PAH Ruggedness test

The report on the ruggedness test is compiled from the regular progress reports as well as the presentations at the HORIZONTAL meetings.

Content:

1. Introduction

This standard includes **16 PAH according to EPA 610** (1982) as well as
* 6 PAH for Drinking Water Analysis

	Toxicity Equivalency Factor	
Naphthalene (2 rings)	-	developed
Acenaphthalene (3 rings)	-	according
Acenaphthene (3 rings)	-	to WHO
Fluorene (3 rings)	-	guidelines
Phenanthrene (3 rings)	-	especially
Anthracene (3 rings)	-	for food
Fluoranthene * (4 rings)	-	
Pyrene (4 rings)	-	
Benzo(a)anthracene (4 rings)	0.1	
Chrysene (4 rings)	0.01	
Benzo(b)fluoranthene* (5 rings)	0.1	
Benzo(k)fluoranthene* (5 rings)	0.1	
Benzo(a)pyrene* (5 rings)	1.0	
Indeno(1,2,3-cd)pyrene* (6 rings)	0.1	
Dibenz(ah)anthracene (5 rings)	1.0	
Benzo(ghi)perylene* (6 rings)	0.01	

2. Limitations and requirements for an analytical method due to different properties of specific PAH

Naphthalene is highly volatile and good soluble in water
Precaution: for losses during sampling and pretreatment

Higher PAH are not good soluble in unpolar solvents
Ideal solvents: Toluene, methylene chloride, acetone
Precaution: for solubility problem during extraction procedure and concentration steps.

Extreme clean up conditions are not applicable for PAH, because they are not as stable as PCB

HPLC/DAD/FLD (ideal eluents: methanol, acetonitrile), difficulties in identification, quenching effects by matrix
UV-DAD not as sensitive as FLD
Acenaphthylene cannot be analysed by HPLC/FLD
Precaution: for losses due to exchange of solvents

GC/MS (ideal solvent: Hexane, heptane, i-octane, toluene), coelution problems

Extraction

Depending on the test sample, origin, moisture content 3 extraction methods are prescribed:
<u>Method 1: Shaking at least for 6 h with acetone/hexane like solvent</u>
Applicable for field moist or dried samples of sandy soil, sludge, sediment, bio waste and compost(lower contamination level 0.001- 10 mg/kg individual PAH)

<u>Method 2: Soxhlet / Pressurised liquid extraction with toluene</u>
Applicable for dried samples of highly contaminated soil, sludge, sediment, suspended solids, waste, bio waste and compost

<u>Method 3 :Shaking at least for 6 h with acetone/hexane like solvent/NaCl</u>
Applicable for wet samples (water content less than 50 %) of soil like materials (peat), bio waste and compost with high organic matter

Depending on the expected PAH content and on the homogeneity of the sample, the following dried amounts are to be used for extraction:
5 - 20g of soil; 2 -10 g of sewage sludge, 5 - 20 g of compost or 2 – 20 g of waste

Clean-up

Clean up is only necessary to remove the present disturbing components. When they are not present, clean-up is not necessary!
PAH are in contrary to the PCB not so stable and persistent so that extreme clean up conditions are not applicable
Usual clean up steps:
- Gel permeation chromatography – for removal high molecular organic matrices
- DMF/ Cyclohexane – Liquid-liquid partition- removal of fats, oils, lipids
- Desactivated Silica gel – for removal of aliphatic hydrocarbons

- Desactivated Aluminium oxide – for removal of more polar compounds, fats, triglycerides

Concentration or dilution step
Prior to measurement, depending on contamination level and extraction solvent, concentration, dilution or exchange of solvent has to be done:
Conditions for HPLC
Toluene extract: dilution (10:1) with acetonitrile and injection volume not more than 10 µL→ HPLC/FLD
(Otherwise toluene peak disturbs the measurement of fast eluted PAH as naphthalene etc.)
Hexane like extract →Exchange of solvent to acetonitrile or DMF → HPLC/FLD (losses of high volatile PAH as naphthalene etc. possible)

Performance criteria for analytical measurement

GC-MS
Internal calibration method
Use of internal standards: deuterated or 13C PAH
Recovery check of internal standards during whole procedure by introducing injection standard!
Good recoveries not necessarily mean good extractability of PAH
Use of proper GC-column, able to separate critical pairs
Care of GC-MS- identification criteria

HPLC/UV-FLD
External calibration method
Recovery check of an internal standard during the whole procedure (e.g. 6-methylchrysene)
Use of proper HPLC-column, able to separate critical pairs

Conclusion: HPLC method is to be used only for highly contaminated samples and for screening

3. State of the art of the analytical methods applied by the routine laboratories

was investigated in BAM PT- Scheme for contaminated soil (10th. Round- January 2005)

Determination of PAH in soil (Gas works sites) 129 participants

Extraction technicque

Soxhlet:	36
Sonication:	53
Shaking:	26
ASE:	6
Mix:	8

Extraction solvent

Acetone/hexane like:	33
Acetonitrile:	30
Toluene:	17
Tetrahydrofurane:	5
Hexane like:	32
Acetone:	6

Clean up 44

Measurement:

GC-MS: 53
HPLC-UV/FLD: 75

Mean value(Sum PAH) of the PT round: 468 mg/kg rel. comparability std. VR = 16.9%
BAM value: Sum PAH: 520 ± 25 mg/kg; ASE Methanol (100°C/140 bar) HPLC-FLD
BAM value: Sum PAH: 595 ± 35 mg/kg; ASE Toluene (100°C/140 bar) GC-MS

Conclusions: For this higher level of PAH-contamination laboratories applied GC-MS and HPLC-UV/FLD approximately the same ratio(53:75), where else the extraction by toluene/ASE gives the highest value of PAH

Comparison HPLC/FLD-GC/MSD
(BAM values- at least 4 independent analysis)

PAH	Mean values HPLC/FLD (Extraction with methanol)mg/kg	Mean values GC/MSD (Extraction with toluene)mg/kg
Naphthalene	7,3	9,3
Acenaphthylene	22,8	8,3
Acenaphthene	1,3	3,0
Fluorene	9,1	10,0
Phenanthrene	121,0	139,3
Anthracene	6,7	7,3
Fluoranthene	91,4	110,0
Pyrene	94,1	113,3
Benz[a]anthracene	26,9	36,0
Chrysene	31,9	50,3
Benzo[b]fluoranthene	29,3	24,0
Benzo[k]fluoranthene	12,9	14,0
Benzo[a]pyrene	15,7	19,3
Dibenz[a,h]anthracene	2,4	4,0
Benzo[ghi]perylene	18,9	23,0
Indeno[1,2,3-cd]pyrene	27,9	24,0
Sum	519,6	595,3

