

MANUAL TAR MEASURING METHOD

Phase 2

ROUND ROBIN TEST 01

*Energy Research Programme EFP 2002
Environmentally friendly production of power and heat*

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Table of Contents

1	Introduction	3
2	Participating Laboratories.....	5
3	The Results of the Laboratories.....	7
3.1	Round 01 - Synthetic tar	7
3.2	Evaluation of results from round 01	21
3.2.1	SYNTAR 01, Pyridine	23
3.2.2	SYNTAR 01, Toluene.....	24
3.2.3	SYNTAR 01, Phenol.....	26
3.2.4	SYNTAR 01, Indene	28
3.2.5	SYNTAR 01, Guaiacol	30
3.2.6	SYNTAR 01, Naphthalene.....	32
3.2.7	SYNTAR 01, 4-methylguaiacol (creosol).....	34
3.2.8	SYNTAR 01, Phenanthrene	36
3.2.9	SYNTAR 01, Fluoranthene.....	38
3.2.10	SYNTAR 01, Pyrene.....	40
3.2.11	SYNTAR 02, Pyridine	42
3.2.12	SYNTAR 02, Toluene.....	43
3.2.13	SYNTAR 02, Phenol.....	45
3.2.14	SYNTAR 02, Indene	47
3.2.15	SYNTAR 02, Guaiacol	49
3.2.16	SYNTAR 02, Naphthalene.....	50
3.2.17	SYNTAR 02, 4-methylguaiacol (creosol).....	52
3.2.18	SYNTAR 02, Phenanthrene	53
3.2.19	SYNTAR 02, Fluoranthene.....	55
3.2.20	SYNTAR 02, Pyrene.....	57
3.2.21	SYNTAR 03, Blind sample.....	59
3.3	Analysis precision.....	60
4	References	63

1 Introduction

In connection with thermal conversion (gasification) of solid biomass, measurements of pollution in producer gas are required. Gas pollution is very complex as it may consist of both solid substances (particulate, soot), drops (aerosol, fog) and a large number of organic compounds (alcohols, organic acids, "tar", PAHs). For a number of years, Danish Technological Institute, Centre for Combustion and Engine Technology, has worked on developing a suitable measuring method, which can quantify the total spectrum of pollution. In connection with the Danish Energy Research Programme EFP 2000 the report "Verification and Validation of Manual Tar Measurement Method" \1\ was published.

At European level different initiatives were taken in order to solve the same problem. The previously published reports "Provisional Protocol for the Sampling and Analysis of Tar and Particulates in the Gas from Large-Scale Biomass Gasifiers" \2\ and "Protocol for the Sampling and Analysis of Particulate and Organic Contaminants in the Gas from Small-Scale Biomass Gasifiers" \3\ have - together with the results of a parallel measurement \4\, which were carried out in Denmark by four European laboratories - resulted in an EU project (ERK6-CT-1999-20002) with the purpose of creating one protocol covering the whole field. In the following this project is called *Tar Guideline* \5\.

In 2002, the EU Commission decided to subsidise a project (ENK5-CT-2002-80648) "Tar Measurement Standard" with the primary objective to standardise the Tar Guideline in order to reduce the technical and non-technical risks of implementation of biomass based CHP systems in the future. Work package WP2 is critical in this project and it shall provide data on

accuracy and reproducibility

of the draft standard according to requirements for CEN. These data will be provided by the group of technical experts (ECN, BTG, CIRAD, DTI, NREL, TU Graz, UMSICHT, Unizar, and VTT) who have collected and will include these data in their current national R&D projects plus in additional national projects aimed to provide these data. The necessity of a national R&D effort is based on the fact, that the EU project only supports the standardisation activity. DTI and VTT are responsible for collection and interpretation of data. The data will be used in WP1 by the CEN working group for the standardisation of the Tar Guideline.

One of the objectives of the present EFP 2002 project is to contribute to the procurement of data. In this context DTI organised a Round Robin Test consisting of three rounds (WP2, Task 2.3, Round Robin on gas chromatographic and gravimetric methods). In the first round synthetic samples with about 10 tar compounds representing updraft and downdraft or fluidised bed gasifiers were analysed gas chromatographically by the participating laboratories. On the basis of the results of round 01, real samples from updraft and downdraft or fluidised bed gasifiers shall be analysed gas chromatographically and gravimetrically (residue of evaporation) in round 02. This round has shown that it is necessary to tightening up the description of the gravimetric analysis method because of varying results. It was decided to carry out a third round only for gravimetric analysis. The present report concerns the results of the first round of the Round Robin Test on synthetic tars. Round 2 and 3 will be reported separately.

2 Participating Laboratories

In March 2003, 16 laboratories, which take an active part in gasification of biomass and tar measurement, were asked if they were interested in participating in a Round Robin Test on tar analysis. 12 laboratories expressed their interest and received detailed information. After this, nine laboratories agreed to participate in the test. In April 2003 - in connection with round 01 - they received three synthetic tar samples including one blind sample. One laboratory informed the coordinator that it wanted to withdraw and two laboratories did not report their results.

Consequently round 01 includes results from six laboratories.

Laboratories involved in this Round Robin Test are listed below in alphabetical order:

- BTG Biomass Technology Group B.V. - Enschede, The Netherlands
- CIRARD Forêt - Montpellier, France
- DTI - Danish Technological Institute - Aarhus, Denmark
- ECN Biomass - Energy Research Centre of the Netherlands - Petten, The Netherlands
- NREL - National Renewable Energy Laboratory - Golden, CO, USA
- VTT Energy - Espoo, Finland

The participating laboratories were given arbitrarily code numbers so the results would be anonymous.

3 The Results of the Laboratories

3.1 Round 01 - Synthetic tar

The laboratories individual results are presented in a table like the paragon shown below:

- 1) Round Robin Test on Tar, May 2003
- 2) Round 01 - Synthetic tar

3) Laboratory code No. x

4) Table 1

Sample identification	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	1	2	3	4	5	6			Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]	CV %
Sub sample No.												

5)

Number of comp.												
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6)

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7) Table 2

Used apparatus, sample preparation and analysis condition

The table shall be read as follows:

- 1) Title of the test and months of completion.
- 2) Number of round and type of sample.
- 3) Code no. of the laboratory.
- 4) Table 1: Column 1 contains the sample identity and the compounds in the performance test. Column 2-7 contain the analysis results of the laboratory in question for the sub divided sample. Column 8 contains the nominal value for the forwarded test matrix (determined by weight). Column 9 contains the uncertainty of the nominal value of every compound. Column 10 contains the mean value of the 6 analysis results. Column 11 contains the mean values deviation from the nominal value. Column 12 contains the standard deviation of the repeated analysis results and column 13 contains the coefficient of variation.

$$CV = \frac{STDev \cdot 100}{Mean Value} [\%]$$

- 5) The number of compounds reported by the laboratory and the average CV.
- 6) The numerically mean deviation from the nominal value (which means, the deviations are added without sign).
- 7) Table 2: Contains information about used apparatus, sample preparation and analysis condition. The level of information is voluntary.

In the following, the results of the participating laboratories are presented.

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO.: Co-ordinator

SYNTAR 01	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.000					
Toluene	4.32	4.75	4.84	4.5	5.4	4.39	4.384	0.033	4.70	7.21	0.398	8.47
Phenol	58.7	60.5	62.8	59.8	62	58.9	55.00	0.41	60.5	9.91	1.662	2.75
Indene	6.82	6.96	7.27	6.91	7.38	6.71	6.500	0.049	7.01	7.82	0.262	3.74
Guaiacol	93	95.9	98.3	95.5	99.7	92.9	88.60	0.66	95.9	8.22	2.748	2.87
Naphthalene	5.91	6.16	6.34	6.08	6.50	6.02	5.960	0.045	6.17	3.50	0.217	3.52
4-methylguaiacol	161	167	173	163	174	162	144.8	1.1	167	15.10	5.680	3.41
Phenanthrene	3.71	3.61	3.57	3.55	3.47	3.49	3.600	0.027	3.57	-0.93	0.087	2.44
Fluoranthene	0.471	0.455	0.44	0.43	0.433	0.394	0.509	0.004	0.437	-14.1	0.026	5.97
Pyrene	0.247	0.243	0.24	0.22	0.23	0.23	0.292	0.002	0.235	-19.5	0.010	4.29

Number of comp.	9	9	9	9	9	9	Mean of CV's %	4.16
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Numerically mean deviation from nominal value %	9.6
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Used apparatus, sample preparation and analysis condition
GC/MS-SIM, HP 6890/5973 Internal standard added. Analysed directly by GC/MS full scan.

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 5

SYNTAR 01	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	< 1	< 1	< 1	< 1	< 1	< 1	0.000					
Toluene	4.80	4.58	4.69	4.71	4.65	4.69	4.384	0.033	4.69	6.9	0.072	1.53
Phenol	66.0	63.9	64.2	64.4	63.8	64.3	55.00	0.41	64.4	17.2	0.787	1.22
Indene	7.19	6.98	7.05	7.04	6.98	7.06	6.500	0.049	7.05	8.5	0.078	1.11
Guaiacol	103.1	99.7	100.5	100.7	99.8	100.6	88.60	0.66	100.7	13.7	1.227	1.22
Naphthalene	6.87	6.70	6.72	6.74	6.75	6.71	5.960	0.045	6.75	13.2	0.060	0.90
4-methylguaiacol	167	162	163	164	162	163	144.80	1.1	164	13.0	1.726	1.06
Phenanthrene	4.21	4.02	4.07	4.11	4.08	4.08	3.600	0.027	4.09	13.7	0.063	1.54
Fluoranthene	0.715	0.593	0.619	0.567	0.605	0.605	0.509	0.004	0.617	21.3	0.051	8.25
Pyrene	0.365	0.371	0.317	0.309	0.334	0.334	0.292	0.002	0.338	15.9	0.025	7.40

Number of comp.	9	9	9	9	9	9	Mean of CV's %	2.69
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Numerically mean deviation from nominal value %	13.7
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Comments on Lab 5's results:

On 1 December Lab 5 forwarded a correction of its results as agreed in the project group. The results were obtained by using a different calibration factor compared to the original results, which were about 25% lower than the corrected data shown above.

Used apparatus, sample preparation and analysis condition
GC/FID, Shimadzu GC 17A, split injector GC-column: J&W DB 5.625, 30 m x 0.25 mm, df = 0.5 µm Oven temp.: 50 °C 4 min, 25 °C/min 150 °C 0 min, 5 °C/min 300 °C 10 min Analysis of pyridine GC-column: ZB-WAX, 30 m x 0.25 mm, df = 0.25 µm (Phenomenex) Oven temp.: 50 °C 5 min, 10 °C/min 240 °C

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 6

SYNTAR 01	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine							0.000					
Toluene	4.81	4.28	4.05	4.31	4.29	4.14	4.384	0.033	4.31	-1.6	0.262	6.07
Phenol	52.5	52.8	52.9	53.3	53.2	52.9	55.00	0.41	52.9	-3.7	0.272	0.51
Indene	6.24	6.31	6.41	6.47	6.46	6.37	6.500	0.049	6.38	-1.9	0.090	1.41
Guaiacol	83.9	83.0	83.4	84.0	83.1	83.2	88.60	0.66	83.4	-5.8	0.427	0.51
Naphthalene	5.83	5.85	5.87	5.67	5.82	5.86	5.960	0.045	5.82	-2.4	0.073	1.26
4-methylguaiacol							144.80	1.1				
Phenanthrene	3.93	3.33	3.26	3.38	3.34	3.29	3.600	0.027	3.42	-4.9	0.251	7.33
Fluoranthene	0.438	0.458	0.532	0.468	2.40	0.484	0.509	0.004	0.797	56.5	0.786	98.7
Pyrene							0.292	0.002				

Number of comp.	7	7	7	7	7	7	Mean of CV's %	16.5
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Numerically mean deviation from nominal value %	11.0
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Used apparatus, sample preparation and analysis condition

GC/FID, HP 5890, HP 3396A integrator
 Column: HP Ultra 2 (crosslinked 5% Ph Me silicone) 50 m x 0.32 mm, film thickness 0.52 µm
 Injector: Split/splitless injector 290 °C
 Carrier gas: Helium, injector pressure about 120 kPa, total flow about 20 ml/min
 Oven temp.: 50 °C 5 min, heating rate 3 °C /min to 160 °C, then 10 °C/min to 290 °C
 ISTD = n-dodecane

Comments:

A peak was detected at runtime of 6.26 min (before pyridine) in every sample (impurity?).
 An unknown peak was detected between naphthalene and dodecane, which is expected to be 4-methylguaiacol (we had no model compound for 4-methylguaiacol).
 Detection limit is approx. 0.5 mg/l.

