CCQM-K39, Determination of Chlorinated Pesticides in Solution

Final Report

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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-P31c study are summarized below for the chlorinated pesticides. After review of the P31c 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 chlorinated pesticides in solution (CCQM-K39) with a concurrent second pilot study for the chlorinated pesticides in solution (CCQM-P31c.1).

Chlorinated pesticides are anthropogenic compounds that persist in the environment, particularly in lipophilic matrices, for many years after use has been halted. Four pesticides were target analytes for the studies: Lindane (*gamma*-HCH); 4,4'-DDE; 4,4'-DDT; and trans-nonachlor. Three of the pesticides targeted have been target compounds in previous studies (CCQM-K5 4,4'-DDE in Fish Oil, CCQM-P10 *gamma*-HCH in Fish Oil, and CCQM-K21 4,4'-DDT in Fish Oil). *Trans*-nonachlor was selected for these studies as a representative from the chlordane family of pesticides.

This report summarizes the results previously reported for CCQM-P31c and the results for CCQM-K39. The results for CCQM-P31c.1 are presented in a separate report.

PILOT STUDY SUMMARY

A pilot study (CCQM-P31c) for chlorinated pesticides in solution was organized by NIST in 2003/2004. Fourteen laboratories received samples for CCQM-P31c with ten returning data. The CCQM-P31c Organic Solution – Chlorinated Pesticides contained 15 chlorinated pesticides (4 pesticides to be determined plus 11 additional pesticides) in *iso*-octane at concentrations of 10 ng/g to 600 ng/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-P31c Organic Solutions – Chlorinated Pesticides, four participating laboratories used gas chromatography with electron capture detection (GC-ECD) while the remaining participants used GC with mass spectrometric detection (GC/MS). The gravimetrically prepared concentrations for the targeted pesticides ranged from 25.6 ng/g for lindane to 592 ng/g for 4,4'-DDE. For the data submitted, the agreement with the gravimetrically prepared concentrations was within ±11%. Three of the ten laboratories submitting data for this study did not report values for *trans*-nonachlor. In general, there was more variability observed in the pesticide data than in the data from the PAH and PCB exercises that were conducted at the same time; however, the majority of the results still agreed with the gravimetric values to within ±5%.

KEY COMPARISON – MATERIALS AND CONDUCT OF STUDY

The CCQM-K39 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-K39 were:

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

BAM switched to participation in the pilot study at the time that the data were submitted to the coordinating laboratory. 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 eight chlorinated pesticides: lindane (*gamma*-HCH); *alpha*-HCH; 2,4'-DDE; 4,4'-DDE; 4,4'-DDD; 4,4'-DDT; *cis*-chlordane; and *trans*-nonachlor. Additional compounds were included to check the identification of the compounds as well the quantification of the target analytes. The concentrations of the targeted pesticides ranged from 34 ng/g for lindane to 318 ng/g for 4,4'-DDE. Each solution was ampouled in 2 mL ampoules with approximately 1.2 mL of solution per ampoule.

For CCQM-K39, 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. All of the laboratories participating in CCQM-K39 used GC/MS with isotopically labeled pesticides as internal standards/surrogates.

RESULTS

Nine laboratories received samples (see above), and seven returned data for 4,4'-DDE, 4,4'-DDT, and lindane while five returned data for *trans*-nonachlor in CCQM-K39. 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 four 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 graphs of degree of equivalence 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]

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 four chlorinated pesticides in the solution distributed for the CCQM-K39 study ranged from 34 ng/g for lindane to 320 ng/g for 4,4'-DDE. 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:

4,4'-DDE	318.0 ng/g ± 5.4 ng/g
4,4'-DDT	56.8 ng/g ± 1.7 ng/g
Lindane	33.9 ng/g ± 0.9 ng/g
trans-Nonachlor	46.6 ng/g ± 2.7 ng/g

As seen in Figure 1, the majority of the data reported by the laboratories for the selected chlorinated pesticides overlapped the uncertainty of the KCRV. The median values from the participant results were lower than the gravimetric values: -0.3% for 4,4'-DDE; -0.4% for 4,4'-DDT; -1.2% for lindane; and -1.1% for *trans*-nonachlor.

