Report: M/424 – CEN-Inter Laboratory Trial for validation (PAH) / prEN 16691:2014

"Water quality — Determination of Polycyclic Aromatic Hydrocarbons (PAH) in whole water samples — Method using disk based solid phase extraction (SPE) combined with gas chromatography mass spectrometry (GC-MS)"

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1. Introduction

Standardization needs with respect to analytical methods, fit for the purpose of Water Framework Directive (WFD) monitoring, have been highlighted at various occasions over the last years in bilateral discussions among the European Commission (DG Environment, Water & Marine Unit) and CEN/TC 230 "Water analysis".

As a result of all technical discussions the European Commission decided to mandate the development and/or the enhancement of analytical methods (chemical and biological) to CEN. This Mandate (M/424) considers different technical developments, of which the development of standards and the interlaboratory validation of the developed methods are important requirements.

This report describes the interlaboratory trial which was organized for the validation of standard PrEN 16691 "Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS). This standard describes a method for the determination of polycyclic aromatic hydrocarbons (PAH) using a disk based solid-phase extraction followed by gas chromatography-mass spectrometry (GC-MS) in whole water samples which contain up to 500 mg/l of suspended particulate matter (SPM).

The objective was to develop a method for the quantitative determination of 7 PAH (six classified as priority hazardous PAH and one priority PAH), listed Table 1. During the development there was a request from the Dutch mirror group to enlarge the scope of standard PrEN 16691 "Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS) to all 16 EPA PAH. The laboratories that participated in the validation were asked to voluntarily report on the additional 9 EPA PAH. The additional PAH used, including the mass of the ions are listed in Table 2.

Table 1   Substances (PAH) included in the interlaboratory trial on PrEN 16691

Name	Molecular formula	CAS registry No.	Molar mass	Annual average environmental quality standards (AA-EQS) in ng/l – surface water –	
			g/mol	Inland	Other
Anthracene	$C_{12}H_8$	120-12-7	178,23	100	100
Fluoranthene	$C_{16}H_{10}$	206-44-0	202,26	100	100
Benzo[b]fluoranthene	$C_{20}H_{12}$	205-99-2	252,32	Σ= 30	Σ= 30
Benzo[k]fluoranthene	$C_{20}H_{12}$	207-08-9	252,32		
Benzo[a]pyrene	$C_{20}H_{12}$	50-32-8	252,32	50	15
Benzo[ghi]perylene	$C_{22}H_{12}$	191-24-2	276,34	Σ= 2	Σ= 2
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	193-39-5	276,34		

Table 2   Additional PAH included in the interlaboratory trial on PrEN 16691

Name	Molecular formula	CAS registry No.	Molar mass	Diagnostic ion	
			g/mol	1 (m/z)	2 (m/z)
Naphtalene	$C_{10}H_8$	91-20-3	128.17	128(100)	102(1)
Fluorene	$C_{13}H_{10}$	86-73-7	166.22	165(100)	166(81)
Acenaphthene	$C_{12}H_{10}$	83-32-9	154.21	153(100)	154(70)
Acenaphthylene	$C_{12}H_8$	208-96-8	152.20	152(100)	150(3)
Phenanthrene	$C_{12}H_8$	85-01-8	178.23	178(100)	152(12)
Pyrene	$C_{16}H_{10}$	129-00-0	202.26	202(100)	200(2)
Chrysene	$C_{18}H_{12}$	218-01-0	228.29	228(100)	226(6)
Benzo[a]anthracene	$C_{18}H_{12}$	56-55-3	228.29	228(100)	226(3)
Dibenzo[a,h]anthracene	$C_{22}H_{14}$	53-70-3	278.35	278(100)	139(9)
Note: figures in parentheses are the relative intensities of the fragment ion					

The interlaboratory trial was designed to serve as a validation exercise and not as proficiency testing. Therefore, it was mandatory for all participants, included in the evaluation process, to strictly follow the procedure as prescribed in the draft standard. Therefore prEN 16691:2014 "Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS that had been made available for each participant early 2014.

2. Principle

The PAH 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 disk.

The extract is concentrated by evaporation. Prior to injection, an injection standard is added to each extract, and an aliquot is injected into the gas chromatograph. 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.

3. Interlaboratory trial design and sample preparation

Announcement of the interlaboratory-trial   November 2013
Deadline 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 5725-2:1994   August 2014

Each participant received 3 samples and one ampoule for spiking:

Sample type 1:	Low level sample containing SPM	2x 1 000 ml
Sample type 2	High level sample containing SPM	2x 1 000 ml
Sample type 3	Sample without SPM to be spiked with the supplied solution in the ampoule	2x 1 000 ml
Ampoule:	Spike solution containing 16 PAH in methanol. This solution was used to spike Sample 3 (100µL) and was shipped separately from the samples.	

EC-JRC-IRMM (Geel, Belgium) was asked for support, and provided testing materials for the intercomparison. The planning, preparation, conceptual proof of homogeneity and stability of the test samples for the trial was provided by EC-JRC-IRMM.

Preparation of the samples

1. Bottles were pre-cleaned with mineral water and acetone at TNO and sent to JRC- IRMM by courier.
2. Selection of the water matrix
   The most suitable water matrix for the preparation of the test material was carefully selected.
   - Type-1 water was ruled out because of its low ionic strength, it would certainly not be representative of an environmental water sample.
   - Use of tap water was also ruled out because of the content of disinfection compounds.
   - The use of natural waters directly from a lake or a river would imply a pre-treatment of the water like filtration, an exhaustive analysis of blanks and needing extra water in case of the repetition of the whole process.
   - Bottled mineral water (Spa-Reine) offered a good compromise concerning all the aspects mentioned above with a typical composition as given in Table 3.

Table 3. Major components present in SPA Reine mineral water (still), data taken from label.

Ion / parameter Concentration	mg/l
Ca^{2+}	4.5
Mg^{2+}	1.3
Na^+	3.0
K^+	0.5
Cl^-	5.0
SO_4^{2-}	4.0
NO_3^-	1.9
HCO_3^-	15
SiO_2	7
Dry residue	33
Ion / parameter	**Value**
pH	6

3. Three different types of each sample were prepared (Table 4). Each type of sample was made in duplicate. Therefore each participating laboratory received 6 bottles.

Table 4. Sample types in the CEN424/TC230 validation

Sample Type	Replicates	Composition	Description/Comments
1	A and B	Low SPM	20 mg SPM/l targeted
2	A and B	High SPM	200 mg SPM/l targeted
3	A and B	Spike	SPA mineral water

Samples were not stabilized using chemicals. Any storage of samples was to be carried out by refrigeration after arrival according to EN-ISO- 5667-3:2012 "*Water quality - Sampling - Part 3: Preservation and handling of water samples*"

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

      1) Sample 1: concentrations close to the corresponding environmental quality standards (EQS) for inland surface water up to 3-times EQS.

      2) Sample 2: concentrations 5 to 20 times EQS for inland surface water.

3) Sample 3: Spike – Sample without SPM to be spiked with the supplied solution in the ampoule.

4) Blank: Regular laboratory procedural blank. The blank was not supplied.

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 analysis from each of the 3 samples and procedural blanks.

4. Ampouling of the spiking solution
    This solution was prepared by mixing individual certified reference materials (CRM) solutions. TNO brought the spiking solutions of PAHs in methanol to JRC-IRMM for filling and flame-sealing in ampoules. Sample Type 3 was to be subsequently spiked with 100 µl of this spiking standard by the participating laboratories in the validation. In total 2.7 ml of the spiking solutions were filled manually into 3 ml amber glass ampoules using a glass-syringe.

5. Sample preparation
    Bottles corresponding to sample types 1 and 2 (Table 4) were prepared on June the 2nd 2014. The slurry addition technique developed during the EMRP-ENV08 project (http://www.emrp-waterframeworkdirective.bam.de/en/home/index.htm) was used to spike the samples with suspended particulate matter (SPM) in the form of a model SPM. For this concept, finely milled soil and sediments were reproducibly added as slurry to the water samples. The top particle size of these model-SPMs was in the range from 9 to 12.5 µm which corresponds to natural SPM in many respects. The analytes are strongly bound to this model-SPM and therefore mimics the situation in natural waters which should present a similar challenge for analysis as routine whole-water samples.

6. Packing and shipping
    The sample bottles were individually packed in boxes which were placed in cardboard boxes filled with shock absorbing materials.
    An information sheet was added inside each of the boxes with instructions for storage and use for the laboratories.

4. Homogeneity and stability of test samples

Conceptual proof with respect to homogeneity and stability of the final water samples has been collected during the EMRP-ENV08 project. Additionally the CEN work package leader s for the PAH validation has provided additional essential data.

Between-unit heterogeneity has been assessed on 5 units of the final samples with SPM loads employed during the validation (from 20 mg/l). Samples were checked with respect to stability for a period of 1 month at +18 °C and +4 °C, respectively (Figure 1). The conclusion was that all samples should be shipped with overnight courier and stored at +4 °C until analysis. Under these conditions the samples were deemed stable for the lifetime of the intercomparison (4 weeks).
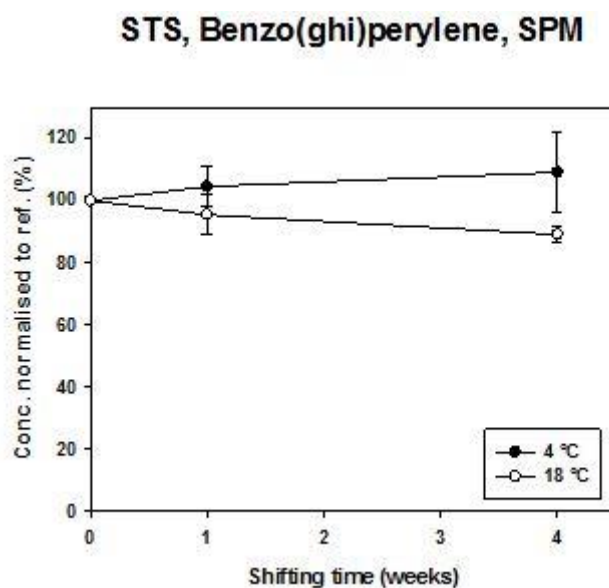
Figure 1. Example of the target analytes in the test materials containing SPMs over for 4 weeks. Benzo(ghi)perylene is shown as representative of PAH.

Since the addition of target analytes was based on slurry addition it was important to asses if there was a change in the density in the constantly mixed slurry over time. Therefore aliquots of the slurry were placed on pre-weighed petri dishes at different times.

Two petri dishes were filled at the beginning, two in the middle and two at the very end of the sample preparation sequence. The petri dishes were left to air-drying in a clean bench and the dry mass of the loaded SPM was determined.

No trend or difference was observed for the added SPM amounts between the beginning and the end of the preparation sequence (Table 5).

Table 5. SPM amounts added to samples type 1 and 2, n = 6

Sample type	Model SPM (mg/L)	Blank SPM (mg/L)
PAH type 1[a]	20.20 ± 0.83	-
PAH type 2[b]	49.18 ± 0.31	147.32 ±0.37

a) Derived from **ERM-CZ100**
b) Derived from the PAH model SPM developed in EMRP ENV08

In Table 6 and 7 certified- and additional information PAH mass fractions are given for ERM-CZ100 (for more details see Certificate of Analysis issued by JRC-IRMM). In Table 8 and 9 the estimated PAH mass fractions are given for the model SPM and the blank SPM. The bold printed compounds represent the PAH relating to the mandate.

Table 6. Certified values for ERM-CZ100

Fine Dust (PM$_{10}$-like)		
PAH	**Mass Fraction**	
	Certified value [ng/g]	Uncertainty [ng/g]
Benzo(b)fluoranthene	1420	140
Benzo(k)fluoranthene	670	60
Benzo(a)pyrene	720	50
Indeno[1,2,3-cd]pyrene	1070	100
Benzo[a]anthracene	910	70
Dibenzo[a,h]anthracene	180	40

Table 7 . Additional information values for ERM-CZ100

PAH	**Mass Fraction**
	Value [ng/g]
Anthracene	280
Fluoranthene	4670
Benzo[ghi]perylene	1760
Phenanthrene	2230
Pyrene	4590
Chrysene	1610

Table 8. Estimated values for Model SPM

Model SPM		
PAH	**Mass Fraction**	
	Estimated value [ng/g]	Uncertainty [ng/g][1]
Naphtalene	1195	193
Anthracene	534	69
Fluoranthene	9512	231
Benzo(b)fluoranthene	3111	65
Benzo(k)fluoranthene	2314	510
Benzo(a)pyrene	2330	172
Indeno(1,2,3-cd)pyrene	2607	95
Benzo(g,h,i)perylene	3055	65

1. The estimated uncertainty only comprises contributions from between-bottle heterogeneity and uncertainty from SPM characterisation whithout the uncertainty contribution from short term stability.

Table 9. Estimated values for blank SPM

PAH	Mass Fraction	
	Estimated value [ng/g]	Uncertainty [ng/g][1]
Naphtalene	47.5	19.5
Anthracene	6.5	1.9
Fluoranthene	57.6	6.5
Benzo(b)fluoranthene	46.1	2.7
Benzo(k)fluoranthene	34.2	10.0
Benzo(a)pyrene	56.0	17.6
Indeno(1,2,3-cd)pyrene	47.0	6.2
Benzo(g,h,i)perylene	45.6	4.1

1. The estimated uncertainty only comprises the uncertainty contribution from a limited Blank SPM characterisation.

The physio-chemical interactions taking place when adding SPM to pre-filled water bottles are not known in detail. In addition, no characterisation of the final samples took place due to time-restraints coupled with potential stability issues when extending the necessary life-time for the prepared samples. Therefore all concentrations in the final water samples based on slurry addition are *estimated.*

5. Technical aspects

5.1 Participants

The 6 samples were shipped to the 19 participants on June the 3rd 2014. The next day the information for executing the trial was send. This email contained

- a copy of the prEN 16691: 2014 **"**Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS),
- a document with trial information for participants
- a spreadsheet for reporting the results
- a spreadsheet for the method characteristics

The deadline for reporting the results was set to July the 15th 2014.

Table 10. Overview geographical spread of participants

Country	Number of participating laboratories
Belgium	2
France	2
Germany	2
Luxemburg	1
Netherlands	4
Norway	1
Portugal	1
Spain	4
UK	2

Four laboratories did not report any results. All four labs were contacted separately to ask for the delay. One of them did not report, without any further comments. One could not report due to supply issues. One lab decided not to report because the recovery results of the analysed samples (internal standards?), done by GC-MS, were too low. One lab send an email on August the 20th , one month after official closing for reporting results of the ILT, that it was not possible to report due to delivery problems of the deuterated internal standard mix.

Results from three laboratories were excluded from evaluation as the results for the sample 3 (spiking) were very different from the expected value (>50% difference). Individual results for sample 3, from the other laboratories that differ more than 50% were not included in the evaluation either.

Two laboratories used a triple quad MS. This is not strictly according to the standard. It was decided to include these results in the graphics and mark them with TQ. In the statistical evaluation these results are also included. (CEN/TC 230/WG1 has to decide to include these results or not.)

One laboratory sent in 2 sets of results. Only one set was partly used.

A total of 12 laboratories (2 TQ included) reported 13 sets of results which were included in the evaluation process according to ISO 5725-2:1994.

5.2 Examples of reported procedural details

For reporting of the results all participants received a spread sheet. This sheet was used by all participants. Additionally, participants were asked to fill in an Excel spreadsheet 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.

The reported technical details of the 12 laboratories whose results are included in the statistical evaluation, including the 2 labs that used TQ, are in table 11.

Table 11. Summary of reported technical details

Technical detail		Number of reports
Sample preparation	a) manually	9
	b) automated	3
Disk: Type of adsorbent:	a) C18	3
	b) DVB	8
	c) mixed	1
Disk diameter:	47 – 50 mm	all
Extraction within:	a)<7 days	6
	b)>7 days	6
	c)< 50 days	all
Clean-up:	a) Yes (2)	**2**
	No (10	**10**
Solvent evaporation:	a) vacuum (ambient air)	6
	b) nitrogen (N$_2$)	5
	c) no solvent evaporation	1
Injection standard for volume control added:		all
Final volume:	a) < 0,5 ml	6
	b) 0,5 – 1 ml	6
	c) >1 ml	1
GC Columns according recommendations in clause 6.6 of prEN 16691:2014		all
Dimensions [length (m) x diameter (µm) x film (µm)]:	20 x 0.18 x 0.18	2
	30 x 0.25 x 0.25	7
	60 x 0.25 x 0.25	3
Injector: Type:	a) fixed temp	8
	b) PTV	4
Injection mode:	a) splitless	10
	b) LVI	1
	c) open split	1
Mass spectrometer type:	a) Q-pol-EI-MS (SIM)	10
	b) Q-pol-MS (MS/MS)	2
	c) ion-trap MS	1
Reported LOQ (ng/l):	a) 0,1 – 1	6
	b) > 1	3
	c) not reported	3
Matrix used for blank:	a) Milli-Q	8
	b) Mineral water	4
Parameter reported by labs:	a) all 7 PAH from the mandate	13
	b) all 16 EPA PAH	8
	c) nearly all 16 EPA PAH	10
Labelled internal stds:	a) Yes	12
	b) No	0
Certified calibration stds	a) Yes	11
	b) No	1

The average recovery for the labelled internal standards is given in table 12.

Table 12. Recovery of labelled internal standards

PAH	% avg recovery	% sd
Anthracene-D	82	24
Fluoranthene-D	92	21
Benzo[b]fluoranthene-D	96	25
Benzo[k]fluoranthene-D	89	25
Benzo[a]pyrene-D	96	29
Benzo[ghi]perylene-D	85	23
Indeno[1.2.3-cd]pyrene-D	88	35

Naphtalene-D	74	28
Fluorene-D	83	26
Acenaphthene-D	72	29
Acenaphthylene-D	75	26
Phenanthrene-D	84	23
Pyrene-D	94	16
Chrysene-D	85	26
Benzo[a]anthracene-D	105	29
Dibenzo[a.h]anthracene-D	88	32

6. Annex: Data evaluation according ISO 5725-2:1994

6.1 Results of the interlaboratory trial for the validation of "prEN 16691

"Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS)

Table 13: Sample 1: Low PAH-level sample containing 20mg/L suspended particulate matter (SPM) **Matrix: Mineral water, spiked with PAH containing SPM**

Sample 1									
Measurand	l	n	o %	X ng/l	$\overline{\overline{x}}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
Anthracene	10	20	0.0	5.66	3.44	60.89	1.67	48.4	1.15	33.4
Fluoranthene	13	26	0.0	94.3	51.2	54.26	21.38	41.8	8.82	17.2
Benzo[b]fluoranthene	11	22	8.3	28.7	33.2	115.69	10.56	31.8	5.18	15.6
Benzo[k]fluoranthene	11	22	8.3	13.5	17.4	128.65	8.25	47.4	2.77	15.9
Benzo[a]pyrene	8	16	33.3	14.5	13.5	92.69	2.58	19.1	0.563	4.2
Benzo[ghi]perylene	10	20	16.7	35.6	34.2	96.10	6.50	19.0	6.50	19.0
Indeno[1,2,3-cd]pyrene	7	14	36.4	21.6	22.5	104.23	1.67	7.4	0.927	4.1
Naphtalene	4	8	20.0		7.75		4.01	51.8	1.20	15.5
Fluorene	6	12	0.0		3.24		1.50	46.3	0.580	17.9
Acenaphthene	4	7	22.2		2.28		2.49	109.5	0.064	2.8
Acenaphthylene	8	16	0.0		2.99		2.50	83.6	0.473	15.8
Phenanthrene	8	16	0.0	45.0	18.6	41.40	5.96	32.0	1.99	10.7
Pyrene	9	18	0.0	92.7	51.5	55.59	19.48	37.8	10.51	20.4
Chrysene	8	16	11.1	32.5	30.3	93.15	10.36	34.2	1.45	4.8
Benzo[a]anthracene	6	12	14.3	18.4	16.6	90.04	2.93	17.7	1.63	9.8
Dibenzo[a,h]anthracene	7	14	22.2	3.64	4.09	112.25	1.29	31.6	1.09	26.7
Explanation of symbols:										
l	number of laboratories after outlier rejection									
n	number of individual test results after outlier rejection									
o	percentage of outliers									
X	estimated value *(reference value)*									
$\overline{\overline{x}}$	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									

Table 14:   Sample 2:   High PAH-level sample containing 200mg/L suspended particulate matter (SPM) Matrix: Mineral water, spiked with PAH containing SPM

