CCQM-K95

"Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea"

Final Report

October 2014

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A key comparison and parallel pilot study agreed upon by the Organic Analysis Working Group (OAWG) of the CCQM and coordinated by GLHK and NIM.

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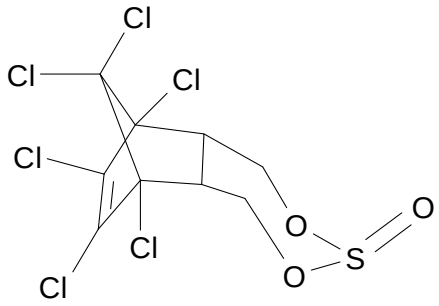
1 Introduction

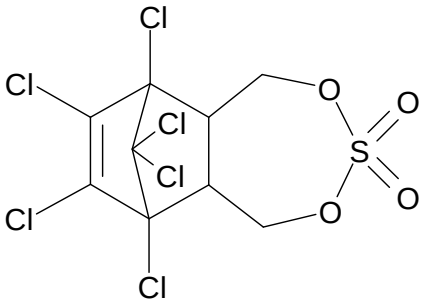
In the OAWG Paris meeting in April 2011, the OAWG agreed on a suite of Track A studies meant to support the assessment of measurement capabilities needed for the delivery of measurement services within the scope of the OAWG Terms of Reference. One of the studies discussed and agreed upon for the suite of ten Track A studies that support the 5-year plan of the CCQM Core Competence assessment was CCQM-K95 "Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea". The study involved extraction, clean-up, analytical separation, and selective detection of the analytes concerned in a food matrix and was designed to test the capabilities for determining mid-polarity analytes in a food matrix. This comparison was co-organised by the Government Laboratory of Hong Kong Special Administrative Region (GLHK) and the National Institute of Metrology, China (NIM). To allow wider participation, a pilot study, CCQM-P136, was run in parallel with this key comparison.

2 Measurands

Mass fractions (μg/kg) of two incurred organochlorine pesticides, namely beta-endosulfan and endosulfan sulphate, in tea were to be determined.



Beta-Endosulfan
(synonym: Endosulfan-II)
CAS No.: 33213-65-9
MW: 407
log K_{ow}: 3.83



Endosulfan Sulphate
CAS No.: 1031-07-8
MW: 423
log K_{ow}: 3.66

3 Study material

3.1 Preparation

The testing material was prepared by GLHK. About 10 kilograms of dried green tea were purchased from the local market in Shenzhen, China. The tea was then ground to powder by high speed blenders at ambient temperature of about 20°C and sieved

through 200-μm sieves. The sample powder (≤ 200 μm) was collected and then placed into a 3-dimensional rotating drum for mixing for 7 days. The homogenised sample powder was then disinfected by γ-irradiation at a dose of about 1 kGy and packed into pre-cleaned and nitrogen-flushed amber glass bottles at about 20 grams each. The bottles were purged with nitrogen before being screw capped. A total of 432 bottles of material were prepared. Each bottle was individually vacuum-sealed in a plastic bag and then stored at about 4°C.

3.2 Homogeneity study

Twelve bottles of the material were randomly selected for the homogeneity study. Two 1-gram test portions from each sample bottle were taken for duplicate analysis. The samples were analysed using a validated method employing isotope dilution GC-NCI-MS technique. In brief, about 1 gram of tea sample spiked with known amounts of beta-endosulfan-$^{13}C_9$ and endosulfan sulphate-$^{13}C_9$ internal standards (purchased from the Cambridge Isotope Laboratories, Inc.) was immersed in a minimal amount of water overnight for wetting. The sample was then dried with acrylate type absorbent polymer. The analytes were extracted from the sample by Soxhlet extraction using ethyl acetate for 16 hours. The extract was concentrated by rotary evaporation to just dryness. The residue was reconstituted with 10 mL of acetonitrile / toluene (3:1). The reconstituted solution then underwent Carb/NH_2 SPE clean-up followed by florisil SPE clean-up. The eluate was concentrated to just dryness and then reconstituted with 500 μL *iso*-octane for GC-NCI-MS analysis using a DB-17MS (30 m × 0.25 mm, 0.25 μm) column. The contents of beta-endosulfan and endosulfan sulphate in each sample were determined using the calibration curve approach by plotting the signal ratio against amount ratio of the respective native and labelled compounds. The sequence of measurement was in a random order to allow distinction between the measurement trend and samples batch trend. The analytical results without moisture content correction (as the variation due to moisture correction was insignificant compared with that of the method precision) were used for evaluating the material homogeneity during the study.

Sample homogeneity was evaluated by using one-way ANOVA with *F*-test in accordance with the requirements as stipulated in ISO Guide 35 and the results are summarised in Tables 1 – 2. The statistical results showed the calculated *F*-values of both analytes were below the *F*-critical values indicating that the inhomogeneity of the study material was insignificant.

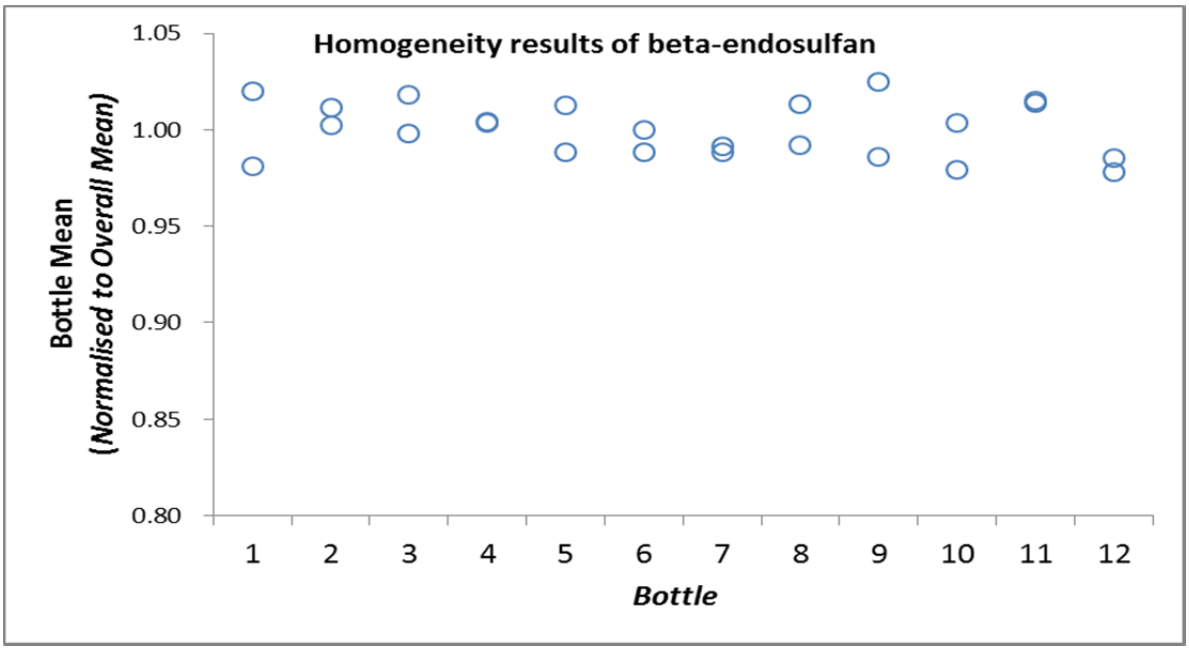


Figure 1 ***Graphical presentation of homogeneity results for beta-endosulfan.***

Table 1 **Summary of ANOVA for homogeneity test of beta-endosulfan in the testing material.**

Source of variances	*SS*	*DF*	*MS*	*F*	*P-value*	F_{Crit}
Between bottles	869.11	11	79.01	0.751	0.678	2.717
Within bottles	1261.7	12	105.14			

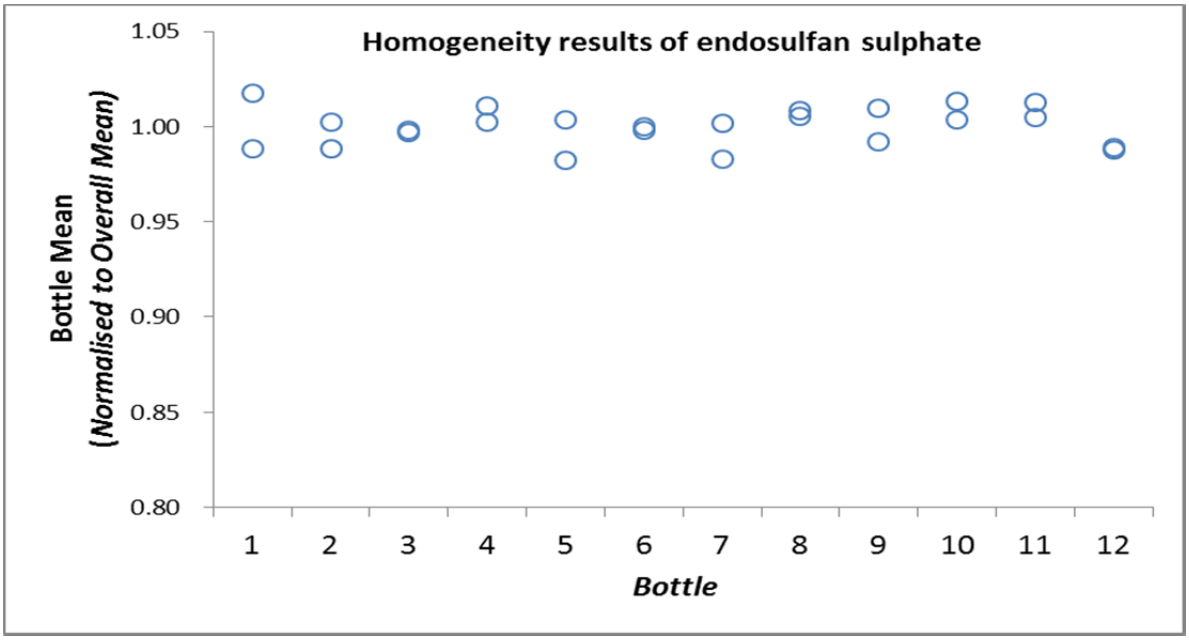


Figure 2 ***Graphical presentation of homogeneity results for endosulfan sulphate.***

Table 2 Summary of ANOVA for homogeneity test of endosulfan sulphate in the testing material.

Source of variances	*SS*	*DF*	*MS*	*F*	*P-value*	F_{Crit}
Between bottles	239.32	11	21.757	0.956	0.526	2.717
Within bottles	272.96	12	22.747			

3.3 Stability study

A total of 8 bottles of material were randomly selected for the short-term stability study. This study was designed to test for the material stability under transportation conditions. The selected bottles in the study were stored at an elevated temperature of 30°C adopting an "*isochronous*" design approach, in which all measurements were carried out under repeatability conditions. The GC-NCI-MS method used for the homogeneity study was employed in the stability study. The contents of beta-endosulfan and endosulfan sulphate in each selected bottle were analysed in duplicate. The analytical results without moisture content correction were used for evaluating the material stability during the study. The results of the samples stored at 30^{o}C for one, two and four weeks were compared with the mean results of the samples which were stored at the reference temperature of -18°C over the whole stability study period. The data of the study were evaluated by trend analysis with linear regression and Student's *t*-test.

The statistical results shown in Table 3 indicated that no significant trend at 95% confidence level was detected as the absolute values of b_1 (i.e. slope of the regression line) were smaller than the critical values of b_1 which were the uncertainty associated with the slope of the regression line for the stability at 30°C for 4 weeks times the respective Student's *t*-factor. Hence, the instability of the material was insignificant at the study temperature over the study period.

Table 3 Summary of stability study results.

Descriptions	Beta-endosulfan	Endosulfan sulphate
Storing conditions	30ºC for 7, 14, 28 days	30ºC for 7, 14, 28 days
Mean ($\bar{y}$)	680.6 µg/kg	464.0 µg/kg
Slope of the regression line (b_1)	-0.0203	-0.0446
Intercept of the regression line (b_0)	680.8	464.5
Variance of the points (s^2)	1.787	0.115
Standard deviation of the points (s)	1.34	0.34
Uncertainty associated with slope [$s(b_1)$]	0.0646	0.0164
Student's t-test ($t_{0.95, n-2}$)	4.303	4.303
Critical value of b_1 [$t_{0.95, n-2} \times s(b_1)$]	0.2778	0.0705

The stability of the study material was also evaluated through ANOVA test on the regression with results summarised in Tables 4 and 5. The obtained respective p-values for both measurands (all greater than 0.05) indicated that the regressions were insignificant at 95% confidence level.

Table 4 Summary of ANOVA test for the short-term stability study of beta-endosulfan in the testing material at 30ºC

	Degree of Freedom	*SS*	*MS*	*F*	*p-value*
Regression	1	0.1775	0.1775	0.0993	0.782
Residual	2	3.574	1.787		
Total	3	3.751			

Table 5 Summary of ANOVA test for the short-term stability study of endosulfan sulphate in the testing material at 30ºC

	Degree of Freedom	*SS*	*MS*	*F*	*p-value*
Regression	1	0.8518	0.8518	7.40	0.113
Residual	2	0.2301	0.1150		
Total	3	1.082			

4 Sample distribution and results submission

Eighteen NMIs/DIs participated in CCQM-K95. Two bottles of sample each

containing about 20 grams of the dried tea powder with cold packs in a foam box were sent to each participant *via* couriers at end of November 2011. A temperature strip was attached on each bottle for the purpose of monitoring the maximum temperature exposure during the transportation. Relevant documents, including Technical Protocol, Sample Receipt Form, Result Report Form and Type A Competency Template were sent to participants by e-mail. Participants were asked to check the physical conditions of the sample upon receipt of the sample pack. All samples were received by the participants in good condition not later than the first week of January 2012.

Participants were requested to determine the mass fractions (in μg/kg) of the two pesticides on a dry mass basis in one of the bottles with their preferred methods. The organisers recommended a minimum sample size of 1 gram for testing with the following protocol for determination of moisture content:

(i) a minimum of three separate portions (recommended size of 1 gram each) of the sample should be taken;

(ii) place the portions over anhydrous calcium sulphate (DRIERITE®) in a desiccator at room temperature for a minimum of 10 days until a constant mass is reached; and

(iii) perform moisture content determination at the same time as the test sample portions are to be analysed.

The participants were requested to fill in the test results, extraction method(s), post-extraction clean-up method, transformation procedures, analytical instrumental details, measurement equation, source(s) of calibrant(s) and internal standard(s), uncertainty estimation details and additional observation(s), if any, in the Results Report Form provided and send the completed form to the organisers by e-mail to ccqm-oc@govtlab.gov.hk before the final deadline for submission of results on 18 March 2012. In addition, for this Type A core competency key comparison, participants were also requested to analyse their competency underpinning the measurement and return the completed Type A Competency Template to the organisers.

5 Reference materials used by the participating laboratories

The information on the reference materials used by the participating laboratories is given in Table 6. BVL, CMQ, HSA, LGC and NMIA used certified reference materials (P1369 and P1372) supplied by NMIA as calibrants. GLHK and NIST used

the standard reference materials (SRM 2275) supplied by NIST; and NIST, in this study, confirmed the concentration values of their standard reference material by comparing with the calibration solution prepared from neat beta-endosulfan and endosulfan sulphate of which the purities were assessed using GC-FID and DSC. BQSF, DMSc used reference materials from two sources, namely the National Institute of Metrology of Thailand (NIMT) and NMIA respectively, and their reported results were the average of all analytical results calculated using both sources of standards. BAM, CENAM, INMETRO, KRISS, NIM, NMIJ, NRC and UME assessed the purity of the calibrants they used, in which BAM assessed the purity of their commercial calibrants by using GC-FID with different polarity columns. INTI and VNIIM did not carry out any in-house assessment of the commercial calibrants they used when they submitted the results in this comparison.

Table 6 Summary of information on the reference materials used by participants.

NMI/DI	Source(s)	Purities and their expanded MU	Technique(s) used for purity assessment, if in-house assessment made
BVL CMQ HSA LGC NMIA	NMIA	NMIA P1369 Beta-endosulfan: 99.3 ± 0.8% NMIA P1372 Endosulfan sulfate: 97.9 ± 3.0 %	-
GLHK	NIST	NIST SRM 2275 Chlorinated Pesticide Solution in Isooctane, Beta-endosulfan: 2.943 ± 0.069 mg/kg, Endosulfan Sulfate : 2.926 ± 0.087 mg/kg	-

NMI/DI	Source(s)	Purities and their expanded MU	Technique(s) used for purity assessment, if in-house assessment made
BQSF, DMSc	NIMT and NMIA	(i) Source 1 Purity assessed by NIMT on the standards supplied by Dr. Ehrenstorfer: *Beta-endosulfan: 99.4 ± 0.4% *Endosulfan sulfate: 98.5 ± 0.4% (ii) Source 2 Source of standards from NMIA *Beta-endosulfan: 99% minimum (P1369) *Endosulfan sulfate: 99.2 ± 0.3% (P1372) *The purities were from the report ID P1369.2007.01 and P1372.2009.01 respectively.	-
NMIJ	Wako	Beta-endosulfan: 99.75 ± 0.08% Endosulfan sulfate: 98.75 ± 0.35 %	Mass balance approach: GC-FID, HPLC-UV, Karl-Fischer coulometry.
NIM	Dr. Ehrenstorfer GmbH	Beta-endosulfan: 99.6 ± 1.0% Endosulfan sulfate: 98.9 ± 1.2 %	Mass balance approach: GC-FID, GC-MS and Karl-Fischer coulometry.
KRISS	Dr. Ehrenstorfer GmbH	Beta-endosulfan: 99.17 ± 0.13% Endosulfan sulfate: 98.92 ± 0.08 %	Mass balance approach: *GC-FID, Karl-Fischer coulometry and TGA.
NRC	Sigma-Aldrich	Beta-endosulfan: 99.6 ± 1.0% Endosulfan sulfate: 70.0 ± 2.0 %	qNMR with benzoic acid (NIST, SRM 350b) as internal standard.
INMETRO	Beta-endosulfan: Fluka Endosulfan sulfate: Dr. Ehrenstorfer	Beta-endosulfan: 98.0 ± 4.0% Endosulfan sulfate: 96.7 ± 1.9%	qNMR with benzoic acid (NIST, SRM 350b) as internal standard.
BAM	Dr. Ehrenstorfer GmbH	Beta-endosulfan: 99.1 ± 0.2% Endosulfan sulfate: 98.2 ± 0.5 %	GC-FID with columns of different polarity.
CENAM	Commercial Source	*Beta-endosulfan : 98.59± 0.56% *Endosulfan sulfate : 96.10±0.64%	GC-FID with two different columns and *Karl-Fischer coulometry

NMI/DI	Source(s)	Purities and their expanded MU	Technique(s) used for purity assessment, if in-house assessment made
UME	Sigma-Aldrich	Beta-endosulfan : 98.35 ± 0.44% Endosulfan Sulfate: 97.44 ± 0.25%	(i) Mass balance approach: GC-ECD, TGA, Karl-Fischer coulometry, headspace-GC/MS; (ii) qNMR with benzoic acid (NIST, SRM 350b) as internal standard for confirmation. *Endosulfan Sulfate was purified by Prep HPLC before purity assessment.
NIST	NIST	NIST SRM 2275 Chlorinated Pesticide Solution in Isooctane, Beta-endosulfan: 2.943 ± 0.069 mg/kg, Endosulfan Sulfate : 2.926 ± 0.087 mg/kg	GC-FID and DSC as confirmation techniques to verify the certified values of SRM 2275 valid.
INTI	Dr. Ehrenstorfer GmbH	*Beta-endosulfan : 96.1 ± 4.42 %* *Endosulfan Sulfate: 99.9 ± 5.07 %*	*GC-MS
VNIIM	Cambridge Isotope Laboratories	*Beta-endosulfan solution in nonane: 99.5 ± 3.4 μg/kg *Endosulfan sulphate solution in nonane: 99.8 ± 3.6 μg/kg	*External calibration using NIST SRM 2275 as calibration solution by GC-MS.

