

REPORTS OF FINNISH ENVIRONMENT INSTITUTE
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SYKE Proficiency Test 2/2006

**Volatile organic compounds and mineral oils
from water and polluted soil**

**Irma Mäkinen
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The publication is available only in printed

Edita Prima Oy, Helsinki 2006
ISBN 952-11-2330-3 (pbk.)
ISSN 1796-1718 (print)

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1 INTRODUCTION

The Finnish Environment Institute carried out the proficiency test for the analysis of mineral oils (middle and heavy fractions) and volatile organic compounds in water and in soil in February 2006. The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1¹, ILAC Requirements², ISO13528³ and IUPAC Recommendations⁴.

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratory
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The responsibilities in organizing the proficiency test were as follows:

Irma Mäkinen, SYKE, coordinator
Pirjo Sainio, analytical expert (mineral oils)
Jari Nuutinen, analytical expert (volatile organic compounds).

2.2 Participants

In total, the samples were delivered to 20 laboratories, from which three laboratories did not reported the results (Appendix 1). The laboratories 15, 16 and 17 reported their results after the dead line.

2.3 Samples and their delivery

The samples were as follows:

Sample/Analytes	Code	Sample amount	Remarks
Standard mixture/mineral oils (in hexane)	S1	≈ 1.5 ml	
Standard mixture/mineral oils (in iso-propanol)	L1	≈ 1.5 ml	The addition solution for the sample V1 (200 µl)
Water/mineral oils	V1	1 l	
Soil/mineral oils	M1	50 g	
Standard mixture/volatile organics ¹⁾ (in methanol)	S2	≈ 1.5 ml	
Water/volatile organics ¹⁾	V2	250 ml	
Soil/ volatile organics ¹⁾	M2	20 g soil 4.0 ml H ₂ O 21 ml MeOH	

¹⁾ MTBE, TAME, benzene, ethylbenzene, toluene, styrene, o-xylene, m-xylene, p-xylene, trichloroethene, tetrachloroethene

The preparation of the samples is presented in Appendix 2.

The samples were delivered on 7 February 2006 and they were asked to analyze as follows:

- 8–9 February 2006 – water/volatile organic compounds
- before 17 February 2006 – water and soil/mineral oils, soil/volatile organic compounds.

The results were asked to return before the 21 February 2006.

2.4 Testing of homogeneity

Homogeneity of the samples M1, M2, and V2 was tested (Appendix 3). The samples were regarded homogenous.

2.5 Testing of stability

The ampoules S1 and L1, and the soil sample M1 for analysis of mineral oils were tested after preparation and during the time of analysis (Appendix 4). There were not significant changes of concentrations.

The samples S2, V2, and M2 were tested during the distribution and in time of analysis. The samples were kept at the room temperature and in cool during the delivering. The concentrations of MTBE and TAME were slightly decreased in those test samples kept at the room temperature during the sample distribution. However, the highest temperature detected by the laboratory after receiving of the samples was 13 °C and most laboratories were received the samples in a few hours. Thus the temperature had not caused similar changes of concentrations as in testing of the samples at two different temperatures. There were also some changes in the concentrations of ethylbenzene and styrene in the sample V2. The target standard deviation was increased in evaluation of the results of ethylbenzene (30 %→ 40 %) and the performance of the laboratories in the analysis of styrene has not been evaluated for the sample V2. No changes of concentrations were obtained in testing of the soil sample M2.

2.6 Comments sent by the participants

The participants sent comments on their own results and methods (Appendix 5). Also the concentrations of the synthetic samples have been commented.

2.7 Analytical methods

The analytical methods used by the participants are presented in Appendix 6.1.

Mineral oils were mainly extracted with hexane from the water sample V1 and with the mixture of acetone–hexane from the soil sample M1. Both shaking and sonication was used as the extraction method.

Volatile organics were mainly analyzed without extraction from the water sample V2. For extraction of the soil sample M2 methanol (added during sample preparation) was mainly used. The lengths of the GC columns varied 15 m to 60 m. About a half of the laboratories used FID detector. In these cases the overlapping of the peaks might have had an effect on the results. On the other hand this can be overcome by using MS as a detector. The methods used by the participants based on several ISO or EPA references.

2.8 Data treatment

2.8.1 Testing of outliers and normality of data

The participants were requested to report the duplicate results in the analysis of the samples S1 and S2, four replicates in the analysis of the samples M1 and M2 and three replicates in the analysis of the water sample V2. Measurement uncertainties were asked to report for each result, too.

Before the statistical treatment, the data was tested according to Kolmogorov-Smirnov normality test. Outliers were rejected according to the Hampel test in calculation of the mean values. Also before calculation of the robust mean, two outliers were rejected, since the results deviated at least 50 % of the robust mean⁴.

2.8.2 Assigned values and their uncertainties

The calculated concentration was used as the signed value in analysis of the synthetic samples S1 and S2 as well as in analysis of the water samples V1 and V2 (Appendix 7). The robust mean was used as the assigned value in the analysis of the soil samples M1 and M2.

The uncertainty of the assigned values was calculated on the basis of the preparation of the samples S1, S2, V1, and V2. The uncertainties were smaller than 0,5 %. The uncertainties of the soil samples M1 and M2 were estimated on the basis of the robust standard deviation of the results and it varied from 16 % to 42 % (at the 95 % confidence interval). It was largest in analysis of tetrachloroethene and trichloroethene in the analysis of the sample M2. Particularly, in these two cases the low number of the participants (< 10) had an influence on the uncertainty of the assigned values

2.8.3 Uncertainties reported by the participants

Most participants reported their measurement uncertainties and it was mainly estimated using the data of validation and internal quality control (Appendix 8). In analysis of the water and soil samples the uncertainties varied mainly from 10 % to 40 %, but also higher uncertainties were reported. On the other hand, in some cases the uncertainty estimates seemed to be too low comparing with the performance of the laboratory.

2.8.4 Target value for total deviation

The target value for the total deviation (s_{target} , %) used for calculation of the z scores was estimated on basis of the type of the sample, the contents of the sample, the results of stability testing and the uncertainties of the assigned values. The s_{target} was 20 % in the analysis of the synthetic samples (at the 95 % confidence interval). In the analysis of the water and soil samples it was 25 % or 30 % except the results of ethylbenzene. In this case the target value of 40 % was used.

2.8.5 Evaluation of performance

The performance evaluation was carried out by using the z scores. The z scores were calculated using the following equation:

$$z = (x_i - X)/s$$

where

x_i = the reported value of the participant

X = the assigned value

s = the target total standard deviation (s_{target}).

z scores can be interpreted as follows:

$ z \leq 2$	“satisfied” results
$2 < z < 3$	“questionable” results
$ z \geq 3$	“unsatisfied” results.

The calculated z scores are presented in the results of each participant (Appendix 11) and the summary of z scores is presented in Appendix 12. Explanations to terms are presented in Appendix 10. The organizing laboratory SYKE has the code 8 in the results.

3 RESULTS AND PERFORMANCE

3.1 Variation of the results

The robust standard deviation varied from 7.2 % to 35 % in the analysis of mineral oils (Table 1). The variation was highest in the analysis of the water sample V1 (0.88 mg/l). The results varied from 19 % to 22 % in the analysis of the water samples in the proficiency test 8/2004⁵. In analysis of the soil sample the standard deviation (12 %) was less than the respective standard deviation in the proficiency test 4/2004⁶. In the analysis of mineral oils particularly from waters the use of two different techniques in extraction (shaking or sonication) increases the variation of the results (Appendix 6.2).

In the analysis of volatile organics from the synthetic sample S2 the results varied from 7.2 % to 30 %. The variation was highest in analysis of TAME and toluene. The laboratory 3 complained about too low concentration in order to dilute the sample S2 using the solvent, which the laboratory normally used.

In the analysis of volatile organics from the water sample V2 the results varied from 6.8 % to 31 %. In this case the results varied most in the analysis of benzene and TAME. In this proficiency test the results of the synthetic sample and water sample varied more than in the proficiency test 8/2003⁷, when the concentrations of volatile organics were higher than in this PT. As have been shown here again the concentrations affects to the variation of the results.

In the analysis of the soil sample M2 the results varied less (15 % - 25 %) than in the analysis of the synthetic sample S2 or the water sample V2.

Table 1. Summary of the proficiency test 2/2006

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
Min.oil-GC	M1	mg/kg	925	942.73	924.69	904.00	114.16	12,3	15	30	87
	S1	mg/ml	5	5.30	5.17	5.08	0.37	7,2	15	20	80
	V1	mg/l	0,88	0.79	0.78	0.72	0.27	34,9	16	30	67
TetraCE	M2	mg/kg	1,72	1.74	1.72	1.75	0.44	25,4	9	30	78
	S2	µg/ml	0,9	0.91	0.92	0.93	0.069	7,5	9	20	67
	V2	µg/l	11,84	11.55	11.04	11.10	1.05	9,5	9	25	78
TriCE	M2	mg/kg	0,676	0.68	0.68	0.71	0.17	25,1	9	30	56
	S2	µg/ml	0,36	0.40	0.40	0.39	0.080	19,9	9	20	56
	V2	µg/l	9,44	9.23	8.85	8.90	0.60	6,8	9	25	78
VOC-Benzene	M2	mg/kg	3,68	3.58	3.68	3.59	0.67	18,2	14	30	93
	S2	µg/ml	2,01	2.11	2.18	2.13	0.33	15,2	14	20	64
	V2	µg/l	11,19	9.79	9.68	9.72	3.04	31,4	14	25	71
VOC-Et.benzene	M2	mg/kg	3,28	3.18	3.28	3.18	0.59	17,9	14	30	79
	S2	µg/ml	1,74	1.77	1.78	1.79	0.35	19,9	14	20	64
	V2	µg/l	17,9	17.56	17.92	18.15	3.15	17,6	14	40	79
VOC-m/p-Xylene	M2	mg/kg	5,63	5.37	5.63	5.79	1.12	19,9	14	30	79
	S2	µg/ml	2,93	2.91	2.97	2.96	0.32	10,9	14	20	71
	V2	µg/l	28,6	27.20	28.62	28.35	4.51	15,8	14	30	71
VOC-MTBE	M2	mg/kg	3,13	3.17	3.13	3.21	0.48	15,3	10	25	90
	S2	µg/ml	1,68	1.70	1.69	1.66	0.31	18,5	10	20	70
	V2	µg/l	9,41	9.39	9.34	9.21	2.47	26,4	10	25	60
VOC-o-Xylene	M2	mg/kg	4,31	4.12	4.31	4.55	0.80	18,5	14	25	86
	S2	µg/ml	2,19	2.27	2.30	2.36	0.33	14,3	14	20	64
	V2	µg/l	23,02	20.87	22.31	22.45	3.67	16,5	14	25	79
VOC-Styrene	M2	mg/kg	1,72	1.73	1.72	1.69	0.28	16,3	9	25	100
	S2	µg/ml	0,89	0.86	0.86	0.88	0.13	15,6	9	20	89
	V2	µg/l	9,05	9.05	9.05	8.97	2.54	28	8		
VOC-TAME	M2	mg/kg	1,41	1.42	1.41	1.50	0.29	20,7	10	25	100
	S2	µg/ml	0,78	0.74	0.74	0.75	0.21	28,7	10	20	60
	V2	µg/l	10,98	10.54	10.54	10.35	3.08	29,2	10	25	70
VOC-Toluene	M2	mg/kg	4,15	3.76	4.15	4.02	0.74	17,9	14	25	71
	S2	µg/ml	2,19	1.99	1.99	2.08	0.59	29,4	14	20	50
	V2	µg/l	16,22	13.97	14.61	14.00	2.02	13,8	14	25	71

where

Ass. val.	the assigned value
Mean	the mean value
Mean rob	robust mean
Md	the median value
SD rob	the robust standard deviation
SD rob %	the robust standard deviation as percents
Num of Labs	the number of participants
2*Targ. SD %	the target total deviation (95 % confidence interval)
Accepted z-val %	the satisfied z values: the results (%), where $ z \leq 2$.

In this proficiency test the repeatability (the within-laboratory standard deviation, s_w) varied from 2.6 to 8.6 % and the reproducibility (the between-laboratory standard deviation, s_l) varied from 3.2 to 30 % (Table 1). The ratio s_l/s_w , the robustness of the methods, was mainly higher than three and in several cases even higher than five. The ratio s_l/s_w should be between 2 and 3 for robust methods⁷.

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

Analyte	Sample	Unit	Ass. val	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Ac- cepted z-val %
Min.oil-GC	M1	mg/kg	925	942,7	910	50,56	152,1	160,3	5,4	16	17	30	15	87
	S1	mg/ml	5	5,299	5,085	0,2064	0,5809	0,6165	3,9	11	12	20	15	80
TetraCE	M2	mg/kg	1,72	1,735	1,75	0,08283	0,442	0,4497	4,8	25	26	30	9	78
	S2	µg/ml	0,9	0,9122	0,9095	0,02625	0,02914	0,03922	2,9	3,2	4,3	20	9	67
	V2	µg/l	11,84	11,55	11,1	0,3681	1,611	1,652	3,2	14	14	25	9	78
TriCE	M2	mg/kg	0,676	0,6769	0,71	0,04828	0,2051	0,2107	7,1	30	31	30	9	56
	S2	µg/ml	0,36	0,3969	0,3903	0,01872	0,09036	0,09228	4,7	23	23	20	9	56
	V2	µg/l	9,44	9,227	8,939	0,2678	1,386	1,411	2,9	15	15	25	9	78
VOC-Benzene	M2	mg/kg	3,68	3,576	3,59	0,1541	0,7872	0,8021	4,3	22	22	30	14	93
	S2	µg/ml	2,01	2,115	2,111	0,1158	0,3324	0,352	5,5	16	17	20	14	64
	V2	µg/l	11,19	9,789	9,72	0,4244	2,875	2,906	4,3	29	30	25	14	71
VOC-Et.benzene	M2	mg/kg	3,28	3,177	3,12	0,1386	0,7586	0,7712	4,4	24	24	30	14	79
	S2	µg/ml	1,74	1,766	1,785	0,06452	0,3448	0,3508	3,7	20	20	20	14	64
	V2	µg/l	17,9	17,56	18,15	1,187	4,913	5,055	6,8	28	29	40	14	79
VOC-m/p-Xylene	M2	mg/kg	5,63	5,373	5,39	0,2476	1,327	1,35	4,6	25	25	30	14	79
	S2	µg/ml	2,93	2,91	2,958	0,1148	0,5134	0,5261	3,9	18	18	20	14	71
	V2	µg/l	28,6	27,2	27,9	0,8365	7,379	7,426	3,1	27	27	30	14	71
VOC-MTBE	M2	mg/kg	3,13	3,169	3,21	0,1769	0,4074	0,4442	5,6	13	14	25	10	90
	S2	µg/ml	1,68	1,705	1,661	0,0741	0,3378	0,3458	4,3	20	20	20	10	70
	V2	µg/l	9,41	9,391	9,205	0,4363	2,25	2,292	4,6	24	24	25	10	60
VOC-o-Xylene	M2	mg/kg	4,31	4,116	4,45	0,1787	0,9329	0,9499	4,3	23	23	25	14	86
	S2	µg/ml	2,19	2,265	2,29	0,0598	0,381	0,3856	2,6	17	17	20	14	64
	V2	µg/l	23,02	20,87	22,3	0,7433	5,446	5,496	3,6	26	26	25	14	79
VOC-Styrene	M2	mg/kg	1,72	1,731	1,69	0,06066	0,2567	0,2637	3,5	15	15	25	9	100
	S2	µg/ml	0,89	0,8583	0,8815	0,03388	0,1188	0,1236	3,9	14	14	20	9	89
	V2	µg/l	9,05	9,053	8,97	0,4425	2,223	2,266	4,9	25	25		8	
VOC-TAME	M2	mg/kg	1,41	1,419	1,5	0,08827	0,2589	0,2736	6,2	18	19	25	10	100
	S2	µg/ml	0,78	0,7434	0,7477	0,06403	0,1826	0,1935	8,6	25	26	20	10	60
	V2	µg/l	10,98	10,54	10,35	0,5777	2,698	2,759	5,5	26	26	25	10	70
VOC-Toluene	M2	mg/kg	4,15	3,764	4,02	0,2106	1,126	1,146	5,6	30	30	25	14	71
	S2	µg/ml	2,19	1,991	2,08	0,08158	0,5211	0,5275	4,1	26	26	20	14	50
	V2	µg/l	16,22	13,97	14,3	0,4174	3,572	3,596	3	26	26	25	14	71

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

3.2 Comments on the results

In the analysis of mineral oils from the water sample V1 the expected concentration was 0.88 mg/l. The use of sonication as the extraction technique gives the recovery of about 80 %, where as the recovery was about 107 % in use of the stirring technique. Similar difference between the results obtained using stirring and sonication can slightly be seen in the analysis of mineral oils from soil (Appendix 6.2). In the analysis of mineral oils extraction and clean-up are the most crucial steps⁸. Extraction time and magnetic stirring speed are the crucial parameters particularly for the analysis of water samples⁸. In this proficiency test the laboratories used mainly Florisil for clean-up.

In general, the participants used different methods or the modifications of the EPA methods, the ISO or the EN standards or the standard proposals^{9, 10, 11, 12} (Appendix 6.1). In the analysis of all samples the participants mainly used the internal standards. Only four laboratories (lab 2, 7, 13 and 14) did not use the internal standards and two participants did not report details of their methods. In use of the internal standard the changes of injection, the proportion of extraction volume and matrix (v/v or v/w) or other interferences do not affect the results. In addition, the length of the column in VOC analysis may affect the results obtained with FID, if a good enough separation was not reached with the compounds. Normally styrene and o-xylene has a small difference in their retention times, as well as benzene and TAME. But they can be separated with MS, since their identification ions differ from each other.

In the analysis of the water sample V2 the laboratories 1 and 3 extracted the water sample. The laboratory 3 obtained the satisfied results, but the laboratory 1 reported too low values in analysis of the water sample V2 and in the analysis of the soil sample M2 as well.

Into the soil sample M2 methanol had been added during the sample preparation. The laboratory 1 added also pentane before extraction. Five laboratories (lab 1, 4, 6, 8 and 12) used shaking and one laboratory (lab 7) used sonication as the extraction technique. Other laboratories did not report the extraction technique. The laboratories 6, 8 and 12 from those using the shaking technique reported the satisfied results in the analysis of the synthetic sample S2. When their mean value obtained from the sample M2 was compared with the robust mean value of all laboratories, it was from 2.8 % to 15.5 % higher than the robust mean (Table 3). Thus the shaking technique had clearly been more effective than other procedures in extraction of the soil sample M2.

Table 3. The mean value of the results obtained by the laboratories 6, 8 and 12 comparing with the robust mean of all results (the assigned value, AV) in the analysis of the soil sample M2.

Lab	TetraCE	TriCE	Benzene	Ethylbenzene	m,p-Xylene	MTBE	o-Xylene	Styrene	TAME	Toluene
6	1.783	0.742	4.447	3.395	6.475	3.163	5.065	2.042	1.5	4.67
8	1.887	0.722	4.361	3.684	6.28	3.538	4.954	2.077	1.655	4.816
12	1.635	0.682	3.555	3.063	5.175	3.502	3.888	1.703	1.732	4.135
$\bar{X}_{lab\ 6,8,12}$	1.77	0.715	4.12	3.38	5.98	3.40	4.64	1.94	1.63	4.54
AV	1.72	0.676	3.68	3.28	5.63	3.13	4.31	1.72	1.41	4.15
Difference-%	2.8	5.8	12.0	3.1	6.2	8.7	7.6	12.8	15.5	9.4

Also the figures of kernel density functions show, that some laboratories reported too low values in the analysis of the sample V2 as well as in the sample M2 (Appendix 6.3).

3.3 Estimation of performance

In this proficiency test 74 % of the participating laboratories reported satisfied results (Appendix 12). This estimation was based on the target value of the total deviation in calculating of z scores at the 95 % confidence interval. The target value of the total deviation was 20 % in the analysis of the synthetic samples (S1 and S2), from 25 % to 30 % in the analysis of the soil samples (M1 and M2) and from 25 % to 40 % in the analysis of the water samples (V1 and V2). The laboratory performance did not be evaluated in analysis of styrene from the soil sample M2 because of a possible instability of this compound.

The laboratories used many different methods or the method modifications; in particular, in the analysis of volatile organics. The VOC results varied also in analysis of the synthetic sample S2. Extraction techniques might have had some effect on the results obtained in the analysis of mineral oils from water and soil as well as in analysis of volatile organics from soil.

In the proficiency test 8/2003 80 % of the laboratories reported the satisfied results in the analysis of VOC's from soil and water. In the analysis of mineral oils from soil (SYKE PT 4/2004) and from water (SYKE PT 8/2004) the 90 % and 88 % of the results were satisfied. However, in this proficiency test the concentrations of mineral oils and volatile organics were lower than in the former PTs. which might have effected on the performance of the laboratories, too.

4 SUMMARY

The Finnish Environment Institute carried out the proficiency test for the analysis of mineral oils (middle and heavy fractions) and volatile organic compounds in water and in soil. In total, the samples were delivered to 20 laboratories, from which three laboratories did not reported the results.

One synthetic sample, one soil sampale and one water sample were delivered to the laboratories for the analysis of different compounds.

In particular, the laboratories used many different methods or the method modifications. The robust standard deviation varied from 7.2 % to 30 % in the analysis of mineral oils and from 6.8 % to 31 % in the analysis of volatile organics. The use of different methods or the method variations, particularly different extraction techniques might have had some effect on variation of the results particularly in the analysis of mineral oils from soil and water as well as in the analysis of volatile organics from soil.

In this proficiency test, the calculated concentrations were used as the assigned values for the synthetic samples and the water samples. The robust mean was used the assigned value in the analysis of the soil samples. When the target value of the total standard deviation varied from 25 % to 40 % in calculating of z scores at the 95 % confidence interval. In total, 74 % of the participating laboratories reported the satisfied results.

5 YHTEENVETO

Suomen ympäristökeskus järjesti helmikuussa 2006 pätevyyskokeen mineraaliöljyjen (keskiraskaat ja raskaat öljyjakeet) ja haihtuvien orgaanisten yhdisteiden määrittämiseksi vedestä ja maasta. Näytteet toimitettiin 20 laboratoriolle, joista kolme ei palauttanut tuloksia. Eri yhdisteitä varten toimitettiin synteettinen näyte, vesinäyte ja maanäyte.

Varsinkin haihtuvien orgaanisten yhdisteiden analysoinnissa käytettiin useita menetelmiä tai menetelmävariaatioita, millä on voinut olla vaikutusta tuloksiin. Jonkin verran todettiin näytteiden uuttotekniikalla olevan vaikutusta mineraaliöljyjen määrittämisessä maasta ja vedestä sekä haihtuvien orgaanisten yhdisteiden määrittämisessä maasta.

