CCQM-K40

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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-P31b study are summarized below for the PCB congeners. After review of the P31b results at the April 2004 OWG meeting and the October 2004 OAWG meeting (Beijing 2004), it was decided to proceed with a key comparison study for PCB congeners in solution (CCQM-K40) with a concurrent second pilot study for the PCB congeners in solution (CCQM-P31b.1). CCQM-K40 was designed as part of a suite of CCQM studies designed to enable evaluation of various uncertainty components of the measurement process for the determination of PCB congeners in marine tissue samples. The meta-results from this suite of studies will be provided in a separate report.

PCBs consist of 209 possible congeners depending on the substitution of the chlorine atoms around the biphenyl molecule. PCBs have been widely used as industrial fluids, flame retardants, diluents, hydraulic fluids, and dielectric fluids for capacitors and transformers. As a class of compounds, they are environmentally stable and tend to bioaccumulate. Of the 209 possible congeners, approximately 150 congeners have been reported in the environment. Congener specific PCB methods, typically based on gas chromatography (GC) with electron capture detection (ECD) or mass spectrometric (MS) detection, are designed to measure selected priority congeners. However, the congeners of interest change with the study and intended customer.

For both the pilot CCQM-P31b.1 and the key CCQM-K40, studies, five target PCB congeners were selected as representative of the measurement of individual congeners in milticomponent PCB congener solutions used as calibrants. The target congeners spanned the volatility range and the typical concentration range for the 150 congeners found in environmental samples, and included some potential problematic GC separations. PCB 28 (2,4,4’-trichlorobiphenyl) is volatile and under certain conditions coelutes with PCB 31. PCB 101 (2,2’,4,5,5’-pentachlorobiphenyl) has the potential coelution with a minor congener, PCB 90 (2,2’,3,4’,5-pentachlorobiphenyl). PCB 153 (2,2’,4,4’,5,5’-hexachlorobiphenyl) is typically one of the most abundant congeners and potentially coelutes with PCB 132 (2,2’,3,3’,4,6’-hexachlorobiphenyl). PCB 105 (2,3,3’,4,4’-pentachlorobiphenyl) is typically at a lower concentration and may change elution order with PCB 132 depending on the analytical conditions. Finally, PCB 170

(2,2',3,3',4,4',5-heptachlorobiphenyl) is one of the less volatile congeners, is typically found at lower concentrations, and can potentially coelute with PCB 190 (2,3,3',4,4',5,6-heptachlorobiphenyl).

This report summarizes the results previously reported for CCQM-P31b and the results for CCQM-K40. The results for CCQM-P31b.1, CCQM-P57, and CCQM-P67 are presented in separate reports.

PILOT STUDY SUMMARY

The CCQM-P31b pilot study for PCB congeners in solution was coordinated by NIST with samples distributed November 2003. Ten laboratories participated

The solution distributed in CCQM-P31b contained 18 PCB congeners (the 5 congeners to be determined plus 13 additional congeners) in *iso*-octane. The PCB congeners targeted in CCQM-P31b ranged in gravimetrically prepared concentration from 137 ng/g for PCB 170 to 1078 ng/g for PCB 153. The participating laboratories' data ranged from -13% to +6% of the gravimetrically prepared concentrations, but the majority of the data agreed with the gravimetrically prepared concentrations to within ±5%. For this study, NRCCRM used GC-ECD while the other laboratories used GC/MS so both methods were validated in the pilot study.

KEY COMPARISON – MATERIALS AND CONDUCT OF STUDY

The CCQM-K40 key comparison study for PCB congeners in solution was coordinated by NIST with samples distributed in December 2004 according to the project protocol agreed to at the October 2004 OAWG meeting. The laboratories receiving samples for CCQM-K40 were:

	BAM	[Germany]
	CENAM	[Mexico]
	IRMM	[Belgium]
	KRISS	[Korea]
	LGC	[United Kingdom]
	LNE	[France]
	NIST	[USA]
	NMIJ	[Japan]
and	NRCCRM	[China].

All results in this report were received prior to the April 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 PCB congeners: PCB 28 (2,4,4'-trichlorobiphenyl), 52 (2,2',5,5'-tetrachlorobiphenyl), 66 (2,3',4,4'-tetrachlorobiphenyl), 101 (2,2',4,5,5'-pentachlorobiphenyl), 105 (2,3,3',4,4'-pentachlorobiphenyl), 118 (2,3',4,4',5-pentachlorobiphenyl), 138 (2,2',3,4,4',5'-hexachlorobiphenyl), 153 (2,2',4,4',5,5'-hexachlorobiphenyl), 180 (2,2',3,4,4',5,5'-heptachlorobiphenyl), and 196 (2,2',3,3',4,4',5',6-octachlorobiphenyl). As agreed to by

the OAWG, additional congeners were included to check the identification of the compounds as well the quantification of the target analytes. The target PCB 170 was not present in the solution. The concentrations of the targeted congeners ranged from 90 ng/g to 360 ng/g. Each solution was ampouled in 2 mL ampoules with approximately 1.2 mL of solution per ampoule. 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

Nine laboratories received samples (see above) and returned data for CCQM-K40. The results were presented by the coordinating laboratory and the individual participants and discussed at the April 2005 CCQM OAWG meeting in Sèvres. 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.[1] Figure 2 displays the agreement between the gravimetric and participant measurement results.

