

## CCQM-K38: Determination of PAHs in Solution

Final Report: October 11, 2005

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## 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 analytes. Appropriate value assignments and uncertainty calculations for these calibration solutions are critical. For the Mutual Recognition Arrangement (MRA) developed by the CIPM, there are numerous Calibration and Measurement Capability Claims (CMCs) published in Category 3 Organic Solutions in the CIPM MRA Appendix C. Additional CMCs in this category are being proposed and reviewed. Evidence of successful participation in formal, relevant international comparisons is needed to support these claims.

A CCQM pilot study conducted in 2004 was comprised of three parts: CCQM-P31a Organic Solution – Polycyclic Aromatic Hydrocarbons (PAHs), CCQM-P31b Organic Solution – Polychlorinated Biphenyl (PCB) Congeners, and CCQM-P31c Organic Solution – Chlorinated Pesticides. The results from the CCQM-P31a study are summarized below for the PAHs. After review of the P31a results at the April 2004 Organic Analytical Working Group (OAWG) meeting and the October 2004 OAWG meeting (Beijing 2004), it was decided to proceed with a key comparison study for PAHs in solution (CCQM-K38) with a concurrent second pilot study for the PAHs in solution (CCQM-P31a.1). CCQM-K38 was conducted during the same time period as a PAHs in soil pilot study (CCQM-P69) coordinated by CENAM and BAM.

PAHs result from combustion sources and are ubiquitous in environmental samples. For both the pilot CCQM-P31a.1 and the key CCQM-K38, studies, five target PAHs, phenanthrene, fluoranthene, benz[*a*]anthracene (B[*a*]A), benzo[*a*]pyrene (B[*a*]P), and benzo[*ghi*]perylene (B[*ghi*]P), were selected as representative of the measurement of individual compounds in multicomponent PAH solutions used as calibrants. The target congeners spanned the volatility range and the typical concentration range for the PAHs found in environmental samples, and included some potential problematic GC separations. Phenanthrene and anthracene are isomers that elute very close to each other using most chromatographic phases. Phenanthrene is typically the more abundant of the two and thus may overwhelm the anthracene peak. Fluoranthene and pyrene are also isomers but are typically well resolved on most chromatographic phases. B[*a*]A, chrysene, and triphenylene are isomers, and although B[*a*]A is typically baseline separated from chrysene and triphenylene, chrysene and triphenylene are difficult to separate on most chromatographic phases. B[*a*]P is typically baseline separated from benzo[*e*]pyrene and perylene but occurs at lower concentrations than B[*e*]P and equal or higher concentrations than perylene. B[*ghi*]P and indeno[1,2,3-*cd*]pyrene are isomers and are well separated using most chromatographic phases. Dibenz[*a,h*]pyrene, however, differs in molecular mass by just 2 units thus resulting in a fragment ion at the same mass as the B[*ghi*]P and is closely eluting on most chromatographic phases with B[*ghi*]P.

This report summarizes the results previously reported for CCQM-P31a and the results for CCQM-K38. The results for CCQM-P31a.1 are presented in a separate report.

## PILOT STUDY SUMMARY

A pilot study (CCQM-P31a) for PAHs in solution was organized by NIST in 2003/2004. Eleven laboratories received the samples for CCQM-P31a with nine returning data. The CCQM-P31a Organic Solution – PAHs contained 35 PAHs (the 5 PAHs to be determined plus 30 additional PAHs) in toluene at concentrations of 1 µg/g to 15 µg/g ampouled in 2 mL ampoules with approximately 1.2 mL of solution per ampoule. The participating laboratories received six ampoules of the appropriate solution. The exercise instructions requested the analysis of duplicate subsamples from each of four ampoules using the laboratory's analytical procedure for determination of the concentrations (mass fraction basis) of the target analytes in the study.

For CCQM-P31a Organic Solutions – PAHs, all of the participating laboratories used gas chromatography with mass spectrometric detection (GC/MS) except for KRISS. KRISS used GC with flame ionization detection (GC-FID) for their analyses. BAM submitted data that was a combined value from two GC/MS methods, a liquid chromatography with diode array detection (LC-DAD) method, and a LC with fluorescence detection (LC-FLD) method. The gravimetrically prepared concentrations of the PAHs targeted in CCQM-P31a ranged from 4.39 µg/g for B[a]A to 11.7 µg/g for phenanthrene. Excluding one outlier, the laboratories' data ranged from -13% to +18% of the gravimetrically prepared concentrations with the majority of the data agreeing with the gravimetric values to within ±5%.