Sample 2										
Measurand	l	n	o %	X ng/l	$\overset{=}{x}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
Anthracene	11	20	0.0	27.2	22.6	82.9	10.83	48.0	2.77	12.3
Fluoranthene	13	24	0.0	476.3	223	46.9	80.39	36.0	18.41	8.2
Benzo[b]fluoranthene	12	23	0.0	159.8	190	118.9	40.11	21.1	20.25	10.7
Benzo[k]fluoranthene	10	19	17.4	118.8	77.9	65.5	13.57	17.4	8.99	11.5
Benzo[a]pyrene	13	25	0.0	122.8	108	87.9	24.27	22.5	8.19	7.6
Benzo[ghi]perylene	12	23	0.0	156.9	145	92.4	30.25	20.9	12.73	8.8
Indeno[1,2,3-cd]pyrene	10	19	9.5	135.1	144	106.9	16.65	11.5	4.93	3.4
Naphtalene	6	12	0.0	65.8	29.3	44.5	11.38	38.9	6.61	22.6
Fluorene	6	12	0.0		9.45		2.91	30.8	0.852	9.0
Acenaphthene	7	13	0.0		5.24		3.57	68.1	0.415	7.9
Acenaphthylene	8	15	0.0		43.3		22.70	52.4	9.91	22.9
Phenanthrene	8	16	0.0		153		48.81	31.8	10.95	7.1
Pyrene	9	17	0.0		213		60.88	28.6	14.19	6.7
Chrysene	8	16	11.1		159		46.78	29.4	20.88	13.1
Benzo[a]anthracene	5	10	28.6		128		14.74	11.5	2.54	2.0
Dibenzo[a,h]anthracene	9	18	0.0		29.6		5.06	17.1	2.46	8.3
Explanation of symbols:	see sample 1									

Table 15: Sample 3:   PAH sample without suspended particulate matter (SPM) **Matrix: Mineral water, spiked with PAH**

Sample 3										
Measurand	l	n	o %	X ng/l	$\overset{=}{x}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
Anthracene	11	22	0.0	**_100_**	102.7	102.7	18.66	18.2	9.48	9.2
Fluoranthene	13	26	0.0	**_100_**	100.5	100.5	13.71	13.6	5.48	5.5
Benzo[b]fluoranthene	11	22	8.3	**_30_**	27.9	93.1	3.01	10.8	1.41	5.0
Benzo[k]fluoranthene	11	22	8.3	**_30_**	28.5	94.9	2.55	9.0	0.91	3.2
Benzo[a]pyrene	13	26	0.0	**_50_**	50.4	100.7	5.12	10.2	3.21	6.4
Benzo[ghi]perylene	11	22	8.3	**_20_**	19.0	95.0	2.71	14.3	1.24	6.5
Indeno[1,2,3-cd]pyrene	10	20	9.1	**_20_**	19.6	98.2	2.16	11.0	1.28	6.5
Naphtalene	6	12	0.0	**_100_**	99.8	99.8	10.77	10.8	5.41	5.4
Fluorene	5	10	16.7	**_50_**	50.7	101.4	2.19	4.3	1.22	2.4
Acenaphthene	7	14	0.0	**_100_**	107.5	107.5	14.70	13.7	6.78	6.3
Acenaphthylene	8	16	0.0	**_100_**	106.5	106.5	19.48	18.3	10.70	10.0
Phenanthrene	8	16	0.0	**_50_**	49.7	99.3	6.30	12.7	1.71	3.4
Pyrene	9	18	0.0	**_50_**	52.9	105.7	6.19	11.7	0.97	1.8
Chrysene	8	16	11.1	**_30_**	27.8	92.7	6.55	23.5	1.36	4.9
Benzo[a]anthracene	7	14	0.0	**_30_**	29.3	97.6	4.17	14.2	2.29	7.8
Dibenzo[a,h]anthracene	9	18	0.0	**_20_**	20.6	102.8	3.48	16.9	2.20	10.7
Explanation of symbols:	see sample 1									

6.2 Sample 1: Graphical presentation of the results interlaboratory trial for the validation of "prEN 16691 "Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS)

Sample 1:   Low level samples containing SPM
Matrix: Mineral water, spiked with SPM