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 congeners in the solution distributed for the CCQM-K40 study ranged from not present (PCB 170) to 352 ng/g (PCB 153). 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 2). The KCRVs and associated uncertainties are as follows:

PCB 28	171.9 ng/g ± 3.2 ng/g
PCB 101	254.5 ng/g ± 5.3 ng/g
PCB 105	93.7 ng/g ± 1.7 ng/g
PCB 153	351.9 ng/g ± 4.5 ng/g

As seen in Figure 1, the majority of the data reported by the laboratories for the selected PCB congeners overlapped the uncertainty of the KCRV.

The agreement between the gravimetric value and the participant results is shown in Figure 2. The median values were lower than the gravimetric values for the four congeners: -0.3% for PCB 28; -1.7% for PCB 101; -1.2% for PCB 105; and -1.7% for PCB 153.

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 PCB congeners (congener numbers 28, 101, 105, 153, and 170) in a solution using GC/MS-based methods.

The PCB congeners measured in CCQM-K40 were selected to be representative of PCB congeners typically used as calibrants in the determination of the approximately 150 congeners found in environmental samples and to provide the typical analytical measurement challenges encountered in the value-assignment of these PCB calibration solutions, such as volatility losses and resolution from potential interferences and other PCB congeners present as components in the solution during chromatographic separation. The abilities demonstrated by the laboratories that provided comparable measurements for all five congeners (including the non-detection of PCB 170) in this Key Comparison should be indicative of their ability to provide reference measurements for a suite of PCB congeners in solutions when present at levels greater than 90 ng/g provided the laboratory demonstrates an acceptable degree of separation of the PCB congeners in the specific solution being analyzed.

REFERENCE

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

Table 1. Results and Summary Statistics for CCQM-K40 Organic Solution – PCBs. All Values as Mass Fractions, ng/g

	PCB 28				PCB 101				PCB 105				PCB 153			
Participant	Value	u_c	k	U_{95}	Value	u_c	k	U_{95}	Value	u_c	k	U_{95}	Value	u_c	k	U_{95}
BAM	170.9	4.5	1.99	8.9	250.7	3.9	2.78	10.8	93.8	2.1	2.14	4.5	344.3	4.4	2.07	9.1
CENAM	164.37	1.23	2	2.5	248.30	1.81	2	3.63	90.10	0.71	2	1.42	342.12	2.82	2	5.64
IRMM	167.0	2.0	2	4.0	249.7	3.5	2	7.0	89.8	1.3	2	2.6	346.0	4.2	2	8.4
KRISS	171.72	0.27	2.04	0.55	255.41	1.00	2.07	2.07	93.67	0.65	2.09	1.36	348.78	0.69	2.08	1.44
LGC	176.0	0.78	2	1.6	258.5	1.21	2	2.4	94.2	0.75	2	1.5	348.5	1.24	2	2.5
LNE	152.3	2.8	2	5.6	225.8	4.6	2	9.2	82	5	2	10	329.2	4.9	2	9.8
NIST	173.4	0.7	2.1	1.5	247.2	2.3	2.0	4.5	92.6	4.1	2.0	7.9	343.4	3.9	2.1	8.4
NMIJ	171.9	1.7	2	3.5					93.4	1.0	2	1.9	354.20	3.6	2	7.2
NRCCRM	171.34	2.5	2	5.1	255.23	3.6	2	7.2	92.27	1.3	2	2.6	349.97	5.0	2	9.9
Gravimetric	171.9			2.4	254.5			3.1	93.7			1.2	351.9			3.6
N	9				8				9				9			
Mean	168.8				248.9				91.3				345.2			
SD	7.0				10.1				3.8				7.1			
ExU		2.2				3.0				2.4				3.7		
Median	171.3				250.2				92.6				346.0			
MADe	3.1				6.0				1.8				4.1			
MADe&ExU	3.8				6.7				3.0				5.5			
$Ts_{1\text{-}0.95,N\text{-}1}$	2.3				2.4				2.3				2.3			
U_{95}(Values)	8.7				15.8				6.9				12.8			
$\%U_{95}$(Values)	5.1				6.3				7.4				3.7			
U_{95}(Median)	2.9				5.6				2.3				4.3			