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 four chlorinated pesticides

(4,4'-DDE, 4,4'-DDT, lindane, and *trans*-nonachlor) in a solution using GC/MS-based methods.

The chlorinated pesticides measured in CCQM-K39 were selected to be representative of various types of chlorinated pesticides typically used as calibrants in the determination of the chlorinated pesticides found in environmental samples and to provide the typical analytical measurement challenges encountered in the value-assignment of these chlorinated pesticide calibration solutions, such as volatility losses and resolution from potential interferences and other pesticides present as components in the solution during chromatographic separation. The abilities demonstrated by the laboratories that provided comparable measurements for the pesticides in this Key Comparison should be indicative of their ability to provide reference measurements for a suite of chlorinated pesticides in solutions when present at levels greater than 30 ng/g provided the laboratory demonstrates an acceptable degree of separation of the pesticides 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-K39 Organic Solution – Chlorinated Pesticides. All Values as Mass Fractions, ng/g

Participant	Source of calibrants	4,4'-DDE			4,4'-DDT			Lindane		
		Value	Combined Std Unc	Expanded Std Unc	Value	Combined Std Unc	Expanded Std Unc	Value	Combined Std Unc	Expanded Std Unc
CENAM	DMR-277a CENAM	296.3	2.8	5.6	56.61	0.73	1.45	34.91	0.38	0.77
JRC-IRMM	Accustandard	304.4	1.6	3.2	54.9	0.3	0.5	31.9	0.3	0.6
KRISS	NIST RMs crystals	319.3	0.54	1.08	57.1	0.31	0.65	33.5	0.14	0.31
NIST	SRM 2261	317	1.82	3.64	55.5	0.61	1.23	33.5	0.41	0.83
NMIJ	NMIJ CRM	318.0	3.2	6.5	56.7	0.6	1.2	33.5	0.3	0.7
NRCCRM	NRCCRM CRMs for crystal DDE, DDT, and Lindane; Accustandard for *trans* -nonachlor	317.2	4.6	9.2	56.53	1.21	2.42	33.03	0.47	0.94
VNIIM	LGC solution NE7551	308.56	1.80	3.61	57.36	0.56	1.12	33.09	0.27	0.53
gravimetric		318	1.2	2.4	56.8	0.4	0.8	33.9	0.2	0.4
N		7			7			7		
Mean		311.5			56.4			33.3		
SD		8.7			0.9			0.9		
Median		317.0			56.6			33.5		
MADe		3.4			0.7			0.6		
ExU		2.6			0.7			0.3		
MADe & ExU		4.3			1.0			0.7		
$T_{s[1-0.95,N-1]}$		2.45			2.45			2.45		
U_{95} (Values)		10.5			2.4			1.7		
%U_{95}(Values)		3.3			4.3			5.1		
U_{95}(Median)		4.0			0.9			0.6		

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. $Ts_{1-0.95,N-1}$: Student's t 95% confidence coverage factor. U_{95}(Value): $Ts_{1-0.95,N-1} \times (MADe\&ExU)$, 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-K39 Organic Solution – Chlorinated Pesticides.
All Values as Mass Fractions, ng/g

| Participant | Source of calibrants | trans-nonachlor | | |
		Value	Combined Std Unc	Expanded Std Unc
CENAM	DMR-277a CENAM	44.15	0.50	1.00
JRC-IRMM	Accustandard	44.0	0.4	0.9
KRISS	NIST RMs crystals			
NIST	SRM 2261	46.1	0.52	1.03
NMIJ	NMIJ CRM			
NRCCRM	NRCCRM CRMs for crystal DDE, DDT, and Lindane; Accustandard for *trans* -nonachlor	46.17	0.61	1.22
VNIIM	LGC solution NE7551	47.96	1.46	2.93
gravimetric		46.6	0.3	0.6
N		5		
Mean		45.7		
SD		1.6		
Median		46.1		
MADe		2.8		
ExU		0.8		
MADe & ExU		2.9		
$T_{s[1-0.95,N-1]}$		2.78		
U_{95} (Values)		8.0		
$\%U_{95}$(Values)		17.3		
U_{95}(Median)		3.6		

