CCQM-K131
Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile

OAWG Track A Key Comparison

Final Report
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SUMMARY

Solutions of organic analytes of known mass fraction are typically used to calibrate the measurement processes used to determine these compounds in matrix samples. Appropriate value assignments and uncertainty calculations for calibration solutions are critical for accurate measurements. Evidence of successful participation in formal, relevant international comparisons is needed to document measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs). To enable NMIs and DIs to update or establish their claims, in 2015 the Organic Analysis Working Group (OAWG) sponsored CCQM-K131 "Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile".

Polycyclic aromatic hydrocarbons (PAHs) result from combustion sources and are ubiquitous in environmental samples. The PAH congeners, benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), and naphthalene (Nap) were selected as the target analytes for CCQM-K131. These targets span the volatility range of PAHs found in environmental samples and include potentially problematic chromatographic separations. Nineteen NMIs participated in CCQM-K131. The consensus summary mass fractions for the three PAHs are in the range of (5 to 25) μg/g with relative standard deviations of (2.5 to 3.5) %.

Successful participation in CCQM-K131 demonstrates the following measurement capabilities in determining mass fraction of organic compounds of moderate to insignificant volatility, molar mass of 100 g/mol up to 500 g/mol, and polarity $pK_{ow} < -2$ in a multicomponent organic solution ranging in mass fraction from 100 ng/g to 100 μg/g: (1) value assignment of primary reference standards (if in-house purity assessment carried out), (2) value assignment of single and/or multi-component organic solutions, and (3) separation and quantification using gas chromatography or liquid chromatography.

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ACRONYMS

ACN	acetonitrile
BaA	benz[*a*]anthracene, $C_{18}H_{12}$
BAM	Bundesanstalt fuer Materialforschung und –pruefung, DI: Germany
BaP	benzo[*a*]pyrene, $C_{20}H_{12}$
BVL	Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, DI: Germany
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CENAM	Centro Nacional de Metrologia, NMI: Mexico
CIPM	International Committee for Weights and Measures
CMC	Calibration and Measurement Capability
CRM	certified reference material
CV	coefficient of variation, expressed in %: CV = $100 \cdot s/\bar{x}$
DI	designated institute
DoE	degrees of equivalence
EXHM	Chemical Metrology Laboratory, DI: Greece
GC-MS	gas chromatography with mass spectrometry detection
GLHK	Government Laboratory, Hong Kong, DI: Hong Kong
HSA	Health Sciences Authority, DI: Singapore
ID	isotope dilution
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia, NMI: Brazil
INRiM	Istituto Nazionale di Ricerca Metrologica, NMI: Italy
JCTLM	Joint Committee for Traceability in Laboratory Medicine
KC	Key Comparison
KCRV	Key Comparison Reference Value
KEBS	Kenya Bureau of Standards, NMI: Kenya
KRISS	Korea Research Institute of Standards and Science, NMI: Republic of Korea
LC-MS	liquid chromatography with mass spectrometry detection
LC-MS/MS	liquid chromatography with tandem mass spectrometry detection
LNE	Laboratoire National de Métrologie et d'Essais, NMI: France
PAH	polycyclic aromatic hydrocarbon
Nap	naphthalene, $C_{10}H_8$
NIM	National Institute of Metrology, NMI: China
NIST	National Institute of Standards and Technology, NMI: USA
NMI	national metrology institute
NMIJ	National Metrology Institute of Japan, NMI: Japan
NMISA	National Metrology Institute South Africa, NMI: South Africa
OAWG	Organic Analysis Working Group
pK_{ow}	Negative base-10 logarithm of the octanol-water partition coefficient
RMP	Reference Measurement Procedure
SRM	Standard Reference Material, a NIST CRM
TBD	To Be Determined
UME	National Metrology Institute of Turkey, NMI: Turkey
VNIIM	D.I. Mendeleyev Institute for Metrology, NMI: Russia
VSL	VSL Dutch Metrology Institute, NMI: the Netherlands

SYMBOLS

d_i	degree of equivalence: x_i - KCRV
$\%d_i$	percent relative degree of equivalence: $100 \cdot d_i$/KCRV
k	coverage factor: $U(x) = k \cdot u(x)$
MAD_E	median absolute deviation from the median (MAD)-based estimate of s: $MAD_E = 1.4826 \cdot MAD$, where $MAD = median(\lvert x_i - median(x_i) \rvert)$
n	number of quantity values in a series of quantity values
s	standard deviation of a series of quantity values: $s = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$
t_s	Student's t-distribution expansion factor
$u(x_i)$	standard uncertainty of quantity value x_i
$\bar{u}(x)$	pooled uncertainty: $\bar{u}(x) = \sqrt{\sum_{i=1}^{n} u^2(x_i)/n}$
$U(x)$	expanded uncertainty
$U_{95}(x)$	expanded uncertainty defined such that $x \pm U_{95}(x)$ is asserted to include the true value of the quantity with an approximate 95 % level of confidence
$U_{k=2}(x)$	expanded uncertainty defined as $U_{k=2}(x) = 2 \cdot u(x)$
x	a quantity value
x_i	the i^{th} member of a series of quantity values
$\bar{x}$	mean of a series of quantity values: $\bar{x} = \sum_{i=1}^{n} x_i/n$

INTRODUCTION

Solutions of known mass fraction of organic analytes of interest are typically used to calibrate the measurement processes used in the determination of these compounds in matrix samples. Appropriate value assignments and uncertainty calculations for calibration solutions are critical for accurate measurements. Evidence of successful participation in formal, relevant international comparisons is needed to document measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs).

In 2004, the Organic Analysis Working Group (OAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) sponsored a set of three related Pilot studies of low-molar mass non-polar organic analytes in organic solvents: CCQM-P31a polycyclic aromatic hydrocarbons (PAHs), CCQM-P31b polychlorinated biphenyl congeners, and CCQM-P31c chlorinated pesticides. Based upon the results from these studies, the OAWG concluded that demonstrating competency with PAH solutions was sufficient to document capability claims for stable low-polarity calibration solutions. Eight NMIs participated in the 2005 OAWG-sponsored key comparison (KC) CCQM-K38 Determination of PAHs in Solution [1]. To enable the CCQM-K38 participants to update their competency claims and allow other NMIs and DIs to demonstrate their competencies, in 2015 the OAWG sponsored CCQM-K131 "Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile".

PAHs result from combustion sources and are ubiquitous in environmental samples. The target PAH congeners, benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), and naphthalene (Nap), span the volatility range of PAHs found in environmental samples and include potentially problematic chromatographic separations. These measurands can be successfully evaluated using either gas chromatography (GC) or liquid chromatography (LC) in conjunction with various detection methods including but not limited to isotope dilution mass spectrometry (IDMS). The method(s) used by participants in CCQM-K131 are intended to represent the way they deliver calibration solution services to their customers.

The following sections of this report document the timeline of CCQM-K131, the measurands, study material, participants, results, and the measurement capability claims that participation in CCQM-K131 can support. The Appendices reproduce the official communication materials and summaries of information about their results provided by the participants.

TIMELINE

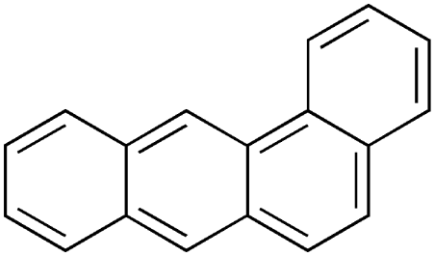
Table 1 lists the timeline for CCQM-K131.

Table 1: Timeline for CCQM-K131

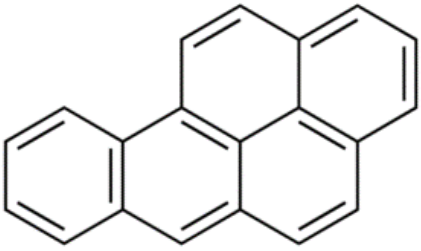
Date	Action
Apr 2014	Proposed to CCQM
Apr 2015	Draft protocol presented to OAWG as a potential Track A Key Comparison
May 2015	OAWG authorized CCQM-K131 as a Track A Key Comparison; protocol approved
Jul 2015	Call for participation to OAWG members
Dec 2015 to Apr 2016	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
Sep 2016	Results due to coordinating laboratory: revised from Feb 2016 to accommodate participants who received samples late or experienced equipment difficulties
Sep 2016	Draft A report distributed to OAWG
Apr 2017	Draft B report distributed to OAWG
Apr 2018	(Draft) Final report delivered to OAWG Chair

MEASURANDS

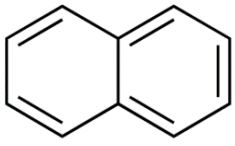
At the October 2014 OAWG meeting, the decision was made to conduct this study in conjunction with CCQM-K95.1 "Low-Polarity Analytes in a Botanical Matrix: Polycyclic Aromatic Hydrocarbons (PAHs) in Tea" to minimize duplication of effort. CCQM K95.1 and -K131 focus on the same two PAHs: BaA, a four-ring *cata*-condensed PAH of molar mass 228 g/mol, and BaP, a five-ring *peri*-condensed PAH of molar mass 252 g/mol. At the April 2015 OAWG meeting, Nap, a volatile two-ring *cata*-condensed PAH of molar mass 128 g/mol was added to the list of CCQM-K131 measurands to enable claims for volatile analytes in organic solutions. The molecular structures of these analytes are displayed in Figure 1.



Benz[*a*]anthracene
BaA



Benzo[*a*]pyrene
BaP



Naphthalene
Nap

Figure 1: Structures of Benz[*a*]anthracene, Benzo[*a*]pyrene, and Naphthalene

STUDY MATERIALS

NIST has produced seven PAHs in acetonitrile (ACN) solution SRMs over the past 30 years, each containing the 16 PAHs identified as priority pollutants by the U.S. Environmental Protection Agency. NIST has available a number of prepared and ampouled solutions related to the production and certification of these SRMs. One of these ampouled solution materials was chosen as the study material for CCQM-K131. The identity of the solution was known only to the study's originator. Comparison of the consensus results to the certified values of the seven 1647-series SRMs indicates that the test sample used in CCQM-K131 was the master solution for SRM 1647a, issued in 1988.

Each participant received four ampoules, each containing 1.2 mL of a solution of 16 PAHs in ACN. Three of these ampoules were to be used in determining the results to be reported; the additional ampoule was for practice and/or screening analysis.

Homogeneity and Stability Assessment of Study Material

Based on previous experience at NIST with these PAHs in ACN solutions, the test solution is homogeneous. Analysis of the solution by liquid chromatography with UV detection (10 µL injections) provided measurements with a coefficient of variation (CV, percent relative standard deviation) of less than 1.9 %.

NIST has not performed a formal stability study for these specific PAHs in ACN solution. However, we have not observed any stability issues with very similar materials, all stored at room temperature.

PARTICIPANTS AND INSTRUCTIONS

The call for participation was distributed in Jul-2015 with the intent to distribute samples in Sep-2015, receive results in Dec-2015, and discuss results at the Spring OAWG meeting, Apr-2016. Appendix A reproduces the Call for Participation; Appendix B reproduces the study Protocol. Due to shipping practicalities, sample shipping was delayed to Dec-2015. Due to customs issues, the last set of materials was delivered in Apr-2016. Because of these delays, the deadline for submission of results was several times postponed with a final deadline of Sep-15-2016 to enable discussion of results at the Fall 2016 OAWG meeting.

Table 2 lists the institutions that received CCQM-K131 samples.

Table 2: Institutions Receiving CCQM-K131 Samples

NMI or DI	Code	Contact
Bundesanstalt fuer Materialforschung und –pruefung	BAM	Rosemarie Philipp
Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	BVL	Rudolf Hackenberg
Centro Nacional de Metrologia	CENAM	Mariana Arce Osuna
Chemical Metrology Laboratory EXHM/GCSL-EIM	EXHM	Charalampos Alexopoulos
Government Laboratory, Hong Kong	GLHK	Pui-kwan Chan
Health Sciences Authority, Singapore	HSA	Tang Lin Teo
Instituto Nacional de Metrologia, Qualidade e Tecnologia	INMETRO	Eliane Cristina Pires do Rego
Istituto Nazionale di Ricerca Metrologica	INRiM	Michela Sega
Kenya Bureau of Standards	KEBS	Luvonga Caleb
Korea Research Institute of Standards & Technology	KRISS	Byungjoo Kim
Laboratoire National de Métrologie et d'Essais	LNE	Julie Cabillic, Carine Fallot
National Institute of Metrology, China	NIM	Tang Hua
National Institute of Standards and Technology	NIST	Lane Sander
National Metrology Institute of Japan	NMIJ	Nobuyasu Itoh
National Metrology Institute of South Africa	NMISA	Laura Quinn
National Metrology Institute of Turkey TÜBİTAK UME	UME	Ahmet Ceyhan Gören
D.I. Mendeleyev Institute for Metrology	VNIIM	Anatoliy Krylov, Alena Mikheeva
VSL Dutch Metrology Institute	VSL	Annarita Baldan

RESULTS

Participants were requested to report a single estimate of the mass fraction (μg/g) for each of the target PAHs based on measurements for one subsample from each of three ampoules of the solution (i.e., three independent replicates). In addition to the quantitative results, participants were to describe their analytical methods, approach to uncertainty estimation, and the Core Competencies they felt were demonstrated in this study. Appendices C, D, and E reproduce the several report forms.

Methods Used by Participants

Participants were instructed to base their measurement method on either GC or LC with a quantification approach based on internal or external standards or IDMS. The methods employed in this study are intended to represent the way the NMI delivers this measurement service.

CCQM-K131 results were received from 18 of the 19 institutions that received samples; KEBS withdrew from participation because of equipment difficulties. Brief descriptions of the analytical methods used by the participants, including sample preparation, analytical technique, and quantification approach are summarized in Appendix F. The participants' approaches to estimating uncertainty are provided in Appendix G. The participants' results as reported are provided in Appendix H.

Calibration Materials Used by Participants

Participants established the metrological traceability of their results using certified reference materials (CRMs) with stated traceability and/or commercially available high purity materials for which they determined the purity. Table 3 lists the CRMs that were used. Table 4 lists how participants established traceability. If through their own measurements, Table 4 lists the material, its assigned purity, the method used, and how the participant had demonstrated their competence in the use of the method(s).

Table 3: Certified Reference Materials Used

CRM	Provider	Analyte	Mass Fraction[a] Delivered, μg/g	Mass Fraction[a] Source Material, %	In-house Purity Methods Used to Value-Assign Source Material[b]
SRM 1647f	NIST	BaA	5.16 ± 0.07	99.84 ± 0.11	DSC
		BaP	6.22 ± 0.11	99.3 ± 0.7	qNMR, DSC
		Nap	25.31 ± 0.35	99.24 ± 0.78	qNMR, DSC
SRM 2260a	NIST	BaA	4.415 ± 0.078	99.79 ± 0.21	DSC
		BaP	4.71 ± 0.17	99.5 ± 0.5	qNMR, DSC
		Nap	11.43 ± 0.30	99.4 ± 0.4	qNMR, DSC
CRM 4213-a	NMIJ	BaP	99.2 ± 3.0	99.23 ± 3.83	DSC, FPD

a Stated as Value ± U_{95}(Value)

b DSC: Differential scanning calorimetry
FPD: Freezing point depression
qNMR: Quantitative nuclear magnetic resonance

Table 4: Metrological Traceability of Participants' Results

NMI/DI	Analyte	Source of Traceability	Material	Mass Fraction[a] Purity, %	Purity Techniques[b]	Evidence of Competence
BAM	BaA BaP Nap	SRM 1647f	N/A			
BVL	BaA BaP	SRM 2260a	N/A			
CENAM	BaA BaP	CENAM	Supelco Ultrascientific	98.68 ± 0.12 99.12 ± 0.76	MB	Successful participation in CCQM-P.20.b,c,f CCQM-K55.a,b
EXHM	BaA BaP	SRM 1647f	N/A			
GLHK	BaA BaP	SRM 1647f	N/A			
HSA	BaA BaP Nap	SRM 1647f HSA HSA	N/A Cerilliant SCB-007 Sigma-Aldrich 84679	 99.38 ± 0.51 99.61 ± 0.62	 MB MB	 Successful participation in CCQM-K55.b-d
INMETRO	BaA BaP Nap	INMETRO	Sigma-Aldrich Supelco Fluka	98.71 ± 0.99 92.41 ± 0.78 88.7 ± 1.7[c]	qNMR, MB	Successful participation in CCQM-P150.a,b CCQM-K55.a-d
INRiM	BaA BaP Nap	SRM 2260a	N/A			
KRISS	BaA BaP Nap	KRISS	BCR-271 Supelco Fluka	98.78 ± 0.55 98.81 ± 017 99.85 ± 0.06	MB	Successful participation in CCQM-P117.a, CCQM-K55.b-d
LNE	BaA BaP Nap	SRM 1647f	N/A			

NMI/DI	Analyte	Source of Traceability	Material	Mass Fraction[a] Purity, %	Purity Techniques[b]	Evidence of Competence
NIM	BaA BaP Nap	NIM	Cerilliant Cerilliant AccuStandard	99.69 ± 0.37 99.30 ± 0.29 99.84 ± 0.15	qNMR, GC-FID, HPLC-DAD	Successful participation in CCQM-P20.a,c-f, CCQM-K55.a-d
NIST	BaA BaP Nap	NIST	BCR-271, vial 110 BCR-51, vial 44 Fluka 2366751182	98.79 ± 0.15 99.3 ± 0.4 99.24 ± 0.39	DSC qNMR, DSC qNMR, DSC	Successful participation in CCQM-P20.a-f, CCQM-K55.a-d
NMIJ	BaP	NMIJ	NMIJ CRM 4213-a	N/A		
	Nap		TCI (Zone Refined, Product N0004, lot QCNQJ-IN)	100.0 ± 0.7	qNMR, GC-FID	Successful participation in CCQM-K55.b
NMISA	BaA BaP Nap	SRM 1647f	N/A			
UME	BaA BaP Nap	UME	Supelco 4-8563 Supelco 4-8564 Fluka 8467	98.08 ± 0.30 94.12 ± 0.52 99.90 ± 0.22	qNMR	Successful participation in CCQM-K55.a-d
VNIIM	BaA BaP	SRM 1647f	N/A			
VSL	Nap	VSL	Sigma-Aldrich MKBT5870V	99.990 ± 0.019	MB	Successful participation in CCQM-P20.b, CCQM-K10, -K22, -K47

a Stated as Value ± U_{95}(Value)

b DSC: Differential scanning calorimetry
GC-FID: Gas chromatography with flame ionization detection
HPLC-DAD: High pressure liquid chromatograph with diode-array detection
MB: Mass balance
qNMR: Quantitative nuclear magnetic resonance

c Result was withdrawn due to miss-assigned purity. Revised purity: 99.20 ± 0.31 %.

Participant Results

The CCQM-K131 results for the determination of BaA, BaP, and Nap are detailed in Table 5 and presented graphically in Figure 2.

BVL was unable to reproduce their reported result for BaP and chose to withdraw it from use in statistical estimates. They were unable to identify a cause of the discordance given the resources available. This result is displayed in *red italic font* in Table 5 and as a solid blue square in Figure 2.

Using an additional set of samples, INMETRO revised their analytical method and revised the purity of their standards. They chose to withdraw their reported result for Nap from use in statistical estimates. This result is displayed in *red italic font* in Table 5 and as a solid blue square in Figure 2. Their revised values for all three measurands are displayed as open diamonds in Figure 2; these revised values are not used elsewhere in this report.

NMISA discovered a transcriptional error that affected their reported results. At the Fall 2017 meeting in Ottawa, Canada, following International Committee for Weights and Measures (CIPM) guidelines the OAWG withdrew the NMISA results for BaA and BaP from use in statistical estimates. The original NIMSA results for these two measurands are displayed in *red italic font* in Table 5 and as solid blue squares in Figure 2. The revised values for all three measurands are displayed as open diamonds in Figure 2; these revised values are not used elsewhere in this report.