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: $\sqrt{(MADe^2+ExU^2)}$, the total dispersion of the reported values. $Ts_{1\text{-}0.95,N\text{-}1}$: Student's t 95% confidence coverage factor
U_{95}(Value): $Ts_{1\text{-}0.95,N\text{-}1} \times$ (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

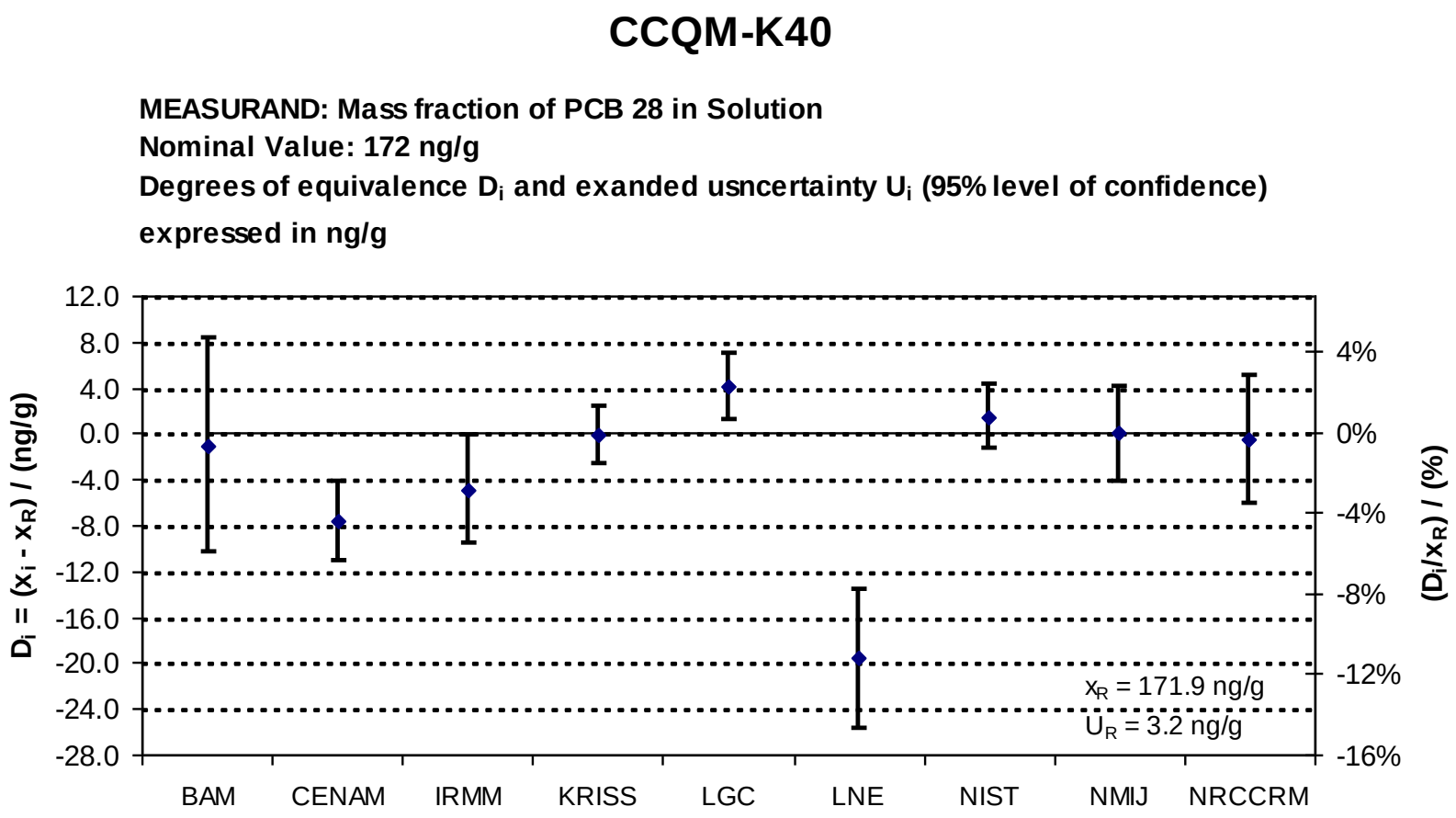
Table 1, Continued. Results and Summary Statistics for CCQM-K40 Organic Solution – PCBs. All Values as Mass Fractions, ng/g

	PCB 70			
Participant	Value	u_c	K	U_{95}
BAM	nd			
CENAM	nd			
IRMM	nd			
KRISS	nd			
LGC	nd			
LNE	5.8	0.9	2	1.8
NIST	nd			
NMIJ	nd			
NRCCRM	nd			
Gravimetric	0			

