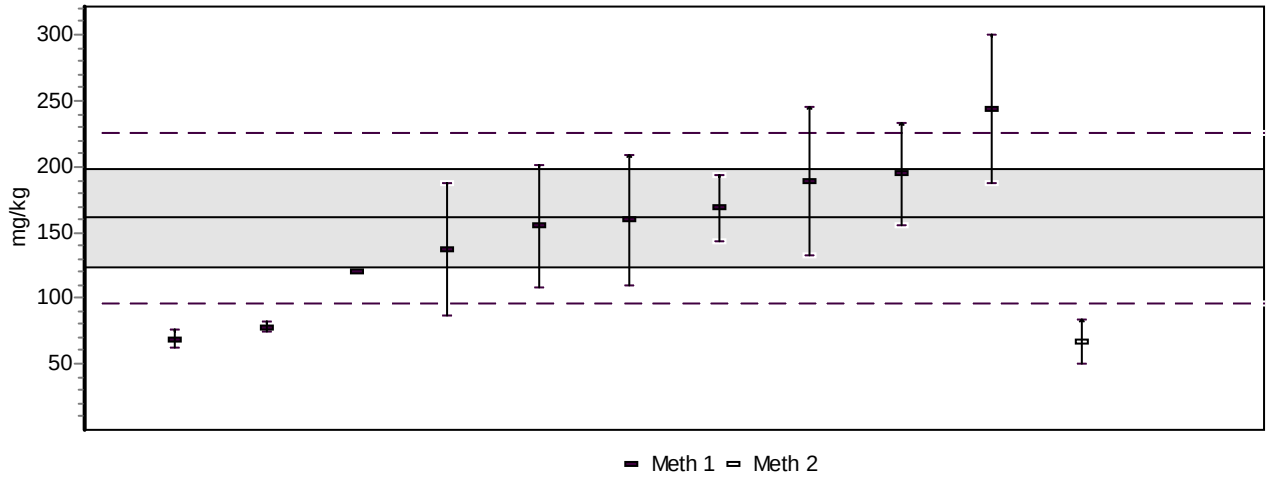
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* N2O