Table 5: Reported Results for BaA, BaP, and Nap, µg/g

	Benz[*a*]anthracene (BaA)				Benzo[*a*]pyrene (BaP)				Naphthalene (Nap)			
NMI/DI	***x***	***u*(*x*)**	***k***	***U*(*x*)**	***x***	***u*(*x*)**	***k***	***U*(*x*)**	***x***	***u*(*x*)**	***k***	***U*(*x*)**
BAM	4.81	0.05	2.00	0.10	6.07	0.08	2.00	0.15	25.30	0.43	2.00	0.85
BVL	4.99	0.05	2.00	0.10	*5.56*	*0.10*	*2.00*	*0.20*	-	-	-	-
CENAM	5.01	0.06	2.00	0.13	6.47	0.12	2.00	0.23	-	-	-	-
EXHM	4.71	0.08	2.12	0.16	5.87	0.10	2.11	0.21	-	-	-	-
GLHK	4.87	0.08	2	0.16	6.08	0.12	2	0.25	-	-	-	-
HSA	4.901	0.040	2	0.080	6.09	0.066	2	0.13	25.29	0.193	2	0.39
INMETRO	4.91	0.077	2.00	0.15	6.39	0.097	2.57	0.25	*27.4*	*0.79*	*2.45*	*1.9*
INRiM	5.12	0.06	2	0.12	6.28	0.08	2	0.17	25.32	0.31	2	0.63
KRISS	4.785	0.034	2.26	0.076	5.989	0.037	2.18	0.081	25.08	0.12	2.31	0.28
LNE	4.88	0.06	2	0.12	6.03	0.08	2	0.15	23.95	0.28	2	0.55
NIM	4.88	0.049	2	0.10	6.10	0.074	2	0.15	25.19	0.27	2	0.53
NIST	4.94	0.029	2.20	0.063	6.16	0.042	2.23	0.094	25.66	0.184	2.12	0.391
NMIJ	-	-	-	-	6.26	0.13	2.00	0.26	25.35	0.26	2.57	0.66
NMISA	*5.16*	*0.08*	*2.09*	*0.16*	*6.22*	*0.10*	*2.06*	*0.20*	25.31	0.30	2.05	0.62
UME	4.99	0.06	2	0.12	6.23	0.10	2	0.20	25.32	0.22	2	0.43
VNIIM	4.82	0.046	2	0.09	6.02	0.066	2	0.13	-	-	-	-
VSL	-	-	-	-	-	-	-	-	25.2	0.5	2	1.0
n	14				14				11			
$\bar{x}$	4.90				6.15				25.18			
s	0.10				0.16				0.43			
$\bar{u}$	0.06				0.09				0.30			
CV	2.1 %				2.7 %				1.7 %			

Results in *red italic font* have been withdrawn from statistical consideration;
- = no result reported for this measurand;
n = number of results included in summary statistics; $\bar{x}$ = mean; *s* = standard deviation;
$\bar{u} = \sqrt{\sum_i^n u^2(x_i)/n}$ (the "average" reported uncertainty); CV = $100 \cdot s/\bar{x}$.
±

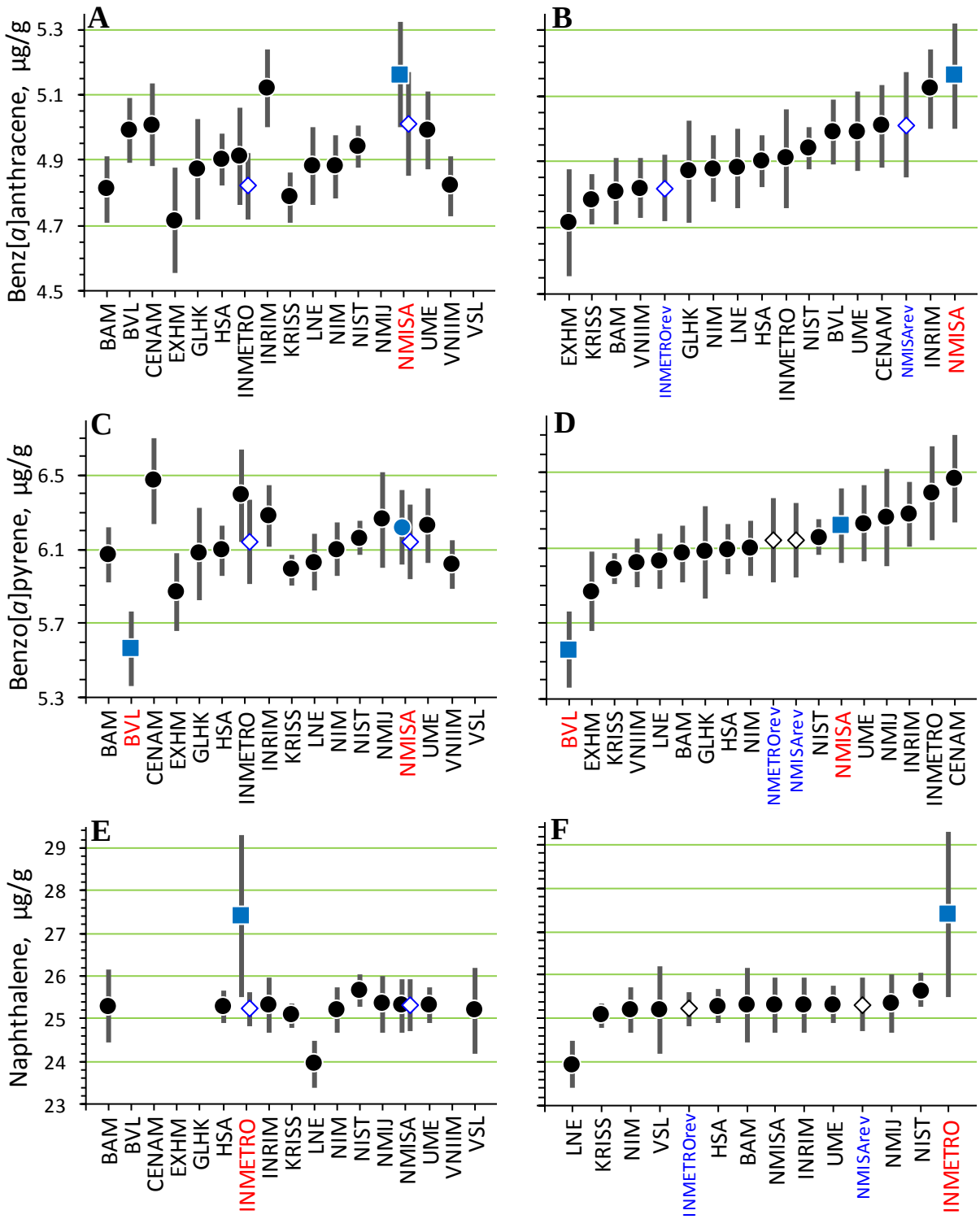


Figure 2: Dot-and-Bar Display of Reported Results for BaA, BaP, and Nap, µg/g

Panels A and B display results for BaA, panels C and D for BaP, and panels E and F for Nap. Panels A, C, and D display results sorted alphabetically by participant acronym, panels B, D, and F display results sorted by increasing reported value. Symbols represent reported mean values, x, bars represent 95 % expanded uncertainties, $U(x)$. Solid blue squares with red labels represent values withdrawn from statistical consideration; open diamonds with blue labels represent revised values. The thin horizontal gridlines are provided for visual guidance.

Within- and Between-Measurand Comparisons

Comparison of measurement results for two measurands in the same sample can help differentiate systematic measurement system biases from sample-specific issues or measurement imprecision. When systematic biases are dominant, the correlation between pair sets of results should be strongly positive. The square of the correlation coefficient, R^2, directly estimates the fraction of the between-participant covariance that is attributable to the systematic biases. Figure 3 presents Youden-style [2] comparisons for the three between-measurand comparisons.

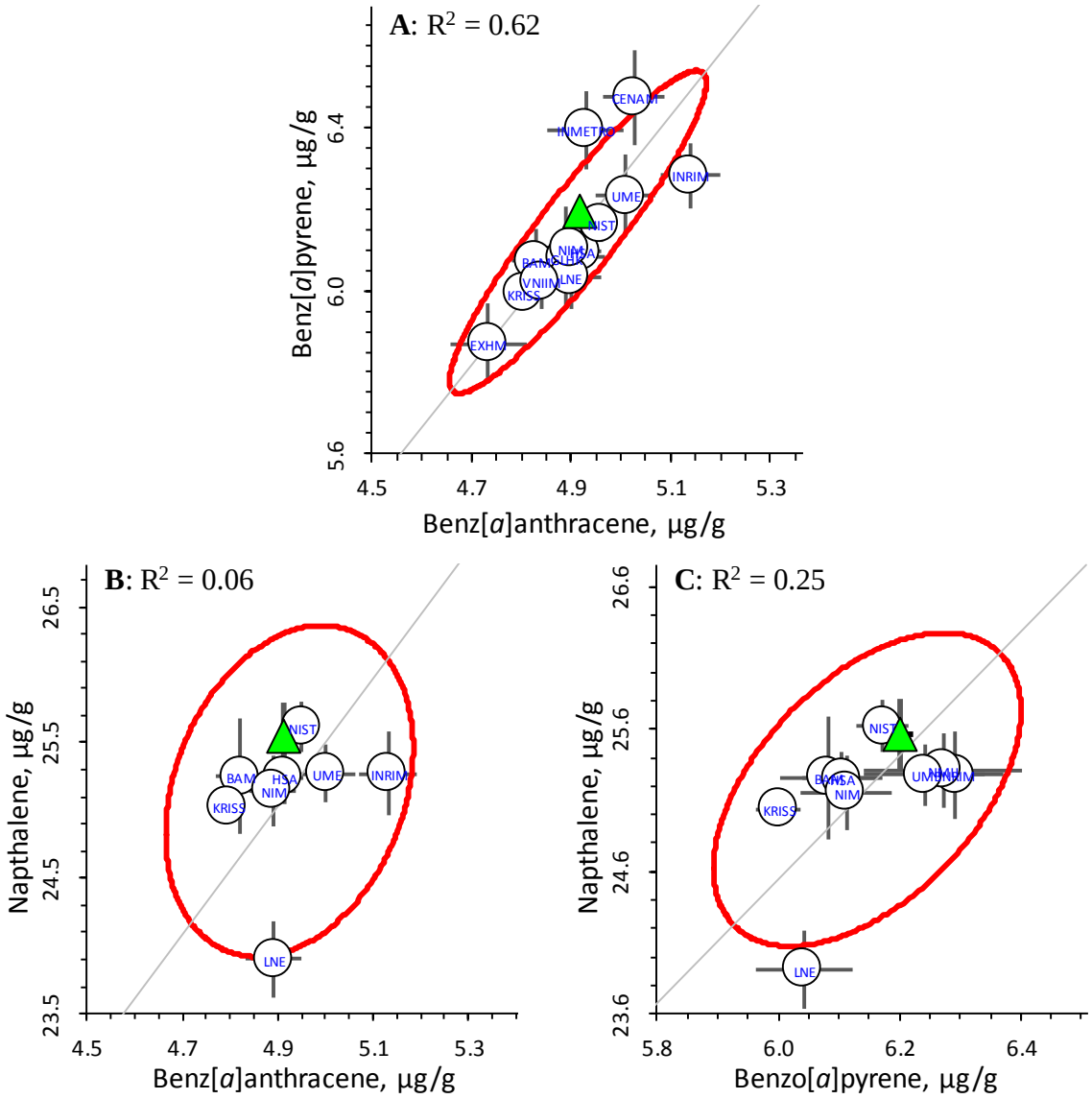


Figure 3: Between-Measurand Comparisons

Each panel displays the bivariate distribution of the reported results for two measurands, excluding the withdrawn results. Panel A displays results for BaA (X-axis) and BaP (Y-axis), B for BaA (X-axis) and Nap (Y-axis), and C for BaP (X-axis) and Nap (Y-axis). Open circles each represent a {measurand-X, measurand-Y} pair of results; bars span $x_i \pm u(x_i)$. The green triangles denote the certified values of SRM 1647a. The ellipses bound approximate 95 % bivariate distributions. The diagonal line marks where the pairs would be expected to lie if the measurements of the two measurands were perfectly correlated; it is provided for visual guidance.

Hypothesis: Origin of Correlation Between BaA and BaP

The majority of the {BaA, BaP} result pairs cluster tightly along the line of perfect correlation, strongly suggestive of a participant-specific measurement bias that impacts both measurands. Figure 4 displays the BaA and BaP results coded by whether the participant assigned the purity of their standard and by analytical method. Neither factor appears to explain the observed bias.

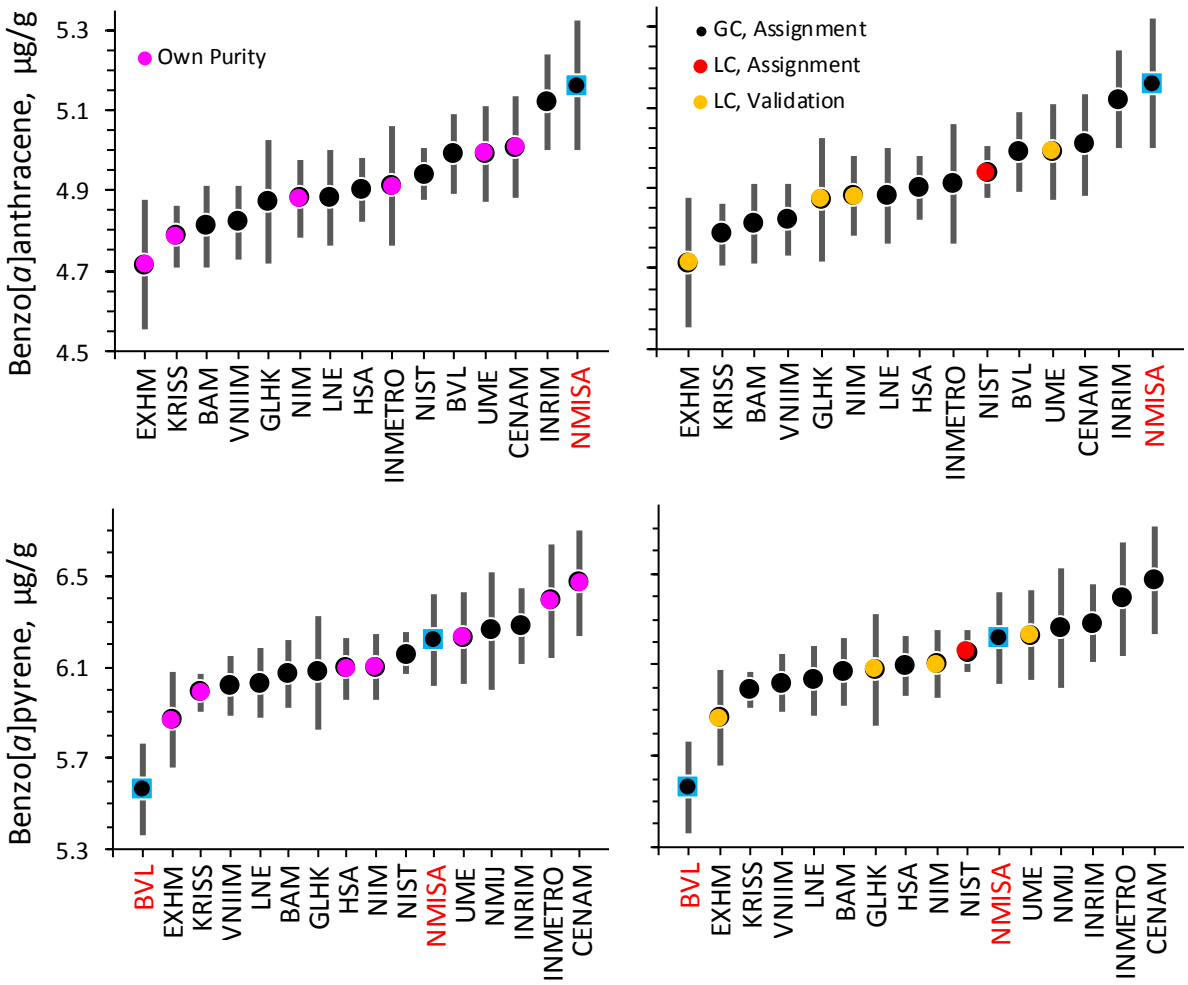


Figure 4: Association of BaA and BaP Values with Purity Assessment, Analytical Method

Symbols represent reported mean values, x, bars represent 95 % expanded uncertainties, $U(x)$. Black dots in the left-hand panels mark results from participants that calibrated with a CRM, magenta dots mark results from participants that determined calibrant purity. Black dots in the right-hand panels mark results determined using gas chromatography (GC), red dots mark results from liquid chromatography (LC), yellow dots mark results validated using LC. The blue squares with red labels represent values withdrawn from statistical consideration.

Table 6 lists other possible bias sources using external calibration. The use of an internal standard (IS) could compensate for some of these biases, depending on when the IS is added.

Table 6: Possible Sources of Bias with External Calibration

Measurement Bias	Summary of Causes
positive bias (true sample concentration is less than assigned value)	**positive measurement biases result from:** 1) *response* of sample is greater than truth a) coeluting interferences in the sample b) evaporation of sample solvent 2) *response* of calibrant is less than truth (Response Factor biased low) a) loss of analyte in calibrant b) analyte volatilizes in calibrant c) overestimate of reference standard purity
negative bias (true sample concentration is greater than assigned value)	**negative measurement biases result from:** 1) *response* of sample is less than truth a) volatile analyte in sample 2) *response* of calibrant is greater than truth (Response Factor biased high) a) concentration of analyte in calibrant b) evaporation of calibrant solvent c) underestimate of reference standard purity d) coeluting interferences in the calibrant

Hypothesis: Origin of Extreme Nap Values

Excluding the two most extreme results, there is no evidence of significant correlation between Nap and either BaA or BaP results. Figure 5 displays the Nap results coded by whether the participant assigned the purity of their standard and by analytical method. INMETRO reports that their withdrawn high value reflects an over-estimated purity.

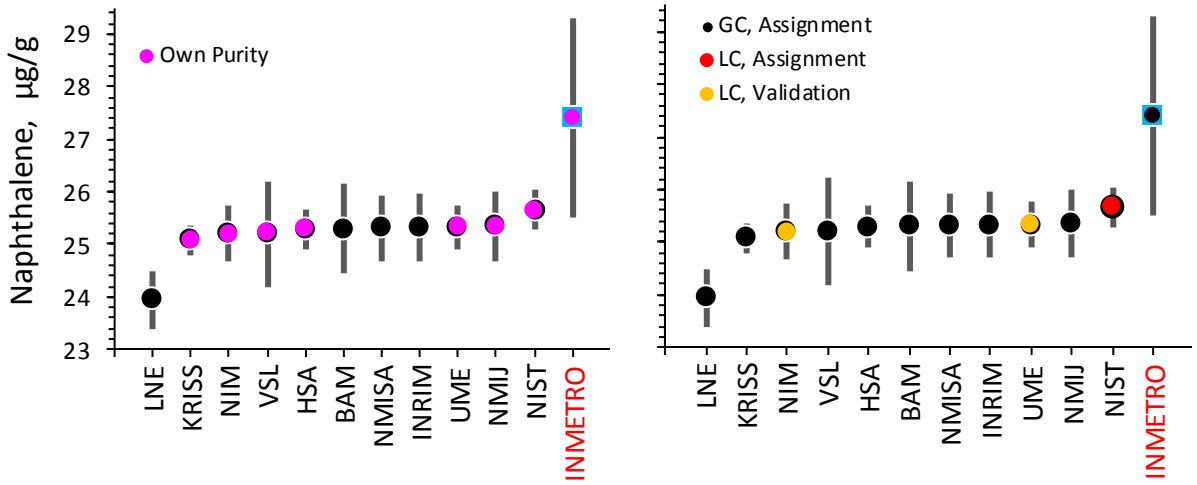


Figure 5: Association of Nap Values with Purity Assessment, Analytical Method

Symbols represent reported mean values, x, bars represent 95 % expanded uncertainties, $U(x)$. Black dots in the left-hand panel marks results from participants that calibrated with a CRM, magenta dots mark results from participants that determined their own calibrant purity values. Black dots in the right-hand panel marks results determined using gas chromatography (GC), red dots mark results from liquid chromatography (LC), yellow dots mark results validated using LC. The blue squares with red labels represent values withdrawn from statistical consideration.

Neither factor appears to explain LNE's result. LNE reviewed their results and found no issue with their method. Given that Nap is much more volatile than BaA and BaP, the low value is compatible with volatile loss in the samples during handling.

Performance Relative to Past Studies

Figure 6 displays CCQM-K131 participant results along with those from previous OAWG assessments of organic measurands in various solvents. In addition to CCQM-K38, these include: CCQM-K39 Determination of Chlorinated Pesticides in Solution [3], CCQM-K40 Determination of PCB Congeners in Solution [4], and CCQM-K49 Volatile Organic Compounds in Methanol [5].

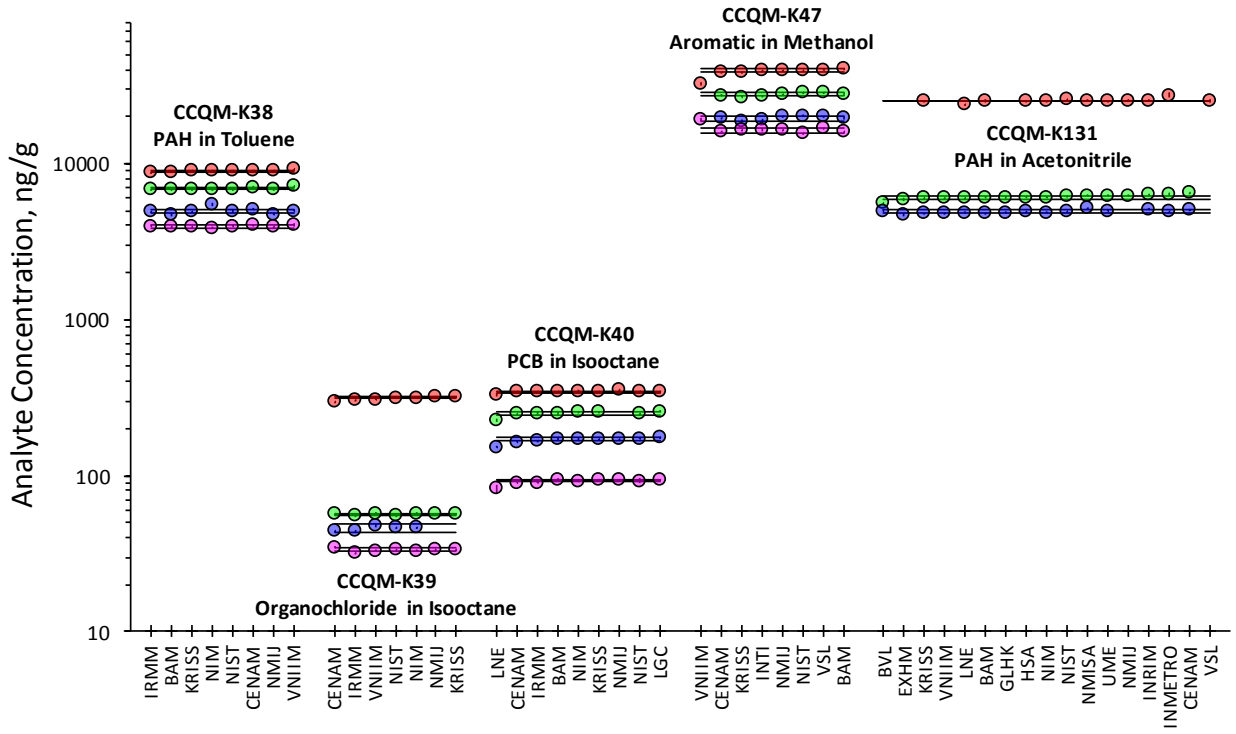


Figure 6: Participant Results in CCQM-K131 and Previous Key Comparisons

Figure 7 displays the standard deviation of the participant results as a function of measurement mean relative to the "Horwitz Curve." The summary estimates exclude the withdrawn BaP and Nap results. The empirical Horwitz function describes the inter-laboratory variability expected for a given mass fraction of an arbitrary analyte in an arbitrary matrix.