Table 2. Participant Uncertainty Budgets for CCQM-K40

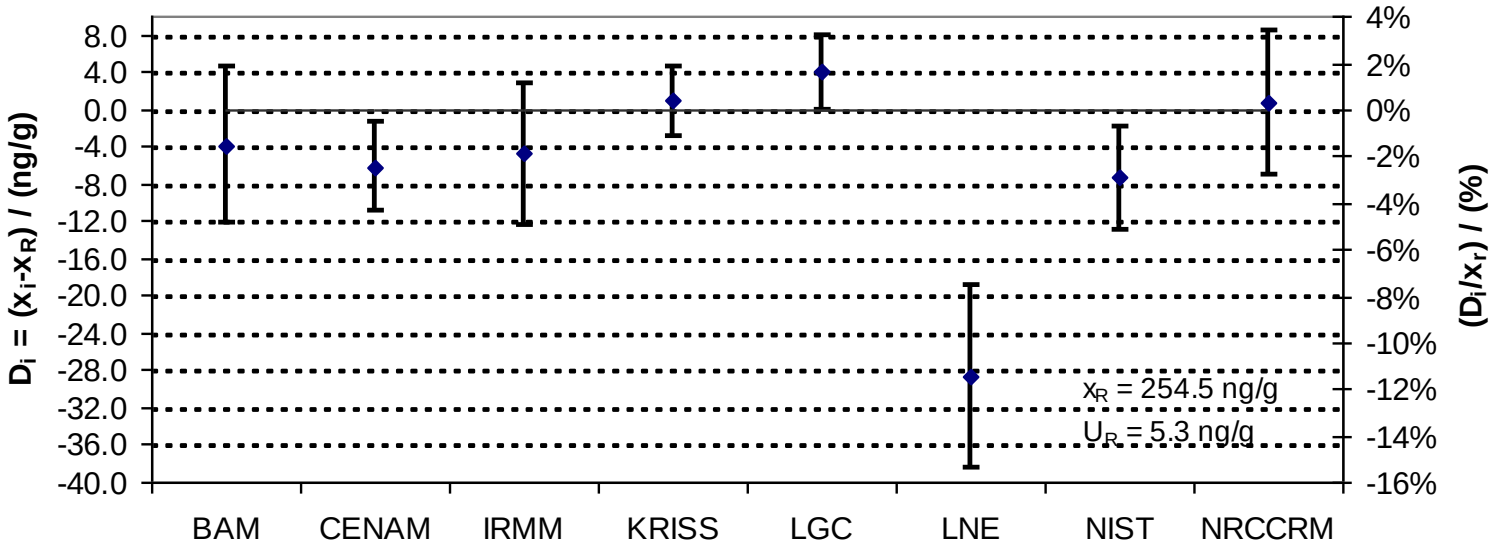
Participant	Component	Type	df
BAM	Precision of the method	A	3
	the measurement, weighing out the sample		
	spiking the internal standard		
	calibration		
	Concentration of the calibration solution	B	100
LNE	Ratio measurement in sample	A	
	Ratio measurement in standard	A	
	Masses	B	large
	Uncertainty of the concentration of SRM used for calibration	B	large
	Fidelity		
CENAM	Mean standard deviation of the measurements	A	3
	Calibration curve	B	large
	Standard for calibration	B	large
IRMM	Relative standard deviation of analyte concentration determined	A	3
	Relative standard deviation of response factor determined	A	
	Uncertainty of the standards used	B	large
KRISS	Standard solution		
	Purity		
	Repeatability of gravimetric preparation		
	Isotope Ratio Standard (repeatability of gravimetric preparation)		
	Repeatability of analysis		
	Measurement of isotope ratio of sample		
	Weighing of sample taken for analysis		
	Weighing of IS solution added to the sample		
	Measurement uncertainty		
	Measurement of isotope ratio (standard + IS mix)		
LGC	Standard deviation of the mean of the four concentrations determined for each congener	A	3
	Masses and primary standard mass fraction	B	large
NIST	Method precision	A	3
	Measurement of calibration solutions	A	5
	Certified concentrations of SRM used to prepare calibration solutions	B	large
NMIJ	Precision for the entire method	A	19
	Measurement of the area ratio for the samples		
	Measurement of the area ratio for the standard		
	Balance linearity	B	large
	Concentration of the calibration solution	B	large
NRCCRM	Method precision	A	3
	Mass fraction of the calibration solution	B	large

Figure 1. Degrees of Equivalence Graphs for each Congener in CCQM-K40. Shown is the KCRV (equivalent to the gravimetric value) ± expanded uncertainty (U) of the KCRV (a combination of the uncertainty in the gravimetric preparation and median absolute deviations from the median value)