Legend: ——— overall mean
         TQ   Laboratory used triple quad

Outliers: A   outlying single result of one laboratory (not detectable in duplicate analysis),
         B   outlying laboratory mean,
         C   outlying within-laboratory variance
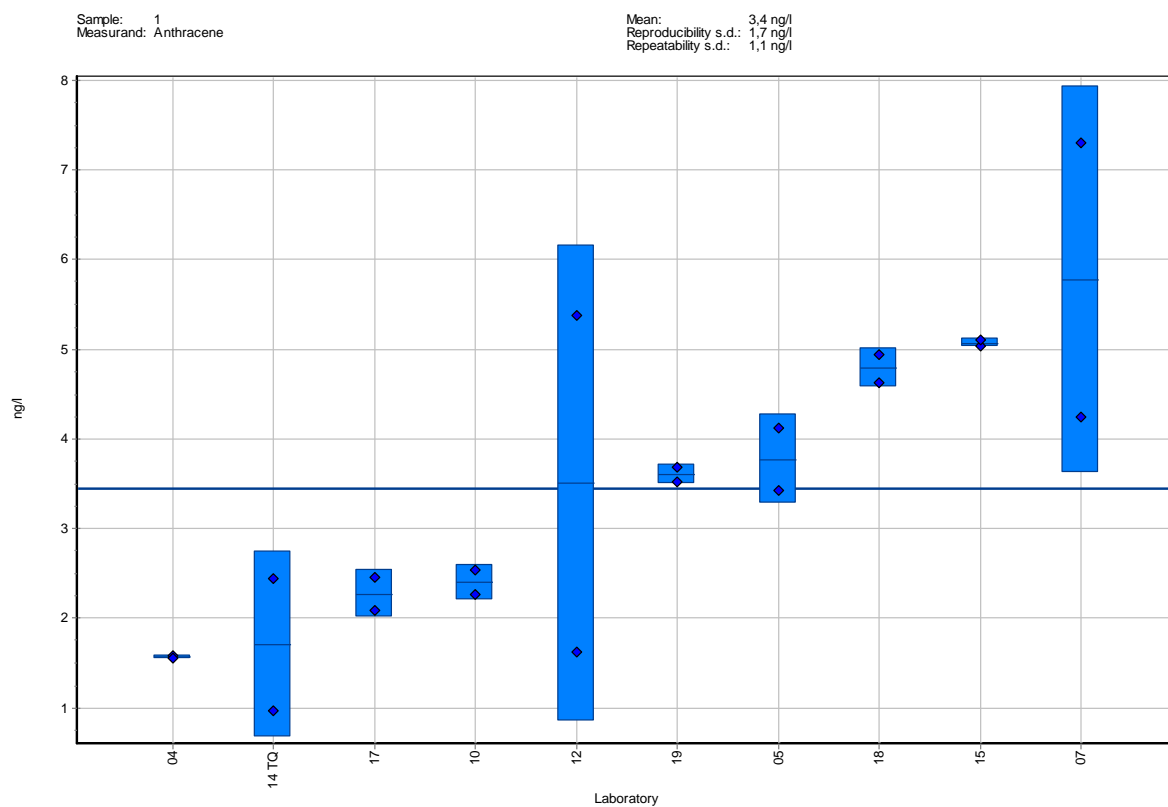
Figure 2: Anthracene, sample 1
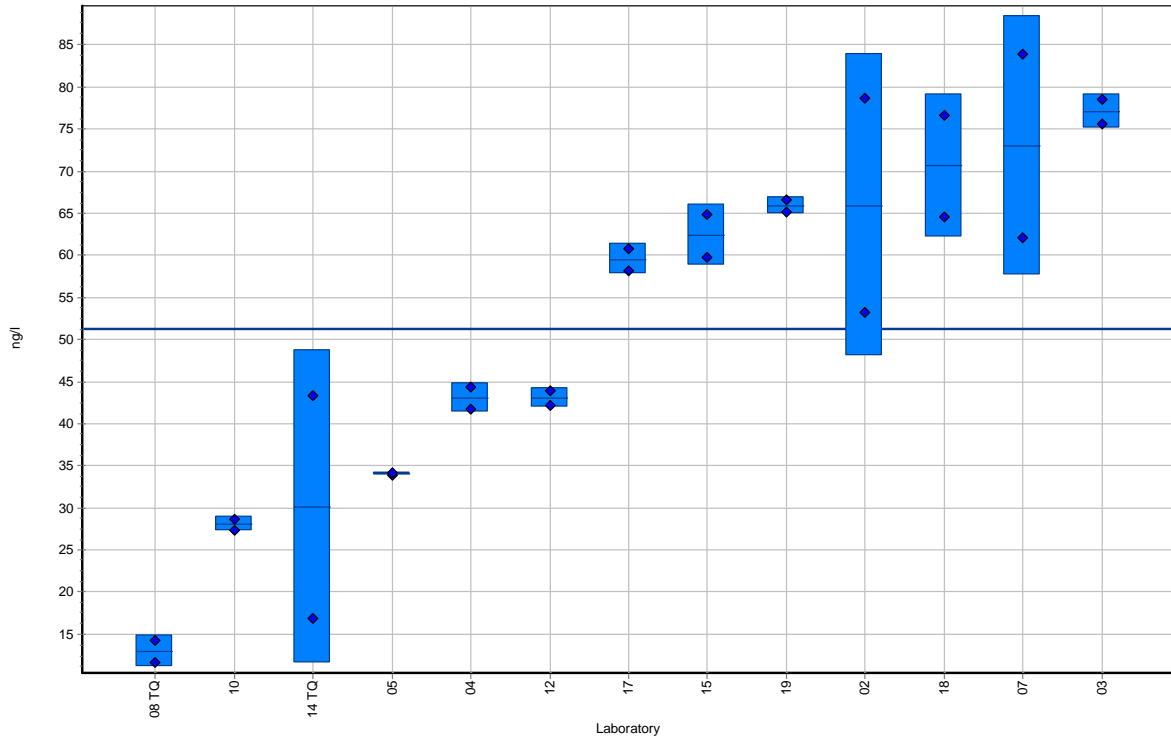
Figure 3: Fluoranthene, sample 1
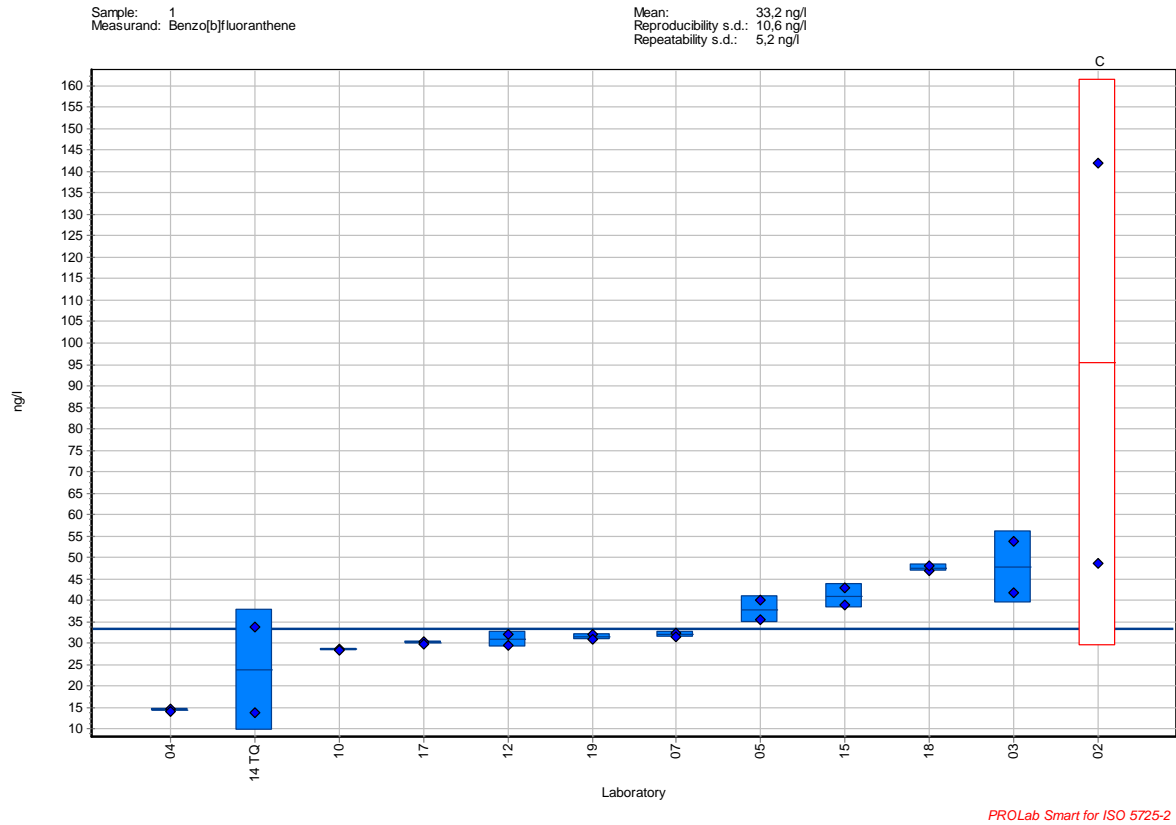
Figure 4: Benzo[b]fluoranthene, sample 1
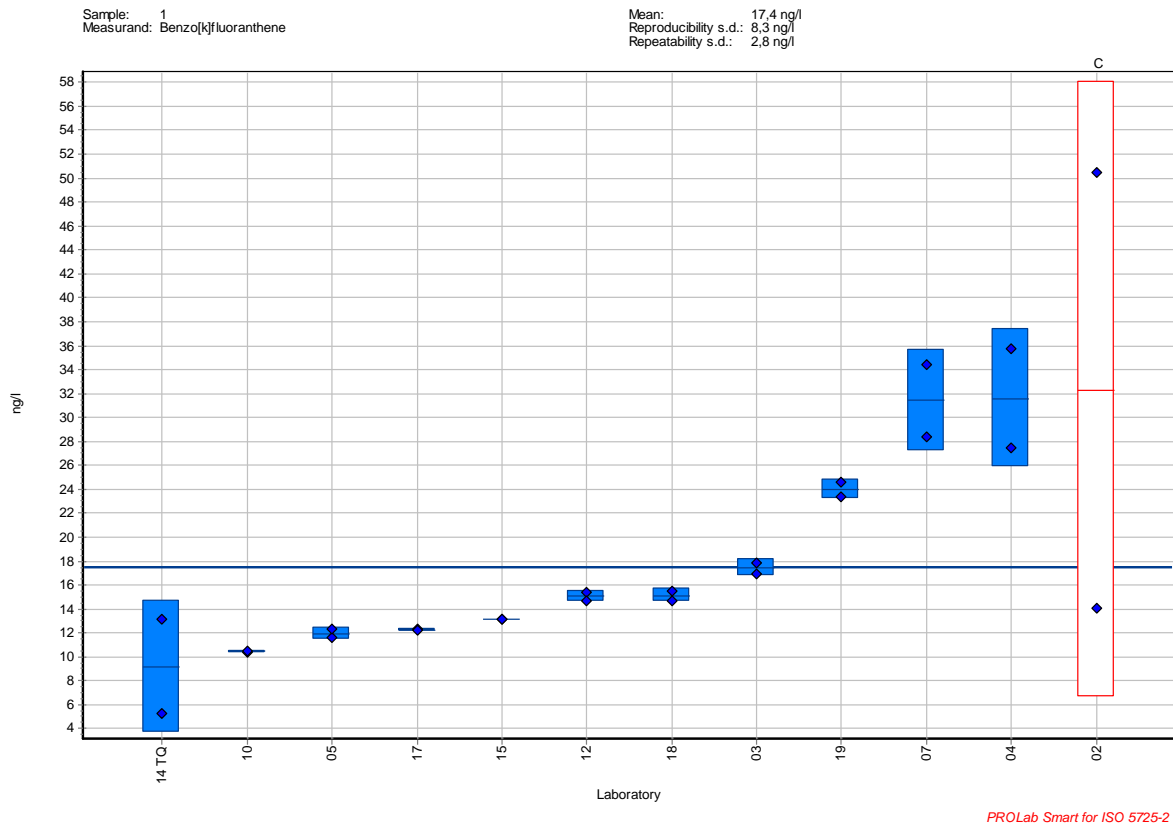
Figure 5: Benzo[k]fluoranthene, sample 1
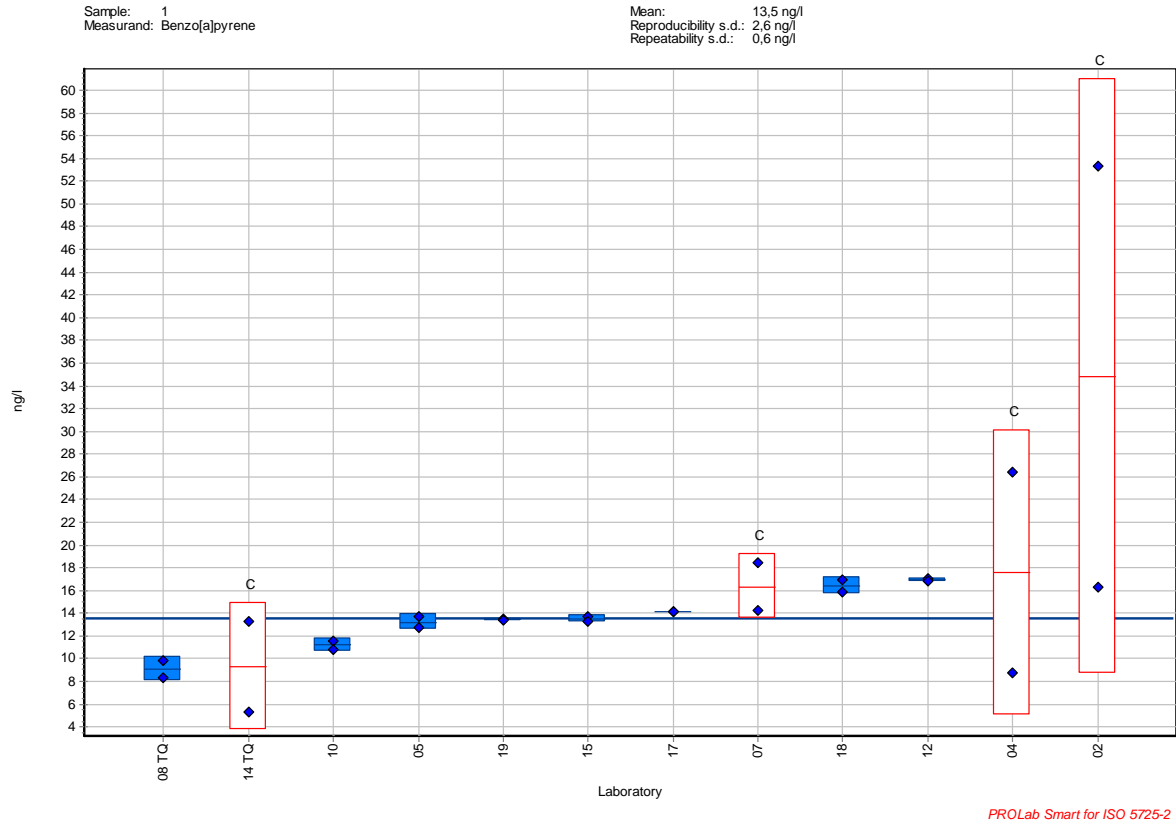
Figure 6: Benzo[a]pyrene, sample 1
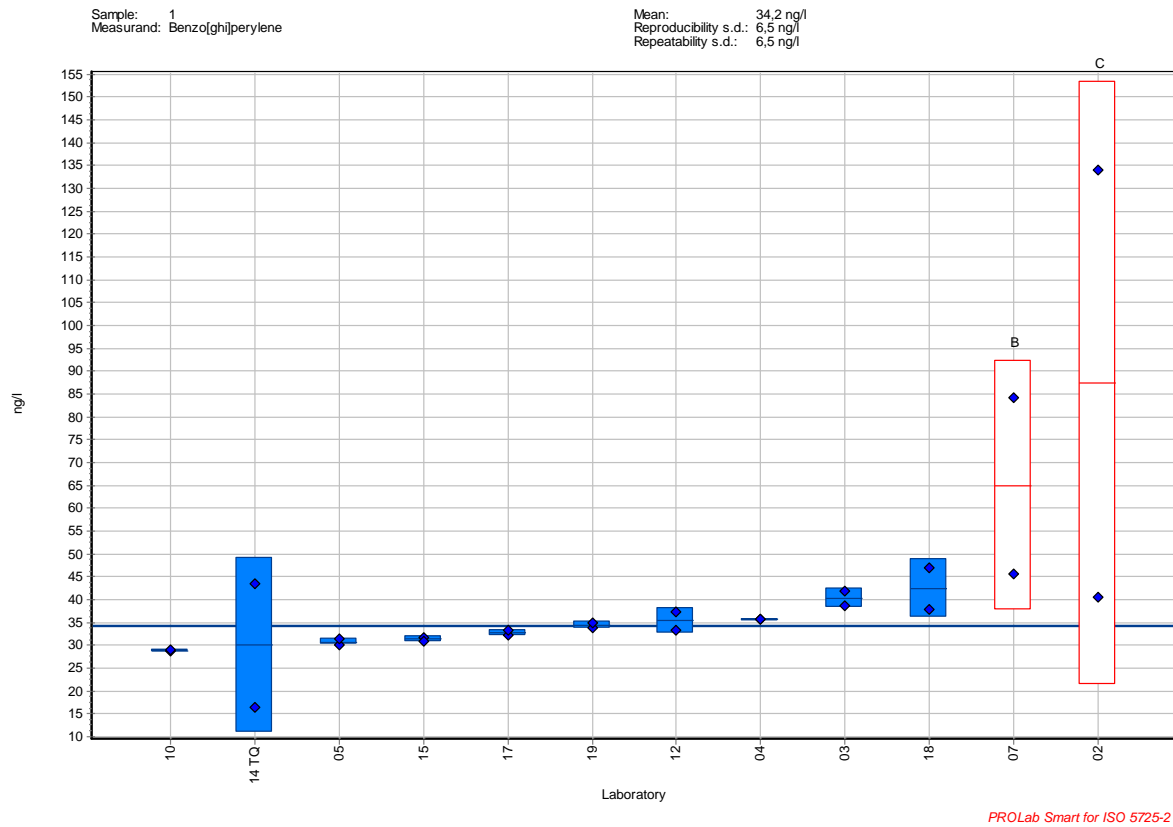
Figure 7: Benzo[ghi]perylene, sample 1
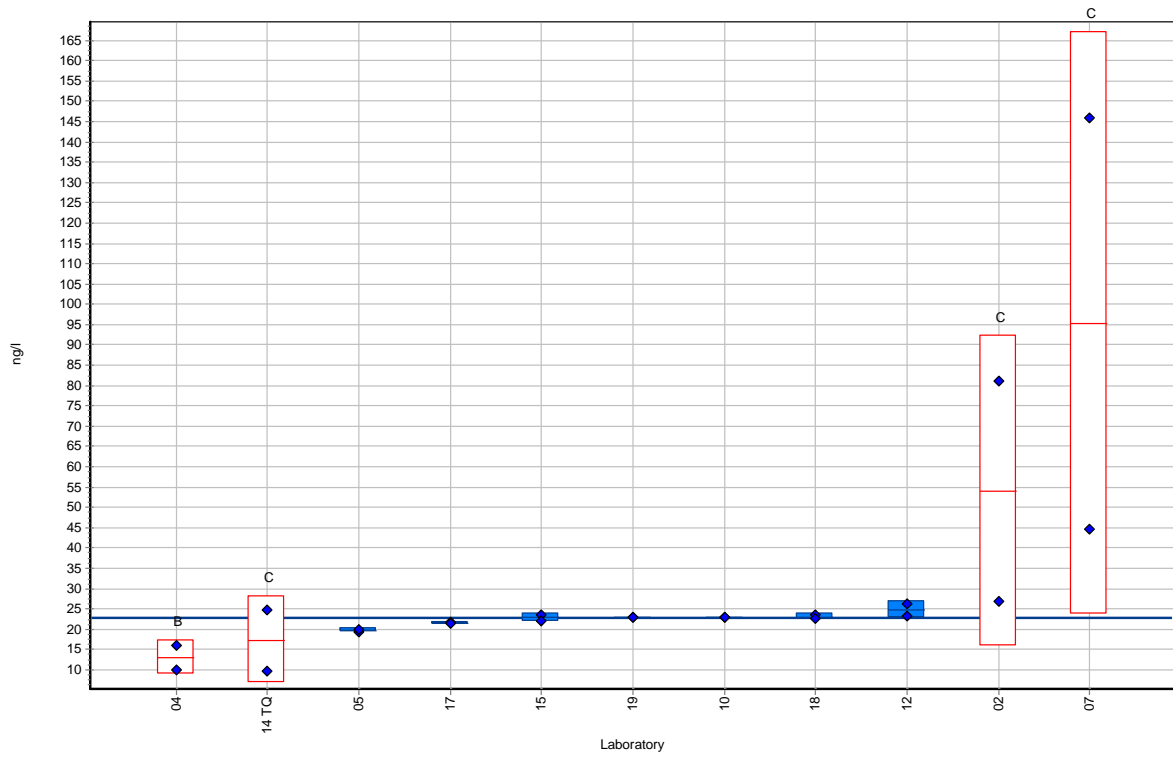
Figure 8: Indeno[1,2,3-cd]pyrene, sample 1
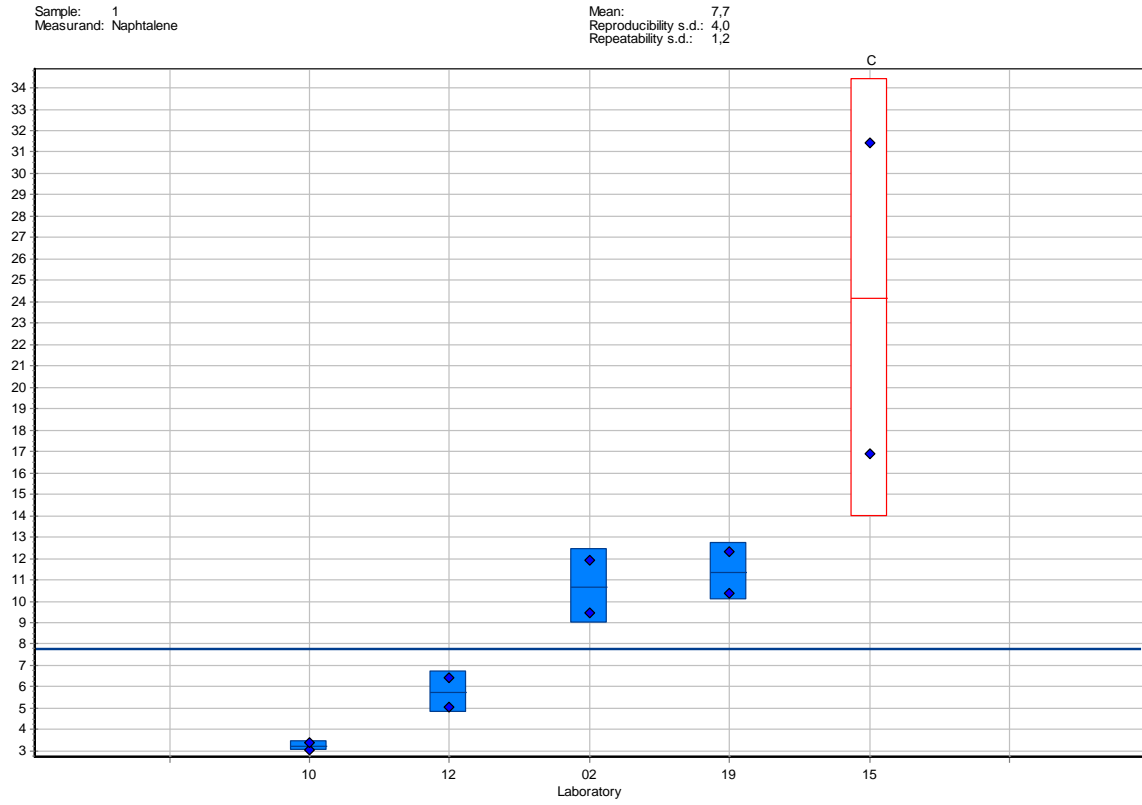
Figure 9: Naphtalene, sample 1
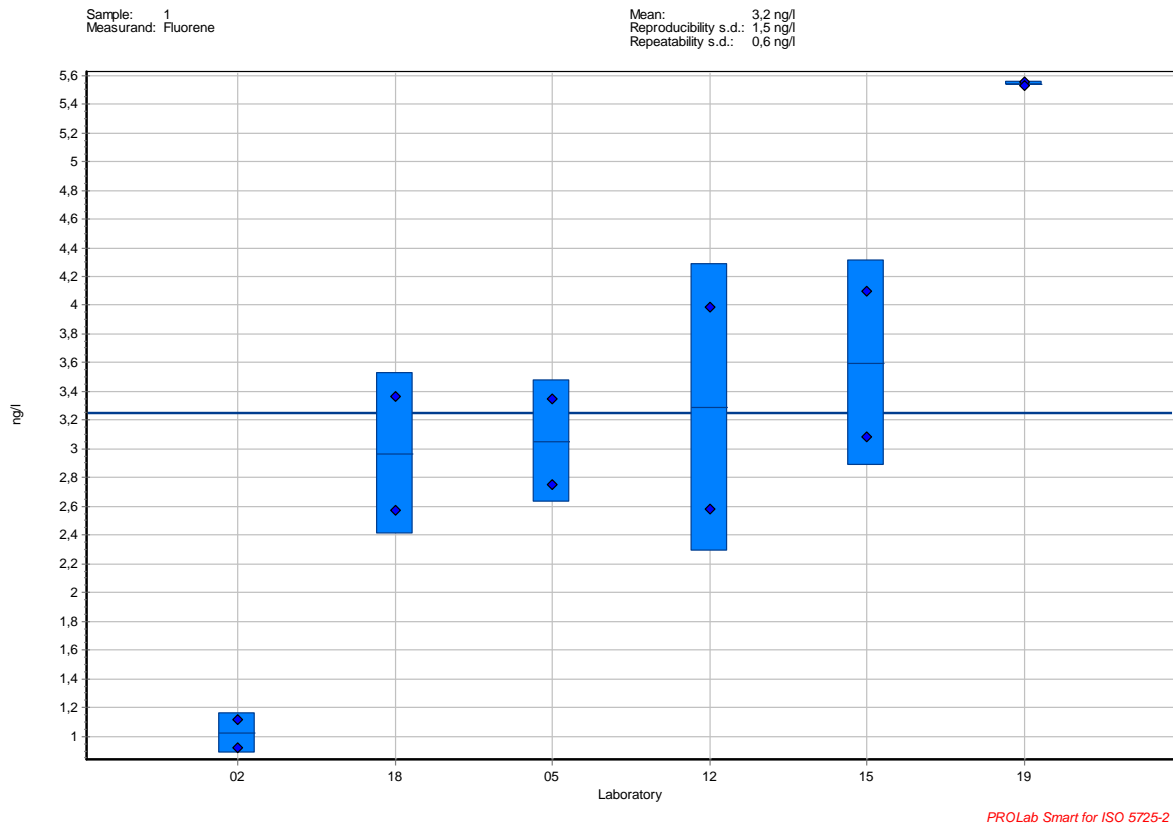
Figure 10: Fluorene, sample 1
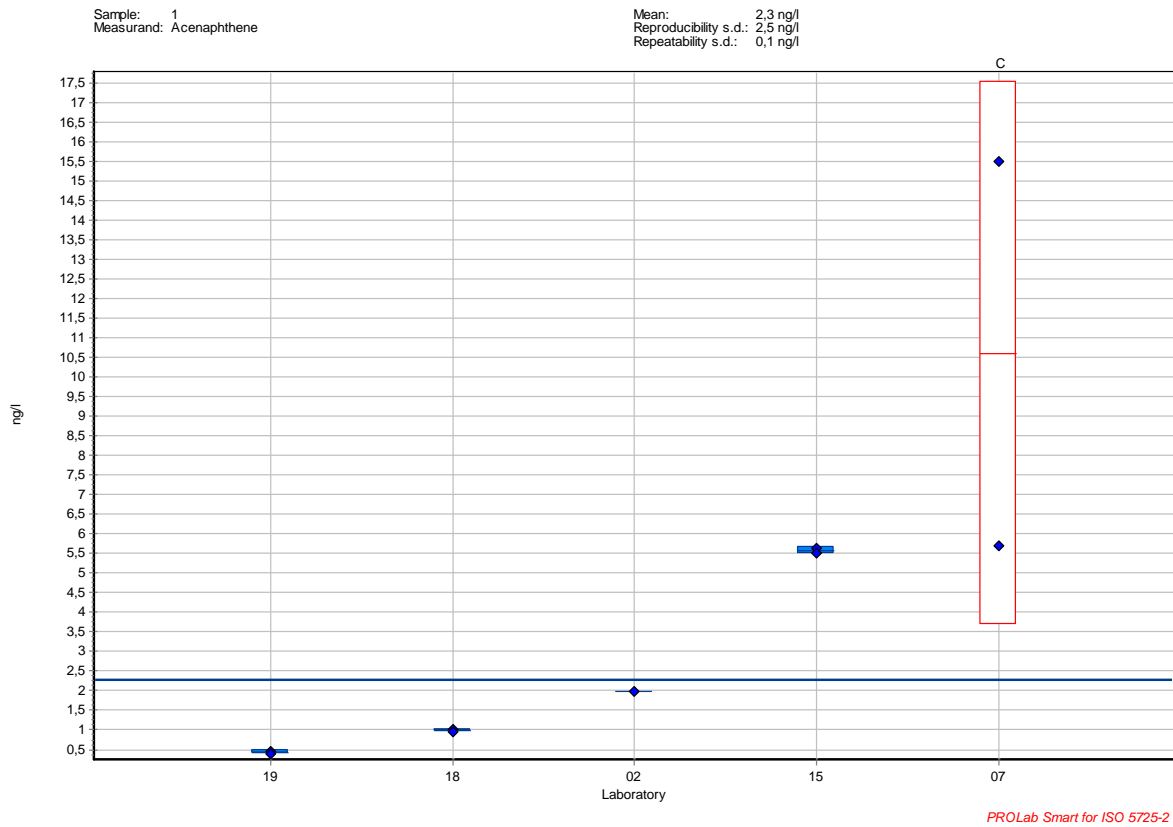
Figure 11: Acenaphthene, sample 1
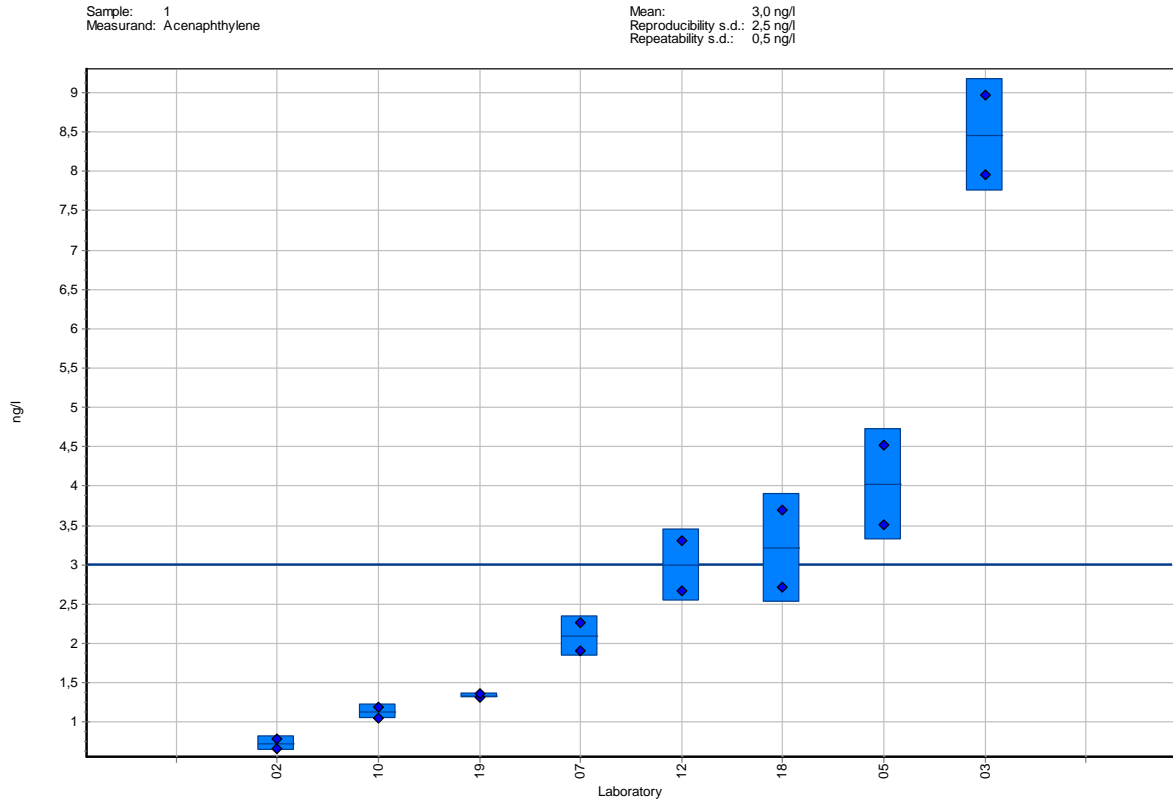
Figure 12: Acenaphthylene, sample 1
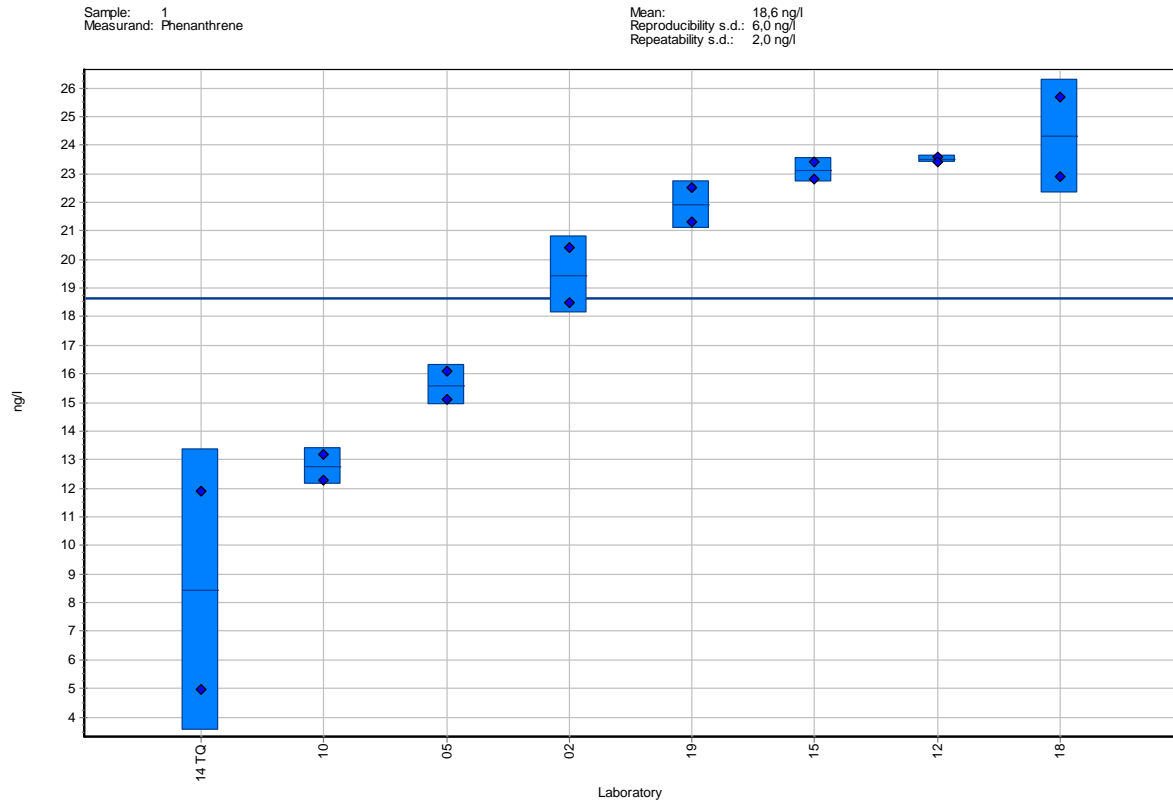
Figure 13: Phenanthrene, sample 1
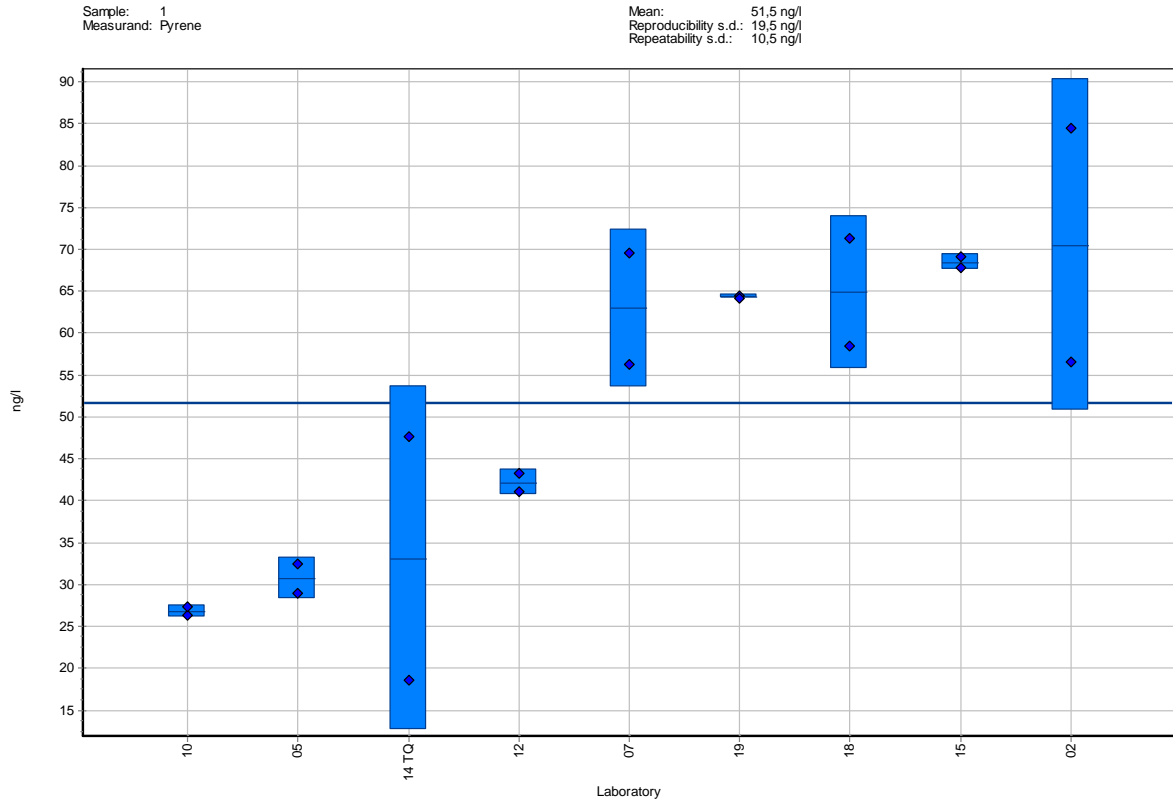
Figure 14: Pyrene, sample 1
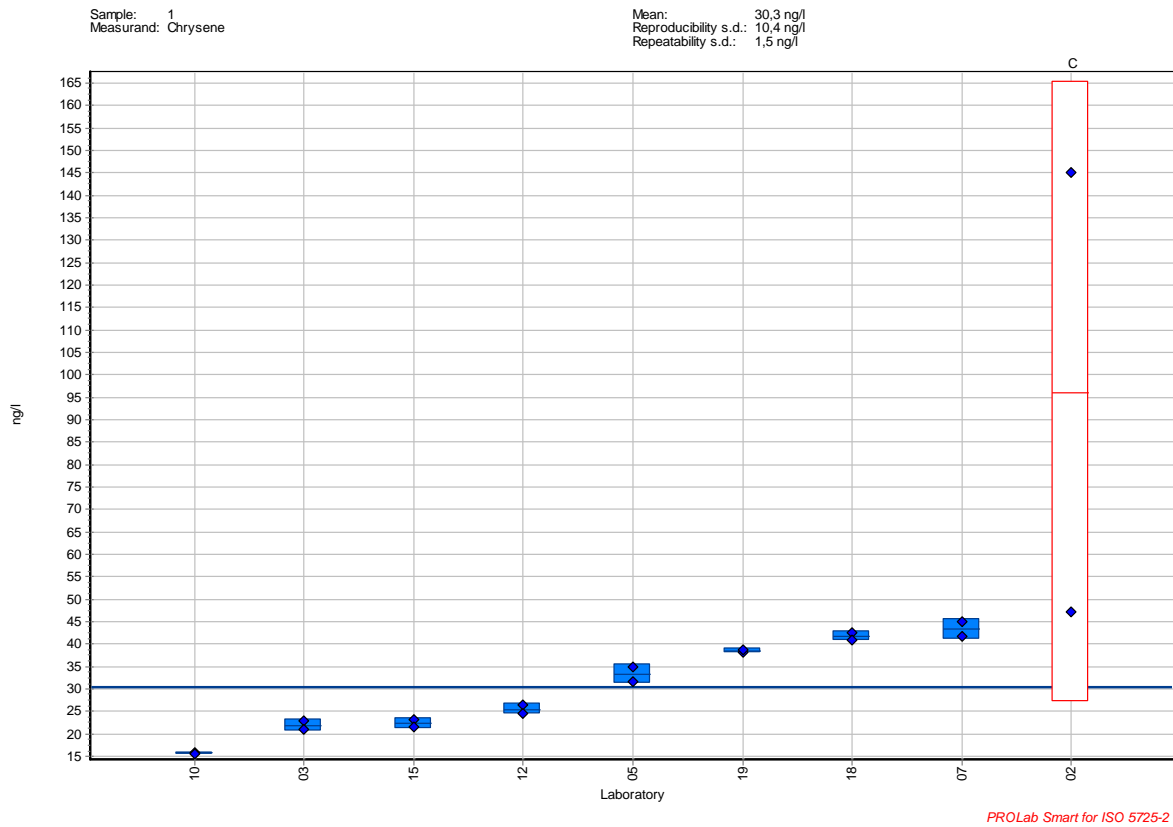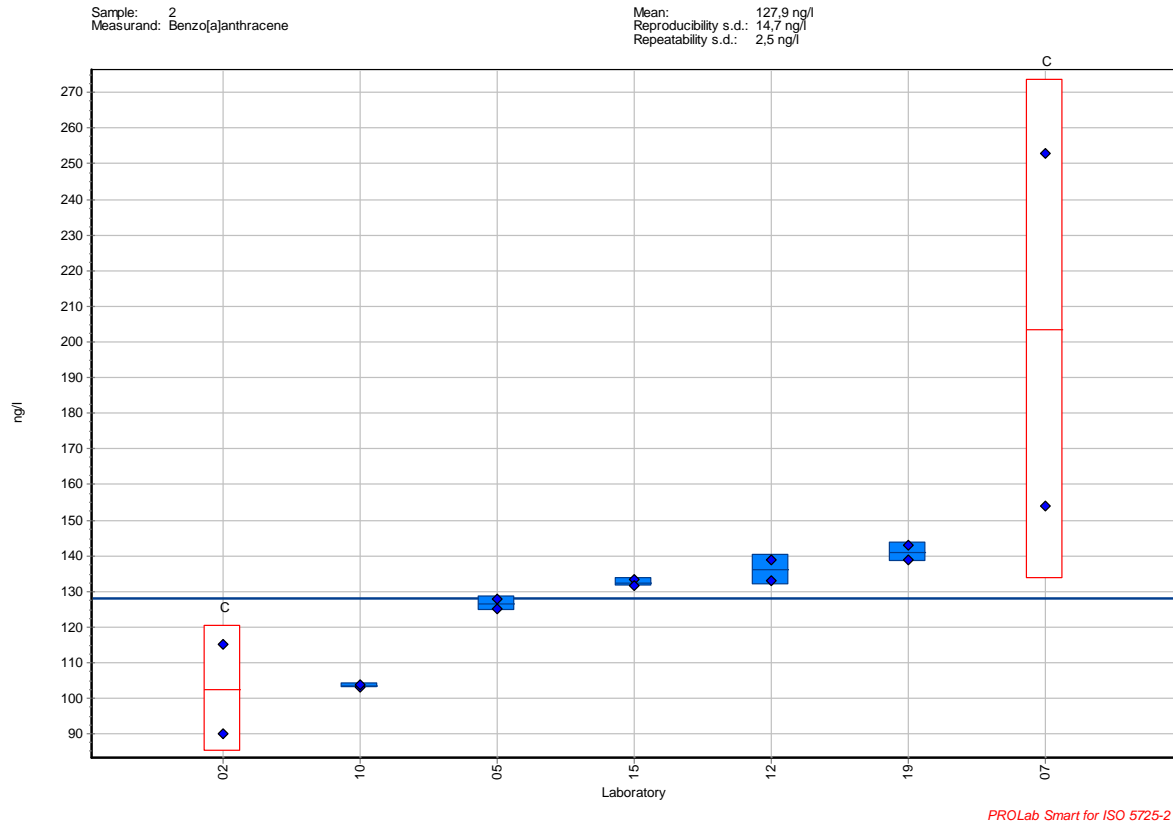
Figure 15: Chrysene, sample 1
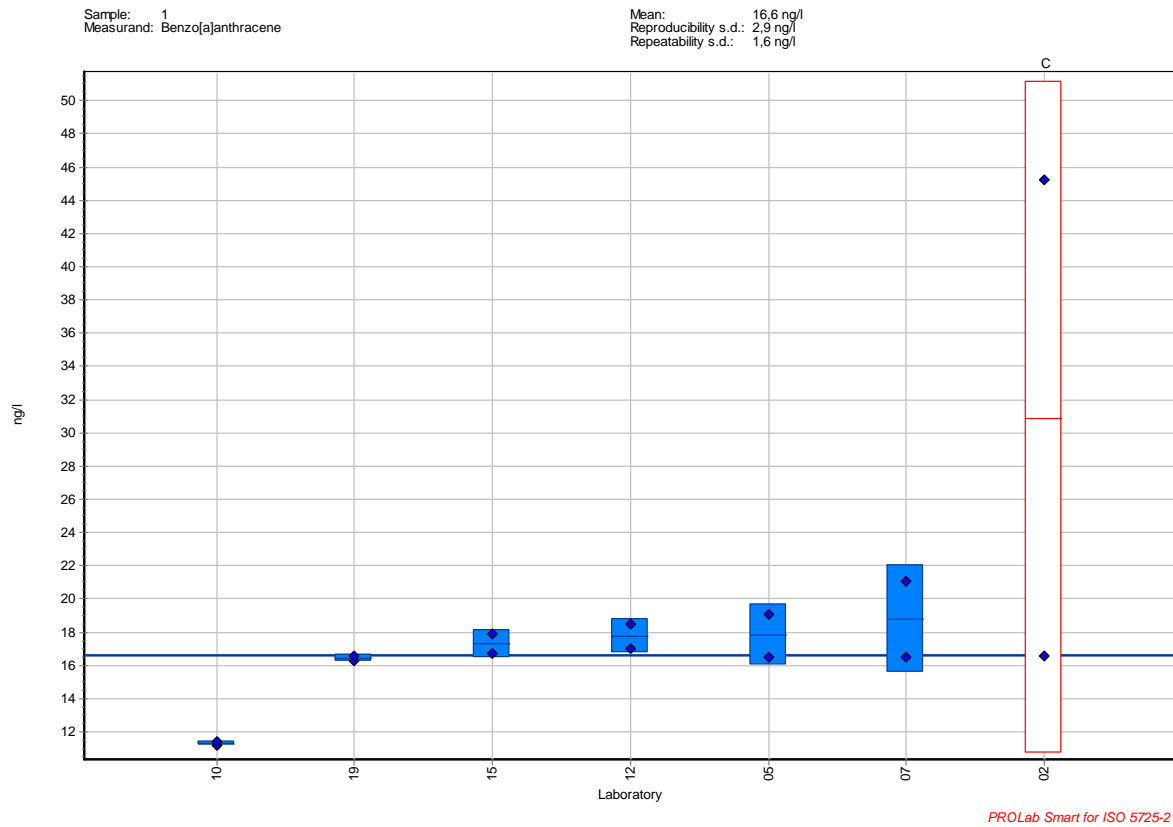
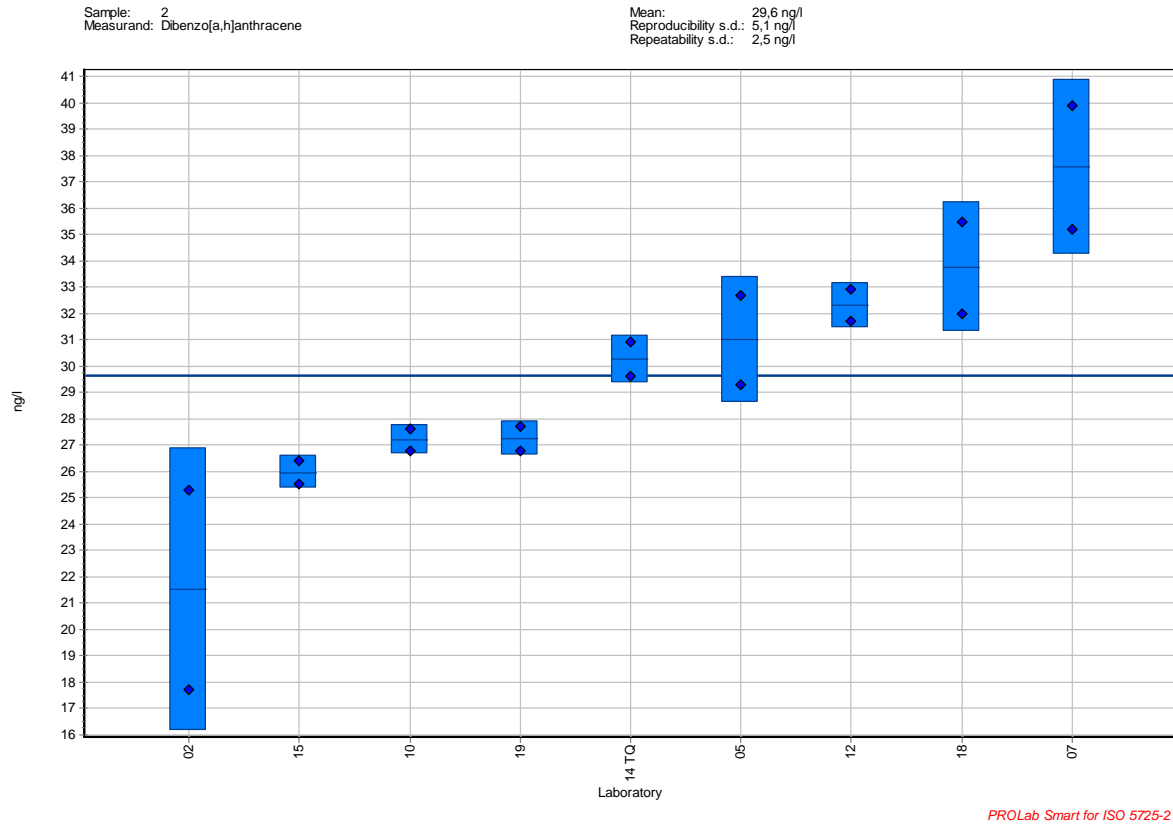**Figure 16: Benzo[a]anthracene, sample 1**
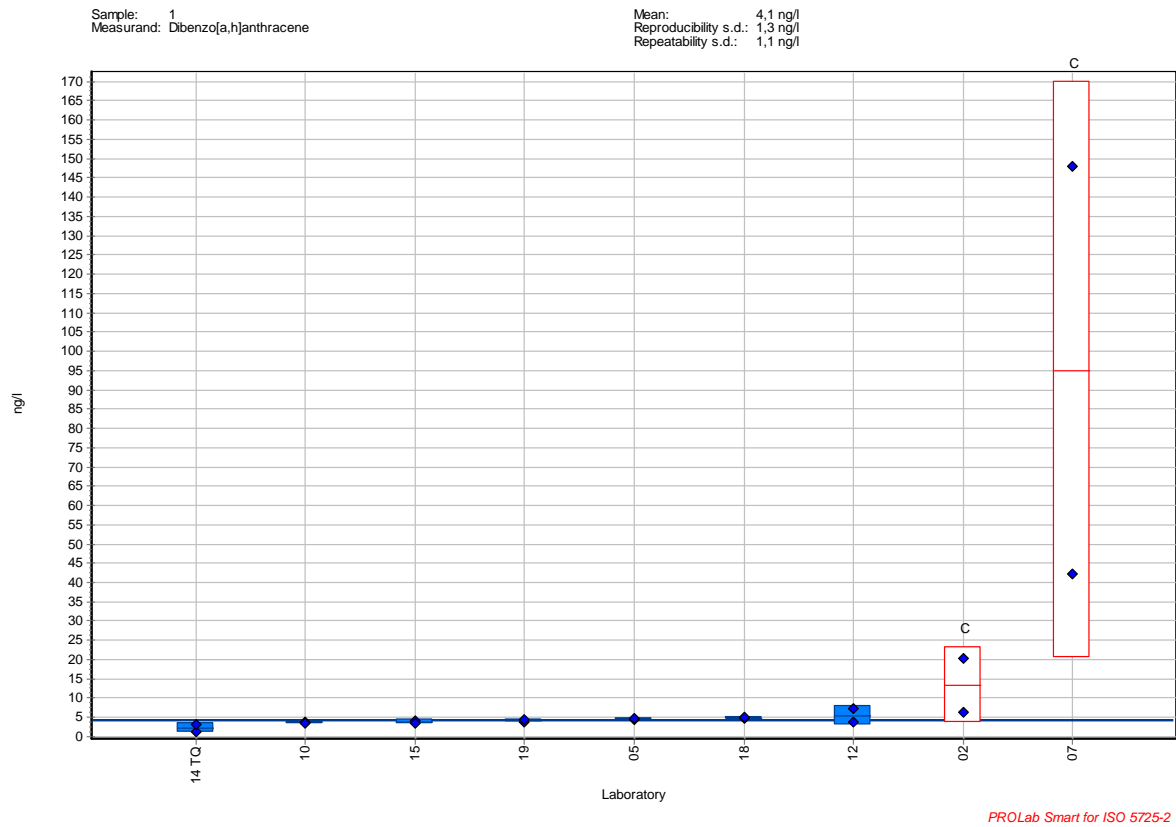
Figure 17: Dibenzo[a,h]anthracene, sample 1