*Additional information provided by participants after the issue of result summary report in April 2012.

6 Methods used by the participating laboratories

The methods for extraction, clean-up and instrumental analysis used by participating laboratories are summarised in Table 7.

Different extraction methods for the analytes were used among the participants. CENAM (for endosulfan sulphate only), GLHK, LGC and NIM used Soxhlet extraction; CMQ, HSA, NMIA, and UME employed the pressurized liquid extraction / accelerated solvent extraction method to extract the analytes from the matrix. Ultrasonic extraction was adopted by BAM, NIST and VNIIM. Other solvent

extraction approaches were employed by BQSF DMSc, BVL, CENAM, INMETRO, INTI, KRISS, NMIA, NMIJ and NRC. For clean-up procedures, most laboratories applied solid phase extraction (SPE) or dispersive SPE. CENAM did not use any clean-up procedures. For the instrumental analysis, all laboratories employed GC technique for chromatographic separation. Most laboratories used MS related techniques for detection and quantification, whereas CENAM and INTI used micro-ECD for their quantitative measurement. Most laboratories used isotope dilution mass spectrometry (IDMS) with the corresponding $^{13}C_9$ and/or d_4 isotopic compounds as internal standard for calibration. CENAM and INMETRO used endosulfan sulphate-d_4 and aldrin respectively as the internal standard for both analytes. INTI quantified the levels of both analytes by using external standard calibration. NMIJ applied matrix-matched calibration in their quantification. For reference purposes, NMIJ prepared and presented in the OAWG Meeting in April 2012 the Youden plots of the participants' results distribution according to the extraction method, extraction solvents and analytical quantitation techniques respectively (Appendix I).

Most of the participants applied the suggested protocol for moisture determination except INMETRO who determined the moisture content by drying the sample in a vacuum oven at 97.5°C for 5 hours as described in an AOAC method. BAM clarified that the moisture data obtained according to the protocol was used for the final dry mass correction and coulometric Karl-Fischer titration was used as an additional plausibility check to determine the moisture content, as they found exact weighing of the dried tea samples difficult due to the hydroscopic nature of the sample. The discrepancy between two methods has not been taken into account in their uncertainty budget.

Table 7 Summary of the methodologies used by the participants.

NMI/DI	Sample size (g)	Extraction method(s)	Extraction Solvent(s)	Clean-up method(s)	Analytical instrument(s) used	Chromatographic Column(s)	Method of quantification	Type of calibration(s)
INTI	4	Solvent extraction; followed by liquid extraction by petroleum ether with water and NaCl.	acetonitrile:water (65:35).	Florisil column with 200ml ethyl ether:petroleum ether (10:90) and 200ml ethyl ether:petroleum ether (50:50).	GC-μECD.	CP-SIL24CB and DB-1701.	External standard	Single point quantification and calibration curve verification.
NMIA	1	Method 1: Accelerated solvent extraction. Method 2: Acetate-buffered QuEChERS with 10 mL of water added to the sample.	Method 1: acetone/ethyl acetate/hexane (1/2/1). Method 2 QuEChERS : 1 % acetic acid in acetonitrile .	Both methods use dispersive SPE technique with 900 mg $MgSO_4$/300 mg PSA/150 mg carbon.	GC-MSD Agilent 5975 MSD, GC-MS-MS Thermo TSQ Quantum XLS.	J&W Scientific DB-17MS, 30 m × 0.25 mm , 0.25 µm; DB-5MS, 30 m × 0.25 mm, 0.25 µm.	IDMS, $^{13}C_9$ beta-endosulfan and $^{13}C_9$ endosulfan sulfate.	single point and bracketing.
INMETRO	1	Solvent extraction.	Ethyl acetate.	SPE technique with 500 mg of porous graphitic carbon (hypercarb) and 500 mg of aminopropylsilane.	Agilent 6890 GC coupled to Agilent 5975 MSD	Factor Four VF-1ms, 30 m × 0,25 mm, 0.25 µm.	Internal calibration for β-endosulfan and IDMS for endosulfan sulfate	6- point calibration curve.
NRC	1	Dispersive extraction into solvent.	Ethanol/toluene (50/50).	EnviroClean CUMPSCB2CT dSPE tube.	Agilent 6890 single quadrupole GC-MS, CH_4 negative CI.	Zebron ZB-5MS, 30 m × 0.25 mm, 0.25 µm.	IDMS	Matching.
CMQ	1	Accelerated solvent extraction.	n-hexane/acetone (3/1).	SPE columns in series Florisil/EnviCarb+Envicarb with mixture of acetonitrile-toluene (3:1) as eluant.	GC-MS: Agilent Technologies GC System model 7890A and Triple axis Detector model 5975C.	DB-5MS + DG., 30 m (+10 m Duraguard), × 0.25mm, 0.25 µm.	IDMS	single-point.

NMI/DI	Sample size (g)	Extraction method(s)	Extraction Solvent(s)	Clean-up method(s)	Analytical instrument(s) used	Chromatographic Column(s)	Method of quantification	Type of calibration(s)
NIM	1	Soxhlet extraction at 70°C for 48h.	acetone/hexane (7/3).	GPC with mobile phase: ethyl acetate/cyclohexane = 1/1, followed by SPE with ENVI-Carb SPE Tubes (0.5 g/6mL) & LC-Alumina_N SPE Tubes (2 g/6 mL) with acetone/hexane (1/9) as eluant.	GC-High resolution mass spectrometer (HRMS)(MAT 900-Trace GC Thermo finnigan).	J&W DB-5MS 30 m × 0.25 mm, 0.25 µm.	IDMS.	single-point.
BAM	1	Sample added with 2ml water, mixed and let soak for 30 minutes in ultrasonic bath before solvent extraction.	acetonitrile	QuEChERS method with 150 mg $MgSO_4$ + 25 mg PSA + 25 mg GCB (PSA, GCB: bulk SPE sorbents).	GC-MS (Negative Chemical Ionziation); Agilent GC 6890N + Agilent MSD 5975B.	SGE BPX35, 60 m × 0.32 mm, 0.25 µm.	IDMS	9-point calibration curve.
BVL	1	Solvent extraction.	ethanol/toluene (1/1)	d-SPE tube (UCT ENVIRO-CLEAN extraction column, CUMPSCB2CT, 150 mg of $MgSO_4$, 50 mg of primary secondary amine (PSA), 50 mg of graphitized carbon black GCB); followed by GPC with BioBeads S-X3 and ethyl acetate/cyclohexan (1:1) as mobile phase.	GC/MS (Agilent 6890 / 5973N); measure with GC-MS/NCI or GC-MS/EI.	DB 5 MS, 30 m × 0.25 mm, 0.25 µm.	Internal standard calibration.	5-point calibration curve.
GLHK	1	Soxhlet extraction for 16 hours from wetted sample.	ethyl acetate	SPE: (1) Carb/NH_2; (2) Florisil.	(1) GC-NCI-MS: Agilent 6890 GC with Agilent 5973 MS; (2) GC-EI-HRMS: Agilent 6890N GC with Waters AutoSpec-Ultima MS.	(1) GC-NCI-MS: DB-17MS, 30 m × 0.25 mm, 0.25 µm; (2) GC-EI-HRMS: DB-5MS, 30 m × 0.25 mm, 0.25 µm.	IDMS.	(1) GC-NCI-MS: 7-point calibration; (2) GC-EI-HRMS: Bracketing.

NMI/DI	Sample size (g)	Extraction method(s)	Extraction Solvent(s)	Clean-up method(s)	Analytical instrument(s) used	Chromatographic Column(s)	Method of quantification	Type of calibration(s)
NMIJ	1	Extraction was carried out by liquid/solid extraction with homogenization.	acetonitrile	The extract was shaken with sodium chloride (10 g) and 0.5 mol/L phosphate buffer solution (pH7.0, 20mL) followed by SPE clean-up (graphite carbon/primary secondary amine silica gel layered cartridge (1 g/500 mg)) with toluene/acetonitrile (1:3) as eluant. Further clean-up was carried out by using silica gel SPE cartridge with hexane/acetone (17:3) as eluant.	GC/MS (an Agilent Technologies 6890GC and a 5973N MSD).	DB-35MS, 30 m × 0.25 mm, 0.25 µm.	IDMS.	Single point with matrix-matched calibration solution prepared by mixing with calibration solution and cleaned up extracts of blank green tea.
KRISS	2	Liquid/Liquid extraction after equilibrating for 2 hrs with water.	water/acetonitrile	Florisil SPE clean-up using hexane/acetone (80/20) as eluant.	GC/MS Jeol Mstation.	Rts-5ms, 30 m × 0.25 mm, 0.25 µm.	IDMS.	Single-point calibration.
CENAM	1	β-endosulfan: solid-liquid extraction Endosulfan sulfate: Soxhlet extraction with acetone. 4 subsamples were measured, 10 hours (8 circles per hour).	acetone and ethyl acetate	No clean up procedures.	GC-µECD Agilent 6890N.	HP-5, 30m × 0.32mm, 0.25 µm.	Internal standard.	5-point calibration curve.
VNIIM	2	Ultrasonic extraction.	acetone/hexane (50/50), 4 x 20 mL	Florisil column clean-up with 50% ethyl ether in hexane as eluant.	GC/MS-EI Agilent 5975C.	HP-5MS, 30 m × 0.25 mm, 0.25 µm.	IDMS.	Single point.

NMI/DI	Sample size (g)	Extraction method(s)	Extraction Solvent(s)	Clean-up method(s)	Analytical instrument(s) used	Chromatographic Column(s)	Method of quantification	Type of calibration(s)
HSA	1	Accelerated solvent extraction: Each sample blend was extracted 6 times with approximately 30 mL of hexane and acetone (1:1 v/v) at a temperature of 70 °C after a static time of 3 minutes.	acetone/hexane (1/1)	SupelClean LC-Florisil SPE cartridges and eluted with 7 mL of ethyl acetate/ hexane (15/85 v/v) mixture, then further clean-up using ENVI-Carb SPE cartridges with ethyl acetate as eluent.	The study samples were analyzed using a Thermo Scientific DFS High Resolution GC/MS equipped with a Thermo Scientific TRACE GC ULTRA.	Restek Rxi-XLB, 30 m × 0.250 mm, 0.25 µm.	Exact matching IDMS.	Single point.
BQSF, DMSc	1	1 g sample was soaked in 50 mL water for 30 min. It was homogenized with acetone and filtered. Filtrate was diluted with water and extracted by hexane.	acetone/hexane	4 g Florisil column with 100 mL of dichloromethane:hexane:acetonitrile (50:49.65:0.35) as eluent.	GC-uECD Agilent Technologies 6890N GC-MS Agilent Technologies 6890N - 5973 inert.	DB5ms and DB-35ms.	IDMS-Exact matching within 80%.	Single-point calibration.
UME	1	Pressurized solvent extraction under temperature 100^{o}C, pressure 100 bar, static time, 5min for 3 cycles.	n-hexane	Glass column (30 cm x 1.5 cm (L/ID)) filled with 7 g of florisil and 1 g of anhydrous sodium sulfate. 60 mL n-hexane was used for the elution step.	Triple-quadrupole GC-MS/MS was used (TSQ Quantum XLS-GC-MS/MS, Thermo Scientific).	TG-5SILMS, 30 m × 0.25 mm, 0.25 µm.	IDMS.	Six concentration levels calibration curve was used for the calibration. The concentration of isotopic labelled compounds was kept constant and equal to the middle concentration value of calibration range at each level.

NMI/DI	Sample size (g)	Extraction method(s)	Extraction Solvent(s)	Clean-up method(s)	Analytical instrument(s) used	Chromatographic Column(s)	Method of quantification	Type of calibration(s)
LGC	1	Soxhlet extraction with extraction solvent spiked with accurately weighed labelled internal standard ($^{13}C_9$) in Soxhlet apparatus for 24 hours.	Hexane/acetone (3/1)	SPE column composed of 2 g anhydrous sodium sulfate, 500 mg Supelco LC-NH2, 500 mg Supelco EnviCarb with a total volume of 13 mL acetonitrile/toluene (3/1) as eluent.	GC-MS with NCI detection (Agilent 5975c), using methane as CI gas.	Rxi-5 HT, 30 m × 0.25 mm, 0.25 µm.	Exact matching double IDMS.	Bracketing.
NIST	1.1	Sonication using 10 mL hexane:acetone (1:1) as extraction solvent-sonicate 30 min remove solvent and add fresh solvent - repeat sonication and solvent removal another 2 times for a total of 30 mL used for extraction.	hexane:acetone (1/1)	SPE using two NH2 Plus SPE columns in series conditioned and eluted with 20 mL of 20% methylene chloride in hexane (v%).	GC/MS (Aglient 7890A/5975C).	50% phenyl methylpolysiloxane 60 m × 0.25 mm, 0.25 µm.	Internal standard.	Bracketing.

7 Results reported by participating laboratories

The results reported by participating laboratories are summarised in Tables 8 and 9 and the summary plots are given in Figures 3 and 4.

Table 8 Summary of CCQM-K95 results for beta-endosulfan.

NMI/DI	Bottle no.	Moisture content (%)	Mass fraction (μg/kg) (on dry mass basis)	Combined standard uncertainty (μg/kg)	Coverage factor (*k*)	Expanded uncertainty (μg/kg)
BVL	*45*	*5.03*	*454*	*27.7*	*2*	*55.4*
INMETRO	*16*	*7.1538*	*530*	*16*	*2.13*	*35*
CENAM	*42*	*6.634*	*535.7*	*32.3*	*2.57*	*82.9*
UME	*37*	*4.97*	*540*	*7.50*	*2*	*15.0*
NIST	*7*	*5.195*	*569*	*8.95*	*2*	*17.9*
NIM	18	6.67	679.7	16.3	2	32.6
LGC	21	6.81	687	9	2	18
INTI	*34*	*7.23*	*693*	*28*	*2*	*57*
NMIA	5	6.8	718	22	2.23	49
KRISS	50	7.12	720	8.4	2.45	21
NMIJ	3	5.7	727	11	2	22
BAM	*20*	*6.55*	*732.5*	*4.4*	*2.57*	*11.3*
NRC	30	7.12	741	22	2	45
GLHK	27	6.48	750	24	2	48
VNIIM	*11*	*3.4*	*750*	*24*	*2*	*48*
CMQ	31	6.07	755	11	2	22
BQSF, DMSc	*25*	*6.92*	*778*	*23.5*	*2.45*	*57.5*
HSA	36	6.83	809	32	2	65

The measurement results of NMI/DI with *italic fonts* were excluded on technical grounds in the KCRV calculation. BAM, INTI and VNIIM did not establish a proper metrological traceability for the calibrants they used. BVL, CENAM, NIST and UME agreed that their results should not be incorporated due to problems with their extractions. INMETRO informed that their reported results were not corrected for recovery and the factor of recovery was not considered in their uncertainty budget though they had observed a significant recovery effect. Hence, INMETRO agreed that their results should not be included for the KCRV calculation. The reported results of BQSF, DMSc were excluded as there was traceability problem with one of the reference standards they used as calibrants. BQSF, DMSc had provided additional data after the release of results in April 2012 on the results which was based on NIMT standards only. The results of beta-endosulfan was 760 μg/kg with u_c= 25.1 μg/kg, U=61.4 μg/kg where *k*=2.45.

Table 9 Summary of CCQM-K95 results for endosulfan sulphate.

NMI/DI	Bottle no.	Moisture content (%)	Mass fraction (μg/kg) (on dry mass basis)	Combined standard uncertainty (μg/kg)	Coverage factor (*k*)	Expanded uncertainty (μg/kg)
BVL	*45*	*5.03*	*275*	*17.1*	*2*	*34.1*
INMETRO	*16*	*7.1538*	*292*	*5.2*	*2.21*	*12*
INTI	*34*	*7.23*	*348*	*21*	*2*	*43*
NIST	*7*	*5.195*	*355*	*5.67*	*2*	*11.3*
NIM	18	6.67	455.1	13.0	2	26.0
LGC	21	6.81	463	11	2	22
CMQ	31	6.07	470	6	2	12
VNIIM	*11*	*3.4*	*486*	*12*	*2*	*24*
HSA	36	6.83	486	16	2	32
NMIA	5	6.8	501	14	2.16	31
NMIJ	3	5.7	505	13	2	25
KRISS	50	7.12	514	5	2.57	13
NRC	30	7.12	517	21	2	42
GLHK	27	6.48	523	20	2	40
BAM	*20*	*6.55*	*532.6*	*3.4*	*2.57*	*8.7*
CENAM	42	6.634	549.1	36.1	2.78	100.1
UME	37	4.97	555	6.90	2	13.8
BQSF, DMSc	*25*	*6.92*	*574*	*31.1*	*2.57*	*79.9*

The measurement results of NMI/DI with *italic fonts* were excluded on technical grounds in the KCRV calculation. INTI and VNIIM did not establish a proper metrological traceability for the calibrants they used; BVL and NIST agreed that their results should not be incorporated due to problems with their extractions. INMETRO informed that their reported results were not corrected for recovery and the factor of recovery was not considered in their uncertainty budget though they had observed a significant recovery effect. Hence, INMETRO requested that their result should not be included for the KCRV calculation. The reported results of BQSF, DMSc were excluded as there was traceability problem with one of the reference standards they used as calibrants. BQSF, DMSc had provided additional data after the release of results in April 2012 on the results which was based on NIMT standards only. The results of endosulfan sulphate was 500 μg/kg with u_c=8.2 μg/kg, U=21.0 μg/kg where k=2.57.

8 Approaches to Uncertainty Estimation

The relative standard uncertainties of the results and the major contributions in the uncertainty

budgets are summarised in Table 10. The full uncertainty evaluation reported by participants is given in Appendix II.

