REPORTS OF FINNISH ENVIRONMENT INSTITUTE 5| 2011

Proficiency Test SYKE 8a/2010

Volatile organic compounds in water and soil

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

Finnish Environment Institute

REPORTS OF FINNISH ENVIRONMENT INSTITUTE 5 | 2011

Proficiency Test SYKE 8a/2010

Volatile organic compounds in water and soil

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

Helsinki 2011

Finnish Environment Institute

REPORTS OF FINNISH ENVIRONMENT INSTITUTE 5 | 2011
Finnish Environment Institute SYKE

The organizer of the intercomparison test:
Finnish Environment Institute SYKE, Laboratories
Hakuninmaantie 6, 00430 Helsinki
phone +358 20 610 123, fax +358 9 495 913
Publication is available only in the internet :
www.environment.fi/publications

ISBN 978-952-11-3854-6 (PDF)
ISSN 1796-1726 (online)

CONTENT

APPENDIXES

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 (EN ISO/IEC 17025) ja vertailumittausten järjestäjä Proftest SYKE PT01 (EN ISO/IEC 17043, www.finas.fi).

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

Parhaat kiitokset yhteistyöstä kaikille osallistujille!

PREFACE

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

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

Thank you for your co-operation!

Helsingissä 10. helmikuuta 2011 / Helsinki 10 February 2011

Marja Luotola

Laboratorionjohtaja / Chief of Laboratory

1 INTRODUCTION

In November 2010 the Finnish Environment Institute (SYKE) carried out the proficiency test (PT) for the analysis of volatile organic compounds (VOC) 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 Recommendations [3]. The SYKE laboratory has been accredited by the Finnish Accreditation Service as a proficiency testing provider Proftest SYKE PT01 (www.finas.fi) on the field of the present PT.

2 ORGANIZING OF THE PROFICIENCY TEST

2.1 Responsibilities

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

The responsibilities in organizing the PT were as follows:

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

2.2 Participants

In total, 13 laboratories (Appendix 1) from Denmark, Finland, Italy and Sweden participated in this PT. Eight laboratories used an accredited method at least for some of VOC compounds. The organizing laboratory (SYKE) had the code 2 in the result tables.

2.3 Samples and their delivery

The artificial sample A1V as well as the addition standard solution for the water sample G2V and the soil sample M3V was prepared gravimetrically from individual compounds by diluting to the final concentration (Appendix 2).

Both the soil sample M3V and the ground water sample G2V were spiked with a known amount of the addition solution. The preparation of the samples is presented in Appendix 2.

The samples were delivered 16 November 2010. They were requested to be analysed and reported at the latest 26 November 2010.

2.4 Homogeneity and stability studies

Homogeneities of the sample G2V and the sample M3V were tested by analysing tetrachloroethene, 1,2,4-trichlorobenzene, o-xylene and MTBE as triplicate determinations from seven sub samples (Appendix 3). Both samples were considered to be homogenous.

The stabilities of the samples A1V and M3V were checked during the sample transport to the participants. The sample vials were weighed at SYKE before the delivering and reweighed at the participating laboratory after the receiving. The differences of these two measurements should be < 0.5 %. During the transport no evaporation of solvent was observed.

The stability test was carried out for all samples A1V, G2V and M3V. One part of the samples was stored at the room temperature and the other part at the temperature 4 °C degrees over night. The samples were analysed 20 November (Appendix 4).

According to the test the increased temperature did not cause significant change in the samples A1V and M3V. The test results of the sample G2V were slightly inconsistent. Only one laboratory reported the temperature of the samples to be higher than 10 °C. However, the results of this participant for the sample G2V were satisfactory ($z < 2$).

2.5 Feedback from the proficiency test

Appendix 5.1 contains the comments sent by the participants. The weight of the groundwater sample G2V was asked to report unnecessarily because the initial weight was not given and evaporation of water during the transport was not probable.

Consequently Appendix 5.2 contains the provider´s comments to the participants. Only one participant sent the results a day after the deadline. However the results could be included in the preliminary data treatment. After sending the preliminary results the coordinator informed the participants that due to low number of the participants both unit errors and the results, which had been entered on inappropriate line, would be corrected by Proftest. No participant reported this kind of errors. As well according to the provider's observation the participants reported their results correctly in this PT. Only method descriptions of two participants were lacking.

2.6 Processing of the data

2.6.1 Testing of outliers and normality of data

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

2.6.2 Assigned value

The assigned values and their uncertainties are presented in Appendix 6. The calculated concentrations were used as the assigned values for the concentrations of all measurements in the artificial sample A1V. The uncertainty of the assigned value given is the expanded combined uncertainty based on the combination of uncertainties associated with individual operations involved in the preparation of the sample. In all cases the uncertainty was less than 1 % and the main individual resource of the uncertainty was the uncertainty of the impurity in the stock solution.

The robust means of the reported results were used as the assigned value for the concentrations of the measurements in both the water G2V and the soil M3V samples. The uncertainty of the assigned value was calculated using the robust standard deviation of the reported results as follows:

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

where:

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

In the samples G2V and M3V the uncertainties of the assigned values varied from 5.1 % to 17 %. After reporting of the preliminary results no significant correction of the assigned value has been done.

2.6.3 Standard deviation for proficiency assessment and z score

The evaluation of the participants was based on z scores, which were calculated using the estimated standard deviation for proficiency assessment. The estimation of the target standard deviation was based on the type of sample, the concentration of the analyte in the sample, the results of homogeneity and stability tests and the uncertainty of the assigned value. In the performance evaluation z scores were interpreted as follows:

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

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

- G2V: 124TCBz, 12DCEa, CCl_4, DCM, ETBz, mpXyl, MTBE, TAME, TeCEe
- M3V: 124TCBz, 12DCEa, DCM, mpXyl, oXyl, TAME

However, the ratios u / s_p were in every case < 0.7.

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 fulfilled in most cases, which weakened the evaluation of performance.

3 RESULTS AND CONCLUSIONS

3.1 Results

The results and the performance of each laboratory are presented in Appendix 7 and the summary of the results in Table 1. The results and their uncertainties are presented graphically in Appendix 8. Explanations for the result sheets are presented in Appendix 9.

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

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
124TCBz	A1V	µg/ml	1,35	1.34	1.35	1.29	0.26	19,1	12	15	58
	G2V	µg/l	2,82	3.03	2.82	2.97	0.51	18,1	9	25	75
	M3V	mg/kg	2,23	2.11	2.10	2.18	0.41	19,7	12	30	92
12DCEa	A1V	µg/ml	1,02	1.00	1.03	0.98	0.18	17,4	13	15	54
	G2V	µg/l	8,9	8.90	8.90	9.10	1.13	12,7	10	25	100
	M3V	mg/kg	2,47	2.09	2.09	2.13	0.49	23,3	13	30	69
Bz	A1V	µg/ml	3,26	3.20	3.26	3.18	0.51	15,6	13	15	62
	G2V	µg/l	8,3	8.29	8.30	8.36	0.90	10,9	10	25	100
	M3V	mg/kg	4,22	4.15	4.15	4.28	0.47	11,2	13	30	92
c12DCEe	A1V	µg/ml	1,59	1.58	1.62	1.58	0.26	16,1	11	15	64
	G2V	µg/l	13,1	13.14	13.14	13.40	1.28	9,7	8	25	100
	M3V	mg/kg	2,91	2.93	2.91	2.93	0.33	11,2	11	30	91
CCl4	A1V	µg/ml	0,61	0.67	0.70	0.70	0.16	22,6	13	15	36
	G2V	µg/l	4,29	4.29	4.29	4.40	0.90	21	10	25	89
	M3V	mg/kg	1,19	1.11	1.19	1.18	0.18	15,4	13	30	75
CHCl3	A1V	µg/ml	1,24	1.27	1.30	1.29	0.29	22,2	13	15	54
	G2V	µg/l	9,87	9.87	9.87	9.80	1.09	11,1	10	25	100
	M3V	mg/kg	2,39	2.38	2.39	2.41	0.34	14,3	13	30	92
DCM	A1V	µg/ml	1,1	1.20	1.20	1.17	0.22	18,4	12	15	58
	G2V	µg/l	8,96	8.96	8.96	9.11	1.28	14,3	10	25	100
	M3V	mg/kg	2,37	2.36	2.37	2.54	0.41	17,2	11	30	91
ETBz	A1V	µg/ml	3,31	3.28	3.28	3.04	0.66	20,2	13	15	69
	G2V	µg/l	6,51	6.51	6.51	6.21	1.07	16,4	10	25	90
	M3V	mg/kg	4,49	4.48	4.49	4.67	0.73	16,2	13	30	92
mpXYL	A1V	µg/ml	5,1	4.94	5.17	4.98	1.59	30,6	13	15	46
	G2V	µg/l	10,9	10.19	10.86	10.01	1.67	15,4	10	25	80
	M3V	mg/kg	7,21	7.12	7.21	7.47	1.56	21,7	13	30	77
MTBE	A1V	µg/ml	6,27	6.07	6.14	5.96	0.67	11	12	15	83
	G2V	µg/l	20,5	20.77	20.54	21.10	2.63	12,8	10	25	90
	M3V	mg/kg	12,4	12.37	12.44	12.72	1.78	14,3	12	30	100
oXYL	A1V	µg/ml	3,36	3.37	3.37	3.17	0.66	19,5	13	15	69
	G2V	µg/l	6,53	6.66	6.53	6.26	0.76	11,6	10	25	80
	M3V	mg/kg	4,75	4.76	4.75	4.92	0.95	20	13	30	85
TAME	A1V	µg/ml	5,44	4.98	5.20	4.99	1.20	23	10	15	60
	G2V	µg/l	17,1	16.88	17.10	17.00	2.94	17,2	10	25	80
	M3V	mg/kg	11	10.91	10.99	11.10	1.55	14,1	10	30	100
TCEe	A1V	µg/ml	2,45	2.33	2.39	2.38	0.41	17,1	13	15	62
	G2V	µg/l	17,9	17.70	17.94	17.98	2.10	11,7	10	25	90
	M3V	mg/kg	4,6	4.66	4.60	4.67	0.34	7,3	13	30	92
TECEe	A1V	µg/ml	3,15	3.07	3.15	3.25	0.60	19	13	15	62
	G2V	µg/l	22,2	22.07	22.17	21.60	3.31	14,9	10	25	90
	M3V	mg/kg	6,06	6.06	6.06	6.41	0.82	13,5	13	30	92
TOL	A1V	µg/ml	4,16	4.16	4.27	4.11	0.68	15,8	13	15	69
	G2V	µg/l	9,83	9.81	9.83	9.69	1.20	12,2	10	25	100
	M3V	mg/kg	5,69	5.62	5.69	5.84	0.57	10	13	30	92

where

Ass. val.	the assigned value
Mean	the mean value
Mean rob	the robust mean
Md	the median value
SD %	the standard deviation as percent
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 target value for total deviation at the 95% confidence interval ($= 2 \cdot s_p$)
Accepted z-val%	the satisfactory z values: the results (%), where $\lvert z \rvert \leq 2$.

The robust deviations in the results of aromatic compounds varied from 10 % to 31 % and in the results of chlorinated compounds from 9.7 % to 23.3 %. Consequently the robust deviations of the results of oxygenates were between 11 and 23 %. The high deviation of the TAME and m/p xylene results from the synthetic sample indicated possible calibration problems.

3.2 Analytical methods

The analytical methods used by the participants are presented in Appendix 10.1.

VOC compounds in water
VOC compounds were determined using the methods which were based on several ISO standards [4-7]. All participants used either headspace or purge&trap -technique, but liquid-liquid extraction was not used. Most participants used GC-MS technique and only one participant (lab 11) GC-FID technique. With the GC-MS technique at least toluene-d8 was used as internal standard.

VOC compounds in soil
Determination of VOC compounds from soil samples were also based on several standard methods or EPAs methods [6–9]. Extraction was mostly done by shaking and only one participant heated the sample in headspace vial. Most participants used headspace as injection technique and three participants used purge&trap technique and only one split-technique. Equipment technique was mostly GC-MS and only one participant (lab 11) used GC-FID.

Statistical comparison between GC-MS and GC-FID was not possible, but according to the graphical presentation (Appendix 8) the results of the lab 11 (GC-FID) did not deviate from the other results. Method comparison was done between injection techniques and before method comparison the results were coded by coordinator as follows:

- Method 1: Headspace
- Method 2: Purge & Trap
- Method 3: Split
- Method 4: Unspecified method

No significant difference could be obtained between the methods. According to the graphical presentation the unsatisfactory results were not due to the applied technique (Appendix 10.2).

3.3 Uncertainties of the results

Most laboratories (85 %) reported the expanded uncertainties with their results (Appendix 9). The reported uncertainties varied largely especially in the analysis of water samples (Table 2). Most laboratories estimated uncertainties using the data of validation and internal quality control (Meth 3). Reported evaluation procedures of the uncertainities did not explain the high variation between uncertainties between the laboratories (Appendix 11). It is evident that harmonization in the estimation of uncertainties should be done.

Table 2. The ranges of the reported expanded uncertainties in the analysis of water and soil samples

Compounds	Uncertainties in water analysis, %	Uncertainties in soil analysis, %
Aromatics	10–100	15–55
Chlorinated compounds	10–100	10–55
Oxygenates	10–50	20–55

4 EVALUATION OF PERFORMANCE

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

When accepting deviations of 15 % from the assigned values for artificial sample A1V, 63 % of the results of the aromatic hydrocarbons, 64 % of the results of the chlorinated hydrocarbons and 72 % the oxygenate results (MTBE and TAME) were satisfactory. In this PT the number of satisfactory results was at the same level as in the previous PT 8/2008 [11].

Consequently, when accepting deviations of 25 % from the assigned value in the determination of ground water sample G2V, 90 % of the results of the aromatic compounds, 93 % of the results of the chlorinated hydrocarbons and 85 % of the oxygenate results were satisfactory. In this PT the number of the satisfactory results was slightly higher than in the previous PT 8/2008 [11], where on an average 85 % of the results of the aromatic compounds were satisfactory.

When accepting deviations of 30 % from the assigned values for the soil sample M3V, 88 % of the results of the aromatic hydrocarbons, 87 % of the results of the chlorinated hydrocarbons and 100 % of the oxygenate results were satisfactory. The number of the satisfactory results in this PT was remarkable higher than in the previous PT 8/2008 [11], where on an average 78 % of the results were satisfactory.

In total, 79 % of the total result data in this PT were satisfactory. More than the half of the participants used accredited methods. There was not any difference in performance between the accredited and not accredited determinations (Appendix 12).

For the priority substances (Table 3) mentioned in the European Union ground water directive (2006/118/EC) the amount of the accepted z-values of the participants results for G2V sample were from 75 % to 100 % (Table 1). Environmental quality standard values (EQS) for the ground waters in the directive are higher than the assigned value in this proficiency test for c12DCEe, CHCl3, DCM, oXYL, TAME and TOL, and lower than the assigned value for 124TCBz, 12DCEa, Bz, CCl4, ETBz, mpXYL, MTBE, TCEe and TECEe. The limit of quantitation for the priority substances should be 1/3 of the EQS values.

Table 3 The environmental quality standard (EQS) values for the compounds in ground waters

Compound	EQS µg/l		Compound	EQS µg/l
Benzene	0.5		Chloroform	100
Ethylbenzene	1.0		1,2-Dichloroethane	1.5
Toluene	12		1,2-Dichloroethene	25
Σ (o-, m-, p-Xylene)	10		Dichloromethane	10
Σ (Trichlorobenzenes)	2.5		MTBE	7.5
Carbontetrachloride	2		TAME	60
Σ (Trichloroethene and Tetrachloroethene)	5			

Σ = sum of compounds

5 SUMMARY

Proftest SYKE carried out the proficiency test for the determinations of volatile organic compounds (VOC) in water and soil samples in November 2010. In total, 13 laboratories participated in the proficiency test. One artificial sample (A1V), one ground water sample (G2V) and one soil sample (M3V) were delivered to the laboratories.

The calculated concentrations (sample A1V) or the robust mean of the results reported by the participants (samples G2V and M3V) were used as the assigned values for measurands. The uncertainties of the calculated assigned values were less than 1 %. Respectively the uncertainties of the consensus assigned values (the robust mean) were from 5.1 % to 16 %.

In total, 79 % of the total result data in this PT were satisfactory when the deviations of 15–30 % from the assigned values were accepted.

6 YHTEENVETO

Proftest SYKE järjesti pätevyyskokeen haihtuvien orgaanisten yhdisteiden määrityksistä vesi- ja maanäytteistä marraskuussa 2010. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 13 laboratoriota.

Synteettisessä näytteessä (A1V) mittaussuureen vertailuarvona käytettiin laskennallista pitoisuutta (teoreettinen arvo) ja vesi- ja maanäytteissä (G2V ja M3V) osallistujien raportoimien tulosten keskiarvoa (sopimusarvo). VOC-yhdisteiden laskennallisten vertailuarvojen laajennetut epävarmuudet olivat alle 1 %. Yhdisteestä ja raportoitujen tulosten hajonnasta riippuen vertailuarvon laajennettu epävarmuus 5.1–16 %, kun vertailuarvona käytettiin sopimusarvoa.

Synteettisten näytteiden tuloksissa sallittiin 15 %:n poikkeama vertailuarvosta, jolloin aromaattisten yhdisteiden tuloksista hyväksyttäviä oli 63 %, öljyn lisäaineiden tuloksista (MTBE ja TAME) 72 % ja kloorattujen hiilivetyjen tuloksista 64 %. Vuoden 2008 vastaavassa vertailussa hyväksyttävien tulosten määrä oli samaa tasoa.

Vesinäytteiden tuloksissa sallittiin 25 %:n poikkeama vertailuarvosta, jolloin aromaattisten yhdisteiden tuloksista oli hyväksyttäviä 90 %, öljyn lisäainetuloksista 85 % ja kloorattujen hiilivetyjen tuloksista 93 %. Vuoden 2008 vastaavassa vertailussa aromaattisten yhdisteiden tuloksista oli hyväksyttäviä 70 %, öljyn lisäaineiden tuloksista 78 % ja kloorattujen hiilivetyjen tuloksista 88 %.

Maanäytteen tulosten sallittiin poiketa vertailuarvosta 30 %, jolloin aromaattisten hiilivetyjen tuloksista oli hyväksyttäviä 88 %, öljyn lisäaineiden tuloksista 100 % ja kloorattujen hiilivetyjen tuloksia 87 %. Vuoden 2008 vastaavassa vertailussa sekä aromaattisten yhdisteiden että kloorattujen hiilivetyjen tuloksista oli hyväksyttäviä 74 % ja öljyn lisäaineiden tuloksista 80 %.

Euroopan unionin pohjavesidirektiivissä (2006/118/EY, valtioneuvoston asetus 341/2009) prioriteetti aineiden (Table 3) z-arvoista G2V näytteessä 75–100 % oli hyväksyttyjä (Table 1). Pohjavesidirektiivin yhdisteiden ympäristölaatunormit (EQS) ovat korkeammat kuin tässä pätevyyskokeessa tavoitearvot seuraaville yhdisteille; c12DCEe, CHCl3, DCM, oXYL, TAME ja TOL, ja alemmat kuin tavoitearvot seuraaville yhdisteille; 124TCBz, 12DCEa, Bz, CCl4, ETBz, mpXYL, MTBE, TCEe ja TECEe. Direktiivissä mainittujen yhdisteiden määritysrajojen tulisi olla kolmasosa EQS-arvoista.

Tässä pätevyyskokeessa koko aineistossa hyväksyttäviä tuloksia oli yhteensä 79 %. Akkreditoitujen ja akkreditoimattomien määritysten tuloksissa hyväksyttäviä oli saman verran. Vesi- ja maanäytteiden VOC-tuloksissa oli enemmän hyväksyttäviä tuloksia kuin vuoden 2008 vastaavassa vertailussa, kun taas synteettisen näytteen tuloksissa hyväksyttäviä tuloksia lähes saman verran.

7 REFERENCES

1 ISO/IEC 17043, 2010. Conformity assessment – General requirements for proficiency testing.

2 ISO 13528, 2005. Statistical methods for use in proficiency testing by interlaboratory comparisons.

3 Thompson. M., Ellison. S.L. R., Wood. R., 2005. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC). International Union of Pure and Applied Chemistry. Analytical. Applied and Clinical Chemistry Division. Interdivisional Working Party for Harmonization of Quality Assurance Schemes for Analytical Laboratories.

4 ISO 10301:1997, Water quality – Determination of highly volatile halogenated hydrocarbons – Gas chromatographic methods

5 ISO 11423-1:1997, Water quality - Determination of benzene and some derivatives - Part 1: Head-space gas chromatographic method

6 ISO 15680:2003, Water quality – Gas-chromatographic determination of number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption.

7 ISO 22155:2005, Soil quality – Gas chromatographic quantitative determination of volatile aromatic and halogenated hydrocarbons and selected ethers – Static headspace method.

8 EPA 5035A, Closed-system purge-and-trap and extraction for volatile organics in soil and waste samples.

9 EPA 8260C, Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS).

10 ISO 15009:2002, Soil quality – Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons – Purge-and-trap method with thermal desorption.

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

PARTICIPANTS IN THE PT SYKE 8a/2010

Comie stc, Siffano, Italy

Ekokem Oy Ab, Riihimäki, Finland

Eurofins Environment Sweden AB, Lidköping, Sweden

Eurofins Miljø A/S, Vejen, Denmark

Eurofins Scientific Finland Oy, Tampere, Finland

Finnish Environment Institute, SYKE, Helsinki, Finland

Kokemäenjoen vesistön vesiensuojelu ry, Hämeenlinna, Finland

Lapin Vesitutkimus Oy, Rovaniemi, Finland

MetropoliLab Oy, Helsinki, Finland

NabLabs Ympäristöanalytiikka Oy, Oulu, Finland

Novalab Oy, Karkkila, Finland

Ramboll Analytics Oy, Lahti, Finland

SGS Inspection Services Oy, Hamina, Finland

PREPARATION OF THE SAMPLES

Each individual stock solution was prepared by weighting methanol (10 ml) and from 0.15 to 33 g of the pure compound into a vial. The concentrations of the analytes in the individual stock solutions have been presented in the table 1 below.

The mixture 1 was prepared by weighing from 0.5 to 3.0 ml of the individual stock solutions (compounds shown in the table 1) into a vial, the final volume of the mixture 1 was 11.6 ml. The mixture 2 was prepared by weighing from 0.9 to 4.6 ml of the individual stock solution (compounds shown in the table 1) into a vial, the final volume of the mixture 2 was 18.5 ml. The mixture 3 was prepared by weighing from 6.0 to 7.0 ml of the individual stock solution (compounds shown in the table 1) into a vial, the final volume was 13 ml.

Table 1. Concentrations of the stock solutions and the mixtures

Compound producer, purity	**Stock solution, mg/ml**	**Mixture 1 mg/ml**	**Mixture 2 mg/ml**	**Mixture 3 mg/ml**
Benzene Fluka, 99.9 %	16.44	2.72		
Ethylbenzene Fluka, >99.5 %	16.70	2.75		
Toluene Fluka, 99.9 %	16.67	3.46		
o-Xylene Fluka, 99.5 %	16.79	2.80		
p-Xylene Fluka, 99.5 %	16.79	4.25		
1,2,4-Trichlorobenzene Fluka, 99.5 %	28.22	1.13		
Carbontetrachloride Ehrenstorfer, 99.5 %	31.54		1.58	
Chloroform Fluka, > 99.9 %	29.64		3.18	
1,2-Dichloroethane Ehrenstorfer, 99.5 %	24.86		2.62	
cis-1,2-Dichloroethene Fluka, > 97 %	25.02		4.09	
Dichloromethane Aldrich, > 99.9	26.12		2.83	
Trichloroethene Riedel-de Haën, 99.9 %	29.05		6.32	
Tetrachloroethene Fluka, >99.9 %	32.75		8.11	
MTBE Sigma Aldrich, 99.8 %	14.82			8.00
TAME Aldrich, ≥ 97 %	15.11			6.95

PREPARATION OF THE SAMPLES

The addition solution 1 was prepared by weighting 10 ml of methanol, 1.5 ml of the mixture 1, 0.5 ml of the mixture 2 and 0.9 ml of the mixture 3 into a vial. The sample A1V was prepared by diluting 1 ml of the addition solution 1 with 95 ml methanol (Table 2).

The addition solution 2 was prepared by weighting 4 ml of the mixture 1, 4 ml of the mixture 2 and 3 ml of the mixture 3 into a vial. Addition solution 2 was diluted three times with methanol in ratio 1:10 (v/v) and the final methanol solution (195 ml) was diluted with 20 litre of ground water to get the sample G2V (Table 2).

The addition solution 3 was prepared by weighting 45 ml of methanol, 2 ml of the mixture 1, 1 ml of the mixture 2 and 2 ml of the mixture 3. The sample M3V was made by mixing 20 g of dry soil, 4 ml of water, 1 ml of the addition solution 3 and 20 ml of methanol (Table 2).

Table 2. Concentrations of the addition solutions (1, 2, 3) and the samples (A1V, G2V, M3V)

Measurement	**Addition solution 1 mg/ml**	**Addition solution 2 mg/ml**	**Addition solution 3 mg/ml**	**A1V µg/ml**	**G2V µg/l**	**M3V mg/kg**
Benzene	0.306	0.981	0.108	3.26	10.72	5.38
Ethylbenzene	0.310	0.995	0.109	3.31	10.87	5.46
Toluene	0.390	1.251	0.137	4.16	13.67	6.86
o-Xylene	0.315	1.011	0.111	3.36	11.05	5.55
p-Xylene	0.478	1.534	0.168	5.10	16.76	8.42
1,2,4-Trichlorobenzene	0.127	0.407	0.045	1.35	4.45	2.23
Carbontetra-chloride	0.058	0.584	0.30	0.61	6.38	1.49
Chloroform	0.116	1.174	0.060	1.24	12.82	2.99
1,2-Dichloroethane	0.095	0.968	0.049	1.02	10.57	2.47
cis-1,2-Dichloroethene	0.149	1.507	0.077	1.59	16.46	3.84
Dichloromethane	0.103	1.042	0.053	1.10	11.39	2.66
Trichloroethene	0.230	2.330	0.119	2.45	25.46	5.95
Tetrachloroethene	0.295	2.989	0.153	3.15	32.65	7.63
MTBE	0.587	2.162	0.297	6.27	23.61	14.87
TAME	0.510	1.877	0.258	5.44	20.51	12.91

TESTING OF HOMOGENEITY

The homogeneities of the samples G2V and M3V were tested by analysing seven sub samples.

Analyte / Sample	**Conc.** µg/l or mg/kg	**s_p%**	**s_p**	**s_a**	**s_a / s_p**	**Was s_a / s_p < 0.5?**	**s_{bb}**	**s_{bb}^2**	**c**	**Was s_{bb}^2 < c?**
o-Xylene/G2V	7.97	12.5	1.00	0.18	0.2	yes	0.12	0.02	0.23	yes
o-Xylene/M3V	5.07	15	0.76	0.14	0.2	yes	0.15	0.02	0.14	yes
1,2,4-TCBz/G2V	3.23	12.5	0.40	0.14	0.3	yes	0.10	0.01	0.06	yes
1,2,4-TCBz/M3V	2.11	15	0.32	0.10	0.3	yes	0.02	< 0.01	0.31	yes
TECEe/G2V	26.8	12.5	3.35	1.04	0.3	yes	0.73	0.54	3.66	yes
TeCEe/M3V	6.96	15	1.04	0.32	0.3	yes	0.21	0.04	0.30	yes
MTBE/G2V	21.1	12.5	2.63	0.25	0.1	yes	0.17	0.03	1.40	yes
MTBE/M3V	12.5	15	1.88	0.54	0.3	yes	0.38	0.14	1.11	yes

Conc. = Concentration
s_p = Target deviation, 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 = 2.01 when the number of sub samples is 7
F2 = 1.25 when the number of sub samples is 7

Conclusion: In each case $s_a / s_p < 0.5$ and $s_{bb}^2 < c$. The samples could be regarded as homogenous.

TESTING OF STABILITY

The samples were distributed 16 November 2010 and they were asked to analyse before 19 November 2010.

Sample A1V / concentration µg/ml

Analyte	**Assigned value**	**16 Nov**	**19 Nov 4 °C**	**19 Nov 25 °C**	D	**0.3 · s_p**	**Test pasted?**
Benzene	3.26	3.19	3.16	3.18	0.02	0.07	Yes
Ethylbenzene	3.31	3.17	2.99	3.03	0.04	0.07	Yes
Toluene	4.16	4.16	4.04	4.11	0.07	0.09	Yes
o-Xylene	3.36	3.22	3.13	3.19	0.06	0.07	Yes
m/p-Xylene	5.10	5.10	4.83	4.89	0.06	0.11	Yes
1,2,4-Trichlorobenzene	1.35	1.37	1.28	1.29	0.01	0.03	Yes
Carbontetra-chloride	0.61	0.80	0.73	0.75	0.01	0.02	Yes
Chloroform	1.24	1.28	1.22	1.23	0.01	0.03	Yes
1,2-Dichloroethane	1.02	1.06	0.99	1.00	0.01	0.02	Yes
cis-1,2-Dichloroethene	1.59	1.61	1.57	1.58	0.01	0.04	Yes
Dichloromethane	1.10	1.10	1.08	1.09	0.02	0.02	Yes
Trichloroethene	2.45	2.40	2.42	2.43	0.01	0.05	Yes
Tetrachloroethene	3.15	3.37	3.35	3.41	0.06	0.07	Yes
MTBE	6.27	5.65	5.62	5.68	0.05	0.13	Yes
TAME	5.44	4.96	4.91	4.92	0.01	0.11	Yes

Conclusion: The stability of the samples during the transport was good.

TESTING OF STABILITY

The samples were distributed 16 November 2010 and they were asked to analyse before 19 November 2010.

Sample G2V / concentration µg/l

Analyte	**Assigned value**	**16 Nov**	**19 Nov 4 °C**	**19 Nov 25 °C**	D	**0.3 · s_p**	**Test pasted?**
Benzene	8.30	9.31	8.65	8.74	0.13	0.32	Yes
Ethylbenzene	6.51	7.81	6.74	6.48	0.26	0.25	No
Toluene	9.83	11.31	10.02	10.41	0.39	0.38	No
o-Xylene	6.53	7.97	6.82	6.93	0.10	0.26	Yes
m/p-Xylene	10.9	13.48	12.14	12.40	0.26	0.46	Yes
1,2,4-Trichlorobenzene	2.82	3.16	3.45	2.16	1.29	0.13	No
Carbontetra-chloride	4.29	6.03	5.45	5.84	0.39	0.20	No
Chloroform	9.87	11.99	11.63	11.56	0.06	0.44	Yes
1,2-Dichloroethane	8.90	10.47	10.56	10.22	0.35	0.40	Yes
cis-1,2-Dichloroethene	13.1	14.58	14.27	14.36	0.09	0.53	Yes
Dichloromethane	8.96	10.26	10.50	10.36	0.13	0.39	Yes
Trichloroethene	17.9	20.68	19.82	20.72	0.90	0.74	No
Tetrachloroethene	22.2	27.88	25.55	28.38	2.83	0.96	No
MTBE	20.5	20.74	20.98	20.29	0.69	0.79	Yes
TAME	17.1	18.22	17.59	17.23	0.35	0.66	Yes

The stability results were within the daily variation of the method and as well as the variation between the bottles. When the samples were delivered to the participants only one laboratory reported the temperature of the samples to be higher than 10 °C. The results of this laboratory for the sample G2V were satisfactory ($z < 2$).

Conclusion: The stability of the samples during the transport was mainly good.

TESTING OF STABILITY

The samples were distributed 16 November 2010 and they were asked to analyse before 19 November 2010.

Sample M3V / concentration mg/kg

Analyte	**Assigned value**	**28 Oct**	**19 Nov 4 °C**	**19 Nov 25 °C**	D	**0.3 · s_p**	**Test pasted?**
Benzene	4.22	4.73	3.88	4.02	0.14	0.18	Yes
Ethylbenzene	4.49	4.90	4.18	4.26	0.08	0.19	Yes
Toluene	5.69	6.16	5.53	5.63	0.10	0.25	Yes
o-Xylene	4.75	5.17	4.44	4.48	0.05	0.20	Yes
m/p-Xylene	7.21	7.83	6.76	6.86	0.10	0.30	Yes
1,2,4-Trichlorobenzene	2.23	2.07	1.96	1.98	0.02	2.09	Yes
Carbontetra-chloride	1.19	1.34	1.35	1.37	0.03	0.06	Yes
Chloroform	2.39	2.76	2.37	2.40	0.02	0.11	Yes
1,2-Dichloroethane	2.47	2.36	2.08	2.10	0.03	0.09	Yes
cis-1,2-Dichloroethene	2.91	3.42	2.86	2.95	0.09	0.13	Yes
Dichloromethane	2.37	2.23	2.35	2.25	0.10	0.11	Yes
Trichloroethene	4.60	3.92	4.57	4.62	0.06	0.21	Yes
Tetrachloroethene	6.06	6.64	7.08	7.12	0.04	0.32	Yes
MTBE	12.4	12.85	10.76	11.02	0.27	0.48	Yes
TAME	11.0	11.59	9.16	9.30	0.13	0.41	Yes

Conclusion: The stability of the samples during the transport was good.

