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Helsinki 2008

Finnish Environment Institute

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CONTENT

1 INTRODUCTION

The Finnish Environment Institute (SYKE) carried out the proficiency test for the determination of organotins (tributyltin, TBT and triphenyltin, TPhT) from the polluted sediment in November 2007. The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1 [1], ILAC Requirements [2], ISO 13528 [3] and IUPAC Recommendations [4]. SYKE is the Proficiency Testing Provider No. PT01 accredited by the Finnish Accreditation Service. The proficiency testing service in SYKE conforms to the requirements of the Guide ISO/IEC 43-1:1997. However, the organizing of tests for measurement of organotins does not include in the accreditation scope.

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratory
Hakuninmaantie 6, 00430 Helsinki
tel. +358 20 490 123, telecopy +358 20 490 2890

Testing laboratory:
City of Helsinki, Environment Centre

The responsibilities in organizing the proficiency test were as follows:
Irma Mäkinen, SYKE, coordinator
Jari Nuutinen, SYKE, preparation of the artificial sample
Raija Ivalo, Pirkanmaa Environment Centre, preparation of the sediment sample in co-work with SYKE
Pirjo Tikkanen, City of Helsinki, analytical expert.

2.2 Participants

In total, the samples were delivered to eight laboratories and each laboratory reported also the results (Appendix 1). Five participants were from Finland and three participants from other European countries.

The code of the testing laboratory (City of Helsinki, Environment Laboratory) was 8 in the result sheets and in the figures.

2.3 Samples and their delivery

One synthetic sample (A1) and one sediment sample (S1) was delivered to the participants. The sample A1 was prepared from a organotin mixture stock solution and the sample S1 was a sea sediment sample provided by VTT (Espoo) and prepared by SYKE in co-work with the Pirkanmaa Environment Centre (Appendix 2).

The samples were delivered on 13 November 2007 and they were asked to analyse before 12 December 2007. The results were asked to return before 21 December 2007.

The preliminary lists of the results were delivered on 10 January 2008.

2.4 Testing of samples

2.4.1 Homogeneity study

Homogeneity of the artificial sample A1 was tested as duplicate determination from three ampoules. There were not systematic differences between the obtained results from different ampoules (Appendix 3).

Homogeneity of the sediment sample S1 was tested from nine bottles. The sample S1 was considered homogenous.

2.4.2 Stability study

The artificial sample A1 was analyzed twice and there were not systematic differences between the results obtained in the time scale of two weeks. (Appendix 3). The stability of the sample S1 was not tested.

2.5 Comments sent by the participants

The participants sent comments dealing with analytical problems (Appendix 4).

2.6 Analytical methods

Except one laboratory the participants did not reported the reference of their analytical methods (Appendix 5). However, there is available the ISO/DIS 23161 for analysis of organotins from soil [5].

The sediment sample was extracted using seven different sample intakes (0.5 g – 4 g) and solvents or solvent mixtures (Appendix 5). Fairly few participants reported their solvents, but at least methanol, acetic acid+methanol, methylen chloride or tropolene-ether-hexane was used. Extraction methods, extraction time and clean-up procedures also varied. TBT and TPhT was determined mainly after derivatisation. Only the laboratory eight had determined TBT and TPhT without derivatisation.

Organotins were mainly measured by the GC-MS-method, but also GC-PPPD and GC-AED-method was used. The laboratory 8 determined organotins using the HPLC-MS-method.

Several standards or standard mixtures were used as internal standards. The laboratory 8 used the standard addition method.

2.7 Data treatment

2.7.1 Testing of outliers and normality of data

The participants were requested to report the triplicate 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. The data was normal except the results obtained in analysis of TPhT from the sample S1. Outliers were rejected according to the Hampel test in calculation of the mean values. Also before calculation of the final robust mean one outlier was rejected in analysis of TPhT from the sample S1. This outlier deviated more than 200 % from the robust mean [4].

2.7.2 Assigned values and their uncertainties

The calculated concentration of the artificial sample A1 was used as the assigned value in analysis of TBT and TPhT. The expanded uncertainty calculated on the basis of the sample preparation was 0.5 % at the 95% confidence level (Appendix 2).

The robust mean was used as the assigned value in analysis of the sediment sample S1 (Appendix 2). The uncertainty of the assigned values in analysis of the sediment sample was calculated using the robust standard deviation. Thus it depended on the variation of the results and the number of the participants. The uncertainty of the assigned value in analysis of TPhT (20 %) was slightly lower than in analysis of TBT (24 %) at the 95% confidence interval due to rejecting of one result in analysis of TPhT.

2.7.3 Uncertainties reported by participants

Most participants reported their measurement uncertainties (Appendix 9). In analysis of the sediment sample S1 the uncertainties varied mainly from 30 % to 40 %. There were not systematic differences between the uncertainties estimated by different procedures, e.g. between the uncertainties estimated using the data obtained in internal quality control or in analysis of certified reference materials.

2.7.4 Target value for total deviation

The target value for the total deviation (s_{target}) was 30 % in analysis of the synthetic sample A1 and 40 % in analysis of the sediment sample S1 (at the 95% confidence interval). E.g. in the EC Draft of technical specifications for chemical analysis and monitoring of water status for the pollutants of WFD has proposed, that the minimum performance criteria for methods of analysis should be based on an uncertainty of measurement of 50 % or below at the 95 % confidence interval [6].

2.7.5 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 deviation (s_{target}).

z scores can be interpreted as follows:

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

The calculated z scores are presented in the results of each participant (Appendix 7) and the summary of z scores is presented in Appendix 10. Explanations to terms are presented in Appendix 6.