## KEY COMPARISON – MATERIALS AND CONDUCT OF STUDY

The CCQM-K38 key comparison study for PAHs in solution was coordinated by NIST with samples distributed in June 2005 according to the project protocol agreed to at the April 2005 OAWG meeting. The laboratories receiving samples for CCQM-K38 were:

BAM	[Germany]
CENAM	[Mexico]
INMETRO	[Brazil]
JRC-IRMM	[EC]
KRISS	[Korea]
LGC	[Great Britain]
LNE	[France]
NIST	[USA]
NMIJ	[Japan]
NRCCRM	[China]
VNIIM	[Russia]

Three of the laboratories, INMETRO, LGC, and LNE, did not return data. All results in this report were received prior to the September 2005 OAWG meeting.

The study material was gravimetrically prepared, and the gravimetric concentrations were adjusted for assessed purity of component materials. The solution used contained 10

PAHs: phenanthrene, anthracene, fluoranthene, pyrene, B[a]A, chrysene, B[e]P, B[a]P, B[ghi]P, and indeno[1,2,3-*cd*]pyrene. Additional compounds were included to check the identification of the compounds as well the quantification of the target analytes. The concentrations of the targeted congeners ranged from 3.9 µg/g for B[a]A to 8.9 µg/g for fluoranthene. Each solution was ampouled in 2 mL ampoules with approximately 1.2 mL of solution per ampoule.

For CCQM-K38, each participating laboratory received five ampoules of the solution. The exercise instructions requested the analysis of one aliquot from each of four ampoules using the laboratory's analytical procedure for determination of the concentrations (mass fraction basis) of the target analytes in the study.

## RESULTS

Eleven laboratories received samples (see above), and eight returned data for CCQM-K38. The results were presented by the coordinating laboratory and the individual participants and discussed at the September 2005 CCQM OAWG meeting at IRMM in Geel, Belgium. Table 1 presents all results for the five target analytes, the Key Comparison Reference Values (KCRVs) based on the gravimetric preparation, and several summary statistics characterizing the reported values: the expected value, the expected measurement uncertainty, the among-participant variability, the expected total variability, and 95% confidence intervals for the population and on the expected value. The degree of equivalence graphs relative to the KCRV are shown in Figure 1. The uncertainty of the KCRV is estimated from a combination of the uncertainty in the gravimetric preparation and the adjusted median absolute deviation from the median value.<sup>1</sup>

Table 2 presents the uncertainty calculations for each of the participants. Each participant used different approaches to the calculation of standard uncertainty. Some of the common sources of uncertainty noted were the measurement precision and the purity of the standards used.

## DISCUSSION

The gravimetric concentrations of the five PAHs in the solution distributed for the CCQM-K38 study ranged from 3.9 µg/g for B[a]A to 8.9 µg/g for fluoranthene. Based on discussions at the September 2005 CCQM OAWG meeting in Geel, Belgium, the KCRV for each congener in the solution is defined as the gravimetric concentration, and the uncertainty of the KCRV is a combination of the uncertainty of the gravimetric concentration and the median absolute deviation from the median value (MADE in Table 1). The KCRVs and associated uncertainties are as follows:

Phenanthrene	5473 ng/g ± 141 ng/g
Fluoranthene	8906 ng/g ± 196 ng/g
Benz[a]anthracene	3952 ng/g ± 95 ng/g

Benzo[*a*]pyrene      4956 ng/g ± 153 ng/g

Benzo[*ghi*]perylene    6872 ng/g ± 146 ng/g

As seen in Figure 1, the majority of the data reported by the laboratories for the selected PAHs overlapped the uncertainty of the KCRV. The median values from the participant results were within 1% of the gravimetric values: -0.5% for phenanthrene; 0.2% for fluoranthene; -0.2% for B[*a*]A; -0.1% for B[*a*]P; and -0.1% for B[*ghi*]P.

