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SYKE Proficiency Test 7/2005

PAHs from polluted soil

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The organizer of the proficiency test:
Finnish Environment Institute (SYKE), Laboratory
Hakuninmaantie 6, 00430 Helsinki
tel. +358 9 403 000, telecopy +358 9 4030 0890

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CONTENT

APPENDIXES

1 INTRODUCTION

The Finnish Environment Institute carried out the proficiency test for the determination of PAHs from polluted soil in November 2005. The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1[1], ILAC Requirements[2], ISO/DIS 13528[3] and IUPAC Recommendations[4].

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratory
Hakuninmaantie 6, 00430 Helsinki
tel. +358 9 403 000, telecopy +358 9 4030 0890

The responsibilities in organizing the proficiency test were as follows:
Irma Mäkinen, SYKE, coordinator
Pirjo Sainio, analytical expert

2.2 Participants

In total, the samples were delivered to 10 laboratories, from which two laboratories did not reported the results (Appendix 1).

2.3 Samples and their delivery

One synthetic sample (S1) and one soil sample (M1) was delivered to the participants. The sample S1 was synthetic and the sample M2 was a soil sample prepared by a German PT provider (Appendix 2).

The samples were delivered on 29 November 2005 and they were asked to analyze before the 31 January 2006.

The results were asked to return before the 3 February 2006.

The preliminary lists of the results were delivered on 10 February 2006.

2.4 Comments sent by the participants

The participants sent comments on the result sheets and on their own results.

2.5 Analytical methods

The standard for analysis of PAHs from soil (ISO 18287) has been published in 2006[6]. The standard method is applicable for all types of soil and it is based on extraction with acetone and petroleum ether. Therefore the new standard method is not yet widely used. The method published by Nordtest (Report TR 329) was used by few participants[7]. Some participants used their own "in house" methods (Appendix 4).

The soil sample was extracted using seven different solvents or solvent mixtures (Appendix 4). The mixture of acetone and hexane or the mixture of hexane and dichloromethane was most commonly used. The sample intake of 2 g – 20 g was used. Extraction was carried out mainly by shaking or/and by soxhlet. Only one participant (lab 3) used solely sonication for extraction of the soil sample M1.

PAHs were mainly measured by GC-MS- method. The length of the column was 30 m except on the laboratory 7, which used 60 m column. One laboratory (lab 2) reported the results of the synthetic sample S1 using HPLC in measurement.

Several standards or standard mixtures were used as internal standards, which were mainly deuterated.

2.6 Data treatment

2.6.1 Testing of outliers and normality of data

The participants were requested to report the duplicate results. 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 not more than one outlier, which deviated at least 50% of the robust mean[4], was rejected.

2.6.2 Assigned values and their uncertainties

The reported value for the reference material was used as the signed value in analysis of the synthetic sample S1. The provider reported that the expanded uncertainty is ± 1.0% at the 95% confidence level.

The robust-mean was used as the assigned value in analysis of the soil sample M1 (Appendix 2). The assigned value can be regarded indicative in analysis of benzo(a)anthracene, benzo(k)fluoranthene, dibenzo(ah)anthracene, fluorene and naphthalene from the soil sample M1 because of the variation of the results, the calculated uncertainty of the assigned value and the low number of the reported results. The assigned values estimated in the SYKE PT were somewhat higher than the assigned value in a German test carried out in 2003, in which 59 laboratories were participated. In the SYKE PT the results obtained by some laboratories from the synthetic sample S1 were higher (> 10%) than the calculated concentration, which might have had some effect on the results of the soil sample M1, too. Further, differences in analytical methods can have had also an effect on the assigned values in two different PTs. The HPLC technique is commonly used in Germany in analysis of PAHs. In this PT the results of the soil sample M1 were obtained using the GC technique.

The uncertainty of the assigned values was calculated using the robust standard deviation. It varied from 8.8% to 60%, (at the 95% confidence interval) and it was largest in analysis of naphthalene. In most

cases the uncertainty was less than 25%. The uncertainty of the assigned value was high (60%) in analysis of naphthalene because of a few results. However, the calculated assigned value (0.097 mg/kg) was close to the value reported in the German PT (0.118 mg/kg). In the final data treatment the performance of the laboratories had not been evaluated in analysis of naphthalene from the soil sample M1.

2.6.3 Uncertainties reported by the participants

Most participants reported their measurement uncertainties (Appendix 6 and 7). In analysis of the soil sample the uncertainties varied mainly from 25% to 40%, but also much higher uncertainties were reported. If the laboratory reported same uncertainty for the sample S1 as for the sample M1, it seemed to be too high for the sample S1 (Appendix 7). On the other hand, in some cases the estimates for the sample M1 seemed to be too low comparing with the performance of the laboratory.

There were not systematic differences between the uncertainties estimated by different procedures, e.g. between the uncertainties estimated using the validation data or the Eurachem Guide[8] (Appendix 6).

2.6.4 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 PAH contents in the sample and the uncertainties of the assigned values. The s_{target} was 20% in analysis of the synthetic sample S1 and 30% or 40% in analysis of the soil sample M1 (at the 95% confidence interval) except the results of benzo(k)fluoranthene. In this case the target value 50% was used.

2.6.5 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:

$\lvert z \rvert \leq 2$	"satisfied" results
$2 < \lvert z \rvert < 3$	"questionable" results
$\lvert z \rvert \geq 3$	"unsatisfied" results.

The calculated z scores are presented in the results of each participant (Appendix 9) and the summary of z scores is presented in Appendix 10. Explanations to terms are presented in Appendix 8.

3. RESULTS AND PERFORMANCE

3.1 Results

For the individual PAHs abbreviations explained in Appendix 2, have been used in the result sheet. All results reported by the laboratories are presented in Appendix 5. Statistically treated results for each la-

boratory are presented in Appendix 9. The graphical presentations of the results and the uncertainty estimations are presented in Appendix 7.

The results were asked to report as duplicates in analysis of the sample M1 (Appendix 5). The repeatability (the within-laboratory standard deviation, s_w) of PAHs varied from 2.9% to 15% and the reproducibility (the between-laboratory standard deviation, s_t) was between 11% and 53% (Table 1). The ratio s_t/s_w, a measure for the robustness of the methods used, was mainly higher than three in seven cases. It was higher than four in case of acenaphthalene, benzo(k)fluoranthene, fluoranthene, fluorene and pyrene. On the other hand, the within-laboratory standard deviation (s_w) was fairly high in analysis of naphthalene. The ratio s_t/s_w should be between 2 and 3 for robust methods[7].

Table 1. Results of the duplicate determinations (ANOVA statistics)

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Accepted. z-val %
A-naphthy	M1	mg/kg	0,266	0,2637	0,274	0,007627	0,05111	0,05168	2,9	19	20	40	8	88
Acenaph	M1	mg/kg	0,166	0,1737	0,164	0,006093	0,02218	0,023	3,5	13	13	30	6	83
Anthrac	M1	mg/kg	0,562	0,5531	0,56	0,03377	0,1255	0,13	6,1	23	23	30	9	78
Benzo-A-P	M1	mg/kg	3,15	3,197	2,96	0,295	0,7083	0,7673	9,2	22	24	40	9	100
Benzo-ant	M1	mg/kg	3,36	3,403	3,52	0,2	0,5478	0,5832	5,9	16	17	30	8	100
Benzo-B-F	M1	mg/kg	3,69	3,817	3,81	0,4413	0,663	0,7965	12	17	21	30	8	88
Benzo-K-F	M1	mg/kg	2,76	2,996	3,01	0,2568	1,293	1,318	8,6	43	44	50	8	75
Benzo-per	M1	mg/kg	2,09	2,077	2,18	0,2237	0,2231	0,3159	11	11	15	30	9	100
Chrysene	M1	mg/kg	3,21	3,349	3,17	0,2275	0,5277	0,5747	6,8	16	17	30	9	78
Dibenz-ah	M1	mg/kg	0,596	0,6049	0,635	0,08153	0,1382	0,1605	13	23	27	40	8	88
Fluoran	M1	mg/kg	6,9	7,039	6,55	0,2176	1,359	1,377	3,1	19	20	40	9	89
Fluorene	M1	mg/kg	0,215	0,2387	0,24	0,01941	0,07873	0,08108	8,1	33	34	40	7	71
Indeno	M1	mg/kg	2,27	2,291	2,2	0,227	0,4666	0,5189	9,9	20	23	40	9	100
Napht	M1	mg/kg	0,097	0,1017	0,1	0,01485	0,05212	0,05419	15	51	53	50	6	33
Phenan	M1	mg/kg	3,17	3,287	3,21	0,1265	0,3245	0,3483	3,8	9,9	11	30	9	89
Pyrene	M1	mg/kg	5,78	6,261	6,1	0,312	1,586	1,616	5	25	26	30	9	78
tot-PAH	M1	mg/kg	37,7	38,79	37,8	1,934	7,39	7,639	5	19	20	30	9	89

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

The robust standard deviation varied from 7.8% to 17.5% in analysis of the synthetic sample S1 and from 8.7% to 62% in analysis of the soil sample M1. It was highest in analysis of naphthalene (62%) and benzo(k)fluoranthene (35%) from the soil sample M1. In the PT results presented in the standard ISO 18287 the results varied generally from 20% to 70% and the variation was highest in analysis of naphthalene, acenaphthylene and/or dibenz(ah)antracene[6].

The variation of the results can be also seen in the Figure 1. Most results are fairly comparable e.g. in analysis of benzo(ghi)perylene and fluoranthene, but the results varied much more in analysis of naphthalene. The values obtained by the laboratories 4 and 6 in analysis of naphthalene might have been arisen from evaporation of naphthalene during the sample handling.

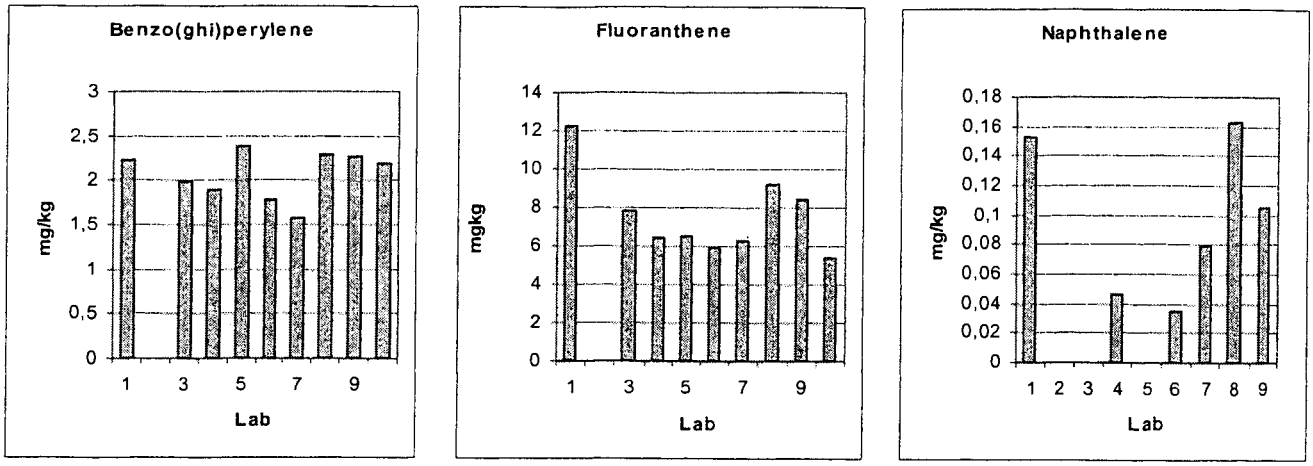

Figure 1. Results in analysis of benzo(ghi)perylene, fluoranthene and naphthalene

Table 2. Summary of the proficiency test

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
Acenaph	M1	mg/kg	0,166	0.17	0.18	0.18	0.031	17,2	7	30	83
	S1	µg/ml	10	10.32	10.45	10.45	0.81	7,8	10	20	80
A-naphthy	M1	mg/kg	0,266	0.26	0.28	0.29	0.055	19,6	8	40	88
	S1	µg/ml	10	10.00	9.84	9.74	1.01	10,3	10	20	90
Anthrac	M1	mg/kg	0,562	0.55	0.58	0.58	0.13	22,4	9	30	78
	S1	µg/ml	10	10.50	10.54	10.55	1.15	10,9	10	20	90
Benzo-ant	M1	mg/kg	3,36	3.40	3.35	3.52	0.66	19,7	8	30	100
	S1	µg/ml	10	10.45	10.43	10.37	1.06	10,2	9	20	100
Benzo-A-P	M1	mg/kg	3,15	3.20	3.15	2.96	0.77	24,6	9	40	100
	S1	µg/ml	10	10.42	10.56	10.50	1.84	17,5	10	20	70
Benzo-B-F	M1	mg/kg	3,69	3.82	3.78	3.81	0.69	18,2	8	30	88
	S1	µg/ml	10	10.76	10.80	10.70	0.85	7,9	9	20	78
Benzo-K-F	M1	mg/kg	2,76	3.00	2.84	3.01	1.38	48,8	8	50	75
	S1	µg/ml	10	10.13	10.13	9.87	0.80	7,9	9	20	89
Benzo-per	M1	mg/kg	2,09	2.08	2.09	2.18	0.26	12,4	9	30	100
	S1	µg/ml	10	10.70	10.71	10.68	0.88	8,2	10	20	100
Chrysene	M1	mg/kg	3,21	3.35	3.31	3.22	0.44	13,4	9	30	78
	S1	µg/ml	10	10.22	10.45	10.25	1.45	13,9	10	20	80
Dibenz-ah	M1	mg/kg	0,596	0.60	0.60	0.64	0.17	28,6	8	40	88
	S1	µg/ml	10	10.47	10.35	10.21	1.15	11,1	10	20	90
Fluoran	M1	mg/kg	6,9	7.04	7.23	6.68	1.62	22,4	9	40	89
	S1	µg/ml	10	10.62	10.62	10.35	1.34	12,6	10	20	80
Fluorene	M1	mg/kg	0,215	0.24	0.23	0.24	0.077	33,3	7	40	71
	S1	µg/ml	10	10.16	10.16	10.25	1.21	11,9	10	20	100
Indeno	M1	mg/kg	2,27	2.29	2.27	2.20	0.56	24,6	9	40	100
	S1	µg/ml	10	10.39	10.50	10.09	1.56	14,9	10	20	70
Napht	M1	mg/kg	0,097	0.10	0.097	0.10	0.061	62,4	7	50	33
	S1	µg/ml	10	9.80	9.92	10.17	1.42	14,4	10	20	90
Phenan	M1	mg/kg	3,17	3.29	3.17	3.20	0.34	10,9	9	30	89
	S1	µg/m	10	10.15	10.15	10.25	1.51	14,8	10	20	90
Pyrene	M1	mg/kg	5,78	6.26	6.03	6.10	1.35	22,5	9	30	78
	S1	µg/ml	10	10.55	10.54	10.25	1.27	12,1	10	20	80
tot-PAH	M1	mg/kg	37,7	38.79	37.72	37.80	6.42	17	9	30	89
	S1	µg/ml	160	165.53	165.53	164.00	16.95	10,2	10	20	100

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 $\lvert z \rvert \leq 2$.

3.2 Comments on the results

In analysis of the synthetic sample S1 12% of the results were not satisfied (Appendix 10). In that case the results deviated more than 20% from the assigned value probably because of differences in calibration and internal standards. The laboratories 5 and 9 did not report in each case satisfied result for the sample S1. However, their results in analysis of the sample M1 were mainly satisfied maybe because of the larger percent value of the target deviation. Also in the CoEPT Project for harmonization of PT organizing in Europe fairly high standard deviations were obtained in analysis of naphthalene[10]. In this project the standard deviation of the results varied from 20% to 59%, when seven PT organizers reported the results of naphthalene. The robust standard deviation of the SYKE PT data in this project in analysis of naphthalene was 39%, when 19 laboratories reported the results[10,11].

In this PT the participants used seven different solvents or solvent combinations in extraction (Appendix 4). Since the ISO 18287 is new, any participants did not use the mixture of acetone and petroleum ether in the extraction as it is described in the standard method[6]. Acetone is an efficient extractant to break down soil aggregates and petroleum ether increases the efficiency of the extraction. According to the report of the European project HORIZONTAL a polar solvent should be used in determination of PAHs because of their limited solubility in unpolar solvent[12]. The extraction of PAHs from different matrices is more crucial than the procedure and the extraction devices itself. The choice of solvents has to be made in accordance with the expected contamination level and also to be applicable to the measurement procedures. Only one laboratory (lab 3) used sonication in extraction, but it has not clearly effected on the results (Appendix 9). The ISO 18287 recommends use a shaking machine for extraction[6].

The length of the GC-column was 30 m except in the laboratory 7, which used the column with the length of 60 m. The used calibration range varied greatly from one laboratory to the other, but the number of calibration points was at least four. Internal standards (e.g. deuterated PAHs) were used for quantification by GC-MS. The substance that is similar in physical and chemical properties (e.g. extraction behaviour, retention time) to those of compounds to be analysed shall always be chosen to be as the internal standard. Since the properties of 16 PAHs in question varied a lot, it shall be more than one internal standard to give proper result and quality for all PAHs also in difficult cases.

The total PAH had been calculated as the sum of each 16 PAHs. The results of the total PAH agreed rather well (Appendix 7). One laboratory (lab 1) had reported too high value.

3.3 Estimation of performance

In this PT test 87% of the participating laboratories reported satisfied results. 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 analysis of the synthetic sample and from 30% to 50% in analysis of the soil sample (Appendix 10). The laboratory performance did not be evaluated in analysis of naphthalene from the soil sample because of a few participants and the large uncertainty of the assigned value.

The participants used many different methods; in particular, different extraction solvents for analysis of PAHs from soil and this might have had some effect on the variation of the results. The variation of the results in analysis of the soil sample agreed well a variation in some international proficiency tests[6,10]. The results varied also in analysis of the synthetic sample. Due to this variation some laboratories should re-examine their calibration procedures. Use of a sufficiently effective polar solvent is crucial in analysis of PAHs.

Especially for slightly polluted soil samples the use of proper pre-treatment methods (extraction, cleanup and concentration) affect to the quality of results in analysis of PAHs from soils.

4 SUMMARY

The Finnish Environment Institute carried out the proficiency test for the determination of PAHs from polluted soil in November 2005. In total 11 laboratories participated in the proficiency test. Two laboratories did not report the results.

One synthetic sample and one soil sampale were delivered to the participating laboratories.

The method published by Nordtest (Report TR 329), the draft standard ISO/DIS 18287 or their modifications were rather commonly used in analysis of PAHs. The robust standard deviation varied from 7.8% to 17.5% in analysis of the synthetic sample and from 8.7% to 62% in analysis of the soil sample. It was highest in analysis of naphthalene (62%) and benzo(k)fluoranthene (35%) in the soil sample. The use of different methods or method variations might have had some effect on variation of the results. There was a variation e.g. in extraction solvents and in internal standards. Use of a sufficiently effective polar solvent is crucial in analysis of PAHs from polluted soil.

In this proficiency test, the robust mean value was used as the assigned value. When the target value of the total deviation was 20% for synthetic sample and from 30% to 50% for the soil sample in calculating of z scores at the 95% confidence interval, 87% of the participating laboratories reported satisfied results.

Especially for slightly polluted soil samples the use of proper pre-treatment methods (extraction, cleanup and concentration) affect to the quality of results in analysis of PAHs from soils.

5 YHTEENVETO

Suomen ympäristökeskus järjesti marraskuussa 2005 pätevyyskokeen 16 PAH -yhdisteen määrittämiseksi maasta. Pätevyyskokeeseen osallistui kaikkiaan 11 laboratoriota. Pätevyyskokeeseen ilmoittautuneista laboratorioista kaksi ei palauttanut tuloksia.

Pätevyyskokeen näytteenä oli yksi synteettinen näyte ja yksi maanäyte.

Analysoinnissa käytettiin useita menetelmiä, yleisimmin Nordtest -raportin TR 329 mukaista menetelmää tai standardiehdotuksen ISO/DIS 18287 mukaista menetelmää. Mm. määritykseen käytetty näytemäärä, uuttoliuottimet ja kalibrointiliuokset vaihtelivat eri laboratorioissa. Riittävän polaarisen liuottimen käyttö on ensisijaisen tärkeää PAH -yhdisteiden uutossa maanäytteistä. Tulosten hajonta oli 7,8 % – 17,5 % eri PAH -yhdisteille synteettisen näytteen analysoinnissa ja 8,7 % - 62 % maanäytteen analysoinnissa. Tulosten hajonta oli suurin naftaleenin ja bentso(k)fluoranteenin määrityksessä. Tulosten hajontaa oli todettavissa myös synteettisen näytteen määrityksessä. Tulosten hajonta maanäytteen määrityksessä oli kuitenkin samaa suuruusluokkaa kuin kansainvälisissä pätevyyskokeissa.