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 7

SYNTAR 01	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	4 U	4 U	4 U	4 U	4 U	4 U	0.000					
Toluene	5.5	5.2	5.3	4.7	5.3	5.3	4.384	0.033	5.22	19.0	0.271	5.20
Phenol	58	51	56	45	50	52	55.00	0.41	52.0	-5.5	4.604	8.85
Indene	C	C	C	C	C	C	6.500	0.049				
Guaiacol	99	83	96	81	82	85	88.60	0.66	87.7	-1.1	7.789	8.88
Naphthalene	7.2	6.5	6.8	5.8	6.4	6.5	5.960	0.045	6.53	9.6	0.463	7.09
4-methylguaiacol	167	143	161	135	142	146	144.80	1.1	149	2.9	12.313	8.26
Phenanthrene	3.8	3.2	3.7	3.2	3.2	3.4	3.600	0.027	3.42	-5.1	0.271	7.94
Fluoranthene	0.5	0.4	0.5	0.4	0.4	0.4	0.509	0.004	0.433	-14.9	0.052	11.92
Pyrene	0.3	0.3	0.3	0.3	0.2	0.2	0.292	0.002	0.267	-8.7	0.052	19.36

Number of comp.	8	8	8	8	8	8	Mean of CV's %	9.69
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Numerically mean deviation from nominal value %	8.3
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Used apparatus, sample preparation and analysis condition
<p>GC/MS, Agilent 6890 GC, Agilent 5973 MSD, Agilent 7673 Autosampler Column: 30 m x 0.25 mm, DB-5 0,25 µm film Split injector 275 °C MSD transfer line 300 °C</p> <p>Sample was injected as received, column flow 1 ml/min helium (constant flow mode) Split ratio 30:1 Oven temp. 50 °C 5 min, ramp 8 °C/min to 250 °C, hold 0 min, ramp 20 °C/min to 300 °C hold 2.5 min</p> <p>Calibration was carried out by external standard.</p> <p>Comment: Indene was detected by GC/MS, but not calibrated due to lack of standard. Even on a clean system, performance for phenol, guaiacol and methylguaiacol deteriorated. (expressive tailing) over repeated injection.</p>

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 14

SYNTAR 01	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine							0.000					
Toluene	3.09	2.49	2.56	2.52	2.51	2.54	4.384	0.033	2.62	-40.3	0.231	8.83
Phenol	109	114	106	119	108	118	55.00	0.41	113	105	5.420	4.81
Indene	5.40	4.46	4.40	4.43	4.41	4.42	6.500	0.049	4.59	-29.4	0.400	8.71
Guaiacol	82.5	90.4	99.3	88.7	91.9	101	88.60	0.66	92.3	4.14	6.847	7.42
Naphthalene	9.02	7.04	7.57	7.83	6.92	7.13	5.960	0.045	7.58	27.2	0.782	10.32
4-methylguaiacol	133	148	162	143	154	160	144.80	1.1	150	3.62	10.89	7.26
Phenanthrene							3.600	0.027				
Fluoranthene							0.509	0.004				
Pyrene							0.292	0.002				

Number of comp.	6	6	6	6	6	6	Mean of CV's %	7.89
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Numerically mean deviation from nominal value %	34.9
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Comments on Lab 14's results:

The results shown above include corrected numbers as a consequence of a discussion between the lab and the coordinator. The coordinator pointed out to the lab that obviously some of the previous results were incorrect. The lab found two processing errors, which it rectified. By this the mean value for phenol was corrected from 3.8 mg/l to 113 mg/l and the mean value for indene changed from 74.9 mg/l to 4.59 mg/l.

Used apparatus, sample preparation and analysis condition
GC/FID, Chrompack CP 9002 Liquid sampler: CP 9050 Column: non-polar capillary CP-Sil 8CB ISTD for aromates: 0.0319 g Tert. Butyl-cyclo-hexane, 30.433 g DCM, added 50 µl ISTD for phenols: 0.032 g Tert. 4-ethyl-phenol, 30.1208 g IPA, added 50 µl + 50 µl BSTA Carrier gas: Helium, 60 kPa initial pressure Start temp. 50 °C, final temp. 280 °C, different oven programming for aromates and phenols

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 18

SYNTAR 01	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine							0.000					
Toluene	7.03	6.97	7.08	7.01	7.11	6.94	4.384	0.033	7.02	60.2	0.064	0.92
Phenol	56.4	56.5	56.6	56.3	56.5	56.4	55.00	0.41	56.5	2.6	0.083	0.15
Indene	8.48	8.55	8.55	8.11	8.43	8.64	6.500	0.049	8.46	30.2	0.186	2.19
Guaiacol	90.1	90.1	90.2	89.4	90.2	90.1	88.60	0.66	90.0	1.6	0.302	0.34
Naphthalene	6.48	6.46	6.49	6.45	6.48	6.45	5.960	0.045	6.47	8.5	0.017	0.27
4-methylguaiacol	154	154	154	153	154	154	144.80	1.1	154	6.3	0.335	0.22
Phenanthrene	3.86	3.75	3.82	3.77	3.78	3.77	3.600	0.027	3.79	5.3	0.041	1.07
Fluoranthene	0.72	0.62	0.63	0.63	0.6	0.56	0.509	0.004	0.627	23.1	0.053	8.42
Pyrene	0.53	0.45	0.4	0.39	0.37	0.36	0.292	0.002	0.417	42.7	0.064	15.30

Number of comp.	9	9	9	9	9	9	Mean of CV's %	3.21
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Numerically mean deviation from nominal value %	20.1
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Comments on Lab 18's results:

On 17 June the lab stated that it always has integration problems with toluene due to a small and very wide peak, so quantitative analysis was not performed. In the subsequent statistic analysis the toluene value was not recognised as an outlier, but anyhow the value was suspect and therefore it was rejected.

Used apparatus, sample preparation and analysis condition
HPLC with UV-DAD detector, KONTRON/BIO-TEK Column: UP 5 ODB-25k (C18 type) No sample preparation. Oven temp.: 20 °C Eluent: Methanol/acetonitrile/water Injection volume: 10 µl

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO.: Coordinator

SYNTAR 02	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	0.868	0.744	0.83	0.81	0.705	0.834	0.720	0.005	0.799	10.9	0.062	7.71
Toluene	1.51	1.86	1.76	1.76	1.75	1.59	1.640	0.012	1.71	3.96	0.129	7.57
Phenol	4.92	4.9	4.78	4.67	4.56	4.66	4.400	0.033	4.7	7.92	0.143	3.02
Indene	4.37	4.64	4.51	4.44	4.26	4.16	4.550	0.034	4.40	-3.37	0.173	3.93
Guaiacol	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.000					
Naphthalene	105	138	127	128	120	119	119.00	0.89	123	3.22	11.089	9.03
4-methylguaiacol	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.434	0.003				
Phenanthrene	25.6	25.4	25.2	25.1	24.5	24.8	25.700	0.193	25.1	-2.33	0.400	1.59
Fluoranthene	8.02	7.52	7.53	7.39	7.33	7.25	7.630	0.057	7.51	-1.6	0.274	3.65
Pyrene	2.06	1.92	1.88	1.83	1.81	1.82	2.340	0.018	1.89	-19.4	0.095	5.01

Number of comp.	8	8	8	8	8	8	Mean of CV's %	5.19
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Numerically mean deviation from nominal value %	6.6
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Used apparatus, sample preparation and analysis condition
GC/MS-SIM, HP 6890/5973 Internal standard added. Analysed direct by GC/MS full scan.

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 5

SYNTAR 02	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	< 1	< 1	< 1	< 1	< 1	< 1	0.720	0.005				
Toluene	1.91	1.96	1.95	1.94	1.97	1.94	1.640	0.012	1.95	18.7	0.021	1.07
Phenol	5.11	5.11	5.12	5.17	5.10	5.13	4.400	0.033	5.12	16.4	0.026	0.50
Indene	4.83	4.90	4.94	4.89	4.88	4.89	4.550	0.034	4.89	7.4	0.035	0.71
Guaiacol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.000					
Naphthalene	135	136	136	136	136	136	119.00	0.89	136	13.9	0.473	0.35
4-methylguaiacol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.434	0.003				
Phenanthrene	30.7	31.0	31.2	31.1	31.0	31.0	25.700	0.193	31.0	20.5	0.177	0.57
Fluoranthene	9.58	9.76	9.84	9.76	9.70	9.68	7.630	0.057	9.72	27.4	0.089	0.91
Pyrene	2.73	2.82	2.76	2.76	2.76	2.76	2.340	0.018	2.76	18.2	0.029	1.04

Number of comp.	7	7	7	7	7	7	Mean of CV's %	0.74
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Numerically mean deviation from nominal value %	17.5
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Comments on Lab 5's results:

On 1 December Lab 5 forwarded a correction of its results as agreed in the project group. The results shown above are obtained by using a different calibration factor.

Used apparatus, sample preparation and analysis condition
GC/FID, Shimadzu GC 17A, split injector GC-column: J&W DB 5.625, 30m x 0.25 mm, df = 0.5 µm Oven temp.: 50 °C 4 min, 25 °C/min 150 °C 0 min, 5 °C/min 300 °C 10 min Analysis of pyridine GC-column: ZB-WAX, 30 m x 0.25 mm, df = 0.25 µm (Phenomenex) Oven temp.: 50 °C 5 min, 10 °C/min 240 °C

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 6

SYNTAR 02	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine							0.720	0.005				
Toluene	1.82	1.80	1.74	1.82	1.78	1.69	1.640	0.012	1.78	8.27	0.050	2.83
Phenol	3.71	3.78	3.61	3.67	3.56	3.70	4.400	0.033	3.67	-16.54	0.077	2.11
Indene	4.41	4.42	4.39	4.41	4.34	4.41	4.550	0.034	4.40	-3.38	0.029	0.67
Guaiacol							0.000					
Naphthalene	115	114	115	115	113	114	119.00	0.89	114	-3.91	0.534	0.47
4-methylguaiacol							0.434	0.003				
Phenanthrene	25.0	25.0	24.9	24.9	24.6	24.8	25.700	0.193	24.9	-3.27	0.168	0.68
Fluoranthene	7.42	7.42	7.43	7.25	7.17	7.18	7.630	0.057	7.31	-4.17	0.125	1.71
Pyrene	2.25	2.19	2.48	1.84	2.18	2.04	2.340	0.018	2.16	-7.59	0.213	9.84

Number of comp.	7	7	7	7	7	7	Mean of CV's %	2.61
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Numerically mean deviation from nominal value %	6.7
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Used apparatus, sample preparation and analysis condition

GC/FID, HP 5890, HP 3396A integrator
 Column: HP Ultra 2 (crosslinked 5% Ph Me silicone) 50 m x 0.32 mm, film thickness 0.52 µm
 Injector: Split/splitless injector 290 °C
 Carrier gas: Helium, injector pressure about 120 kPa, total flow about 20 ml/min
 Oven temp.: 50 °C 5 min, heating rate 3 °C /min to 160 °C, then 10 °C/min to 290 °C
 ISTD = n-dodecane

Comments:

A peak was detected at runtime of 6.26 min (before pyridine) in every sample (impurity?).
 An unknown peak was detected between naphthalene and dodecane, which is expected to be 4-methylguaiacol (we had no model compound for 4-methylguaiacol).
 Detection limit is approx. 0.5 mg/l