Table 10 Summary of relative standard uncertainty of participants and the factors contributed in their uncertainty budget

NMI/DI	Relative standard uncertainty (%)		Contributions to the measurement uncertainty budget
	Beta-endosulfan	Endosulfan sulphate	
INTI	4.0	6.0	(i) Repeatability – standard deviation of sample results (ii) Bias – relative difference of recovery
NMIA	3.1	2.8	(i) Precision effects related to peak area ratio measurements and mass measurements (ii) Maximum bias in mass of calibration solution added to calibration blend (iii) Maximum bias in mass of internal standard added to sample blend (iv) Maximum bias in mass of internal standard added to calibration blend (v) Maximum bias in mass of sample added to sample blend (vi) Potential bias due to effects of the matrix on measurement of chromatographic peak areas (vii) Precision effects related to mass fraction of analyte calibration solution (viii) Precision of measurement of moisture content (ix) Bias due to method trueness assessed via an independent method
INMETRO	3.0	1.8	(i) Area ratio (ii) Mass of internal standard solution (iii) Internal standard solution mass fraction (iv) Sample mass (v) Dry mass correction (vi) Repeatability (vii) Purity of standard (viii) Calibration curve
NRC	3.0	4.1	(i) Mass fraction of analyte in sample (ii) Mass of calibration solution (iii) Mass of sample (iv) Mass of labeled spike added to sample solution (v) Mass of labeled spike added to calibration solution (vi) Signal ratio from native to labeled in sample solution and in calibration solution (vii) Dry mass correction (viii) Uncertainty of a series of independent determinations
CMQ	1.5	1.3	(i) Mass fraction of analyte in sample (ii) Mass of internal standard solution added to sample blend (iii) Mass of sample added to sample blend (iv) Mass of reference standard solution added to calibration blend (v) Mass of internal standard solution added to calibration blend (vi) Peak area ratio of analyte to internal standard in sample blend solution (vii) Peak area ration of analyte to internal standard in calibration blend solution (viii) Dry mass correction (ix) Blend-to-blend variation

NMI/DI	Relative standard uncertainty (%)		Contributions to the measurement uncertainty budget
	Beta-endosulfan	Endosulfan sulphate	
NIM	2.4	2.9	(i) Method precision (ii) Recovery of extraction procedure (iii) Purity of standard (iv) Mass fraction of internal standard (v) Mass fraction of sample (vi) Mass fraction of calibration standard (vii) Matrix effects in calibration blend
BAM	0.6	0.6	(i) Method precision (ii) Purity of standard (iii) Dry mass correction
BVL	6.0	6.2	(i) Calibration solution (ii) Sample weight (iii) Sample spike (iv) Dry mass correction (v) Method reproducibility
GLHK	3.2	3.8	(i) Purity of standard (ii) Method precision (iii) Method bias (iv) Uncertainty from moisture content
NMIJ	1.5	2.6	(i) Variability of analytical values (ii) Ratio of peak area of analyte and internal standard (iii) Calibration solution (iv) Weighing uncertainty (v) Purity of standard (vi) Spiking uncertainty (vii) Dry mass correction
KRISS	1.2	1.0	(i) Purity of standard (ii) Gravimetric preparation of standard solution (iii) Gravimetric preparation for calibration isotope standard mixtures (iv) Dry mass correction (v) Method precision
CENAM	6.0	6.6	(i) Calibration curve (ii) Dilution factor (iii) Mass fraction of sample (iv) Repeatability (v) Dry mass correction
VNIIM	3.17 (3.35, revised)*	2.48 (2.84 revised)*	(i) Mass concentration of calibrant* (ii) Mass fraction of sample (iii) Response factor (iv) Mass of internal standard added to sample before extraction (v) Method precision
HSA	4.0	3.3	(i) Method precision (ii) Bias in different extraction and clean-up methods (iii) IDMS results from different ion pairs (iv) Mass fraction of calibration solution (v) Comparison from matrix and non-matrix matched calibration blends (vi) Blend preparation masses (vii) Dry mass correction (viii) Peak area ratios in the sample and calibration blends
BQSF, DMSc	3.0	5.4	(i) Method precision (ii) Mass fraction of calibration solution (iii) Mass fraction of internal standard in sample blend (iv) Mass fraction of internal standard in calibration blend (v) Mass fraction of sample in sample blend (vi) Dry mass correction (vii) Purity of standard (viii) Concentration of working standards

NMI/DI	Relative standard uncertainty (%)		Contributions to the measurement uncertainty budget
	Beta-endosulfan	Endosulfan sulphate	
UME	1.4	1.2	(i) Naive stock solution (ii) Labeled stock solution (iii) Mass of sample (iv) Spiked volume of internal labeled standard (v) Mass of final sample (vi) Calibration graph
LGC	1.3	2.4	(i) Mass fraction of replicate sample extracts (ii) Individual sample uncertainties (iii) Dry mass correction (iv) Preparation of calibration blends
NIST	1.6	1.6	(i) Measurement of samples (ii) Measurement of calibration standards (iii) Dry mass correction (iv) Certified concentration of calibration solution

*VNIIM revised their reported standard uncertainties after they completed the purity assessment of their calibrants.

9 Key Comparison Reference Value (KCRV) calculation

A result summary report and the draft A report were sent to participants in early April 2012 and early November 2012 for discussion in the OAWG meetings in Paris, France and in Hong Kong, China respectively. For beta-endosulfan, the eighteen results spread from 454 μg/kg to 809 μg/kg, with five of the results below 570 μg/kg and thirteen results above 670 μg/kg. For endosulfan sulphate, the eighteen results spread from 275 μg/kg to 574 μg/kg, with four of the results below 360 μg/kg and fourteen results above 450 μg/kg. GLHK reported at the OAWG meeting in April 2012 that presence of traces of water in the solvent or wetting the sample before extraction was critical for complete extraction of beta-endosulfan and endosulfan sulphate from the matrix. A summary of the extraction efficiency study is illustrated in Appendix III.

Subsequent to the meeting, NIST reported that 720 μg/kg beta-endosulfan and 510 μg/kg endosulfan sulphate were found in the sample after wetting of the sample prior to extraction. BVL also reported after further investigation that beta-endosulfan at 680μg/kg and endosulfan sulphate at 509 μg/kg were found in the sample after wetting of the sample prior to extraction. Furthermore, BVL also revised their moisture content estimate of the sample to 6.3%. CENAM reported that the solid-liquid extraction method which they adopted for the extraction of beta-endosulfan did not give complete recovery. By using the standard addition method, an average of 721.4 μg/kg beta-endosulfan with relative standard uncertainty of 16% was obtained.

In consideration of the findings in the follow-up studies, BVL and NIST agreed not to include their beta-endosulfan and endosulfan sulphate results for KCRV calculation and CENAM and

UME agreed not to include their beta-endosulfan results for KCRV calculation.

INMETRO agreed not to include their results in KCRV calculation because of incomplete extraction and recovery correction was not applied.

At the OAWG meeting held in November 2012, NIM reported their additional studies showing that the extraction efficiency for labeled internal standards and the analytes were not equal either in Soxhlet extraction or ASE extraction. NIM reported that wetting of the samples prior to ASE extraction would give better extraction efficiency, and a similar observation was also found by GLHK on Soxhlet extraction with wetted samples. NIM also noted that the matrix effect and injection sequence would affect the signal ratio between analytes and labeled internal standards.

As agreed in the OAWG meetings, the results of BAM and INTI were not included in the KCRV calculation as their in-house purity assessment appeared not complete in a way to establish the metrological traceability for the commercial calibrants they used.

The reported results of BQSF, DMSc were the average of all analytical results calculated by the use of both sources of standards from NIMT and NMIA. However, their NMIA standard purity values were not the current NMIA certified purity values for these materials. As agreed in the OAWG meeting in Nov 2012, their results were not included in the KCRV calculation. BQSF, DMSc repeated the calculation using NIMT standards as calibrants and obtained the results as follows: beta-endosulfan at mass fraction 760 µg/kg with u_c= 25.1 µg/kg, U=61.4 µg/kg where k=2.45 and endosulfan sulphate at mass frraction 500 µg/kg with u_c=8.2 µg/kg, U=21.0 µg/kg where k=2.57.

VNIIM re-determined the purity of their calibrants against a NIST SRM after the comparison. As a result they increased their reported relative combined standard uncertainties of both analytes slightly from 3.17% to 3.35% for beta-endosulfan and 2.48% to 2.84% for endosulfan sulphate. However, the uncertainty component due to this process was not included in their original uncertainty budget. As such, the original results of VNIIM were not included in the KCRV calculation.

To conclude, 9 sets of valid results were used for the KCRV calculation for beta-endosulfan (Table 8) and 11 sets of valid results were used for the KCRV calculation for endosulfan sulphate (Table 9).

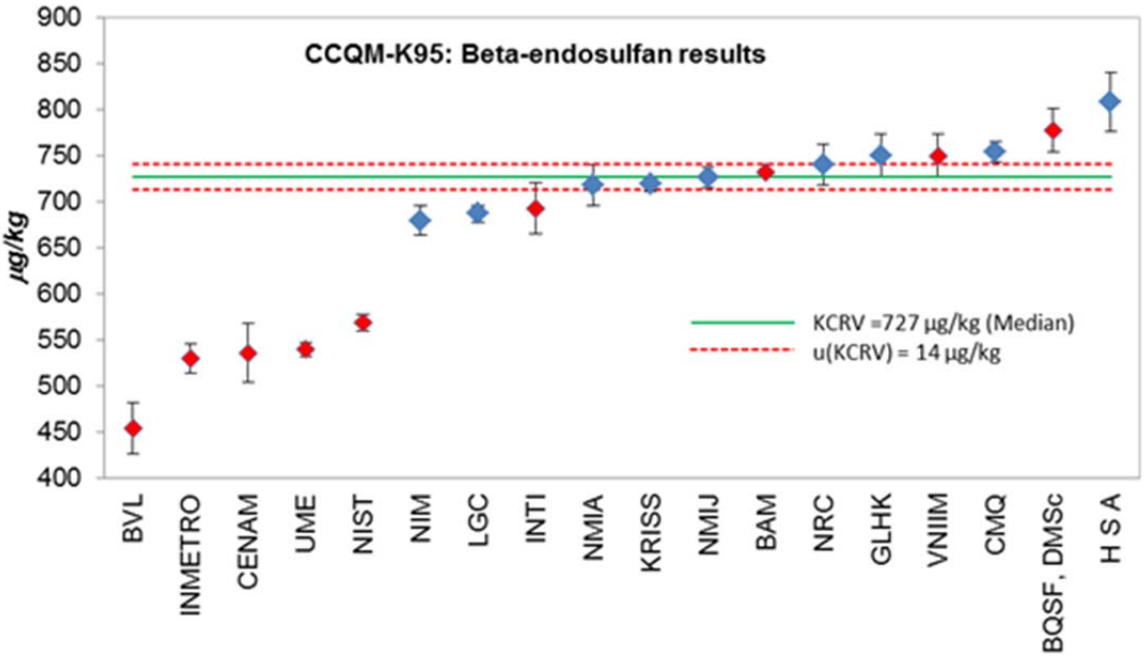
Table 11 summarises the provisional KCRVs and their associated standard uncertainty u (KCRV) using the following three different statistical approaches, i.e. arithmetic mean (standard deviation), median (*MADe*) and MM-median (S(MM-median)), with all valid data.

Table 11 Results of provisional KCRVs and the associated uncertainties calculated by different approaches.

		beta-endosulfan	Endosulfan sulphate
1.	*Arithmetic Mean*	732 μg/kg	503 μg/kg
	Standard deviation (SD)	39 μg/kg	33 μg/kg
	No. of data used (N)	9	11
	Standard uncertainty $(= SD\sqrt{N})$	13 μg/kg	10 μg/kg
2.	*Median*	727 μg/kg	505 μg/kg
	MADe [median absolute deviation (MAD) multipled by 1.483]	34 μg/kg	28 μg/kg
	No. of data used (N)	9	11
	Standard uncertainty $(= 1.25 \times MADe / \sqrt{N})$	14 μg/kg	11 μg/kg
3.	*MM-median*	728 μg/kg	504 μg/kg
	S(MM-median)	38 μg/kg	38 μg/kg
	No. of data used (N)	9	11
	Standard uncertainty $(= S(MM - median) / \sqrt{N})$	13 μg/kg	11 μg/kg

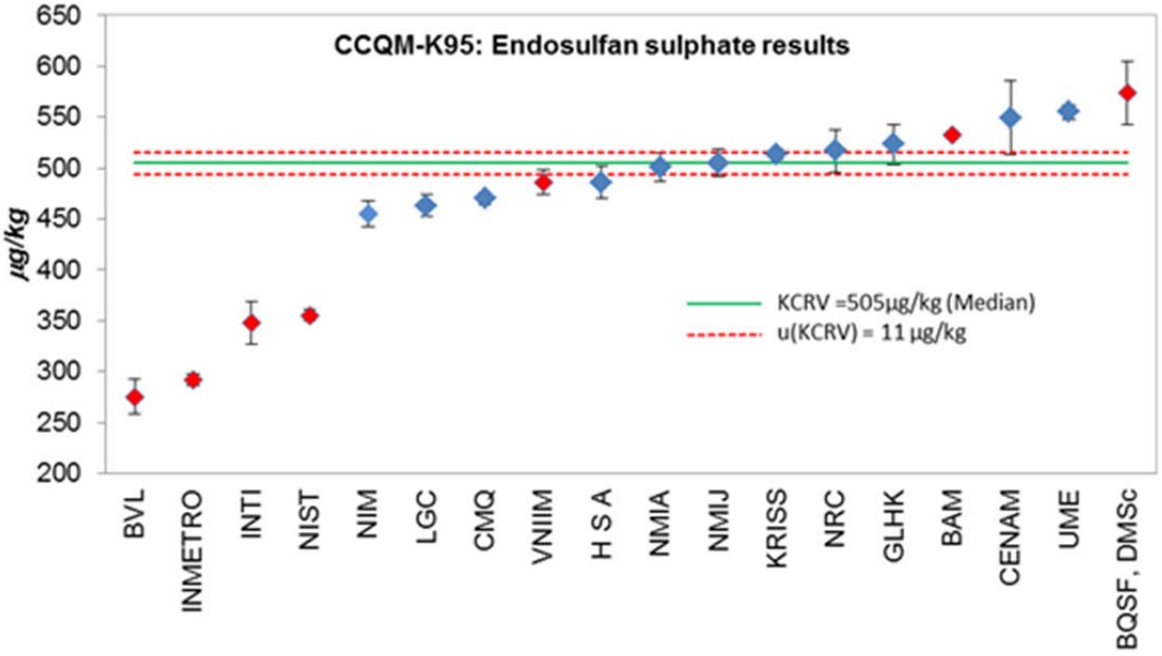
Considering no significant difference among the calculated KCRV results from the three different approaches, the piloting institutes, GLHK and NIM recommended the use of median approach for calculation of KCRVs as it is robust, simple to calculate and understand, and has a very clear relationship with the data from which it was derived. The OAWG agreed to such recommendation at the OAWG meeting in November 2012.

The participants' data, the KCRV and its associated standard uncertainty of beta-endosulfan and endosulfan sulphate are plotted in Figures 3 and 4.



◆ Data included for KCRV calculation; ◆ Data excluded from KCRV calculation.

Figure 3 ***CCQM-K95: KCRV for beta-endosulfan and its standard uncertainty with participants' results and the associated reported standard uncertainties.***



◆ Data included for KCRV calculation; ◆ Data excluded from KCRV calculation.

Figure 4 ***CCQM-K95: KCRV for endosulfan sulphate and its standard uncertainty with participants' results and the associated reported standard uncertainties.***

10 Degrees of equivalence (DoE) calculation

The DoE (D_i, $U(D_i)$)for each participant was calculated according to the following equation:

$$D_i = X_i - X_{ref}$$

where D_i is the degree of equivalence of participant i;
X_i is the reported result of participant i; and
X_{ref} is the KCRV value.

The uncertainty associated with D_i for each participant was estimated as follows:

$$u(D_i) = \sqrt{u^2(X_i) + u^2(X_{ref})}$$

The expanded uncertainty of the D_i [$U(D_i)$] with coverage factor k =2 and at 95% level of confidence was calculated as follows:

$$U(D_i) = 2 \times u(D_i)$$

Table 12 Degrees of equivalence [D_i] and their expanded uncertainties with k=2 and at 95% level of confidence [$U(D_i)$].

	Beta-endosulfan					Endosulfan sulphate				
	D_i		$U(D_i)$		$\frac{D_i}{U(D_i)}$	D_i		$U(D_i)$		$\frac{D_i}{U(D_i)}$
	(µg/kg)	(%)	(µg/kg)	(%)		(µg/kg)	(%)	(µg/kg)	(%)	
INTI	-34	-4.7	63	8.6	-0.54	-157	-31	47	9.3	-3.34
NMIA	-9	-1.2	52	7.2	-0.17	-4	-0.8	35	7.0	-0.11
INMETRO	-197	-27	43	5.9	-4.61	-213	-42	24	4.7	-9.01
NRC	14	1.9	52	7.2	0.27	12	2.4	47	9.3	0.25
CMQ	28	3.9	36	4.9	0.78	-35	-6.9	24	4.8	-1.44
NIM	-47.3	-6.5	43	5.9	-1.10	-49.9	-9.9	34	6.6	-1.49
BAM	5.5	0.8	30	4.1	0.19	27.6	5.5	22	4.4	1.24
BVL	-273	-38	61	8.4	-4.45	-230	-46	40	8.0	-5.71
GLHK	23	3.2	56	7.7	0.41	18	3.6	45	9.0	0.40
NMIJ	0	0.0	36	4.9	0.00	0	0.0	34	6.6	0.00
KRISS	-7	-1.0	33	4.5	-0.21	9	1.8	23	4.6	0.38
CENAM	-191.3	-26	71	9.7	-2.71	44.1	8.7	75	15	0.59
VNIIM	23	3.2	56	7.7	0.41	-19	-3.8	32	6.3	-0.59
HSA	82	11	70	9.6	1.17	-19	-3.8	39	7.7	-0.49
BQSF, DMSc	51	7.0	55	7.5	0.93	69	14	66	13	1.05
UME	-187	-26	32	4.4	-5.83	50	9.9	25	5.0	1.97
LGC	-40	-5.5	34	4.6	-1.19	-42	-8.3	31	6.1	-1.37
NIST	-158	-22	34	4.6	-4.71	-150	-30	24	4.8	-6.23