FEEDBACK FROM THE PARTICIPANTS

Lab	Comment	Action/SYKE
all	The weight after receiving of the sample V2G was asked to report although the initial weight was not given in the covering letter with the samples.	Evaporation of water samples is not probable.
3	The samples arrived to the local bus station 15 November late afternoon.	The delivering time is from 8 to 16 o'clock and it will be written down in the consignment note.
9	In the sheet of the notification of sample receiving the formula for the calculation of the weight difference-% could be added.	This good idea will be taken into account in next PTs.

FEEDBACK TO THE PARTICIPANTS

Lab	Comments from the provider
4	Method description was lacking.
12	Method description was lacking.
13	The participant sent the results 29 November, but did not inform the provider that the results are not arriving on time.

ASSIGNED VALUES AND THEIR UNCERTAINTIES

Analyte Abbreviation	Sample	Assigned value	Unit	Evaluation of the assigned value	Uncertainty ($U = 2\ u_c$) %
Benzene Bz	A1V	3.26	µg/ml	Calculated	< 1
	G2V	8.30	µg/l	Robust mean	8.6
	M3V	4.22	mg/kg	Robust mean	7.7
Ethylbenzene ETBz	A1V	3.31	µg/ml	Calculated	< 1
	G2V	6.51	µg/l	Robust mean	13
	M3V	4.49	mg/kg	Robust mean	11
Tolune TOL	A1V	4.16	µg/ml	Calculated	< 1
	G2V	9.83	µg/l	Robust mean	9.6
	M3V	5.62	mg/kg	Robust mean	6.9
o-Xylene oXYL	A1V	3.36	µg/ml	Calculated	< 1
	G2V	6.53	µg/l	Robust mean	9.2
	M3V	4.75	mg/kg	Robust mean	14
m/p-Xylene mpXYL	A1V	5.10	µg/ml	Calculated	< 1
	G2V	10.9	µg/l	Robust mean	12
	M3V	7.21	mg/kg	Robust mean	15
1,2,4-Trichlorobenzene 124TCBz	A1V	1.35	µg/ml	Calculated	< 1
	G2V	2.96	µg/l	Robust mean	15
	M3V	2.23	mg/kg	Robust mean	14
Carbontetrachloride CCl4	A1V	0.61	µg/ml	Calculated	< 1
	G2V	4.29	µg/l	Robust mean	17
	M3V	1.17	mg/kg	Robust mean	10
Chloroform CHCl3	A1V	1.24	µg/ml	Calculated	< 1
	G2V	9.87	µg/l	Robust mean	8.7
	M3V	2.39	mg/kg	Robust mean	9.9
1,2-Dichloroethane 12DCEa	A1V	1.02	µg/ml	Calculated	< 1
	G2V	8.90	µg/l	Robust mean	10
	M3V	2.47	mg/kg	Robust mean	16
cis-1,2-Dichloroethene c12DCEe	A1V	1.59	µg/ml	Calculated	< 1
	G2V	13.1	µg/l	Robust mean	8.6
	M3V	2.99	mg/kg	Robust mean	8.5
Dichloromethane DCM	A1V	1.10	µg/ml	Calculated	< 1
	G2V	8.89	µg/l	Robust mean	11
	M3V	2.37	mg/kg	Robust mean	13
Trichloroethene TCEe	A1V	2.45	µg/ml	Calculated	< 1
	G2V	17.9	µg/l	Robust mean	9.3
	M3V	4.60	mg/kg	Robust mean	5.1
Tetrachloroethene TECEe	A1V	3.15	µg/ml	Calculated	< 1
	G2V	22.2	µg/l	Robust mean	12
	M3V	6.06	mg/kg	Robust mean	9.4
MTBE	A1V	6.27	µg/ml	Calculated	< 1
	G2V	20.5	µg/l	Robust mean	10
	M3V	12.4	mg/kg	Robust mean	10
TAME	A1V	5.44	µg/ml	Calculated	< 1
	G2V	17.1	µg/l	Robust mean	14
	M3V	11.0	mg/kg	Robust mean	11

LIITE 7. RESULTS OF EACHLABORATORY

APPENDIX 7.

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
124TCBz	µg/ml	A1V		0,593	yes	1,35	15	1,41	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		0,979	yes	2,82	25	3,165	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		-0,105	yes	2,23	30	2,195	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		3,268	yes	1,02	15	1,27	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		0,566	yes	8,9	25	9,53	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		1,012	yes	2,47	30	2,845	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-0,184	yes	3,26	15	3,215	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		-0,048	yes	8,3	25	8,25	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		0,292	yes	4,22	30	4,405	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		-0,671	yes	1,59	15	1,51	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		-0,214	yes	13,1	25	12,75	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		0,424	yes	2,91	30	3,095	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		1,770	yes	0,61	15	0,691	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		1,231	yes	4,29	25	4,95	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		0,644	yes	1,19	30	1,305	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		0,753	yes	1,24	15	1,31	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		0,361	yes	9,87	25	10,32	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		1,032	yes	2,39	30	2,76	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		1,030	yes	1,1	15	1,185	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		0,232	yes	8,96	25	9,22	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		0,689	yes	2,37	30	2,615	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-0,967	yes	3,31	15	3,07	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-0,055	yes	6,51	25	6,465	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		-0,134	yes	4,49	30	4,4	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-0,327	yes	5,1	15	4,975	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-0,701	yes	10,9	25	9,945	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		-0,129	yes	7,21	30	7,07	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-0,797	yes	6,27	15	5,895	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		0,312	yes	20,5	25	21,3	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		0,618	yes	12,4	30	13,55	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-0,694	yes	3,36	15	3,185	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		0,122	yes	6,53	25	6,63	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		0,000	yes	4,75	30	4,75	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-1,924	yes	5,44	15	4,655	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		-0,398	yes	17,1	25	16,25	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		-0,242	yes	11	30	10,6	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		0,245	yes	2,45	15	2,495	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		0,737	yes	17,9	25	19,55	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		0,522	yes	4,6	30	4,96	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		0,614	yes	3,15	15	3,295	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		0,739	yes	22,2	25	24,25	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		0,699	yes	6,06	30	6,695	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		0,112	yes	4,16	15	4,195	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		0,334	yes	9,83	25	10,24	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		0,188	yes	5,69	30	5,85	5,816	5,659	0,6445	11,3	12	1	0	13

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 2																
124TCBz	µg/ml	A1V		-0,840	yes	1,35	15	1,265	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		-1,007	yes	2,82	25	2,465	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		-0,792	yes	2,23	30	1,965	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-0,654	yes	1,02	15	0,97	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		0,620	yes	8,9	25	9,59	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-1,039	yes	2,47	30	2,085	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-0,450	yes	3,26	15	3,15	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		-0,135	yes	8,3	25	8,16	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		-0,498	yes	4,22	30	3,905	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		-0,293	yes	1,59	15	1,555	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		0,076	yes	13,1	25	13,22	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		-0,069	yes	2,91	30	2,88	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		2,295	yes	0,61	15	0,715	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		1,315	yes	4,29	25	4,995	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		0,840	yes	1,19	30	1,34	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		-0,430	yes	1,24	15	1,2	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		0,438	yes	9,87	25	10,41	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		-0,070	yes	2,39	30	2,365	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		-0,485	yes	1,1	15	1,06	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		0,295	yes	8,96	25	9,29	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		-0,028	yes	2,37	30	2,36	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-1,269	yes	3,31	15	2,995	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		0,498	yes	6,51	25	6,915	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		-0,401	yes	4,49	30	4,22	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-0,640	yes	5,1	15	4,855	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		1,017	yes	10,9	25	12,29	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		-0,375	yes	7,21	30	6,805	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-1,287	yes	6,27	15	5,665	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		-0,453	yes	20,5	25	19,34	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		-0,782	yes	12,4	30	10,95	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-0,873	yes	3,36	15	3,14	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		0,496	yes	6,53	25	6,935	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		-0,386	yes	4,75	30	4,475	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-1,176	yes	5,44	15	4,96	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		-0,299	yes	17,1	25	16,46	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		-1,021	yes	11	30	9,315	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		-0,191	yes	2,45	15	2,415	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		0,476	yes	17,9	25	18,96	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		-0,058	yes	4,6	30	4,56	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		0,254	yes	3,15	15	3,21	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		0,807	yes	22,2	25	24,44	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		1,117	yes	6,06	30	7,075	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		-0,385	yes	4,16	15	4,04	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		-0,004	yes	9,83	25	9,825	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		-0,158	yes	5,69	30	5,555	5,816	5,659	0,6445	11,3	12	1	0	13

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 3																
124TCBz	µg/ml	A1V		-5,037	yes	1,35	15	0,84	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		-2,043	yes	2,82	25	2,1	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		-2,362	yes	2,23	30	1,44	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-2,353	yes	1,02	15	0,84	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		-1,335	yes	8,9	25	7,415	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-2,726	yes	2,47	30	1,46	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-2,965	yes	3,26	15	2,535	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		-1,764	yes	8,3	25	6,47	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		-1,359	yes	4,22	30	3,36	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		-2,096	yes	1,59	15	1,34	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		-0,885	yes	13,1	25	11,65	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		-0,710	yes	2,91	30	2,6	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		-4,481	yes	0,61	15	0,405	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		-2,135	yes	4,29	25	3,145	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		-2,493	yes	1,19	30	0,745	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		-5,054	yes	1,24	15	0,77	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		-1,074	yes	9,87	25	8,545	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		-1,688	yes	2,39	30	1,785	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		-1,394	yes	1,1	15	0,985	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		-0,603	yes	8,96	25	8,285	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		-0,999	yes	2,37	30	2,015	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-6,908	H	3,31	15	1,595	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-5,161	H	6,51	25	2,31	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		-1,767	yes	4,49	30	3,3	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-5,791	yes	5,1	15	2,885	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-5,336	H	10,9	25	3,63	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		-1,498	yes	7,21	30	5,59	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-1,967	yes	6,27	15	5,345	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		0,820	yes	20,5	25	22,6	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		-0,806	yes	12,4	30	10,9	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-6,944	H	3,36	15	1,61	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		-5,201	H	6,53	25	2,285	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		-1,930	yes	4,75	30	3,375	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-5,466	yes	5,44	15	3,21	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		-3,111	yes	17,1	25	10,45	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		-1,918	yes	11	30	7,835	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		-4,299	yes	2,45	15	1,66	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		-2,498	yes	17,9	25	12,31	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		-0,007	yes	4,6	30	4,595	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		-3,852	yes	3,15	15	2,24	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		-2,178	yes	22,2	25	16,16	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		-1,001	yes	6,06	30	5,15	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		-3,782	yes	4,16	15	2,98	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		-1,872	yes	9,83	25	7,53	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		-1,687	yes	5,69	30	4,25	5,816	5,659	0,6445	11,3	12	1	0	13

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 4																
124TCBz	µg/ml	A1V		2,370	yes	1,35	15	1,59	1,285	1,333	0,2608	19,5	12	0	0	12
	mg/kg	M3V		-1,794	yes	2,23	30	1,63	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		3,137	yes	1,02	15	1,26	0,98	0,9918	0,1364	13,7	12	1	0	13
	mg/kg	M3V		-2,024	yes	2,47	30	1,72	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		2,086	yes	3,26	15	3,77	3,17	3,181	0,3937	12,3	12	1	0	13
	mg/kg	M3V		-1,232	yes	4,22	30	3,44	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		2,851	yes	1,59	15	1,93	1,555	1,552	0,1909	12,3	10	1	0	11
	mg/kg	M3V		-0,825	yes	2,91	30	2,55	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		5,027	yes	0,61	15	0,84	0,7005	0,6547	0,1289	19,6	8	3	2	13
	mg/kg	M3V		-0,896	yes	1,19	30	1,03	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		2,473	yes	1,24	15	1,47	1,25	1,268	0,2973	23,4	12	1	0	13
	mg/kg	M3V		-1,116	yes	2,39	30	1,99	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		3,273	yes	1,1	15	1,37	1,175	1,212	0,2293	18,9	12	0	0	12
	mg/kg	M3V		-1,828	yes	2,37	30	1,72	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		2,135	yes	3,31	15	3,84	3,035	3,262	0,4515	13,8	11	2	0	13
	mg/kg	M3V		-1,128	yes	4,49	30	3,73	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		3,111	yes	5,1	15	6,29	4,94	4,997	1,2	24,0	12	1	0	13
	mg/kg	M3V		-0,851	yes	7,21	30	6,29	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		1,127	yes	6,27	15	6,8	5,9	6,024	0,5837	9,7	11	1	0	12
	mg/kg	M3V		-1,839	yes	12,4	30	8,98	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		1,349	yes	3,36	15	3,7	3,175	3,357	0,4656	13,8	11	2	0	13
	mg/kg	M3V		-1,698	yes	4,75	30	3,54	4,83	4,838	0,8333	17,2	12	1	0	13
TCEe	µg/ml	A1V		2,939	yes	2,45	15	2,99	2,31	2,295	0,3188	13,8	12	1	0	13
	mg/kg	M3V		-0,797	yes	4,6	30	4,05	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		1,947	yes	3,15	15	3,61	3,17	3,035	0,468	15,4	12	1	0	13
	mg/kg	M3V		-1,199	yes	6,06	30	4,97	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		2,372	yes	4,16	15	4,90	4,065	4,13	0,579	14,0	12	1	0	13
	mg/kg	M3V		-1,277	yes	5,69	30	4,60	5,816	5,659	0,6445	11,3	12	1	0	13
Laboratory 5																
124TCBz	µg/ml	A1V		0,741	yes	1,35	15	1,425	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		1,262	yes	2,82	25	3,265	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		0,015	yes	2,23	30	2,235	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		0,131	yes	1,02	15	1,03	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		0,589	yes	8,9	25	9,555	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-1,066	yes	2,47	30	2,075	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		0,736	yes	3,26	15	3,44	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		1,123	yes	8,3	25	9,465	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		1,209	yes	4,22	30	4,985	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		0,252	yes	1,59	15	1,62	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		1,099	yes	13,1	25	14,9	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		0,596	yes	2,91	30	3,17	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V			H	0,61	15	<0,5	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		-1,473	yes	4,29	25	3,5	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		-3,557	yes	1,19	30	0,555	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		-1,398	yes	1,24	15	1,11	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		0,332	yes	9,87	25	10,28	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		-0,683	yes	2,39	30	2,145	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		3,515	yes	1,1	15	1,39	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		1,286	yes	8,96	25	10,4	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		1,238	yes	2,37	30	2,81	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		1,229	yes	3,31	15	3,615	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		1,770	yes	6,51	25	7,95	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		1,455	yes	4,49	30	5,47	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		1,987	yes	5,1	15	5,86	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		1,615	yes	10,9	25	13,1	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		1,553	yes	7,21	30	8,89	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-0,627	yes	6,27	15	5,975	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		0,527	yes	20,5	25	21,85	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		0,403	yes	12,4	30	13,15	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		2,401	yes	3,36	15	3,965	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		2,842	yes	6,53	25	8,85	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		2,084	yes	4,75	30	6,235	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-2,169	yes	5,44	15	4,555	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		0,117	yes	17,1	25	17,35	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		0,151	yes	11	30	11,25	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		-1,197	yes	2,45	15	2,23	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		-0,045	yes	17,9	25	17,8	17,98	17,79	2,441	13,7	10	0	0	10

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
	mg/kg	M3V		-0,725	yes	4,6	30	4,1	4,632	4,685	0,4746	10,1	12	1	0	13
Laboratory 5																
TECEe	µg/ml	A1V		0,804	yes	3,15	15	3,34	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		1,099	yes	22,2	25	25,25	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		0,429	yes	6,06	30	6,45	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		1,058	yes	4,16	15	4,49	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		1,196	yes	9,83	25	11,3	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		0,773	yes	5,69	30	6,35	5,816	5,659	0,6445	11,3	12	1	0	13
Laboratory 6																
124TCBz	µg/ml	A1V		-2,370	yes	1,35	15	1,11	1,285	1,333	0,2608	19,5	12	0	0	12
	mg/kg	M3V		-0,718	yes	2,23	30	1,99	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-0,654	yes	1,02	15	0,97	0,98	0,9918	0,1364	13,7	12	1	0	13
	mg/kg	M3V		-0,877	yes	2,47	30	2,145	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-2,106	yes	3,26	15	2,745	3,17	3,181	0,3937	12,3	12	1	0	13
	mg/kg	M3V		-0,434	yes	4,22	30	3,945	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		-2,725	yes	1,59	15	1,265	1,555	1,552	0,1909	12,3	10	1	0	11
	mg/kg	M3V		-0,390	yes	2,91	30	2,74	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		0,546	yes	0,61	15	0,635	0,7005	0,6547	0,1289	19,6	8	3	2	13
	mg/kg	M3V		0,868	yes	1,19	30	1,345	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		-2,151	yes	1,24	15	1,04	1,25	1,268	0,2973	23,4	12	1	0	13
	mg/kg	M3V		-0,405	yes	2,39	30	2,245	2,365	2,384	0,3281	13,7	12	1	0	13
ETBz	µg/ml	A1V		-1,813	yes	3,31	15	2,86	3,035	3,262	0,4515	13,8	11	2	0	13
	mg/kg	M3V		0,289	yes	4,49	30	4,685	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		0,052	yes	5,1	15	5,12	4,94	4,997	1,2	24,0	12	1	0	13
	mg/kg	M3V		1,244	yes	7,21	30	8,555	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-0,936	yes	6,27	15	5,83	5,9	6,024	0,5837	9,7	11	1	0	12
	mg/kg	M3V		0,922	yes	12,4	30	14,12	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-1,409	yes	3,36	15	3,005	3,175	3,357	0,4656	13,8	11	2	0	13
	mg/kg	M3V		0,400	yes	4,75	30	5,035	4,83	4,838	0,8333	17,2	12	1	0	13
TCEe	µg/ml	A1V		-2,204	yes	2,45	15	2,045	2,31	2,295	0,3188	13,8	12	1	0	13
	mg/kg	M3V		-0,109	yes	4,6	30	4,525	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		-3,069	yes	3,15	15	2,425	3,17	3,035	0,468	15,4	12	1	0	13
	mg/kg	M3V		-0,594	yes	6,06	30	5,52	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		-1,410	yes	4,16	15	3,72	4,065	4,13	0,579	14,0	12	1	0	13
	mg/kg	M3V		0,258	yes	5,69	30	5,91	5,816	5,659	0,6445	11,3	12	1	0	13
Laboratory 7																
124TCBz	µg/ml	A1V		3,012	yes	1,35	15	1,655	1,285	1,333	0,2608	19,5	12	0	0	12
	mg/kg	M3V		0,658	yes	2,23	30	2,45	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		0,261	yes	1,02	15	1,04	0,98	0,9918	0,1364	13,7	12	1	0	13
	mg/kg	M3V		5,884	H	2,47	30	4,65	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		0,614	yes	3,26	15	3,41	3,17	3,181	0,3937	12,3	12	1	0	13
	mg/kg	M3V		6,051	H	4,22	30	8,05	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		1,048	yes	1,59	15	1,715	1,555	1,552	0,1909	12,3	10	1	0	11
	mg/kg	M3V		8,339	H	2,91	30	6,55	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		2,678	yes	0,61	15	0,7325	0,7005	0,6547	0,1289	19,6	8	3	2	13
	mg/kg	M3V		5,658	H	1,19	30	2,2	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		2,366	yes	1,24	15	1,46	1,25	1,268	0,2973	23,4	12	1	0	13
	mg/kg	M3V		7,280	H	2,39	30	5	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		3,818	yes	1,1	15	1,415	1,175	1,212	0,2293	18,9	12	0	0	12
	mg/kg	M3V		17,950	H	2,37	30	8,75	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		3,766	yes	3,31	15	4,245	3,035	3,262	0,4515	13,8	11	2	0	13
	mg/kg	M3V		11,890	H	4,49	30	12,5	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		3,686	yes	5,1	15	6,51	4,94	4,997	1,2	24,0	12	1	0	13
	mg/kg	M3V		9,052	H	7,21	30	17	7,205	7,31	1,427	19,5	12	1	0	13
oXYL	µg/ml	A1V		3,929	yes	3,36	15	4,35	3,175	3,357	0,4656	13,8	11	2	0	13
	mg/kg	M3V		13,680	H	4,75	30	14,5	4,83	4,838	0,8333	17,2	12	1	0	13
TCEe	µg/ml	A1V		-0,762	yes	2,45	15	2,31	2,31	2,295	0,3188	13,8	12	1	0	13
	mg/kg	M3V		4,928	H	4,6	30	8	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		2,116	yes	3,15	15	3,65	3,17	3,035	0,468	15,4	12	1	0	13
	mg/kg	M3V		4,884	H	6,06	30	10,5	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		1,795	yes	4,16	15	4,72	4,065	4,13	0,579	14,0	12	1	0	13
	mg/kg	M3V		5,108	H	5,69	30	10,05	5,816	5,659	0,6445	11,3	12	1	0	13

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 8																
124TCBz	µg/ml	A1V		-0,914	yes	1,35	15	1,258	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		-0,262	yes	2,82	25	2,728	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		0,614	yes	2,23	30	2,436	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-0,190	yes	1,02	15	1,006	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		-0,990	yes	8,9	25	7,799	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		0,084	yes	2,47	30	2,501	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		2,806	yes	3,26	15	3,946	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		-0,481	yes	8,3	25	7,801	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		0,363	yes	4,22	30	4,45	4,215	4,173	0,4678	11,2	12	1	0	13
CCl4	µg/ml	A1V		3,585	yes	0,61	15	0,774	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		-1,782	yes	4,29	25	3,335	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		-0,233	yes	1,19	30	1,148	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		0,871	yes	1,24	15	1,321	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		-1,016	yes	9,87	25	8,616	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		1,254	yes	2,39	30	2,84	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		0,806	yes	1,1	15	1,167	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		-0,498	yes	8,96	25	8,402	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		0,990	yes	2,37	30	2,722	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		0,769	yes	3,31	15	3,501	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-0,222	yes	6,51	25	6,329	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		1,163	yes	4,49	30	5,273	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		3,953	yes	5,1	15	6,612	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-0,055	yes	10,9	25	10,82	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		0,737	yes	7,21	30	8,008	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		2,362	yes	6,27	15	7,38	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		-0,521	yes	20,5	25	19,16	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		0,462	yes	12,4	30	13,26	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		0,319	yes	3,36	15	3,441	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		-0,268	yes	6,53	25	6,312	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		1,035	yes	4,75	30	5,488	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		3,276	yes	5,44	15	6,777	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		1,165	yes	17,1	25	19,59	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		1,336	yes	11	30	13,21	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		1,293	yes	2,45	15	2,688	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		-0,630	yes	17,9	25	16,49	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		1,857	yes	4,6	30	5,881	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		1,380	yes	3,15	15	3,476	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		-0,714	yes	22,2	25	20,22	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		1,161	yes	6,06	30	7,116	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		3,059	yes	4,16	15	5,114	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		-0,631	yes	9,83	25	9,055	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		0,866	yes	5,69	30	6,429	5,816	5,659	0,6445	11,3	12	1	0	13

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 9																
12DCEa	µg/ml	A1V		-2,294	yes	1,02	15	0,8445	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		-0,679	yes	8,9	25	8,145	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-2,888	yes	2,47	30	1,4	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-0,348	yes	3,26	15	3,175	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		0,135	yes	8,3	25	8,44	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		-0,024	yes	4,22	30	4,205	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		1,048	yes	1,59	15	1,715	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		0,733	yes	13,1	25	14,3	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		-0,115	yes	2,91	30	2,86	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		1,858	yes	0,61	15	0,695	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		1,734	yes	4,29	25	5,22	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		-0,056	yes	1,19	30	1,18	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		0,968	yes	1,24	15	1,33	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		1,159	yes	9,87	25	11,3	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		-0,112	yes	2,39	30	2,35	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		0,909	yes	1,1	15	1,175	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		0,915	yes	8,96	25	9,985	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		-0,844	yes	2,37	30	2,07	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-1,954	yes	3,31	15	2,825	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-1,352	yes	6,51	25	5,41	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		0,067	yes	4,49	30	4,535	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-2,288	yes	5,1	15	4,225	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-1,277	yes	10,9	25	9,16	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		-0,620	yes	7,21	30	6,54	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-0,255	yes	6,27	15	6,15	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		0,566	yes	20,5	25	21,95	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		-0,914	yes	12,4	30	10,7	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-1,845	yes	3,36	15	2,895	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		-0,404	yes	6,53	25	6,2	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		0,232	yes	4,75	30	4,915	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		0,245	yes	5,44	15	5,54	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		1,076	yes	17,1	25	19,4	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		-0,488	yes	11	30	10,2	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		0,354	yes	2,45	15	2,515	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		0,849	yes	17,9	25	19,8	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		-0,159	yes	4,6	30	4,49	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		-1,291	yes	3,15	15	2,845	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		-0,396	yes	22,2	25	21,1	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		-0,671	yes	6,06	30	5,45	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		-0,737	yes	4,16	15	3,93	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		0,081	yes	9,83	25	9,93	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		-0,152	yes	5,69	30	5,56	5,816	5,659	0,6445	11,3	12	1	0	13

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																
124TCBz	µg/ml	A1V		-1,432	yes	1,35	15	1,205	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		1,362	yes	2,82	25	3,3	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		-1,599	yes	2,23	30	1,695	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-0,719	yes	1,02	15	0,965	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		0,944	yes	8,9	25	9,95	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-0,837	yes	2,47	30	2,16	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-0,777	yes	3,26	15	3,07	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		1,639	yes	8,3	25	10	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		0,079	yes	4,22	30	4,27	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		-1,342	yes	1,59	15	1,43	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		0,275	yes	13,1	25	13,55	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		0,607	yes	2,91	30	3,175	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		-2,951	yes	0,61	15	0,475	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		1,138	yes	4,29	25	4,9	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		-0,868	yes	1,19	30	1,035	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		-1,398	yes	1,24	15	1,11	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		0,592	yes	9,87	25	10,6	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		0,140	yes	2,39	30	2,44	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		0,849	yes	1,1	15	1,17	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		1,062	yes	8,96	25	10,15	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		0,506	yes	2,37	30	2,55	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-0,967	yes	3,31	15	3,07	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		1,770	yes	6,51	25	7,95	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		-0,401	yes	4,49	30	4,22	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-0,784	yes	5,1	15	4,8	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		0,917	yes	10,9	25	12,15	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		-0,573	yes	7,21	30	6,59	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-0,744	yes	6,27	15	5,92	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		2,478	yes	20,5	25	26,85	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		0,027	yes	12,4	30	12,45	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-1,111	yes	3,36	15	3,08	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		0,882	yes	6,53	25	7,25	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		-0,695	yes	4,75	30	4,255	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-0,306	yes	5,44	15	5,315	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		2,058	yes	17,1	25	21,5	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		-0,091	yes	11	30	10,85	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		-2,068	yes	2,45	15	2,07	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		1,274	yes	17,9	25	20,75	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		0,101	yes	4,6	30	4,67	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		-2,243	yes	3,15	15	2,62	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		1,622	yes	22,2	25	26,7	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		-0,127	yes	6,06	30	5,945	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		-0,785	yes	4,16	15	3,915	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		1,685	yes	9,83	25	11,9	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		-0,387	yes	5,69	30	5,36	5,816	5,659	0,6445	11,3	12	1	0	13

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

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 11																
124TCBz	µg/ml	A1V		-1,086	yes	1,35	15	1,24	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V				2,82	25	<6,0	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		-0,194	yes	2,23	30	2,165	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-2,288	yes	1,02	15	0,845	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		1,258	yes	8,9	25	10,3	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		0,229	yes	2,47	30	2,555	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-1,411	yes	3,26	15	2,915	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		-0,096	yes	8,3	25	8,2	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		0,237	yes	4,22	30	4,37	4,215	4,173	0,4678	11,2	12	1	0	13
CCl4	µg/ml	A1V			H	0,61	15	<1,00	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V				4,29	25	<20	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V			H	1,19	30	<2,5	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		13,710	H	1,24	15	2,515	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V			H	9,87	25	<15	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		0,642	yes	2,39	30	2,62	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		-0,364	yes	1,1	15	1,07	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V			H	8,96	25	<15	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		0,802	yes	2,37	30	2,655	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-1,188	yes	3,31	15	3,015	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-0,934	yes	6,51	25	5,75	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		0,631	yes	4,49	30	4,915	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-0,837	yes	5,1	15	4,78	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-0,991	yes	10,9	25	9,55	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		0,550	yes	7,21	30	7,805	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-1,478	yes	6,27	15	5,575	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		-0,234	yes	20,5	25	19,9	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		0,403	yes	12,4	30	13,15	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-1,210	yes	3,36	15	3,055	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		-0,894	yes	6,53	25	5,8	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		0,477	yes	4,75	30	5,09	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-1,066	yes	5,44	15	5,005	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		-0,187	yes	17,1	25	16,7	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		0,727	yes	11	30	12,2	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		-1,796	yes	2,45	15	2,12	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		-0,112	yes	17,9	25	17,65	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		0,196	yes	4,6	30	4,735	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		-1,587	yes	3,15	15	2,775	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		-0,631	yes	22,2	25	20,45	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		0,187	yes	6,06	30	6,23	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		-1,234	yes	4,16	15	3,775	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		-0,513	yes	9,83	25	9,2	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		0,310	yes	5,69	30	5,955	5,816	5,659	0,6445	11,3	12	1	0	13

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 12																
124TCBz	µg/ml	A1V		-0,494	yes	1,35	15	1,3	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		-0,340	yes	2,82	25	2,7	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		-0,090	yes	2,23	30	2,2	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		-0,261	yes	1,02	15	1,0	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		-0,449	yes	8,9	25	8,4	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-0,459	yes	2,47	30	2,3	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		-1,063	yes	3,26	15	3,0	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		0,096	yes	8,3	25	8,4	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		0,284	yes	4,22	30	4,4	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		0,922	yes	1,59	15	1,7	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		-0,061	yes	13,1	25	13	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		1,581	yes	2,91	30	3,6	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		1,967	yes	0,61	15	0,7	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		0,205	yes	4,29	25	4,4	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		1,176	yes	1,19	30	1,4	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		-0,430	yes	1,24	15	1,2	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		-0,057	yes	9,87	25	9,8	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		0,865	yes	2,39	30	2,7	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		-4,848	yes	1,1	15	0,7	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		-1,661	yes	8,96	25	7,1	9,11	9,073	1,059	11,6	8	1	1	10
	mg/kg	M3V		-0,759	yes	2,37	30	2,1	2,455	2,412	0,3458	14,3	10	1	0	11
ETBz	µg/ml	A1V		-1,249	yes	3,31	15	3,0	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-1,118	yes	6,51	25	5,6	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		-0,876	yes	4,49	30	3,9	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		-7,059	yes	5,1	15	2,4	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-4,404	yes	10,9	25	4,9	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		-3,153	yes	7,21	30	3,8	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		-0,149	yes	6,27	15	6,2	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		-0,976	yes	20,5	25	18	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		1,398	yes	12,4	30	15	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		-0,635	yes	3,36	15	3,2	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		-1,139	yes	6,53	25	5,6	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		-0,772	yes	4,75	30	4,2	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		-1,569	yes	5,44	15	4,8	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		-0,047	yes	17,1	25	17	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		0,606	yes	11	30	12	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		-0,272	yes	2,45	15	2,4	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		-0,849	yes	17,9	25	16	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		0,290	yes	4,6	30	4,8	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		1,058	yes	3,15	15	3,4	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		-0,793	yes	22,2	25	20	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		-0,396	yes	6,06	30	5,7	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		0,128	yes	4,16	15	4,2	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		-0,431	yes	9,83	25	9,3	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		0,129	yes	5,69	30	5,8	5,816	5,659	0,6445	11,3	12	1	0	13

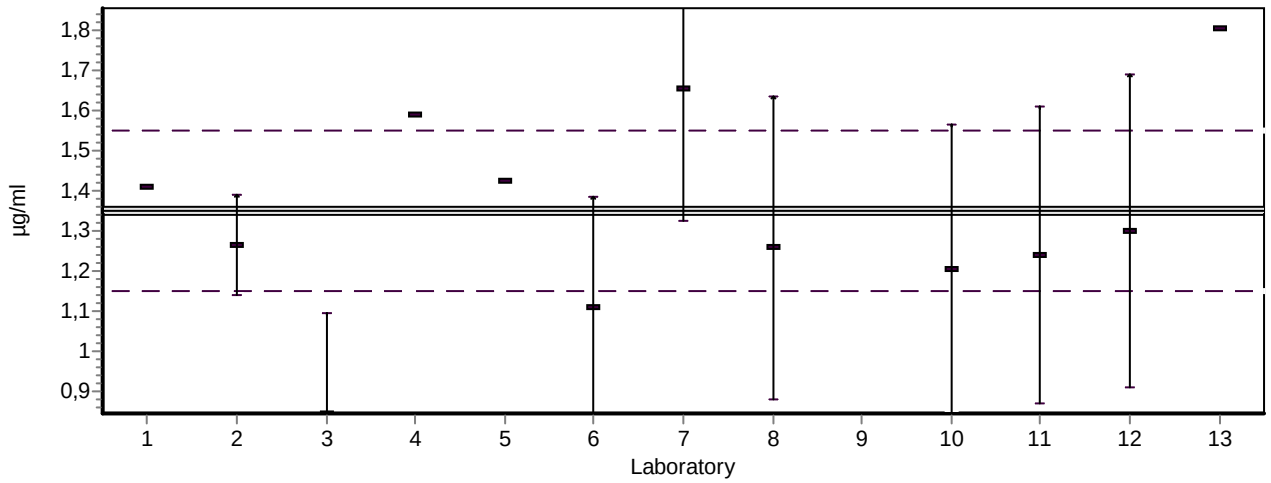
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