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



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



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

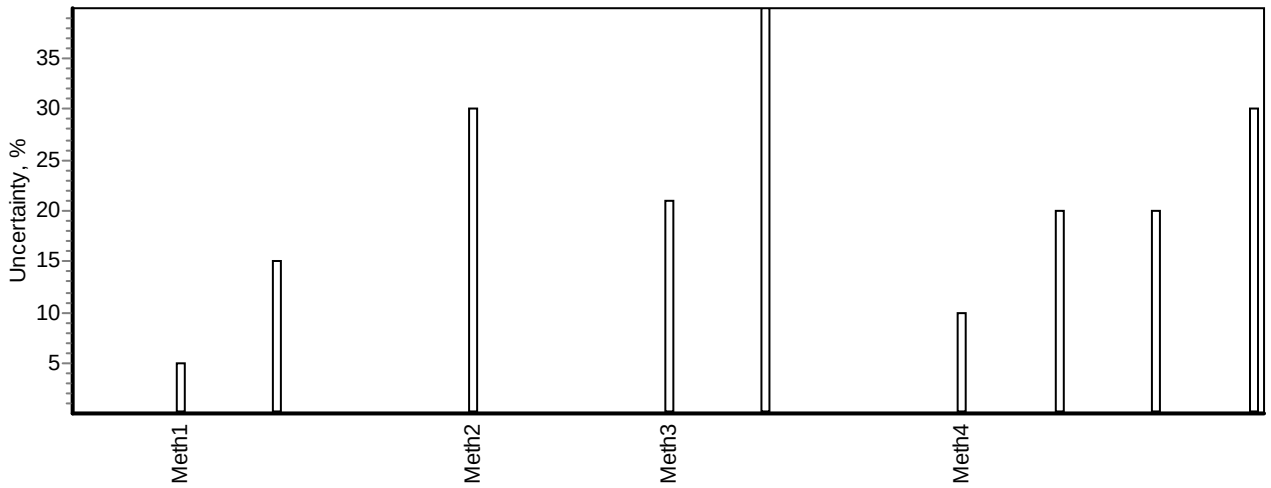
8. No uncertainty estimation

IQC = internal quality control

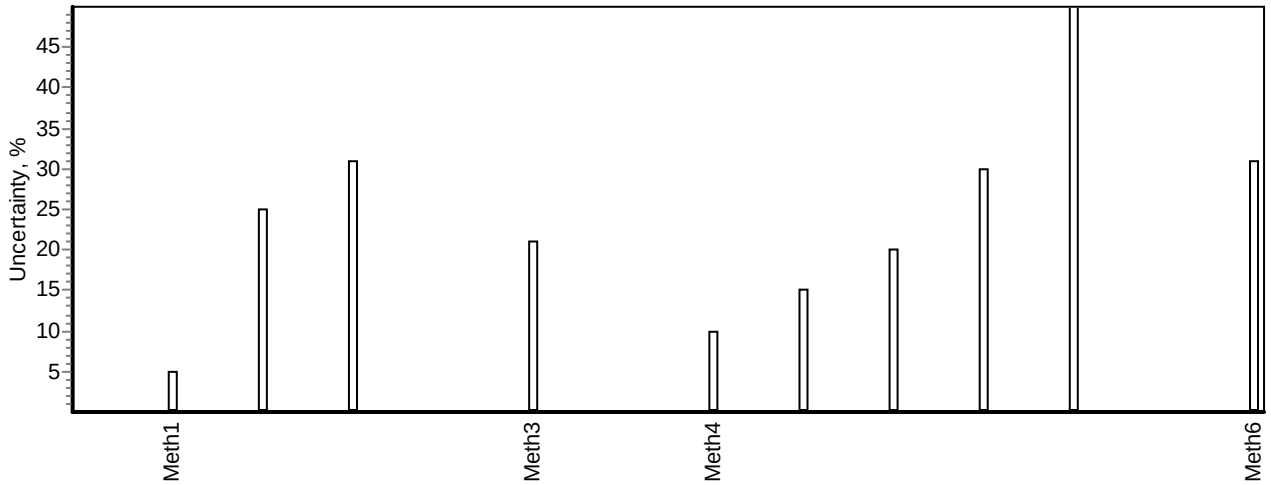
[1)] http://www.nordtest.info
[2)] http://www.eurachem.org

LIITE 12.
APPENDIX 12.

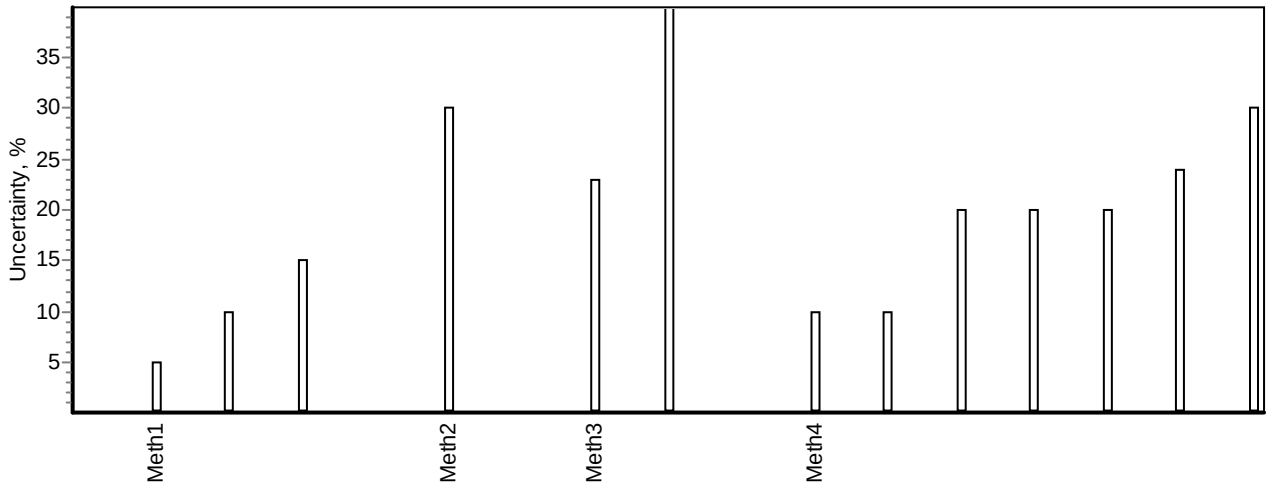
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* A1O