Tulosten hajonta oli 7,2 % – 30 % mineraaliöljyjen määrittämisessä ja 6,8 % – 31 % haihtuvien orgaanisten yhdisteiden analysoinnissa. Tulosten hajontaa vaikutti mm. erilaisten menetelmien ja eri uuttotekniikoiden käyttö mittauksessa olleiden eroavaisuuksien ohella.

Vertailuarvona käytettiin laskennallista pitoisuutta synteettisten näytteiden ja vesinäytteiden sekä robustikeskiarvoa maanäytteiden tulosten arvioinnissa. Tässä pätevyyskokeessa 74 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin 25 % – 30 % mineraaliöljyjen analysoinnissa ja 25 % – 40 % haihtuvien orgaanisten yhdisteiden analysoinnissa (95 % merkitsevyystaso).

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APPENDIX 1. PARTICIPANTS IN THE SYKE PROFICIENCY TEST 2/2006

AnalyCen, Lidköping, Sweden

AnalyCen, Tampere, Finland

Ekokem Oy Ab, Riihimäki, Finland

Eurofins Norge, Oslo, Norway

Golder Associates Oy, Helsinki, Finland

Helsingin kaupungin ympäristölaboratorio, Helsinki, Finland

Insinööritoimisto Paavo Ristola Oy, Hollola, Finland

Jyväskylän yliopisto, ympäristön tutkimuskeskus, Jyväskylä, Finland

Karlshamn Kraft AB, Karlshamn, Sweden

NabLabs Ympäristöanalytiikka Oy, Helsinki, Finland

NabLabs Ympäristöanalytiikka Oy, Oulu, Finland

Neste Oil Oyj Porvoon jalostamon laboratorio, Porvoo, Finland

Novalab Oy, Karkkila, Finland

SGS Inspection Services Oy, Hamina, Finland

SIA "Vides Audits", Riika, Latvia

Suomen ympäristökeskus (SYKE), laboratorio, Helsinki, Finland

Suunnittelukeskus Oy, Ympäristölaboratorio, Helsinki, Finland

APPENDIX 2. PREPARATION OF THE SAMPLES

Mineral oils (middle and heavy fractions) – the samples S1 and V1

Sample S1

Solutions	Preparation
Diesel/Fuel oil (BAM KS 5004)	498.80 mg oil in 99.7 ml of hexane => 5.00 mg/ml

The ampoule S1 (2 ml) was sent to the participants.

Sample V1; L1 – the standard mixture for analysis of the water sample V1

Solutions	Preparation
I Diesel/Fuel oil (BAM KS 5002)	2927.21 mg oil in 49,814 ml of hexan => 58.76 mg/ml
II Lubricating oil (BAM KS 5003)	2927.25 mg oil in 49.761 ml of isopropanol => 58.83 mg/ml
L1	2,5 ml I + 5 ml II into 100 ml of isopropanol => 4.42 mg/ml
V1	200 µl into 1 litre of water => 0.88 mg/l

The ampoule L1 (2 ml) was sent to the participants. The final water sample V1 was prepared at the participating laboratory by adding 200 µl of the sample L1 into the 1l of the water sample V1.

Sample M1

The polluted soil taken from the oil-contaminated site close to Tampere. The soil was dried at room temperature and it was sieved through a 0.250 µm sieve. The soil was mixed by a mechanized sample mixer. The soil was distributed in sub samples of 50 g using a rotary sample divider equipped with vibratory sample feeder.

Volatile organics – the samples S2 and M2

Samples S2 and M2

Compound (producer) (purity)	Preparation of the stock solution ²⁾ (1:50 dilution with MeOH) ($m_{\text{compound}} / V_{\text{MeOH}}$)	Preparation of the addition solution for samples S2 and M2 ²⁾ ($V_{\text{stock solution}} \rightarrow m_{\text{compound}}$) ($m_{\text{compound}} / V_{\text{MeOH}}$)	S2 ($\mu\text{g/ml}$) (Addition solution / MeOH:Ha) (1.976 g / 79.107 g)	M2 ³⁾ (mg/kg) 20.0 g soil ⁴⁾ , 4.0 ml H ₂ O, 1.0 ml addition solution, 20.0 ml MeOH
MTBE (Rathburn 7229) (HPLC grade)	141.0 mg / 10.121 ml ¹⁾ = 13.932 mg/ml	0.475 ml * 13.932 mg/ml = 6.62 mg 6.62 mg / 98.52 ml ¹⁾ = 0.067 mg/ml	1.68 $\mu\text{g/ml}$	3.36 mg/kg
TAME (Fluka, 67849) ($\geq 97\%$)	162.5 mg / 10.152 ml ¹⁾ = 16.007 mg/ml	0.191 ml * 16.007 mg/ml = 3.06 mg 3.06 mg / 98.52 ml ¹⁾ = 0.031 mg/ml	0.78 $\mu\text{g/ml}$	1.55 mg/kg
Benzene (Riedel-de-Haen, 32212) ($> 99.7\%$)	167.1 mg / 10.157 ml ¹⁾ = 16.452 mg/ml	0.481 ml * 16.452 mg/ml = 7.92 mg 7.92 mg / 98.52 ml ¹⁾ = 0.080 mg/ml	2.01 $\mu\text{g/ml}$	4.02 mg/kg
Ethylbenzene (Fluka, 03080) ($> 99\%$)	173.2 mg / 10.137 ml ¹⁾ = 17.085 mg/ml	0.401 ml * 17.085 mg/ml = 6.85 mg 6.85 mg / 98.52 ml ¹⁾ = 0.069 mg/ml	1.74 $\mu\text{g/ml}$	3.47 mg/kg
Tolene (Fluka, 98680) ($> 99.9\%$)	172.1 mg / 10.137 ml ¹⁾ = 16.978 mg/ml	0.508 ml * 16.978 mg/ml = 8.62 mg 8.62 mg / 98.52 ml ¹⁾ = 0.088 mg/ml	2.19 $\mu\text{g/ml}$	4.38 mg/kg
Styrene (Fluka, 85959) (99.5 %)	180.5 mg / 10.160 ml ¹⁾ = 17.766 mg/ml	0.197 ml * 17.766 mg/ml = 3.50 mg 3.50 mg / 98.52 ml ¹⁾ = 0.036 mg/ml	0.89 $\mu\text{g/ml}$	1.78 mg/kg
o-Xylene (Fluka 95660) ($> 99.5\%$)	170.8 mg / 10.168 ml ¹⁾ = 16.798 mg/ml	0.515 ml * 16.798 mg/ml = 8.65 mg 8.65 mg / 98.52 ml ¹⁾ = 0.088 mg/ml	2.19 $\mu\text{g/ml}$	4.39 mg/kg
m-Xylene (Fluka 95670) ($> 99.5\%$)	165.6 mg / 10.131 ml ¹⁾ = 16.347 mg/ml	0.511 ml * 16.347 mg/ml = 8.35 mg 8.35 mg / 98.52 ml ¹⁾ = 0.085 mg/ml	2.12 $\mu\text{g/ml}$	4.24 mg/kg
p-Xylene (Fluka 95680) ($> 99.5\%$)	166.8 mg / 10.147 ml ¹⁾ = 16.438 mg/ml	0.193 ml * 16.438 mg/ml = 3.18 mg 3.18 mg / 98.52 ml ¹⁾ = 0.032 mg/ml	0.81 $\mu\text{g/ml}$	1.61 mg/kg
Trichloroethene (Fluka, 02667) ($> 99.9\%$)	142.5 mg / 10.046 ml ¹⁾ = 14.185 mg/ml	0.099 ml * 14.185 mg/ml = 1.41 mg 1.41 mg / 98.52 ml ¹⁾ = 0.014 mg/ml	0.36 $\mu\text{g/ml}$	0.71 mg/kg
Tetrachloroethene (Fluka, 02666) ($> 99.9\%$)	169.7 mg / 10.064 ml ¹⁾ = 16.863 mg/ml	0.210 ml * 16.863 mg/ml = 3.54 mg 3.54 mg / 98.52 ml ¹⁾ = 0.036 mg/ml	0.90 $\mu\text{g/ml}$	1.79 mg/kg

¹⁾ the final volume of the methanol (Fluka, purge&trap grade, 65553) and the compound²⁾ the solvents were made by weighing, the content of the compounds in the solutions were calculated from the weighing results³⁾ 1,0 ml of the addition solution was added to the sample bottles (additions were done by weighing)⁴⁾ the polluted soil was prepared from the same batch as the sample M1

Sample V2

Compound ⁽¹⁾	Stock solution ⁽²⁾	Preparation of the stock solution B ⁽²⁾ ($V_{\text{stock solution}} \rightarrow m_{\text{compound}}$) ($m_{\text{compound}} / V_{\text{MeOH}}$)	Preparation of the addition solution for sample V2	V2 ($\mu\text{g/l}$)
MTBE	13.932 mg/ml	0.49 ml * 13.932 mg/ml = 6.885 mg 6.885 mg / 10.056 ml ¹⁾ = 0.685 mg/ml	<p>Dilution of the stock solution B with MeOH in three steps (I, II and III):</p> <p>I 4 ml (stock solution B) + 25 ml MeOH 3.147 g + 19.603 g</p> <p>II 5 ml (dilution I) + 45 ml MeOH 3.962 g + 35.435 g</p> <p>III 30 ml (dilution II) + 260 ml MeOH 23.68 g + 203.72 g</p> <p>290 ml of the addition solution (dilution III) was mixed with 30.0 l river water</p>	9.41 $\mu\text{g/l}$
TAME	16.007 mg/ml	0.50 ml * 16.007 mg/ml = 8.032 mg 8.032 mg / 10.056 ml ¹⁾ = 0.799 mg/ml		10.98 $\mu\text{g/l}$
Benzene	16.452 mg/ml	0.50 ml * 16.452 mg/ml = 8.182 mg 8.182 mg / 10.056 ml ¹⁾ = 0.814 mg/ml		11.19 $\mu\text{g/l}$
Ethylbenzene	17.085 mg/ml	1.00 ml * 17.085 mg/ml = 17.077 mg 17.077 mg / 10.056 ml ¹⁾ = 1.698 mg/ml		23.35 $\mu\text{g/l}$
Toluene	16.978 mg/ml	0.70 ml * 16.978 mg/ml = 11.861 mg 11.861 mg / 10.056 ml ¹⁾ = 1.179 mg/ml		16.22 $\mu\text{g/l}$
Styrene	17.766 mg/ml	0.52 ml * 17.766 mg/ml = 9.179 mg 9.179 mg / 10.056 ml ¹⁾ = 0.913 mg/ml		12.55 $\mu\text{g/l}$
o-Xylene	16.798 mg/ml	1.00 ml * 16.798 mg/ml = 16.832 mg 16.832 mg / 10.056 ml ¹⁾ = 1.674 mg/ml		23.02 $\mu\text{g/l}$
m-Xylene	16.347 mg/ml	1.01 ml * 16.347 mg/ml = 16.471 mg 16.471 mg / 10.056 ml ¹⁾ = 1.638 mg/ml		22.52 $\mu\text{g/l}$
p-Xylene	16.438 mg/ml	0.50 ml * 16.438 mg/ml = 8.198 mg 8.198 mg / 10.056 ml ¹⁾ = 0.815 mg/ml		11.21 $\mu\text{g/l}$
Trichloroethene	14.185 mg/ml	0.49 ml * 14.185 mg/ml = 6.904 mg 6.904 mg / 10.056 ml ¹⁾ = 0.687 mg/ml		9.44 $\mu\text{g/l}$
Tetrachloroethene	16.863 mg/ml	0.51 ml * 16.863 mg/ml = 8.659 mg 8.659 mg / 10.056 ml ¹⁾ = 0.861 mg/ml	11.84 $\mu\text{g/l}$	

¹⁾ the same producer and purity as in preparation of the sample S2 and M2

²⁾ the stock solution B was made from the same stock solutions as in preparation of the sample S2 and M2

APPENDIX 3. TESTING OF HOMOGENEITY

Sample S1 (mineral oils)

The homogeneity was tested by analysis of nine ampoules: The recovery varied from 98.4 % to 101 %.

Sample L1 (mineral oils)

The sample L1 was used for preparation of the sample V1.

The homogeneity was tested by analysis of nine ampoules: The recovery varied from 98.3 % to 99.9 %.

Sample S2 (VOCs)

Homogeneity was tested by analyzing trichloroethene and benzene from three samples. The differences between three ampoules were smaller than 2 %.

Samples M1, V2 and M2

The homogeneity was tested from 10 samples.

Analyte/ Sample	Concentration	Starget %	Target	S _a	S _a /S _{target}	Was S _a /S _{target} <0.5?	S _{bb}	S _{bb} ²	c	S _{bb} ² <c
Mineral oils/M1	925 mg/kg	15	138.8	5,82	0.066	yes	2.47	6.09	1350	yes
Trichloroethene/V2	8.65 µg/l	12.5	1.081	0.112	0.103	yes	0.100	0.010	0.21	yes
Tetrachloroethene/V2	11.2 µg/l	1,5	1.40	0.208	0.148	yes	0.116	0.013	0.375	yes
Benzene/V2	11.41 µg/l	12.5	1.43	0.142	0.100	yes	0.132	0.017	0.365	yes
MTBE/V2	0.794 µg/l	12.5	1.22	0.167	0.136	yes	0.118	0.014	0.280	yes
TAME/V2	11.28 µg/l	12.5	1.41	0.242	0.172	yes	0.151	0.023	0.396	yes
Toluene/V2	15.65 µg/l	12.5	1.96	0.269	0.137	yes	0.186	0.035	0.723	yes
Ethylbenzene/V2	21.66 µg/l	15	3.25	0.389	0.120	yes	0.297	0.088	1.94	yes
m,p-Xylene/V2	31.11 µg/l	15	4.67	0.461	0.099	yes	0.292	0.085	3.90	yes
o-Xylene/V2	22.58 µg/l	12.5	2.82	0.686	0.243	yes	0.486	0.236	1.82	yes
Styrene/V2	13.19 µg/l	15	1.98	0.193	0.098	yes	0.142	0.020	0.701	yes
Trichloroethene/M2	0.701 mg/kg	15	0.105	0.016	0.152	yes	0.003	< 0.001	0.002	yes
Tetrachloroethene/M2	1.87 mg/kg	15	0.281	0.049	0.174	yes	0.034	0.001	0.016	yes
Benzene/M2	4.35 mg/kg	15	0.653	0.103	0.157	yes	0.073	0.005	0.083	yes
MTBE/M2	3.52 mg/kg	12.5	0.44	0.152	0.345	yes	0.109	0.012	3.52	yes
TAME/M2	1.66 mg/kg	12.5	0.208	0.081	0.389	yes	0.057	0.003	0.014	yes
Toluene/M2	4.82 mg/kg	12.5	0.603	0.162	0.269	yes	0.115	0.013	0.088	yes
Ethylbenzene/M2	3.66 mg/kg	15	0.549	0.077	0.140	yes	0.055	0.003	0.057	yes
m,p-Xylene/M2	6.24 mg/kg	15	0.936	0.215	0.230	yes	0.152	0.023	0.194	yes
o-Xylene/M2	4.91 mg/kg	12.5	0.614	0.092	0.150	yes	0.065	0.004	0.072	yes
Styrene/M2	2.07 mg/kg	12.5	0.259	0.029	0.112	yes	0.019	< 0.001	0.012	yes

In each case $s_a/s_{target} < 0.5$. The variation between bottles s_{bb} was smaller than the criteria $c = F1 \cdot s_{all}^2 + F2 \cdot s_a^2$, where $s_{all}^2 = (0.3s_{target})^2$ and $F1 = 1.88$ and $F2 = 1.01$, when the number of the bottles was 10 (the samples M1, M2 and V2). In each case the $s_{bb}^2 < c$.

APPENDIX 4. TESTING OF STABILITY

The samples were distributed 7 February and they were asked to analyze as follows:

- 8 – 9 February 2006 / volatile organics in water (V2)
- until 17 February 2006 / mineral oils in soil and water, volatile organics in soil (S1, M1, V1+L1, S2 and M2).

Mineral oils

Sample	Date	Result mg/ml	Calculated con- centration
S1	7 Feb 2006	5.00 mg/ml	5.00
	8 Feb 2006	5.00 mg/ml	
L1	4 Feb 2006	0.856 mg/ml	0.88
	14 Feb 2006	0.870 mg/ml	
M1	7 Feb 2006	908 mg/kg	
	9 Feb 2006	914 mg/kg	

Volatile organics

Samples S2 and V2

Sample/Analyte	7 Feb		9 Feb	9 Feb	D= Test 4°- Test 25°	S _{target}	0,3S _{target}	Was D < 0,3S _{target} ?	13 Feb
	AV	Distrib.	Test 4 °	Test 25 °					Test 4 °
S2/MTBE	1.68	1.71	1.71	1.79	-0.080	0.168	0.050	No	1.75
S2/Benzene	2.01	2.202	2.13	2.185	0.055	0.201	0.060	Yes	2.19
S2/TAME	0.78	0.766	0.781	0.81	-0.029	0.078	0.023	No	0.791
S2/Trichloroethene	0.36	0.361	0.348	0.346	0.002	0.036	0.011	Yes	0.358
S2/Toluene	2.19	2.27	2.27	2.30	0.030	0.219	0.066	Yes	2.111
S2/Tetrachloroethene	0.9	0.978	0.91	0.921	-0.011	0.090	0.027	Yes	0.954
S2/Ethylbenzene	1.74	1.69	1.76	1.72	0.040	0.174	0.052	Yes	1.771
S2/m,p-Xylene	2.93	2.86	2.95	2.89	0.060	0.293	0.088	Yes	2.978
S2/o-Xylene	2.19	2.28	2.36	2.33	0.030	0.219	0.066	Yes	2.377
S2/Styrene	0.89	0.955	0.951	0.952	0.002	0.089	0.027	Yes	0.961
V2/MTBE	9.41	10.18	10.60	10.63	-0.030	1.220	0.366	Yes	10.45
V2/Benzene	11.19	11.61	11.55	11.26	0.290	1.430	0.430	Yes	10.94
V2/TAME	10.98	11.35	12	1.93	0.030	1.410	0.420	Yes	11.66
V2/Trichloroethene	9.44	8.79	8.9	8.79	0.110	1.080	0.324	Yes	8.76
V2/Toluene	16.22	15.5	15.7	15.3	0.400	1.960	0.588	Yes	14.53
V2/Tetrachloroethene	11.84	11.01	11.23	11.03	0.200	1.400	0.420	Yes	11.03
V2/Ethylbenzene	17.9	19.50	18.67 x)	17.40	1.270	3.580	1.074	No	16.11
V2/m,p-Xylene	2.93	29.6	29.42	28.81	0.390	4.670	1.401	Yes	26.28
V2/o-Xylene	23.02	22.72	22.91	22.66	0.250	2.820	0.846	Yes	21.73
V2/Styrene	9.05	12.08	10.9 x)	9.89	1.010	No evaluation			9.08

x) the results of triplicates varied

Sample M2

		7 Feb	20 Feb	17 Feb	D=Test 4°-Test 25°			
Sample/Analyte	AV	Distrib.	Test 4 °	Test 25 °		s_{target}	$0,3s_{target}$	Was D< $0,3s_{target}$?
M2/MTBE	3.13	3.58	3.54	3.45	0.090	0.440	0.132	Yes
M2/Benzene	3.68	4.57	4.36	4.29	0.070	0.653	0.196	Yes
M2/TAME	1.41	1.66	1.65	1.62	0.030	0.208	0.062	Yes
M2/Trichloroethene	0.676	0.77	0.722	0.716	0.006	0.105	0.032	Yes
M2/Toluene	4.15	4.97	4.82	4.75	0.030	0.603	0.181	Yes
M2/Tetrachloroethene	1.72	2.09	1.89	1.89	0.000	0.281	0.084	Yes
M2/Ethylbenzene	3.28	3.81	3.68	3.66	0.020	0.549	0.165	Yes
M2/m,p-Xylene	5.63	6.7	6.28	6.29	-0.010	0.936	0.281	Yes
M2/o-Xylene	4.31	5.21	4.95	4.93	0.020	0.614	0.184	Yes
M2/Styrene	1.72	2.17	2.08	2.07	0.010	0.259	0.078	Yes

APPENDIX 5. COMMENTS SENT BY THE PARTICIPANTS

Lab	Comment	Action/SYKE
1	In a plastic bottle the text (<i>kylmävaraaja</i> = freezer) was in Finnish. All marking should be in English.	All text will be in English in future.
3	<p>The sample M2: The laboratory does not use the head space technique. The sample had to be moved into another bottle, which might have resulted in some loss of VOC-compounds.</p> <p>The samples V1 and V2: The laboratory was still testing the method during the PT.</p> <p>The sample S2: The concentration of the synthetic samples should be higher in order to dilute them with a proper solvent used by a participant.</p> <p>The range for measuring (C10-C40) should be informed in the sample letter</p>	<p>The comments will be taken into account</p>
6	Each participant was not able to report the results within the deadline. They should be mentioned in the report in future.	The comment will be taken into account
15	The laboratory has reported much lower concentrations than the assigned values in analysis of VOCs. The clear reasons have not been found, but the participant has done strict control procedures	