## **CONCLUSIONS AND HOW FAR DOES THE LIGHT SHINE?**

This Key Comparison study demonstrated a high level of equivalence in capabilities of the participating NMIs to successfully identify and measure five PAHs (phenanthrene, fluoranthene, benz[*a*]anthracene, benzo[*a*]pyrene, and benzo[*ghi*]perylene) in a solution using GC/MS-based methods.

The PAHs measured in CCQM-K38 were selected to be representative of PAHs typically used as calibrants in the determination of the PAHs found in environmental samples and to provide the typical analytical measurement challenges encountered in the value-assignment of these PAH calibration solutions, such as volatility losses and resolution from potential interferences and other PAHs present as components in the solution during chromatographic separation. The abilities demonstrated by the laboratories that provided comparable measurements for all five PAHs in this Key Comparison should be indicative of their ability to provide reference measurements for a suite of PAHs in solutions when present at levels greater than 3 µg/g provided the laboratory demonstrates an acceptable degree of separation of the PAHs in the specific solution being analyzed.

## **REFERENCE**

1. S. Ellison, Robust Statistics Toolkit (RobStat.xla) Excel add-in, [www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/RobustStatistics.asp](http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/RobustStatistics.asp)

Table 1. Results and Summary Statistics for CCQM-K38 Organic Solution – PAHs. All Values as Mass Fractions, ng/g

Participant	Source of calibrants	phenanthrene			fluoranthene			B[a]A		
		Value	Combined Std Unc	Expanded Std Unc	Value	Combined Std Unc	Expanded Std Unc	Value	Combined Std Unc	Expanded Std Unc
BAM	SRM 2260a	5371	33	81	8874	60	155	3933	29	60
CENAM	CENAM DMR-275a	5404.1	68.9	143.0	9001.9	95.3	201.0	4014.4	61.7	132.4
JRC-IRMM	Dr Ehrenstorfer for phen & BaP and BCR for remainder	5609.9	40.3	80.7	8716.1	61.8	123.6	3989.8	40.4	80.8
KRISS	TCI for phen, Aldrich for BaP and BCR for remainder	5357	26	54	8914	72	156	3904	30	64
NIST	2260a	5440	32	63	8928	49	97	3956	41	81
NMIJ	Supelco for phen, AccuStandard for BghiP, and TCI for remainder	5451	29	57	9008	47	94	3922	23	46
NRCCRM	Accustandard	5755	149	297	8919	146	292	3889	69	139
VNIIM	SRM 2260a	5539.79	29.54	59.08	9180.10	63.79	127.58	4040.74	56.52	113.04
	gravimetric	5473	32	64	8906	46	92	3952	21	42
	N	8			8			8		
	Mean	5491.0			8942.6			3956.1		
	SD	136.4			131.9			54.3		
	Median	5446			8924			3945		
	MADe	82.0			95.0			64.0		
	MADe & ExU	104.2			124.4			79.1		
	$T_{s[1-0.95,N-1]}$	2.36			2.36			2.36		
	$U_{95}$ (Values)	246.4			294.3			187.2		
	% $U_{95}$ (Values)	4.5			3.3			4.7		
	$U_{95}$ (Median)	87.1			104.0			66.2		

N: Number of values. Mean: Mean of values. SD: Standard deviation of values. ExU: pooled  $u_c$ , the expected uncertainty. Median: Median of values. MADe: Median absolute deviations from the median, a robust estimate of the SD. MADe&ExU:  $\sqrt{(\text{MADe}^2 + \text{ExU}^2)}$ , the total dispersion of the reported values.  $T_{s[1-0.95,N-1]}$ : Student's t 95% confidence coverage factor.  $U_{95}$ (Value):  $T_{s[1-0.95,N-1]} \times (\text{MADe\&ExU})$ , the uncertainty on the population of values. % $U_{95}$ (Value):  $100 \times U_{95}$ (Value)/Median.  $U_{95}$ (Median):  $U_{95}$ (Value) /  $\sqrt{N}$ , the uncertainty on the expected value