The (1.7 to 2.7) % CVs of the three CCQM-K131 measurands agree well with those observed in the previous relevant CCQM studies. Using the robust median and median absolute deviation from the median (MAD_E) estimates of location and dispersion, the best-fit relationship among the 19 available {median, MAD_E} pairs is a CV of 2.6 % for mass fractions from 30 ng/g to 40 µg/g. This suggests that the chemical nature of the analytes (PAH, organochloride, and aromatic) and their solvent matrix (toluene, isooctane, methanol, and acetonitrile) used in these studies has had little or no effect on the variability of the measurement processes.

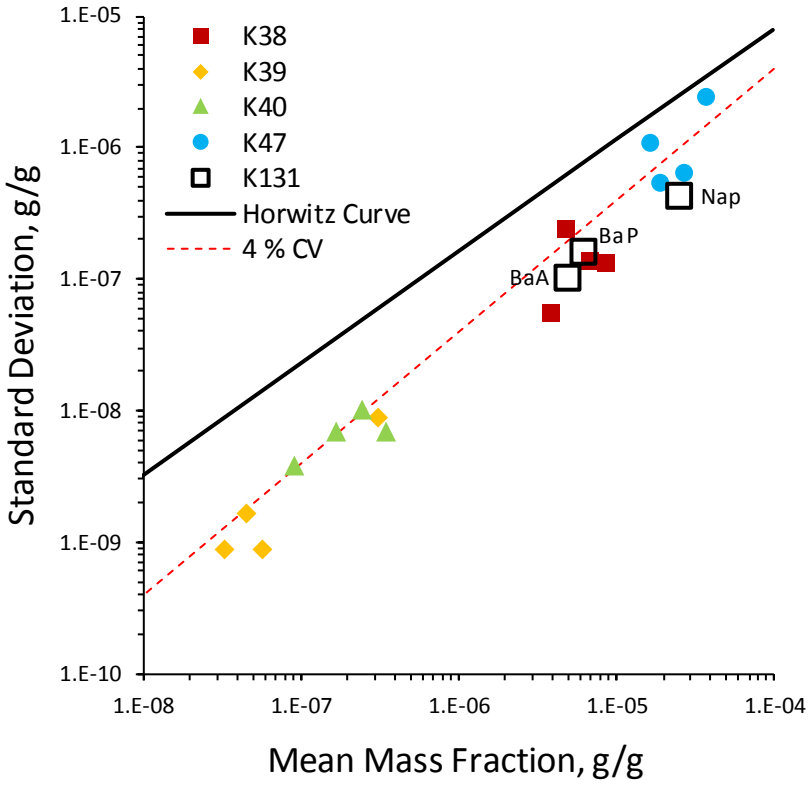


Figure 7: Summary Performance Relative to the Horwitz Curve

KEY COMPARISON REFERENCE VALUE (KCRV)

The reported BaA and BaP values do not agree within their stated uncertainties, implying that there is significant unexplained between-participant variance. This over-dispersion has been termed "excess variance" or "dark uncertainty" [6,7]. For both BaA and BaP, all of the confirmed values appear to be drawn from rectangularly distributed (uniform) populations; that is, they are unimodal with a fairly constant probability over the range. For such data, use of robust estimators of location and dispersion such as the median and adjusted median absolute deviation from the median (MAD_E) is inefficient [6]. However, one or potentially two of the reported values for Nap are separated from the other values. For such potentially multi-modal data, robust estimators may be appropriate.

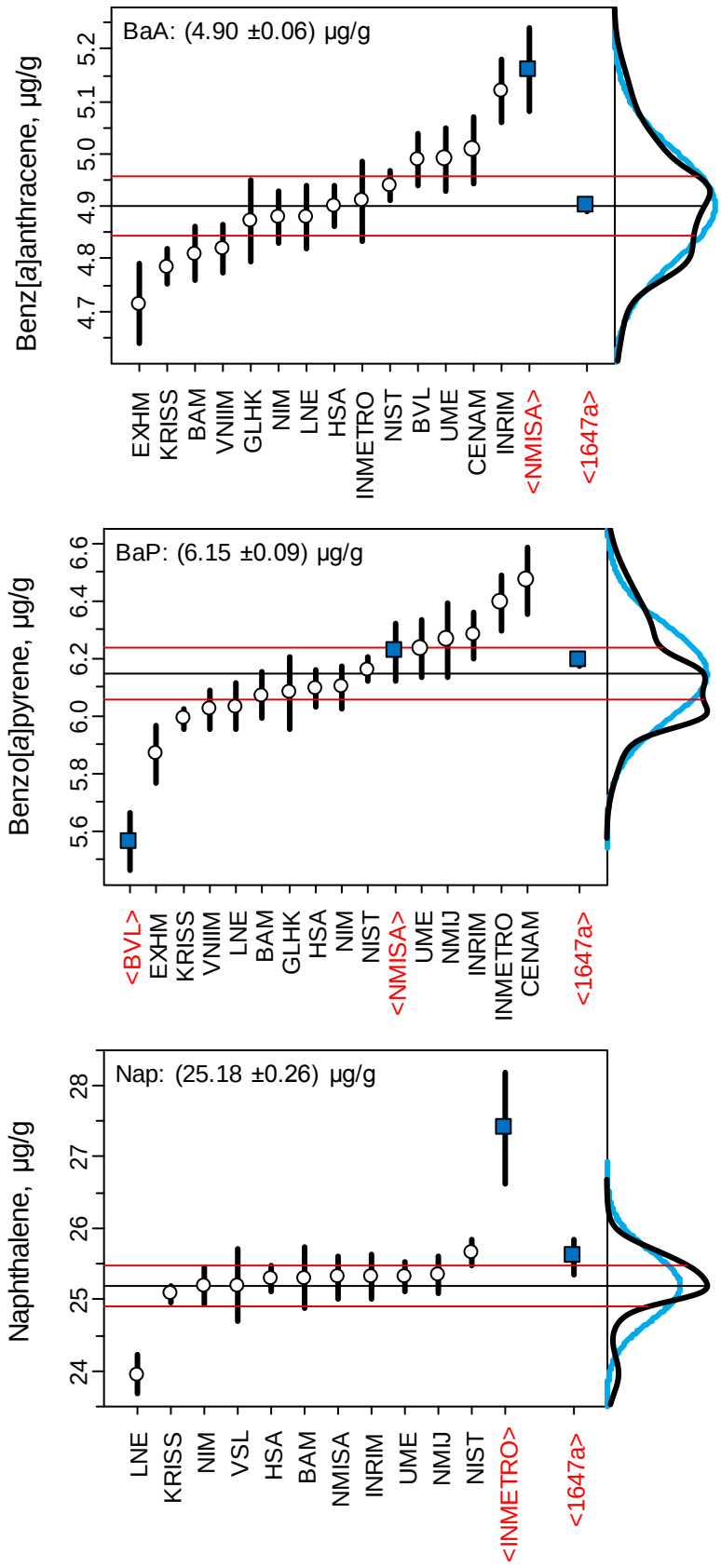
There is therefore no clear choice about which estimators are most appropriate to use as Key Comparison Reference values (KCRV) and associated uncertainties for the CCQM-K131 measurands. Table 7 lists candidate KCRV values, X, standard uncertainties, $u(X)$, and 95 % expanded uncertainties, $U_{95}(X)$, for the following plausible choices: the equally-weighted arithmetic mean and standard deviation of the mean (Mean), the robust median and MAD_E of the median (Median), the DerSimonian-Laird variance-weighted mean (DL-Mean), and hierarchical Bayesian analysis (Bayes) [8]. The Mean and Median do not use reported measurement uncertainties in any way. The DL-Mean and Bayes estimators use the reported uncertainties, albeit in different ways. The Mean, Median, and DL-Mean summaries were calculated using relevant equations in [6]; the Bayes summary was calculated using the NIST Consensus Builder (NICOB) [9].

Table 7: Candidate KCRVs for the CCQM-K131 Measurands

		BaA, µg/g			BaP, µg/g			Nap, µg/g		
Estimator	***u*?**[a]	X	$u(X)$	$U_{95}(X)$	X	$u(X)$	$U_{95}(X)$	X	$u(X)$	$U_{95}(X)$
Mean[b]	No	4.901	0.028	0.060[c]	6.146	0.044	0.095[c]	25.18	0.13	0.29[c]
Median[b]	No	4.891	0.038	0.081[c]	6.095	0.045	0.097[c]	25.30	0.03	0.06[c]
DL-Mean[b]	Yes	4.901	0.027	0.058[c]	6.131	0.039	0.085[c]	25.19	0.13	0.29[c]
Bayes[d]	Yes	4.901	0.028	0.056[e]	6.132	0.042	0.084[e]	25.19	0.12	0.24[e]

a) Does the estimator utilize the information in the reported uncertainties?
b) Estimated using equations in [6]
c) $U_{95}(X) = t_s \cdot u(X)$, where t_s is the appropriate two-tailed Student's t critical value for 95 % coverage.
d) Estimated using NICOB [9]
e) $U_{95}(X)$ estimated as one-half of the estimate's 95 % credible interval.

At Fall 2017 meeting in Ottawa, Canada, the OAWG agreed to use the DL-Mean for the three measurands. Figure 8 displays the DL-Mean values and uncertainties for BaA, BaP, and Nap.



These panels display the Key Comparison Reference Values (KCRVs) relative to the reported results for Benz[*a*]anthracene (BaA), Benzo[*a*]pyrene (BaP), and Naphthalene (Nap). Participant results are sorted by increasing reported value. The symbols represent the reported mean values, x; bars their standard uncertainties, $u(x)$. The solid blue squares with red labels represent values that were not used in estimating the KCRV. The value labeled <1647a> represents the value assigned by NIST to this material in 1988.

The black horizontal line in each panel denotes the KCRV for that measurand. The bracketing red lines denote the approximate 95 % level of confidence interval about the KCRV. The black curve along the right edge of each multiple is the empirical probability density function for the reported values. The blue curve along the right edge represents the probability density function for a normal distribution having mean KCRV and standard deviation U_{95}(KCRV)/2.

Figure 8: Key Comparison Reference Values for BaA, BaP, and Nap

DEGREES OF EQUIVALENCE (DoE)

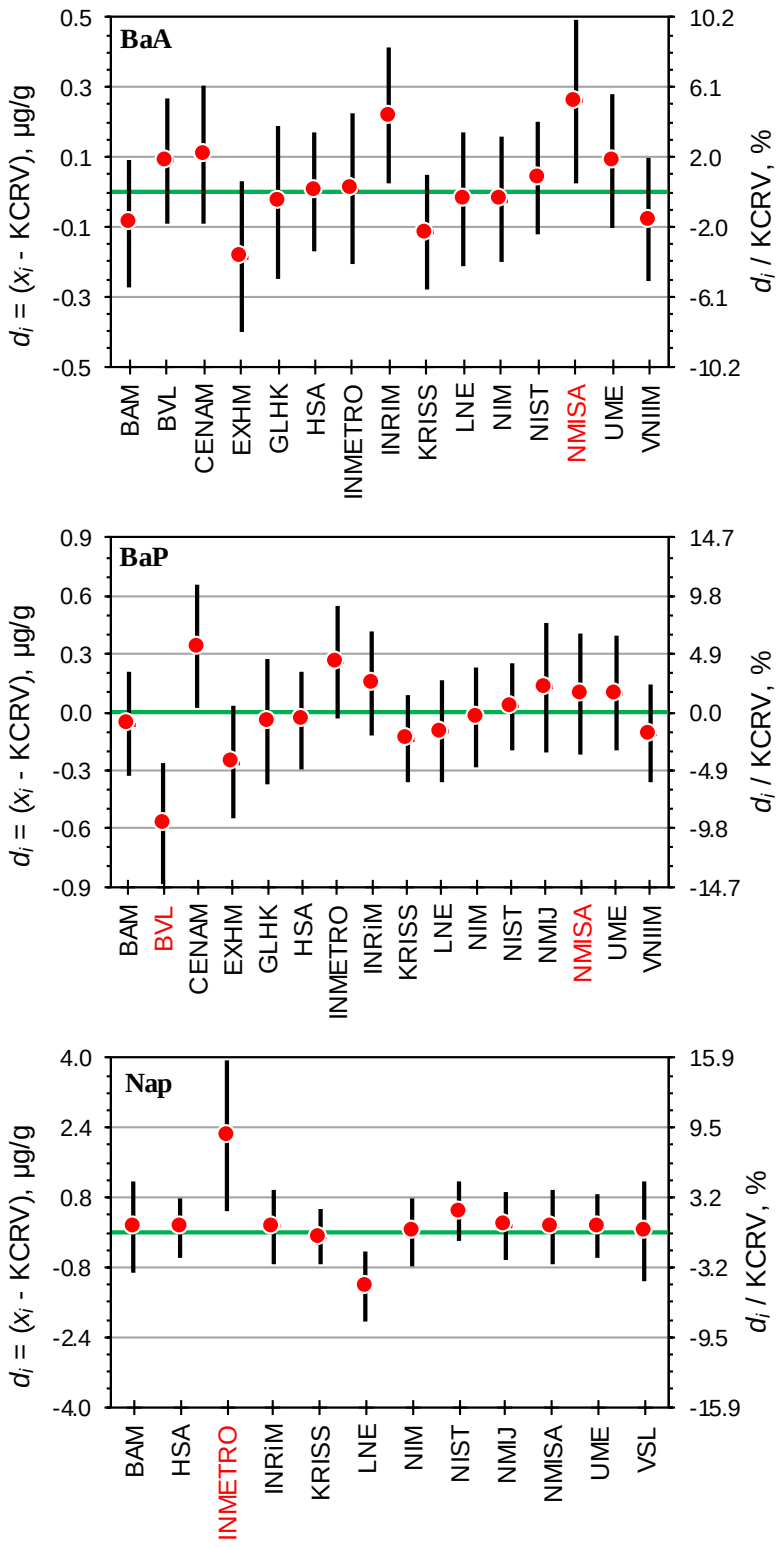
The absolute degrees of equivalence (DoE) for the participants in CCQM-K131 are estimated as the signed difference between the combined value and the KCRV: $d_i = x_i - \text{KCRV}$. Since the KCRV is estimated from consensus of all results, the nominal k=2 expanded uncertainty on the d_i, $U_{k=2}(d_i)$, is estimated as twice the square root of the sum of the squares of the standard uncertainties of the two components minus twice the covariance between the x_i and the KCRV:

$$U_{k=2}(d_i) = 2\sqrt{u^2(x_i) + u^2(\text{KCRV}) - 2\text{cov}(x_i, \text{KCRV})}.$$

To enable comparison with the DoE estimates from other studies, it is convenient to also express the d_i and $U_{k=2}(d_i)$ as percentages relative to the KCRV: $\%d_i = 100 \cdot d_i/\text{KCRV}$ and $U_{k=2}(\%d_i) = 100 \cdot U_{k=2}(d_i)/\text{KCRV}$. Table 8 lists the numeric values of d_i, $U_{k=2}(d_i)$, $\%d_i$, and $U_{k=2}(\%d_i)$ for BaA, BaP, and Nap. Figure 9 displays the estimated DoE for the three CCQM-K131 measurands relative to the DL-Mean KCRVs. Each panel displays both the absolute $d_i \pm U_{k=2}(d_i)$ and relative $\%d_i \pm U_{k=2}(\%d_i)$.

Table 8: Degrees of Equivalence

	Benz[*a*]anthracene (BaA)				Benzo[*a*]pyrene (BaP)				Naphthalene (Nap)			
	µg/g		%		µg/g		%		µg/g		%	
NMI/DI	***d***	***U*$_{k=2}$(*d*)**	***%d***	***U*$_{k=2}$(*%d*)**	***d***	***U*$_{k=2}$(*d*)**	***%d***	***U*$_{k=2}$(*%d*)**	***d***	***U*$_{k=2}$(*d*)**	***%d***	***U*$_{k=2}$(*%d*)**
BAM	-0.09	0.18	-1.9	3.7	-0.06	0.27	-1.0	4.3	0.11	1.03	0.4	4.1
BVL	0.09	0.18	1.8	3.7	-0.57	0.31	-9.3	5.1				
CENAM	0.11	0.20	2.2	4.0	0.34	0.32	5.5	5.2				
EXHM	-0.19	0.22	-3.8	4.4	-0.26	0.29	-4.3	4.8				
GLHK	-0.03	0.22	-0.6	4.4	-0.05	0.32	-0.8	5.2				
HSA	0.00	0.17	0.0	3.5	-0.04	0.25	-0.7	4.1	0.10	0.69	0.4	2.8
INMETRO	0.01	0.22	0.2	4.4	0.26	0.29	4.2	4.7	2.21	1.72	8.8	6.8
INRIM	0.22	0.19	4.5	4.0	0.15	0.27	2.4	4.3	0.13	0.85	0.5	3.4
KRISS	-0.12	0.17	-2.4	3.4	-0.14	0.23	-2.3	3.7	-0.11	0.62	-0.4	2.5
LNE	-0.02	0.19	-0.4	4.0	-0.10	0.27	-1.7	4.3	-1.24	0.80	-4.9	3.2
NIM	-0.02	0.18	-0.4	3.7	-0.03	0.26	-0.5	4.2	0.00	0.79	0.0	3.1
NIST	0.04	0.16	0.8	3.3	0.03	0.23	0.5	3.7	0.47	0.68	1.9	2.7
NMIJ					0.13	0.34	2.1	5.5	0.16	0.78	0.6	3.1
NMISA	0.26	0.23	5.3	4.8	0.09	0.31	1.4	5.1	0.12	0.83	0.5	3.3
UME	0.09	0.19	1.8	4.0	0.10	0.29	1.6	4.8	0.13	0.72	0.5	2.9
VNIIM	-0.08	0.18	-1.7	3.6	-0.11	0.25	-1.8	4.1				
VSL									0.01	1.15	0.0	4.6



These panels display the Degrees of Equivalence (DoE) for Benz[a]anthracene (BaA), Benzo[a]pyrene (BaP), and Naphthalene (Nap) basing the KCRV on the DerSimonian-Laird variance-weighted mean (DL-Mean). Results are sorted alphabetically by participant acronym. Dots represent the DoE, bars their approximate 95 % expanded uncertainties, U_{95}(DoE). Values with red labels are estimated from values that were not used in estimating the KCRV.

The axis to the left edge of each panel displays the absolute DoE, *d*, in units of µg/g. The axis to the right edge displays the relative DoE, %*d* = 100×*d*/KCRV, as percent. The thick green horizontal line denotes perfect agreement with the KCRV.

Figure 9: Degrees of Equivalence for BaA, BaP, and Nap

Degrees of Equivalence for Participants

All but one of the participants in CCQM-K131 reported results on more than one measurand. For these participants a combined relative DoE, %D, can be estimated from the relative degrees of equivalence, %d_i, of the measurands they reported using the NICOB "Linear Pool" estimator [9]. This estimator models each %d_i as a N(%d_i, u^2(%d_i)) normal (Gaussian) distribution and combines them into a single distribution.

Table 9 lists the %D values for the 16 participants that reported results for more than one measurand. The composite distributions are not necessarily unimodal or symmetric, so are best characterized using their (2.5, 50, and 97.5) % percentiles: $D_{2.5\%}$, $D_{50\%}$, and $D_{97.5\%}$. The median, $D_{50\%}$, is a robust estimate for the participant DoE; the interval from $D_{2.5\%}$ to $D_{97.5\%}$ is its 95 % uncertainty interval. If a symmetric 95 % expanded uncertainty for %D is required, a conservative estimate is

$$U_{95}(\%D) = \mathrm{MAX}(D_{50\%} - D_{2.5\%}, D_{97.5\%} - D_{50\%})$$

where "MAX" is the function "return the maximum of the two values." Figure 14 displays the %D and 95 % uncertainty interval for each participant.

Table 9: Composite Relative Degrees of Equivalence, %D

NMI/DI	$\%D_{2.5\%}$	$\%D_{50\%}$	$\%D_{97.5\%}$	$U_{95}(\%D)$
BAM	-5.0	-0.8	3.7	4.5
BVL	-13.4	-2.8	4.9	10.6
CENAM	-1.2	3.7	9.8	6.1
EXHM	-8.6	-4.1	0.4	4.6
GLHK	-5.5	-0.7	4.0	4.8
HSA	-3.8	0.0	3.3	3.8
INMETRO	-3.1	4.0	13.6	9.6
INRIM	-2.1	2.4	7.5	5.1
KRISS	-5.6	-1.6	1.6	4.0
LNE	-7.3	-2.3	2.8	5.0
NIM	-4.2	-0.3	3.5	3.9
NIST	-2.5	1.1	4.3	3.7
NMIJ	-2.8	1.2	6.7	5.5
NMISA	-2.7	2.0	8.7	6.7
UME	-2.4	1.2	5.6	4.4
VNIIM	-5.5	-1.7	2.1	3.8

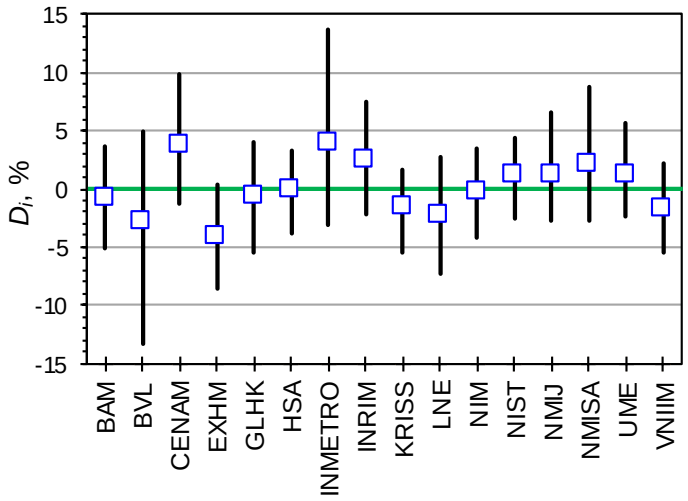


Figure 10: Composite Relative Degrees of Equivalence for Participants

The open squares represent the relative Degrees of Equivalence, %D, for each participant, estimated from the composite distribution of the relative DoE, %d = 100×d/KCRV, for the measurands reported by the participant. The bars span the central 95 % of the composite distribution. Results are sorted alphabetically by participant acronym.

