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Oil hydrocarbons in water and soil

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Proftest SYKE

FINAS Finnish Accreditation Service PT01 (EN ISO/IEC 17043)

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ABSTRACT

Interlaboratory Proficiency Test 13/2017
Proftest SYKE carried out the proficiency test (PT) for analysis of oil hydrocarbons in water and soil in November 2017. Three types of samples were delivered to the participants: synthetic sample, surface water and soil samples. In total, 16 participants joined in the PT. In this proficiency test 76 % of the results were satisfactory when deviation of 20–40 % from the assigned value was accepted.

Basically, either the calculated concentration, the robust mean, or the median of the results reported by the participants was used as the assigned value for measurands. The evaluation of the performance of the participants was carried out using the z scores.
Warm thanks to all the participants of this proficiency test!

Keywords: water analysis, soil analysis, oil hydrocarbons, proficiency test, interlaboratory comparisons

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 13/2017
Proftest SYKE järjesti marraskuussa 2017 pätevyyskokeen öljyhiilivetyjä vedestä ja maasta analysoiville laboratorioille. Pätevyyskokeen osallistujille toimitettiin synteettinen, pintavesi- ja maanäyte. Pätevyyskokeessa oli 16 osallistujaa. Koko tulosaineistossa hyväksyttäviä tuloksia oli 76 %, kun vertailuarvosta sallittiin 20–40 %:n poikkeama.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Testisuureen vertailuarvona käytettiin joko laskennallista pitoisuutta tai osallistujien ilmoittamien tulosten perusteella laskettua robustia keskiarvoa tai mediaania.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, maa-analyysi. öljyhiilivedyt, pätevyyskoe, vertailumittaus

SAMMANDRAG

Provningsjämförelse 13/2017
Proftest SYKE genomförde en provningsjämförelse i november 2017, som omfattade bestämningen av olja kolväten i ytvatten och i förorenad jord. Tillsammans 16 laboratorier deltog i jämförelsen. I jämförelsen var 76 % av alla resultaten tillfredsställande, när total deviation på 20–40 % från referensvärdet accepterades.

Som referensvärde av analytens koncentration användes teoretiska värdet, robust medelvärdet eller medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, jordanalyser, olja kolväte, provningsjämförelse, interkalibrering

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of oil hydrocarbons (>C10-C40 and C5-C10) in water and soil in November 2017 (OIL 13/2017). The purpose of this PT was to ensure the comparability and accuracy of the results of the participants.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope with the exception of the C5–C10 measurements.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4 (formerly Hakuninmaantie 6), FI-00430 Helsinki, Finland
Phone: +358 295 251 000, Email: proftest@environment.fi

The responsibilities in organizing the proficiency test

Riitta Koivikko	coordinator
Jari Nuutinen	substitute for coordinator
Keijo Tervonen	technical assistance
Sari Lanteri	technical assistance
Markku Ilmakunnas	technical assistance
Ritva Väisänen	technical assistance
Anne Markkanen	technical assistance
Helena Pyykönen	technical assistance
Helena Kutramoinen	technical assistance

Analytical expert Jari Nuutinen

2.2 Participants

In total 16 laboratories participated in this proficiency test (Appendix 1), 13 participants from Finland and three participants from abroad. Altogether 63 % of the participants used accredited

analytical methods at least for a part of the measurements. For this proficiency test, the organizer has the code 4 (SYKE, Helsinki, T003, www.finas.fi/sites/en) in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic sample, surface water and soil samples. The synthetic samples A1O and A2B were prepared from the traceable commercial reference material produced by BAM, Dr. Ehrenstorfer, Ultra Scientific and AccuStandard. The oil contaminated soil sample M3O was collected from the site of former gasoline station from southern Finland. The soil sample M4B was prepared from VOC free soil material which was spiked with C5-C10 compounds and preserved with methanol. The surface water sample N5O was collected from the lake Kattilajärvi, Southern Finland and spiked with diesel and lubricating oils. The sample preparation is described in details in the Appendix 2.

When preparing the samples, the purity of the used sample vessels was secured by using new sample vessels as well as checking blank samples in each sample patch. According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 13 November 2017 to the participants abroad and on 14 November 2017 to the national participants. The samples arrived to the participants mainly on 15 November 2017. Participants 9 and 11 received the samples on 16 November 2017.

The samples were requested to be measured latest on 1 December 2017.

The results were requested to be reported latest on 1 December 2017 and all participants delivered the results accordingly. The preliminary results were delivered to the participants via ProftestWEB and email on 8 December 2017.

2.4 Homogeneity and stability studies

Based on the earlier similar PTs, the synthetic samples as well as water and soil samples are known to be homogenous and stable. Here, the soil sample M3O (>C10-C40) was mixed and divided to new vessels, the homogeneity of the sample was tested by analyzing >C10-C40 as duplicate determinations from four subsamples (Appendix 3). The homogeneity of the soil sample M4B was tested from 4 sub samples and the homogeneity of the water sample N5O was tested from three sub sample (Appendix 3). According to the homogeneity test results the samples M3O and N5O were considered homogenous. The criterion for homogeneity was not fulfilled for the sample M4B and the performance evaluation is weakened.

The stability of the samples A1O, M3O and N5O was checked by analyzing the samples before they were distributed to the participants as well as during or in the end of the requested time of analysis (Appendix 4). The stability criterion was fulfilled for the sample A1O and M3O and the samples were considered stable. For the sample N5O the stability criterion was not fulfilled, but some of the stability test measurement results could be questionable (Appendix 4).

Further, the synthetic samples (A1O, A2B and the addition solution L5O) as well as sample M4B were weighed at SYKE before the delivery and reweighed by the participants after the sample receiving. The difference of these two measurements was allowed to be < 1 %. If the difference was higher, the sample was replaced, which was the case for three participants.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants mainly dealt with their reporting errors with the samples. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed from the data more than $s_{rob} \times 5$ or 50 % from the robust mean were rejected before the statistical results handling. The replicate results were tested using the Cochran test. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

The calculated concentration of the certified reference material was used as the assigned values for the >C10-C40 in synthetic sample A1O and for C5-C10 in synthetic sample A2B. For the calculated assigned values the expanded measurement uncertainty (k=2) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the purity and/or concentration in the stock solutions.

For the other samples and measurands the robust mean or median (n_{stat}<12) of the reported participant results was used as the assigned value. The uncertainty was calculated using the robust standard deviation or standard deviation, respectively [2, 4].

The used assigned values are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned values was statistically tested [2, 3].

The assigned values **have not been changed** after reporting the preliminary results.

The expanded uncertainty of the calculated assigned values were 0.6 % (A1O, >C10-C40) and 2.4 % (A2B, C5-C10). When using the robust mean or median of the participant results as the

assigned value, the uncertainties of the assigned values varied from 4.5 % to 18.5 % (Appendix 6).

2.6.3 Standard deviation for proficiency assessment and z score

The standard deviation for proficiency assessment was estimated on the basis of the uncertainty of the assigned values, the concentrations of the measurands, the results of homogeneity and stability tests, and the long-term variation in the former proficiency tests. The standard deviation for the proficiency assessment ($2\times s_{pt}$, at the 95 % confidence level) was set to 20–40 % depending on the measurement. After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.

When using the robust mean or median as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standard deviation (sd, when $n_{stat}<12$) of the reported results [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned value[1] and/or for the reliability of the standard deviation for proficiency assessement[2] was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurand
M3O	>C10-C40[1,2], >C21-C40[1,2]
M4B	C5-C10[1]
N5O	>C10-C40[1]

3 Results and conclusions

3.1 Results

The terms in the results tables are explained in the Appendix 7. The results and the performance of each participant are presented in Appendix 8 and the summary of the results in Table 1. The results of the replicate determinations are presented in Table 2 (ANOVA statistics). The reported results with their expanded uncertainties (k=2) are presented in Appendix 9. The summary of the z scores is shown in Appendix 10 and z scores in the ascending order in Appendix 11.

Table 1. The summary of the results in the proficiency test OIL 13/2017.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n (all)	Acc z %
>C10-C21	A1O	mg/ml	1.11	1.11	1.13	1.11	0.10	8.6	30	9	89
	M3O	mg/kg	534	523	523	534	84	16.1	30	10	100
>C10-C40	A1O	mg/ml	2.32	2.21	2.18	2.25	0.20	9.2	20	15	93
	M3O	mg/kg	1988	1979	1988	2122	490	24.7	35	12	92
	N5O	mg/l	0.59	0.61	0.64	0.59	0.17	26.7	35	15	53
>C21-C40	A1O	mg/ml	1.09	1.08	1.08	1.09	0.12	10.9	30	9	100
	M3O	mg/kg	1579	1495	1511	1579	419	27.7	40	10	80
C5-C10	A2B	µg/ml	102	111	111	117	49	43.8	30	11	27
	M4B	mg/kg	5.53	5.89	5.89	5.53	1.63	27.8	40	10	60

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

The robust standard deviation of oil hydrocarbons (>C10-C40) was for the synthetic sample A1O 9 %, for the soil sample M3O 25 %, and for the water sample N5O 27 % (Table 1). The robust standard deviations were slightly higher when compared to the previous similar proficiency test Proftest SYKE OIL 09/2014 [5], where the deviations were 6 %, 21 % and 23 %, respectively.

For volatile oil hydrocarbons (C5-C10) the robust standard deviation was 44 % for the synthetic sample A2B and 28 % for the soil sample M4B. In the previous similar proficiency test, the deviations were 34 % and 35 %, respectively [5].

