CEN/TC 230/WG 1
Physical and biochemical methods
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Secretariat: DIN

EN 16693 (OCP) ILC report

Date of document	2014-09-02
Expected action	Next Meeting
Due Date	2014-10-21

– Report –

EN 16693 – interlaboratory trial for validation on OCPs (CEN/TC 230/WG 1 – M/424)

Water quality — Determination of organochlorine pesticides (OCP) in whole water samples — Method using disk based solid phase extraction (SPE) combined with gas chromatography mass spectrometry (GC-MS)

provided by

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Muelheim an der Ruhr, September 2014

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Content

1 General

This interlaboratory trial for validation was organized within the standardization project for establishing EN 16693. This European Standard specifies a method dedicated for the determination organochlorine pesticides (OCP) in surface water samples containing amounts of suspended particulate matter (SPM) up to 500 mg/l ("whole water samples") by means of disk based solid-phase extraction followed by gas chromatography-mass spectrometry (GC-MS). The method is applicable to drinking water and ground water as well. The following parameters listed in Table 1 below were included in the ring trial for measurement.

Table 1 OCP-Listing of substances included in the interlaboratory trial for validation on EN 16693

Name	Molecular formula	CAS registry No.	Molar mass	Annual average environmental quality standards (AA-EQS) in µg/l – surface water –	
			g/mol	Inland	Other
Alachlor *	$C_{14}H_{20}ClNO_2$	15972-60-8	269,77	0,3	0,3
Cyclodiene pesticides:				Σ= 0,01	Σ= 0,005
Aldrin *	$C_{12}H_8Cl_6$	309-00-2	364,91		
Dieldrin *	$C_{12}H_8Cl_6O$	60-57-1	380,91		
Endrin *	$C_{12}H_8Cl_6O$	72-20-8	380,91		
Isodrin *	$C_{12}H_8Cl_6$	465-73-6	364,91		
DDT-total:				Σ= 0,025	Σ= 0,025
op´-DDT *	$C_{14}H_9Cl_5$	789-02-6	354,49		
pp´-DDT *	$C_{14}H_9Cl_5$	50-29-3	354,49		
pp´-DDD *	$C_{14}H_{10}Cl_4$	72-54-8	320,04		
pp´-DDE *	$C_{14}H_8Cl_4$	72-55-9	318,03		
Hexachlorobenzene (HCB) *	C_6Cl_6	118-74-1	284,80	0,01	0,01
Hexachlorobutadiene (HCBD) *	C_4Cl_6	87-68-3	260,76	0,1	0,1
Hexachlorocyclohexane: **				Σ= 0,02	Σ= 0,002
alpha-HCH *	$C_6H_6Cl_6$	319-84-6	290,83		
beta-HCH *	$C_6H_6Cl_6$	319-85-7	290,83		
delta-HCH *	$C_6H_6Cl_6$	319-86-8	290,83		
gamma-HCH *	$C_6H_6Cl_6$	58-89-9	290,83		
Pentachlorobenzene *	C_6HCl_5	608-93-5	250,34	0,007	0,0007
Trichlorobenzene: **				Σ= 0,4	Σ= 0,4
1,2,3-TCB *	$C_6H_3Cl_3$	87-61-6	181,45		
1,2,4-TCB *	$C_6H_3Cl_3$	120-82-1	181,45		
1,3,5-TCB *	$C_6H_3Cl_3$	108-70-3	181,45		
Endosulfan: **				Σ= 0,005	Σ= 0,0005
Endosulfan-I (alpha) *	$C_9H_6Cl_6O_3S$	959-98-8	406,93		
Endosulfan-II (beta) *	$C_9H_6Cl_6O_3S$	33213-65-9	406,93		

(*) Parameter to be analysed within the interlaboratory trial for validation
(**) Mixture of isomers

The ring trial was designed to serve as a validation exercise and not a proficiency testing trial. Therefore, it was mandatory for all participants to be included in the evaluation process to strictly follow the procedure as prescribed in the draft standard (prEN 16693) that had been made available for each participant early in 2014.

2 Principle

The organochlorine pesticides present in the whole water sample are extracted by means of solid-phase extraction using solid-phase extraction disks (SPE-disks). Samples shall not be filtered. An internal standard mixture is added to the sample prior to extraction. Extraction by SPE-disks includes a combined extraction of both the analytes dissolved in the liquid phase of the sample and those adsorbed to the suspended particulate matter. The latter is extracted within the elution step of the procedure.

The extract is concentrated by evaporation and the analytes are separated, identified and quantified by means of capillary gas chromatography with mass spectrometric detection (GC-MS) using electron impact (EI) ionisation mode. Compounds endosulfan-I (alpha) and endosulfan-II (beta) may require additional efforts on sample enrichment by either large volume injection (LVI) of sample extract evaporation of solvent extracts down to a lower final volume.

3 PT design and sample preparation

- **Announcement of the interlab-trial: November 2013**
- **Expression of interest by labs: December, 15th 2013**
- **Final registration of participants: January 2014**
- **Dispatch of samples: June, 3rd 2014**
- **Deadline for results: July, 15th 2014**
- **Evaluation according ISO 5725-2: August 2014**

Each participant got 4 samples

Sample 1: Low level sample without SPM (2x 1000 mL);
Sample 2: Low level sample containing SPM (2x 1000 mL);
Sample 3: High level sample containing SPM (2x 1000 mL);
Sample 4: Blank sample (2x 1000 mL).

The matrix of each sample had been surface water surface water taken from an urban and industrialized area (river Ruhr in Muelheim, Germany). The water was filtered using a glass-fibre filter prior to OCP and/or sediment spiking. Each sample had been prepared from one 50-litre-batch of filtered surface water (glass container) as follows:

Sample 1: OCP batch spiking-A → bottling of empty glass bottles
Sample 2: OCP batch spiking-B → bottling of glass bottles containing 20 mg of CRM
Sample 3: OCP batch spiking-C → bottling of glass bottles containing 200 mg of CRM
Sample 4: batch of surface water → bottling of empty glass bottles

SPM spiking had been carried out by using commercially available certified reference material (CRM, pesticides Clay Loam 1, CRM847-50G, Lot-No 002405), weighed to each bottle.

- All samples contained 200 µl/l acetone as solutizer.
- **Sample conservation** was by addition of 40 mg/l of sodium azide to each surface water batch

The following information in terms of anticipated concentrations were announced to all participants in advance:

1) Sample 1+2: concentrations close to the corresponding environmental quality standards for inland surface water (EQS) up to 3-times EQS, except for some organochlorine pesticides where concentrations may be below EQS
2) Sample 3: concentrations 5 to 20 times EQS for inland surface water, except for some organochlorine pesticides where concentrations may be below EQS
3) Sample 4: Blank – If the result is < LOQ, the laboratory has to report actually applied LOQ in "µg/l" (e. g. "< 0,001").
4) Concentrations of individual substances spiked are in the range from 0,01 µg/l to 0,50 µg/l.
5) All analytes listed in Table 1 are present (spiked) in quantifiable concentrations in samples 1, 2 and 3.

All participants had to work on 2 independent replicate analyses on each sample.

4 Stability testing

Stability testing had been carried out on 16 measurement days by IWW Water Centre, Muelheim an der Ruhr, Germany. Concentrations for individual substances in these experiments range from 0,5 µg/l to 5 µg/l. Results of stability testing experiments are listed in Table 2 and Figure 1 for spiked surface water samples. Results of each parameter are expressed as “mean” and are calculated from 7-12 individual measurements. It can be seen from the results that all samples are stable for more than 14 days, most of them even for more than 3 weeks.

Table 2

Interlaboratory trial for validation EN 16693 / stability testing

OCP-spiked surface water

substance name	recovery of samples analysed after 4, 7, 12, 15 and 21 days all values listed in each column are derived from 7 to 12 individual measurements and calculated as "mean".					moving average of mean recovery values in %			
	samples (after 4 d)	samples (after 7 d)	samples (after 12 d)	samples (after 15 d)	samples (after 21 d)	after 4-7 d	after 7-12 d	after 12-15 d	after 15-21 d
Alachlor	89	122	105	83	101	5	13	-6	-8
Aldrin	82	98	90	127	100	-10	-6	9	14
Dieldrin	103	89	99	107	101	-4	-6	3	4
Endrin	111	105	86	110	91	8	-5	-2	1
Isodrin	89	113	95	95	107	1	4	-5	1
op´-DDT	103	84	93	109	108	-6	-11	1	8
pp´-DDT	72	106	90	118	111	-11	-2	4	14
pp´-DDD	87	108	94	110	100	-2	1	2	5
pp´-DDE	90	89	112	112	98	-10	1	12	5
Hexachlorobenzene (HCB)	82	93	104	100	116	-13	-2	2	8
Hexachlorobutadiene (HCBD)	106	84	101	103	95	-5	-8	2	-1
alpha-HCH	80	94	97	86	110	-13	-5	-9	-2
beta-HCH	98	97	107	89	107	-3	2	-2	-2
delta-HCH	88	92	114	106	94	-10	3	10	0
gamma-HCH	70	104	108	92	120	-13	6	0	6
Pentachlorobenzene	111	86	97	90	112	-2	-9	-7	1
1,2,3-TCB	107	80	124	82	69	-7	2	3	*-25*
1,2,4-TCB	92	75	128	87	41	-17	1	8	*-36*
1,3,5-TCB	129	121	117	76	44	25	19	-4	*-40*
Endosulfan-I (alpha)	75	112	106	124	102	-6	9	15	13
Endosulfan-II (beta)	106	116	92	91	86	11	4	-9	-12

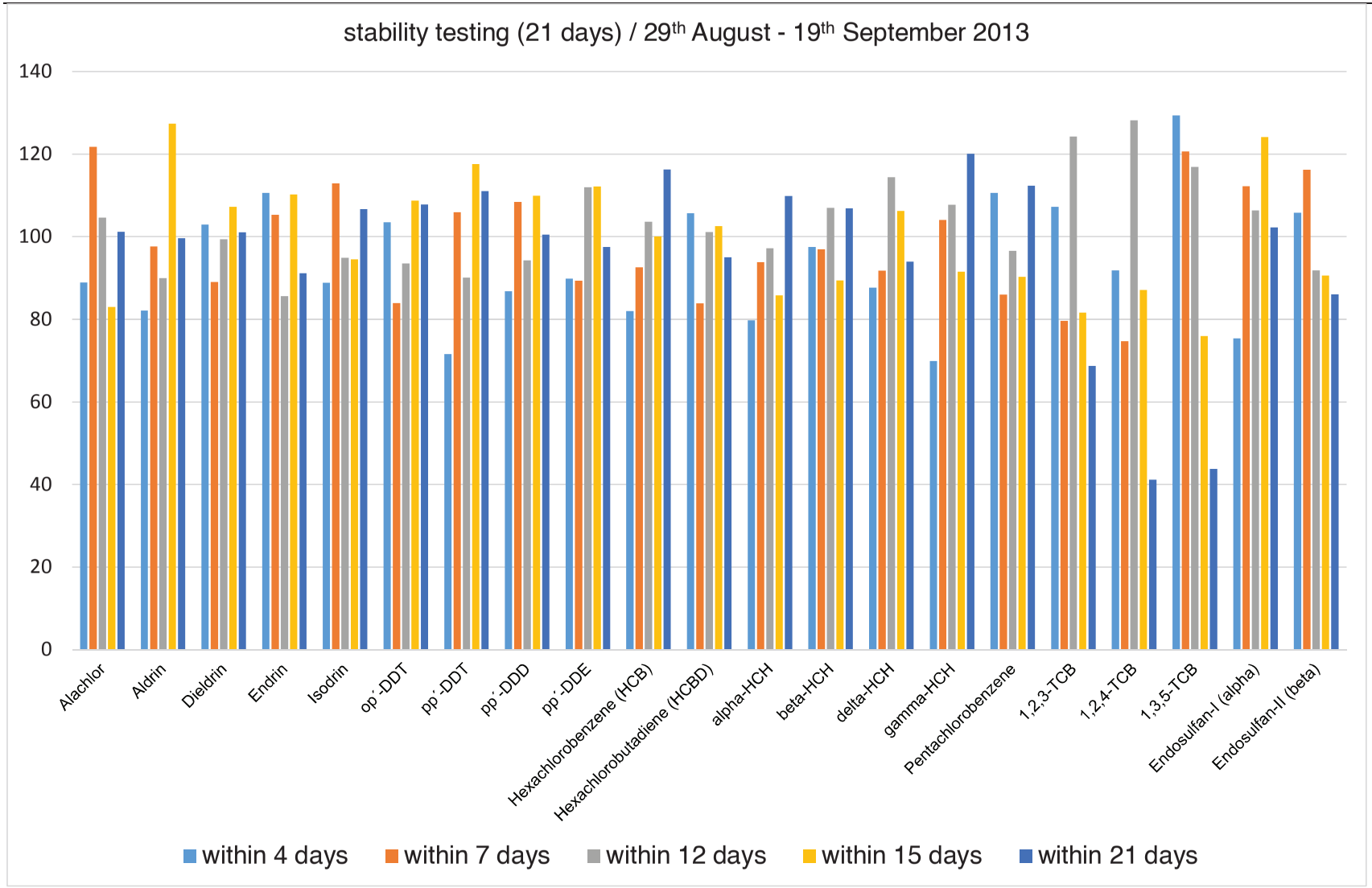

Figure 1: Stability testing experiments carried out on 16 measurement days. Each bar shows results derived from 7-12 individual measurements calculated as "mean".

5 Technical aspects

5.1 Participants

All samples were shipped to the 17 participating laboratories on June, 3rd 2014.

17 Participants out of 10 countries

- Belgium 3x
- France 1x
- Germany 2x
- Italy 1x
- Lithuania 1x
- Netherlands 2x
- Norway 1x
- Portugal 1x
- Spain 3x
- United Kingdom 2x

Four labs did not submit results, one of them without any comment. Results from one lab had to be excluded from evaluation because of significant deviation from the procedure prescribed in the draft standard.

A total of 12 labs reported results to be included in the evaluation process according ISO 5725-2.

5.2 Examples of reported procedural details

An electronic record sheet (EXCEL file) was distributed by e-mail to all participants on 3rd of June 2014. Data submission of results was exclusively done electronically using partly inaccessible EXCEL data reporting spreadsheets enabling subsequent automatic data transfer for computerized evaluation.

Finally, participants were asked to fill in some attached Excel spreadsheets which included a comprehensive questionnaire for additional information on procedural details. This included general information about the measurements and procedural details as well as on interferences observed. In some cases a choice between pre-set options was offered by tick-boxes.

Examples of reported technical details:

Sample preparation: a) manually (11x), b) automated (2x).

Disk: Type of adsorbent: a) C18 (8x), b) DVB (4x), c) mixed (1x).

Diameter: 47 – 50 mm (all)

Drying of disk: a) vacuum supported by N_2 (3x), b) vacuum (ambient air) (9x), c) nitrogen (N_2) (1x).

Drying time: a) < 10 min (3x), b) 10 – 15 min (4x), c) > 15 min (6x).

Solvent evaporation: a) vacuum supported by N_2 (1x), b) vacuum (ambient air) (2x), c) nitrogen (N_2) (9x), d) no solvent evaporation (1x).

Injection standard for volume control added: (10x)

Final volume: a) < 0,5 ml (2x), b) 0,5 – 1 ml (9x), c) > 15 min (2x).

Columns according recommendations in clause 6.8 of prEN 16693: (all)

Dimensions [length (m) x diameter (μm) x film (μm)]:
20 x 0,18 x 0,18 (2x),
25 x 0,33 x 0,20 (1x),
30 x 0,25 x 0,25 (8x),
60 x 0,25 x 0,25 (2x).

Injector: Type: a) fixed temp. (5x), b) PTV (8x).

Septum included: a) yes (11x), septum purge on b) no (septumless) (2x).

Injection mode: a) splitless (9x), b) LVI (3x), c) open split (0,5) (1x).

Mass specrometer type: a) Q-pol-EI-MS (SIM) (6x), b) Q-pol-MS (MS/MS) (4x), c) ion-trap MS (2x), d) HRMS (SIM) (1x).

Reported LOQ (ng/L): a) 0,1 – 1 (7x), b) > 1 (5x), c) not reported (1x).

Parameter analysed by labs: a) all (6x), b) nearly all (3x).

Internal standards used (all in all 28):

- HCB (^{13}C6) (7x)
- pp´-DDT (^{13}C12) (6x)
- Alachlor (D13) (4x)
- 1,2,3-TCB (D3) (4x)
- pp´-DDE (^{13}C12) (3x)
- Endosulfan-I (alpha) (D4) (3x)
- HCBD (^{13}C4) (3x)
- gamma-HCH (^{13}C6) (3x)
- Alachlor (^{13}C6) (1x)
- op-DDT (^{13}C12) (1x)
- op´-DDT (D8) (1x)
- pp´-DDT (D8) (1x)
- pp´-DDD (^{13}C12) (1x)
- op´-DDE (^{13}C12) (1x)
- Endrin (^{13}C12) (1x)
- alfa-HCH (D6) (1x)
- beta-HCH (^{13}C) (1x)
- gamma-HCH (D6) (1x)
- 1,2,3-TCB (D3) (1x)
- 1,3,5-TCB (D3) (1x)
- 1,2,4,5-TCB (^{13}C) (1x)

other:

- Chrysene (D12) (1x)
- Fluoranthene (D10) (1x)
- Mirex (1x)
- Naphtalene(D8) (1x)
- PCB118 (^{13}C12) (1x)
- Phenantrene (D10) (1x)
- Tetrachloro-m-xylene (1x)

The majority of labs included 3-6 internal standards (max: 8).

6 Annex: Data evaluation according ISO 5725-2

CEN/TC 230/WG 1
Physical and biochemical methods
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Results and graphics interlaboratory trial OCP EN 16693

Date of document	2014-08-29
Expected action	Info

Background

This document contains the results of the interlaboratory trial to validate the method described in EN 16693 "Water quality — Determination of organochlorine pesticides (OCP) in whole water samples – Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)"

For all samples the graphical presentations of the results are included in this document.

Results of the Interlaboratory Trial for the validation of EN 16693
"Determination of organochlorine pesticides (OCP) with SPE-disks combined with GC-MS"

Sample 1: Low OCP-level sample without suspended particulate matter (SPM)
Matrix: Filtered surface water, spiked with OCP

Sample 1

Measurand	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	µg/l	µg/l	%	µg/l	%	µg/l	%
Alachlor	8	16	11,1	0,1625	0,1381	85,0	0,0276	20,0	0,0140	10,1
Aldrin	10	20	0,0	0,0150	0,0126	83,7	0,0026	21,1	0,0010	7,9
Dieldrin	12	23	0,0	0,0200	0,0213	106,3	0,0064	30,1	0,0018	8,5
Endrin	10	20	9,1	0,0200	0,0199	99,3	0,0065	33,0	0,0010	5,2
Isodrin	8	16	11,1	0,0200	0,0166	83,1	0,0038	23,0	0,0008	4,8
op´-DDT	12	24	0,0	0,0360	0,0389	108,0	0,0166	42,7	0,0034	8,7
pp´-DDT	12	24	0,0	0,0227	0,0265	116,6	0,0098	37,2	0,0021	7,8
pp´-DDD	10	20	16,7	0,0361	0,0365	101,1	0,0118	32,4	0,0030	8,4
pp´-DDE	11	22	8,3	0,0450	0,0391	86,9	0,0123	31,5	0,0024	6,2
Hexachlorobenzene	10	20	0,0	0,0240	0,0207	86,0	0,0077	37,3	0,0015	7,4
Hexachlorobutadiene	9	18	0,0	0,1134	0,0706	62,3	0,0195	27,6	0,0056	7,9
alpha-HCH	11	22	8,3	0,0299	0,0246	82,2	0,0104	42,3	0,0016	6,4
beta-HCH	12	24	0,0	0,0303	0,0288	94,9	0,0121	42,2	0,0020	7,1
delta-HCH	11	22	0,0	0,0374	0,0391	104,6	0,0109	27,9	0,0018	4,7
gamma-HCH	12	23	0,0	0,0299	0,0266	89,0	0,0139	52,2	0,0022	8,4
Pentachlorobenzene	9	18	0,0	0,0151	0,0156	103,0	0,0095	60,8	0,0028	18,1
1,2,3-TCB	7	14	12,5	0,3247	0,2491	76,7	0,0695	27,9	0,0072	2,9
1,2,4-TCB	7	14	12,5	0,2573	0,2239	87,0	0,0587	26,2	0,0109	4,9
1,3,5-TCB	8	16	11,1	0,2700	0,2109	78,1	0,0532	25,2	0,0088	4,2
Endosulfan-I (alpha)	10	20	0,0	0,0131	0,0118	89,7	0,0039	33,5	0,0019	15,8
Endosulfan-II (beta)	10	20	0,0	0,0132	0,0102	77,3	0,0036	35,1	0,0009	9,3

Explanation of symbols:

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
X	assigned value (reference value)
$\bar{\bar{x}}$	overall mean of results (without outliers)
η	recovery rate
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

Sample 2: **Low OCP-level sample containing 20 mg SPM**
Matrix: **Filtered surface water, spiked with OCP and SPM**

Sample 2

Measurand	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	µg/l	µg/l	%	µg/l	%	µg/l	%
Alachlor	8	16	11,1	0,3251	0,2663	81,9	0,0470	17,6	0,0220	8,3
Aldrin	9	18	10,0	0,0203	0,0173	85,1	0,0046	26,4	0,0023	13,6
Dieldrin	10	20	16,7	0,0265	0,0279	105,3	0,0038	13,6	0,0021	7,6
Endrin	11	22	0,0	0,0275	0,0320	116,2	0,0084	26,4	0,0039	12,1
Isodrin	10	20	0,0	0,0300	0,0248	82,5	0,0120	48,3	0,0028	11,3
op´-DDT	11	22	8,3	0,0540	0,0455	84,2	0,0108	23,8	0,0052	11,4
pp´-DDT	11	22	8,3	0,0306	0,0306	100,0	0,0093	30,3	0,0045	14,8
pp´-DDD	10	20	16,7	0,0497	0,0458	92,2	0,0140	30,5	0,0034	7,4
pp´-DDE	12	24	0,0	0,0584	0,0530	90,8	0,0166	31,2	0,0037	7,0
Hexachlorobenzene	10	20	0,0	0,0300	0,0249	82,8	0,0074	29,7	0,0016	6,4
Hexachlorobutadiene	9	18	0,0	0,1701	0,0938	55,1	0,0309	33,0	0,0103	11,0
alpha-HCH	11	22	8,3	0,0493	0,0424	85,9	0,0165	38,9	0,0024	5,7
beta-HCH	12	24	0,0	0,0523	0,0543	103,9	0,0254	46,7	0,0071	13,2
delta-HCH	11	22	0,0	0,0612	0,0633	103,4	0,0217	34,4	0,0098	15,6
gamma-HCH	12	24	0,0	0,0516	0,0463	89,6	0,0187	40,4	0,0037	7,9
Pentachlorobenzene	8	16	11,1	0,0189	0,0149	79,0	0,0052	35,1	0,0013	8,4
1,2,3-TCB	8	16	0,0	0,4059	0,2921	72,0	0,1304	44,6	0,0740	25,3
1,2,4-TCB	8	16	0,0	0,3859	0,3324	86,1	0,0880	26,5	0,0610	18,4
1,3,5-TCB	9	18	0,0	0,3240	0,2768	85,4	0,1095	39,6	0,0722	26,1
Endosulfan-I (alpha)	10	20	0,0	0,0139	0,0137	98,6	0,0047	34,6	0,0020	14,8
Endosulfan-II (beta)	10	20	0,0	0,0150	0,0134	89,3	0,0045	33,8	0,0012	9,1

Explanation of symbols: see sample 1

Sample 3: **High OCP-level sample containing 200 mg SPM**
Matrix: **Filtered surface water, spiked with OCP and SPM**

Sample 3

Measurand	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	µg/l	µg/l	%	µg/l	%	µg/l	%
Alachlor	7	14	22,2	0,4334	0,3652	84,3	0,0729	19,9	0,0240	6,6
Aldrin	11	22	0,0	0,1850	0,1511	81,7	0,0326	21,6	0,0114	7,5
Dieldrin	12	24	0,0	0,1250	0,1323	105,8	0,0442	33,4	0,0090	6,8
Endrin	11	22	8,3	0,1834	0,1830	99,8	0,0762	41,7	0,0121	6,6
Isodrin	10	20	0,0	0,1800	0,1478	82,1	0,0417	28,2	0,0127	8,6
op´-DDT	9	18	25,0	0,2400	0,1968	82,0	0,0705	35,8	0,0083	4,2
pp´-DDT	11	22	8,3	0,1612	0,1715	106,4	0,0663	38,7	0,0139	8,1
pp´-DDD	10	20	16,7	0,3406	0,3028	88,9	0,1035	34,2	0,0212	7,0
pp´-DDE	11	22	8,3	0,2056	0,2069	100,6	0,0585	28,3	0,0138	6,7
Hexachlorobenzene	10	20	0,0	0,1080	0,0906	83,9	0,0219	24,2	0,0070	7,7
Hexachlorobutadiene	9	18	0,0	0,3969	0,2181	55,0	0,0929	42,6	0,0086	4,0
alpha-HCH	10	20	16,7	0,2243	0,1751	78,0	0,0686	39,2	0,0102	5,8
beta-HCH	10	20	16,7	0,2164	0,1946	89,9	0,0730	37,5	0,0116	5,9
delta-HCH	10	20	9,1	0,2527	0,2185	86,5	0,0614	28,1	0,0181	8,3
gamma-HCH	11	22	8,3	0,2274	0,1957	86,1	0,0647	33,1	0,0063	3,2
Pentachlorobenzene	8	16	11,1	0,0906	0,0749	82,7	0,0167	22,3	0,0056	7,4
1,2,3-TCB	7	14	12,5	0,4871	0,3614	74,2	0,1295	35,8	0,0245	6,8
1,2,4-TCB	7	14	12,5	0,5065	0,3754	74,1	0,1357	36,1	0,0190	5,1
1,3,5-TCB	8	16	11,1	0,4860	0,3518	72,4	0,1598	45,4	0,0127	3,6
Endosulfan-I (alpha)	11	22	0,0	0,0871	0,0814	93,4	0,0304	37,4	0,0074	9,1
Endosulfan-II (beta)	10	20	9,1	0,0621	0,0623	100,3	0,0381	61,2	0,0054	8,7

Explanation of symbols: see sample 1

Graphical presentation of the results of the Interlaboratory Trial for the validation of EN 16693
Determination of organochlorine pesticides (OCP) with SPE-disks combined with GC-MS

Sample 1: **Low OCP-level sample without suspended particulate matter (SPM)**
Matrix: **Filtered surface water, spiked with OCP**

Legend: reference value
overall mean

Outliers: A outlying single result of one laboratory,
B outlying laboratory mean,
C outlying within-laboratory variance