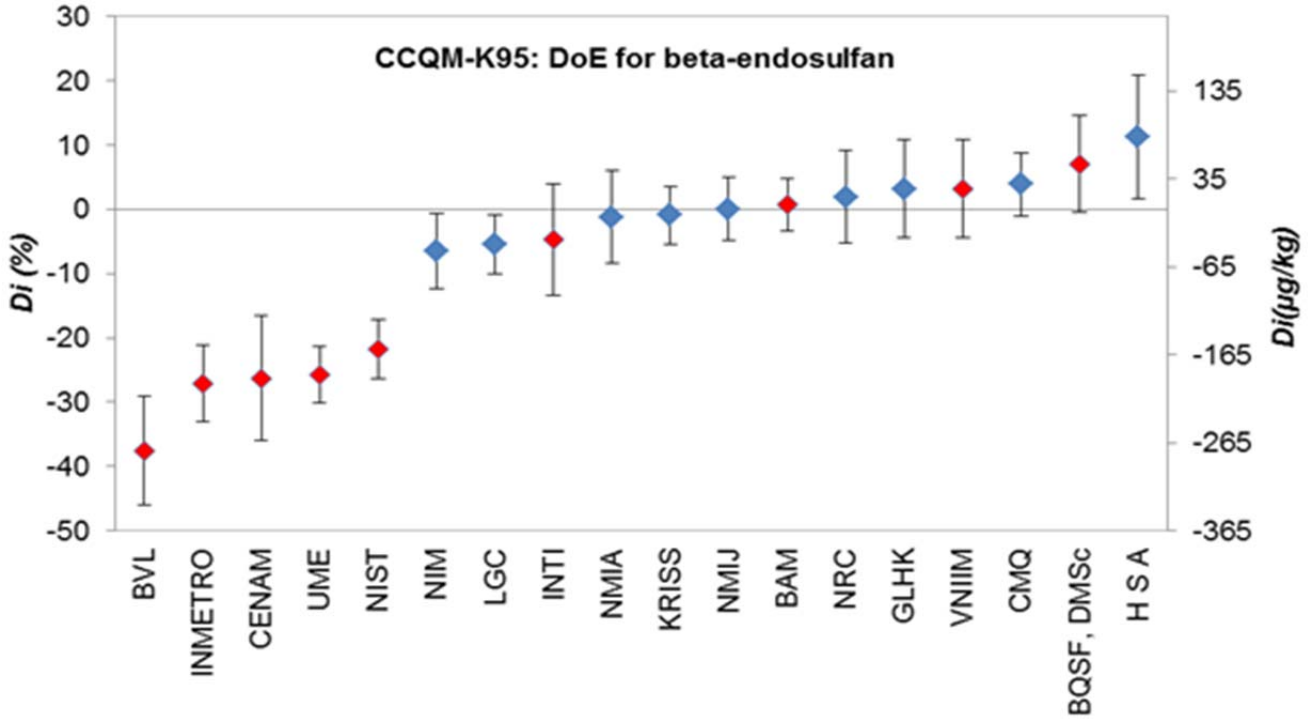


Figure 5 ***CCQM-K95: Plot of degrees of equivalence [D_i] of beta-endosulfan and their expanded uncertainties with k=2 and at 95% level of confidence [$U(D_i)$].***

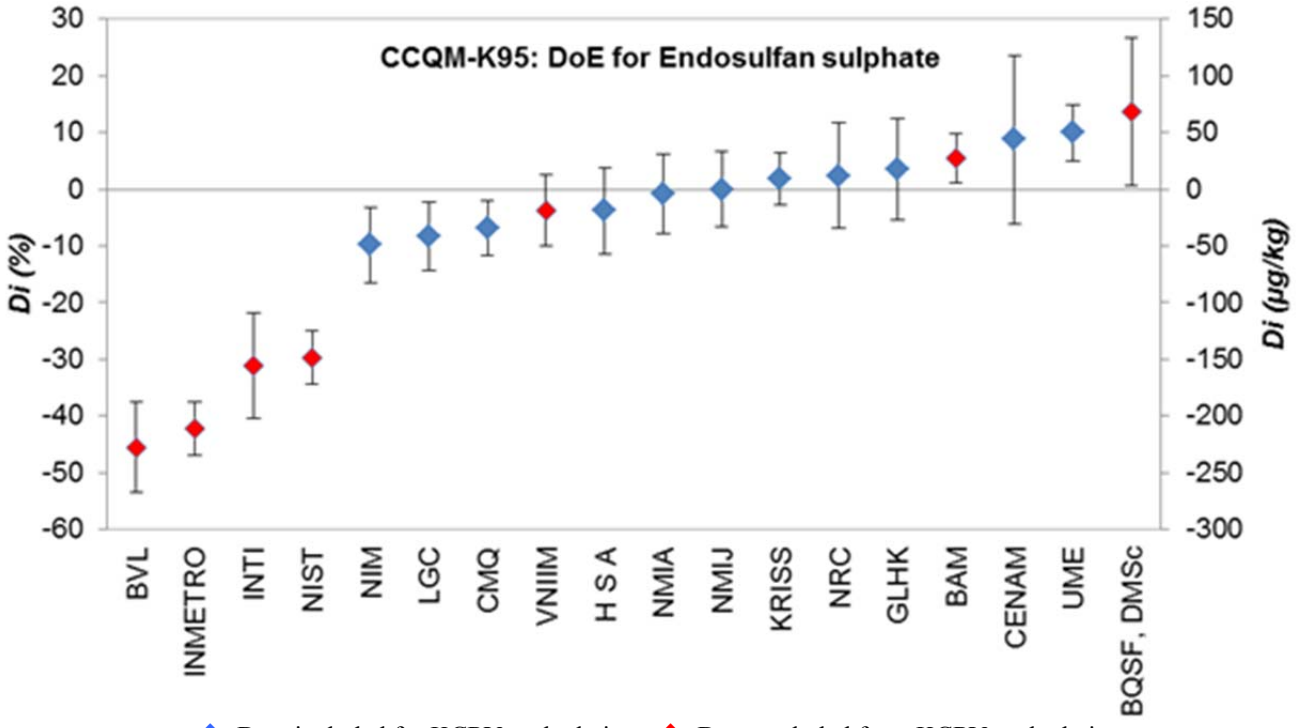


Figure 6 ***CCQM-K95: Plot of degrees of equivalence [D_i] of endosulfan sulphate and their expanded uncertainties with k=2 and at 95% level of confidence [$U(D_i)$].***

11 Core Competency and How far does the light shine?

This Track A comparison is part of a suite of studies designed and meant to support (as a set of studies) the assessment of measurement capabilities needed for delivery of measurement services within the scope of the OAWG Terms of Reference. This CCQM-K95 "Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea" study provides the means for assessing measurement capabilities for (i) value assignment of primary references; (ii) value assignment (including verification) of single and multi-component formulated solutions; (iii) extraction of analytes of interest from matrix; (iv) clean-up and separation of analytes of interest from other undesirable interfering matrix or extract components; (v) transformation, if any; and (vi) analytical separation and specificity in a plant matrix. Generally, it specifically demonstrates a laboratory's capabilities in determining the mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity pK_{ow} < -2 in low fat, low protein plant matrices. The Analysis Space Model and the AOAC food-matrix triangle are shown in Figures 7 and 8 for easy reference. This tea matrix would be expected to fall into segment "5" of the AOAC food-matrix triangle as a low fat and low protein material. Competency tables underpinning their core competency of participants are given in Appendix IV.

12 Conclusion

Participants' capabilities in measuring mid-polarity analytes in food matrix were being demonstrated through this key comparison. Most of the participating NMIs/DIs successfully measured beta-endosulfan and endosulfan sulphate in the sample though there is room for further improvement for some participants. This key comparison involved not only extraction, clean-up, analytical separation and selective detection of the analytes in a complex food matrix, but also the pre-treatment procedures of the material before the extraction process. The problem of incomplete extraction of the incurred analytes from the sample matrix may not be observed simply using spike recovery.

The relative standard deviations for the data included in the KCRV calculation in this key comparison were less than 7% which were acceptable given the complexity of the matrix, the level of the analytes and the complexity of the analytical procedure.

13 Acknowledgement

The contributions from the participating NMIs/DIs are highly appreciated and acknowledged. The coordinating laboratories would also like to thank Dr. Lindsey Mackay, the chair of OAWG, for providing guidance throughout the course of this study.

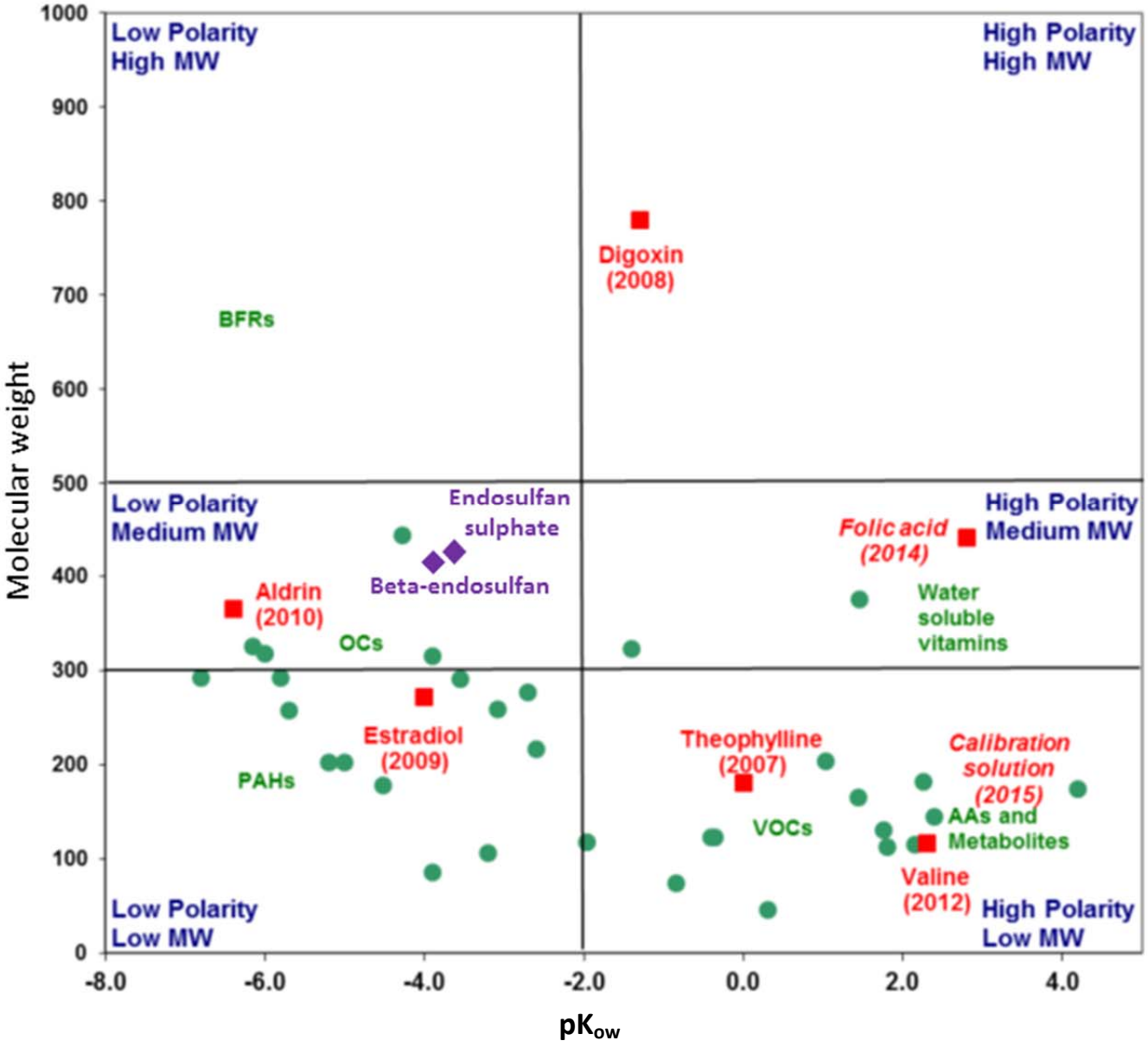


Figure 7 Analysis Space Model

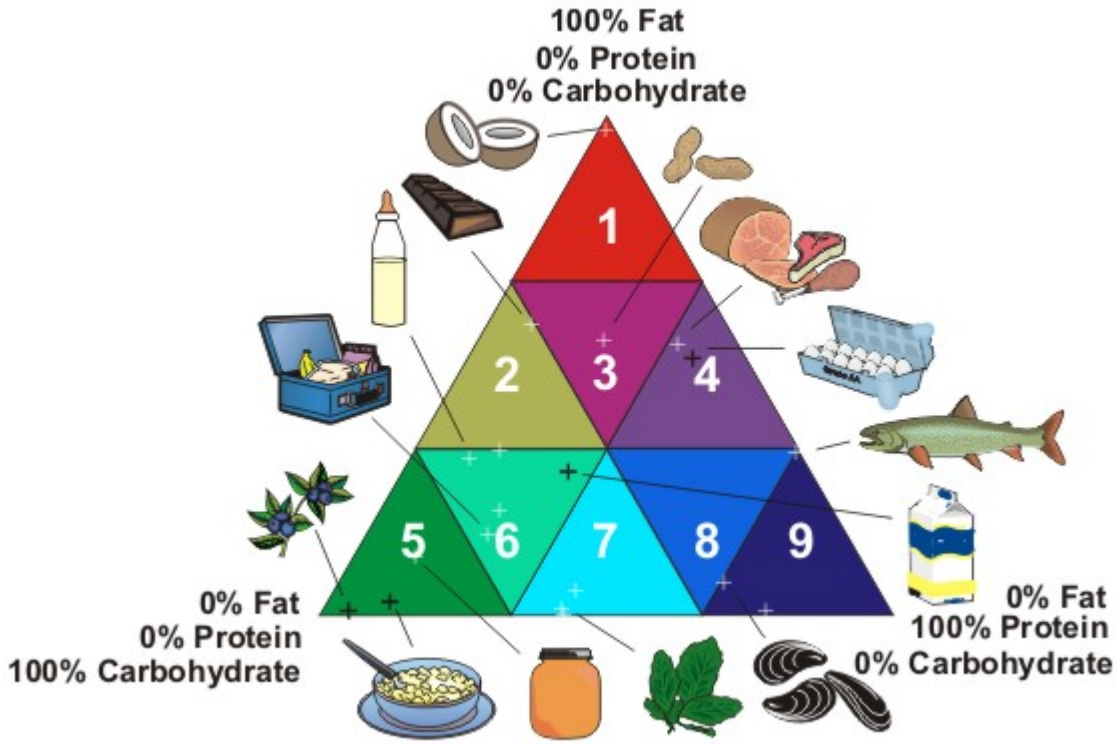


Figure 8 ***AOAC Food-matrix Triangle (by courtesy of NIST)***

Appendix I: Youden plots of the participants' results distribution

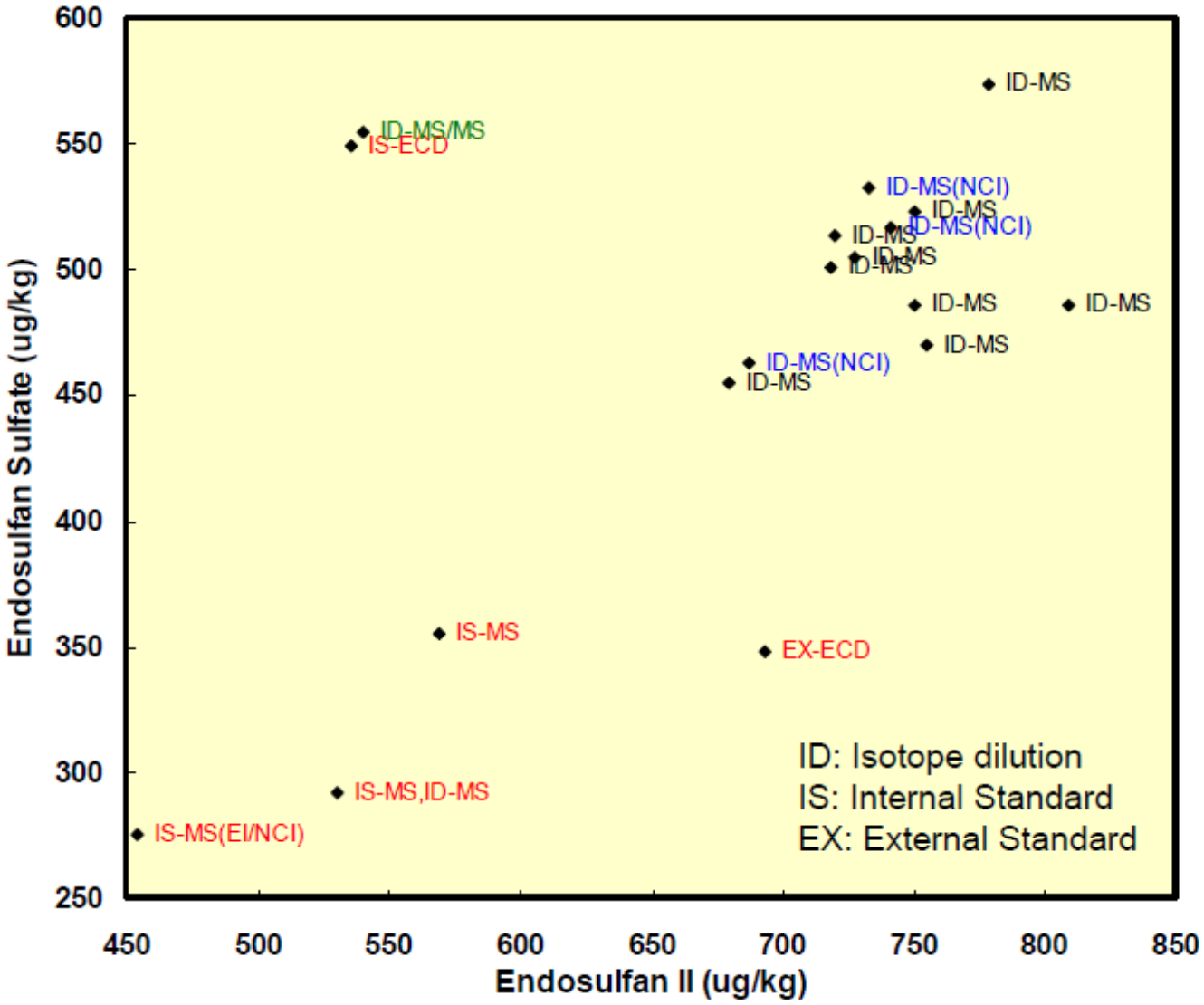


Figure AI-1 ***Youden Plot of CCQM-K95 participants' results distribution with respect to the quantitation techniques used (by courtesy of NMIJ)***