In this PT the participants were requested to report duplicate results for all measurements (except sample N5O, where one result was requested). The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2. The estimation of the robustness of the methods could be done by the ratio s_b/s_w, which should not exceed 3 for robust methods. For oil hydrocarbons (>C10-C40) the ratio varied in this test from 2.9 to 8.1, which was higher than in the previous similar proficiency test, where the ratio for oil hydrocarbons (>C10-C40) varied from 1.7 to 2.6 [5].

Table 2. The summary of repeatability on the basis of duplicate determinations (ANOVA) statistics.

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
>C10-C21	A1O	mg/ml	1.11	1.11	0.0914	0.160	0.184	7.9	14	16	1.7
	M3O	mg/kg	534	523	7.79	75.2	75.6	1.5	14	14	9.7
>C10-C40	A1O	mg/ml	2.32	2.21	0.0887	0.260	0.275	4.1	12	13	2.9
	M3O	mg/kg	1988	1979	55.4	447	451	2.8	23	23	8.1
	N5O	mg/l	0.59	0.61	0	0	0	0	0	0	-
>C21-C40	A1O	mg/ml	1.09	1.08	0.0520	0.102	0.114	4.8	9.4	11	2.0
	M3O	mg/kg	1579	1495	60.6	399	403	4.1	27	27	6.6
C5-C10	A2B	µg/ml	102	111	6.58	42.5	43.0	5.9	38	39	6.5
	M4B	mg/kg	5.53	5.89	0.246	1.43	1.45	4.2	24	25	5.8

s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t**:** reproducibility standard error.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. The details of the used methods were collected from the participants with an electronic questionnaire delivered together with the samples. Altogether 10 participants (63 %) replied to the questionnaire. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendices 12 and 13. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. However, in this PT there were not enough results for statistical comparison. Thus, the comparison is based on the graphical result evaluation.

Oil hydrocarbons (>C10-C40) in water

Majority of the participants (90 %) determined oil hydrocarbons in water using the method based on the standard EN ISO 9377-2 [6] and one participant used other method. The water sample was mainly extracted with hexane; also pentane and heptane were used for extraction. Five participants removed the polar substances by clean up on Florisil/Na_2SO_4, three participants used Al_2O_3, one participant used Florisil and one used Silica gel 60/ Na_2SO_4. The purified aliquot was analyzed by GC-FID (13 participants) or by GS-MS (2 participants). Several different injectors were used (split/splitless, on-column, and MMI-solvent vent). In the graphical evaluation between different methods results analysed by GC-MS are higher that the results analyzed by GC-FID. 62 % of the GC-FID results were satisfactory whereas both results achieved with GC-MS were unsatisfactory (Appendices 12, 13).

Oil hydrocarbons (>C10-C40) in soil

Most participants used the method based on ISO 16703 (or modification, 7 participants) to determine oil hydrocarbons in soil [7]. One participant used also EN 14039 [8] and one participant used other method. The soil sample M4O was mainly extracted with acetone/hexane followed by shaking or sonication, also acetone/heptane and acetone/hexane/water/methanol mixtures were used for the extraction. Most of the participants (70 %) purified the extract on Florisil/Na_2SO_4, also Florisil, Al_2O_3, Na_2SO_4, and silica gel 60/Na_2SO_4 were used. The aliquot was analyzed using GC-FID (10 participants) or GC-MS (2 participants). Statistical comparison between the applied methods could not be done due to low number of the results, but according to the graphical evaluation systematic differences between the used methods were not observed (Appendices 12, 13).

Volatile oil hydrocarbons (C5-C10) in soil

Four participants determined C5-C10 in soil using headspace GC-MS, three participants used GC-FID, two participants used GC-MS and one participant used HS-GC-FID. Five participants used the method based on ISO 22155 (or modification) [9] and two participants used other methods (e.g. extraction with methanol, static head-space GC-MS). According to graphical evaluation no systematic differences were observed between the used methods. Despite several different measurement methods, six participants (60 %) had satisfactory results for soil sample M4B, but only three participants (27 %) for synthetic sample A2B. Four participants have accredited the C5-C10 determination for the soil samples.

The Environmental Administration in Finland has published *Risk assessment and sustainable risk management of contaminated land* –report [10, in Finnish] where recommendation has been given how the volatile oil hydrocarbons (C5-C10) should be determined. The recommendation is based on the consensus by the workgroup of Finnish laboratory representatives conducting analyses on oil hydrocarbons. In summary, the volatile oil hydrocarbons (C5-C10) are recommended to be determined from total ion chromatogram (TIC) with headspace-GC-MS instrument (HS-GC-MS). The C5-C10 result is calculated as the sum of all the compound signals from n-pentane to n-decane (including these signals). The calibration should be done with a mixture of several hydrocarbons (including both linear, iso- and cycloalkanes, and aromatic hydrocarbons). The standard ISO 16558-1 lists the compounds which can be used for the calibration [11].

3.3 Uncertainties of the results

In total 94 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 9). The range of the reported uncertainties varied between the measurements and the sample types. The uncertainties were not reported for all the results where accredited methods were used.

Several approaches were used for estimating of measurement uncertainty (Appendix 14). The most used approach was based on the data obtained from method validation. Three participants used MUkit measurement uncertainty software for the estimation of their uncertainties. The free software is available on the webpage: www.syke.fi/envical/en [12]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 3. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurand	A1O %	M3O %	N5O %	A2B %	M4B %
>C10-C21	13-40	18-40	-	-	-
>C10-C40	7.4-40	10-40	10-42	-	-
>C21-C40	13-40	13-40	-	-	-
C5-C10	-	-	-	20-40	20-45

4 Evaluation of the results

The evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for the proficiency assessment (Appendix 6). The z scores were interpreted as follows:

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

In total, 76 % of the results were satisfactory when total deviation of 20–40 % from the assigned values were accepted. Altogether 63 % of the participants used accredited analytical methods at least for a part of the measurements and 79 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 4. In the previous similar PT, Proftest SYKE OIL 09/2014 [5], the performance was satisfactory for 77 % of the all participants.

Table 4. Summary of the performance evaluation in the proficiency test OIL 13/2017.

Measurand	Satisfactory results (%)	2 × s_{pt}, %	Remarks
>C10-C21	95	30	Excellent performance for sample M3O (100 %). In the OIL 09/2014 the performance was satisfactory for 69 % of the results [5].
>C10-C40	93	20–35	Good performance for samples A1O and M3O. Low performance for sample N5O. The criterion for the reliability of the assigned value was not fulfilled for N5O, thus the performance evaluation is weakened. The stability test results were not all considered reliable for the sample N5O. For the sample M3O, the criteria for the reliability of the assigned value and of the standard deviation were not fulfilled and the performance evaluation is weakened. In the OIL 09/2014 the performance was satisfactory for 87 % of the results [5].
>C21-C40	90	30–40	Excellent performance for sample A1O (100 %). For the sample M3O, the criteria for the reliability of the assigned value and of the standard deviation were not fulfilled and the performance evaluation is weakened. In the OIL 09/2014 the performance was satisfactory for 80 % of the results [5].
C5-C10	44	30–40	Low performance, especially for sample A2B, where only three satisfactory results. The criteria for the homogeneity and for the reliability of the assigned value were not fulfilled for M4B, thus the performance evaluation is weakened. In the OIL 09/2014 the performance was satisfactory for 63 % of the results [5].

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of oil hydrocarbons (>C10-C40 and C5-C10) in water and soil in November 2017 (OIL 13/2017). Three types of samples were delivered to the participants: synthetic sample, surface water and soil samples. In total 16 laboratories participated in this proficiency test.

Either the calculated concentration, robust mean, or median (n_{stat}<12) of the reported participant results was used as the assigned value. The uncertainty for the assigned value was estimated at the 95 % confidence level and for calculated assigned values it was 0.6–2.4 % and for the assigned values based on the robust mean or median of the reported participant results the uncertainty was 4.5–18.5 %.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. In this proficiency test 76 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value 20 to 40 %. About 63 % of the participants used accredited methods and 79 % of their results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti marraskuussa 2017 pätevyyskokeen öljyhiilivetyjä vedestä ja maasta analysoiville laboratorioille (OIL 09/2017). Pätevyyskokeen osallistujille toimitettiin synteettinen, pintavesi- ja maanäyte. Pätevyyskokeessa oli 16 osallistujaa.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa tai mediaania. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 0,6–2,4 % laskennallista vertailuarvoa käytettäessä ja kun vertailuarvo määritettiin muilla keinoin, sen laajennettu epävarmuus vaihteli välillä 4,5–18,5 %.

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 20–40 %. Koko aineistossa hyväksyttäviä tuloksia oli 76 %. Noin 63 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 79 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Czech Republic	ALS Czech Republic s.r.o.
Finland	Ahma Ympäristö Oy, Rovaniemi
	Borealis Polymers Oy, laboratoriopalvelut, Kulloo
	Eurofins Environment Testing Finland Oy, Lahti
	Fortum Waste Solutions Oy, Riihimäki
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere
	Metropolilab Oy
	Nablabs Oy / Jyväskylä
	Neste Oyj / Laadunvarmistus, Naantali
	Neste Oyj, Tutkimus ja kehitys/Vesilaboratorio, Kulloo
	Novalab Oy
	SGS Finland Oy, Kotka
	SSAB Europe Raahe, Raahe
	SYKE Ympäristökemia Helsinki
Hungary	DUNAFERR LABOR Nonprofit Kft. Szénkémiai A. Foosztály
Lithuania	Environmental Protection Agency, Klaipeda

APPENDIX 2: Preparation of the samples

Oil hydrocarbons (middle and heavy fractions, >C10-C40) - the samples A1O and N5O
All the dilutions were made by weighting.