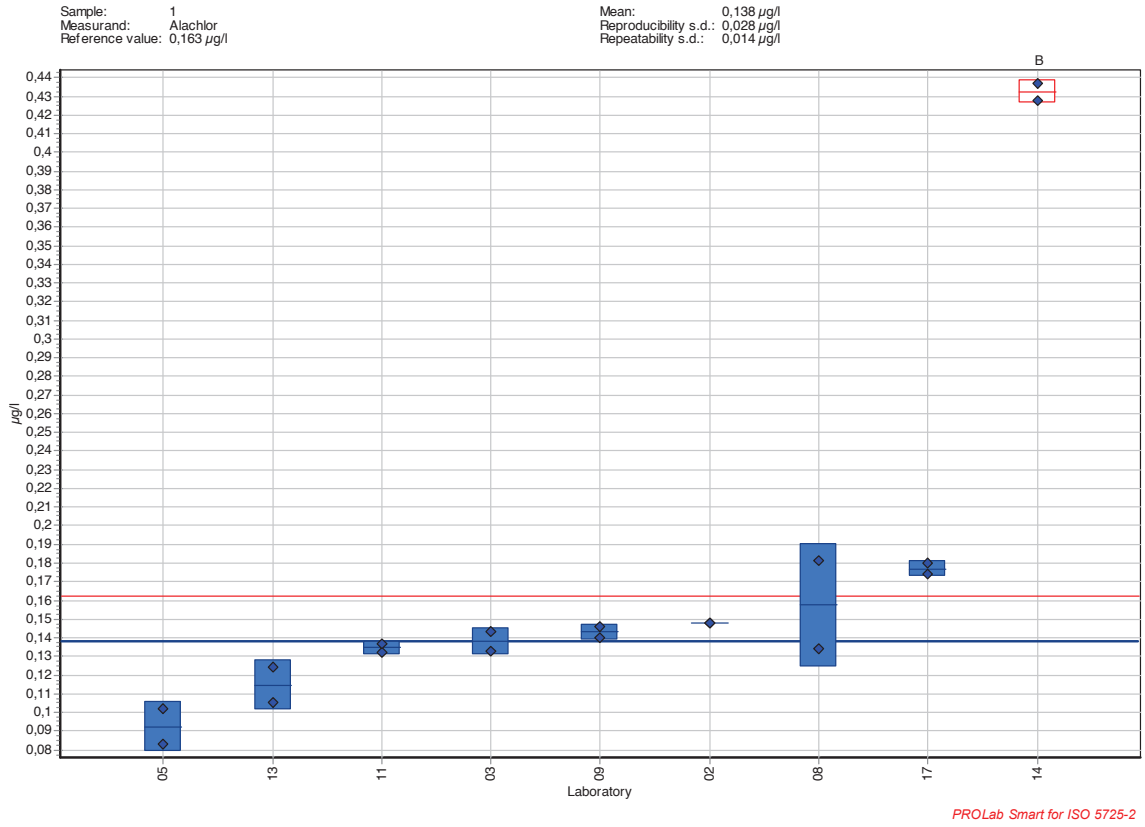

Figure 1: Alachlor, sample 1

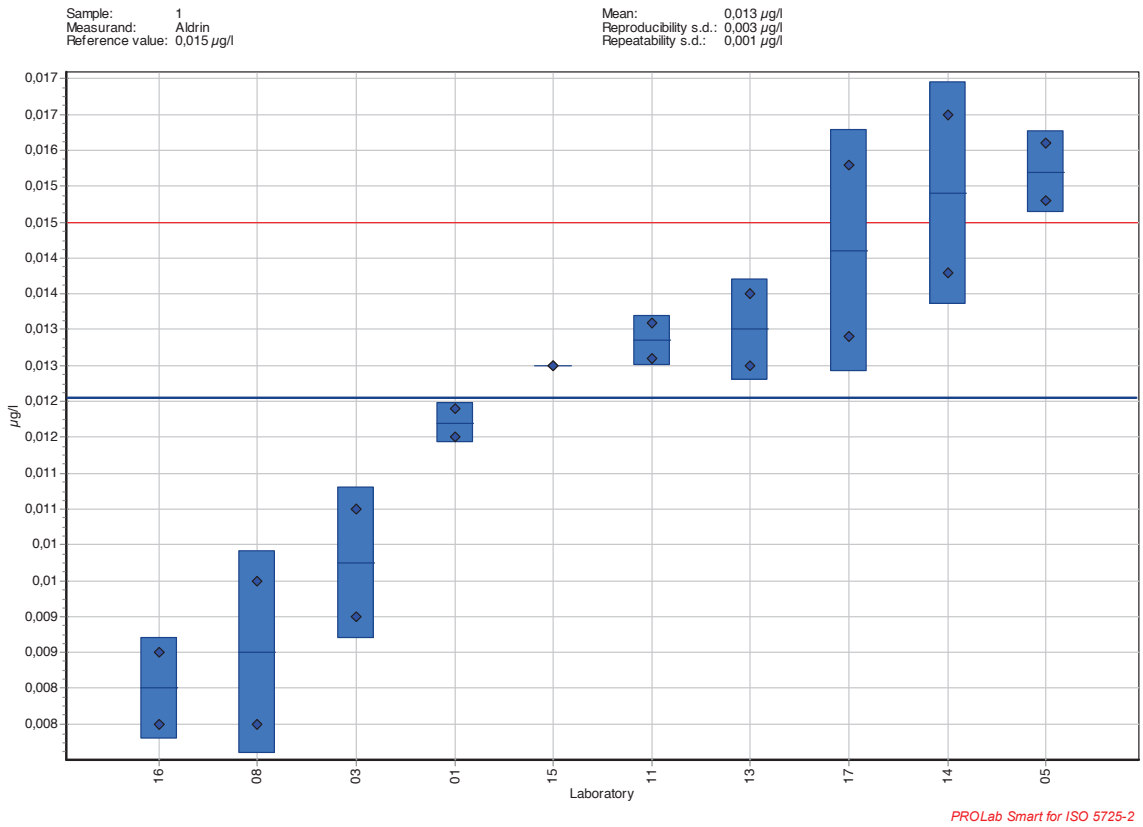

Figure 2: Aldrin, sample 1

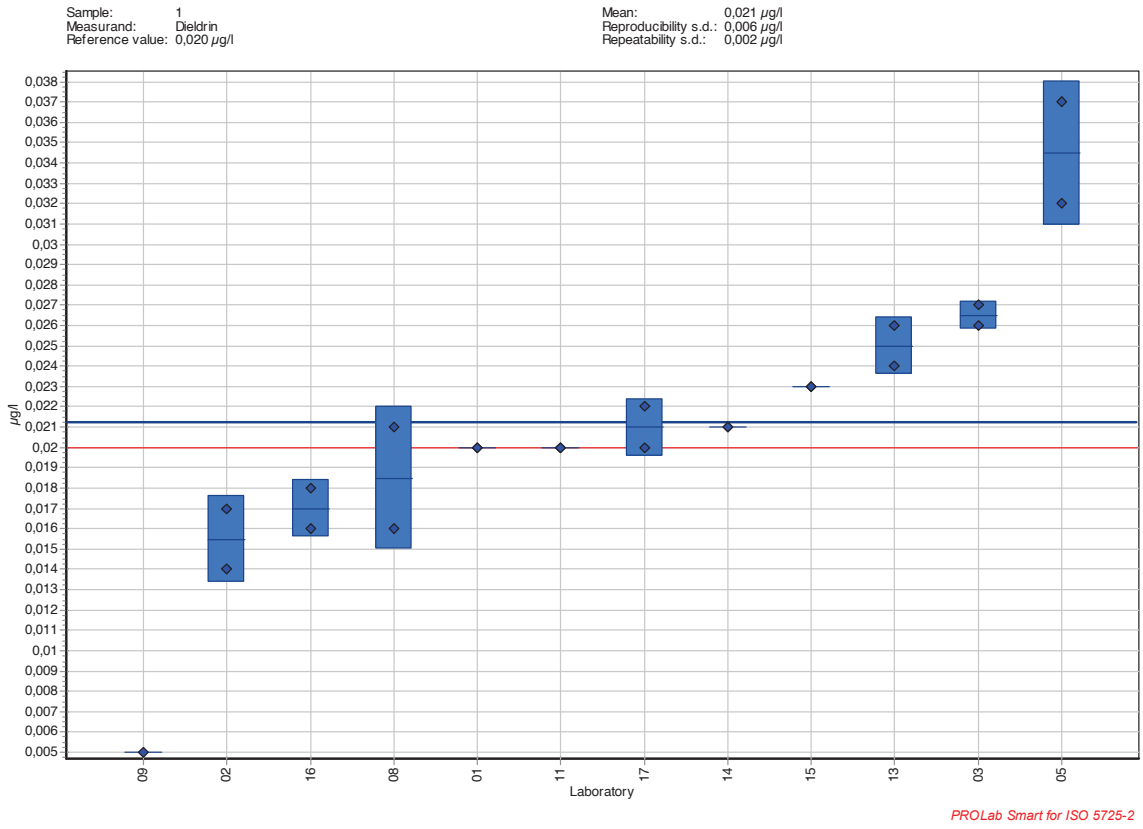

Figure 3: Dieldrin, sample 1

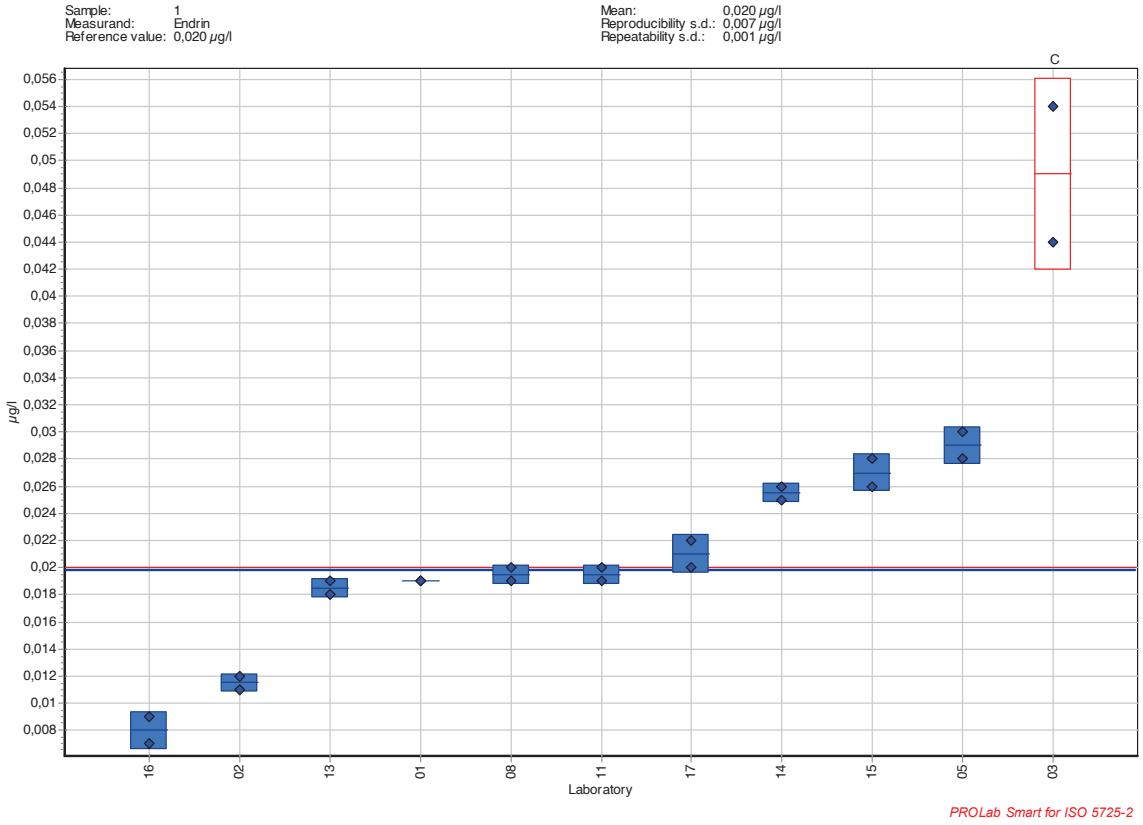

Figure 4: Endrin, sample 1

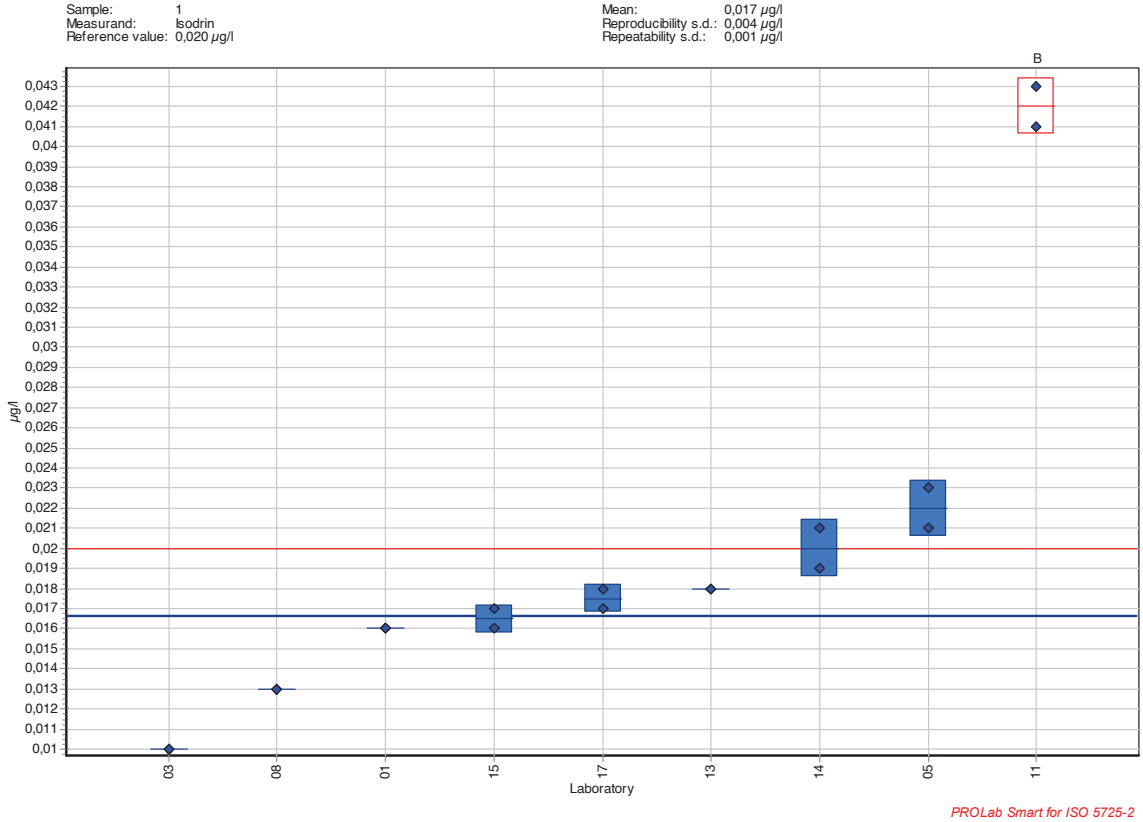

Figure 5: Isodrin, sample 1

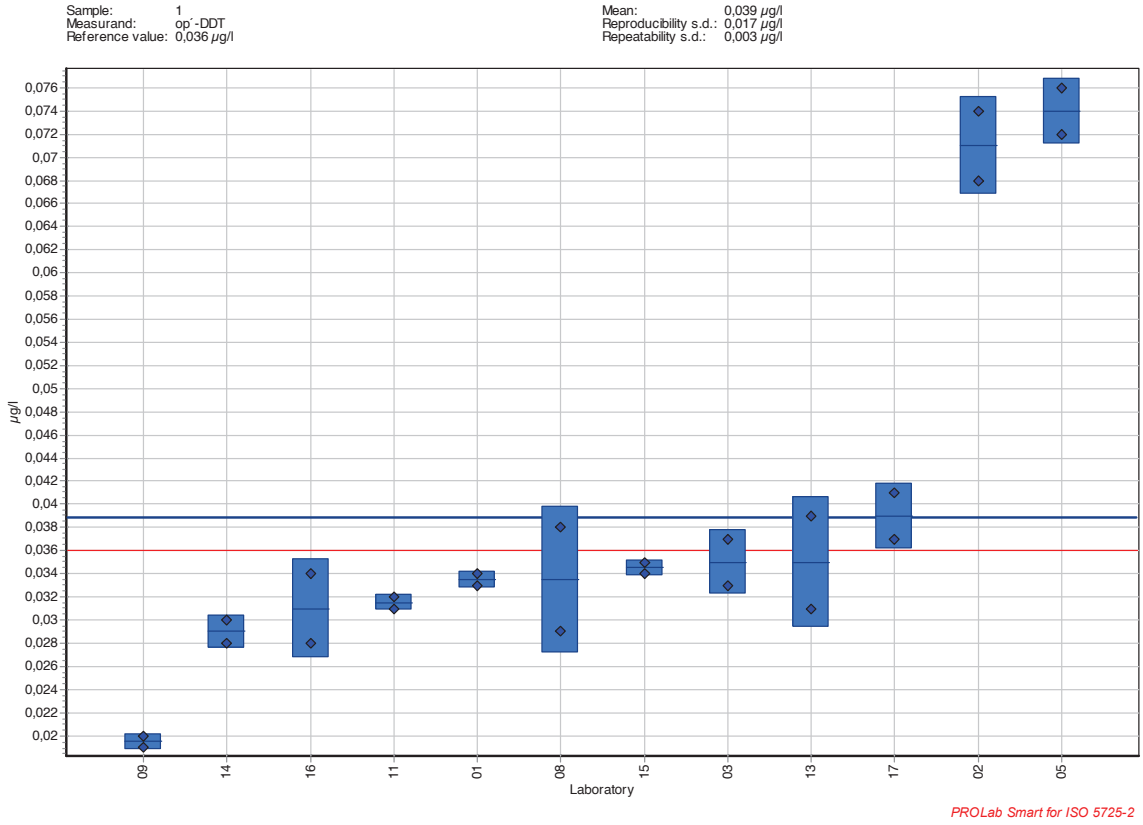

Figure 6: op‘-DDT, sample 1

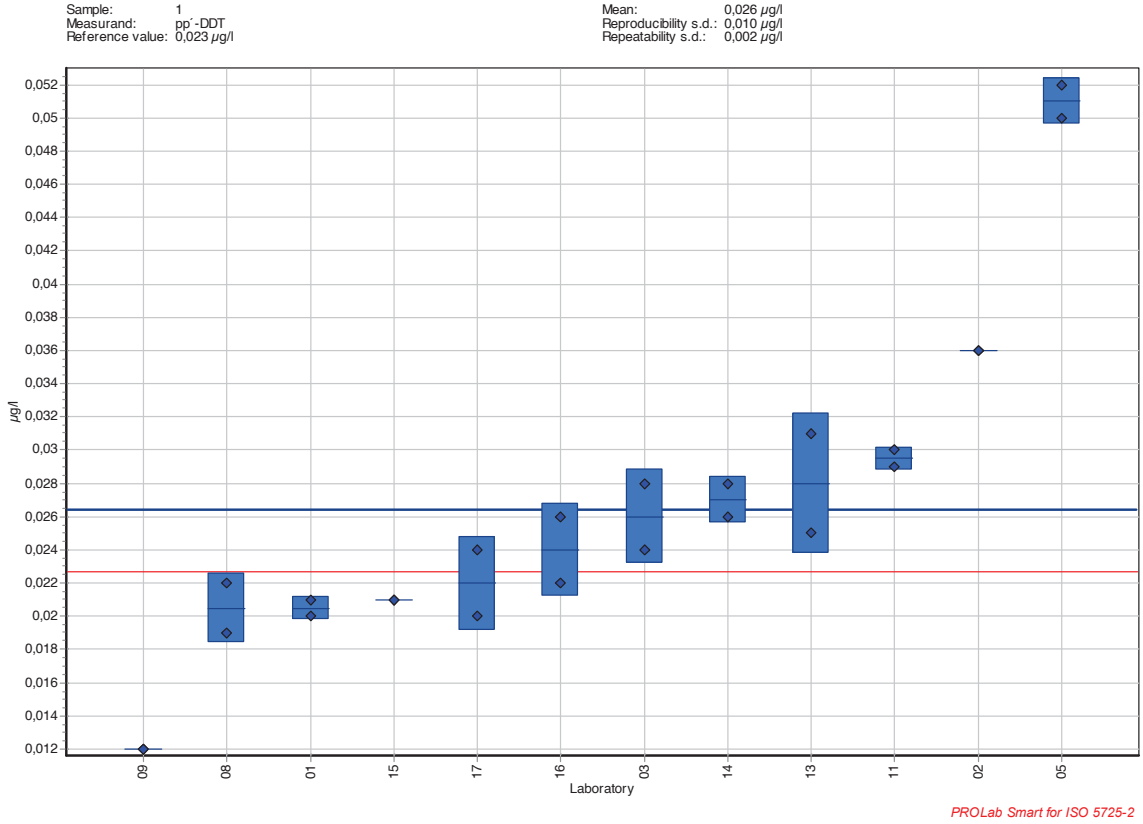

Figure 7: pp‘-DDT, sample 1

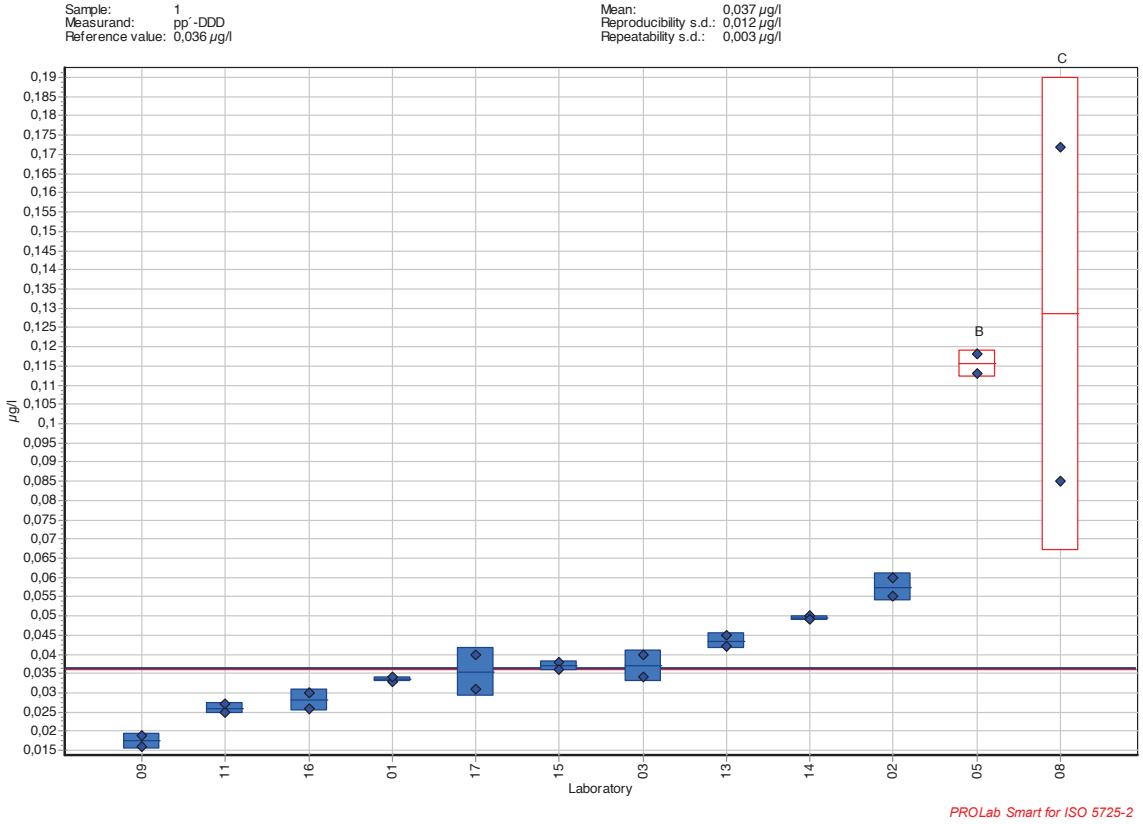

Figure 8: pp‘-DDD, sample 1

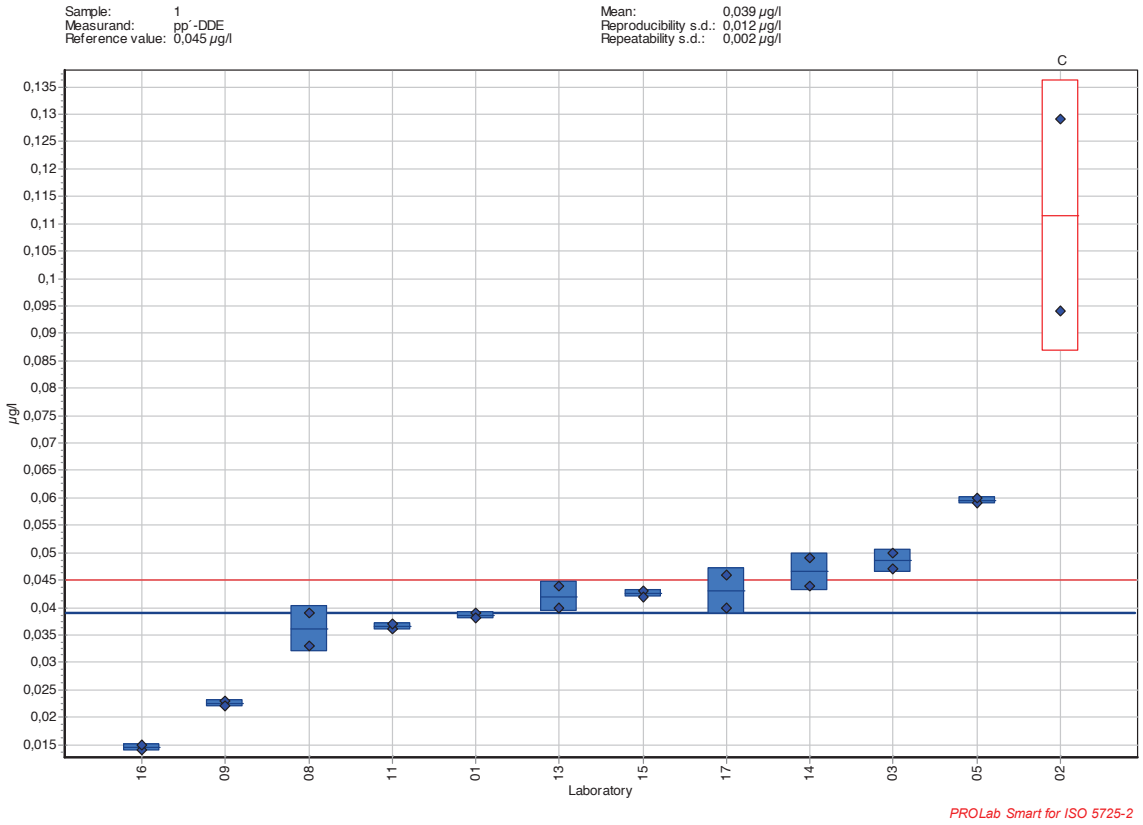

Figure 9: pp‘-DDE, sample 1

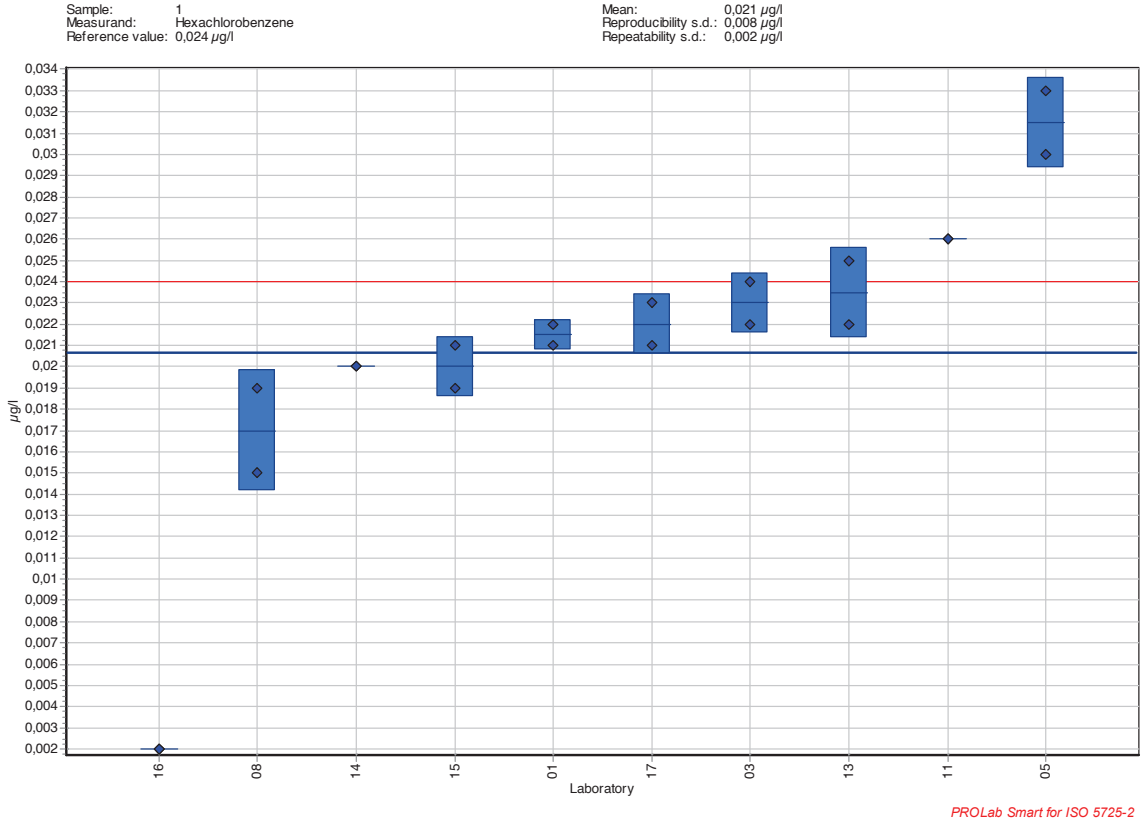