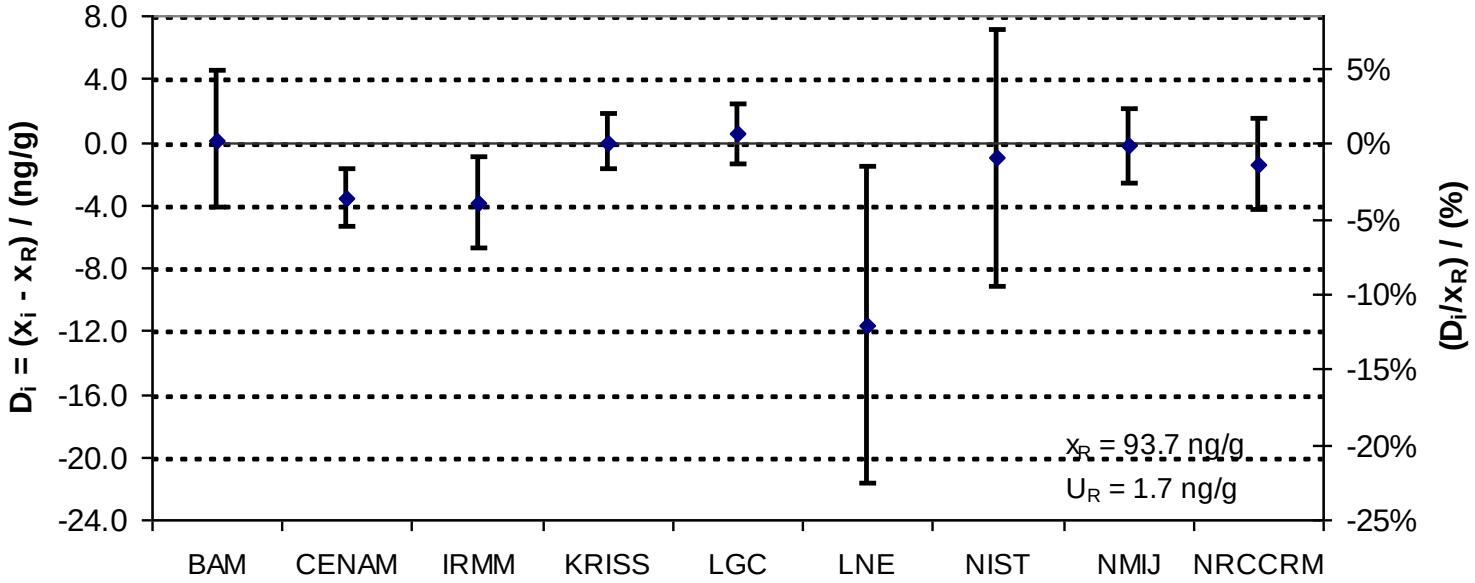
CCQM-K40

MEASURAND: Mass fraction of PCB 101 in Solution
Nominal Value: 255 ng/g
Degrees of equivalence Di and exanded usncertainty Ui (95% level of confidence) expressed in ng/g



CCQM-K40

MEASURAND: Mass fraction of PCB 105 in Solution
Nominal Value: 94 ng/g
Degrees of equivalence Di and exanded usncertainty Ui (95% level of confidence) expressed in ng/g



CCQM-K40

MEASURAND: Mass fraction of PCB 153 in Solution
Nominal Value: 352 ng/g
Degrees of equivalence Di and exanded usncertainty Ui (95% level of confidence) expressed in ng/g