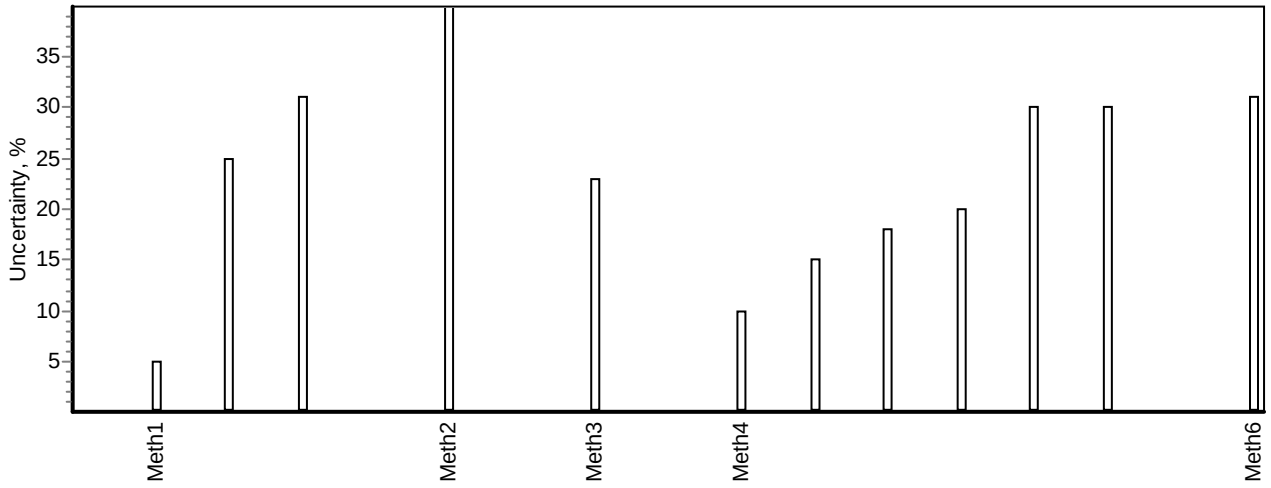
Analyytti *(Analyte)* **>C10-C21** Näyte *(Sample)* M3O