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 7

SYNTAR 02	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	4 U	4 U	4 U	4 U	4 U	4 U	0.720	0.005				
Toluene	2	2.1	2.2	2	2	2.2	1.640	0.012	2.08	27.0	0.098	4.72
Phenol	5.8	5.7	5 U	5.5	5 U	5 U	4.400	0.033	5.7	28.8	0.153	2.70
Indene	C	C	C	C	C	C	4.550	0.034				
Guaiacol	6 U	6 U	6 U	6 U	6 U	6 U	0.000					
Naphthalene	118	118	122	115	117	123	119.00	0.89	119	-0.14	3.061	2.58
4-methylguaiacol	7 U	7 U	7 U	7 U	7 U	7 U	0.434	0.003				
Phenanthrene	26	26	26	25	25	26	25.700	0.193	25.7	-0.13	0.516	2.01
Fluoranthene	7.7	7.6	7.4	7.5	7.2	7.3	7.630	0.057	7.45	-2.36	0.187	2.51
Pyrene	2	2	1.9	1.9	1.8	1.9	2.340	0.018	1.92	-18.1	0.075	3.93

Number of comp.	6	6	6	6	6	6	Mean of CV's %	3.07
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Numerically mean deviation from nominal value %	12.8
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Used apparatus, sample preparation and analysis condition
<p>GC/MS, Agilent 6890 GC, Agilent 5973 MSD, Agilent 7673 Autosampler Column: 30 m x 0.25 mm, DB-5 0,25 µm film Split injector 275 °C MSD transfer line 300 °C</p> <p>Sample was injected as received, column flow 1 ml/min helium (constant flow mode) Split ratio 30:1 Oven temp. 50 °C 5 min, ramp 8 °C/min to 250 °C, hold 0 min, ramp 20 °C/min to 300 °C hold 2.5 min</p> <p>Calibration was carried out by external standard.</p> <p>Comment: Indene was detected by GC/MS, but not calibrated due to lack of standard. Even on a clean system, performance for phenol, guaiacol and methylguaiacol deteriorated (expressive tailing) over repeated injection.</p>

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 14

SYNTAR 02	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine							0.720	0.005				
Toluene	2.31	1.87	1.93	1.42	1.87	1.71	1.640	0.012	1.85	12.9	0.291	15.74
Phenol	12.4	10.3	10.9	11.0	10.0	10.9	4.400	0.033	10.9	148	0.825	7.56
Indene	5.96	4.48	4.48	4.26	4.14	4.02	4.550	0.034	4.55	0.10	0.711	15.62
Guaiacol	14.4	14.1	14.6	14.0	14.3	14.5	0.000		14.3	∞	0.220	1.53
Naphthalene	131	91.7	90.5	84.8	87.3	78.8	119.00	0.89	94.1	-20.9	18.9	20.06
4-methylguaiacol	175	164	172	162	164	174	0.434	0.003	169	39000	5.80	3.44
Phenanthrene	27.5	19.2	19.2	17.7	17.9	17.4	25.700	0.193	19.8	-22.9	3.84	19.38
Fluoranthene	8.52	6.37	6.03	5.86	5.87	5.24	7.630	0.057	6.32	-17.2	1.14	18.02
Pyrene							2.340	0.018				

Number of comp.	8	8	8	8	8	8	Mean of CV's %	12.67
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Numerically mean deviation from nominal value %	-
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Comments on Lab 14's results:

The above results include corrected numbers as a consequence of a discussion between the lab and the coordinator. The coordinator pointed out to the lab that obviously some of the previous results were wrong. The lab found one processing error, which it rectified. Therefore the mean value for phenol was corrected from 113 mg/l to 10.9 mg/l.

Used apparatus, sample preparation and analysis condition
GC/FID, Chrompack CP 9002 Liquid sampler: CP 9050 Column: non-polar capillary CP-Sil 8CB ISTD for aromates: 0.0319 g Tert. Butyl-cyclo-hexane, 30.433 g DCM, added 50 µl ISTD for phenols: 0.032 g Tert. 4-ethyl-phenol, 30.1208 g IPA, added 50 µl + 50 µl BSTA Carrier gas: Helium, 60 kPa initial pressure Start temp. 50 °C, final temp. 280 °C, different oven programming for aromates and phenols

Round Robin Test on Tar, May 2003

Round 01 - Synthetic tar

LABORATORY CODE NO. 18

SYNTAR 02	Measured value [µg/ml]						Nominal value [µg/ml]	U _{nom} [µg/ml]	Statistics			
	Sub sample No.	1	2	3	4	5			6	Mean value [µg/ml]	Deviat from nom. %	STDev [µg/ml]
Pyridine	<5	<5	<5	<5	<5	<5	0.720	0.005				
Toluene	5.29	5.34	5.4	5.47	5.35	5.15	1.640	0.012	5.33	225	0.109	2.04
Phenol	4.55	4.31	4.31	4.2	4.56	4.49	4.400	0.033	4.40	0.08	0.150	3.40
Indene	4.94	5.01	5.29	5.17	5.26	4.98	4.550	0.034	5.11	12.3	0.151	2.96
Guaiacol	<1	<1	<1	<1	<1	<1	0.000					
Naphthalene	105	106	106	105	106	106	119.00	0.89	105.67	-11.2	0.516	0.49
4-methylguaiacol	<1	<1	<1	<1	<1	<1	0.434	0.003				
Phenanthrene	27.0	27.2	27.2	27.2	27.1	27.2	25.700	0.193	27.2	5.64	0.077	0.28
Fluoranthene	7.99	8.02	8.01	8.05	8.03	8.02	7.630	0.057	8.02	5.11	0.020	0.25
Pyrene	2.37	2.31	2.40	2.40	2.39	2.39	2.340	0.018	2.38	1.57	0.034	1.45

Number of comp.	7	7	7	7	7	7	Mean of CV's %	1.55
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Numerically mean deviation from nominal value %	37
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Comments on Lab 18's results:

On 17 June the coordinator received corrected values for SYNTAR 02 - naphthalene from lab 18, which had detected a problem with its calibration curves for naphthalene. The mean value was corrected from 488 mg/l to 105.67 mg/l. The project group accepted the new values and they appear from the table above. Furthermore, the lab stated that it always has integration problems with toluene due to a small and very wide peak, so quantitative analysis was not carried out. In the subsequent statistic analysis the toluene value was recognized as an outlier and was rejected.

Used apparatus, sample preparation and analysis condition
HPLC with UV-DAD detector, KONTRON/BIO-TEK Column: UP 5 ODB-25k (C18 type) No sample preparation Oven temp.: 20 °C Eluent: Methanol/acetonitrile/water Injection volume: 10 µl

3.2 Evaluation of results from round 01

The aim of the evaluation is to show an illustrative picture of the individual laboratories' performance compared to each other and compared to the nominal value. In addition to this, the primary aim of the evaluation at single round level is to identify outliers in the reported results. Primarily, focus is on comparison of accuracy and repeatability of the individual labs and the reproducibility between labs. This includes a control of the presence of systematic errors. Outliers in the reported data should be eliminated from the data set that qualifies for an estimate of the accuracy and reproducibility of the tar measuring method.

The following graphs show the results of the laboratories' as the range of observations (the difference between the largest observation and the smallest observation), where the data mark indicates the mean value (mean of lab).

- The green line in the graphs represents the nominal value of the tar compound in the test matrix. The test matrix is made by weighing the compounds on a scales with an accuracy of 0.1 mg. The mass of the individual compounds ranges from 0.05 g to 0.5 g. After weighing, the finale test matrix was prepared by volumetric dilution.
- The bold, red line in the graph represents the mean value of the participating laboratories' results (mean of lab means).
- The two thin red lines represent the limits of the 95% confidence interval (CI) of the mean of lab means. The 95% CI is a range of values the mean of lab means takes with probability 95%.

The statistic analysis of the reported data was carried out in accordance with ISO 5725-2:1994. The analysis includes testing for outlying lab means and analysis of variances. Variances are examined for outliers according to Cochran's test, the homogeneity of variances is tested and finally the statistic significance of differences between labs is tested. Outlying lab means are tested by means of three different methods: Dixon's test, Nalimov t-test and Grubb's test.

According to ISO 5725 the definition of outlier depends on the probability level (P) of the Cochran's and Dixon's test. If $P \leq 1\%$, i.e. the test statistic is larger than its 1% critical value. In this case the item is called a statistic outlier, which can be discarded after thoroughly investigation.

The received results were examined by the co-ordinator and compared with the nominal value. After this, it was investigated if errors could be explained and corrected. The outcome of this investigation appears from comments on the individual laboratories' results in paragraph 3.1. Remaining outliers, which could not be explained, were discarded as real outliers not belonging to the experiment. Particularly in cases where several unexplained outliers occur at different levels within the same lab, it was decided to discard the data from such an outlying laboratory. In the following statistic outliers are printed in red colour.

Finally, the methods precision is calculated. Within labs the analysis precision is expressed by the repeatability value "r" - the value below which the absolute difference between two single test results obtained under repeatability conditions may be expected to lie with a probability of 95%.

The repeatability conditions are the conditions where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

Between labs the analysis precision is expressed by the reproducibility value "R" - the value below which the absolute difference between two single test results obtained under reproducibility conditions may be expected to lie with a probability of 95%. The reproducibility conditions are the conditions where test results are obtained with the same method on identical test material in different laboratories with different operators using different equipment. These values "r" and "R" appear from paragraph 3.3.

3.2.1 SYNTAR 01, Pyridine

Nominal value: 0.000

Statistic analysis was not carried out. Laboratories reported values either below detection limit or no information (blank cells in the report). This means that all participants agreed on the nominal value of zero. In fact the compound was not added to the solution.

3.2.2 SYNTAR 01, Toluene

Lab	Sample #1 mg/l	Sample #2 mg/l	Sample #3 mg/l	Sample #4 mg/l	Sample #5 mg/l	Sample #6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	4.32	4.75	4.84	4.5	5.4	4.39	4.70	0.398	0.418
Lab 5	4.80	4.58	4.69	4.71	4.65	4.69	4.687	0.072	0.076
Lab 6	4.81	4.28	4.05	4.31	4.29	4.14	4.313	0.264	0.277
Lab 7	5.5	5.2	5.3	4.7	5.3	5.3	5.217	0.271	0.285
Lab 14	3.09	2.49	2.56	2.52	2.51	2.54	2.618	0.231	0.243
Lab 18	7.03	6.97	7.08	7.01	7.11	6.94	7.023	0.064	0.068

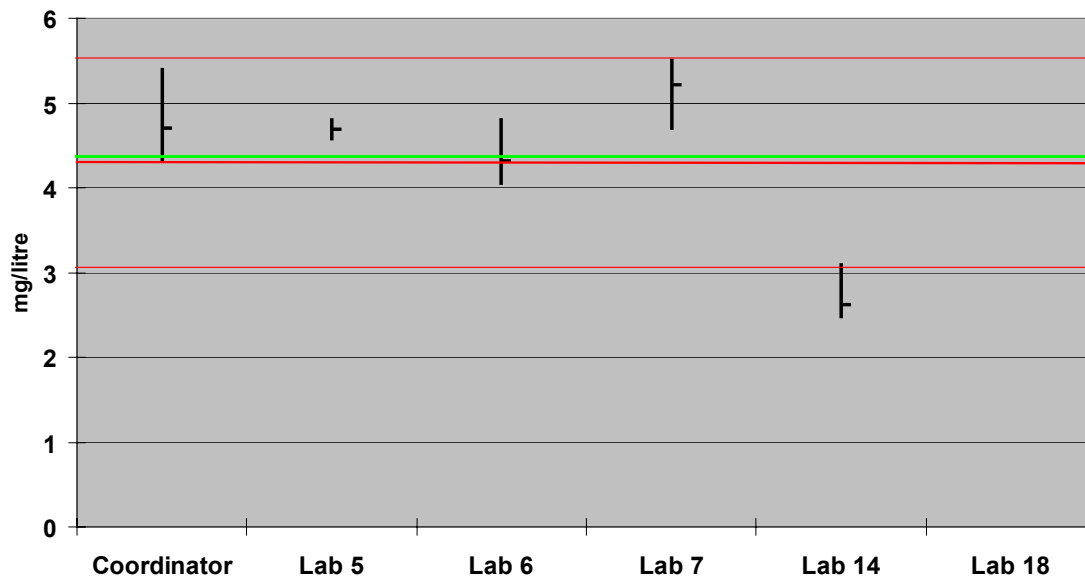
Comments on Lab 18's results on toluene, see paragraph 3.1

TESTING OF OUTLYING LAB MEANS

Dixon's test: Outlier detected. Lab 18 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)
 Nalimov t-test: Outlier detected. Lab 18 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)
 Grubb's test: No outlier detected

Lab 18's results were discarded and a new statistic analysis was carried out based on the results of the remaining labs.