Table 2. Participant Uncertainty Budgets for CCQM-K39

Participant	Component	Type	df
CENAM	Repeatability of replicates in independent measurements of calibration curve	A	
	Bias of control sample value with a reference value	B	
	Difference between results changing column in GC/MS	A	
	Standard deviation in sample concentration results	A	
JRC-IRMM	Uncertainty of the standards used (weighings, dilutions, and purity)		
	Relative standard deviation of results (analyte concentration		
KRISS	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		
	Measurement of isotope ratio of standard + IS		
NIST	Method precision	A	3
	Measurement of calibration solutions	A	5
	Certified concentrations of SRM used to prepare calibration solutions	B	large
NMIJ	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-K39. 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-K39

**MEASURAND: Mass fraction of 4,4'-DDE in solution**
Nominal Value: 318 ng/g
Degrees of equivalence D_i and exanded usncertainty U_i (95% level of confidence)
expressed in ng/g

$X_R = 318.0$ ng/g
$U_R = 5.4$ ng/g
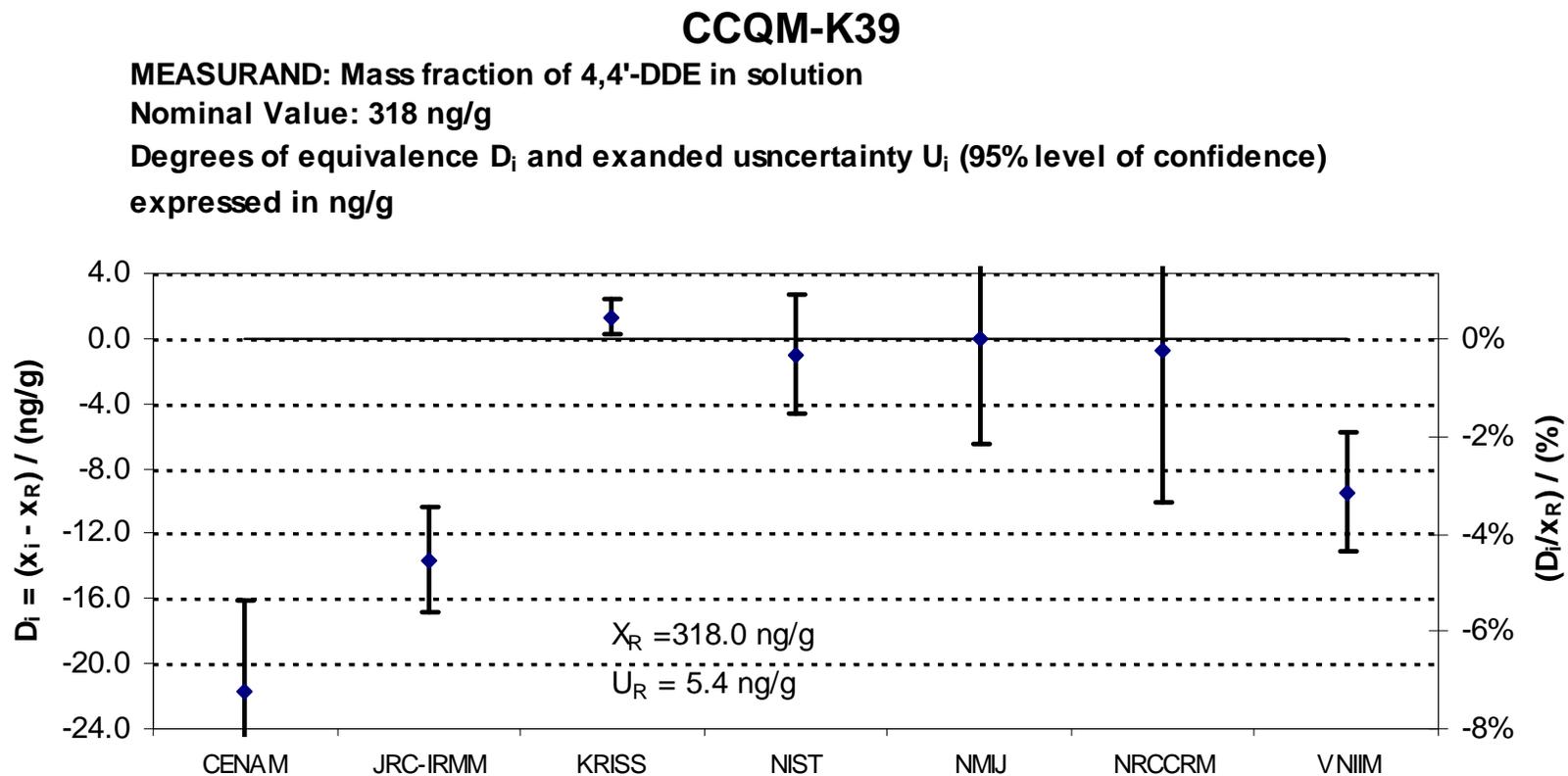
CCQM-K39