6.3 Sample 2: Graphical presentation of the results interlaboratory trial for the validation of "prEN 16691 "Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS)

Sample 2:   High level samples containing SPM
Matrix: Mineral water, spiked with SPM

Legend: ────── overall mean
                   TQ   Laboratory used triple quad

Outliers: A   outlying single result of one laboratory (not detectable in duplicate analysis),
                   B   outlying laboratory mean,
   C   outlying within-laboratory variance
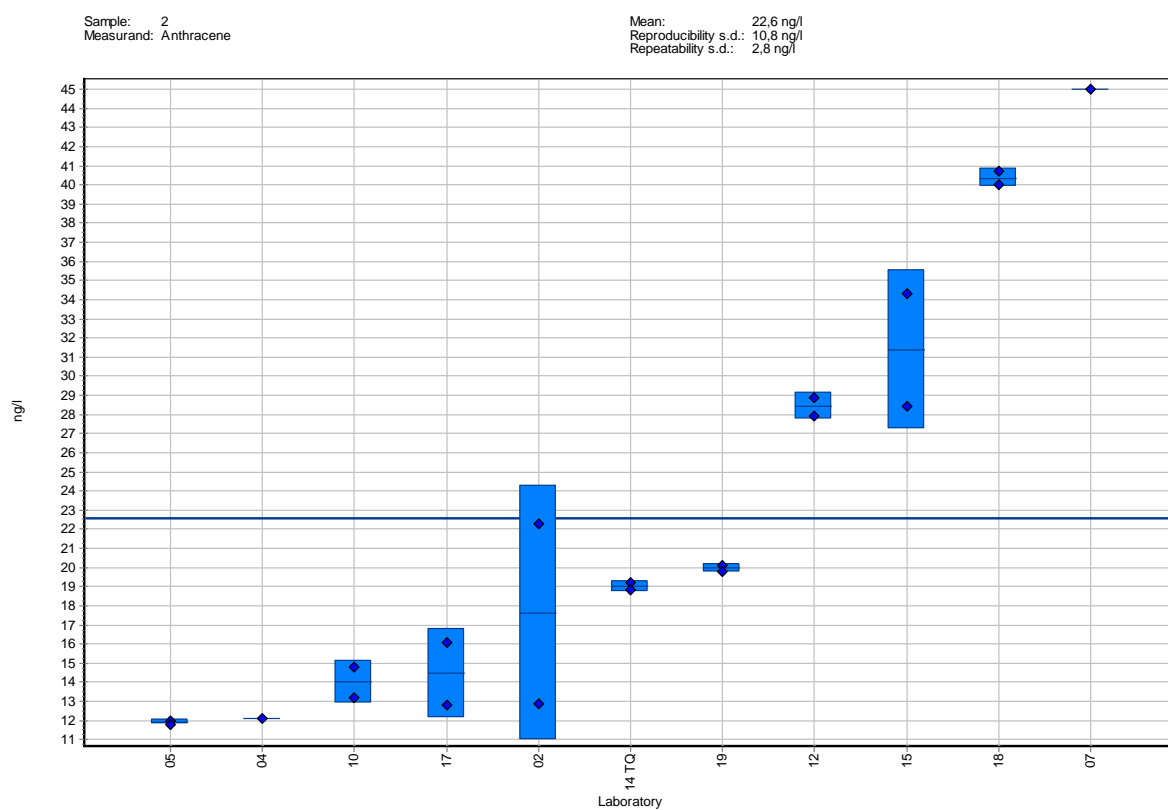
Figure 18: Anthracene, sample 2