APPENDIX 6.1. ANALYTICAL METHODS

Mineral oils / Water - V1												
Lab	Extr.solvent /Vol.	Extr.method/Time	Separation	Concentration	Clean-up	Detector/T°C	Injection, vol.	Column m/mm/µm	Oven-T °C	Standard, Range	Reference	
2	n-hexane/50 ml	Stirring/60 min	Microseparator	1 ml, rotavapor	Florisil, 2 g	GC-FID/330°	autosampler, 1µl	Rtx-5; 30/0.53/0.50	60° - 320°	Diesel fuel+Motor oil (1:1); 0.1-1 mg/l	EN ISO 9379-2	
3	pentane	Shaking	Funnel		Florisil	GC-FID					EN ISO 9377-2	
4	heptane/4 ml	Shaking/40 min	Centrifugation		Al ₂ O ₃	GC-FID/300°	automatic split, 2 µl	12/0.32/0.25	60° - 300°	0.1-2 mg/l	EN ISO 9379-2+ CEN WG	
5	n-hexane/50 ml	Shaking/30 min	Funnel		Florisil	GC-FID/325°	automatic split, 20 µl	P-Ci/ISCB; 25/1.0/0.53	50° - 310°	Gas+Lubrig.oil; 0.1-5.0 mg/50 ml	EN ISO 9377-2	
6	n-hexane/50+20 ml	Stirring/60+20 min	Manual	N ₂	Florisil	GC-FID	splitless, 2 µl	Pre-col. +DB-1; 15/0.53/0.15	40° - 325°	0.3-8 mg/ml	ISO 9377-2	
7	n-hexane/50 ml	Stirring/30 min	Funnel	1 ml	Florisil	GC-FID/325°	on-column	HP-5; 15/0.53/1	60° - 320°	20-1000 mg/l	ISO 9377-2	
8	n-hexane/30 ml	Stirring/30 min	Pipetting	N ₂	Florisil/Na ₂ SO ₄	GC-FID/360°	on-column	Pre-col. +S/GE BPX; 5.5/0.32/1	60° - 330°	BAM 5004; 0.05-10.07 mg/mL	ISO 9377-2	
9	n-hexane/50 ml	Stirring/30 min	Funnel	rotavapor+N ₂	Florisil/Na ₂ SO ₄	GC-FID/300°	automatic, 1 µl	HP-5; 15/0.32/0.25	40° - 300°	0-1 µg/ml	ISO 9377-2	
10	n-hexane/50 ml	Stirring/30 min	Funnel	N ₂	Al ₂ O ₃	GC-FID/350°	automatic split, 2 µl	DB-5; 30/0.32/0.25	40° - 320°	0.05-8 mg/l	EN ISO 9377-2	
11	pentane/50 ml	Shaking/50 min	Pipetting		Florisil/Na ₂ SO ₄	GC-MS	splitless, 1 µl	MSD; 26.5/0.25/250	40° - 300°	0-1000 mg/l	ISO 9377-2(mod.)	
12	n-hexane/20 ml	Shaking/60 min	Phase separation		Florisil	GC-FID/400°	PTV, 40 µl	30/0.25/0.25	40° - 355°	0-10 mg/l	EN ISO 9377-2	
13	n-hexane/50 ml	Shaking/30 min	Funnel	vac.-sentrig.	Florisil/Na ₂ SO ₄	GC-FID/360°	on-column, 2 µl	BPX-5; 20/0.32/1	50° - 340°	0.2-1.2 mg/ml	EN ISO 9377-2	
14	n-hexane/50 ml	Shaking/30-45 min	Standing	1 ml	Florisil	GC-FID/300°	on-column, 0.25 µl	DB-1; 25/0.32/0.25	60° - 300°	Diesel+Lubrig.oil (1:1); 0.08-16 mg/ml	ISO 9377-2(mod.)	
15	n-hexane/50 ml	Shaking/60 min	Funnel	N ₂	Florisil	GC-FID/300°	splitless, 1 µl	15/0.32/0.25	50° - 300°	50-1600 mg/l	EN ISO 9377-2	

VOCs/Soil M2

Lab	Intake	Extr. solvent/Vol.	Extr. method/Time	Sampling technique	Separation	Detector/°C	Injection, vol.	Column, m/mm/µm	Oven-T °C	Standard, Range	Reference
1	8	pentane, 20 ml	Shaking/16 h		Centrifugation	GC-FID/325°	splitless, 2 µl	30/0.25/0.25	40° - 310°	1-chloro-4-fluorobenzen, N-triacontane, 0.1-10 mg/l	
2	> 30 g			purge&trap		GC-FID/190°		MXI: 60/0.53/3	40° - 180°	No 0.1-10 µg/l	EPA 5030 & 8021
3						GC-MSD					ISO/DIS 16203
4	20 g	methanol/20 ml	Shaking/40 min	head space	Centrifugation	GC-MS	split, 1 ml	30/0.25/0.25	40° - 260°	D-8 toluene, 0.5-2000µg/l	ISO Soil quality, EPA 8270
6	20 g	methanol/21 ml + water/4ml	Shaking/30 min	purge&trap	Manual	GC-MSD	automatic	HP-5MS, 30/0.25/0.25	-220°	D-8 toluene	ISO 15009
7	20 g	methanol/21 ml	Ultrasonic/10 min	head space	Pipetting	GC-FID/300°		HP 5 and HP 1701	40° - 275°	No 2-10 000 µg/l	EPA 5021, ISO 11423-1
8	20 g	methanol/21 ml	Shaking/30 min	head space	Settling Pipetting	GC-MSD	split, 1 ml	RTX-VMS; 30/0.25/1.4	40° - 225°	α,α-trifluoro-toluene, 4-bromo-fluorobenzene, 1-47 µg/l	ISO/CD 22155
10	10-15 g			head space		GC-FID/250°	2 ml	NB-54, 25/0.32/1, NB-311; 25/0.32/3	40° - 220°	benzodifluoride	
12	25 g	methanol	Shaking/30 min	purge&trap	Settling	GC-MSD	thermo desorptor	HP-5MS; 30/0.25/0.2	35° - 280°	D8- toluene, 0.05-15 mg/kg	
13	20 g	methanol/25 ml		head space		GC-FID/260° and 300°C	1 ml	DB-624; 30/0.25/1.4, HP-1; 25/0.2/0.33	35° - 200°	No 3.5-15 µg/l	ISO 11423 (mod.)
14	20 g	methanol/21 ml		head space	equilibrium, liquid/gas	GC-FID/250°	split, 1 ml	DB-1; 60/0.32/1	→ 200°	No 0.01-0.25 mg/l	ISO/CD 22155
15				head space		GC-MS	split	60/0.25/1.4	40° - 200°	fluorobenzene D8-toluene	EPA 8260B and 5021, ISO/DIS 22155
17				Head space		GC-FID/300°	splitless, 1 µl	15/0.32/0.25	50° - 300°	dichlorobenzene 50-1600 mg/l	

Lab 16 did not report the method.

VOCs / Water -V2

Lab	Extr. solvent/ Vol.	Separation	Sampling technique	Detector/T°C	Injection, vol.	Column m/m/m/µm	Oven/T °C	Internal standard, Range	Reference
1	pentane, 2 ml	Centrifugation		GC-FID/325°	splitless, 2 µl	30/0.25/0.25	40° - 310°	1-chloro-4-fluorobenzene 0.1-12.5mg/l	EPA 5030 & 8021
2	pentane		purge&trap	GC-FID/190°		MX-T; 60/0.53/3	40° - 180°	No 0.1-10 µg/l	
3				GC-MS					
4			head space	GC-MS	split, 1 ml	30/0.25/0.25	40° - 260°	D8-toluene 00.00005-2 mg/l	ISO/TC 190, EPA 8270
6			purge&trap	GC-MSD		HP 5MS; 30/0.25/0.25	45° - 220°	D8 toluene, 4-200 µg/l	EN ISO 15680
7			head space	GC-FID/300°	1 ml	HP-5&1701; 60/0.32/1	40° - 275°	No 2-10 000 µg/l	ISO 11423-1
8			head space	GC-MS	split, 1 ml	RTX-VMS; 30/0.25/1.4	40° - 225°	α,α,α-trifluoro-toluene, 4-bromo-fluoro- benzene 1-47 µg/l	ISO/DIS 10301
10			Head space	GC-FID/250°	2 ml	NB-54; 25/0.32/1, NB-31125/0.32/3	40° - 220°	benzodifluoride	
12			purge&trap	GC-MSD	thermo desorptor	HP-5MS; 30/0.25/0.2	35° - 280°	bromobenzene, 0.2-24 or 9-100 µg/l	
13			head space	GC-FID/260° and 300°C	1 ml	DB-624; 30/0.25/1.4, HP-1;25/0.2/0.33	35° - 200°	No 3.5-15 µg/l	ISO 11423 (mod.)
14		equilib. liquid/gas	head space	GC-FID/250°	split, 1 ml	DB-1; 60/0.32/1	→200°	No 0.01-0.25 mg/l	NM 356; ISO 11423-1 EPA 8260B, EN ISO 10301
15			head space	GC-MS	split	60/0.25/1.4	40° - 200°	fluorobenzene	
17				GC-FID/300°	splitless, 1 µl	15/0.32/0.25	50° - 300°	D8- toluene 50-1600 mg/l	

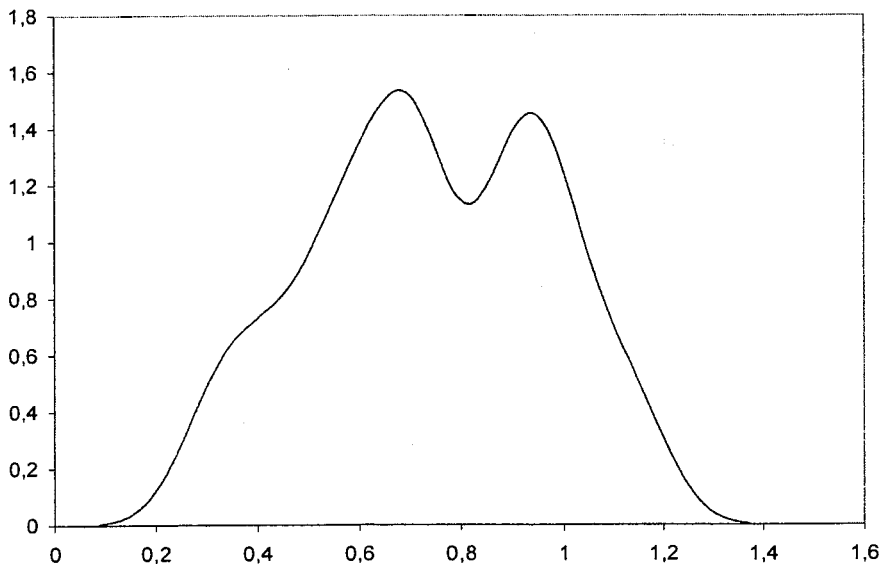
Lab 16 did not report the
method.

APPENDIX 6.2 KERNEL DENSITY FUNCTIONS OF THE RESULTS OBTAINED IN ANALYSIS OF MINERAL OILS

The sample V1

The participants used stirring or shaking method in extraction of the water sample V1. The Kernel density function was drawn after rejection the results of the laboratories (the labs 2, 7 and 9), which did not obtain the accepted results in analysis of the synthetic sample S1. The density distribution is not unimodal, a clear evidence of bimodality can be seen. The first top (about 0.7 mg/l) represents mainly the results obtained using the stirring technique in extraction. On the other hand the second top (about 0.95 mg/l) represents mainly the results obtained using the shaking technique in extraction.

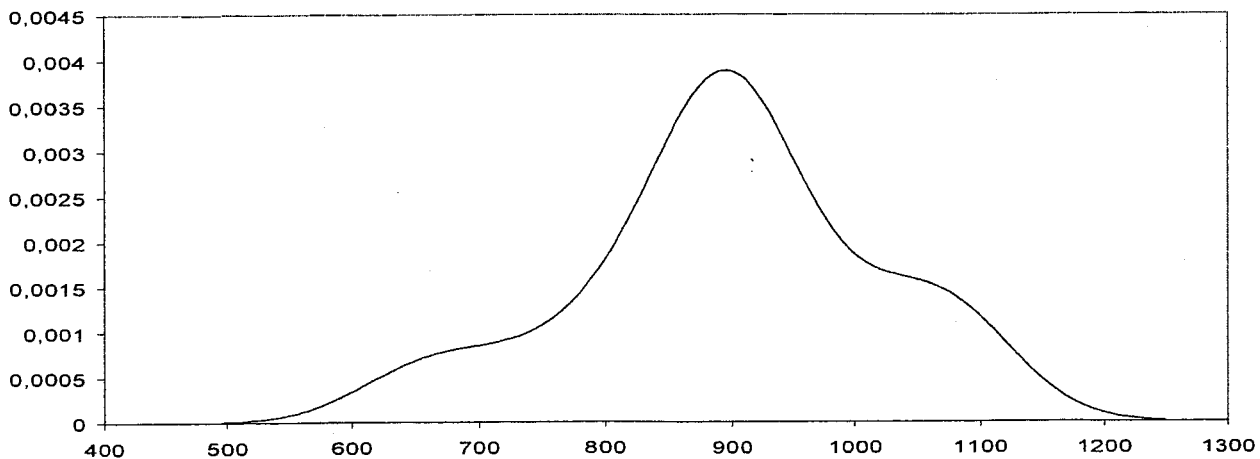
Kernel Density Plot
Fixed h: 0.08 Mineral oil/V1 (lab 2, 7 and 9 missing)



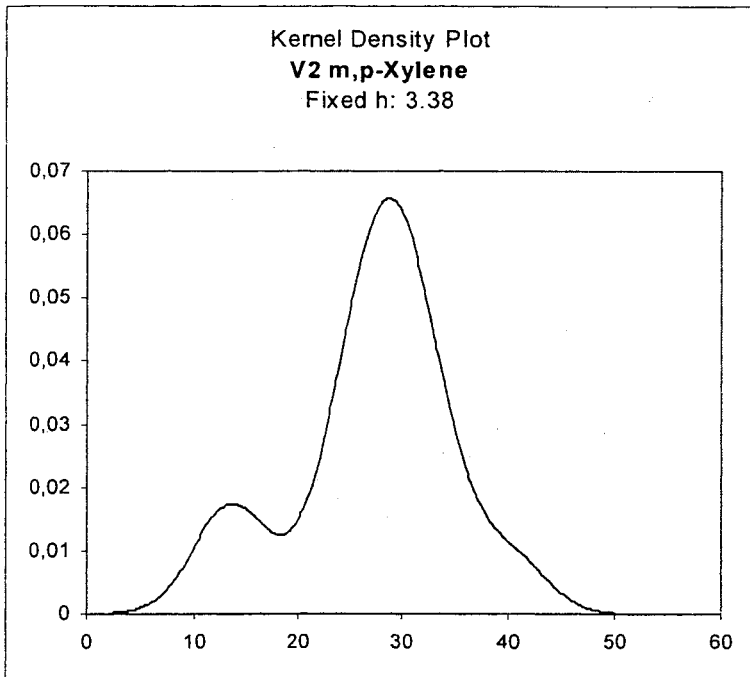
The sample M1

An evidence of multimodality (several tops in the distribution) can be seen also in analysis of the soil sample.

Kernel Density Plot
hOpt = 56.2 Mineral oil/M1 (lab 2, 7, 5 and 9 missing)



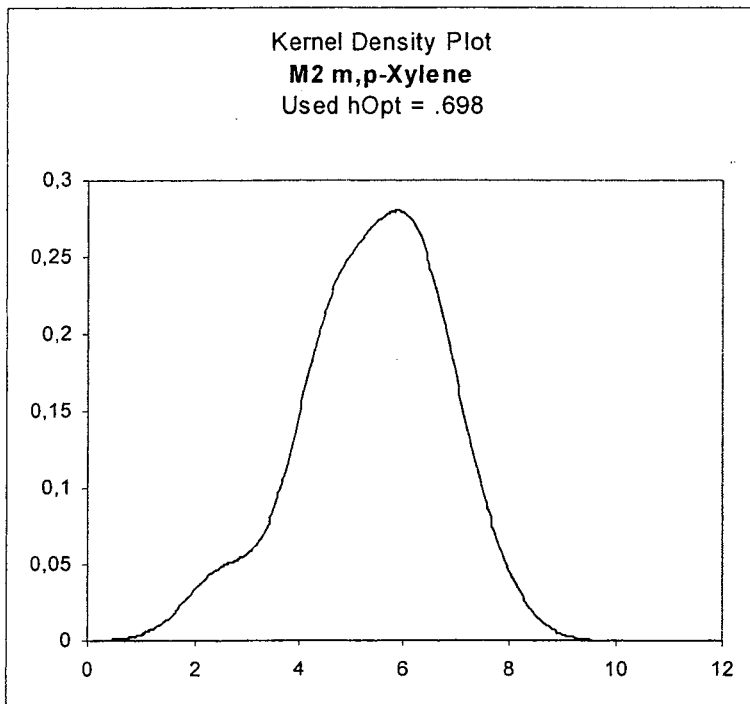
APPENDIX 6.3 KERNEL DENSITY FUNCTIONS OF THE RESULTS OBTAINED IN ANALYSIS OF TWO VOLATILE ORGANIC COMPOUNDS



The assigned value (the calculated value): 28,6 µg/l

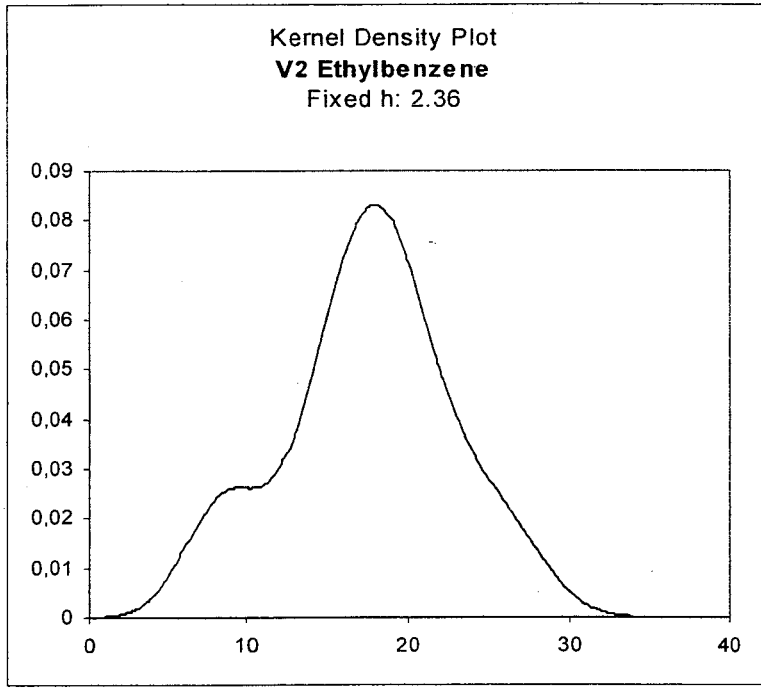
The results of the laboratories in the order of magnitude: 1, 15, 10, 14, 16, 13, 7, 17, 8, 3, 12, 6 and 4.

In analysis of the sample V2 the function was cleanly unimodal.



The assigned value (the robust mean): 5,63 mg/kg

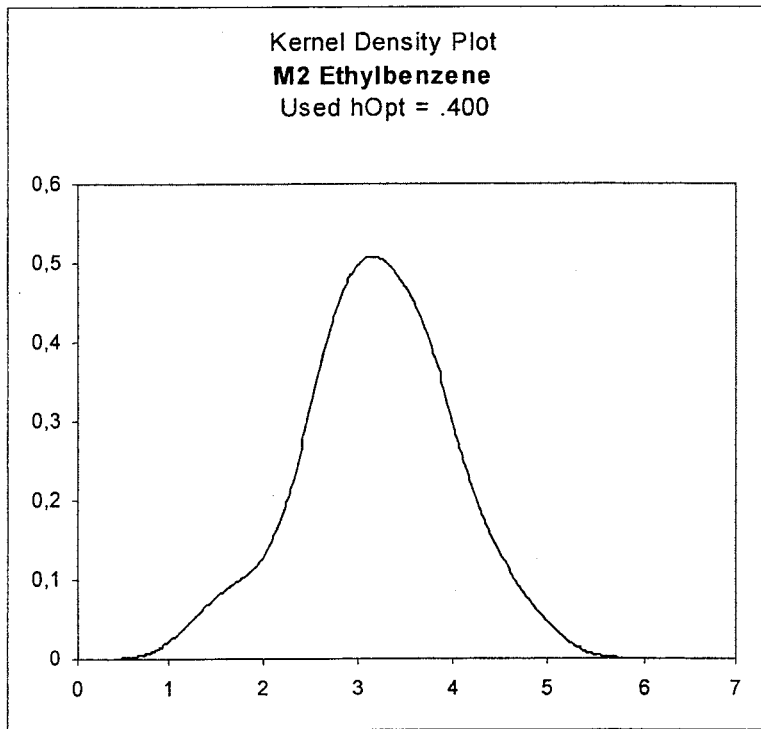
The results of the laboratories in the order of magnitude: 1, 15, 10, 17, 13, 12, 14, 16, 7, 8, 6, 3 and 4.



The assigned value (the calculated value): 17,9 µg/l.

The results of the laboratories in the order of magnitude: 1, 15, 16, 10, 14, 13, 17, 3, 7, 8, 6, 12, 2 and 4.

In analysis of the sample V2 the function was slightly unimodal.



The assigned value (the robust mean): 3.28 mg/kg.

The results of the laboratories in the order of magnitude: 1, 15, 17, 10, 13, 14, 12, 6, 16, 8, 7, 3 and 4.