USE OF CCQM-K131 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines

Successful participation in CCQM-K131 demonstrates the following measurement capabilities in determining mass fraction of organic compounds of moderate to insignificant volatility, molar mass of 100 g/mol up to 500 g/mol, and polarity $pK_{ow} < -2$ in a multicomponent organic solution ranging in mass fraction from 100 ng/g to 100 µg/g.

1) value assignment of primary reference standards (if in-house purity assessment carried out),
2) value assignment of single and/or multi-component organic solutions,
3) separation and quantification using gas or liquid chromatographic analytical systems.

Core Competency Statements

Tables 10a to 10q list the Core Competencies claimed by the participants in CCQM-K131. The information in these Tables is as provided by the participants; however, the presentation of many entries has been condensed and standardized. Details of the analytical methods used by each participant in this study are provided in Appendix F.

CCQM is considering the application of "broader-scope" Calibration and Measurement Capabilities (CMCs). Appendix I presents a prototype "broader-scope" CMC that could be claimed on the basis of successful participation in CCQM-K131 and relevant previous CCQM Key Comparisons.

Table 10a: Core Competencies Demonstrated in CCQM-K131 by BAM

CCQM-K131	***BAM***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information as Provided by *BAM***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	Calibration solution NIST SRM 1647f Priority PAHs in Acetonitrile
Identity verification of analyte(s) in calibration material	✓	GC-MS, retention time and mass spectra
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	N/A	
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	GC-MS, retention time and mass spectra
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) internal standard (deuterated or ^{13}C labelled) b) 5-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample	N/A	
Other	N/A	

Table 10b: Core Competencies Demonstrated in CCQM-K131 by BVL

CCQM-K131	***BVL***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Calibration solution PAH in toluene, NIST standard reference material 2260a
Identity verification of analyte(s) in calibration material	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	N/A	
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Chromatographic retention time, mass ratio
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	×	GC-HRMS
Calibration approach for value-assignment of analyte(s) in matrix	×	a) isotopic dilution mass spectrometry b) 4-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample	N/A	
Other	N/A	

The BVL result for BaP is not consistent with the KCRV for that measurand and yields a DoE that does not cross zero. Since no specific cause could be identified, the inconsistency could arise from the analytical system and/or the calibration approach.

Table 10c: Core Competencies Demonstrated in CCQM-K131 by CENAM

CCQM-K131	***CENAM***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Highly pure substances: BaA, Supelco; BaP, Ultrascientific
Identity verification of analyte(s) in calibration material	✓	GC-MS/MS: ions 228.1-226.1 for BaA, retention time to separate of Chrysene; ions 252.1-250.1 for BaP.
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	Mass Balance For organic impurities; GC FID with two columns, 5 % phenyl polysyloxane and 50 % phenyl polysyloxane. For water content Karl Fischer titration Value assignment: BaA: (986.8 ± 1.2) mg/g BaP: (981.2 ± 7.6) mg/g
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time and MRM ion pairs ions 228.1-226.1 for BaA, retention time to separate of Chrysene; ions 252.1-250.1 for BaP.
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS/MS
Calibration approach for value-assignment of analyte(s) in matrix	×	IDMS single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample	✓	SRM 1647c was used as control RM, mainly to approach the target value.
Other		

The CENAM result for BaP is not consistent with the KCRV for that measurand and yields a DoE that does not cross zero. This inconsistentcy has been traced to a procedural oversight in the preparation of a calibration solution.

Table 10d: Core Competencies Demonstrated in CCQM-K131 by EXHM

CCQM-K131	***EXHM***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		calibration solution: NIST SRM 1647f calibrants: "pure" BaA & BaP
Identity verification of analyte(s) in calibration material	✓	GC-IT-MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	qNMR used to assess purity of in-house calibrants; but calibrants value-assigned against NIST SRM 1647f
For calibrants which are a calibration solution: Value-assignment method(s)	✓	Used values from NIST calibration certificate confirmed against in-house calibrants
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	GC-IT-MS (retention time, mass spec ion ratios)
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-IT-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	IDMS single-point (exact matching)
Verification method(s) for value-assignment of analyte(s) in sample	✓	HPLC-FLD – external standard
Other	✓	HPLC-FLD – external standard

Table 10e: Core Competencies Demonstrated in CCQM-K131 by GLHK

CCQM-K131	***GLHK***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Calibration solution from NIST (NIST SRM 1647f)
Identity verification of analyte(s) in calibration material	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	N/A	
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	1) HPLC-UV, identification by a) chromatographic retention times with authentic standards and b) Specific absorption wavelengths 2) GC-MS, identification by a) chromatographic retention time and b) molecular weight of the fragment
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	1) HPLC-UV 2) GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	1) HPLC-UV, quantification by external standardization and calibration by bracketing technique 2) GC-MS, quantification by IDMS and calibration using exact matching technique
Verification method(s) for value-assignment of analyte(s) in sample	✓	Results of HPLC-UV and GC-MS are compared and verified with each other.
Other	N/A	

Table 10f: Core Competencies Demonstrated in CCQM-K131 by HSA

CCQM-K131	***HSA***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓,×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		BaA: BCR-271, IRMM BaP: Cerilliant SCB-007 Nap: Sigma-Aldrich 84679
Identity verification of analyte(s) in calibration material	✓	Comparison with SRM 1647f using: 1) retention time and m/z ratio on the GC-MS, 2) retention time on HPLC at λ = 254 nm
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	BaP and Nap: determined in-house by mass balance. BaA: Verified with NIST SRM 1647f.
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention times, SIM mode with one ion on GC-MS.
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	Agilent 7890A/5975C GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	Single-point, exact-matching IDMS
Verification method(s) for value-assignment of analyte(s) in sample	✓	NIST SRM 1647f analyzed in parallel with each sample solution for quality control (QC). QC results were all within the expanded uncertainty of the certified values for BaA, BaP, and Nap
Other	N/A	

Table 10g: Core Competencies Demonstrated in CCQM-K131 by INMETRO

CCQM-K131	***INMETRO***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Pure materials assessed in house by qNMR: Nap: Fluka, (0.887 ± 0.017) g/g BaA: Aldrich, (0.9871 ± 0.0099) g/g BaP: Supelco, (0.9241 ± 0.0078) g/g
Identity verification of analyte(s) in calibration material	✓	GC-MS, NMR
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	×	Analyte mass fraction/purity of pure standards were established by qNMR and cross-checked by mass balance
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time, mass spectrum
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) Quantification mode used: IDMS b) Calibration mode used: six-point calibration curve, using isotopically labelled analog compounds as internal standards
Verification method(s) for value-assignment of analyte(s) in sample	N/A	
Other	N/A	

The INMETRO result for Nap is not consistent with the KCRV for that measurand and yields a DoE that does not cross zero. The inconsistency was determined to arise from the purity assessment procedure used, which has since been revised.

Table 10h: Core Competencies Demonstrated in CCQM-K131 by INRiM

CCQM-K131	***INRiM***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Calibration solutions were used: NIST SRM 2260a to prepare standard solutions for the quantification of the analytes; NIST SRM 2269 for BaA-d_{12} used as Internal Standard; NIST SRM 2270 for Nap-d_8 and BaP-d_{12} used as Internal Standards
Identity verification of analyte(s) in calibration material	✓	GC-MS in full scan mode
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	N/A	
For calibrants which are a calibration solution: Value-assignment method(s)	✓	By gravimetric dilution of NIST SRM 2260a
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time and molecular ion
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	×	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) Quantification mode: external standard plus perdeuterated PAHs as internal standards both in the sample and in the calibration solutions b) Calibration mode: single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample	N/A	
Other	N/A	

The INRiM result for BaA is not consistent with the KCRV for that measurand and yields a DoE that does not cross zero. On review, INRiM determined that their chromatographic separation of BaA was incomplete and affected by coelution.

Table 10i: Core Competencies Demonstrated in CCQM-K131 by KRISS

CCQM-K131	***KRISS***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Neat commercial calibrants for Nap (Fluka), BaA (BCR), BaP (SUPELCO). Purities of three compounds were assayed by KRISS with mass-balance method.
Identity verification of analyte(s) in calibration material	✓	GC-MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	GC-FID for structurally related impurities, Karl-Fischer coulometry for water, thermogravimetric analysis for non-volatiles, headspace-GC-MS for residual solvents.
For calibrants which are a calibration solution: Value-assignment method(s)	✓	Calibration solutions were gravimetrically prepared in KRISS and verified by cross-checking of multiple calibration solutions. Secondary confirmation by comparison with NIST SRM 1647f
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	GC retention time, mass spec ion ratios, comparison of GC-MS measurement results by low resolution SIM
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS (low resolution) in SIM mode, split injection
Calibration approach for value-assignment of analyte(s) in matrix	✓	IDMS with exact matching single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample	✓	NIST SRM 1647f
Other	N/A	

Table 10j: Core Competencies Demonstrated in CCQM-K131 by LNE

CCQM-K131	***LNE***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Calibration solution: NIST SRM 1647
Identity verification of analyte(s) in calibration material	✓	Retention time, mass spectrum, abundance of characteristic ions, comparison with the bibliography, comparison with NIST mass spectral library
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	N/A	
For calibrants which are a calibration solution: Value-assignment method(s)	✓	NIST SRM 1647
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time, specific ions
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system: non-volatiles	✓	GC-MS
Analytical system: semi-volatiles	×	
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) Quantification mode used: IDMS b) Calibration mode used: 5-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample	N/A	
Other	N/A	

The LNE result for Nap is not consistent with the KCRV for that measurand and yields a DoE that does not cross zero. The DoE for BaA and BaP are consistent with their KCRVs. This is compatible with the analytical system being sensitive to analyte volatility.

Table 10k: Core Competencies Demonstrated in CCQM-K131 by NIM

CCQM-K131	***NIM***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Highly-pure substance was used. BaA & BaP: Cerilliant NAP AccuStandard.
Identity verification of analyte(s) in calibration material	✓	GC-MS, NMR
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	GC-FID, HPLC-DAD, NMR
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Comparison of retention time in HPLC-DAD analysis of each analyte in sample with that in calibration solution
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	HPLC-DAD and GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) BaA-d_{12} & BaA-d_{12} used as internal standards for BaA and BaP, respectively. External standard method was used for value-assignment of Nap. b) Single-point calibration was used for all three analytes.
Verification method(s) for value-assignment of analyte(s) in sample	✓	GC-IDMS method and external standard method by HPLC-DAD was used for BaA & BaP as verification method. GC-IDMS method and internal standard method were used for Nap as verification method. SRM 1647f was used as a control sample.
Other	N/A	

Table 10l: Core Competencies Demonstrated in CCQM-K131 by NIST

CCQM-K131	***NIST***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Calibration solutions were gravimetrically prepared from highly-pure substances.
Identity verification of analyte(s) in calibration material	✓	Nap: pure material; Fluka lot 2366751182 BaA: pure material; BCR-271; vial 110 BaP: pure material; BCR-51; vial 44
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	Nap & BaP: qNMR and DSC BaA: DSC
For calibrants which are a calibration solution: Value-assignment method(s)	✓	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Identification by liquid chromatography retention time comparison with SRM 1647f
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	LC-absorbance; detection at 254 nm
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) quantification mode: external standard b) calibration mode: 3-point calibration with averaged response factors
Verification method(s) for value-assignment of analyte(s) in sample	✓	SRM 1647f used as a control sample
Other	N/A	

Table 10m: Core Competencies Demonstrated in CCQM-K131 by NMIJ

CCQM-K131	***NMIJ***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Pure material for naphthalene and calibration solution (NMIJ CRM 4213-a) for BaP
Identity verification of analyte(s) in calibration material	✓	Retention time in GC-FID and retention time with mass spectra in GC-MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	Purity assessment by qNMR and GC-FID
For calibrants which are a calibration solution: Value-assignment method(s)	✓	Gravimetric preparation
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time and mass spectra
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-FID and GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) IDMS (Nap-d_8 and BaP-d_{12}) b) single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample	✓	LC-UV and another GC-FID using self-made calibration solution (prepared from qNMR assessed neat Nap and BaP) and SRM1647f
Other	N/A	

Table 10n: Core Competencies Demonstrated in CCQM-K131 by NMISA

CCQM-K131	***NMISA***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		NIST SRM 1647f
Identity verification of analyte(s) in calibration material	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	N/A	
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time; mass spectrum ion ratios and diode array detector spectrum relative to NIST SRM 1647f
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	✓	Gravimetric dilution
Analytical system	✓	GC-TOFMS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) Quantification mode: double IDMS; internal standard and external standard Deuterated PAH and NIST 1647f respectively b) Calibration mode used (single-point calibration, multi-point calibration and bracketing)
Verification method(s) for value-assignment of analyte(s) in sample	✓	LC-DAD using a Waters PAH column and ACN/water mobile phase
Other	N/A	

The NMISA result for BaA is not consistent with the KCRV for that measurand and yields a DoE that does not cross zero. This inconsistentcy arose from a transcriptional error and not any of the competencies listed above.

Table 10o: Core Competencies Demonstrated in CCQM-K131 by UME

CCQM-K131	***UME***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		Highly pure substances BaA: Supelco 4-8563, BaP: Supelco 4-8564 Nap: Fluka 8467 used with in-house purity assessment.
Identity verification of analyte(s) in calibration material	✓	GCMS/MS Retention time, Parent/ Product Ion, NIST Mass Spectral Library
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	Purity assessment of pure substances were established by qNMR, traceability through UME CRM 1301 Chloramphenicol Primary Calibrant
For calibrants which are a calibration solution: Value-assignment method(s)	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Comparison of retention time, Parent/ Product Ions of each analyte in GC-MS/MS and LC/MS analysis.
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS/MS and LC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) Quantification mode used: IDMS b) Calibration mode used :6-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample	✓	GC-MS/MS was used for value assignment. LC-MS was used for confirmation.
Other	N/A	

Table 10p: Core Competencies Demonstrated in CCQM-K131 by VNIIM

CCQM-K131	***VNIIM***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**
Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.		
Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		NIST SRM 1647f
Identity verification of analyte(s) in calibration material	✓	Retention time Full mass spectrum
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)		
For calibrants which are a calibration solution: Value-assignment method(s)	✓	In accordance with Certificate of Analysis SRM 1647f
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time Full mass spectrum
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	✓	a) IDMS b) Single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample	N/A	
Other	N/A	

Table 10q: Core Competencies Demonstrated in CCQM-K131 by VSL

CCQM-K131	***VSL***	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**

Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.

Competency	**✓, ×, or N/A**	**Specific Information**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	Naphthalene (99.9 %) Sigma-Aldrich, MKBT5870V Acetonitrile (99.99 %) Sigma-Aldrich, STBF8730V
Identity verification of analyte(s) in calibration material	✓	GC-MS: mass spectrum and retention time
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s)	✓	Purity: Mass balance *Acetonitrile*; GC-MS and GC-FID for structurally related impurities and naphthalene. Residue on evaporation for solids. *Naphthalene*; GC-MS and GC-FID for structurally related impurities and acetonitrile. Both: Karl-Fischer Coulometry (oven method) for water content
For calibrants which are a calibration solution: Value-assignment method(s)	✓	Calibration solutions were gravimetrically prepared by VSL using the value-assigned pure materials, verified by cross-checking of multiple calibration solutions. Secondary confirmation with NIST SRM 1647f
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	GC-MS: Mass spectrum and retention time.
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-MS and GC-FID
Calibration approach for value-assignment of analyte(s) in matrix	✓	External calibration with errors-in-variables regression
Verification method(s) for value-assignment of analyte(s) in sample	✓	SRM 1647f used for quality control
Other	N/A	

CONCLUSIONS

Participants in CCQM-K131 demonstrated their ability to identify and quantify moderate to very low volatility non-polar organic compounds in a multicomponent calibration solution at mass fractions of a few μg/g. Three results were excluded from use in defining the consensus KCRVs for identified cause; one result was withdrawn by the submitter as a suspected technical outlier of unidentified cause. All but two of the remaining 39 reported results agreed with the consensus KCRVs within the combined 95 % expanded uncertainties. The central 50 % of all reported results were within ±1.6 % of the consensus KCRVs with a median 95 % expanded uncertainty of 4.0 %.

The results for the two very low volatility measurands, BaA and BaP, do not agree within their stated uncertainties, appear to be rectangularly distributed, and are highly correlated with each other. This suggests that there are participant-specific biases in the analytical methods used for these measurands. The source(s) of this "dark uncertainty" has not been identified.

With the exception of one modestly low value, the results for the moderately volatile Nap do agree within their stated uncertainties, appear normally distributed, and are not correlated with the BaA and BaP results. This suggests that there were no significant unknown biases in the measurement processes for this measurand.

The (1.7 to 2.7) % CV of the non-excluded results for the three measurands, estimated using the robust median and MAD_E, are typical of the CVs observed in earlier calibration solution KCs. The best-fit relationship among the 19 available {median, MAD_E} pairs is a CV of 2.6 % over mass fractions from 30 ng/g to 40 μg/g.

ACKNOWLEDGEMENTS

The study coordinators thank all of the participating laboratories for providing the requested information during the course of this study.

REFERENCES

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http://www.bipm.org/utils/common/pdf/final_reports/QM/K39/CCQM-K39.pdf

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APPENDIX A: Call for Participation

From: Lindsey.Mackay@measurement.gov.au
Date: Tue, July 21, 2015 8:14 AM -0400

To: [OAWG contact list]

Subject: Comparison protocols for CCQM-K131 and K95.1 (PAHs in solution and tea)

Dear OAWG colleagues

Please find attached the protocols and associated documentation for two upcoming key comparisons. Many thanks to Steve Wise at NIST for providing them and for coordinating these studies.

CCQM-K95.1 is a repeat of the Track A comparison for pesticides in tea, the specific measurand in this case is PAHs in tea. Only laboratories that would like to improve upon their performance in the original CCQM-K95 comparison need to participate.
The second comparison is a Track A comparison for non-polar analytes in organic solutions, in this case the measurand is PAHs in Acetonitrile. All NMIs/DIs with CMCs related to the How Far the Light Shines statement for this Track A comparison would be expected to participate.
Both comparisons will occur in the Sep – Dec 2015 timeframe. Please complete the attached registration forms and return them to stephen.wise@nist.gov by 28 August.

Best regards
Lindsey

Attachments:
CCQM 95_1 Participant Registration form.docx
CCQM K95_ 1 PAH in Mate Tea protocol July2015.docx
K95_1 Core Competency Table .doc
Reporting Form CCQM-K95_1.xlsx
CCQM K131 PAH in Acetonitrile protocol July2015.docx
CCQM K131 Participant Registration.docx
K131 Core Competency Table .doc
Reporting Form CCQM-K131.xlsx

APPENDIX B: Protocol

CCQM-K131 Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile

Key Comparison
Track A

Coordinating Laboratory: NIST
Study Protocol
July 20, 2015

Introduction

CCQM-P31a "Polycyclic Aromatic Hydrocarbons in Solution" was conducted in 2004 using a candidate CRM (now SRM 2260a Polycyclic Aromatic Hydrocarbons in Toluene) containing 35 PAHs. This pilot study was followed with a key comparison, CCQM-K38 PAHs in Solution (Toluene) in 2005, using a solution containing 10 PAHs. In both studies five representative PAHs were measured: phenanthrene, fluoranthene, benz[*a*]anthracene, benzo[*a*]pyrene, and benzo[*ghi*]perylene. Since these studies were conducted over 10 years ago, the OAWG has requested that another study be conducted for determination of nonpolar organic compounds in solution. CCQM-K131 "Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile" will be conducted in 2015 to meet this need. At the October 2014 OAWG meeting, it was recommended that this key comparison be conducted in parallel with K95.1 "Low-Polarity Analytes in a Botanical Matrix: Polycyclic Aromatic Hydrocarbons (PAHs) in Tea" to minimize the duplication of effort between these two studies involving PAH measurements.

Study Material

NIST has produced a number of PAHs in acetonitrile solution SRMs over the past 30 years each containing the 16 PAHs identified as priority pollutants by the U.S. Environmental Protection Agency (EPA). The most recent in this series is SRM 1647f Priority Pollutant Polycyclic Aromatic Hydrocarbons in Acetonitrile issued in September 2014. NIST has available a number of previously prepared and ampouled solutions that were used in the certification of these SRMs. One of these ampouled solution materials would serve as the study material for CCQM-K131. The study material would be 1.2 mL of acetonitrile solution of the 16 PAHs in a sealed amber ampoule.

Measurands

At the October 2014 OAWG meeting, the decision was made to conduct this study in conjunction with K95.1 and to focus on the same two PAHs in this study (K131), i.e., benz[*a*]anthracene and benzo[*a*]pyrene, which represent a four-ring *cata*-condensed PAH of molar mass 228 g/mol and a five-ring *peri*-condensed PAH of molar mass 252 g/mol. At the April 2015 OAWG meeting, there was a request to add a volatile PAH, such as naphthalene, to the list of measurands for K131 to allow laboratories to underpin claims for volatile analytes in organic solutions. Therefore, naphthalene (two-ring *cata*-condensed PAH of molar mass 128 g/mol) was added as an "optional" measurand for laboratories wanting to make claims for volatile organic compounds in an organic solution.

Homogeneity and Stability Assessment
Based on previous experience at NIST with these PAHs in acetonitrile solutions, the test solution is homogeneous. Analysis of the solution by liquid chromatography with UV detection (10 µL injections) provided measurements with less than 1.9 % (SD) for n = 40.

NIST has not performed a formal stability study for this specific PAHs in acetonitrile solution. However, with over 30 years' experience in preparing such PAHs in acetonitrile SRMs, we have not observed any stability issues with these solutions. Therefore, we anticipate that the PAHs would be stable in the solution material during the period of the study.