MEASURAND: Mass fraction of 4,4'-DDT in solution

Nominal Value: 56.8 ng/g

Degrees of equivalence D_i and exanded usncertainty U_i (95% level of confidence)
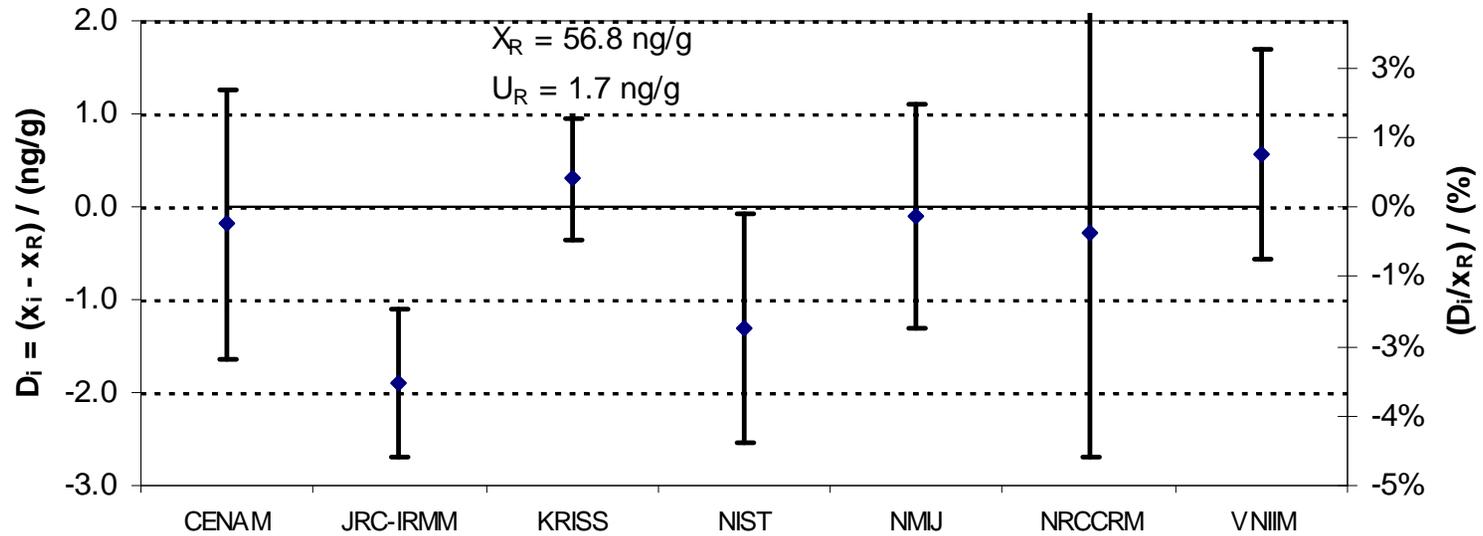
expressed in ng/g