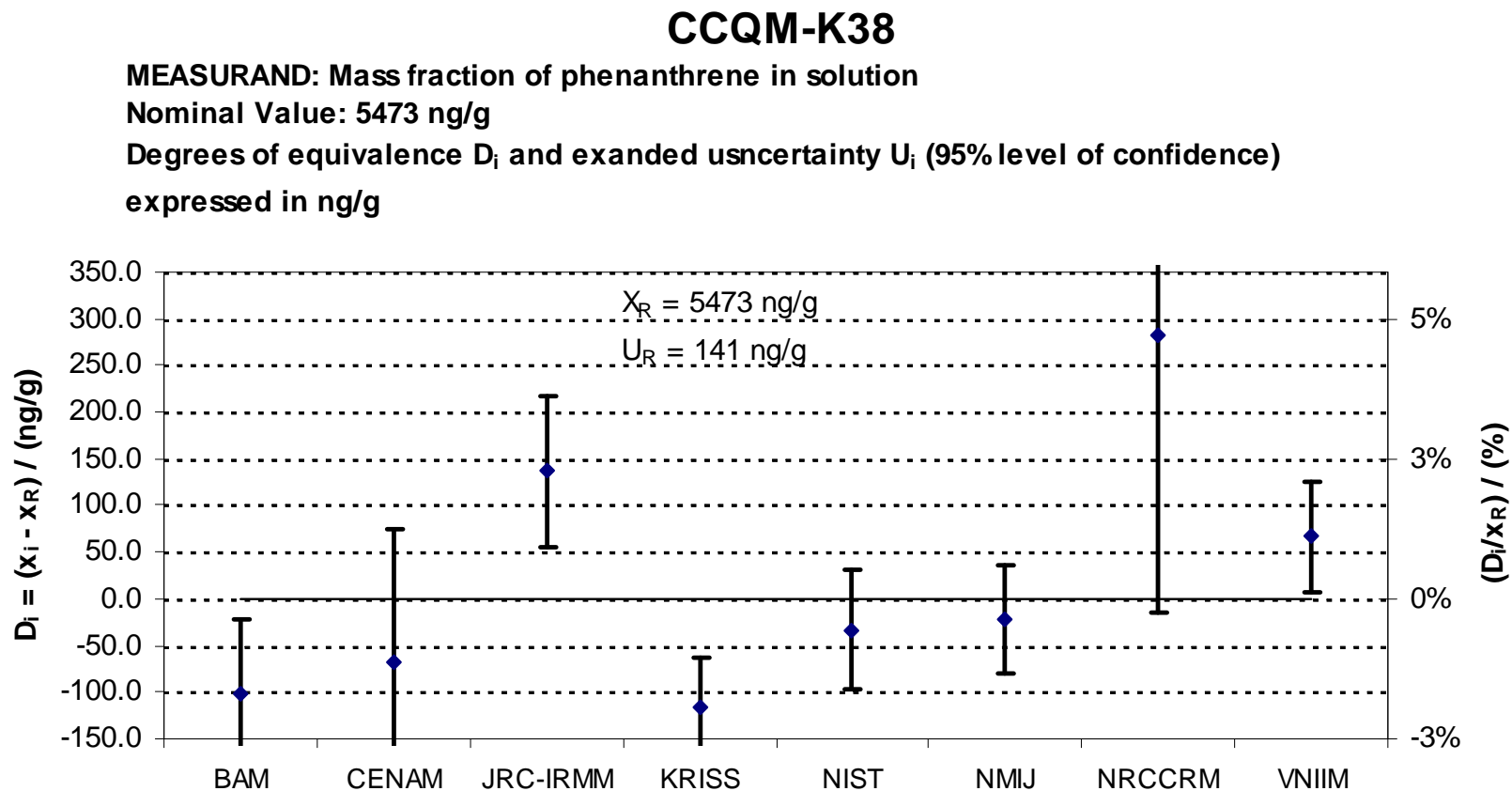
Table 1, Continued. Results and Summary Statistics for CCQM-K38 Organic Solution – PAHs. All Values as Mass Fractions, ng/g