SYNTAR 01 - Toluene



Second statistic analysis:

TESTING OF OUTLYING LAB MEANS

Dixon's test: No outlier detected
 Nalimov t-test: Lab 14 is an outlier (a = 0.05)
 Grubb's test: Lab 14 is an outlier (a = 0.05)

TESTING OF VARIANCES

Cochran test: Pass # 1: No outlier detected
 Bartlett test: Lab variances homogeneous?
 No (a = 0.05)
 Yes (a = 0.01)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes (a = 0.05), Yes (a = 0.01)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	4.384 mg/l	Between labs STDev:	0.991 mg/l
Mean of lab means:	4.307 mg/l	Within labs STDev:	0.269 mg/l
Half width 95% CI:	1.238 mg/l	StDev of lab means:	0.997 mg/l
Upper limit of 95% CI	5.545 mg/l	Lower limit of 95% CI	3.069 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s _r		r		s _R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
4.4	0.269	6.1	0.753	17.1	1.027	23.3	2.875	65.3

3.2.3 SYNTAR 01, Phenol

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	58.7	60.5	62.8	59.8	62	58.9	60.45	1.662	1.744
Lab 5	66.0	63.9	64.2	64.4	63.8	64.3	64.43	0.802	0.841
Lab 6	52.5	52.8	52.9	53.3	53.2	52.9	52.933	0.288	0.302
Lab 7	58	51	56	45	50	52	52	4.604	4.832
Lab 14	109	114	106	119	108	118	113		
Lab 18	56.4	56.5	56.6	56.3	56.5	56.4	56.457	0.083	0.087

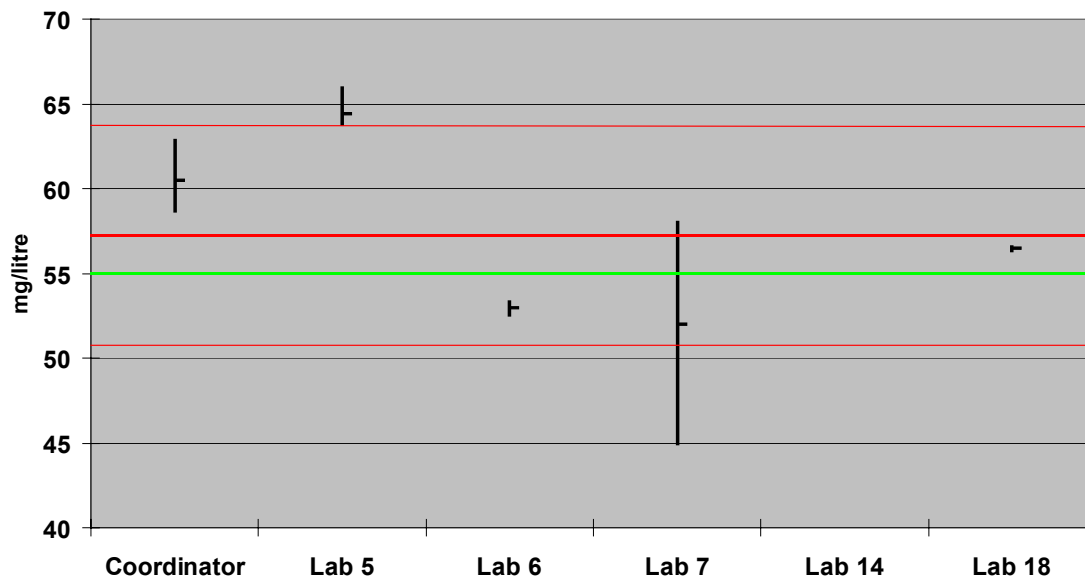
Comments on Lab 14's results on phenol, see paragraph 3.1

TESTING OF OUTLYING LAB MEANS

Dixon's test: Outlier detected. Lab 14 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)
 Nalimov t-test: Outlier detected. Lab 14 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)
 Grubb's test: No outlier detected

Lab 14's results were discarded and a new statistic analysis was carried out based on the results of the remaining labs.

SYNTAR 01 - Phenol



Second statistic analysis:

TESTING OF OUTLYING LAB MEANS

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

TESTING OF VARIANCES

Cochran test:
 Pass #1: Lab 7 is an outlier at $\alpha = 0.01$ and 0.05
 Pass #2: Coord. is an outlier at $\alpha = 0.01$ and 0.05
 Pass #3: Lab 5. is an outlier at $\alpha = 0.01$ and 0.05
 Pass #4: Lab 6 is an outlier at $\alpha = 0.05$
 Pass #5: Outliers NOT detected
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	55.00 mg/l	Between labs STDev:	5.133 mg/l
Mean of lab means:	57.25 mg/l	Within labs STDev:	2.223 mg/l
Half width 95% CI:	6.472 mg/l	StDev of lab means:	5.212 mg/l
Upper limit of 95% CI	63.73 mg/l	Lower limit of 95% CI	50.78 mg/l

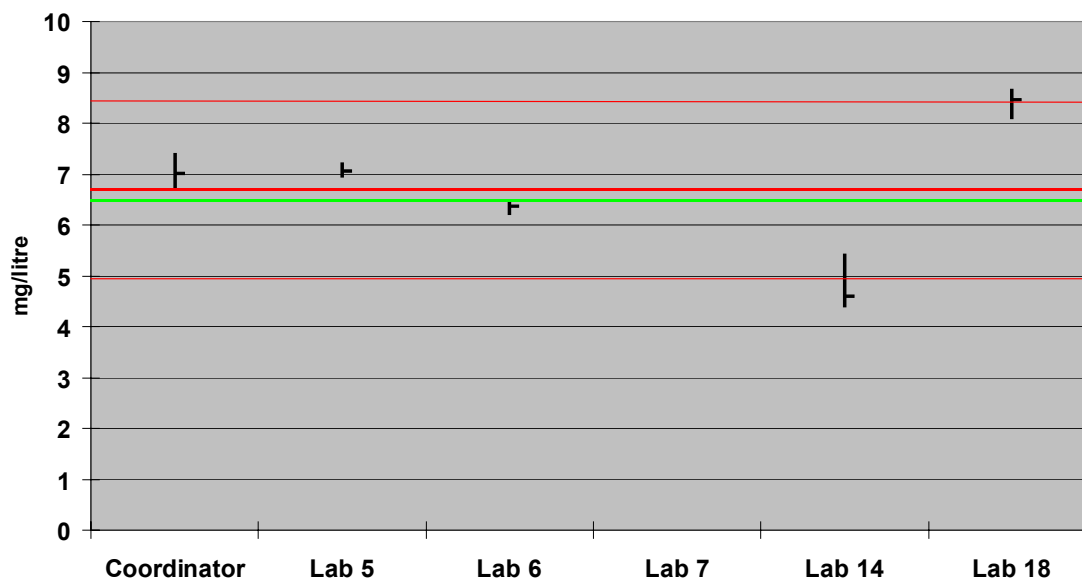
Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	S_r		r		S_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
55	2.223	4.0	6.224	11.3	5.594	10.2	15.662	28.5

3.2.4 SYNTAR 01, Indene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	6.82	6.96	7.27	6.91	7.38	6.71	7.008	0.262	0.275
Lab 5	7.19	6.98	7.05	7.04	6.98	7.06	7.050	0.077	0.081
Lab 6	6.24	6.31	6.41	6.47	6.46	6.37	6.377	0.089	0.094
Lab 7	C	C	C	C	C	C			
Lab 14	5.40	4.46	4.40	4.43	4.41	4.42	4.587	0.400	0.419
Lab 18	8.48	8.55	8.55	8.11	8.43	8.64	8.46	0.186	0.195

"C" = The analyte is determined to be present.

SYNTAR 01 - Indene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test: Lab 14 is an outlier at $\alpha=0.05$
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

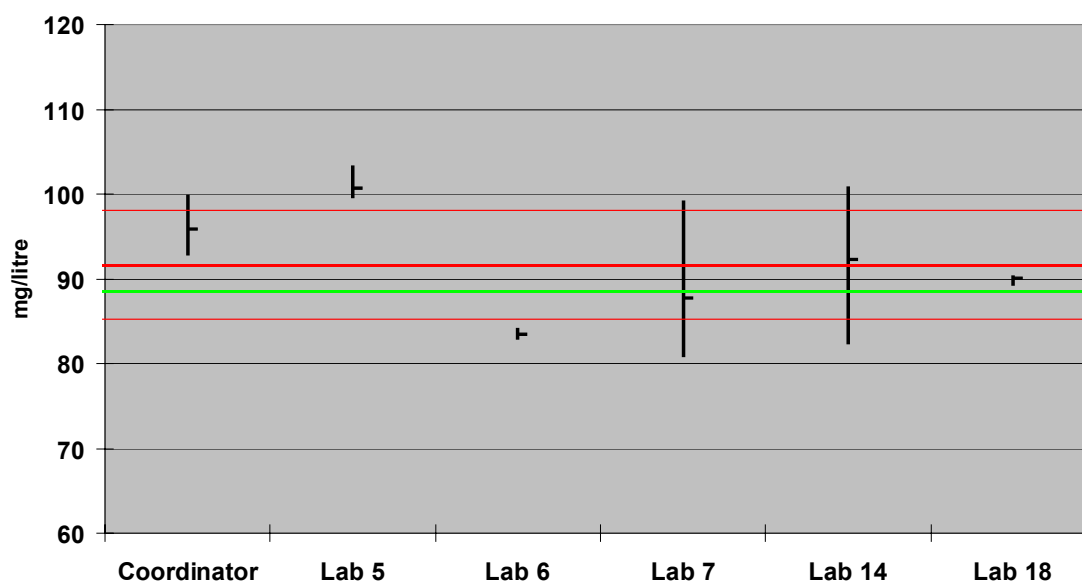
Nominal value:	6.50 mg/l	Between labs STDev:	1.401 mg/l
Mean of lab means:	6.696 mg/l	Within labs STDev:	0.235 mg/l
Half width 95% CI:	1.743 mg/l	StDev of lab means:	1.404 mg/l
Upper limit of 95% CI	8.440 mg/l	Lower limit of 95% CI	4.953 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
6.5	0.235	3.6	0.658	10.1	1.421	21.9	3.978	61.2

3.2.5 SYNTAR 01, Guaiacol

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	93	95.9	98.3	95.5	99.7	92.9	95.833	2.748	2.884
Lab 5	103.1	99.7	100.5	100.7	99.8	100.6	100.73	1.234	1.295
Lab 6	83.9	83.0	83.4	84.0	83.1	83.2	83.433	0.423	0.444
Lab 7	99	83	96	81	82	85	87.667	7.789	8.174
Lab 14	82.5	90.4	99.3	88.7	91.9	101	92.266	6.847	7.185
Lab 18	90.1	90.1	90.2	89.4	90.2	90.1	90.017	0.306	0.321

SYNTAR 01 - Guaiacol



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Lab 7 is an outlier at $\alpha = 0.05$
 Pass #2: Lab 14 is an outlier at $\alpha = 0.01$ and 0.05
 Pass #3: Coord. is an outlier at $\alpha = 0.01$ and 0.05
 Pass #4: Lab 5 is an outlier at $\alpha = 0.01$ and 0.05
 Pass #5: Outliers NOT detected
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Due to satisfactory Dixon's test, no outliers are discarded.