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 13																
124TCBz	µg/ml	A1V		4,519	yes	1,35	15	1,808	1,285	1,333	0,2608	19,5	12	0	0	12
	µg/l	G2V		4,851	yes	2,82	25	4,53	2,97	3,054	0,7607	24,9	8	0	1	9
	mg/kg	M3V		1,973	yes	2,23	30	2,89	2,18	2,125	0,4021	18,9	12	0	0	12
12DCEa	µg/ml	A1V		6,928	H	1,02	15	1,55	0,98	0,9918	0,1364	13,7	12	1	0	13
	µg/l	G2V		-0,517	yes	8,9	25	8,325	9,1	8,927	1,032	11,5	10	0	0	10
	mg/kg	M3V		-1,615	yes	2,47	30	1,872	2,115	2,101	0,4377	20,8	12	1	0	13
Bz	µg/ml	A1V		8,307	H	3,26	15	5,291	3,17	3,181	0,3937	12,3	12	1	0	13
	µg/l	G2V		-0,578	yes	8,3	25	7,7	8,36	8,283	0,9974	12,0	10	0	0	10
	mg/kg	M3V		-0,208	yes	4,22	30	4,088	4,215	4,173	0,4678	11,2	12	1	0	13
c12DCEe	µg/ml	A1V		7,610	H	1,59	15	2,498	1,555	1,552	0,1909	12,3	10	1	0	11
	µg/l	G2V		-0,806	yes	13,1	25	11,78	13,4	13,15	1,256	9,6	8	0	0	8
	mg/kg	M3V		-0,635	yes	2,91	30	2,633	2,91	2,914	0,3053	10,4	10	1	0	11
CCl4	µg/ml	A1V		10,590	H	0,61	15	1,095	0,7005	0,6547	0,1289	19,6	8	3	2	13
	µg/l	G2V		-0,177	yes	4,29	25	4,195	4,4	4,287	0,8231	19,2	9	0	1	10
	mg/kg	M3V		-0,135	yes	1,19	30	1,166	1,169	1,103	0,264	23,9	10	2	1	13
CHCl3	µg/ml	A1V		7,753	yes	1,24	15	1,961	1,25	1,268	0,2973	23,4	12	1	0	13
	µg/l	G2V		-0,754	yes	9,87	25	8,94	9,8	9,871	1,022	10,3	8	1	1	10
	mg/kg	M3V		-0,163	yes	2,39	30	2,332	2,365	2,384	0,3281	13,7	12	1	0	13
DCM	µg/ml	A1V		7,067	yes	1,1	15	1,683	1,175	1,212	0,2293	18,9	12	0	0	12
	µg/l	G2V		-1,000	yes	8,96	25	7,84	9,11	9,073	1,059	11,6	8	1	1	10
ETBz	µg/ml	A1V		6,924	H	3,31	15	5,029	3,035	3,262	0,4515	13,8	11	2	0	13
	µg/l	G2V		-0,387	yes	6,51	25	6,195	6,41	6,56	0,9451	14,4	9	1	0	10
	mg/kg	M3V		0,998	yes	4,49	30	5,162	4,56	4,545	0,663	14,5	12	1	0	13
mpXYL	µg/ml	A1V		8,029	C	5,1	15	8,171	4,94	4,997	1,2	24,0	12	1	0	13
	µg/l	G2V		-0,785	yes	10,9	25	9,83	10,57	10,51	2,029	19,3	9	1	0	10
	mg/kg	M3V		2,133	yes	7,21	30	9,517	7,205	7,31	1,427	19,5	12	1	0	13
MTBE	µg/ml	A1V		4,920	H	6,27	15	8,584	5,9	6,024	0,5837	9,7	11	1	0	12
	µg/l	G2V		-1,458	yes	20,5	25	16,77	21,1	20,92	2,872	13,7	10	0	0	10
	mg/kg	M3V		-0,069	yes	12,4	30	12,27	12,72	12,41	1,505	12,1	12	0	0	12
oXYL	µg/ml	A1V		6,593	H	3,36	15	5,021	3,175	3,357	0,4656	13,8	11	2	0	13
	µg/l	G2V		-0,227	yes	6,53	25	6,345	6,384	6,72	0,9548	14,2	9	1	0	10
	mg/kg	M3V		1,371	yes	4,75	30	5,727	4,83	4,838	0,8333	17,2	12	1	0	13
TAME	µg/ml	A1V		4,763	H	5,44	15	7,383	4,95	4,99	0,9468	18,9	9	1	0	10
	µg/l	G2V		-1,401	yes	17,1	25	14,11	17	16,87	3,137	18,5	10	0	0	10
	mg/kg	M3V		0,379	yes	11	30	11,63	11,1	10,85	1,54	14,1	10	0	0	10
TCEe	µg/ml	A1V		7,875	H	2,45	15	3,897	2,31	2,295	0,3188	13,8	12	1	0	13
	µg/l	G2V		-0,114	yes	17,9	25	17,64	17,98	17,79	2,441	13,7	10	0	0	10
	mg/kg	M3V		-0,015	yes	4,6	30	4,59	4,632	4,685	0,4746	10,1	12	1	0	13
TECEe	µg/ml	A1V		7,945	C	3,15	15	5,027	3,17	3,035	0,468	15,4	12	1	0	13
	µg/l	G2V		-0,031	yes	22,2	25	22,11	21,6	22,18	3,194	14,4	10	0	0	10
	mg/kg	M3V		0,438	yes	6,06	30	6,458	6,325	6,129	0,716	11,6	12	1	0	13
TOL	µg/ml	A1V		8,428	H	4,16	15	6,79	4,065	4,13	0,579	14,0	12	1	0	13
	µg/l	G2V		-0,037	yes	9,83	25	9,785	9,69	9,833	1,238	12,5	10	0	0	10
	mg/kg	M3V		0,171	yes	5,69	30	5,835	5,816	5,659	0,6445	11,3	12	1	0	13

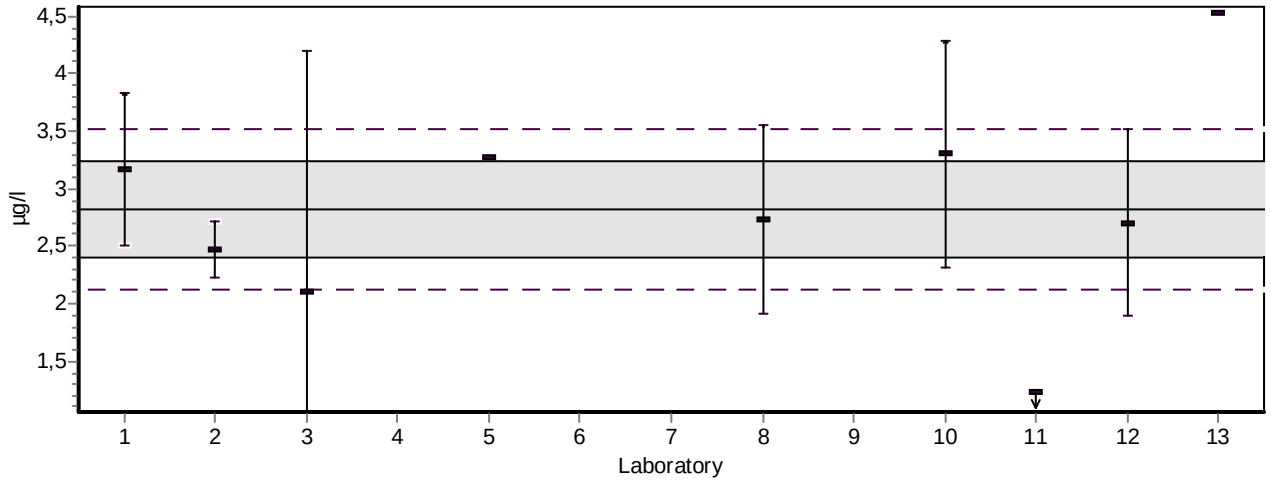
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

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

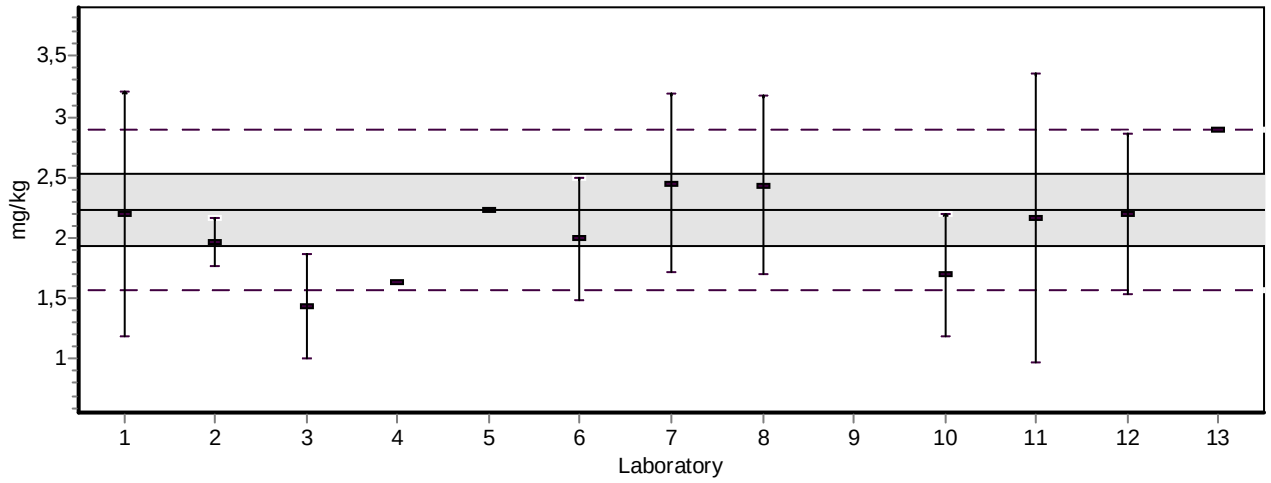
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* A1V



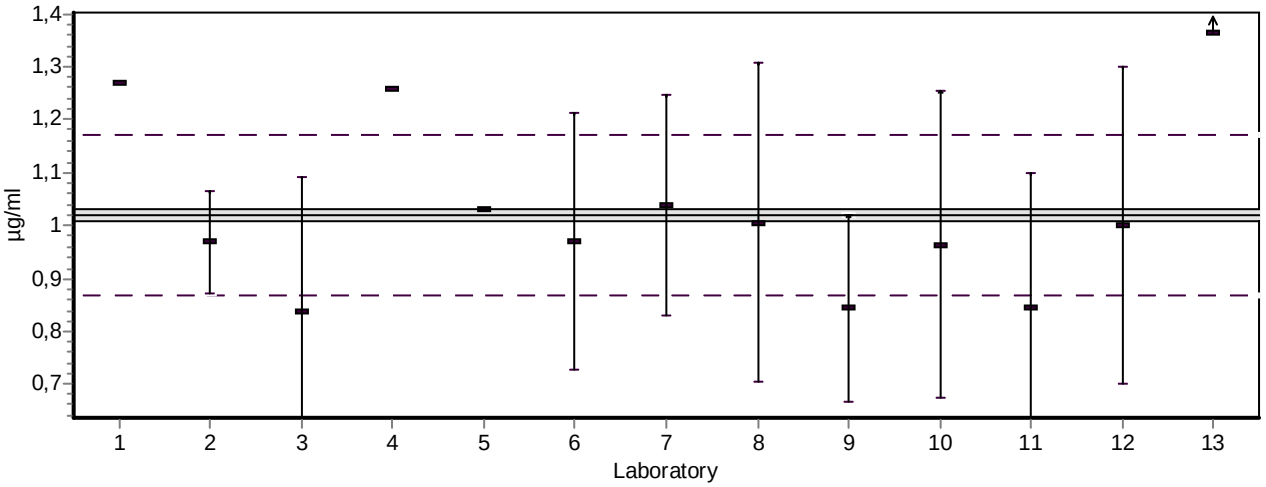
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* G2V



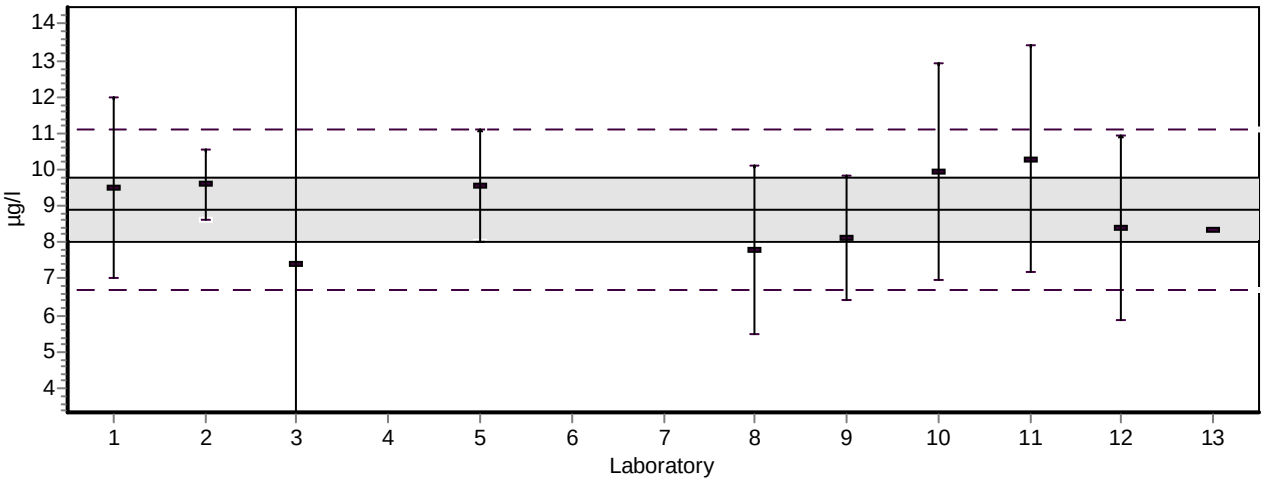
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* M3V



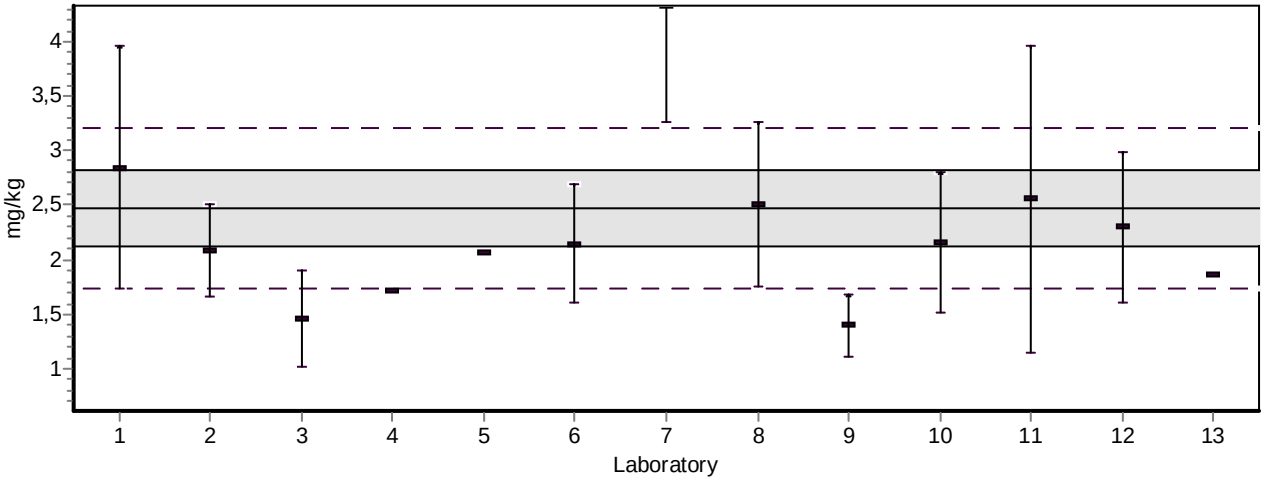
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* A1V



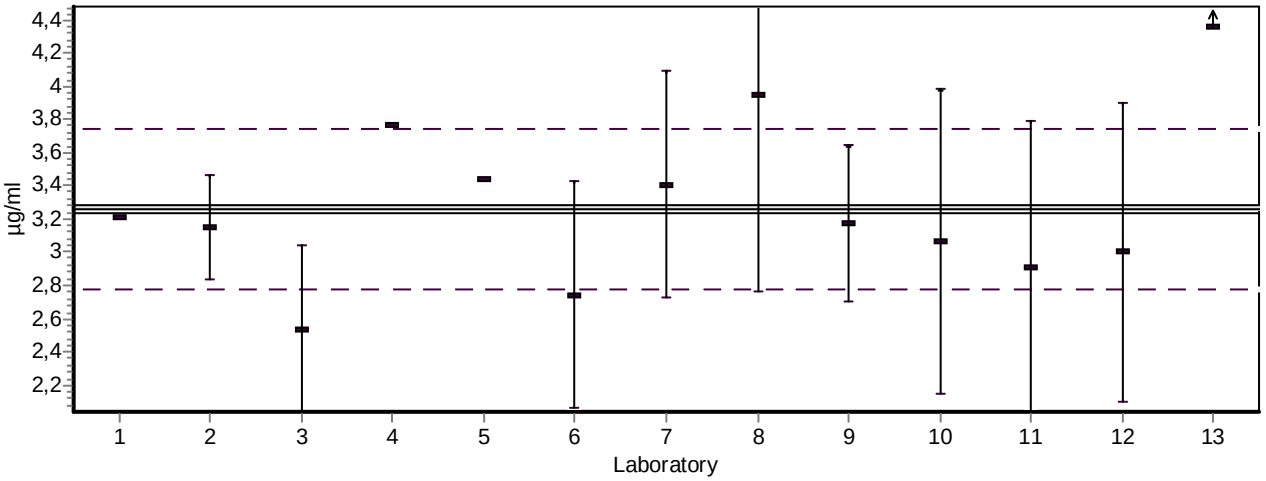
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* G2V



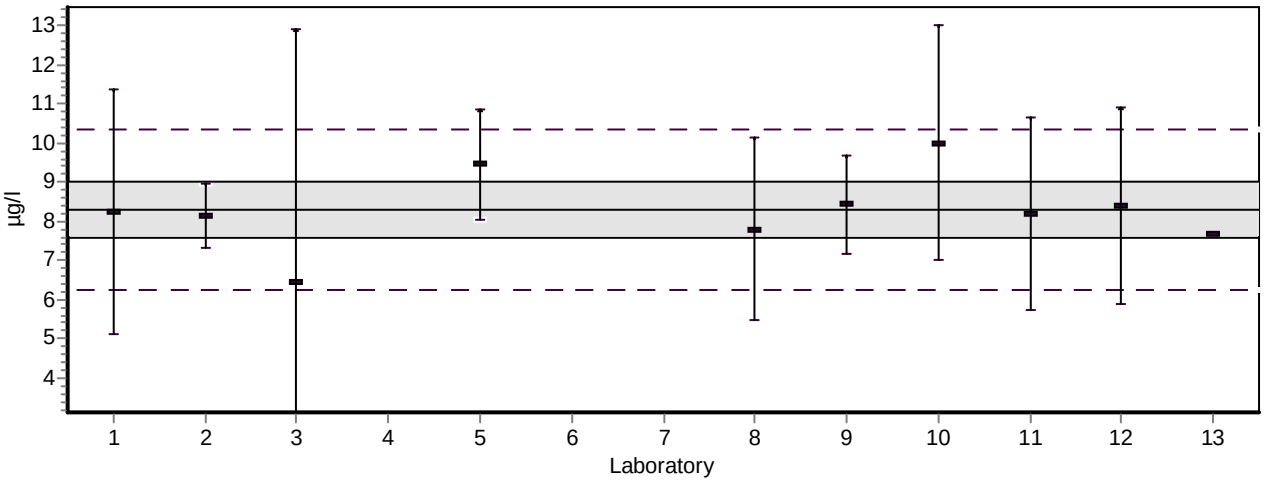
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* M3V



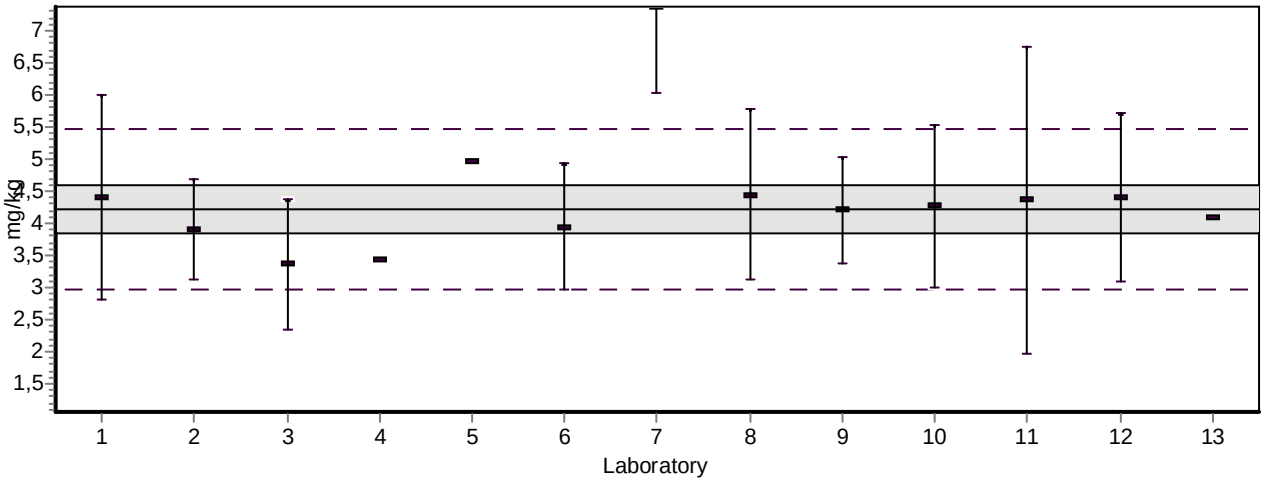
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* A1V



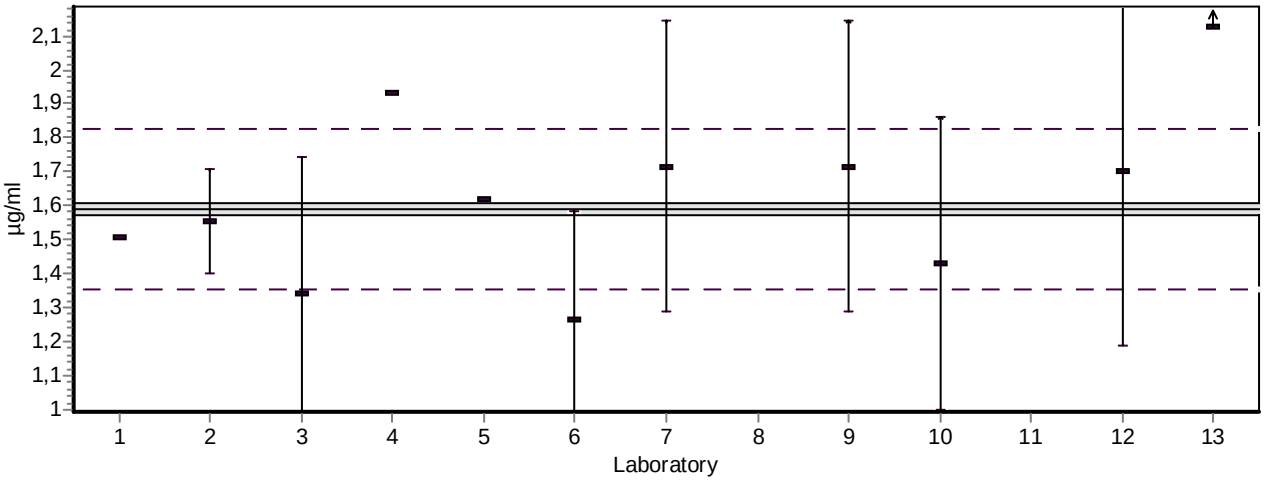
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* G2V



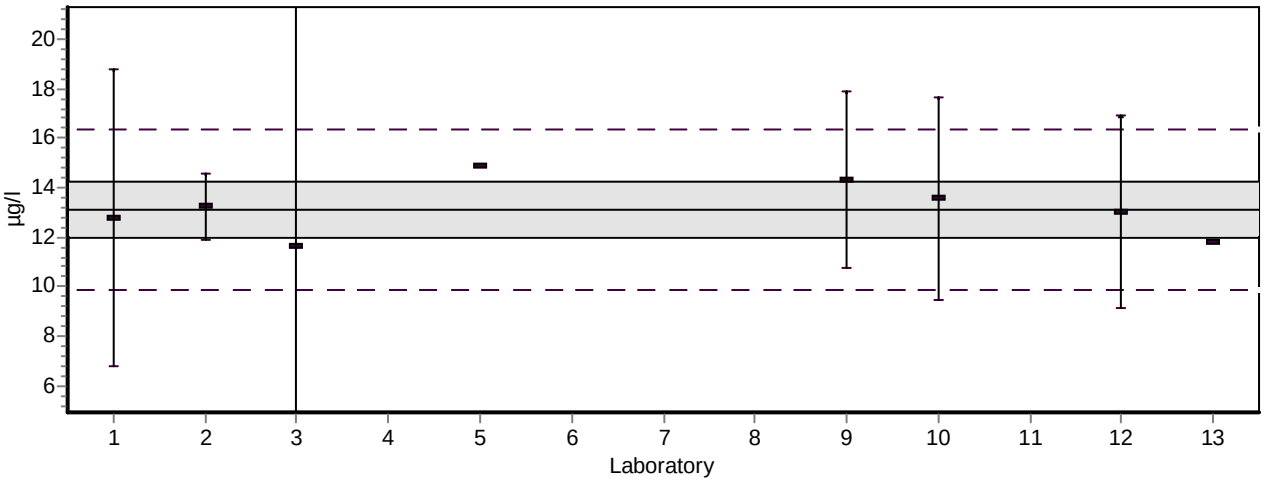
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* M3V



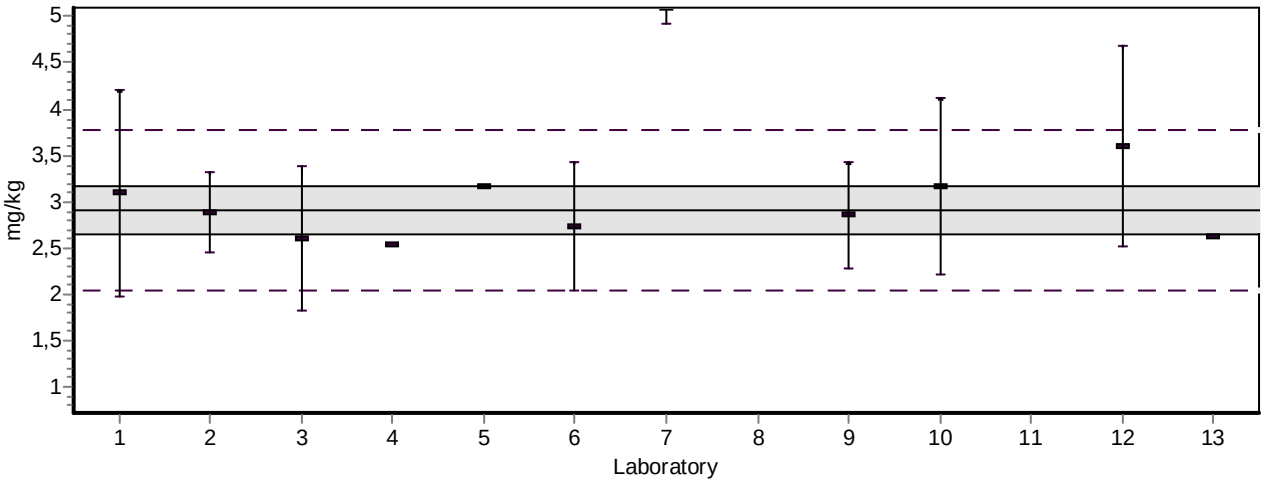
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* A1V



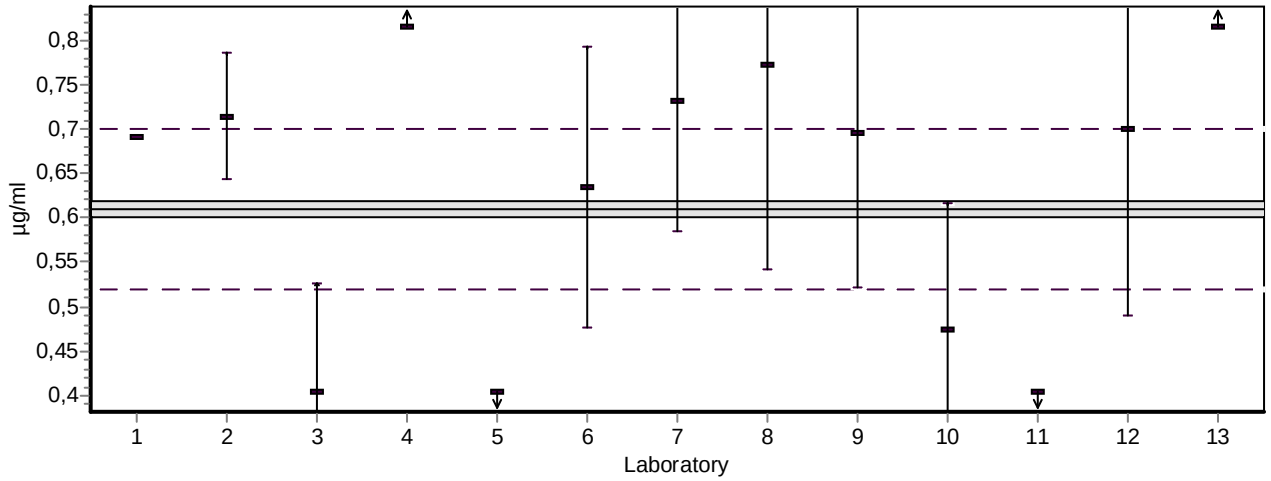
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* G2V



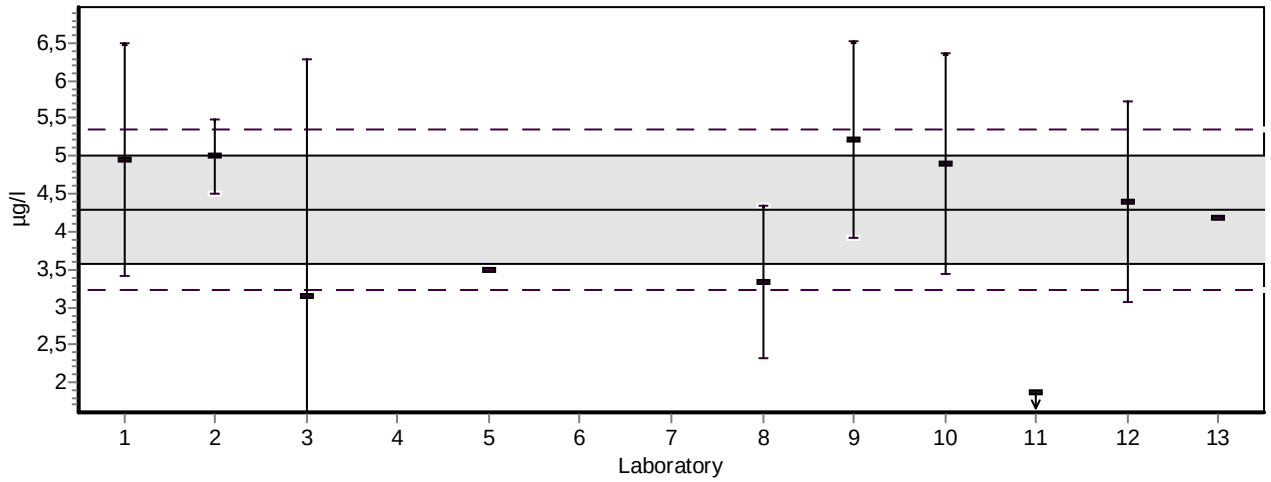
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* M3V