Methods
Participants are expected to perform measurements by using either gas chromatography (GC) or liquid chromatography (LC). An isotope dilution quantification approach may be used, but is not required for this study. Other approaches involving internal or external standards are acceptable, and the methods should represent the way the NMI delivers this measurement service.

Reference Standards Available
Solution CRMs for the target PAHs for use as calibrants are available from NIST (SRM 2260a Aromatic Hydrocarbons in Toluene) and SRM 1647f Priority Pollutant PAHs in Acetonitrile (both contain benz[*a*]anthracene and benzo[*a*]pyrene), IRMM (ERM-AC213) (contains benz[*a*]anthracene only), and NMIJ (CRM 4213-a) (contains benzo[*a*]pyrene only). A high-purity PAH CRM is available from IRMM for benz[*a*]anthracene (BCR-271). Isotopically-labeled (deuterium or carbon-13) PAHs for use as internal standards, if an isotope dilution approach is used, are commercially available from a number of sources.

Study Guidelines
Each participant will receive four ampoules, each containing 1.2 mL of solution (three ampoules will be required for analysis and an additional ampoule is available for practice and/or screening analysis. Samples can be stored at room temperature.

Participants are requested to report a single estimate of the mass fraction (µg/kg) for each of the two or three target PAHs based on measurements for one subsample from each of three ampoules of the solution (i.e., three independent replicates). Participants may use either GC or LC analysis.

Submission of Results
Each participant must provide results using the reporting sheet provided with the samples including a core competency table. The results should be sent via email to the study coordinator (stephen.wise@nist.gov) before the submission deadline. Submitted results are considered final and no corrections or adjustments of analytical data will be accepted unless approved by the OAWG. The results must include: (1) mass fractions of the each of the two or three PAHs, and (2) the standard and expanded uncertainties with detailed description of the full uncertainty budget. A description of the analytical procedure (GC or LC column; chromatographic conditions, quantification approach) should be provided in the reporting forms. Details should

also be provided concerning calibration and internal standards used with appropriate purity statement and/or laboratory assessment.

How Far Does the Light Shine?

Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity $pK_{ow} < -2$, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.

Time Schedule

This study will be conducted in parallel with K95.1 Low-Polarity Analytes in a Botanical Matrix: Polycyclic Aromatic Hydrocarbons (PAHs) in Tea. Call for participants in K131 will be in August 2015. Samples for K131 and K95.1 would be distributed together in September 2015. The deadline for submission of results would be December 15, 2015. The first discussion of the results would be during the OAWG meeting in Paris in April 2016.

APPENDIX C: Registration Form

Registration Form

CCQM-K131 Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile

ORGANIZATION / DEPARTMENT / LABORATORY

FULL ADDRESS FOR SHIPMENT OF SAMPLES (no PO box)

CONTACT PERSON

E-MAIL AND TELEPHONE

Will you also be participating in CCQM-K95.1 Low-Polarity Analytes in a Botanical Matrix: Polycyclic Aromatic Hydrocarbons (PAHs) in Tea?

Yes ____ No _____

Date _____

Please complete the form and send it back to stephen.wise@nist.gov **before August 28, 2015**.

APPENDIX D: Reporting Form

The original form was distributed as an Excel workbook. The following are pictures of the relevant portions of the workbook's three worksheets.

"Participant Details" worksheet

CCQM-K131

Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile

Data Submission Form

Please complete all pages of the reporting form and submit it by email before December 15, 2015 to:
stephen.wise@nist.gov

Reporting Date	
Institute	
Submitted by (name)	
E-mail address	

"Results" Worksheet

CCQM-K131 RESULTS

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)				
Benz[*a*]anthracene				
Benzo[*a*]pyrene				

"Analytical Information" Worksheet

Information about the analytical procedure

Sample amount used for analysis g

Sample pre-treatment (if applicable)

"Analytical Information" Worksheet (Continued)

Analytical instrumentation used
(e.g., LC, GC, GC-MS, etc.)

Chromatographic Column
(i.e., specify tpe and manufacturer)

Chromatographic Conditions
(e.g., GC temperature program, LC mobile phase and gradient)

Calibration type / details
(e.g., single-point, bracketing /
external calibration, internal standard calibration, IDMS)

Calibration standards
(e.g., source, purity, and traceability of standards)

Internal standards used (if applicable)
(Please specify the compounds, sourse, and at which stage of
the analysis were the internal standards added)

"Analytical Information" Worksheet (Continued)

Purity assessment of the calibrant (if applicable) (e.g. methods used for value assignment/verification)	
Estimation of impurities (if applicable) (e.g. type of impurity, mass fraction, uncertainty)	
Indicate ion/MRM monitored in Mass Spectrometer (if applicable)	
Measurement equation and uncertainty budget (please include breakdown of the budget, describing individual uncertainty contributions and how they were combined)	
Additional Comments or Observations	

APPENDIX E: Core Competency Table Form

CCQM OAWG: Competency Template for Analyte(s) in Matrix

CCQM-K131	*NMI*	**Low-Polarity Analytes in a Multicomponent Organic Solution: Polycyclic Aromatic Hydrocarbons (PAHs) in Acetonitrile**

Scope of Measurement: Participation in this Track A study "Low-Polarity Analytes in a Multicomponent Organic Solution is intended to demonstrate the following measurement capabilities: (1) value assignment of primary reference standards (if in-house purity assessment carried out); (2) value assignment of single and/or multi-component organic solutions; (3) separation and quantification using gas chromatography or liquid chromatography. This study would demonstrate the laboratory's capabilities in determining mass fraction of organic compounds, with molar mass of 100 g/mol to 500 g/mol and having polarity pK_{ow} < -2, in a multicomponent organic solution ranging in mass fraction from 100 µg/kg to 100 µg/g.

Competency	✓, ×, or N/A	Specific Information as Provided by *NMI/DI*
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		*Indicate if you used a "pure material" or a calibration solution. Indicate its source and ID, e.g. CRM identifier*
Identity verification of analyte(s) in calibration material.		*Indicate method(s) you used to identify analyte(s)*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).		*Indicate how you established analyte mass fraction/purity (i.e., mass balance (list techniques used), qNMR, other)*
For calibrants which are a calibration solution: Value-assignment method(s).		*Indicate how you established analyte mass fraction in calibration solution*
Sample Analysis Competencies		
Identification of analyte(s) in sample		*Indicate method(s) you used to identify analyte(s) in the sample (i.e., Retention time, mass spec ion ratios, other)*
Extraction of analyte(s) of interest from matrix		*Indicate extraction technique(s) used, if any, (i.e. Liquid/liquid, Soxhlet, ASE, other)*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)		*Indicate cleanup technique(s) used, if any (i.e., SPE, LC fractionation, other)*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)		*Indicate chemical transformation method(s), if any, (i.e., hydrolysis, derivatization, other)*
Analytical system		*Indicate analytical system (i.e., LC-MS/MS, GC-HRMS, GC-ECD, other)*
Calibration approach for value-assignment of analyte(s) in matrix		*a) Indicate quantification mode used (i.e., IDMS, internal standard, external standard, other)* *b) Indicate calibration mode used (i.e., single-point calibration, bracketing, x-point calibration curve, other)*
Verification method(s) for value-assignment of analyte(s) in sample (if used)		*Indicate any confirmative method(s) used, if any.*
Other		*Indicate any other competencies demonstrated.*

Instructions:

- In the middle column place a tick, cross or say the entry is not applicable for each of the competencies listed (the first row does not require a response)
- Fill in the right hand column with the information requested in blue in each row
- Enter the details of the calibrant in the top row, then for materials which would not meet the CIPM traceability requirements the three rows with a # require entries.

APPENDIX F: Summary of Participants' Analytical Information

The following Tables summarize the detailed information about the analytical procedures each participant provided in their "Analytical Information" worksheets. The presentation of the information in many entries has been consolidated and standardized.

The participant's measurement uncertainty statements are provided verbatim in Appendix G.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in these Tables to specify adequately experimental conditions or reported results. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology or other participant in this Key Comparison, nor does it imply that the equipment, instruments, or materials identified are necessarily the best available for the purpose.

Table F-1: Summary of Sample Size, Extraction, and Cleanup for CCQM-K131

NMI	Sample Size (g)	Pre-treatment	Analytical Technique
BAM	≈0.156	Not applicable	GC-MS
BVL	0.076	None	GC-high resolution MS
CENAM	0.38		GC-MS/MS: Agilent GC 7890 MS 7000QQQ
EXHM	0.15		GC-IT-MS: Thermo Trace Ultra GC PolarisQ ion trap MS
GLHK Method 1	0.2	Vortex before use	GC-MS
GLHK Method 2	0.13	Vortex before use	HPLC-UV
HSA	0.2	Gravimetrically diluted, mixed IS added and vortexed	GC-MS: Agilent 7890A GC, 5975C MS
INMETRO	0.3	Not applicable	GC-MS: Agilent 6890N and 5975B (MSD)
INRiM	1 µL per GC run	Not applicable	GC-MS
KRISS	0.38	Not applicable	GC-MS Jeol JMS-800D
LNE	0.070	Not applicable	GC-MS
NIM Method 1	0.2367	0.3 mL sample solution was transferred into sample vial and weighed, then 0.4 mL internal standard solution was transferred into same vial and weighed	HPLC-DAD Shimadzu LC-20AT
NIM Method 2	0.2367	0.3 mL sample solution was transferred into sample vial and weighed, then 0.4 mL internal standard solution was transferred into same vial and weighed	GC-MS/MS TSQ Quantum XLS
NIST	0.120	None	LC/UV absorbance @254 nm
NMIJ	0.15	Dilution with ACN solution containing Nap-d_8 and BaP-d_{12} comparable to analytes	GC-FID, GC-MS
NMISA	0.0938	Gravimetrically diluted for GC analysis by a factor of ≈ 22.79	GC-TOFMS
UME Method 1	0.1	Dilution with Acetonitrile solution containing Nap-$d_{8,}$ BaP-d_{12} and BaA-d_{12}.	Triple Quadrupole GC-MS/MS. Thermo Scientific TSQ GC-MS/MS
UME Method 2	0.1	Dilution with water and Acetonitrile solution containing Nap-$d_{8,}$ BaP-d_{12} and BaA-d_{12}.	LC-MS, Thermo Scientific ORBITRAP Q-Exactive system

Table F-1: Summary of Sample Size, Extraction, and Cleanup (Continued)

NMI	Sample Size (g)	Pre-treatment	Analytical Technique
VNIIM	0.0158 to 0.0166	Added successively: 20 µL sample (by mass), 20 µL (by mass) ^{13}C-labeled IS CIL ES-4087 in *n*-nonane; 2 drops toluene to mix the nonane and ACN	GC-MS: Agilent 5973N/6890
VSL	0.25 per replicate		GC-FID for quantification GC-MS for qualitative analysis

Table F-2: Summary of Analytical Techniques for CCQM-K131

NMI	Chromatographic Column	Mass Spectrometry and Chromatographic Conditions	ion/MRM monitored
BAM	DB-EUPAH 60 m×0.25 mm×0.25 µm	He, 1 mL/min 60 °C (1 min), 45 °C/min to 200 °C, 10 °C/min to 320 °C (33 min)	Nap: 128, Nap-d_8: 136 BaA: 228, BaA-d_{12}: 240 BaP: 252, BaP-$^{13}C_4$: 256
BVL	Optima 35 MS (Macherey & Nagel) 30 m×0.25 mm×0.25 µm precolumn deactivated	He, 1 ml/min, splitless @280 °C 80 °C (2 min), 30 °C/min to 240 °C, 3.0 °C/min to 270 °C 2.0 °C/min to 285 °C, 8 °C/min to 330 °C	BaA: 228.0933 BaA-d_{12}: 240.1687 BaP: 252.0933 BaP-d_{12}: 264.1687
CENAM	HP-50 60 m×0.25 mm×0.25 µm	1.1 mL/min 100 °C (1 min), 40 °C/min to 280 °C (45 min)	BaA: 228.1/226.1; BaA-d_{12}:240.1/236.1 BaP: 252.1/250.1 BaP-d_{12}: 264.1/260.1
EXHM	Agilent J&W DB-35 ms 30 m×0.25 mm×0.25 µm	**MS**: 230 °C, 5.6 V, max energy 0.43, damping gas 2 ml/min **GC**: transfer line 280 °C, PTV injector 10 µL inj, 85 °C initial, 25 mL/min split flow, 160 kPa, evaporation 15 °C/s to 85 °C (30 s), transfer 15 °C/s to 300 °C, clean 14.5 °C/s to 320 °C (28 min) Flow: He, 1.5 mL/min (0 to 15 min), 0.1 mL/min to 2 mL/min (13 min) Oven: 80 °C (3 min), 50 °C/min to 270 °C (18 min), 50 °C/min to 320 °C (7 min)	BaA: 228 (226/224) BaA-d_{12}: 240 (236/232) BaP: 252 (250/246) BaP-d_{12}: 264 (260/258)
GLHK Method 1	Agilent DB-17MS 60 m×0.25 mm×0.25 µm	85 °C (1 min), 30 °C/min to 210 °C (8 min), 5 °C/min to 250 °C (8 min), 5 °C/min to 300 °C (40 min)	BaA: 228/226 BaA-$^{13}C_6$: 234 BaP: 252/253 BaP-$^{13}C_4$: 256
GLHK Method 2	Restek Pinnacle II PAH 150 mm×3.0 mm; Waters PAH 250 mm×3.0 mm	Flow 1.1 ml/min; 45 %/55 % ACN/water, 6.5 min to 60 %/40 % ACN/water, 1.5 min to 70 %/30 % ACN/Water, 4 min to 100 % ACN (3 min), switch to 45 %/55 % ACN/water (2 min)	

Table F-2: Summary of Analytical Techniques for CCQM-K131 (Continued)

NMI	Chromatographic Column	Mass Spectrometry and Chromatographic Conditions	ion/MRM monitored
HSA	Restek Rxi-PAH 40 m×0.18 mm×0.07 µm	**MS**: Source 280 °C, quadrapole 180 °C, transfer line 280 °C **GC**: He, 0.5 mL/min, 1.5 µL, Inlet 275 °C, split ratio 20:1 110 °C (1 min), 40 °C/min to 210 °C, 3 °C/min to 260 °C 11 °C/min to 300 °C (6 min)	Nap: 128, Nap-$^{13}C_6$: 134 BaA: 228, BaA-$^{13}C_6$: 234 BaP: 252, BaP-$^{13}C_4$: 256
INMETRO (Original)	Varian VF-5MS 60 m×0.25 mm×0.25 µm	**MS**: Ion source 250 °C, quadrupole 150 °C **GC**: He, 1.0 mL/min, 1 µL, splitless, inlet 290 °C, 60 °C (2 min), 20 °C/min to 120 °C (2 min) 6 °C/min to 180 °C (2 min), 3 °C/min to 290 °C (19.33 min)	Nap: 128, Nap-d_8: 136 BaA: 228, BaA-d_{12}: 240 BaP: 252, BaP-d_{12}: 264
INMETRO (Revised)	Varian VF-5MS 10 m×0.15 mm×0.15 µm	**MS**: Ion source 250 °C, quadrupole 150 °C **GC**: He, 1.0 mL/min, 1 µL, pulsed split, inlet 300 °C 70 °C (2 min), 25 °C/min to 150 °C (2 min), 30 °C/min to 200 °C (2 min), 8 °C/min to 280 °C (4 min)	Nap: 128, Nap-d_8: 136 BaA: 228, BaA-d_{12}: 240 BaP: 252, BaP-d_{12}: 264
INRiM	Thermo Scientific TR-5ms 30 m×0.25 mm×0.25 µm	He, 1.2 mL/min, 1 µL, Inlet 300 °C, transfer 270 °C, splitless 70 °C (2 min), 25 °C/min to 180 °C, 5 °C/min to 300 °C (3 min)	Nap: 128, Nap-d_8: 136 BaA: 228, BaA-d_{12}: 240 BaP: 252, BaP-d_{12}: 264
KRISS	Rxi-17sil MS 60 m×0.25 mm×0.25 µm	**MS**: EI, 1000 resolution **GC**: He, 1.5 mL/min, split, 1 µL BaA & BaP: 80 °C (2 min), 30 °C/min to 220 °C, 3 °C/min to 320 °C (20 min) Nap: 80 °C (5 min), 5 °C/min to 150 °C, 30 °C/min to 320 °C (30 min)	Nap: 128.06 Nap-d_8: 136.11 BaA: 228.09 BaA-d_{12}: 240.17 BaP: 252.09 BaP-d_{12}: 264.17
LNE	Agilent DB-EUPAH 60 m×0.25 mm×0.25 µm	He, 1.2 mL/min, splitless, 1 µL, Injector: 280 °C, 60 °C, 45 °C/min to 200 °C, 10 °C/min to 250 °C 30 °C/min to 320 °C (26 min)	Nap: 128/127 Nap-$^{13}C_6$: 134/135 BaA: 228/114 BaA-$^{13}C_6$: 234/117 BaP: 252/250 BaP-$^{13}C_4$: 256/128

Table F-2: Summary of Analytical Techniques for CCQM-K131 (Continued)

NMI	Chromatographic Column	Mass Spectrometry and Chromatographic Conditions	ion/MRM monitored
NIM Method 1	Waters PAH C18 4.6 mm×250 mm 5 µm diameter particles	Injection: 10 µL, Flow:1.0 mL/min, Temp:27 °C, Detector: UV254 UV272 Gradient: 5 min, 40 %/60 % ACN/Water, 20 min to 100 % ACN (30 min), 37 min to 40 %/60 % ACN/Water (46 min)	
NIM Method 2	Agilent DM-5 50 m×0.25 mm×0.25 µm	Inlet: 280 °C Injection: 1 µL, gradient flow: 0.8 mL/min (10 min), 2.4 mL/min (30 min), 1.2 mL/min (17 min); Temperature program: 60 °C (1 min), 25 °C/min to 180 °C, 10 °C/min to 200 °C, 3 °C/min to 230 °C, 1.5 °C/min to 240 °C, 1 °C/min to 265 °C, 20 °C/min to 300 °C (20 min)	Nap: 128, Nap-d_8: 136 BaA: 228, BaA-$^{13}C_6$: 234 BaP: 252/250 BaP-$^{13}C_4$: 256
NIST	Agilent Eclipse PAH 4.6 mm×100 mm, 1.8 µm diameter particles	column temperature 25 °C, flow rate 1.5 mL/min 50 % (by volume) ACN in water, 3 min equilibration, 2 min post injection; 10 min linear gradient to 100 % ACN	
NMIJ	GC-FID: Agilent, DB-5MS, 60 m×0.25 mm×0.25 µm GC-MS: Agilent, DB-17MS, 30 m×0.25 mm×0.25 µm	**GC-FID**: He, 36 cm/s 50 °C (2 min), 2.5 °C/min to 300 °C (20 min) **GC-MS**: He, 36 cm/s; 50 °C (2 min), 10 °C/min to 240 °C, 1.25 °C/min to 300 °C (10 min)	Nap: 128.1, Nap-d_8: 136.1 BaP: 252.1, BaP-d_{12}: 264.2
NMISA	Restek Rxi-PAH 60 m×0.25 mm×0.10 µm	**MS**: Detector 1800 V, electron energy -70 V, source 250 °C, acquisition rate 10 spectra/s **GC**: He, 1.5 mL/min, inlet 300 °C, transfer line 275 °C 65 °C (0.5 min), 5 °C/min to 170 °C, 3 °C/min to 250 °C 10 °C/min to 340 °C (10 min)	Nap: 128 BaA: 228 BaP: 252
UME Method 1	Agilent DB EUPAH 60 m×0.25 mm×0.25 µm	**MS**: source 275 °C, transfer: 300 °C **GC**: He, 1 mL/min, splitless, 1 µL, inlet: 300 °C, 60 °C (90 s), 45 °C /min to 200 °C, 0 °C /min to 320 °C (33 min)	Nap: 128/102 (40 V) Nap-d_8: 136/108 (50 V) BaA: 228/226 (40 V) BaA-d_{12}: 240/236 (48 V) BaP: 252/250 (48 V) BaP-d_{12}: 264.260 (55 V)

Table F-2: Summary of Analytical Techniques for CCQM-K131 (Continued)

NMI	Chromatographic Column	Mass Spectrometry and Chromatographic Conditions	ion/MRM monitored
UME Method 2	Agilent Eclipse PAH 2.1 mm×50 mm×1.8 µm	autosampler, injection: 2 µL, column: 35 °C, flow: 0.35 mL/min, phases: A = 10:90 ACN:water, B = ACN Gradient: 0.5 min 35 %/65 % A/B, 5 min to 100 % B (7 min), 1 min to 35 %/65 % A/B (1.5 min)	Nap: 128/102 (40 V) Nap-d_8: 136/108 (50 V) BaA: 228/226 (40 V) BaA-d_{12}: 240/236 (48 V) BaP: 252/250 (48 V) BaP-d_{12}: 264.260 (55 V)
VNIIM	Rtx-5MS, 30 m×0.25 mm×0.10 µm	**MS**: source 230 °C, quadrapole 150 °C, transfer 280 °C TIC (33 to 350) m/z **GC**: He, 1 ml/min, splitless, 1 µl, injector: 280 °C 70 °C (5 min), 10 °C/min to 280 °C (20 min)	BaA: 228, BaA-$^{13}C_6$: 234 BaP: 252, BaP-$^{13}C_4$: 256
VSL	Agilent 19091J-413 HP-5 5 % Phenyl Methyl Siloxane 30 m×320 µm×0.25 µm	Split 1:10, inlet 325 °C 50 °C (5 min); 3 °C/min to 119 °C; 30 °C/min to 249 °C	