Figure 10: Hexachlorobenzene, sample 1

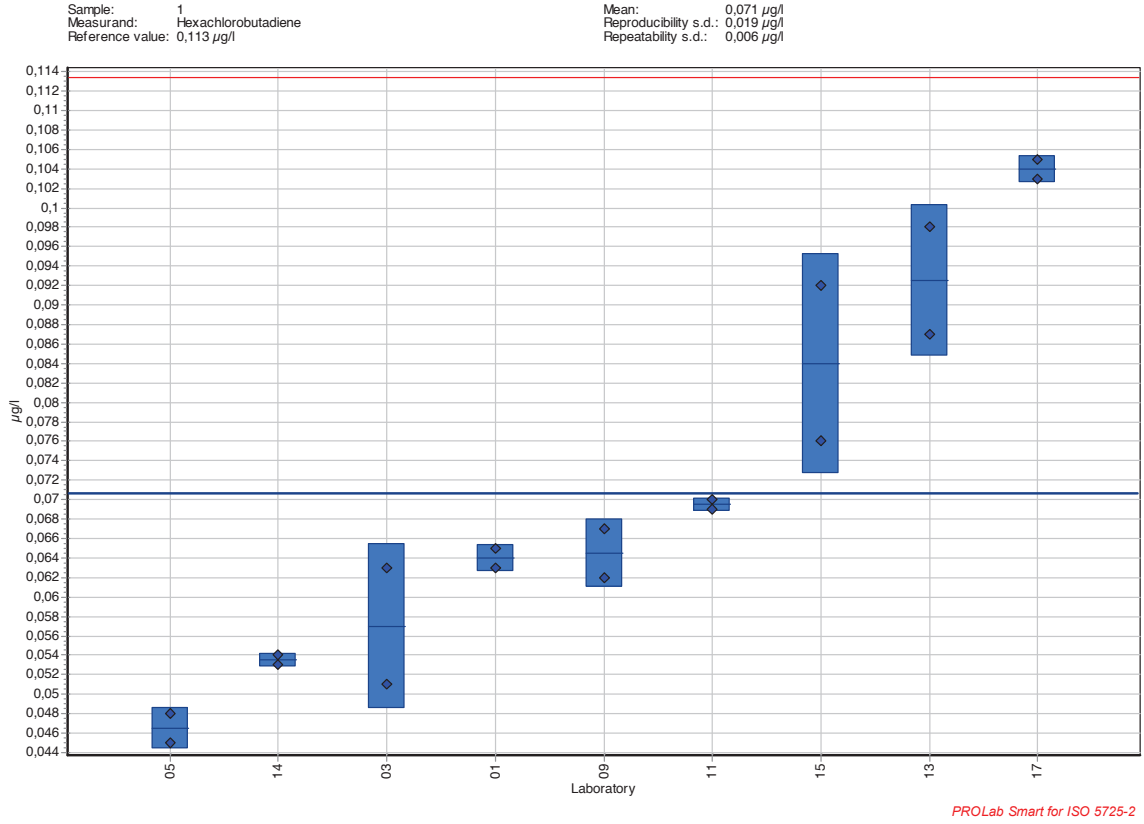

Figure 11: Hexachlorobutadiene, sample 1

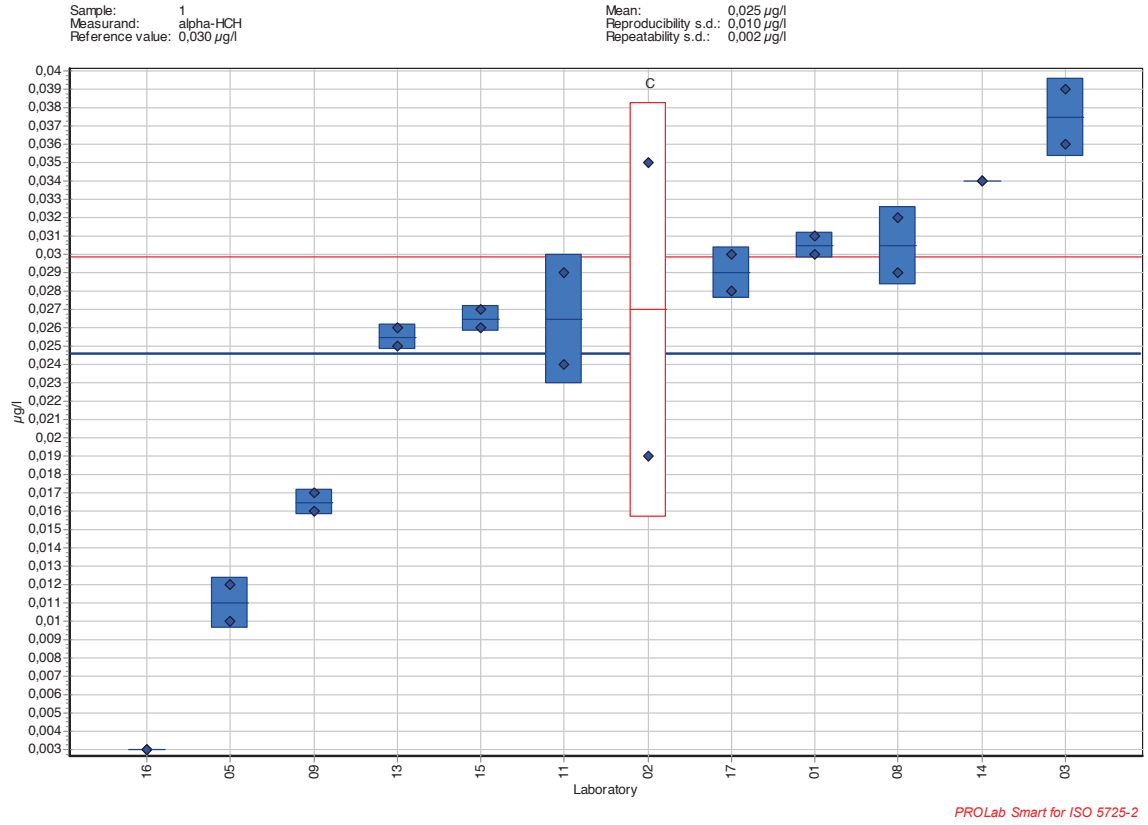

Figure 12: alpha-HCH, sample 1

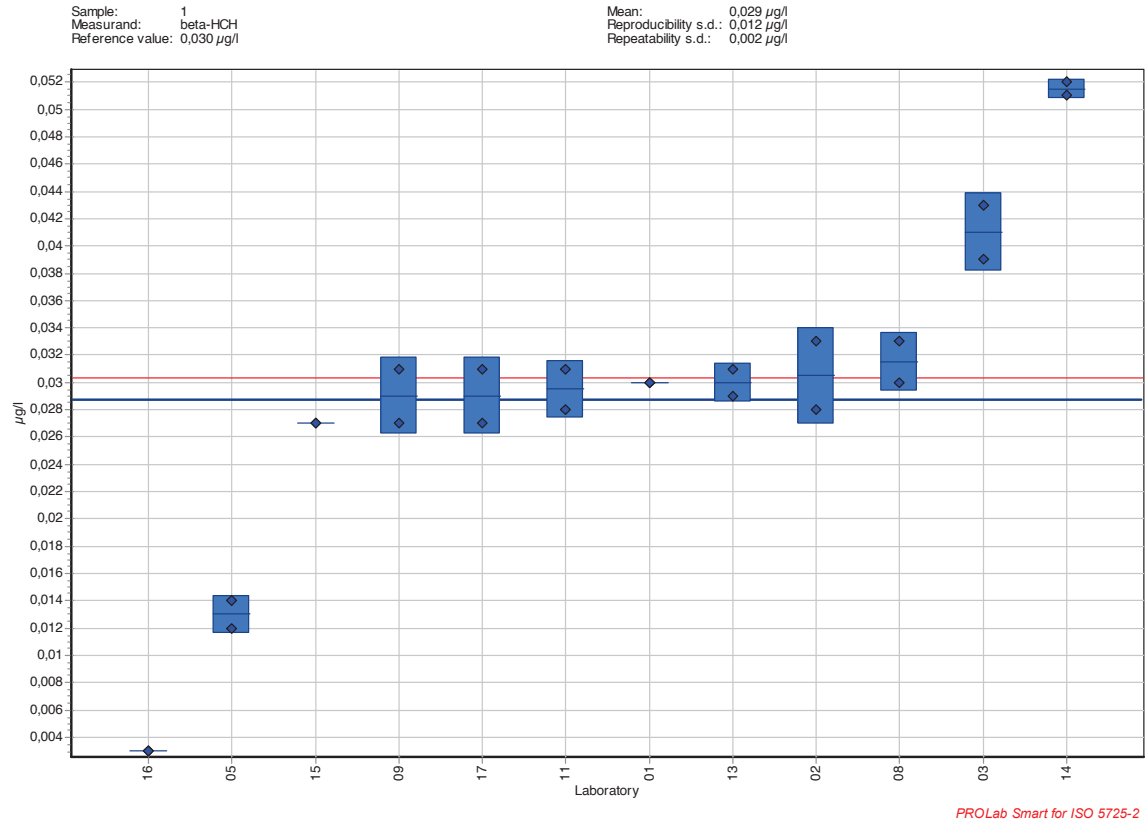

Figure 13: beta-HCH, sample 1

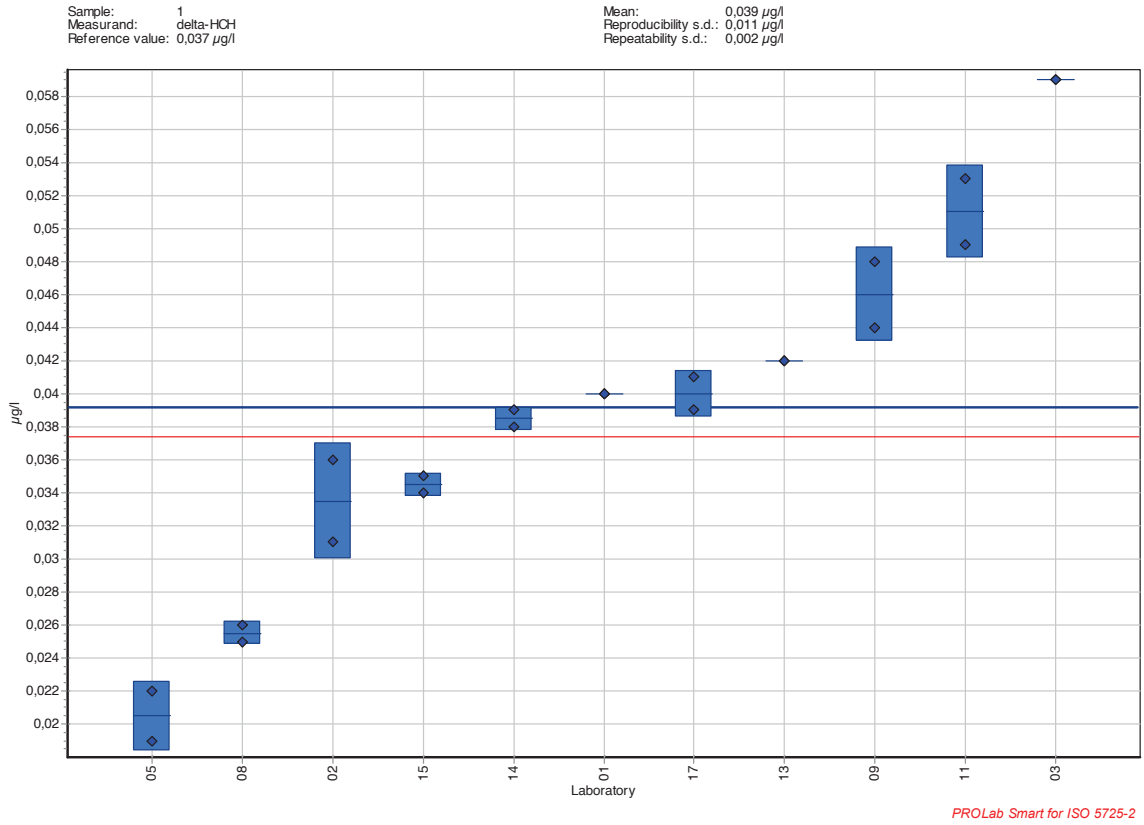

Figure 14: delta-HCH, sample 1

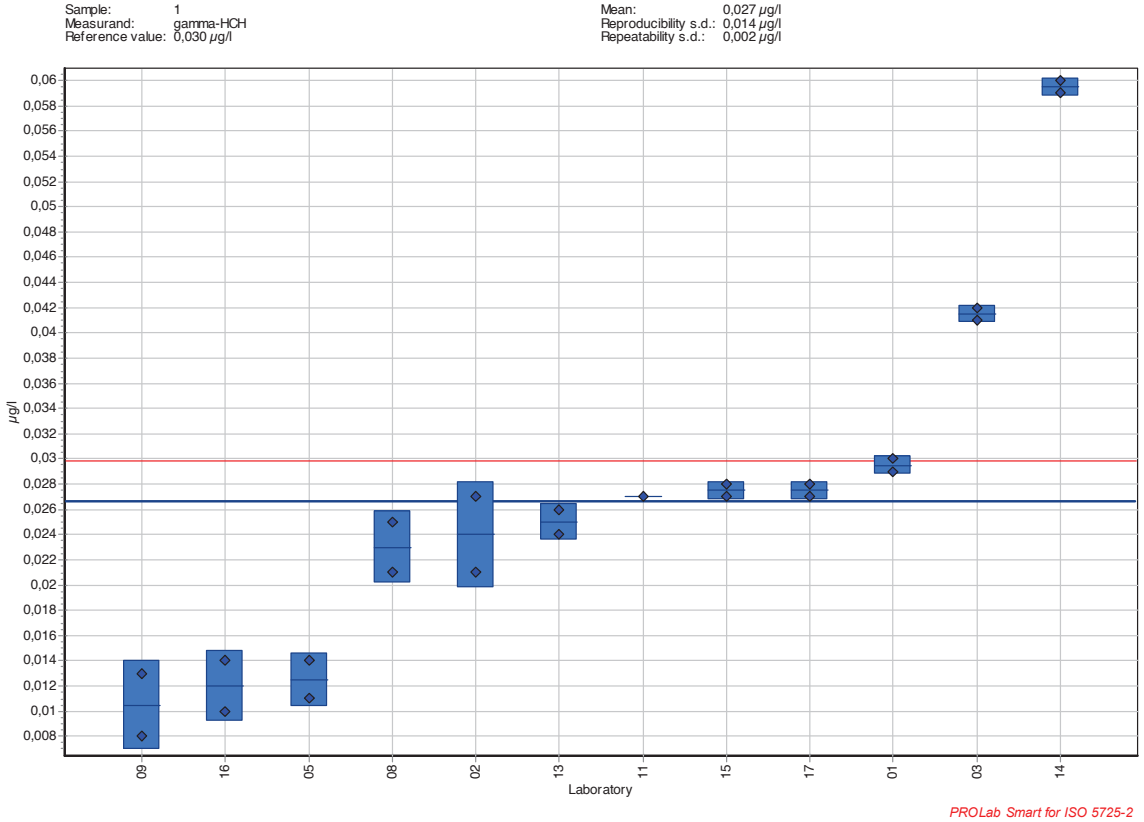

Figure 15: gamma-HCH, sample 1

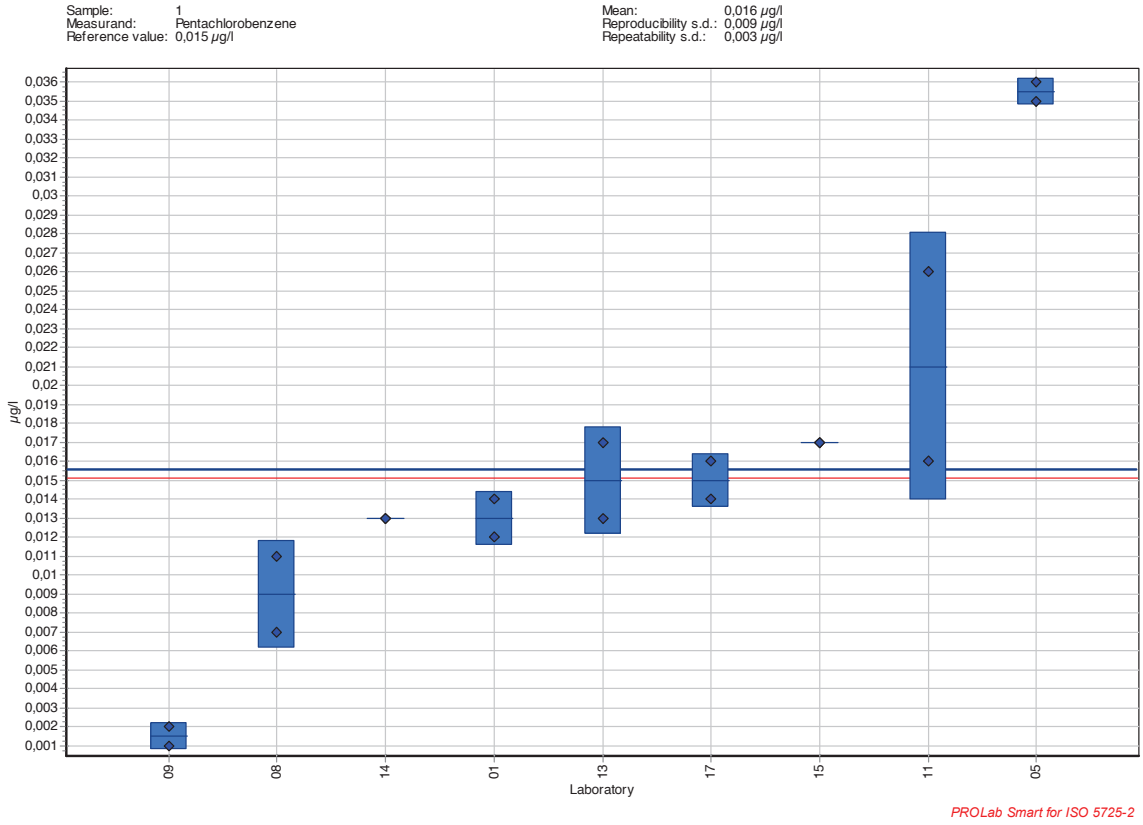

Figure 16: Pentachlorobenzene, sample 1

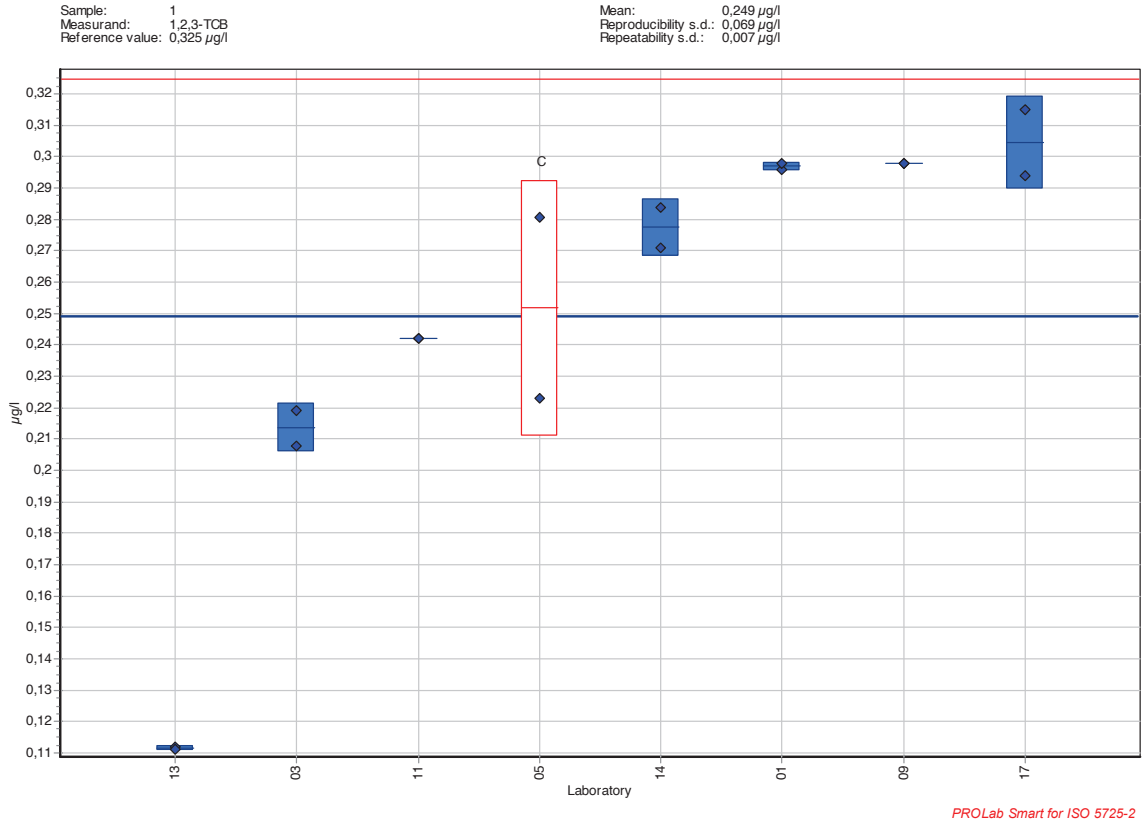

Figure 17: 1,2,3-TCB, sample 1

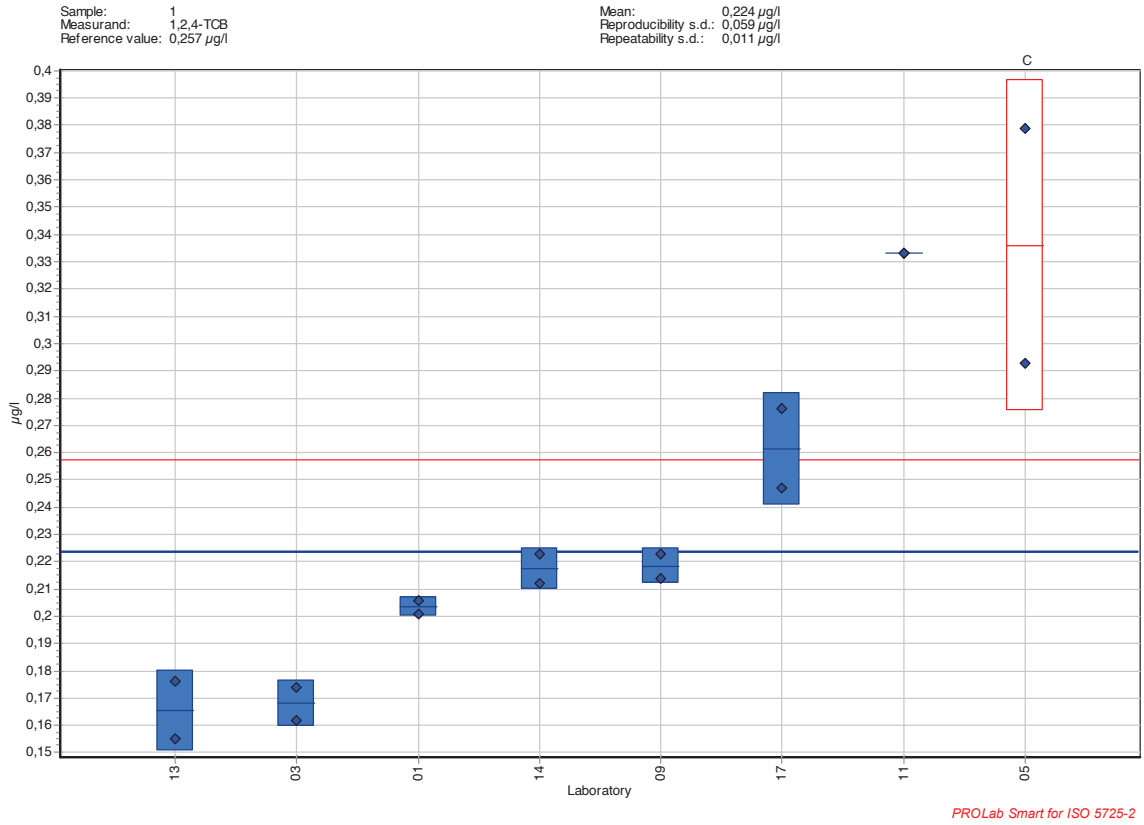

Figure 18: 1,2,4-TCB, sample 1

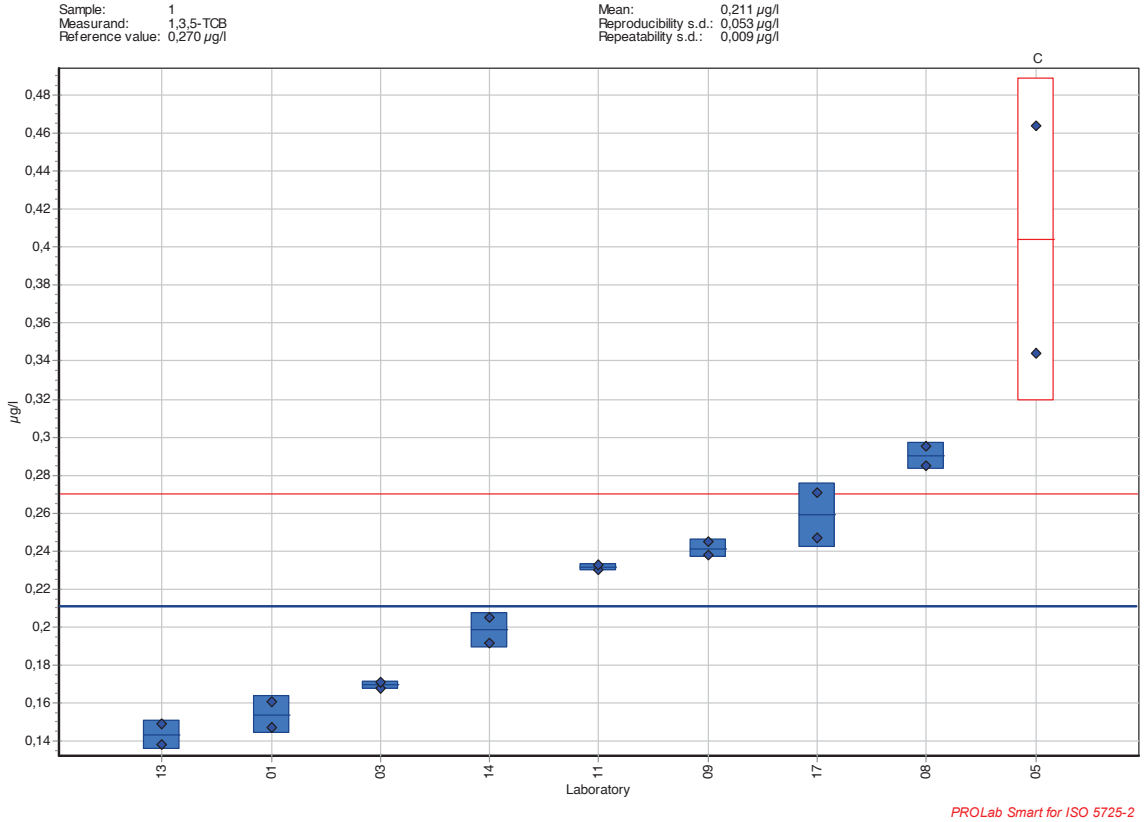