Figure 19: Fluoranthene, sample 2
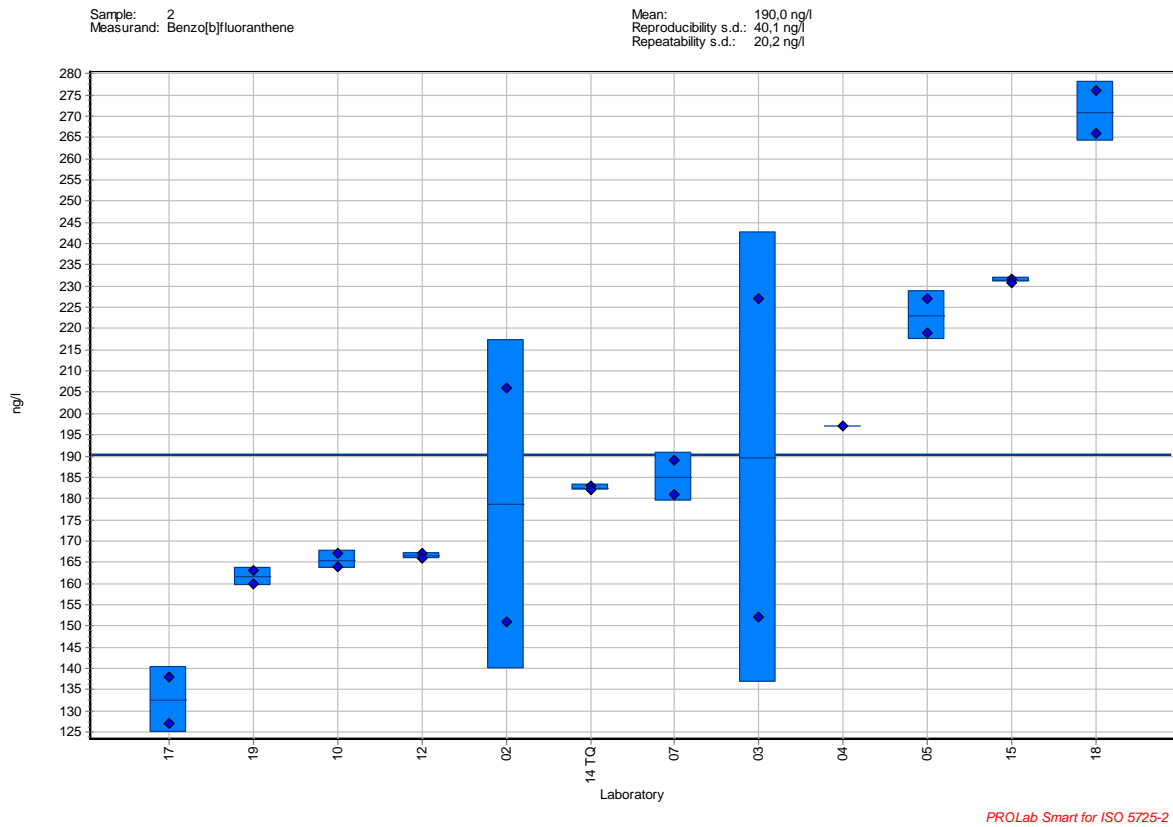
Figure 20: Benzo[b]fluoranthene, sample 2
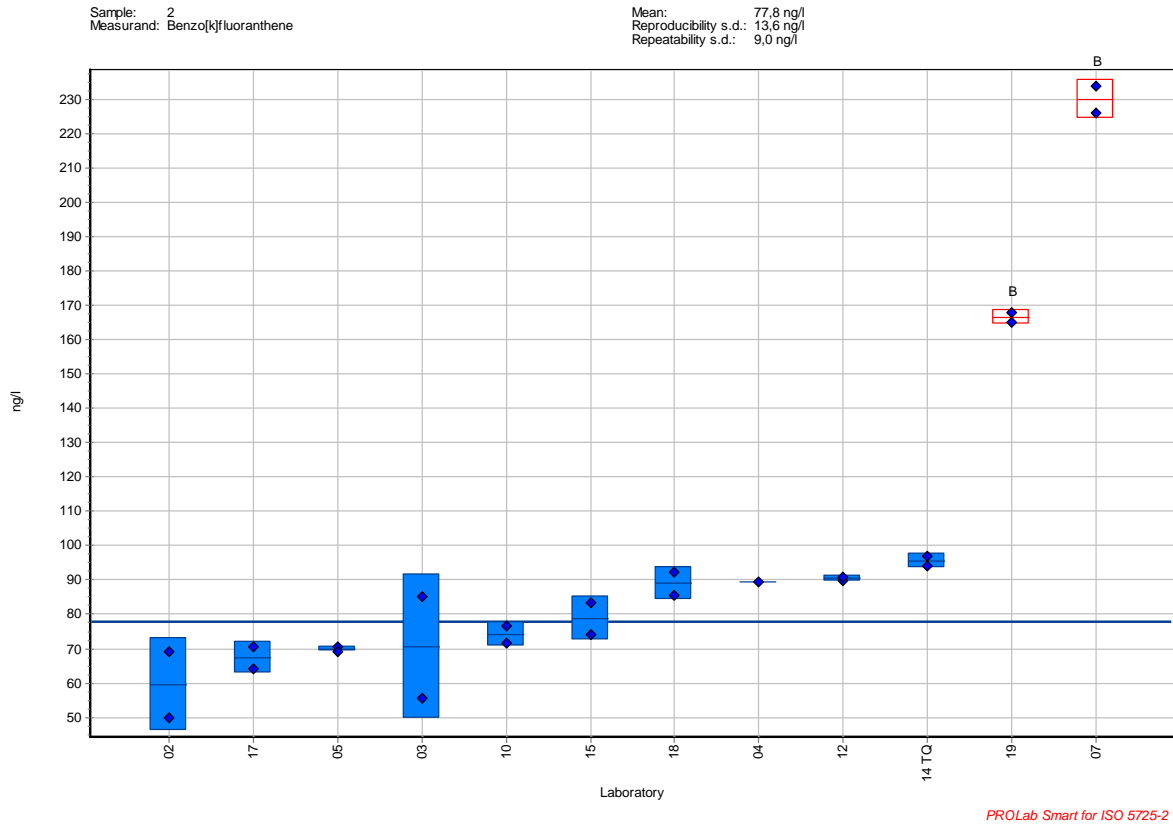
Figure 21: Benzo[k]fluoranthene, sample 2
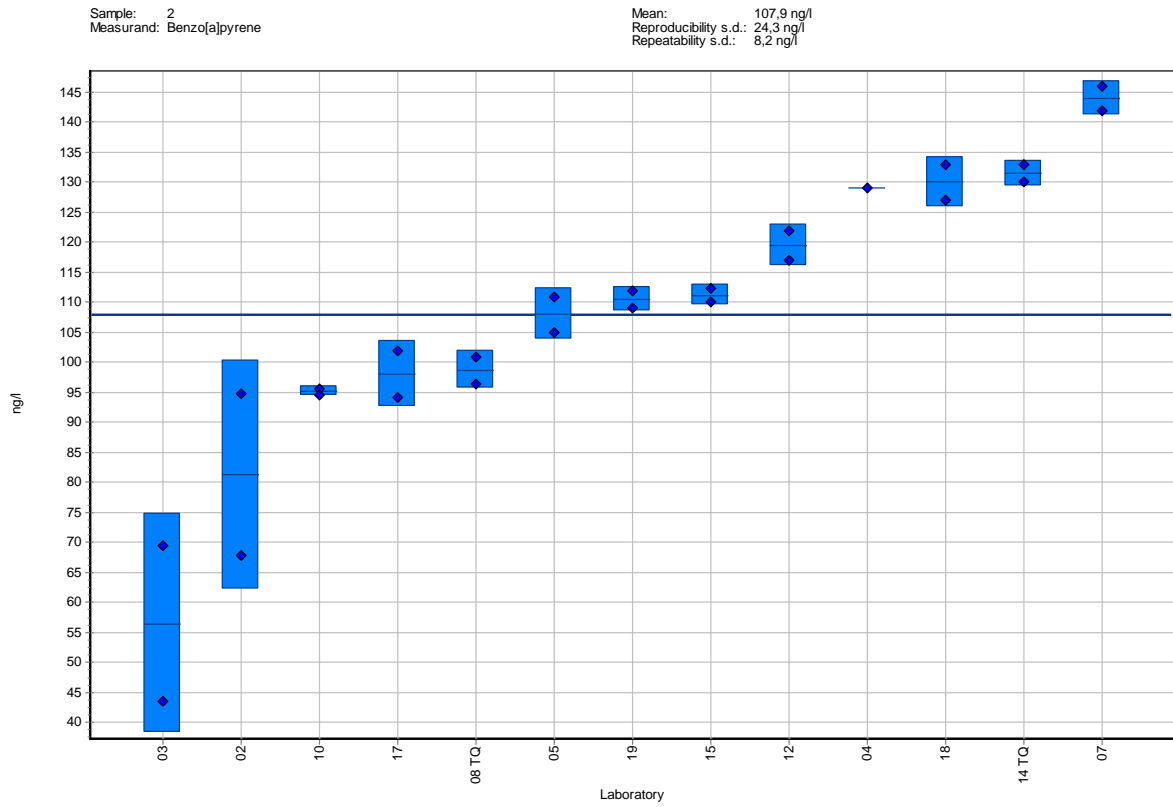
Figure 22: Benzo[a]pyrene, sample 2

Sample: 2
Measurand: Benzo[ghi]perylene

Mean: 145,0 ng/l
Reproducibility s.d.: 30,2 ng/l
Repeatability s.d.:   12,7 ng/l

ng/l

Laboratory

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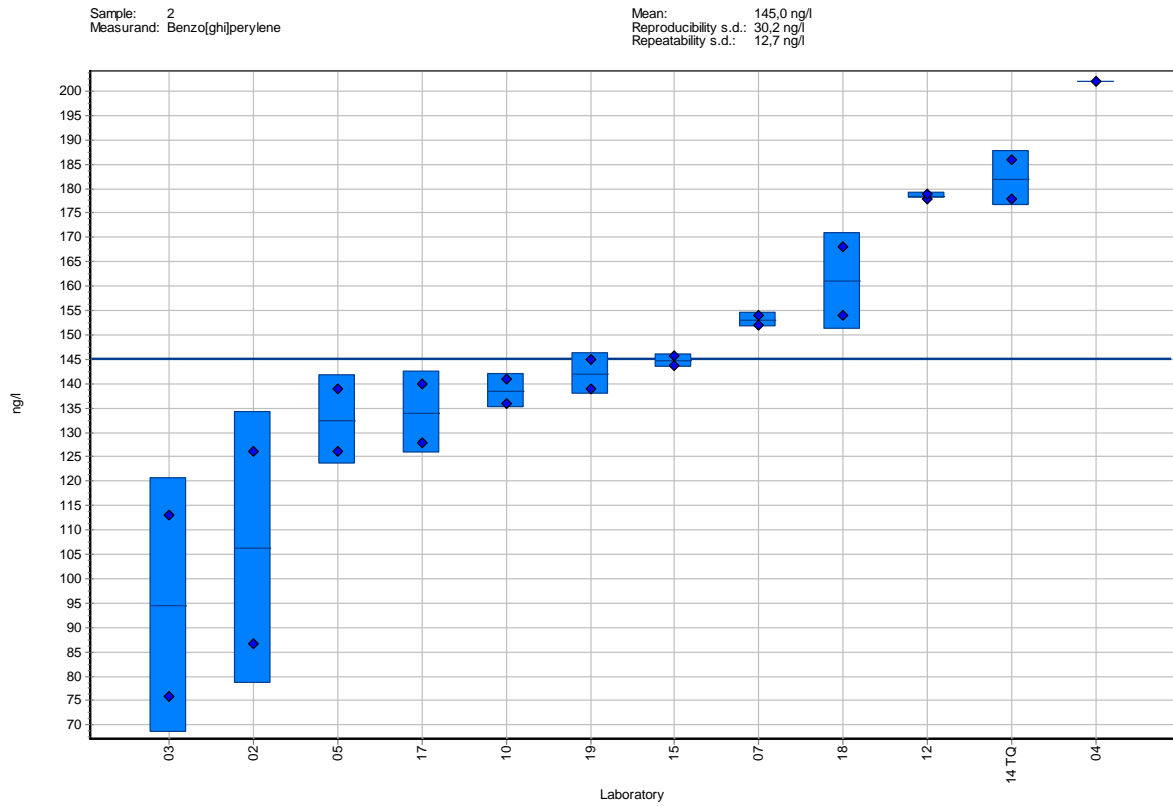
Figure 23: Benzo[ghi]perylene, sample 2
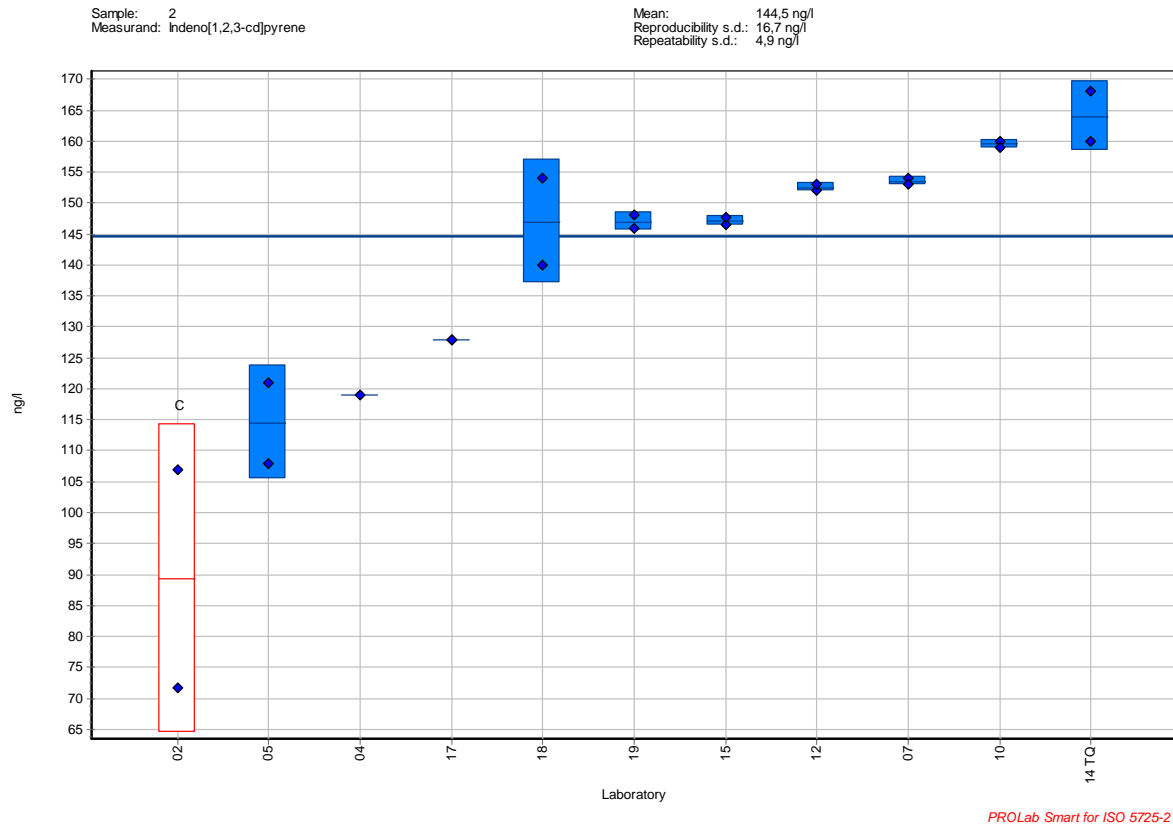
Figure 24: Indeno[1,2,3-cd]pyrene, sample 2
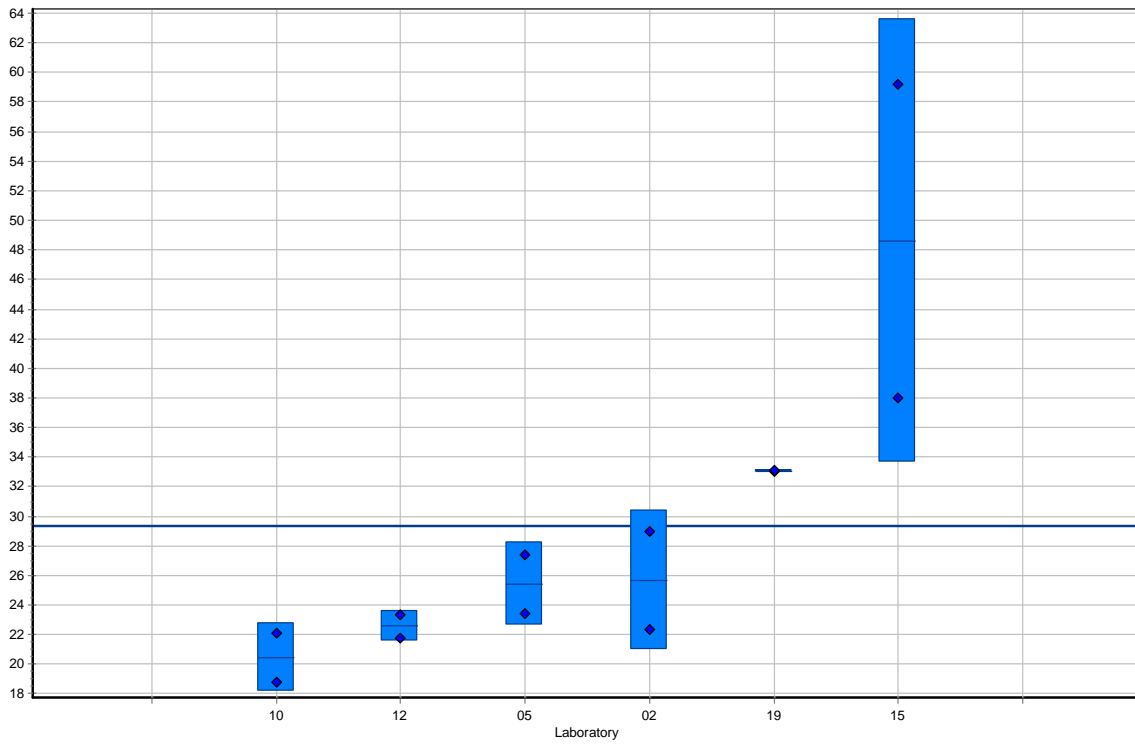
Figure 25: Naphtalene, sample 2
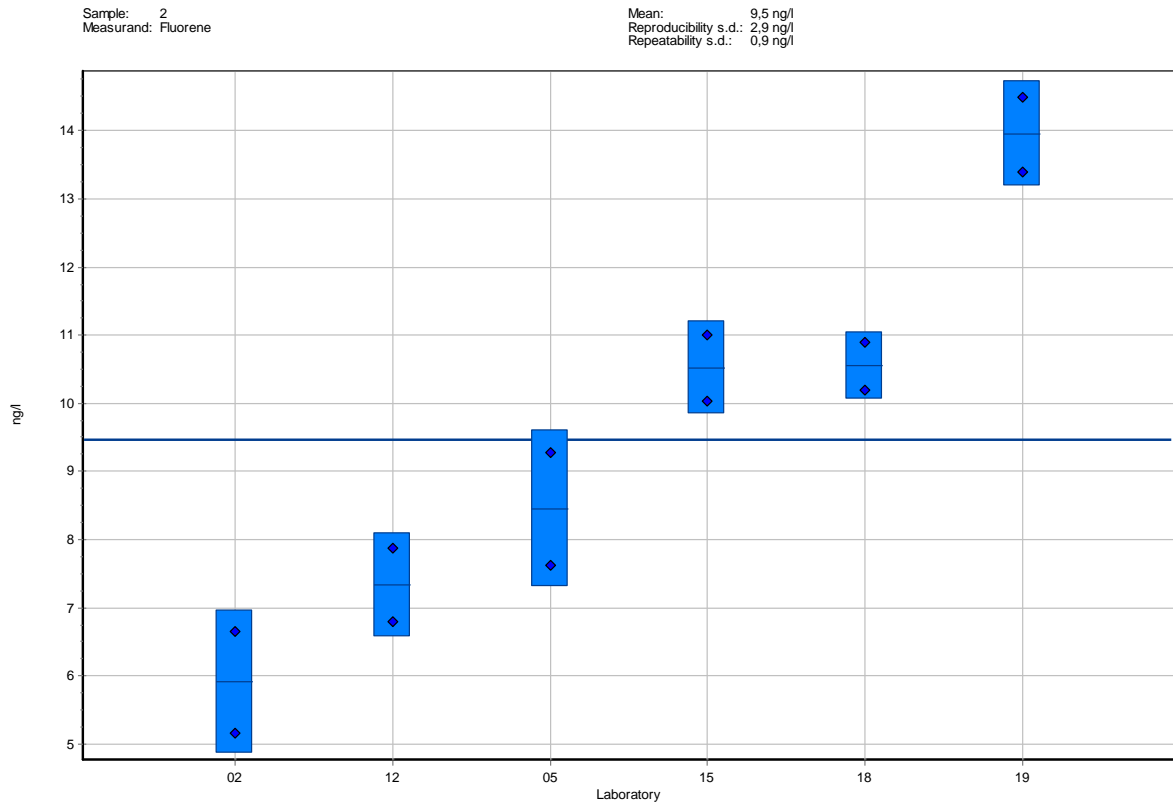
Figure 26: Fluorene, sample 2
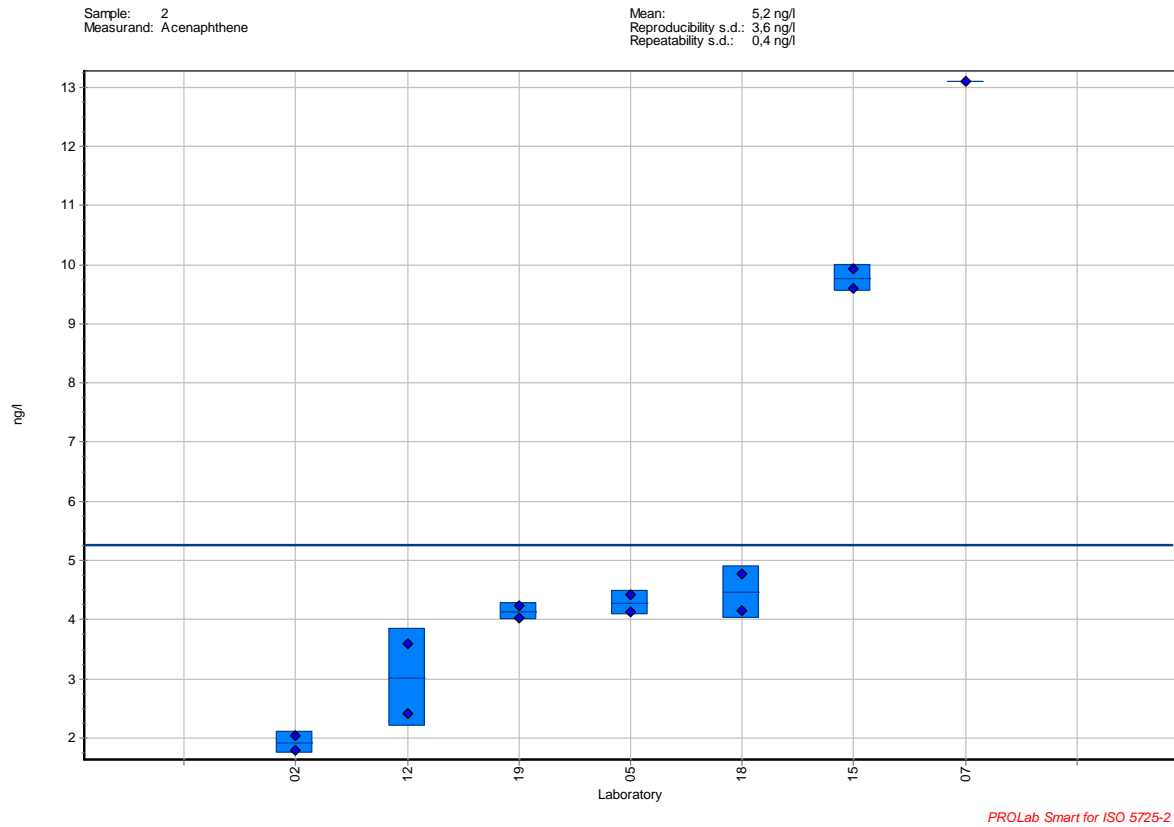
Figure 27: Acenaphthene, sample 2
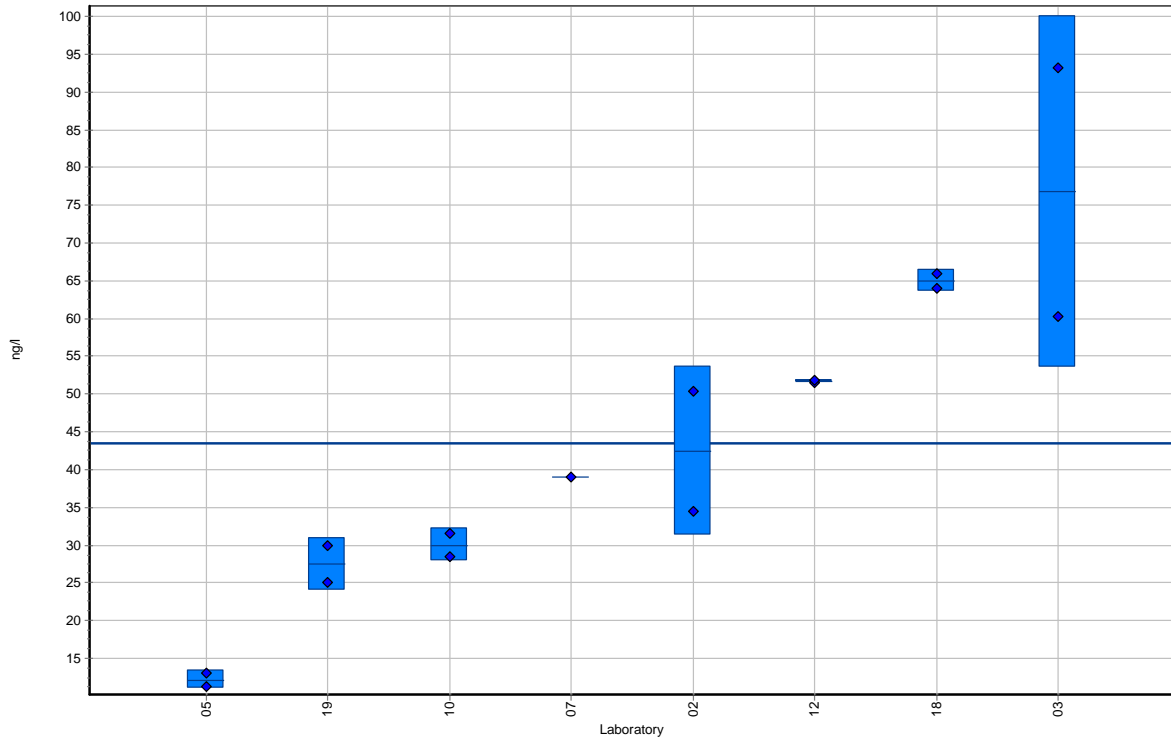
Figure 28: Acenaphthylene, sample 2