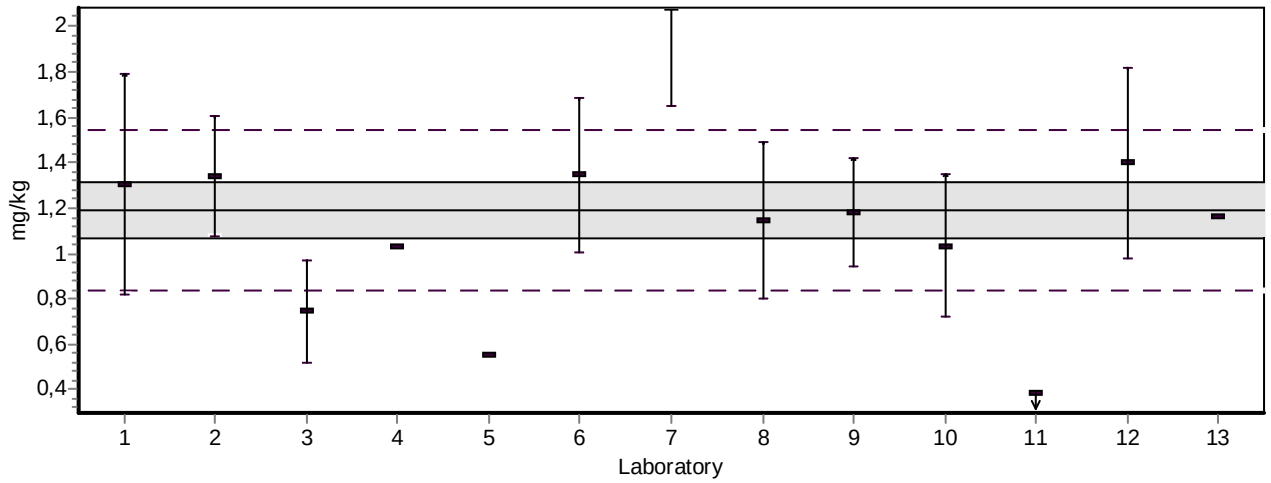
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* A1V



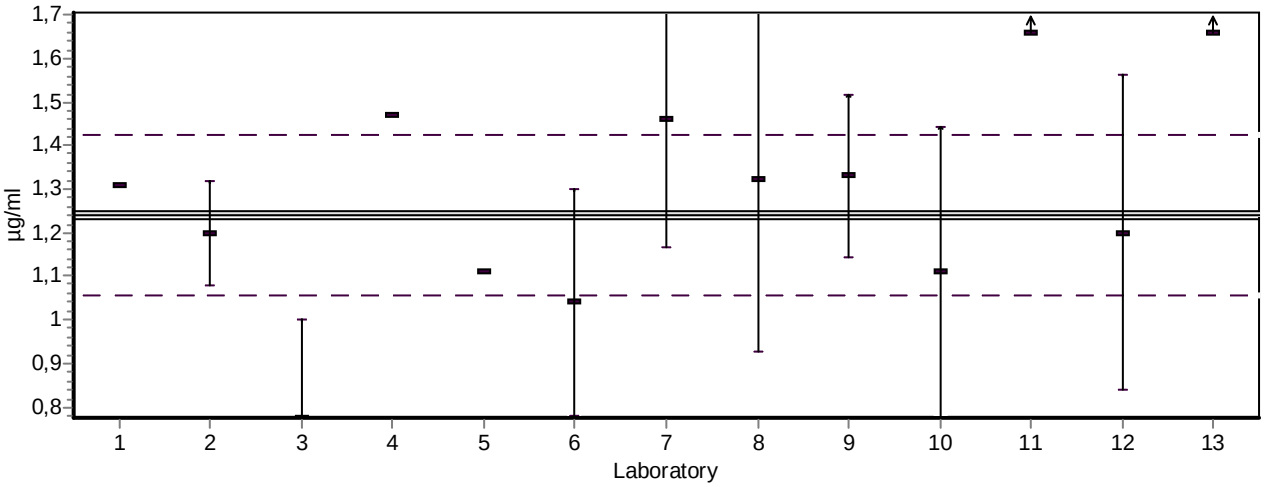
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* G2V



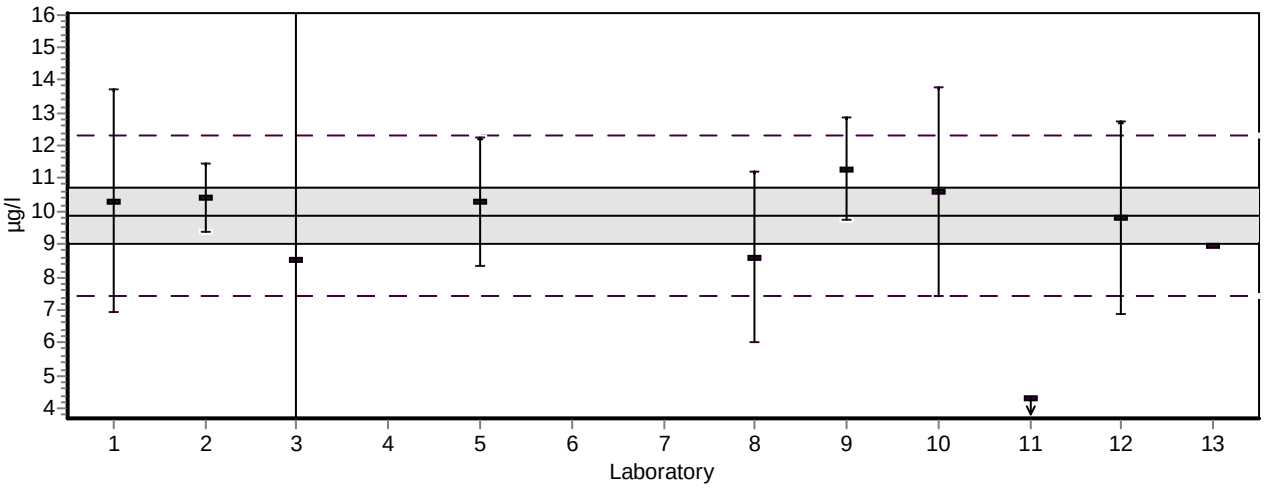
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* M3V



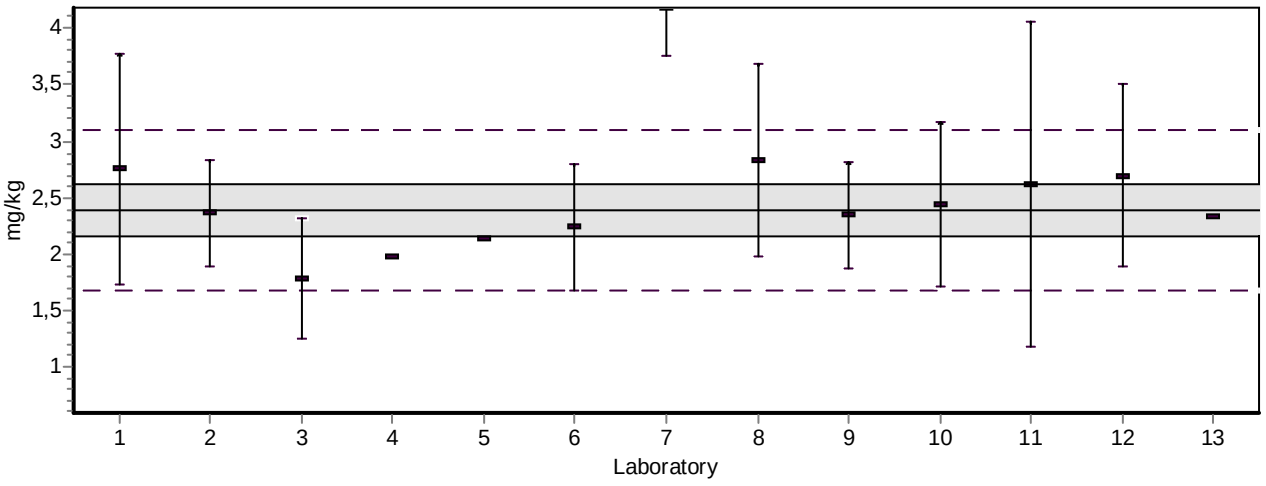
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* A1V



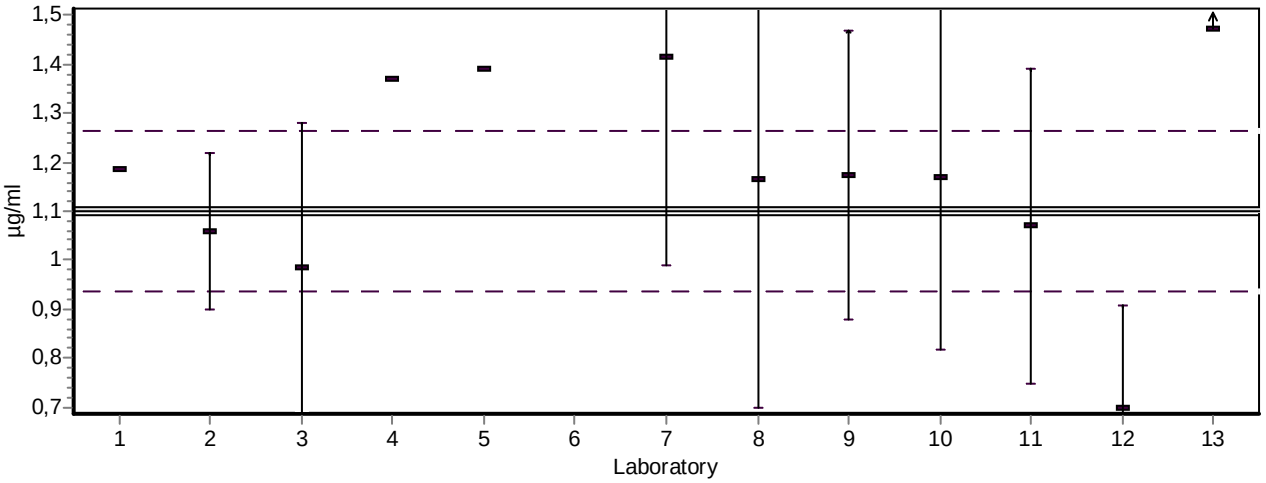
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* G2V



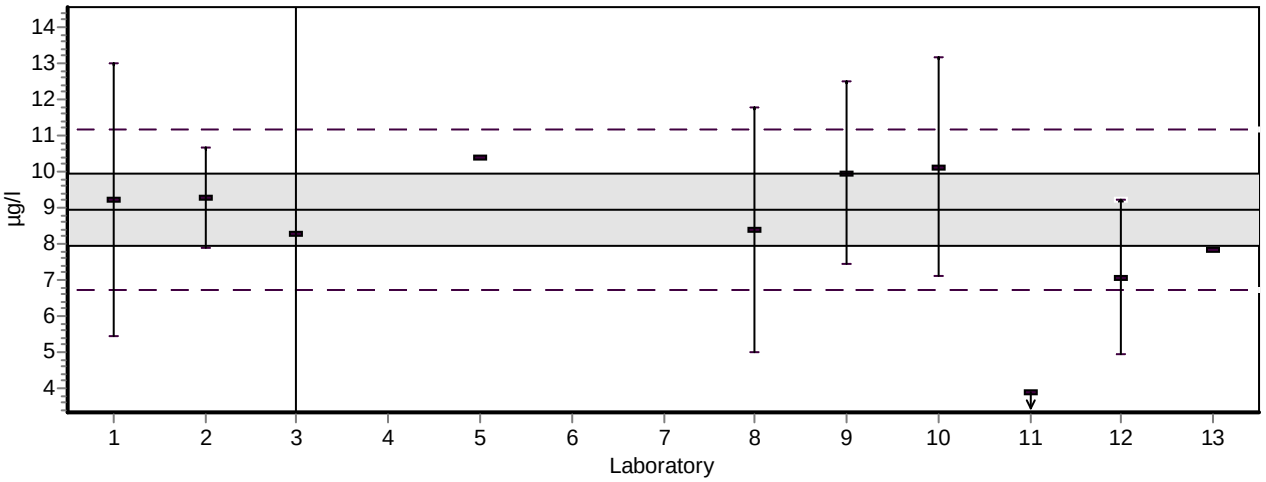
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* M3V



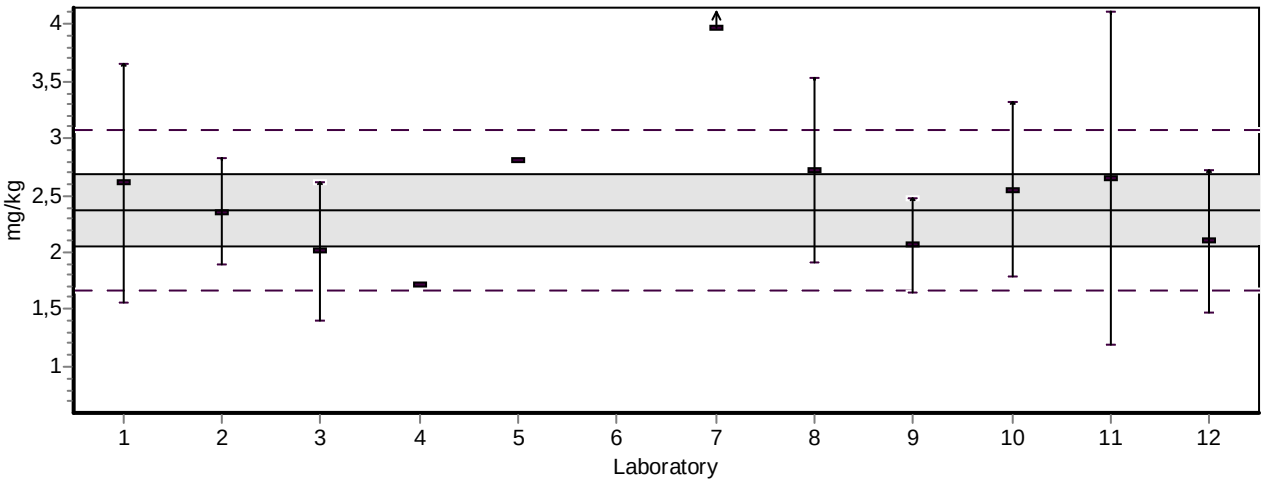
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* A1V



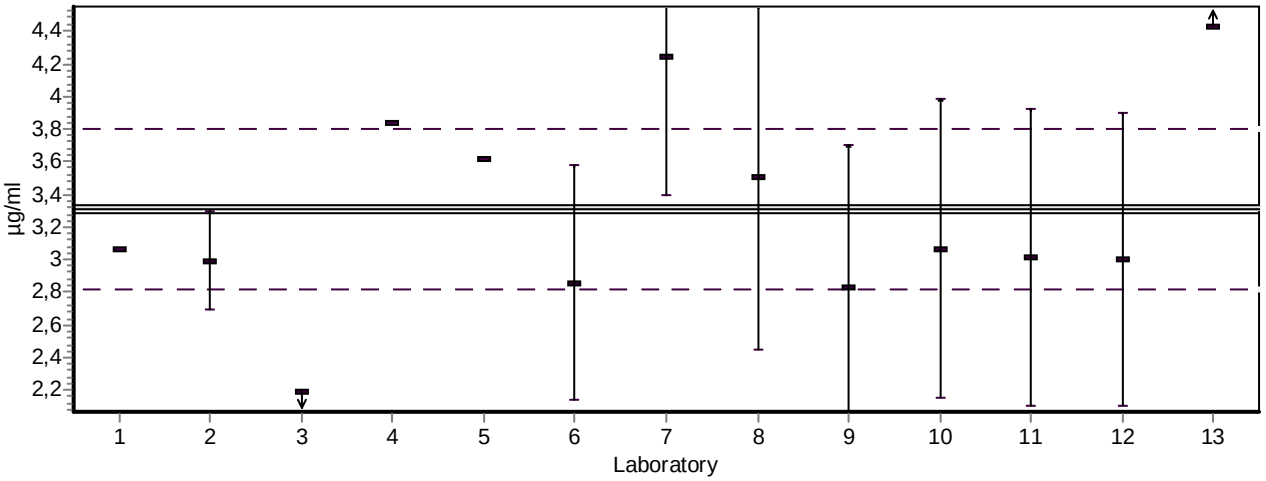
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* G2V



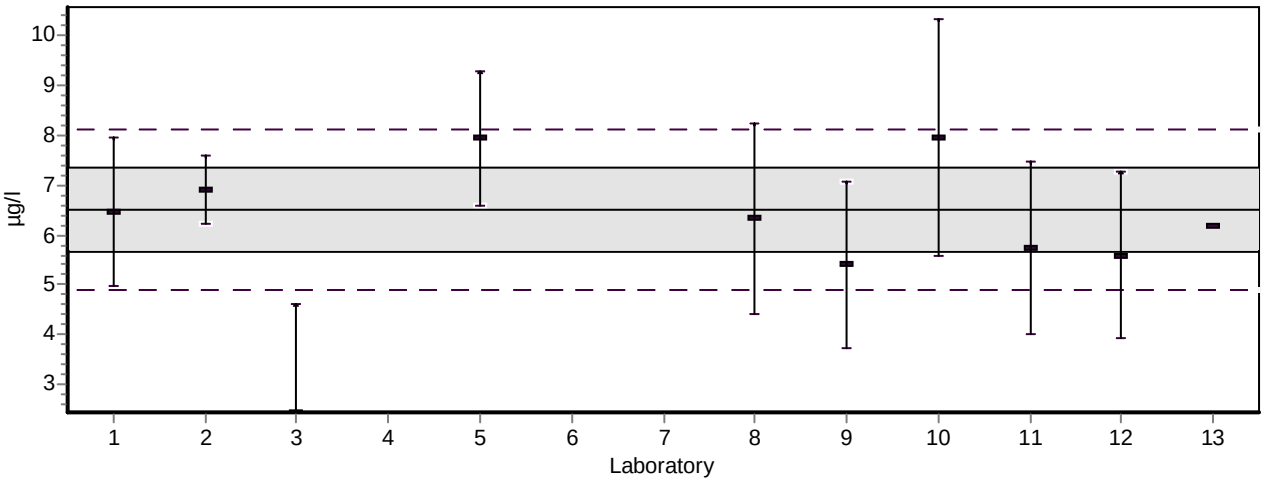
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* M3V



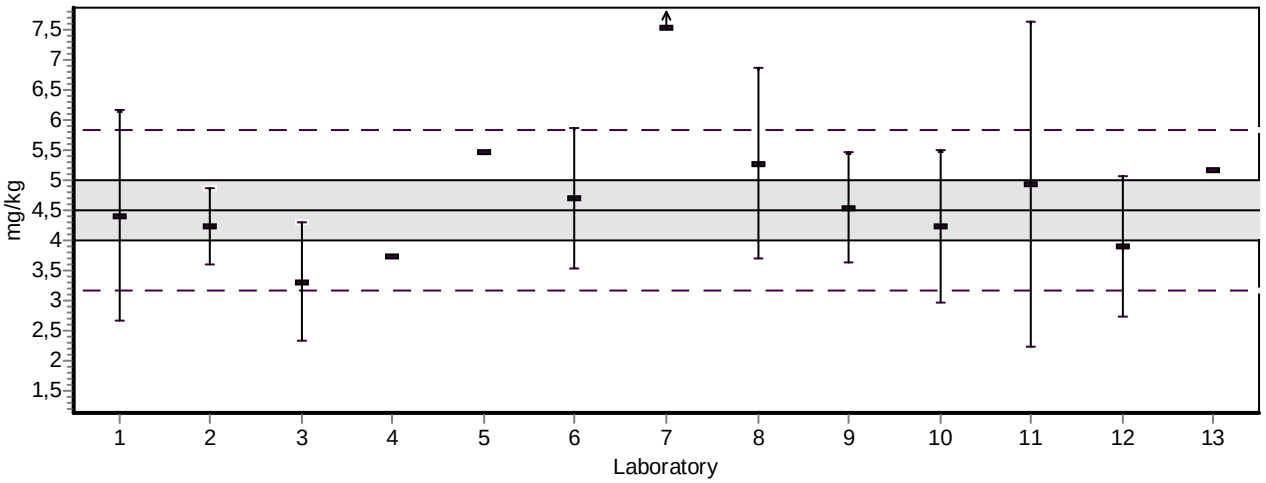
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* A1V



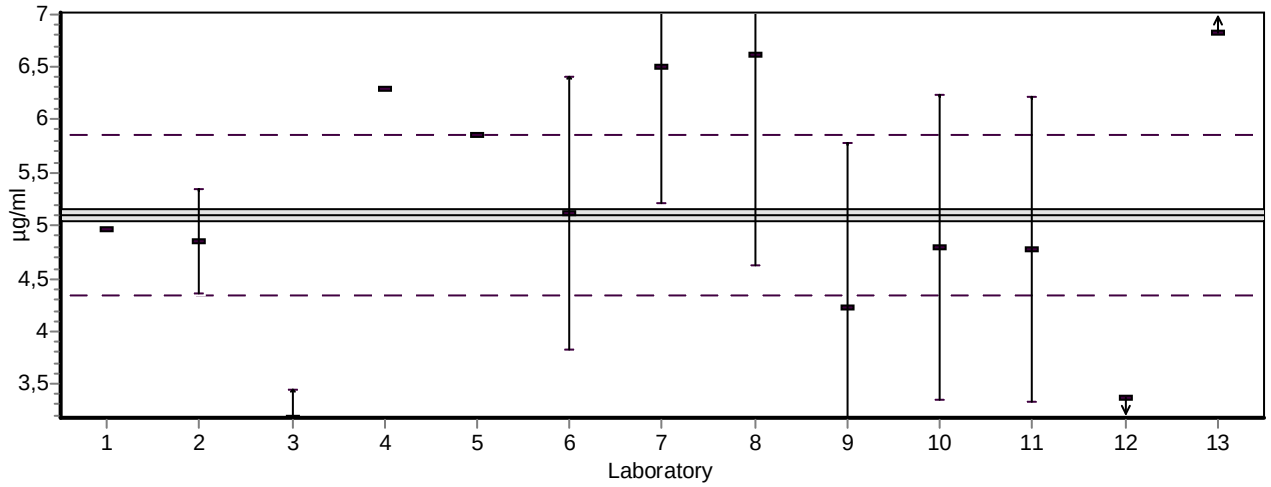
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* G2V



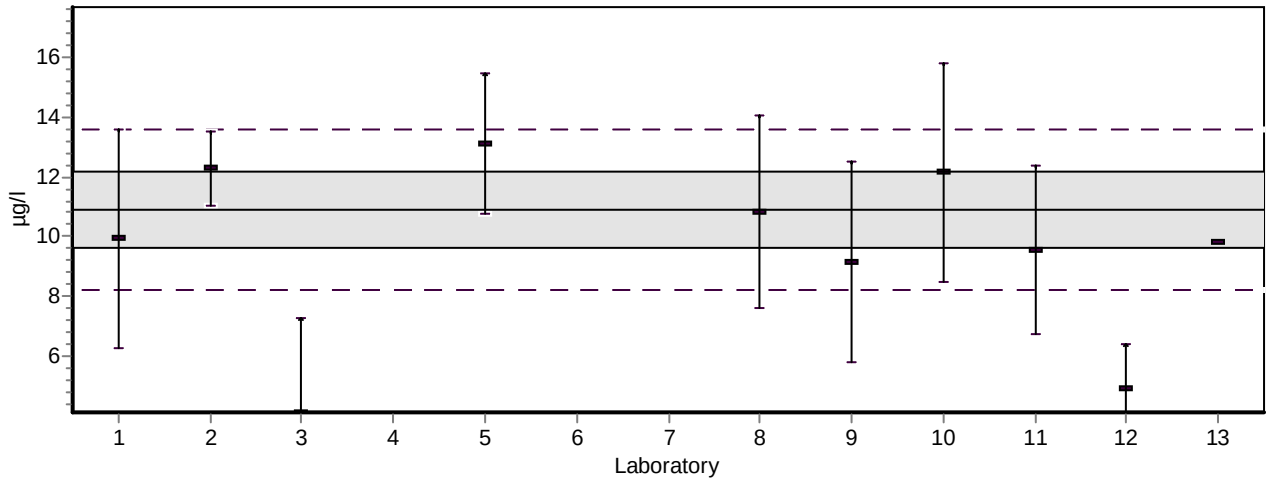
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* M3V



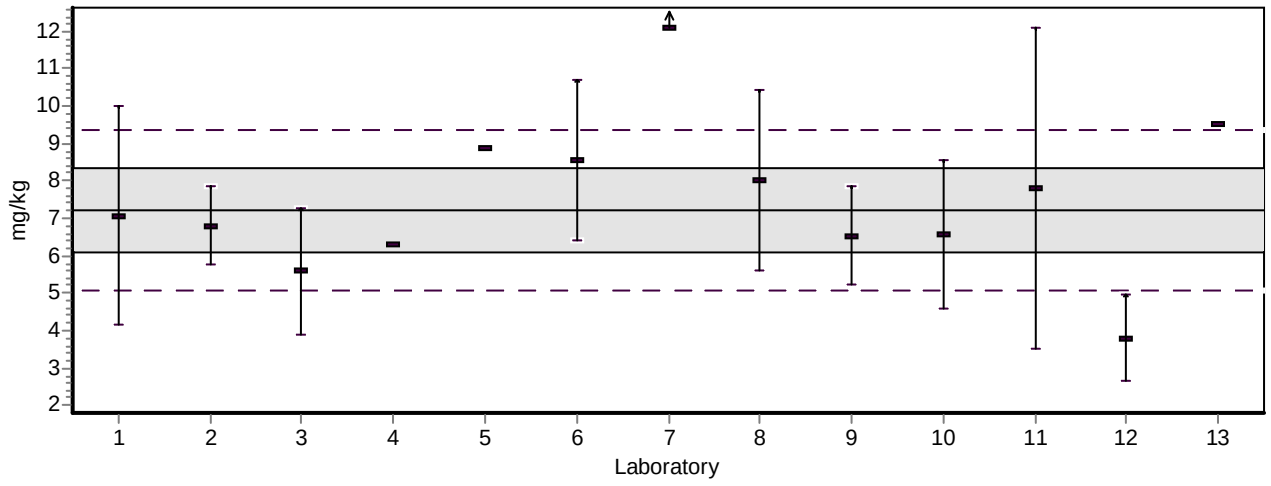
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* A1V



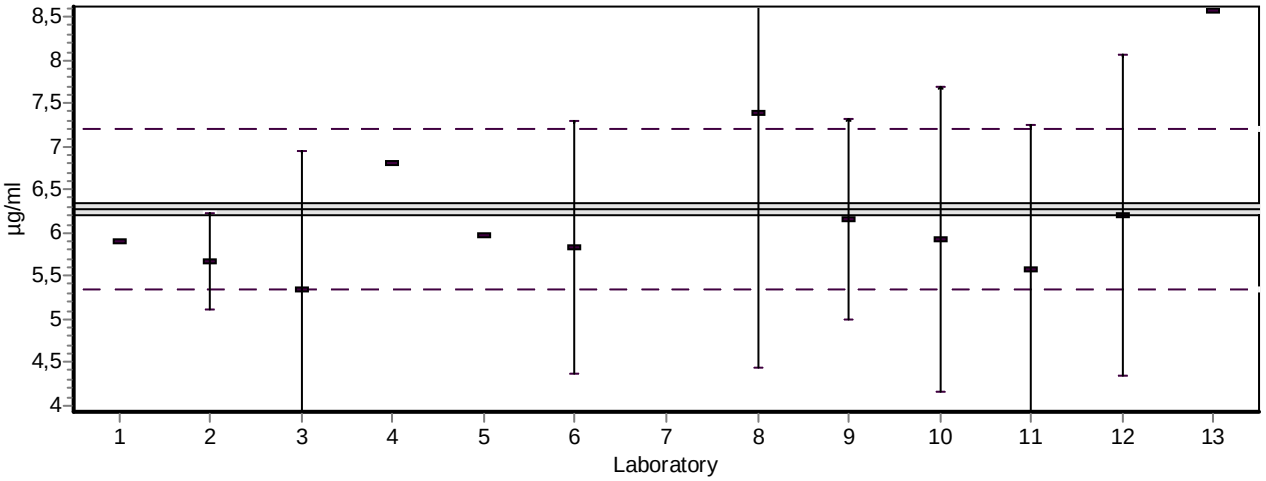
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* G2V



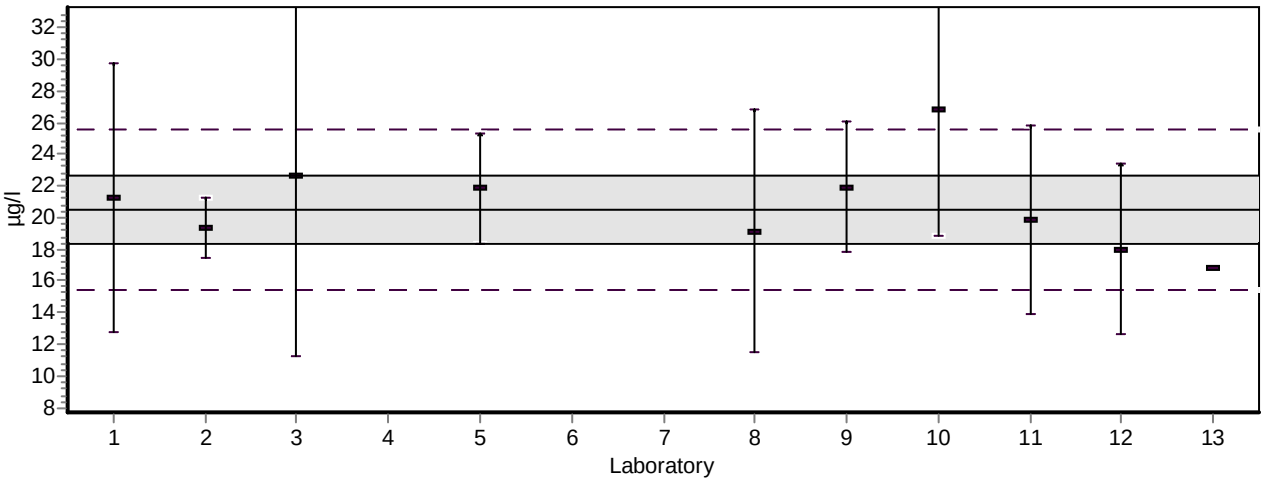
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* M3V



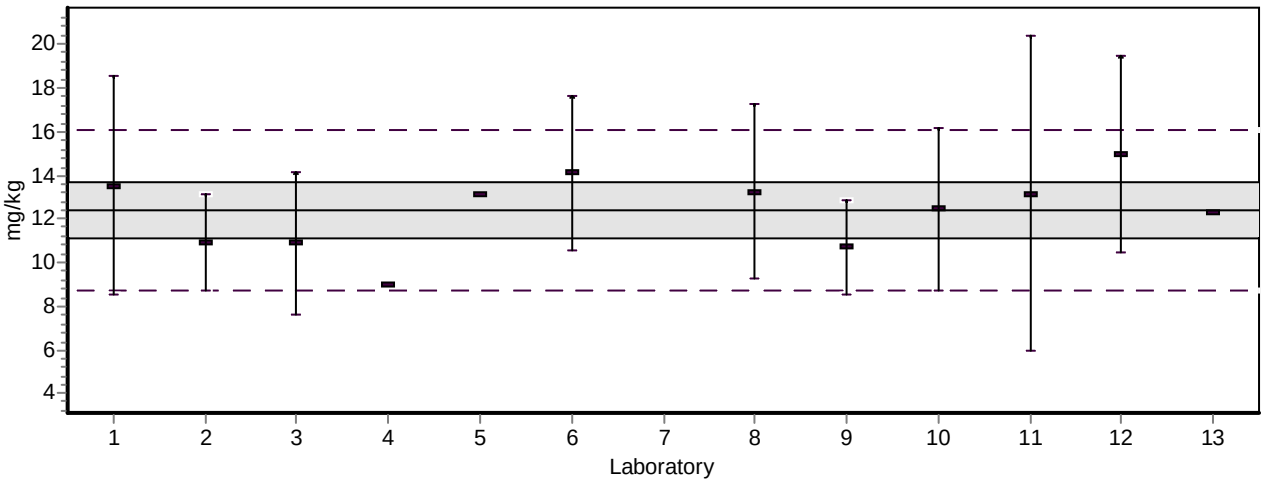
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* A1V



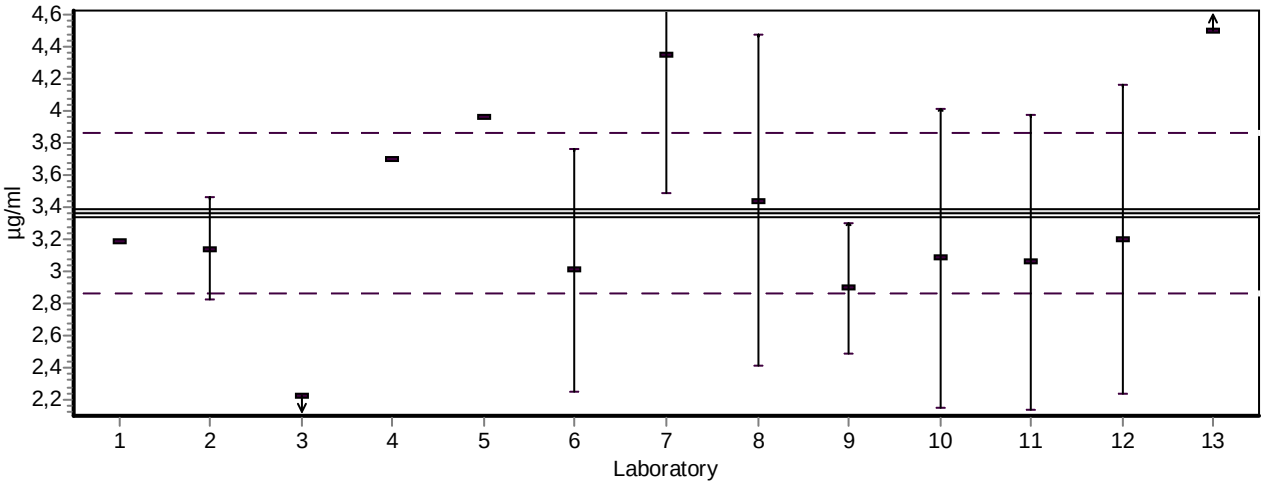
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* G2V