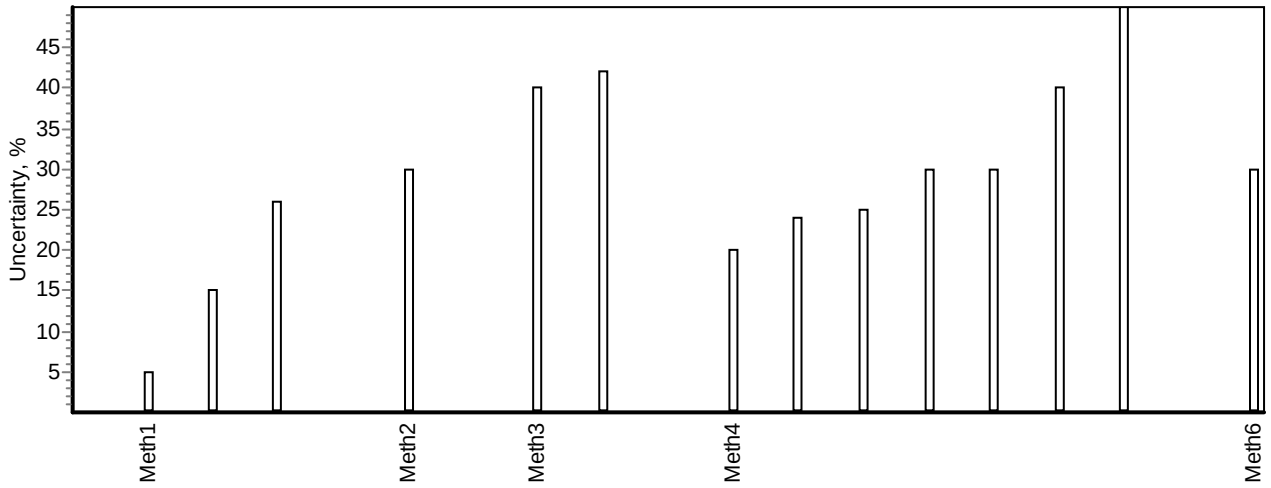
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* A1O



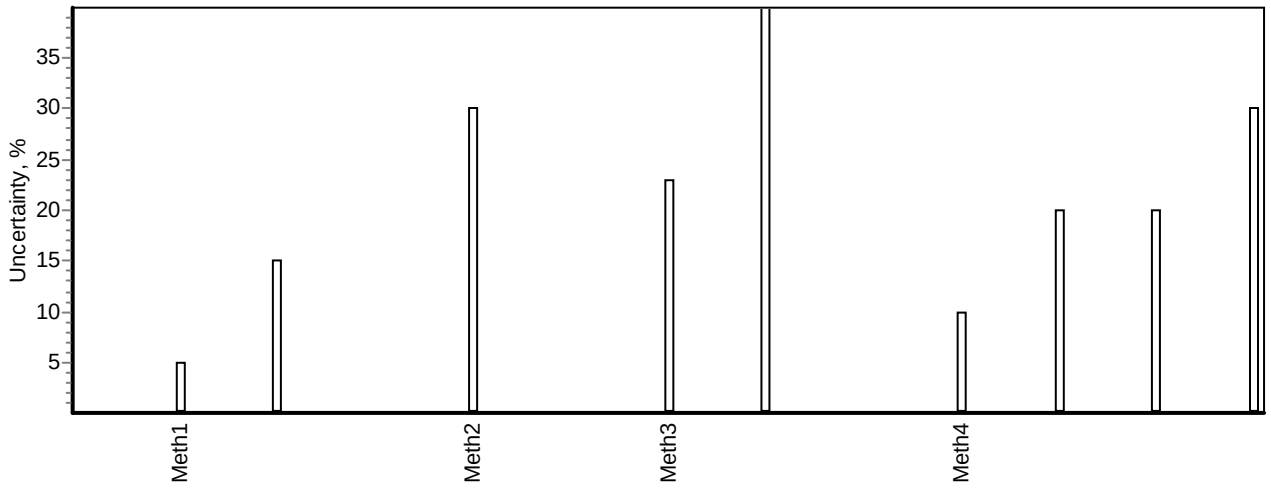
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* M3O