Extraktion with ASE200 at 100°C and 140bar

4. Existing Validation data for different matrices

Sludge
sewage sludge (method 2 extraction, method 3 extraction, HPLC/FLD)
Sum PAH 40ppm level- DIN 38414-S23:2002

Industrial sludge **- -**

Sediment, suspended solids
(method 2 extraction, method 3 extraction, HPLC/FLD)
Sum PAH 7ppm level- DIN 38414-S23:2002)

Waste
soil like waste **- -**
building materials containing tar particles, cresote wood **- -**

Soil improvers
Compost (stabilised) **- -**
Biowaste(not stabilised) **- -**

Soil
sandy (method 3 extraction, GC/MS)
Sum PAH 120 and 30 ppm levels- ISO 18287:2006

(method 1 extraction, GC/MS and HPLC/UV/FLD)
Sum PAH 55 and 65 ppm levels - ISO 18287:2006

Clay **- -**
organic rich **- -**

(- - not existing)

5. Available certified reference materials

Sediment CRM 535(IRMM)
Sewage sludge CRM 088 (IRMM)
Contaminated soil ERM CC014(BAM) 58 ppm(sum)
Contaminated soil ERM CC013(BAM) 99 ppm(sum)
Sewage Sludge ERM ?? (LGC) PAH content ?
Annex II: Certificates of BAM certified reference materials

6. Samples for ruggedness test

The playground samples for ruggedness test were provided by European Commision JRC- IES-Soil and Waste Unit, ISPRA.
PAH are analysed by HPLC-FLD after extraction of 5-10 g of samples with toluene using ASE (100°C/140 bars, 2 extraction cycles). The extract about 20 mL was filled up to 50 mL toluene. 2 independent extractions were made. 5 µL of extract were injected into HPLC-UV/FLD- System without any dilution and clean up.
Please see: SWCT report No. 01/08/2004: Analytical Report, Characterisation of "Playground samples" to be used in the context of Project HORIZONTAL-Organic parameters

Project HORIZONTAL „Playground“ sample		Sum PAK mg/kg
CW 1	Composted garbage	10,5
CW 5	Compost	2,5
SL 4	Sludge of domestic origin	13,1
SL 11	Sewage sludge, electronic industry	0,1
SO 1	Brown soil	0,06
SO 4	Clay soil	0,25
SO 7	Rice soil	16,4
SO 8	Mineralised soil	2,1
SO 9	Sludge-amended soil	4,5
SO 13	Terra rossa <2mm	0,45
SO 16 R	EUROSOIL 3R	0,44
S 38	Chinese sediment	3,8

PAK (mg/kg)	**CW1-1**	**CW1-2**	**CW5-1**	**CW5-2**	**SL4-1**	**SL4-2**	**SL11-1**	**SL11-2**	**SO1-1**	**SO1-2**	**SO4-1**	**SO4-2**
Naphthalin	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Acenaphthylen	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Acenaphthen	0,11	0,14	<0,01	<0,01	1,12	1,09	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Fluoren	0,04	0,02	<0,01	<0,01	1,48	1,31	<0,01	<0,01	0,02	<0,01	<0,01	<0,01
Phenanthren	0,69	0,79	0,17	0,17	3,64	3,28	0,06	0,03	0,02	0,02	0,05	0,08
Anthracen	0,15	0,18	0,03	0,03	0,25	0,28	0,03	0,05	<0,01	<0,01	<0,01	<0,01
Fluoranthen	2,11	1,74	0,60	0,51	2,37	2,29	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Pyren	0,90	1,14	0,45	0,38	1,46	1,40	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Benzo(a)anthracen	1,01	1,08	0,27	0,26	0,86	0,81	<0,01	<0,01	<0,01	0,02	0,02	0,03
Chrysen	1,16	1,19	0,31	0,31	0,93	0,82	<0,01	<0,01	0,01	0,01	0,04	0,04
Benzo(b)fluoranthen	1,48	1,61	0,29	0,28	0,62	0,59	<0,01	<0,01	<0,01	0,02	0,06	0,09
Benzo(k)fluoranthen	0,64	0,65	0,13	0,13	0,30	0,29	<0,01	<0,01	0,01	0,01	0,02	0,03
Benzo(a)pyren	0,74	0,72	0,17	0,18	0,30	0,34	<0,01	<0,01	0,01	<0,01	0,02	0,04
Benzo(g,h,i)perylen	0,72	0,86	0,16	0,13	0,24	0,27	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Dibenz(a,h)anthracen	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Indeno(1,2,3)pyren	0,71	0,46	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Summe	**10,45**	**10,58**	**2,56**	**2,38**	**13,56**	**12,76**	**0,10**	**0,08**	**0,06**	**0,07**	**0,22**	**0,30**

PAK (mg/kg)	SO7-1	SO7-2	SO8-1	SO8-2	SO9-1	SO9-2	SO13-1	SO13-2	SO16R-1	SO16R-1	S38-1	S38-2
Naphthalin	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Acenaphthylen	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Acenaphthen	0,14	0,13	0,04	0,03	0,06	0,07	0,03	<0,01	<0,01	<0,01	0,18	0,21
Fluoren	0,03	0,06	0,03	0,01	0,05	0,04	<0,01	<0,01	<0,01	<0,01	0,39	0,42
Phenanthren	2,35	2,37	0,31	0,30	0,46	0,46	0,09	0,17	0,04	0,08	1,47	1,47
Anthracen	0,17	0,18	0,04	0,04	0,07	0,08	<0,01	0,01	0,01	0,02	0,05	0,05
Fluoranthen	3,25	3,32	0,36	0,32	0,66	0,80	<0,01	0,11	0,07	0,09	0,58	0,80
Pyren	2,46	2,55	0,37	0,36	0,51	0,50	0,05	0,09	0,07	0,04	0,29	0,26
Benzo(a)anthracen	1,42	1,46	0,23	0,22	0,42	0,41	0,04	0,08	0,04	0,05	0,17	0,19
Chrysen	1,45	1,51	0,22	0,20	0,39	0,39	0,04	0,07	0,05	0,06	0,23	0,24
Benzo(b)fluoranthen	1,63	1,65	0,17	0,21	0,59	0,57	0,02	0,04	0,07	0,07	0,16	0,18
Benzo(k)fluoranthen	0,72	0,73	0,09	0,09	0,24	0,25	0,01	0,02	0,03	0,03	0,07	0,07
Benzo(a)pyren	1,37	1,34	0,20	0,20	0,36	0,37	0,01	0,04	0,04	0,04	0,08	0,09
Benzo(g,h,i)perylen	1,35	1,25	<0,01	0,19	0,63	0,66	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Dibenz(a,h)anthracen	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Indeno(1,2,3)pyren	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Summe	**16,33**	**16,55**	**2,06**	**2,17**	**4,43**	**4,61**	**0,28**	**0,62**	**0,42**	**0,47**	**3,67**	**3,96**

7. Limits of Detection (LOD)

Please see in Annex I: Determination of LOD for HPLC-FLD, GC-MS (quadropol) and GC-MS(Ion Trap)

Limit of detection according to DIN 32645 for PAH in solution
When 10 g of soild material(soil,sludge or compost) are extracted with appropriate amount of extraction solvent,
if necessary clean up and the final extract brought to a volume of 10mL will give LOD of specific PAH in solid.