Participant	Source of calibrants	B[a]P			B[ghi]P		
		Value	Combined Std Unc	Expanded Std Unc	Value	Combined Std Unc	Expanded Std Unc
BAM	SRM 2260a	4665	106	273	6768	93	296
CENAM	CENAM DMR-275a	5103.8	64	142.6	7067.3	48.7	101.0
JRC-IRMM	Dr Ehrenstorfer for phen & BaP and BCR for remainder	4890.2	28.4	56.8	6829.3	25.3	50.5
KRISS	TCI for phen, Aldrich for BaP and BCR for remainder	4973	25	51	6886	34	67
NIST	2260a	4922	89	178	6880	47	94
NMIJ	Supelco for phen, AccuStandard for BghiP, and TCI for remainder	4756	26	52	6850	35	71
NRCCRM	Accustandard	5464	81	162	6801	77	152
VNIIM	SRM 2260a	4957.81	61.63	123.26	7158.94	67.37	134.75
gravimetric		4946	26	52	6872	34	68
	N	8			8		
	Mean	4966.5			6905.1		
	SD	241.9			136.4		
	Median	4940			6865		
	MADe	158.0			74.0		
	ExU	66.8			57.8		
	MADe & ExU	171.5			93.9		
	$T_{s[1-0.95,N-1]}$	2.36			2.36		
	$U_{95}$ (Values)	405.6			222.0		
	% $U_{95}$ (Values)	8.2			3.2		
	$U_{95}$ (Median)	143.4			78.5		

Table 2. Participant Uncertainty Budgets for CCQM-K38

Participant	Component	Type	df
BAM	Precision of the method	A	3
	Uncertainty of the calibrant	B	100
CENAM	Mass ratio of standard low level	A	large
	Mass ratio of standard high level	A	large
	Mass of sample	B	large
	Mass of labeled in sample	B	large
	Unlabeled /labeled area ratio of high level standard	A	3
	Unlabeled /labeled area ratio of low level standard	A	3
	Unlabeled /labeled area ratio of sample	A	3
	Concentration in standard solution	A	large
	Concentration in sample	A	3
JRC-IRMM	Uncertainty of the standards used (weighings, dilutions, and purity)		
KRISS	Relative standard deviation of results (analyte concentration		
	Standard solution - purity and repeatability of gravimetric preparation		
	Isotope ratio Standard		
	Repeatability of analysis -includes measurement of isotope ratio of sample, weighing of sample taken for analysis, and weighing of IS solution added to sample		
	Measurement uncertainty		
NIST	Measurement of isotope ratio of standard + IS		
	Method precision	A	3
	Measurement of calibration solutions	A	5
NMIJ	Certified concentrations of SRM used to prepare calibration solutions	B	large
	Method precision	A	15
	Purity of reference standard	B	large
	Preparation of calibration solution	B	large
	Ratio, calibration solution	B	large
	Ratio, sample	B	large
	Balance linearity, calibration solution	B	large
	Balance linearity, sample spike	B	large
	Balance linearity, calibration spike	B	large
Balance linearity, sample mass	B	large	
NRCCRM	Method precision	A	3
	Mass fraction calibration solution	B	large
VNIIM	Gravimetric preparation of calibration solutions		
	Gravimetric preparation of internal standard solution		
	Gravimetric preparation of sample solution		
	Relative standard deviation of SRM concentrations		
	Relative standard deviation of the response factor		
	Relative standard deviation of the results		

Figure 1. Degrees of Equivalence Graphs for each Congener in CCQM-K38. Shown is the KCRV (equivalent to the gravimetric value)  $\pm$  expanded uncertainty (U) of the KCRV (a combination of the uncertainty in the gravimetric preparation and median absolute deviations from the median value)