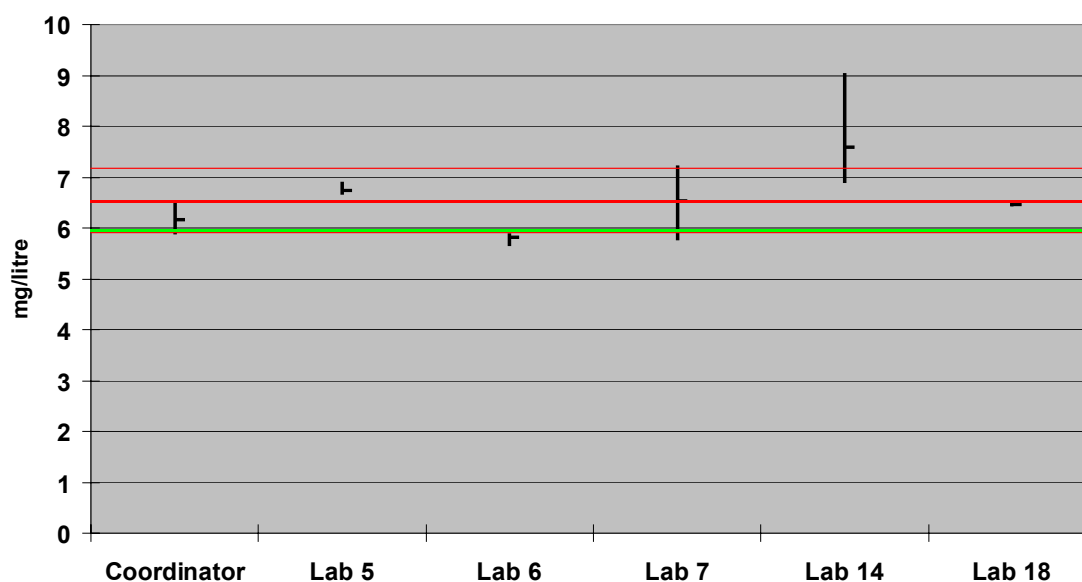
Nominal value:	88.60 mg/l	Between labs STDev:	5.842 mg/l
Mean of lab means:	91.667 mg/l	Within labs STDev:	4.414 mg/l
Half width 95% CI:	6.415 mg/l	StDev of lab means:	6.113 mg/l
Upper limit of 95% CI	98.082 mg/l	Lower limit of 95% CI	85.251 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
90	4.414	4.9	12.359	13.7	7.322	8.1	20.502	22.8

3.2.6 SYNTAR 01, Naphthalene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	5.91	6.16	6.34	6.08	6.50	6.02	6.168	0.217	0.228
Lab 5	6.87	6.70	6.72	6.74	6.75	6.71	6.748	0.062	0.066
Lab 6	5.83	5.85	5.87	5.67	5.82	5.86	5.817	0.074	0.078
Lab 7	7.2	6.5	6.8	5.8	6.4	6.5	6.533	0.463	0.486
Lab 14	9.02	7.04	7.57	7.83	6.92	7.13	7.584	0.782	0.821
Lab 18	6.48	6.46	6.49	6.45	6.48	6.45	6.468	0.017	0.018

SYNTAR 01 - Naphthalene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected

Nalimov t-test: Lab 14 is an outlier ($\alpha = 0.05$)

Grubb's test: No outlier detected

Cochran test:

Pass #1: Lab 14 is an outlier at $\alpha = 0.01$ and 0.05

Pass #2: Lab 7 is an outlier at $\alpha = 0.01$ and 0.05

Pass #3: Coord. is an outlier at $\alpha = 0.01$ and 0.05

Pass #4: Outliers NOT detected

Bartlett test: Lab variances homogeneous?

No ($\alpha = 0.05$)

No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Because of satisfactory Dixon's test no outliers are discarded.

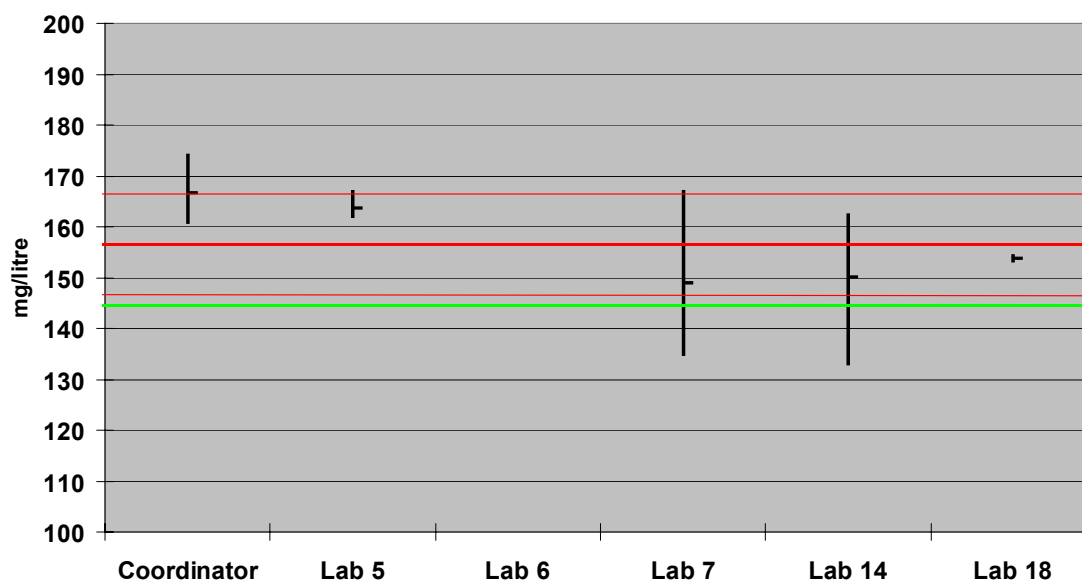
Nominal value:	5.960 mg/l	Between labs STDev:	0.579 mg/l
Mean of lab means:	6.553 mg/l	Within labs STDev:	0.384 mg/l
Half width 95% CI:	0.629 mg/l	StDev of lab means:	0.600 mg/l
Upper limit of 95% CI	7.183 mg/l	Lover limit of 95% CI	5.924 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
6	0.384	6.4	1.075	17.9	0.695	11.6	1.945	32.4

3.2.7 SYNTAR 01, 4-methylguaiacol (creosol)

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	161	167	173	163	174	162	166.67	5.68	5.961
Lab 5	167	162	163	164	162	163	163.5	1.871	1.963
Lab 6									
Lab 7	167	143	161	135	142	146	149	12.313	12.921
Lab 14	133	148	162	143	154	160	150.04	10.893	11.432
Lab 18	154	154	154	153	154	154	153.89	0.335	0.351

SYNTAR 01 - 4-methylguaiacol



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: No outlier detected
 Bartlett test: Lab variances homogeneous?
 No (a = 0.05)
 No (a = 0.01)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes (a = 0.05), Yes (a = 0.01)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

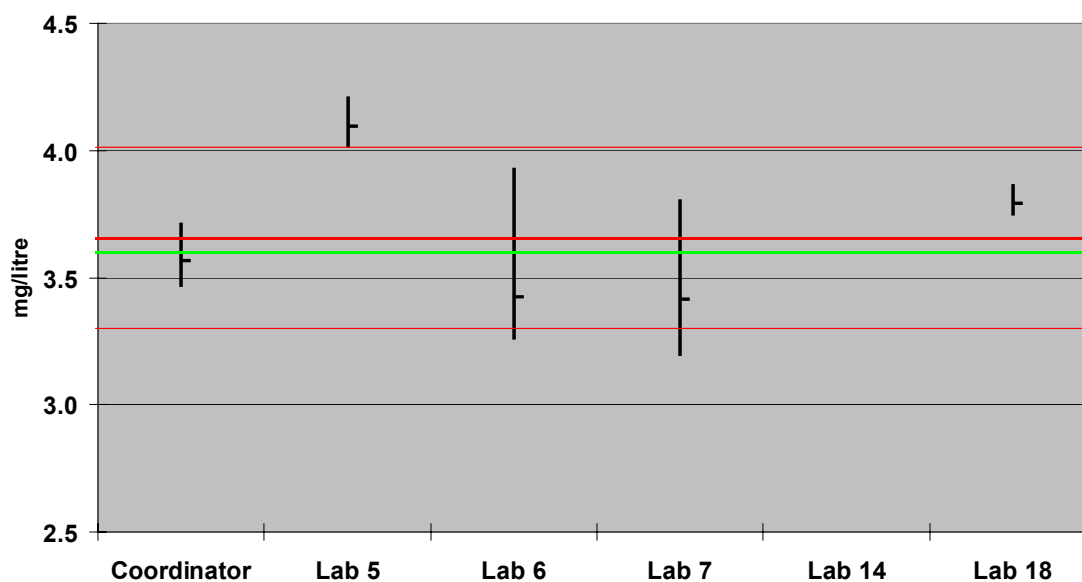
Nominal value:	144.8 mg/l	Between labs STDev:	7.363 mg/l
Mean of lab means:	156.6 mg/l	Within labs STDev:	7.848 mg/l
Half width 95% CI:	9.971 mg/l	StDev of lab means:	8.030 mg/l
Upper limit of 95% CI	166.6 mg/l	Lower limit of 95% CI	146.6 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s _r		r		s _R		R	
150	mg/l	%	mg/l	%	mg/l	%	mg/l	%
		7.848	5.2	21.97	14.6	10.76	7.2	30.13

3.2.8 SYNTAR 01, Phenanthrene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	3.71	3.61	3.57	3.55	3.47	3.49	3.567	0.087	0.091
Lab 5	4.21	4.02	4.07	4.11	4.08	4.08	4.095	0.063	0.067
Lab 6	3.93	3.33	3.26	3.38	3.34	3.29	3.422	0.252	0.265
Lab 7	3.8	3.2	3.7	3.2	3.2	3.4	3.417	0.271	0.285
Lab 14									
Lab 18	3.86	3.75	3.82	3.77	3.78	3.77	3.792	0.041	0.043

SYNTAR 01 - Phenanthrene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Outliers NOT detected
 Bartlett test: Lab variances homogeneous?
 No (a = 0.05)
 No (a = 0.01)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes (a = 0.05), Yes (a = 0.01)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

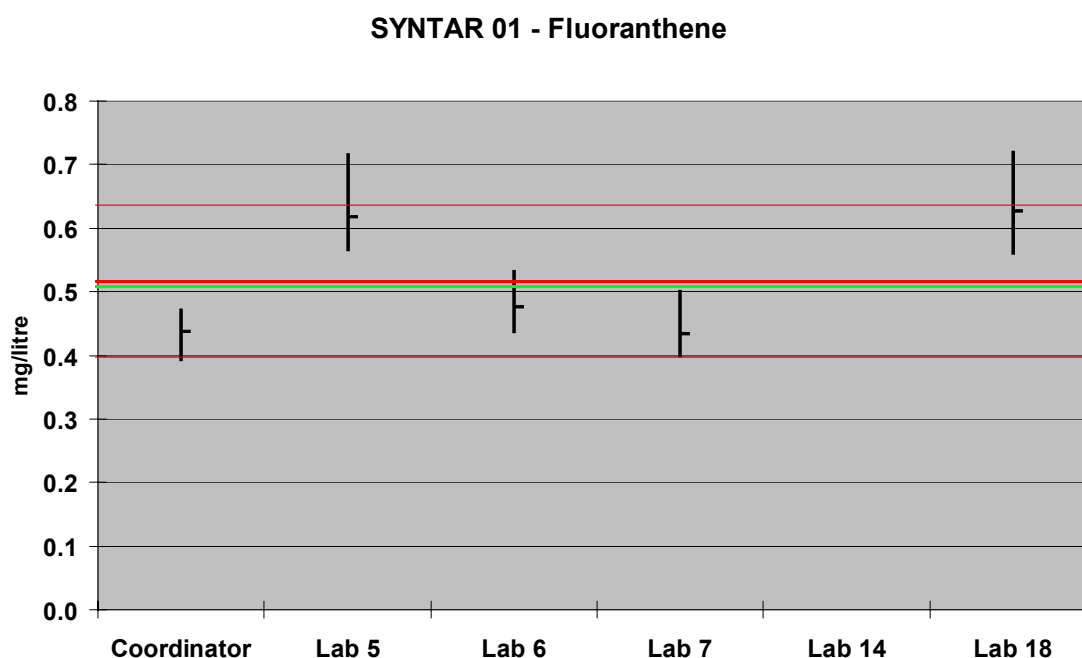
Nominal value:	3.60 mg/l	Between labs STDev:	0.279 mg/l
Mean of lab means:	3.658 mg/l	Within labs STDev:	0.174 mg/l
Half width 95% CI:	0.357 mg/l	StDev of lab means:	0.288 mg/l
Upper limit of 95% CI	4.016 mg/l	Lower limit of 95% CI	3.301 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	S _r		r		S _R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
3.6	0.174	4.8	0.487	13.5	0.329	9.1	0.921	25.6

3.2.9 SYNTAR 01, Fluoranthene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	0.471	0.455	0.44	0.43	0.433	0.394	0.437	0.026	0.027
Lab 5	0.715	0.593	0.619	0.567	0.605	0.605	0.617	0.051	0.053
Lab 6	0.438	0.458	0.532	0.468	2.40	0.484	0.476	0.035	0.044
Lab 7	0.5	0.4	0.5	0.4	0.4	0.4	0.433	0.052	0.054
Lab 14									
Lab 18	0.72	0.62	0.63	0.63	0.6	0.56	0.627	0.053	0.055

Lab 6's sample # 5 is obviously an error. It was decided to discard this value.