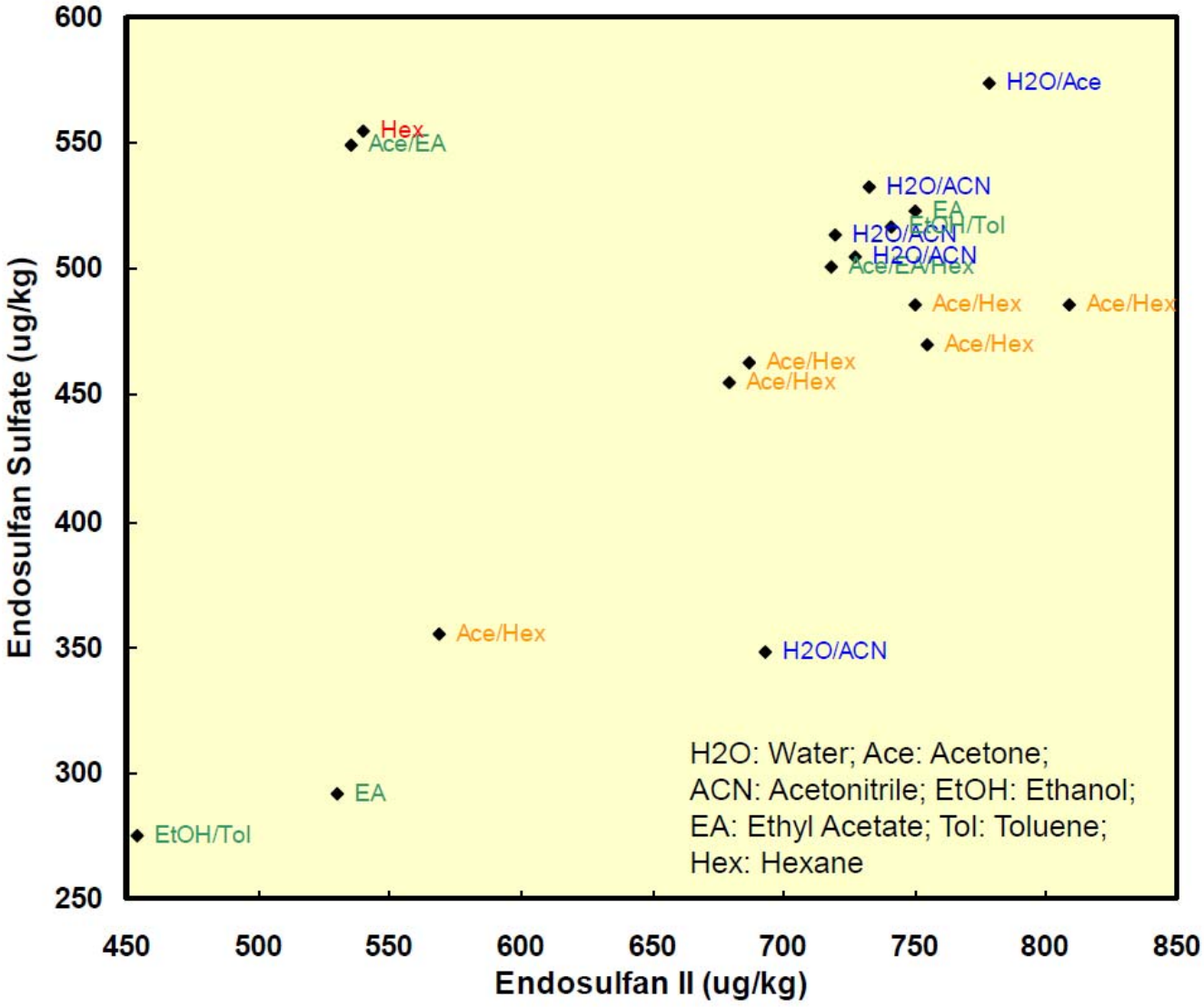


Figure AI-2 ***Youden Plot of CCQM-K95 participants' results distribution with respect to the extraction solvents used (by courtesy of NMIJ)***

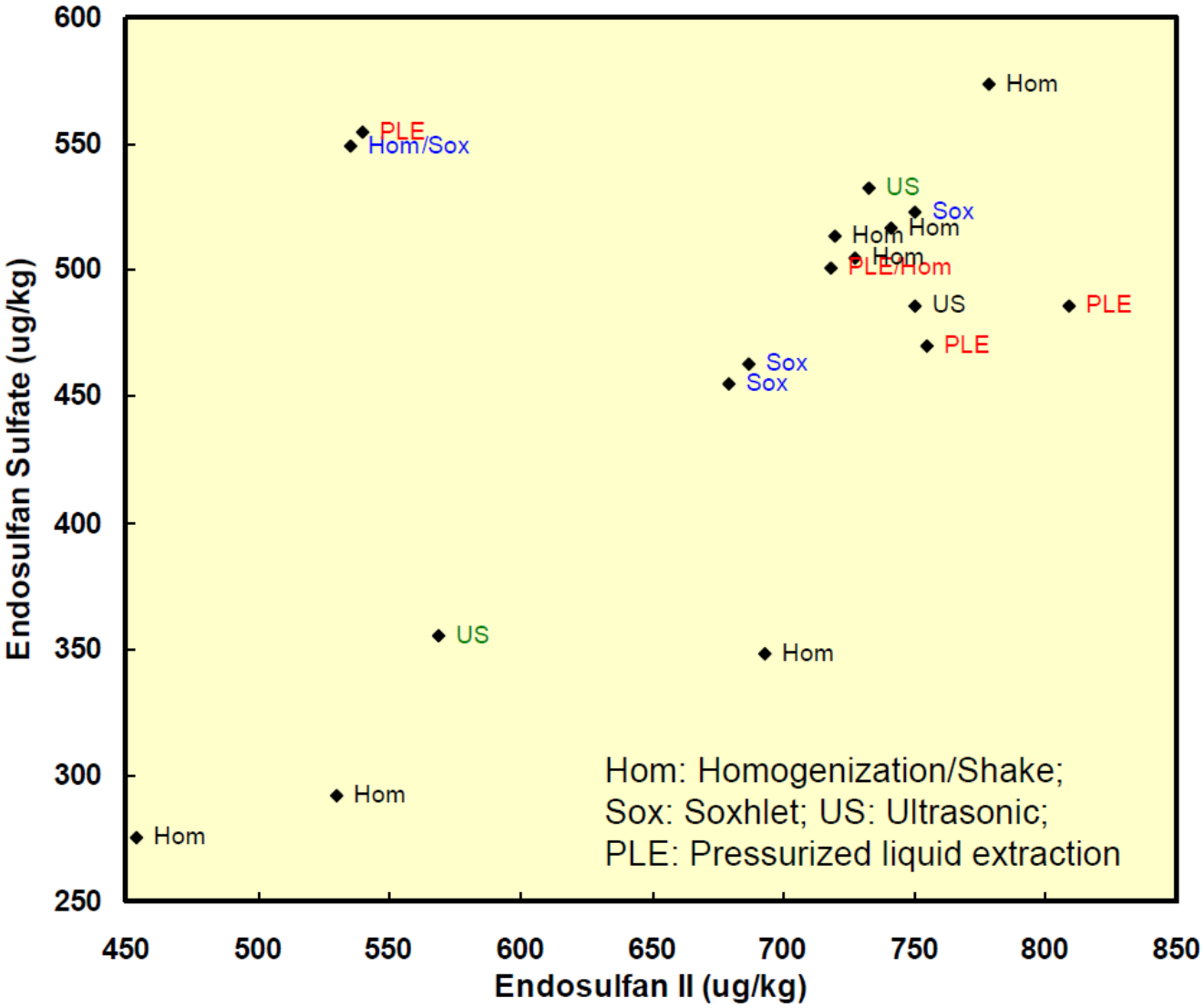


Figure AI-3 ***Youden Plot of CCQM-K95 participants' results distribution with respect to the extraction methods used (by courtesy of NMIJ)***

Appendix II: Measurement Equations and the Uncertainty Estimation of Participants

Measurement equations used to calculate the mass fraction of each analyte, the uncertainties estimation for each factor and the full uncertainty budget of each participant were listed below:

INTI - Argentina

Analyte concentration = (Analyte area/Standard area) x Standard concentration x Dilution factor

Two uncertainty sources were considered as representative and combined quadratically to obtain the combined uncertainty. The first one was the repetibility, which was measured as the standard deviation of the sample results (two duplicates, two times). The second source, was the bias, which was measured as the standard deviation of the relative differences between the nominal value and the obtained value of three recovery tests, that where carried out together with the samples. The expanded uncertainty was obtained by multiplying the combined uncertainty by a cover factor of k=2 (95% confidence).

Full uncertainty budget has not been provided.

NMIA – Australia

The measurement equations used to calculate the mass fraction of each analyte is as follows;

$$\omega_X = \omega_Z \bullet \frac{M_Y}{M_X} \bullet \frac{M_{Zc}}{M_{Yc}} \bullet \frac{R_B}{R_{Bc}} \bullet (p + 1)$$

where;

ω_x = mass fraction of analyte in sample

ω_z = mass fraction of analyte in the calibration standard solution used to prepare calibration blend

M_y = mass of internal standard solution added to sample blend

M_{yc} = mass of internal standard solution added to calibration blend

M_x = mass of sample added to sample blend

M_{zc} = mass of calibration standard solution added to calibration blend

R_b = observed isotope amount ratio in sample/internal standard blend

R_{bc} = observed isotope amount ratio in standard/internal standard calibration blend

p = moisture content expressed as a mass fraction of the dry mass of the sample

All masses and mass fractions used to calculate ωx were determined using balances calibrated with metrological traceability to the SI unit of the kilogram through Australian national standards for mass. Isotope amount ratios were determined by measurement of peak areas in chromatographic traces for characteristic ions of analytes and internal standards. 13 sub-samples from bottle 5 of the study material were analysed by two methods in four batches during February 2012. Moisture content was determined according to the study protocol.

Tables showing the measurement uncertainty budgets for beta-endosulfan and endosulfan sulfate are provided to the right of this cell.

A standard uncertainty was estimated for all components in the measurement equation. These were combined using derived sensitivity coefficients to estimate a combined standard uncertainty in the reported result for each analyte in the CCQM-K95 study sample. The total effective degrees of freedom was determined using the Welch-Satterthwaite equation to calculate the appropriate coverage (k) factor to expand the combined standard uncertainty to a 95% confidence interval for reporting. To ensure that all likely sources of bias would be accounted for in the final uncertainty budget a trueness factor was also included. This factor was assigned a nominal value of one and an uncertainty representing the potential magnitude of undetected bias due to factors affecting the measured peak area ratios such as the degree of matching of sample and calibration blends and stability of reference standard solutions. The magnitude of the uncertainty in the trueness factor was estimated by the approach described in ISO Guide 35 (Section 7.9) for estimating potential between group variance when an ANOVA indicates insufficient within group precision.

Uncertainty budget for β-endosulfan

Parameter	Source of uncertainty	x_i	$u(x_i)$	Degrees of freedom ($_i$)	Source of data
Measurement precision for ω_x (including precision for R_B, R_{Bc}, M_x, M_y, M_z and M_{yc})	Precision effects related to peak area ratio measurements and mass measurements	668.0	6.2	9	Standard deviation of the mean of 13 independent determinations on the study material over 4 separate batches using two extraction methods and two determination methods
M_{Zc} (g)	Maximum bias in mass of calibration solution added to calibration blend	0.16	0.00014	Large	Certified balance linearity
M_Y (g)	Maximum bias in mass of internal standard added to sample blend	0.16	0.00014	Large	Certified balance linearity
M_{Yc} (g)	Maximum bias in mass of internal standard added to calibration blend	0.16	0.00014	Large	Certified balance linearity
M_X (g)	Maximum bias in mass of sample added to sample blend	1	0.00014	Large	Certified balance linearity
R_b/R_{bc}	Potential bias due to effects of the matrix on measurement of chromatographic peak areas	1	0.013	11	Standard deviation of the normalised results for individual samples when measured by six different NCI/MS and EI/MS/MS ion pairs
ω_Z ($\mu g. g^{-1}$)	Precision effects related to mass fraction of analyte calibration solution	3.48	0.048	24	Purity/dilution masses/observed standard solution preparation variability
p+1	Precision of measurement of moisture content	1.07	0.0019	11	Standard deviation of the mean of measured moisture content in four sub-samples of the study material
$F_{trueness}$	Bias due to method trueness	1	0.022	3	Between batch standard deviation

Uncertainty budget for endosulfan sulfate

Parameter	Source of uncertainty	x_i	$u(x_i)$	Degrees of freedom ($_i$)	Source of data
Measurement precision for ω_x (including precision for R_B, R_{Bc}, M_x, M_y, M_z and M_{yc})	Precision effects related to ratio measurements and mass measurements	466	3.7	9	Standard deviation of the mean of 13 independent determinations on the study material over 4 separate batches using two extraction methods and two determination methods
M_{Zc} (g)	Maximum bias in mass of calibration solution added to calibration blend	0.16	0.00014	Large	Certified balance linearity
M_Y (g)	Maximum bias in mass of internal standard added to sample blend	0.16	0.00014	Large	Certified balance linearity
M_{Yc} (g)	Maximum bias in mass of internal standard added to calibration blend	0.16	0.00014	Large	Certified balance linearity
M_X (g)	Maximum bias in mass of sample added to sample blend	1	0.00014	Large	Certified balance linearity
R_b/R_{bc}	Potential bias due to effects of the matrix on measurement of chromatographic peak areas	1	0.0051	11	Standard deviation of the normalised results for individual samples when measured by six different NCI/MS and EI/MS/MS ion pairs
ω_Z ($\mu g. g^{-1}$)	Precision effects related to mass fraction of analyte calibration solution	2.43	0.045	33	Purity/dilution masses/observed standard solution preparation variability
p+1	Precision of measurement of moisture content	1.07	0.0019	11	Standard deviation of the mean of measured moisture content in four sub-samples of the study material
$F_{trueness}$	Bias due to method trueness	1	0.019	3	Between batch standard deviation

Brazil – INMETRO

$$W_{Analite} = \left(\frac{R - b}{a} \right) \times \left(\frac{m_{IS\_sol} \times W_{lS}}{m_{sample} \times f} \right)$$

a and b: angular and linear coefficients, respectively;
R: sample area ratio;
m_{IS_sol} : internal standard solution mass added to the sample;
m_{sample}: sample mass;
W_{IS}: intenal standard solution mass fraction;
f: dry mass correction factor.

		β-endosulfan		Endosulfan sulphate	
Source	Description	u (standard uncertainty) µg/kg	contribution (%)	u (standard uncertainty) µg/kg	contribution (%)
Area ratio	Type A uncertainty: starndard deviation of the mean.	6,8	17,2	1,76	11,2
Mass of internal standard solution	Type B uncertainty: obtained from the weight certificate	0,025	0,0	0,014	0,0
Internal standard solution mass fraction	Type B uncertainty obtained from the certificates. The sources considered were the masses obtained during the solution preparation	0,34	0,0	0,34	0,4
Sample mass	Type B uncertainty: obtained from the weight certificate	0,0059	0,0	0,0033	0,0
Dry mass correction factor	Type A uncertainty: starndard deviation of the mean of 3 determinations. Type B sources were also considered such as the wet and dry masses in the glass dishes.	0,068	0,0	0,038	0,0
Repeatability	Type A uncertainty: starndard deviation of the mean of 3 determinations	4,3	7,0	1,7	10,2
Purity of the standard	Type A uncertainty: standard deviation of the mean of 3 qNMR determinations. Other sources were also considered such as the Internal Standard purity and the masses and molar masses of analyte and internal standard.	5,1	9,5	2,9	31,1
Calibration curve	Standard erros of linear and angular coefficients, obtained from the linear regression of calibration curve	13	66,3	3,6	47,1
Overall		16	100	5,2	100,0

The sources that are part of the measurand equation were combined and the result was relatively combined with the uncertainties of purity and repeatability.

Canada – NRC-INMS

Measurement equation:

$$w = \frac{R_{sam}}{R_{cal}} \cdot \frac{m_{ssam}}{m_{scal}} \cdot \frac{m_{cal}}{m_{sam}} \cdot \frac{1}{d_w} \cdot w_{cal}$$

where:

$$\frac{\boldsymbol{R}_{sam}}{\boldsymbol{R}_{cal}} = \frac{\left(\boldsymbol{R}_s^* - \boldsymbol{R}_b^*\right)}{\left(\boldsymbol{R}_b^* - \boldsymbol{R}_{sp}\right)} \cdot \frac{\left(\boldsymbol{R}_{sp} - \boldsymbol{R}_b\right)}{\left(\boldsymbol{R}_b - \boldsymbol{R}_s\right)}$$

and:

$\boldsymbol{w}$ = mass fraction of analyte in sample
$\boldsymbol{R}_{sam}$ = corrected ratio of signal from native to labelled in sample solution
$\boldsymbol{R}_{cal}$ = corrected ratio of signal from native to labelled in calibration solution
$\boldsymbol{m}_{ssam}$ = mass of labelled spike added to sample solution
$\boldsymbol{m}_{scal}$ = mass of labelled spike added to calibration solution
$\boldsymbol{m}_{cal}$ = mass of calibration solution
$\boldsymbol{m}_{sam}$ = mass of sample
$\boldsymbol{d}_w$ = dry weight fraction of $\boldsymbol{m}_{sam}$
$\boldsymbol{w}_{cal}$ = mass fraction of calibration solution
$\boldsymbol{R}_b$ = ratio of signal from native to labelled in sample solution blend
$\boldsymbol{R}_b$* = ratio of signal from native to labelled in spiked calibration solution
$\boldsymbol{R}_s$* = ratio of signal from native to labelled in the native calibrant
$\boldsymbol{R}_{sp}$ = ratio of signal from native to labelled in the spike

Uncertainty calculations:

The overall uncertainty was calculated from individual combined estimates (u_i) according to the measurement equation:

$$u_i = w\sqrt{\left(\frac{u\left(R_{sam}/R_{cal}\right)}{R_{sam}/R_{cal}}\right)^2 + \left(\frac{u\left(m_{ssam}\right)}{m_{ssam}}\right)^2 + \left(\frac{u\left(m_{scal}\right)}{m_{scal}}\right)^2 + \left(\frac{u\left(m_{cal}\right)}{m_{cal}}\right)^2 + \left(\frac{u\left(m_{sam}\right)}{m_{sam}}\right)^2 + \left(\frac{u\left(d_w\right)}{d_w}\right)^2 + \left(\frac{u\left(w_{cal}\right)}{C_{cal}}\right)^2}$$

combined with the uncertainty of a series of independent determinations by the type B on bias method (NIST):

$$u_c = \sqrt{s_m^2 + \frac{1}{n}\sum u_i^2}$$

where: s_m is the standard deviation of a series of determinations (n=6) and u_i is the uncertainty of the individual estimates for i = [1..n].