APPENDIX 7. ASSIGNED VALUES AND THEIR UNCERTAINTIES

The samples M1 and M2

Analyte	Sample	Assigned value	Estimation of assigned value	Uncertainty (U = 2 u _c)
Mineral oils	M1	925 mg/kg	Robust mean	16 %
Tetrachloroethylen	M2	1.72 mg/kg	Robust mean	42 %
Trichloroethylen	M2	0.676 mg/kg	Robust mean	41 %
VOC-Benzene	M2	3.68 mg/kg	Robust mean	24 %
VOC-Ethylbenzene	M2	3.28 mg/kg	Robust mean	24 %
VOC-m/p-Xylene	M2	5.63 mg/kg	Robust mean	26 %
VOC-MTBE	M2	3.13 mg/kg	Robust mean	24 %
VOC-o-Xylene	M2	4.31 mg/kg	Robust mean	25 %
VOC-Styrene	M2	1.72 mg/kg	Robust mean	27 %
VOC-TAME	M2	1.41 mg/kg	Robust mean	33 %
VOC-Toluene	M2	4.15 mg/kg	Robust mean	24 %

The uncertainty of was estimated using the equation:

$$U = 2 \cdot 2,23 \cdot s_{rob} / \sqrt{n} \text{ (at 95 \% confidence interval)}$$

The samples S1, S2, V1 and V2:

Analyte	Sample	Assigned value	Estimation of assigned value	Uncertainty (U = 2 u _c)
Mineral oils	S1	5.00 mg/kl	Calculated concentration	< 0.5 %
	V1	0.88 mg/l	Calculated concentration	< 0.5 %
Tetrachloroethylen	S2	0.900 µg/ml	Calculated concentration	< 0.5 %
	V2	11.84 µg/l	Calculated concentration	< 0.5 %
Trichloroethylen	S2	0.360 µg/ml	Calculated concentration	< 0.5 %
	V2	9.44 µg/l	Calculated concentration	< 0.5 %
VOC-Benzene	S2	2.01 µg/ml	Calculated concentration	< 0.5 %
	V2	11.19 µg/l	Calculated concentration	< 0.5 %
VOC-Ethylbenzene	S2	1.74 µg/ml	Calculated concentration	< 0.5 %
	V2	17.9 µg/l	Calculated concentration	< 0.5 %
VOC-m/p-Xylene	S2	2.93 µg/ml	Calculated concentration	< 0.5 %
	V2	28.6 µg/l	Calculated concentration	< 0.5 %
VOC-MTBE	S2	1.68 µg/ml	Calculated concentration	< 0.5 %
	V2	9.41 µg/l	Calculated concentration	< 0.5 %
VOC-o-Xylene	S2	2.19 µg/ml	Calculated concentration	< 0.5 %
	V2	23.02 µg/l	Calculated concentration	< 0.5 %
VOC-Styrene	S2	0.89 µg/ml	Calculated concentration	< 0.5 %
	V2	9.05 µg/l	Calculated concentration	< 0.5 %
VOC-TAME	S2	0.78 µg/ml	Calculated concentration	< 0.5 %
	V2	10.98 µg/l	Calculated concentration	< 0.5 %
VOC-Toluene	S2	2.19 µg/ml	Calculated concentration	< 0.5 %
	V2	16.22 µg/l	Calculated concentration	< 0.5 %

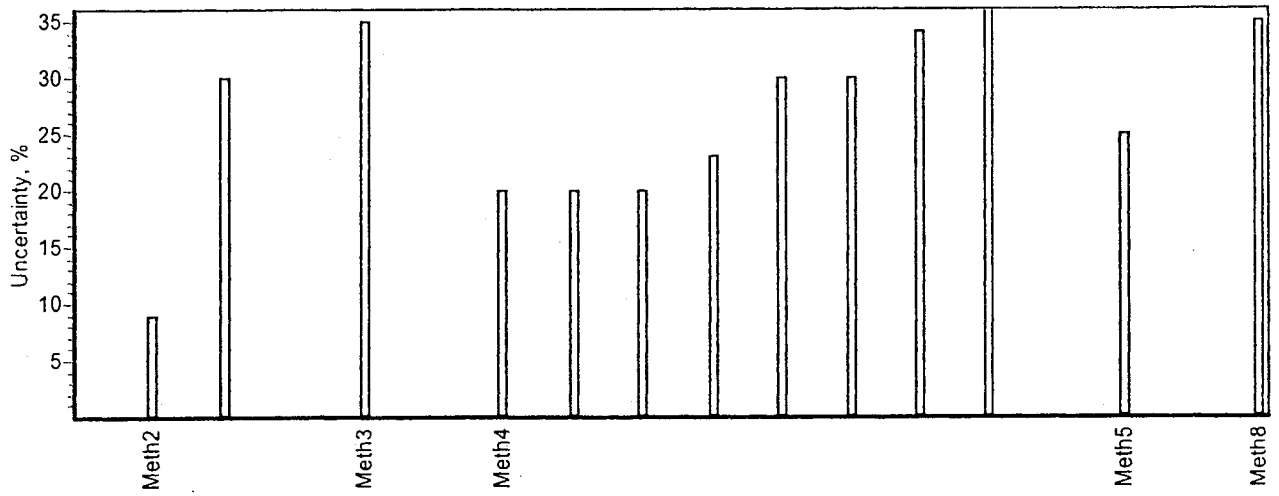
The uncertainty was estimated on the basis of the sample preparation

APPENDIX 8. MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS

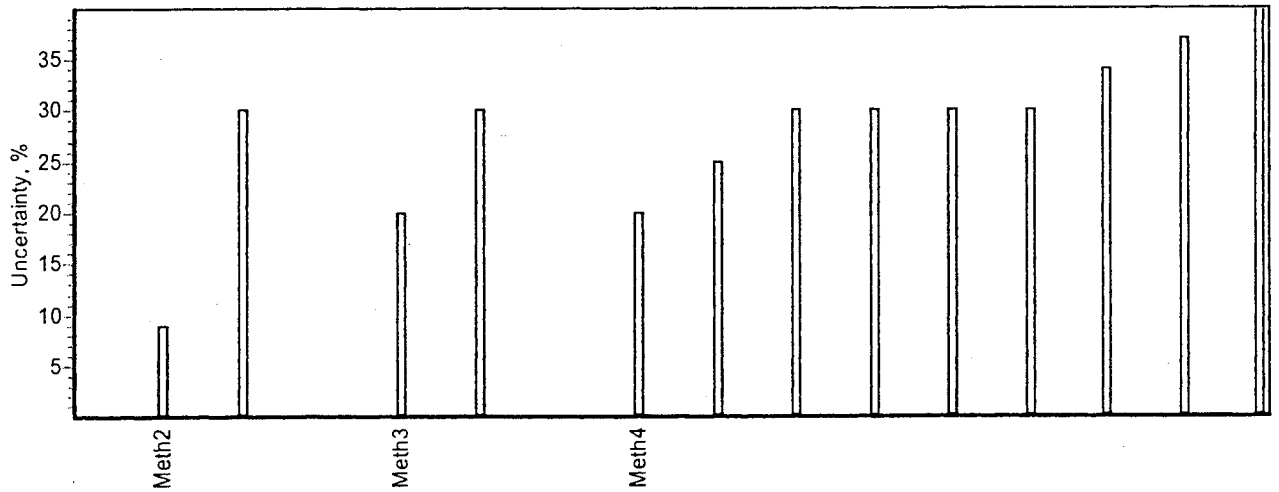
Uncertainties were estimated using the procedures as follows:

- Meth 1: using the variation of the results in X chart (for artificial samples)
- Meth 2: using the variation of the results in X chart and the variation of the replicates (t %- or R-chart)
- Meth 3: using the variation of the data obtained in analysis of CRM
- Meth 4: using the data obtained in method validation (and IQC)
- Meth 5: using the EURACHEM- Guide "Quantifying Uncertainty in Analytical measurements"
- Meth 6: adapting the EURACHEM- Guide "Quantifying Uncertainty in Analytical measurements" (e.g. pre-treatment, calibration, measurement)
- Meth 7: using the the NORDTEST report TR 537 "handbook for calculation of Measurement Uncertainty"
- Meth 8: other procedure

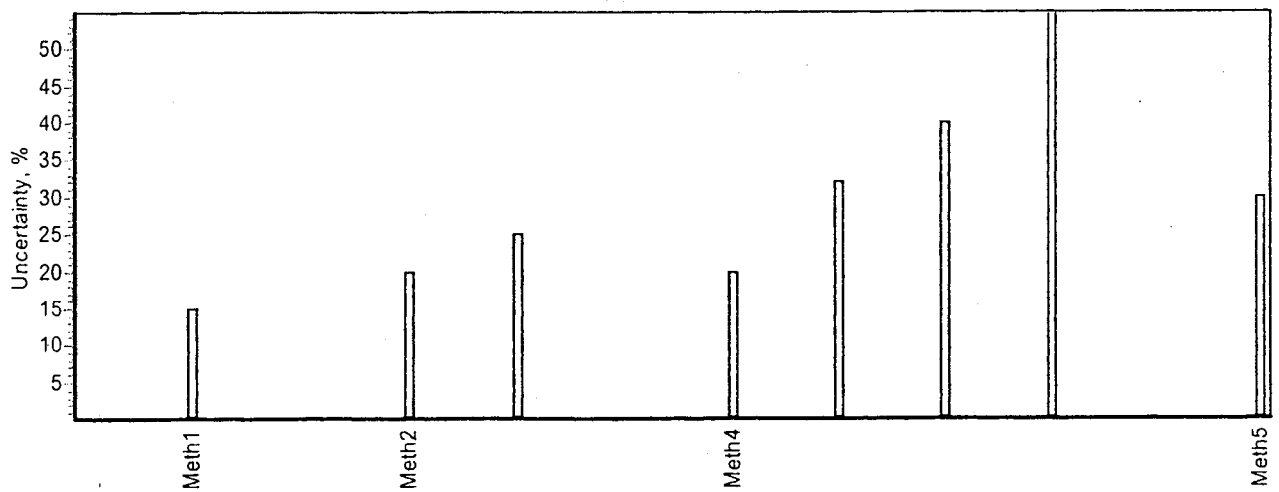
Analyytti (Analyte) **Min.oil-GC** Näyte (Sample) M1



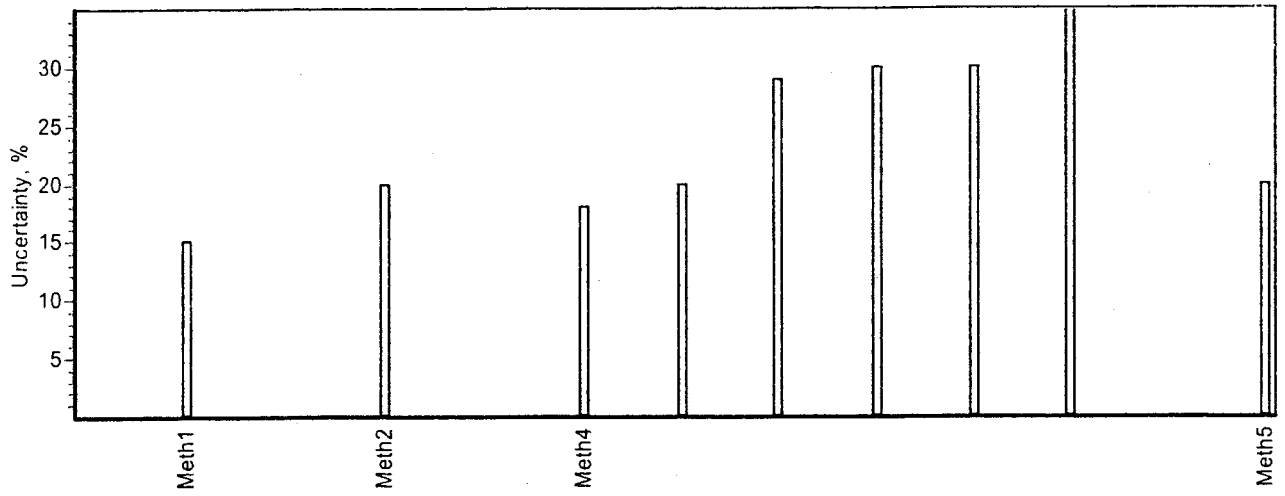
Analyytti (Analyte) **Min.oil-GC** Näyte (Sample) V1



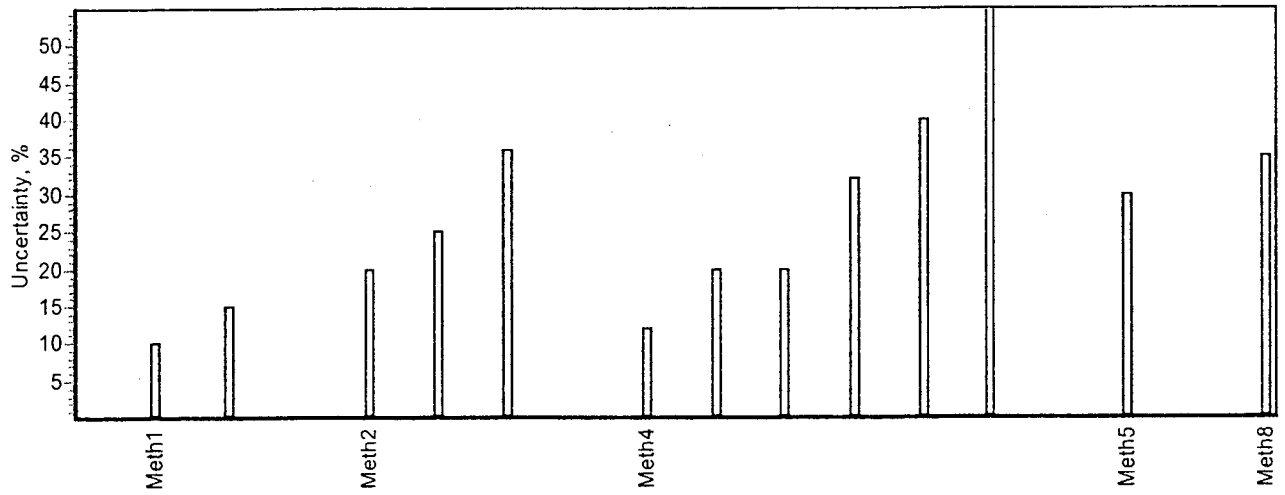
Analyytti (Analyte) **TetraCE** Näyte (Sample) M2



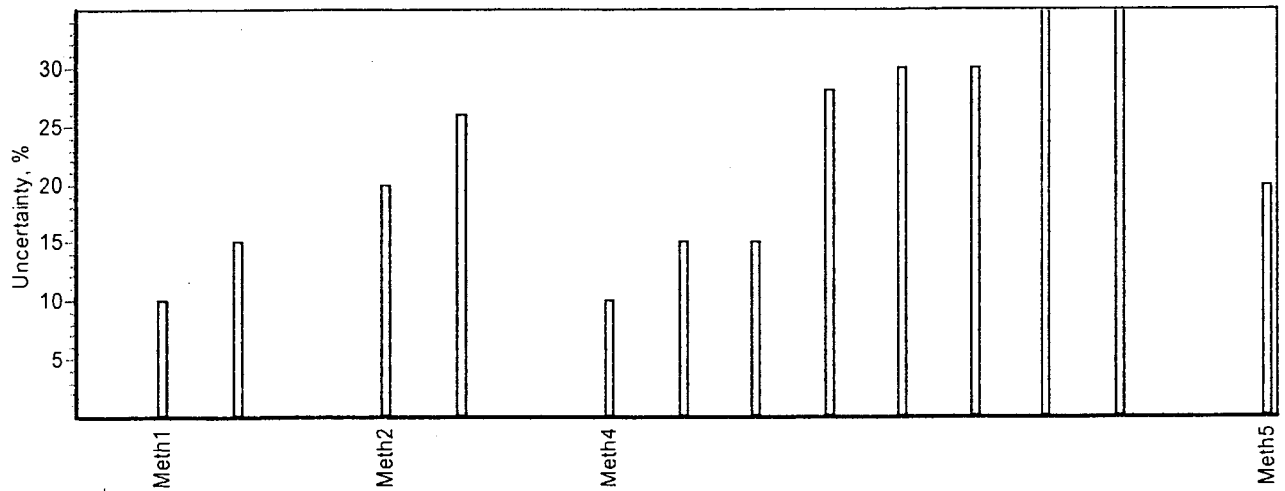
Analyytti (Analyte) **TetraCE** Näyte (Sample) **V2**



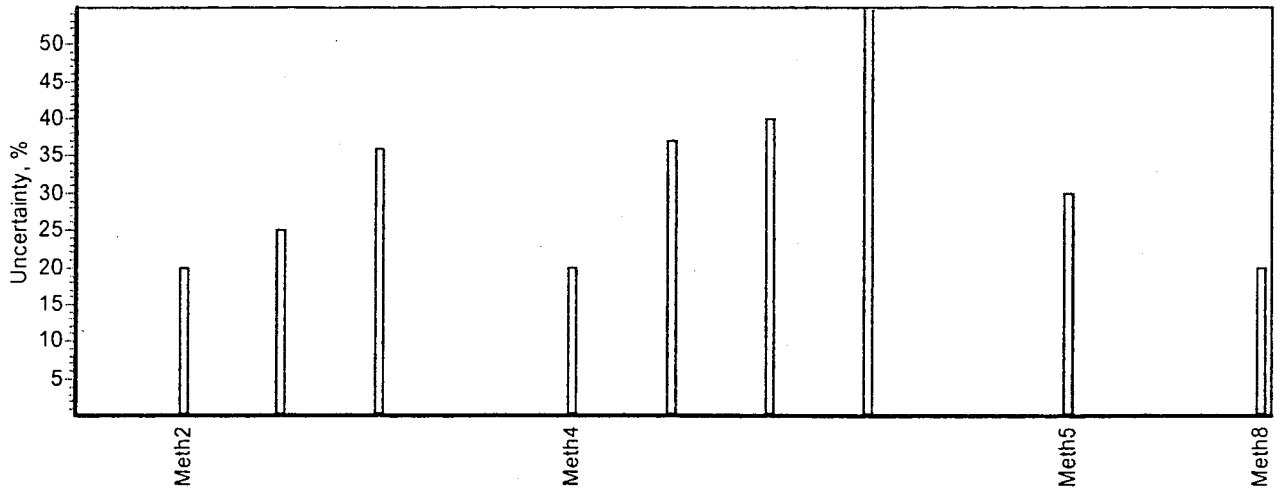
Analyytti (Analyte) **VOC-Benzene** Näyte (Sample) **M2**



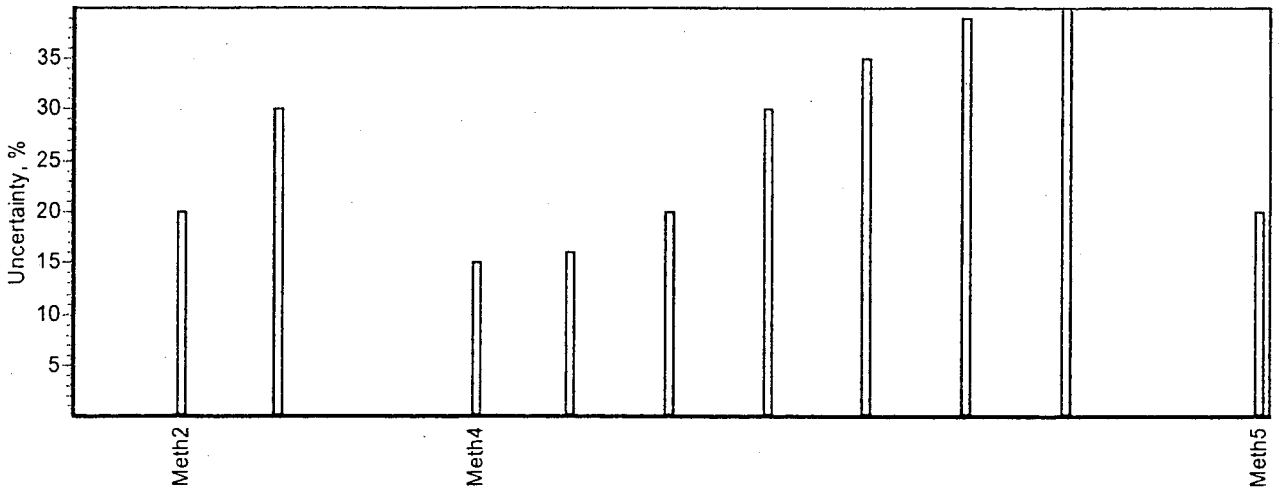
Analyytti (Analyte) **VOC-Benzene** Näyte (Sample) **V2**



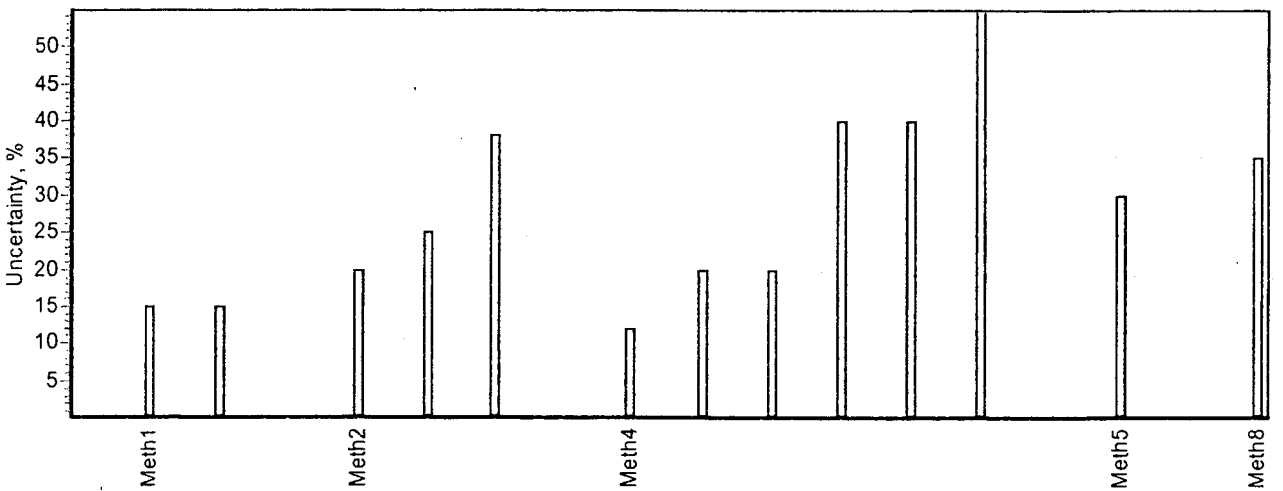
Analytytti (Analyte) **VOC-MTBE** Näyte (Sample) M2



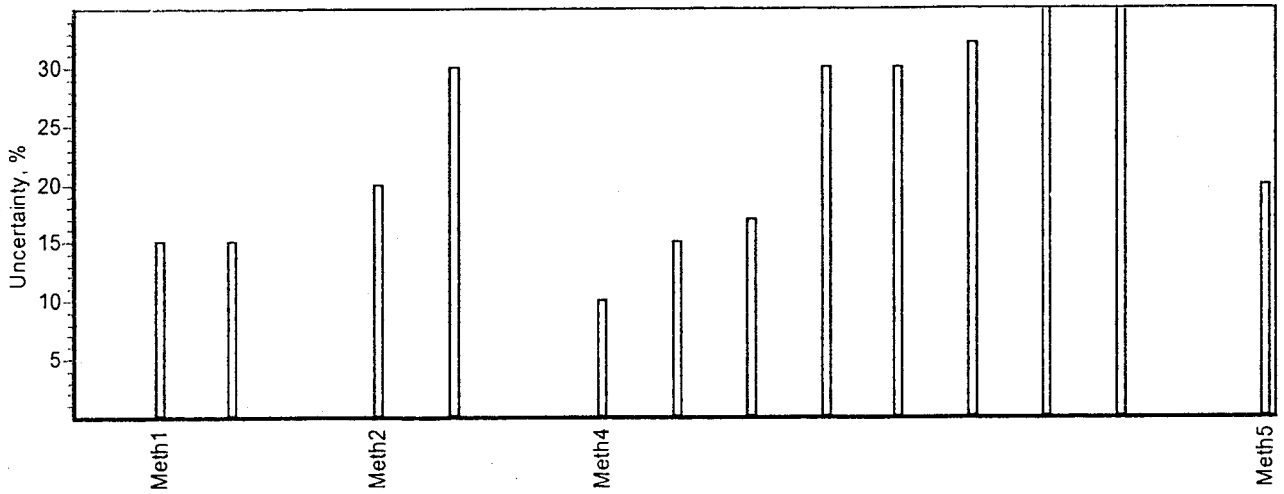
Analytytti (Analyte) **VOC-MTBE** Näyte (Sample) V2