Sample A1O:

Solutions	Preparation
Diesel Oil (without additives DIN H53)	124.98 mg
Lubricating oil (BAM-K009)	103.88 mg
Hexane	65.52 g → c = 2.319 mg/ml

The vial A1O (V = 3 ml) was sent to the participants.

Sample N5O:

Solutions	Preparation
A: Diesel Oil (without additives DIN H53)	605.42 mg oil in 6.09 g hexane
B: Lubricating oil (BAM-K009)	602.07 mg oil in 2.01 g hexane and 4.82 g isopropanol
L5O	5.0 ml A + 7.0 ml B into 99.5 ml of isopropanol → c = 7.330 mg/ml
N5O	100 µl L5O into 1 litre of water → c = 0.733 mg/l

The vial L5O (V = 2 ml) and surface water sample N5O (V = 1.0 litre) were sent to the participants.

Oil hydrocarbons (C5-C10) - the samples A2B and M4B
All the dilutions were made by weighting.

A2B was made from Naphtha (20.01 mg/ml, AccuStandard, Catalog No. HS-003S-40X) and addition solution for M4B was made by mixing BETX mixture (Ultra Scientific BETX Mixture, Product Number: BTX-2000N) and Naphtha (20.01 mg/ml, AccuStandard, Catalog No. HS-003S-40X).

BTEX mixture in methanol: Benzene 2.010 mg/ml, Ethylbenzene 2.005 mg/ml, Toluene 2.008 mg/ml, o-Xylene 2.009 mg/ml, m-Xylene 2.009 mg/ml, and p-Xylene 2.009 mg/ml.

A2B was made by mixing 0.513 ml Naphtha and 100.26 ml methanol. The vial A2B (V = 3 ml) was sent to the participants.

Final theoretical concentration for the A2B was 101.93 µg/ml.

Addition solution A for the M4B was made by mixing 0.148 ml BETX mixture, 0.236 ml Naphtha, and 50.14 ml methanol.

M4B was made by adding 20 g soil, 4 ml water, 1 ml addition solution A and 20 ml methanol (JT Baker, Purge&Trap quality).

Final theoretical concentration for the sample M4B (C5-C10) was 6.437 mg/kg.

APPENDIX 3: Homogeneity of the samples

The homogeneity of the samples M3O and M4B was tested by analyzing >C10-C40 or C5-C10, respectively, as duplicate measurements from four sub samples.

Criteria for homogeneity

$\mathbf{s_{anal}/s_{pt}<0.5}$ and $\mathbf{s_{sam}^2<c}$, where

s_{pt} = standard deviation for proficiency assessment
s_{anal} = analytical deviation, standard deviation of the results within sub samples
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_{pt})^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Sample / Measurand	Concentration mg/kg	n	s_{pt} %	s_{pt}	s_{anal}	s_{anal}/s_{pt}	s_{anal}/s_{pt} < 0.5?	s_{sam}	s_{sam}^2	c	s_{sam}^2 < c?
M3O / >C10-C40	1782	4	17.5	312	66.0	0.21	Yes	0.00	0.00	34981	Yes
M4B / C5-C10	5.89	4	20	1.18	0.19	0.16	Yes	0.67	0.45	0.43	No

The homogeneity of the sample N5O was tested by three replicated measurements.

Criteria for homogeneity

$\mathbf{s_{sam} < 0.5 \times s_{pt}}$

Sample / Measurand	Concentration mg/l	n	s_{pt} %	s_{pt}	0.5 × s_{pt}	s_{sam}	s_{sam} < 0.5 × s_{pt}?
N5O / >C10-C40	0.601	3	17.5	0.105	0.053	0.034	Yes

Conclusion: The samples M3O and N5O were considered to be homogenous. For the sample M4B the criterion of $s_{sam}^2 < c$ was not fulfilled. Thus the performance evaluation is weakened for sample M4B.

APPENDIX 4: Stability of the samples

The samples were delivered to the participants on 13-14 November 2017 and they were requested to be analysed latest on 1 December 2017.

The stability of the samples was tested by analysing the samples stored at temperatures 4 ° C and 25 ° C.

Criterion for stability: D < 0.3 × s_{pt}, where

D = |the difference of the results of the samples stored at temperatures 4 ° C and 20 ° C|

s_{pt} = standard deviation for proficiency assessment

Sample Measurand [unit]	Assigned value	29.11.2017 4°C [µg/ml]	29.11.2017 20°C [µg/ml]	D	0.3 × s_{pt}	D < 0.3 × s_{pt} ?
A1O >C10-C40 [mg/ml]	2.32	2.14	2.13	0.01	0.07	Yes
M3O >C10-C40 [mg/kg]	1988	2490	2404	86	104	Yes
N5O >C10-C40 [mg/l]	0.59	0.40	0.54	0.14	0.03	No

Conclusion: The criterion for stability was fulfilled for the samples A1O and M3O. For the sample N5O the criterion was not fulfilled and the difference was also not within the expanded measurement uncertainty (15 %). The result for the sample kept at 4 °C is lower than the median of the participant results and also lower than the mean of the homogeneity results. Therefore the stability test results are not fully reliable.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments to the results	Action / Proftest
4	The participant informed that they reported <C10-C40 result for the sample N5O in wrong unit. The corrected result was: 0.400 mg/l	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the result had been reported correctly, the result would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
5, 12, 15	For these participants the deviation of replicate measurements for some measurands and samples were high and their results were Cochran outliers. The provider recommends the participant to validate their deviation of replicate measurements.
6	After the delivery of the preliminary results the participant ordered a new A1O sample. They informed the result to the provider and that result was satisfactory.

APPENDIX 6: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
>C10-C21	A1O	mg/ml	1.11	0.05	4.5	Median	0.15
	M3O	mg/kg	534	51	9.6	Median	0.32
>C10-C40	A1O	mg/ml	2.32	0.01	0.6	Calculated value	0.03
	M3O	mg/kg	1988	354	17.8	Robust mean	0.51
	N5O	mg/l	0.59	0.08	13.5	Median	0.39
>C21-C40	A1O	mg/ml	1.09	0.07	6.7	Median	0.22
	M3O	mg/kg	1579	268	17.0	Median	0.43
C5-C10	A2B	µg/ml	102	2	2.4	Calculated value	0.08
	M4B	mg/kg	5.53	1.02	18.5	Median	0.46

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 7: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The reference value
2×s_{pt} %	The standard deviation for proficiency assessment at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
sd	Standard deviation
sd %	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

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

Robust analysis

The items of data are 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)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i $(i = 1, 2 \ldots p)$:

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

The new values of x^* and s^* are calculated 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 [2].

APPENDIX 8: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C40	mg/ml	A1O		0.13	2.32	20	2.35	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		0.47	1988	35	2150	2122	1979	449	22.7	12
	mg/l	N5O		3.29	0.59	35	0.93	0.59	0.61	0.13	21.3	10

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		-0.36	1.11	30	1.05	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		-0.94	534	30	459	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		-1.44	2.32	20	1.99	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		-0.58	1988	35	1785	2122	1979	449	22.7	12
	mg/l	N5O		-0.02	0.59	35	0.59	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		-0.95	1.09	30	0.93	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		-0.80	1579	40	1325	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		3.24	102	30	152	117	111	43	38.7	8
	mg/kg	M4B		2.21	5.53	40	7.98	5.53	5.89	1.44	24.5	7

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		0.18	1.11	30	1.14	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		-0.10	534	30	526	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		-0.97	2.32	20	2.10	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		-0.08	1988	35	1960	2122	1979	449	22.7	12
	mg/l	N5O		0.15	0.59	35	0.61	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		-0.83	1.09	30	0.96	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		-0.46	1579	40	1435	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		2.48	102	30	140	117	111	43	38.7	8
	mg/kg	M4B		1.51	5.53	40	7.20	5.53	5.89	1.44	24.5	7

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		-0.57	1.11	30	1.02	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		0.00	534	30	534	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		-0.80	2.32	20	2.14	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		1.37	1988	35	2464	2122	1979	449	22.7	12
	mg/l	N5O		3868.38	0.59	35	400.00	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		0.18	1.09	30	1.12	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		1.11	1579	40	1931	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		1.93	102	30	132	117	111	43	38.7	8
	mg/kg	M4B		-0.03	5.53	40	5.50	5.53	5.89	1.44	24.5	7

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		-0.36	1.11	30	1.05	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		1.91	534	30	687	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		0.04	2.32	20	2.33	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		0.87	1988	35	2290	2122	1979	449	22.7	12
	mg/l	N5O		3.36	0.59	35	0.94	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		1.13	1.09	30	1.28	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		0.07	1579	40	1600	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		4.18	102	30	166	117	111	43	38.7	8
	mg/kg	M4B		4.63	5.53	40	10.65	5.53	5.89	1.44	24.5	7

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C40	mg/ml	A1O		-3.77	2.32	20	1.45	2.25	2.21	0.19	8.5	14
	mg/l	N5O		-1.26	0.59	35	0.46	0.59	0.61	0.13	21.3	10

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		0.71	1.11	30	1.23	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		0.70	534	30	590	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		0.00	2.32	20	2.32	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		0.88	1988	35	2293	2122	1979	449	22.7	12
	mg/l	N5O		2.23	0.59	35	0.82	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		0.01	1.09	30	1.09	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		0.39	1579	40	1703	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		-1.54	102	30	79	117	111	43	38.7	8
	mg/kg	M4B		5.13	5.53	40	11.20	5.53	5.89	1.44	24.5	7