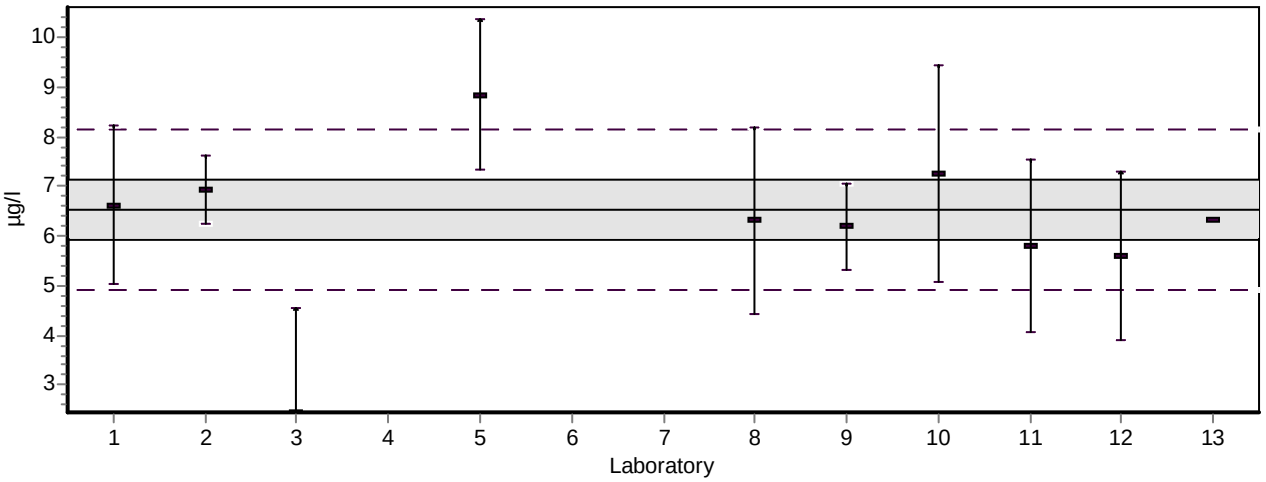
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* M3V



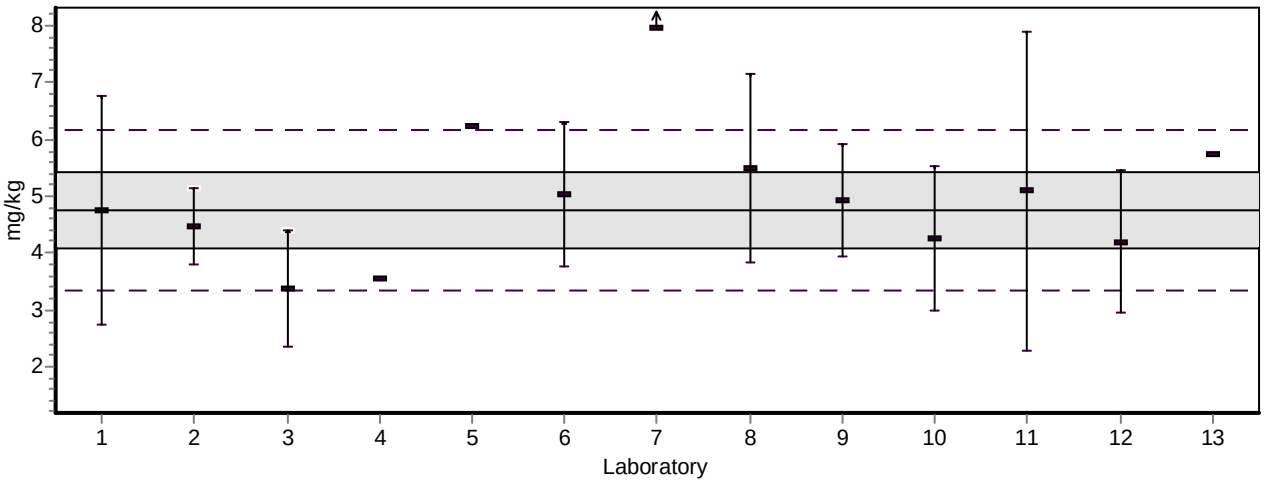
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* A1V



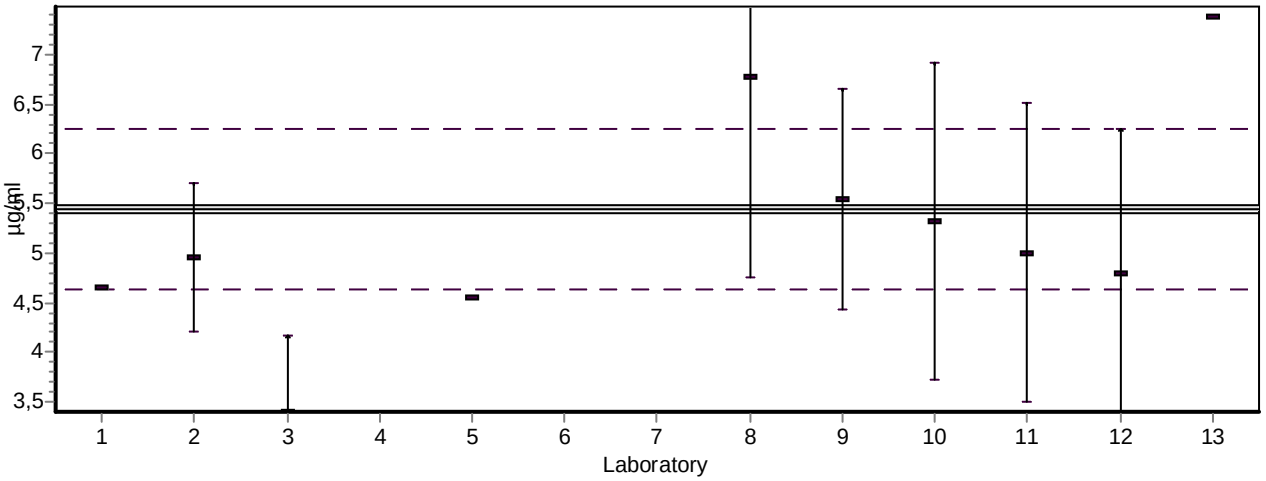
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* G2V



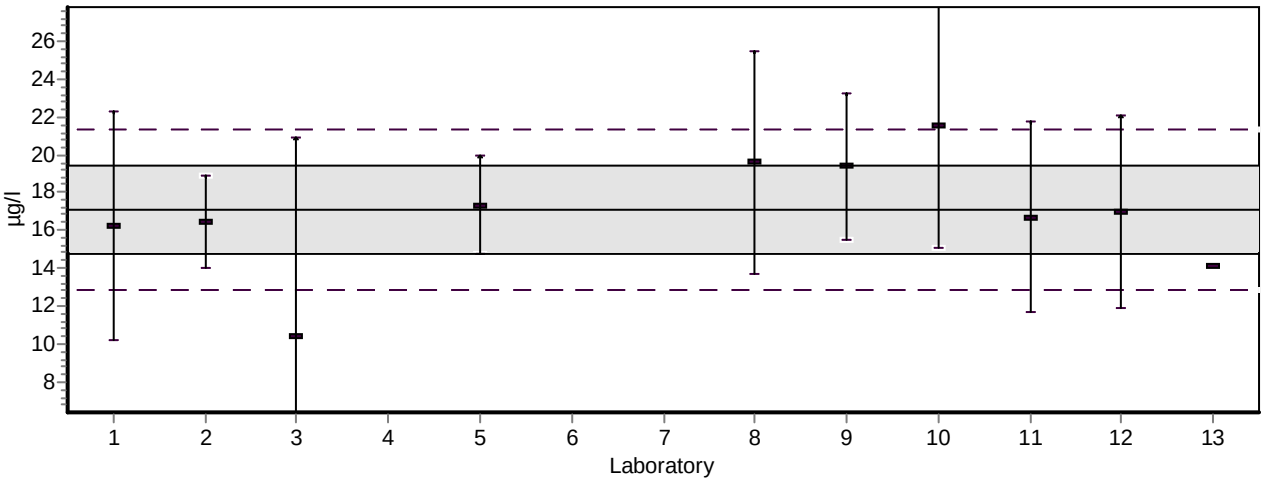
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* M3V



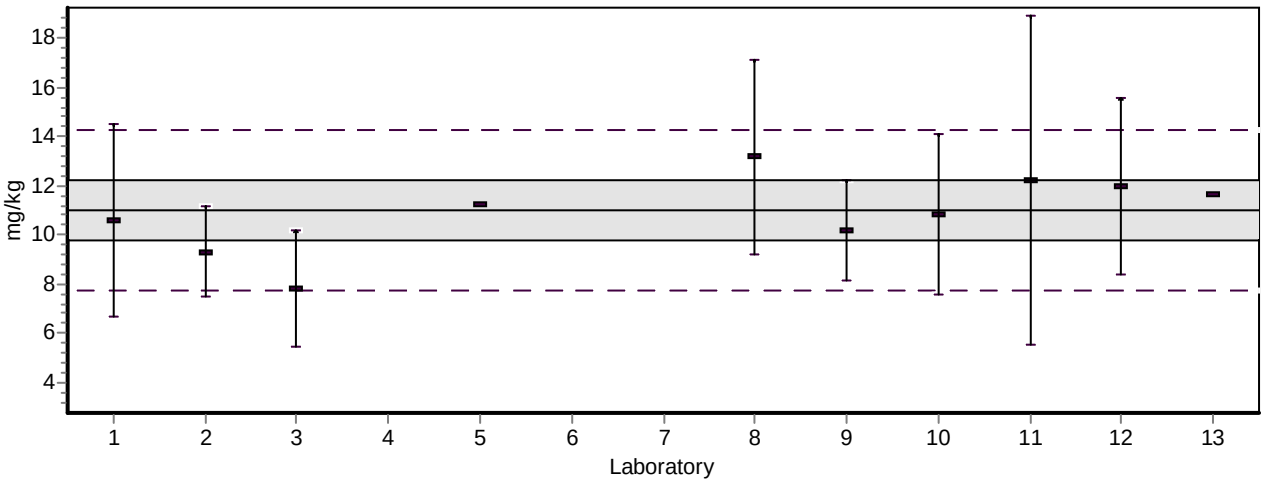
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* A1V



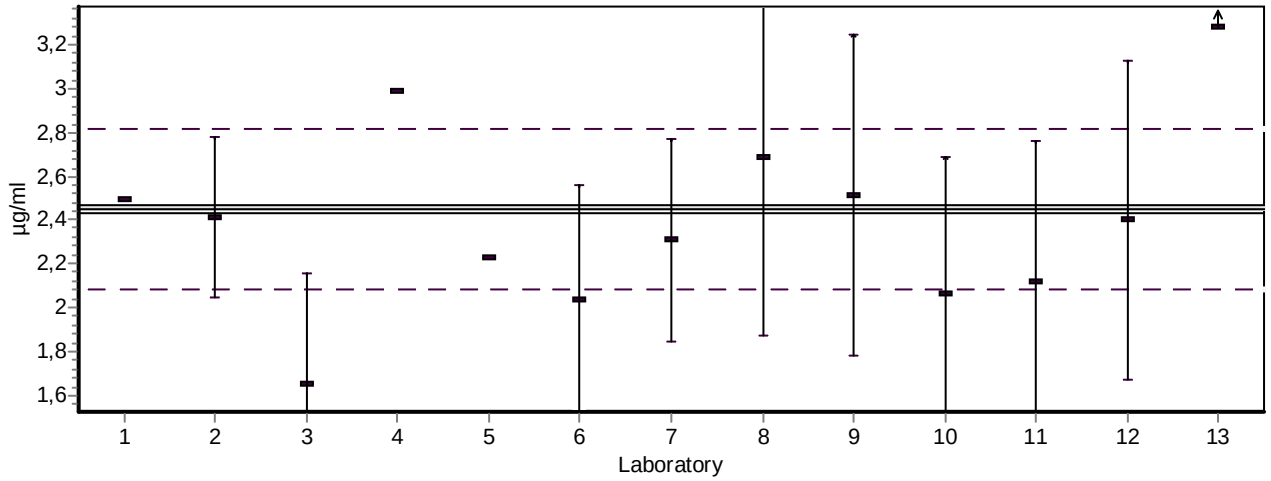
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* G2V



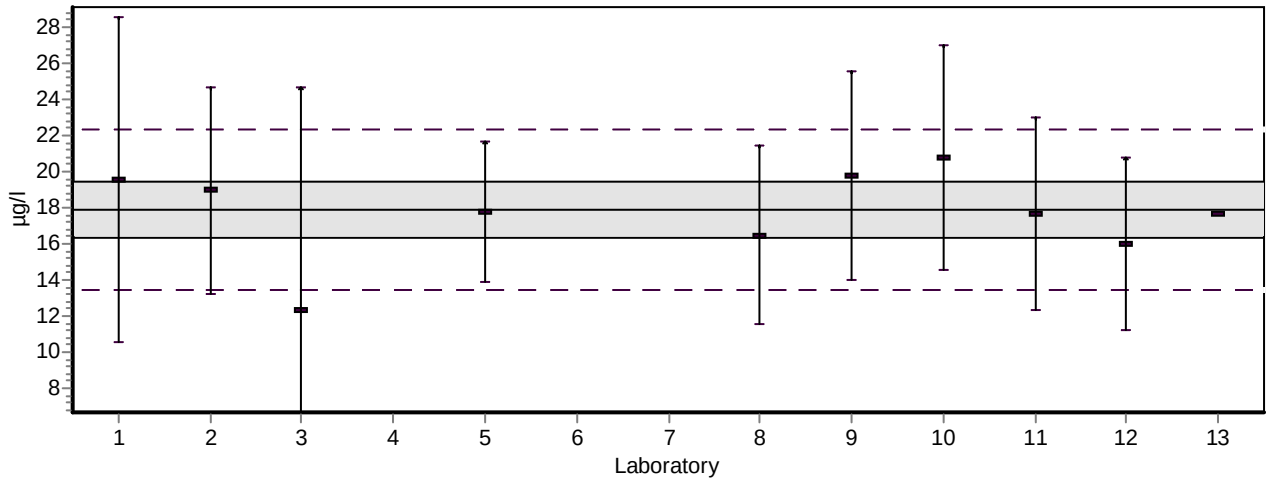
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* M3V



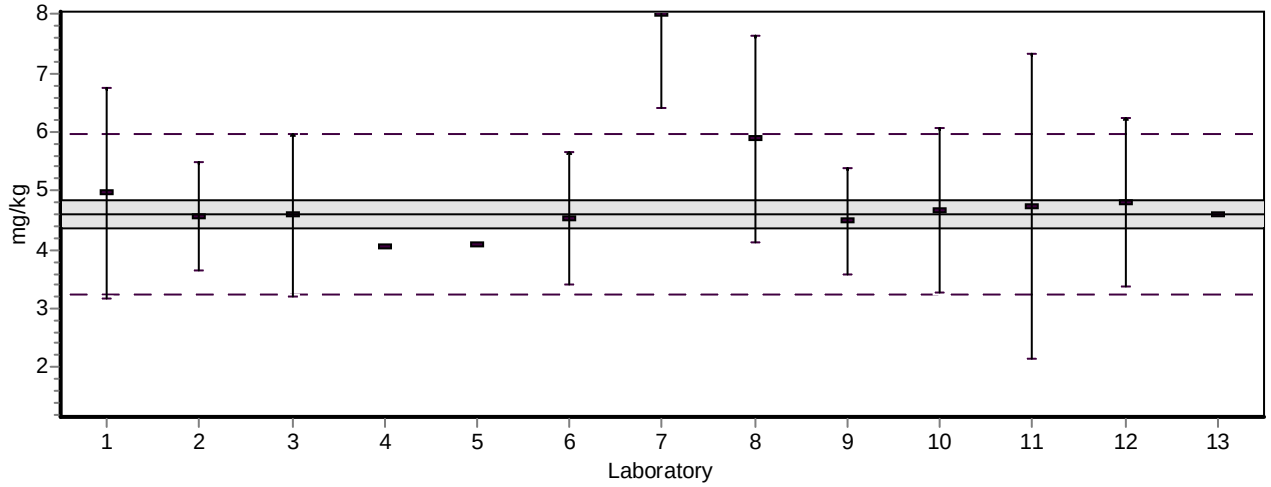
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* A1V



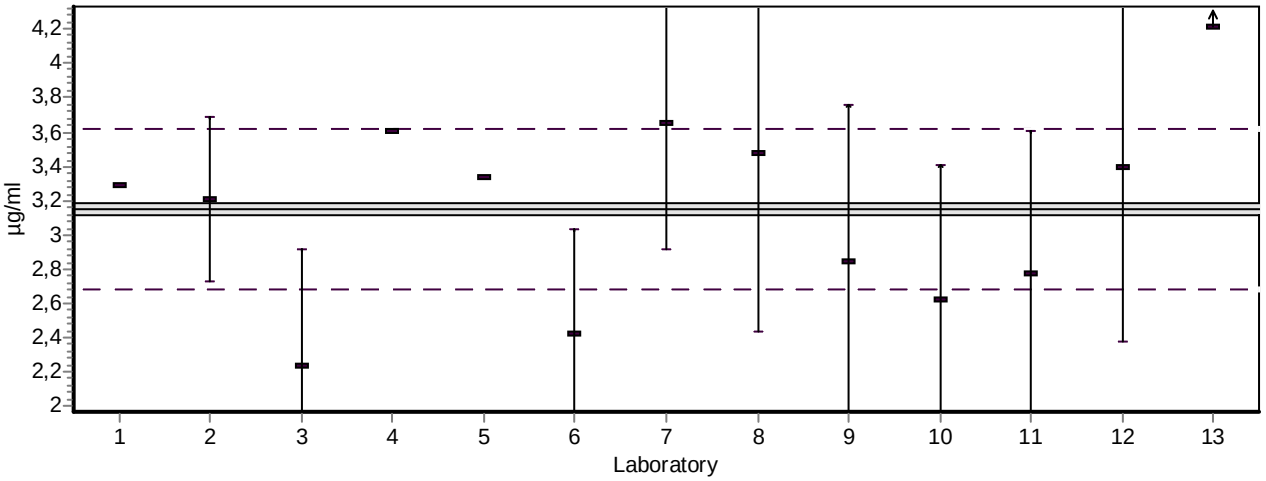
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* G2V



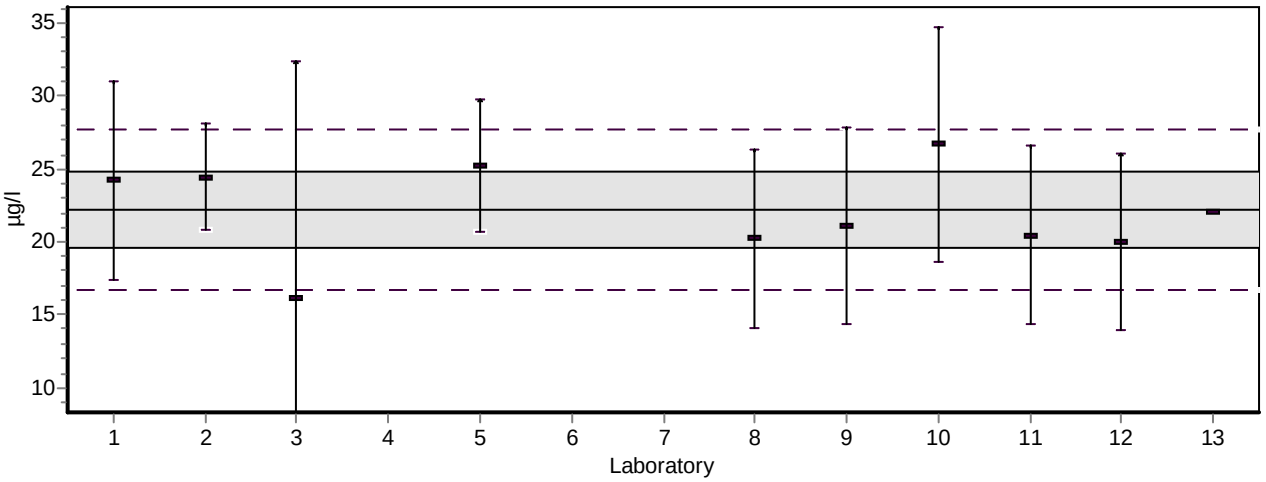
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* M3V



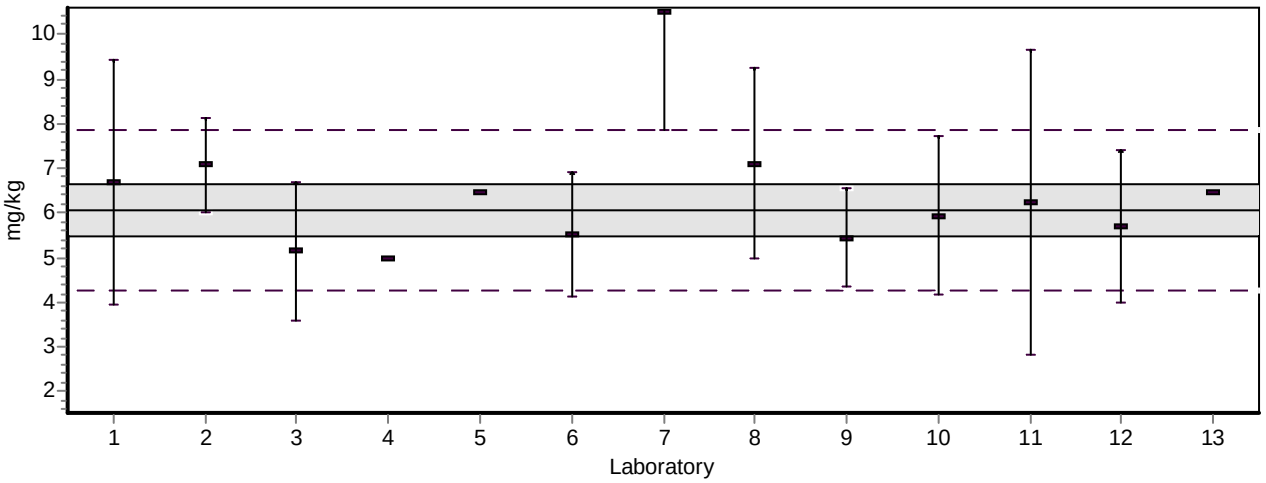
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* A1V



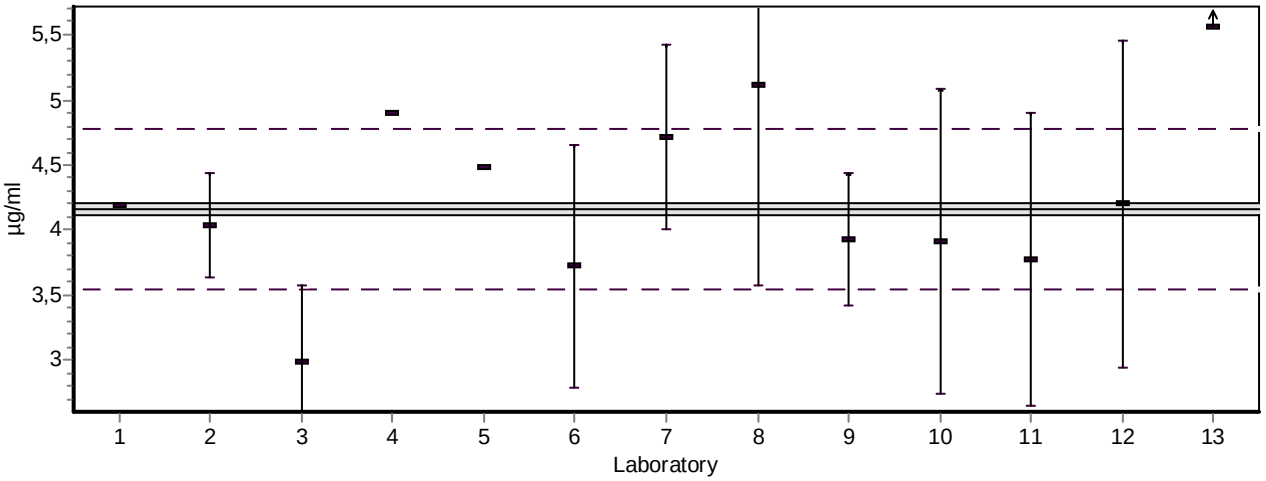
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* G2V



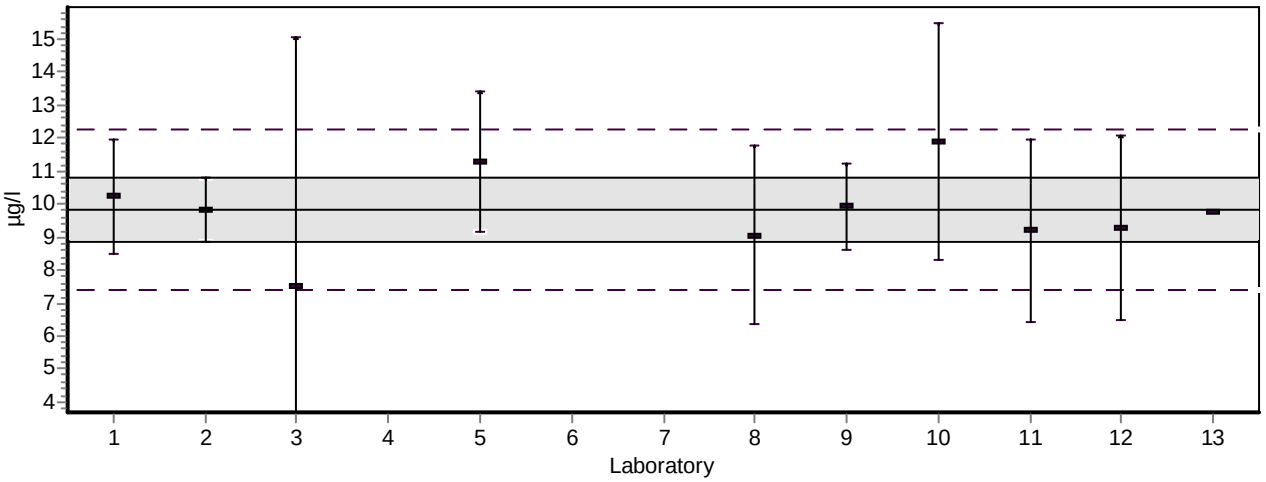
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* M3V



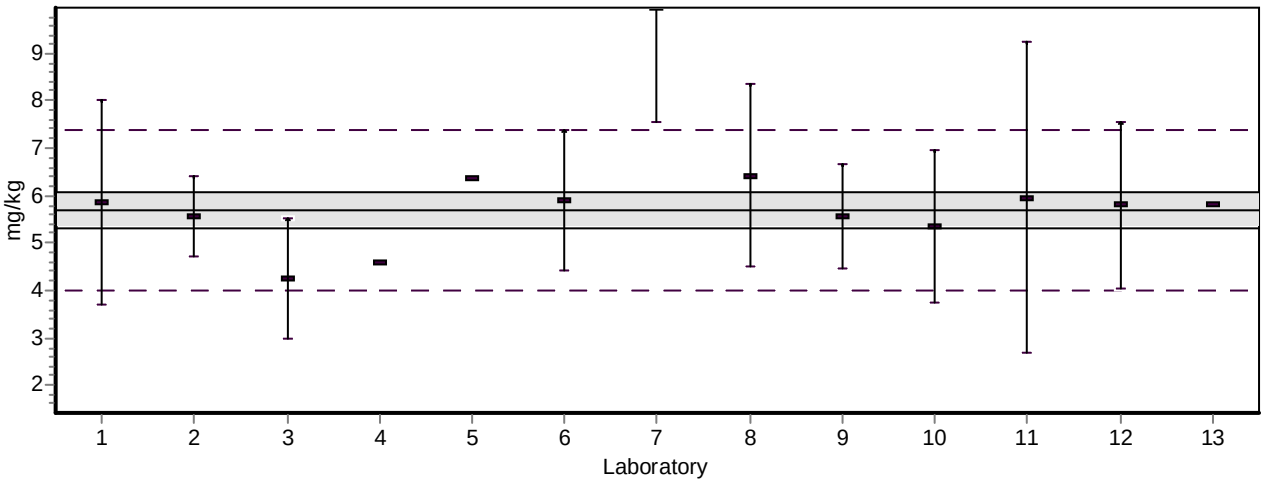
Analyytti *(Analyte)* **TOL** Näyte *(Sample)* A1V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* G2V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* M3V



EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant (Appendixes 7 and 8)

Sample The code of the sample

z-Graphics z score - the graphical presentation

z score calculated as follows:

$z = (x_i - X)/s_p$, where

x_i = the result of the individual laboratory

X = the reference value (*the assigned value*)

s_p = the target value of the standard deviation for proficiency assessment

Outl test OK yes - the result passed the outlier test

H = Hampel test (a test for the mean value)

In addition, in robust statistics some results deviating from the original robust mean have been rejected

Assigned value the reference value

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

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

Md. Median

Mean Mean

Robust mean Robust mean

SD Standard deviation

SD% Standard deviation, %

SD %rob Robust standard deviation, %

Passed The results passed the outlier test

Missing i.e. < DL

Num of labs the total number of the participants

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)

Q – questionable ($2 < z < 3$), positive error, the result deviates more than $2 \cdot s_p$ from the assigned value

q – questionable ($-3 > z < -2$), negative error, the result deviates more than $2 \cdot s_p$ from the assigned value

U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 \cdot s_p$ from the assigned value

u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 \cdot s_p$ from the assigned value

Robust analysis

The items of data is sorted into increasing order, x_1, x_2, x_i,…,x_p.

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

X^* = median of x_i (i = 1, 2,…p)

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

For each x_i (i = 1, 2,…p) is calculated:

$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$

$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$

$x_i^* = x_i$ otherwise

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

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

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

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

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

Annex C ISO 13528 2005 [3].