	HPLC-Fluorescence		GC-MS/SIM(quad)		GC-MS(ion trap)	
	Solution	**Solid**	Solution	**Solid**	Solution	**Solid**
PAK	(ng/ml)	**(µg/kg)**	(ng/ml)	**(µg/kg)**	(ng/ml)	**(µg/kg)**
Naphthaline	15	**15**	1	**1**	16	**16**
Acenaphthylene			5	**5**	8	**8**
Acenaphthene	15	**15**	1	**1**	4	**4**
Fluorene	8	**8**	0.6	**0.6**	8	**8**
Phenanthrene	5	**5**	0.06	**0.06**	5	**5**
Anthracene	7	**7**	0.1	**0.1**	7	**7**
Fluoranthene	12	**12**	1	**1**	8	**8**
Pyrene	9	**9**	3	**3**	8	**8**
Benzo(a)anthracene	3	**3**	0.2	**0.2**	6	**6**
Chrysene	4	**4**	2	**2**	9	**9**
Benzo(b)fluoranthen	7	**7**	0.6	**0.6**	8	**8**
Benzo(k)fluorathene	3	**3**	5	**5**	14	**14**
Benzo(a)pyrene	4	**4**	2	**2**	10	**10**
Benzo(g,h,i)perylene	8	**8**	3	**3**	6	**6**
Dibenz(a,h)anthracene	8	**8**	3	**3**	12	**12**
Indeno(1,2,3-cd)pyrene	11	**11**	2	**2**	2	**2**

8. Comparison of analytical methods

In the frame work of the certification of PAH content in contaminated soil candidate reference material a comparability the results by different analytical methods was investigated in 2006.

Contaminated soil sample, 6 independent replicates for each method

	Method No. mg/kg											
PAH	**1**	**SD**	**2**	**SD**	**3**	**SD**	**4**	**SD**	**5**	**SD**	**6**	**SD**
Napthalene	**2,26**	0,18	**1,95**	0,31	**2,91**	0,08	**2,75**	0,04	**2,05**	0,08	**2,75**	0,09
Acenaphthylene			**0,69**	0,12	**0,89**	0,07	**1,52**	0,03	**0,739***	0,06		
Acenaphthene	**0,65**	0,06	**0,76**	0,02	**0,82**	0,01	**0,77**	0,01	**2,47**	0,05	**0,74**	0,01
Fluorene	**1,00**	0,08	**1,24**	0,07	**1,17**	0,07	**1,11**	0,03	**1,13**	0,04	**1,17**	0,00
Phenanthrene	**11,13**	0,58	**12,40**	0,29	**12,68**	0,27	**11,28**	0,30	**12,64**	0,14	**11,93**	0,03
Anthracene	**1,36**	0,03	**1,44**	0,09	**1,81**	0,04	**1,03**	0,02	**1,28**	0,04	**1,52**	0,02
Fluoranthene	**11,48**	0,39	**12,63**	0,32	**13,71**	0,25	**12,99**	0,27	**13,69**	0,53	**12,82**	0,02
Pyrene	**9,43**	0,25	**9,99**	0,40	**9,59**	0,12	**9,73**	0,17	**9,24**	0,40	**9,34**	0,07
Benz(a)anthracene	**5,14**	0,16	**7,72**	1,23	**5,57**	0,17	**5,81**	0,19	**6,24**	0,55	**5,31**	0,08
Chrysene	**4,06**	0,13	**5,74**	0,40	**5,36**	0,26	**6,61**	0,33	**5,03**	0,08	**4,72**	0,05
Benz(b)fluoranthene	**8,09**	0,34	**8,13**	0,18	**5,92**	0,17	**6,37**	0,28	**7,35**	0,38	**9,02**	0,06
Benz(k)fluoranthene	**3,32**	0,18	**4,50**	0,93	**3,27**	0,09	**6,00**	1,03	**3,02**	0,06	**3,25**	0,02
Ben(a)pyrene	**4,77**	0,51	**4,27**	0,29	**3,73**	0,27	**5,30**	0,15	**5,74**	0,21	**5,29**	0,03
Indeno(1,2,3 -cd)pyrene	**5,64**	0,38	**4,23**	0,29	**4,26**	0,17	**4,92**	0,21	**5,19**	0,26	**7,07**	0,12
Dibenz[a,h]anthracene			**1,19**	0,09	**1,39**	0,10	**0,92**	0,05	**1,71**	0,07	**0,53**	0,03
Benzo(ghi)perylene	**4,31**	0,13	**5,81**	0,99	**4,23**	0,13	**5,14**	0,10	**4,79**	0,20	**4,20**	0,05

The significant differences of results are marked yellow.

Method comparison

Contaminated soil sample, 6 independent replicates

Method No.	Detection tech.	Extraction	Extraction solvent
1	GC-MS	ASE	Toluene
2	GC-MS	Soxhlet	Toluene
3	GC-MS	flexIKA	Toluene
4	GC-MS	Ultrasonic	Cyclohexan/Aceton
5	HPLC	Ultrasonic	Cyclohexan/Aceton
6	HPLC	ASE	Methanol

* UV measurement

Sewage Sludge

In the frame work of the International Measurement Program (IMEP 21) of the Institute of Reference Materials and Measurements (IRMM) of the European Commission for the contribution of the measurement results for the certified reference values, we have investigated also the comparability of the results by different analytical methods. For this sewage sludge matrix different clean up procedures had to be applied to get chromatograms free of disturbances.
4-16 independent measurements were made for each method.
Please see: IMEP-21 Certification Report EUR 2006:Trace Elements, PCBs, PAHs in Sewage Sludge and also :Reports to Participants EUR 2242 EN(2006)