Table F-3: Summary of Calibrants and Standards for CCQM-K131

NMI	Type of Calibration	Calibrants	Internal Standards
BAM	internal standard 5 calibration points linear regression	NIST SRM 1647f	BaP-$^{13}C_4$, CIL BaA and Nap, Dr Ehrenstorfer PAH Mix 9 deuterated Weighed to the sample solution
BVL	internal standard	NIST SRM 2260a	BaA-d_{12} & BaP-$d_{12,}$ Promochem
CENAM	single point IDMS	Commercial sources	BaA-d_{12} 98.7 % CIL BaP-d_{12} 98 % CDN isotopes
EXHM	single point, exact matching IDMS	NIST SRM 1647f In-house calibrant purities by qNMR BaA: SigmaAldrich (98.5±0.3) % BaP: SigmaAldrich (96.7±0.4) %	BaA-d_{12} & BaP-d_{12}, Chem Service, added to the diluted sample
GLHK Method 1	single point, exact matching IDMS	NIST 1647f	BaA-$^{13}C_6$ & BaP-$^{13}C_4$, CIL
GLHK Method 2	bracketing	NIST 1647f	
HSA	single point, exact matching IDMS	Purities by HSA mass balance BaP: Cerilliant, (99.38 ±0.51) % Nap: SigmaAldrich, (99.61±0.32) % BaA: BCR-271, (99.84 ± 0.09*) % * The purity was verified with NIST SRM 1647	BaA-$^{13}C_6$, CIL CLM-3602-1.2, BaP-$^{13}C_4$, CIL CLM-2722-1.2, Nap-$^{13}C_6$, CIL CLM-1332-1.2 The mixed solution was diluted, added gravimetrically into sample solutions and calibration solutions.
INMETRO (Original)	IDMS	Purities by INMETRO BaA: Aldrich, 98.71 % BaP: Supelco, 92.41 % Nap: Fluka, 88.7 %	Nap-d_8, BaA-d_{12} & BaP-d_{12} CIL Toluene with all IS added to sample & calibrants just prior to injection
INMETRO (Revised)		Purities by INMETRO BaA: Aldrich, (98.66 ± 0.28) % BaP: Supelco, (92.41± 0.78) % Nap: Fluka, (99.20 ± 0.31) %	Nap-d_8, BaA-d_{12} & BaP-d_{12} CIL Toluene with all IS added to sample & calibrants just prior to injection

Table F-3: Summary of Calibrants and Standards for CCQM-K131 (Continued)

NMI	Type of Calibration	Calibrants	Internal Standards
INRiM	single point calibration with external standard; internal standards in both sample and calibration solutions	NIST SRM 2260a, gravimetric dilution; Mass standards traceability to INRiM	BaA-d_{12}: NIST SRM 2269 Nap-d_8 & BaP-d_{12}: NIST SRM 2270 all added prior to the injection
KRISS	Single-point with exact matching double ID for IDMS	Purities by KRISS BaA: BCR, 98.789 % BaP: SUPELCO 98.81 % Nap: Fluka, 99.85 %	Nap-d_8 SUPELCO BaA-d_{12} & BaP-d_{12} CIL weighed into 0.5 mL sample to achieve 1:1 ratio
LNE	five point IDMS	NIST SRM 1647f	Nap-$^{13}C_6$, BaA-$^{13}C_6$, & BaP-$^{13}C_4$; CIL
NIM Method 1 Method 2	Internal standard for BaA & BaP External standard for Nap	Purities by NIM BaA: Cerilliant, 99.69 % BaP: Cerilliant, 99.30 % Nap: AccuStandard, 99.84	Nap-d_8, BaA-d_{12}, BaA-$^{13}C_6$, BaP-d_{12}, & BaP-$^{13}C_4$, CIL
NIST	External 3-point calibration with averaged response factors	Purity by NIST DSC BaA: BCR-271, 99.84 %Purity by NIST Purity by NIST qNMR and DSC BaP: BCR-51, 99.3 % Nap: Fluka, 99.235 %	
NMIJ	single point IDMS	BaP: NMIJ CRM 4213-a Nap: TCI, N0004, Lot: QCNQJ-IN	Nap-d_8, BaP-d_{12}
NMISA	Double IDMS (bracketing)	NIST SRM 1647f	PAH cocktail for CARB method 429 (D, 99.6 %) CIL added at start of analysis

Table F-3: Summary of Calibrants and Standards for CCQM-K131 (Continued)

NMI	Type of Calibration	Calibrants	Internal Standards
UME	IDMS, 6-point calibration	Purity by UME, traceability through UME CRM 1301 Chloramphenicol Primary Calibrant BaA: Supelco 4-8563 (98.08 ±0.30) % BaP: Supelco 4-8564 (94.12±0.52) % Nap: Fluka 8467 (99.90 ± 0.22) %	Nap-d_8 99 % DLM-365-5 CIL BaA-d_{12} 98 % DLM-610-0.1 CIL BaP-d_{12} 97 % DLM-258-0.1 CIL
VNIIM	single point IDMS	NIST SRM 1647f in ACN using the procedure like sample pre-treatment	US EPA 16 PAH ^{13}C Cocktail; CIL ES-4087 Lot ER10161401 Internal standards were added to the sample immediately after weighing the sample
VSL	External calibration with 9 standards of nominal value {1,5,10,15,20,25,30,35,50} µg/g, linearity of method and detection (0.1 to 100) µg/g, range used for calibration (1 to 50) µg/g Gravimetric preparation of 3 different stock solutions. Each stock is gravimetrically diluted to desired mass fraction to obtain a set of calibrants. Each calibrant decanted into 3 sample vials and directly analyzed.	Purity by VSL ACN SigmaAldrich, (99.912 ± 0.007) % Nap SigmaAldrich, (99.990 ± 0.019) %	

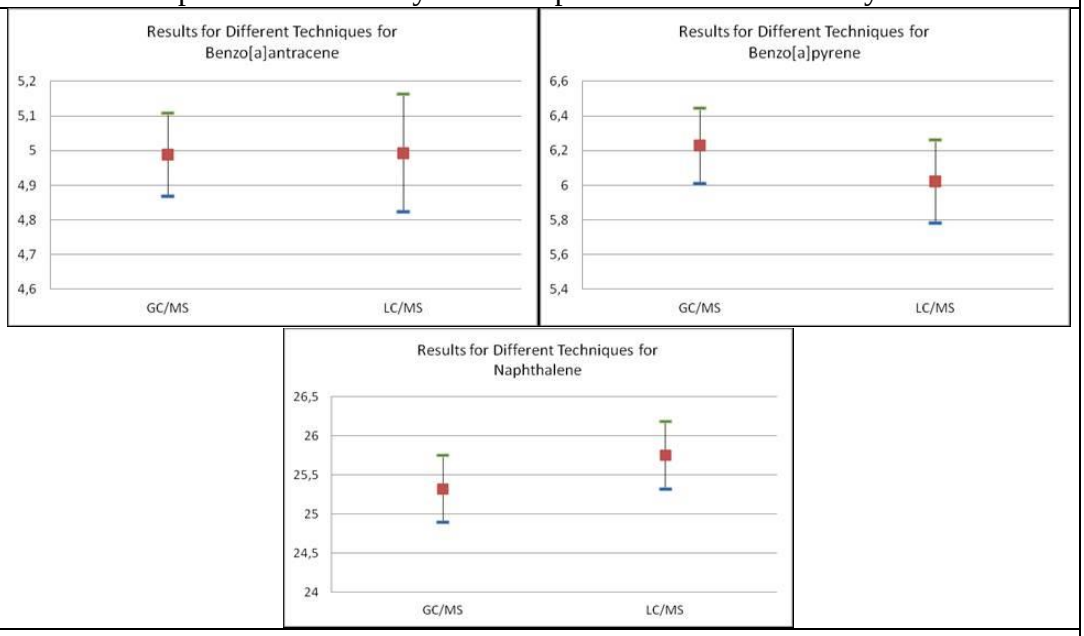
Table F-4: Summary of Assessment and Verification Methods for CCQM-K131

NMI	Purity Assessment	Result Verification	Impurities
CENAM	GC-FID with two different columns and determination of water content by Karl Fischer titration		
EXHM	In-house calibrant purities by qNMR	Comparison with NIST SRM 1647f, values used as reported in the certificate	
HSA	In-house evaluation of BaP and Nap using mass balance approach. Structurally related organics: HPLC-DAD with Eclipse PAH LC column, confirmed using Kinetex C18, using relative peak area approach. Moisture: Mettler Toledo Karl Fisher Coulometer, validated using NIST SRM 2890 Volatile organics: Headspace GC-MS with capillary DB-624 column, TGA Total non-volatiles: TGA BaA purity verified by comparison with NIST SRM 1647f	Comparison with NIST SRM 1647f	Structurally related organics: BaP: 5.85 mg/g Nap: 3.70 mg/g. Moisture: BaP: 0.32 mg/g; Nap: 0.19 mg/g. Volatile organics: BaP & Nap: 0 mg/g, uncertainty estimated from the LOD for the detected dichloromethane (2.3 mg/g). Total non-volatiles: BaP & Nap: 0 mg/g with associated uncertainty estimated from the LOD (5.0 mg/g).
INMETRO	qNMR, Sigma-Aldrich traceCERT dimethyl sulfone as IS		
KRISS	GC-FID for structurally related organics, Karl-Fischer Coulometry for water, thermogravimetric analysis for non-volatiles, headspace-GC-MS for residual solvents	Secondary confirmation by comparison with NIST SRM 1647f	Organic similars only detected with GC-FID. No other impurities detected in any calibrant

Table F-4: Summary of Assessment and Verification Methods for CCQM-K131 (Continued)

NMI	Purity Assessment	Result Verification	Impurities
NIM	GC-FID, HPLC-DAD, NMR	GC-IDMS Confirmation by comparison with NIST SRM 1647f in HPLC-DAD & GC-IDMS analysis. GC-IDMS method and external standard method by HPLC-DAD were used for BaA & BaP as verification method. GC-IDMS method and internal standard method were used for Nap as verification method.	
NIST	Nap and BaP: qNMR and DSC BaA: DSC	Comparison with NIST SRM 1647f	
NMIJ	Nap assessed with qNMR, GC-FID	LC-UV and another GC-FID using self-made calibration solution (prepared from qNMR assessed neat Nap and BaP) NIST SRM 1647f	Dibenzo[*b*]thiophen (0.05 %, g/g; not considered)
UME	qNMR	NIST SRM 2260a	
VSL	Nap and ACN assessed by mass balance GC-MS in solution with methanol for organics Coulometric Karl-Fisher for water Residue on drying (ACN) for unknown content	NIST SRM 1647f was used for quality control	Nap: no organic impurities (LoQ $\leq 0.1\times10^{-6}$) g/g H_2O $(100 \pm 185)\times10^{-6}$ g/g ACN: no organic impurities (LoQ $\leq 0.1\times10^{-6}$) g/g H_2O (0.000826 ± 0.000005) g/g unknown content (0.00005 ± 0.00005) g/g

Table F-5: Additional Comments for CCQM-K131

NMI	Additional Comments
EXHM	Three 0.150 g samples taken from each ampoule, diluted 1:10 with ACN. 0.155 g of each diluted sample was spiked with IS solutions and diluted 1:10 with (50:50) acetone/cyclohexane. Samples were measured against in-house PAH standards prepared at "exactly matching" concentrations. All samples were prepared directly after ampoule opening. All measurements were carried out within 24 hours.
HSA	NIST SRM 1647f was analysed in parallel with each sample blend for quality control (QC). The QC results were all within the expanded uncertainty of the certified values for BaA, BaP, and Nap. Subsamples from each reporting ampoule were also measured with LC-DAD (Agilent 1260 Infinity Quaternary System), using internal calibration method (n-butyl paraben as the internal standard). The results were used to estimate the uncertainty in the use of different instruments.
NIST	Prior to beginning measurements, autosampler function was critically evaluated by multiple replicate injections of an unretained compound. After proper function was observed, injection reproducibility was 0.3 % for N=37. The use of the Eclipse PAH column provides selectivity for the separation of BaA and chrysene isomers.
UME	
VSL	Regression performed using an errors-in-variables approach. The mass fraction of the unknown was determined by a searching algorithm, given the coefficients of the straight line and the response. The associated standard uncertainty was obtained by applying the law of propagation of uncertainty from the GUM. The resulting mass fractions and associated standard uncertainties were used as input for the data-analysis. The final result is calculated as a weighted mean, using a meta-analysis approach on the mass fractions from the 9 measurements. The standard deviation is approximately τ = 0.70 µg/g (ppm) using the DerSimonian-Laird model. The calculations have been performed in R using the package metafor.

APPENDIX G: Summary of Participants' Uncertainty Estimation Approaches

The following are images or verbatim copies of the uncertainty-related information provided by the participants in the "Analytical Information" worksheet of the "Reporting Form" Excel workbook or in separate documents. Information is grouped by participant and presented in alphabetized acronym order.

Uncertainty Information from BAM

measurement equation:

$$x_{sample} = \frac{r - i_c}{sl} \cdot \frac{m_{is}}{m_{sample}} \cdot F_{purity}$$

symbol	**parameter description**
r	area ratio native/internal std
i_c	intercept of calibration line
sl	slope of calibration line
m_is	mass of internal standard added to sample
m_sample	mass sample
F_purity	purity correction factor
x_sample	**result**

coverage factor k = 2

		u_rel		
uncertainty estimate		**Nap**	**B(a)A**	**B(a)P**
residual scatter of calibration		0.015	0.005	0.006
estimate combining u(ic), u(sl), and covar		0.002	0.004	0.003
SD of replicate weighings, converted to u_rel		0.003	0.003	0.003
SD of replicate weighings of mass standard, converted to u_rel		0.001	0.001	0.001
certificate uncertainty NIST SRM 1647f, includes purity		0.007	0.007	0.009
		0.017	**0.009**	**0.012**
	expanded relative uncertainty U:	0.033	0.019	0.023
	expanded uncertainty U µg/g:	0.845	0.091	0.142
	standard uncertainty u µg/g	0.423	0.046	0.071

C(sample) = [A(analyte)*m(is)]/[A(is)*RF(mean)]*1/m(sample)
C(sample): concentration of analyte in sample [ng/g]
A(analyte); A(is): chromatographic peak area of analyte; peak area internal standard
m(is): mass of internal standard [ng]
RF(mean): average response factor from four calibration points;
m(sample): weight of sample aliquot [g]
Response Factor = [Area(analyte)/Area(int. standard)]/[mass(int. standard)/mass(analyte)]

uncertainty components:
weighing (sample, internal standard, calibrant)
variation of response factor
uncertainty of calibrant (see certificate NIST 2260a)
combined uncertainty = sqrt (sum of squared standard uncertainties)

Uncertainty budget K131 (PAH in solution)

standard uncertainties, relative values u(x)/X

	BaA [%]	BaP [%]	Comment
Weighing processes			
weighing of sample	0.66	0.66	76 +/- 0,5 mg
addition of internal standard solution	0.23	0.23	220 +/- 0,5 mg
Calibration			
Uncertainty of calibrant	0.59	1.20	NIST 2260a, see certificate
weighing NIST 2260a	0.057	0.057	876 +/- 0,5 mg
variation response factor	0.3	1.1	accounts for injection and integration bias
combined standard uncertainty [%]	0.96	1.77	
expanded uncertainty (k=2) [%]	**1.9**	**3.5**	

mean RF	std. dev.	CV [%]	
1.024	0.003	0.3	(BaA)
1.126	0.012	1.1	(BaP)

Uncertainty Information from CENAM

$$w_x = \frac{m_{Ix} \cdot R_x \cdot m_0}{m_x \cdot R_0 \cdot m_{I0}} \cdot w_0$$

m_0	Mass of measurand for calibration solution
m_{I0}	Mass of labeled compound for calibration solution
m_x	Sample mass
m_{Ix}	Mass of labeled solution for sample
R_0	Area ratio for calibration solution
R_x	Area ratio for sample
w_0	Mass fraction of measurand in calibration solution
w_x	Mass fraction of measurand in sample

Several uncertainty sources were combined: The budget of each uncertainty by ampule is shown un next figure.The expanded uncertainty was obtained by multiplying the combined standards uncertainty by the cover factor with a 95 % level of confidence k =2.

Paramerter	Value	units	uncertainty source	standard uncertainty
Mass of measurand for calibration solution	**0.38670**	g	and calibration	0.00006
Mass of labeled compound for calibration solution	**0.38546**	g	and calibration	0.00006
Sample mass	**0.38422**	g	and calibration	0.00004
Mass of labeled solution for sample	**0.38786**	g	and calibration	0.00004
Area ratio for calibration solution	**1.0397**		Experimental, repeatibility	0.0088
Area ratio for sample	**1.0049**		Experimental, repeatibility	0.0059
Mass fraction of measurand in calibration solution	**5.1792**	mg/kg	repeatability and purity	0.0178

Uncertainty Information from EXHM

The measurement equation is:

$$w_{A,S} = w_{A,C} \frac{m_{S,in}}{m_{S,dil}} \times \frac{m_{is,S}}{m_{D,S}} \times \frac{m_{A,C}}{m_{is,C}} \times \frac{R_S}{R_C}$$

where $w_{A,S}$ = dry mass fraction of the analyte (B[a]A or B[a]P) in the sample, (μg/g)
$w_{A,C}$ = mass fraction of the analyte (B[a]A or B[a]P) in the calibration solution, (μg/g)
$m_{S,in}$ = the mass of sample in the diluted sample (g)
$m_{S,dil}$ = the total mass of the diluted sample (g)
$m_{is,S}$ = mass of internal standard solution added to sample blend, (g)
$m_{D,S}$ = mass of diluted test material in sample blend, (g)
$m_{A,C}$ = mass of the analyte (B[a]A or B[a]P) solution added to calibration blend, (g)
$m_{is,C}$ = mass of internal standard solution added to calibration blend, (g)
R_S = measured peak area ratio of the selected ions in the sample blend
R_C = measured peak area ratio of the selected ions in the calibration blend

The equation used to estimate standard uncertainty is:

$$u(w_{BS}) = \sqrt{(s_R)^2 + \sum \left(C_j u(m_i)\right)^2 + \sum \left(C_j u(R_i)\right)^2 + \left(C_j u(w_{MC})\right)^2}$$

where s_R is the standard deviation under reproducibility conditions, n the number of determinations and C_j the sensitivity coefficients associated with each uncertainty component (masses, ion ratios and calibrant concentration). The uncertainty of the peak area ratios was considered to have been included in the estimation of method precision.

Uncertainty estimation was carried out according to JCGM 100: 2008. The standard uncertainties were combined as the sum of the squares of the product of the sensitivity coefficient (obtained by partial differentiation of the measurement equation) and standard uncertainty to give the square of the combined uncertainty. The square root of this value was multiplied by a coverage factor (95 % confidence interval) from the t-distribution at the total effective degrees of freedom obtained from the Welch-Satterthwaite equation to give the expanded uncertainty.

The uncertainty budgets for BaA and BaP are:

Benz[*a*]anthracene

uncertainty component (typical values)	symbol	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	C_i x u_i	$(C_i \times u_i)^2$
method precision		4,714	1,000	0,0586	0,0124	0,059	0,003
mass fraction of BaA in the calibration solution, (µg/g)	$w_{A,c}$	0,6461	7,268	0,0068	0,0105	0,049	0,002
the mass of sample in the diluted sample (g)	$m_{s,in}$	0,15000	-48,456	0,00003	0,0002	-0,001	0,000
the total mass of the diluted sample (g)	$m_{s,dil}$	1,50000	4,846	0,00006	0,0000	0,000	0,000
mass of BaA-d_{12} solution added to sample blend, (*g*)	$m_{is,S}$	0,16000	7,268	0,00003	0,0002	0,000	0,000
mass of diluted test material in sample blend, (*g*)	$m_{D,S}$	0,15500	-46,893	0,00003	0,0002	-0,001	0,000
mass of BaA solution added to calibration blend, (*g*)	$m_{is,C}$	0,11300	7,268	0,00003	0,0003	0,000	0,000
mass of BaA-d_{12} solution added to calibration blend, (*g*)	$m_{A,C}$	0,16000	-45,428	0,00003	0,0002	-0,001	0,000
measured peak area ratio of the selected ions in the sample blend	R_S	0,9970		considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	R_C	1,0000		estimation of method precision			

result (µg/kg)	4,714
combined standard uncertainty (µg/g)	0,077
relative uncertainty (%)	1,6
effective degrees of freedom	16,7
coverage factor	2,12
expanded uncertainty (µg/kg)	0,162

Benzo[*a*]pyrene

uncertainty component (typical values)	symbol	value	sensitivity coefficient	standrard uncertainty	relative uncertainty	C_i x u_i	$(C_i \times u_i)^2$
method precision		5,867	1,000	0,0704	0,0120	0,070	0,005
mass fraction of BaP in the calibration solution, (µg/g)	$w_{A,c}$	0,6604	8,894	0,0079	0,0120	0,070	0,005
the mass of sample in the diluted sample (g)	$m_{s,in}$	0,15000	-39,161	0,00003	0,0002	-0,001	0,000
the total mass of the diluted sample (g)	$m_{s,dil}$	1,50000	3,916	0,00006	0,0000	0,000	0,000
mass of BaP-d_{12} solution added to sample blend, (*g*)	$m_{is,S}$	0,16000	5,874	0,00003	0,0002	0,000	0,000
mass of diluted test material in sample blend, (*g*)	$m_{D,S}$	0,15500	-37,898	0,00003	0,0002	-0,001	0,000
mass of BaP solution added to calibration blend, (*g*)	$m_{is,C}$	0,13800	5,874	0,00003	0,0002	0,000	0,000
mass of BaP-d_{12} solution added to calibration blend, (*g*)	$m_{A,C}$	0,16000	-36,713	0,00003	0,0002	-0,001	0,000
measured peak area ratio of the selected ions in the sample blend	R_S	0,9990		considered to be included in the			
measured peak area ratio of the selected ions in the calibration blend	R_C	1,0000		estimation of method precision			

result (µg/g)	5,867
combined standard uncertainty (µg/g)	0,100
relative uncertainty (%)	1,7
effective degrees of freedom	17,8
coverage factor	2,11
expanded uncertainty (µg/g)	0,210