3 RESULTS AND PERFORMANCE

3.1 Variation of the results

The results were asked to report as triplicates in analysis of the samples. The repeatability (s_w) and the reproducibility (s_t) were as follows (see also table 1):

- s_w-TBT: 5.2 % (A1) and 5.4 % (S1)
- s_w-TPhT: 5.9 % (A1) and 7.1 % (S1)
- s_t-TBT: 36 % (A1) and 16 % (S1)
- s_t-TPhT: 49 % (A1) and 21 % (S1).

The ratio s_t/s_w, a measure for the robustness of the methods used, was higher than three in analysis of the artificial sample A1. The ratio s_b/s_w should be between 2 and 3 for robust methods [7].

Table 1. Results of the triplicate 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 %
TBT	A1	µg/ml	64,63	70,12	71,4	3,649	25,04	25,31	5,2	36	36	30	8	50
	S1	µg/kg	335	365,3	366	19,78	54,38	57,86	5,4	15	16	40	8	88
TPhT	A1	µg/ml	64,63	58,23	63,25	3,445	28,39	28,6	5,9	49	49	30	8	62
	S1	µg/kg	160	160,5	155	11,33	31,13	33,13	7,1	19	21	40	8	88

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

The summary of all results is presented in Table 2. The robust standard deviations were much higher (TBT: 32 % and TPhT: 46 %) in analysis of the artificial sample A1 than in analysis of the sediment sample S1 (TBT: 27 % and TPhT: 22 %). The robust standard deviation in analysis of TPhT (20 %) was slightly lower than in analysis of TBT (24 %) at the 95% confidence interval due to rejecting of one results in the data of TPhT.

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%
TBT	A1	µg/ml	64,63	69.43	71.58	71.40	22.97	32,1	8	30	50
	S1	µg/kg	335	354.03	335.07	363.50	91.16	27,2	8	40	100
TPhT	A1	µg/ml	64,63	58.03	67.44	69.40	30.96	45,9	8	30	63
	S1	µg/kg	160	160.49	160.49	159.50	36.08	22,5	8	40	88

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 $\| z \| \leq 2$.

3.2 Comments on results

In analysis of the artificial sample A1 two laboratories reported about analytical problems relating to equipment, derivation step or standards (Appendix 3). The results of these laboratories deviated most from the assigned value in analysis of the sample A1 (Appendix 5). In preparation of the standards the laboratory 4 uses normally cyclohexane instead of methanol. However, the solvent was reported to the participants beforehand in the invitation letter. It was also important in analysis of the sample A1, that the ampoule was mixed properly e.g. using ultrasonic bath before further dilution of the sample.

On the basis of the results of the sediment sample S1 the laboratories 2 and 4 have had also analytical problems. The laboratory 2 reported the low result in analysis of TBT and the large result in analysis of TPhT. Thus the calibration has not been a problem alone. The laborary 4 reported too large result in analysis of TPhT due to problems in derivatisation step.

3.3 Estimation of performance

In this PT test 75 % of the participating laboratories reported satisfactory results. This estimation was based on the target value of the total deviation in calculating of z scores at the 95 % confidence interval (Appendix 10). The target value of the total deviation was 30 % in analysis of the artificial sample and 40 % in analysis of the sediment sample. The participants had more problems in analysis of the artificial sample than in analysis of the sediment sample. In analysis of the sediment sample 100 % of TBT-results and 88 % of TPhT-results were considered satisfactory.

The participants used, in particular, different extraction solvents, extraction methods and different internal standards for analysis of organotins and these differences might have had some effect on the variation of the results. Two laboratories reported the results with highest deviations from the assigned value due to analytical problems.

In the QUASIMEME laboratory performance study in 2005 the variation of the results in analysis of TBT from two sea sediments was fairy similar as in this proficiency test [8]. The results varied 21 %, when the concentration of TBT was 224 µg/kg and 149 µg/kg.

4 SUMMARY

The Finnish Environment Institute (SYKE) carried out the proficiency test for the determination of organotins (tributyltin TBT and triphenyltin TPhT) from polluted sediment in November 2007. One artificial sample and one sediment sample was delivered to eight participating laboratories.

The robust standard deviations were much higher (TBT: 32 % and TPhT: 46 %) in analysis of the artificial sample than in analysis of the sediment sample (TBT: 27 % and TPhT: 22 %). Two participants reported having analytical problems particularly in analysis of the artificial sample.

In this proficiency test, the robust mean value was used as the assigned value. When the target total deviation was 30 % for the artificial sample and 40 % for the sediment sample in calculating of z scores at the 95 % confidence interval, 75 % of the participating laboratories reported satisfactory results. In analysis of the sediment sample 100 % of TBT-results and 88 % of TPhT-results were considered satisfactory.

5 YHTEENVETO

Suomen ympäristökeskus järjesti marraskuussa 2007 pätevyyskokeen organotinayhdisteiden (TBT ja TPhT) analysoimiseksi sedimentistä. Osallistujille toimitettiin yksi synteettinen näyte ja yksi sedimenttinäyte. Pätevyyskokeeseen osallistui kahdeksan laboratoriota.

Analyysimenetelmät erosivat toisistaan mm. uuttoliuosten, uuttotekniikan ja sisäisen standardin suhteen. Tulosten hajonta oli suurempi synteettisen näytteen (TBT: 32 % ja TPhT: 46 %) kuin sedimenttinäytteen analysoinnissa (TBT: 27 % ja TPhT: 22 %). Tulosten hajontaan vaikutti kahdella laboratoriolla esiintyneet analyyttiset ongelmat erityisesti synteettisen näytteen analysoinnissa.