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Outliers NOT detected
 Bartlett test: Lab variances homogeneous?
 Yes (a = 0.05)
 Yes (a = 0.01)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes (a = 0.05), Yes (a = 0.01)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

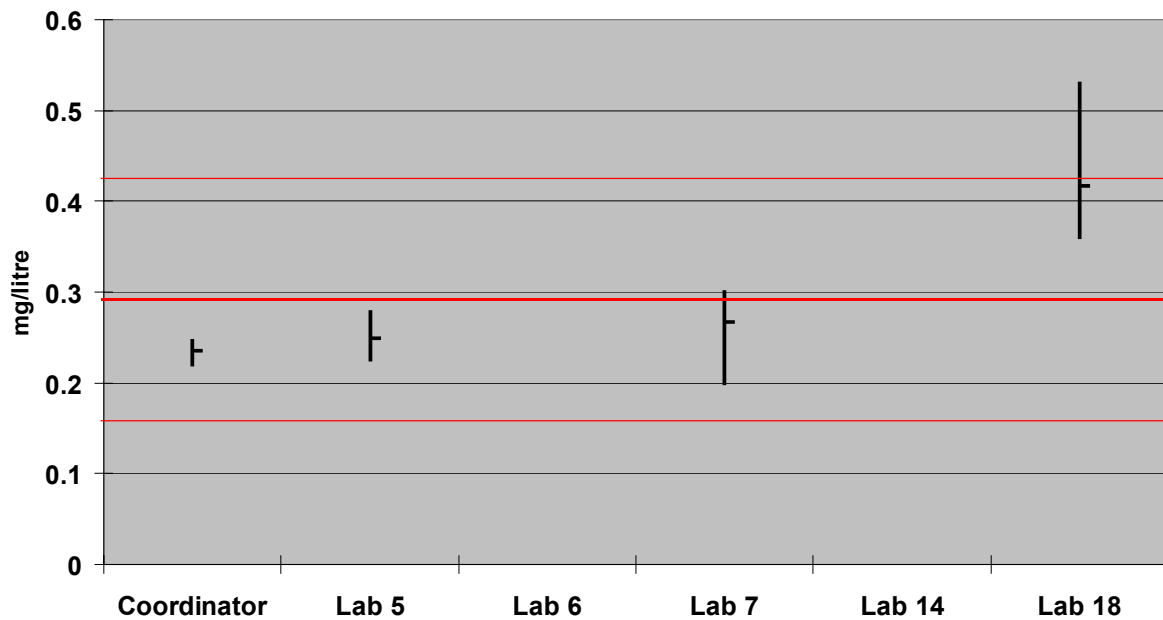
Nominal value:	0.509 mg/l	Between labs STDev:	0.096 mg/l
Mean of lab means:	0.518 mg/l	Within labs STDev:	0.045 mg/l
Half width 95% CI:	0.120 mg/l	StDev of lab means:	0.096 mg/l
Upper limit of 95% CI	0.638 mg/l	Lower limit of 95% CI	0.398 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s _r		r		s _R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0.5	0.045	9.0	0.126	25.2	0.106	21.2	0.297	59.4

3.2.10 SYNTAR 01, Pyrene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	0.247	0.243	0.24	0.22	0.23	0.23	0.235	0.010	0.011
Lab 5	0.365	0.371	0.317	0.309	0.334	0.334	0.338	0.025	0.026
Lab 6									
Lab 7	0.3	0.3	0.3	0.3	0.2	0.2	0.267	0.052	0.054
Lab 14									
Lab 18	0.53	0.45	0.4	0.39	0.37	0.36	0.417	0.064	0.067

SYNTAR 01 - Pyrene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Outliers NOT detected
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	0.292 mg/l	Between labs STDev:	0.079 mg/l
Mean of lab means:	0.314 mg/l	Within labs STDev:	0.043 mg/l
Half width 95% CI:	0.129 mg/l	StDev of lab means:	0.081 mg/l
Upper limit of 95% CI	0.443 mg/l	Lower limit of 95% CI	0.186 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0.3	0.043	14.3	0.120	40.0	0.090	30.0	0.252	83.9

3.2.11 SYNTAR 02, Pyridine

Nominal value: 0.720

Statistic analysis was not carried out. Only the coordinator found pyridine in the test matrix (mean of lab = 0.799). The other laboratories reported values either below detection limit or no information (blank cells in the report).

3.2.12 SYNTAR 02, Toluene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	1.51	1.86	1.76	1.76	1.75	1.59	1.705	0.129	0.135
Lab 5	1.91	1.96	1.95	1.94	1.97	1.94	1.945	0.021	0.022
Lab 6	1.82	1.80	1.74	1.82	1.78	1.69	1.776	0.050	0.053
Lab 7	2	2.1	2.2	2	2	2.2	2.083	0.098	0.103
Lab 14	2.31	1.87	1.93	1.42	1.87	1.71	1.852	0.291	0.306
Lab 18	5.29	5.34	5.4	5.47	5.35	5.15	5.33		

Comments on Lab 18's results on toluene, see paragraph 3.1

TESTING OF OUTLYING LAB MEANS

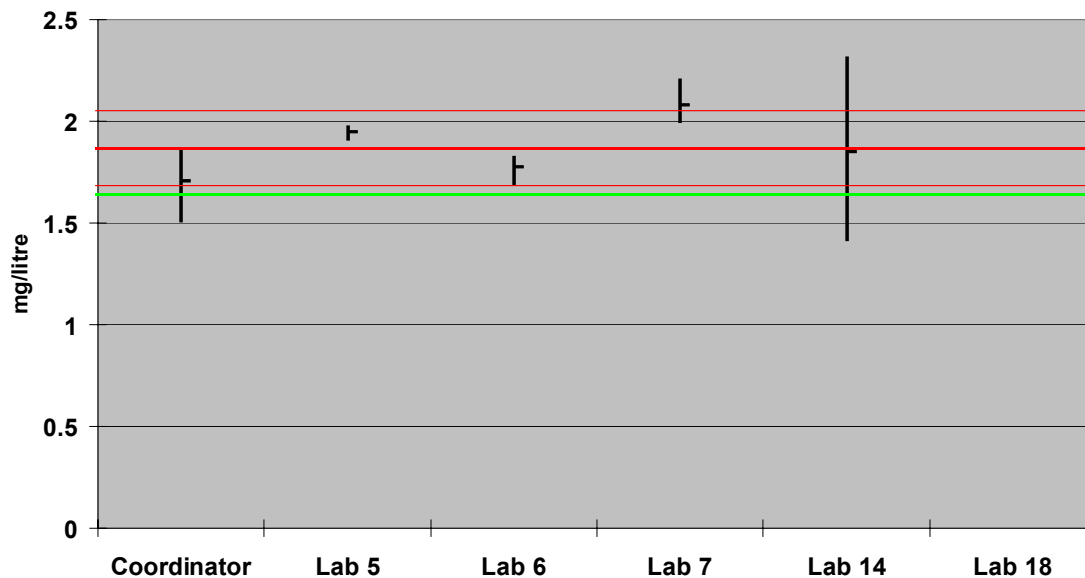
Dixon's test: Outlier detected. Lab 18 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)

Nalimov t-test: Outlier detected. Lab 18 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)

Grubb's test: No outlier detected

Lab 18's results were discarded and a new statistic analysis was carried out based on the results of the remaining labs.

SYNTAR 02 - Toluene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Lab 14 is an outlier at $\alpha = 0.01$ and 0.05
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	1.640 mg/l	Between labs STDev:	0.135 mg/l
Mean of lab means:	1.872 mg/l	Within labs STDev:	0.151 mg/l
Half width 95% CI:	0.184 mg/l	StDev of lab means:	0.148 mg/l
Upper limit of 95% CI	2.056 mg/l	Lower limit of 95% CI	1.688 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
1.7	0.151	8.9	0.423	24.9	0.203	11.9	0.567	33.4

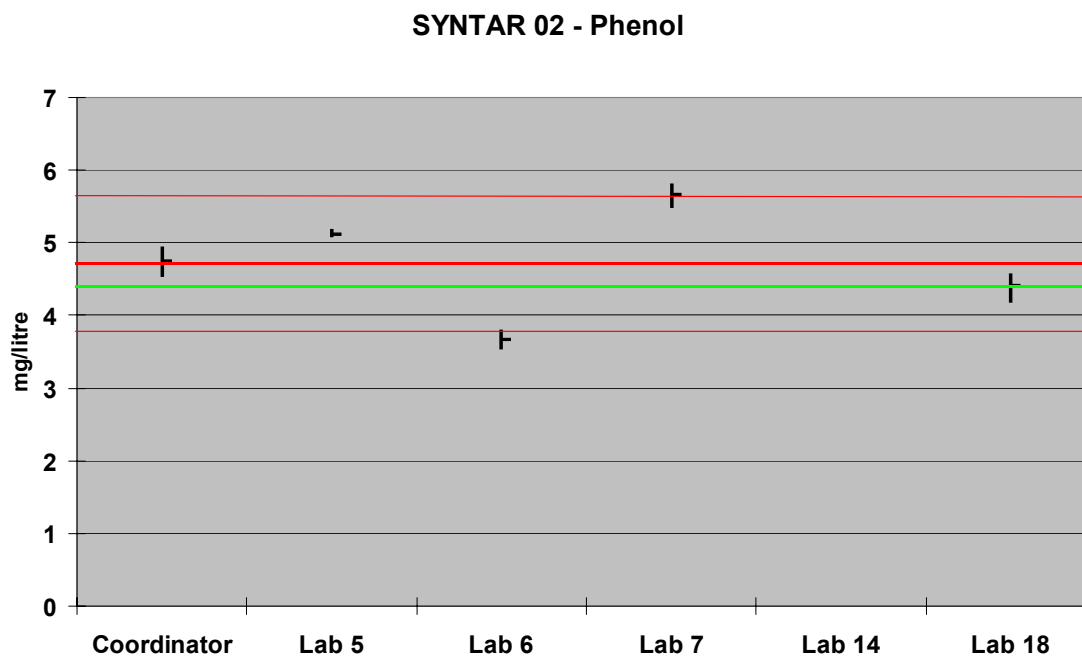
3.2.13 SYNTAR 02, Phenol

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	4.92	4.9	4.78	4.67	4.56	4.66	4.748	0.143	0.151
Lab 5	5.11	5.11	5.12	5.17	5.10	5.13	5.123	0.025	0.026
Lab 6	3.71	3.78	3.61	3.67	3.56	3.70	3.672	0.077	0.081
Lab 7	5.8	5.7	5 U	5.5	5 U	5 U	5.667	0.153	0.379
Lab 14	12.4	10.3	10.9	11.0	10.0	10.9	10.9		
Lab 18	4.55	4.31	4.31	4.2	4.56	4.49	4.403	0.150	0.157

TESTING OF OUTLYING LAB MEANS

Dixon's test: Outlier detected. Lab 14 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)
 Nalimov t-test: Outlier detected. Lab 14 is an outlier at ($\alpha = 0.05$ and $\alpha = 0.01$)
 Grubb's test: No outlier detected

Lab 14's results were discarded and a new statistic analysis was carried out based on the results of the remaining labs.