Uncertainty Information from GLHK

BaA: GC-MS	Value x	Standard uncertainty $u(x_i)$	Relative uncertainty $u(x_i)/x_i$
Mass fraction of spike solution	5.1600	3.50E-02	6.78E-03
Weight of internal standard in sample blend	0.05667	1.00E-04	1.76E-03
Weight of sample	0.20818	1.00E-04	4.80E-04
Weight of internal standard in calibration blend	0.05702	1.00E-04	1.75E-03
Weight of standard added to calibration blend	0.20045	1.00E-04	4.99E-04
Isotope ratio of sample	1.005	1.82E-03	1.81E-03
Isotope ratio ofcalibration blend	1.021	5.06E-03	4.95E-03
Run to run variability	1.000	1.94E-03	1.94E-03
Combined uncertainty (ug/g)			0.045
Expanded uncertainty (ug/g)			0.089
Relative Expanded Uncertainty (%)			1.833
BaP: GC-MS	**Value x**	**Standard uncertainty $u(x_i)$**	**Relative uncertainty $u(x_i)/x_i$**
Mass fraction of spike solution	6.2200	5.50E-02	8.84E-03
Weight of internal standard in sample blend	0.05667	1.00E-04	1.76E-03
Weight of sample	0.20818	1.00E-04	4.80E-04
Weight of internal standard in calibration blend	0.05702	1.00E-04	1.75E-03
Weight of standard added to calibration blend	0.20045	1.00E-04	4.99E-04
Isotope ratio of sample	0.998	7.39E-04	7.40E-04
Isotope ratio ofcalibration blend	0.977	4.74E-04	4.85E-04
Run to run variability	1.000	3.85E-03	3.85E-03
Combined uncertainty (ug/g)			0.061
Expanded uncertainty (ug/g)			0.122
Relative Expanded Uncertainty (%)			2.004

BaA: HPLC-UV	Value x	Standard uncertainty $u(x_i)$	Relative uncertainty $u(x_i)/x_i$
Standard purity and weighing of standard 1	1.02170	0.00707	0.006920
Standard purity and weighing of standard 2	1.27937	0.00886	0.006925
Weighing of sample	0.57383	0.000022993	0.000040
Precision of replicate analyse	1	0.0085612	0.008561
Combined rel uncertainty			**0.0130**
Expanded rel uncertainty			**0.0260**
BaP: HPLC-UV	**Value x**	**Standard uncertainty $u(x_i)$**	**Relative uncertainty $u(x_i)/x_i$**
Standard purity and weighing of standard 1	1.27428	0.0115	0.009025
Standard purity and weighing of standard 2	1.54000	0.0139	0.009026
Weighing of sample	0.57383	0.000022993	0.000040
Precision of replicate analyse	1	0.012395	0.012395
Combined rel uncertainty			**0.0178**
Expanded rel uncertainty			**0.0356**

Uncertainty Information from GLHK (Continued)

Calculation of Measurement Uncertainty of combined results (GC-MS & HPLC-UV):

$$U_{Combined} = \sqrt{U_{GCMSD}^2 + U_{LCUVD}^2}$$

Expanded uncertainty = 2 x $U_{combined}$ (k=2)

Where

U_{GCMSD} = standard uncertainty of analyte measured by GC-MS

U_{LCUVD} = standard uncertainty of analyte measured by HPLC-UV

Uncertainty Information from HSA

(i) Measurement equation used to determine the mass fraction of the measurands

$$C_X = C_Z \cdot \frac{m_Y \cdot m_{Zc}}{m_X \cdot m_{Yc}} \cdot \frac{R_Y - R_B}{R_B - R_X} \cdot \frac{R_{Bc} - R_Z}{R_Y - R_{Bc}}$$

where

C_Z =	mass fraction of benz[a]anthracene/benzo[a]pyrene/naphthalene in the calibration standard solution used to prepare the calibration blend
m_Y =	mass of internal standard solutions added to the sample blend
m_{Yc} =	mass of internal standard solutions added to the calibration blend
m_{Zc} =	mass of standard solutions added to the calibration blend
m_X =	mass of study sample solution in the sample blend
	$m_x = m_x'/D_f$, where D_f represents the dilution factor ($D_f = w_{final\ solution}/w_{initial\ sample}$) and m'_x represents mass of the diluted sample solution
R_X =	observed isotope abundance ratio in the study sample
R_Y =	observed isotope abundance ratio in the internal standard
R_Z =	observed isotope abundance ratio in the calibration standard
R_B =	observed isotope abundance ratio in the sample blend
R_{Bc} =	observed isotope abundance ratio in the calibration blend

(ii) Uncertainty Budget

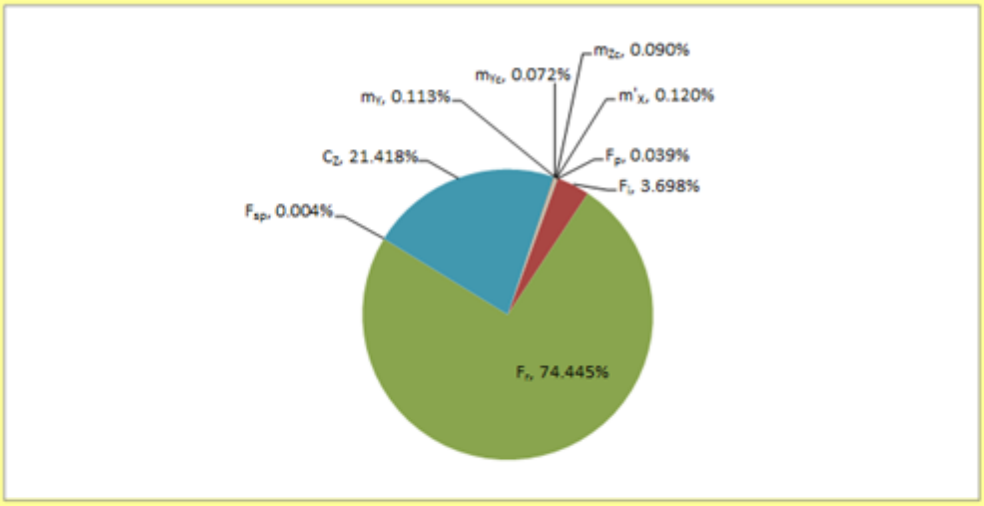
$$C_X = F_p.F_i.F_{sp}.F_r.C_Z \cdot \frac{m_Y \cdot m_{Zc}}{m_X \cdot m_{Yc}} \cdot \frac{R_Y - R_B}{R_B - R_X} \cdot \frac{R_{Bc} - R_Z}{R_Y - R_{Bc}}$$

where

additional factors (F) contributing to biases in the result value of benz[a]anthracene/benzo[a]pyrene/naphthalene were included, with an uncertainty associated to each factor.

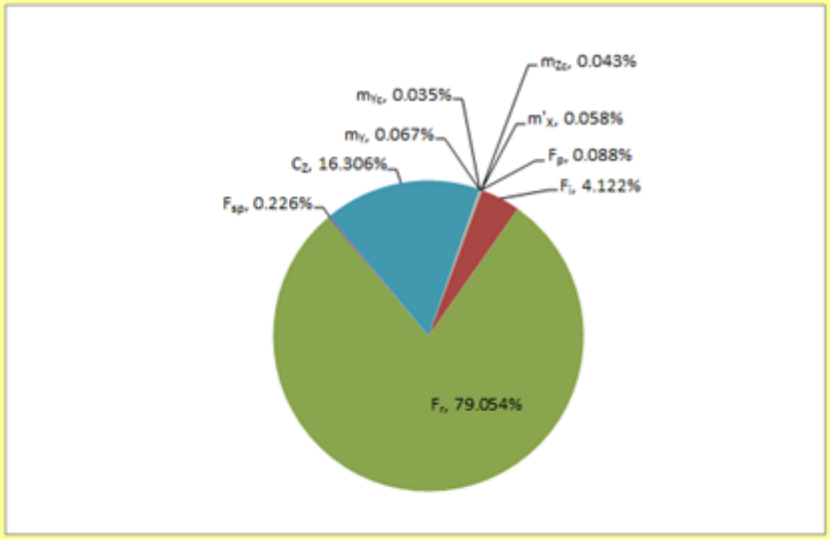
F_p =	Factor representing method precision
F_i =	Factor representing any bias in the result due to choice of instrument
F_{sp} =	Factor representing any bias in the result due to sample preparation
F_r =	Factor representing method recovery

The full uncertainty budget for the determination of benz[a]anthracene is given in the Table below:



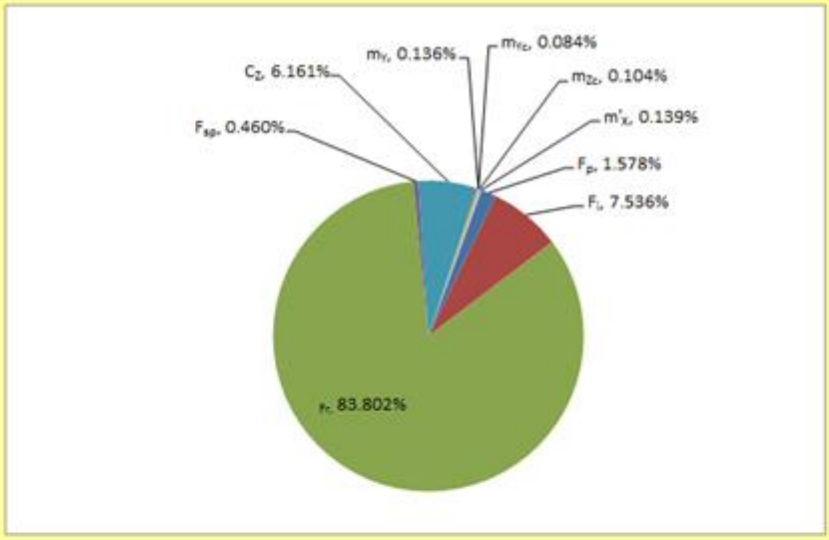
Parameter	x_i	u_{xi}	u_{xi}/x_i	Contribution	Sources of uncertainty
F_p	1	0.00016	0.0161%	0.039%	Standard deviation of the mean of three results
F_i	1	0.00158	0.1576%	3.698%	Comparison of mean results obtained using GC-MS and LC-DAD.
F_r	1	0.00707	0.7070%	74.445%	Method recovery using NIST SRM 1647f as quality control.
F_{sp}	1	0.00005	0.0054%	0.004%	Dilution of study sample: uncertainty in weighing based on balance calibration certificate
C_z	0.4515	0.00171	0.3792%	21.418%	Uncertainty in the purity value of benz[a]anthracene certified reference material (BCR-271). Uncertainty in weighing based on balance calibration certificate. Bias in the preparation of calibration blends.
m_y	0.3077	0.0000849	0.0276%	0.113%	Uncertainty in weighing based on balance calibration certificate.
m_{yc}	0.3849	0.0000849	0.0220%	0.072%	
m_{zc}	0.3448	0.0000849	0.0246%	0.090%	
m'_x	0.2991	0.0000849	0.0284%	0.120%	
R_x, R_y, R_z	Negligible				
R_p, R_{sc}	Uncertainty included in method precision				

The full uncertainty budget for the determination of benzo[a]pyrene is given in the Table below:



Parameter	x_i	u_{xi}	u_{xi}/x_i	Contribution	Sources of uncertainty
F_p	1	0.00032	0.0322%	0.088%	Standard deviation of the mean of three results
F_i	1	0.00221	0.2206%	4.122%	Comparison of mean results obtained using GC-MS and LC-DAD.
F_r	1	0.00966	0.9659%	79.054%	Method recovery using NIST SRM 1647f as quality control.
F_{sp}	1	0.00052	0.0517%	0.226%	Dilution of study sample: uncertainty in weighing based on balance calibration certificate
C_z	0.6006	0.00263	0.4387%	16.306%	Uncertainty in the purity value of benzo[a]pyrene (SCB-007) determined in-house. Uncertainty in weighing based on balance calibration certificate. Bias in the preparation of calibration blends.
m_y	0.2760	0.0000778	0.0282%	0.067%	Uncertainty in weighing based on balance calibration certificate.
m_{yc}	0.3814	0.0000778	0.0204%	0.035%	
m_{zc}	0.3457	0.0000778	0.0225%	0.043%	
m'_x	0.2968	0.0000778	0.0262%	0.058%	
R_x, R_y, R_z	Negligible				
R_s, R_{sc}	Uncertainty included in method precision				

The full uncertainty budget for the determination of naphthalene is given in the Table below:



Parameter	x_i	u_{xi}	u_{xi}/x_i	Contribution	Sources of uncertainty
F_p	1	0.00096	0.0957%	1.578%	Standard deviation of the mean of three results
F_I	1	0.00209	0.2091%	7.536%	Comparison of mean results obtained using GC-MS and LC-DAD.
F_r	1	0.00697	0.6972%	83.802%	Method recovery using NIST SRM 1647f as quality control.
F_{sp}	1	0.00052	0.0517%	0.460%	Dilution of study sample: uncertainty in weighing based on balance calibration certificate
C_Z	2.5571	0.00483	0.1890%	6.161%	Uncertainty in the purity value of naphthanlene (84679 from Sigma Aldrich) determined in-house. Uncertainty in weighing based on balance calibration certificate. Bias in the preparation of calibration blends.
m_Y	0.3022	0.0000849	0.0281%	0.136%	Uncertainty in weighing based on balance calibration certificate.
m_{Yc}	0.3849	0.0000849	0.0220%	0.084%	
m_{Zc}	0.3448	0.0000849	0.0246%	0.104%	
m'_X	0.2991	0.0000849	0.0284%	0.139%	
R_X, R_Y, R_Z	Negligible				
R_{sp}, R_{sc}	Uncertainty included in method precision				

Uncertainty Information from INMETRO

Measurement Equation

$w\_a=((R-b\_0)/b\_1)\times m\_IS/m\_s$

Where, w_a mass fraction of the analyte in the sample

R analyte/intenal standard area ratio

b_0 and b_1 linear and angular coefficients of the calibration curve

m_IS mass of internal standard solution added to the sample

m_s mass of sample

	Naphthalene		Benz[a]anthracene		Benzo[a]pyrene	
Source	standard uncertainty (µg/g)	contribution (%)	standard uncertainty (µg/g)	contribution (%)	standard uncertainty (µg/g)	contribution (%)
Area ratio	0.58	53.4	0.055	51.6	0.077	63.0
Sample mass	0.0014	0.00032	0.00024	0.0010	0.00031	0.0010
Internal standar solution mass	0.0014	0.00032	0.00023	0.0009	0.00031	0.0010
Calibration curve	0.078	0.96	0.030	15.4	0.029	8.8
Purity of the calibration standard	0.28	12.4	0.025	10.3	0.027	7.7
Repeatability	0.46	33.2	0.036	22.7	0.044	20.5
Overall	0.79	100	0.077	100	0.097	100

ISO GUM approach was used to combine the components of uncertainty that are part of the measurement equation and the result was combined with repeatability source using the root mean square.

Uncertainty Information from INRiM

$X_{PAH}=(A_{sample}/A_{IS\_sample})/(\bar{A}_{std}/\bar{A}_{IS\_std})\cdot X_{std}\cdot f_{dil}$

X_{PAH}: mass fraction of each PAH [µg/g]

$(A_{sample}/A_{IS\_sample})$: ratio between the chromatographic areas of each PAH and its Internal standard in each run of the sample solutions [AU]

$(\bar{A}_{std}/\bar{A}_{IS\_std})$: ratio between the mean chromarographic areas of each PAH and its Internal Standard in 3 replicated analyses of calibration solution [AU]

X_{std}: mass fraction of each PAH in the calibration solution [µg/g]

f_{dil}: dilution factor

$u(A_{sample}/A_{IS\_sample})$= standard deviation of repeated measurements

$u(\bar{A}_{std}/\bar{A}_{IS\_std})$: standard deviation of repeated measurements

$u(X_{std})$: gravimetric preparation (SRM certificate, weighing, buoyancy effect)

$u(f_{dil})$: gravimetric dilution

The above measurement equation was used to estimate X_{PAH} in each chromatographic run, with the associated uncertainty. X_{PAH} for each ampoule was determined by calculating the weighted mean. The associated uncertainty was calculated by combining quadratically the standard uncertainty of the weighted mean and a repeatability contribution due to the dispersion of the X_{PAH} values. The same approach was used to calculate the final results, from the estimates and uncertainties obtained from 3 different ampoules.

Uncertainty Information from KRISS

$$C = \frac{M_{is\_sol,spiked} \cdot AR_{sample} \cdot M_{s\_sol,std} \cdot C_{s\_sol}}{W_s \cdot AR_{std} \cdot M_{is\_sol,std}}$$

C_{sample}: is the concentration of analytes in the sample;
$C_{s\text{-}sol}$: is the concentration of the analytes standard solution;
M_{sample}: is the mass of the sample taken for analysis;
$M_{is\text{-}sol,\ spiked}$: is the mass of the isotope standard solution added to the sample aliquot;
$M_{is\text{-}sol,\ std.\ mix.}$: is the mass of the isotope standard solution added to the isotope ratio standard solution;
$M_{s\text{-}sol,\ std.\ mix.}$: is the mass of the standard solution added to the isotope ratio standard solution;
AR_{sample}: is the area ratio of analyte/isotope for sample extract, observed by GC/MS;
$AR_{std.\ mix.}$: is the area ratio of analyte/isotope for the isotope ratio standard solution, observed by GC/MS.

Systematic Uncertainty		Naphthalene		Benz(a)anthracene		Benzo(a)pyrene	
		Usys(rel%)	DOF	Usys(rel%)	DOF	Usys(rel%)	DOF
1	Uncertainty of purity of primary reference material	0.025%	36	0.215%	5	0.073%	9
2	Uncertainty of gravimetric preparation for standard solutions	0.34%	3	0.46%	3	0.29%	3
3	Uncertainty of gravimetric mixing for calibration isotope standard mixtures	0.24%	4	0.31%	4	0.38%	4
4	Area ratio of native/isotope for the calibration standard mixture, observed by GC/MS	0.23%	2	0.34%	3	0.29%	3
	combined systematic unc.	**0.47%**	**7**	**0.68%**	**9**	**0.57%**	**10**

Random uncertainty : Standard deviations (s) of multiple measurement results from six subsamplings
Combined standard uncertainties were obtained by combining systematic uncertainties and random uncertainties as shown below equation

$$u(C_{\text{mean}}) = \sqrt{u^2_{\text{s.p.systematic}} + \frac{s^2}{n}}$$

Uncertainty Information from LNE

$$C_{PAH/sample} = \frac{C_{PAH*/sample} \times m_{PAH*/sample}}{m_{sample}} \times (a \times R_{sample} + b) \times f_{standard} + f_P$$

$C_{PAH/sample}$	mass fraction of PAH in the sample in µg/g
$C_{PAH*/sample}$	mass fraction of PAH* in the sample in µg/g
$m_{PAH*/sample}$	mass of labelled solution in the sample in g
m_{sample}	mass of the sample in g
R_{sample}	unlabeled/labeled ion peak area ratio in the sample
a	gradient of the slope for linear regression plot
b	intercept on y axis for the linear regression plot
$f_{standard}$	correction factor due to the standard solutions uncertainty
f_P	correction factor due to measurment precision

Naphtalene	TYPE (A OR B)	RELATIVE UNCERTAINTY (%)
Preparation of sample blends (weighings)	B	5%
Calibration model	B	1%
Preparation of calibration blend (weighings + CRM uncertainty)	B	31%
Precision	B	63%

Benzo[*a*]Pyrene	TYPE (A OR B)	RELATIVE UNCERTAINTY (%)
Preparation of sample blends (weighings)	B	2%
Calibration model	B	2%
Preparation of calibration blend (weighings + CRM uncertainty)	B	21%
Precision	B	75%

Benz[*a*]Anthracene	TYPE (A OR B)	RELATIVE UNCERTAINTY (%)
Preparation of sample blends (weighings)	B	2%
Calibration model	B	3%
Preparation of calibration blend (weighings + CRM uncertainty)	B	38%
Precision	B	57%

Uncertainty Information from NIM

Measurement equation: $$C_{sample} = \frac{R_{SM} \times C_{calib} \times f_{purity} \times M_{spike(sample)}}{R_{CM} \times M_{sample} \times C_{spike(calib)}}$$

R_{SM} : Area ratio of target compound and labeled compound in sample solution.
R_{CM} : Area ratio of target compound and labeled compound in calibration.
C_{calib}: Mass faction of standard solution,by weighing.

$M_{spike(sample)}$: Mass of labeled compound to added into sample, by weighing .
$C_{spike(calib)}$: Mass fractionof labeled compound to add into calibration soultion, by weighing.
M_{sample}: Sample mass, by weighing.
f_{purity} : Purity of calibrant.

Parameter of **Benz[a]anthracene**	Standard Uncertainty (μg/g)	Degrees of freedom	Type
Method precision	0.038	5	A
Purity of pure standard	0.020	large	A+B
Mass fraction of internal standard	0.003		A+B
Mass fraction of sample	0.003		A+B
Mass fraction calibration standard	0.003		A+B
Influnce of interference peak	0.024	large	B
Combined standard uncertainty	0.049	large	B
Coverage factor	2		
Combined expanded uncertainty	0.10		

Parameter of **Benzo[a]pyrene**	Standard Uncertainty (μg/g)	Degrees of freedom	Type
Method precision	0.059	5	A
purity of pure standard	0.021	large	A+B
Mass fraction of internal standard	0.004		A+B
Mass fraction of sample	0.004		A+B
Mass fraction calibration standard	0.004		A+B
Influnce of interference peak	0.040	large	B
Combined standard uncertainty	0.074	large	B
Coverage factor	2		
Combined expanded uncertainty	0.15		

Parameter of **Naphthalene**	Standard Uncertainty (μg/g)	Degrees of freedom	Type
Method precision	0.20	5	A
purity of pure standard	0.092	large	A+B
Mass fraction of sample	0.015		A+B
Mass fraction of calibration standard	0.015		A+B
Influnce of interference peak	0.15	large	B
Combined standard uncertainty	0.27	large	B
Coverage factor	2		
Combined expanded uncertainty	0.53		

Method precision:	Reproducibility of sample determination
Purity of pure standard:	Type A uncertainty (combined uncertainty of 3 method for purity determination), type B uncertainty (respond factor)were combined.
Mass fraction of internal standard:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty ((linearity of weighing, certificate of calibration,solvent evaporation and influnce from moisture and temperatur during weighing) were combined.
Mass fraction of sample:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty (linearity of weighing, certificate of calibration,solvent evaporation and influnce from moisture and temperatur during weighing) were combined.
Mass fraction calibration standard:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty (linearity of weighing, certificate of calibration,solvent evaporation and influnce from moisture and temperatur during weighing) were combined.
Influnce of interference peak	Type B uncertainty (interference from peak of other compound)

Uncertainty Information from NIST

Mass Fraction = (average response factor) × (detector response)

Type A and Type B uncertainties were considered in the assessment of contributions to measurement uncertainty. No sample processing was required, so replicate injections are suitable for assessing Type A uncertainty. Type A uncertainty resulted from the analyses performed for each of the three samples, each injected 10 times, and from analyses of three independently weighed calibration solutions, each injected 5 times. The RSDs for response factors are based on the standard deviation of the mean.