Sewage sludge IMEP 21

	GC-MS CH/acetone ASE + GPC + silica gel µg/kg	GC-MS CH/acetone ASE (NaCl/H2O) +GPC+ silica gel µg/kg	GC-MS(ion trap) toluene ASE + GPC + silica gel µg/kg	GC-MS (quad) toluene ASE + GPC + silica gel µg/kg	Lab B, GC-MS CH/aceton e Soxhlet + SPE-Silica/Alox µg/kg	HPLC-F Toluene ASE without clean up µg/kg	HLC-F ACN-ASE without clean up µg/kg	HPLC-F CH/acetone Shaking without clean up µg/kg	IMEP 21-Certified values and expanded uncertainty
Naphthalene	210	210	257	168	64	-	203	26	116 ± 27
Acenaphthylen	71	45	54	nd	nd	-		-	
Acenaphthene	84	65	62	nd	nd	-	929	-	
Fluorene	111	93	115	108	73	271	231	-	90 ± 22
Phenanthrene	835	852	823	865	627	761	973	1420	746 ± 18
Anthracene	91	78	92	122	86	146	139	35	104 ± 77
Fluoranthene	650	605	684	984	847	865	959	628	916 ± 63
Pyrene	1344	1241	1366	1401	1155	1043	1317	854	1280 ±120
Benzo(a)anthra	427	340	386	435	338	605	574	477	386 ± 160
Chrysene	890	523	834	306		699	591	540	
Benzo(b/k)fluo.	1319	901	1038	1240	1078	1043	812	557	1110 ± 56
Benzo(a)pyren.	425	316	344	447	319	396	365	176	383 ± 91
Indeno-pyrene	467	239	321	444	296		417	180	370 ± 54
Benzo(ghi)pery .	716	438	533	428	487	584	431	461	508 ± 58
Dibenz(ah)anth	239	91	88			230		82	

nd:_not determined

GC-MS; CH/acetone ASE +GPC + silica gel : ASE-Extraction with cyclohexane/acetone 1:2 ,wash out of acetone with water, volume reduction and GPC and silica gel (10% desactivated) clean up , concentration and GC-MS injection 1 µl

GC-MS; CH/acetone ASE (NaCl/H2O) +GPC+ silica gel:ASE- Extraction with cyclohexane/acetone 1:2 ,wash out of acetone with 30% NaCl in Water, volume reduction and GPC and silica gel (10% desactivated) clean up , concentration and GC-MS injection 1 µl

GC-MS(ion trap;) toluene ASE + GPC + silica gel:ASE- Extraction with toluene , volume reduction and GPC and silica gel (10% desactivated) clean up , concentration and GC-MS injection 1 µl

GC-MS (quad); toluene ASE + GPC + silica gel : ASE- Extraction with toluene , volume reduction and GPC and silica gel (10% desactivated) clean up , concentration and GC-MS injection 1 µl

Lab B, GC-MS; CH/acetone Soxhlet + SPE- Silica/Alumina: Soxhlet-Extraction with cyclohexane/acetone 1:2 ,wash out of acetone with water, volume reduction ,SPE silica gel and aluminium oxide clean up , concentration and GC-MS injection 1 µl

HPLC-F; Toluene ASE without cleanup: ASE extraction with toluene, direct injection of 5 µl of extract without clean up

HLC-F; ACN-ASE without clean up: ASE extraction with acetonitrile, direct injection of 5 µl of extract without clean up

HPLC-F; CH/acetone, shaking without clean up: -Extraction with cyclohexane/acetone 1:2 , by horizontal shaking at least for 6 h, Wash out of acetone with water, volume reduction and change of solvent from cyclohexane to acetonitrile, and injection of 5 µl without clean up

Shaking of the samples with cyclohexane /acetone and change of solvent for HPLC suitable acetonitrile gives losses of volatile PAH.
In GC-MS-Analysis, chrysene peak is partly of fully coeluted with triphenylene peak so that the results are depending upon the peak separation and integration.

9. Introduction of the metrological approach (traceability of measurement results to the International Standard SI unit-amount of substance and uncertainty assessment) in the standardisation procedure

We tried to introduce the metrological approach traceability of measurement results to the International standard SI unit-amount of substance) in the standardisation procedure by taking part or organising the **International Intercomparison of the „Committee of the amount of substance" CCQM of BIPM (International Bureau of weight and measures)** (Key and Pilot CCQM-, Comparisons) at the highest measurement level of National Metrological Institutes (NMI), which are signatory members of the Metre Convention.

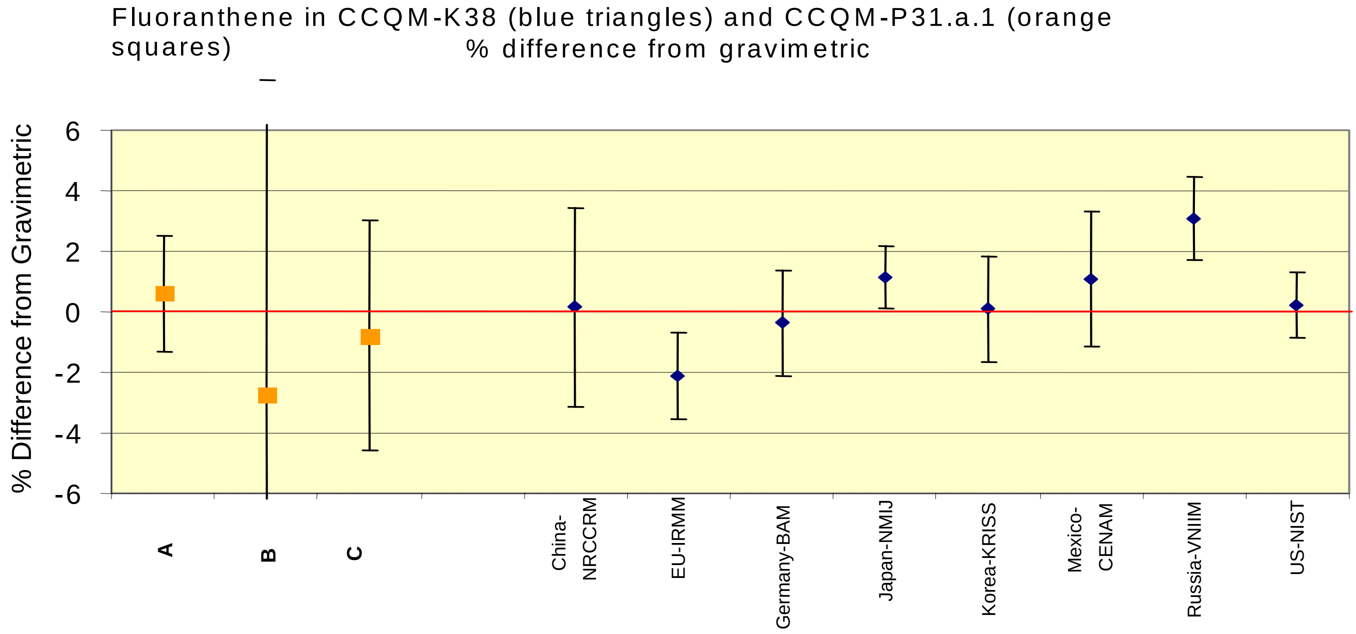
CCQM–K38 and –P31.a.1; Measurement of PAH in standard solution (July-Sep. 2005): is aimed to see how accurate and with which measurement uncertainties the NMI are able to measure PAH in solution.
Coordinating laboratory (NIST- USA)
10 PAHs in hexane:toluene (96:4 volume:volume) – 5 PAHs targeted are to be measured:

- Phenanthrene
- Fluoranthene
- Benz[*a*]anthracene – B[*a*]A
- Benzo[*a*]pyrene – B[*a*]P
- Benzo[*ghi*]perylene – B[*ghi*]P

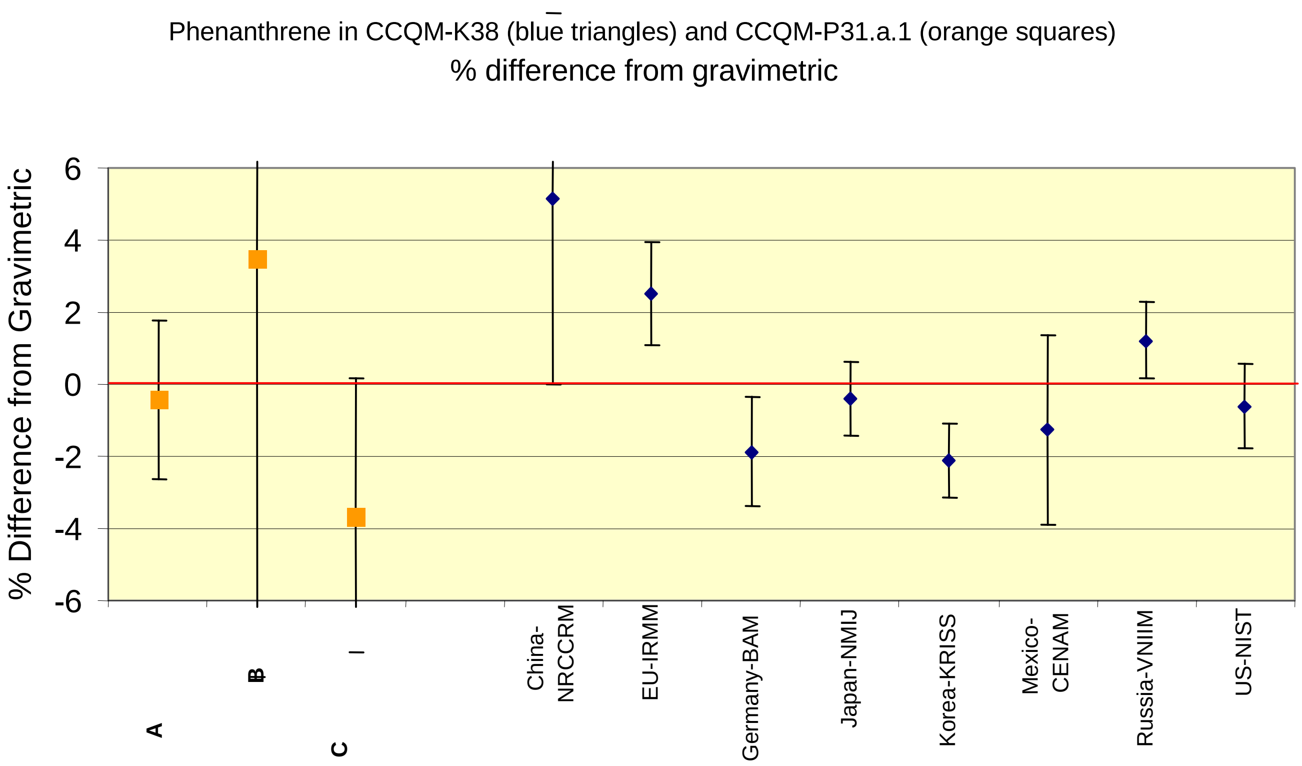
International Participants of NMI

Country	Institute	CCQM-K38	CCQM-P31.a.1
Brazil	INMETRO		
China	NRCCRM	x	
EU	JRC-IRMM-RM	x	
France	LNE		
Germany	BAM	x	
Great Britain	LGC		
Japan	NMIJ	x	
Korea	KRISS	x	
Mexico	CENAM	x	
Russia	VNIIM	x	
US	NIST	x	
Chile	CENMA		
Hong Kong	Government Laboratory		x
Peru	Envirolab Peru		x
South Africa	CSIR-NML		x
# receiving samples		11	4
# returning data		8	3

Example Fluoranthene

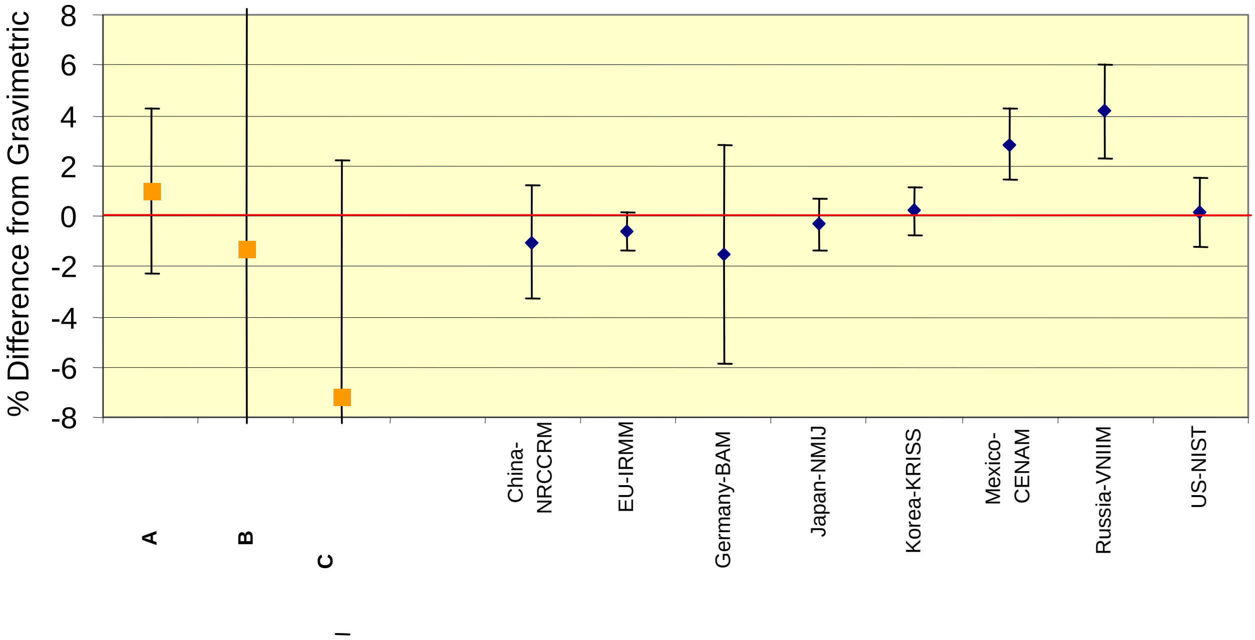


Example Phenanthrene



Example Benzo(ghi)perylene

B[*ghi*]P in CCQM-K38 (blue triangles) and CCQM-P31.a.1 (orange squares)
% difference from gravimetric