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Outlier NOT detected
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 Yes ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

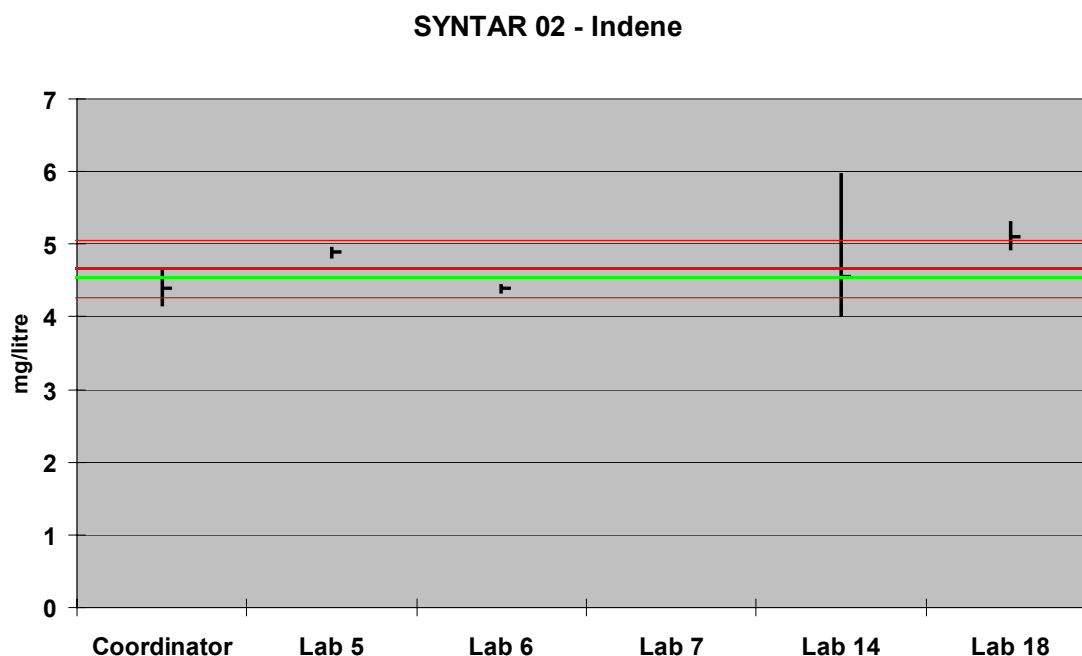
Nominal value:	4.400 mg/l	Between labs STDev:	0.702 mg/l
Mean of lab means:	4.723 mg/l	Within labs STDev:	0.116 mg/l
Half width 95% CI:	0.933 mg/l	StDev of lab means:	0.751 mg/l
Upper limit of 95% CI	5.656 mg/l	Lower limit of 95% CI	3.790 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
4.4	0.116	2.6	0.325	7.4	0.712	16.2	1.992	45.3

3.2.14 SYNTAR 02, Indene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	4.37	4.64	4.51	4.44	4.26	4.16	4.397	0.173	0.181
Lab 5	4.83	4.90	4.94	4.89	4.88	4.89	4.888	0.035	0.037
Lab 6	4.41	4.42	4.39	4.41	4.34	4.41	4.396	0.029	0.031
Lab 7	C	C	C	C	C	C			
Lab 14	5.96	4.48	4.48	4.26	4.14	4.02	4.555	0.711	0.746
Lab 18	4.94	5.01	5.29	5.17	5.26	4.98	5.108	0.151	0.159

"C" = The analyte is determined to be present.



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Lab 14 is an outlier at $\alpha = 0.01$ and 0.05
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	4.550 mg/l	Between labs STDev:	0.286 mg/l
Mean of lab means:	4.669 mg/l	Within labs STDev:	0.335 mg/l
Half width 95% CI:	0.394 mg/l	StDev of lab means:	0.317 mg/l
Upper limit of 95% CI	5.063 mg/l	Lower limit of 95% CI	4.275 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
4.6	0.335	7.3	0.938	20.4	0.440	9.6	1.233	26.8

3.2.15 SYNTAR 02, Guaiacol

Nominal value: 0.000

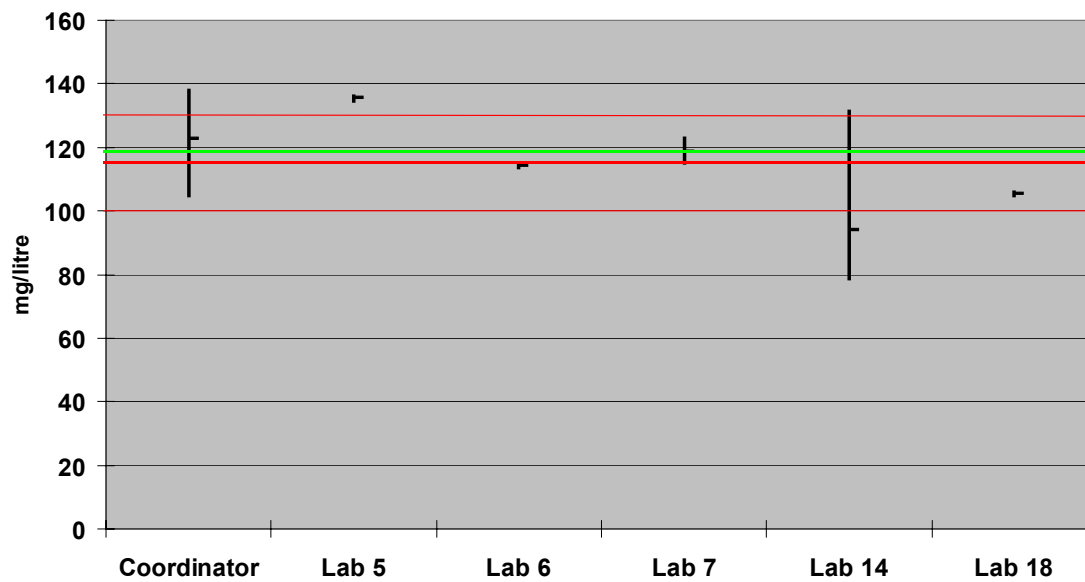
Statistic analysis was not carried out. Most of the laboratories reported values either below detection limit or no information (blank cells in the report). This means that the participants except one are in agreement with the nominal value of zero. In fact, the compound was not added to the solution. In spite of that, Lab 14 found 14.3 mg guaiacol per litre solution.

3.2.16 SYNTAR 02, Naphthalene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	105	138	127	128	120	119	122.83	11.089	11.637
Lab 5	135	136	136	136	136	136	135.83	0.408	0.428
Lab 6	115	114	115	115	113	114	114.35	0.534	0.561
Lab 7	118	118	122	115	117	123	118.83	3.061	3.212
Lab 14	131	91.7	90.5	84.8	87.3	78.8	94.11	18.88	19.814
Lab 18	105	106	106	105	106	106	105.67	0.516	0.542

On June 17 Lab 18's results were corrected from 488 to 105.67 mg/l

SYNTAR 02 - Naphthalene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Lab 14 is an outlier at $\alpha = 0.01$ and 0.05
 Pass #2: Coord. is an outlier at $\alpha = 0.01$ and 0.05
 Pass #3: Lab 7 is an outlier at $\alpha = 0.01$ and 0.05
 Pass #4: Outliers NOT detected
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	119.0 mg/l	Between labs STDev:	13.896 mg/l
Mean of lab means:	115.27 mg/l	Within labs STDev:	9.033 mg/l
Half width 95% CI:	15.088 mg/l	StDev of lab means:	14.377 mg/l
Upper limit of 95% CI	130.36 mg/l	Lower limit of 95% CI	100.18 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
119	9.033	7.6	25.29	21.3	16.57	13.9	46.41	39.0

3.2.17 SYNTAR 02, 4-methylguaiacol (creosol)

Nominal value: 0.434 mg/l

Statistic analysis was not carried out. Most of the laboratories reported values either below detection limit or no information (blank cells in the report). This means that the participants except one are close to the nominal value of 0.434 mg/l. The only exception is Lab 14 that found 169 mg creosol per litre solution.

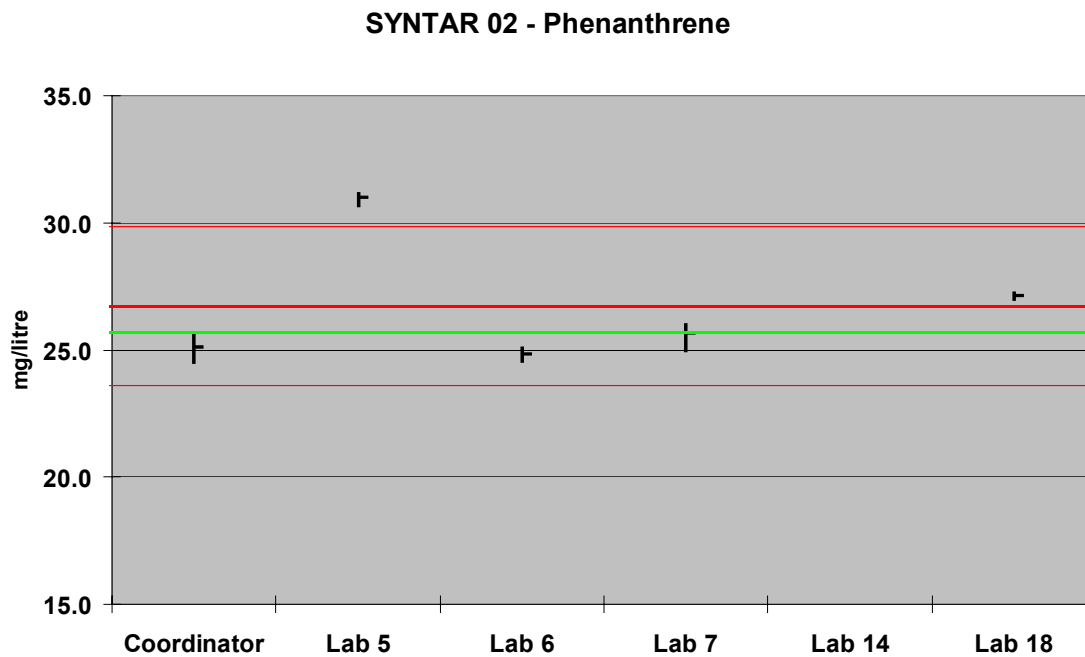
3.2.18 SYNTAR 02, Phenanthrene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	25.6	25.4	25.2	25.1	24.5	24.8	25.10	0.40	0.42
Lab 5	30.7	31.0	31.2	31.1	31.0	31.0	31.0	0.167	0.176
Lab 6	25.0	25.0	24.9	24.9	24.6	24.8	24.86	0.168	0.176
Lab 7	26	26	26	25	25	26	25.667	0.516	0.542
Lab 14	27.5	19.2	19.2	17.7	17.9	17.4	19.8		
Lab 18	27.0	27.2	27.2	27.2	27.1	27.2	27.15	0.077	0.081

TESTING OF OUTLYING LAB MEANS

Dixon's test: No outlier detected
 Nalimov t-test: Outlier detected. Lab 14 is an outlier at ($\alpha = 0,05$ and $\alpha = 0,01$)
 Grubb's test: No outlier detected

Lab 14's results were discarded and a new statistic analysis was carried out based on the results of the remaining labs.



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected

Nalimov t-test: Lab 5 is an outlier at $\alpha = 0.05$

Grubb's test: No outlier detected

Cochran test:

Pass #1: Lab 7 is an outlier at $\alpha = 0.05$

Pass #2: Coord. is an outlier at $\alpha = 0.01$ and 0.05

Pass #3: Outliers NOT detected

Bartlett test: Lab variances homogeneous?