Figure 19: 1,3,5-TCB, sample 1

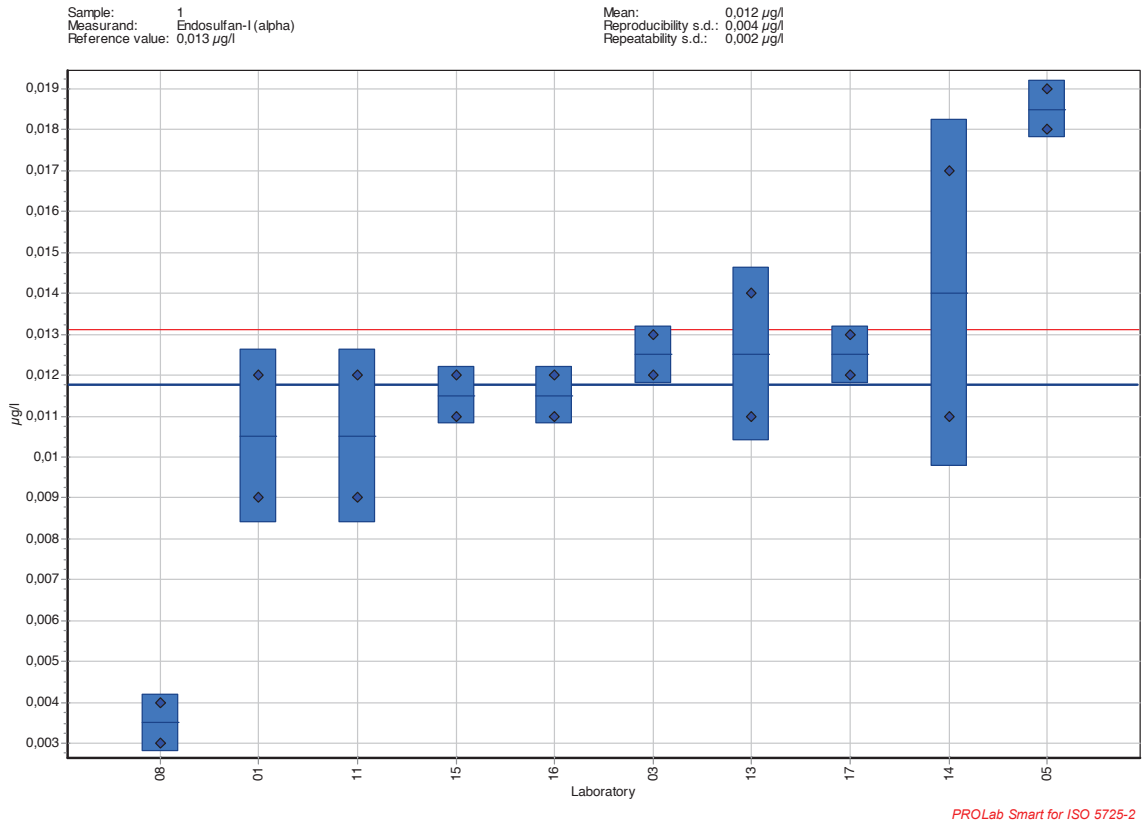

Figure 20: Endosulfan-I (alpha), sample 1

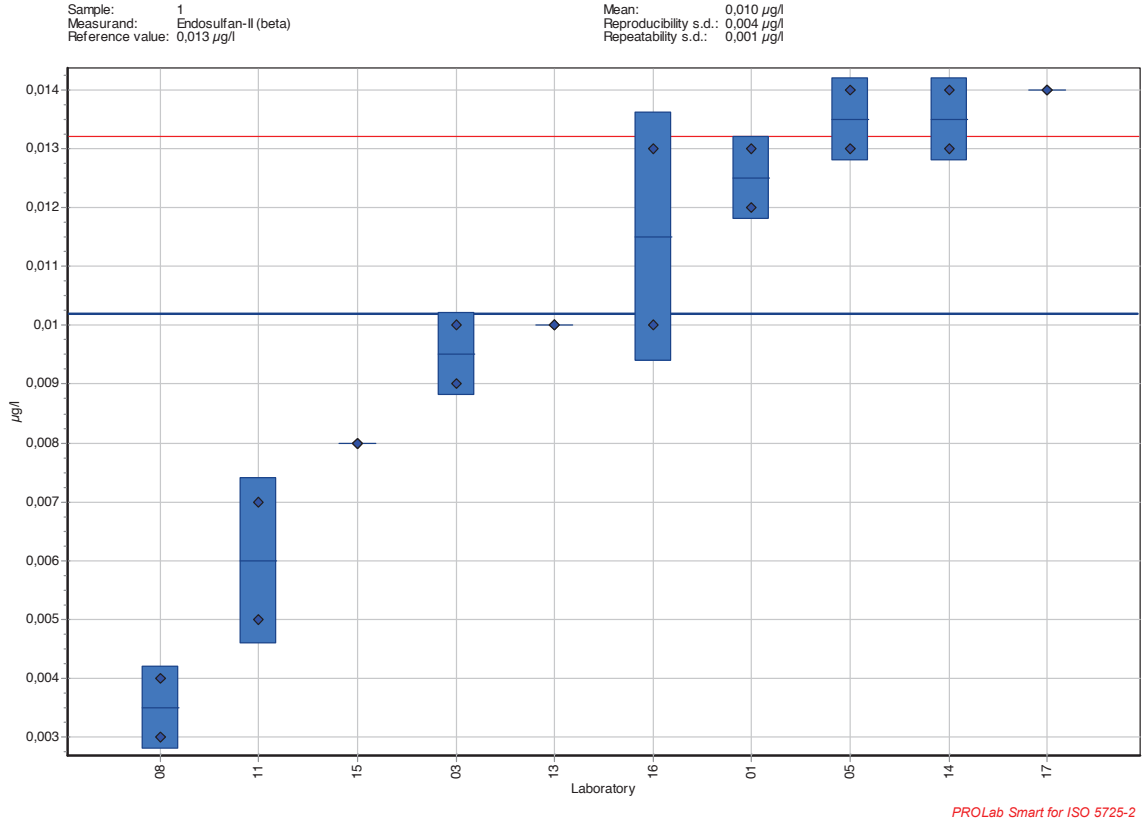

Figure 21: Endosulfan-II (beta), sample 1

Graphical presentation of the results of the Interlaboratory Trial for the validation of EN 16693
Determination of organochlorine pesticides (OCP) with SPE-disks combined with GC-MS

Sample 2: **Low OCP-level sample containing 20 mg SPM**
Matrix: **Filtered surface water, spiked with OCP and SPM**

Legend: ——— reference value
——— overall mean

Outliers: A outlying single result of one laboratory,
B outlying laboratory mean,
C outlying within-laboratory variance