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C40	mg/ml	A1O		-0.23	2.32	20	2.27	2.25	2.21	0.19	8.5	14
	mg/l	N5O		2.13	0.59	35	0.81	0.59	0.61	0.13	21.3	10

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C40	mg/ml	A1O		-1.81	2.32	20	1.90	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		-1.66	1988	35	1410	2122	1979	449	22.7	12
	mg/l	N5O		-1.72	0.59	35	0.41	0.59	0.61	0.13	21.3	10
C5-C10	µg/ml	A2B		-2.58	102	30	63	117	111	43	38.7	8
	mg/kg	M4B		0.59	5.53	40	6.18	5.53	5.89	1.44	24.5	7

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C40	mg/ml	A1O		-0.28	2.32	20	2.26	2.25	2.21	0.19	8.5	14
	mg/l	N5O		-0.27	0.59	35	0.56	0.59	0.61	0.13	21.3	10

Participant 11													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C40	mg/ml	A1O		-1.13	2.32	20	2.06	2.25	2.21	0.19	8.5	14

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		2.85	1.11	30	1.59	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		-1.41	534	30	421	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		1.38	2.32	20	2.64	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		-2.41	1988	35	1150	2122	1979	449	22.7	12
	mg/l	N5O		3.62	0.59	35	0.96	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		-0.19	1.09	30	1.06	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		-2.70	1579	40	727	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		-3.24	102	30	53	117	111	43	38.7	8
	mg/kg	M4B		-0.19	5.53	40	5.33	5.53	5.89	1.44	24.5	7

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		-0.17	1.11	30	1.08	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		-1.25	534	30	434	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		-1.08	2.32	20	2.07	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		-1.75	1988	35	1380	2122	1979	449	22.7	12
	mg/l	N5O		-0.08	0.59	35	0.58	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		-0.63	1.09	30	0.99	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		-2.00	1579	40	946	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		-5.45	102	30	19	117	111	43	38.7	8
	mg/kg	M4B		-1.84	5.53	40	3.50	5.53	5.89	1.44	24.5	7

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		0.24	1.11	30	1.15	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		0.02	534	30	536	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		-0.04	2.32	20	2.31	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		0.30	1988	35	2093	2122	1979	449	22.7	12
	mg/l	N5O		0.10	0.59	35	0.60	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		0.43	1.09	30	1.16	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		-0.07	1579	40	1558	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		42.81	102	30	757	117	111	43	38.7	8
	mg/kg	M4B		18.15	5.53	40	25.60	5.53	5.89	1.44	24.5	7

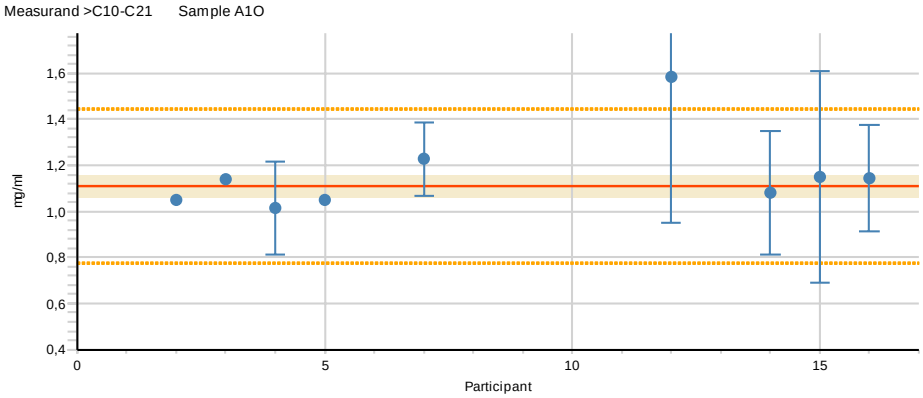
Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/ml	A1O		0.21	1.11	30	1.14	1.11	1.11	0.07	6.4	8
	mg/kg	M3O		1.50	534	30	655	534	523	75	14.4	9
>C10-C40	mg/ml	A1O		-0.32	2.32	20	2.25	2.25	2.21	0.19	8.5	14
	mg/kg	M3O		1.11	1988	35	2375	2122	1979	449	22.7	12
	mg/l	N5O		0.71	0.59	35	0.66	0.59	0.61	0.13	21.3	10
>C21-C40	mg/ml	A1O		0.21	1.09	30	1.12	1.09	1.08	0.11	10.0	9
	mg/kg	M3O		0.96	1579	40	1883	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		0.06	102	30	103	117	111	43	38.7	8
	mg/kg	M4B		0.00	5.53	40	5.53	5.53	5.89	1.44	24.5	7

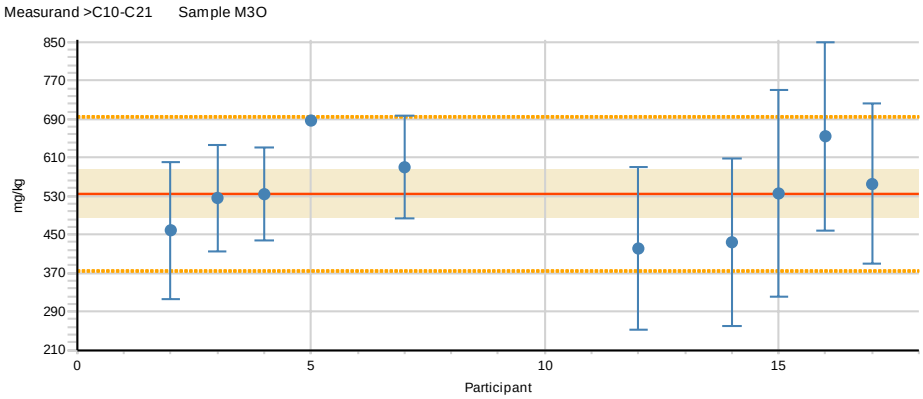
Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
>C10-C21	mg/kg	M3O		0.26	534	30	555	534	523	75	14.4	9
>C10-C40	mg/kg	M3O		1.19	1988	35	2403	2122	1979	449	22.7	12
	mg/l	N5O		6425.28	0.59	35	664.00	0.59	0.61	0.13	21.3	10
>C21-C40	mg/kg	M3O		0.85	1579	40	1847	1579	1495	401	26.8	10
C5-C10	µg/ml	A2B		5.29	102	30	183	117	111	43	38.7	8

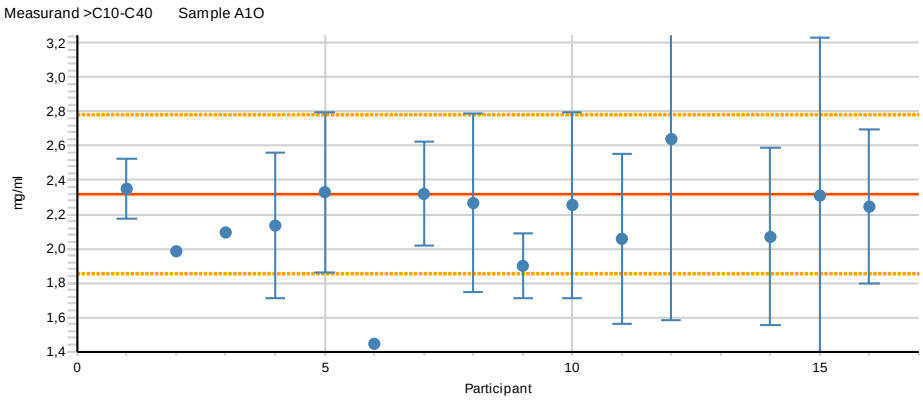
APPENDIX 9: Results of participants and their uncertainties

In figures:

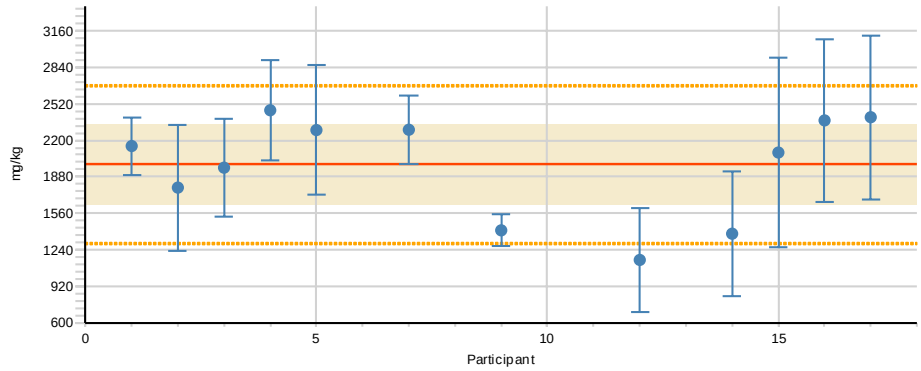
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