Conclusions:
For the Pilot Comparison Study - the majority of the data agree with the gravimetric value to within ± 4%
For the Key Comparison Study – the majority of the data agree with the gravimetric value to within ± 2%

CCQM-P69, Measurement of PAHs in Soil/Sediment(July-September 2005)
Coordinating laboratories; BAM-Germany/CENAM-Mexico
5 PAHs are to be measured as examples:

- Phenanthrene
- Fluoranthene
- Benz[*a*]anthracene – B[*a*]A
- Benzo[*a*]pyrene – B[*a*]P
- Benzo[*ghi*]perylene – B[*ghi*]P

International Participants of NMI

- CHINA NRCCRM
- EC IRMM
- GERMANY BAM
- HONG KONG HKSAR
- JAPAN NMIJ
- KOREA KRISS
- MEXICO CENAM
- UK LGC
- USA NIST

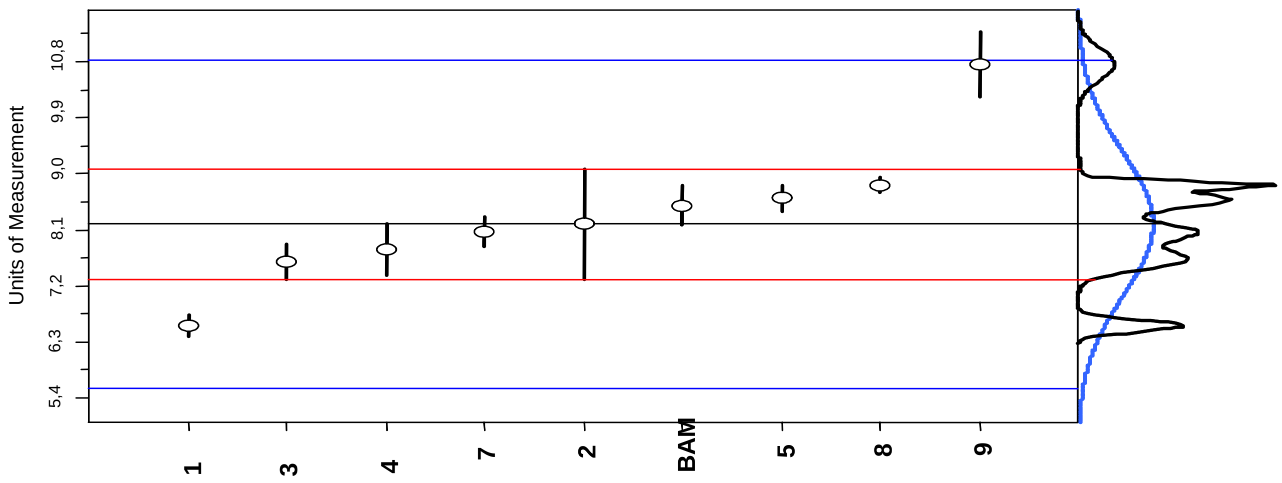
11 Laboratories received sample
9 Laboratories reported the measurement results to the coordinators

Extraction Methods

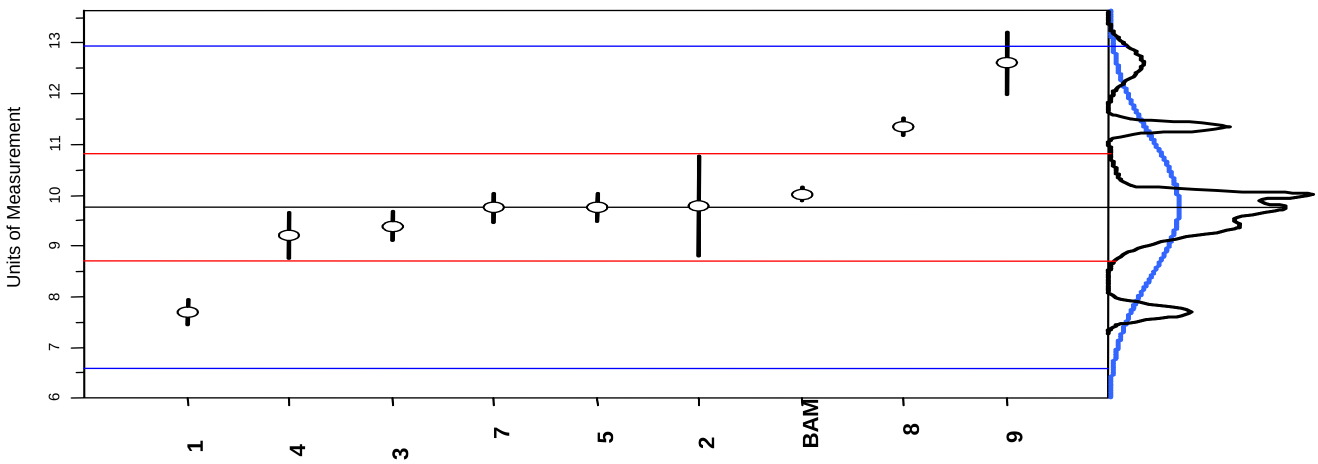
Participant	Amount of sample used for Extraction (g)	Method and solvent used for extraction	Internal standards	Type of calibration
5	5	Pressurized Fluid Extraction (PFE) using toluene at 150 degrees C (15 MPa) for 10 min (3 cycles)	5 corresponding perdeuterated PAH added before extraction	Single point
7	10	ASE solvent?	5 corresponding 13C labelled PAH added before extraction	Single point exact matching
9	9.5	ASE, using dichloromethane at 100 ° C (2000psi) for 10 min (2 cycles)	5 corresponding perdeuterated PAH added before extraction	Bracketing
1	0.5	Soxhlet solvent?	5 corresponding perdeuterated PAH added before sample preparation	Single point
BAM	5	ASE using toluene (100 °C, 140 bar, 2 cycles), Soxhlet with IKAflex in comparison	5 corresponding perdeuterated PAH added to aliquot of extract	3 points calibration
8	10	ASE solvent?	5 corresponding perdeuterated PAH added prior to extraction	Single point
2	10	Soxhlet with acetone: Hexane (1:1,v/v) for 24 hours	5 corresponding perdeuterated PAH added before extraction	Single point
4	1	Soxhlet (50% v/v hexane/acetone) overnight	5 corresponding 13C labelled PAH added prior to extraction	Single point
3	3	Soxhlet , with toluene and Dicloromethane	5 corresponding perdeuterated PAH added before extraction	5 points calibration

All the laboratories applied GC-MS method with deuterated PAH as internal standards
BAM-method: Extraction with toluene/ASE/Soxhlet and GC-MS