Response factors:
Naphthalene: RSD = 0.439 %
Benz[*a*]anthracene: RSD = 0.387 %
Benzo[*a*]pyrene: RSD = 0.413 %

Potential biases due to purity corrections were considered. The Type B uncertainty for Naphthalene was estimated using a bootstrap procedure based on a Gaussian random effects model for the between-method effects, and for Benz[*a*]anthracene and Benzo[*a*]pyrene, the Type B uncertainty was estimated from the certificates of analysis reported for the BCR CRM reference standards.

Purity:
Naphthalene: 0.3 %
Benz[*a*]anthracene: 0.045 %
Benzo[*a*]pyrene: 0.2 %

In the total run order of measurements, there are 5 sets of 6 consecutive measurements each; the mean analyte level was estimated as the mean of these 5-set means, with a Type A uncertainty being the standard error of the mean of the set means. Since each set has 6 observations, the mean of the set means equals the mean of the measurements.

An analysis of variance was run that modeled the effects of the measurement sets and the samples. In addition to the sets, the model showed small but statistically significant effects for sample. However, due to the solution nature of the material, which is presumed homogenous, it is considered very likely that any such effects, which are small in magnitude, are due to measurement variability rather than the material inhomogeneity.

The combined uncertainty incorporates Type A and Type B uncertainties, consistently with the ISO GUM.

Uncertainty Information from NMIJ

Canal = Fmethod * Fsample * Fcal * R(sample) * Ccal * (Mcal * Msur(sample)) / (Msample * Msur(calib))

where,

Canal is a concentration of analyte in the sample (mg/kg),

Fmethod is a factor for difference of measurement,

Type A uncertainty (from ANOVA of analytial results obtained with GC-FID and GC-MS)

Fsample is a factor for reproducibility of sample solution preparation (CCQM sample + surrogate),

Type A uncertainty (from ANOVA, n=3)

Fcal is a factor for reproducibility of calibration solution preparation,

Type A uncertainty (from ANOVA, n=4)

R(sample) is a Rsample / Rcalibration,

Rsample is a ratio of peak area of analyte / surrogate observed for the sample solution,

Rcalibration is a ratio of peak area of analyte / surrogate observed for the calibration solution,

Type A uncertainty (repeatability of measurement, n=5)

Ccal is concentration of analyte in the calibration solution, (mg/kg)

u(Ccal) is uncertainty of concentration in calibration solution prepared from neat naphthalene or NMIJ CRM BaP

Mcal is mass of the standard solution of analytes taken for preparation of the calibration solution,

Type B uncertainties (linearity of weighing, certificate of calibration) were combined.

Msur(sample) is mass of the surrogates solution added to the sample, (mg)

Type B uncertainties (linearity of weighing, from certificate of calibration) were combined.

Msample is mass of the CCQM sample taken for measurement, (mg)

Type B uncertainties (linearity of weighing, certificate of calibration) were combined.

Msur(calib) is mass of the surrogate solution taken for preparation of the calibration solution, (mg)

Type B uncertainty (linearity of weighing, from certificate of calibration) were combined.

Table. Evaluation of uncertainty

	Value, xi	Uncertainty, u(xi)	degree of freedom	type of uncertainty
Fmethod: Naphthalene	1.0000	0.0023	4	A
Fmethod: Benzo[a]pyrene	1.0000	0.0075	4	A
R(sample): Naphthalene	0.82758	0.00048	4.05	A
R(sample): Benzo[a]pyrene	0.9557	0.0015	4.48	A
Fcal: Naphthalene	1.0000	0.0088	3	A
Fcal: Benzo[a]pyrene	1.0	0.0	3	A
Mcal (mg)	158.19	0.024	large	B
Ccal: Naphthalene (mg/kg)	29.49	0.10	large	A + B
Ccal: Benzo[a]pyrene (mg/kg)	6.40	0.13	large	A + B
Fsample: Naphthalene	1.0000	0.0030	2	A
Fsample: Benzo[a]pyrene	1.0	0.0	2	A
Msur(sample) (mg)	745.70	0.024	large	B
Msur(calib) (mg)	740.68	0.024	large	B
Msample (mg)	152.52	0.024	large	B

	Concentration (mg/kg)	combined uncertainty (mg/g)	k	expanded uncertainty (mg/kg)
Naphthalene	25.35	0.26	2.57	0.66
Benzo[a]pyrene	6.26	0.13	2.00	0.26

IDMS measurement equation:

$$W_x = W_z \times \frac{m_z}{m_{yc}} \times \frac{m_y}{m_x} \times \frac{R'_B}{R'_{BC}}$$

W_x	Mass fraction of PAH in test portion µg/g
W_z	Mass fraction of PAH in calibration µg/g
m_z	Mass of CRM solution added to the calibration blend (g)
m_{yc}	Mass of isotope added to calibration blend (g)
m_y	Mass of isotope added to sample blend (g)
m_x	Mass of sample (g)
R'_B	Peak area ratio of analyte/ isotope in sample blend
R'_{BC}	Peak area ratio of analyte/ isotope in calibration blend

Level of confidence is approximately 95%

Naphthalene Factors in uncertainty		x	u	u/x	u/x^2	
Wz	CRM uncertainty	**25.31**	1.75E-01	6.91E-03	4.78E-05	
mz	Weight of calibration blend (g)	0.08	1.00E-06	1.31E-05	1.72E-10	
my	Weight of Isotope added to sample (g)	0.13	1.63E-06	1.25E-05	1.55E-10	
myc	Weight of Isotope added to calibration blend (g)	0.13	1.63E-06	1.25E-05	1.55E-10	
mx	Weight of sampled (g)	0.01	1.63E-06	1.43E-04	2.05E-08	
R'B/R'BC	Ratio of peaks areas of native/ labelled in the samples	4.97	4.84E-02	9.74E-03	9.48E-05	
			Sum	0.02	1.43E-04	
			Veff	28.48	**0.30**	u
			k	**2.05**	**0.62**	U
					2.45	Rel U

Benz[a]anthracene Factors in uncertainty		x	u	u/x	u/x^2	
Wz	CRM uncertainty	**5.16**	3.50E-02	6.78E-03	4.60E-05	
mz	Weight of calibration blend (g)	0.08	1.00E-06	1.31E-05	1.72E-10	
my	Weight of Isotope added to sample (g)	0.13	1.63E-06	1.25E-05	1.55E-10	
myc	Weight of Isotope added to calibration blend (g)	0.13	1.63E-06	1.25E-05	1.55E-10	
mx	Weight of sampled (g)	0.01	1.63E-06	1.43E-04	2.05E-08	
RB	Ratio of peak areas	0.90	1.20E-02	1.34E-02	1.78E-04	
			Sum	0.02	2.25E-04	
			Veff	20.09	**0.08**	u
			k	**2.09**	**0.16**	U
					3.13	Rel U

Benzo[a]pyrene Factors in uncertainty		x	u	u/x	u/x^2	
Wz	CRM uncertainty	**6.22**	5.50E-02	8.84E-03	7.82E-05	
mz	Weight of calibration blend (g)	0.08	1.00E-06	1.31E-05	1.72E-10	
my	Weight of Isotope added to sample (g)	0.13	1.63E-06	1.25E-05	1.55E-10	
myc	Weight of Isotope added to calibration blend (g)	0.13	1.63E-06	1.25E-05	1.55E-10	
mx	Weight of sampled (g)	0.01	1.63E-06	1.43E-04	2.05E-08	
RB	Ratio of peak areas	1.77	2.34E-02	1.32E-02	1.75E-04	
			Sum	0.02	2.53E-04	
			Veff	26.71	**0.10**	u
			k	**2.06**	**0.20**	U
					3.27	Rel U

Uncertainty Information from UME

Uncertainty Calculations

Sources :
1- Mass of sample intake
2- Labelled stock solution
3- Native stock solution
4- Repeatability
5- Calibration graph

$$\frac{u_c(Analyte)}{c_{Analyte}} = \sqrt{(\frac{u(m_{SI})}{m_{SI}})^2 + (\frac{u(c_{LSS})}{c_{LSS}})^2 + (\frac{u(c_{NSS})}{c_{NSS}})^2 + (\frac{u(r)}{r})^2 + (\frac{u(Cal)}{C_0})^2}$$

Uncertainty Budget of BaA			
Parameters	**Value (X)**	**u(x)**	**u(x)/X**
Mass of sample intake (SI)	75	0,0000115	1,53E-07
Labelled stock solution (LSS)	10137,5	71,09	7,01E-03
Native stock solution (NSS)	10060,3	27,24093	2,71E-03
Repeatability (r)	100	0,23678	2,37E-03
Calibration Graph (Cal)	1	0,00915	9,15E-03
Combined Standard Uncertainty	4.99	0,06	0,012
Expanded Uncertainty (k=2)		0,12	
Relative Expanded Uncertainty	2,41 %		

Uncertainty Budget of BaP			
Parameters	**Value (X)**	**u(x)**	**u(x)/X**
Mass of sample intake (SI)	75	0,0000115	1,53E-07
Labelled stock solution (LSS)	10137,5	71,09	7,01E-03
Native stock solution (NSS)	10060,3	27,24093	2,71E-03
Repeatability (r)	100	0,22862	2,29E-03
Calibration Graph (Cal)	0,55	0,00785	1,43E-02
Combined Standard Uncertainty	6.23	0,10	0,016
Expanded Uncertainty (k=2)		0,20	
Relative Expanded Uncertainty	3,26 %		

Uncertainty Budget of Nap			
Parameters	**Value (X)**	**u(x)**	**u(x)/X**
Mass of sample intake (SI)	75	0,0000115	1,53E-07
Labelled stock solution (LSS)	10137,5	71,09	7,01E-03
Native stock solution (NSS)	10060,3	27,24093	2,71E-03
Repeatability (r)	100	0,37559	3,76E-03
Calibration Graph (Cal)	10	0,01647	1,65E-03
Combined Standard Uncertainty	25.32	0,22	0,009
Expanded Uncertainty (k=2)		0,43	
Relative Expanded Uncertainty	1,71 %		

Sources of uncertainty

Source of uncertainty		Type
Standard uncertainty of sample measurements, u_A		A
Calibration, u_{cal}	SRM, u_{SRM}	B
	Weighing of SRM and IS, $u_{solution}$	B
	Relative response factor (RF), u_{RF}	B
Sample, u_{sample}	Weighing of sample and IS, u_{sample}	B

The equation of standard uncertainty is:

$$u = \sqrt{u_A^2 + u_B^2} = \sqrt{u_A^2 + \left[u_{cal}^2 + u_{sample}^2\right]} = \sqrt{u_A^2 + \left[(u_{RF}^2 + u_{solution}^2) + u_{sample}^2\right]}$$

где

u_A – standard uncertainty (type A) of sample results, %;

u_B – standard uncertainty (type B) consisting of standard uncertainty of calibration – u_{cal}, %, and standard uncertainty of sample preparation – $u_{solution}$, %.

In tern u_{cal} consists of $u_{solution}$ – standard uncertainty of calibration solution preparation and

u_{RF} – standard uncertainty of RF (relative Response Factor), %.

1. u_A evaluation

u_A were calculated as standard deviation of the mean based on measurements for four subsamples from each of four ampoules of the solution:

u_A (BaA) = 0,23%;

u_A (BaP) = 0,20 %.

2. u_{cal} evaluation

The equation of u_{cal} is:

$$u_{cal} = \sqrt{u_{SRM}^2 + u_{solution}^2}$$

u_{SRM} were taken from NIST SRM 1647f Certificate of Analysis:

u_{SRM} (BaA)= 0,68 %;

u_{SRM} (BaP)= 0,88 %;

$u_{soltion}$ was calculated by using average mass of SRM and IS (16 mg) and tolerance of the balance (±0,03 mg) and suggesting the quadratic distribution:

$$u_{solution} = \frac{2 * 0{,}03}{16 * \sqrt{3}} * 100$$

$u_{solution}$= 0,22 %.

3. u_{RF} evaluation

u_{RF} were calculated as standard deviation of the RF mean of 7 calibration solutions:
u_{RF} (BaA) = 0,61%;
u_{RF} (BaP) = 0,57 %.

4. u_{sample} evaluation

u_{sample} was calculated by using average mass of sample and IS (16 mg) and tolerance of the balance (±0,03 mg) and suggesting the quadratic distribution:

$$u_{sample} = \frac{2 * 0{,}03}{16 * \sqrt{3}} * 100$$

$u_{solution}$= 0,22 %.

Benz(a)antracene - Combined standard uncertainty and expanded uncertainty

№	Source of uncertainty		Type	Standard uncertainty, %
1	Standard uncertainty of sample measurements, u_A		A	0,23
2	Calibration	SRM, u_{SRM}	B	0,68
3		Weighing of SRM, $u_{solution}$	B	0,22
4		Relative response factor (RF), u_{RF}	B	0,61
5	Sample, u_{sample}	Weighing of sample and IS, u_{sample}	B	0,22
Combined standard uncertainty, u				0,97
Expanded uncertainty, U (k=2)				1,94
Set, U				1,9

Benz(a)pyrene - Combined standard uncertainty and expanded uncertainty

№	Source of uncertainty		Type	Standard uncertainty, %
1	Standard uncertainty of sample measurements, u_A		A	0,20
2	Calibration	SRM, u_{SRM}	B	0,88
3		Weighing of SRM, $u_{solution}$	B	0,22
4		Relative response factor (RF), u_{RF}	B	0,57
5	Sample, u_{sample}	Weighing of sample and IS, u_{sample}	B	0,22
Combined standard uncertainty, u				1,09
Expanded uncertainty, U (k=2)				2,18
Set, U				2,2

Uncertainty Information from VSL

The final result is calculated as a weighted mean, using a meta-analysis approach on the mass fractions from the 3 measurements on 3 vials. The standard deviation is approximately $\tau = 0.70$ ppm using the DerSimonian-Liaird model. The calculations have been performed in R using the package metafor.

The results of the 3 × 3 measurements are obtained as follows. The GC-FID is calibrated with a series of standards, prepared from naphthalene and acetonitrile. The calibration standards have been prepared gravimetrically. Both the naphthalene and acetonitrile have been analysed for the presence of impurities. Appropriate corrections have been applied.

The calibration function is a straight line for each of the 9 measurements. The regression has been performed using an errors-in-variables approach. The mass fraction of the unknown has been determined by a searching algorithm, given the coefficients of the straight line and the response. The associated standard uncertainty has been obtained by applying the law of propagation of uncertainty from the GUM. The resulting mass fractions and associated standard uncertainties have been used as input for the meta-analysis described previously.

APPENDIX H: Participants' Quantitative Results as Reported

The following are pictures of the quantitative results as provided by the participants in the "Results" worksheet of the "Reporting Form" Excel workbook. Information is grouped by participant and presented in alphabetized acronym order.

Quantitative Results from BAM

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.30	0.43	2	0.85
Benz[*a*]anthracene	4.81	0.05	2	0.10
Benzo[*a*]pyrene	6.07	0.08	2	0.15

Quantitative Results from BVL

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	not analyzed			
Benz[*a*]anthracene	4.99	0.05	2	0.1
Benzo[*a*]pyrene	5.56	0.10	2	0.2

Quantitative Results from CENAM

Analytes	Ampoule	Mass Fraction (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Benzo[a]anthracene	**1**	5069	55	2	110
	2	4987	55	2	110
	3	4966	53	2	107
	Mean	5007	63	2	126
Benzo[a]pyrene	**1**	6580	60	2	120
	2	6481	84	2	169
	3	6352	130	2	259
	Mean	6471	116	2	233

Quantitative Results from EXHM

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)				
Benz[*a*]anthracene	4.714	0.076	2.12	0.162
Benzo[*a*]pyrene	5.867	0.100	2.11	0.210

Quantitative Results from GLHK

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	NA			
Benz[a]anthracene	4.87	0.08	2	0.16
Benzo[a]pyrene	6.08	0.12	2	0.25

Quantitative Results from HSA

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.29	0.193	2	0.39
Benz[*a*]anthracene	4.901	0.0402	2	0.080
Benzo[*a*]pyrene	6.09	0.066	2	0.13

Quantitative Results from INMETRO

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	27.4	0.79	2.45	1.9
Benz[*a*]anthracene	4.91	0.077	2.00	0.15
Benzo[*a*]pyrene	6.39	0.097	2.57	0.25

Quantitative Results from INRiM

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.32	0.31	2	0.63
Benz[*a*]anthracene	5.12	0.06	2	0.12
Benzo[*a*]pyrene	6.28	0.08	2	0.17

Quantitative Results from KRISS

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.08	0.12	2.31	0.28
Benz[*a*]anthracene	4.785	0.034	2.26	0.076
Benzo[*a*]pyrene	5.989	0.037	2.18	0.081

Quantitative Results from LNE

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	23.95	0.28	2	0.55
Benz[*a*]anthracene	4.88	0.06	2	0.12
Benzo[*a*]pyrene	6.03	0.08	2	0.15

Quantitative Results from NIM

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.19	0.27	2	0.53
Benz[*a*]anthracene	4.88	0.049	2	0.10
Benzo[*a*]pyrene	6.10	0.074	2	0.15

Quantitative Results from NIST

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.66	0.184	2.12	0.391
Benz[*a*]anthracene	4.94	0.029	2.20	0.063
Benzo[*a*]pyrene	6.16	0.042	2.23	0.094

Quantitative Results from NMIJ

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.35	0.26	2.57	0.66
Benz[*a*]anthracene	N/A	N/A	N/A	N/A
Benzo[*a*]pyrene	6.26	0.13	2	0.26

Quantitative Results from NMISA

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.31	0.30	2.05	0.62
Benz[*a*]anthracene	5.16	0.08	2.09	0.16
Benzo[*a*]pyrene	6.22	0.10	2.06	0.20

Quantitative Results from UME

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.32	0.22	2	0.43
Benz[*a*]anthracene	4.99	0.06	2	0.12
Benzo[*a*]pyrene	6.23	0.10	2	0.20

Quantitative Results from VNIIM

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)				
Benz[*a*]anthracene	4.82	0.046	2	0.09
Benzo[*a*]pyrene	6.02	0.066	2	0.13

Quantitative Results from VSL

Measurand	Mass Fraction (µg/g)	Combined Standard Uncertainty (µg/g)	Coverage Factor (k)	Expanded Uncertainty (µg/g)
Naphthalene (optional)	25.2	0.5	2	1.0
Benz[*a*]anthracene	x	x	x	x
Benzo[*a*]pyrene	x	x	x	x

APPENDIX I: Prototype Broader-Scope Core Competency Claim

Table I-1: Prototype Broader Category 3 Claims
for All Participants

Measurement service	Category 3. Organic Solutions
Measurement service sub-category	PAHs (3.1); PCBs (3.2); Pesticides (3.3); Other (3.4)
Matrix	Single component or multicomponent organic solution
Measurand	Analyte or Component: low-polarity ($pK_{ow} < -2$) organic analyte of low molar mass (100 g/mol to 500 g/mol) Quantity: Mass fraction
Dissemination range of measurement capability	From 0.1 to 100 Unit: μg/g
Dissemination position of expanded uncertainties	Demonstrated range: 3.3 % to 5.5 % (BaA, BaP) 2.7 % to 6.8 % (Nap) Unit: % Coverage factor: 2 or Student's $t_{1-0.95,n-1}$ Level of confidence: 95 % Expanded uncertainty is a relative one: Yes
Example measurands within this scope	PAHs, PCBs, PFOS, xylenes, organochloride pesticides, chlorophenols, bromo(halo)forms, chlorinated industrial solvents (e.g., CCl_4), steroids, fat soluble-vitamins, steroidal-based vitamin metabolites
Supporting Evidence	Successfully participated in CCQM-K131

Table I-2: Prototype Broader Category 1 Claims
for Participants Who Performed In-House Purity Assessment

Measurement service	Category 1. High purity chemicals
Measurement service sub-category	Organic compounds (1.2)
Matrix	High purity [individual primary component]
Measurand	Analyte or Component: low-polarity ($pK_{ow} < -2$) organic analyte of low molar mass (100 g/mol to 500 g/mol) Quantity: Mass fraction %
Dissemination range of measurement capability	From 92 to 100 [purity range of calibrant materials] Unit: %
Dissemination position of expanded uncertainties	Demonstrated range: 3.3 % to 5.5 % (BaA, BaP) 2.7 % to 6.8 % (Nap) Unit: % Coverage factor: 2 or Student's $t_{1\text{-}0.95,n\text{-}1}$ Level of confidence: 95 % Expanded uncertainty is a relative one: Yes
Example measurands within this scope	PAHs, PCBs, PFOS, xylenes, organochloride pesticides, chlorophenols, steroids, fat soluble-vitamins, steroidal-based vitamin metabolites
Supporting Evidence	Successfully participated in CCQM-K131 and participation in CCQM-K55 series