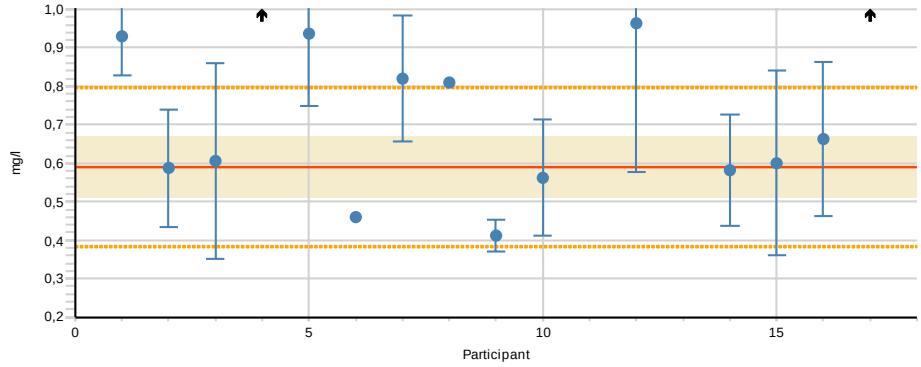




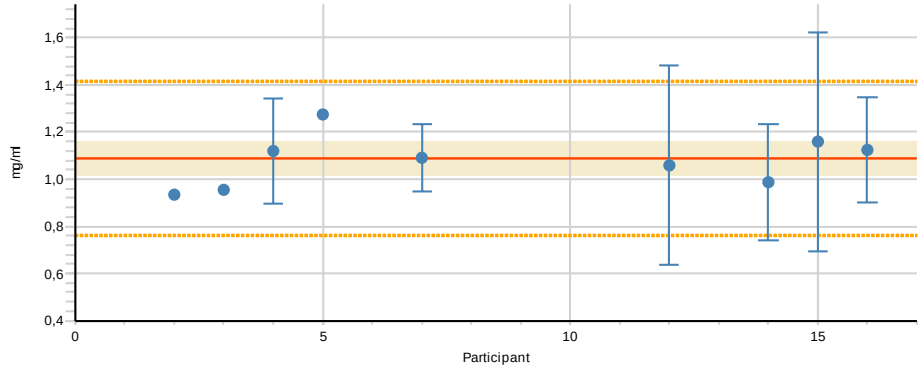
Measurand >C10-C40 Sample M3O



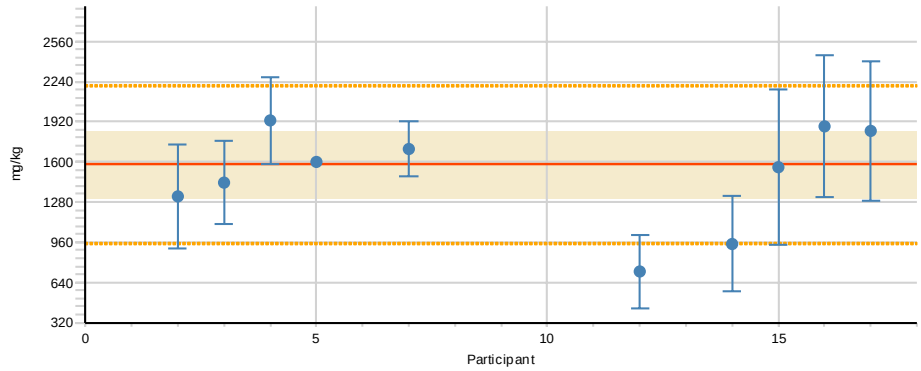
Measurand >C10-C40 Sample N5O



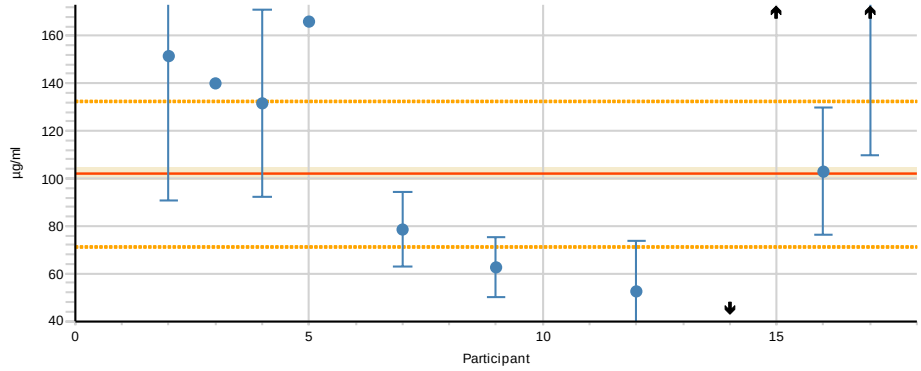
Measurand >C21-C40 Sample A1O



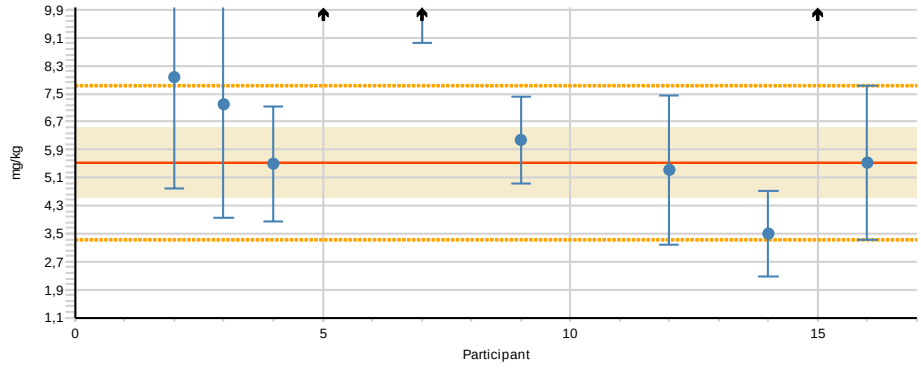
Measurand >C21-C40 Sample M3O



Measurand C5-C10 Sample A2B



Measurand C5-C10 Sample M4B



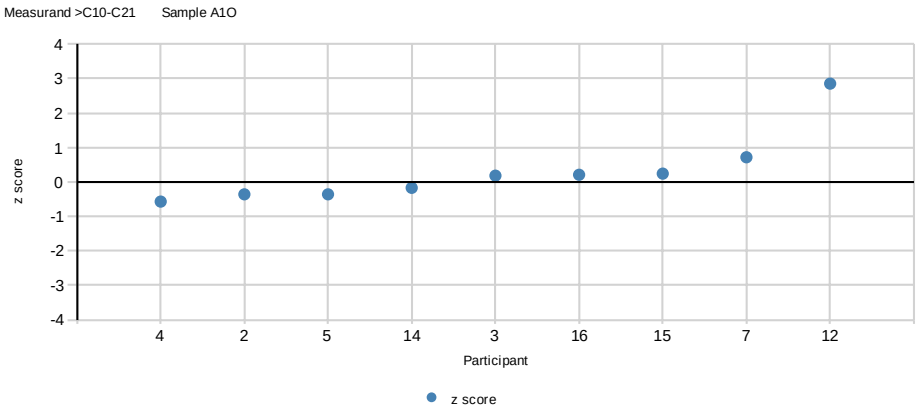
APPENDIX 10: Summary of the z scores

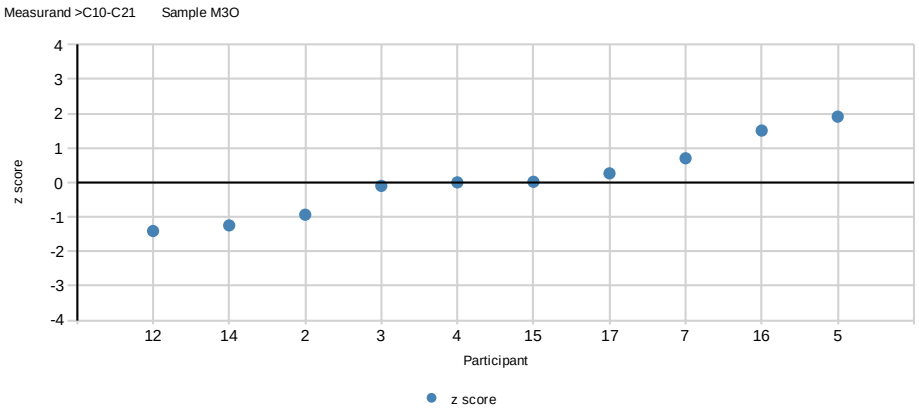
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17		%
>C10-C21	A1O	.	S	*S*	S	*S*	.	S	.	.	.	.	Q	.	*S*	*S*	*S*	.	. . . . .	88.9
	M3O	.	S	S	S	*S*	.	S	.	.	.	.	S	.	S	*S*	*S*	S	. . . . .	100
>C10-C40	A1O	*S*	S	*S*	S	S	*u*	S	*S*	S	*S*	*S*	S	.	S	S	*S*	.	. . . . .	93.3
	M3O	*S*	S	S	S	S	.	S	.	S	.	.	q	.	S	S	*S*	S	. . . . .	91.7
	N5O	*U*	S	S	*U*	U	*S*	Q	*Q*	S	*S*	.	U	.	S	S	*S*	U	. . . . .	53.3
>C21-C40	A1O	.	S	*S*	S	*S*	.	S	.	.	.	.	S	.	*S*	*S*	*S*	.	. . . . .	100
	M3O	.	S	S	S	*S*	.	S	.	.	.	.	q	.	*q*	*S*	*S*	S	. . . . .	80.0
C5-C10	A2B	.	U	*Q*	*S*	*U*	.	*S*	.	q	.	.	u	.	*u*	*U*	*S*	U	. . . . .	27.3
	M4B	.	Q	S	*S*	*U*	.	*U*	.	S	.	.	S	.	*S*	*U*	*S*	.	. . . . .	60.0
%		67	78	89	89	67	50	78	50	80	100	100	44		78	78	100	60		
accredited			9	5	6	3		7		5			9		4	3		5		