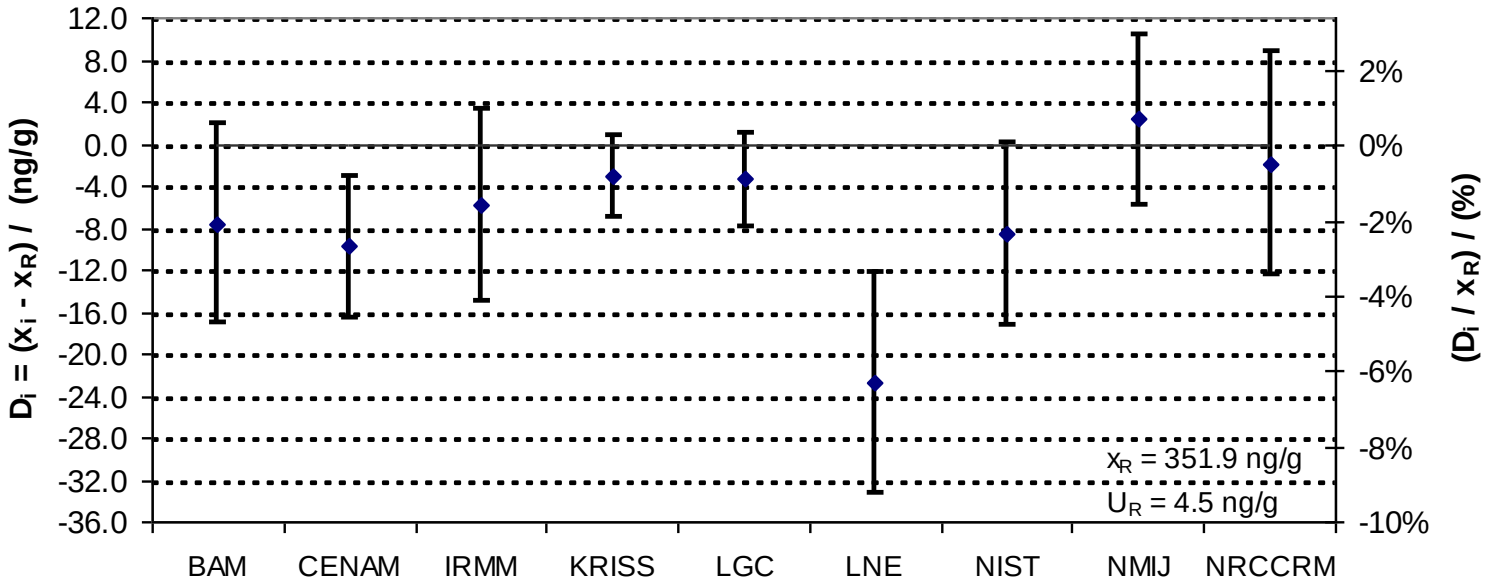
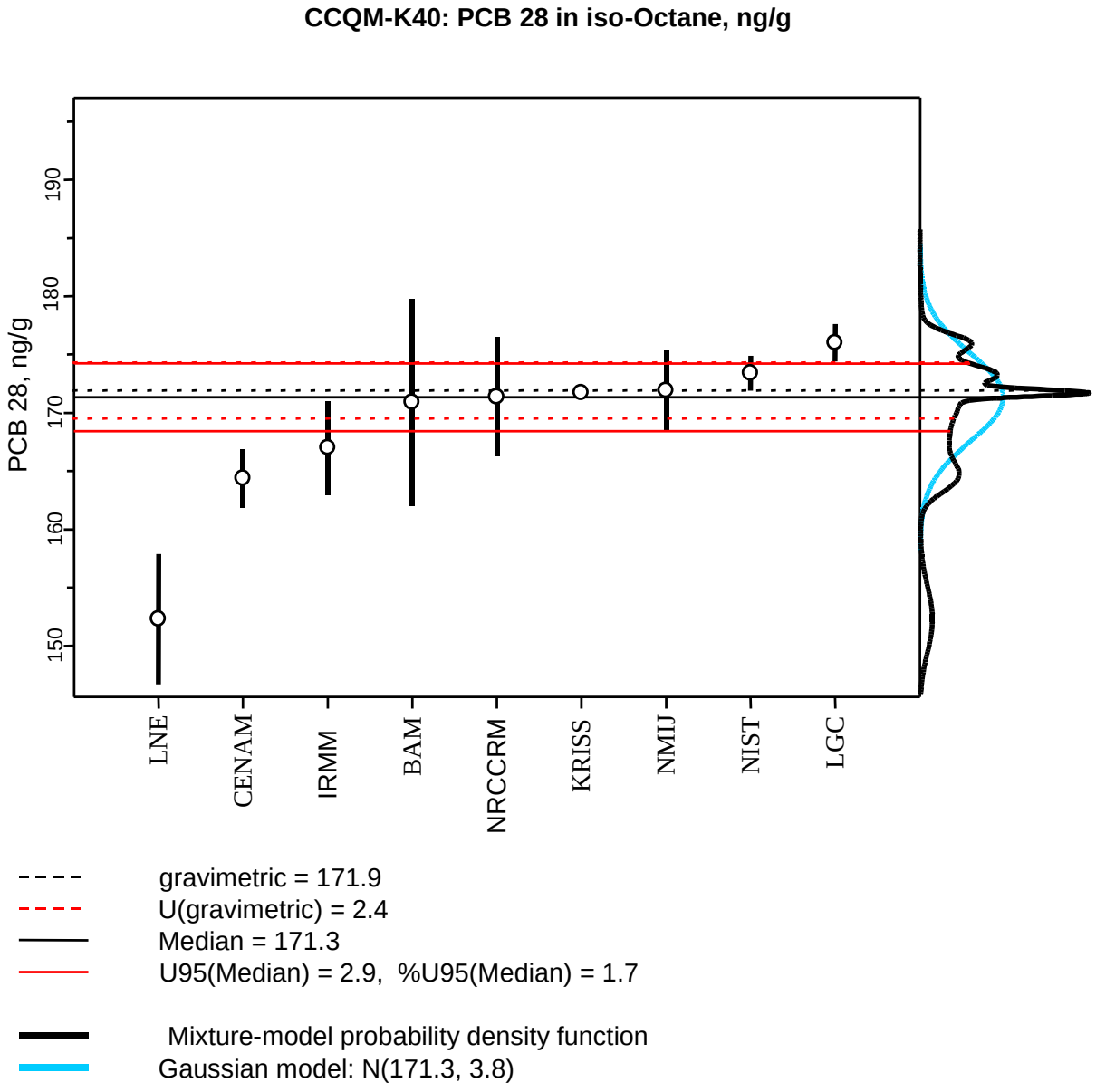