Vertailuarvona käytettiin robusti-keskiarvoa. Tässä pätevyyskokeessa 87 % tuloksista oli tyydyttäviä,

kun kokonaiskeskihajonnan tavoitearvona käytettiin synteettiselle näytteelle 20 % ja maanäytteelle 30 % tai 40 % lukuun ottamatta bentso(k)fluoranteenia, jolle tavoitearvoksi asetettiin 50 % (95 % merkitsevyystaso).

Etenkin vähän saastuneita maita analysoitaessa näytteen esikäsittelyllä (uutolla, puhdistuksella ja konsentroinnilla) on vaikutusta PAH -tulosten laatuun.

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APPENDIX 1. PARTICIPANTS IN THE PROFICIENCY TEST SYKE 7/2005

Alcontrol Ab, Linköping, Sweden

Ekokem Oy Ab, Riihimäki, Finland

EST S.r. l., Grasbobbio, Italy

Golder Associates Oy, Helsinki, Finland

Helsingin kaupungin ympäristökeskus, Helsinki, Finland

Insinööritoimisto Paavo Ristola Oy, Hollola, Finland

Neste Oil Oyj, Porvoo, Finland

SGS Inspection Services Oy, Hamina, Finland

SYKE, Laboratory, Helsinki, Finland

Technologisk Institut, Traastrup, Denmark

APPENDIX 2. SAMPLES

Sample S1

The sample S1 was a synthetic sample prepared from the Dr. Ehrenstorfer Reference Materials, from the the PAH Mix 9 including 16 US EPA PAH-components in cyclohexane (L 20950900CY) or in acetonitrile (L 20950900AL). Concentration of each component was 10 ng/ml (mg/l). The uncertainty of each component was reported to be ± 1% at the 95% confidence level.

Sample M2

The sample M1 was the soil sample prepared by the a German PT provider and it was distributed in a German proficiency test.

The robust mean of the results obtained in the SYKE PT 7/2005 was used as the assigned value for the sample M1.

PAH compound	Abbreviation[3]	Assigned value in a German PT	Assigned value in the SYKE PT 7/2005	Uncertainty (U) of the assgned value [1] (SYKE PT 7/2005)
Naphtalene	Napht	0,118	0,097	60[2]
Acenaphthene	Acenaph	0,169	0,166	9,5
Acenaphthylene	A-naphty	0,159	0,266	17
Fluorene	Fluor	0,171	0,215	26
Phenanthrene	Phenan	2,994	3,17	8,8
Anthracene	Antrac	0,518	0,562	15
Fluoranthene	Fluoran	6,562	6,90	16
Pyrene	Pyrene	5,559	5,78	16
Chrysene	Chrysene	3,073	3,21	7,2
Benzo(a)anthracene	Benzo-ant	2,745	3,36	17
Benzo(b)fluoranthene	Benzo-B-F	2,986	3,69	12
Benzo(k)fluoranthene	Benzo-K-F	1,563	2,76	31
Benzo(a)pyrene	Benzo-A-P	2,939	3,15	20
Dibenz(ah)anthracene	Dibenz-ah	0,478	0,596	25
Indeno(1,2,3-c,d)pyrene	Indeno	2,039	2,27	20
Benzo(ghi)perylene	Benzo-per	2,089	2,09	11
Total PAH	tot-PAH	34,45	37,7	14

[1] The uncertainty at 95 % confidence interval was estimated using the equation: $U = 2 \cdot 1{,}23\ s_{rob}/\sqrt{p}$ (p = the number of the participants)

[2] The performance has not been evaluated.

[3] Abbreviations in the result sheets

APPENDIX 3. COMMENTS SENT BY THE PARTICIPANTS

Comments on the reported results:

Lab 5: The laboratory explained reasons for slightly too high results in analysis of the sample S1. The participant suspected, that the use of a too strong solution in measurement was the reason for too high values.

Lab 8: In the results sheet the results of the sample S1 were asked to report as mg/ml. In order to avoid reporting errors the new results sheets were delivered, in which the results were asked to report as mg/l.

Lab 9: The organizer used the wrong Finnish name for asenaphthene, it is "asenafteeni" instead of "asenaftleeni".

APPENDIX 4. ANALYTICAL METHODS

Soil sample M1

Experimental conditions - intake, treatment

Lab	Intake	Extr.solvent, vol (ml)/time (min)	Extr.method	Separation	Acet/rem.	Drying	Clean-up .
1	10,06 g	hexane+dichloromethane, 200 ml, 10 h	Soxhlet	No	No		Silica-gel
2		hexane+dichloromethane, 200 ml, 10 h		Sentrifugation			
3	5 g	acetone, 30 ml, 30 min	Ultrasonic	Sentrifugation	No	No	No
4	4,8016 g	hexane-acetone (8 ml + 12 ml), 2 h	Shaking table	H_2O-add +Sentrifugation	H_2O-add +Sentrifugation	No	No
5	10 g	hexane-acetone (25 ml + 50 ml), 6 h	Ultrasonic + Shaking	Separatory funnel	H_2O 2x100 ml	Na_2SO_4	Al_2O_3
6		DCM-acetone(3/1)	Ultrasonic + Shaking	Sentrifugation	No		No
7	2 g	acetonitrile-H_2O (1:1) 20 ml, 0,05 M Na-pyro-phospahtedekahydrate, toluene 10 ml, 6 h	Shaking 16 h	Sentrifugation	No	Na_2SO_4	1,5 g Florisil
8	20 g	toluene, 200 ml, 10 h	Soxhlet	No	No	Hood	No
9	7 g	hexane-acetone (1:1), 2 h	Shaking	Sentrifugation			
10	4-10 g	dichloromethane, 120 ml	Soxhlet	No	No	At room-T	No

Experimental conditions- calibration

Lab	Calibration range	No of standards	Internal standard	Calculation of tot-PAH	Comments
1	10-1000 µg/ml	8	chrysene-d12, naphtalene-d8, phenantrene-d12, perylene-d12		
2					
3	1-25 µg/ml	4	chrysene-d12, naphtalene-d8, phenantrene-d12, perylene-d12, acetnaphtene-d12	Sum of 16 PAH's	Nordtest 1143-93, ISO/DIS 18287
4	0,125 -11,25 µg/ml	4	pyrene-d10	Sum of the positive results	
5	0,1-2,5 µg/ml	6	chrysene-d12, naphtalene-d8, phenantrene-d12, perylene-d12, acetnaphtene-d12	Sum of 16 PAH's	ISO/DIS 18287, EPA 8270C
6	0,05-20 µg/g	5	pyrene-d10, benz(a)pyrene-d10		1)
7	0,05-2 µg/lml	6	chrysene-d12, phenantrene-d12, perylene-d12,acetnaphtene-d12	Sum of 16 PAH's	Nordtest 329
8	0,5-100 µg/g	7	1,1'- binaphthyl	Sum of 16 PAH's	In house
9	0,04-10 or 0,04-1 µg/ml	4	chrysene-d12, phenantrene-d10, perylene-d12,acetnaphtene-d12	Sum of 16 PAH's	Nordtest 329
10		4	antracene-d10	Sum of 16 PAH's	2)

1) The value for benzo(k)fluoranthene indicates the sum of benzo(b)- and benzo(k)fluoranthenes.
2) The value for chrysene indicates the sum of chrysene and benzo(a)anthracene. The value for benzo(b)fluoranthene indicates the sum of benzo(b)- and benzo(k)fluoranthene. The peaks co-eluate.

Experimental conditions- GC-conditions

Lab	Equipm.(GC,HPLC), detector, mode	GC-columns and dimens.(m/mm/µm)	Carrier gas and ml/min	Injection technig and T °C	Oven-T °C
1	GC-MS, SIM	DP-5 MS, 30 m, 0,25 mm, 0,25 µm	He, 1 ml/min	Splitless, 280	80-300
2	HPLC				
3	GC-MSD, SCAN mode (single ions)	HP-5 MS, 30 m, 0,25 mm, 0,25 µm	He 5.6, 1 mil/min	Splitless, 300	60-280
4	GC/MS, SIM, MS quad 150°C, MS source 230°C	HP-5 MS, 30 m, 0,25 mm, 0,25 µm	He, 1,3 ml/min	PTV-autosampl., 70-360	60-340
5	GC/MS, SIM, MS quad 150°C, MS source 230°C	DB-XLB, 30 m, 0,25 mm, 0,25µm	He 1,8 ml/min	Pulsed spitless,300	60-325
6	GC/MS, SCAN	CO Sil 8cB, 30 m, 0,25 mm, 0,5µm	He	Splitless 280	35-320
7	GC/MS, SIM, MS quad 150°C, MS source 230°C	Phenomenex Zebrum ZB-5, 60m, 0,25mm, 0,25µm	He 0,7 ml/min	Splitless 250	80-310
8	GC-MS, SIM	HP-5 MS, 30 m, 0,25 mm, 0,25 µm	He 1ml/min	Splitless 280	90-325
9	GS-MS, SIM	HP-5 MS, 30 m, 0,25 mm, 0,25 µm	He 1,3 ml/min	Splitless 280	60-325
10	GS-MS, SIM	DB-5, 30 m, 0,32 mm, 0,25 µm	He 1,5 ml/min	Splitless 100	100-300

APPENDIX 5. RESULTS REPORTED BY THE LABORATORIES

Analyte	Sample	Unit	1			2			3			4			5			6		
A-naphthy	M1	mg/kg	0,490	0,401	1				0,306	0,320	1	0,274		1				0,24	0,26	1
	S1	µg/ml	9,82		1	9,52		2	10,1		1	10,549		1	11,9		1	8,82		1
Acenaph	M1	mg/kg	0,441	0,314	1							0,150		1				0,16	0,16	1
	S1	µg/ml	10,10		1	10,14		2	10,5		1	11,011		1	12,4		1	8,82		1
Anthrac	M1	mg/kg	0,980	1,12	1				0,300	0,320	1	0,518		1	0,55	0,58	1	0,52	0,61	1
	S1	µg/ml	9,21		1	8,28		2	10,9		1	11,165		1	12,4		1	10,17		1
Benzo-A-P	M1	mg/kg	4,15	4,61	1				2,32	2,56	1	2,75		1	2,96	2,94	1	2,50	2,57	1
	S1	µg/ml	9,06		1	6,46		2	11,0		1	11,666		1	10,4		1	9,14		1
Benzo-ant	M1	mg/kg	4,10	4,08	1				3,95	3,95	1	2,64		1	2,96	3,16	1	2,57	3,28	1
	S1	µg/ml	8,92		1	10,37		2	10,3		1	11,029		1	11,2		1	9,32		1
Benzo-B-F	M1	mg/kg	4,04	4,69	1				3,18	3,11	1	3,81		1	3,77	3,87	1			
	S1	µg/ml	9,56		1	10,22		2	10,7		1	11,261		1	10,6		1			
Benzo-K-F	M1	mg/kg	3,56	4,40	1				3,01	2,63	1	1,35		1	1,58	1,53	1	5,38	5,33	1
	S1	µg/ml	9,05		1	9,80		2	10,4		1	10,680		1	9,42		1	18,00		1
Benzo-per	M1	mg/kg	2,27	2,18	1				2,03	1,95	1	1,89		1	2,31	2,46	1	1,83	1,75	1
	S1	µg/ml	10,76		1	11,05		2	9,97		1	11,709		1	10,6		1	9,27		1
Chrysene	M1	mg/kg	4,47	3,66	1				3,22	3,38	1	3,13		1	2,91	3,06	1	3,16	3,10	1
	S1	µg/ml	8,90		1	9,28		2	10,2		1	10,941		1	11,5		1	9,23		1
Dibenz-ah	M1	mg/kg	0,539	0,635	1							0,461		1	0,75	0,78	1	0,52	0,50	1
	S1	µg/ml	9,17		1	10,22		2	9,92		1	11,357		1	10,52		1	8,51		1
Fluoran	M1	mg/kg	11,36	13,16	1				7,80	7,84	1	6,44		1	6,43	6,68	1	5,68	6,13	1
	S1	µg/ml	9,99		1	9,57		2	10,6		1	11,026		1	12,2		1	9,23		1
Fluorene	M1	mg/kg	0,339	0,403	1							0,186		1				0,24	0,24	1
	S1	µg/ml	9,90		1	9,38		2	10,3		1	10,867		1	11,8		1	8,51		1
Indeno	M1	mg/kg	2,57	3,05	1				2,18	2,20	1	1,85		1	2,84	3,11	1	1,66	1,58	1
	S1	µg/ml	10,24		1	6,92		2	9,94		1	11,992		1	11,4		1	9,41		1
Napht	M1	mg/kg	0,173	0,134	1							0,0466		1				0,03	0,04	1
	S1	µg/ml	11,00		1	7,36		2	10,5		1	10,694		1	11,9		1	8,05		1
Phenan	M1	mg/kg	3,92	3,56	1				3,10	3,21	1	2,95		1	3,21	3,26	1	3,18	3,20	1
	S1	µg/m	9,35		1	9,24		2	10,2		1	10,829		1	12,4		1	8,33		1
Pyrene	M1	mg/kg	8,98	10,06	1				6,44	6,56	1	5,34		1	5,92	6,10	1	4,86	4,96	1
	S1	µg/ml	9,62		1	9,94		2	10,4		1	10,978		1	12,2		1	9,27		1
tot-PAH	M1	mg/kg	52,4	56,5	1				37,8	38,0	1	33,8		1	36,8	38,1	1	32,53	33,71	1
	S1	µg/ml	154,68		1	147,82		2	166		1	177,75		1	183		1	144,11		1

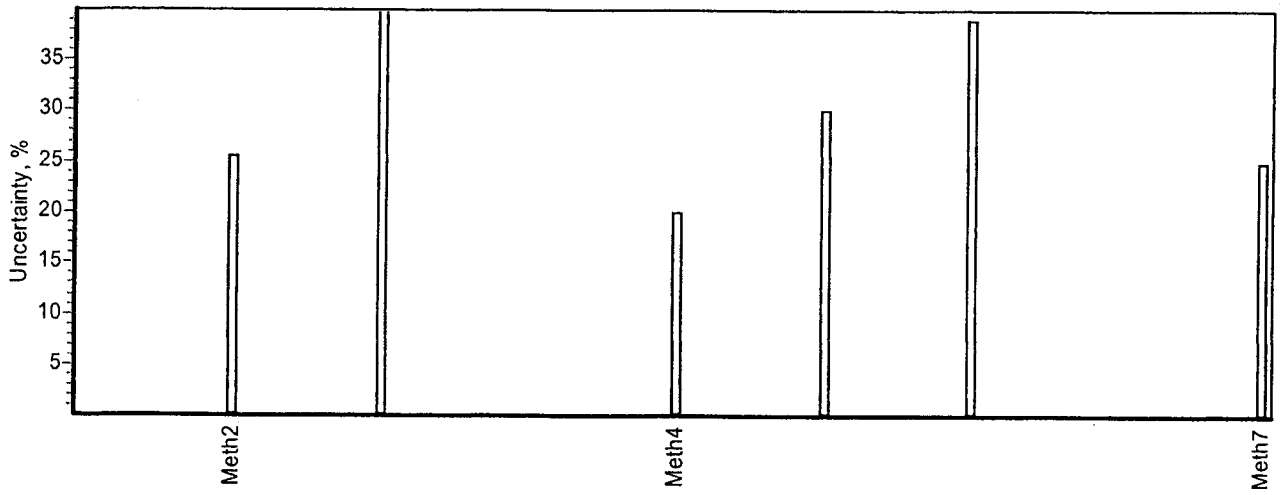
Analyte	Sample	Unit	7			8			9			10		
A-naphthy	M1	mg/kg	0,178	0,177	1	0,291	0,292	1	0,32	0,31	1	0,23	0,23	1
	S1	µg/ml	9,66		1	9,34		1	12,1		1	8,20		1
Acenaph	M1	mg/kg	0,164	0,150	1	0,205	0,204	1	0,19	0,18	1	<0,1	<0,1	1
	S1	µg/ml	10,5		1	10,4		1	13,2		1	9,00		1
Anthrac	M1	mg/kg	0,498	0,461	1	0,737	0,723	1	0,65	0,64	1	0,63	0,56	1
	S1	µg/ml	10,3		1	11,9		1	10,8		1	9,83		1
Benzo-A-P	M1	mg/kg	2,51	2,30	1	3,48	3,53	1	4,09	3,99	1	4,06	3,03	1
	S1	µg/ml	10,3		1	12,4		1	10,6		1	13,2		1
Benzo-ant	M1	mg/kg	2,80	2,69	1	3,55	3,52	1	3,92	3,87	1			
	S1	µg/ml	9,94		1	12,0		1	11,0		1			
Benzo-B-F	M1	mg/kg	2,86	2,78	1	3,92	3,93	1	3,65	3,40	1	5,87	4,38	1
	S1	µg/ml	10,2		1	12,5		1	11,0		1	20,5		1
Benzo-K-F	M1	mg/kg	2,02	1,83	1	3,08	3,08	1	3,17	2,99	1			
	S1	µg/ml	9,87		1	12,0		1	9,84		1			
Benzo-per	M1	mg/kg	1,62	1,52	1	2,25	2,32	1	2,29	2,24	1	2,63	1,77	1
	S1	µg/ml	10,1		1	10,4		1	11,8		1	11,3		1
Chrysene	M1	mg/kg	2,65	2,61	1	4,23	4,20	1	3,17	3,29	1	6,03	5,14	1
	S1	µg/ml	10,3		1	12,2		1	9,45		1	19,7		1
Dibenz-ah	M1	mg/kg	0,334	0,359	1	0,665	0,76	1	0,76	0,76	1	0,76	0,49	1
	S1	µg/ml	10,0		1	11,8		1	13,0		1	10,2		1
Fluoran	M1	mg/kg	6,55	6,02	1	9,18	9,26	1	8,5	8,31	1	5,52	5,25	1
	S1	µg/ml	10,1		1	12,2		1	12,0		1	9,27		1
Fluorene	M1	mg/kg	0,199	0,187	1	0,270	0,279	1	0,26	0,25	1	0,13	0,12	1
	S1	µg/ml	10,2		1	10,9		1	11,1		1	8,61		1
Indeno	M1	mg/kg	1,98	1,92	1	2,50	2,58	1	2,66	2,66	1	2,16	1,45	1
	S1	µg/ml	9,87		1	12,1		1	12,4		1	9,62		1
Napht	M1	mg/kg	0,0802	0,0794	1	0,174	0,152	1	0,11	0,10	1	<0,1	<0,1	1
	S1	µg/ml	9,84		1	9,35		1	10,8		1	8,49		1
Phenan	M1	mg/kg	3,02	2,77	1	3,81	3,82	1	3,08	3,21	1	2,17	2,19	1
	S1	µg/m	10,3		1	11,8		1	10,6		1	8,49		1
Pyrene	M1	mg/kg	5,35	4,95	1	7,55	7,56	1	6,33	6,63	1	4,57	4,28	1
	S1	µg/ml	10,1		1	12,2		1	11,6		1	9,20		1
tot-PAH	M1	mg/kg	32,8	30,8	1	43,0	43,4	1	43,16	42,81	1	34,86	28,89	1
	S1	µg/ml	162		1	183		1	181,3		1	155,6		1

APPENDIX 6. MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS

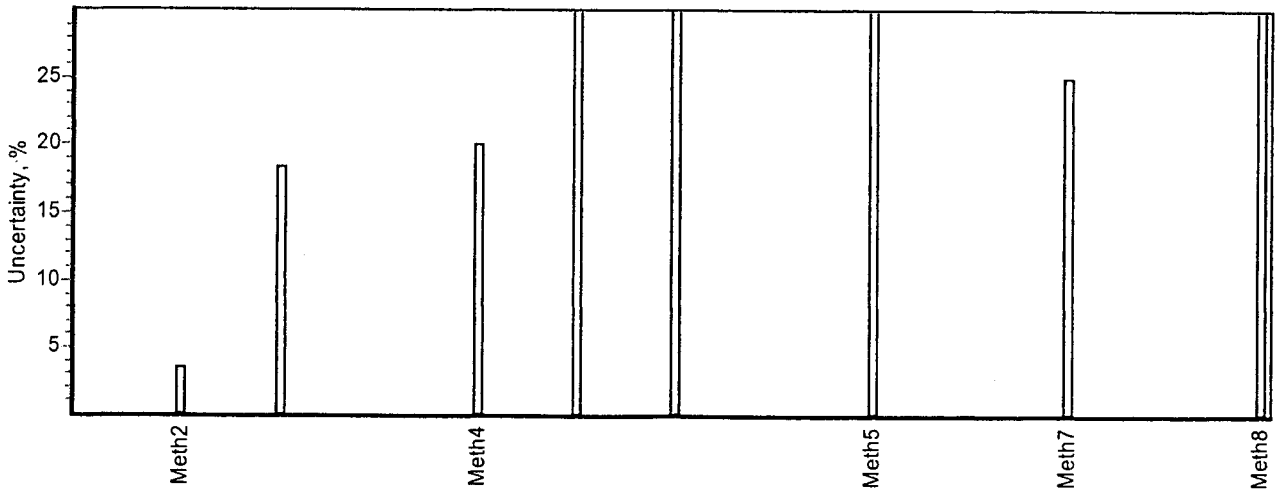
Uncertainties were estimated using the procedures as follows:

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 (r % - 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 7-8: other procedure

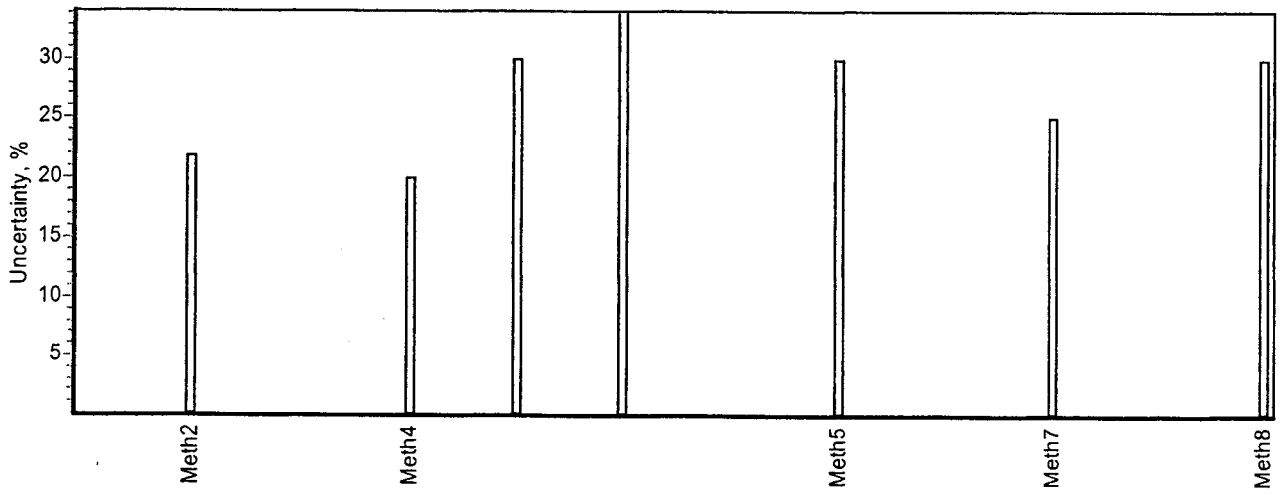
Analyytti *(Analyte)* **Acenaph** Näyte *(Sample)* M1



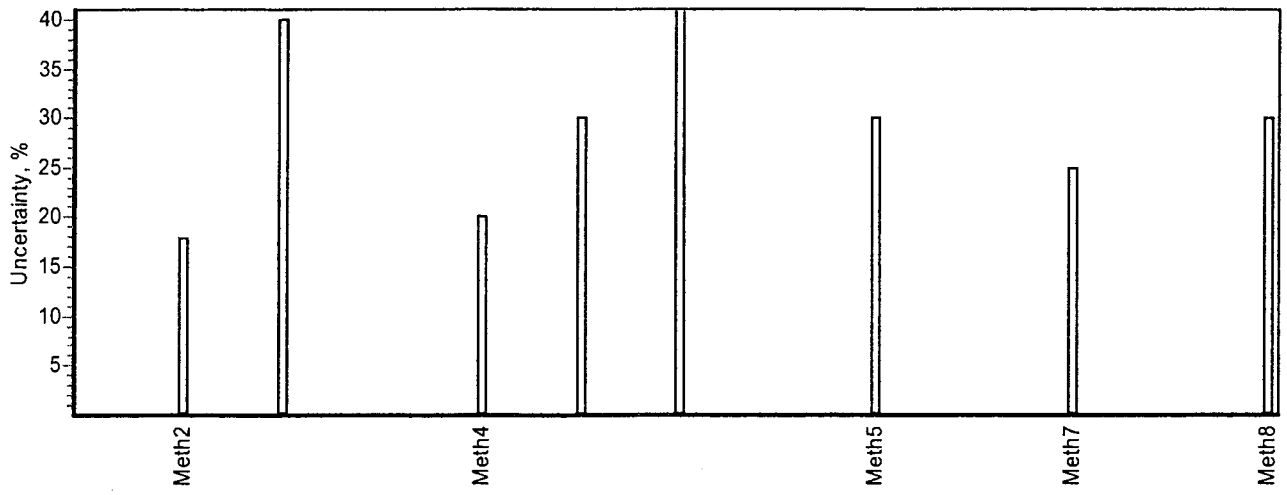
Analyytti *(Analyte)* **Anthrac** Näyte *(Sample)* M1



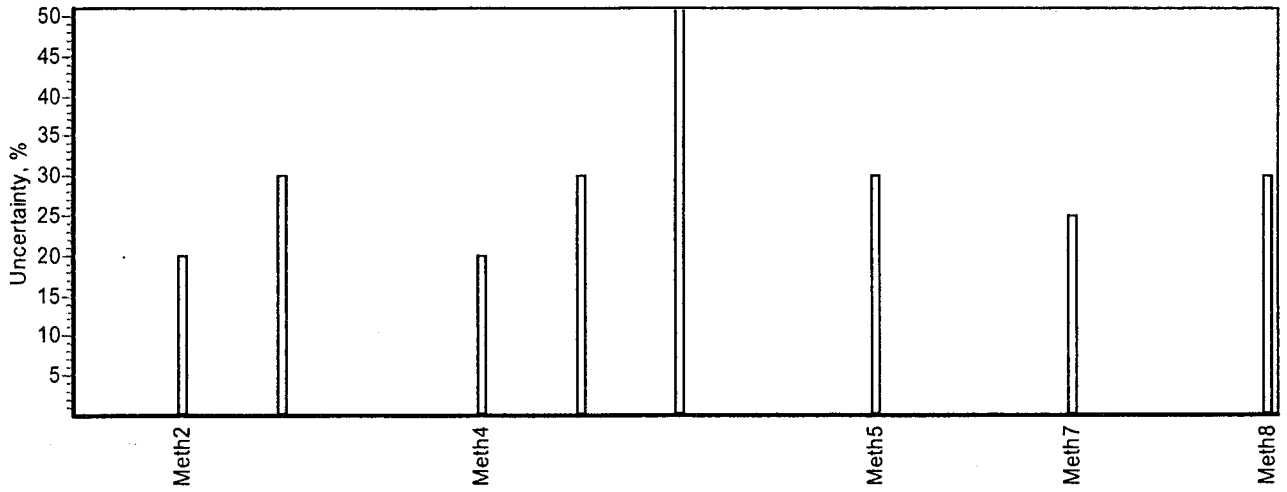
Analyytti *(Analyte)* **Benzo-ant** Näyte *(Sample)* M1



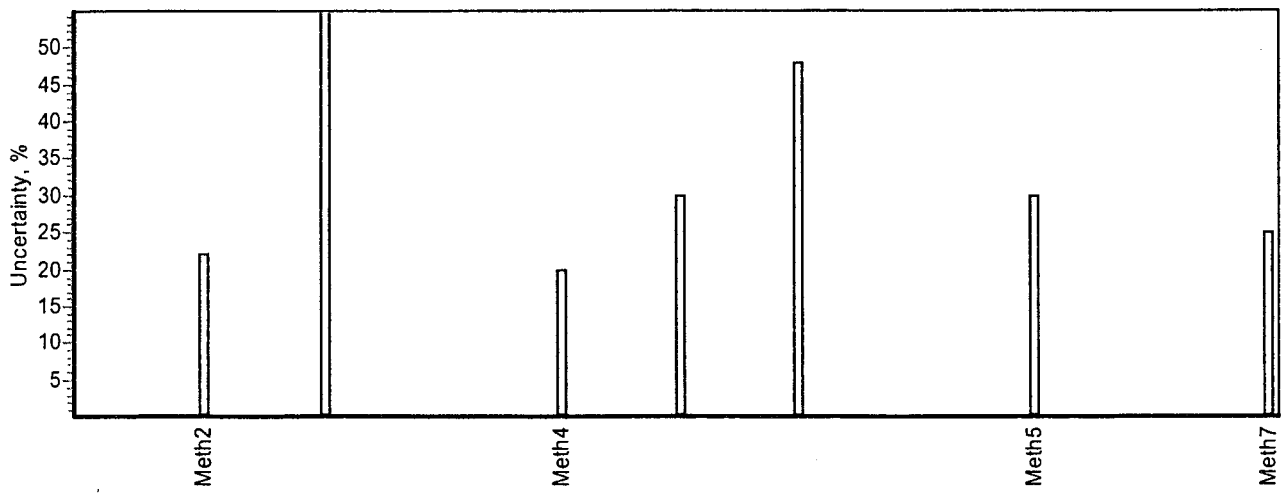
Analyytti *(Analyte)* **Benzo-B-F** Näyte *(Sample)* M1



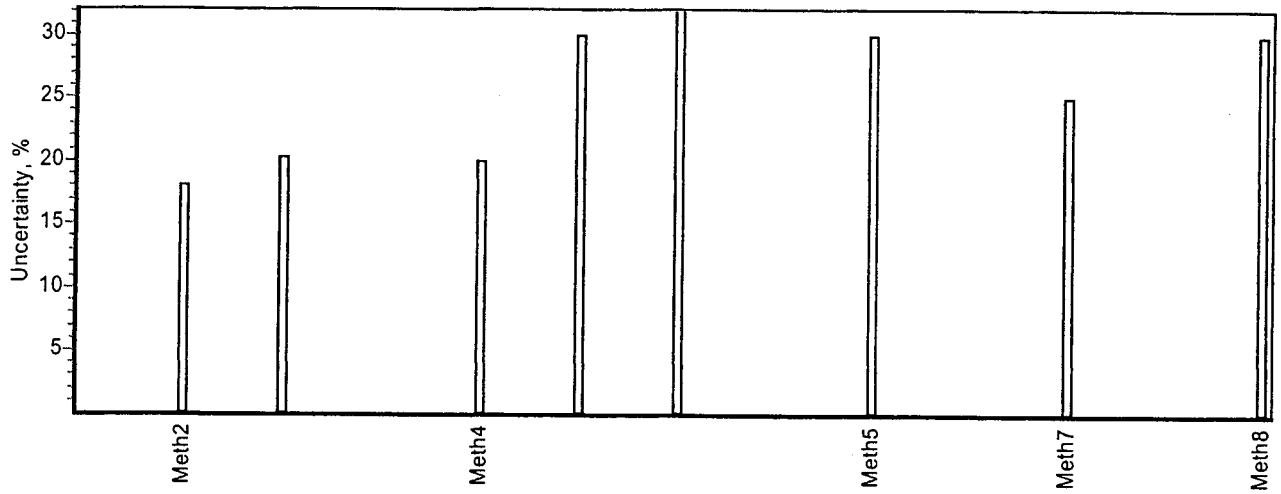
Analyytti *(Analyte)* **Chrysene** Näyte *(Sample)* M1



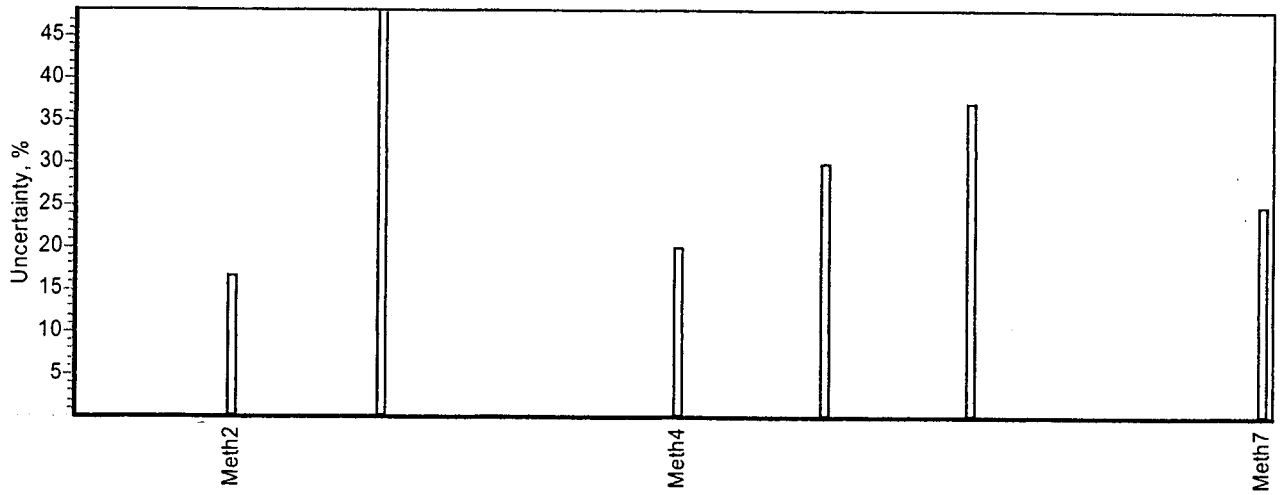
Analyytti *(Analyte)* **Dibenz-ah** Näyte *(Sample)* M1



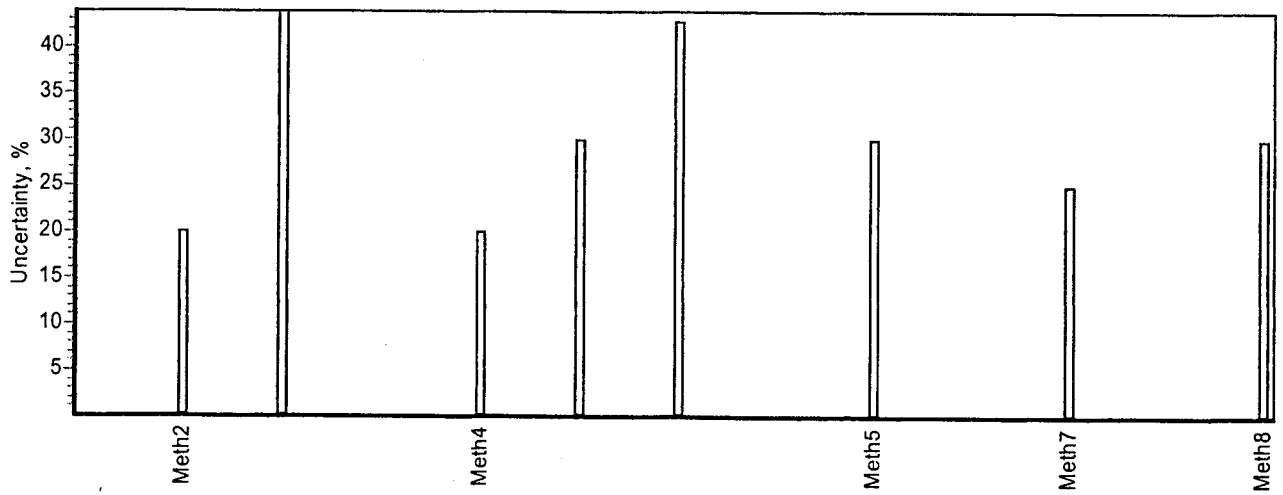
Analyytti *(Analyte)* **Fluoran** Näyte *(Sample)* M1



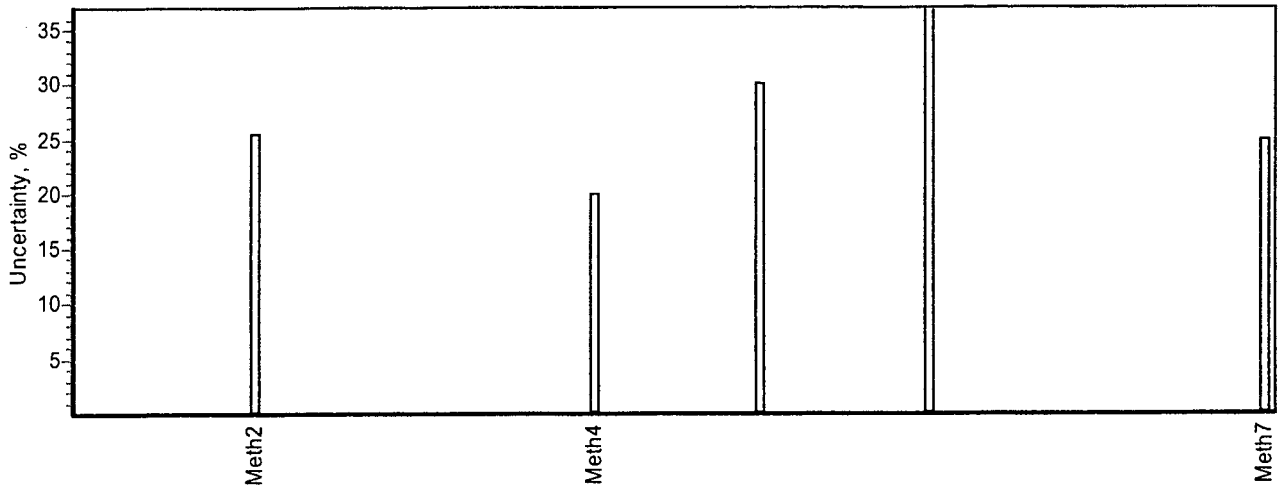
Analyytti *(Analyte)* **Fluorene** Näyte *(Sample)* M1



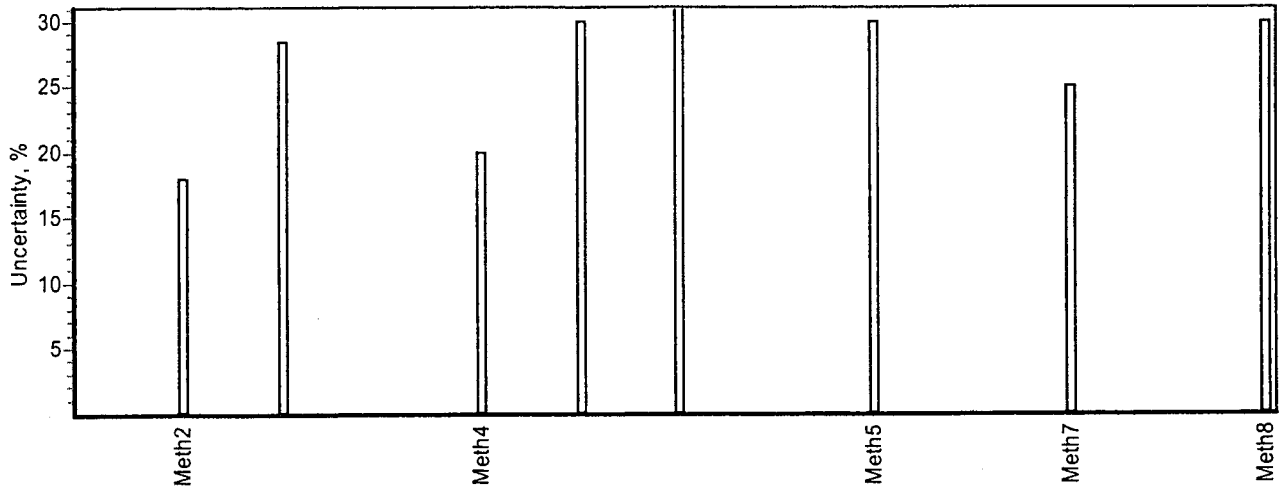
Analyytti *(Analyte)* **Indeno** Näyte *(Sample)* M1



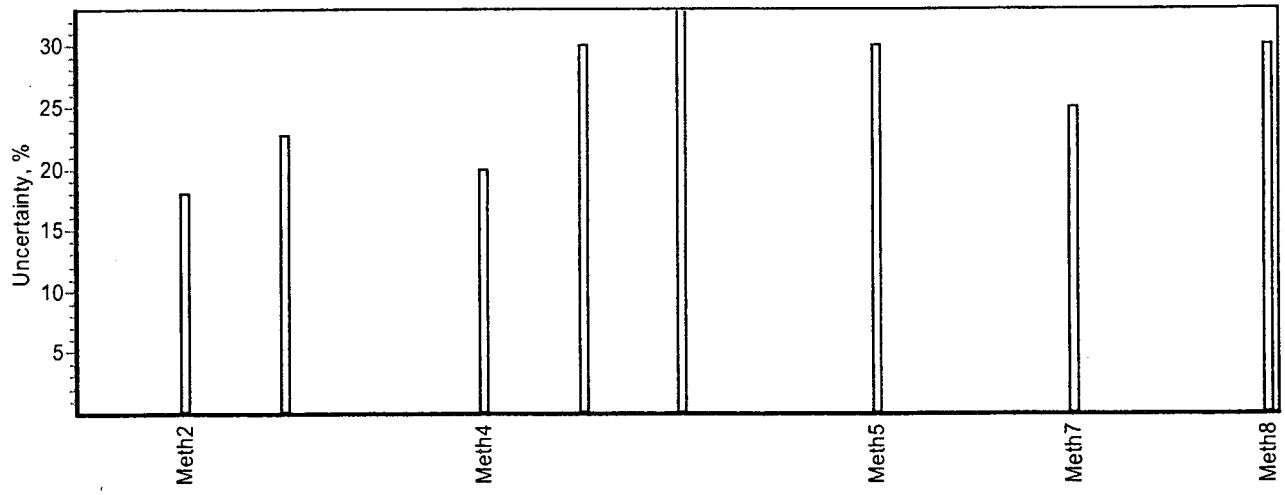
Analyytti *(Analyte)* **Napht** Näyte *(Sample)* M1