Sample: 2
Measurand: Phenanthrene

Mean: 153,5 ng/l
Reproducibility s.d.:   48,8 ng/l
Repeatability s.d.:   11,0 ng/l

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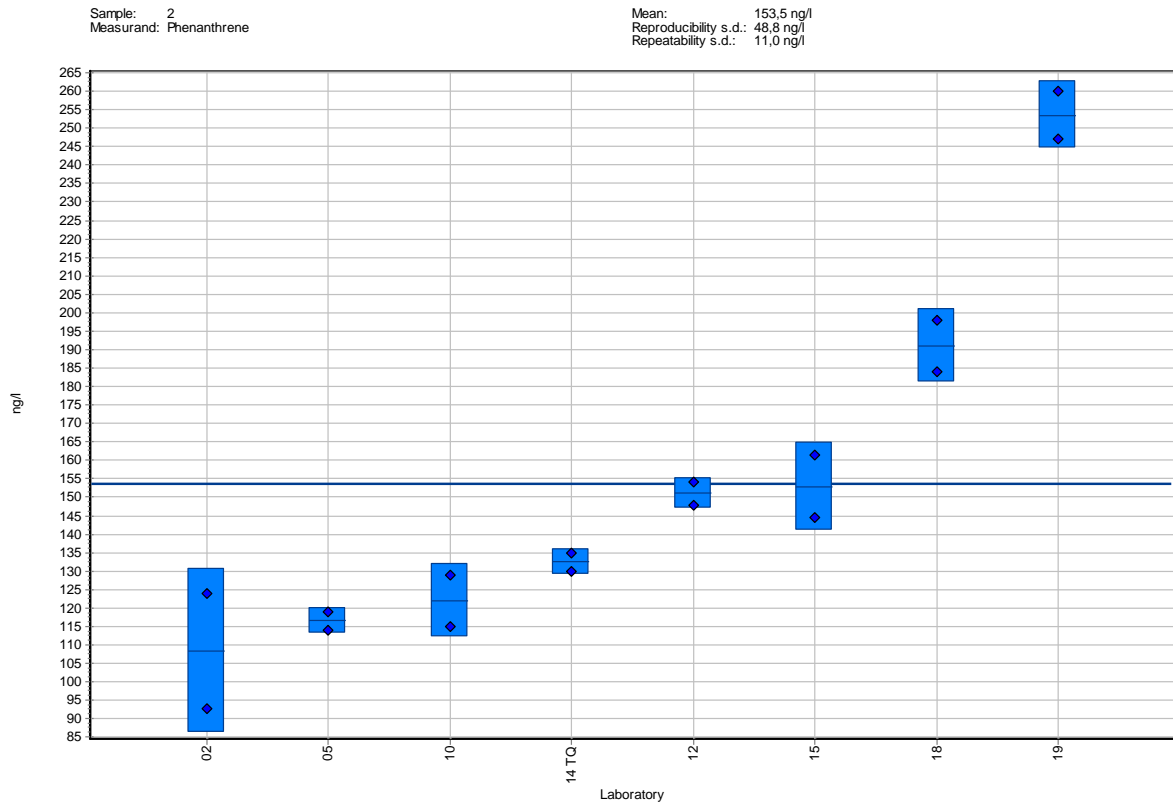
**Figure 29: Phenanthrene, sample 2**
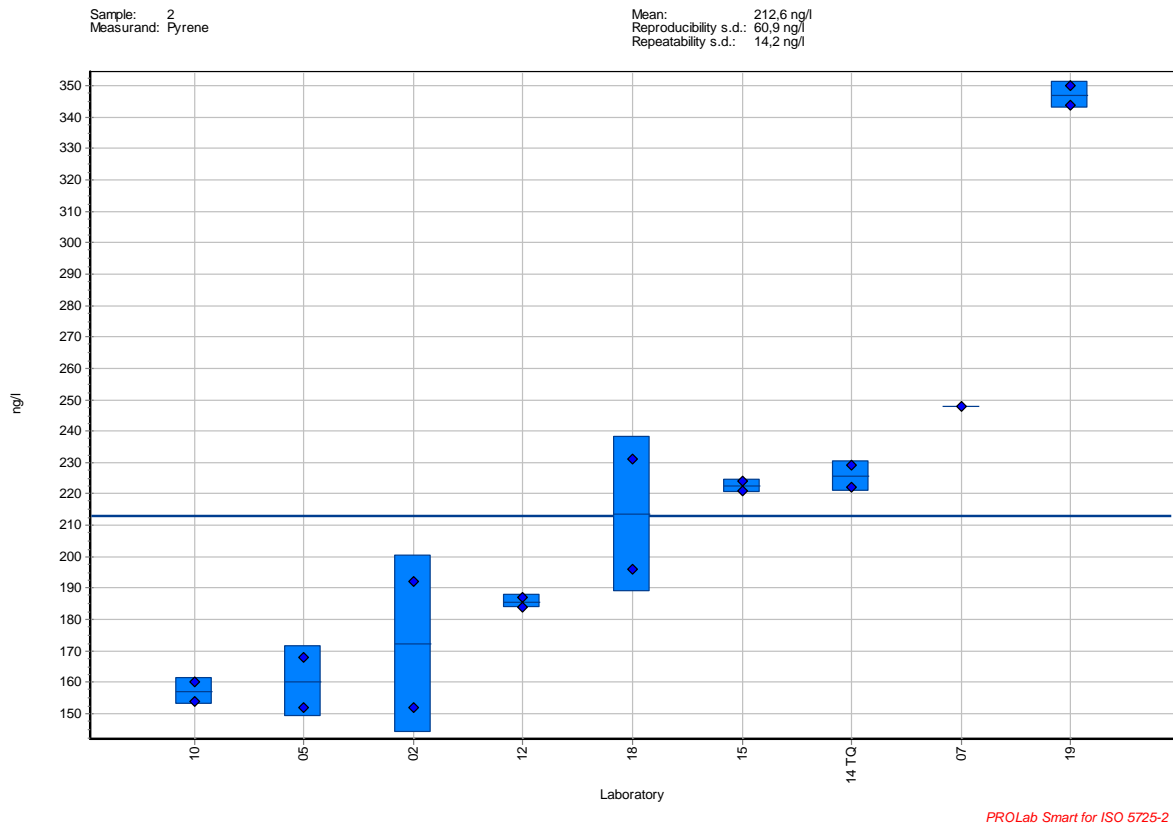
Figure 30: Pyrene, sample 2
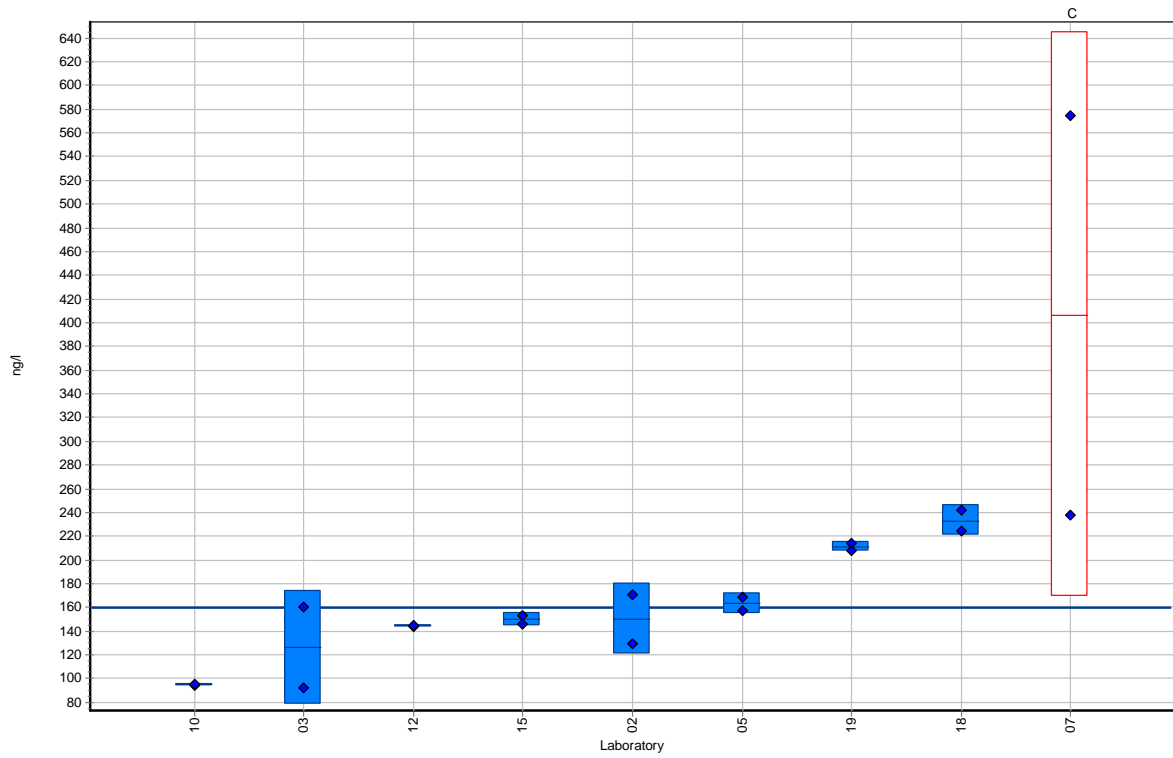
Figure 31: Chrysene, sample 2

Figure 32: Benzo[a]anthracene, sample 2

Figure 33: Dibenzo[a,h]anthracene, sample 2

6.4 **Sample 3: Graphical presentation of the results interlaboratory trial for the validation of "prEN 16691 "** Water quality - Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS)

Sample 3: Sample without SPM spiked with PAH
Matrix: Mineral water

Legend: ———— reference value
———— overall mean
TQ   Laboratory used triple quad

Outliers: A   outlying single result of one laboratory (not detectable in duplicate analysis),
B   outlying laboratory mean,
C   outlying within-laboratory variance
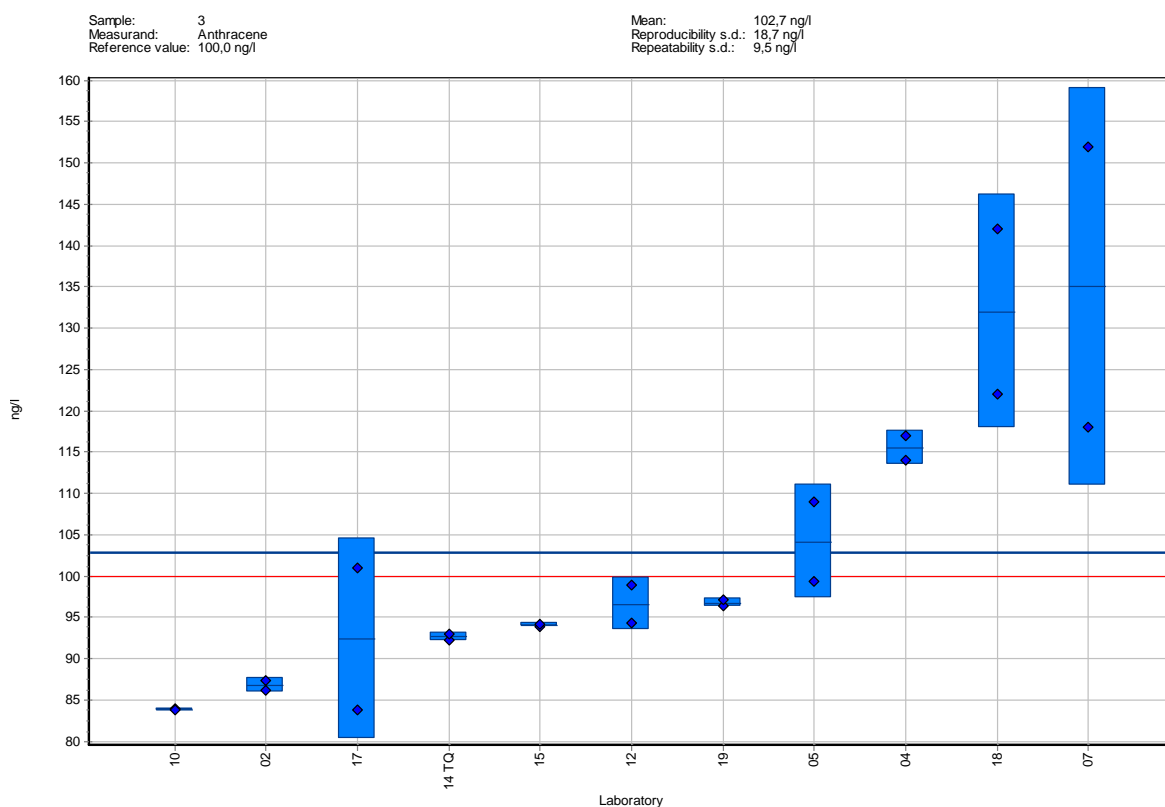
Figure 34: Anthracene, sample 3