Vertailuarvona käytettiin robustia keskiarvoa. Tässä pätevyyskokeessa 75 % tuloksista oli tyydyttäviä, kun kokonaishajonnan tavoitearvona käytettiin synteettiselle näytteelle 30 % ja sedimenttinäytteelle 40 % 95 % merkitsevyystasolla. Sedimenttinäytteen analysoinnissa TBT-yhdisteen tuloksista 100 % ja TPhT-yhdisteen tuloksista 88 % oli tyydyttäviä.

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APPENDIX 1. PARTICIPANTS IN THE PROFICIENCY TEST SYKE 9/2007

AnalyCen AS, Moss, Norway

City of Helsinki, Environment Centre, Helsinki, Finland

GALAB Laboratories GmbH, Geesthacht, Germany

National Public Health Institute, YTOS, KEM, Kuopio, Finland

Norwegian Water Research Institute (NIVA), Oslo, Norway

Ramboll Finland Oy, Lahti, Finland

SGS Inspection Services Oy, Hamina, Finland

University of Jyväskylä, Institute of Environmental Research, Jyväskylä, Finland

APPENDIX 2. SAMPLES

Sample A1

The sample A1 was a synthetic sample prepared from the Organotin – Mix 8 Stock Solution (LGC-Promochem GmbH D-46485 Wesel, the code: SL 31005, Lot: 081507) including eight organotin components in methanol, where the concentration of TBT and TPhT was 1000 µg/ml (± 0.5 %). The stock solution was diluted by weighing 1,617 ml of the stock solution and 23,395 ml of the Fluka methanol 65553 (purge and trap grade). For calculations, density of 0.7914 g/ml was used for methanol. The final concentrations of organotin components (TBT and TPhT) was 64.631 µg/ml.

The prepared dilution was carefully mixed and sampled into a 1.0 ml portions. Small amber glass bottles with a teflon-lined seal and a screw cap were used. Bottles were labelled and numbered according to filling order.

The weight of each tube was recorded at SYKE and at the participating laboratory. The differences of these two weights were as follows:

Tube	SYKE (g)	Participating laboratory (g)	Difference -%
2	4.1934	4.2037	0.25
5	4.1833	4.1890	0.14
7	4.2030	4.2018	-0.03
10	4.2240	4.2287	0.11
14	4.1767	4.1767	0.00
15	4.1870	4.1900	0.07
17	4.1805	4.1805	0.00
19	4.1960	4.1960	0.00

The assigned values and their expanded uncertainties were as follows:

- TBT: 64.63 µg/ml ± 0.5 %
- TPhT: 64.63 µg/ml ± 0.5 %.

The uncertainty was estimated according to the sample preparation.

Sample S1

The sample S1 was prepared from a polluted sediment sample taken from the Baltic Sea. The original sample contained tributyltin chloride (TBT), but it did not contained triphenyltin chloride (TPhT). TBT and TPhT was added into the sediment. The sample was mixed, freezedried and distributed in sub samples of 20 g using a rotary sample divider equipped with vibratory sample feeder.

The dry weight of the sediment sample S1 was 99.2 %.

The robust mean of the results obtained in this proficiency test was used as the assigned value for the sample S1. The assigned values and their expanded uncertainties were as follows:

- TBT: 335 µg/kg ± 24.0 %
- TPhT: 160 µg/kg ± 20.3 %.

The uncertainty was estimated on basis of the robust standard deviation (s_{rob}) of all results reported by the participants (the expanded uncertainty $U = 2 \bullet 1.25 \bullet s_{rob} / \sqrt{n}$, in which n = the number of the participants)

APPENDIX 3. TESTING OF THE SAMPLES

Homogeneity

The synthetic sample A1

Three tubes of the sample A1 were tested. There were not systematic differences between the results.

Organotin	Tube 2	Tube 12	Tube 20
TBT µg/ml	68.3	71.1	69.0
TPhT µg/ml	71.6	73.2	72.8

The calculated concentration of the sample A1 was 64.641 µg/ml.

The sediment sample S1

Homogeneity was tested as duplicate determinations from nine bottles of the sample S1. The analytical variation s_a and the between bottle variation s_{bb} was calculated using one-way variance analysis. For this proficiency test the results were recalculated by taking into account the IUPAC procedure for the treatment of homogeneity testing data and the target values of total deviation [4].

Organo-tin	Conc. µg/kg	$1s_{target}$ %	$0.3s_t$	s_a	s_a %	$s_a/s_{target}<0.5$	s_{bb}	s_{bb} %	$s_{bb}^2 <c$
TBT	348,5	20	20.91	21,57	6.2	yes	15,29	4,4	yes
TPhT	222,6	20	13,36	16,3	7,3	yes	11,56	5,2	yes

The analytical variation s_a was accepted, because $s_a/s_{target} < 0.5$.

The between-bottle variation s_{bb} was smaller than the criteria $c = F1 \bullet s_{all}^2 + F2 \bullet s_a^2$, where
$s_{all}^2 = (0.3s_{target})^2$,
F1 = 1.94 and F2 = 1.11, when nine bottles were tested.

The results showed, that the sample S1 was homogenous.

Stability

The synthetic sample A1

The samples were distributed on 13 November 2007 and they were asked to analyzed before 12 December 2007.