ANALYTICAL METHODS

Water – G2V

Lab	Extraction	Internal standard	Sampling	Equipment	Reference
1	No extraction	Toluene-d8 1,2-Dichlorobenzene-d4	Headspace	GC-MS	ISO 22155
2	No extraction	Toluene-d8, ααα-Trifluorotoluene	Headspace	GC-MS	ISO 10301
3	No extraction	Toluene-d8	Headspace	GC-MS	In house method
5	No extraction	Toluene-d8	Purge & Trap	GC-MS	SFS-EN ISO 15680
8	No extraction	Toluene-d8 Bromobenzene	Headspace	GC-MS	SFS-EN ISO 15680
9	No extraction	Toluene-d8	Headspace	GC-MS	In house method
10	No extraction	Toluene-d8 1,2-Dchloroethana-d4	Headspace	GC-MS	ISO 10301
11	No extraction	No	Headspace	GC-FID	ISO 11423-1
12	No extraction	?	Headspace	GC-MS	ISO 11423-1 EN ISO 10301
13	No extraction	Toluene-d8	Headspace	GC-MS	In house method

Soil – M3V

Lab	Extraction	Internal standard	Sampling / Injection	Equipment	Reference
1	Shaking	Toluene-d8 1,2-Dichlorobenzene-d4	Headspace	GC-MS	ISO 22155
2	Shaking	Toluene-d8 ααα-Trifluorotoluene	Headspace	GC-MS	ISO 22155
3	Shaking	Toluene-d8	Headspace	GC-MS	In house method
4	Shaking	?	Purge & Trap	GC-MS	?
5	Shaking	Toluene-d8	Purge & Trap	GC-MS	SFS-ISO 22155
6	Shaking	Fluorobenzene Clorobenzene-d5 1,4-Dichlorobenzene-d4	Purge & Trap	GC-MS	EPA 5035A EPA 8260C
7	Heating in headspace vial	Toluene-d8 1,4-dichlorobenzene-d4	Headspace	GC-MS	?
8	Shaking	Toluene-d8 Bromobenzene	Headspace	GC-MS	ISO 22155 SFS-EN ISO 15680
9	Shaking	Toluene-d8	Headspace	GC-MS	ISO 22155
10	Shaking	Fluorobenzene	Headspace	GC-MS	ISO 22155
11	Shaking	No	Headspace	GC-FID	SFS-EN ISO 22155
13	Shaking	Toluene-d8	Split	GC-MS	In house method

RESULTS GROUPED ACCORDING TO THE METHODS

No statistical comparison between the different techniques could be done because of the low number of the results. In this appendix the results of the participants are grouped according to the injection techniques as follows:

Meth 1. Headspace

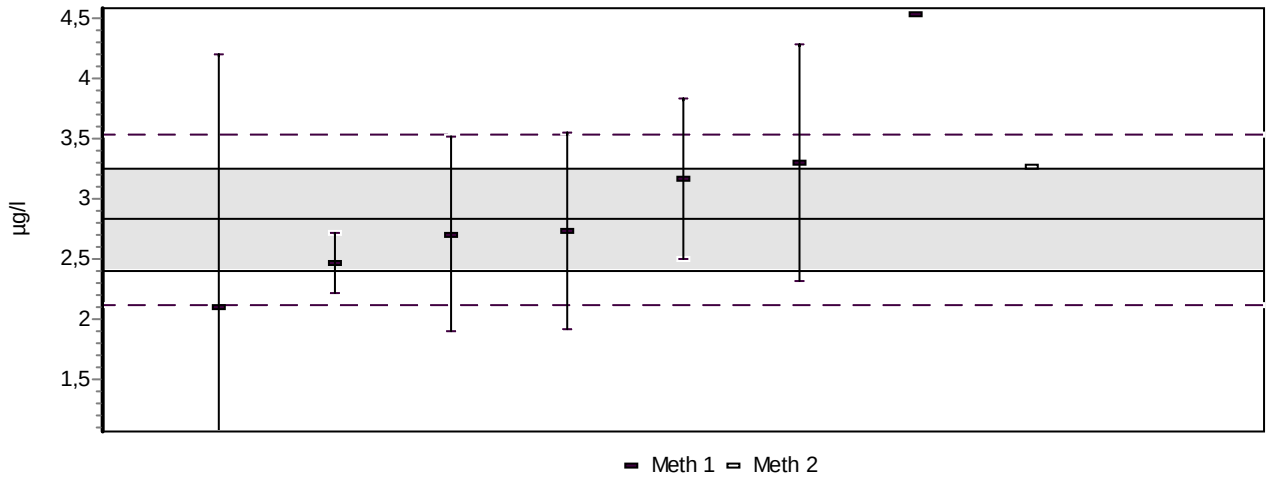
Meth 2. Purge & Trap

Meth 3. Split

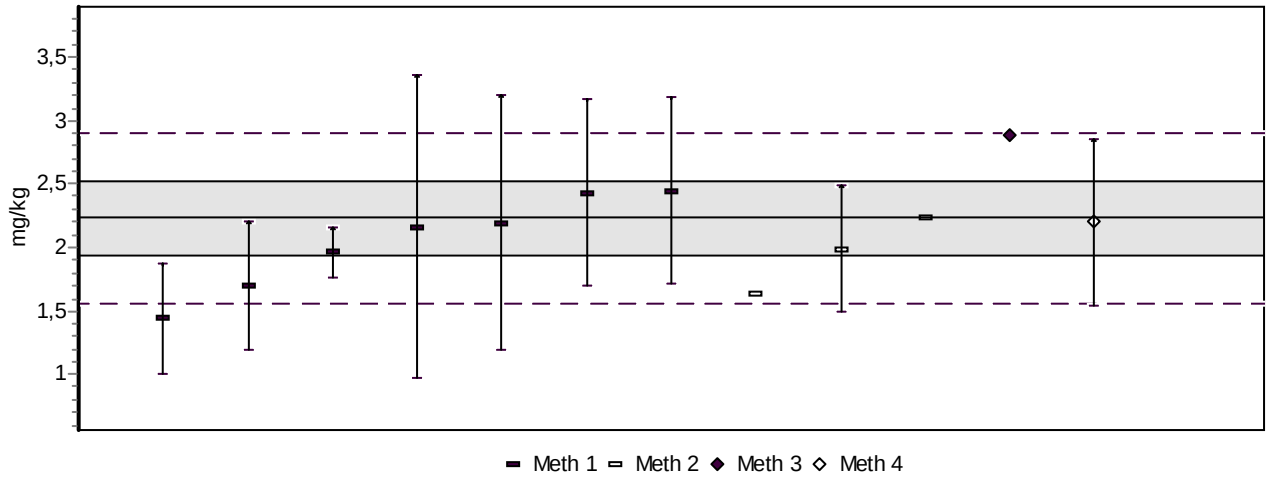
Meth 4. Not specified

LIITE 10.2.
APPENDIX 10.2.

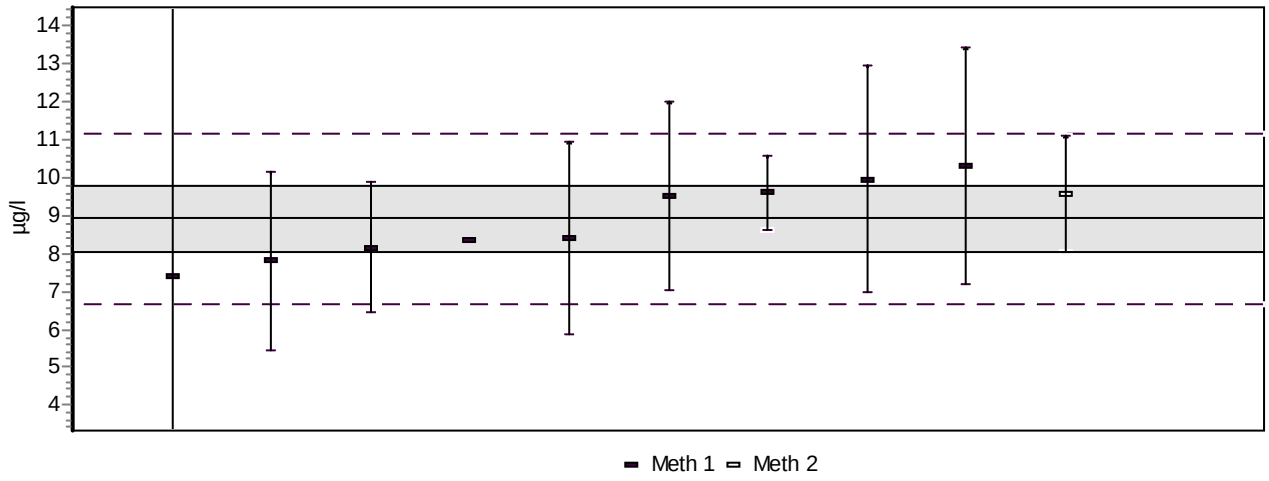
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* G2V



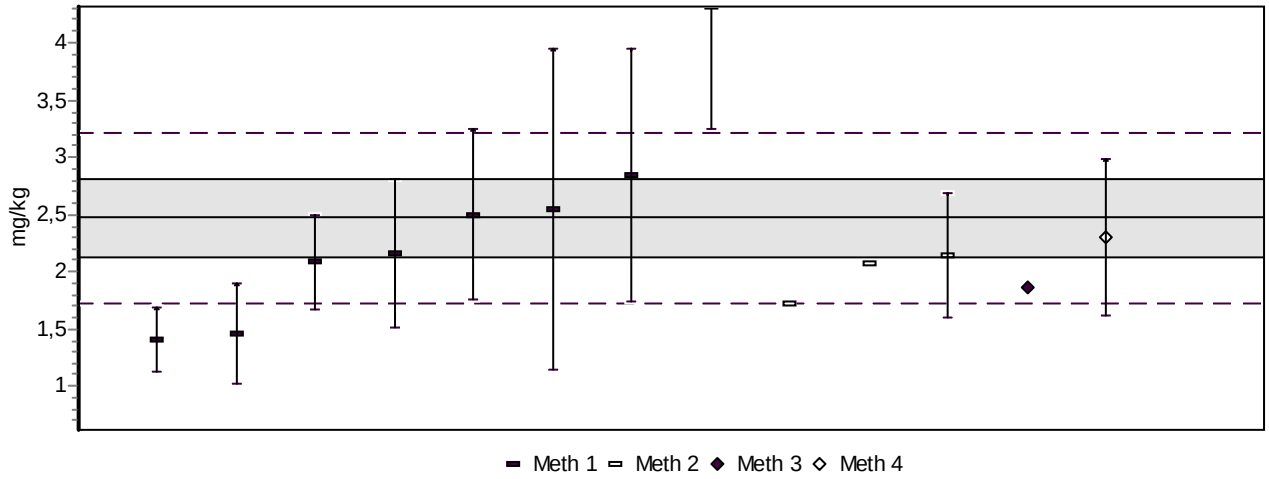
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* M3V



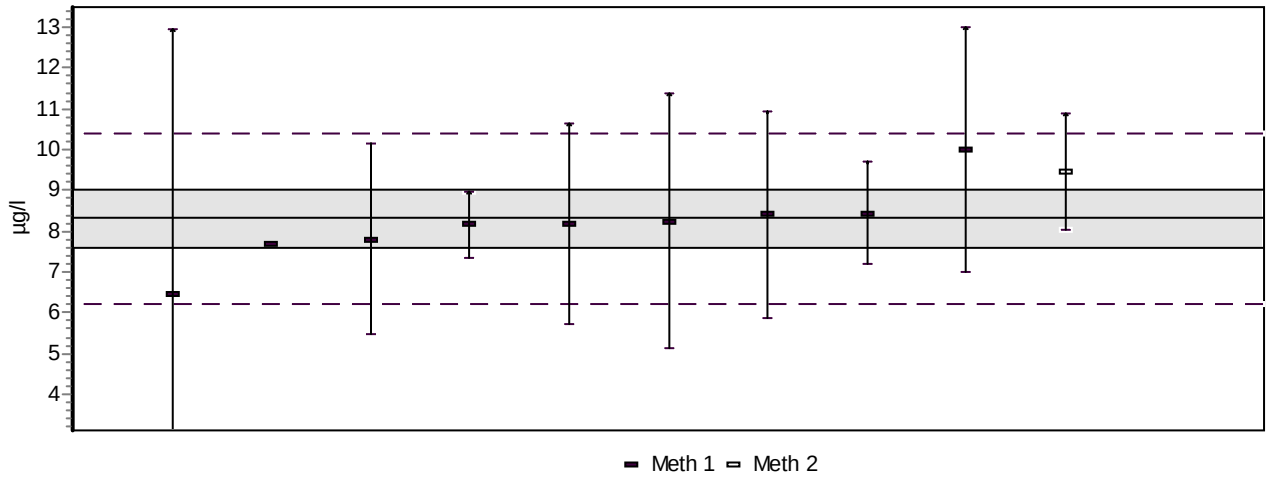
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* G2V



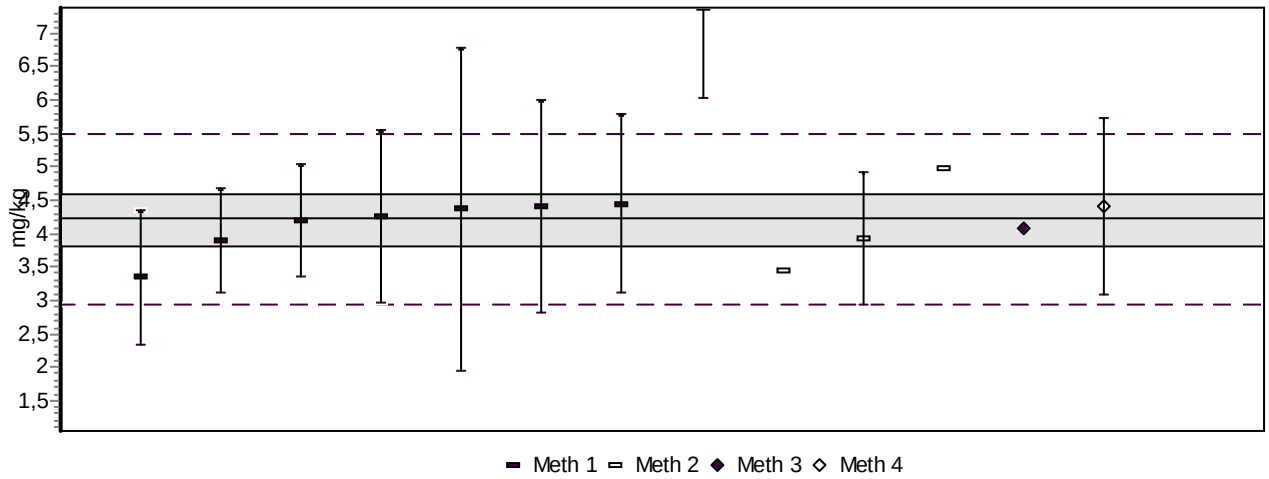
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* M3V



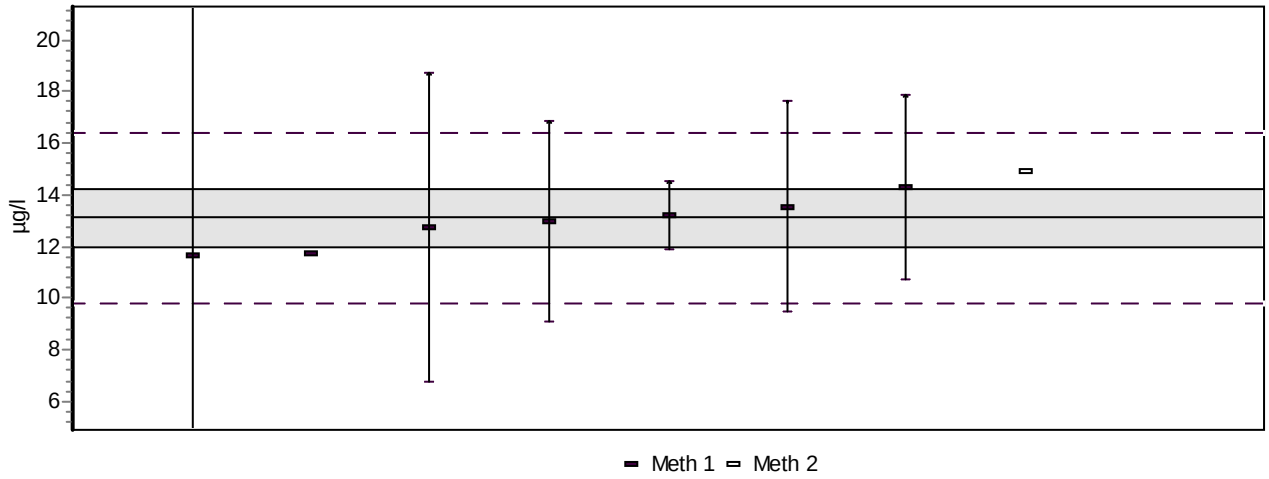
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* G2V



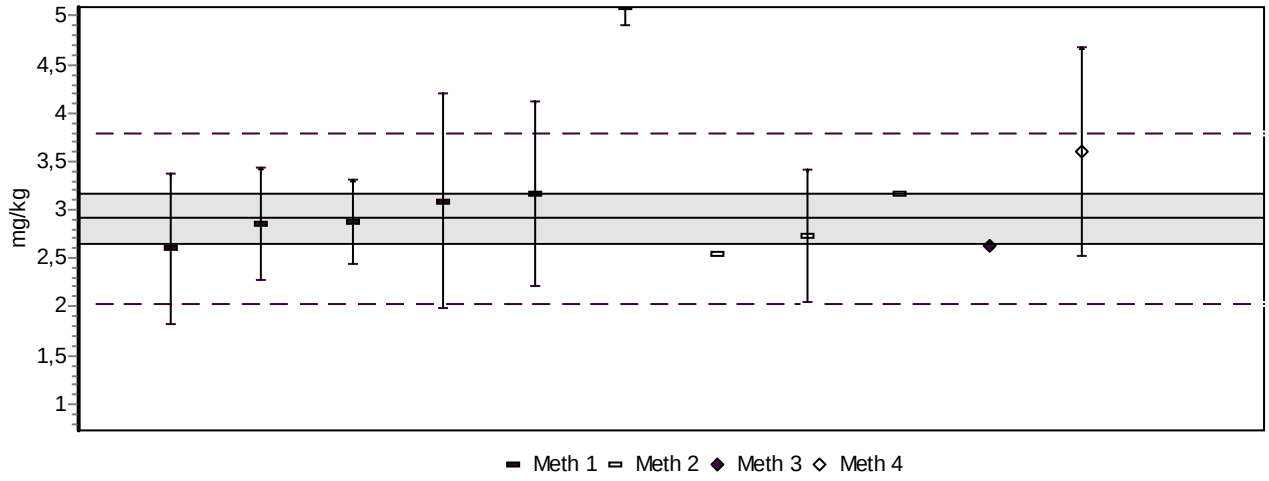
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* M3V



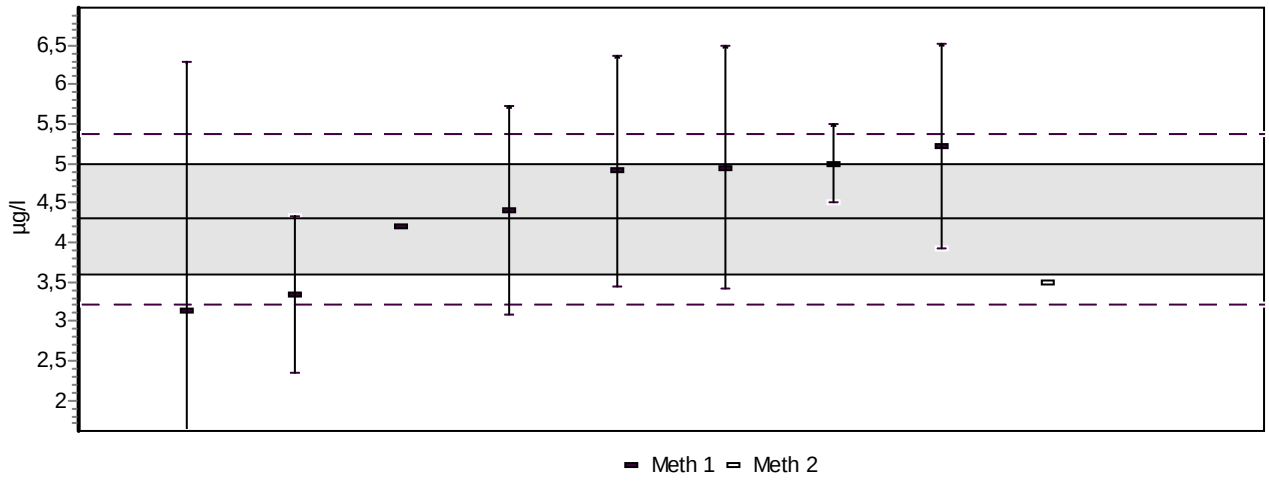
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* G2V



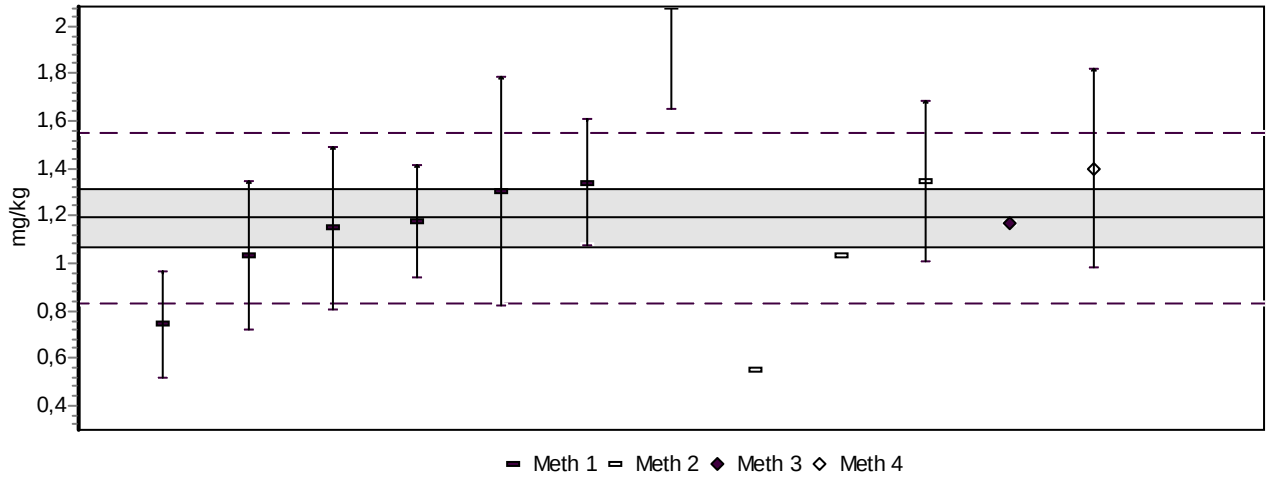
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* M3V



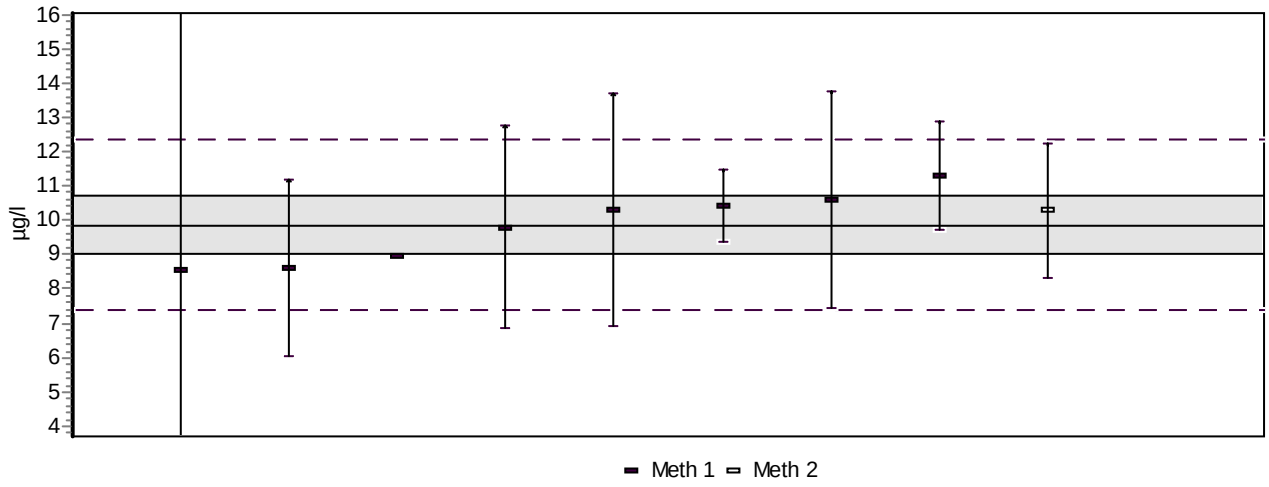
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* G2V



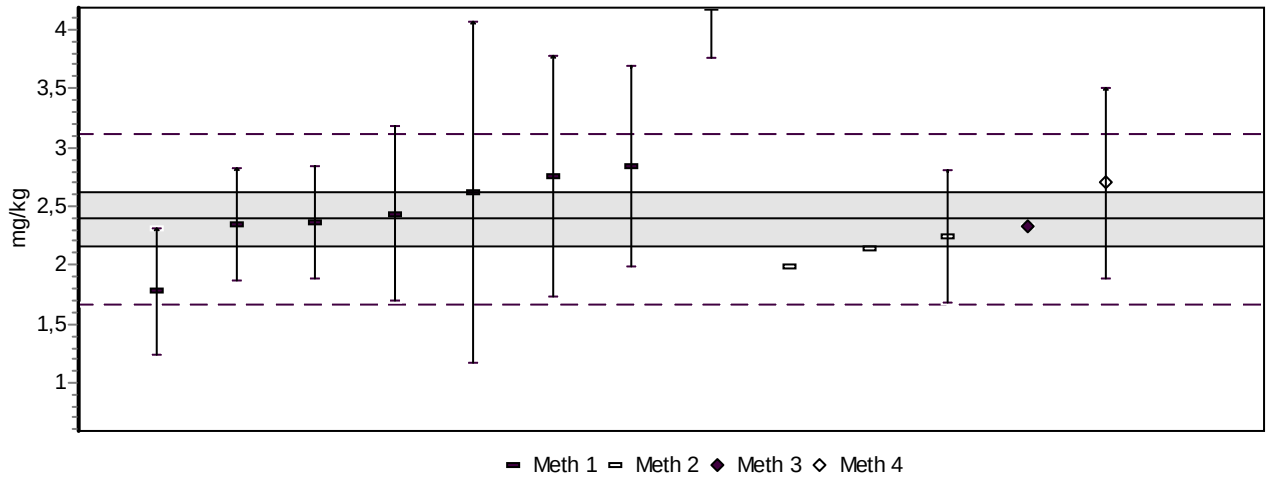
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* M3V



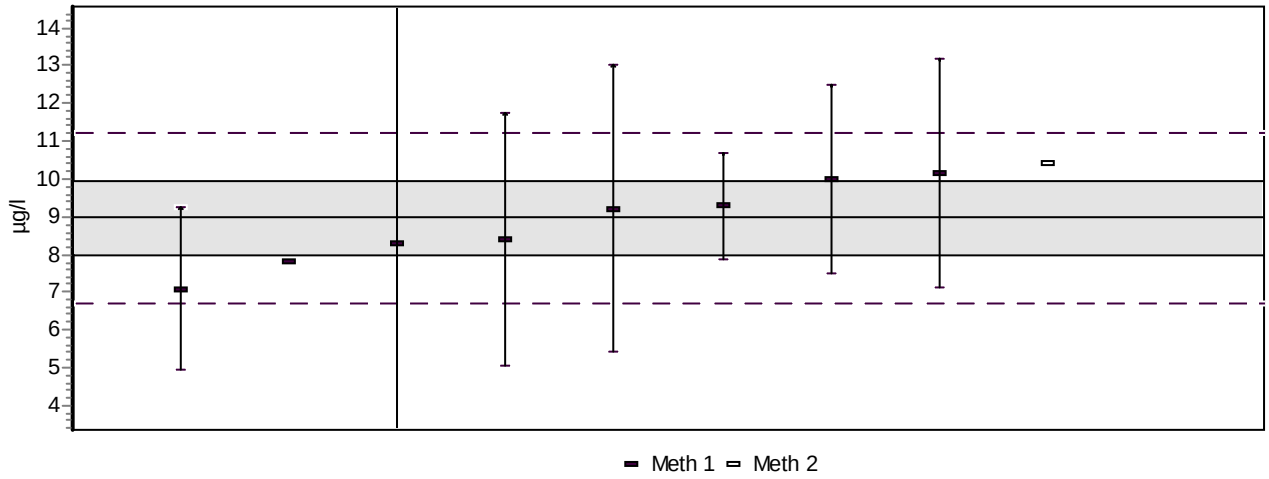
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* G2V



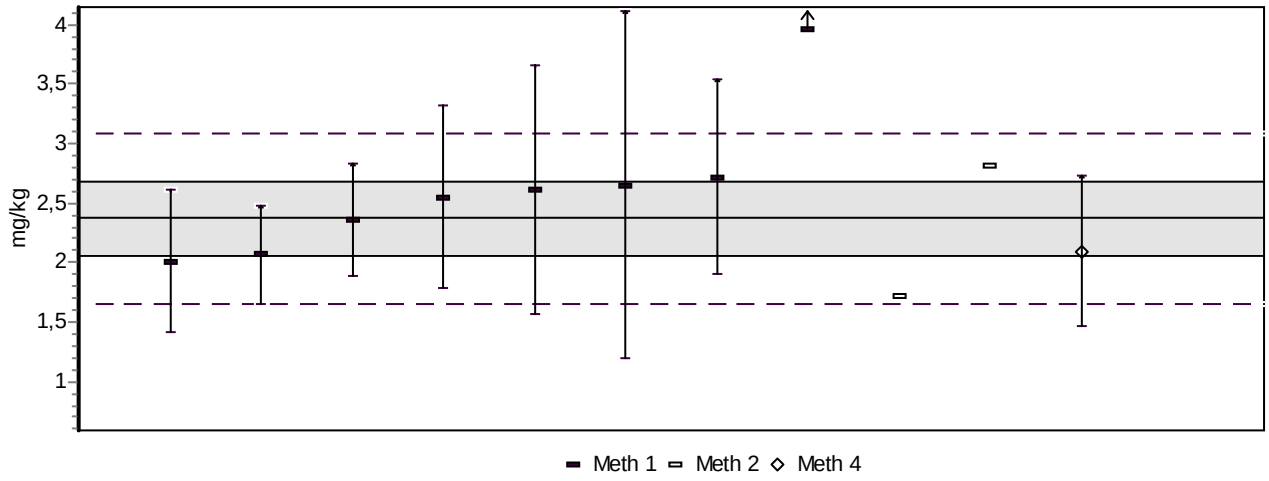
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* M3V



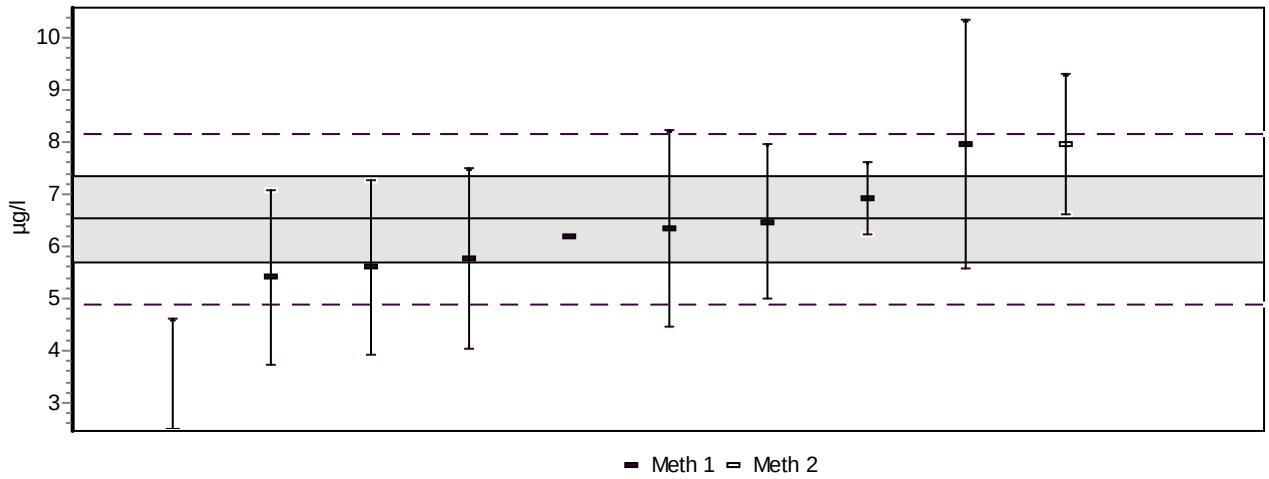
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* G2V



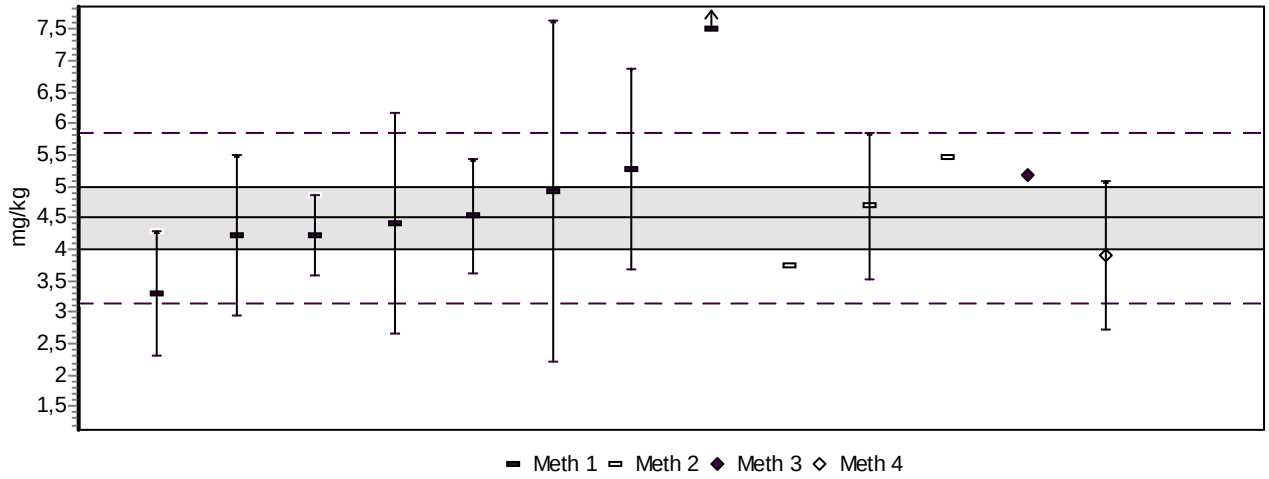
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* M3V



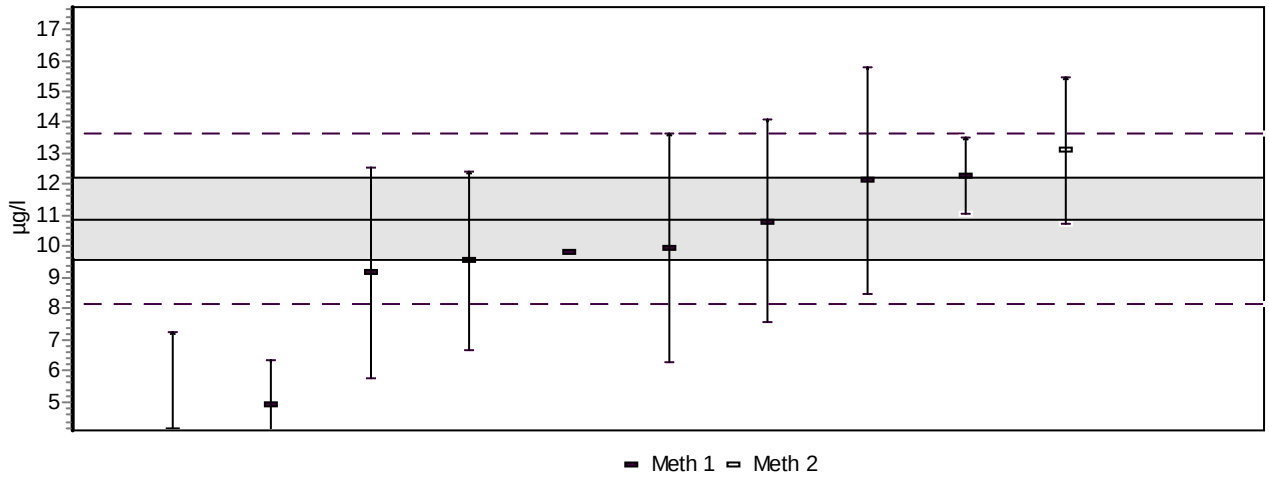
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* G2V