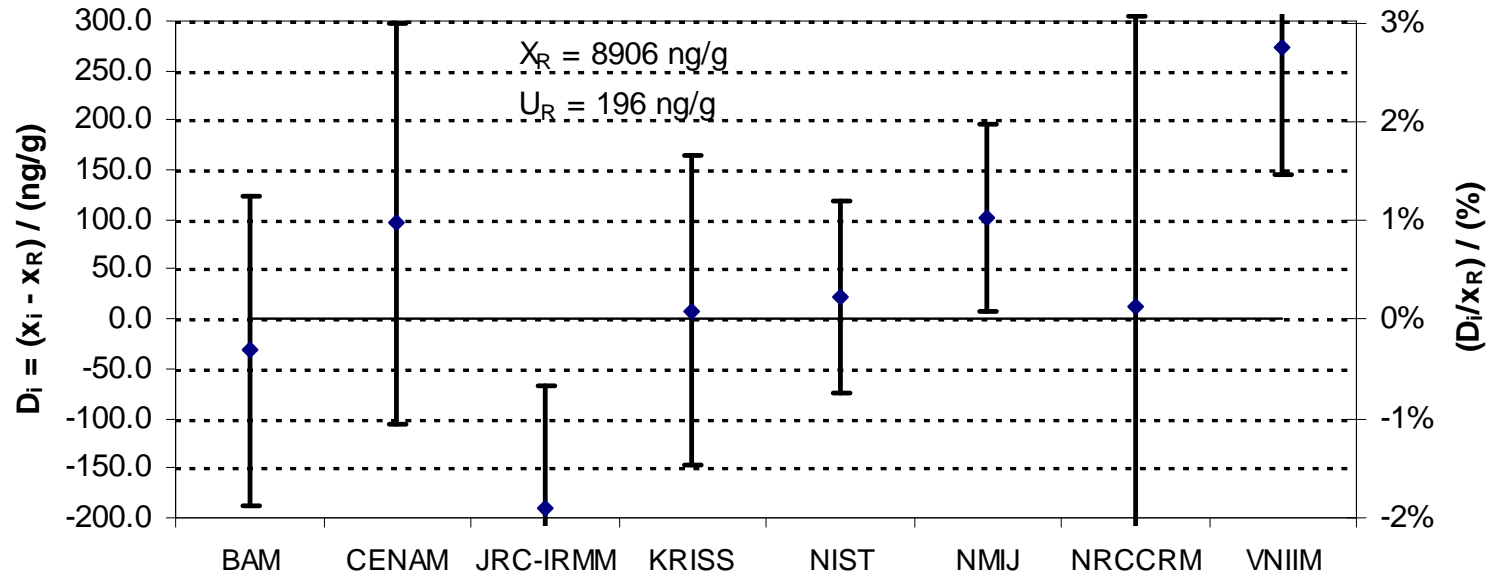


## CCQM-K38

MEASURAND: Mass fraction of fluoranthene in solution

Nominal Value: 8906 ng/g

Degrees of equivalence  $D_i$  and expanded uncertainty  $U_i$  (95% level of confidence) expressed in ng/g