The testing laboratory analyzed the sample A1 the first time on 7 November 2007 and the second time 20 November 2007. The results were as follows:

Organotin	7 November 2007	20 November 2007
TBT µg/ml	69.5	71.8
TPhTµg/ml	72.5	71.8

The sediment sample S1

The stability of the sediment sample was not tested, because the testing laboratory was not able to carry out analysis later in December 2007 because of change of residence. However, the laboratory 6 analyzed the samples as late as 19-20 December 2007 and they results were close to the assigned values (see Appendix 7, the laboratory 6).

APPENDIX 4. COMMENTS SENT BY THE PARTICIPANTS

Comments sent by the participants:

Lab 2: The laboratory had problems with equipment and in particular in derivation step of the sample A1.

Lab 4 : The sample A1 was diluted and tested on GC-MS. The standards of the laboratory were ethylderivates in cyclohexane, thus TBT and TPhT in methanol (the sample A1) had different retention times. The laboratory did not used an internal standard in analysis of the sample A1. The laboratory was unsure, if the response factors were same in use of methanol and cyclohexane.

APPENDIX 5. ANALYTICAL METHODS

TBT and TPhT / Sample S1/Extraction, derivatization and clean-up

Lab	Reference	Sample amount	Extraction Solvent/Time	Derivatisation	Extraction method	Extraction time	Extraction clean-up
1	J. of Chromatography A975 (2002), 319-333	0,5 g	0,02 % tropolone-ether-hexane (8:2)/2x4,0 ml	Acidic	NaCl-leaching, acetic acid-acidification and extraction	2x30 min	Al_2O_3 (3 cm in pasteur-pipet), eluation with 4 % ether-hexane (10 ml)
2				Acidic	Ultrasonic	2x60 min	
3		1 g	10 ml	Acidic	Liquid-liquid extraction	30 min	Al_2O_3
4		1 g	35 ml	Acidic	Liquid-liquid extraction	55 min	
5		3,5 g	Methylenchloride tropolin/50 ml	Hexyl MgBr	Ultrasonic	20 min	Florisil column
6		1 g	12 ml	Acidic	Ultrasonic + shaking	60 min	
7		0,5 g	Acetic acid-methanol (3:1)/4 ml	Tetraethylborate/ tetra-hydrolfurane	Ultrasonic	6x2 min	Silicagel-sodiumsuplphate
8		4 g	Acidic methanol/50-60 ml	No	ASE	5 min	No

TBT and TPhT / Measurement and MS-conditions

Lab	Instru-ment	Injection model	Injection		Colum-oven T	Carrier Gas/Gas flow	Ionization mode	Instrument type	Resolu-tion
			Vol.	T °C					
1	GC-MS	Split/splitless	2 µl	250	50 °C/1 min – 15 °C/1 min –> 280 °C/4 min	Helium/1,0 ml/min		Sector	8000
2	GC-MS	Splittless	2 µl	280	50 °C/2 min – 10 °C/1 min –> 300 °C	Helium/1,0 ml/min	Electron capture	MSD	
3	GC-AED	Split/splitless	1 µl	280	60 °C/ – 10 °C –> 300 °C	Helium/1,6 ml/min			
4	GC-PPPD	Split/splitless	5 µl	260	90 °C/1 min – 15 °C/1 min –> 90 °C -1 °C/1 min –> 99 °C – 17 °C/1 min –> 200 °C – 20 °C/1 min –> 280 °C	Helium/1,5 ml/min			
5	GC-MS	Splitless (pulsed)	2 µl	300	40 °C/1 min – 20 °C/1 min –> 100 °C – 10 °C/1 min –> 300 °C	Helium/1,0 ml/min	Electron capture	Quadropol	Low
6	GC-MS	Splittless	1 µl	300	50 °C/2 min – 6 °C/1 min –> 240 °C/2 min – 20 °C/1 min –> 300 °C/9 min			MS	
7	GC-MS	Splitless (pulsed)	1 µl	250	60 °C/1 min – 10 °C/1 min –> 200 °C/0 min – 2 °C/1 min –> 250 °C/5 min - 10 °C/1 min –>270 °C				
8	HPLC-MS		20 µl	ambient			ESI	triple Quadropol	

TBT and TPhT / Calibration, integration, calculation and analysis dates

Lab	Internal standards	Calibration range	No of calib. points	Curve fitting	Weighing mode	Dates: Extraction and clean-up	Dates: Measurement	Comments
1	Deuterated analogs	5-100 ng/ml	3	Linear		16.-21.11.2007	22.11.2007	
2	Tripropyl- and tripentyltin	5-3000 ng/ml	7	Linear	1/x	19.11.2007	10.12.2007	Problems with derivation step (A1)
3	Tetrapropyl- and tripropyltin, monophenyltin	1-100 ng/ml	6			3.-12.12.2007	5.-12.2007	
4	TPT	1-500 ng/l	7	Quadratic	equal			Standards in cyclohexane – the sample A1 was in methanol
5	Tetrapropyltin	100-5000 ng/ml	4			30.11.2007	30.11.2007	
6	Tetrapropyl- ja dipropyltin, dimethyltin, triphenyltin	20-1000 ng/l	5	Linear		19.11.2007	19.-20.12.2007	
7	Tripropyltin		1			12.12.2007	12.-18.12.2007	
8	None	20-60 ng/ml	3	Linear	equal	19.11.2007	23.11.-5.12.2007	Standard addition procedure

APPENDIX 6. 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)
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:
$X^* = \sum x_i^* / p$