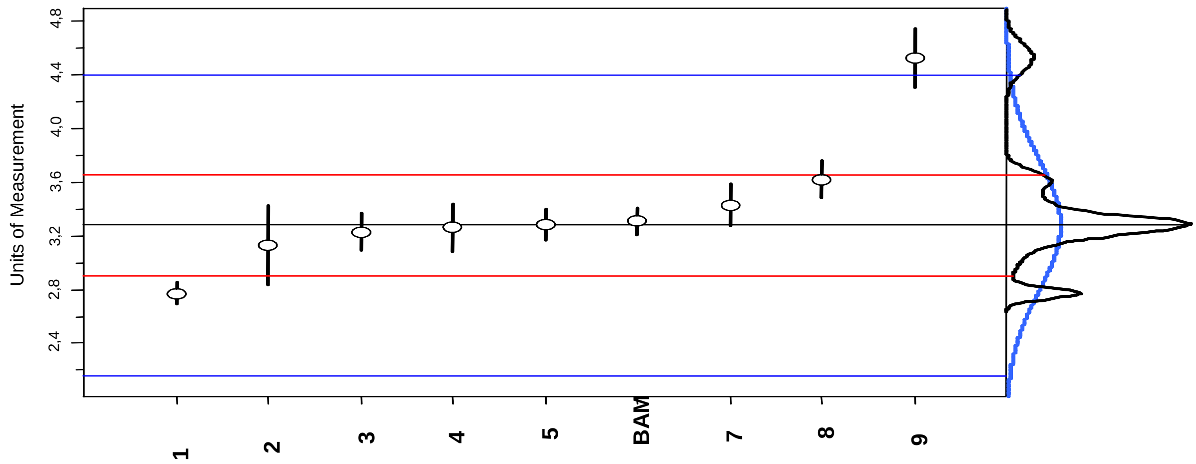
CCQM-P69PAH in soil: **Phenanthrene** µg/g dry soil
The dark and two solid red lines are the median 8.19 and S 0.71(8.7%)



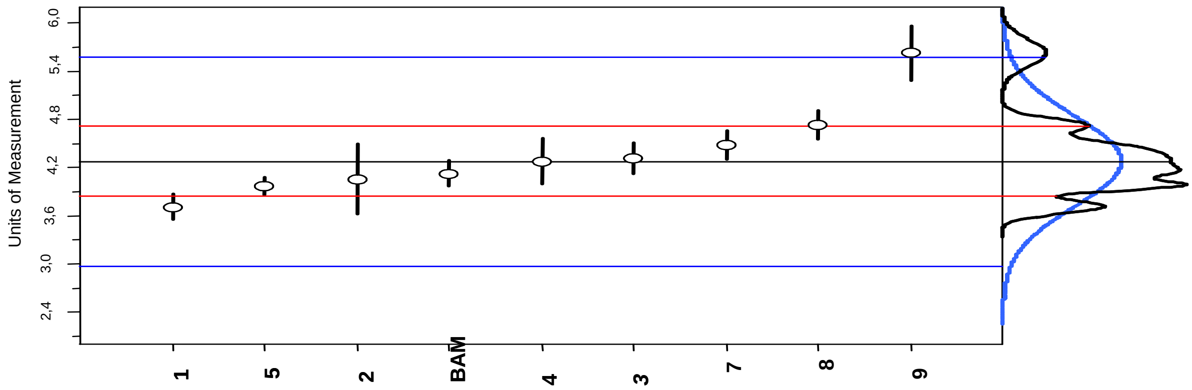
CCQM-P69 PAH in soil: **Fluoranthene** µg/g dry soil
The dark and two solid red lines are the median 9.77 and S 0.96(9.8%)



CCQM-P69 PAH in soil: **Benzo (ghi)perylene** µg/g dry soil
The dark and two solid red lines are the median 3.2 and S 0.27(8.4%)

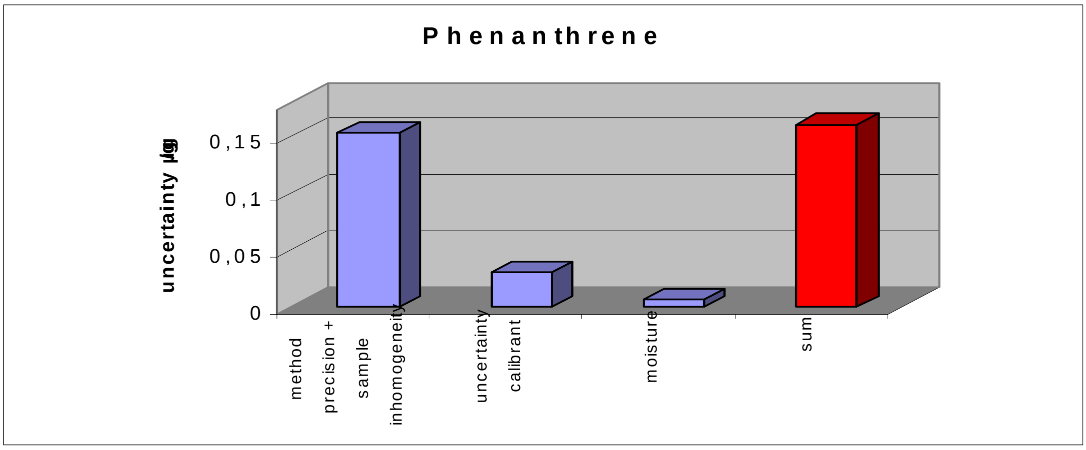


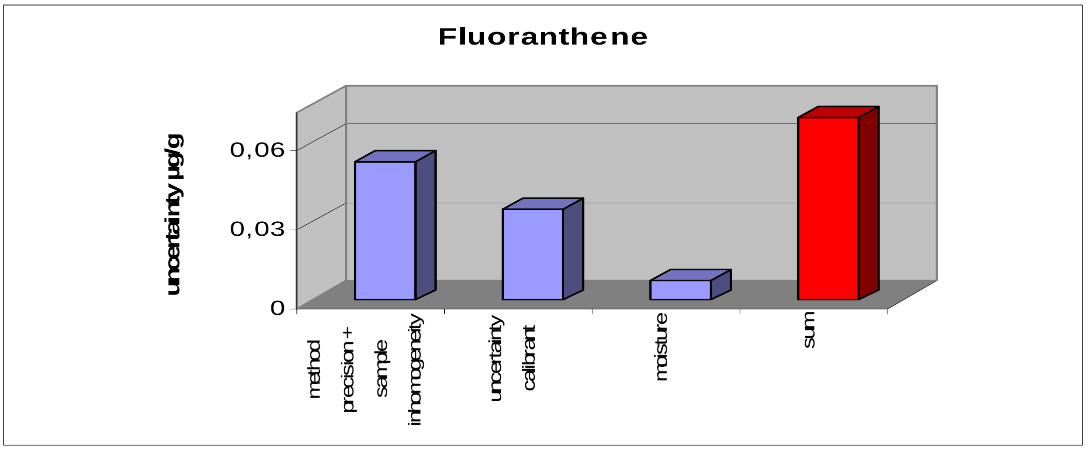
CCQM-P69 PAH in soil: **Benzo (a) pyrene µg/g** dry soil
The dark and two solid red lines are the median 4.28 and S 0.32(7.4%)