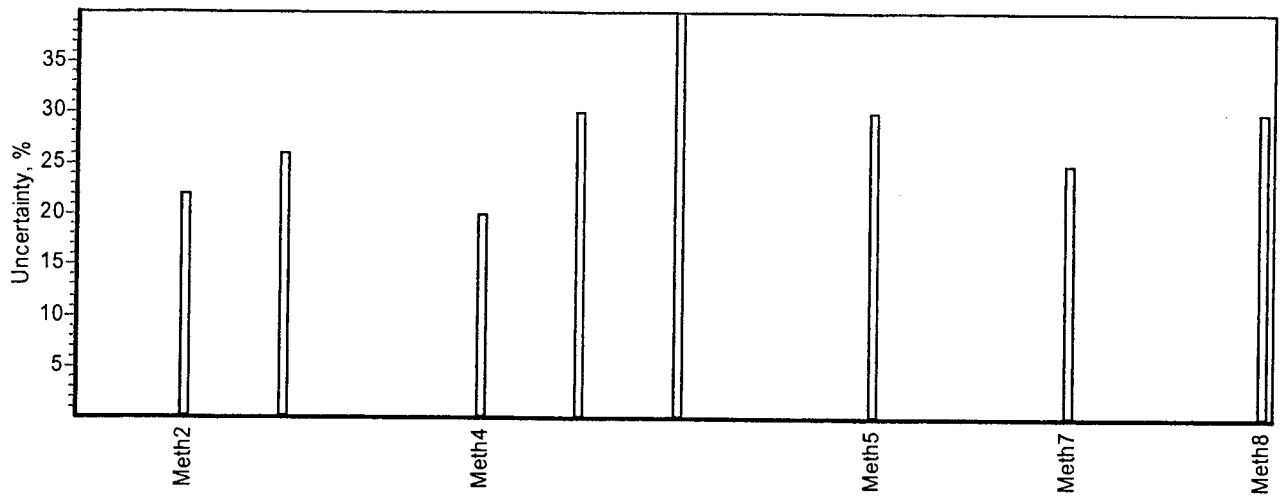
Analyytti *(Analyte)* **Phenan** Näyte *(Sample)* M1



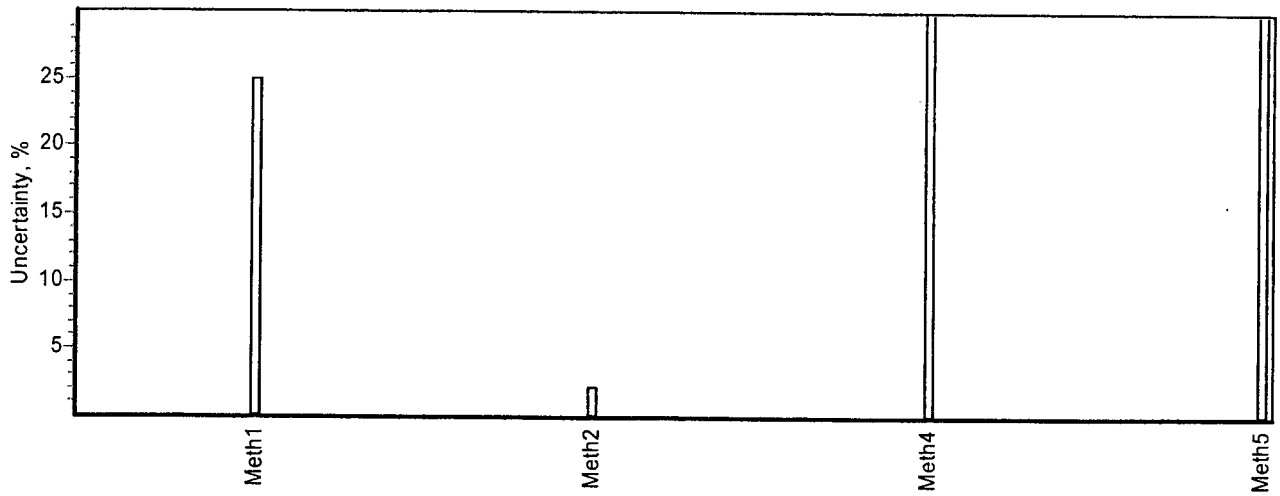
Analyytti *(Analyte)* **Pyrene** Näyte *(Sample)* M1



Analyytti *(Analyte)* **tot-PAH** Näyte *(Sample)* M1

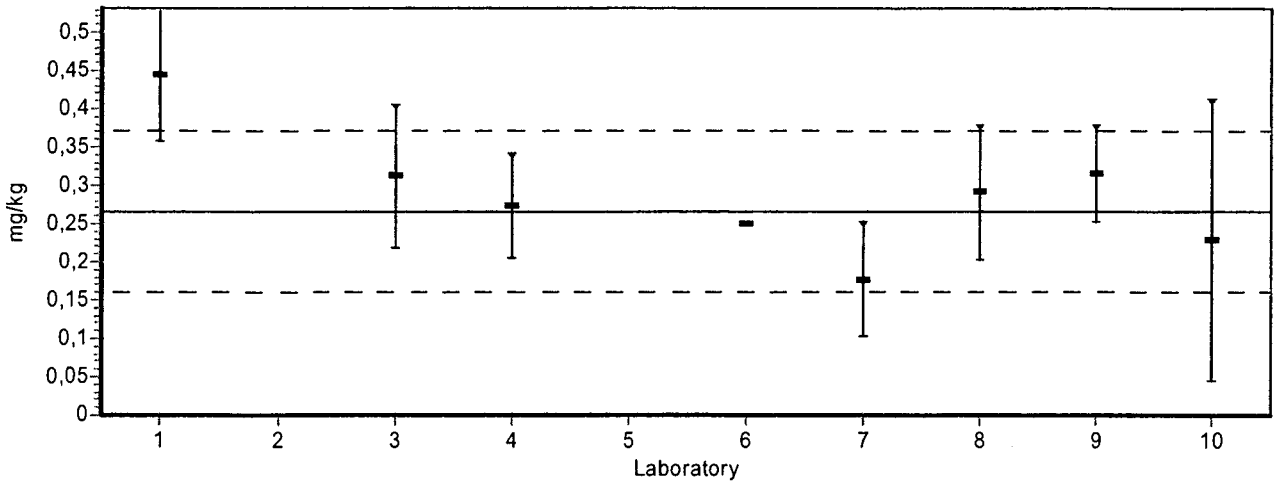


Analyytti *(Analyte)* **tot-PAH** Näyte *(Sample)* S1

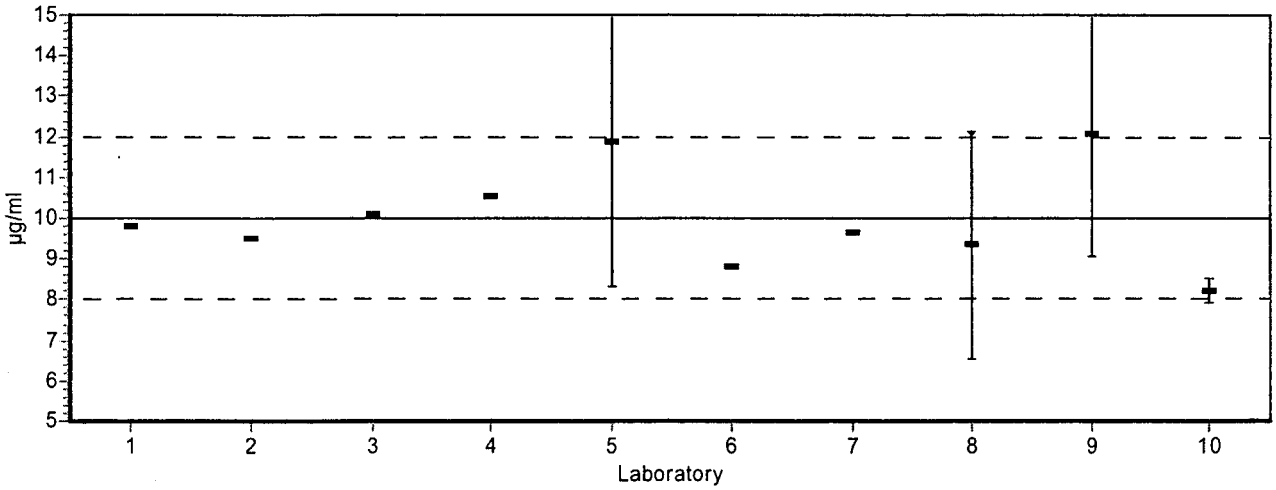


APPENDIX 7. GRAPHICAL PRESENTATION OF THE RESULTS AND THEIR MEASUREMENT UNCERTANTIES

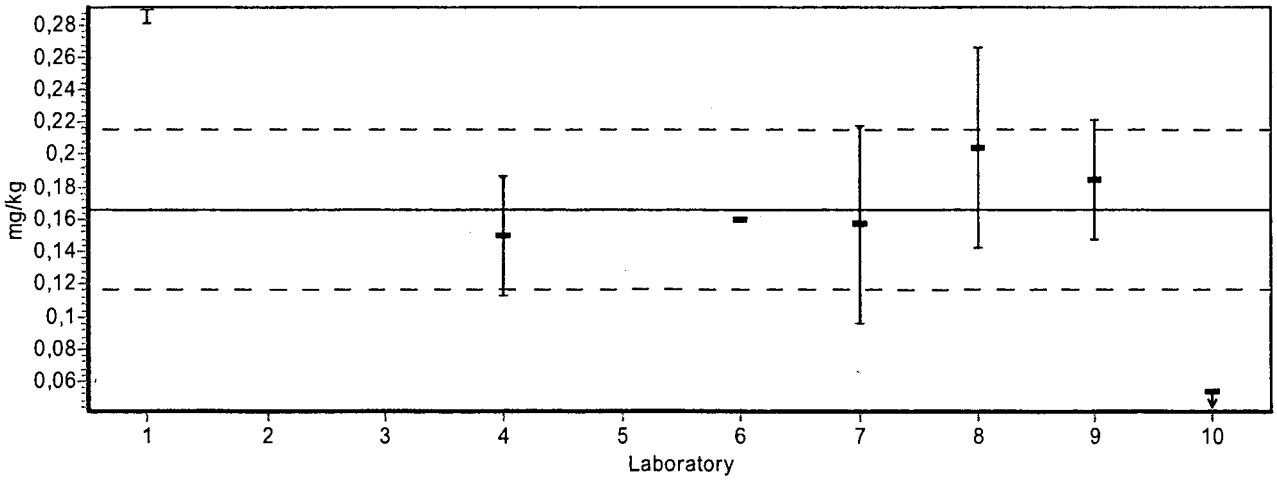
Analyytti *(Analyte)* **A-naphthy** Näyte *(Sample)* M1



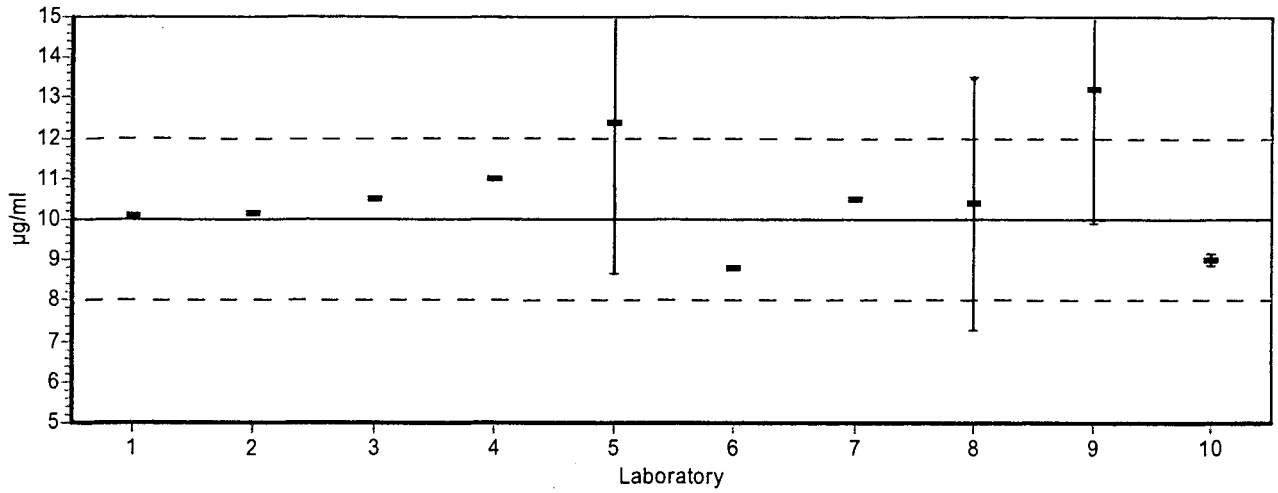
Analyytti *(Analyte)* **A-naphthy** Näyte *(Sample)* S1



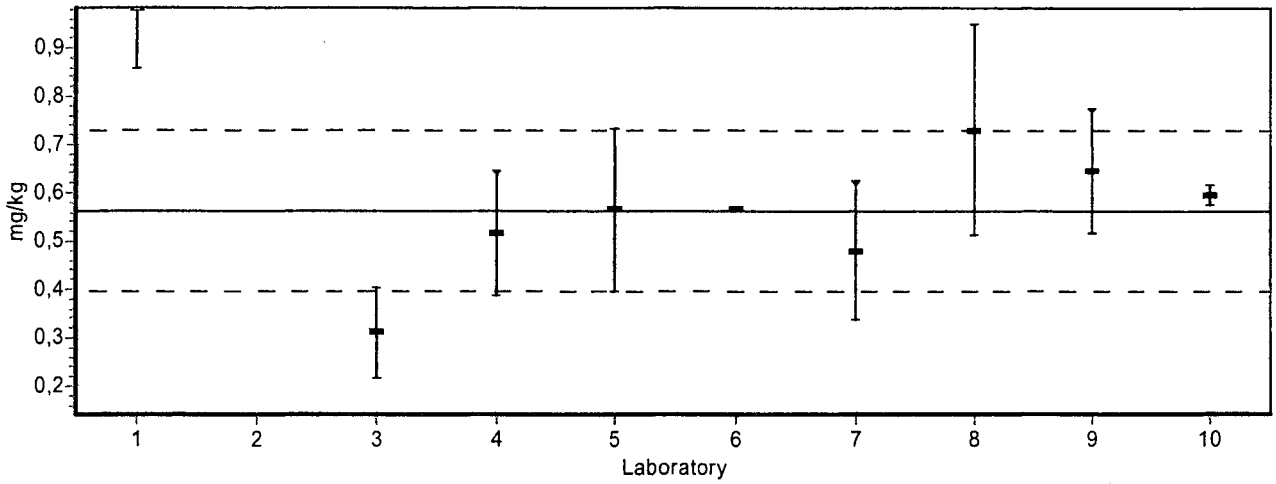
Analyytti *(Analyte)* **Acenaph** Näyte *(Sample)* M1



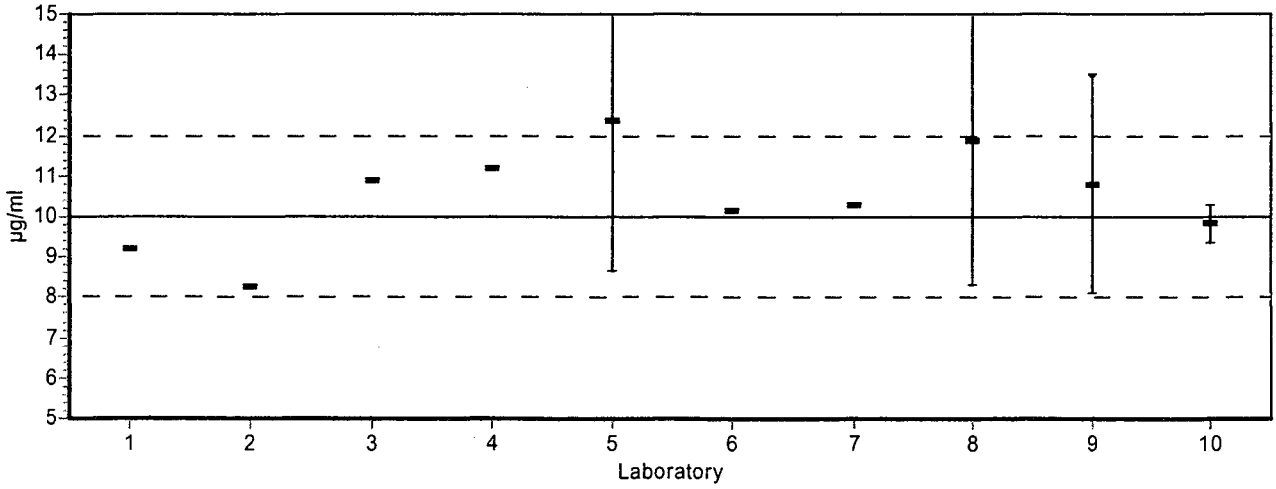
Analyytti *(Analyte)* **Acenaph** Näyte *(Sample)* S1



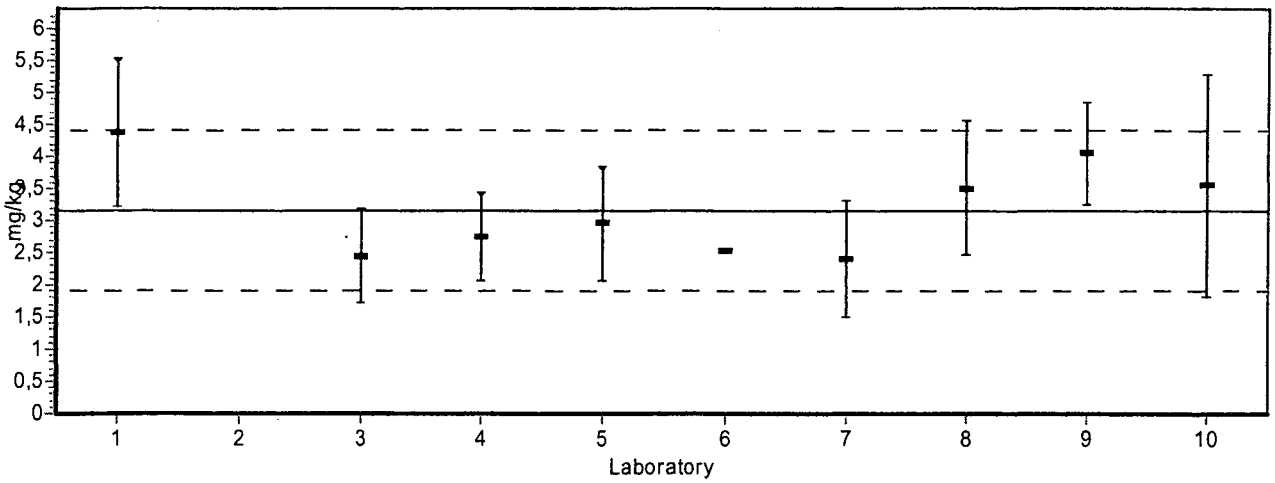
Analyytti *(Analyte)* **Anthrac** Näyte *(Sample)* M1



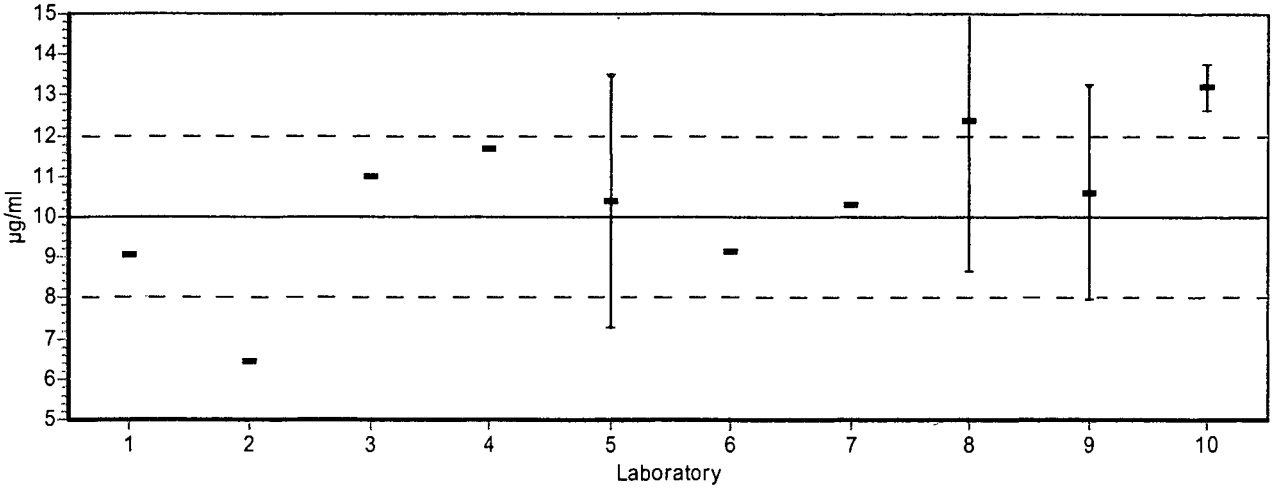
Analyytti *(Analyte)* **Anthrac** Näyte *(Sample)* S1