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

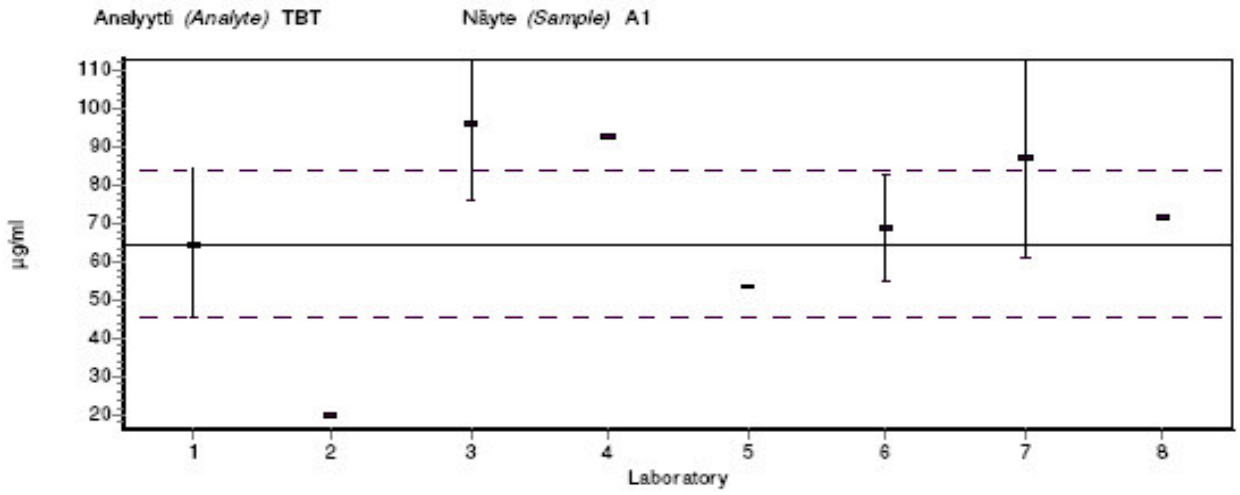
The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergenes.

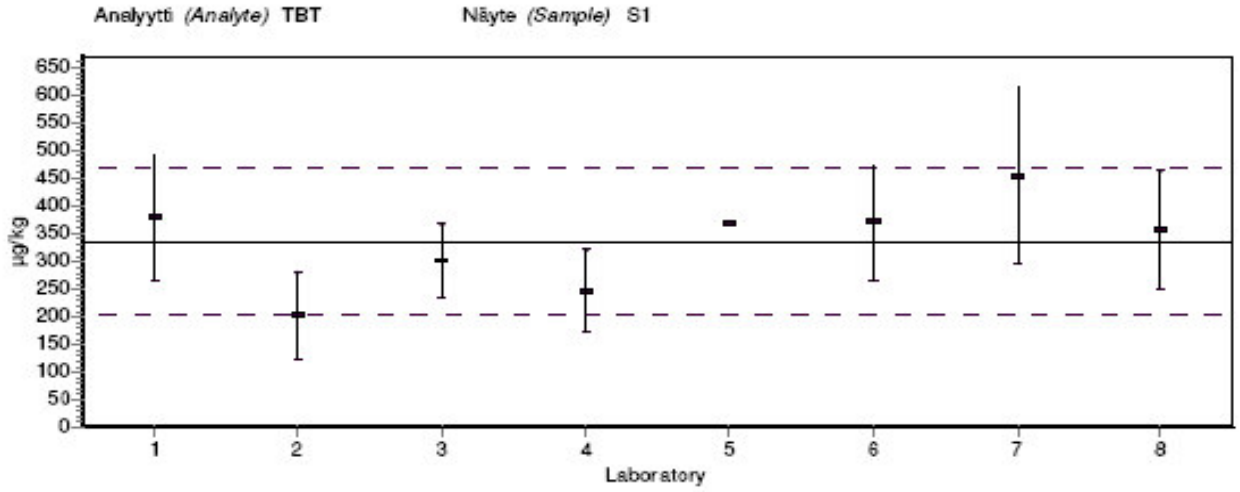
Ref: Statistical methods for use in proficiency testing by interlaboratory comparisons, Annex C (ISO13528).