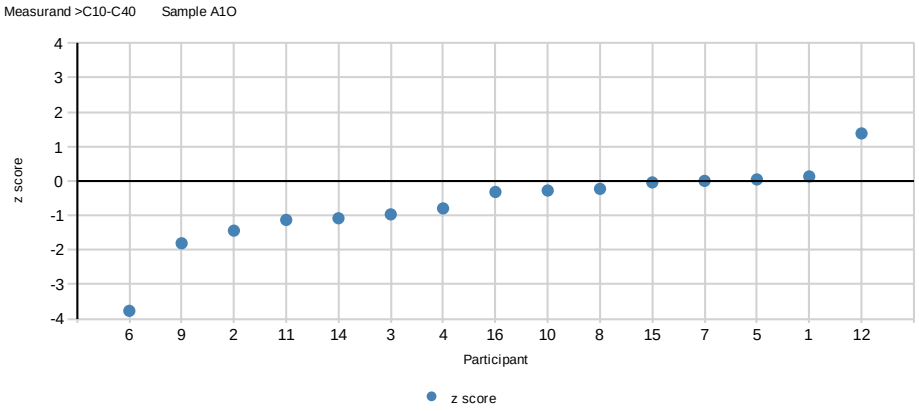
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

Totally satisfactory, % in all: 76 % in accredited: 79 % in non-accredited: 73

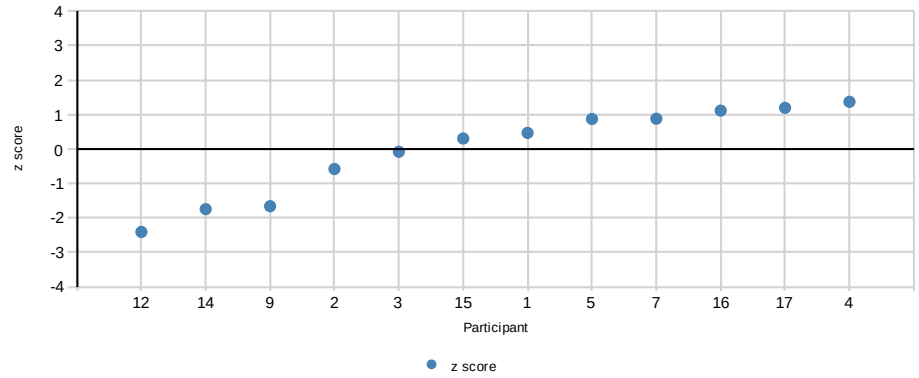
APPENDIX 11: z scores in ascending order



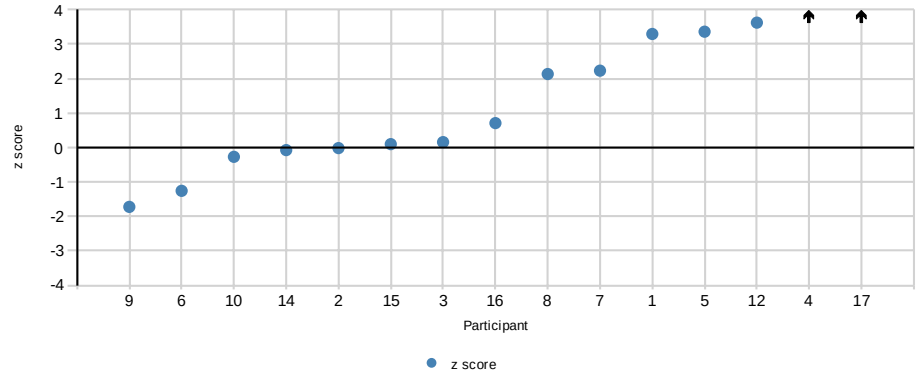




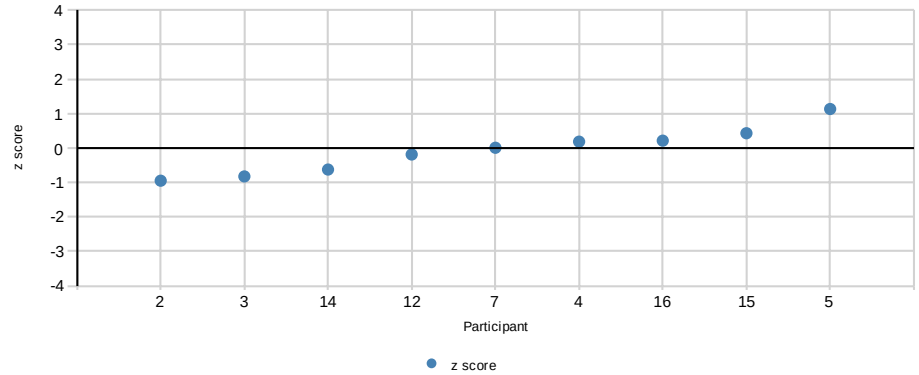
Measurand >C10-C40 Sample M3O



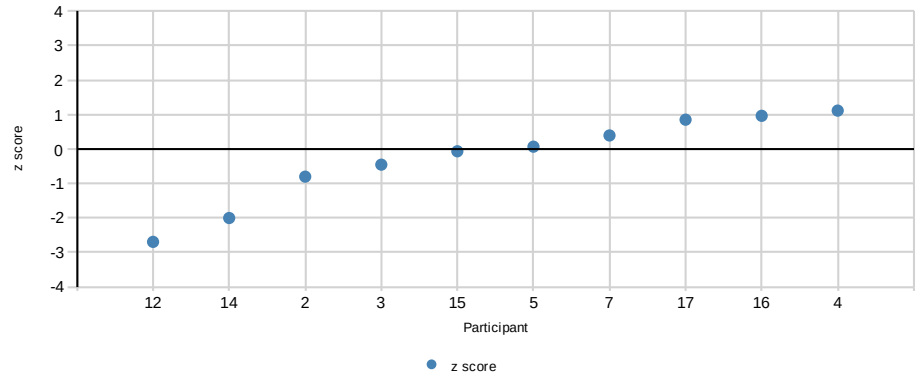
Measurand >C10-C40 Sample N5O



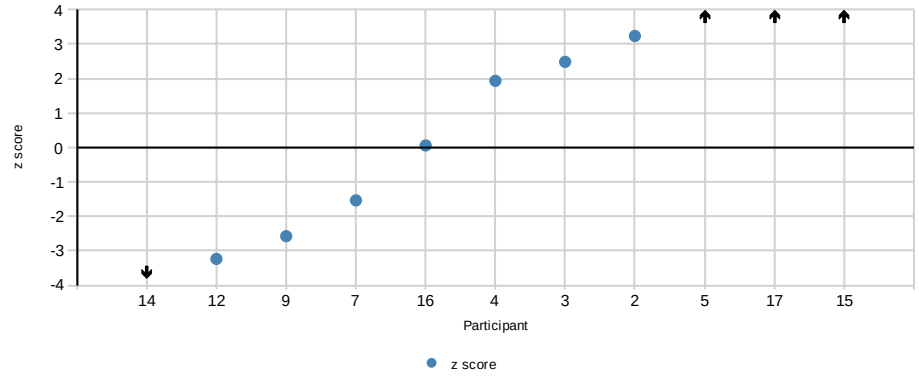
Measurand >C21-C40 Sample A1O



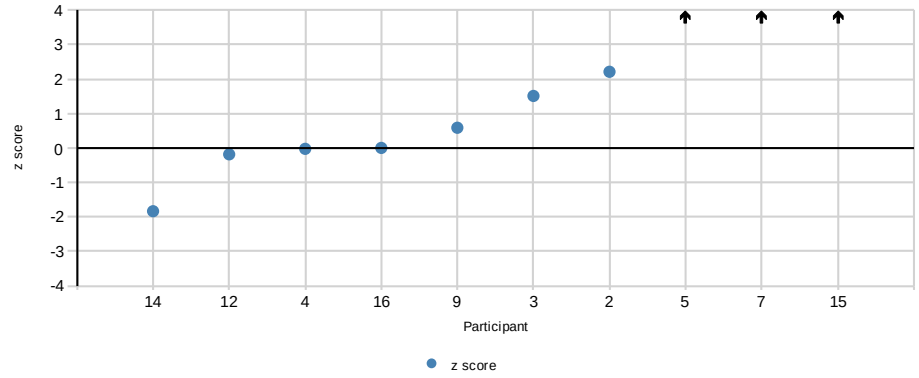
Measurand >C21-C40 Sample M3O



Measurand C5-C10 Sample A2B



Measurand C5-C10 Sample M4B



APPENDIX 12: Analytical methods

To collect the details of the used methods, an electronic questionnaire was delivered to the participants at the same time as the samples. Altogether 10 participants (63 %) replied to the questionnaire. The summaries of the used methods are below.