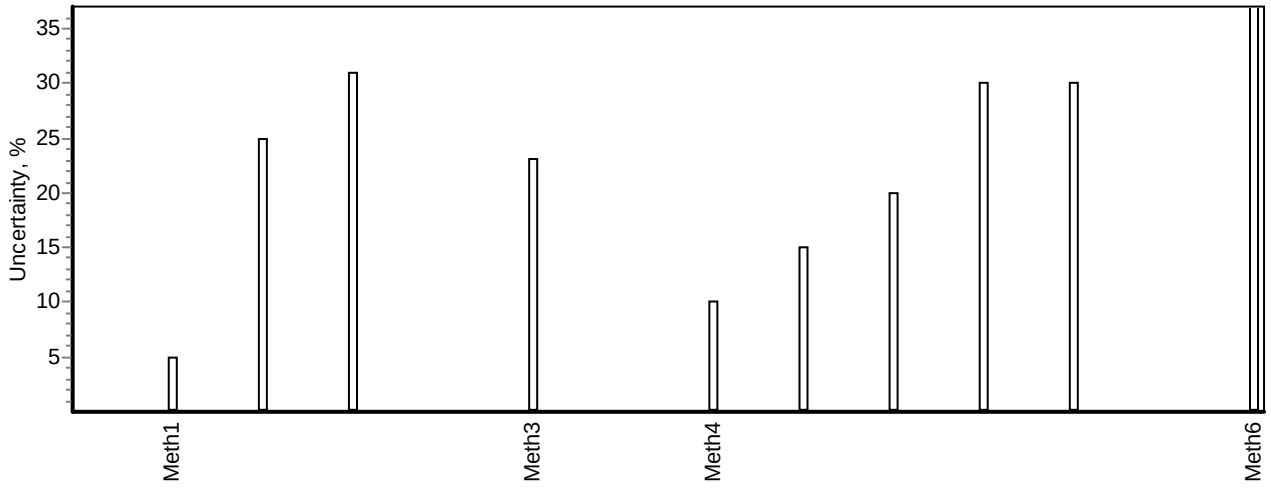
Analyytti *(Analyte)* **>C10-C40** Näyte *(Sample)* N2O



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



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



Documentation page

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Author(s)	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori and Markku Ilmakunnas	
Title of publication	Proficiency Test SYKE 9/2012 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	Proftest SYKE carried out the proficiency test for analysis of oil hydrocarbons from water and soil in October 2012. One artificial sample and one surface water sample and one soil sample for the determination of oil hydrocarbons were distributed. In total, 18 laboratories participated in the PT. Either the calculated concentration or the robust mean value was chosen to be the assigned value for the measurement. The performance of the participants was evaluated by using z scores. In this proficiency test 81 % of the results were satisfactory when the deviation of 20–40 % from the assigned value was accepted.	
Keywords	water analysis, soil analysis, oil hydrocarbons, proficiency test, intercomparison	
Publication series and number	Suomen ympäristökeskuksen raportteja 8 / 2013	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
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Julkaisun nimi	Proficiency Test SYKE 9/2012 Oil hydrocarbons in water and soil.	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä. www.ymparisto.fi/julkaisut	
Tiivistelmä	Proftest SYKE järjesti pätevyyskokeen vesi- ja maanäytteiden öljyhiilivetyjen määrityksistä lokakuussa 2012. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 18 laboratorioita. Määrityksen vertailuarvona käytettiin laskennallista arvoa tai osallistujien tulosten robustia keskiarvoa. Pätevyyden arvioimisessa käytettiin z-arvoa ja sitä laskettaessa tulokselle sallittiin 20–40 %:n poikkeama vertailuarvosta. Kokonaisuudessaan hyväksyttäviä tuloksia oli 81 %.	
Asiasanat	vesianalyysi, maa-analyysi, öljyhiilivedyt, pätevyyskoe, vertailumittaus	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 8 / 2013	
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Projektihankkeen nimi ja projektinumero		
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Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2013	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Februari 2013
Författare	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori och Markku Ilmakunnas	
Publikationens titel	Proficiency Test SYKE 9/2012 Oil hydrocarbons in water and soil.	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under oktober 2012 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av olja kolväte föreningar i grundvatten och i förorenad jord. Proven sändes ut till 18 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 81 % av alla resultaten tillfredsställande, när 20–40 % totalavvikelsen från referensvärdet accepterades.	
Nyckelord	vattenanalyser, jordanalyser, olja kolväte, provningsjämförelse, interkalibrering	
Publikationsserie och nummer	Suomen ympäristökeskuksen raportteja 8 / 2013	
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