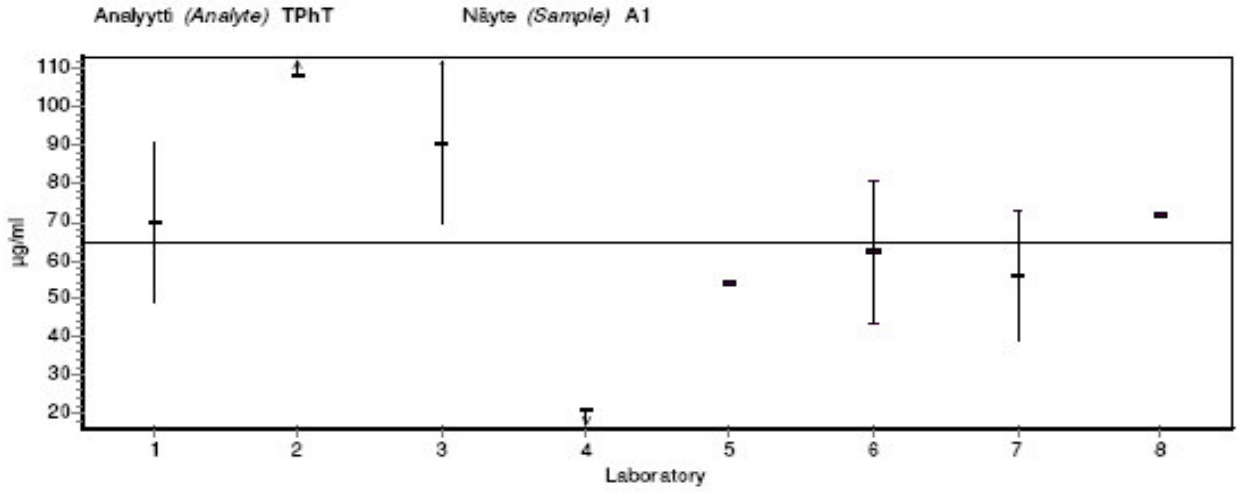
APPENDIX 7. RESULTS OF EACH PARTICIPANT

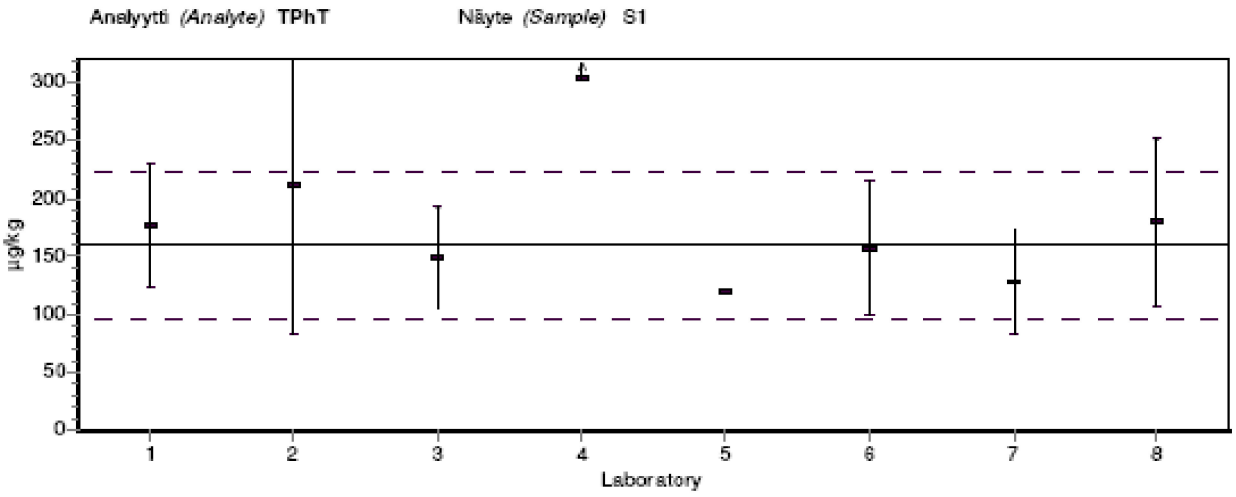
Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
TBT	µg/ml	A1		0,021	yes	64,63	30	64,83	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		0,686	yes	335	40	381	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		0,530	yes	64,63	30	69,77	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		0,523	yes	160	40	176,7	155	160,5	31,63	19,7	7	1	0	8
Laboratory 2																
TBT	µg/ml	A1		-4,614	yes	64,63	30	19,9	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		-1,990	H	335	40	202,3	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		16,300	H	64,63	30	222,7	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		1,615	yes	160	40	211,7	155	160,5	31,63	19,7	7	1	0	8
Laboratory 3																
TBT	µg/ml	A1		3,260	yes	64,63	30	96,23	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		-0,479	yes	335	40	302,9	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		2,691	yes	64,63	30	90,72	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		-0,353	yes	160	40	148,7	155	160,5	31,63	19,7	7	1	0	8
Laboratory 4																
TBT	µg/ml	A1		2,906	yes	64,63	30	92,8	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		-1,313	yes	335	40	247	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		-6,505	yes	64,63	30	1,57	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		12,470	H	160	40	559	155	160,5	31,63	19,7	7	1	0	8
Laboratory 5																
TBT	µg/ml	A1		-1,149	yes	64,63	30	53,5	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		0,483	yes	335	40	367,3	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		-1,096	yes	64,63	30	54	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		-1,240	yes	160	40	120,3	155	160,5	31,63	19,7	7	1	0	8
Laboratory 6																
TBT	µg/ml	A1		0,458	yes	64,63	30	69,07	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		0,522	yes	335	40	370	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		-0,240	yes	64,63	30	62,3	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		-0,083	yes	160	40	157,3	155	160,5	31,63	19,7	7	1	0	8
Laboratory 7																
TBT	µg/ml	A1		2,342	yes	64,63	30	87,33	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		1,766	yes	335	40	453,3	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		-0,890	yes	64,63	30	56	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		-0,990	yes	160	40	128,3	155	160,5	31,63	19,7	7	1	0	8
Laboratory 8																
TBT	µg/ml	A1		0,736	yes	64,63	30	71,77	71,4	70,12	24,21	34,5	8	0	0	8
	µg/kg	S1		0,323	yes	335	40	356,7	366	365,3	55,11	15,0	7	1	0	8
TPhT	µg/ml	A1		0,743	yes	64,63	30	71,83	63,25	58,23	27,15	46,6	7	1	0	8
	µg/kg	S1		0,635	yes	160	40	180,3	155	160,5	31,63	19,7	7	1	0	8