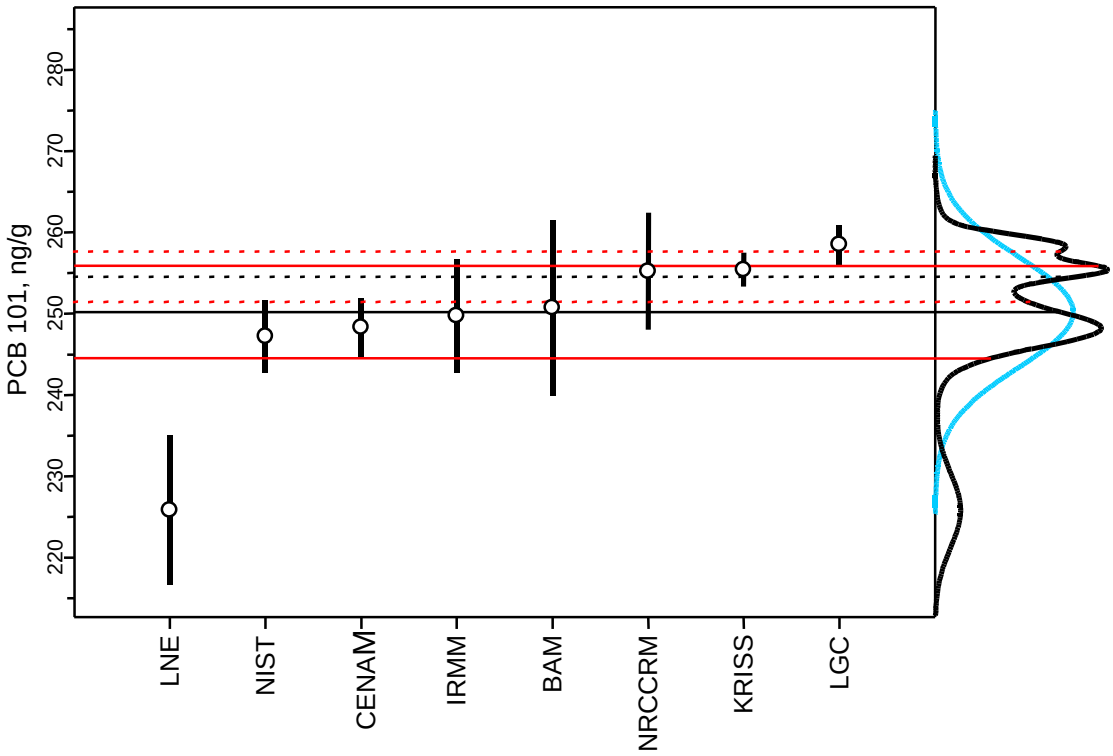