CCQM-K39

MEASURAND: Mass fraction of lindane in solution

Nominal Value: 33.9 ng/g

Degrees of equivalence D_i and exanded usncertainty U_i (95% level of confidence)

expressed in ng/g

$X_R = 33.9$ ng/g

$U_R = 0.9$ ng/g
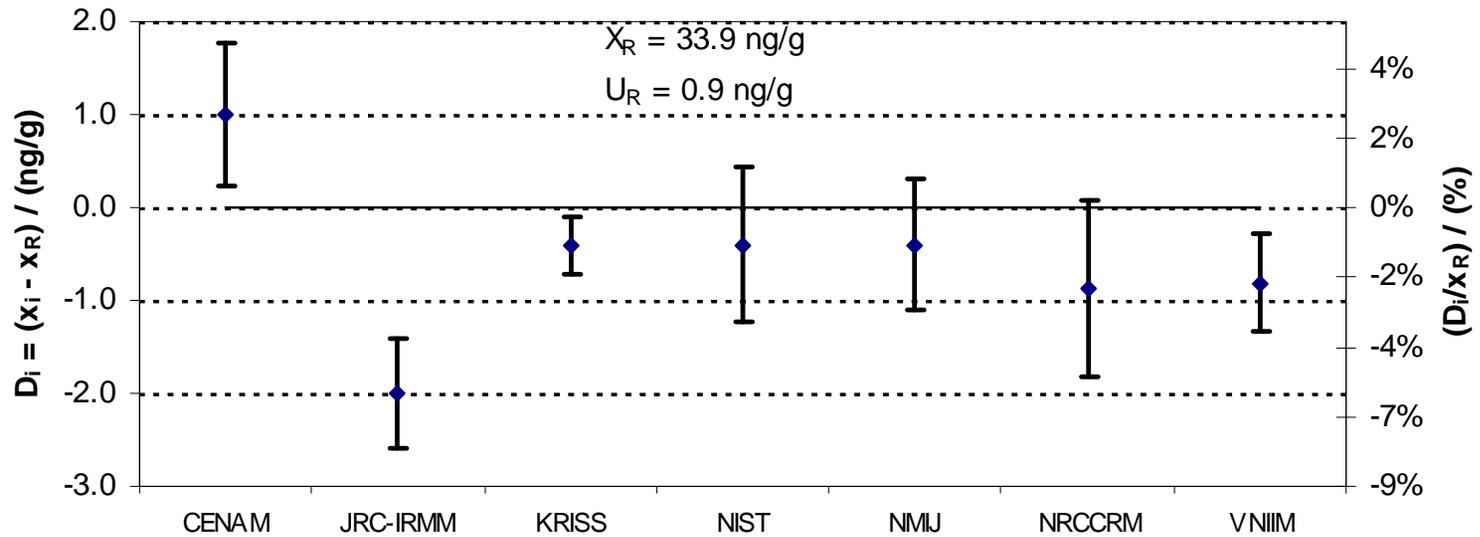
CCQM-K39

MEASURAND: Mass fraction of *trans*-nonachlor in solution

Nominal Value: 46.6 ng/g

Degrees of equivalence D_i and exanded usncertainty U_i (95% level of confidence) expressed in ng/g

$X_R = 46.6$ ng/g
$U_R = 2.7$ ng/g