Water – N5O, Oil hydrocarbons (>C10-C40)

Participant	Reference	Solvent	Extraction	Purification	Injection	Equipment
1	EN ISO 9377-2	n-Hexane	Stirring, 50 ml / 30 min	Al_2O_3	Split, 1 µl	GC-FID
2	EN ISO 9377-2	n-Hexane	Shaking / 50 ml / -	Florisil / Na_2SO_4	Splitless, -	GC-FID
3	EN ISO 9377-2	n-Hexane	Stirring / 30 ml / 60 min	Florisil	MMI[1] Solvent vent, 5 µl	GC-FID
4	EN ISO 9377-2	n-Hexane	Stirring / 30 ml / 60 min	Florisil / Na_2SO_4	On-column, 1 µl	GC-FID
5	EN ISO 9377-2	n-Hexane	Shaking / 20 ml / 10 min	Florisil / Na_2SO_4	Splitless, 0.5 µl	GC-MS
6	EN ISO 9377-2	n-Pentane	Shaking / 50 ml / 30 min	Florisil / Na_2SO_4	Split, 20 µl	GC-FID
7	EN ISO 9377-2	Heptane	Shaking / 4 ml / 40 min	Al_2O_3	On-column, 1 µl	GC-FID
9	Other method	n-Hexane	Shaking / 30 ml / 60 min	Silica gel 60 / Na_2SO_4	Splitless, 1 µl	GC-FID
10	EN ISO 9377-2	n-Hexane	Shaking / 50 ml / 30 min	Florisil / Na_2SO_4	On-column, 1 µl	GC-FID
12	EN ISO 9377-2	n-Hexane	Shaking / 40 ml / 30 min	Al_2O_3	On-column, 3 µl	GC-MS

[1] MMI - Multimode inlet (technique for large volume injection)

Soil – M3O, Oil hydrocarbons (>C10-C40)

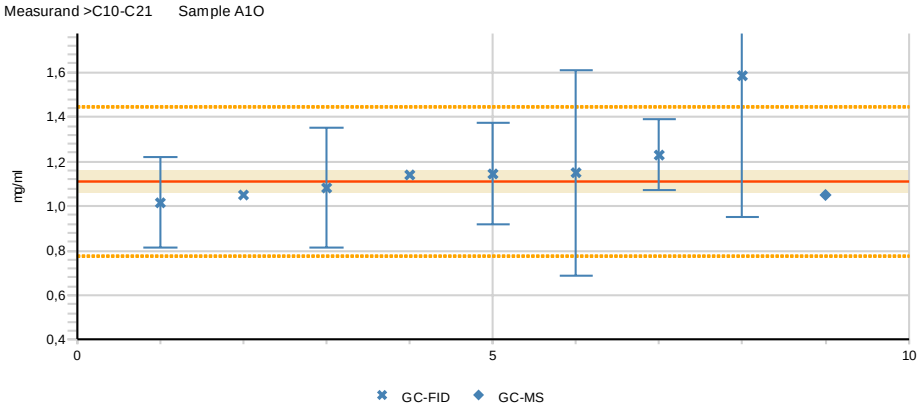
Participant	Reference	Solvent	Extraction	Purification	Injection	Equipment
1	ISO 16703	Acetone / Hexane	Shaking, 10 g / 60 min	Florisil / Na_2SO_4	Split, 1 µl	GC-FID
2	ISO 16703, EN 14039	Acetone / Hexane	Shaking, 20 g / -	Florisil / Na_2SO_4	Splitless, -	GC-FID
3	ISO 16703	Acetone / Hexane	Ultrasonic, 8 g / 30 min	Florisil	MMI Solvent vent, 2 µl	GC-FID
4	ISO 16703	Acetone / Hexane	Shaking, 10 g / 60 min	Florisil / Na_2SO_4	On-column, 1 µl	GC-FID
5	Modified ISO 16703	Acetone / Hexane	Shaking, 20 g / 60 min	Florisil / Na_2SO_4	Splitless, 0.1 µl	GC-MS
7	ISO 16703	Heptane / Acetone	Shaking, 10 g / 40 min	Al_2O_3	Split, 2 µl	GC-FID
9	Other method	Acetone / Hexane	Ultrasonic, 1.5 g / 80 min	Silica gel 60 / Na_2SO_4	Splitless, 1 µl	GC-FID
12	ISO 16703	MeOH, Acetone, Hexane, H_2O	Shaking, 20 g / 30 min	Al_2O_3	Splitless, 1 µl	GC-MS

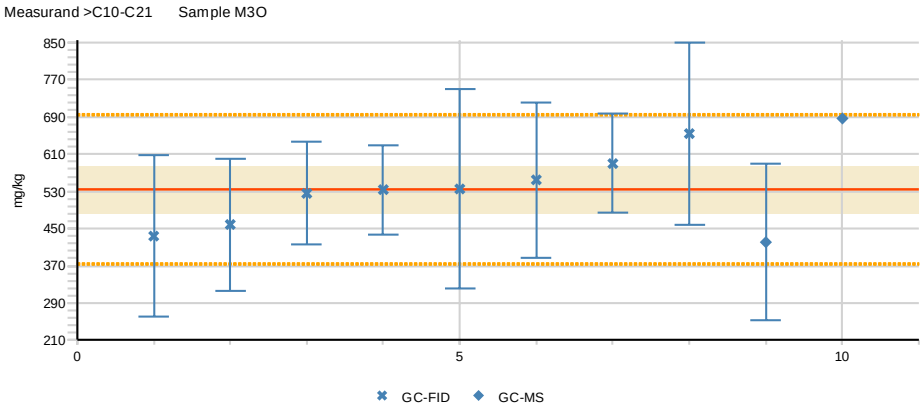
Soil – M4B, Volatile oil hydrocarbons (C5-C10)

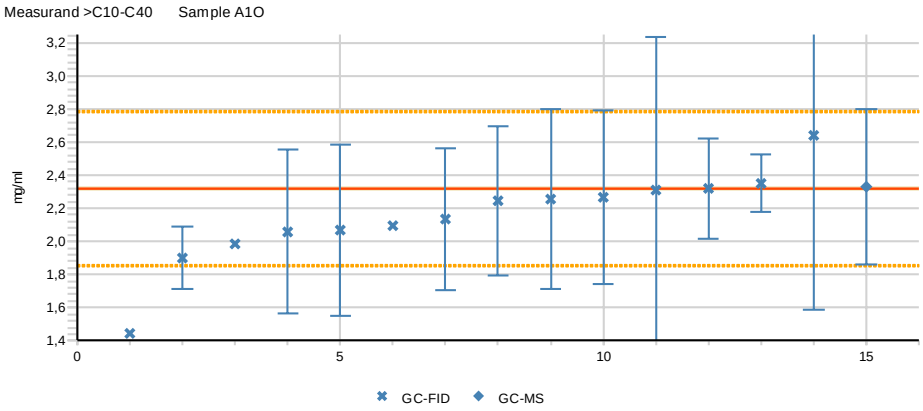
Participant	Reference	MS mode	Standards	Equipment
2	ISO 22155	Headspace	Internal standard, External standard	Headspace GC-MS
3	ISO 22155	Headspace, 1000 µl	Internal standard	Headspace GC-MS
4	ISO 22155	Headspace, 1000 µl	Internal standard	Headspace GC-MS
5	Modified ISO 22155	Headspace, 0.2 µl	Internal standard	GC-MS
7	Other method	Headspace, 1000 µl	External standard	GC-FID
9	Other method	Split, 1 µl	-	GC-FID
12	ISO 22155	Headspace, 3 µl	Internal standard, External standard	GC-MS

APPENDIX 13: Results grouped according to the methods

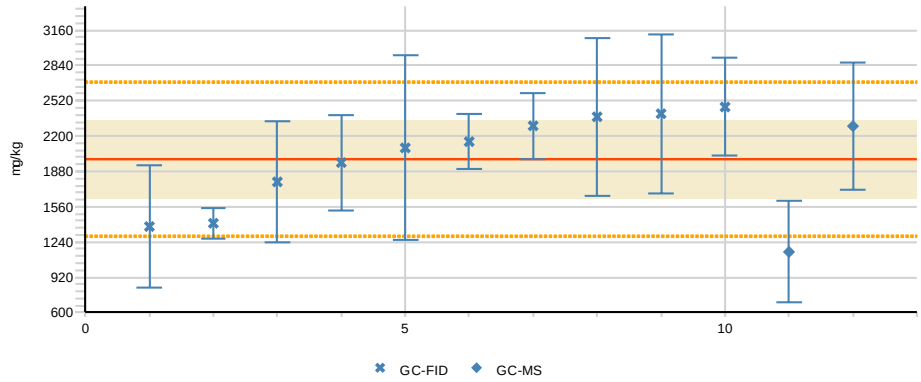
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