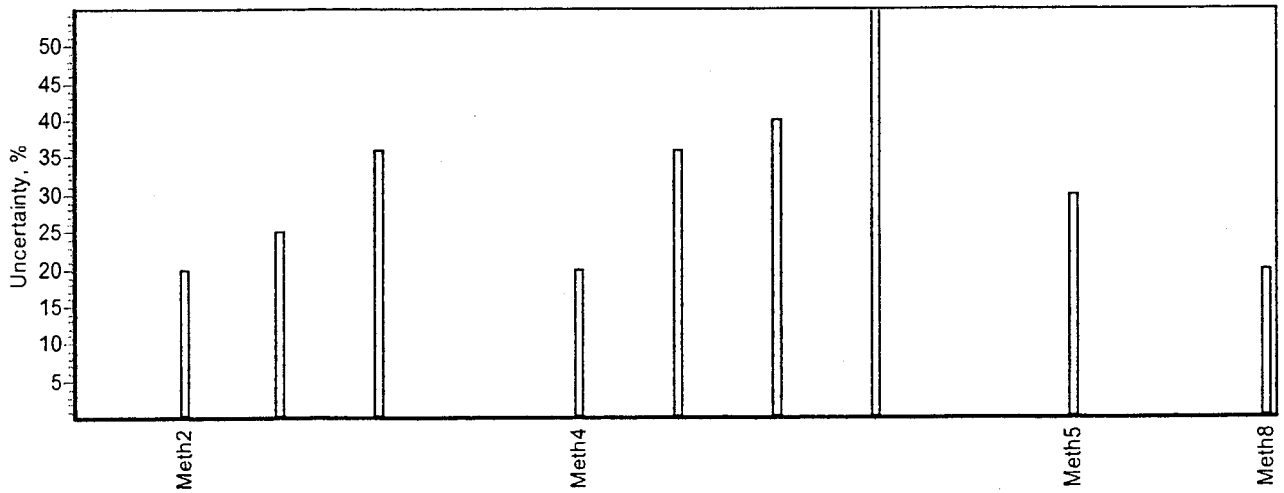
Analytytti (Analyte) **VOC-o-Xylene** Näyte (Sample) M2



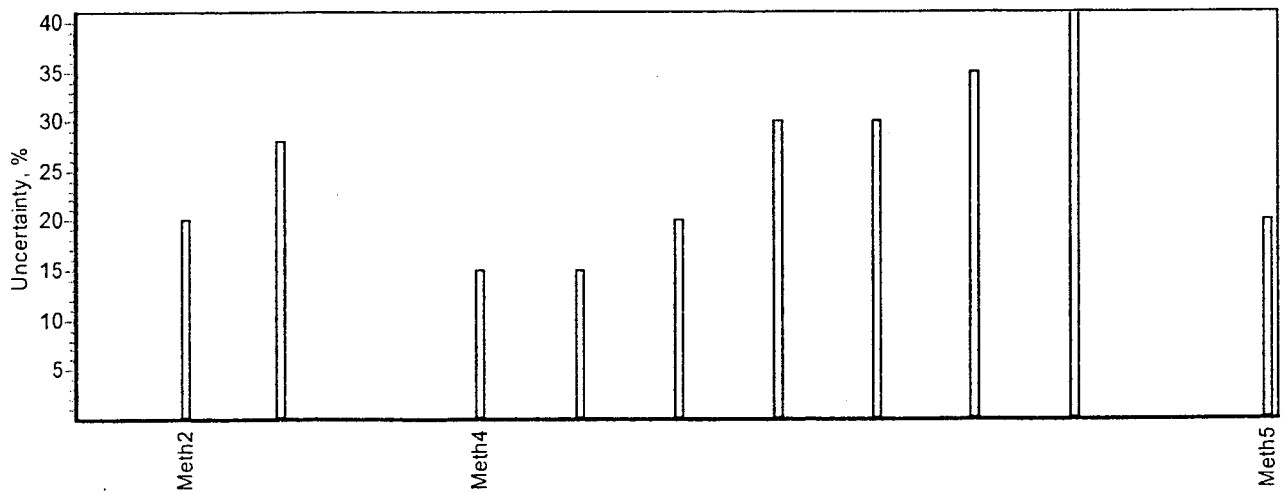
Analyytti (Analyte) **VOC-o-Xylene** Näyte (Sample) V2



Analyytti (Analyte) **VOC-TAME** Näyte (Sample) M2

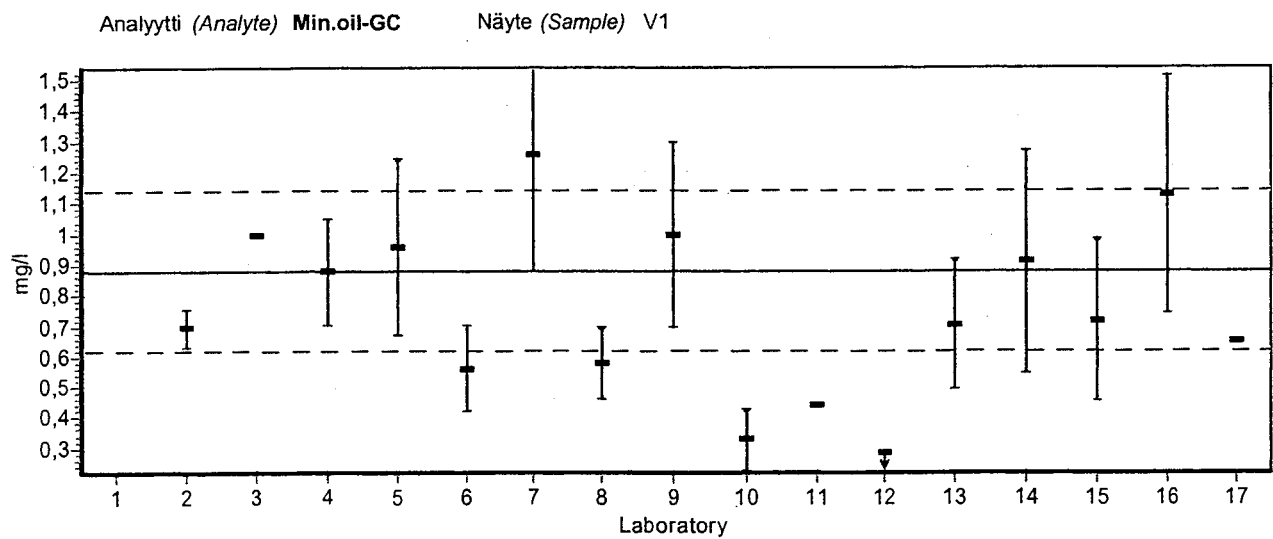
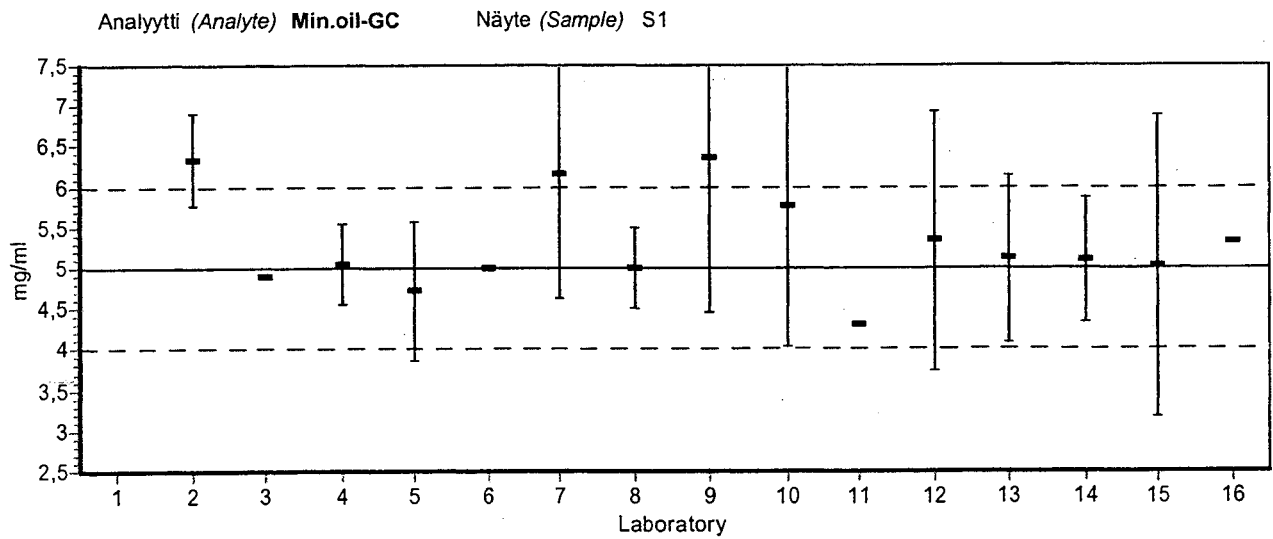
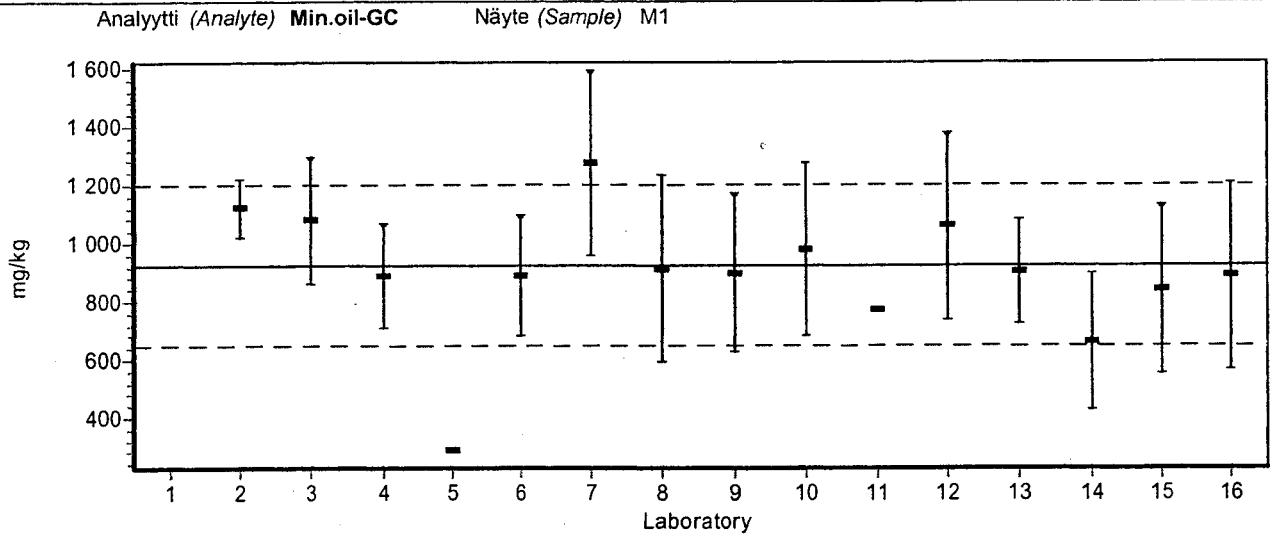


Analyytti (Analyte) **VOC-TAME** Näyte (Sample) V2

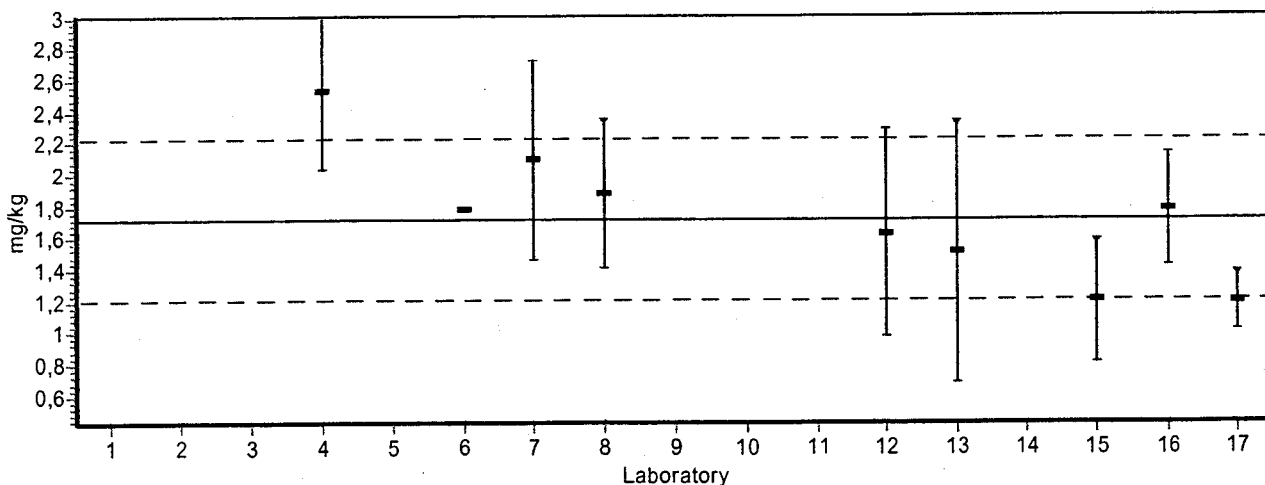


LIITE 9. RESULTS AND UNCERTAINTY ESTIMATES REPORTED BY THE LABORATORIES

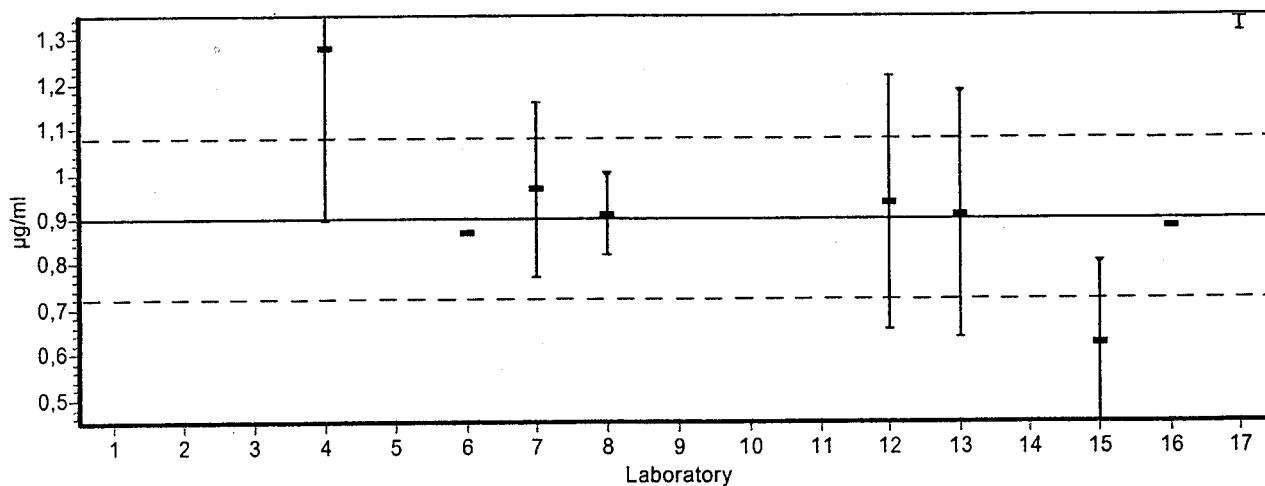
Appendix 9.



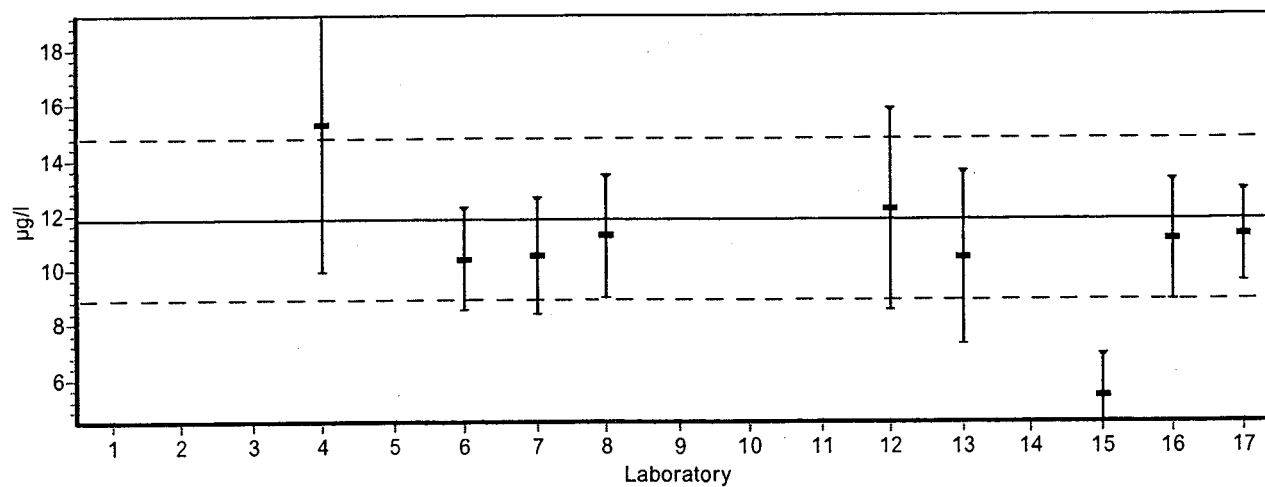
Analyytti (Analyte) **TetraCE** Näyte (Sample) **M2**



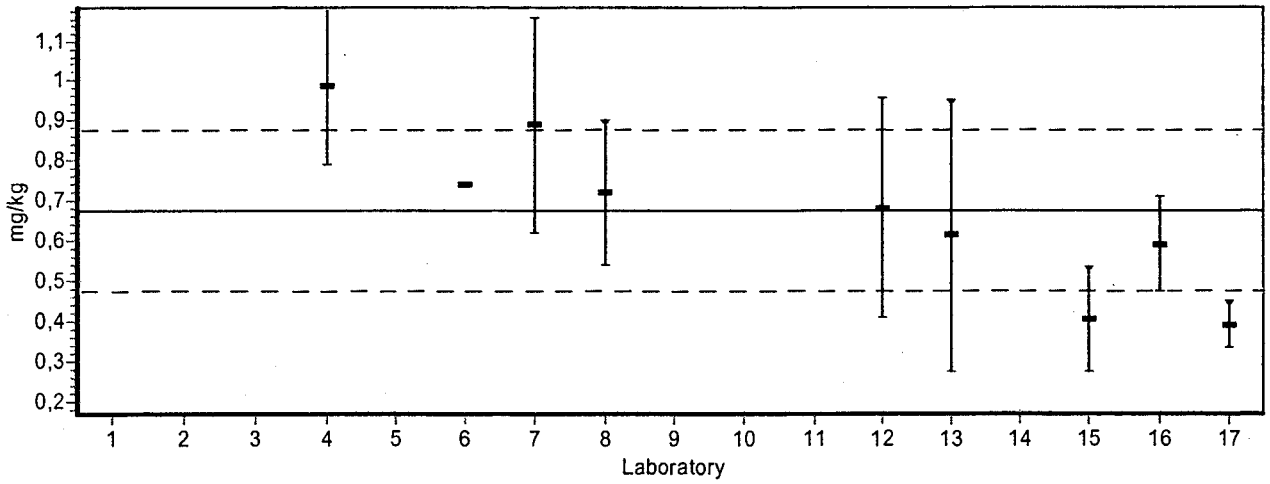
Analyytti (Analyte) **TetraCE** Näyte (Sample) **S2**



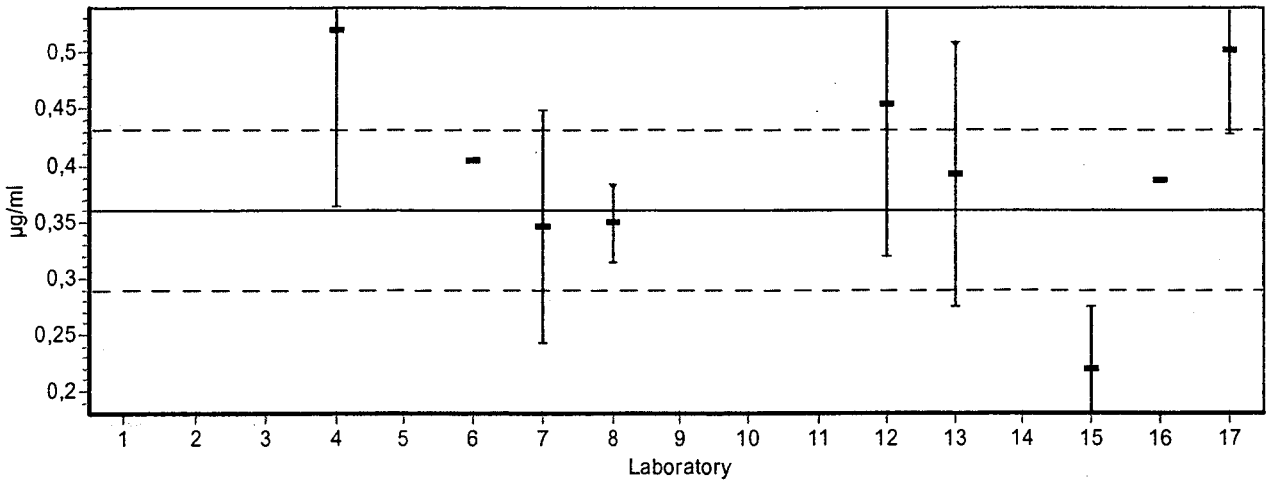
Analyytti (Analyte) **TetraCE** Näyte (Sample) **V2**



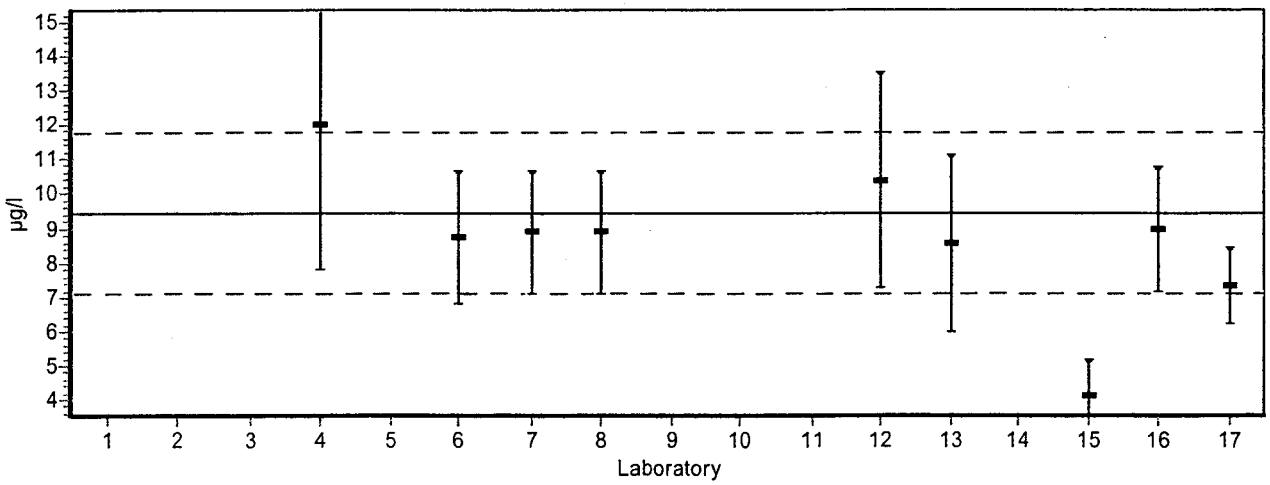
Analyytti (Analyte) TriCE Näyte (Sample) M2