Uncertainty budgets:

Endosulfan sulfate: uncertainty of characterisation for one individual case (u_i):

Component (units)	x_i	$u(x_i)$	$u(x_i)/x_i$ (%)
w_{cal} (µg g^{-1})	8.33043	0.23803	2.86
m_{cal} (g)	0.06227	0.00003	0.05
m_{sam} (g)	1.05084	0.00003	0.003
m_{ssam} (g)	0.04158	0.00003	0.07
m_{scal} (g)	0.04178	0.00003	0.07
R_{sam}/R_{cal}	0.97931	0.01856	1.89
d_w	0.92893	0.00040	0.04
w (µg kg^{-1})	518		
u_i (µg kg^{-1})			18

Endosulfan II: uncertainty of characterisation for one individual case (u_i):

Component (units)	x_i	$u(x_i)$	$u(x_i)/x_i$ (%)
w_{cal} (µg g^{-1})	13.07497	0.13069	0.99
m_{cal} (g)	0.05889	0.00003	0.05
m_{sam} (g)	1.05084	0.00003	0.003
m_{ssam} (g)	0.06121	0.00003	0.05
m_{scal} (g)	0.06252	0.00003	0.05
R_{sam}/R_{cal}	0.94367	0.02150	2.28
d_w	0.92893	0.00040	0.04
w (µg kg^{-1})	729		
u_i (µg kg^{-1})			18

Endosulfan sulfate and endosulfan II: mean and standard deviation (s_m) of a series of determinations:

Endosulfan sulfate	**mean (s_m):**	**517 (10) µg kg^{-1} (n=6)**
Endosulfan II	**mean (s_m):**	**741 (13) µg kg^{-1} (n=6)**

Chile – CMQ

For each sample blend (n=5) the IDMS equation was used:

$$C_X = C_Z \frac{mY\ mZ_c}{mX\ mY_c\ f_{\text{mois}}} \frac{R'_B}{R'_{Bc}}$$

CX = mass fraction of analyte in sample
CZ = mass fraction of reference analyte in reference standard solution
mY = mass of internal standard solution added to sample blend
mX = mass of sample added to sample blend
mZc = mass of reference standard solution added to calibration blend
mYc = mass of internal standard solution added to calibration blend
R′B = peak area ratio of selected ions of analyte to internal standard in sample blend solution
R′Bc= peak area ratio of selected ions of analyte to internal standard in calibration blend solution
fmoist= moisture correction factor

All the sample blends were prepared gravimetrically (mY, mX, mZc, mYc, fmois).

CZ was prepared gravimetrically from traceable standard from NMI Australia with Certificate of purity

R'B and R'Bc were obteined from replicated injections on GCMS

For each sample blend, a full uncertainty budget was calculated by applying the GUM approach to IDMS equation:

Factor	std uncertainty u	Obs
CZ	< 2.0 %	Standard prepared gravimetrically, certified purity from provider (NMI Australia) was taken into account.
mY	0,00005 g	Calibration of balance
mX	0,00005 g	
mZc	0,00005 g	
mYc	0,00005 g	
R'B	< 0.5 %	Replicated injections of sample blend
R'Bc	< 1.5%	Replicated injections of calibration blend

fmoist	0,00005 g	Calibration of balance
For the n=5 aliquots:		
s_{bb}	0.3 - 0.4 %	blend-to-blend variation (standard deviation of the mean for the n=5 aliquots of mass fractions)
u_{av}	< 1.5%	average sample blend uncertainty
Overall standard uncertainty	$u=(s^2_{bb}+u^2_{av})^{1/2}$	
Overall Expanded Uncertainty	U=k*u	k=2

China – NIM

The sample assign process was carried out by singal point method, the formula was shown as following:

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

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}: Sample Purity ,determined by GC-FID, GC/MS and karl fischer coulometry.

f_{dry}: Ratio of the sample mass before drying and after drying

β-endosulfan Parameter	Standard Uncertainty (ug/kg)	Degrees of freedom	Type
Method precision	2.7	5	A
Recovery of extraction procedure	10.2	large	B
purity of pure standard	6.8	large	A+B
Mass fraction of internal standard	1.4	large	A+B
Mass fraction of sample	1.4	large	A+B
Mass fraction calibration standard	1.0	large	A+B
Matrix effects in calibration blend	10.2		B
Combined standard uncertainty	16.3		
Coverage factor	2		
Combined expanded uncertainty	32.6		

endosulfan sulfate Parameter	Standard Uncertainty (ug/kg)	Degrees of freedom	Type
Method precision	2.9	5	A
Recovery of extraction procedure	9.1	large	B
purity of pure standard	5.5	large	A+B
Mass fraction of internal standard	0.9	large	A+B
Mass fraction of sample	0.9	large	A+B
Mass fraction calibration standard	0.7	large	A+B
Matrix effects in calibration blend	6.8	large	B
Combined standard uncertainty	13.0		
Coverage factor	2		
Combined expanded uncertainty	26.0		

Method precision:	reproducibility of sample determination
Recovery of extraction procedure:	Comparison of results from different extraction techniques and different extraction time.
purity of pure standard:	Type A uncertainty (combined uncertainty of 3 method for purity determination),type B uncertainty (FID 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 and solvent evaporation) were combined.
Mass fraction of sample:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty (linearity of weighing, certificate of calibration and influnce from loss of moisture 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) were combined.
Matrix effects in calibration blend:	Comparison of results from calibration blends prepared from solvent and tea matrix

Germany – BAM

$$w_{tea} = \frac{m_{solvent}}{m_{tea}} \times \frac{m_{13_{C\ sol\ ution}} \times c_{13_{C\ sol\ ution}}}{\left(m_{13_{C\ sol\ ution}} + m_{solvent}\right)} \times \frac{\left(\frac{Area_{12_C}}{Area_{13_C}} - a_0\right)}{a_1}$$

$$\frac{\left(\frac{Area_{12_C}}{Area_{13_C}} - a_0\right)}{a_1} = \frac{(f(x) - a_0)}{a_1} = x$$

$f(x) = a_1 x + a_0$ (calibration line)

Uncertainty estimation:
The reported results are the mean of 6 replicate measurements. It was assumed, that the major contributions to the combined uncertainty of that mean arise from the precision of the method, the purity of the calibrant and the dry mass determination.
The standard deviation of the mean of the six replicates was taken as a measure of method precision. This precision estimate covers not only the precision associated with the measurement but also the precision of weighing out the sample, spiking with the internal standard, calibration etc. as these operations were repeated during the course of the experiment. A separate estimate of their individual uncertainties is therefore not required. The purity of the neat calibrant was determined in-house by GC-FID with columns of different polarity. The standard deviation of the mean of the purity results was taken as the uncertainty estimate of the purity of the standard. The uncertainty of the dry mass was assumed to be equal to the standard deviation of the results of the dry mass determination (4 replicates). Uncertainties were propagated according to

$$U_{95\%CI} = k \cdot c \cdot \sqrt{\frac{s^2}{c^2} + \left(\frac{u(p)}{p}\right)^2 + \left(\frac{u(m_d)}{m_d}\right)^2}$$

$U_{95\%CI}$: expanded uncertainty (95% confidence interval) of the mean
k: coverage factor
c: mass fraction, mean of 6 replicates
s: standard deviation of the mean
$u(p)$: uncertainty of the purity p of the calibrant
$u(m_d)$: uncertainty of the dry mass m_d

For the calculation of the expanded uncertainty a coverage factor k=2.57 (t- factor for 5 degrees of freedom) was assumed.
Uncertainty budgets are given below.

		c [µg/kg]	*s* [µg/kg]	$c \times u(p)/p$ [µg/kg]	$c \times u(m_d)/m_d$ [µg/kg]	***u* (combined)** [µg/kg]	***k***	$U_{(95\%CI)}$ [µg/kg]
β-Endosulfan		732,5	4,3	0,6	0,5	4,4	2,57	11,3
Endosulfan-sulphate		532,6	3,1	1,3	0,3	3,4	2,57	8,7

Full uncertainty budget has not been provided.

Germany- BVL

Endosulfansulfat

contributions to measurement uncertainty:

	u		target		u(x)/X [%]	
u calibration solution:	0.257012	ng/g	14.49275	ng/g	1.773	3.144893
u sample weight:	0.02444	g	1000	mg	0.002	5.97E-06
u sample spike:	0.021048	g	14	mg	0.150	0.022603
u dry mass:	0.0027	g	0.9497	g	0.28	0.080827
reproducibility method:	16.1820	ng/g	261	ng/g	6.20	38.44

k= 2
u= 6.45665
U= 12.9133

b-Endosulfan
contributions to measurement uncertainty:

	u	target	u(x)/X	[%]
u calibration solution:	0.06968 ng/g	14.49275 ng/g	0.480793	0.231162
u sample weight:	0.02444 g	1000 mg	0.002444	5.97E-06
u sample spike:	0.021048 g	14 mg	0.150344	0.022603
u dry mass:	0.0027 g	0.9497 g	0.2843	0.080827
reproducibility method:	26.352 ng/g	432 ng/g	6.1	37.21

k= 2
u= 6.127365
U= 12.25473

Hong Kong, China –GLHK

1. Calculate the signal response ratio (*Rsp*) of *beta*-endosulfan and endosulfan sulphate for each standard as follows:

$$Rsp = \frac{A}{A_{IS}}$$

where

A = Q1 peak area of the target analyte
A_{IS} = Q1 peak area of the corresponding labelled standard

2. Calculate the amount ratio (Amt_{Ratio}) of *beta*-endosulfan and endosulfan sulphate for each standard as follows:

$$Amt_{Ratio} = \frac{Amt}{Amt_{IS}}$$

where

Amt = amount of the target analyte used in ng
Amt_{IS} = amount of the corresponding labelled standard used in ng

3. Establish a calibration bracket by plotting the response ratios (*Rsp*) versus the amount ratios (Amt_{Ratio}). Obtain the followin linear equation from the graph.

$$(Rsp) = (m)(Amt_{Ratio}) + b$$

where

Rsp = signal response ratio of the target analyte (*y*-axis)
m = slope of the linear equation
Amt_{Ratio} = amount ratio of the corresponding labelled standard (*x*-axis)
b = *y*-intercept

4. Calculate the amount of *beta*-endosulfan and endosulfan sulphate in sample (*Spl_Amt*) in ng using the following equation:

$$Spl\_Amt = \frac{\left(A_{Spl} / A_{IS}\right) - b}{m} \times Amt_{IS}$$

where

A_{Spl} = Q1 peak area of the target analyte in sample solution
A_{IS} = Q1 peak area of the corresponding labelled standard in sample solution
b = y-intercept of the linear equation as obtained in Clause 3
m = slope of the linear equation as obtained in Clause 3
Amt_{IS} = amount of labelled standard in sample in ng

5. Calculate the concentration of *beta*-endosulfan and endosulfan sulphate (C_{Sample}) in sample in ng/g as follows:

$$C_{Sample} = \frac{Spl\_Amt}{W_{Sample}}$$

where

Spl_Amt = amount of the target analyte found in sample in ng
W_{Sample} = sample used in g

6. The moisture content (%*M*) in the sample is calculated as follows:

$$\%M = \frac{W2 - W3}{W2 - W1} \times 100\%$$

where

W3 = weight of glass vial with sample after drying, in g
W2 = weight of glass vial with sample before drying, in g
W1 = weight of glass vial, in g

7. The moisture-corrected analyte content ($C_{Sample,MC}$), in ng/g or µg/kg is calculated as follows:

$$C_{Sample,MC} = C_{Sample} \div \left(1 - \frac{\%M}{100\%}\right)$$

where

C_{Sample} = concentration of *beta*-endosulfan and endosulfan sulphate in sample as obtained in Clause 5, in ng/g or µg/kg
%*M* = moisture content in sample as obtained in Clause 6

Uncertainties were estimated based on contribution from four factors: 1) purity of reference material, 2) method precision, 3) method bias, 4) uncertainty from moisture content determination. Detailed breakdowns are given as follows:

beta-Endosulfan				
Description	*Value x*		*Std. Unc.*	*Rel. Std. Unc. u(x)*
RM [u(std)]	1		0.011723	0.011723
Precision [u(pres)]	1		0.014304	0.014304
Method Bias [u(bias)]	1		0.025981	0.025981
Moisture [u(water)]	1		0.0048015	0.0048015
Combined Rel. Std. Unc.			0.032250	
Rel. Expanded Unc. (U)			**0.064501**	
		≤	**0.07**	

Endosulfan Sulphate				
Description	*Value x*		*Std. Unc.*	*Rel. Std. Unc. u(x)*
RM [u(std)]	1		0.014867	0.014867
Precision [u(pres)]	1		0.015641	0.015641
Method Bias [u(bias)]	1		0.031178	0.031178
Moisture [u(water)]	1		0.0048015	0.0048015
Combined Rel. Std. Unc.			0.038221	
Rel. Expanded Unc. (U)			**0.076441**	
		≤	**0.08**	

Japan –NMIJ

$$C = F_{\mathrm{ext}} \times \left(\frac{R_{\mathrm{sample}}}{R_{\mathrm{cal}}} - \frac{R_{\mathrm{blank}}}{R_{\mathrm{cal}}}\right) \times \frac{F_{\mathrm{cal}} \times M_{\mathrm{cal}} \times C_{\mathrm{cal}} \times M_{\mathrm{spike(sample)}}}{M_{\mathrm{sample}} \times M_{\mathrm{spike(cal)}} \times F_{\mathrm{dry}}}$$

C: a concentration of analyte in the sample (unit: μg/kg)
F_{ext}: a factor concerning extraction and cleanup step (= 1)
R_{sample}: a ratio of peak area of analyte/internal standard observed for the sample solution
R_{blank}: a ratio of peak area of analyte/internal standard observed for the blank solution
R_{cal}: a ratio of peak area of analyte/internal standard observed for the calibration solution
F_{cal}: a factor of repeatability for preparing calibration solution (= 1)
M_{cal}: a mass of the pesticide solution taken for preparation of the calibration solution (unit: g)
C_{cal}: a concentration of analyte in the calibration solution (unit: μg/kg)
$M_{spike(sample)}$: a mass of the internal standard solution added to the sample (unit: g)
M_{sample}: a mass of the sample taken for analysis (unit: g)
$M_{spike(cal)}$: a mass of the internal standard solution taken for preparation of the calibration solution (unit: g)
F_{dry}: a correction factor for the moisture content of the sample

The uncertainty budget is summarized in the following Table.

	value, x_i	uncertainty, $u(x_i)$	unit	type of uncertainty
F_{ext}: β-endosulfan	1	0.00273	-	A
F_{ext}: Endosulfan sulfate	1	0.00360	-	A
(R_{sample}/R_{cal}): β-endosulfan	0.921	0.0065	-	A
(R_{sample}/R_{cal}): Endosulfan sulfate	0.800	0.0031	-	A
(R_{blank}/R_{cal}): β-endosulfan	-	-	-	A
(R_{blank}/R_{cal}): Endosulfan sulfate	-	-	-	A
$M_{spike(sample)}$	0.33	0.00030	g	B
M_{sample}	1.0	0.00014	g	B
F_{dry}	0.9434	0.00017	-	A
F_{cal}: β-endosulfan	1	0.0127	-	A
F_{cal}: Endosulfan sulfate	1	0.0239	-	A
M_{cal}	0.1204	0.00007	g	B

C_{cal}: β-endosulfan	26368	97	μg/kg	A+B
C_{cal}: Endosulfan sulfate	21076	109	μg/kg	A+B
$M_{spike(cal)}$	1.321	0.00007	g	B
	Concentration (μg/kg)	Combined uncertainty (μg/kg)	k	Expanded uncertainty (μg/kg)
β-endosulfan	727	11	2	22
Endosulfan sulfate	505	13	2	25

(Since β-endosulfan and endosulfan sulfate were not detected in blank samples, we did not include the uncertainties related to R_{blank} in combined uncertainty.)

The uncertainty of tea sample was estimated from $u(C_{ind})$ and $u(C_{com})$.The $u(C_{ind})$ associated with each analytical method was obtained from the uncertainty of R_{sample}, R_{blank}, R_{cal}, F_{ext}, M_{sample}, and $M_{spike(sample)}$. The $u(C_{com})$ that is common to analytical methods was estimated from the uncertainty of F_{cal}, M_{cal}, C_{cal}, and $M_{spike(cal)}$. The uncertainty for each factor was evaluated as described below.

$u(F_{ext})$: based on the variability of analytical values
$u(R_{sample}/R_{cal})$: based on the variability of a ratio of GC/MS peak area of analyte/internal standard
$u(R_{blank})$: not included because target pesticides were not detected (below detection limit) in blank samples.
$u(F_{cal})$: based on the variability of preparing calibration solution
$u(M_{cal})$, $u(M_{sample})$, $u(M_{spike(cal)})$: based on the weighing uncertainty (calculated by using calibration certification of balance)
$u(C_{cal})$: combined the uncertainty for purity of neat pesticides and weighing uncertainty
$u(M_{spike(sample)})$: combined the spiking uncertainty and weighing uncertainty
$u(F_{dry})$: combined the uncertainty for moisuture content and weighing uncertainty

Korea – KRISS

$$C_{\text{sample}} = f \bullet \frac{M_{\text{is-sol,spiked}} \cdot AR_{\text{sample}} \cdot M_{\text{s-sol,std. mix.}} \cdot C_{\text{s-sol}}}{M_{\text{sample}} \cdot AR_{\text{std. mix.}} \cdot M_{\text{is-sol,std.mix.}}}$$

f is dry-mass correction factor

$C_{\text{sample:}}$ is the concentration of analytes in the sample;

$C_{\text{s-sol:}}$ is the concentration of the analytes standard solution;

$M_{\text{sample:}}$ is the mass of the sample taken for analysis;

$M_{\text{is-sol, spiked:}}$ is the mass of the isotope standard solution added to the sample aliquot;

$M_{\text{is-sol, std. mix.:}}$ is the mass of the isotope standard solution added to the isotope ratio standard solution;

$M_{\text{s-sol, std. mix.:}}$ 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;

$AR_{\text{std. mix.:}}$ is the area ratio of analyte/isotope for the isotope ratio standard solution, observed by GC/MS.

Measurement protocol: One subsample and standard solution was run by GC/MS
Combined standard uncertainties were obtained by combining systematic uncertainties and random uncertainties as shown below equation.

$$u_{total} = \sqrt{u^2_{\text{systematic}} + u^2_{\text{random}}}$$

Details for the full uncertainty budget is provided the below table.

	Sources
Systematic	Uncertainty of purity of primary reference material
	Uncertainty of gravimetric preparation for standard solutions
	Uncertainty of gravicmetric mixing for calibration isotope standard mixtures
	Uncertainty of dry mass corrections
Random	Standard deviations of multiple measurement results from five subsamplings which includes uncertainties in GC/MS measurements of standard solution and sample

Full uncertainty budget has not been provided.

Mexico – CENAM

$$w_a = \left(\frac{rA_m - b}{m} \right) \cdot w_{EI} \cdot d$$

Wa = mass fraction of measurand; rA = area ratio: measurand area/ internal standard area; b = intercept of calibration curve (y=mx+b), m = slope of calibration curve (5 independent points); d = dilution factor of sample and internal standard ratio .

Several uncertainty sources were combined: Calibration curve residual variation, dilution factor variation (including weight repeatability and balance calibration); variation IS mass fraction (weighting process variation, variation of purity measurements), repeatability of sample measurements, and variance of dry mass correction. For de combination of all sources (relative uncertainties) Law of Propagation of Uncertainty was used. The expanded uncertainty was obtained by multiplying the combined standards uncertainty by the cover factor with a 95 % level of confidence. The k factor applied is the effective degrees of freedom at n-1.