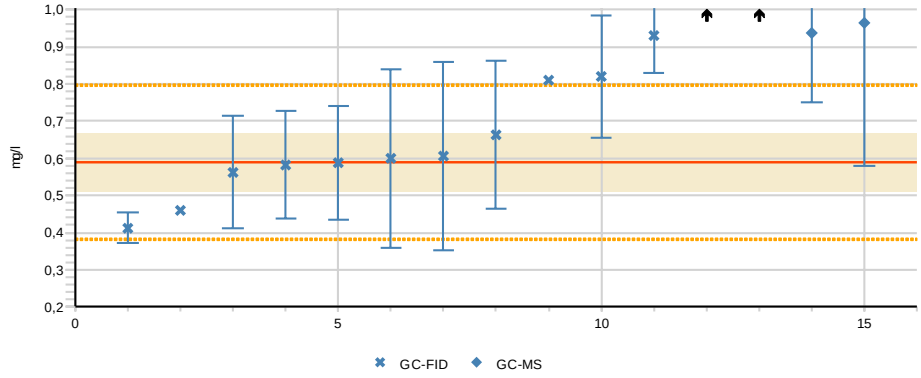




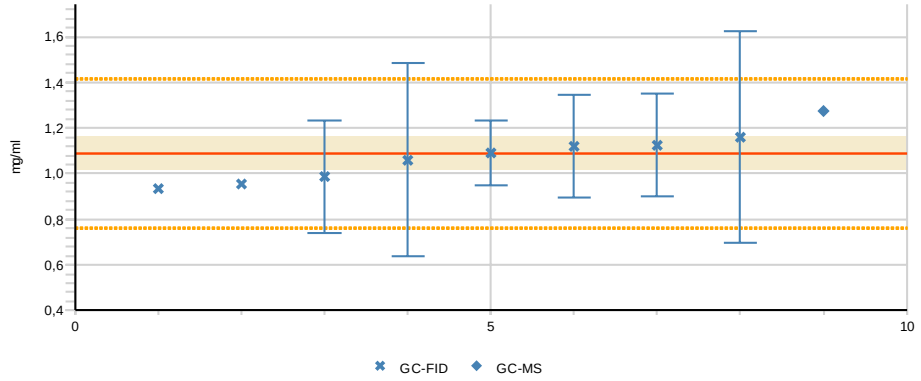
Measurand >C10-C40 Sample M3O



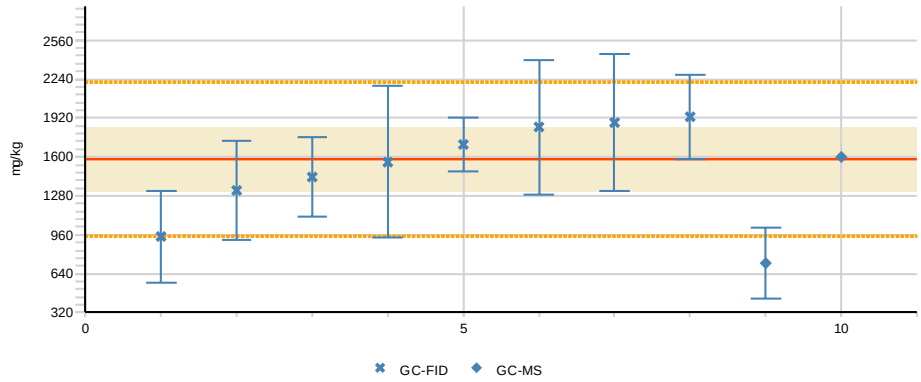
Measurand >C10-C40 Sample N5O



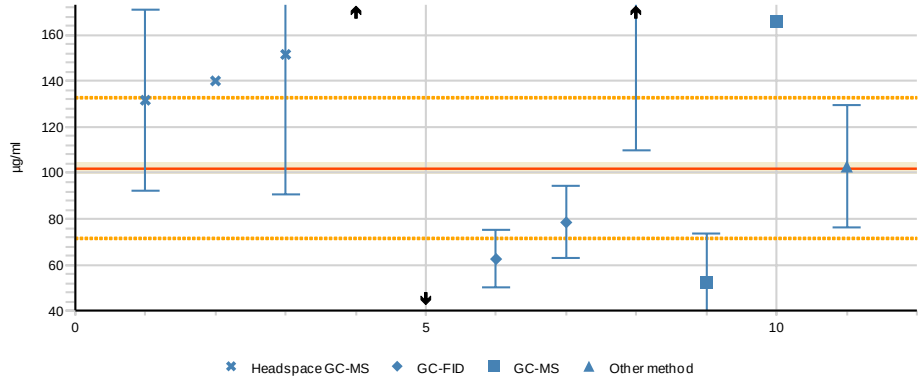
Measurand >C21-C40 Sample A1O



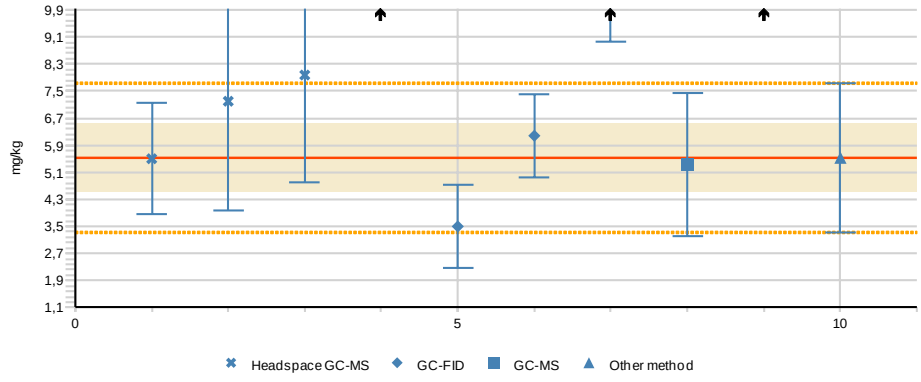
Measurand >C21-C40 Sample M3O



Measurand C5-C10 Sample A2B

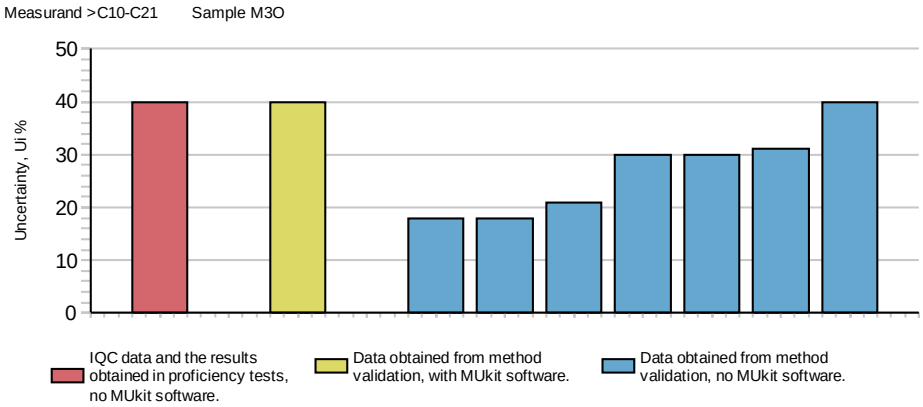


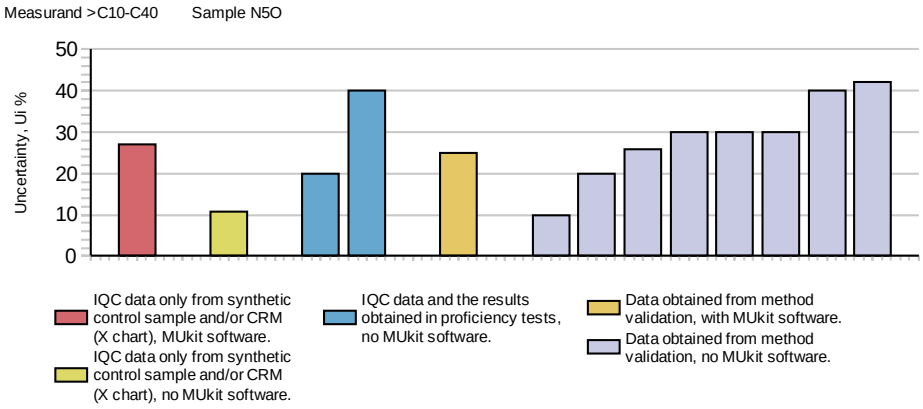
Measurand C5-C10 Sample M4B

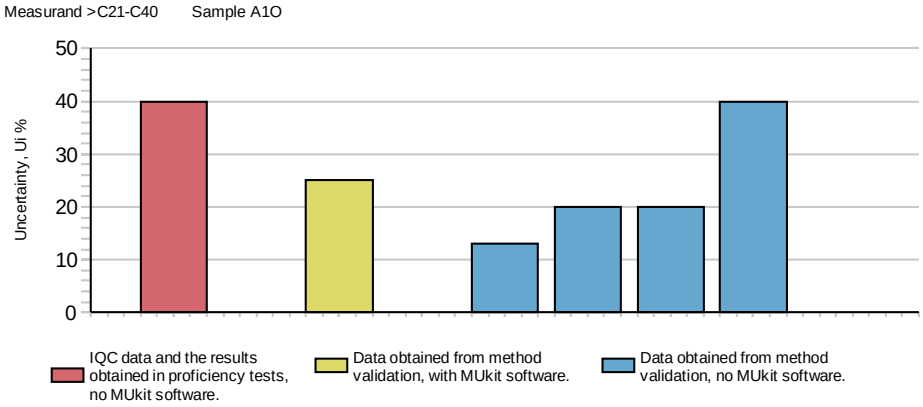


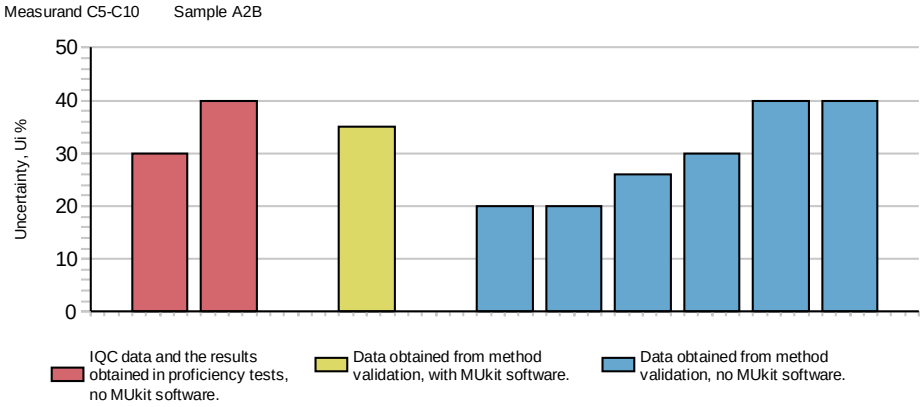
APPENDIX 14: Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [12, 13] or using method validation [13].






Measurand >C21-C40 Sample A1O
Uncertainty, Ui %
50
40
30
20
10
0
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.


Measurand C5-C10 Sample A2B
Uncertainty, Ui %
50
40
30
20
10
0
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

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