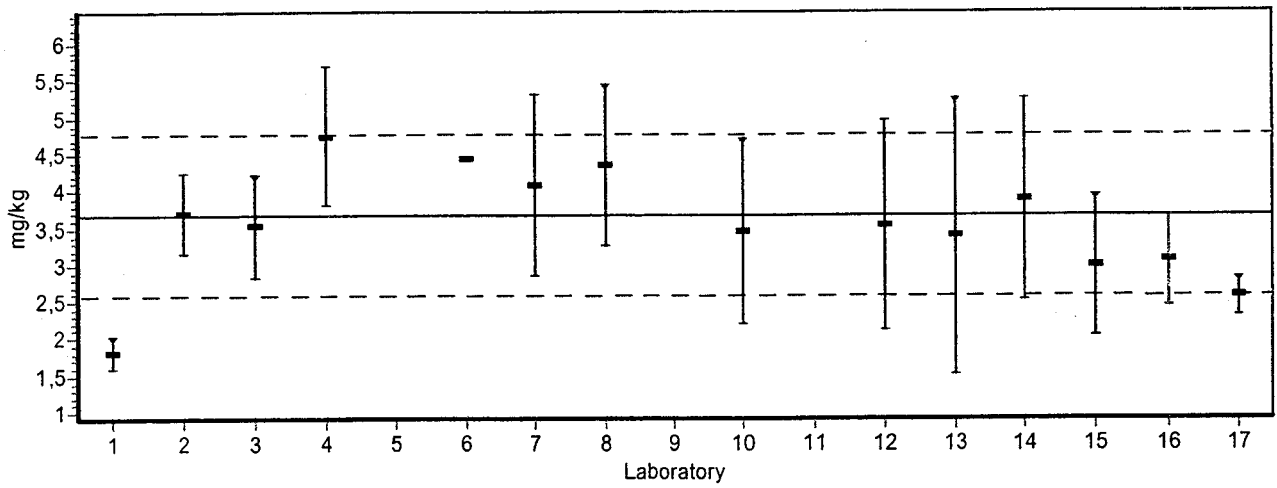
Analyytti (Analyte) TriCE Näyte (Sample) S2



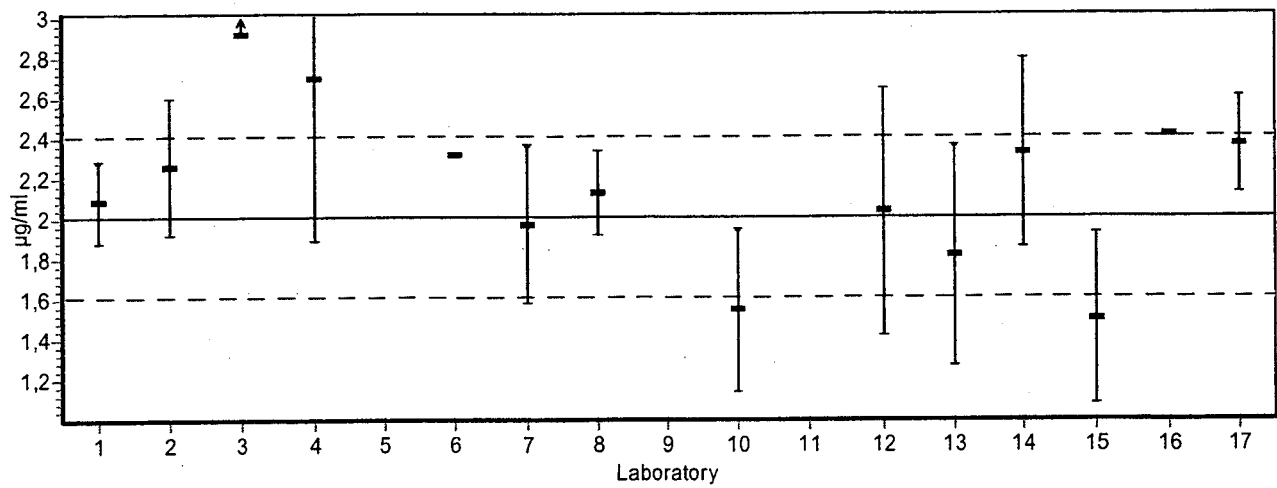
Analyytti (Analyte) TriCE Näyte (Sample) V2



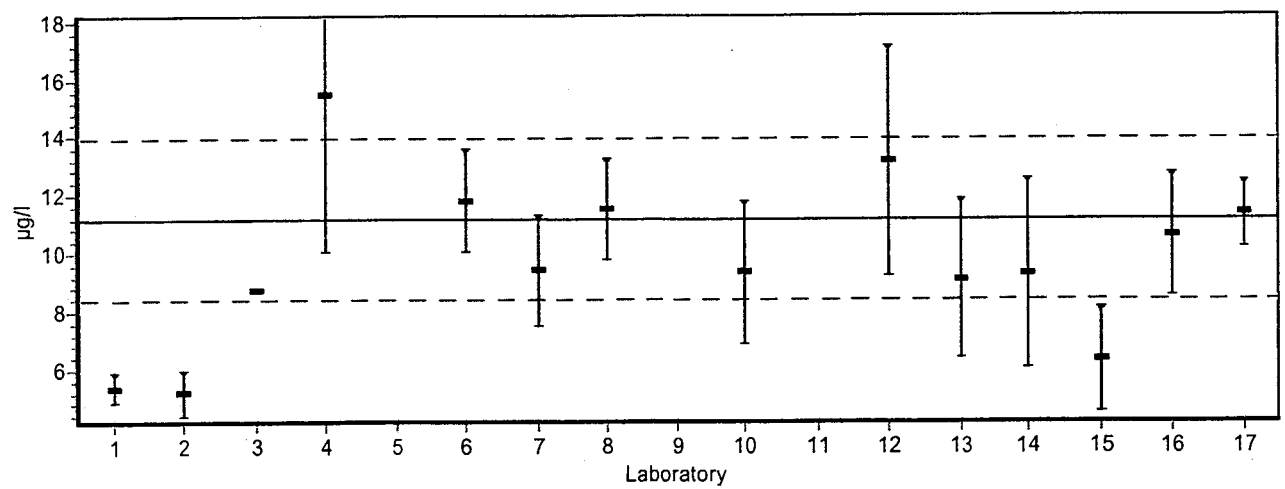
Analyytti (Analyte) VOC-Benzene Näyte (Sample) M2



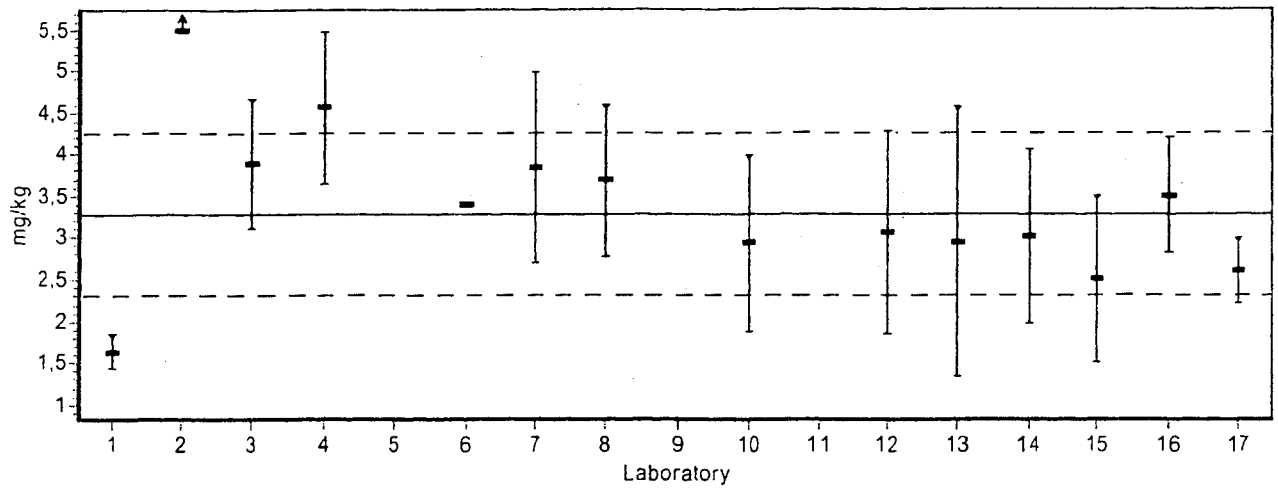
Analyytti (Analyte) VOC-Benzene Näyte (Sample) S2



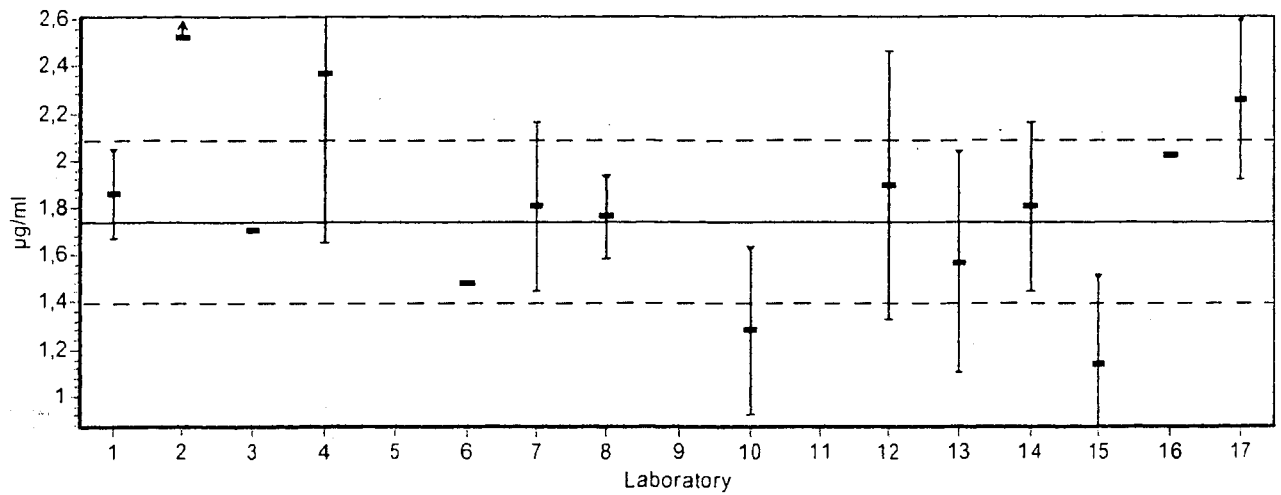
Analyytti (Analyte) VOC-Benzene Näyte (Sample) V2



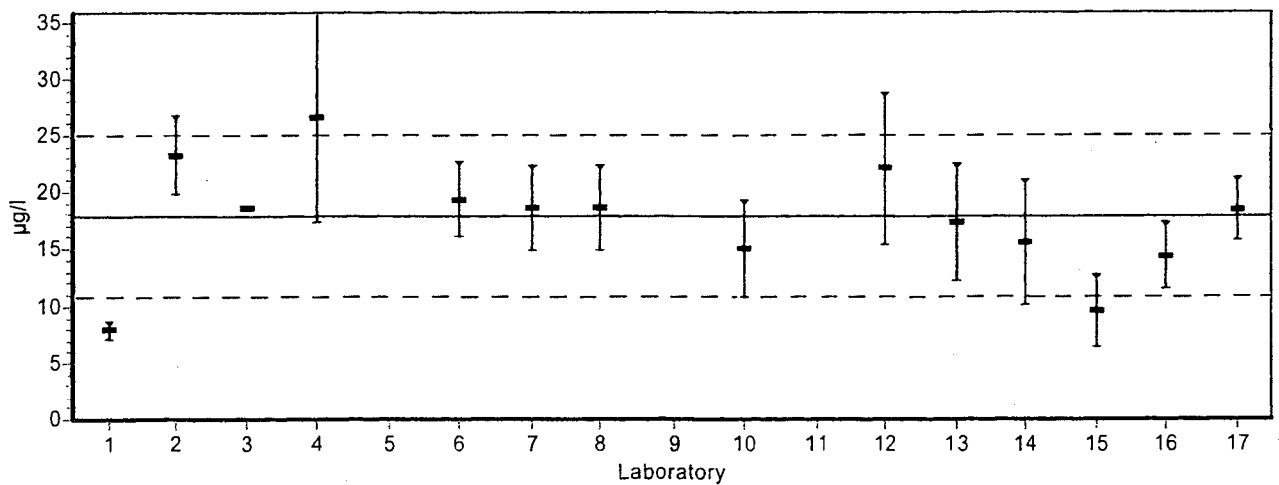
Analyytti (Analyte) VOC-Et.benzene Näyte (Sample) M2



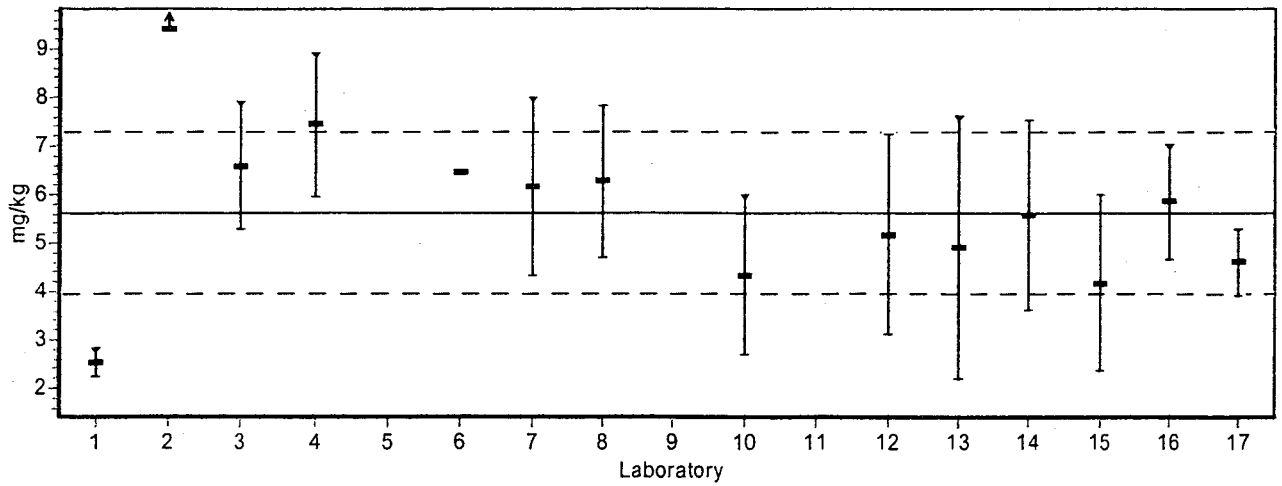
Analyytti (Analyte) VOC-Et.benzene Näyte (Sample) S2



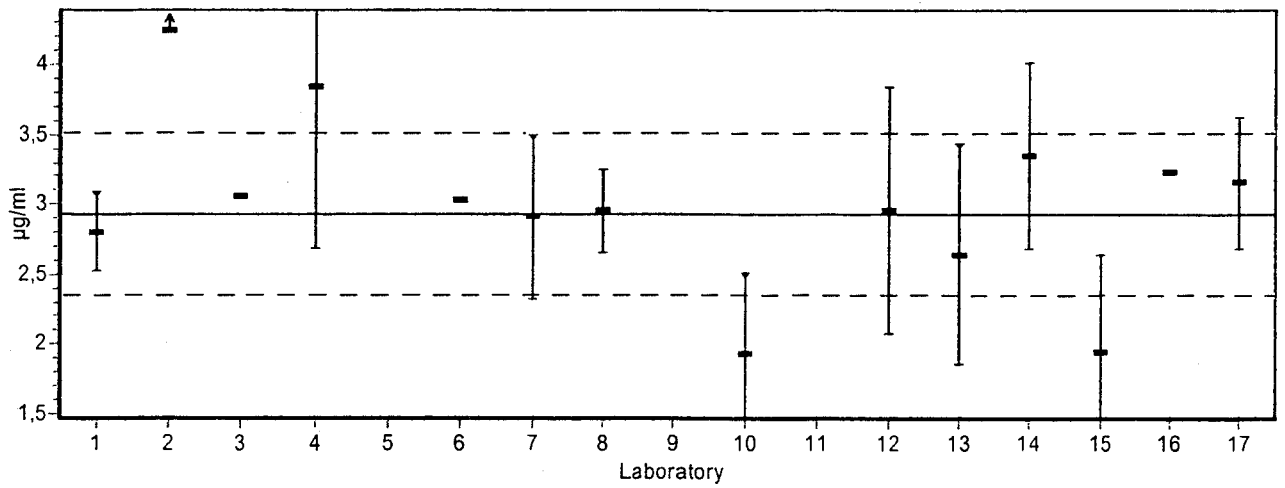
Analyytti (Analyte) VOC-Et.benzene Näyte (Sample) V2



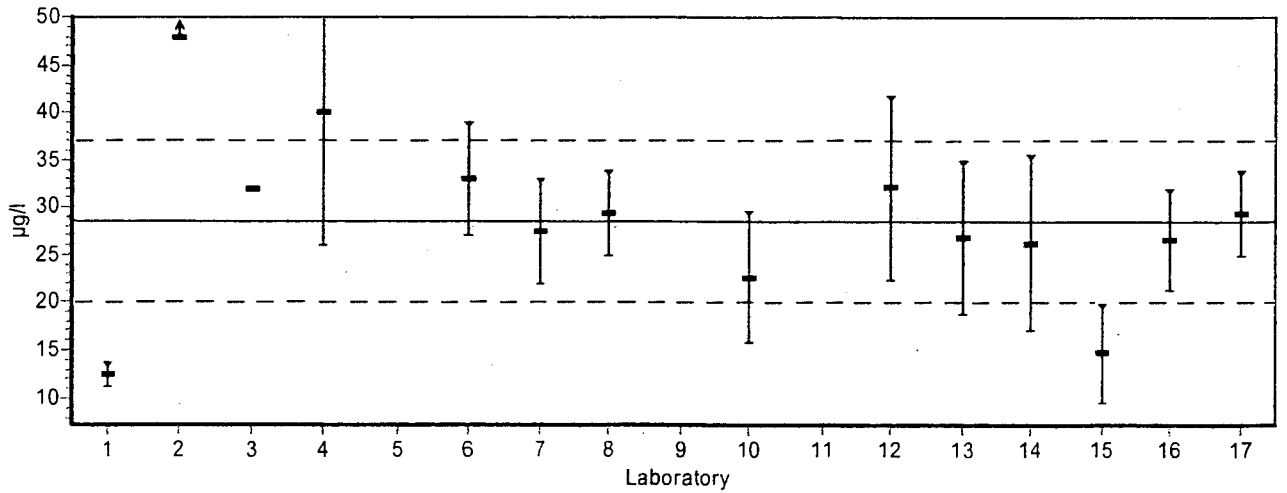
Analyytti (Analyte) VOC-m/p-Xylene Näyte (Sample) M2



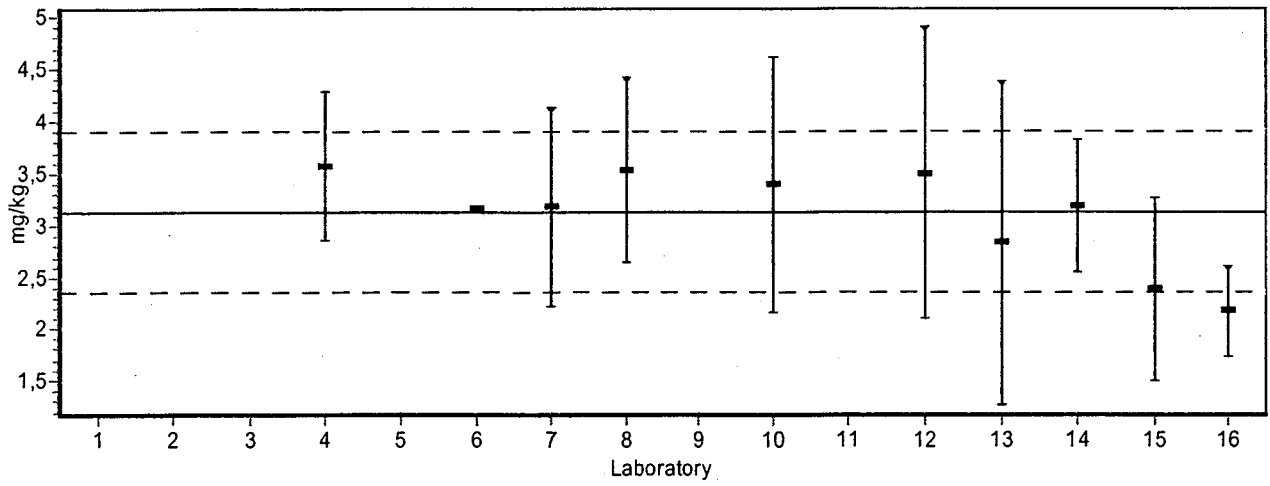
Analyytti (Analyte) VOC-m/p-Xylene Näyte (Sample) S2



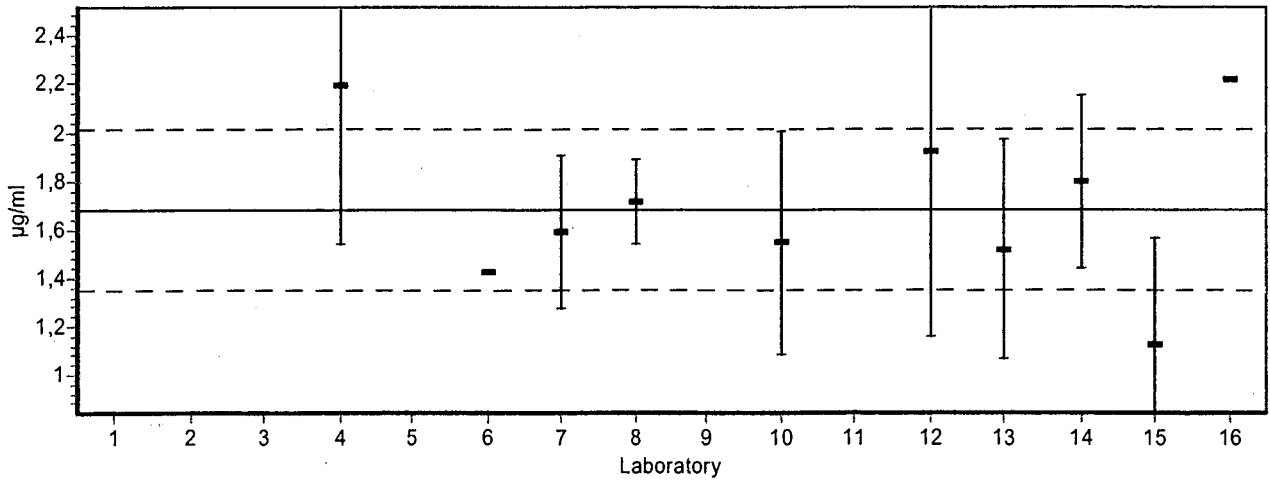
Analyytti (Analyte) VOC-m/p-Xylene Näyte (Sample) V2