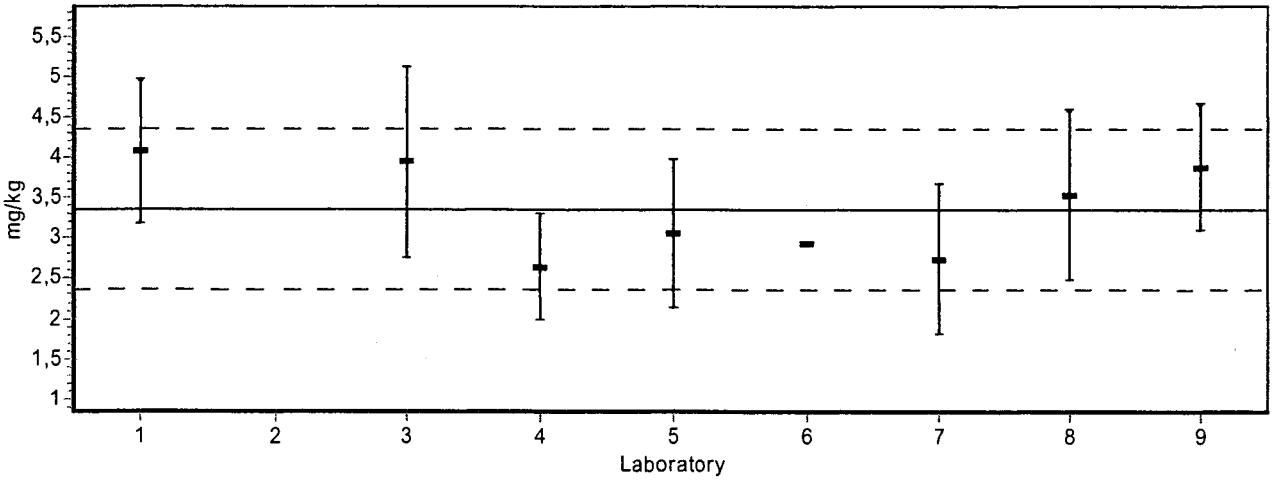
Analyytti *(Analyte)* **Benzo-A-P** Näyte *(Sample)* M1



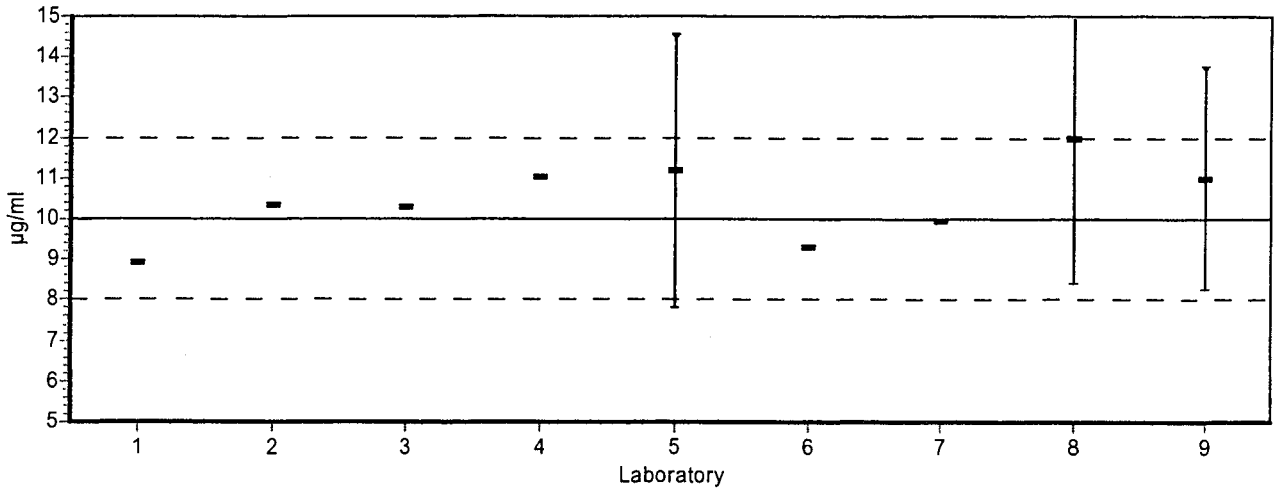
Analyytti *(Analyte)* **Benzo-A-P** Näyte *(Sample)* S1



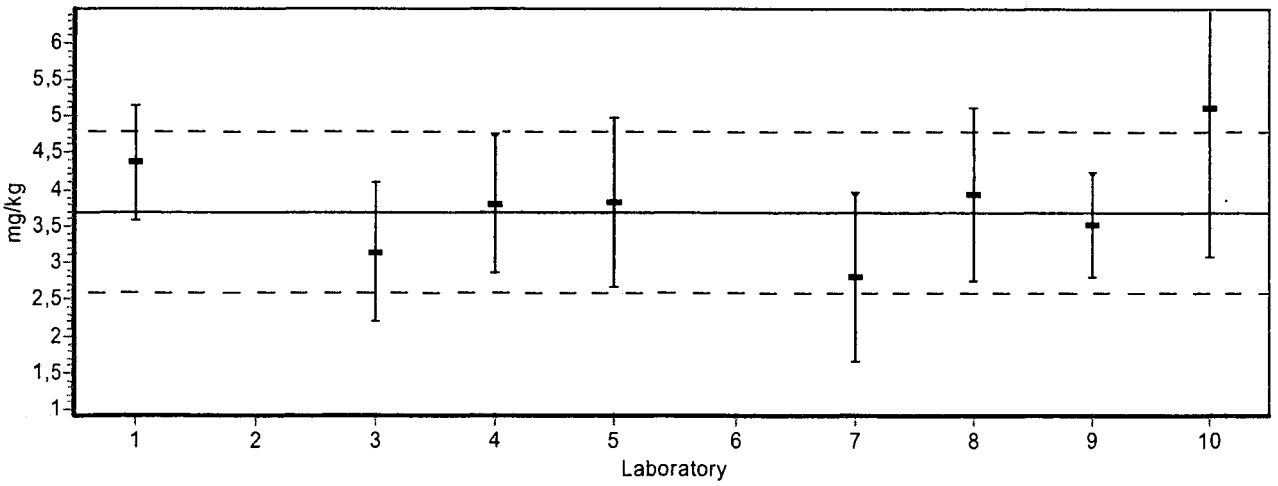
Analyytti *(Analyte)* **Benzo-ant** Näyte *(Sample)* M1



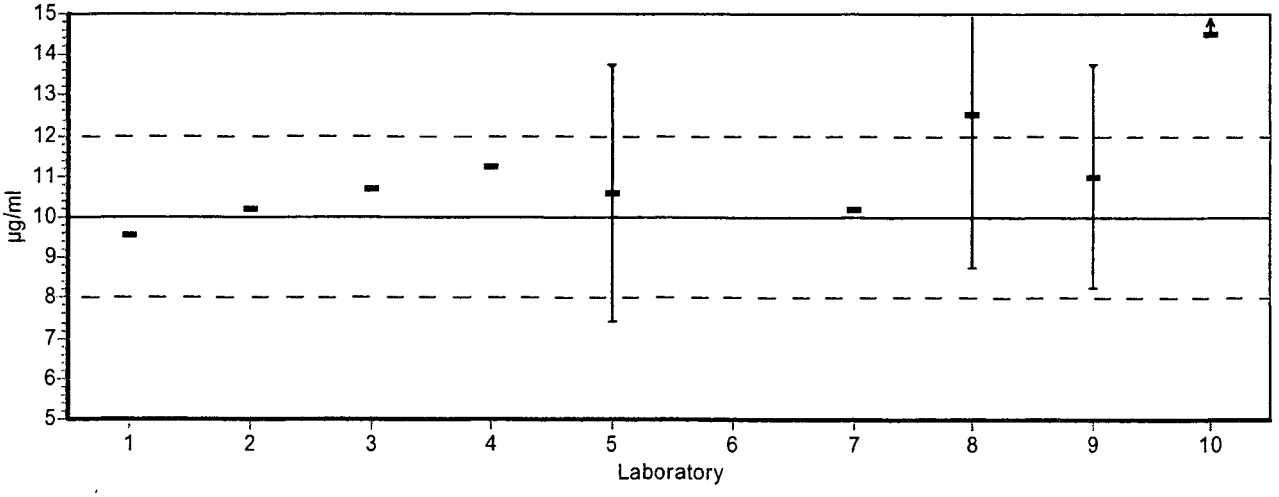
Analyytti *(Analyte)* **Benzo-ant** Näyte *(Sample)* S1



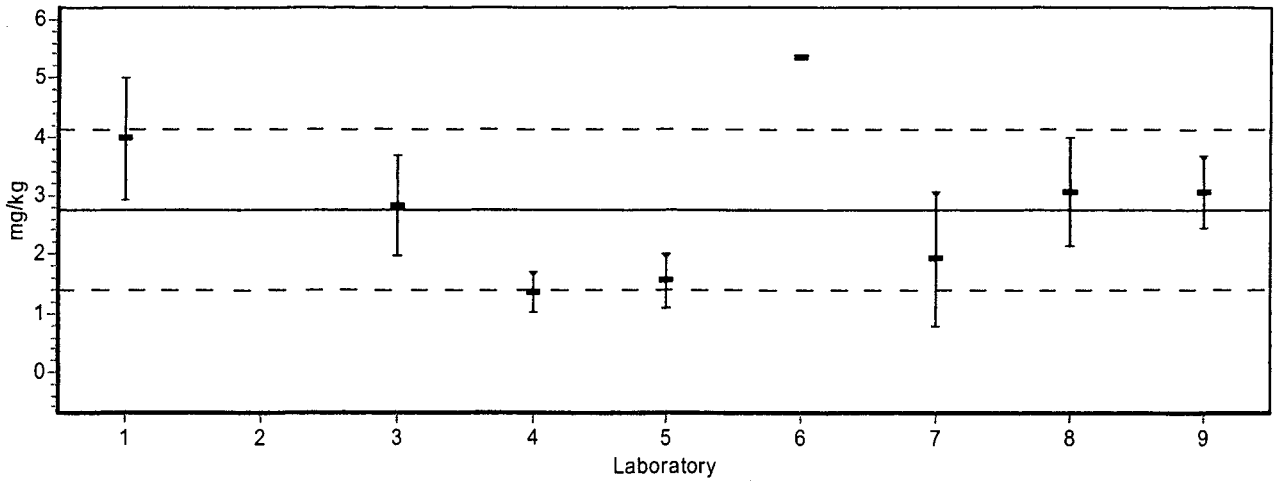
Analyytti *(Analyte)* **Benzo-B-F** Näyte *(Sample)* M1



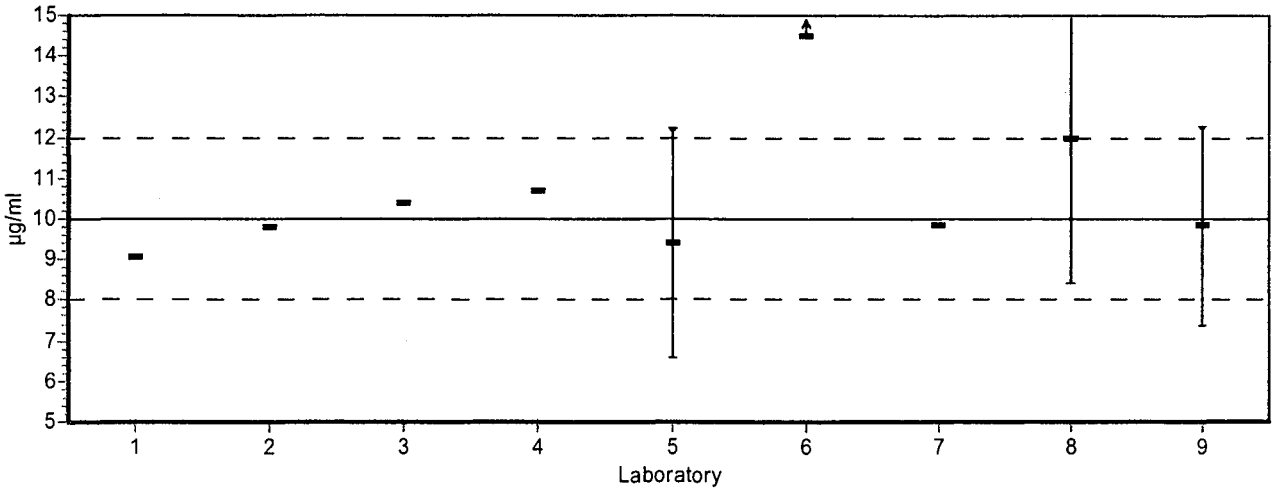
Analyytti *(Analyte)* **Benzo-B-F** Näyte *(Sample)* S1



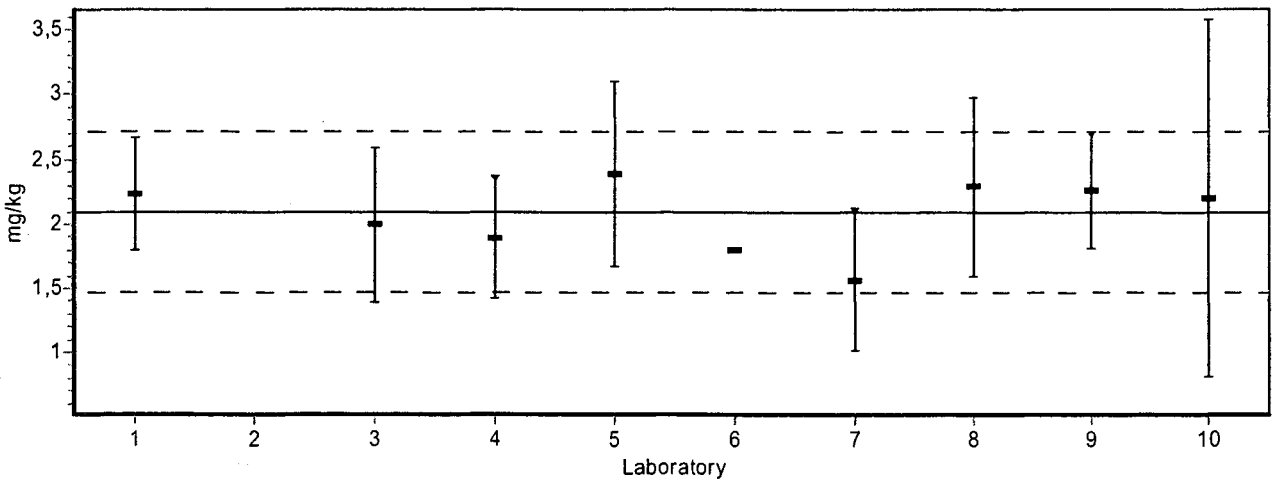
Analyytti *(Analyte)* **Benzo-K-F** Näyte *(Sample)* M1



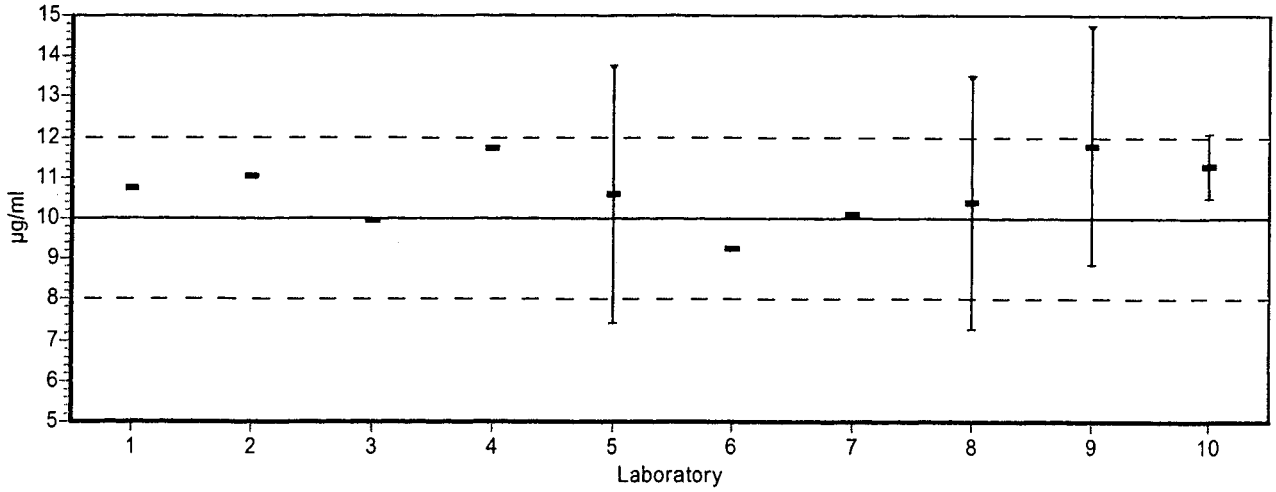
Analyytti *(Analyte)* **Benzo-K-F** Näyte *(Sample)* S1



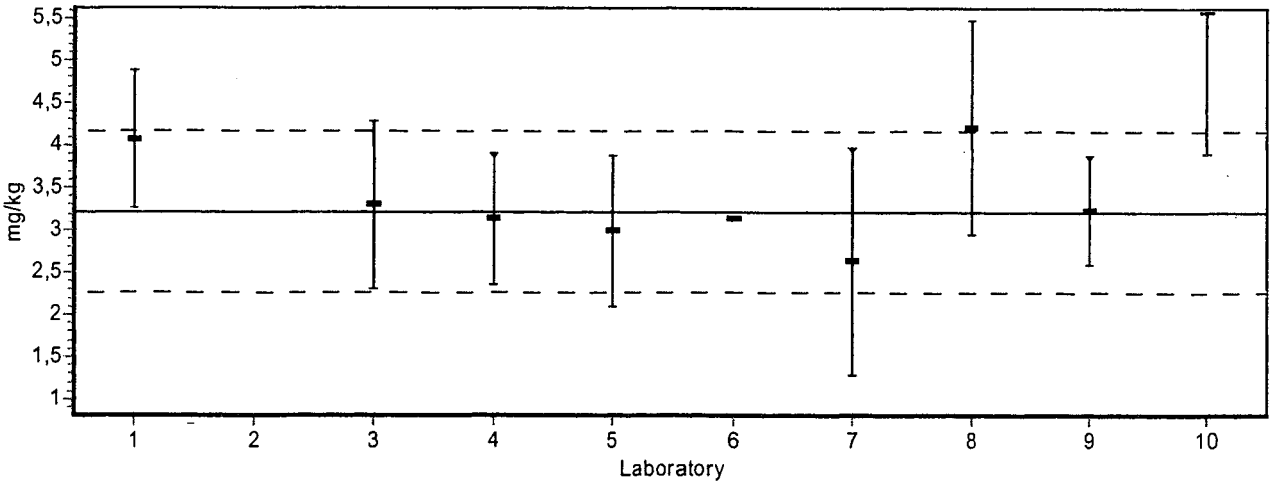
Analyytti *(Analyte)* **Benzo-per** Näyte *(Sample)* M1



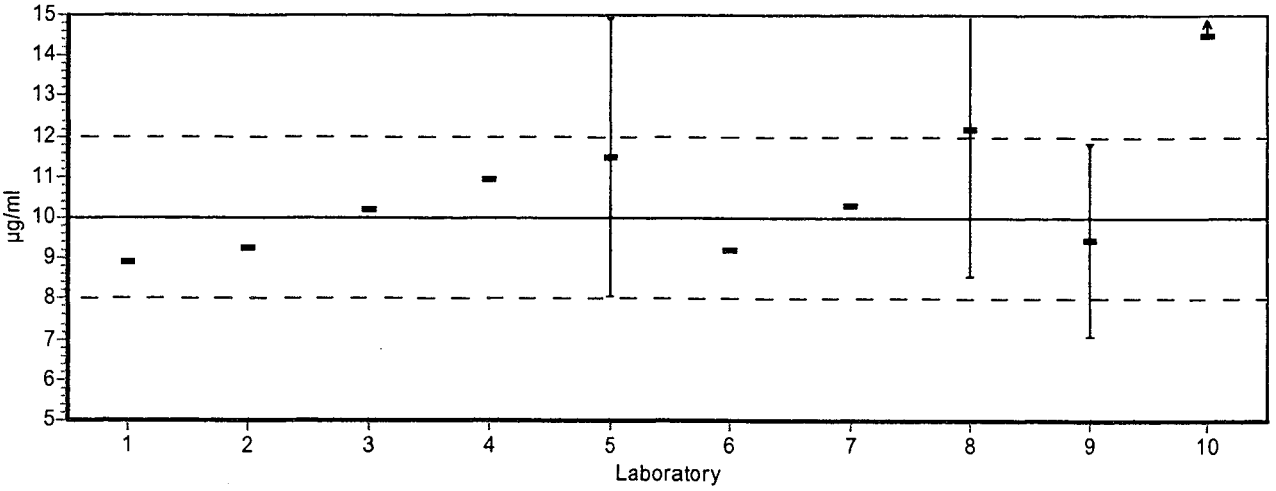
Analyytti *(Analyte)* **Benzo-per** Näyte *(Sample)* S1