No ($\alpha = 0.05$)

No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value: 25.70 mg/l

Mean of lab means: 26.755 mg/l

Half width 95% CI: 0.868 mg/l

Upper limit of 95% CI 29.902 mg/l

Between labs STDev: 2.531 mg/l

Within labs STDev: 0.313 mg/l

STDev of lab means: 2.324 mg/l

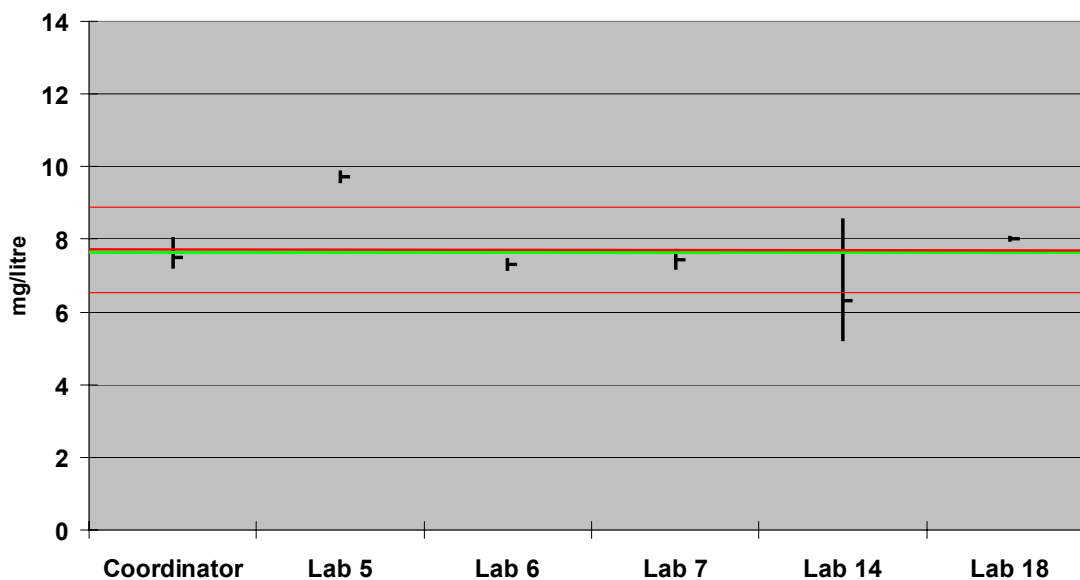
Lower limit of 95% CI 23.608 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
26	0.313	1.2	0.876	3.4	2.55	9.8	7.141	27.5

3.2.19 SYNTAR 02, Fluoranthene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	8.02	7.52	7.53	7.39	7.33	7.25	7.507	0.274	0.287
Lab 5	9.58	9.76	9.84	9.76	9.70	9.68	9.72	0.089	0.093
Lab 6	7.42	7.42	7.43	7.25	7.17	7.18	7.312	0.125	0.131
Lab 7	7.7	7.6	7.4	7.5	7.2	7.3	7.450	0.187	0.196
Lab 14	8.52	6.37	6.03	5.86	5.87	5.24	6.315	1.141	1.197
Lab 18	7.99	8.02	8.01	8.05	8.03	8.02	8.02	0.20	0.21

SYNTAR 02 - Fluoranthene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected

Nalimov t-test: Lab 5 is an outlier at $\alpha = 0.05$

Grubb's test: No outlier detected

Cochran test:

Pass #1: Lab 14 is an outlier at $\alpha = 0.01$ and 0.05

Pass #2: Coord. is an outlier at $\alpha = 0.05$

Pass #3: Lab 7 is an outlier at $\alpha = 0.05$

Pass #4: Outliers NOT detected

Bartlett test: Lab variances homogeneous?

No ($\alpha = 0.05$)

No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

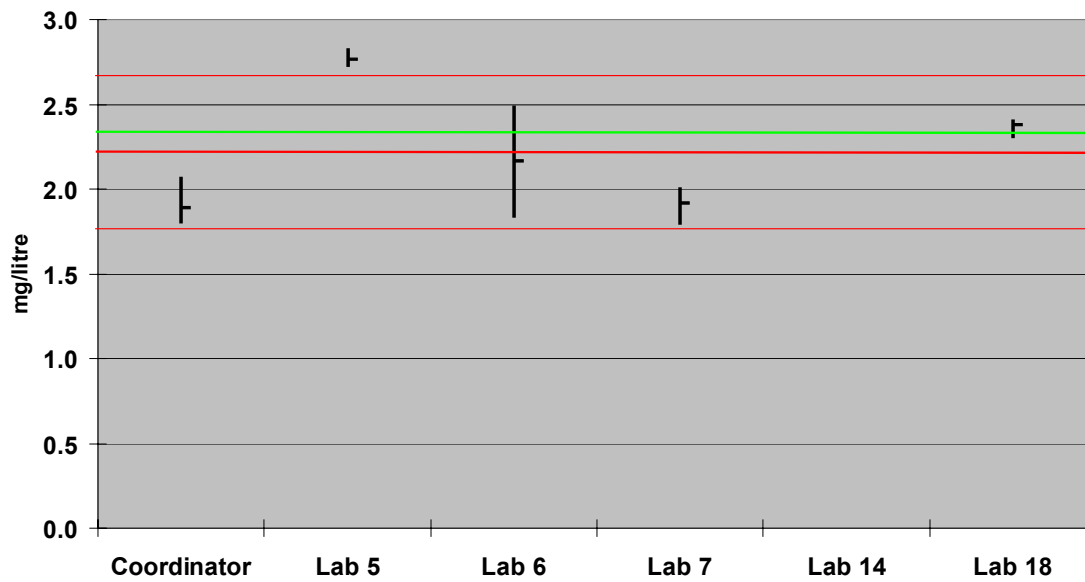
Nominal value:	7.63 mg/l	Between labs STDev:	1.109 mg/l
Mean of lab means:	7.721 mg/l	Within labs STDev:	0.489 mg/l
Half width 95% CI:	1.183 mg/l	StDev of lab means:	1.127 mg/l
Upper limit of 95% CI	8.903 mg/l	Lower limit of 95% CI	6.538 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
8	0.489	6.1	1.369	17.1	1.212	15.2	3.394	42.4

3.2.20 SYNTAR 02, Pyrene

Lab	Sample # 1 mg/l	Sample # 2 mg/l	Sample # 3 mg/l	Sample # 4 mg/l	Sample # 5 mg/l	Sample # 6 mg/l	Mean mg/l	STDev mg/l	H.W. CI (95%) mg/l
Coordin.	2.06	1.92	1.88	1.83	1.81	1.82	1.887	0.095	0.099
Lab 5	2.73	2.82	2.76	2.76	2.76	2.76	2.765	0.029	0.031
Lab 6	2.25	2.19	2.48	1.84	2.18	2.04	2.163	0.213	0.223
Lab 7	2	2	1.9	1.9	1.8	1.9	1.917	0.075	0.079
Lab 14									
Lab 18	2.37	2.31	2.40	2.40	2.39	2.39	2.377	0.034	0.036

SYNTAR 02 - Pyrene



TESTING OF OUTLYING LAB MEANS

TESTING OF VARIANCES

Dixon's test: No outlier detected
 Nalimov t-test: No outlier detected
 Grubb's test: No outlier detected

Cochran test:
 Pass #1: Lab 5 is an outlier at $\alpha = 0.01$ and 0.05
 Bartlett test: Lab variances homogeneous?
 No ($\alpha = 0.05$)
 No ($\alpha = 0.01$)

ANOVA

Snedecor F-test: Difference between labs statistically significant? Yes ($\alpha = 0.05$), Yes ($\alpha = 0.01$)

Snedecor F-test and Bartlett test show that pooling is: NOT ALLOWED

Nominal value:	2.34 mg/l	Between labs STDev:	0.360 mg/l
Mean of lab means:	2.222 mg/l	Within labs STDev:	0.111 mg/l
Half width 95% CI:	0.451 mg/l	StDev of lab means:	0.363 mg/l
Upper limit of 95% CI	2.673 mg/l	Lower limit of 95% CI	1.770 mg/l

Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
	s_r		r		s_R		R	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
2.3	0.111	4.8	0.311	13.5	0.377	16.4	1.055	45.9

3.2.21 SYNTAR 03, Blind sample

Nominal value: 0.000

Statistic analysis was not carried out. Laboratories reported mainly values either below detection limit or no information (blank cells in the report). However, some small quantities of compounds were found.

Lab mean, mg/l	Coordinator	Lab 5	Lab 14	Lab 18
Toluene	0.06	0.217		5.57
Phenol			1.744	
Naphthalene				0.52
Phenanthrene	0.02			
Pyrene				0.08

3.3 Analysis precision

The table below shows the repeatability and reproducibility values for typical test results (levels). The repeatability appears both as a standard deviation and as the value "r" which is explained in paragraph 3.2. The reproducibility again is reported as a standard deviation and as the value "R", see also paragraph 3.2. All four values are also expressed as percentage of the measured concentration. The concentrations are divided into ranges (levels) and the average values for those ranges appear from the table.

Compound	Level mg/l	Repeatability conditions (within labs)				Reproducibility conditions (between labs)			
		s _r		r		s _R		R	
		mg/l	%	mg/l	%	mg/l	%	mg/l	%
Synthetic tar, range < 10 mg/l									
Pyrene	0.3	0.043	14.3	0.120	40.0	0.090	30.0	0.252	83.9
Fluoranthene	0.5	0.045	9.0	0.126	25.2	0.106	21.2	0.297	59.4
Pyrene	2	0.111	4.8	0.311	13.5	0.377	16.4	1.055	45.9
Toluene	2	0.151	8.9	0.423	24.9	0.203	11.9	0.567	33.4
Toluene	4	0.269	6.1	0.753	17.1	1.027	23.3	2.875	65.3
Phenol	4	0.116	2.6	0.325	7.4	0.712	16.2	1.992	45.3
Phenanthrene	4	0.174	4.8	0.487	13.5	0.329	9.1	0.921	25.6
Indene	5	0.335	7.3	0.938	20.4	0.440	9.6	1.233	26.8
Naphthalene	6	0.384	6.4	1.075	17.9	0.695	11.6	1.945	32.4
Indene	7	0.235	3.6	0.658	10.1	1.421	21.9	3.978	61.2
Fluoranthene	8	0.489	6.1	1.369	17.1	1.212	15.2	3.394	42.4
Mean value	3.9	0.214	6.7	0.599	18.8	0.601	16.9	1.683	47.4
Synthetic tar, range 10 to 150 mg/l									
Creosol	150	7.85	5.2	21.97	14.6	10.76	7.2	30.13	20.1
Naphthalene	119	9.03	7.6	25.29	21.3	16.57	13.9	46.41	39.0
Guaiacol	90	4.41	4.9	12.36	13.7	7.32	8.1	20.50	22.8
Phenol	55	2.22	4.0	6.22	11.3	5.59	10.2	15.66	28.5
Phenanthrene	26	0.31	1.2	0.88	3.4	2.55	9.8	7.14	27.5
Mean value	88	4.77	4.6	13.34	12.9	8.60	9.8	24	27.6

For the range from 0.3 to 10 mg/l the difference between two single results found on identical synthetic test material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability value $r = 0.6$ mg/l corresponding to 18.8% of the test result on average not more than once in 20 cases in the normal and correct operation of the method.

For the range from 10 to 150 mg/l the difference between two single results found on identical synthetic test material by one operator using the same apparatus within the shortest feasible time interval will exceed the repeatability value $r = 13.3$ mg/l corresponding to 12.9% of the test result on average not more than once in 20 cases in the normal and correct operation of the method.

For the range from 0.3 to 10 mg/l single results on identical synthetic test material reported by two laboratories will differ more than the reproducibility value $R = 1.7$ mg/l corresponding to 47.4% of the test result on average not more than once in 20 cases in the normal and correct operation of the method.

For the range from 10 to 150 mg/l single results on identical synthetic test material reported by two laboratories will differ more than the reproducibility value $R = 24.0$ mg/l corresponding to 27.6% of the test result on average not more than once in 20 cases in the normal and correct operation of the method.

4 References

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- \5\ "Tar Guideline"; European Commission (DGXII), Danish Energy Agency, Netherlands Agency for Energy and the Environment (Novem), Swiss Federal Office of Energy, US Department of Energy (DoE), National Resources Canada; John Neeft, ECN, The Netherlands, Uwe Zielke, DTI, Denmark, Harrie Knoef and G.J. Buffinga, BTG, The Netherlands, Philipp Hasler, Verenum Research, Switzerland, Pekka Simell and Marjut Suomalainen, VTT Energy, Finland, Krister Sjöström and Claes Brage, KTH, Sweden, M.A. Dorrington and L. Thomas, UK, Claus Greil, Germany, Nick Abatzoglou, Canada, Steve Deutch, USA