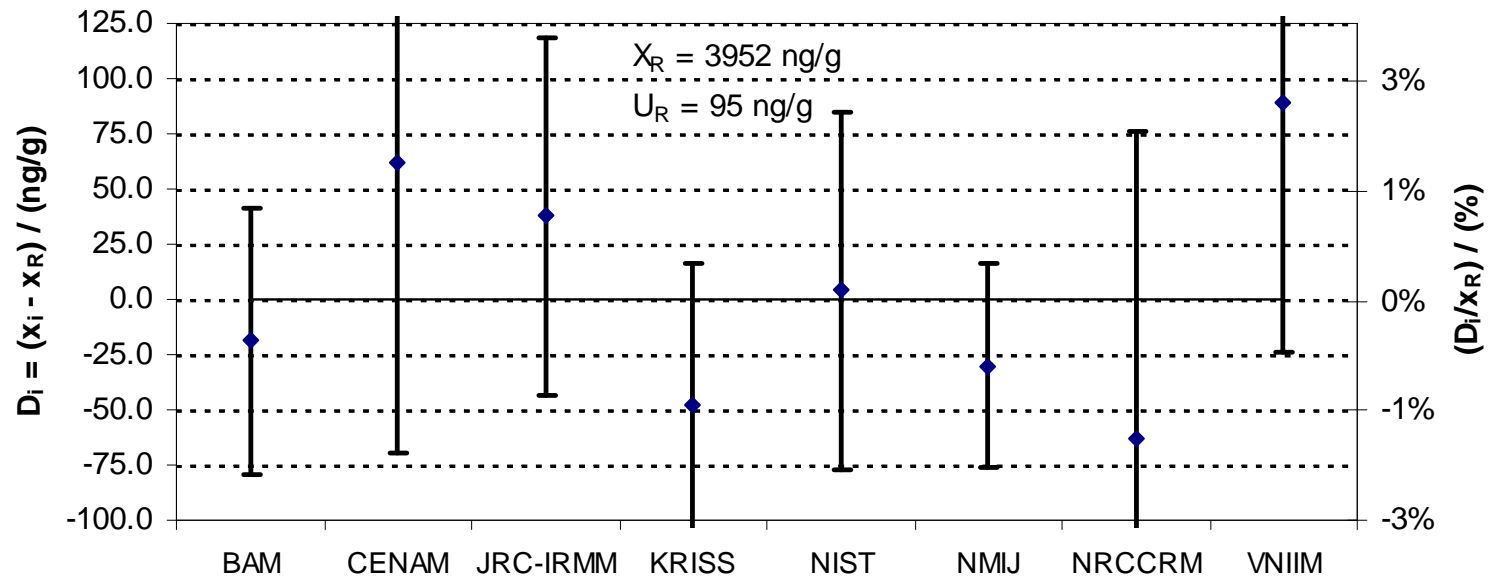
## CCQM-K38

MEASURAND: Mass fraction of benz[a]anthracene in solution

Nominal Value: 3952 ng/g

Degrees of equivalence  $D_i$  and expanded uncertainty  $U_i$  (95% level of confidence)

expressed in ng/g



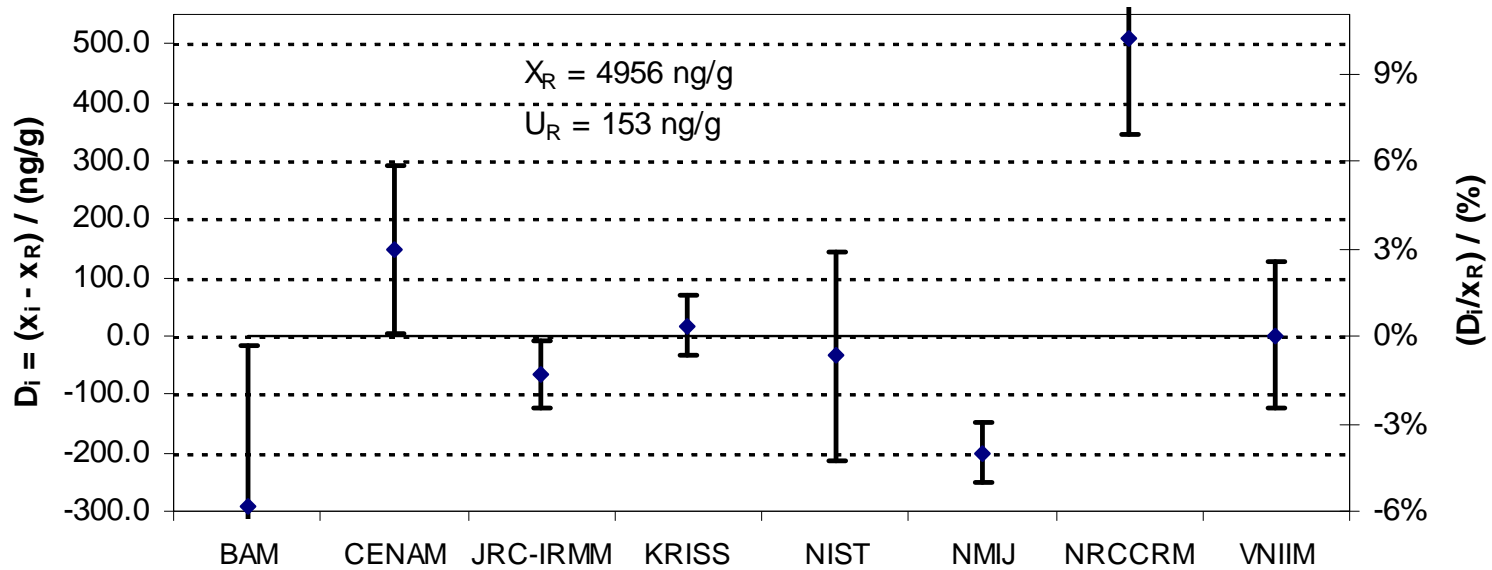
## CCQM-K38

MEASURAND: Mass fraction of benzo[a]pyrene in solution

Nominal Value: 4956 ng/g

Degrees of equivalence  $D_i$  and expanded uncertainty  $U_i$  (95% level of confidence)

expressed in ng/g



## CCQM-K38

MEASURAND: Mass fraction of benzo[ghi]perylene in solution

Nominal Value: 6872 ng/g

Degrees of equivalence  $D_i$  and expanded uncertainty  $U_i$  (95% level of confidence)  
expressed in ng/g