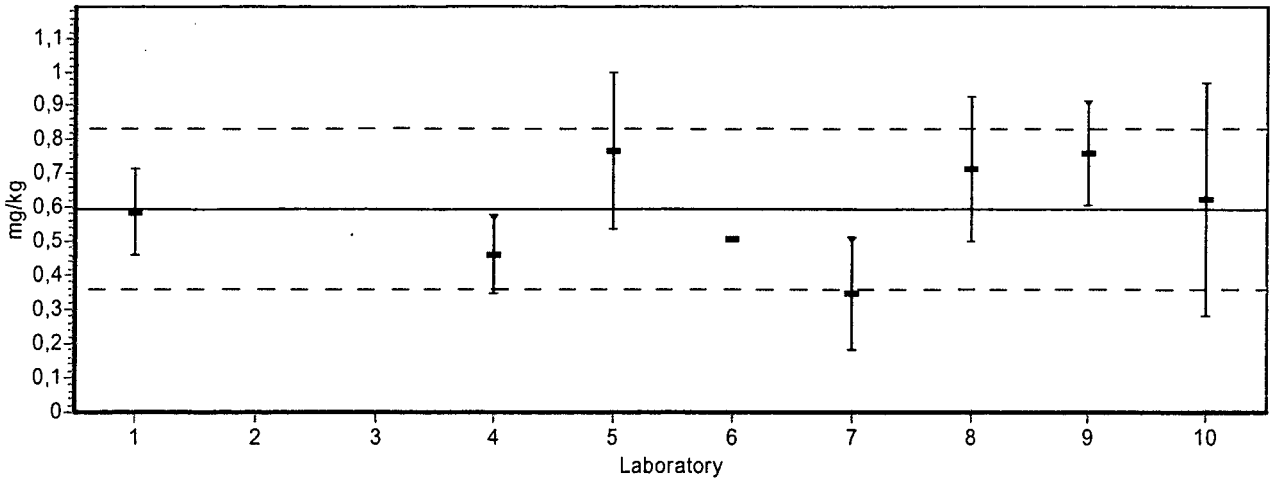
Analyytti *(Analyte)* **Chrysene** Näyte *(Sample)* M1



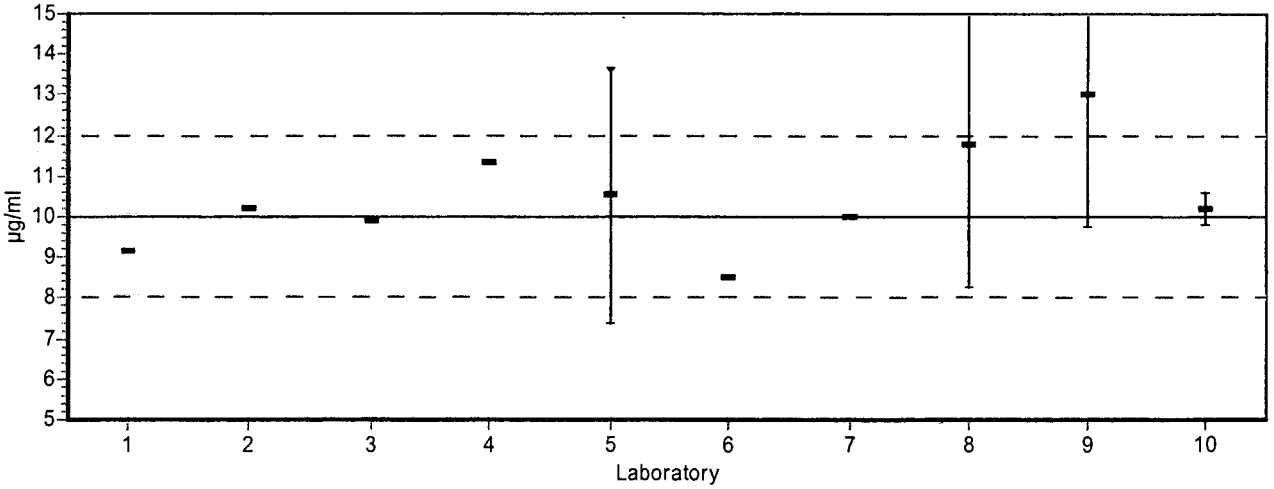
Analyytti *(Analyte)* **Chrysene** Näyte *(Sample)* S1



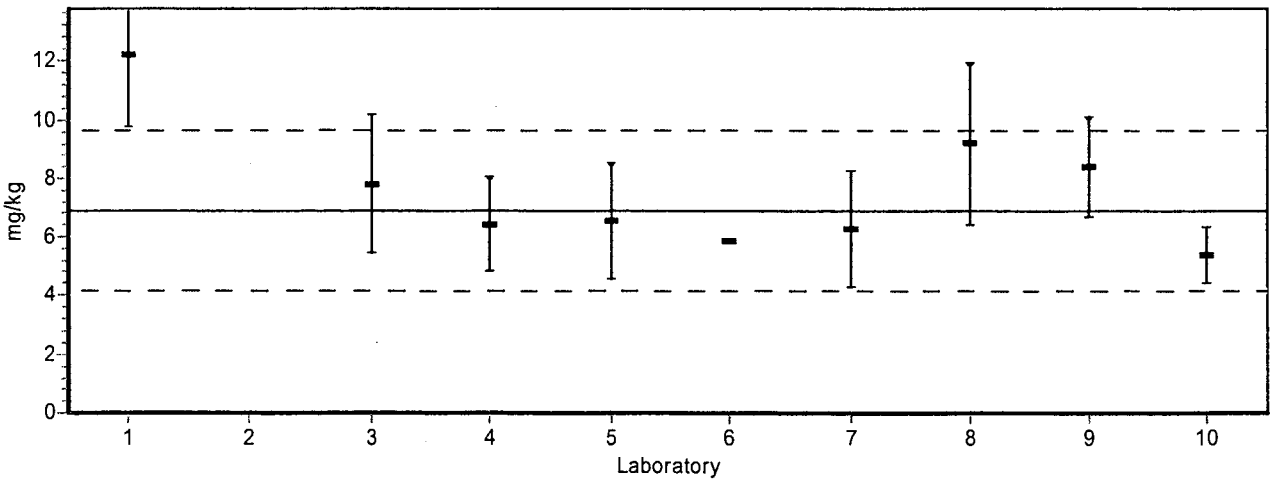
Analyytti *(Analyte)* **Dibenz-ah** Näyte *(Sample)* M1



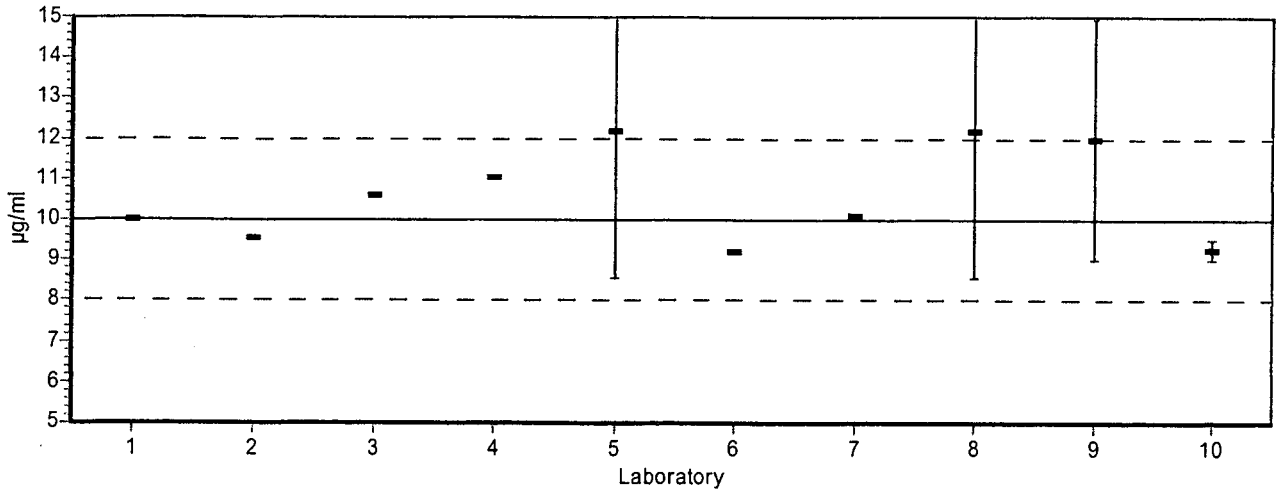
Analyytti *(Analyte)* **Dibenz-ah** Näyte *(Sample)* S1



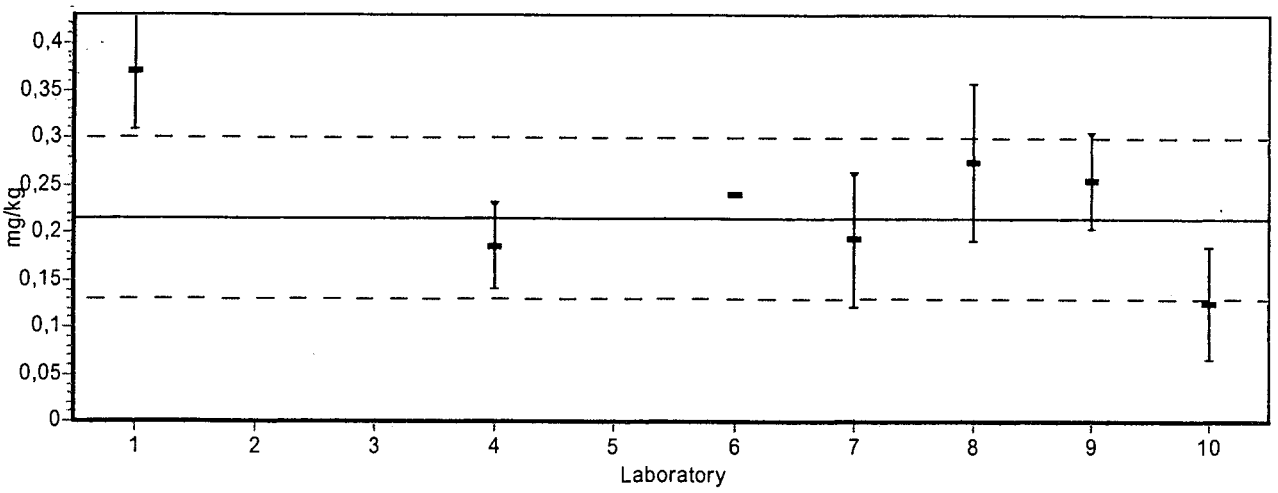
Analyytti *(Analyte)* **Fluoran** Näyte *(Sample)* M1



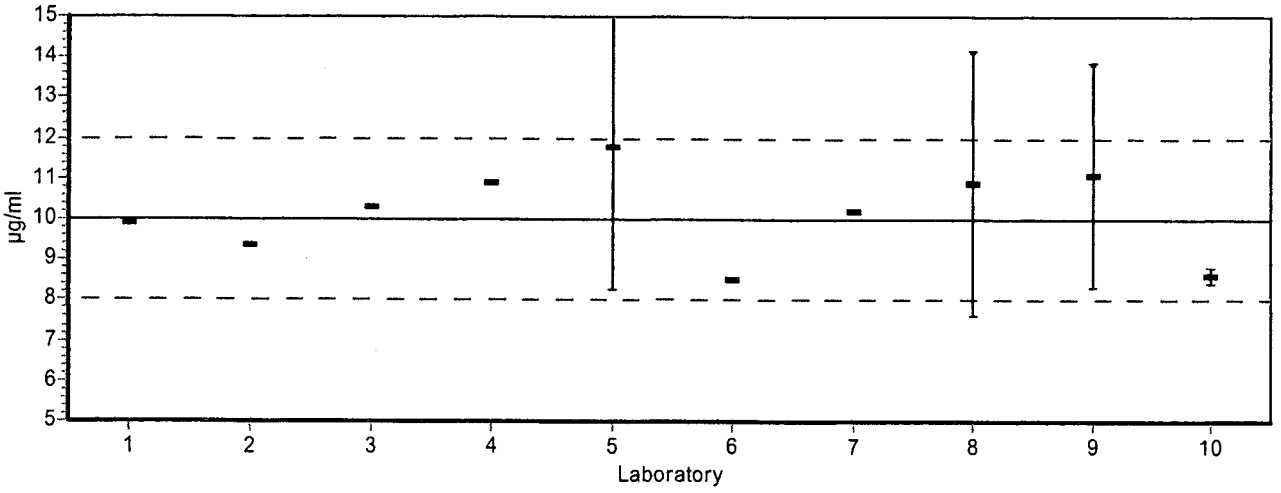
Analyytti *(Analyte)* **Fluoran** Näyte *(Sample)* S1



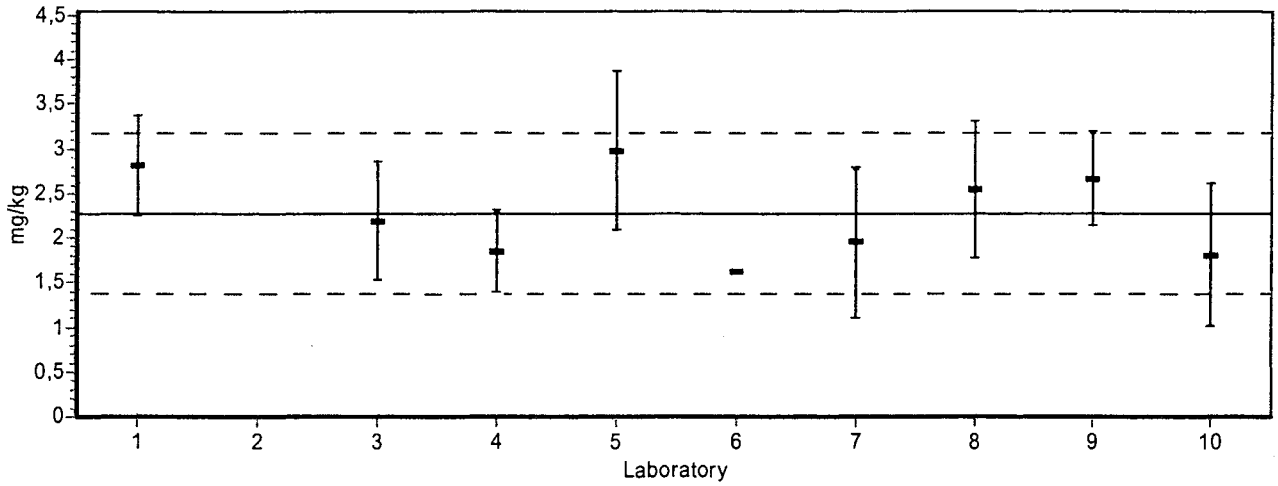
Analyytti *(Analyte)* **Fluorene** Näyte *(Sample)* M1



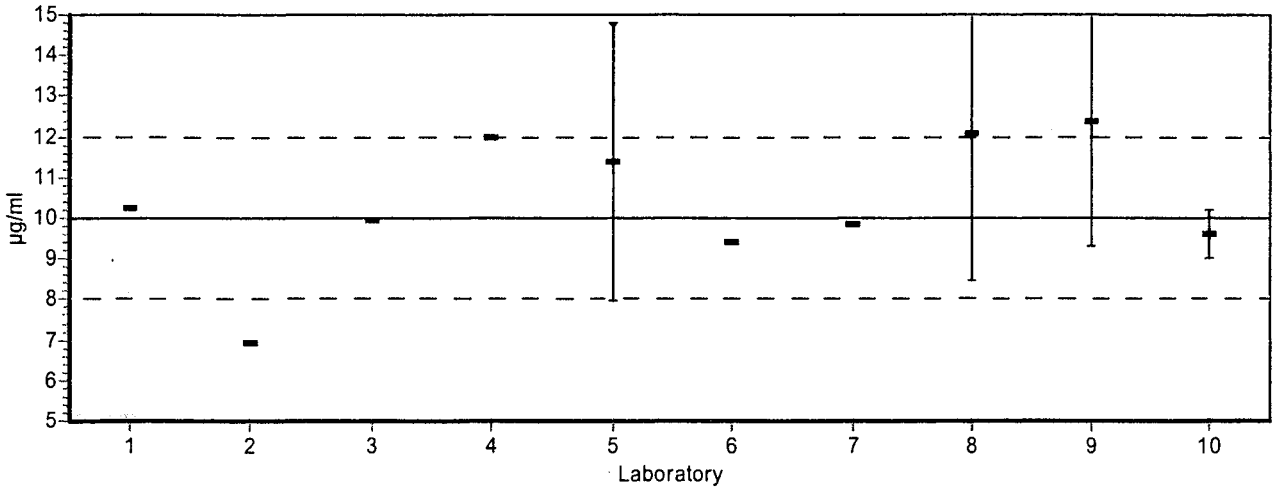
Analyytti *(Analyte)* **Fluorene** Näyte *(Sample)* S1



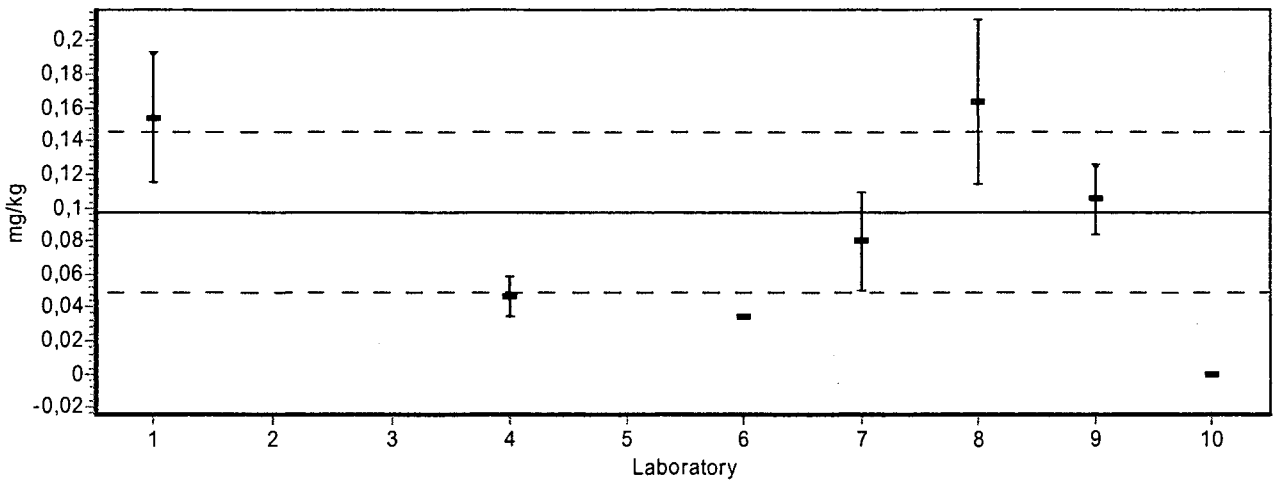
Analyytti *(Analyte)* **Indeno** Näyte *(Sample)* M1



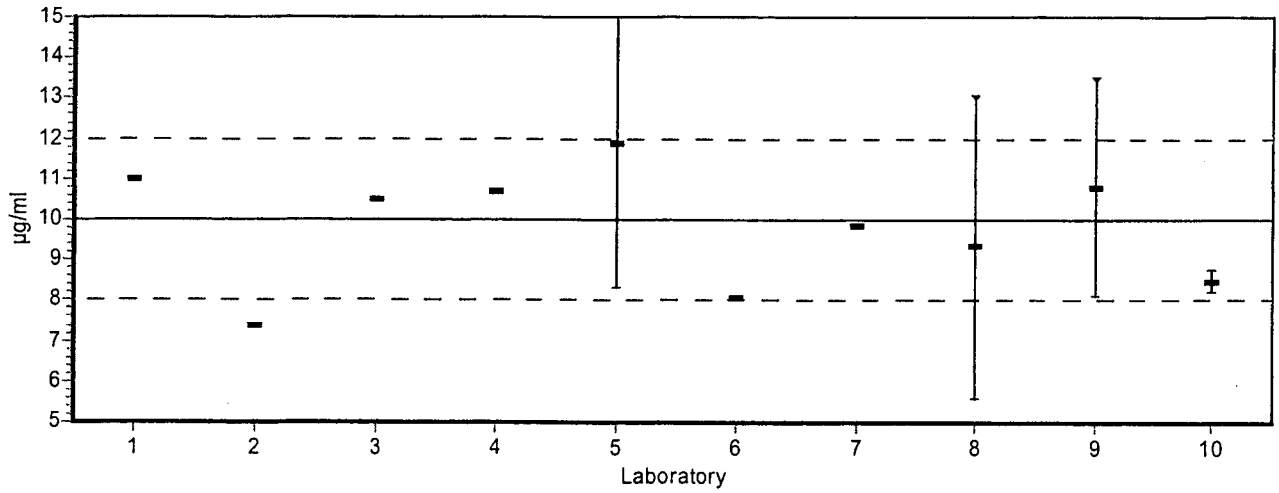
Analyytti *(Analyte)* **Indeno** Näyte *(Sample)* S1