Description	Values	units	Source	Standard uncertainty	distribution type	Relative uncertainty
Calibrarion curve	2.423		Experimental	0.10188	A, normal	4.20%
dilution factor	1.052	g	Exp. and balance certificate	0.000047	A, normal	0.00%
mass fraction of sample	230.971	µg/kg	Experimental	1.356871	A, normal	0.59%
Repeatibility	*535.7*	µg/kg	Experimental	22.83	A, normal	4.26%
Dry mass correction	*93.37*	*g/100g*	Experimental	0.25	*g/100g*	0.27%

Russia – VNIIM

$W=(S_{an}*m_{IS})/(S_{IS}*m*F)$

W - mass fraction of the pesticide in the sample, mkg/kg;

m_{IS} - mass of internal standard added to sample before extraction, mkg;

m - mass of sample, kg;

F - response factor; $F=(S_{an}*C_{IS})/(S_{IS}*C_{an})$

C_{an}- concentration of pesticide in calibration solution;

C_{IS} - concentration of internal standard in calibration solution

S_{an} - peak area for the pesticide;

S_{IS} - peak area for the internal standard

Source of uncertainty	**endosulfan II**	**endosulfan sulfate**
mass of sample (m)	**0.58**	**0.58**
response factor (F)	**1.94**	**1.77**
mass fraction of unlabeled pesticides in calibration solution	0.57	0.57
mass fraction of C13 labeled pesticides in calibration solution	1.73	1.47
volume of the syringe	0.57	0.57
RSD	0.37	0.56
mass of internal standard added to sample before extraction (m_{IS})	**1.82**	**1.57**
volume of the syringe	0.57	0.57
mass fraction of C13 labled pesticides in calibration solution	1.73	1.47
RSD of results, %	**1.63**	**0.47**
comb. std uncertainty	**3.17**	2.48
expanded uncertainty (k=2)	**6.3**	**5**

Singapore – HSA

The mass fraction of endosulfan II and endosulfan sulphate was calculated based on the following exact-matching double isotope dilution measurement equation:

$$C_X = C_Z \cdot \frac{m_Y \cdot m_{Zc}}{m_X \cdot m_{Yc}} \cdot \frac{R_Y - R_B}{R_B - R_X} \cdot \frac{R_{Bc} - R_X}{R_Y - R_{Bc}} \quad \text{— (1)}$$

where

C_X = mass fraction of endosulfan II or endosulfan sulphate in the study sample (based on dry mass)

C_Z = mass fraction of endosulfan II or endosulfan sulphate in the calibration standard solution used to prepare the calibration blends

m_Y = mass of internal standard solution added to the sample blend

m_{Yc} = mass of internal standard solution added to the calibration blend

m_{Zc} = mass of endosulfan II or endosulfan sulphate calibration standard solution added to the calibration blend

m_X = dried mass of study sample in the sample blend

R_X = observed isotope abundance ratio in the study sample

R_Y = observed isotope abundance ratio in the internal standard

R_B = observed isotope abundance ratio in the sample blend

R_{Bc} = observed isotope abundance ratio in the calibration blend

A standard uncertainty was estimated for all components of the measurement equation (Equation 1), which were then combined using respective derived sensitivity coefficients to estimate a combined standard uncertainty in the reported result. The combined uncertainty was then multiplied by a coverage factor of 2 to determine the expanded uncertainty at 95 % confidence interval. Possible sources of biases are accounted for in the final uncertainty budget with the use of the following measurement equation:

$$C_X = F_P \cdot F_s \cdot F_{ip} \cdot C_Z \cdot \frac{m_Y \cdot m_{Zc}}{m_X \cdot m_{Yc}} \cdot \frac{R_Y - R_B}{R_B - R_X} \cdot \frac{R_{Bc} - R_X}{R_Y - R_{Bc}} \quad \text{— (2)}$$

where

additional factors contributing to biases in the result value of endosulfan II or endosulfan sulphate content were included by assigning a value of 1, with an associated uncertainty value to this value.

F_P = factor representing precision effects related to the sampling process of the study sample (1 bottle containing 20 g) and ratio measurements

F_S = factor representing any bias in the result value due to sample extraction parameters and technique, as well as cleanup

F_{ip} = factor representing any bias in the result value due to choice of ion pair/interference effects

Method precision (Fp):
The standard deviation of the mean of the averaged results of each subsample was used to estimate the uncertainty due to method precision. The choice of results of each subsample taken into consideration depends on the R_b/R_{bc} ratio, of which only results with ratios in the range of 0.90 to 1.1 were considered.

Sample extraction technique, parameters and sample cleanup (Fs):
Biases in three different type of sample extraction techniques (accelerated solvent extraction, sonication and shaking); biases in different parameters used in accelerated solvent extraction; and different sample clean up methods, were determined from the standard deviation of the mean of the differences in results obtained.

Comparison of IDMS results from different ion pairs (F_{ip}):
Measurements results calculated from different ion pairs showed insignificant differences (t-test at 95% confidence level). Standard deviation of the mean of differences in the results was included in the measurement uncertainty budget.

Mass fraction of calibration standard solution (C_z):
Uncertainty in the concentration of calibration standard solution was estimated by combining the standard uncertainty of the purity and weighing bias obtained from the balance calibration reports.

Comparison of results obtained from the use of matrix and non-matrix matched calibration blends , as well as preparation of different non-matrix matched calibration blends:
Insignificant differences (t-test, 95% confidence level) were found between results obtained from the use of matrix and non-matrix matched calibration blends and between results obtained using different calibration blends. Standard deviations of the mean of the differences in the results were included in the estimation of uncertainty contributed by Cz.

Blend preparation masses (m_Y, m_{Yc}, m_{Zc}):
Only weighing biases obtained from the balance calibration certificates were considered for uncertainty in the masses of internal standard solutions and calibration standard solutions added to the blends.

Dry sample mass (m_X):
Weighing biases obtained from the balance calibration report and precision from moisture determinations were considered for the combined uncertainty in the dry mass of the study sample. The final moisture content were determined from subsamples, dried over calcium sulphate in a dessication, over a period of 63 days.

Peak area ratios in the sample and calibration blends (R_B and R_{Bc}):

Precision in the measurement of peak area ratios of the analyte and internal standard in the sample and calibration blends were included in the method precision. The effect of bias on these ratios was assumed to be insignificant. This is because any systematic biases should cancel out with exact-matching of the peak areas of the reference standard to internal standard in the calibration blends, as well as matching of the ratio between the sample and calibration blends. Instrumental drifts were also corrected for by bracketing the sample blends with calibration blends.

Observed isotope abundance ratio in the study sample, R_x; internal standard, R_y and sample blend, R_z: Measured isotope abundance ratio of the internal standard, Ry was found to be negligible, but that of the study sample, Rx and sample blend, Rz were found to be sufficiently small to necessitate the use of the full exact matching IDMS equation for calculation purposes. Thus, the standard deviation in the measurements of Rx and Rz were included in the measurement uncertainty.

Please refer to Table 1 for the MU budget of endosulfan II and Table 2 for the MU budget of endosulfan sulphate in the different worksheets for details.

Table 1: Sources of uncertainty for beta-endosulfan

Parameter	x_i	$u(x_i)/xi$	Source of uncertainty data
F_P	1	0.015	Standard deviation of the mean of 11 independent determinations on the study sample
F_s	1	0.030	Uncertainty in the sample preparation, which consists of • Bias in the type of sample extraction technique (accelerated solvent extraction, sonication, shaking) • Bias in the accelerated solvent extraction parameters (temperature, static time, solvent ratio) • Bias in the sample cleanup method
F_{ip}	1	0.007	Comparison of results obtained using different ion pairs
C_Z	9933 μg/kg	0.026	• Uncertainty in the purity value of endosulfan II certified reference material • Uncertainty in weighing based on value from the balance calibration report • Comparison of results obtained from different calibration blends bracketing the same sample blend • Comparison of results obtained from matrix and non-matrix matched calibration blends bracketing the same sample blend
m_Y	0.12701 g	0.001	Uncertainty in weighing based on value from the balance calibration report
m_{Yc}	0.21841 g	0.0005	Uncertainty in weighing based on value from the balance calibration report
m_{Zc}	0.13049 g	0.001	Uncertainty in weighing based on value from the balance calibration report
m_X	0.93868 g	0.001	• Uncertainty in weighing based on value from the balance calibration report • Standard deviation of the mean of moisture content determined from 3 sub-samples
R_x *and* R_z	22	0.103	• Standard deviation of the observed isotope abundance ratio in the study sample • Standard deviation of the observed isotope abundance ratio in the calibration standard
R_y	0.0285	0.075	Standard deviation of the observed isotope abundance ratios in the internal standard
R_B			Uncertainty included in method precision
R_{Bc}			Uncertainty included in method precision

Table 2: Sources of uncertainty for endosulfan sulphate

Parameter	x_i	$u(x_i)/xi$	Source of uncertainty data
F_P	1	0.004	Standard deviation of the mean of 12 independent determinations on the study sample
F_s	1	0.025	Uncertainty in the sample preparation, which consists of • Bias in the type of sample extraction technique (accelerated solvent extraction, sonication, shaking) • Bias in the accelerated solvent extraction parameters (temperature, static time, solvent ratio) • Bias in the sample cleanup method
F_{ip}	1	0.005	Comparison of results obtained using different ion pairs
C_Z	5885 μg/kg	0.025	• Uncertainty in the purity value of endosulfan sulfate certified reference material • Uncertainty in weighing based on value from the balance calibration report • Comparison of results obtained from different calibration blends bracketing the same sample blend • Comparison of results obtained from matrix and non-matrix matched calibration blends bracketing the same sample blend
m_Y	0.12701 g	0.001	Uncertainty in weighing based on value from the balance calibration report
m_{Yc}	0.21841 g	0.0005	Uncertainty in weighing based on value from the balance calibration report
m_{Zc}	0.13049 g	0.001	Uncertainty in weighing based on value from the balance calibration report
m_X	0.93868 g	0.001	• Uncertainty in weighing based on value from the balance calibration report • Standard deviation of the mean of moisture content determined from 3 sub-samples
R_x and R_z	150	0.182	• Standard deviation of the observed isotope abundance ratio in the study sample • Standard deviation of the observed isotope abundance ratio in the calibration standard
R_y	0.0026	0.203	Standard deviation of the observed isotope abundance ratio in the internal standard
R_B			Uncertainty included in method precision
R_{Bc}			Uncertainty included in method precision

Thailand – BQSF, DMSc

$$C_X = C_Z \cdot \frac{M_Y \cdot M_{Zc}}{M_X(1-F) \cdot M_{Yc}} \cdot \frac{R_B}{R_{Bc}}$$

Mzc: Mass of standard in calibration blend, My : Mass of internal standard in sample blend,Myc : Mass of internal standard in calibration blend, Cz: Concentration of native standard added in calibration blend, Mx : Mass of isample in sample blend, F : Dry mass factor, Rb:The ration of native and isotopic ion in sample blend, Rbc:The ration of native and isotopic ion in calibration blend

Combination of Uncertainties		b-Endosulfan							
Factor		Values x	Uncertainty	Divisor	Std uncertain u(x)/divisor	Rel. uncertainty u(x)/(x)	Rel. uncerta u(x)/(x)^2	Rel. uncertainty u(x)/(x)^2 (%)	u(x)/(x)^4
Measurement equation factors									
Method Precision		778.45	52.83613	?6	2.16E+01	2.77E-02	7.68E-04	84.24%	5.90E-07
Mass of STD in calibration blend	Mzc	0.19632	0.000500	2.17	2.87E-04	1.46E-03	2.13E-06	0.23%	4.54E-12
			0.000405	?2	2.87E-04	1.46E-03	2.13E-06	0.23%	4.54E-12
Mass of ISTD in sample blend	My	0.18535	0.000500	2.17	2.24E-04	1.21E-03	1.46E-06	0.16%	2.12E-12
			0.000608	?3	3.51E-04	1.89E-03	3.58E-06	0.39%	1.28E-11
Mass of ISTD in calibration blend	Myc	0.18103	0.000500	2.17	2.24E-04	1.24E-03	1.53E-06	0.17%	2.33E-12
			0.002628	?2	1.86E-03	1.03E-02	1.05E-04	11.55%	1.11E-08
Mass of sample in sample blend	Mx	1.09091	0.000500	2.17	2.24E-04	2.05E-04	4.20E-08	0.00%	1.77E-15
			0.002651	?3	1.53E-03	1.40E-03	1.97E-06	0.22%	3.87E-12
Dry mass factor	F	0.06921	0.000545	?6	2.23E-04	3.21E-03	1.03E-05	1.13%	1.07E-10
Concentration of working	Cz	4.811	-	-	1.88E-02	3.90E-03	1.52E-05	1.67%	2.31E-10
Primary standard purity		0.9940	0.004000	2.0	2.00E-03	2.01E-03	4.05E-06		
stock solution	standard mass	0.01755	0.000059	?5	2.62E-05	3.34E-03	1.11E-05		
	solution mass	17.18343	0.000053	?5	2.39E-05	3.10E-06	9.64E-12		
Intermediated solution	standard mass	0.46583	0.000029	?5	1.28E-05	6.15E-05	3.78E-09		
	solution mass	17.10330	0.000013	?5	5.83E-06	7.62E-07	5.81E-13		
Working solution	standard mass	1.31431	0.000012	?5	5.48E-06	9.32E-06	8.68E-11		
	solution mass	7.59996	0.000000	?5	0.00E+00	0.00E+00	0.00E+00		
Balance	Certificate	50.00000	0.000500	2.17	2.30E-04	4.61E-06	2.12E-11		
Total		1.000				**3.02E-02**	**9.1E-04**	**100.0%**	**8.31E-07**
									1.29E-07
								Veff	6.44

Combination of Uncertainties		Endosulfan sulfate							
Factor		Values x	Uncertainty	Divisor	Std uncertain u(x)/divisor	Rel. uncertainty u(x)/(x)	Rel. uncerta u(x)/(x)^2	Rel. uncertainty u(x)/(x)^2 (%)	u(x)/(x)^4
Measurement equation factors									
Method Precision		573.71	74.36174	?6	3.04E+01	5.29E-02	2.80E-03	95.45%	7.85E-06
Mass of STD in calibration blend	Mzc	0.19632	0.000500	2.17	2.87E-04	1.46E-03	2.13E-06	0.07%	4.54E-12
			0.000405	?2	2.87E-04	1.46E-03	2.13E-06	0.07%	4.54E-12
	My	0.18535	0.000500	2.17	2.24E-04	1.21E-03	1.46E-06	0.05%	2.12E-12
Mass of ISTD in sample blend			0.000608	?3	3.51E-04	1.89E-03	3.58E-06	0.12%	1.28E-11
Mass of ISTD in calibration blend	Myc	0.18103	0.000500	2.17	2.24E-04	1.24E-03	1.53E-06	0.05%	2.33E-12
			0.002628	?2	1.86E-03	1.03E-02	1.05E-04	3.59%	1.11E-08
Mass of sample in sample blend	Mx	1.09091	0.000500	2.17	2.24E-04	2.05E-04	4.20E-08	0.00%	1.77E-15
			0.002651	?3	1.53E-03	1.40E-03	1.97E-06	0.07%	3.87E-12
Dry mass factor	F	0.06921	0.000545	?6	2.23E-04	3.21E-03	1.03E-05	0.35%	1.07E-10
Concentration of working STD	Cz	3.673	-	-	8.32E-03	2.27E-03	5.14E-06	0.18%	2.64E-11
Primary standard purity		0.9850	0.004000	2.0	2.00E-03	2.03E-03	4.12E-06		
stock solution	standard mass	0.01845	0.000019	?5	8.28E-06	1.00E-03	1.01E-06		
	solution mass	17.17589	0.000043	?5	1.93E-05	2.52E-06	6.33E-12		
Intermediated solution	standard mass	0.33817	0.000029	?5	1.28E-05	8.47E-05	7.17E-09		
	solution mass	17.10330	0.000013	?5	5.83E-06	7.62E-07	5.81E-13		
Working solution	standard mass	1.31431	0.000012	?5	5.48E-06	9.32E-06	8.68E-11		
	solution mass	7.59996	0.000000	?5	0.00E+00	0.00E+00	0.00E+00		
Balance	Certificate	50.00000	0.000500	2.17	2.30E-04	4.61E-06	2.12E-11		
Total		1.000				**5.42E-02**	**2.9E-03**	**1.00E+00**	**8.61E-06**
									1.58E-06
								Veff	5.45

Turkey – UME

Calibration graph was drawn as area ratio versus concentration ratio. The responce factor (RF) was calculated by proportioning area ratio (Area of Native Compound /Area of Isotopic Labelled Compound) to the concentration ratio (Concentration of Native Compound/Concentration of Isotopic Labelled Compound). The area values of native and isotopic labelled compounds were obtained as a responce from the instrument. The proper amount of isotopic labelled compounds was determined based on the concentration which is intended to be in the final amount of the sample, just prior to analysis, and added into the sample at the beginning of the method application. The concentration of native compounds in the final sample was determined by using the RF equation. The mass fraction of compounds in the sample intake was concentrated approximately for two times in the final sample, therefore the result was determined by considering this concentration step.