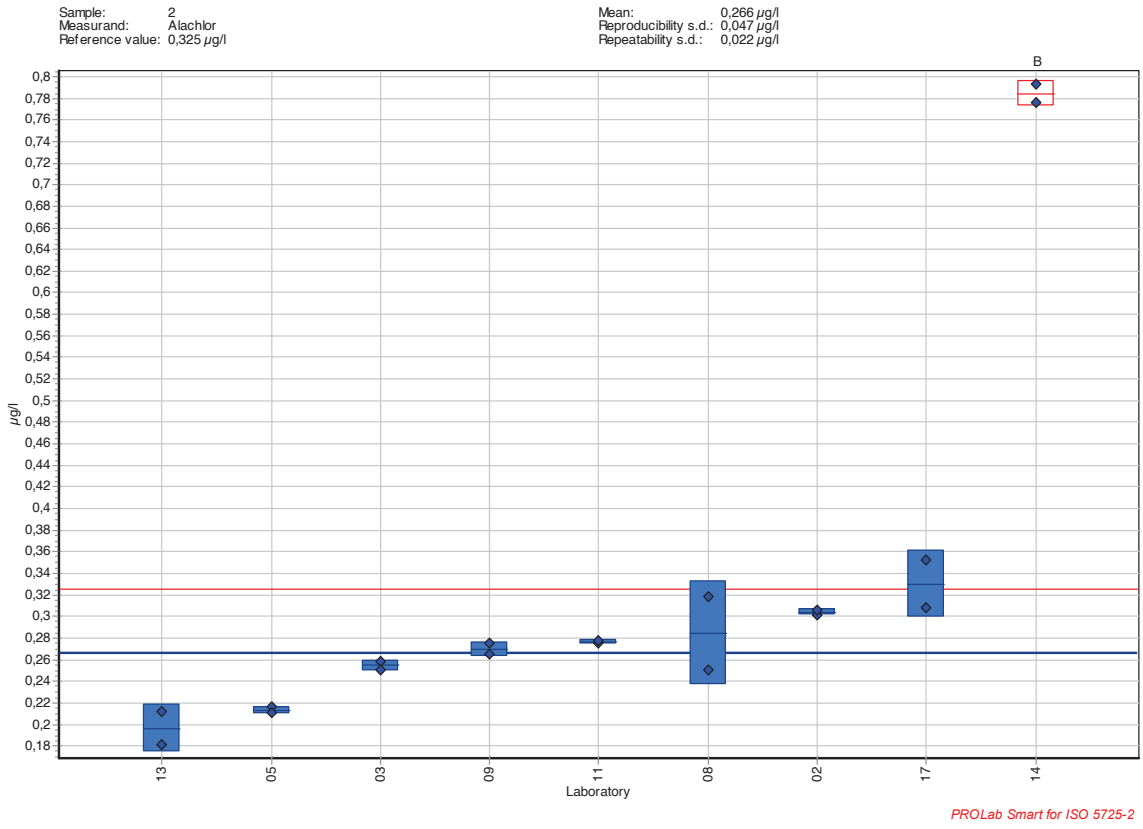

Figure 1: Alachlor, sample 2

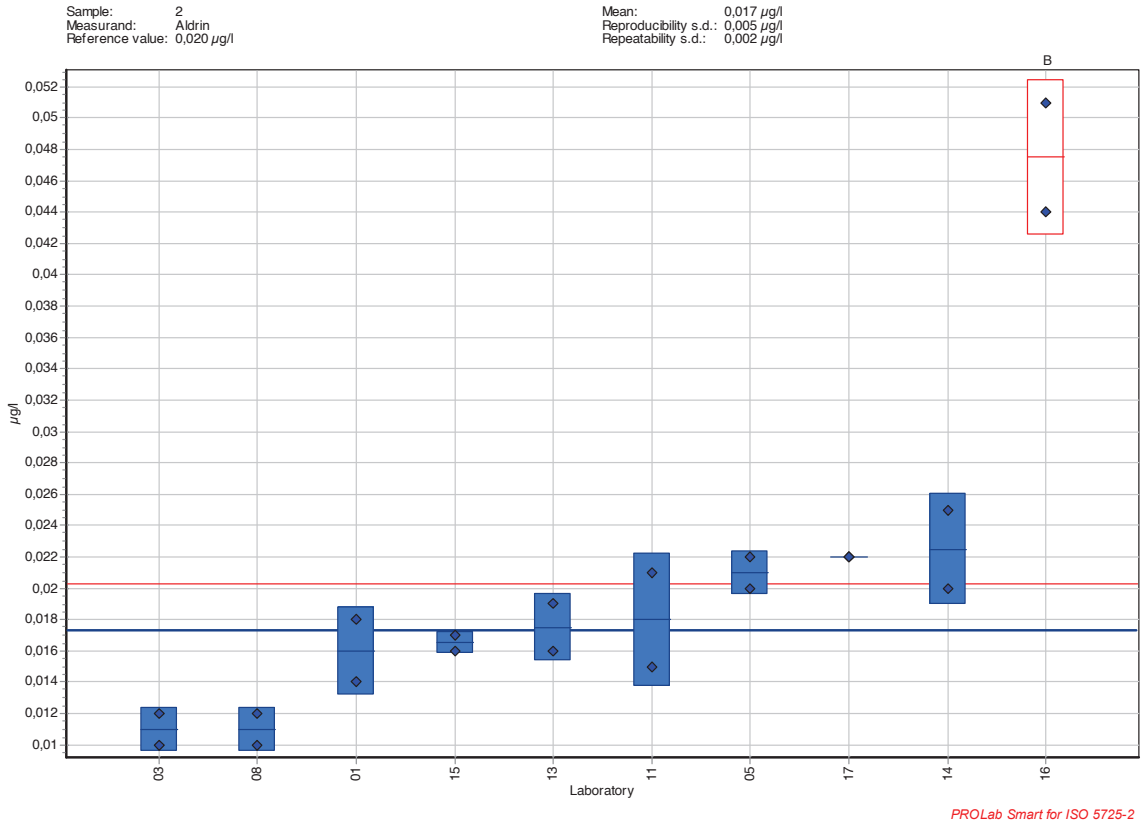

Figure 2: Aldrin, sample 2

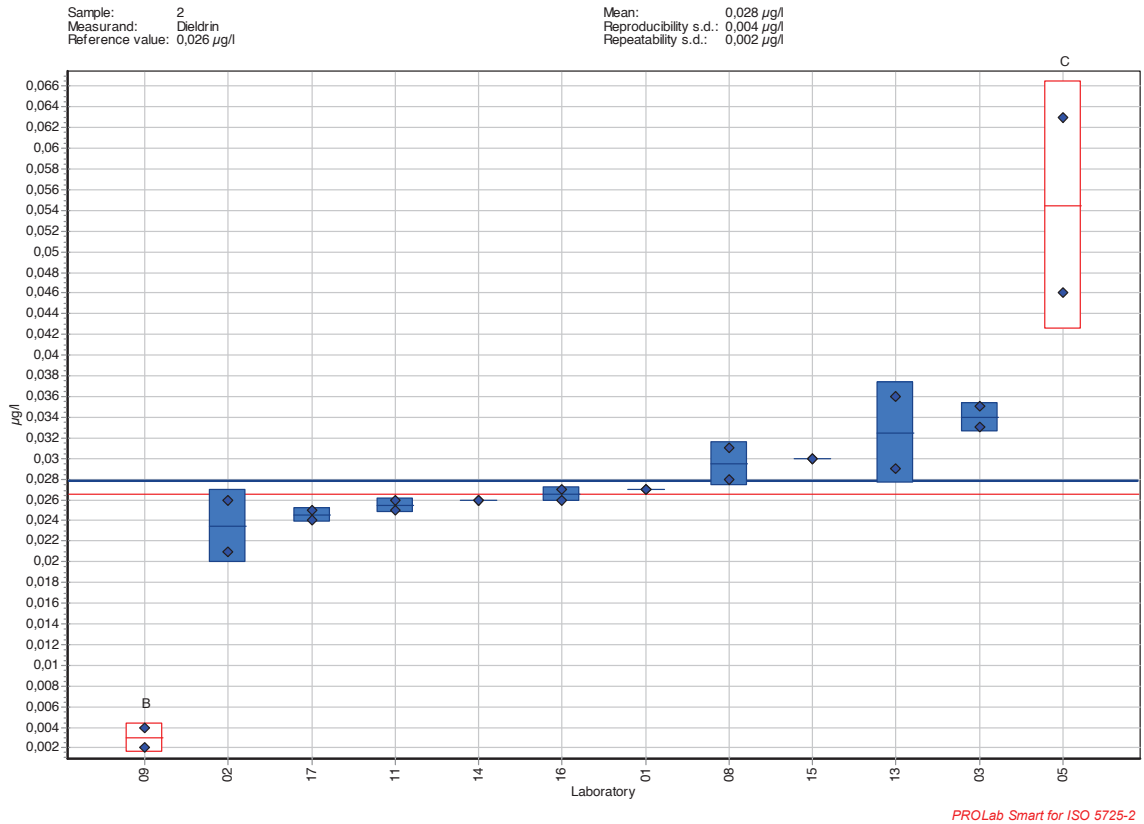

Figure 3: Dieldrin, sample 2

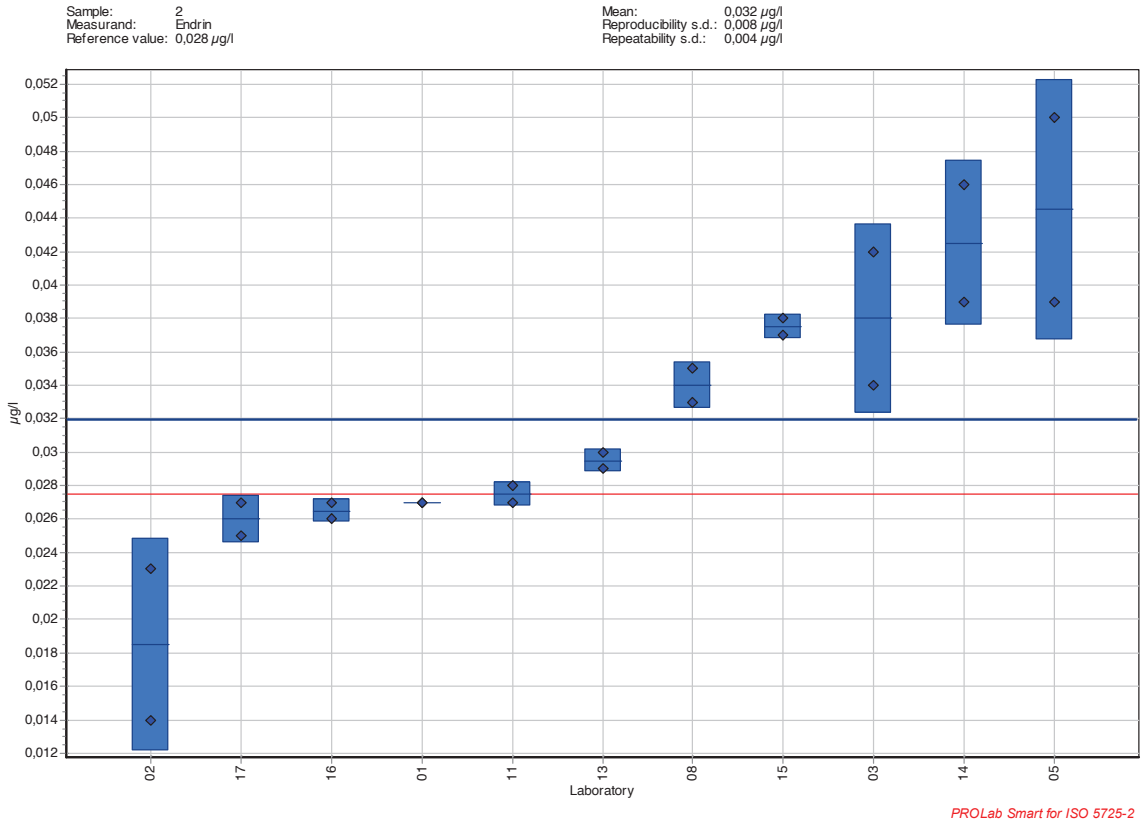

Figure 4: Endrin, sample 2

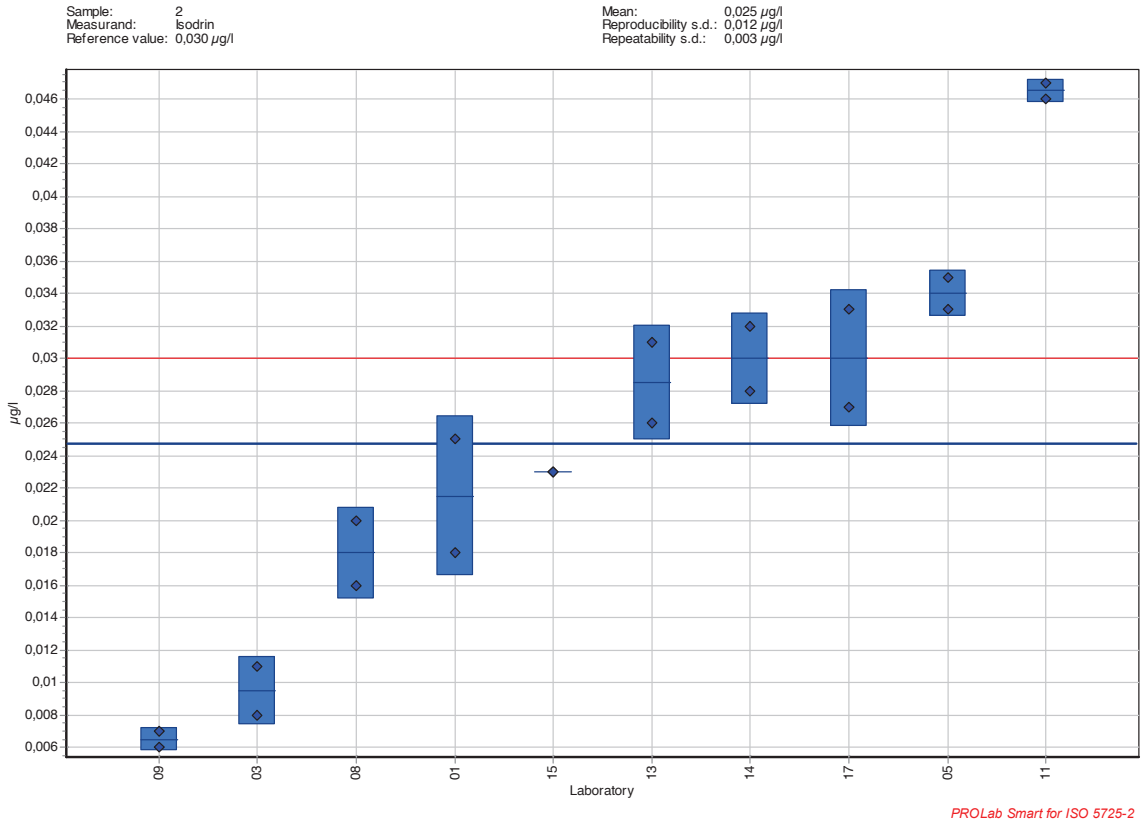

Figure 5: Isodrin, sample 2

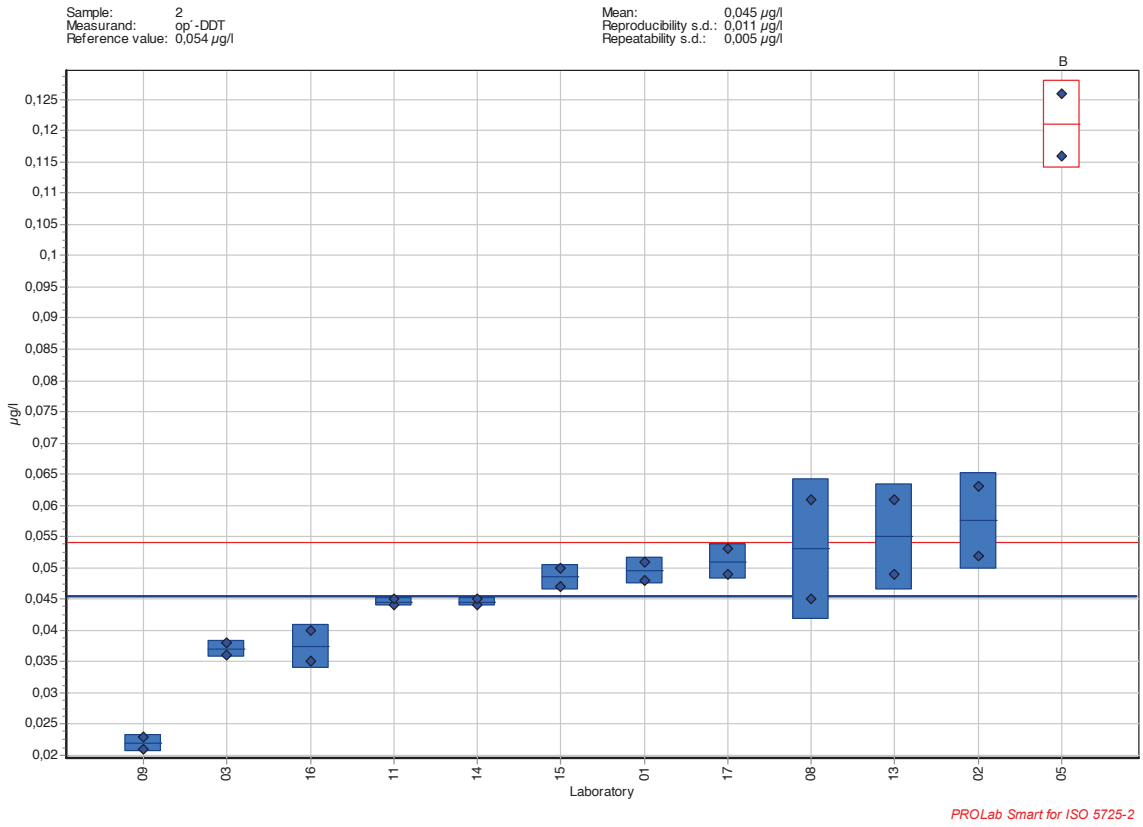

Figure 6: op'-DDT, sample 2

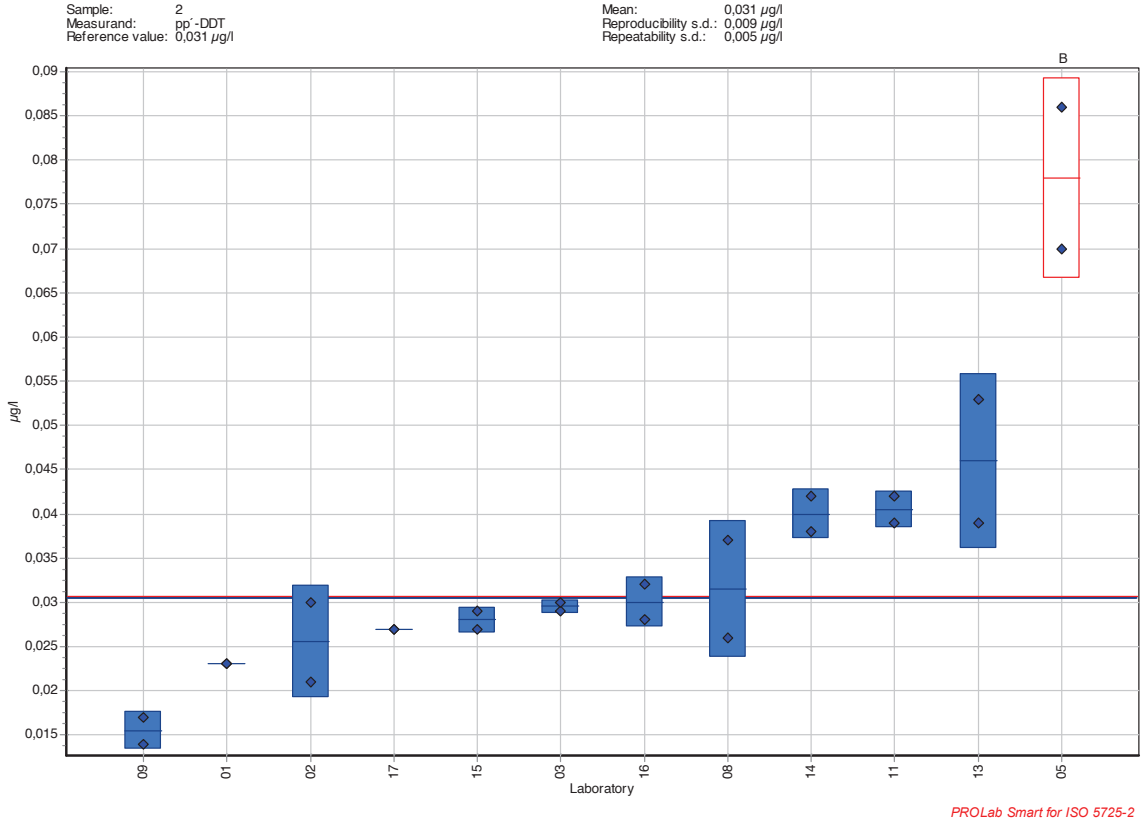

Figure 7: pp'-DDT, sample 2

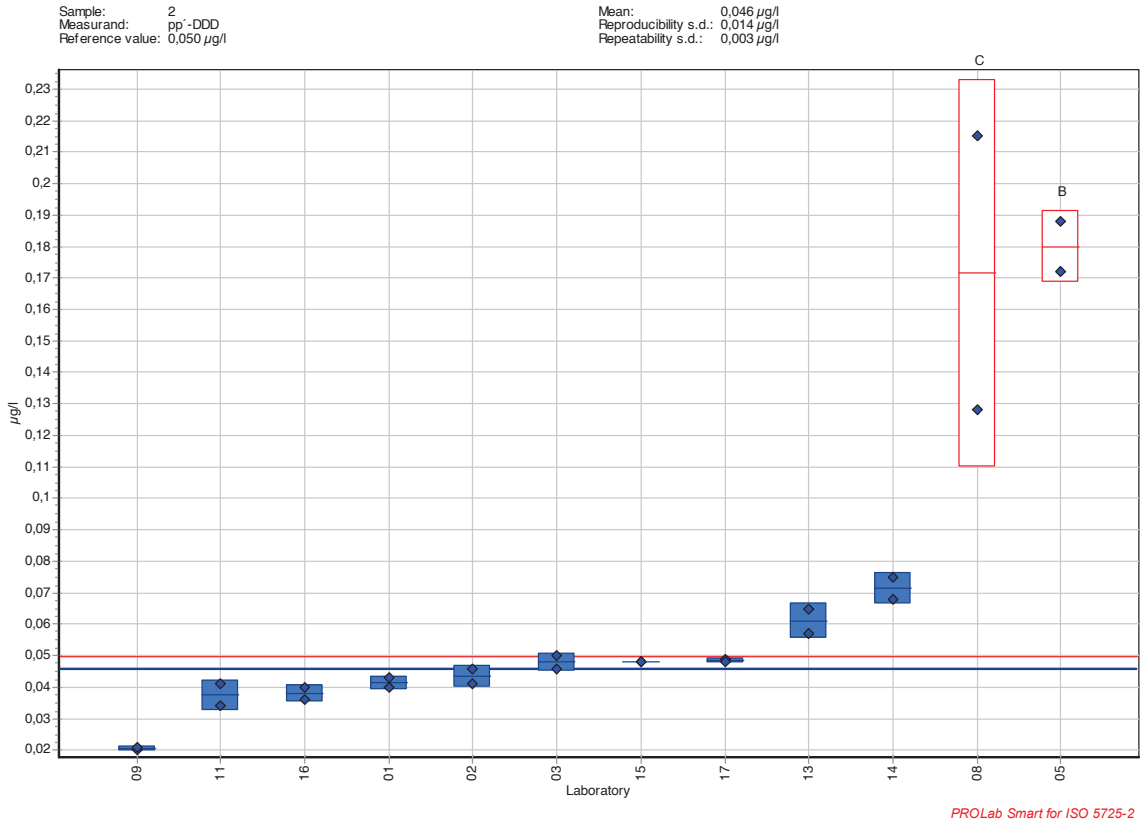

Figure 8: pp‘-DDD, sample 2

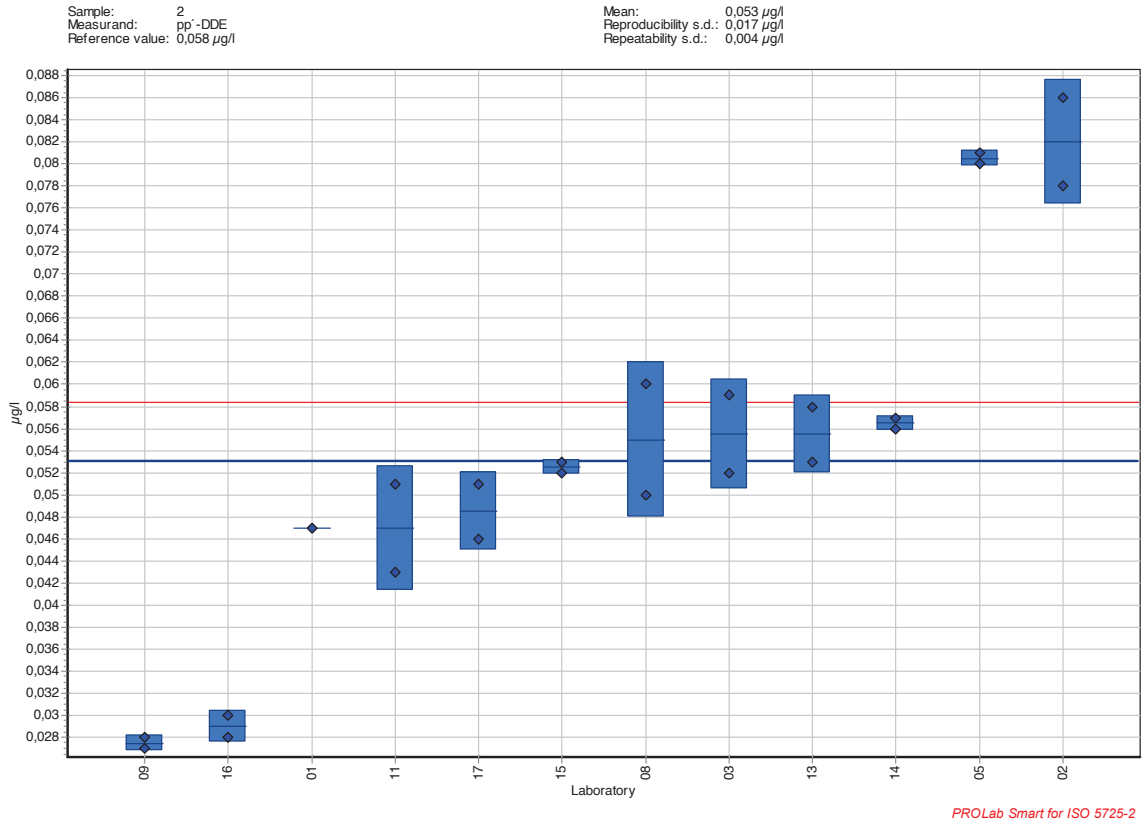

Figure 9: pp‘-DDE, sample 2

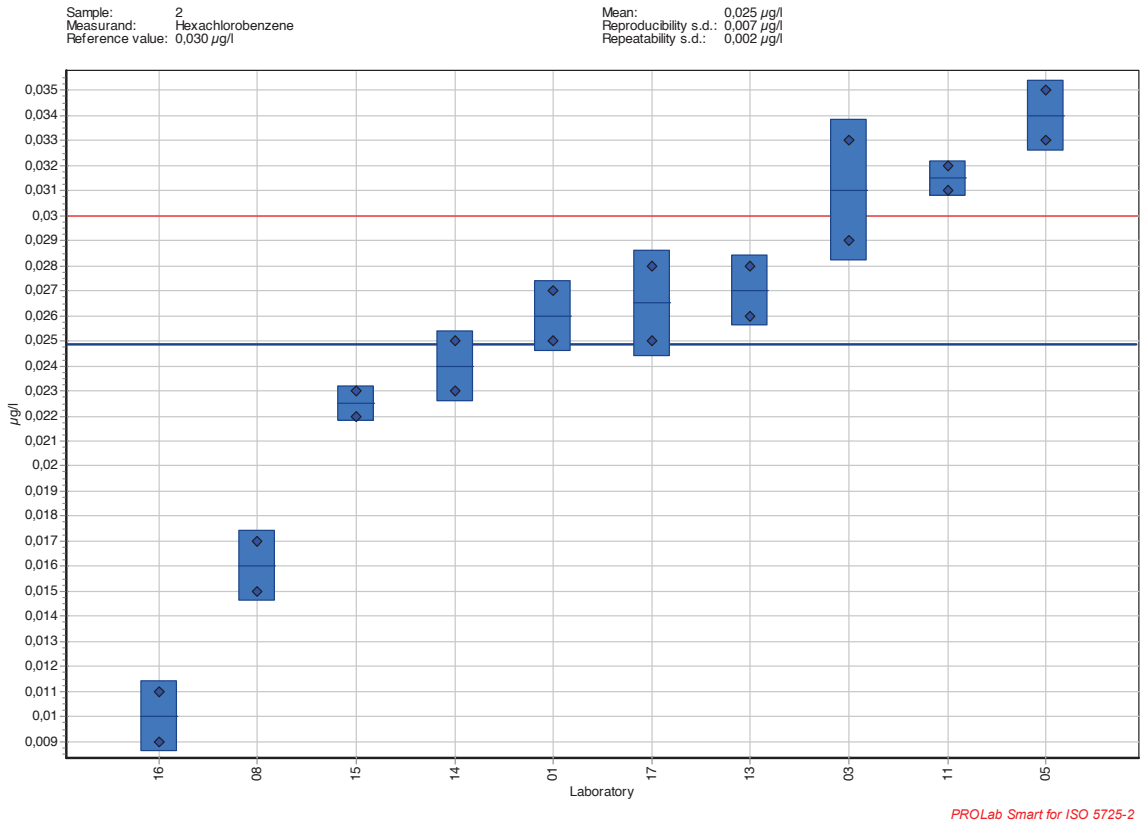

Figure 10: Hexachlorobenzene, sample 2

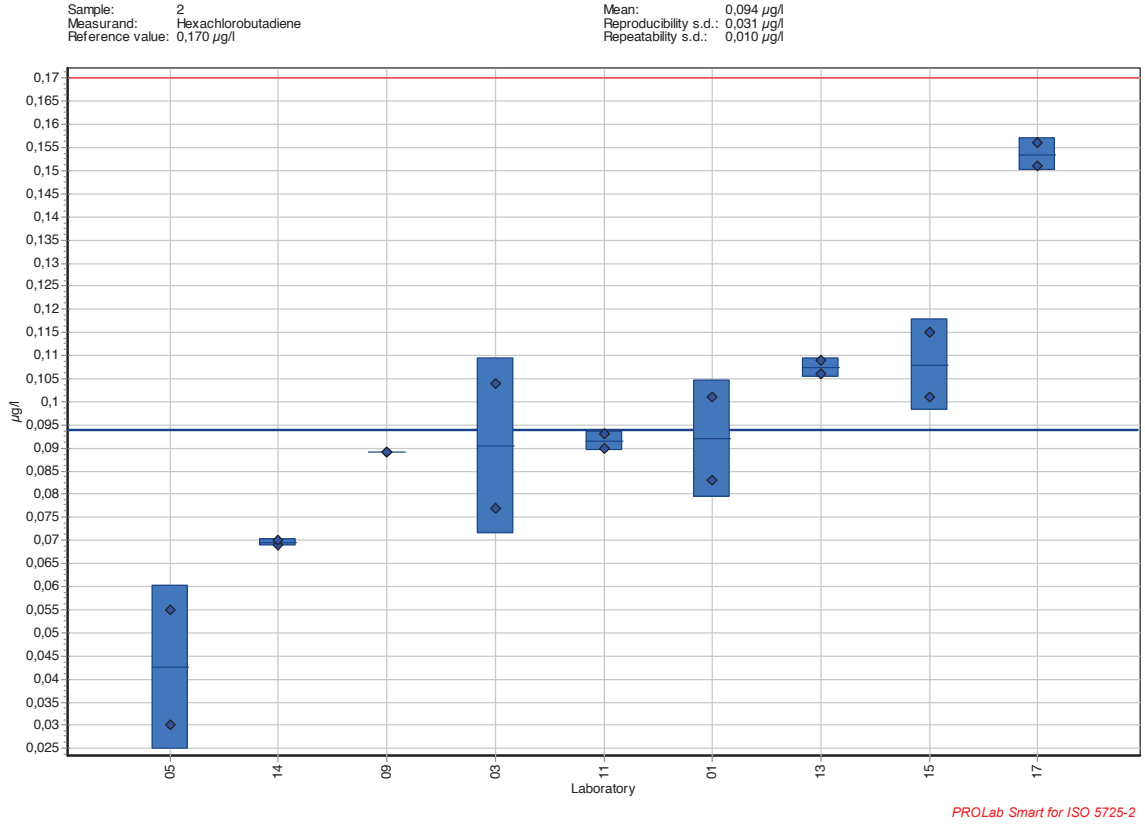

Figure 11: Hexachlorobutadiene, sample 2

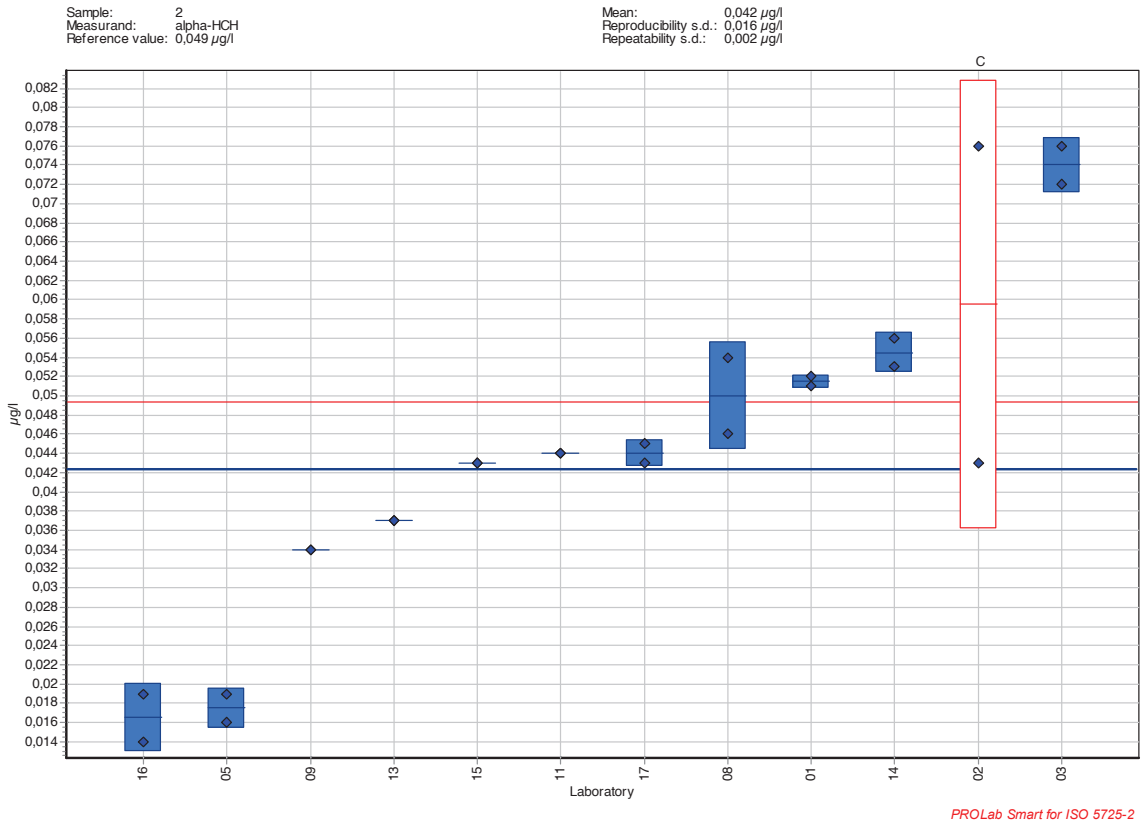

Figure 12: alpha-HCH, sample 2

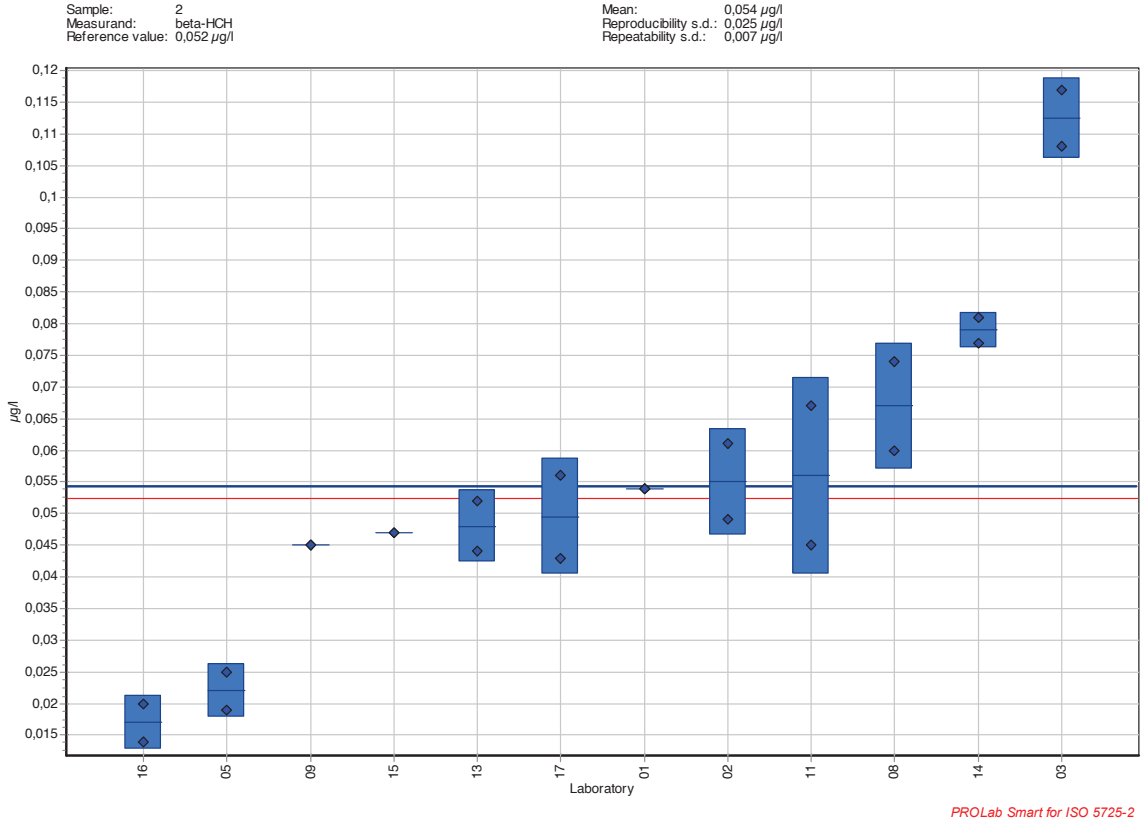

Figure 13: beta-HCH, sample 2

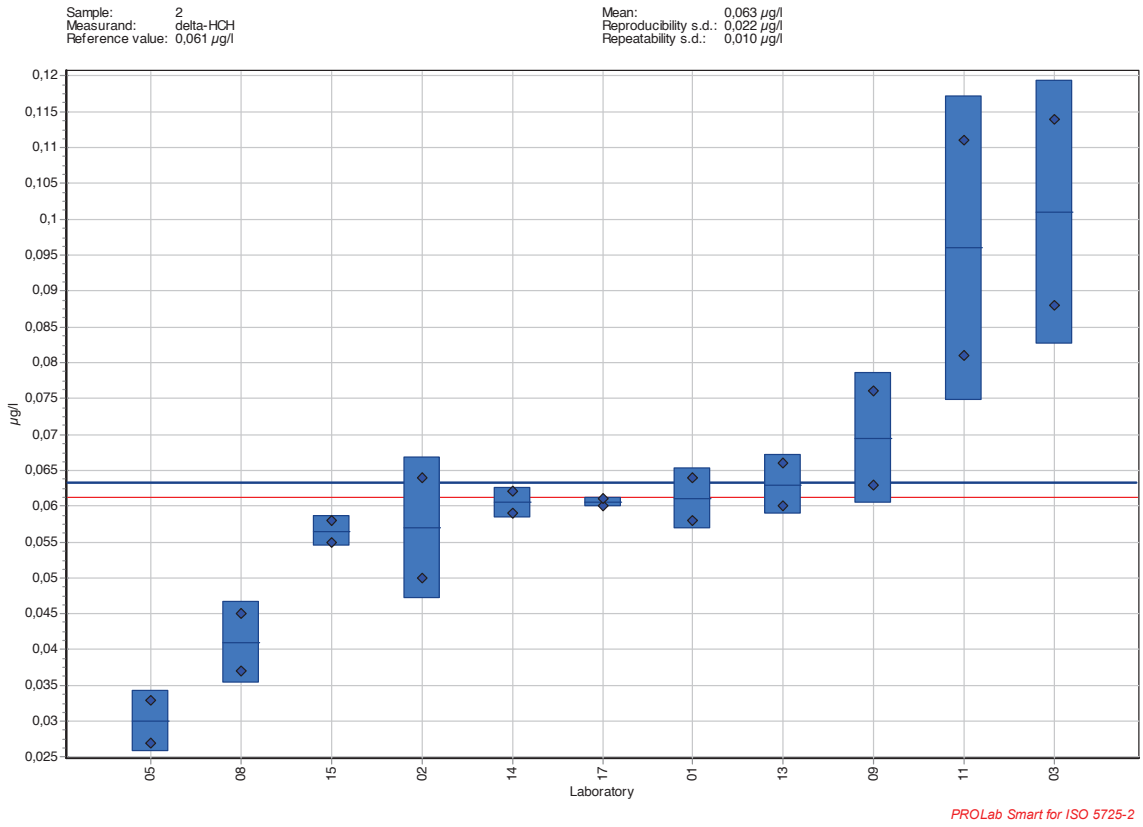

Figure 14: delta-HCH, sample 2