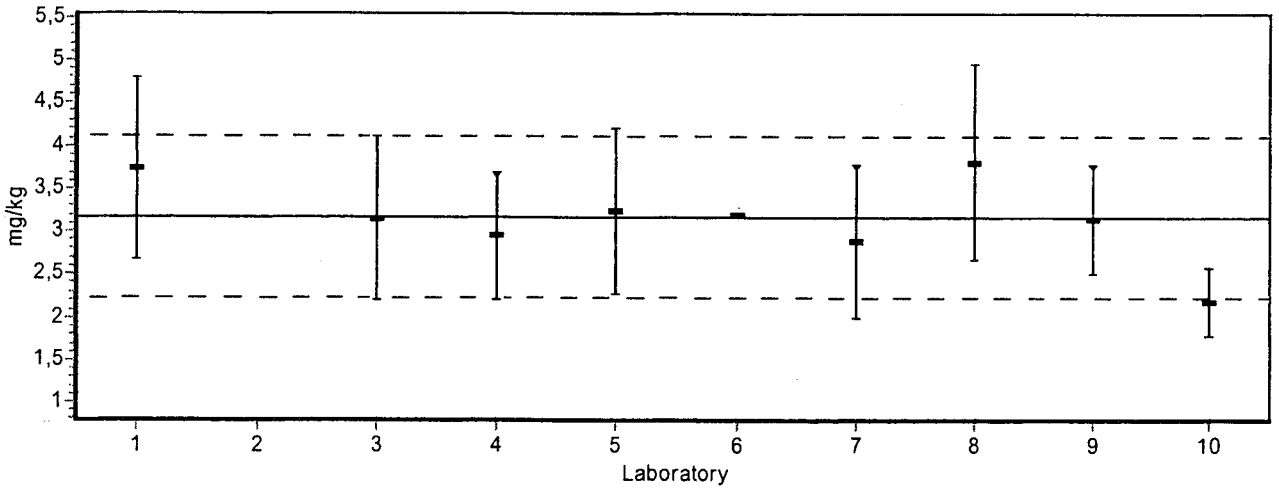
Analyytti *(Analyte)* **Napht** Näyte *(Sample)* M1



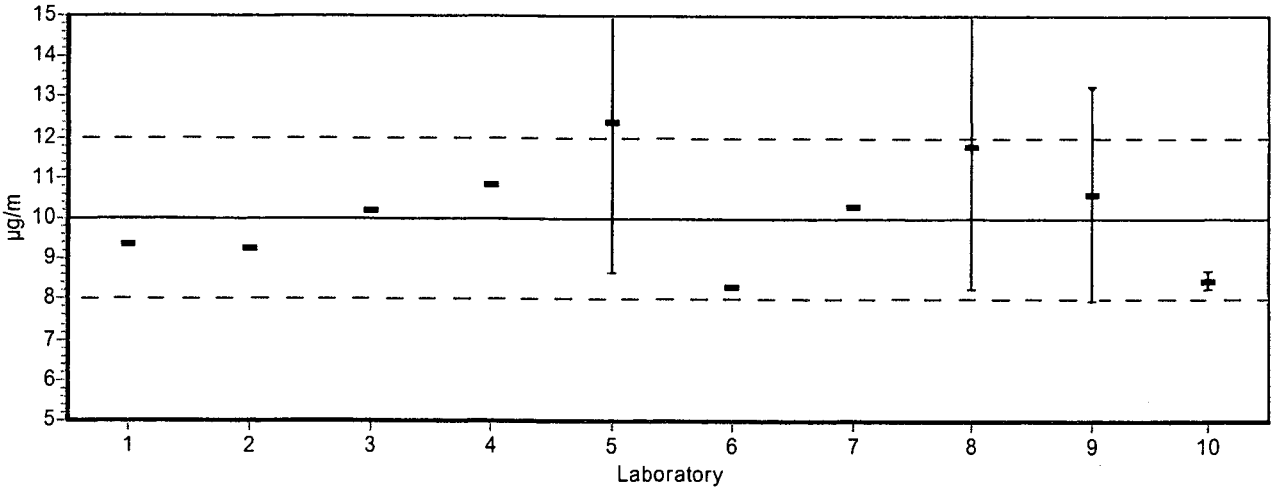
Analyytti *(Analyte)* **Napht** Näyte *(Sample)* S1



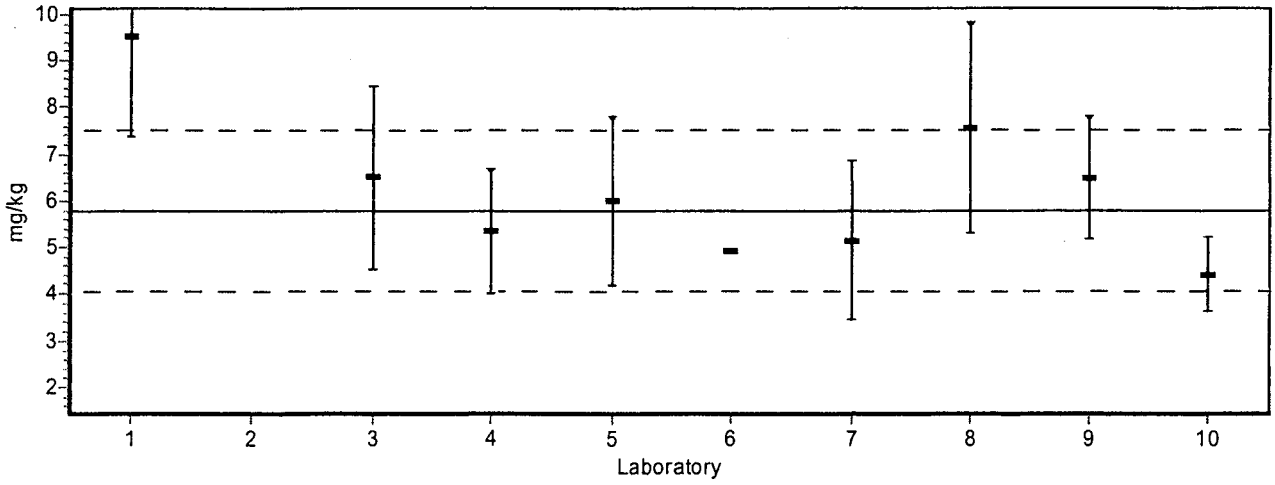
Analyytti *(Analyte)* **Phenan** Näyte *(Sample)* M1



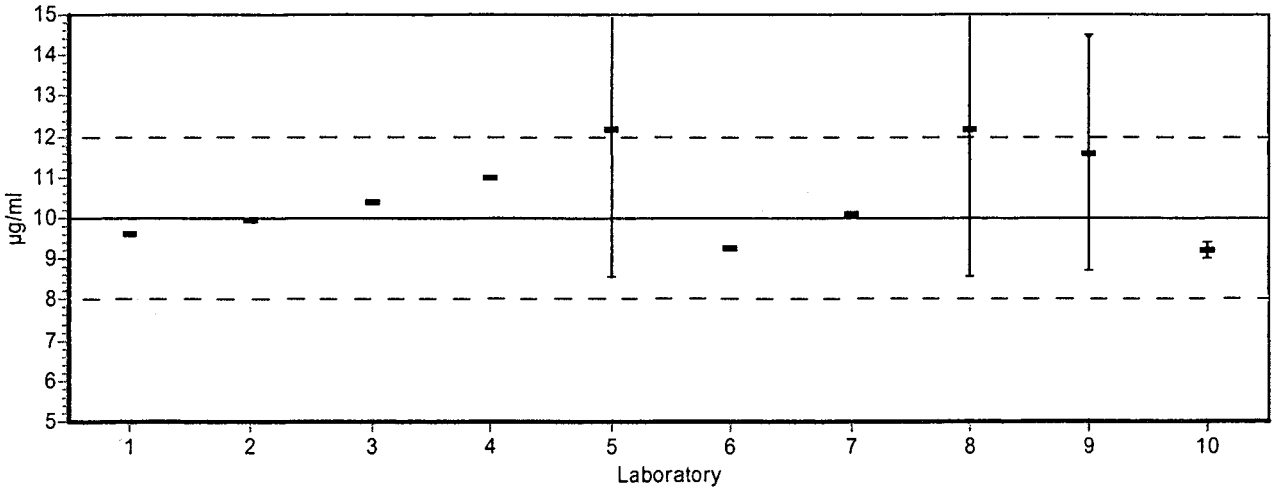
Analyytti *(Analyte)* **Phenan** Näyte *(Sample)* S1



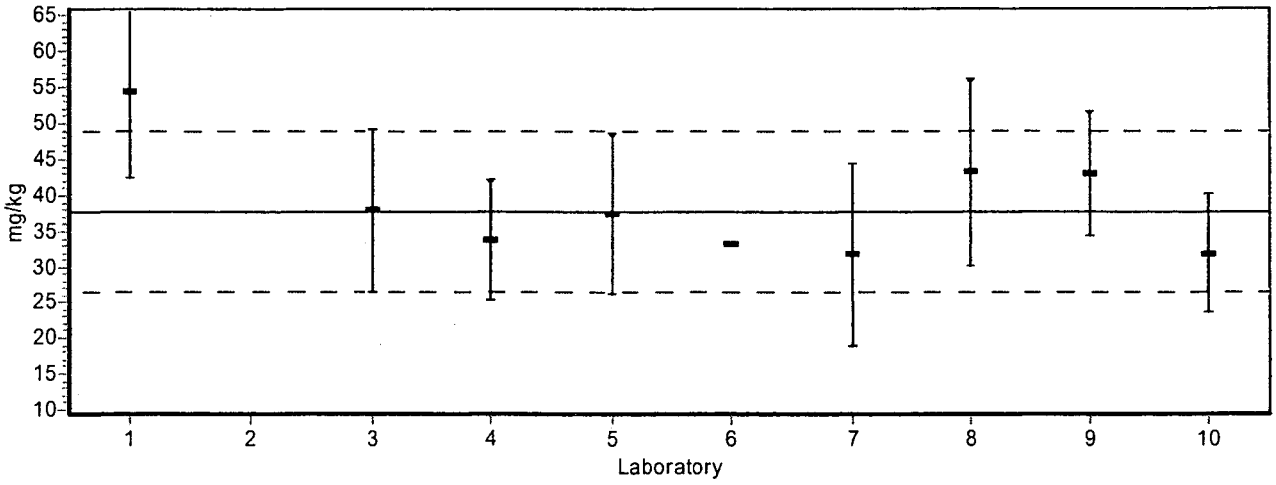
Analyytti *(Analyte)* **Pyrene** Näyte *(Sample)* M1

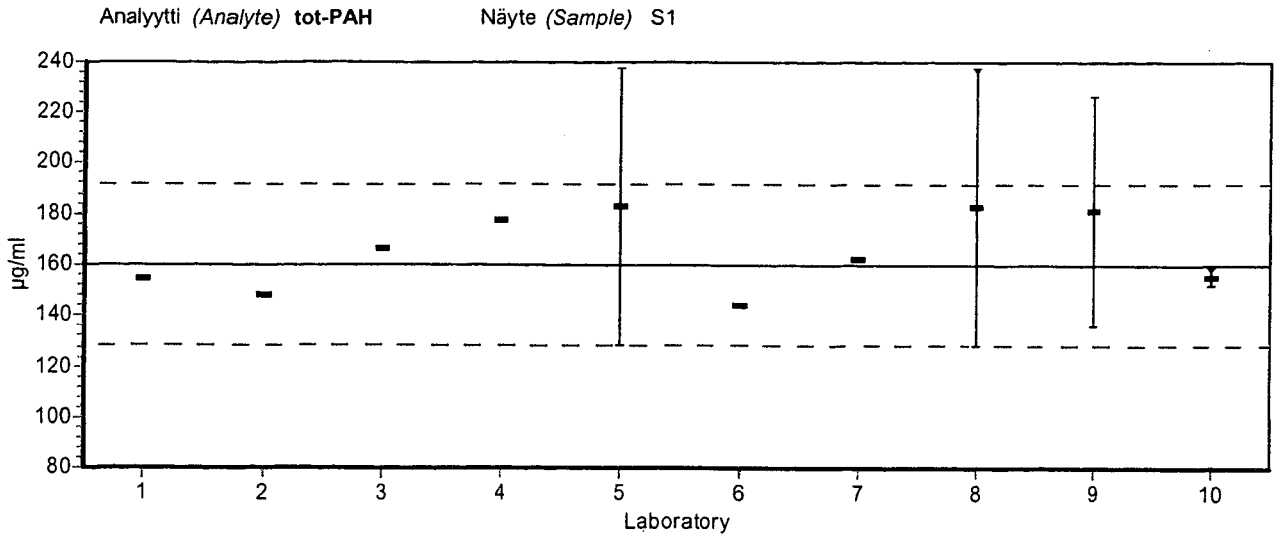


Analyytti *(Analyte)* **Pyrene** Näyte *(Sample)* S1



Analyytti *(Analyte)* **tot-PAH** Näyte *(Sample)* M1




Analyytti (Analyte) tot-PAH
Näyte (Sample) S1
240
220
200
180
160
140
120
100
80
µg/ml
1
2
3
4
5
6
7
8
9
10
Laboratory

APPENDIX 8. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant

Analyte	PAHs
Unit	mg/kg
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 invidual 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 ($-2 \le z \le 2$)
p - questionable ($2 < z \le 3$), positive error, the result > X
n - questionable ($-3 \le z < -2$), negative error, the result < X
P- non- accepted ($z > 3$), positive error, the result >>> X
N- non- accepted ($z < -3$), negative error, the result <<< X (X = the reference value)

Robust analysis

The items of data is sorted into increasing order, $x_1, x_2, \ldots, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
X^* = median of x_i ($i = 1 \ldots p$)
$s^* = 1.483$ median of $| x_i - x^* |$ ($i = 1 \ldots p$)

For each x_i 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 convergenes.