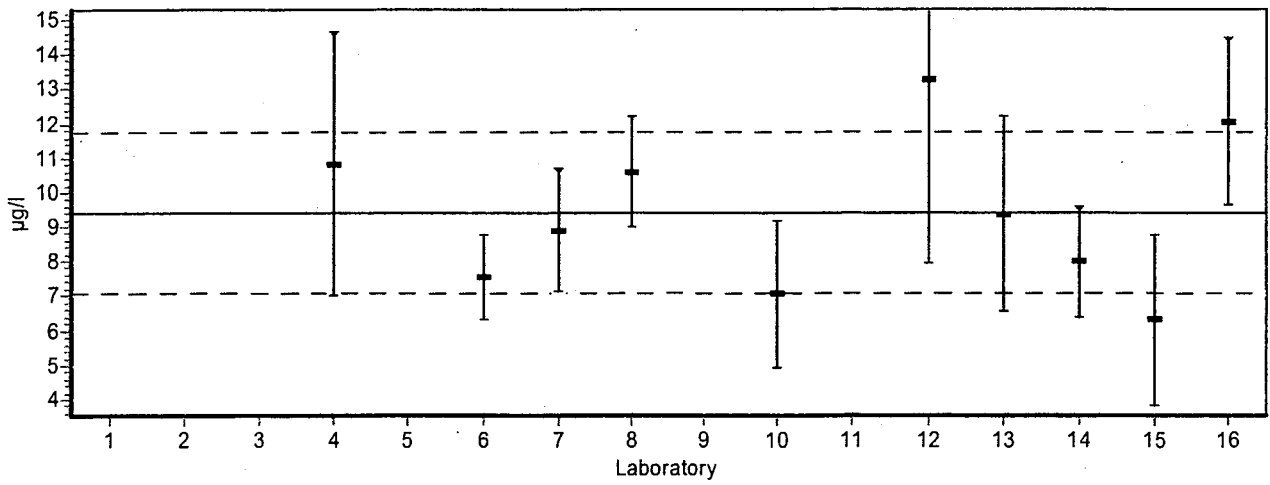
Analyytti (Analyte) VOC-MTBE Näyte (Sample) M2



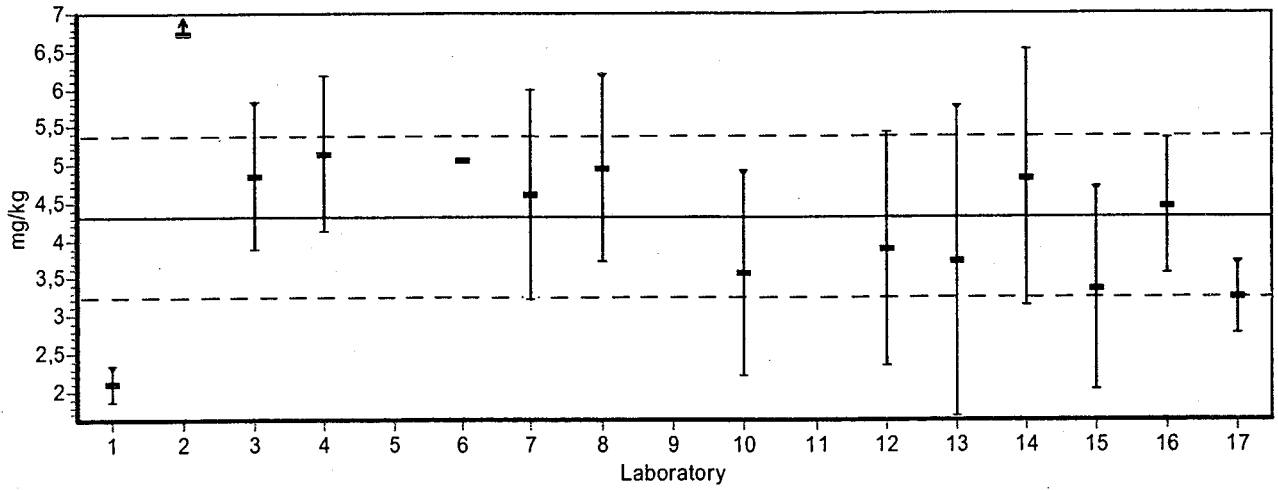
Analyytti (Analyte) VOC-MTBE Näyte (Sample) S2



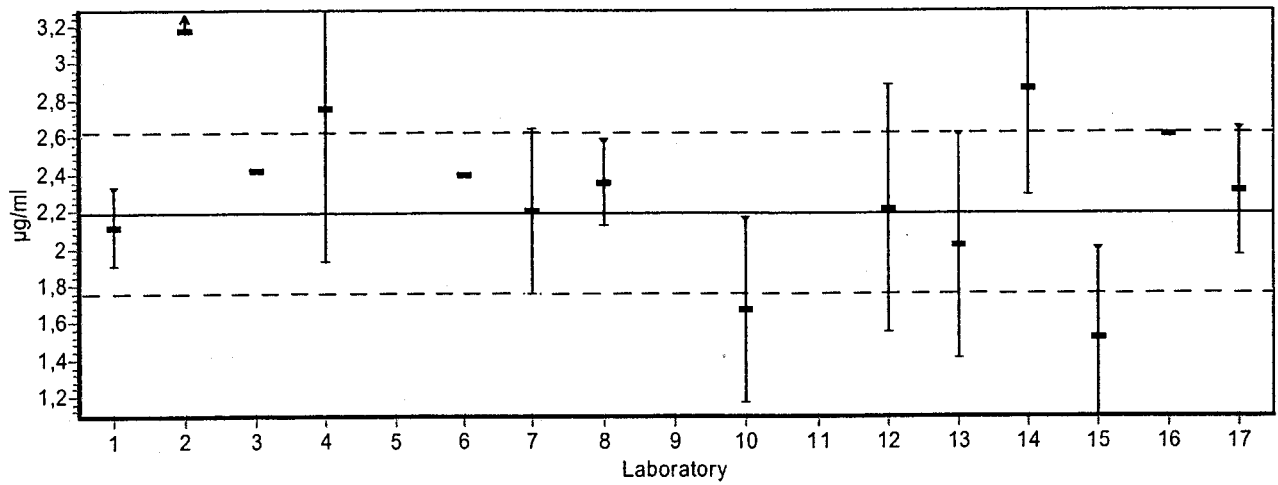
Analyytti (Analyte) VOC-MTBE Näyte (Sample) V2



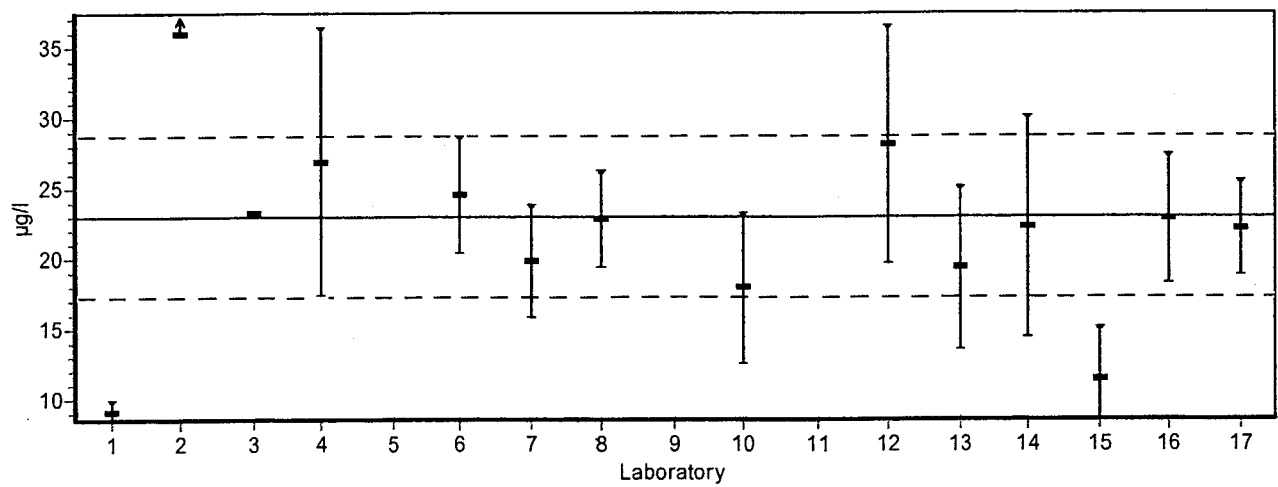
Analyttili (Analyte) VOC-o-Xylene Näyte (Sample) M2



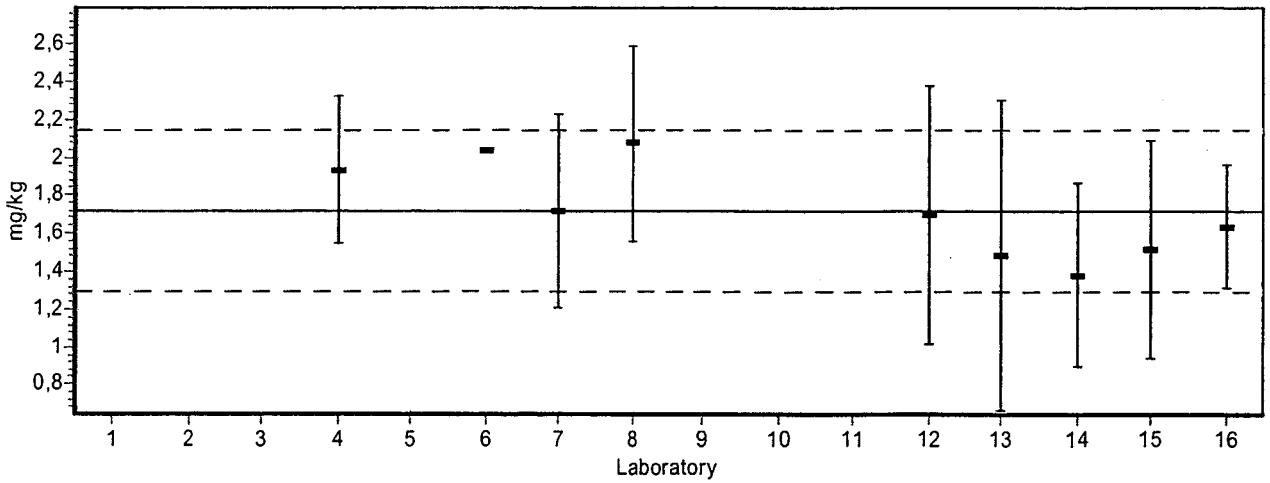
Analyttili (Analyte) VOC-o-Xylene Näyte (Sample) S2



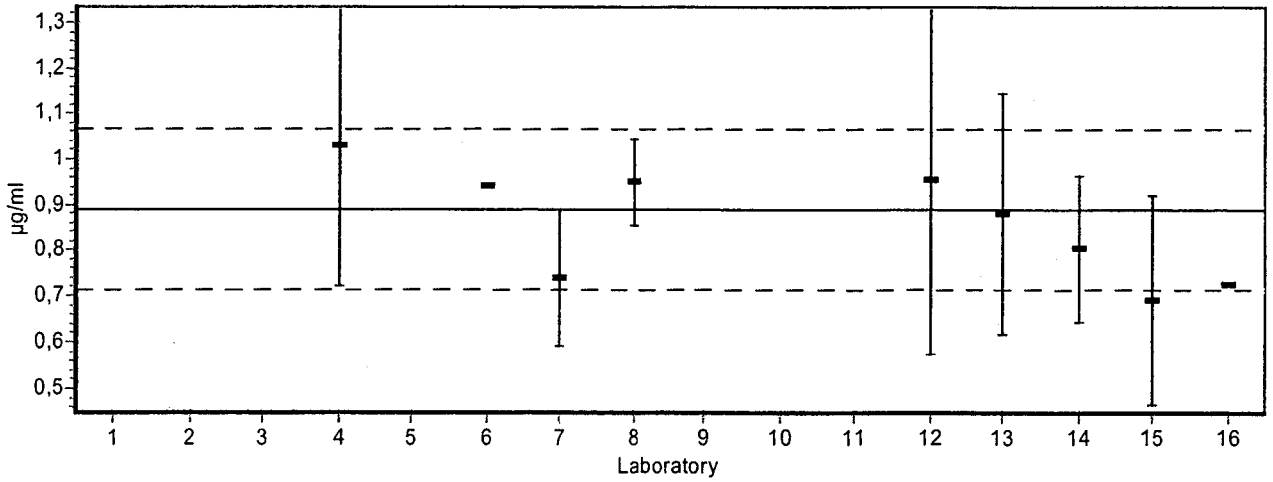
Analyttili (Analyte) VOC-o-Xylene Näyte (Sample) V2



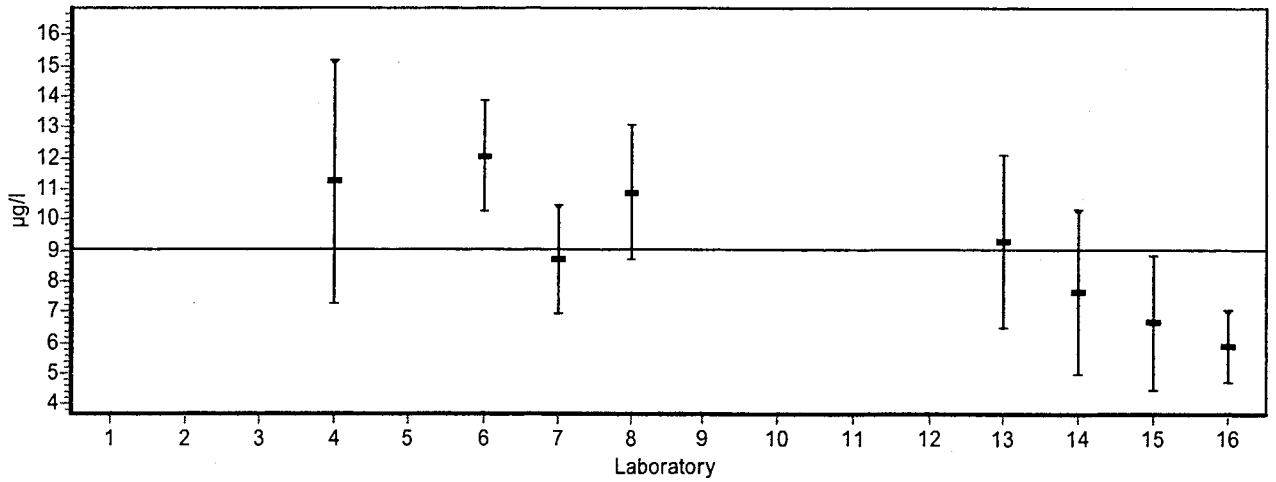
Analyytti (Analyte) VOC-Styrene Näyte (Sample) M2



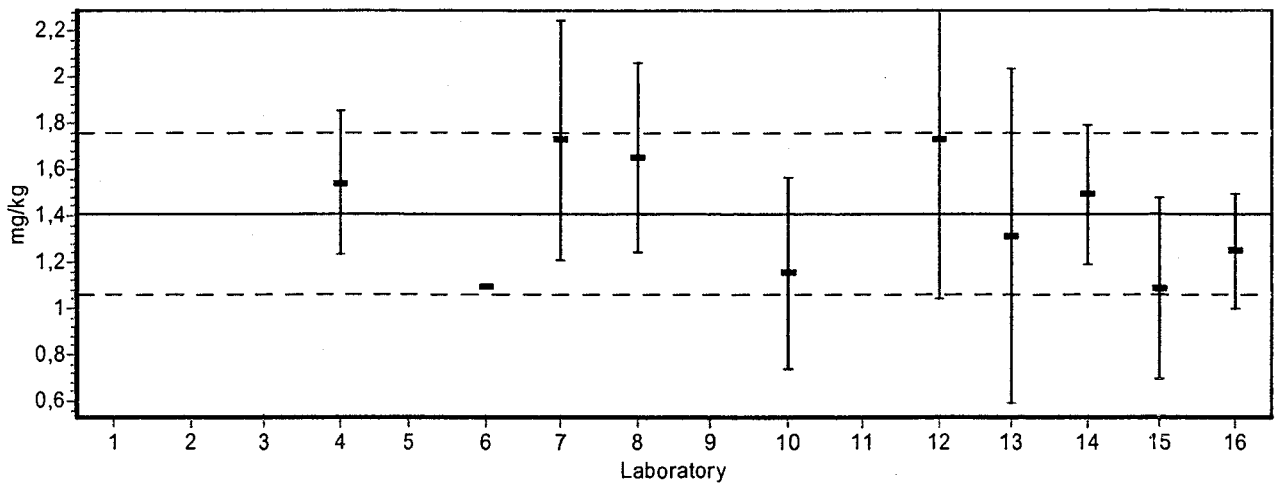
Analyytti (Analyte) VOC-Styrene Näyte (Sample) S2



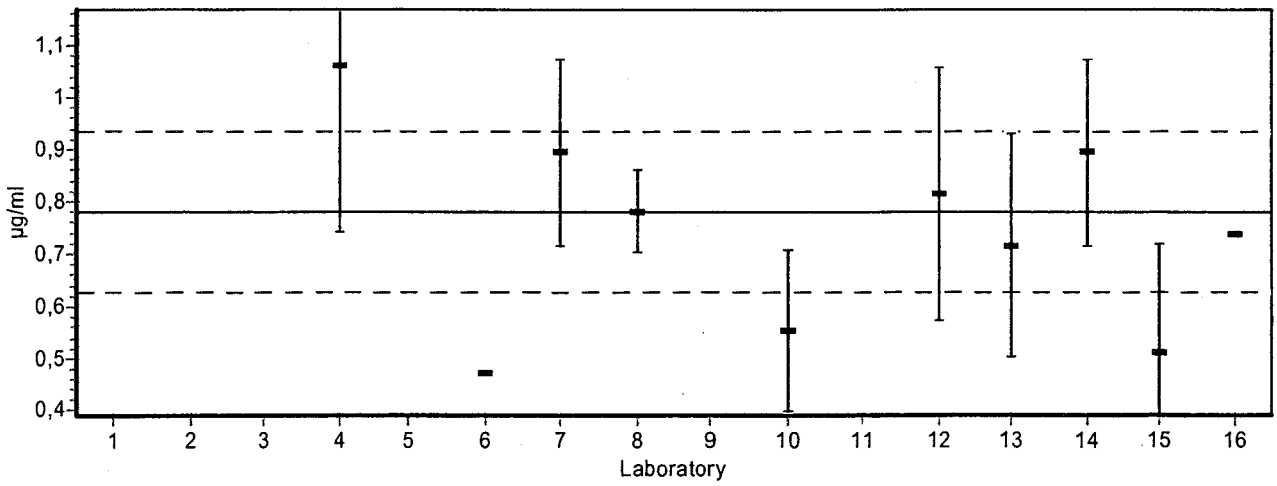
Analyytti (Analyte) VOC-Styrene Näyte (Sample) V2



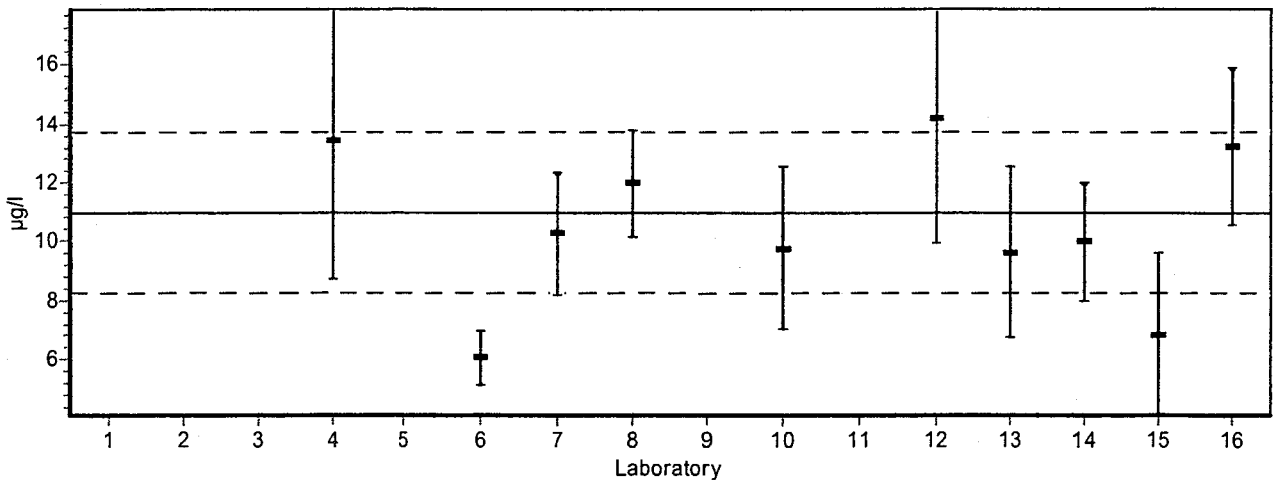
Analyytti (Analyte) **VOC-TAME** Näyte (Sample) M2



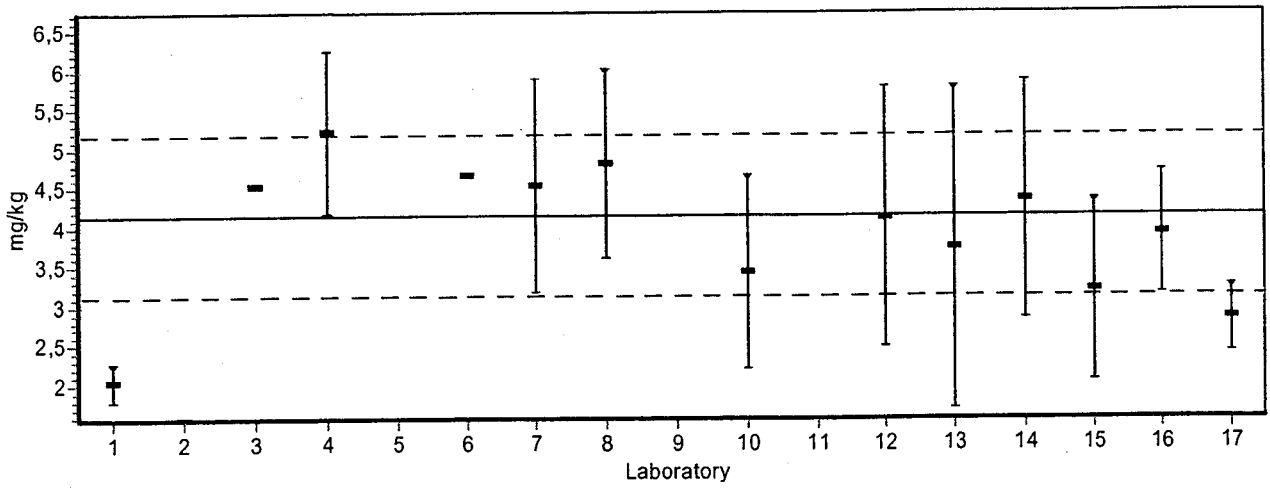
Analyytti (Analyte) **VOC-TAME** Näyte (Sample) S2