Figure 2. Comparison of Gravimetric Preparation and Participant Measurements



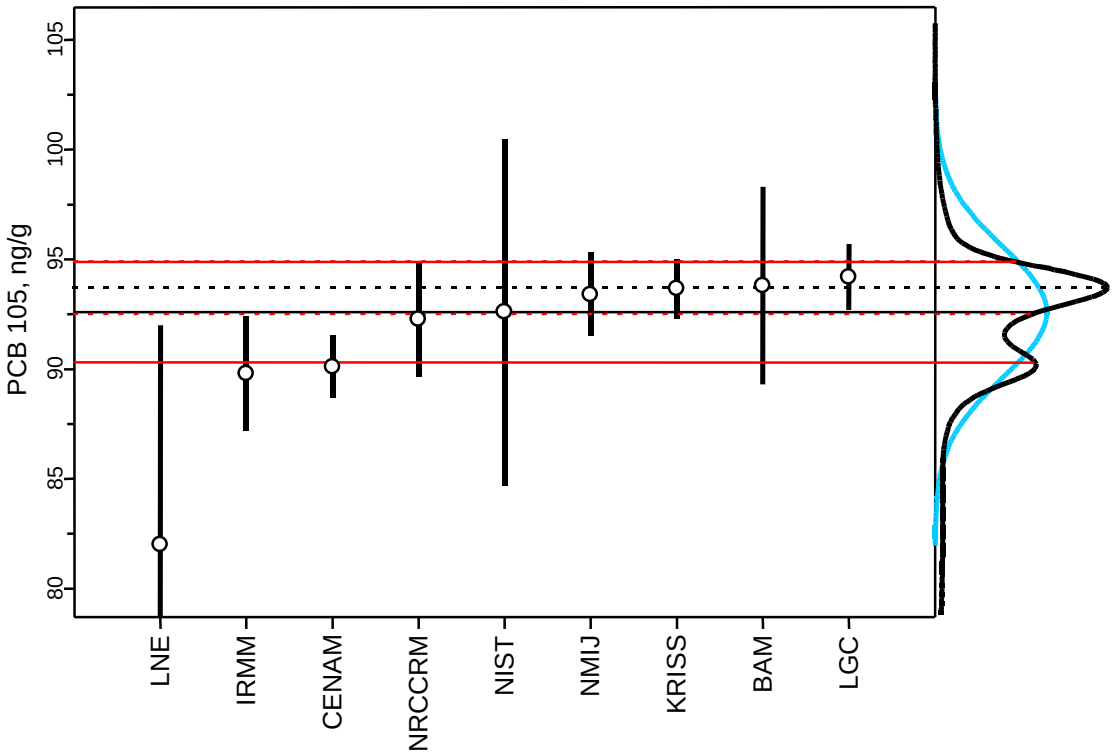
CCQM-K40: PCB 101 in iso-Octane, ng/g



gravimetric = 254.5
U(gravimetric) = 3.1
Median = 250.2
U95(Median) = 5.7, %U95(Median) = 2.3

Mixture-model probability density function
Gaussian model: N(250.2, 6.8)

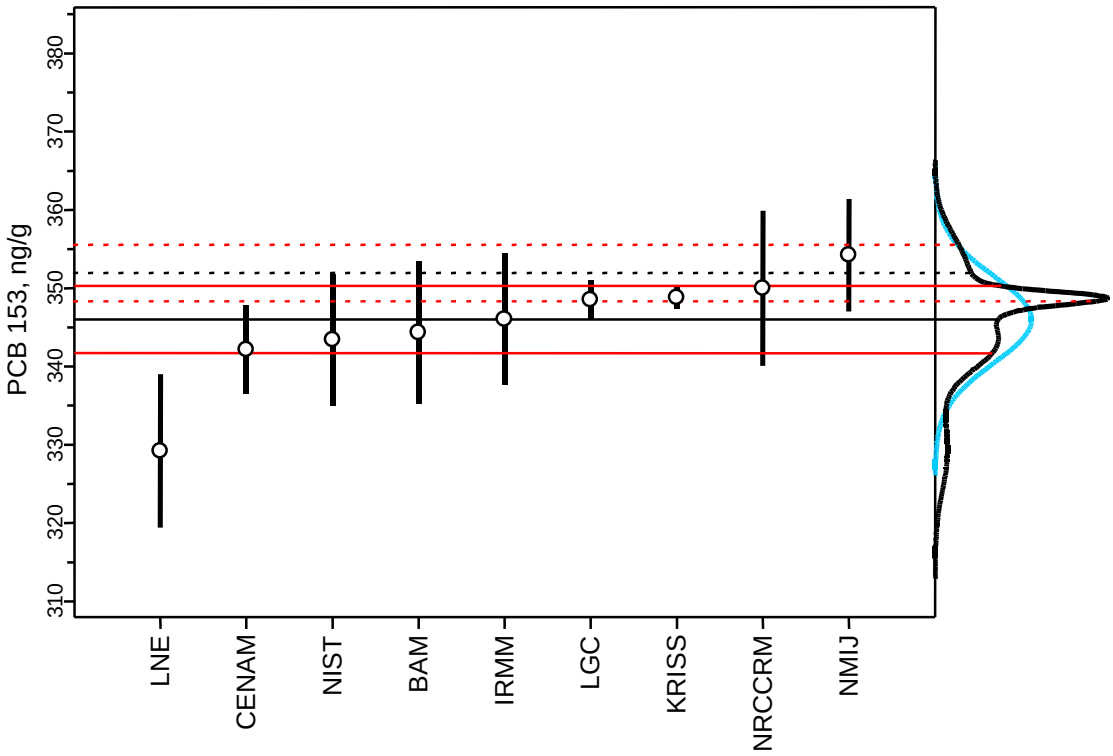
CCQM-K40: PCB 105 in iso-Octane, ng/g



gravimetric = 93.7
U(gravimetric) = 1.2
Median = 92.6
U95(Median) = 2.3, %U95(Median) = 2.5

Mixture-model probability density function
Gaussian model: N(92.6, 3.0)

CCQM-K40: PCB 153 in iso-Octane, ng/g



gravimetric = 351.9
U(gravimetric) = 3.6
Median = 346.0
U95(Median) = 4.3, %U95(Median) = 1.2

Mixture-model probability density function
Gaussian model: N(346.0, 5.6)