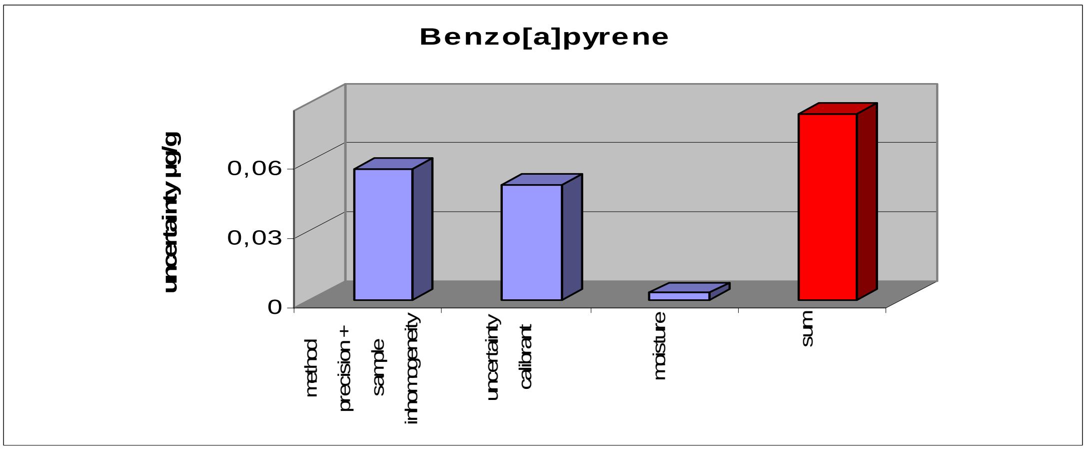


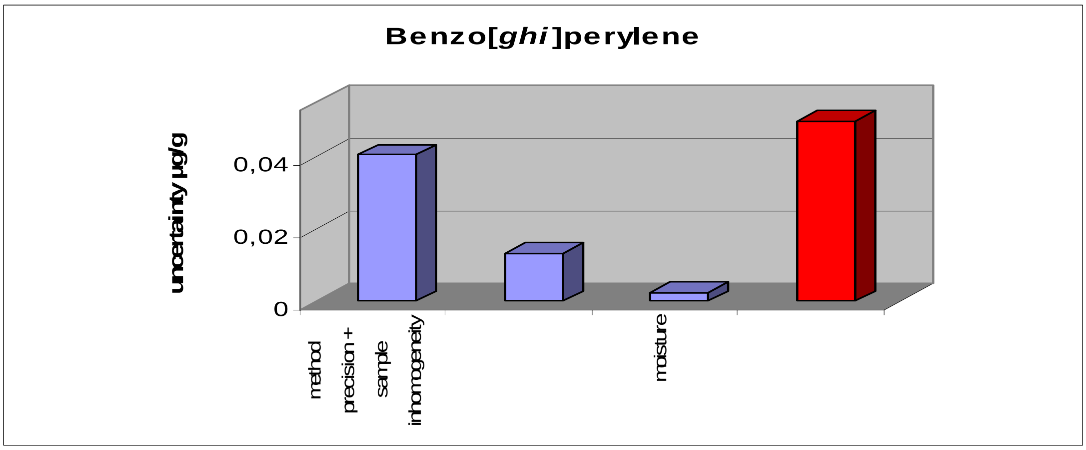
Conclusions: ASE Extraction and GC-MS with the deuterated internal standard is the best appropriate method. The majority of the data agree within ± 8% to ± 10%.

Examples for Uncertainty contributions









Major contributions to the combined uncertainty of the mean

Precision of the method including possible sample inhomogeneity, precision associated with the measurement but also the precision of weighing out the sample, extraction, spiking with the internal standard, calibration, possible inhomogeneity of the sample: *Standard deviation of the mean of the four replicate*

Concentration of the calibration solution (PAH in iso octane)
The expanded uncertainty of the standard solution (NIST SRM-2260a)

	Conc.	Exp. uncertainty
Phenanthrene	11,57	0,35
Fluoranthene	8,324	0,35
Benz[*a*]anthracene	4,415	0,59
Benzo[*a*]pyrene	4,71	1,20
Benzo[*ghi*]perylene	5,669	0,41
	µg/g	**%**

Moisture content of the sample
The moisture content was determined 5 times.
The standard deviation of the mean of these measurements 0,08% was taken as an estimate of the standard uncertainty of moisture content moisture content: 1,77% (5 determinations)

Uncertainty calculation

$$U = k \cdot c \cdot \sqrt{u(c_{st})^2 + \frac{(SD_{results})^2}{n} + \frac{(SD_M)^2}{n_m}}$$

where U : expanded uncertainty
k: coverage factor (k=2-3)
c : average concentration of the analyte
$u(c_{st})$: uncertainty of standards used
SD_{result} : standard deviation of results (analyte concentration determined)
n: number of independent samples analysed
SD_M : standard deviation of moisture determination

Uncertainty budget of PAH determination

PAH	mean	method precision + sample inhomogeneity	uncertainty calibrant	moisture	sum	k
	µg/g	µg/g	µg/g	µg/g	µg/g	
Phenanthrene	8,49	0,15	0,03	0,006	0,16	3,18
Fluoranthene	10,02	0,05	0,03	0,007	0,07	2,45
Benz[a] anthracene	4,54	0,03	0,03	0,003	0,05	2,31
Benzo[a] pyrene	4,13	0,06	0,05	0,003	0,08	2,26
Benzo[ghi] perylene	3,31	0,04	0,01	0,002	0,05	3,18

Comparison of PAH results

PAH	**BAM mean**	BAM Expanded Uncertainty	**CCQM P 69 median**	P 69 1 SD	**Certified Ref. Mat. BAM ERM CC014***	Expanded Uncertainty
	µg/g	µg/g	**µg/g**	µg/g	**µg/g**	µg/g
Phenanthrene	**8,49**	0,50	**8,19**	0,71	**7,5**	0,7
Fluoranthene	**10,02**	0,16	**9,79**	0,96	**9,1**	1,0
Benz[a] anthracene	**4,54**	0,10	**4,29**	0,52	**4,19**	0,4
Benzo[a] pyrene	**4,13**	0,18	**4,28**	0,32	**4,38**	0,2
Benzo[ghi] perylene	**3,31**	0,14	**3,2**	0,27	**3,5**	0,3

*CCQM P69 soil sample and the Certified reference material BAM ERM CCO14 are taken from the bulk material of the same origin