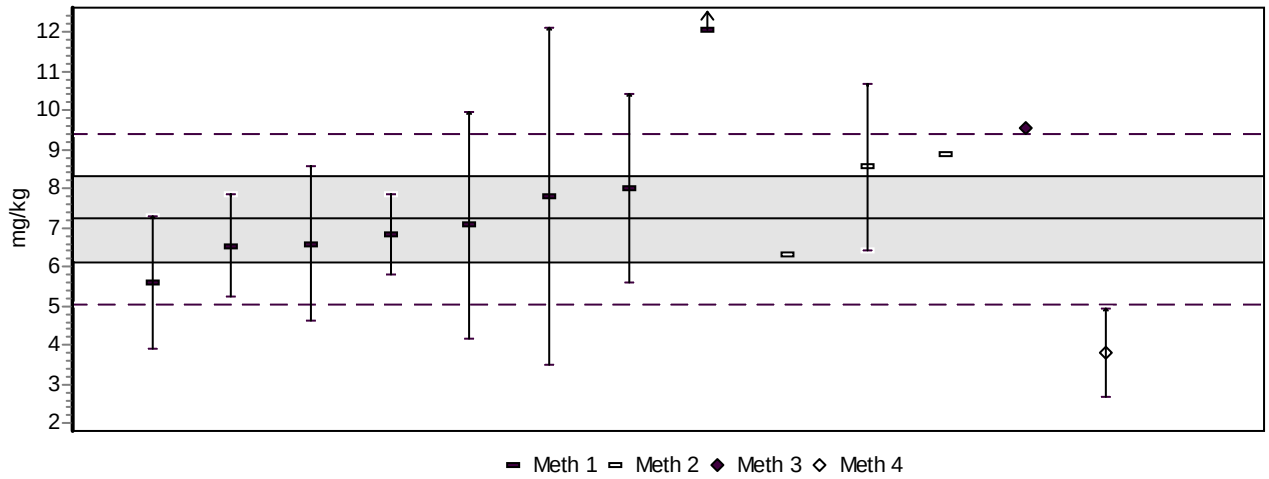
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* M3V



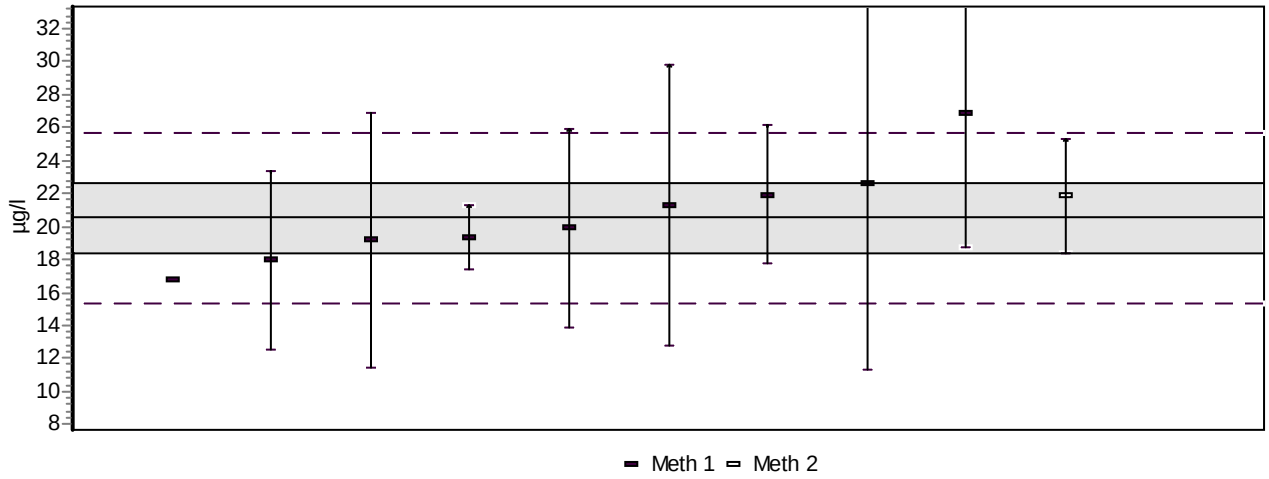
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* G2V



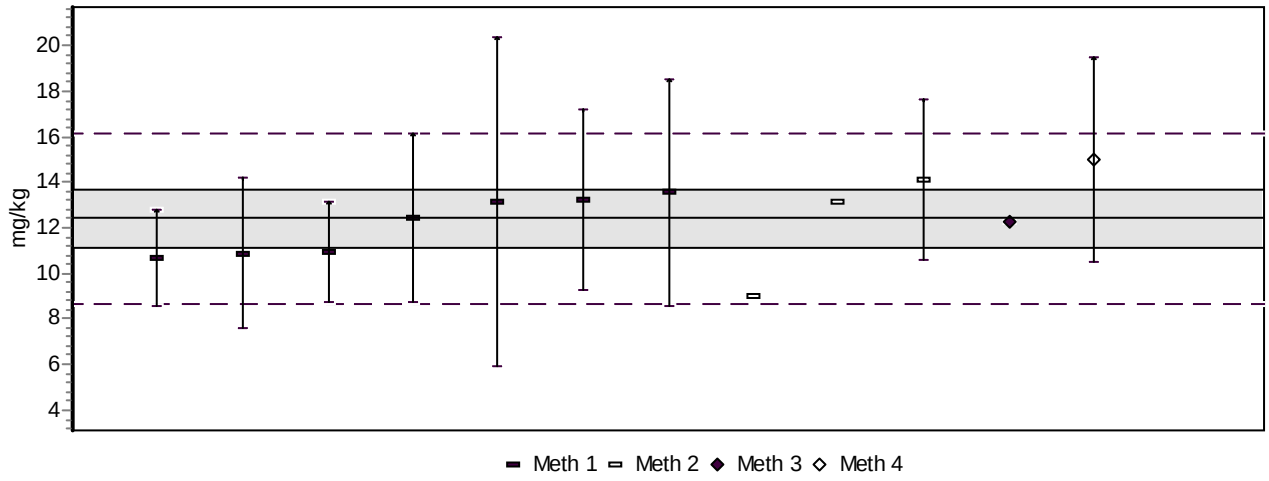
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* M3V



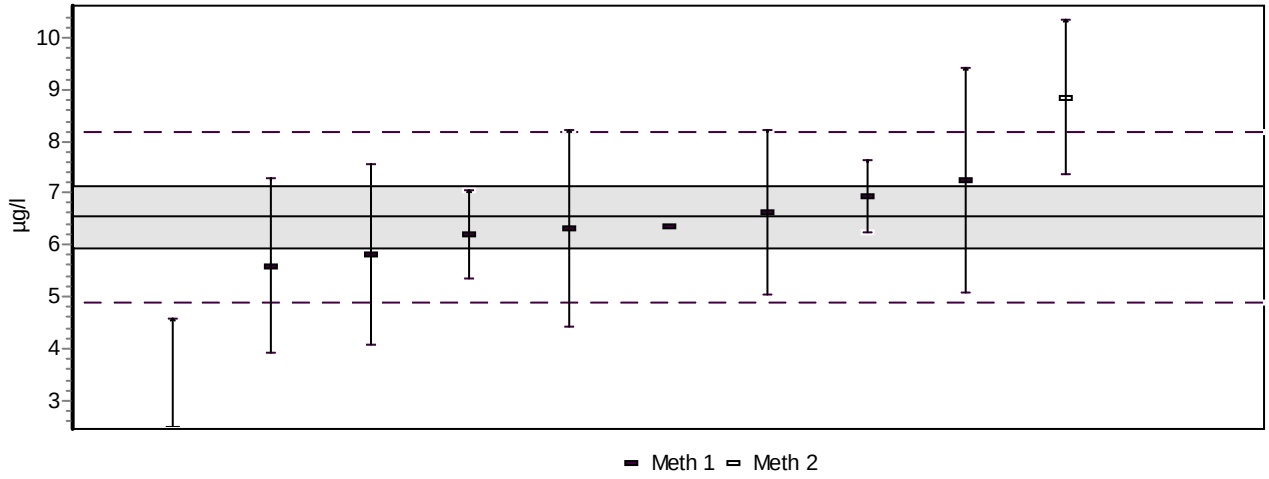
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* G2V



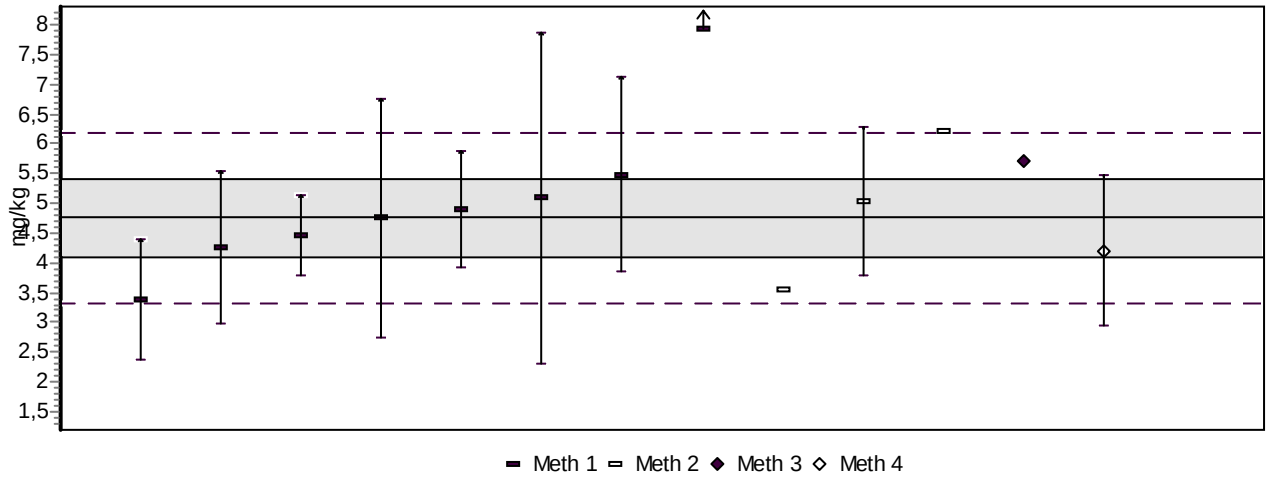
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* M3V



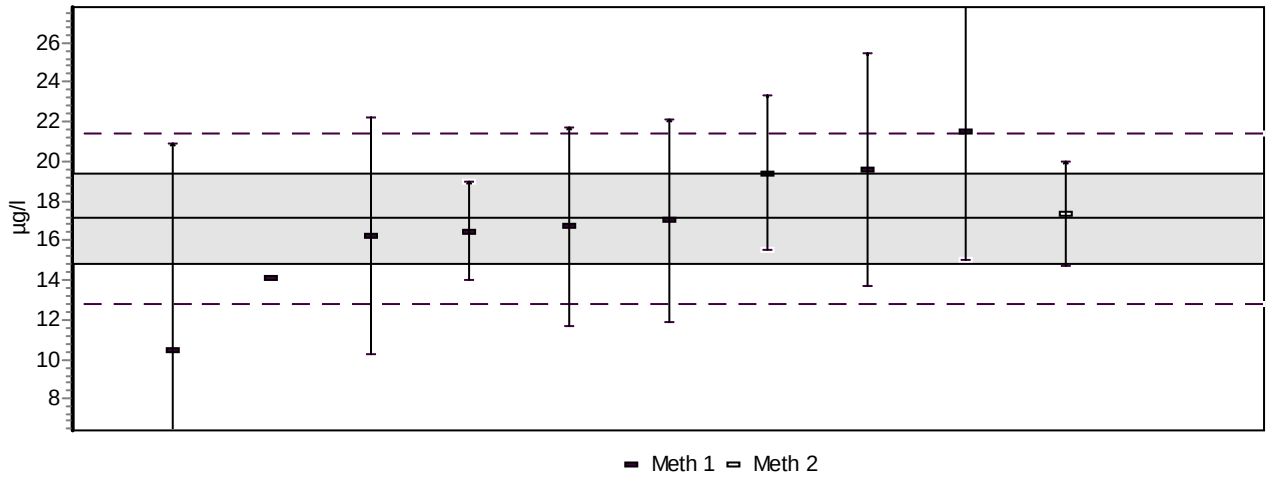
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* G2V



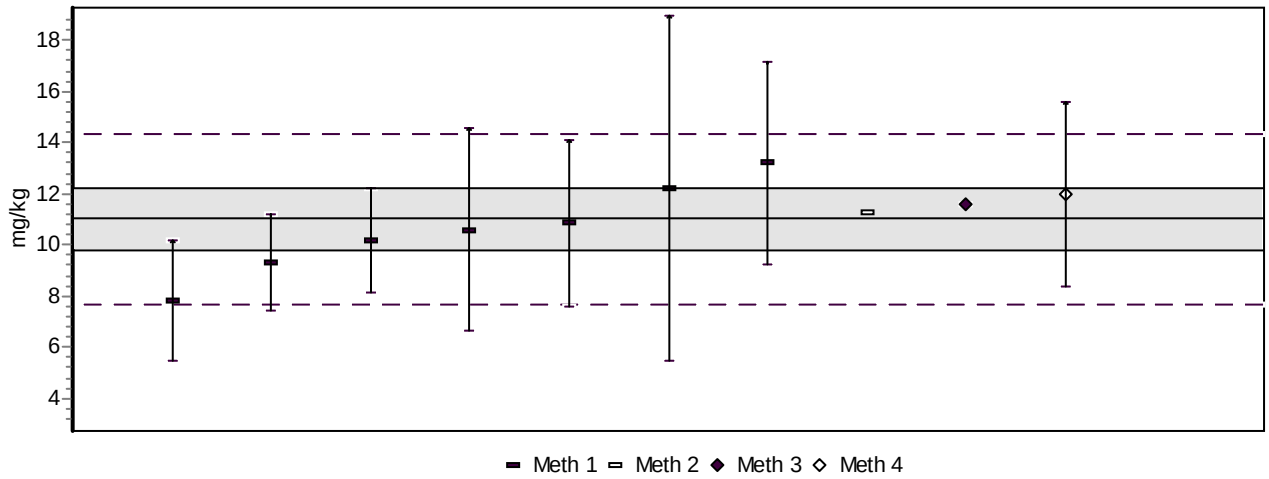
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* M3V



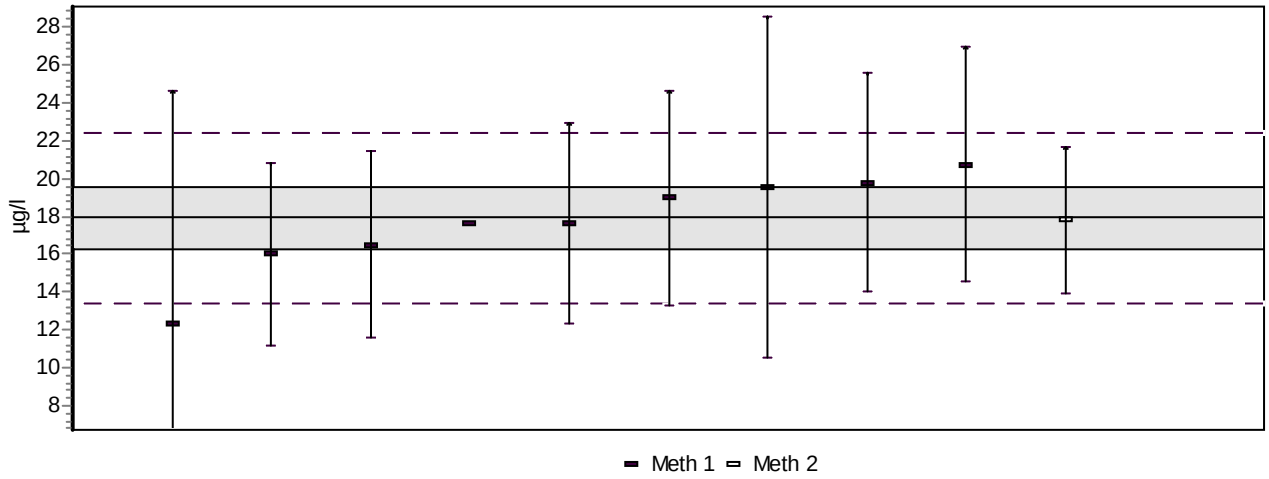
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* G2V



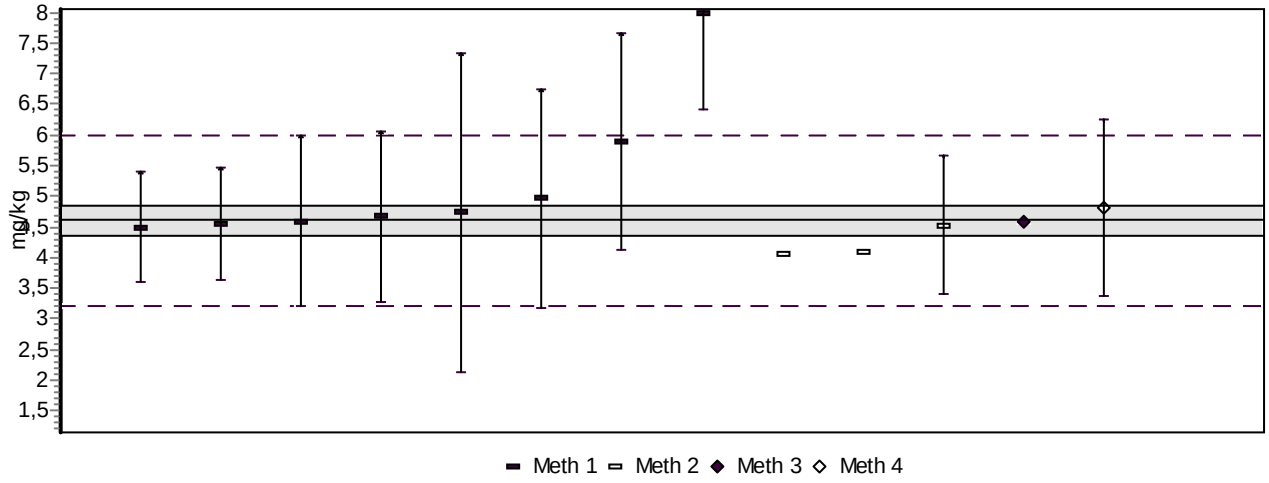
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* M3V



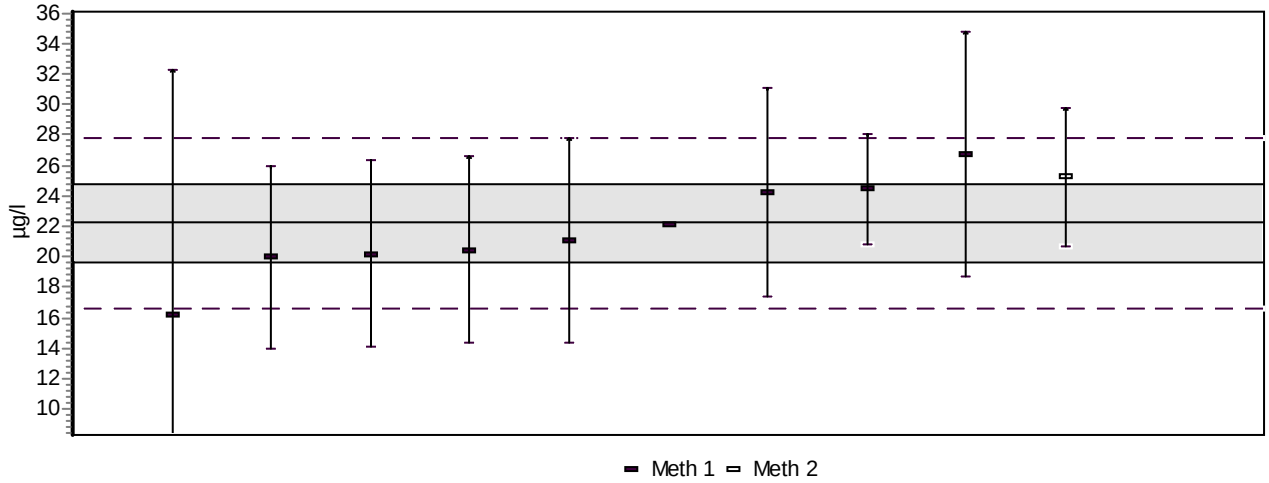
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* G2V



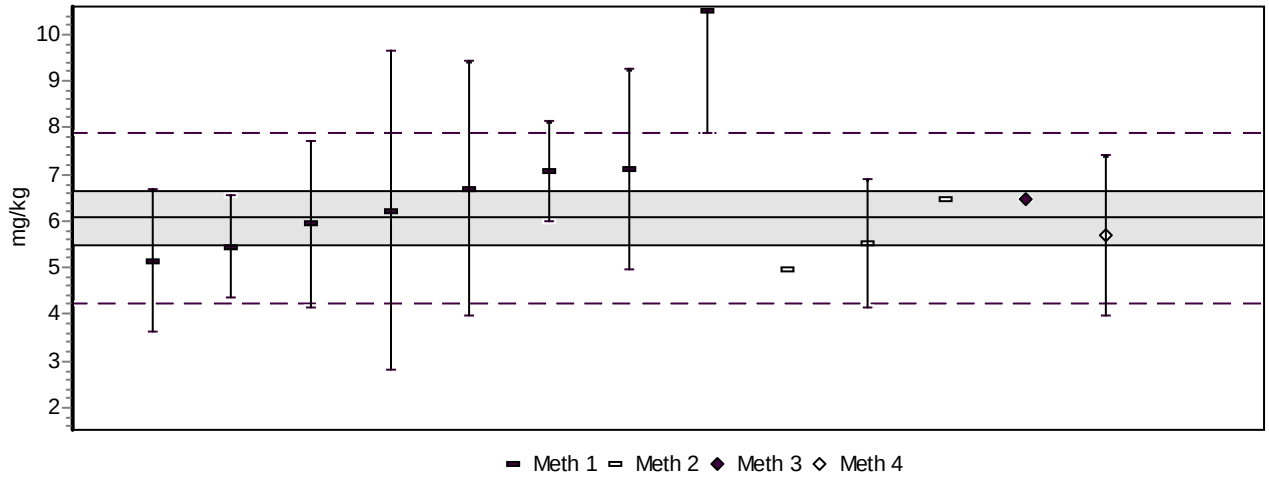
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* M3V



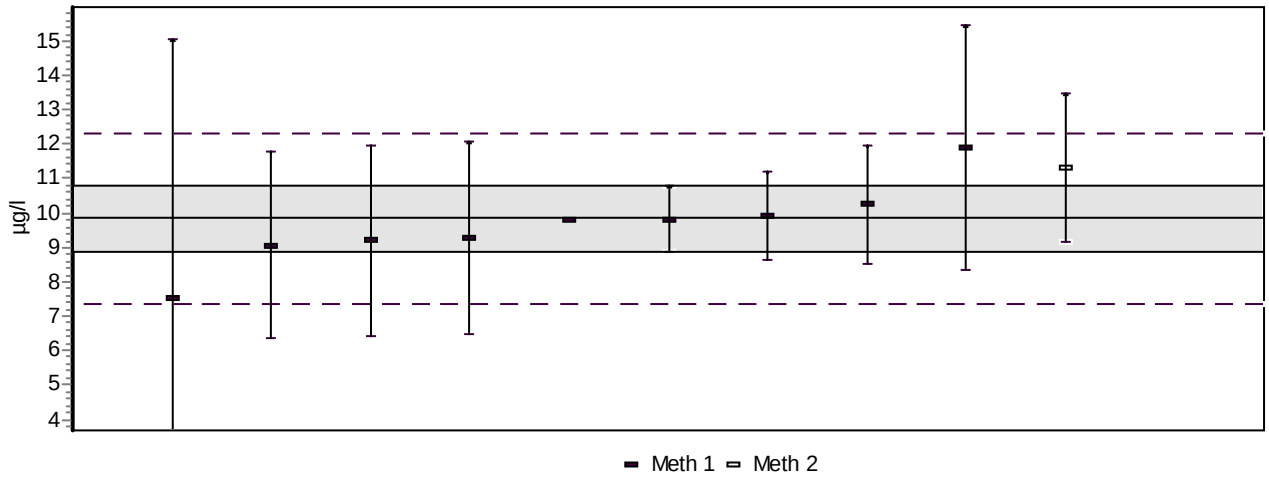
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* G2V



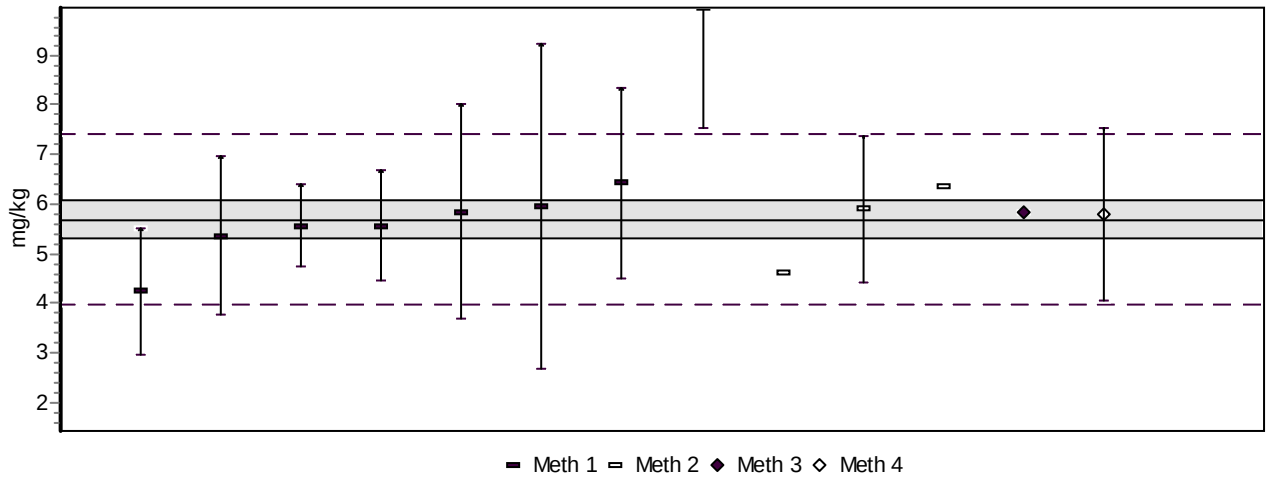
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* M3V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* G2V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* M3V



EXAMPLES OF THE REPORTED MEASUREMENT UNCERTAINTIES GROUPED ACCORDING TO THE EVALUATION PROCEDURE

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

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

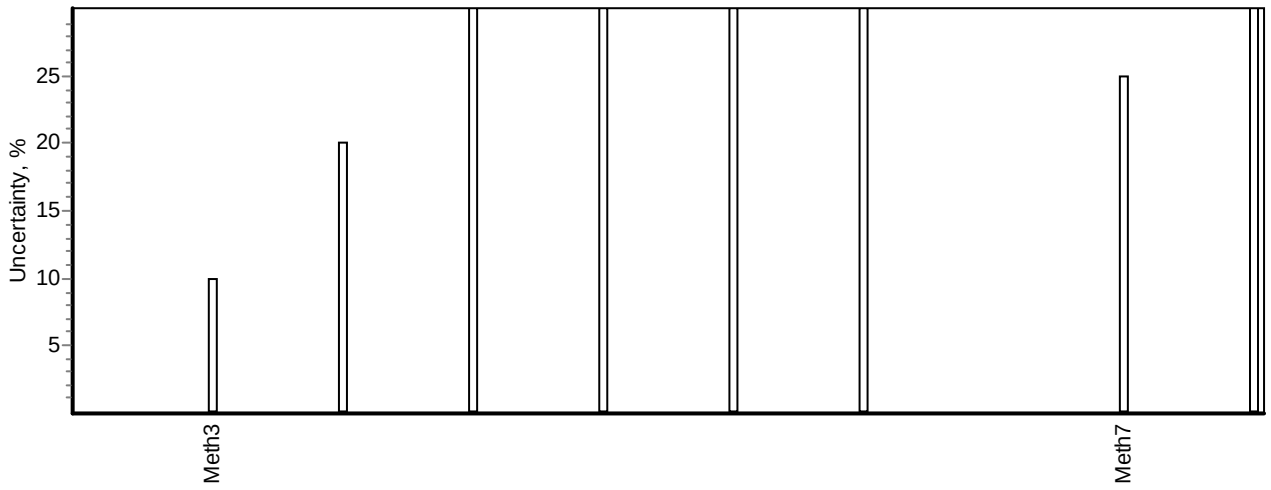
IQC = internal quality control

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

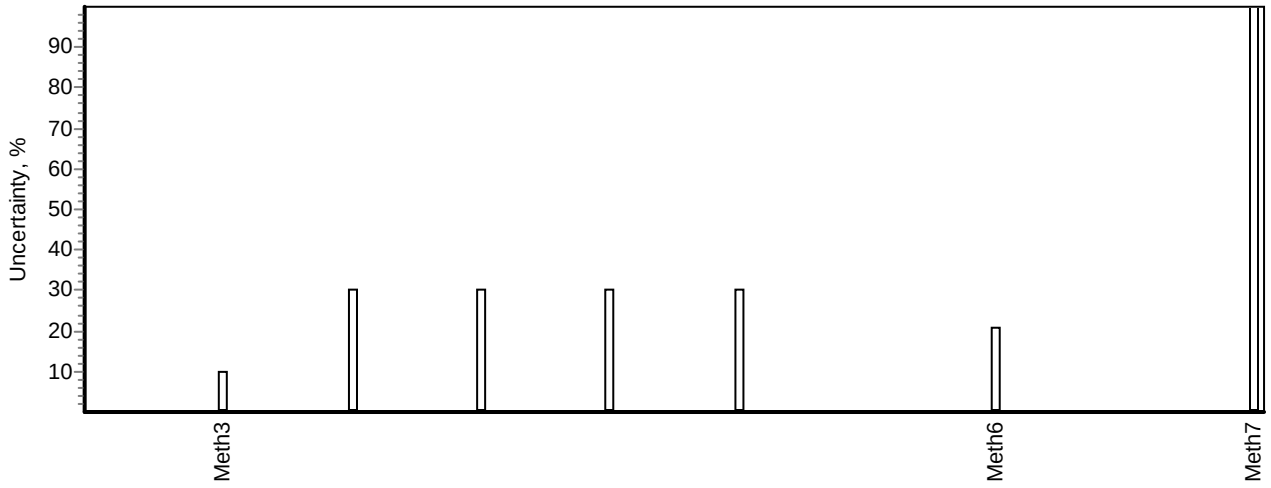
[1)] http://www.nordicinnovation.net
[2)] http://www.eurachem.org

LIITE 11.
APPENDIX 11.