Sample: 3
Measurand: Fluoranthene
Reference value: 100,0 ng/l

Mean: 100,5 ng/l
Reproducibility s.d.: 13,7 ng/l
Repeatability s.d.:   5,5 ng/l
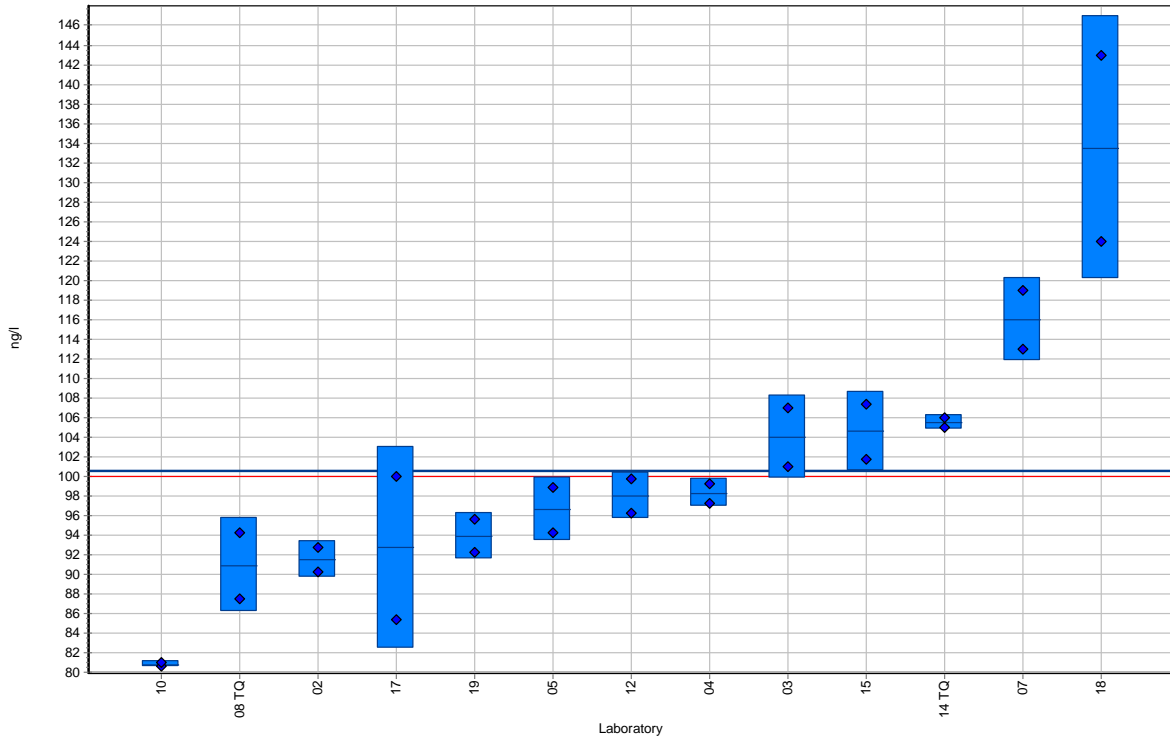
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Figure 35: Fluoranthene, sample 3
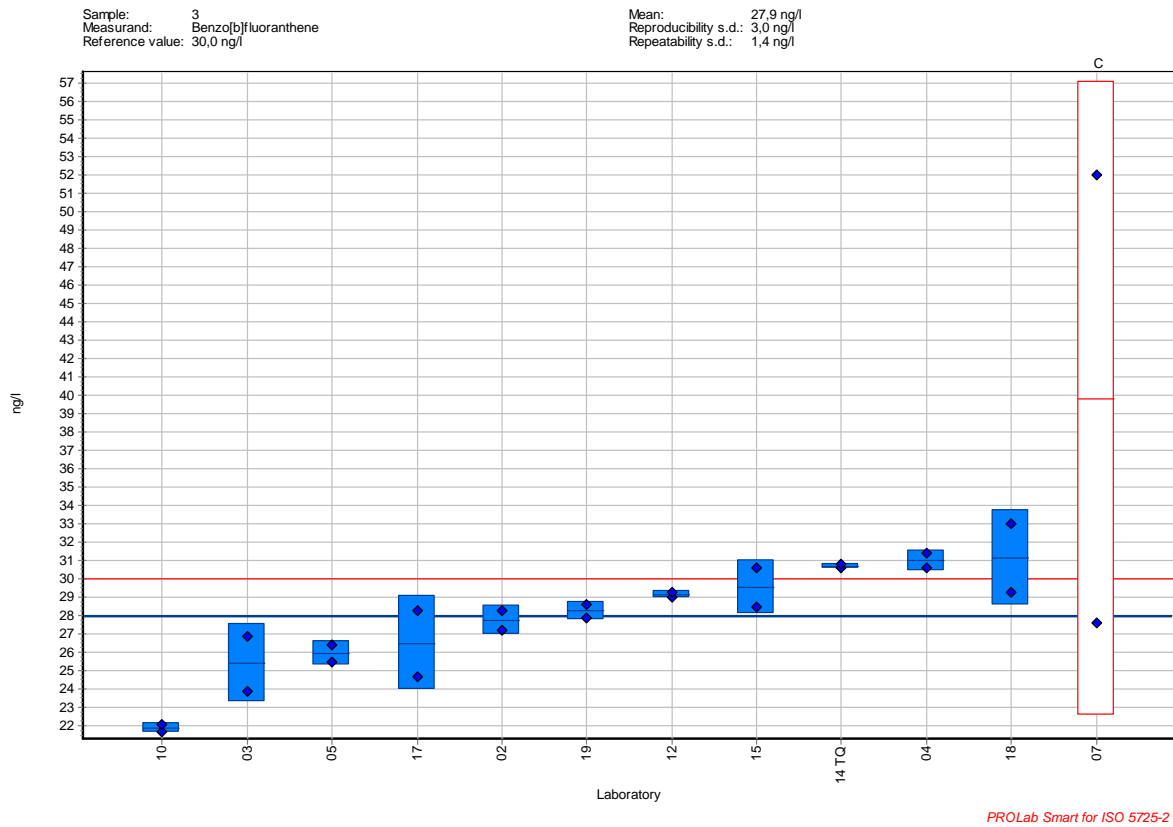
Figure 36: Benzo[b]fluoranthene, sample 3
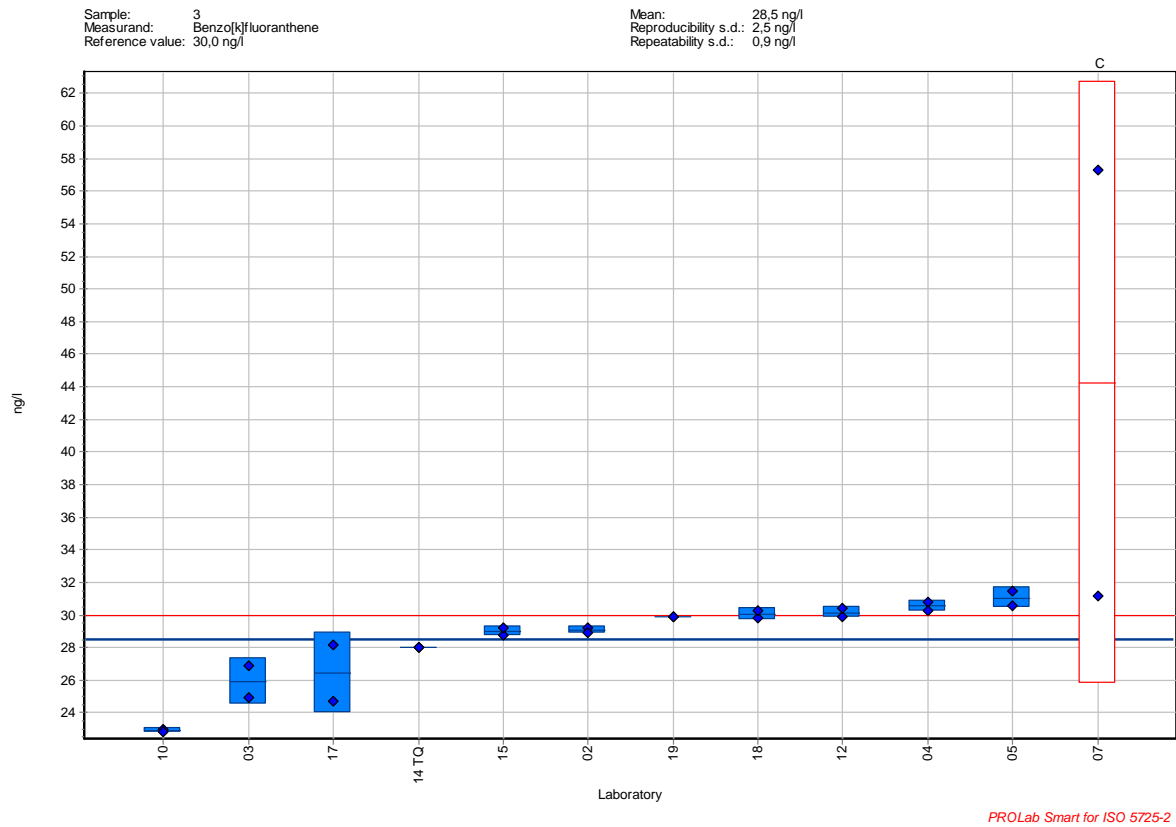
Figure 37: Benzo[k]fluoranthene, sample 3
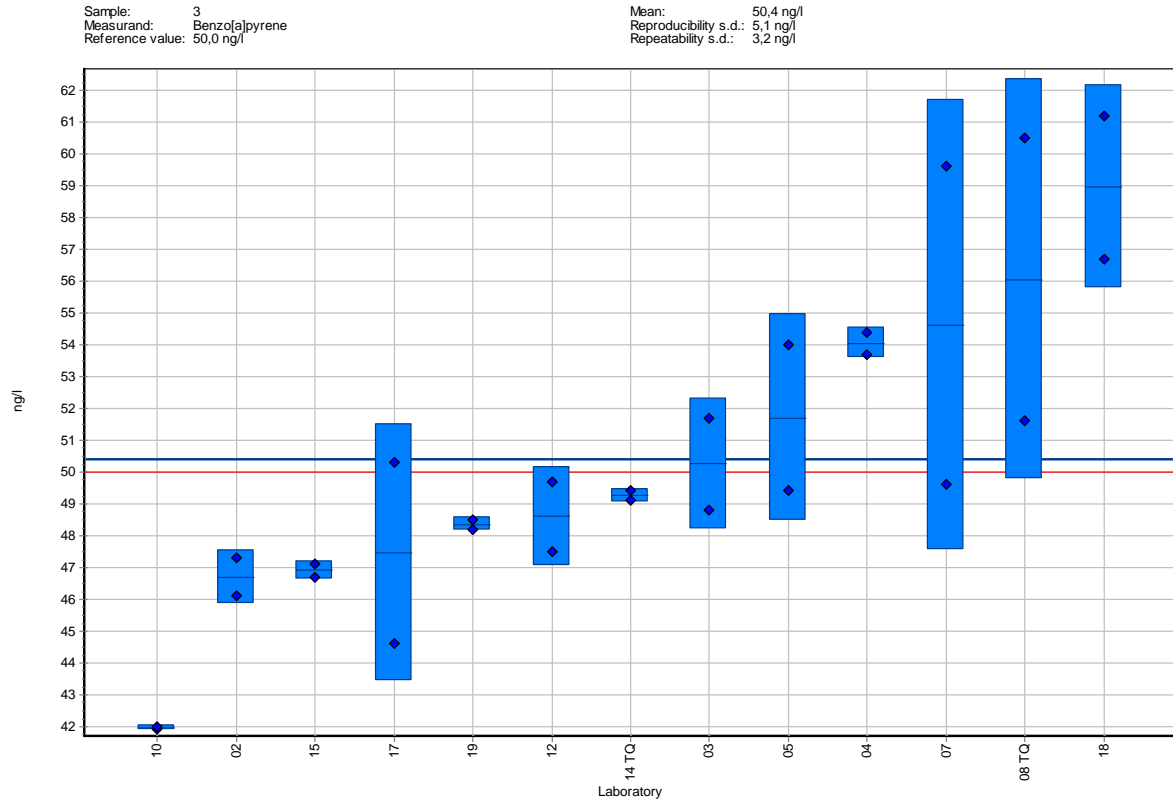
Figure 38: Benzo[a]pyrene, sample 3

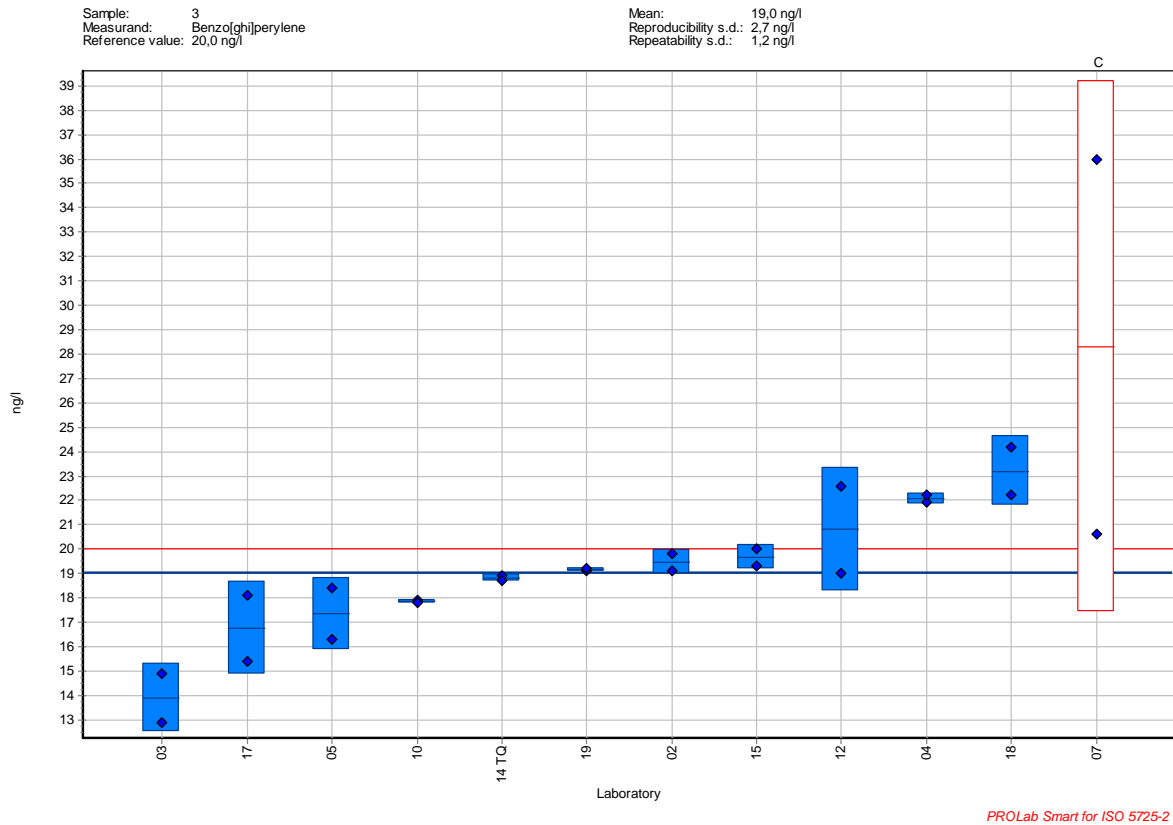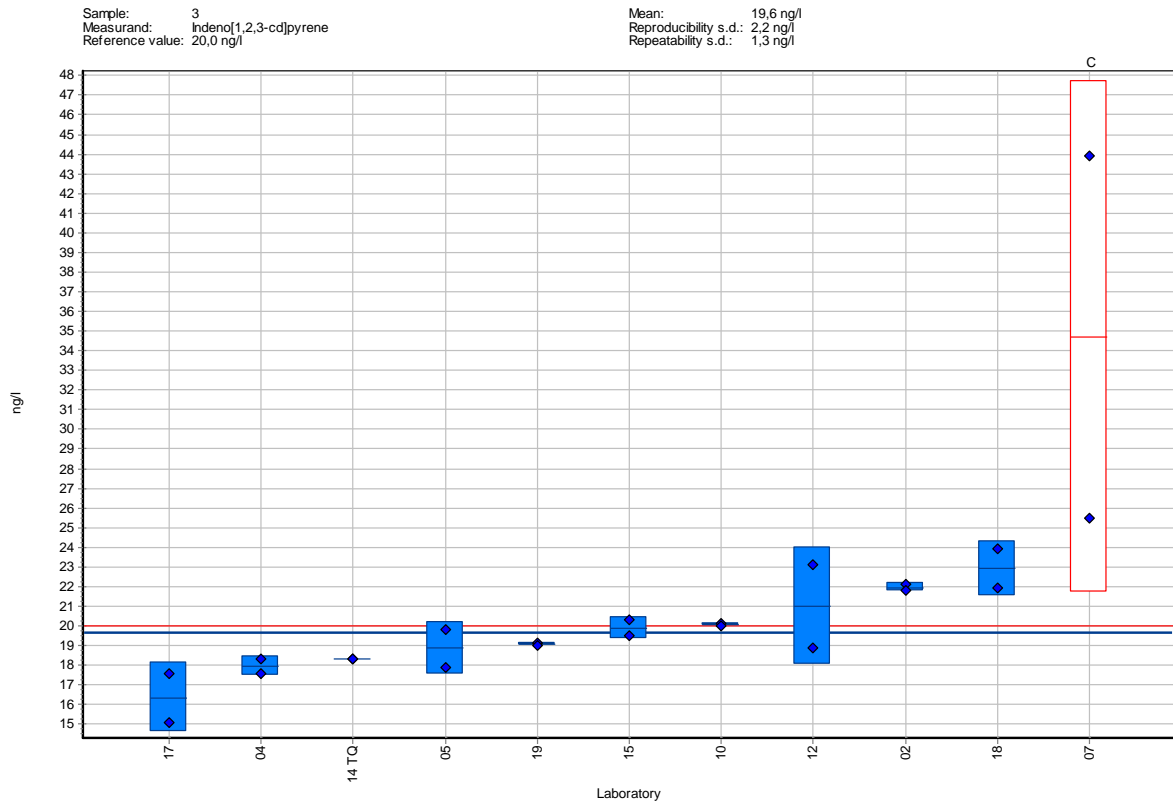**Figure 39: Benzo[ghi]perylene, sample 3**

Sample: 3
Measurand: Indeno[1,2,3-cd]pyrene
Reference value: 20,0 ng/l

Mean: 19,6 ng/l
Reproducibility s.d.: 2,2 ng/l
Repeatability s.d.:   1,3 ng/l

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Figure 40: Indeno[1,2,3-cd]pyrene, sample 3
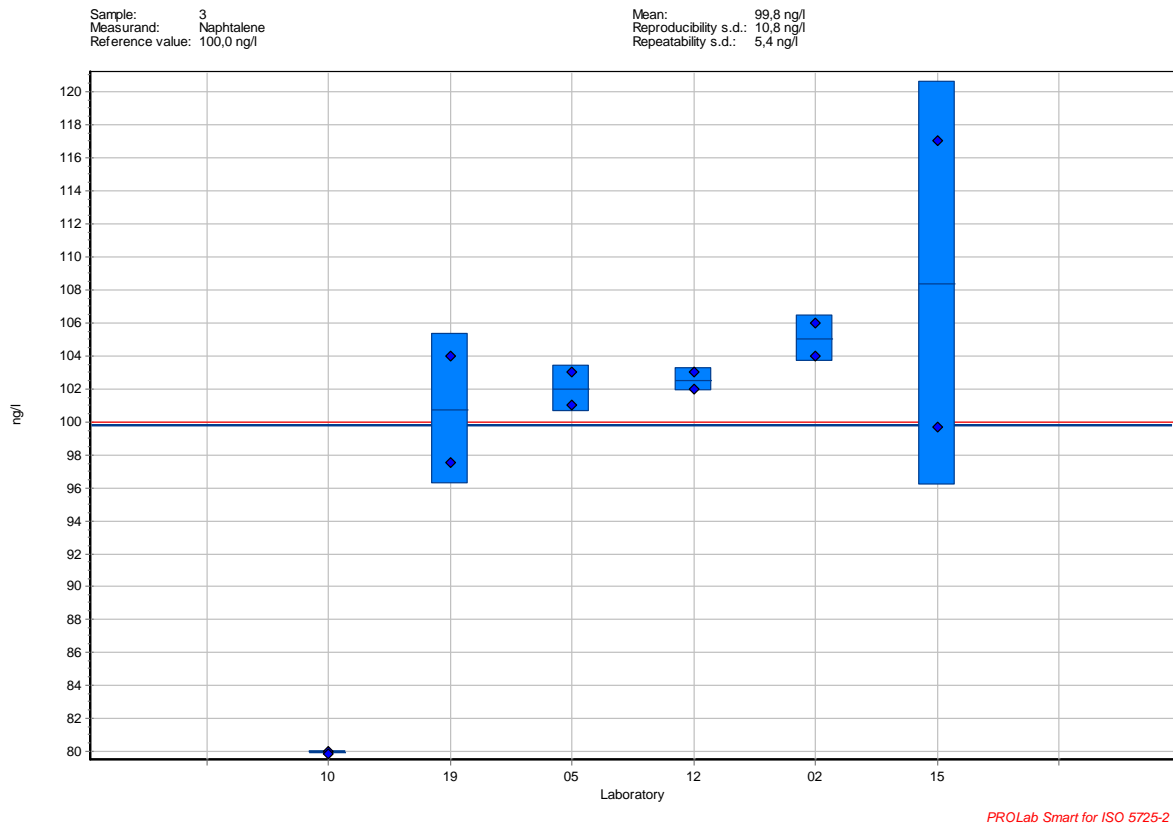
Figure 41: Naphtalene, sample 3
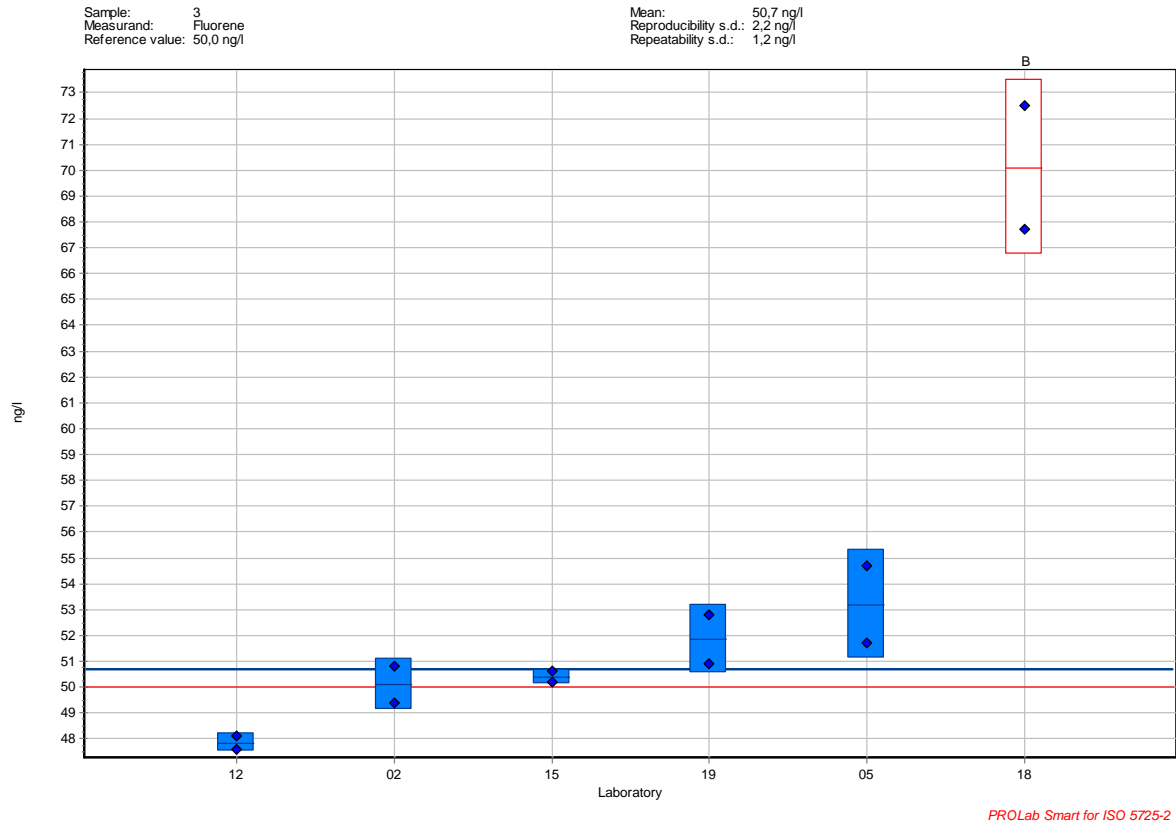
Figure 42: Fluorene, sample 3
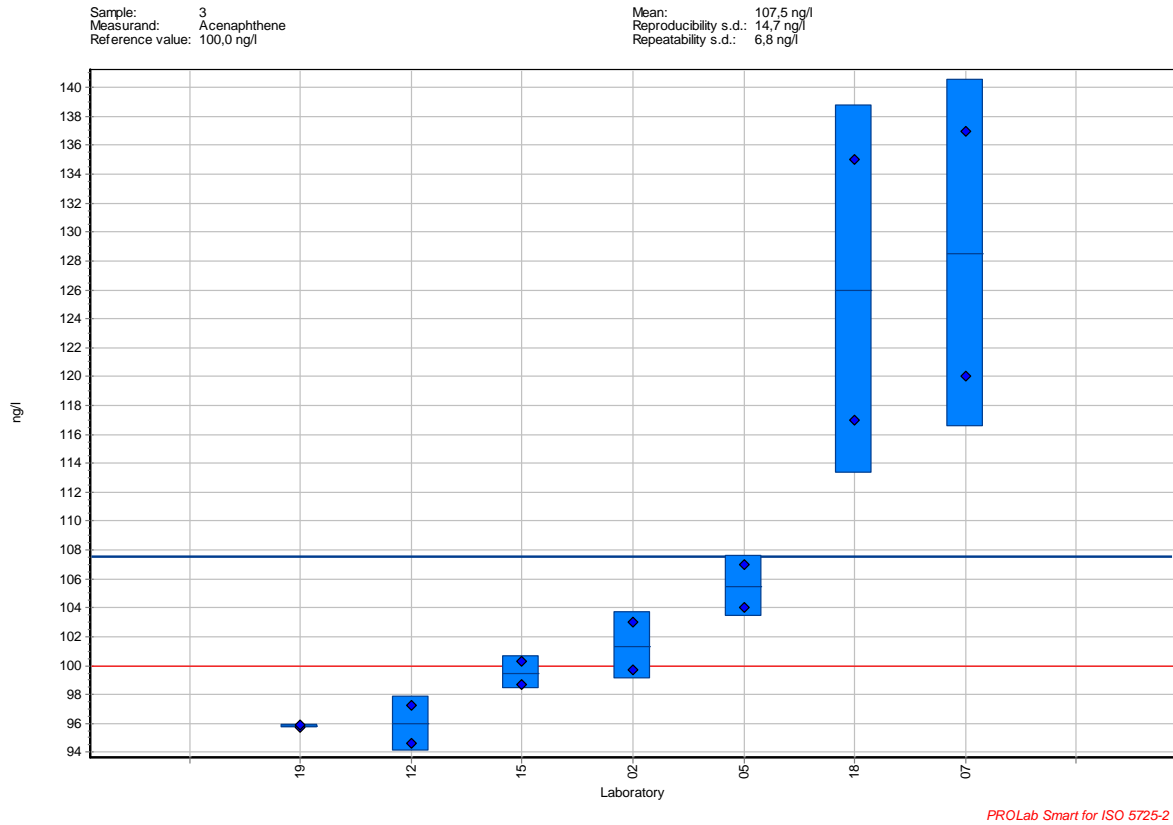
Figure 43: Acenaphthene, sample 3
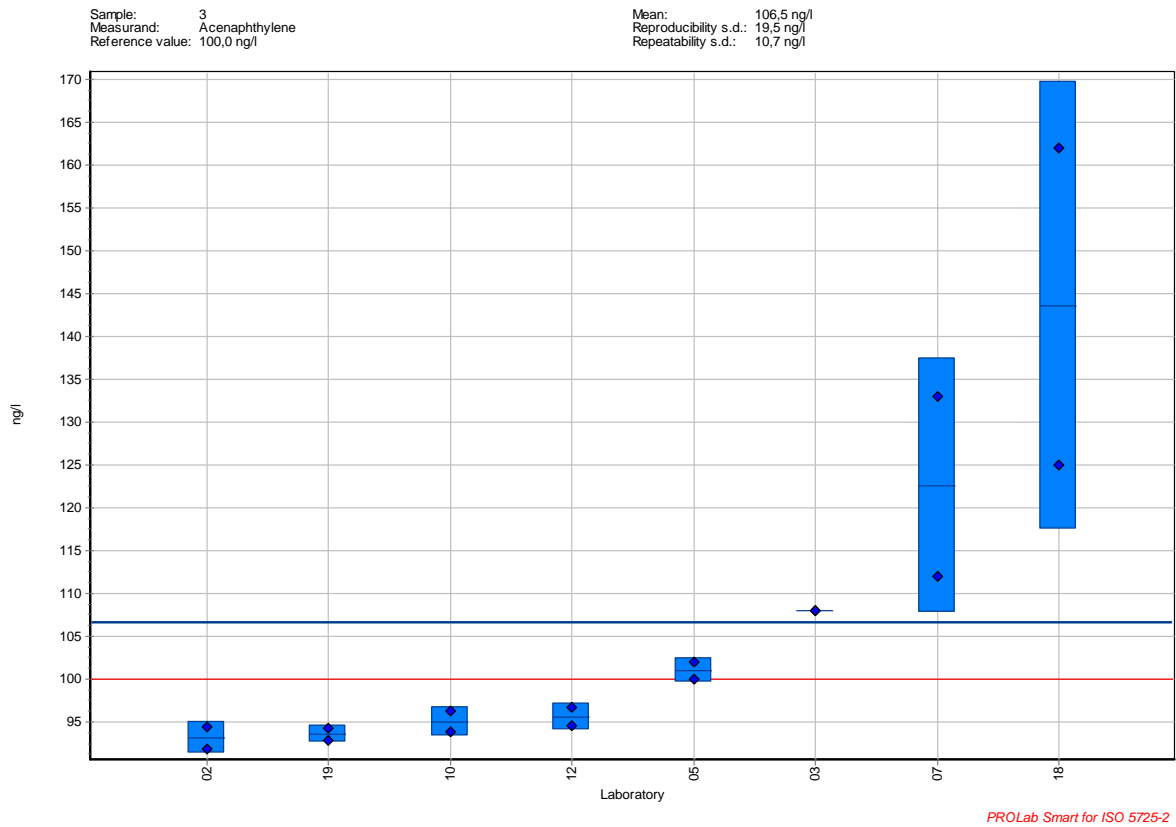
Figure 44: Acenaphthylene, sample 3