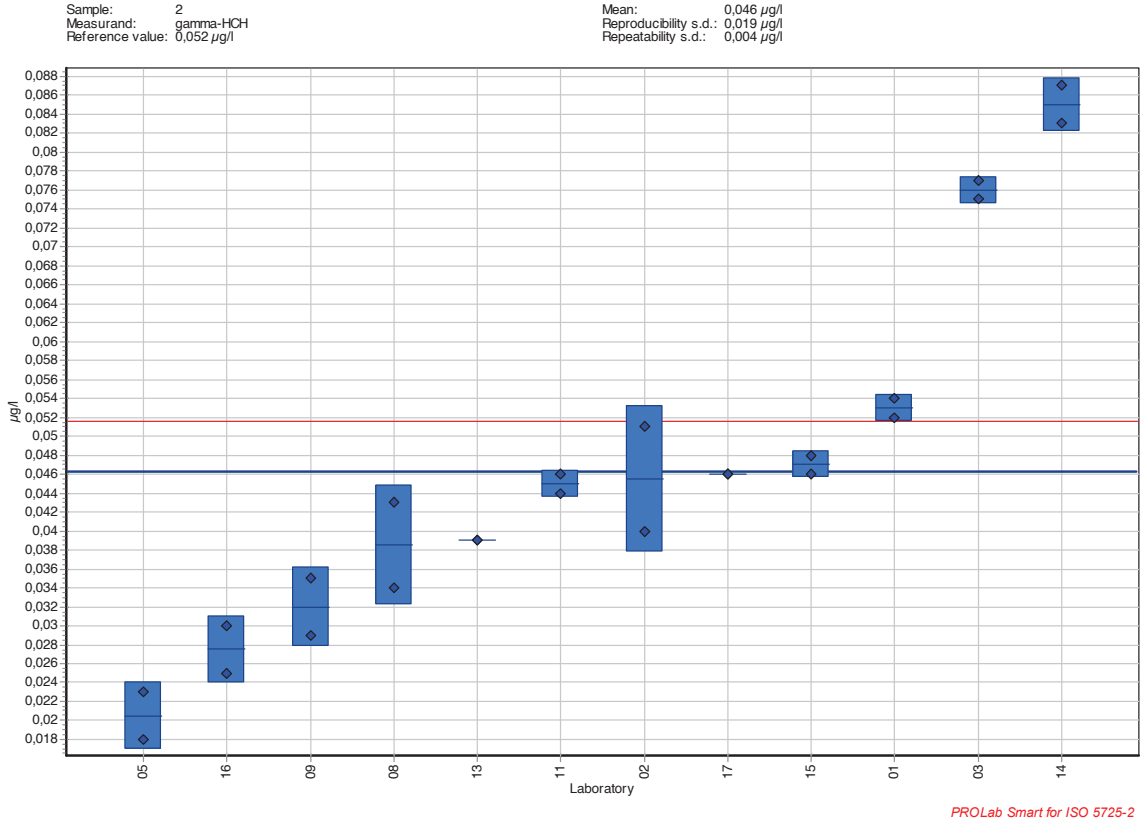

Figure 15: gamma-HCH, sample 2

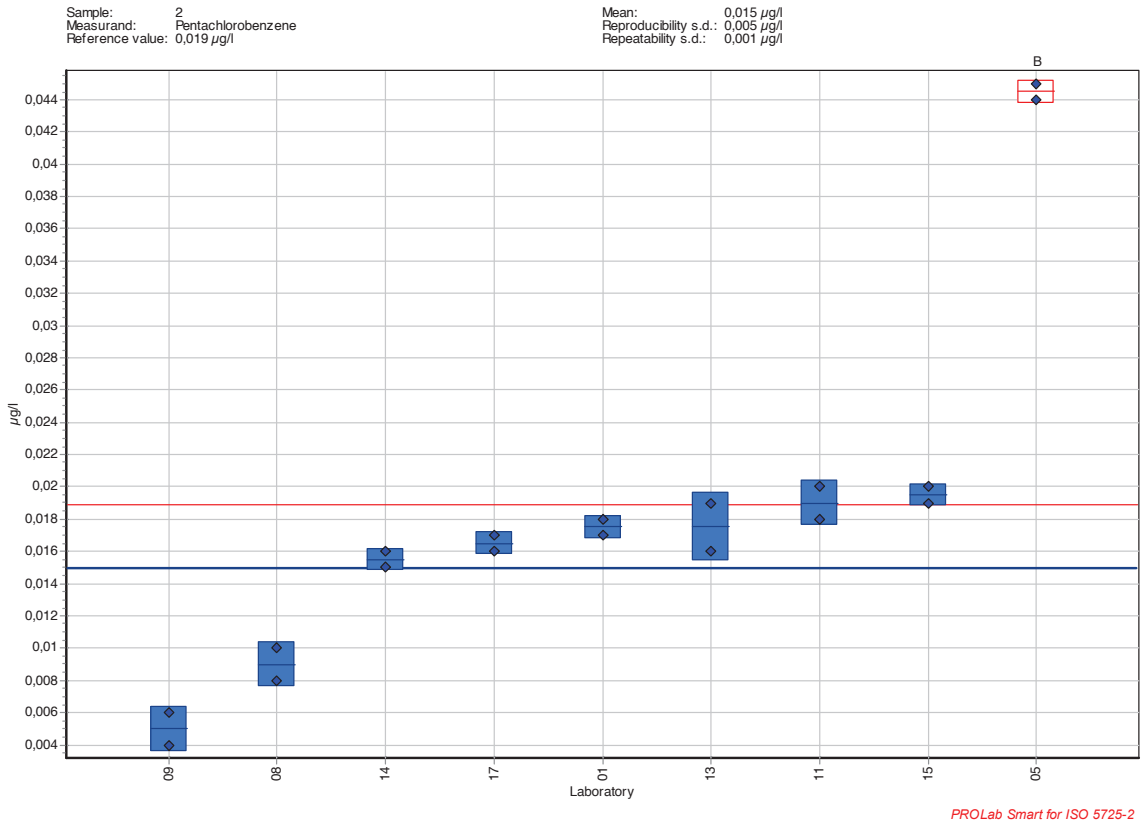

Figure 16: Pentachlorobenzene, sample 2

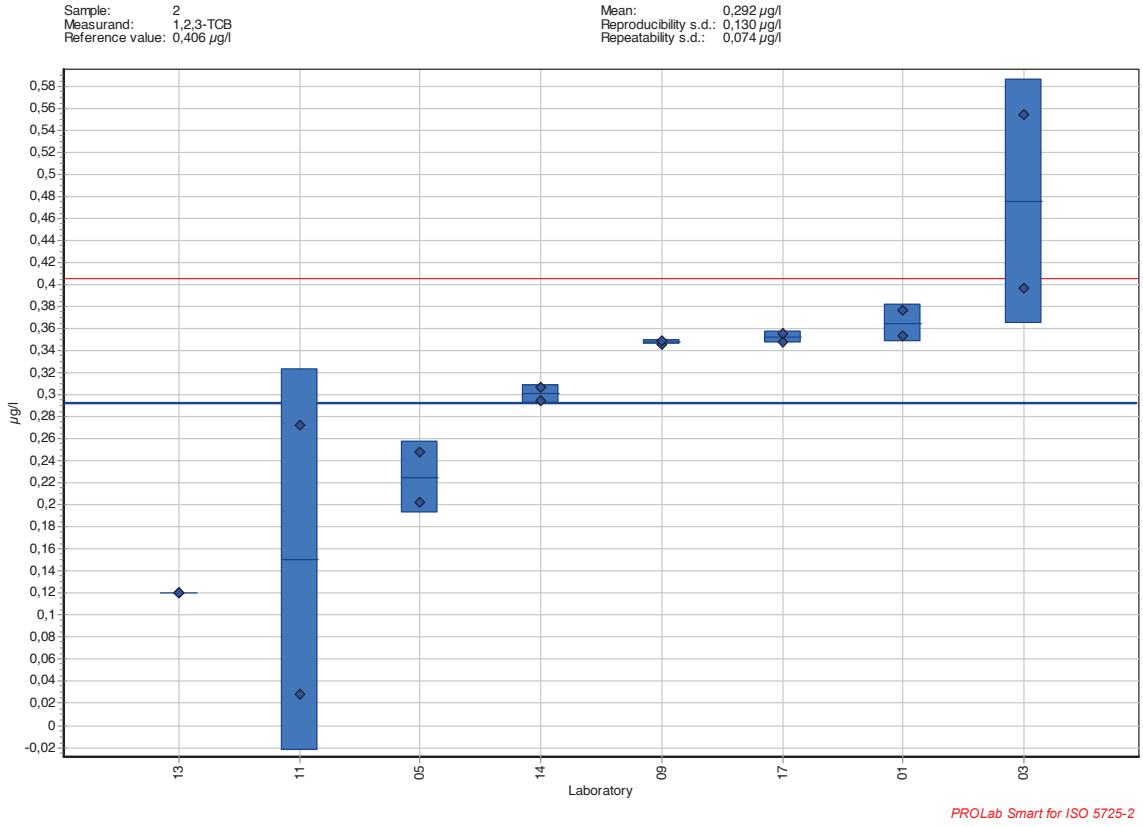

Figure 17: 1,2,3-TCB, sample 2

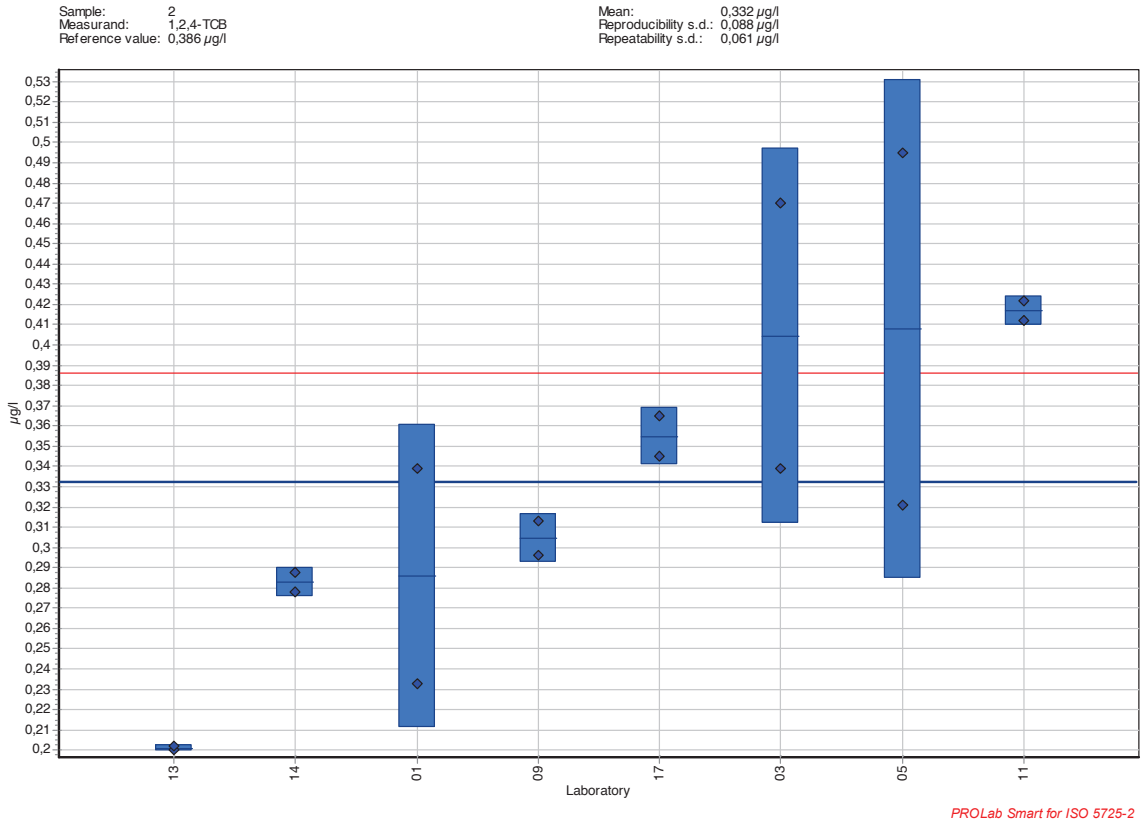

Figure 18: 1,2,4-TCB, sample 2

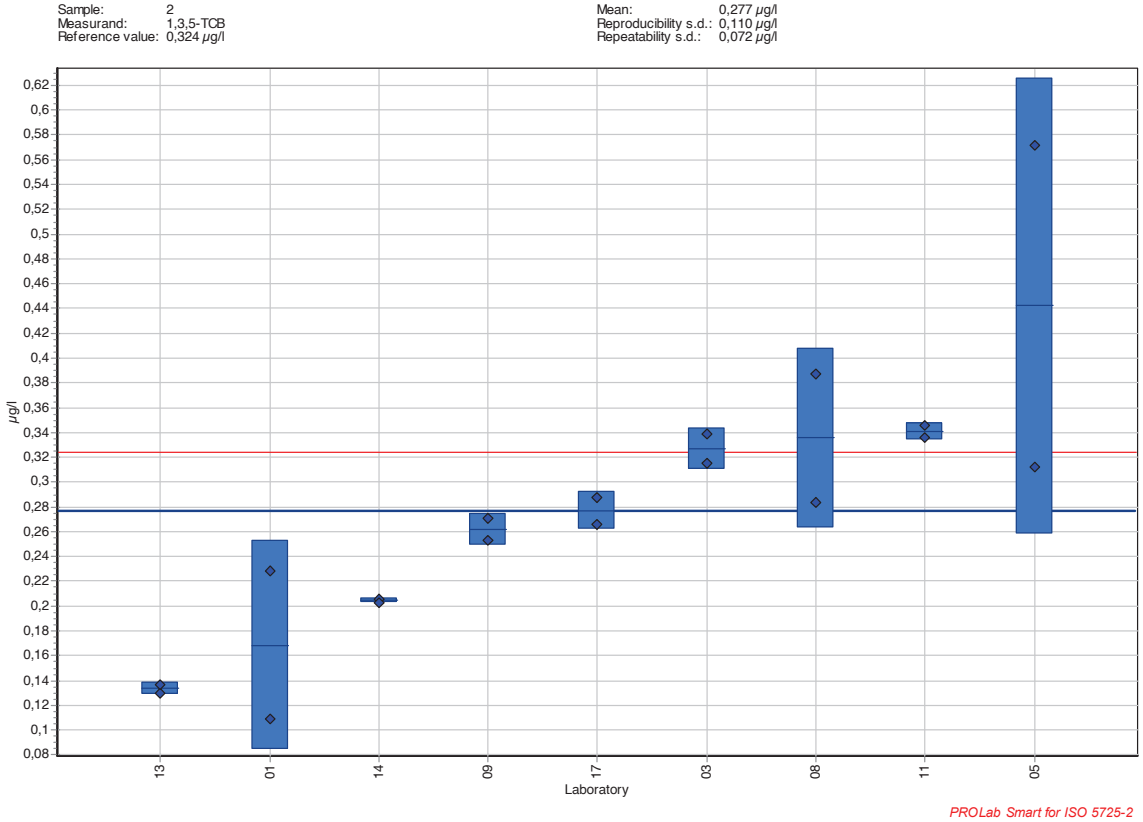

Figure 19: 1,3,5-TCB, sample 2

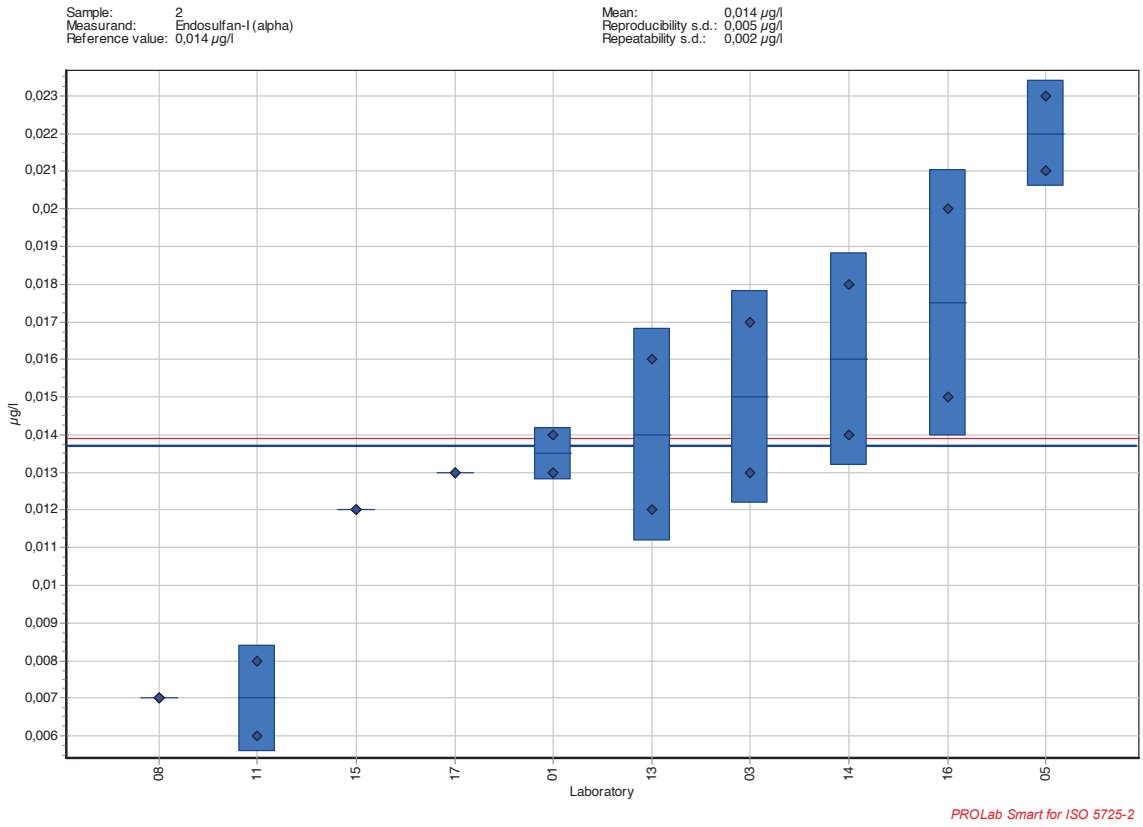

Figure 20: Endosulfan-I (alpha), sample 2

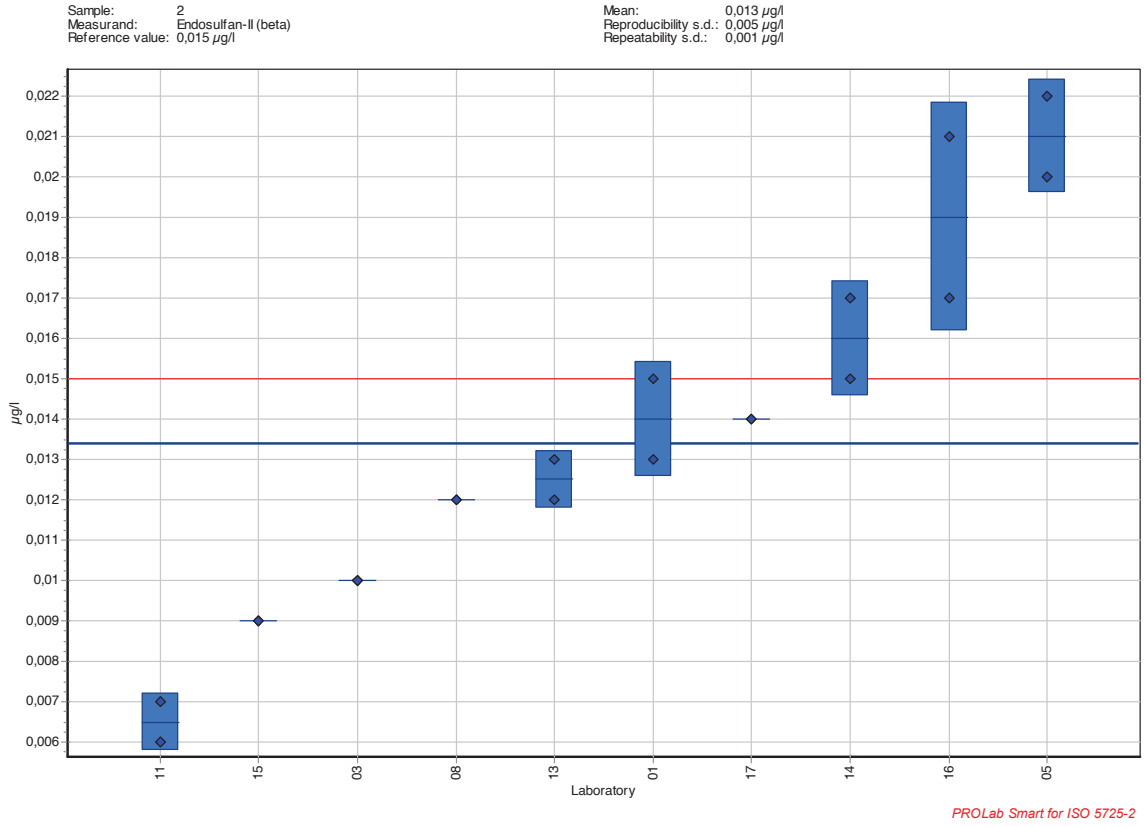

Figure 21: Endosulfan-II (beta), sample 2

Graphical presentation of the results of the Interlaboratory Trial for the validation of EN 16693
Determination of organochlorine pesticides (OCP) with SPE-disks combined with GC-MS

Sample 3: **High OCP-level sample containing 200 mg SPM**
Matrix: **Filtered surface water, spiked with OCP and SPM**

Legend: ——— reference value
——— overall mean

Outliers: A outlying single result of one laboratory,
B outlying laboratory mean,
C outlying within-laboratory variance