APPENDIX 8. RESULTS AND UNCERTAINTY ESTIMATES REPORTED BY PARTICIPANTS





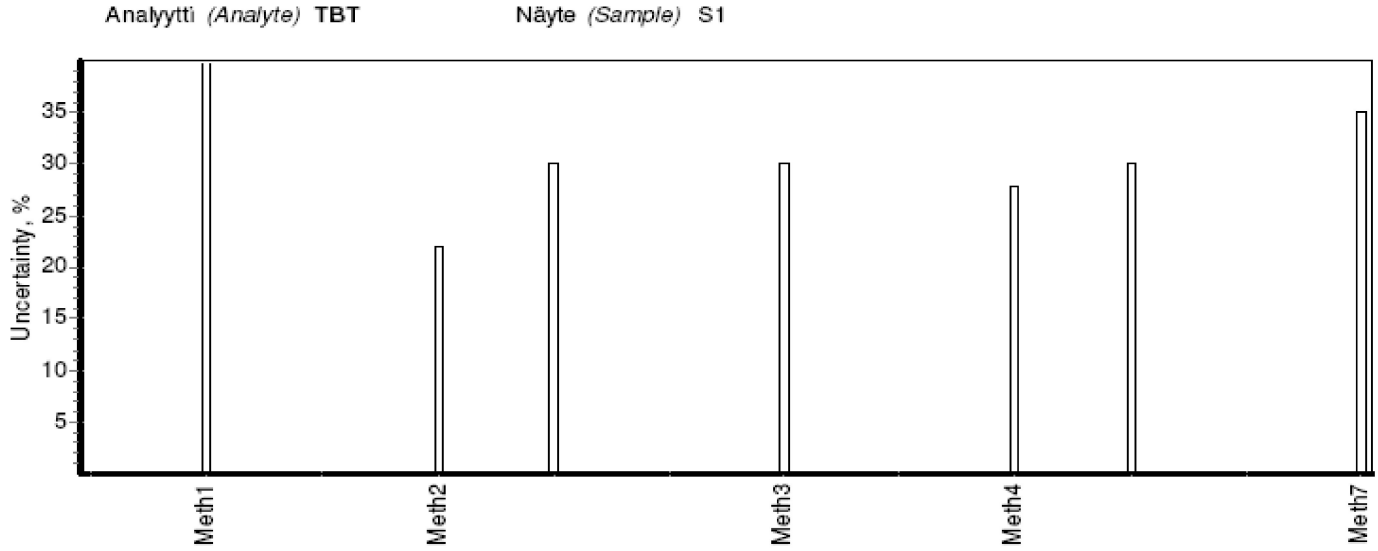


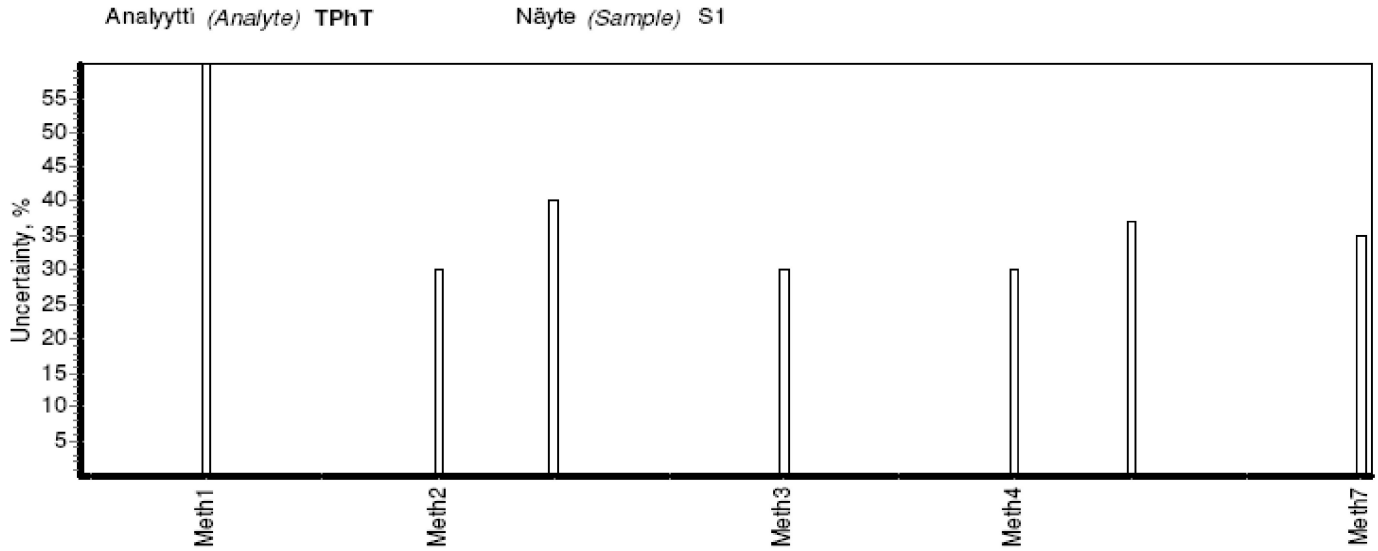

Analyytti (Analyte) TPhT
Näyte (Sample) S1
µg/kg
300
250
200
150
100
50
0
1
2
3
4
5
6
7
8
Laboratory

APPENDIX 9. MEASUREMENT UNCERTAINTIES AND ESTIMATION PROCEDURES REPORTED BY THE PARTICIPANTS

Uncertainties were estimated using the procedures as follows:

1 using the IQC data (X chart)
2 using the IQC data (X-chart and also R- chart or r%-chart for real samples)
3 using the data obtained in method validation and IQC, see e.g. NORDTEST TR 537[1)]
4 using the data obtained in the analysis of CRM (besides IQC data), see e.g.NORDTEST TR 537 [1)]
5 using the IQC data and the results obtained in proficiency tests, see e.g. NORDTEST TR 537[1)]
6 using the "modeling approach" (GUM Guide or EURACHEM Guide Quantifying Uncertainty in Analytical Measurements[2]
7 other procedure
8 no uncertainty estimation





APPENDIX 10. SUMMARY OF Z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	%
TBT	A1	A	**N**	**P**	p	A	A	p	A	50
	S1	A	A	A	A	A	A	A	A	100
TPhT	A1	A	**P**	p	**N**	A	A	A	A	62
	S1	A	A	A	**P**	A	A	A	A	88
% Accredited		100 yes	50	50 yes	25 yes	100	100 yes	75	100 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: 75 In accredited: 75 In non-accredited: 75

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date April 2008
Author(s)	Irma Mäkinen, Jari Nuutinen and Pirjo Tikkanen	
Title of publication	SYKE Proficiency test 9/2007 Organotins from sediment	
Parts of publication/ other project publications	Publication is also available in the internet www.ymparisto.fi/julkaisut	
Abstract	The Finnish Environment Institute (SYKE) carried out the proficiency test for the determination of organotins (tributyltin TBT and triphenyltin TPhT) from the polluted sediment in November 2007. One artificial sample and one sediment sample was delivered to eight participating laboratories. The robust standard deviations were much higher (TBT: 32 % and TPhT: 46 %) in analysis of the artificial sample than in analysis of the sediment sample (TBT: 27 % and TPhT: 22 %). Two participants reported having analytical problems particularly in analysis of the artificial sample. In this proficiency test, the robust mean value was used as the assigned value. When the target total deviation was 30 % for the artificial sample and 40 % for the sediment sample in calculating of z scores at the 95 % confidence interval, 75 % of the participating laboratories reported satisfactory results. In analysis of the sediment sample 100 % of TBT-results and 88 % of TPhT-results were considered satisfactory.	
Keywords	organotins, sediment, environmental laboratories, proficiency test, interlaboratory comparisons	
Publication series and number	Reports of Finnish Environment Institute 12/2008	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
	ISSN 1796-1718 (print) 1796-1726 (online)	ISBN 978-952-11-3106-6 (pbk.) 978-952-11-3107-3 (PDF)
	No. of pages 27	Language english
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Printing place and year	Edita Prima Ltd, Helsinki 2008	
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Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Huhtikuu 2008
Tekijä(t)	Irma Mäkinen, Jari Nuutinen ja Pirjo Tikkanen	
Julkaisun nimi	SYKE pätevyyskoe 9/2007 Organotinayhdisteet sedimentistä	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana myös internetistä www.ymparisto.fi/julkaisut	
Tiivistelmä	Suomen ympäristökeskus järjesti marraskuussa 2007 pätevyyskokeen kahden organotinayhdisteen (tributyylitina TBT ja trifenyylitina TPhT) analysoimiseksi sedimentistä. Osallistujille toimitettiin yksi synteettinen näyte ja yksi sedimenttinäyte. Pätevyyskokeeseen osallistui kahdeksan laboratoriota. Analyysimenetelmät erosivat toisistaan mm. uuttoliuosten, uuttotekniikan ja sisäisen standardin suhteen. Tulosten hajonta oli suurempi synteettisen näytteen (TBT: 32 % ja TPhT: 46 %) kuin sedimenttinäytteen analysoinnissa (TBT: 27 % ja TPhT: 22 %). Tulosten hajontaan vaikutti kahdella laboratoriolla esiintyneet analyyttiset ongelmat erityisesti synteettisen näytteen analysoinnissa. Vertailuarvona käytettiin robustia keskiarvoa. Tässä pätevyyskokeessa 75 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin synteettiselle näytteelle 30 % ja sedimenttinäytteelle 40 % 95 % merkitsevyystasolla. Sedimenttinäytteen analysoinnissa TBT-yhdisteen tuloksista 100 % ja TPhT-yhdisteen tuloksista 88 % oli tyydyttäviä.	
Asiasanat	Organotinayhdisteet, sedimentti, ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailukoe	
Julkaisusarjan nimi ja numero	Reports of Finnish Environment Institute 12/2008	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
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Projektiryhmään kuuluvat organisaatiot		
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Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2008	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum April 2008
Författare	Irma Mäkinen, Jari Nuutinen och Pirjo Tikkanen	
Publikationens titel	Provningsjämförelse 9-2007 Organiska tenföreningar av sediment	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig också på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under november 2007 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av två organiska tenföreningar (TBT, TPhT) av sediment. Ett syntetisk prov och ett sediment prov hade sent till laboratorier. Olika analysmetoder hade användts för analys av organiska tenföreningar. I särskildt, extraktion teknik extraktion-lösningar och kalibreringen varierade i olika labortorier. Som referensvärde (*the assigned value*) användes robust medelvärdet. Resultaten värderades med hjälp av z-värden. Beräkningen av z-värdena baserade sig på totalavvikelser, som sattes till 30 % (syntetiska provet) och till 40 % (sediemntprovet) på 95 % sannolikhetsnivå. I denna provningsjämförelse, 75 % av resultatena var tillfredsställande. I analys av sedimentprovet 100 % av TBT-resultatena och 88 % av TPhT-resultatenavar tillfredsställande.	
Nyckelord	organotin, sediment proven, provningsjämförelse, miljölaboratorier	
Publikationsserie och nummer	Reports of Finnish Environment Institute 12/2008	
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