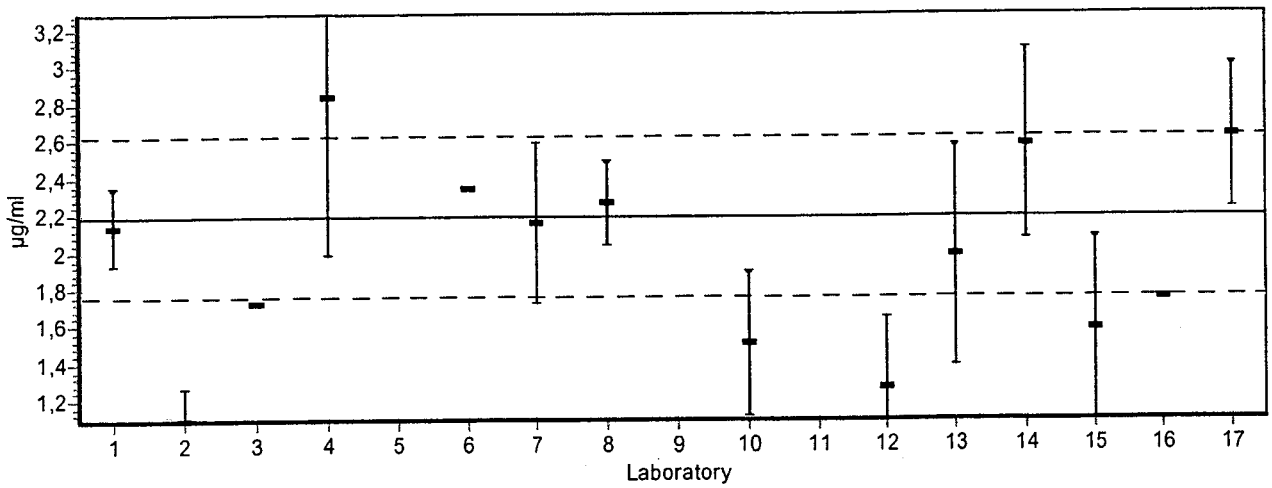
Analyytti (Analyte) **VOC-TAME** Näyte (Sample) V2



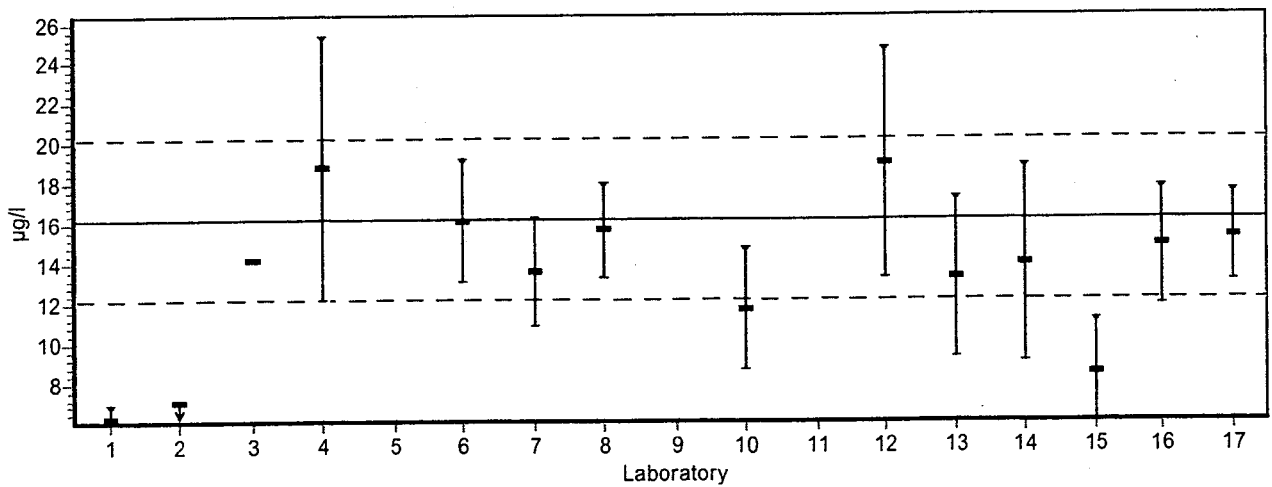
Analyytti (Analyte) VOC-Toluene Näyte (Sample) M2



Analyytti (Analyte) VOC-Toluene Näyte (Sample) S2



Analyytti (Analyte) VOC-Toluene Näyte (Sample) V2



APPENDIX 10. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant

Analyte	
Unit	
Sample	The code of the sample
z-Graphics	z score - the graphical presentation
z-value	z-score, calculated as follows: $z = (x_i - X)/s$, where x_i = the result of the individual laboratory X = the reference value (the assigned value) s = the target value for the total standard deviation (s_{target}).
Outl test OK	yes - the result passed the outlier test H = Hampel test (a test for the mean value) In addition, in robust statistics results deviating at least 50 % from the original robust mean have been rejected.
Assigned value	the reference value
2* Targ SD %	the target total standard deviation (95 % confidence interval).
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores

- A - accepted ($-2 \leq z \leq 2$)
 p - questionable ($2 < z \leq 3$), positive error, the result $> X$
 n - questionable ($-3 \leq z < -2$), negative error, the result $< X$
 P - non- accepted ($z > 3$), positive error, the result $\gg X$
 N - non- accepted ($z < -3$), negative error, the result $\ll X$ (X = the reference value)

Robust analysis

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

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

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

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

For each x_i is calculated:

$$x_i^* = x^* - \varphi \quad \text{if } x_i < x^* - \varphi$$

$$x_i^* = x^* + \varphi \quad \text{if } x_i > x^* + \varphi$$

$$x_i^* = x_i \quad \text{otherwise}$$

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 converges.

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

Analyte	Unit	Sample	z-Graphics						Z-value	Out 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
			-3	-2	-1	0	+1	+2													
	µg/l	V2								yes	9.05		10,9	8,97	9,053	2,17	23,9	8	0	0	8
Laboratory 8																					
VOC-TAME	mg/kg	M2							1,387	yes	1,41	25	1,655	1,5	1,419	0,2634	18,5	10	0	0	10
	µg/ml	S2							0,019	yes	0,78	20	0,7815	0,7477	0,7434	0,1889	25,4	10	0	0	10
	µg/l	V2							0,742	yes	10,98	25	12	10,35	10,54	2,666	25,2	10	0	0	10
VOC-Toluene	mg/kg	M2							1,284	yes	4,15	25	4,816	4,02	3,764	1,114	29,5	14	0	0	14
	µg/ml	S2							0,349	yes	2,19	20	2,266	2,08	1,991	0,5178	26,0	14	0	0	14
	µg/l	V2							-0,258	yes	16,22	25	15,7	14,3	13,97	3,501	25,0	13	1	0	14
Laboratory 9																					
Min.oil-GC	mg/kg	M1							-0,180	yes	925	30	900	910	942,7	156,3	16,5	14	1	0	15
	mg/ml	S1							2,700	yes	5	20	6,35	5,085	5,299	0,607	11,4	15	0	0	15
	mg/l	V1							0,909	yes	0,88	30	1,0	0,719	0,7878	0,2603	33,0	15	0	1	16
Laboratory 10																					
Min.oil-GC	mg/kg	M1							0,393	yes	925	30	979,5	910	942,7	156,3	16,5	14	1	0	15
	mg/ml	S1							1,540	yes	5	20	5,77	5,085	5,299	0,607	11,4	15	0	0	15
	mg/l	V1							-4,182	yes	0,88	30	0,328	0,719	0,7878	0,2603	33,0	15	0	1	16
VOC-Benzene	mg/kg	M2							-0,394	yes	3,68	30	3,463	3,59	3,576	0,78	21,8	14	0	0	14
	µg/ml	S2							-2,289	yes	2,01	20	1,55	2,111	2,115	0,3457	16,3	13	1	0	14
	µg/l	V2							-1,308	yes	11,19	25	9,36	9,72	9,789	2,836	28,9	14	0	0	14
VOC-Et.benzene	mg/kg	M2							-0,706	yes	3,28	30	2,933	3,12	3,177	0,748	23,5	13	1	0	14
	µg/ml	S2							-2,644	yes	1,74	20	1,28	1,785	1,766	0,344	19,4	13	1	0	14
	µg/l	V2							-0,801	yes	17,9	40	15,03	18,15	17,56	4,937	28,1	14	0	0	14
VOC-m/p-Xylene	mg/kg	M2							-1,525	yes	5,63	30	4,343	5,39	5,373	1,309	24,3	13	1	0	14
	µg/ml	S2							-3,413	yes	2,93	20	1,93	2,958	2,91	0,5159	17,7	13	1	0	14
	µg/l	V2							-1,364	yes	28,6	30	22,75	27,9	27,2	7,231	26,5	13	1	0	14
VOC-MTBE	mg/kg	M2							0,671	yes	3,13	25	3,393	3,21	3,169	0,4288	13,5	10	0	0	10
	µg/ml	S2							-0,804	yes	1,68	20	1,545	1,661	1,705	0,337	19,7	10	0	0	10
	µg/l	V2							-2,001	yes	9,41	25	7,057	9,205	9,391	2,215	23,5	10	0	0	10
VOC-o-Xylene	mg/kg	M2							-1,383	yes	4,31	25	3,565	4,45	4,116	0,9214	22,3	13	1	0	14
	µg/ml	S2							-2,374	yes	2,19	20	1,67	2,29	2,265	0,378	16,6	13	1	0	14
	µg/l	V2							-1,756	yes	23,02	25	17,97	22,3	20,87	5,353	25,6	13	1	0	14
VOC-TAME	mg/kg	M2							-1,447	yes	1,41	25	1,155	1,5	1,419	0,2634	18,5	10	0	0	10
	µg/ml	S2							-2,917	yes	0,78	20	0,5525	0,7477	0,7434	0,1889	25,4	10	0	0	10
	µg/l	V2							-0,879	yes	10,98	25	9,773	10,35	10,54	2,666	25,2	10	0	0	10
VOC-Toluene	mg/kg	M2							-1,407	yes	4,15	25	3,42	4,02	3,764	1,114	29,5	14	0	0	14
	µg/ml	S2							-3,128	yes	2,19	20	1,505	2,08	1,991	0,5178	26,0	14	0	0	14
	µg/l	V2							-2,213	yes	16,22	25	11,73	14,3	13,97	3,501	25,0	13	1	0	14
Laboratory 11																					
Min.oil-GC	mg/kg	M1							-1,108	yes	925	30	771,3	910	942,7	156,3	16,5	14	1	0	15
	mg/ml	S1							-1,400	yes	5	20	4,3	5,085	5,299	0,607	11,4	15	0	0	15
	mg/l	V1							-3,333	yes	0,88	30	0,44	0,719	0,7878	0,2603	33,0	15	0	1	16

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

LIITE 12. SUMMARY OF THE z SCORES
Appendix 12.

Analyte	Sample/Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	%
Min.oil-GC	M1	.	A	A	A	N	A	p	A	A	A	A	A	A	A	A	A	A	87
	S1	.	p	A	A	A	A	p	A	p	A	A	A	A	A	A	A	A	80
	V1	.	A	A	A	A	n	p	n	A	N	N	.	A	A	A	A	A	67
TetraCE	M2	.	.	.	P	.	A	A	A	.	.	.	A	A	.	A	A	n	78
	S2	.	.	.	P	.	A	A	A	.	.	.	A	A	.	N	A	P	67
	V2	.	.	.	p	.	A	A	A	.	.	.	A	A	.	N	A	A	78
TriCE	M2	.	.	.	P	.	A	p	A	.	.	.	A	A	.	n	A	n	56
	S2	.	.	.	P	.	A	A	A	.	.	.	p	A	.	N	A	P	56
	V2	.	.	.	p	.	A	A	A	.	.	.	A	A	.	N	A	A	78
VOC-Benzene	M2	N	A	A	A	.	A	A	A	.	A	.	A	A	A	A	A	A	93
	S2	A	A	P	P	.	A	A	A	.	n	.	A	A	A	n	p	A	64
	V2	N	N	A	P	.	A	A	A	.	A	.	A	A	A	N	A	A	71
VOC-Et.benzene	M2	N	P	A	p	.	A	A	A	.	A	.	A	A	A	A	A	A	79
	S2	A	P	A	P	.	A	A	A	.	n	.	A	A	A	N	A	p	64
	V2	N	p	A	P	.	A	A	A	.	A	.	A	A	A	N	A	A	71
VOC-m/p-Xylene	M2	N	P	A	p	.	A	A	A	.	A	.	A	A	A	A	A	A	79
	S2	A	P	A	P	.	A	A	A	.	N	.	A	A	A	N	A	A	71
	V2	N	P	A	p	.	A	A	A	.	A	.	A	A	A	N	A	A	71
VOC-MTBE	M2	.	.	.	A	.	A	A	A	.	A	.	A	A	A	A	n	.	90
	S2	.	.	.	P	.	A	A	A	.	A	.	A	A	A	N	P	.	70
	V2	.	.	.	A	.	A	A	A	.	n	.	P	A	A	n	p	.	60
VOC-o-Xylene	M2	N	P	A	A	.	A	A	A	.	A	.	A	A	A	A	A	A	86
	S2	A	P	A	p	.	A	A	A	.	n	.	A	A	P	N	A	A	64
	V2	N	P	A	A	.	A	A	A	.	A	.	A	A	A	N	A	A	79
VOC-Styrene	M2	.	.	.	A	.	A	A	A	.	.	.	A	A	A	A	A	.	100
	S2	.	.	.	A	.	A	A	A	.	.	.	A	A	A	n	A	.	89
	V2	.	.	.	A	.	p	A	A	A	A	A	n	.	75
VOC-TAME	M2	.	.	.	A	.	A	A	A	.	A	.	A	A	A	A	A	.	100
	S2	.	.	.	P	.	N	A	A	.	n	.	A	A	A	N	A	.	60
	V2	.	.	.	A	.	N	A	A	.	A	.	p	A	A	N	A	.	70
VOC-Toluene	M2	N	N	A	p	.	A	A	A	.	A	.	A	A	A	A	A	n	71
	S2	A	N	n	p	.	A	A	A	.	N	.	N	A	A	n	n	A	50
	V2	N	N	A	A	.	A	A	A	.	n	.	A	A	A	N	A	A	71
%		33	22	89	42	67	88	88	97	67	62	67	87	100	96	39	82	73	
Accredited		yes	yes	yes	yes	yes	yes		yes				yes		yes	yes	yes	yes	

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

%* - percentage of accepted results

Totally accepted, % In all: 74 In accredited: 71

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date	July 2006
Author(s)	Irma Mäkinen, Pirjo Sainio and Jari Nuutinen		
Title of publication	SYKE Proficiency test 2/2006 Volatile organic compounds and mineral oils from water and polluted soil		
Parts of publication/ other project publications			
Abstract	<p>The Finnish Environment Institute carried out the proficiency test for the analysis of mineral oils (middle and heavy fractions) and volatile organic compounds in water and in soil. In total, the samples were delivered to 20 laboratories, from which three laboratories did not reported the results.</p> <p>One synthetic sample, one soil sample and one water sample were delivered to the laboratories for the analysis of different compounds.</p> <p>In particular, the laboratories used many different methods or the method modifications. The robust standard deviation varied from 7.2 % to 30 % in the analysis of mineral oils and from 6.8 % to 31 % in the analysis of volatile organics. The use of different methods or the method variations, particularly different extraction techniques might have had some effect on variation of the results in the analysis of mineral oils from soil and water as well as in the analysis of volatile organics from soil.</p> <p>In this proficiency test, the calculated concentrations were used as the assigned values for the synthetic samples and the water samples. The robust mean was used the assigned value in the analysis of the soil samples. When the target value of the total standard deviation varied from 25 % to 40 % in calculating of z scores at the 95 % confidence interval. In total, 74 % of the participating laboratories reported the satisfied results.</p>		
Keywords	polluted soils, environmental laboratories, proficiency test, interlaboratory comparisons		
Publication series and number	Suomen ympäristökeskuksen moniste 10/2006		
Theme of publication			
Project name and number, if any			
Financier/ commissioner			
Project organization			
	ISSN 1455-0792	ISBN 952-11-2330-3	
	No. of pages 58	Language English	
	Restrictions Public	Price	
For sale at/ distributor	Finnish Environment Institute, Customer service E-mail: neuvonta.syke@ymparisto.fi tel. 358 9 4030 0190, fax 358 9 40300 190		
Financier of publication	Finnish Environment Institute, P.O.Box 140, FIN-00251 Helsinki, Finland		
Printing place and year	Edita Prima Ltd, Helsinki 2006		
Other information			

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisu-aika Heinäkuu 2006
Tekijä(t)	Irma Mäkinen, Pirjo Sainio ja Jari Nuutinen	
Julkaisun nimi	Laboratorioiden välinen pätevyyskoe 2/2006 Haihtuvat orgaaniset yhdisteet ja mineraali öljy vedestä ja maasta	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	<p>Suomen ympäristökeskus järjesti helmikuussa 2006 pätevyyskokeen mineraaliöljyjen (keskiraskaat ja raskaat öljyjakeet) ja haihtuvien orgaanisten yhdisteiden määrittämiseksi vedestä ja maasta. Näytteet toimitettiin 20 laboratoriolle, joista kolme ei palauttanut tuloksia. Eri yhdisteitä varten toimitettiin synteettinen näyte, vesinäyte ja maanäyte.</p> <p>Varsinkin haihtuvien orgaanisten yhdisteiden analysoinnissa käytettiin useita menetelmiä tai menetelmävariaatioita, millä on voinut olla vaikutusta tuloksiin. Jonkin verran todettiin näytteiden uutotekniikalla olevan vaikutusta mineraaliöljyjen määrittämisessä maasta ja vedestä sekä haihtuvien orgaanisten yhdisteiden määrittämisessä maasta.</p> <p>Tulosten hajonta oli 7,2 % – 30 % mineraaliöljyjen määrittämisessä ja 6,8 % – 31 % haihtuvien orgaanisten yhdisteiden analysoinnissa. Tulosten hajontaa vaikutti mm. erilaisten menetelmien ja eri uutotekniikoiden käyttö mittauksessa olleiden eroavaisuuksien ohella.</p> <p>Vertailuarvona käytettiin laskennallista pitoisuutta synteettisten näytteiden ja vesinäytteiden sekä robusti-keskiarvoa maanäytteiden tulosten arvioinnissa. Tässä pätevyyskokeessa 74 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin 25 % – 30 % mineraaliöljyjen analysoinnissa ja 25 % – 40 % haihtuvien orgaanisten yhdisteiden analysoinnissa (95 % merkitsevyystaso).</p>	
Asiasanat	saastuneet maat, ympäristölaboratoriot, pätevyyskoe, vertailumittaus	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen moniste 10/2006	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
	ISSN 1455-0792	ISBN 952-11-2330-3
	Sivuja 58	Kieli englanti
	Luottamuksellisuus Julkinen	Hinta
Julkaisun myynti/ jakaja	Suomen ympäristökeskus, asiakaspalvelu sähköpostiosoite: neuvonta.syke@ymparisto.fi puh. (09) 4030 0119, telefax (09) 4030 0190	
Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Edita Prima Ltd, Helsinki 2006	
Muut tiedot		

Presentationblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Juli 2006
Författare	Irma Mäkinen, Pirjo Sainio och Jari Nuutinen	
Publikationens titel	Provning jämförelse 2/2006	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	<p>Under februari 2005 genomförde Finlands Miljöcentral en provning jämförelse, som omfattade bestämning av avdustande organiska föreningar (VOC föreningar) och mineralolja i vatten och i förorenad jord.</p> <p>Ett syntetiskt prov, ett vattenprov och ett jordprov hade preparats. proven utsändes till 20 laboratorier, men endast 17 laboratorier returnerade resultaten.</p> <p>Olika analysmetoder eller metodapplikationer hade använts för VOC analyser. vilket hade möjliggjort utverkat på resultaten. Extraktion teknik hade verkat på något sätt vid bestämningen av mineralolja i vatten och i jord vid bestämning av VOC föreningar av jord.</p> <p>Resultaten varierade 7,2 % - 30 % vid bestämningen av mineralolja och 6,8 % - 31 % vid bestämningen av VOC föreningar. Olika metoder eller metodvariationer hade verkat på variationen av resultaten.</p> <p>Som referensvärde (<i>the assigned value</i>) användes det teoretiska värdet (syntetiska provet och vattenprovet) och robust-medelvärde (jordprovet). Resultaten värderades med hjälp av z-värden. Beräkningen av z-värden baserade sig på totalstandardavvikelse, som tillsattes 25 % - 40 % (95 % sannolikhetsnivå). I denna provning jämförelse var 74 % av resultaten tillfredsställande.</p>	
Nyckelord	Mineralolja, avdustande organiska föreningar, VOC föreningar, vattenprov, jordprov, provning jämförelse, miljölaboratorier	
Publikationsserie och nummer	Suomen ympäristökeskuksen moniste 10/2006	
Publikationens tema		
Projektets namn och nummer		
Finansiär/ uppdragsgivare		
Organisationer i projektgruppen		
	ISSN 1455-0792	ISBN 952-11-2330-3
	Sidantal 58	Språk Engelska
	Offentlighet offentlig	Pris
Beställningar/ distribution	Finlands miljöcentral, informationstjänsten neuvonta.syke@ymparisto.fi Tfn (09) 4030 0119, fax (09) 4030 0190	
Förläggare	Finlands miljöcentral, PB 140, 00250 Helsingfors	
Tryckeri/ tryckningsort och -år	Edita Prima Ltd, Helsingfors 2006	
Övriga uppgifter		

SYKE PROFICIENCY TEST 2 / 2006
VOLATILE ORGANIC COMPOUNDS AND MINERAL OILS FROM WATER AND POLLUTED SOIL



ISBN 952-11-2330-3 (pbk.)

ISSN 1796-1718 (print.)

FINNISH ENVIRONMENT INSTITUTE