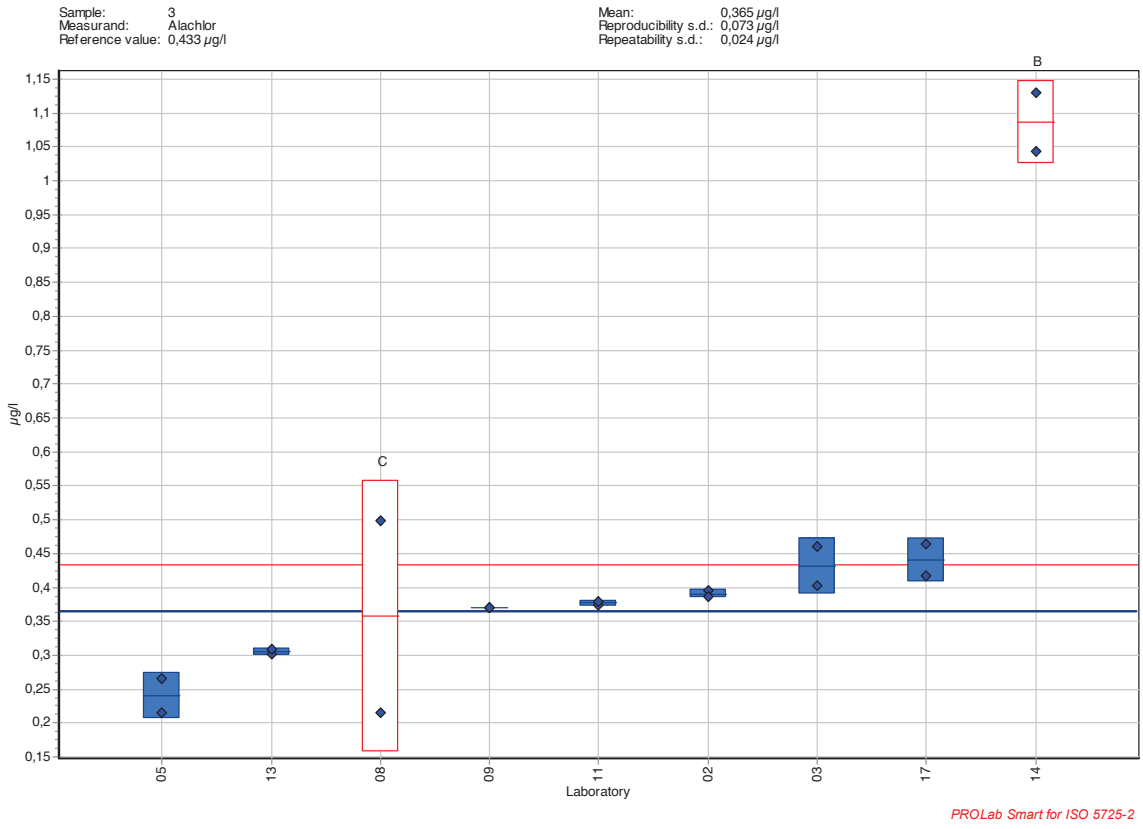

Figure 1: Alachlor, sample 3

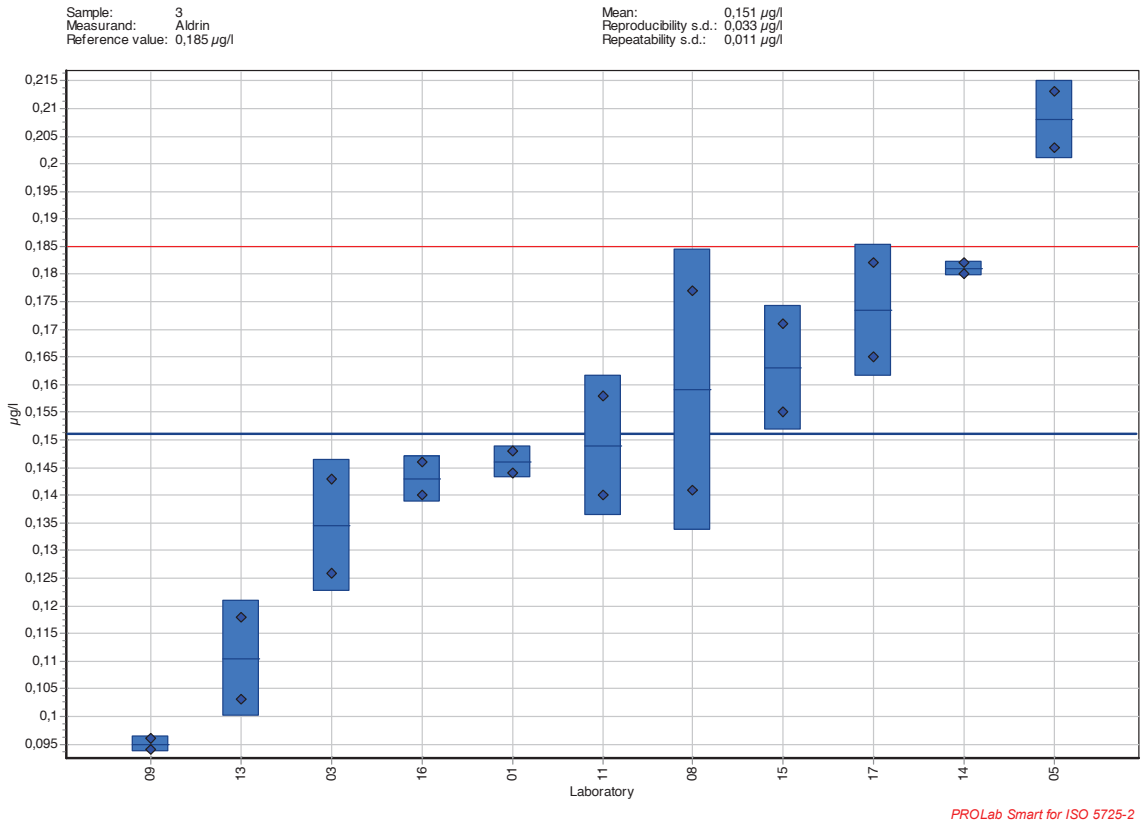

Figure 2: Aldrin, sample 3

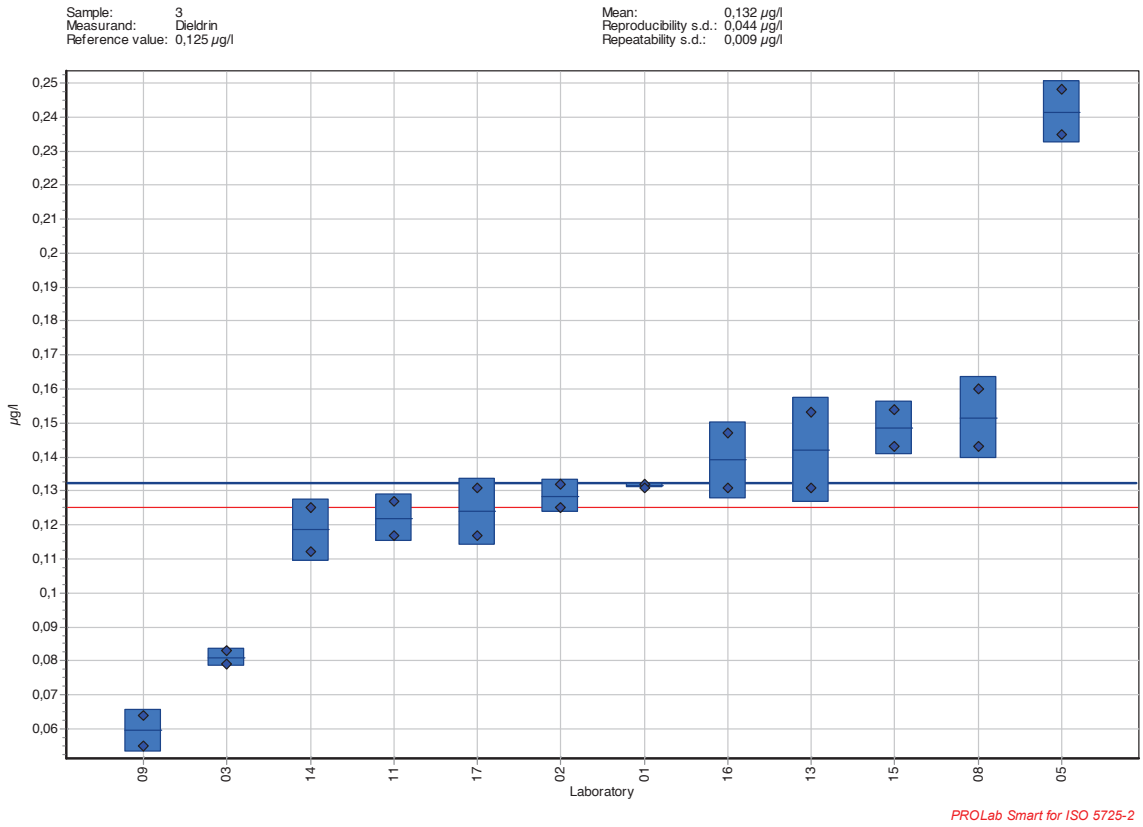

Figure 3: Dieldrin, sample 3

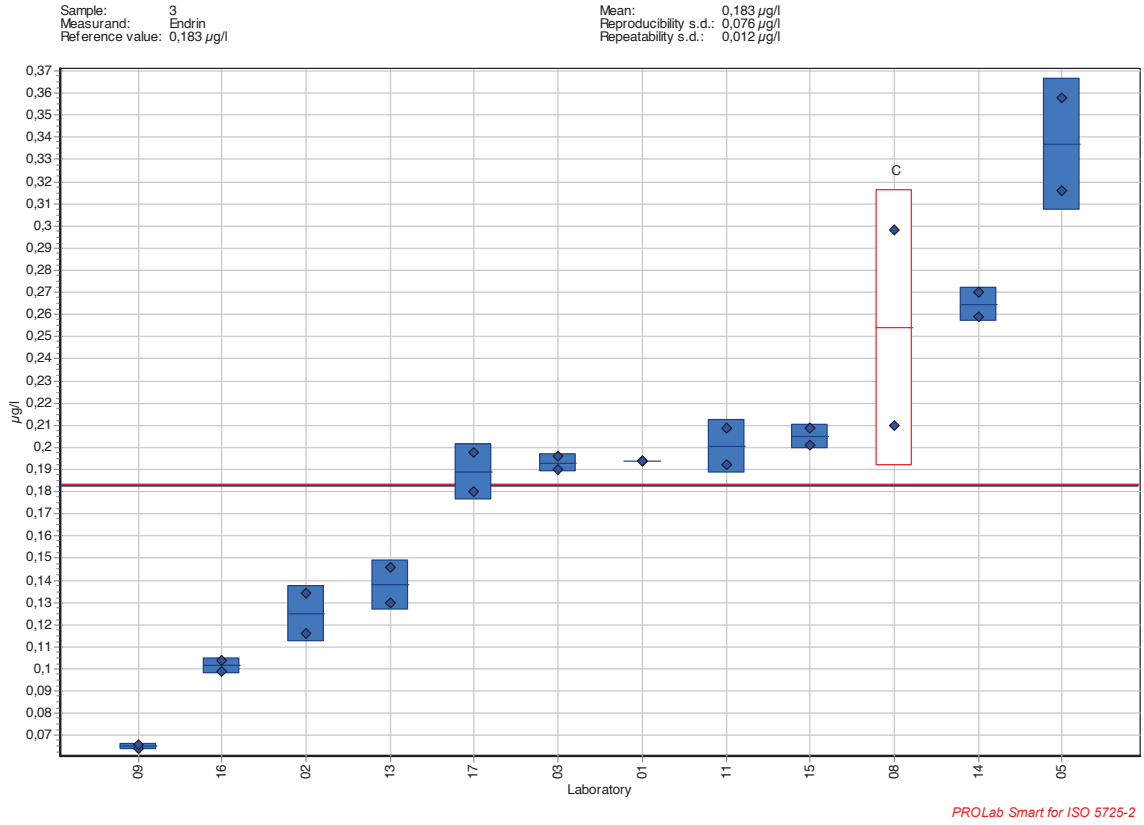

Figure 4: Endrin, sample 3

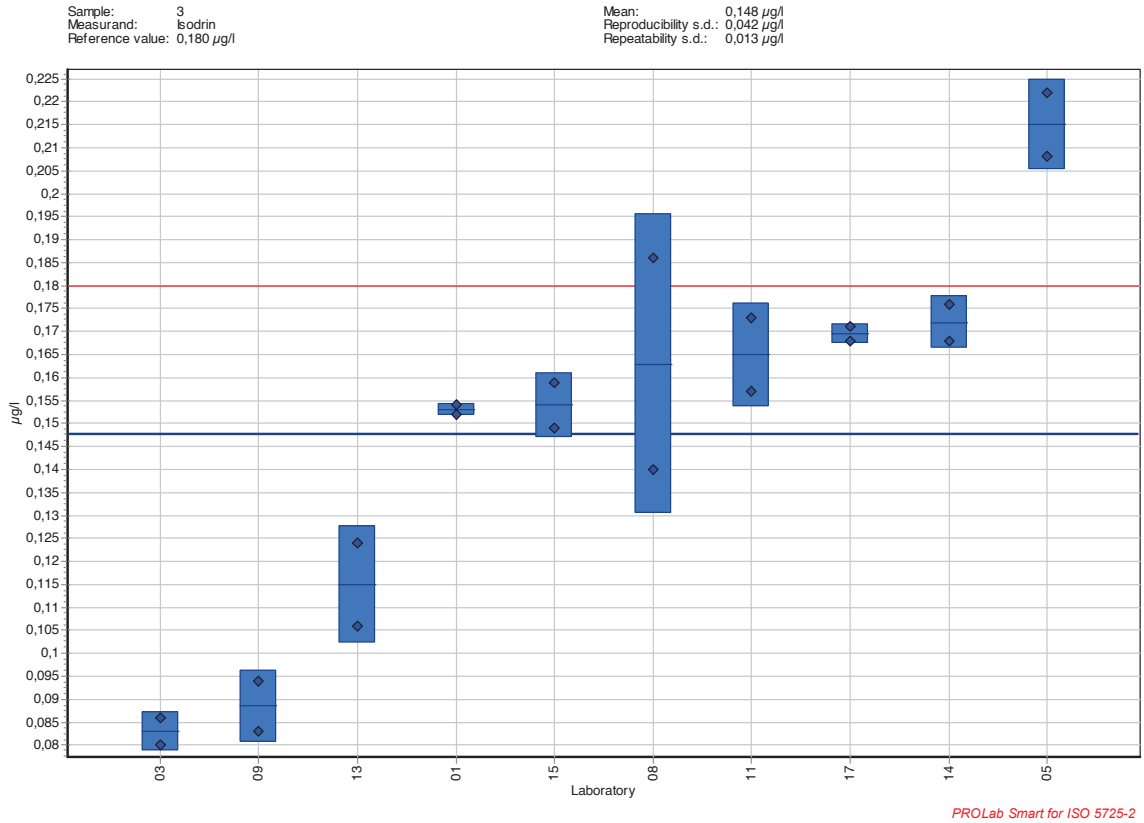

Figure 5: Isodrin, sample 3

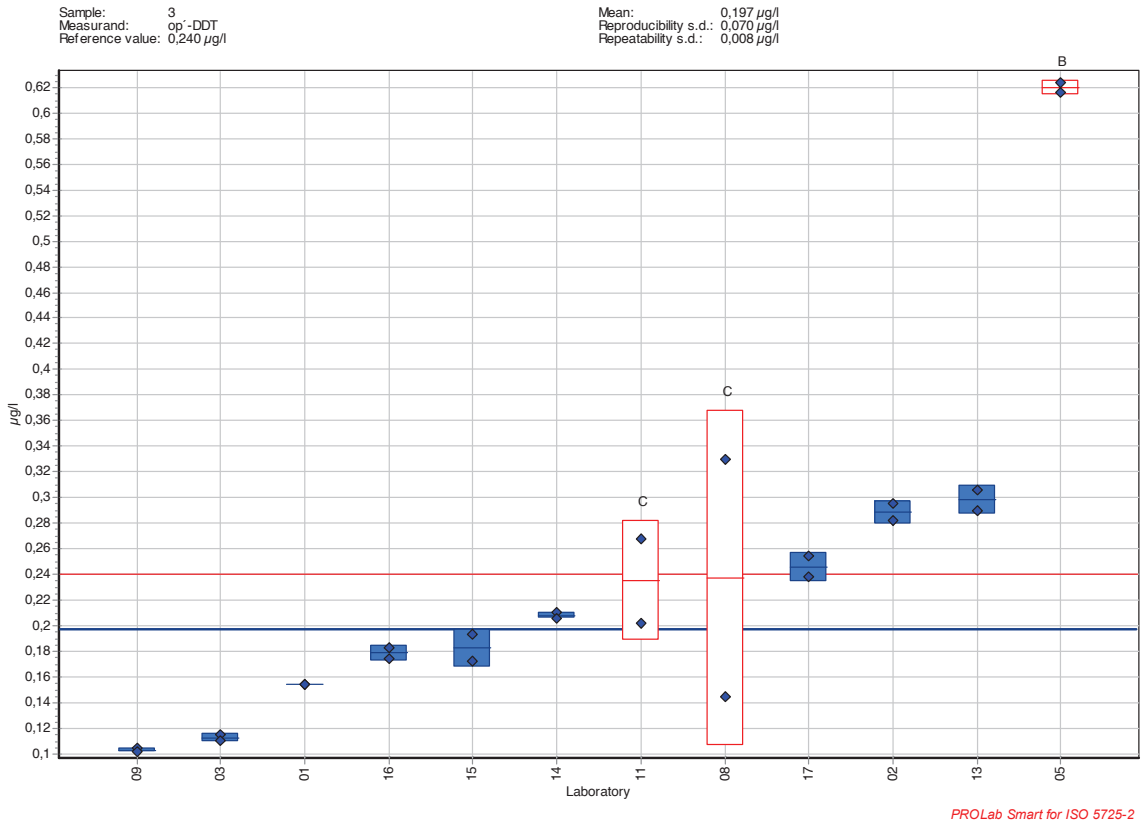

Figure 6: op‘-DDT, sample 3

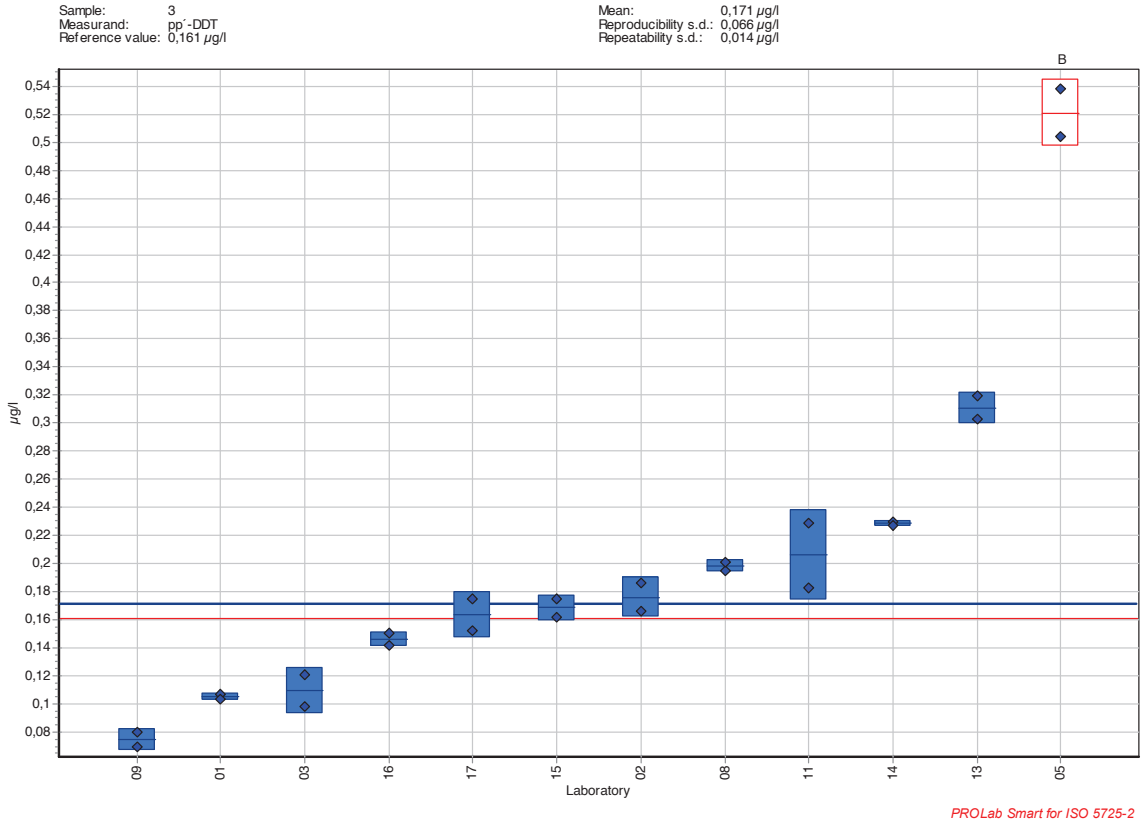

Figure 7: pp‘-DDT, sample 3

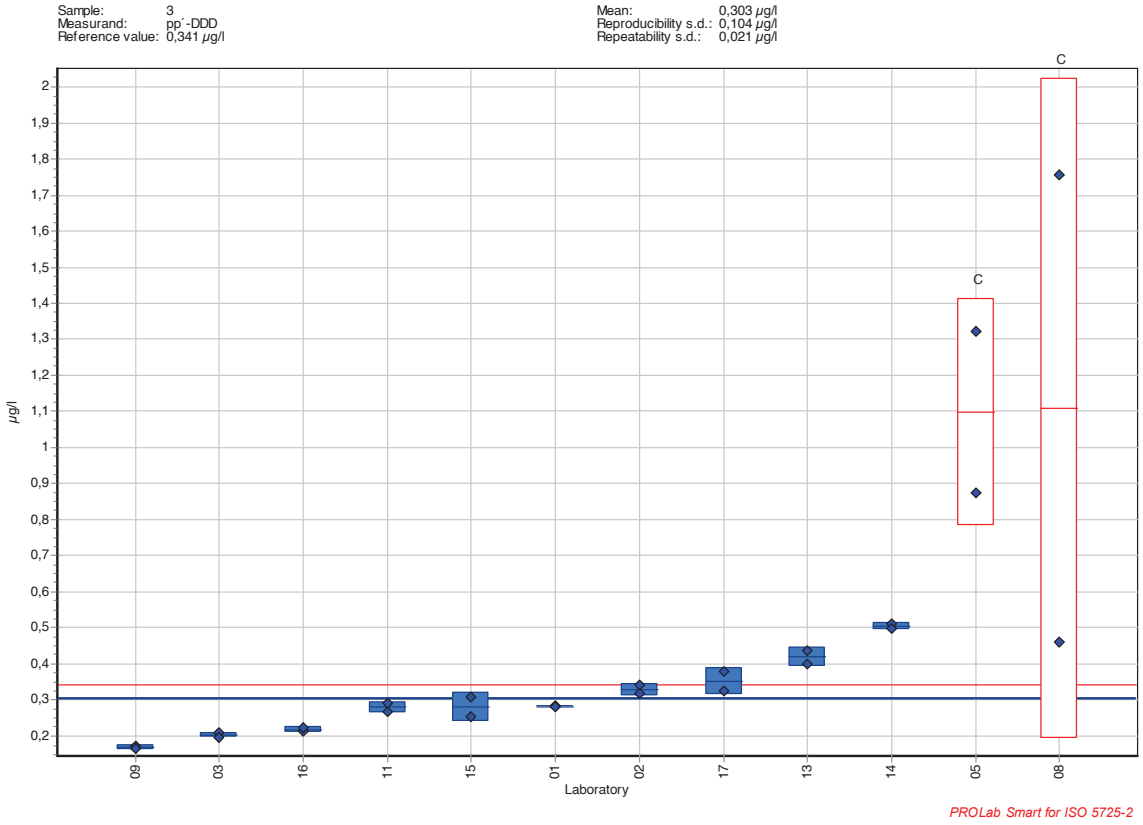

Figure 8: pp‘-DDD, sample 3

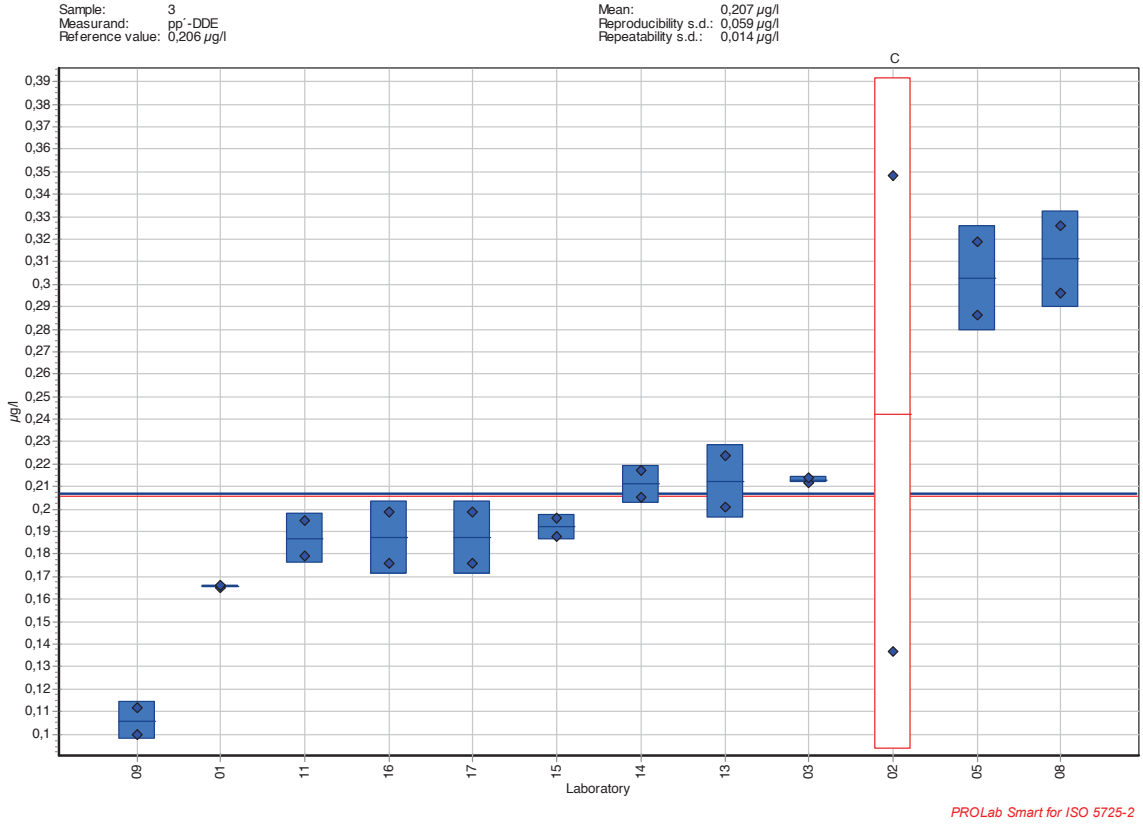

Figure 9: pp‘-DDE, sample 3

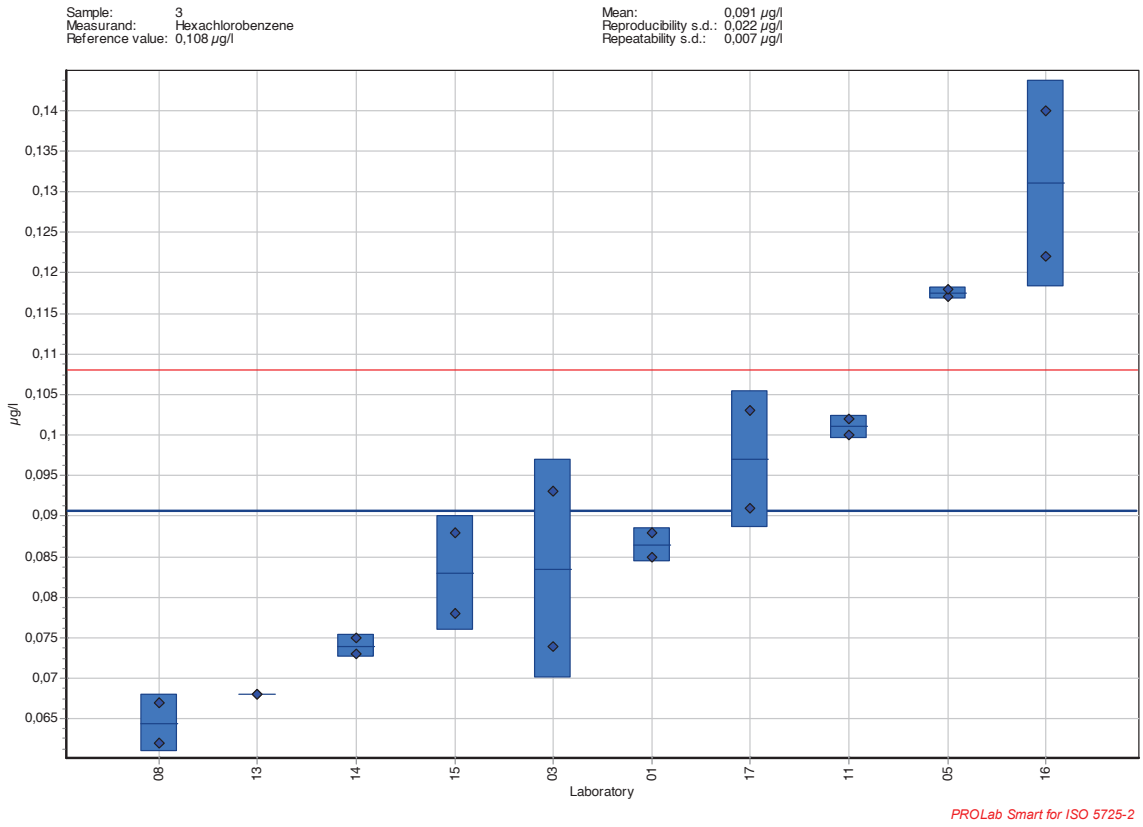

Figure 10: Hexachlorobenzene, sample 3

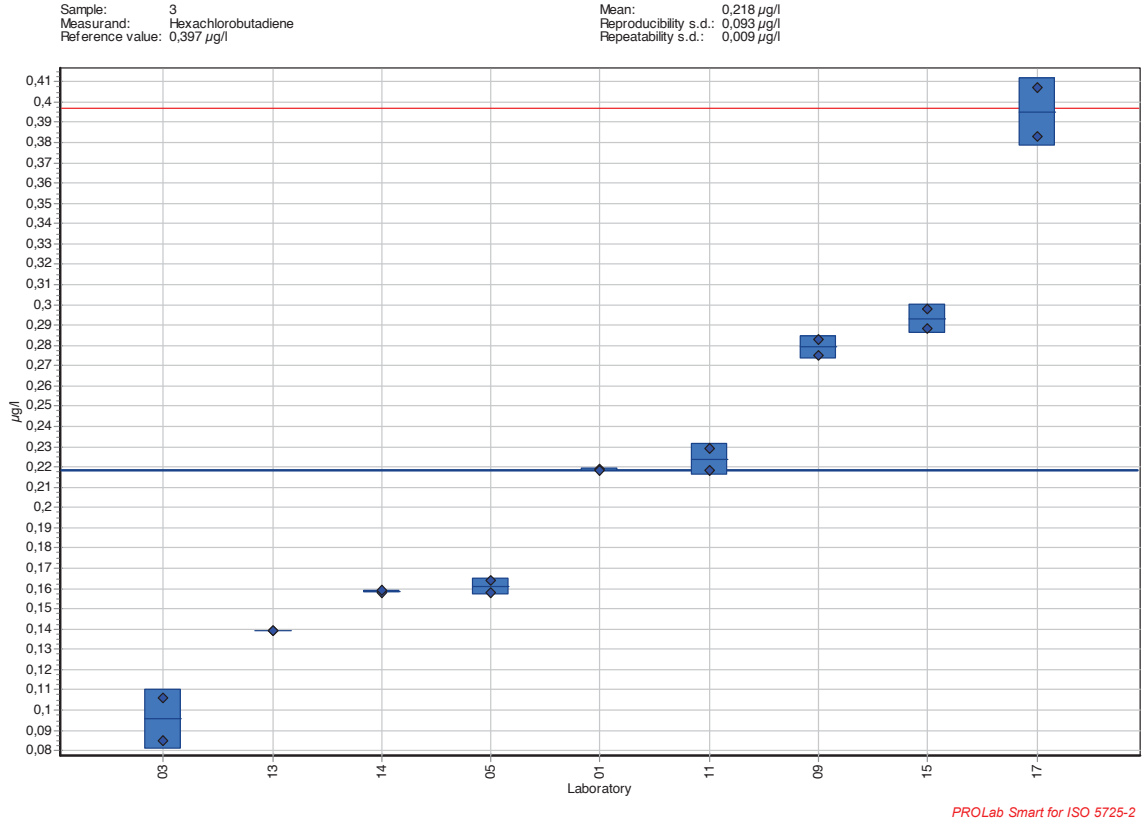

Figure 11: Hexachlorobutadiene, sample 3