Sample: 3
Measurand: Phenanthrene
Reference value: 50,0 ng/l

Mean: 49,7 ng/l
Reproducibility s.d.:   6,3 ng/l
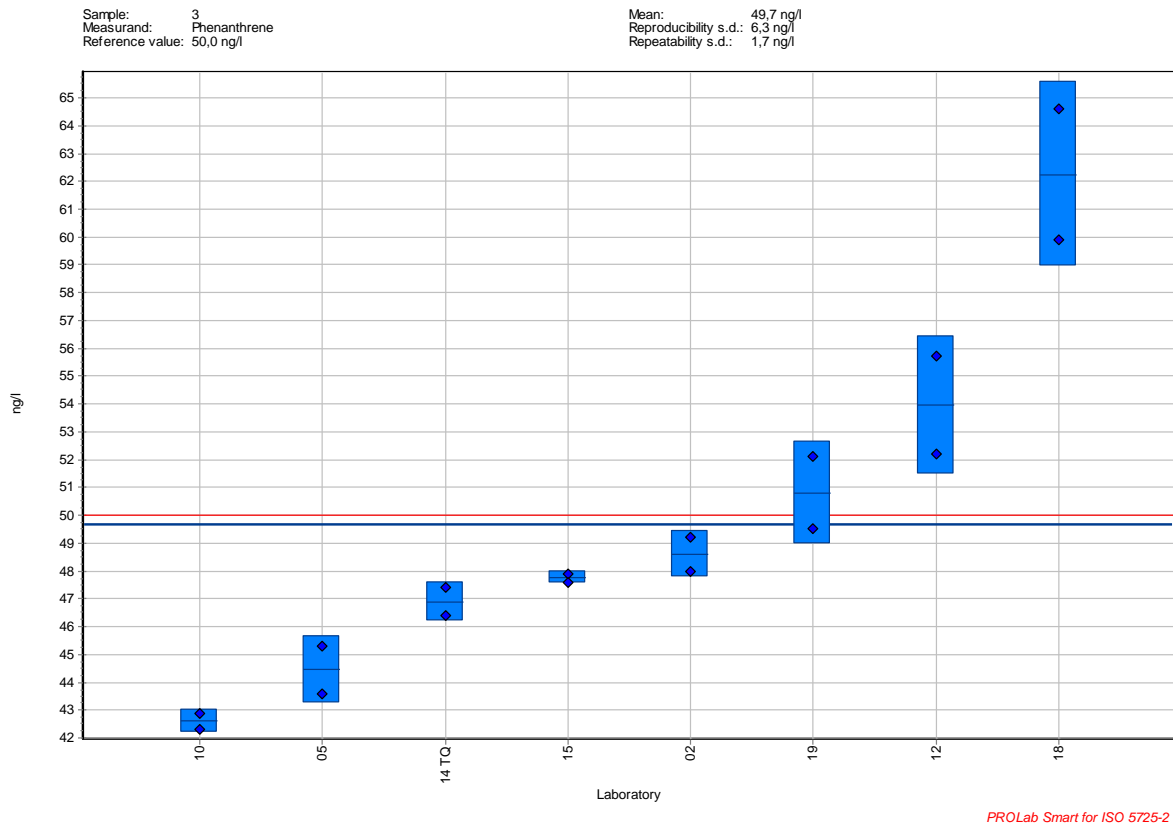Repeatability s.d.:   1,7 ng/l

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Figure 45: Phenanthrene, sample 3
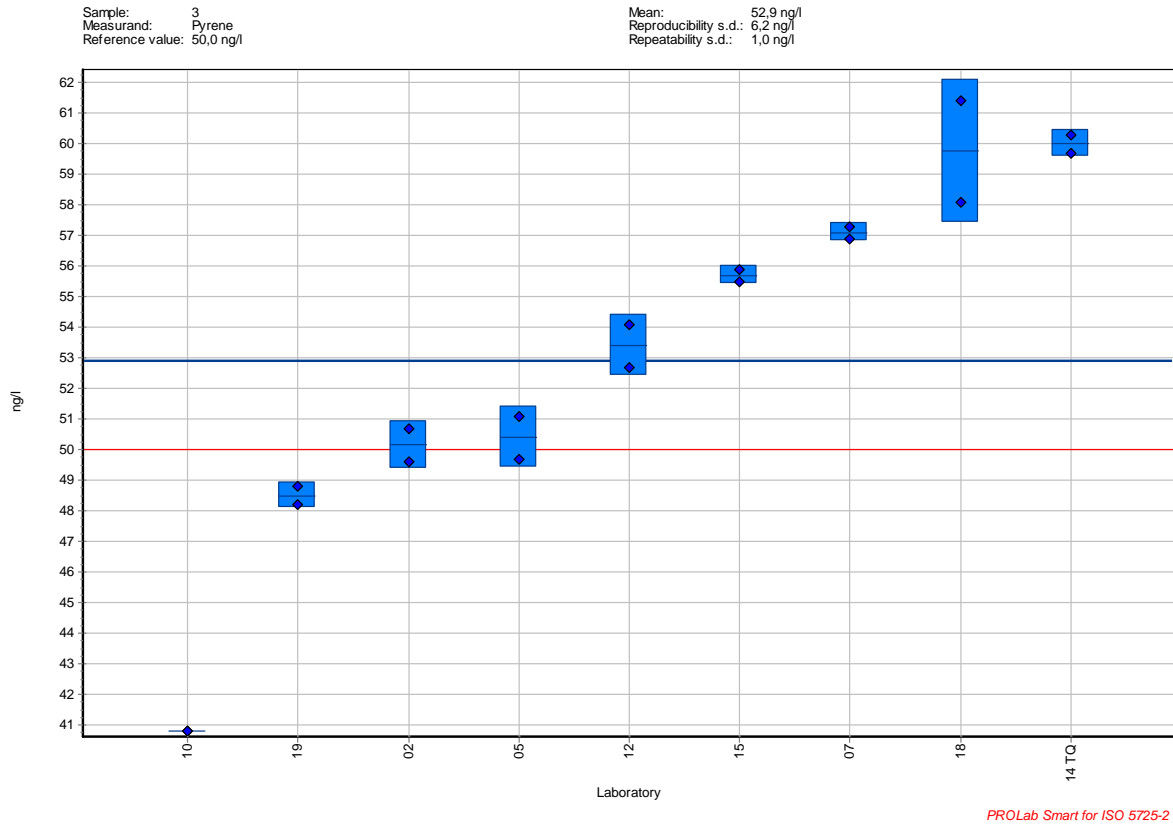
Figure 46: Pyrene, sample 3
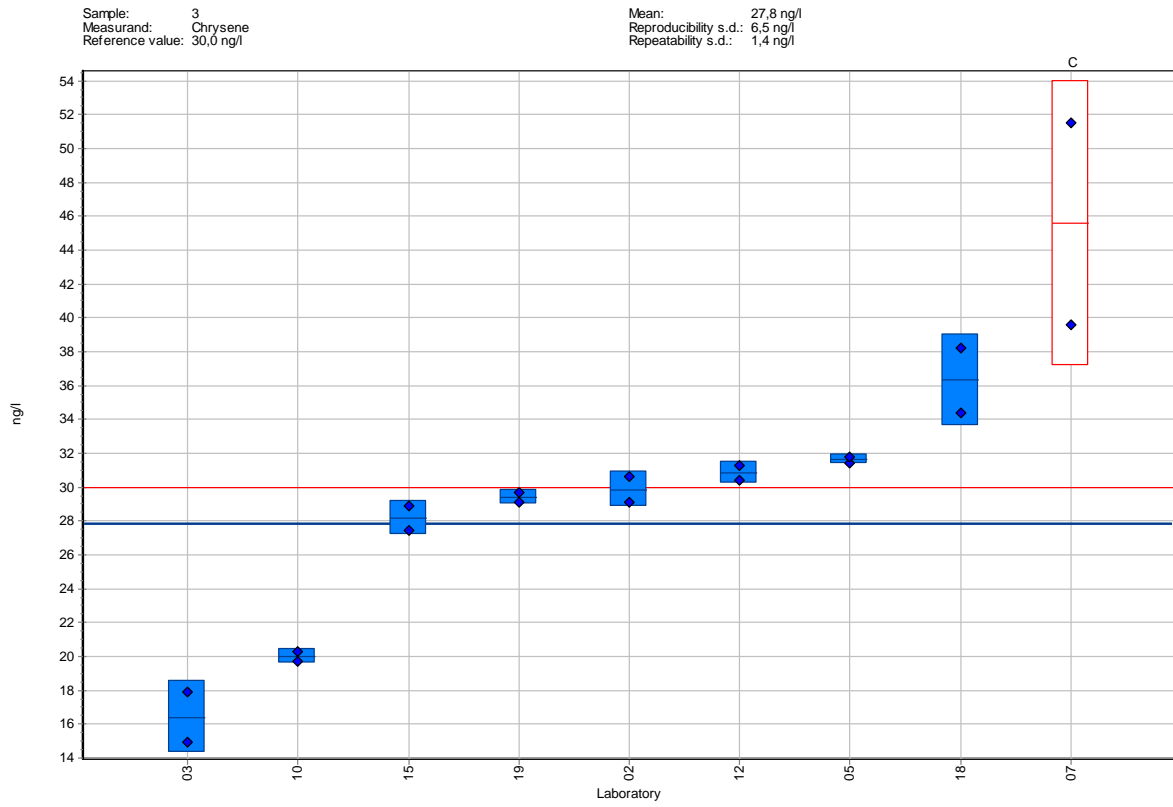
Figure 47: Chrysene, sample 3
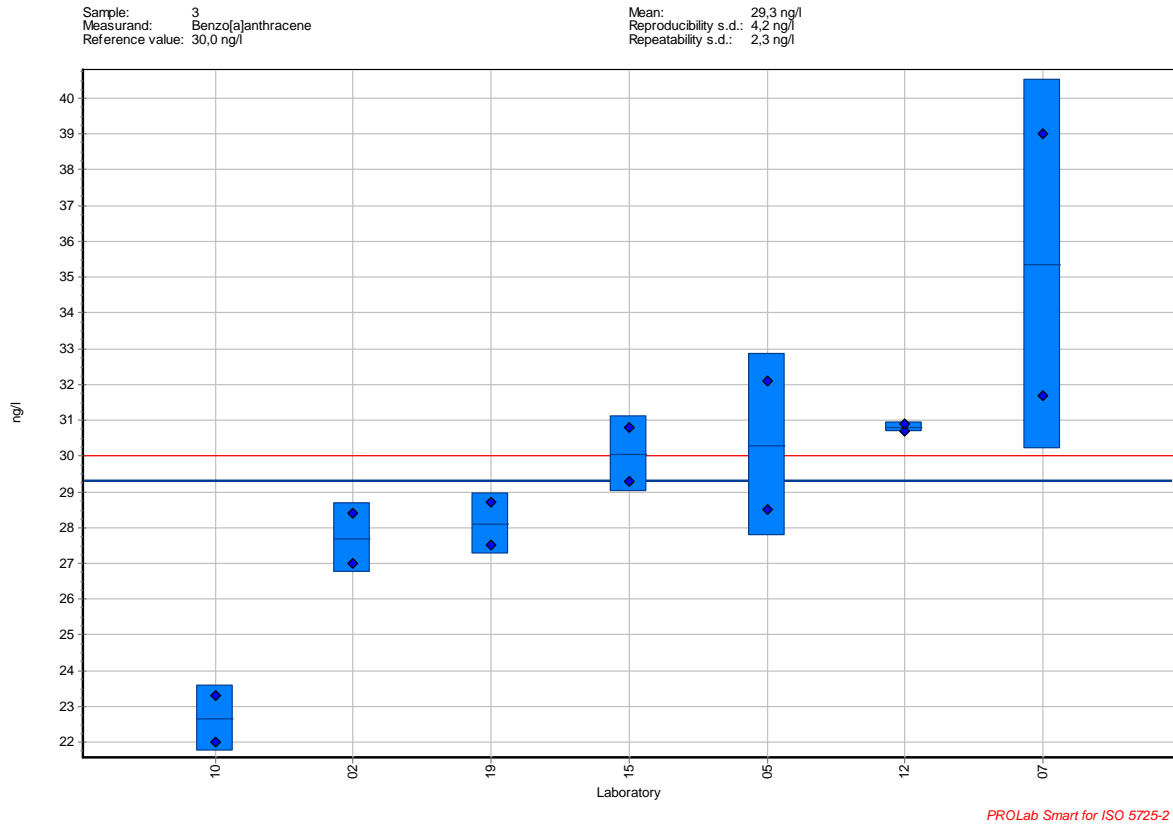
Figure 48: Benzo[a]anthracene, sample 3

Sample: 3
Measurand: Dibenzo[a,h]anthracene
Reference value: 20,0 ng/l

Mean: 20,6 ng/l
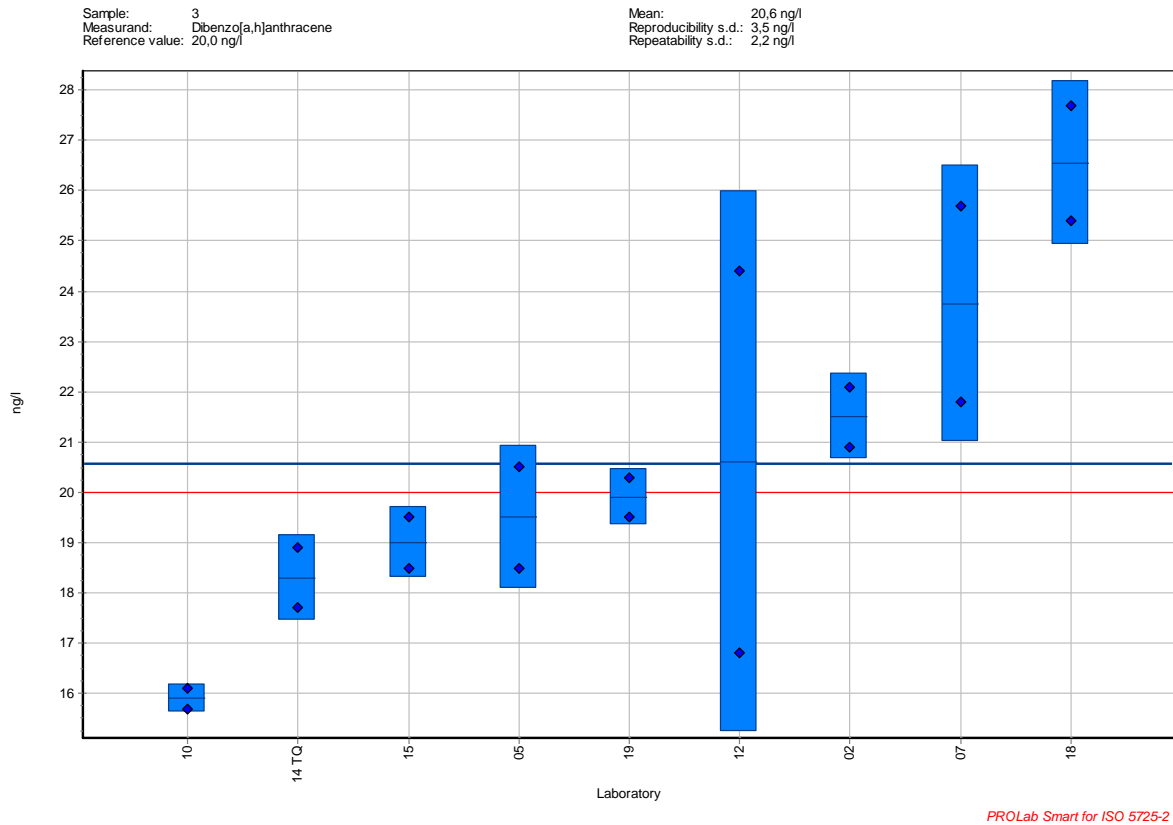Reproducibility s.d.: 3,5 ng/l
Repeatability s.d.:   2,2 ng/l

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Figure 49: Dibenzo[a,h]anthracene, sample 3