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

APPENDIX 9. RESULTS OF EACH PARTICIPANT

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
A-naphthy	mg/kg	M1		3,374	H	0,266	40	0,4455	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		-0,180	yes	10	20	9,82	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1		8,494	H	0,166	30	0,3775	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		0,100	yes	10	20	10,10	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		5,789	H	0,562	30	1,05	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		-0,790	yes	10	20	9,21	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		1,952	yes	3,15	40	4,38	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		-0,940	yes	10	20	9,06	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		1,448	yes	3,36	30	4,09	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		-1,080	yes	10	20	8,92	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		1,220	yes	3,69	30	4,365	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		-0,440	yes	10	20	9,56	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		1,768	yes	2,76	50	3,98	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		-0,950	yes	10	20	9,05	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		0,431	yes	2,09	30	2,225	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		0,760	yes	10	20	10,76	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		1,776	yes	3,21	30	4,065	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		-1,100	yes	10	20	8,90	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		-0,075	yes	0,596	40	0,587	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		-0,830	yes	10	20	9,17	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		3,884	H	6,9	40	12,26	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		-0,010	yes	10	20	9,99	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		3,628	yes	0,215	40	0,371	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		-0,100	yes	10	20	9,90	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		1,189	yes	2,27	40	2,81	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		0,240	yes	10	20	10,24	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1		2,330	yes	0,097	50	0,1535	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		1,000	yes	10	20	11,00	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		1,199	yes	3,17	30	3,74	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		-0,650	yes	10	20	9,35	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		4,314	yes	5,78	30	9,52	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		-0,380	yes	10	20	9,62	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		2,962	yes	37,7	30	54,45	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		-0,333	yes	160	20	154,68	164	165,5	14,94	9	10	0	0	10
Laboratory 2																
A-naphthy	µg/ml	S1		-0,480	yes	10	20	9,52	9,74	10	1,237	12,3	10	0	0	10
Acenaph	µg/ml	S1		0,140	yes	10	20	10,14	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	µg/ml	S1		-1,720	yes	10	20	8,28	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	µg/ml	S1		-3,540	yes	10	20	6,46	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	µg/ml	S1		0,370	yes	10	20	10,37	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	µg/ml	S1		0,220	yes	10	20	10,22	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	µg/ml	S1		-0,200	yes	10	20	9,80	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	µg/ml	S1		1,050	yes	10	20	11,05	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	µg/ml	S1		-0,720	yes	10	20	9,28	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	µg/ml	S1		0,220	yes	10	20	10,22	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	µg/ml	S1		-0,430	yes	10	20	9,57	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	µg/ml	S1		-0,620	yes	10	20	9,38	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	µg/ml	S1		-3,080	yes	10	20	6,92	10,09	10,39	1,655	15,9	10	0	0	10
Napht	µg/ml	S1		-2,640	yes	10	20	7,36	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	µg/m	S1		-0,760	yes	10	20	9,24	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	µg/ml	S1		-0,060	yes	10	20	9,94	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	µg/ml	S1		-0,761	yes	160	20	147,82	164	165,5	14,94	9	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
Laboratory 3																
A-naphthy	mg/kg	M1		0,883	yes	0,266	40	0,313	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		0,100	yes	10	20	10,1	9,74	10	1,237	12,3	10	0	0	10
Acenaph	µg/ml	S1		0,500	yes	10	20	10,5	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		-2,989	yes	0,562	30	0,31	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		0,900	yes	10	20	10,9	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		-1,127	yes	3,15	40	2,44	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		1,000	yes	10	20	11,0	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		1,171	yes	3,36	30	3,95	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		0,300	yes	10	20	10,3	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		-0,985	yes	3,69	30	3,145	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		0,700	yes	10	20	10,7	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		0,087	yes	2,76	50	2,82	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		0,400	yes	10	20	10,4	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		-0,319	yes	2,09	30	1,99	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		-0,030	yes	10	20	9,97	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		0,187	yes	3,21	30	3,3	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		0,200	yes	10	20	10,2	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	µg/ml	S1		-0,080	yes	10	20	9,92	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		0,667	yes	6,9	40	7,82	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		0,600	yes	10	20	10,6	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	µg/ml	S1		0,300	yes	10	20	10,3	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		-0,176	yes	2,27	40	2,19	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		-0,060	yes	10	20	9,94	10,09	10,39	1,655	15,9	10	0	0	10
Napht	µg/ml	S1		0,500	yes	10	20	10,5	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		-0,032	yes	3,17	30	3,155	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		0,200	yes	10	20	10,2	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		0,830	yes	5,78	30	6,5	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		0,400	yes	10	20	10,4	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		0,035	yes	37,7	30	37,9	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		0,375	yes	160	20	166	164	165,5	14,94	9	10	0	0	10
Laboratory 4																
A-naphthy	mg/kg	M1		0,150	yes	0,266	40	0,274	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		0,549	yes	10	20	10,549	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1		-0,643	yes	0,166	30	0,150	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		1,011	yes	10	20	11,011	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		-0,522	yes	0,562	30	0,518	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		1,165	yes	10	20	11,165	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		-0,635	yes	3,15	40	2,75	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		1,666	yes	10	20	11,666	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		-1,429	yes	3,36	30	2,64	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		1,029	yes	10	20	11,029	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		0,217	yes	3,69	30	3,81	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		1,261	yes	10	20	11,261	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		-2,043	yes	2,76	50	1,35	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		0,680	yes	10	20	10,680	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		-0,638	yes	2,09	30	1,89	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		1,709	yes	10	20	11,709	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		-0,166	yes	3,21	30	3,13	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		0,941	yes	10	20	10,941	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		-1,133	yes	0,596	40	0,461	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		1,357	yes	10	20	11,357	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		-0,333	yes	6,9	40	6,44	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		1,026	yes	10	20	11,026	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		-0,674	yes	0,215	40	0,186	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		0,867	yes	10	20	10,867	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		-0,925	yes	2,27	40	1,85	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		1,992	yes	10	20	11,992	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1		-2,078	yes	0,097	50	0,0466	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		0,694	yes	10	20	10,694	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		-0,463	yes	3,17	30	2,95	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		0,829	yes	10	20	10,829	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		-0,507	yes	5,78	30	5,34	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		0,978	yes	10	20	10,978	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		-0,690	yes	37,7	30	33,8	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		1,109	yes	160	20	177,75	164	165,5	14,94	9	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
Laboratory 5																
A-naphthy	µg/ml	S1		1,900	yes	10	20	11,9	9,74	10	1,237	12,3	10	0	0	10
Acenaph	µg/ml	S1		2,400	yes	10	20	12,4	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		0,036	yes	0,562	30	0,565	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		2,400	yes	10	20	12,4	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		-0,318	yes	3,15	40	2,95	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		0,400	yes	10	20	10,4	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		-0,595	yes	3,36	30	3,06	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		1,200	yes	10	20	11,2	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		0,235	yes	3,69	30	3,82	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		0,600	yes	10	20	10,6	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		-1,746	yes	2,76	50	1,555	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		-0,580	yes	10	20	9,42	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		0,941	yes	2,09	30	2,385	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		0,600	yes	10	20	10,6	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		-0,467	yes	3,21	30	2,985	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		1,500	yes	10	20	11,5	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		1,418	yes	0,596	40	0,765	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		0,520	yes	10	20	10,52	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		-0,250	yes	6,9	40	6,555	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		2,200	yes	10	20	12,2	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	µg/ml	S1		1,800	yes	10	20	11,8	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		1,553	yes	2,27	40	2,975	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		1,400	yes	10	20	11,4	10,09	10,39	1,655	15,9	10	0	0	10
Napht	µg/ml	S1		1,900	yes	10	20	11,9	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		0,137	yes	3,17	30	3,235	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		2,400	yes	10	20	12,4	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		0,265	yes	5,78	30	6,01	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		2,200	yes	10	20	12,2	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		-0,044	yes	37,7	30	37,45	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		1,438	yes	160	20	183	164	165,5	14,94	9	10	0	0	10
Laboratory 6																
A-naphthy	mg/kg	M1		-0,301	yes	0,266	40	0,25	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		-1,180	yes	10	20	8,82	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1		-0,241	yes	0,166	30	0,16	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		-1,180	yes	10	20	8,82	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		0,036	yes	0,562	30	0,565	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		0,170	yes	10	20	10,17	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		-0,976	yes	3,15	40	2,535	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		-0,860	yes	10	20	9,14	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		-0,863	yes	3,36	30	2,925	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		-0,680	yes	10	20	9,32	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-K-F	mg/kg	M1		3,761	yes	2,76	50	5,355	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		8,000	H	10	20	18,00	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		-0,957	yes	2,09	30	1,79	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		-0,730	yes	10	20	9,27	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		-0,166	yes	3,21	30	3,13	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		-0,770	yes	10	20	9,23	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		-0,722	yes	0,596	40	0,51	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		-1,490	yes	10	20	8,51	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		-0,721	yes	6,9	40	5,905	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		-0,770	yes	10	20	9,23	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		0,581	yes	0,215	40	0,24	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		-1,490	yes	10	20	8,51	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		-1,432	yes	2,27	40	1,62	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		-0,590	yes	10	20	9,41	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1		-2,557	yes	0,097	50	0,035	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		-1,950	yes	10	20	8,05	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		0,042	yes	3,17	30	3,19	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		-1,670	yes	10	20	8,33	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		-1,003	yes	5,78	30	4,91	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		-0,730	yes	10	20	9,27	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		-0,810	yes	37,7	30	33,12	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		-0,993	yes	160	20	144,11	164	165,5	14,94	9	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
Laboratory 7																
A-naphthy	mg/kg	M1		-1,664	yes	0,266	40	0,1775	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		-0,340	yes	10	20	9,66	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1		-0,361	yes	0,166	30	0,157	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		0,500	yes	10	20	10,5	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		-0,979	yes	0,562	30	0,4795	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		0,300	yes	10	20	10,3	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		-1,183	yes	3,15	40	2,405	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		0,300	yes	10	20	10,3	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		-1,220	yes	3,36	30	2,745	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		-0,060	yes	10	20	9,94	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		-1,572	yes	3,69	30	2,82	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		0,200	yes	10	20	10,2	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		-1,210	yes	2,76	50	1,925	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		-0,130	yes	10	20	9,87	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		-1,659	yes	2,09	30	1,57	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		0,100	yes	10	20	10,1	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		-1,205	yes	3,21	30	2,63	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		0,300	yes	10	20	10,3	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		-2,093	yes	0,596	40	0,3465	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		0,000	yes	10	20	10,0	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		-0,446	yes	6,9	40	6,285	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		0,100	yes	10	20	10,1	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		-0,512	yes	0,215	40	0,193	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		0,200	yes	10	20	10,2	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		-0,705	yes	2,27	40	1,95	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		-0,130	yes	10	20	9,87	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1		-0,709	yes	0,097	50	0,0798	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		-0,160	yes	10	20	9,84	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		-0,578	yes	3,17	30	2,895	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		0,300	yes	10	20	10,3	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		-0,727	yes	5,78	30	5,15	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		0,100	yes	10	20	10,1	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		-1,043	yes	37,7	30	31,8	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		0,125	yes	160	20	162	164	165,5	14,94	9	10	0	0	10
Laboratory 8																
A-naphthy	mg/kg	M1		0,479	yes	0,266	40	0,2915	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		-0,660	yes	10	20	9,34	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1		1,546	yes	0,166	30	0,2045	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		0,400	yes	10	20	10,4	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		1,993	yes	0,562	30	0,73	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		1,900	yes	10	20	11,9	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		0,564	yes	3,15	40	3,505	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		2,400	yes	10	20	12,4	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		0,347	yes	3,36	30	3,535	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		2,000	yes	10	20	12,0	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		0,425	yes	3,69	30	3,925	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		2,500	yes	10	20	12,5	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		0,464	yes	2,76	50	3,08	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		2,000	yes	10	20	12,0	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		0,622	yes	2,09	30	2,285	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		0,400	yes	10	20	10,4	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		2,087	yes	3,21	30	4,215	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		2,200	yes	10	20	12,2	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		0,977	yes	0,596	40	0,7125	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		1,800	yes	10	20	11,8	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		1,681	yes	6,9	40	9,22	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		2,200	yes	10	20	12,2	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		1,384	yes	0,215	40	0,2745	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		0,900	yes	10	20	10,9	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		0,595	yes	2,27	40	2,54	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		2,100	yes	10	20	12,1	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1		2,722	yes	0,097	50	0,163	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		-0,650	yes	10	20	9,35	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		1,356	yes	3,17	30	3,815	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		1,800	yes	10	20	11,8	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		2,047	yes	5,78	30	7,555	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		2,200	yes	10	20	12,2	10,25	10,55	1,138	10,7	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
tot-PAH	mg/kg	M1		0,973	yes	37,7	30	43,2	37,8	38,79	7,426	19,1	9	0	0	9
Laboratory 8																
tot-PAH	µg/ml	S1		1,438	yes	160	20	183	164	165,5	14,94	9	10	0	0	10
Laboratory 9																
A-naphthy	mg/kg	M1		0,921	yes	0,266	40	0,315	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		2,100	yes	10	20	12,1	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1		0,763	yes	0,166	30	0,185	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		3,200	H	10	20	13,2	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		0,985	yes	0,562	30	0,645	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		0,800	yes	10	20	10,8	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		1,413	yes	3,15	40	4,04	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		0,600	yes	10	20	10,6	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-ant	mg/kg	M1		1,062	yes	3,36	30	3,895	3,52	3,403	0,5658	16,6	8	0	0	8
	µg/ml	S1		1,000	yes	10	20	11,0	10,37	10,45	0,9689	9,3	9	0	0	9
Benzo-B-F	mg/kg	M1		-0,298	yes	3,69	30	3,525	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		1,000	yes	10	20	11,0	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-K-F	mg/kg	M1		0,464	yes	2,76	50	3,08	3,01	2,996	1,275	42,5	8	0	0	8
	µg/ml	S1		-0,160	yes	10	20	9,84	9,855	10,13	0,9105	9	8	1	0	9
Benzo-per	mg/kg	M1		0,558	yes	2,09	30	2,265	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		1,800	yes	10	20	11,8	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		0,042	yes	3,21	30	3,23	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		-0,550	yes	10	20	9,45	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		1,376	yes	0,596	40	0,76	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		3,000	yes	10	20	13,0	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		1,091	yes	6,9	40	8,405	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		2,000	yes	10	20	12,0	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		0,930	yes	0,215	40	0,255	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		1,100	yes	10	20	11,1	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		0,859	yes	2,27	40	2,66	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		2,400	yes	10	20	12,4	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1		0,330	yes	0,097	50	0,105	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		0,800	yes	10	20	10,8	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		-0,053	yes	3,17	30	3,145	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		0,600	yes	10	20	10,6	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		0,807	yes	5,78	30	6,48	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		1,600	yes	10	20	11,6	10,25	10,55	1,138	10,7	10	0	0	10
tot-PAH	mg/kg	M1		0,935	yes	37,7	30	42,98	37,8	38,79	7,426	19,1	9	0	0	9
	µg/ml	S1		1,331	yes	160	20	181,3	164	165,5	14,94	9	10	0	0	10
Laboratory 10																
A-naphthy	mg/kg	M1		-0,677	yes	0,266	40	0,23	0,274	0,2637	0,04969	18,8	7	1	0	8
	µg/ml	S1		-1,800	yes	10	20	8,20	9,74	10	1,237	12,3	10	0	0	10
Acenaph	mg/kg	M1			H	0,166	30	<0,1	0,164	0,1737	0,02178	12,5	4	2	1	7
	µg/ml	S1		-1,000	yes	10	20	9,00	10,4	10,32	1,058	10,2	9	1	0	10
Anthrac	mg/kg	M1		0,392	yes	0,562	30	0,595	0,56	0,5531	0,1259	22,7	8	1	0	9
	µg/ml	S1		-0,170	yes	10	20	9,83	10,55	10,5	1,223	11,6	10	0	0	10
Benzo-A-P	mg/kg	M1		0,627	yes	3,15	40	3,545	2,96	3,197	0,7478	23,3	9	0	0	9
	µg/ml	S1		3,200	yes	10	20	13,2	10,5	10,42	1,908	18,3	10	0	0	10
Benzo-B-F	mg/kg	M1		2,593	yes	3,69	30	5,125	3,81	3,817	0,7778	20,3	8	0	0	8
	µg/ml	S1		10,500	H	10	20	20,5	10,65	10,76	0,8792	8,2	8	1	0	9
Benzo-per	mg/kg	M1		0,351	yes	2,09	30	2,2	2,18	2,077	0,3113	14,9	9	0	0	9
	µg/ml	S1		1,300	yes	10	20	11,3	10,68	10,7	0,7994	7,5	10	0	0	10
Chrysene	mg/kg	M1		4,933	H	3,21	30	5,585	3,17	3,349	0,5583	16,6	8	1	0	9
	µg/ml	S1		9,700	H	10	20	19,7	10,2	10,22	1,134	11,0	9	1	0	10
Dibenz-ah	mg/kg	M1		0,243	yes	0,596	40	0,625	0,635	0,6049	0,1565	25,8	8	0	0	8
	µg/ml	S1		0,200	yes	10	20	10,2	10,21	10,47	1,297	12,3	10	0	0	10
Fluoran	mg/kg	M1		-1,098	yes	6,9	40	5,385	6,55	7,039	1,331	18,9	8	1	0	9
	µg/ml	S1		-0,730	yes	10	20	9,27	10,35	10,62	1,183	11,1	10	0	0	10
Fluorene	mg/kg	M1		-2,093	yes	0,215	40	0,125	0,24	0,2387	0,07809	32,7	7	0	0	7
	µg/ml	S1		-1,390	yes	10	20	8,61	10,25	10,16	1,077	10,6	10	0	0	10
Indeno	mg/kg	M1		-1,024	yes	2,27	40	1,805	2,2	2,291	0,5064	22,1	9	0	0	9
	µg/ml	S1		-0,380	yes	10	20	9,62	10,09	10,39	1,655	15,9	10	0	0	10
Napht	mg/kg	M1				0,097	50	<0,1	0,1	0,1017	0,05186	50,9	6	0	1	7
	µg/ml	S1		-1,510	yes	10	20	8,49	10,17	9,798	1,456	14,8	10	0	0	10
Phenan	mg/kg	M1		-2,082	H	3,17	30	2,18	3,21	3,287	0,3381	10,2	8	1	0	9
	µg/m	S1		-1,510	yes	10	20	8,49	10,25	10,15	1,334	13,1	10	0	0	10
Pyrene	mg/kg	M1		-1,563	yes	5,78	30	4,425	6,1	6,261	1,57	25,0	9	0	0	9
	µg/ml	S1		-0,800	yes	10	20	9,20	10,25	10,55	1,138	10,7	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
tot-PAH	mg/kg	M1		-1,030	yes	37,7	30	31,88	37,8	38,79	7,426	19,1	9	0	0	9
Laboratory 10																
tot-PAH	µg/ml	S1		-0,275	yes	160	20	155,6	164	165,5	14,94	9	10	0	0	10

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

APPENDIX 10. SUMMARY OF z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	%
A-naphthy	M1	P	.	A	A	.	A	A	A	A	A	88
	S1	A	A	A	A	A	A	A	A	p	A	90
Acenaph	M1	P	.	.	A	.	A	A	A	A	.	83
	S1	A	A	A	A	p	A	A	A	P	A	80
Anthrac	M1	P	.	n	A	A	A	A	A	A	A	78
	S1	A	A	A	A	p	A	A	A	A	A	90
Benzo-A-P	M1	A	.	A	A	A	A	A	A	A	A	100
	S1	A	N	A	A	A	A	A	p	A	P	70
Benzo-ant	M1	A	.	A	A	A	A	A	A	A	.	100
	S1	A	A	A	A	A	A	A	A	A	.	100
Benzo-B-F	M1	A	.	A	A	A	.	A	A	A	p	88
	S1	A	A	A	A	A	.	A	p	A	P	78
Benzo-K-F	M1	A	.	A	n	A	P	A	A	A	.	75
	S1	A	A	A	A	A	P	A	A	A	.	89
Benzo-per	M1	A	.	A	A	A	A	A	A	A	A	100
	S1	A	A	A	A	A	A	A	A	A	A	100
Chrysene	M1	A	.	A	A	A	A	A	p	A	P	78
	S1	A	A	A	A	A	A	A	p	A	P	80
Dibenz-ah	M1	A	.	.	A	A	A	n	A	A	A	88
	S1	A	A	A	A	A	A	A	A	p	A	90
Fluoran	M1	P	.	A	A	A	A	A	A	A	A	89
	S1	A	A	A	A	p	A	A	p	A	A	80
Fluorene	M1	P	.	.	A	.	A	A	A	A	n	71
	S1	A	A	A	A	A	A	A	A	A	A	100
Indeno	M1	A	.	A	A	A	A	A	A	A	A	100
	S1	A	N	A	A	A	A	A	p	p	A	70
Napht	M1	p	.	.	n	.	n	A	p	A	.	33
	S1	A	n	A	A	A	A	A	A	A	A	90
Phenan	M1	A	.	A	A	A	A	A	A	A	n	89
	S1	A	A	A	A	p	A	A	A	A	A	90
Pyrene	M1	P	.	A	A	A	A	A	p	A	A	78
	S1	A	A	A	A	p	A	A	p	A	A	80
tot-PAH	M1	p	.	A	A	A	A	A	A	A	A	89
	S1	A	A	A	A	A	A	A	A	A	A	100
%		76	82	97	94	83	91	97	74	88	75	
Accredited		yes			yes				yes			

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

%* - percentage of accepted results

Totally accepted, % In all: 86 In accredited: 81

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date April 2006
Author(s)	Irma Mäkinen and Pirjo Sainio	
Title of publication	SYKE Proficiency test 7/2005 PAHs from polluted soil	
Parts of publication/ other project publications		
Abstract	The Finnish Environment Institute carried out the proficiency test for the determination of PAHs from polluted soil in November 2005. In total 11 laboratories participated in the proficiency test. Two laboratories did not report the results. One synthetic sample and one soil sample were delivered to the participating laboratories. The method published by Nordtest (Report TR 329), the draft standard ISO/DIS 18287 or their modifications were rather commonly used in analysis of PAHs. The robust standard deviation varied from 7.8% to 17.5% in analysis of the synthetic sample and from 8.7% to 62% in analysis of the soil sample. It was highest in analysis of naphthalene (62%) and benzo(k)fluoranthene (35%) in the soil sample. The use of different methods or method variations might have had some effect on variation of the results. There was a variation e.g in extraction solvents and in internal standards. The use of a sufficiently effective polar solvent is crucial in analysis of PAHs from polluted soil. In this proficiency test, the robust mean value was used as the assigned value. When the target value of the total deviation was 20% for synthetic sample and from 30% to 50% for the soil sample in calculating of z scores at the 95% confidence interval, 87% of the participating laboratories reported satisfied results. Performance in analysis of naphthalene had not been evaluated. The SYKE proficiency test for analysis of PCB compounds from polluted soils was carried out for the second time. The results were fairly satisfactory in analysis of most PCB congeners, when compared with some international comparisons	
Keywords	PAH-compounds, polluted soils, environmental laboratories, proficiency test, interlaboratory comparisons	
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Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Huhtikuu 2006
Tekijä(t)	Irma Mäkinen ja Pirjo Sainio	
Julkaisun nimi	SYKE pätevyyskoe 7/2005 PAH-yhdisteet maasta	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Suomen ympäristökeskus järjesti marraskuussa 2005 pätevyyskokeen 16 PAH -yhdisteen määrittä-miseksi maasta. Pätevyyskokeeseen osallistui kaikkiaan 11 laboratoriota. Pätevyyskokeeseen il-moittautuneista laboratorioista kaksi ei palauttanut tuloksia. Pätevyyskokeen näytteenä oli yksi synteettinen näyte ja yksi maanäyte. Analysoinnissa käytettiin useita menetelmiä, yleisimmin Nordtestin raportin TR 329 mukaista menetelmää tai standardiehdotuksen ISO/DIS 18287 mukaista menetelmää. Mm. määritykseen käytetty näytemäärä, uuttoliuottimet ja kalibrointiliuokset vaihtelivat eri laboratorioissa. Riittävän polaarisen liuottimen käyttö on ensisijaisen tärkeää PAH -yhdisteiden uutossa maanäytteistä. Tulosten hajonta oli 7,8 % – 17,5 % eri PAH -yhdisteille synteettisen näytteen analysoinnissa ja 8,7 % - 62 % maanäytteen analysoinnissa. Tulosten hajonta oli suurin naftaleenin ja bentso(k)-fluoranteenin määrityksessä. Tulosten hajontaa oli todettavissa myös synteettisen näytteen määri-tyksessä. Tulosten hajonta maanäytteen määrityksessä oli kuitenkin samaa suuruusluokkaa kuin kansainvälisissä pätevyyskokeissa. Vertailuarvona käytettiin robusti-keskiarvoa. Tässä pätevyyskokeessa 87 % tuloksista oli tyydyttä-viä, kun kokonaiskeskihajonnan tavoitearvona käytettiin synteettiselle näytteelle 20 % ja maanäyt-teelle 30 % tai 40 % lukuun ottamatta bentso(k)fluoranteenia, jolle tavoitearvoksi asetettiin 50 % (95 % merkitsevyystaso). Suoriutumiskykyä naftaleenin määrityksessä maanäytteestä ei arvioitu.	
Asiasanat	PAH -yhdisteet, saastuneet maat, ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailukoe	
Julkaisusarjan nimi ja numero	Reports of Finnish Environment Institute 2/2006	
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Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2005	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum April 2006
Författare	Irma Mäkinen och Pirjo Sainio	
Publikationens titel	Provningsjämförelse 7/2005 PAH-föreningar av jord	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	Under november 2005 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av 16 PAH föreningar av jord. Ett syntetisk prov och ett jord prov hade sent till laboratorier. Olika analysmetoder hade användts för PAH analys. Huvudsakligen de var baserade sig på Nordtest metod (Rapport 329) eller standardförslaget ISO/DIS 18287. I särskildt, extraktion-lösningar och kalibreringlösningar varierade i olika labortorier. Som referensvärde (*the assigned value*) användes det teoretiska värdet (syntetiska provet) eller robust-medelvärdet (jordproven). Resultaten värderades med hjälp av z-värden. Beräkningen av z-värdena baserade sig på totalavvikelser, som sattes till 20 % (syntetiska provet) och till 30 % - 50 % (jordprovet) på 95 % sannolikhetsnivå. I denna provningsjämförelse, 87 % av resultatena var tillfredsställande I analys av PCB 101,105, 118 och 138 i jordprovena resultatena var mest tillfredsställande. Bestämningen av PCB 28 och 52 såg ut att vara mest kritisk. Kompetens i bestämningen av naftalen av jordprovet hade inte evaluerats.	
Nyckelord	PAH, jord proven, provningsjämförelse, miljölaboratorier	
Publikationsserie och nummer	Reports of Finnish Environment Institute 2/2006	
Publikationens tema		
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