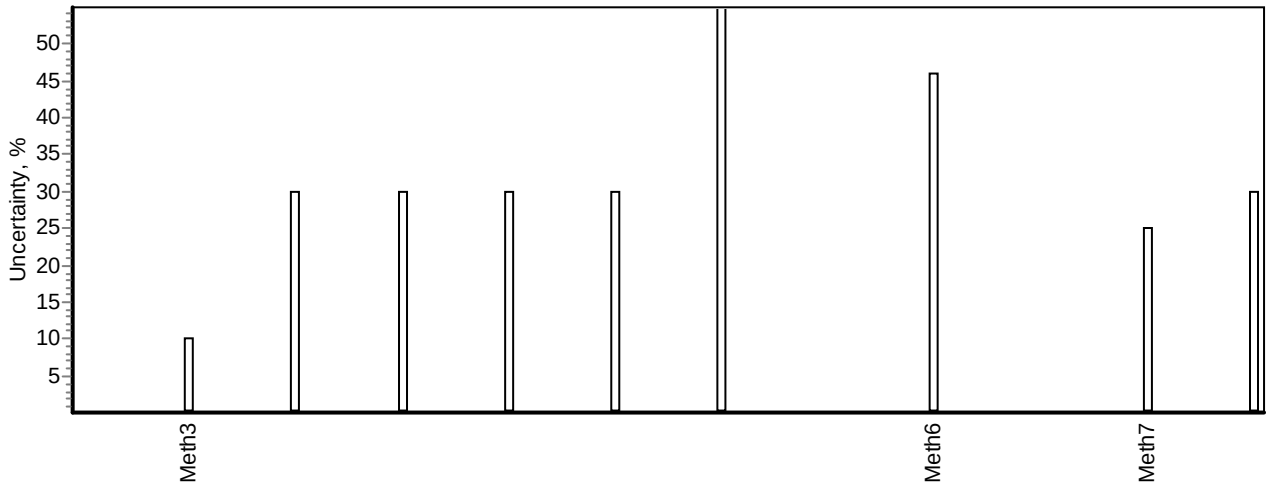
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* A1V



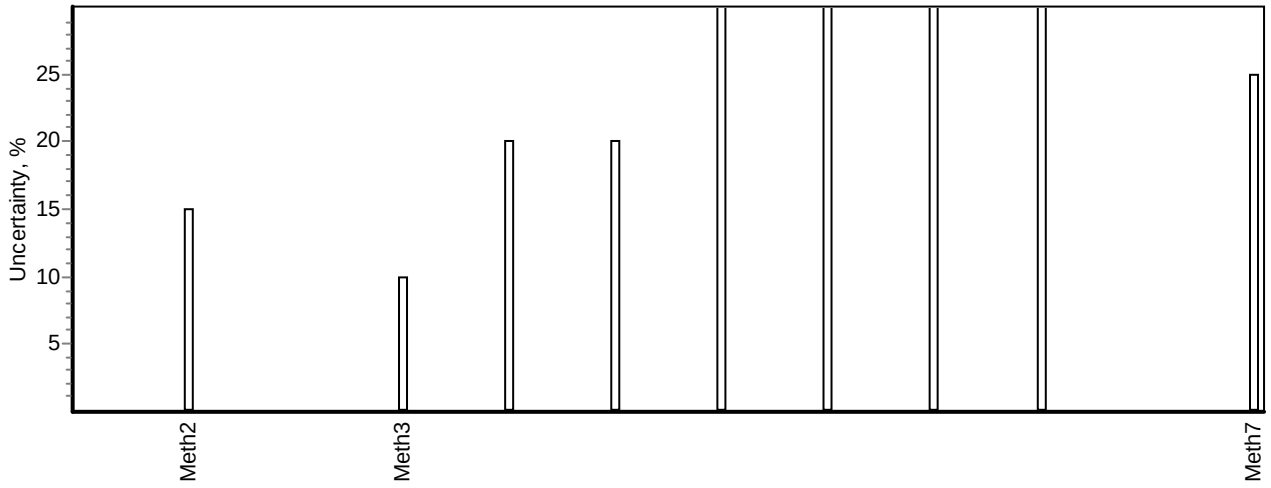
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* G2V



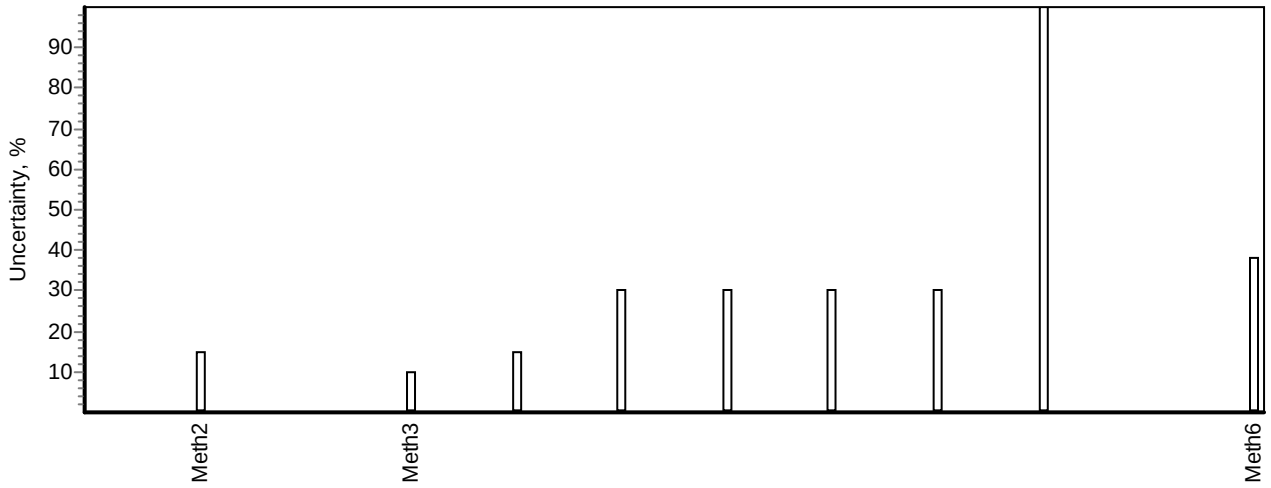
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* M3V



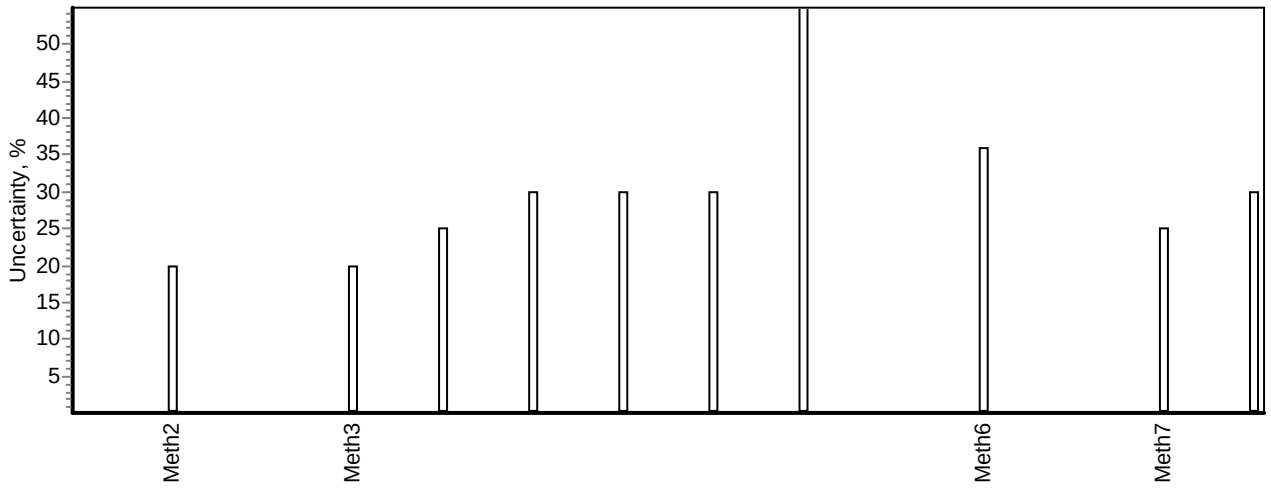
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* A1V



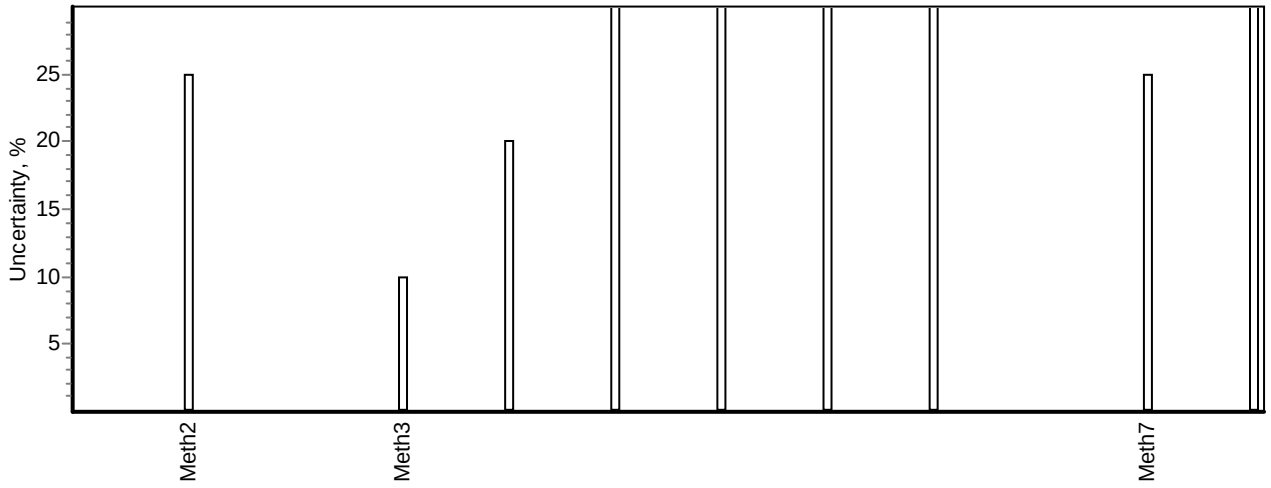
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* G2V



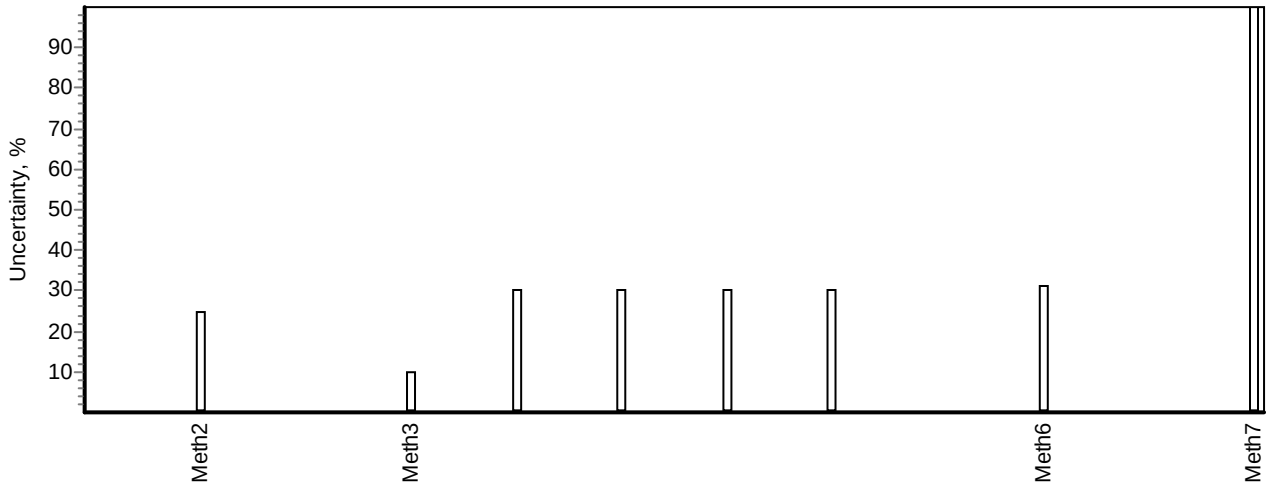
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* M3V



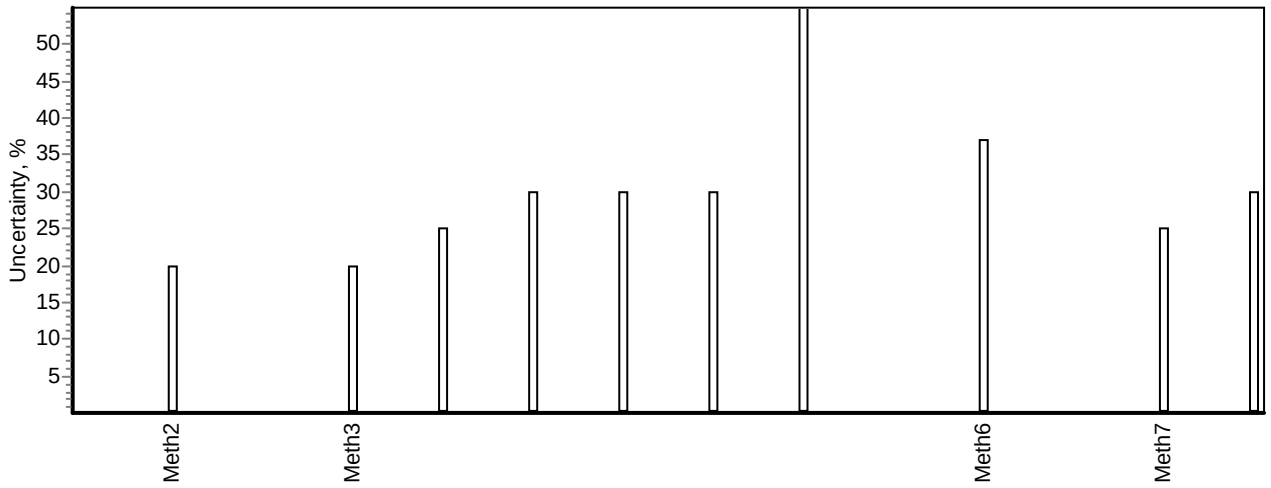
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* A1V



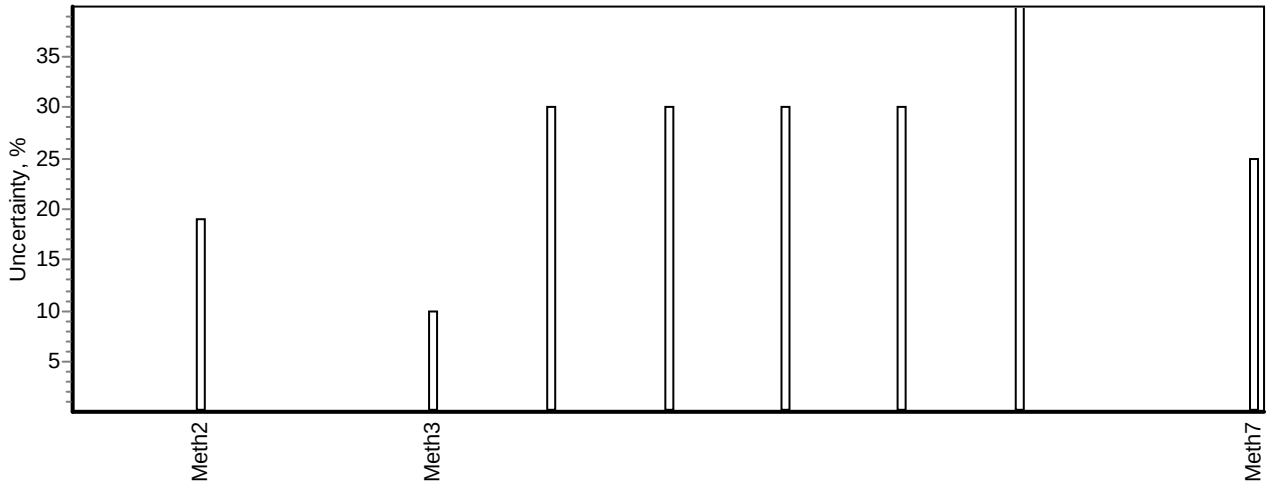
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* G2V



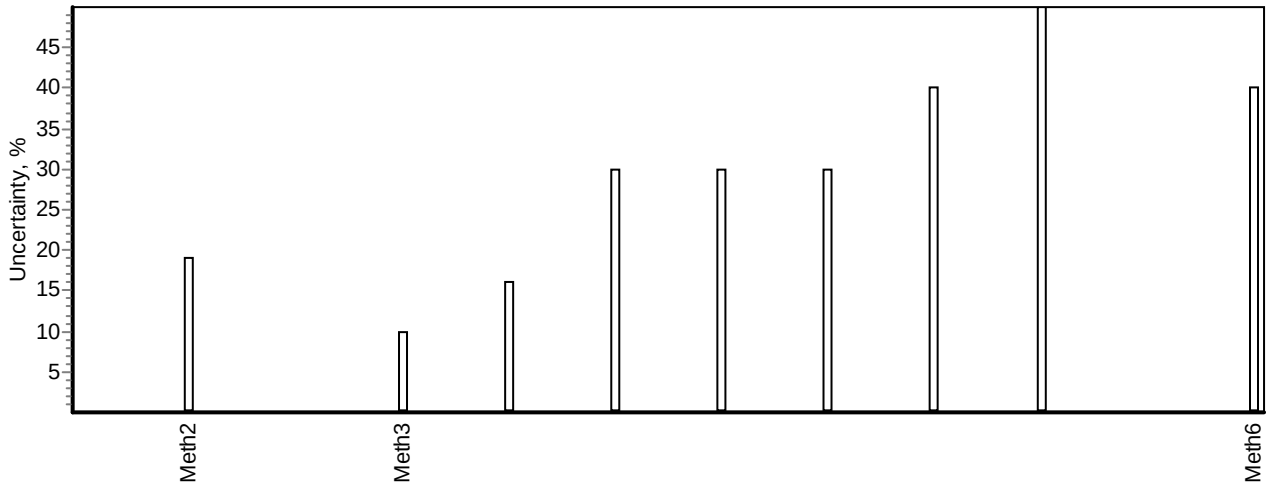
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* M3V



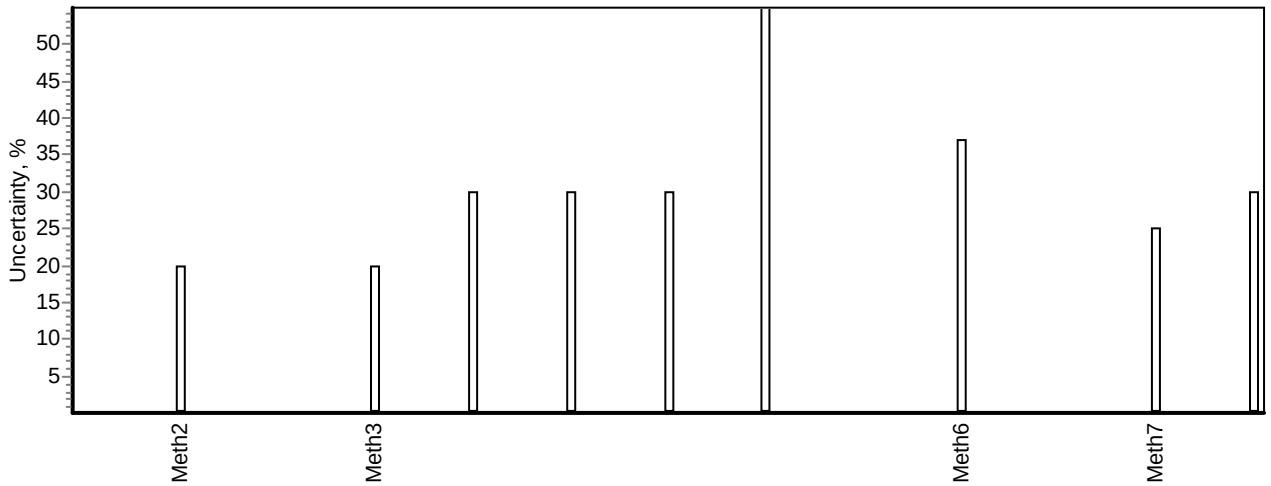
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* A1V



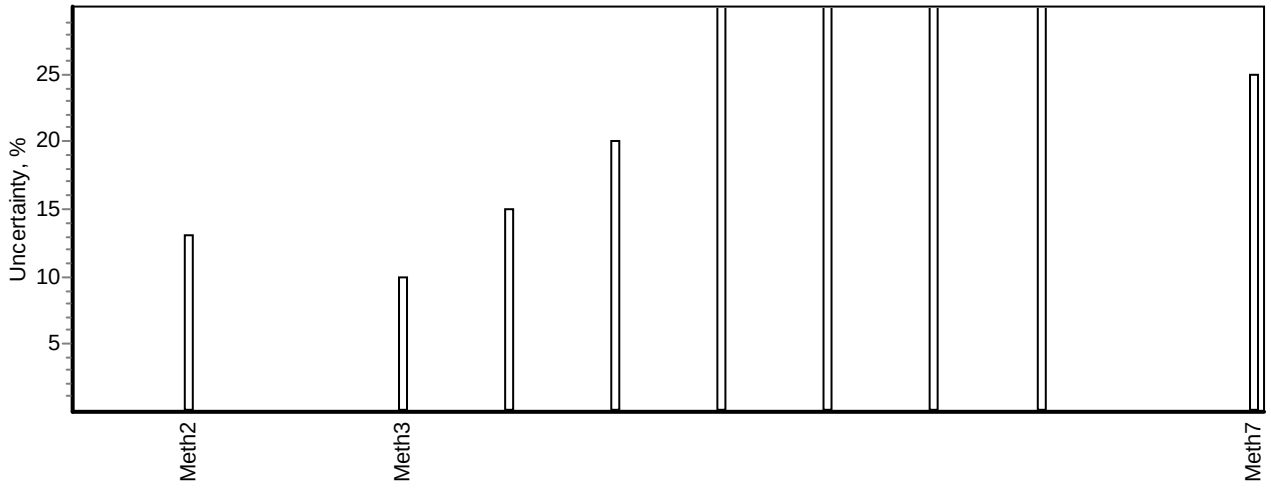
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* G2V



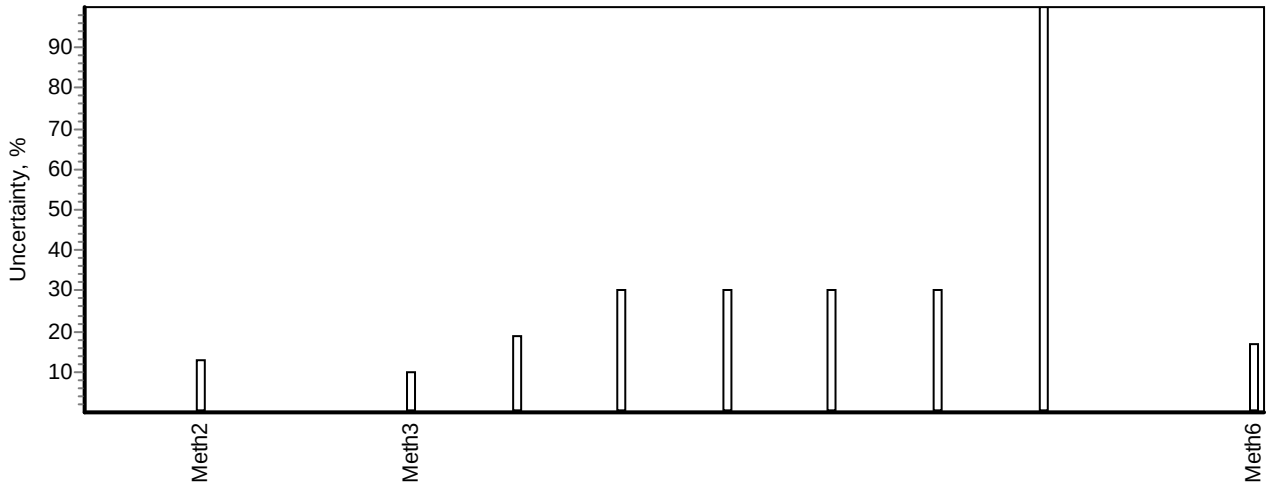
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* M3V



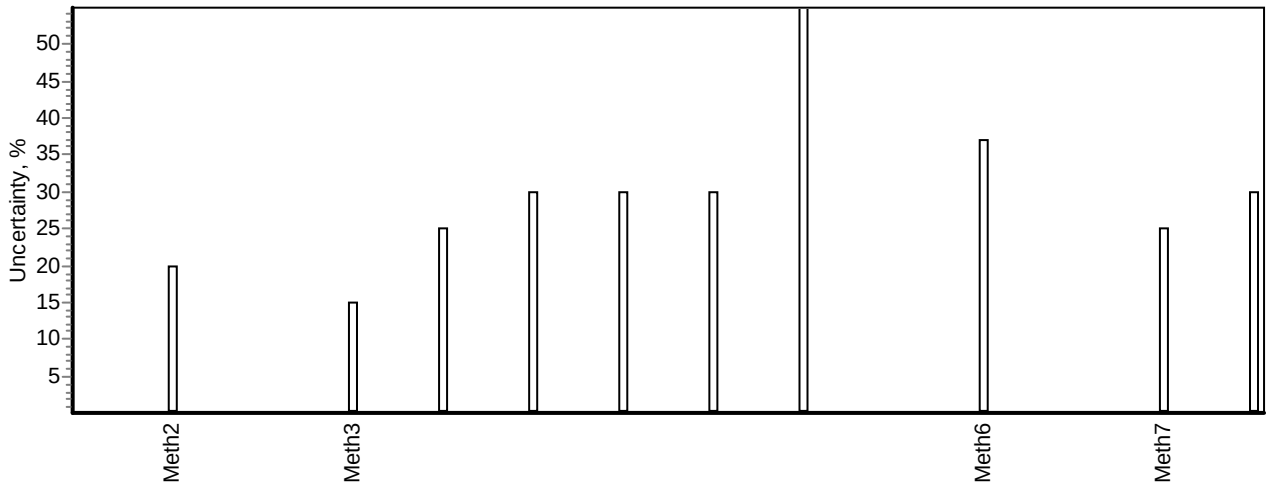
Analyytti *(Analyte)* **TOL** Näyte *(Sample)* A1V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* G2V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* M3V



LIITE 12. SUMMARY OF THE z SCORES

APPENDIX 12.Summary of the z scores

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	%
124TCBz	A1V	S	S	u	Q	S	q	U	S	.	S	S	S	U	58
	G2V	S	S	q	.	S	.	.	S	.	S	.	S	U	75
	M3V	S	S	q	S	S	S	S	S	.	S	S	S	S	92
12DCEa	A1V	U	S	q	U	S	S	S	S	q	S	q	S	U	54
	G2V	S	S	S	.	S	.	.	S	S	S	S	S	S	100
	M3V	S	S	q	q	S	S	U	S	q	S	S	S	S	69
Bz	A1V	S	S	q	Q	S	q	S	Q	S	S	S	S	U	62
	G2V	S	S	S	.	S	.	.	S	S	S	S	S	S	100
	M3V	S	S	S	S	S	S	U	S	S	S	S	S	S	92
c12DCEe	A1V	S	S	q	Q	S	q	S	.	S	S	.	S	U	64
	G2V	S	S	S	.	S	.	.	.	S	S	.	S	S	100
	M3V	S	S	S	S	S	S	U	.	S	S	.	S	S	91
CCl4	A1V	S	Q	u	U	.	S	Q	U	S	q	.	S	U	36
	G2V	S	S	q	.	S	.	.	S	S	S	.	S	S	89
	M3V	S	S	q	S	u	S	U	S	S	S	.	S	S	75
CHCl3	A1V	S	S	u	Q	S	q	Q	S	S	S	U	S	U	54
	G2V	S	S	S	.	S	.	.	S	S	S	.	S	S	100
	M3V	S	S	S	S	S	S	U	S	S	S	S	S	S	92
DCM	A1V	S	S	S	U	U	.	U	S	S	S	S	u	U	58
	G2V	S	S	S	.	S	.	.	S	S	S	.	S	S	100
	M3V	S	S	S	S	S	.	U	S	S	S	S	S	.	91
ETBz	A1V	S	S	u	Q	S	S	U	S	S	S	S	S	U	69
	G2V	S	S	u	.	S	.	.	S	S	S	S	S	S	90
	M3V	S	S	S	S	S	S	U	S	S	S	S	S	S	92
mpXYL	A1V	S	S	u	U	S	S	U	U	q	S	S	u	U	46
	G2V	S	S	u	.	S	.	.	S	S	S	S	u	S	80
	M3V	S	S	S	S	S	S	U	S	S	S	S	u	Q	77
MTBE	A1V	S	S	S	S	S	S	.	Q	S	S	S	S	U	83
	G2V	S	S	S	.	S	.	.	S	S	Q	S	S	S	90
	M3V	S	S	S	S	S	S	.	S	S	S	S	S	S	100
oXYL	A1V	S	S	u	S	Q	S	U	S	S	S	S	S	U	69
	G2V	S	S	u	.	Q	.	.	S	S	S	S	S	S	80
	M3V	S	S	S	S	Q	S	U	S	S	S	S	S	S	85
TAME	A1V	S	S	u	.	q	.	.	U	S	S	S	S	U	60
	G2V	S	S	u	.	S	.	.	S	S	Q	S	S	S	80
	M3V	S	S	S	.	S	.	.	S	S	S	S	S	S	100
TCEe	A1V	S	S	u	Q	S	q	S	S	S	q	S	S	U	62
	G2V	S	S	q	.	S	.	.	S	S	S	S	S	S	90
	M3V	S	S	S	S	S	S	U	S	S	S	S	S	S	92
TECEe	A1V	S	S	u	S	S	u	Q	S	S	q	S	S	U	62
	G2V	S	S	q	.	S	.	.	S	S	S	S	S	S	90
	M3V	S	S	S	S	S	S	U	S	S	S	S	S	S	92
TOL	A1V	S	S	u	Q	S	S	S	U	S	S	S	S	U	69
	G2V	S	S	S	.	S	.	.	S	S	S	S	S	S	100
	M3V	S	S	S	S	S	S	U	S	S	S	S	S	S	92
%		98	98	47	57	86	77	23	86	93	89	94	91	61	
Accredited		yes		yes		yes		yes	yes	yes	yes		yes		

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

%* - percentage of satisfactory results

Totally satisfactory, % In all: 79 In accredited: 79 In non-accredited: 79

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date February 2011
Author(s)	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori and Markku Ilmakunnas	
Title of publication	Proficiency Test SYKE 8a/2010 Volatile organic compounds in water and soil.	
Parts of publication/ other project publications	The publication is available only in the internet www.ymparisto.fi/julkaisut.	
Abstract	The Finnish Environment Institute carried out the proficiency test for analysis of volatile organic compounds from water and soil in November 2010. One artificial sample and one groundwater sample and one soil sample were distributed. In total, 13 laboratories participated in the proficiency test. Either the calculated concentration or the robust mean value was chosen to be the assigned value for the measurand. The performance of the participants was evaluated by using z scores. In this proficiency test 79 % of the results were satisfactory when the deviation of 15–30 % from the assigned value was accepted.	
Keywords	water analysis, soil analysis, volatile organic compounds, VOC, proficiency test, intercomparison	
Publication series and number	Suomen ympäristökeskuksen raportteja 5 / 2011	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
	ISSN 1796-1726 (online)	ISBN 978-952-11-3854-6 (PDF)
	No. of pages 71	Language English
	Restrictions Public	Price
For sale at/ distributor	Finnish Environment Institute, Customer service E-mail: neuvonta.syke@ymparisto.fi Phone +358 20 610 183 Fax +358 9 5490 2190	
Financier of publication	Finnish Environment Institute, P.O.Box 140, FI-00251 Helsinki, Finland	
Printing place and year	Helsinki 2011	
Other information		

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Helmikuu 2011
Tekijä(t)	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori ja Markku Ilmakunnas	
Julkaisun nimi	Proficiency Test SYKE 8a/2010 Volatile organic compounds in water and soil.	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä. www.ymparisto.fi/julkaisut	
Tiivistelmä	Suomen ympäristökeskus järjesti pätevyyskokeen haihtuvien orgaanisten yhdisteiden määrityksistä vesi- ja maanäytteistä marraskuussa 2010. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 13 laboratorioita. Mittaussuureen vertailuarvona käytettiin laskennallista arvoa tai osallistujien tulosten robustia keskiarvoa. Pätevyyden arvioimisessa käytettiin z-arvoa ja sitä laskettaessa tulokselle sallittiin synteettisessä näytteessä 15 %:n, vesinäytteessä 25 %:n ja maanäytteessä 30 %:n poikkeama vertailuarvosta. Kokonaisuudessaan hyväksyttäviä tuloksia oli 79 %.	
Asiasanat	vesianalyysi, maa-analyysi, haihtuvat orgaaniset yhdisteet, VOC, pätevyyskoe, vertailumittaus	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 5 / 2011	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
	ISSN 1796-1726 (verkkoj.)	ISBN 978-952-11-3854-6 (PDF)
	Sivuja 71	Kieli englanti
	Luottamuksellisuus Julkinen	Hinta
Julkaisun myynti/ jakaja	Suomen ympäristökeskus, asiakaspalvelu Sähköpostiosoite: neuvonta.syke@ymparisto.fi puh. 020 610 183 faksi 09 5490 2190	
Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2011	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Februari 2011
Författare	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori och Markku Ilmakunnas	
Publikationens titel	Proficiency Test SYKE 8a/2010 Volatile organic compounds in water and soil.	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under november 2010 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av flyktiga organiska föreningar i grundvatten och i förorenad jord. Proven sändes ut till 13 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 79 % av alla resultaten tillfredsställande, när 15–30 % totalavvikelsen från referensvärdet accepterades.	
Nyckelord	vattenanalyser, jordanalyser, flyktiga organiska föreningar, VOC, provningsjämförelse, interkalibrering	
Publikationsserie och nummer	Suomen ympäristökeskuksen raportteja 5 / 2011	
Publikationens tema		
Projektets namn och nummer		
Finansiär/ uppdragsgivare		
Organisationer i projektgruppen		
	ISSN 1796-1726 (online)	ISBN 978-952-11-3854-6 (PDF)
	Sidantal 71	Språk Engelska
	Offentlighet Offentlig	Pris
Beställningar/ distribution	Finlands miljöcentral, informationstjänsten neuvonta.syke@ymparisto.fi Tfn 020 610 183 Fax 09 5490 2190	
Förläggare	Finlands Miljöcentral, PB 140, 00251 Helsingfors	
Tryckeri/ tryckningsort och –år	Helsingfors 2011	
Övriga uppgifter		

SYKE PROFICIENCY TEST 5/2011

FINNISH ENVIRONMENT INSTITUTE

ISBN 978-952-11-3854-6 (PDF)
ISSN 1796-1726 (online)