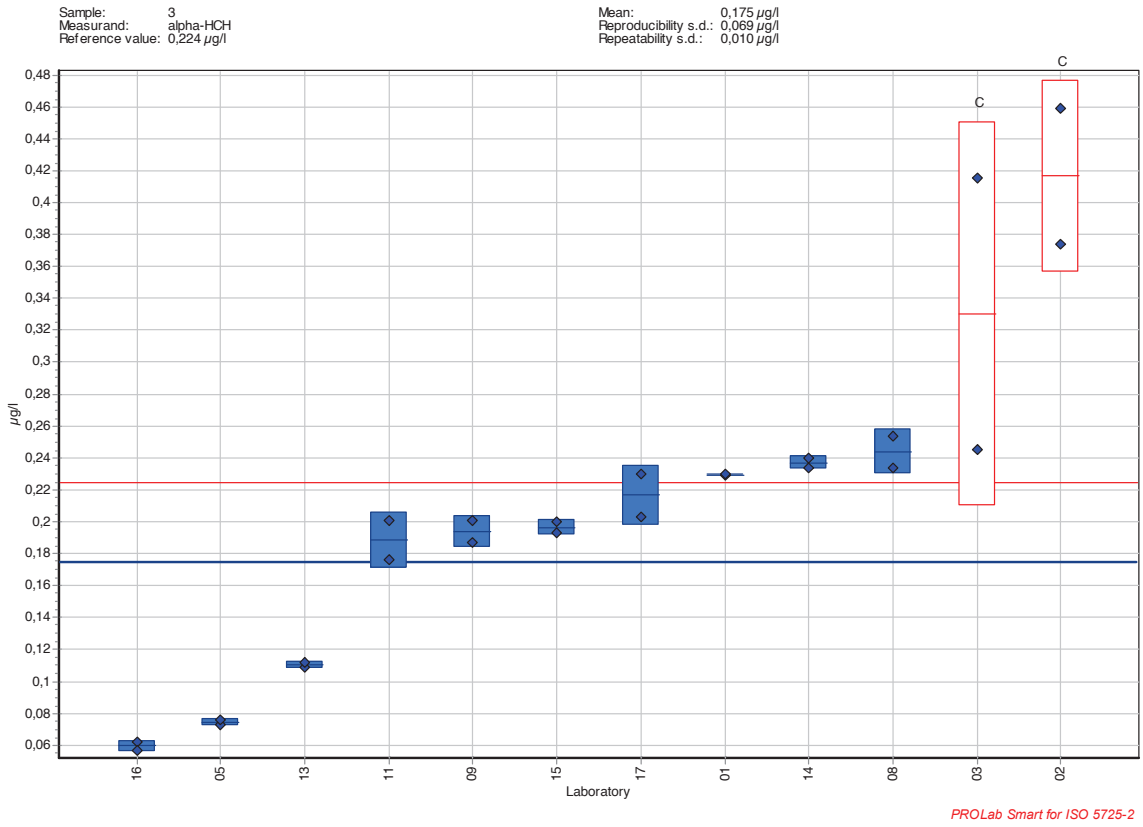

Figure 12: alpha-HCH, sample 3

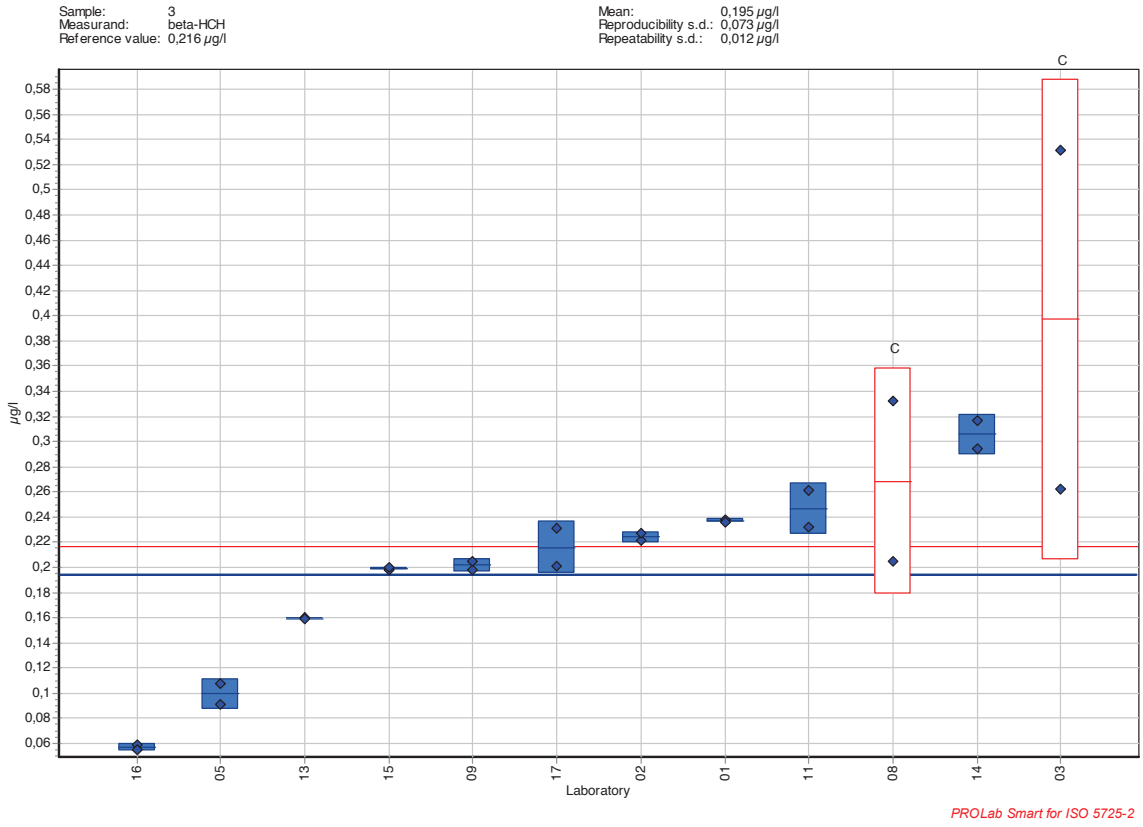

Figure 13: beta-HCH, sample 3

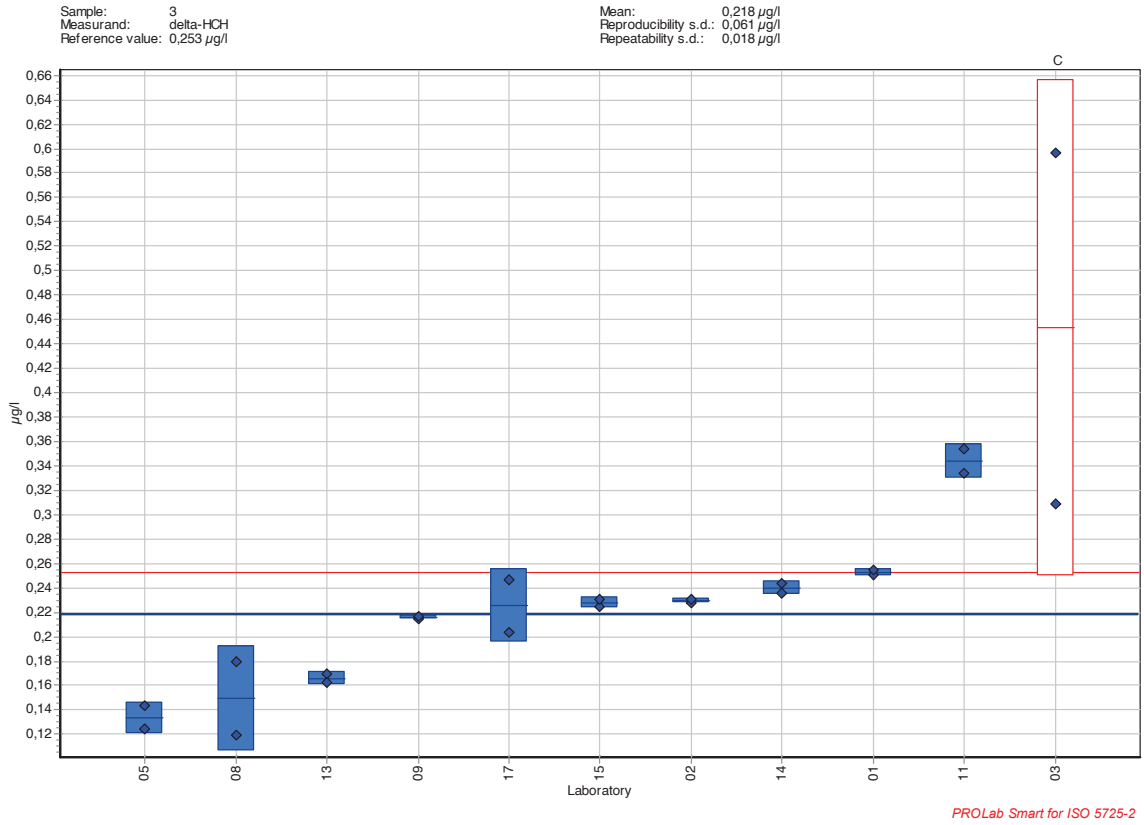

Figure 14: delta-HCH, sample 3

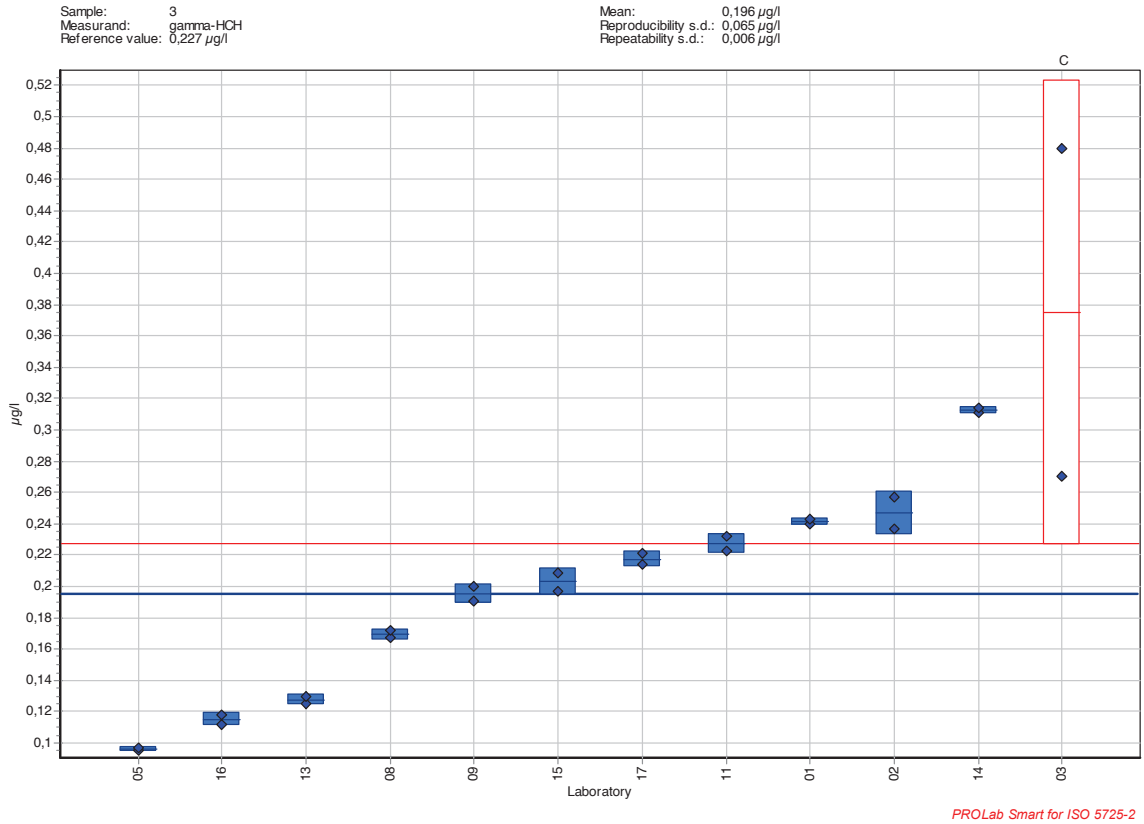

Figure 15: gamma-HCH, sample 3

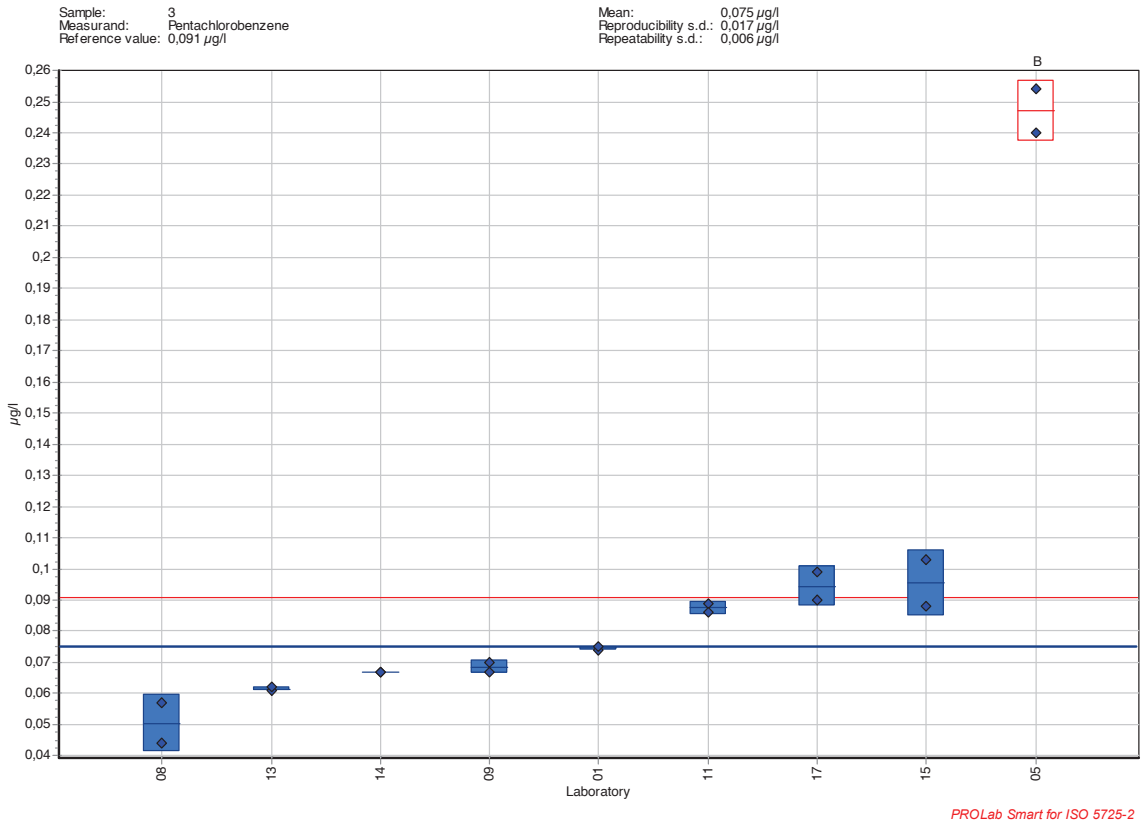

Figure 16: Pentachlorobenzene, sample 3

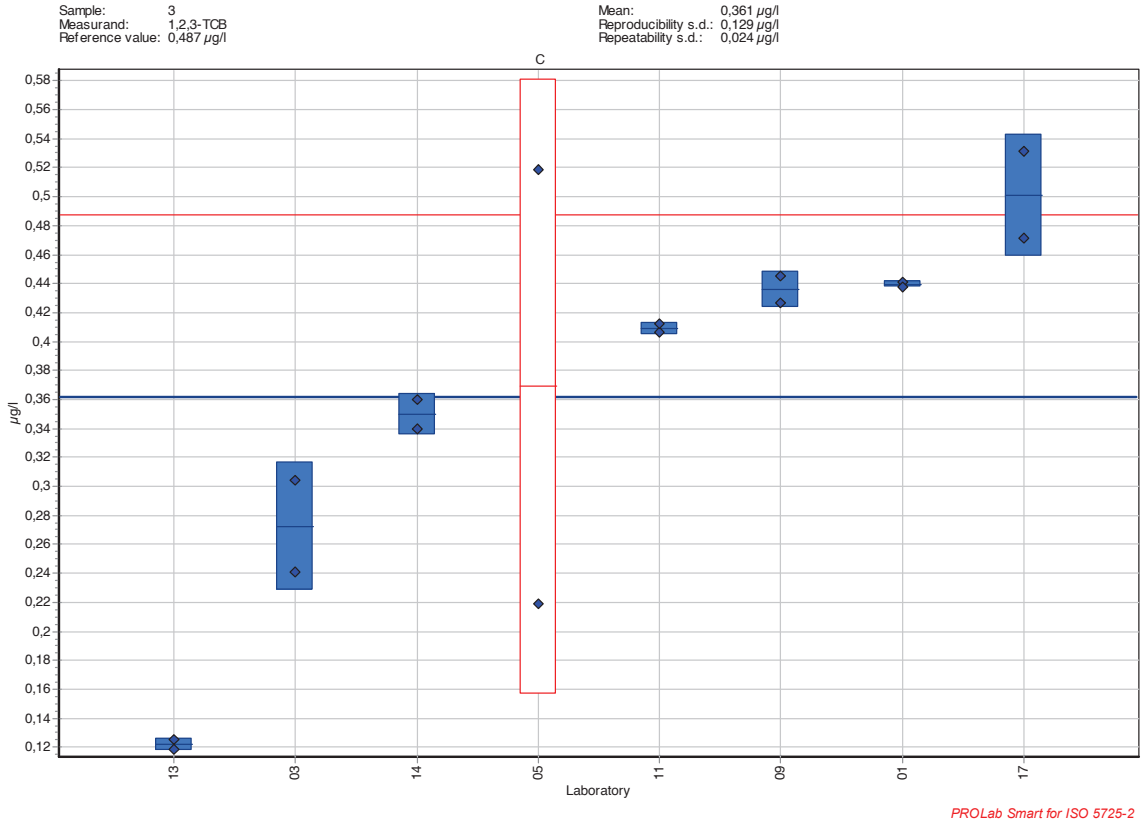

Figure 17: 1,2,3-TCB, sample 3

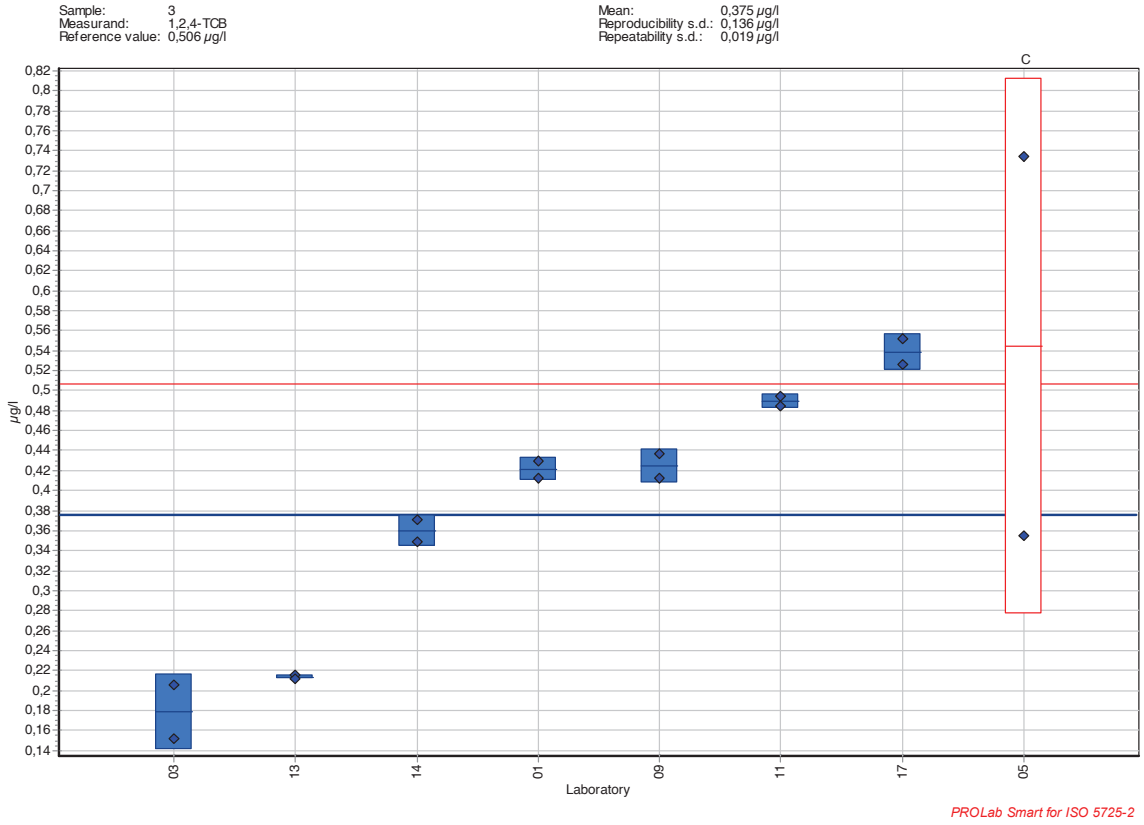

Figure 18: 1,2,4-TCB, sample 3

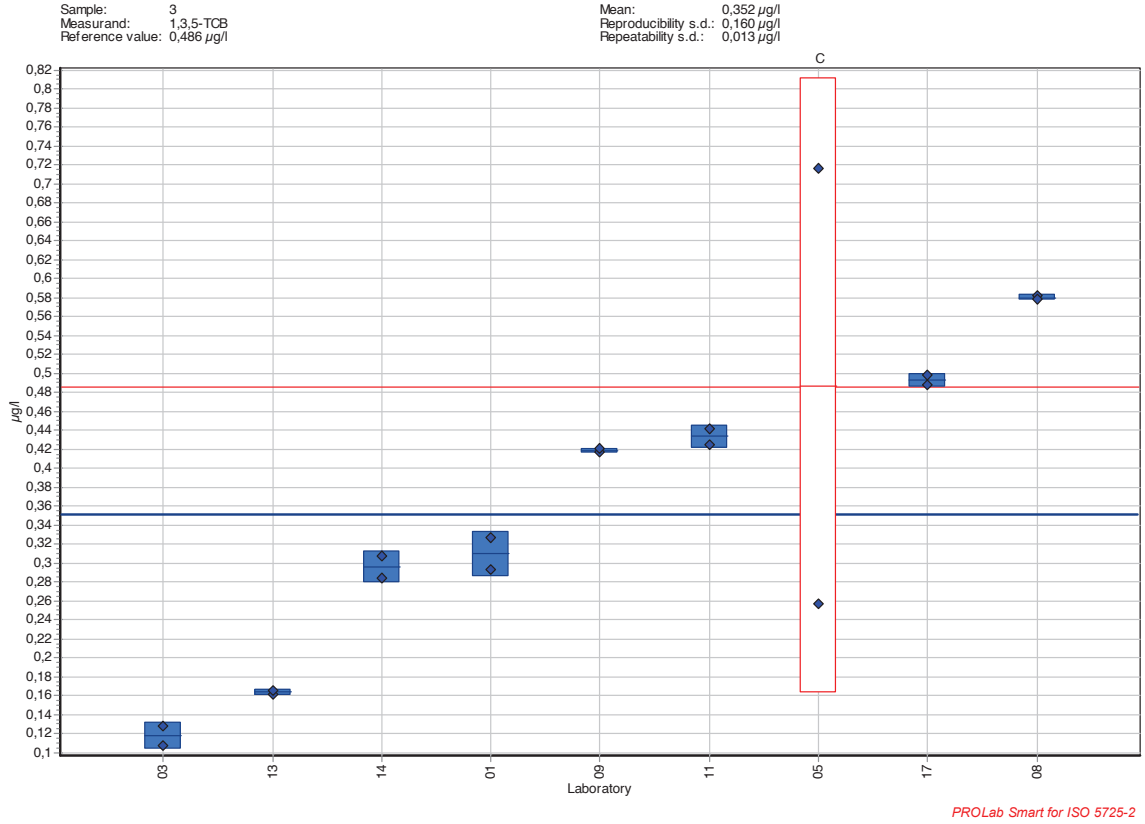

Figure 19: 1,3,5-TCB, sample 3

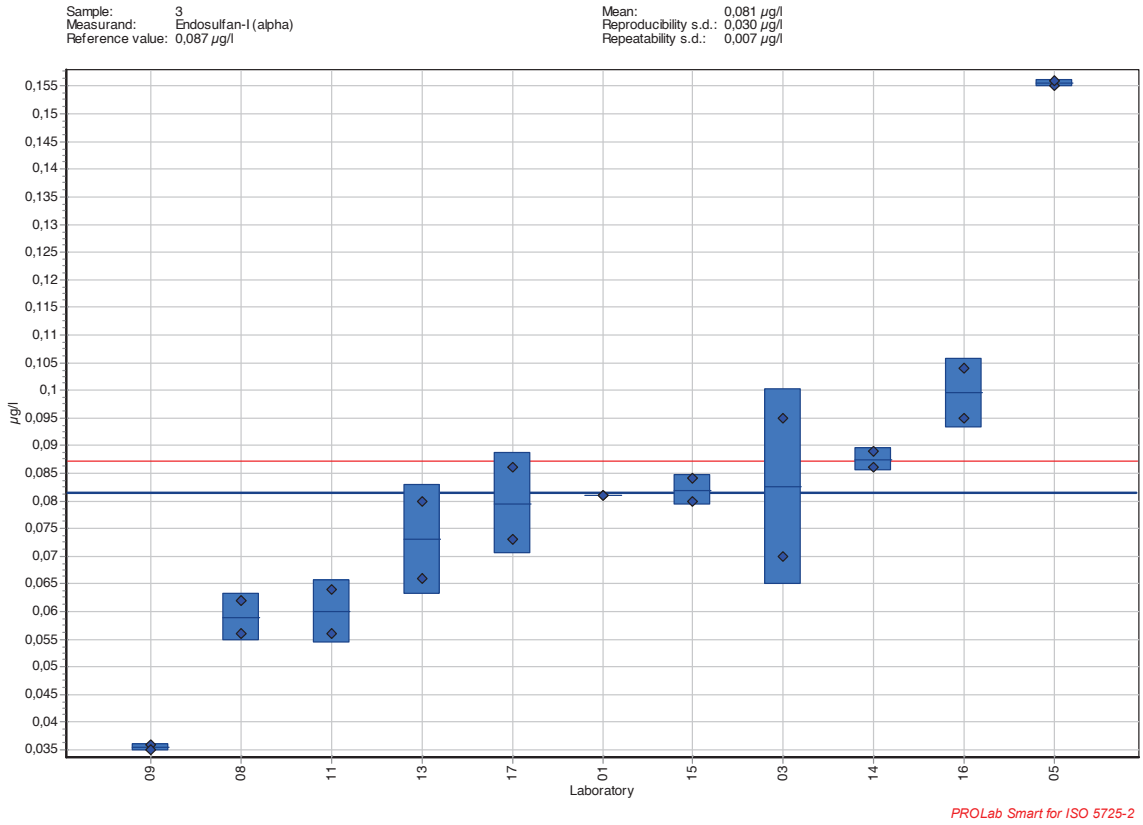

Figure 20: Endosulfan-I (alpha), sample 3

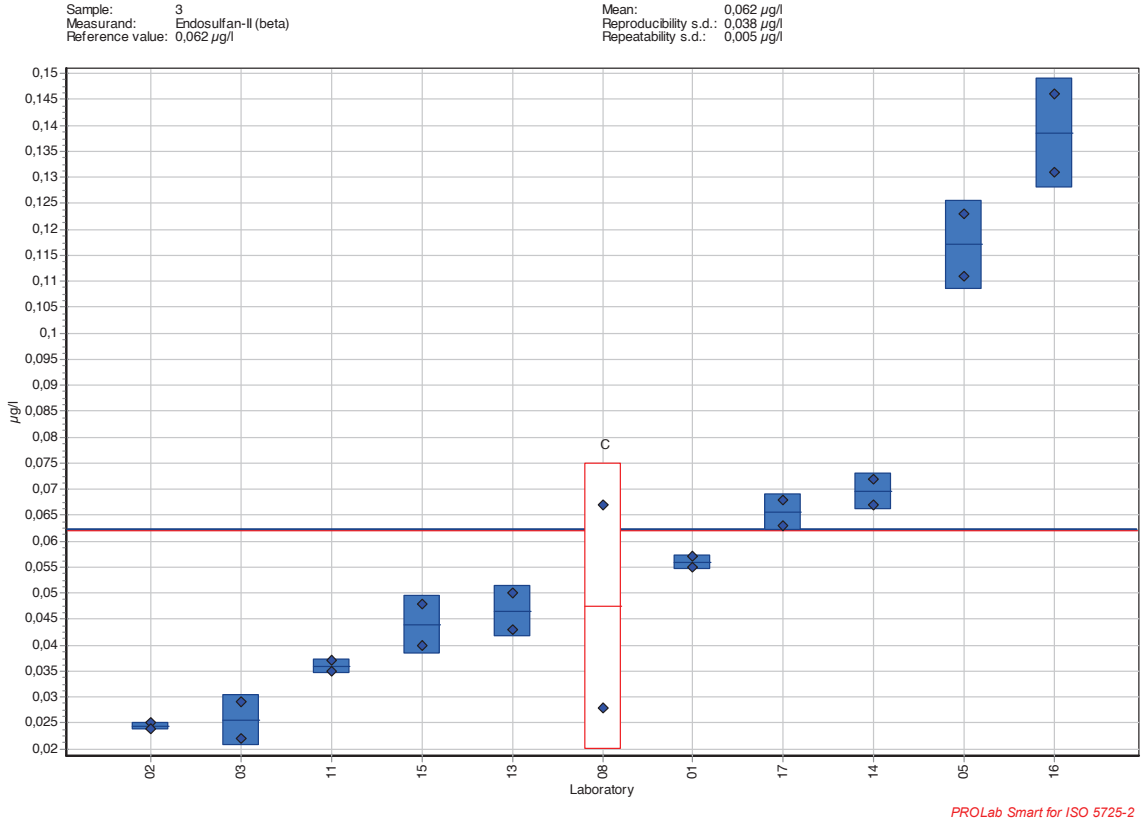

Figure 21: Endosulfan-II (beta), sample 3