Uncertainty Sources

1-Native Compounds Calibration Stock Solution

		Value	Standard Uncertainty
Purity of the Compound		$P_{compound}$	$uP_{Compound}$
Mass			
	Mass of compound	$m_{Compound}$	
	Calibration		$uCm_{Compound}$
	Mass of Solvent	$m_{solvent}$	
	Calibration		$uCm_{solvent}$
	Mass of Tare	m_{tare}	
	Calibration		uCm_{tare}
	Repeatability		uRm

$$u(m_{Compound}) = \sqrt{u_{CmCompound}^{2} + u_{CmSolvent}^{2} + u_{CmTare}^{2} + (u_{Rm})^{2}}$$

Combined Standard Measurement Uncertainty

$$\frac{u_c(NS)}{c_{NS}} = \sqrt{\left(\frac{u(P_{Compound})}{P_{Compound}}\right)^2 + \left(\frac{u(m_{Compound})}{m_{Compound}}\right)^2}$$

2-Isotopic Labelled Compounds Calibration Stock Solution

	Value	Standard Uncertainty
Purity of the Compound $^{13}C_9$	$P_{Compound13C9}$	$uP_{Compound13C9}$
Mass		
Mass of Compound $^{13}C_9$	$m_{E\text{-}II13C9}$	
Calibration		uCm_{C13C9}
Mass of Solvent	$m_{solvent}$	
Calibration		$uCm_{solvent}$
Mass of Tare	m_{tare}	
Calibration		uCm_{tare}
Repeatability		uRm

$$u\left(m_{Compound\,13C9}\right)=\sqrt{u_{CmCompound\,13C9}{}^{2}+u_{CmSolvent}{}^{2}+u_{CmTare}{}^{2}+\left(u_{Rm}\right)^{2}}$$

Combined Standard Measurement Uncertainty

$$\frac{u_c(ILS)}{c_{ILS}}=\sqrt{\left(\frac{u(P_{Compound\,13C9})}{P_{Compound\,13C9}}\right)^2+\left(\frac{u(m_{Compound\,13C9})}{m_{Compound\,13C9}}\right)^2}$$

3-Mass of Sample Intake

	Value	Standard Uncertainty
Mass of green tea sample	$m_{green\ tea}$	
Calibration		$uCm_{greentea}$
Mass of Tare	m_{tare}	
Calibration		uCm_{tare}
Repeatability		uRm

$$u\left(m_{SI}\right)=\sqrt{u_{Rm}{}^{2}+\left(u_{Cmgreentea}\right)^{2}+\left(u_{Cmtare}\right)^{2}}$$

4-Spiked Volume of Isotopic Labelled Compounds Stock Solution

	Value	Standard Uncertainty
Spiked volume of isotopic labelled compounds stock solution	V_{SIL}	uV_{SIL}
Repeatability		u_{RV}
Calibration		u_{CV}
Temperature		u_{TV}

$$u(V_{SIL}) = \sqrt{u_{RV}^{\,2} + u_{CV}^{\,2} + u_{TV}^{\,2}}$$

5-Mass of Final Sample

	Value	Standard Uncertainty
Mass of final sample	$m_{final\ sample}$	
Calibration		$uCm_{finalsample}$
Mass of Tare	m_{tare}	
Calibration		uCm_{tare}
Repeatability		uRm

$$u(m_S) = \sqrt{u_{Rm}^{\,2} + (u_{Cmfinalsample})^2 + (u_{Cmtare})^2}$$

6-Calibration Graph

$$u(c_0) = \frac{S}{B_1}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{S_{xx}}} \qquad Sxx = \sum_{i=1}^{n}(c_i - \bar{c})^2$$

S Residual standard deviation

B1 Slope

p number of measurement to determine c_0

n	number of measurement for the calibration
c_0	determined concentration
$\boxed{\bar{c}}$	mean value of the different calibration standards (n number of measurement)
i	index for the number of calibration standards

COMBINED STANDARD MEASUREMENT UNCERTAINTY

$$\frac{u_c(Greentea)}{c_{greantea}} = \sqrt{\left(\frac{u_c(NS)}{c_{NS}}\right)^2 + \left(\frac{u_c(ILS)}{c_{ILS}}\right)^2 + \left(\frac{u(m_{SI})}{m_{SI}}\right)^2 + \left(\frac{u(V_{SIL})}{V_{SIL}}\right)^2 + \left(\frac{u(m_{FS})}{m_{FS}}\right)^2 + \left(\frac{u(CG)}{CG}\right)^2}$$

Uncertainty Budget of β-Endosulfan

Parameters	Value (X)	u(x)	u(x)/X
Native Stock Solution (µg/kg)	2603	12.412	0.00477
Labelled Stock Solution (µg/kg)	5459	70.969	0.01300
Mass of sample intake (mg)	1000	0.0026	2.616E-06
Spiked volume of ILS (µL)	100	0.0960	0.0009603
Mass of final sample (mg)	500	0.0014	2.83793E-06
Calibration Graph (µg/kg)	500	0.0179	3.58657E-05
Relative Standard Measurement Uncertainty			0.014
Result (µg/kg)	540		
Combined Standard Measurement Uncertainty		7.50	
Expanded Uncertainty (k=2)		15.0	

Uncertainty Budget of Endosulfan Sulfate

Parameters	Value (X)	u(x)	u(x)/X
Native Stock Solution (µg/kg)	2179	6.7270	0.00309
Labelled Stock Solution (µg/kg)	5864	70.373	0.01200
Mass of sample intake (mg)	1000	0.0026	2.616E-06
Spiked volume of ILS (µL)	100	0.0960	0.000960312
Mass of final sample (mg)	500	0.0014	2.83793E-06

Calibration Graph (µg/kg)	500	0.0024	4.81619E-06
Relative Standard Measurement Uncertainty			0.012
Result (µg/kg)	555		
Combined Standard Measurement Uncertainty		6.90	
Expanded Uncertainty (k=2)		13.8	

United Kingdom – LGC

The amount of beta endosulfan (bES) and endosulfan sulfate (ESS) in each of three sample aliquots was calculated using the double IDMS equation:

$$W_{x_i} = W_z \cdot \frac{m_z}{m_{yc}} \cdot \frac{m_y}{m_x} \cdot \frac{R'_B}{R'_{BC}}$$

Where:

W_{xi} = the mass fraction of bES (or ESS) in sample replicate i

W_z = the mass fraction of the natural bES (or ESS) used to prepare the calibration blend – calculated from certificate of analysis of the solid standards and weights from the gravimetric preparation of diluted solvent standard

m_z = mass of the natural bES (or ESS) solution added to the calibration blend – determined by weighing on analytical balance.

m_x = mass of the sample used – determined by weighing on analytical balance.

m_{yc} = mass of the labelled bES (or ESS) solution added to the calibration blend – determined by weighing on analytical balance.

m_y = mass of the labelled bES (or ESS) solution added to the sample blend – determined by weighing on analytical balance.

R'_B = measured ratio of the sample blend – from GC-MS.*

R'_{BC} = average measured ratio of the calibration blend injected before and after the sample – from GC-MS.*

* The measured ratios were as follows:

bES = peak area bES/peak area $^{13}C_9$-bES (m/z 408/417)

ESS = peak area ESS/peak area $^{13}C_9$-ESS (m/z 386/395)

The amount of beta endosulfan (bES) and endosulfan sulfate (ESS) in the sample was calculated by averaging the mass fraction in the three replicates and converting the average to dry mass basis:

$$W_x = \frac{\overline{W}_{x_i}}{dm}$$

Where:

W_x = the mass fraction of bES (or ESS) in the sample

$\overline{W}_{xi}$ = the average mass fraction of bES (or ESS) from the i sample replicates

dm = average dry mass, determined by drying 3 portions of tea sample over calcium sulfate

The uncertainty of each individual measurement was calculated using the following equation:

$$u_{ci} = w_x \sqrt{\left(\frac{u_{Wz}}{w_z}\right)^2 + \left(\frac{u_{p\,R'_B}}{p_{R'_B}}\right)^2 + \left(\frac{u_{p\,R'_{BC}}}{p_{R'_{BC}}}\right)^2 + \left(\frac{um_x}{m_x}\right)^2 + \left(\frac{um_y}{m_y}\right)^2 + \left(\frac{um_z}{m_z}\right)^2 + \left(\frac{um_{yc}}{m_{yc}}\right)^2}$$

Where

u_{Wz} = the standard uncertainty associated with the mass fraction of the calibration solution.

w_z = the mass fraction of the calibration solution.

um_x = the uncertainty associated with the mass of sample used.

m_x = the mass of sample used.

um_y = the uncertainty associated with the mass of labelled bES (or ESS) solution added to the sample blend.

m_y = the mass of labelled bES (or ESS) solution added to the sample blend.

um_z = the uncertainty associated with the mass of bES (or ESS) solution added to the calibration blend.

m_z = the mass of bES (or ESS) solution added to the calibration blend.

um_{yc} = the uncertainty associated with the mass of labelled bES (or ESS) solution added to the calibration blend.

m_{yc} = the mass of labelled bES (or ESS) solution added to the calibration blend.

$u_{PR'B}$ = the standard deviation of ratio R'_B (n=5)

$p_{R'B}$ = the mean of R'_B(n=5)

$u_{PR'BC}$ = the standard deviation of ratio R'_{Bc} (n=5)

$p_{R'BC}$ = the mean of R'_{Bc} (n=5)

The combined final uncertainty for bES was calculated using:

$$u_{bES} = \sqrt{b_{\mathrm{var}}^{\,2} + \bar{u}_{ci}^{\,2} + u_{dm}^{\,2} + u_{blk}^{\,2} + u_{bES\,in\,ESS}^{\,2}}$$

Where

b_{var} = the standard deviation of mass fractions of replicate sample extracts

$\bar{u}_{ci}$ = average of the individual sample uncertainties u_{ci}

u_{dm} = uncertainty of the determination of dry mass

u_{blk} = uncertainty of contribution from tea used for the preparation of calibration blends

$u_{bES\,in\,ESS}$ = uncertainty due to contribution of bES in ESS standard

The combined final uncertainty for ESS was calculated using:

$$u_{ESS} = \sqrt{b_{\mathrm{var}}^{\,2} + \bar{u}_{ci}^{\,2} + u_{dm}^{\,2} + u_{blk}^{\,2}}$$

The final uncertainty for bES and ESS was expanded using a factor of k=2 (95 % confidence).

$$U = 2u$$

Uncertainty budget for bES

Factor		value	standard uncertainty	
mass fraction in solvent standard	w_z	922 ng/g	3.80	gravimetric preparation of spiking standard
mass of sample	m_x	0.9997 g	0.000142	balance standard uncertainty from balance cailbration
mass of the labelled bES (or ESS) solution added to the sample blend	m_y	0.6829 g	0.000142	balance standard uncertainty from balance cailbration
mass of the natural bES (or ESS) solution added to the calibration blend	m_z	0.6839 g	0.000142	balance standard uncertainty from balance cailbration
mass of the labelled bES (or ESS) solution added to the calibration blend	m_{yc}	0.6839 g	0.000142	balance standard uncertainty from balance cailbration
measured peak area ratio bES/13CbES in the sample blend	R'_B	1.023	0.000988	standard deviation of 5 replicate injections
average measured peak area ratio bES/13CbES of the calibration blend injected before and after the sample	R'_{BC}	1.005	0.002490	standard deviation of 5 replicate injections
mass fraction of sample aliquot	w_{xi}	641 ng/g	3.15	$u_c = w_x\sqrt{\left(\frac{u_{Wz}}{w_z}\right)^2+\left(\frac{u_{pR'B}}{p_{R'B}}\right)^2+\left(\frac{u_{pR'BC}}{p_{R'BC}}\right)^2+\left(\frac{um_x}{m_x}\right)^2+\left(\frac{um_y}{m_y}\right)^2+\left(\frac{um_z}{m_z}\right)^2+\left(\frac{um_{yc}}{m_{yc}}\right)^2}$

correction for dry mass

$$W_x = \frac{\overline{W_{xi}}}{dm}$$

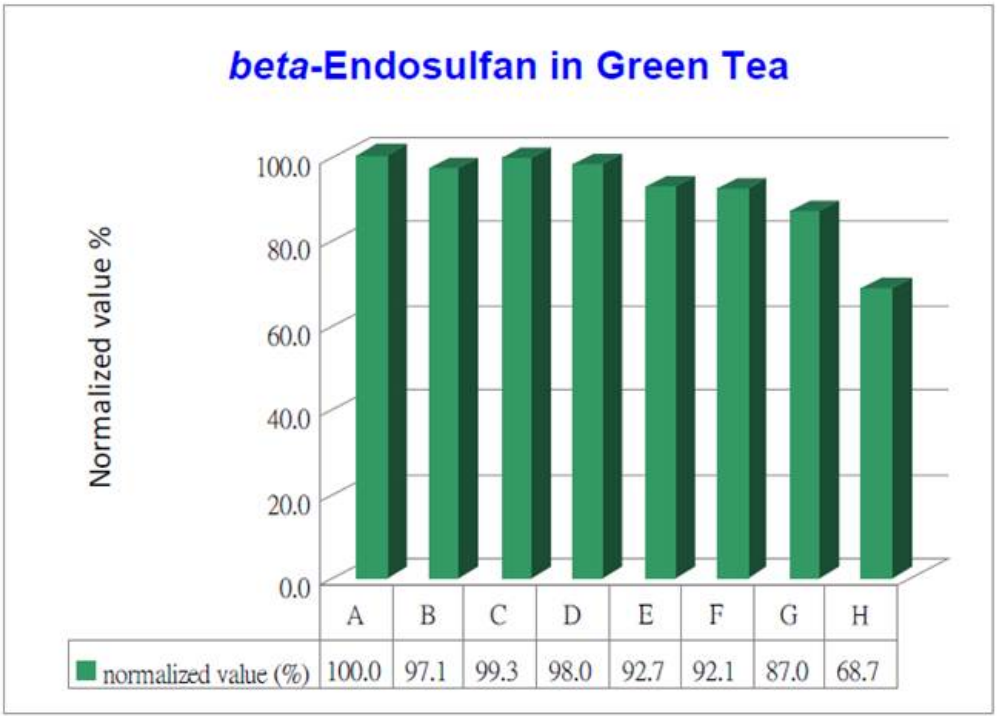
			relative standard uncertainty	
mass fraction, dry mass basis	W_x	687 ng/g		$u_{bES}=\sqrt{b_{\mathrm{var}}^2+\bar{u}_i^2+u_{dm}^2+u_{blk}^2+u_{bESinESS}^2}$
average mass fraction of sample aliquots	$\overline{W_{xi}}$	640 ng/g		sqrt(av(u)^2+bvar^2)
dry mass	dm	0.9319	0.0006	0.0006 standard deviation of 3 replicates
bvar			6.57	0.0103 standard deviation of 3 replicates
average uncertainty of x_i			3.29	0.0051 average of u_i
uncertainty due to contribution in blank tea used to prepare calibration blends	blk		0.89	0.0014 measured by IDMS
uncertainty due to bES in ESS standard	bES in ESS		0.006	0.006 peak area ratio
combined uncertainty	u		9	square root of the sum of squares of the individual uncertainties * w_x
expanded uncertainty, k=2	U		18	2*u

United States – NIST

For calibration solutions - RF =((ng pesticide)/(ng labeled pesticide))*((area labeled pesticide)/(area pesticide)) ; for tea samples ng/g pesticide =(RF*ng/g labeled pesticide*area pesticide)/area labeled pesticide

Table 3 Uncertainty calculations for CCQM-95 Mid Polarity Pesticides in Tea (ng/g dry mass)						
CCQM-K95	endosulfan II	endosulfan sulfate		d.f.		
Measured Value (mean)	568.67	354.97				
Uncertainty Components						
Measurement of Samples	5.97	2.06		5	sd of the conc divided by sqrt of 6	
Measurement of Calib Stds	0.06	0.02		5	=measured value*sqrt[(sd of RF squared/6)]/100.	
drying factor	0.05	0.03		3	=measured value*sqrt[(sd of DF squared/4)]/100.	
Certified Conc of Calib Soln	6.67	5.28		inf	"=rel std unc of calibration solution* measured value	
Combined Standard Unc.	8.95	5.67			=sqrt (sum of squares of above 4)	
k	2	2				
Expanded Uncertainty	17.90	11.33			"=k * comb std unc"	
Expanded Unc as %	3.15%	3.19%				
Information on Calibration Solution						
Certified Concentration (ng/g)	2943	2926				
Standard Uncertainty	34.5	43.5			1/2 of the 95% conf interval	
Rel Std Unc (as %)	1.17%	1.49%				

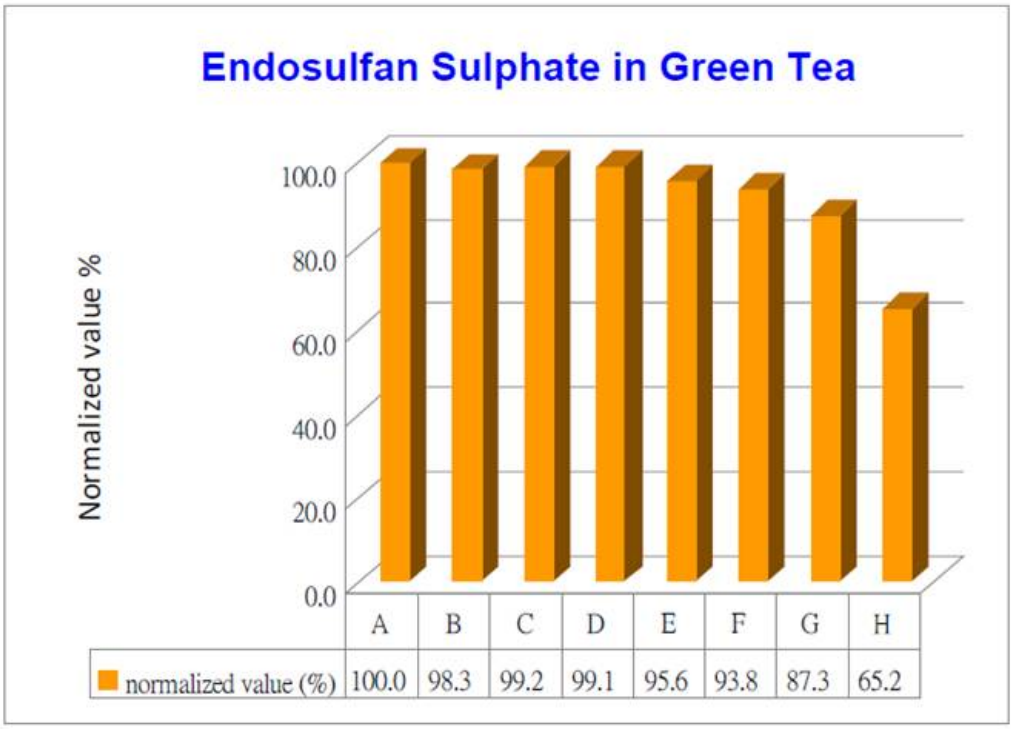
Appendix III Summary of Extraction Efficiency Studies



Entry	Extraction Condition
A	Wet / ethyl acetate / Soxhlet
B	Wet-2days / ethyl acetate / Soxhlet
C	Wet-0.5 g / ethyl acetate / Soxhlet
D	Wet / acetone-hexane/ Soxhlet
E	Wet / ethyl acetate / sonication + shaking
F	Dry / acetone-hexane/ Soxhlet
G	Dry / ethyl acetate / Soxhlet
H	Dry / ethyl acetate / sonication + shaking

Remark: GLHK's unpublished data, for internal reference only.

Figure AIII-1 Extraction efficiency results for beta-endosulfan in green tea



Entry	Extraction Condition
A	Wet / ethyl acetate / Soxhlet
B	Wet-2days / ethyl acetate / Soxhlet
C	Wet-0.5 g / ethyl acetate / Soxhlet
D	Wet / acetone-hexane/ Soxhlet
E	Wet / ethyl acetate / sonication + shaking
F	Dry / acetone-hexane/ Soxhlet
G	Dry / ethyl acetate / Soxhlet
H	Dry / ethyl acetate / sonication + shaking

Remark: GLHK's unpublished data, for internal reference only.

Figure AIII-2 ***Extraction efficiency results for endosulfan sulphate in green tea***

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

CCQM-K95	*NMI*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity pK_{ow} < -2 in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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, eg 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.

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

CCQM-K95	*BAM*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Dr. Ehrenstorfer GmbH.*
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 by columns with different polarity.*
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 spec ion ratios.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/solid, ultrasonic.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*QuEChERS*
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	✓	*IDMS with, 9-point calibration curve*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*BVL*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from NMIA*
Identity verification of analyte(s) in calibration material.[#]	✓	*GC-MS*
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 spec ion ratios.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/solid*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*GPC, mixed cartridges.*
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	✓	*Internal standard with 5-point calibration curve.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*CENAM*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from commercial sources*
Identity verification of analyte(s) in calibration material.#	✓	*GC-MS*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass balance (GC-FID, Karl-Fisher coulometry)*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid, Soxhlet.*
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-µECD*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*Internal standard with 5-point calibration curve*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*By Standard Addition.*
Other	N/A	

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.

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

CCQM-K95	*CMQ*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials form NMIA*
Identity verification of analyte(s) in calibration material.[#]	✓	*GC-MS*
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 spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*ASE*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*IDMS with single-point calibration.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*BQSF, DMSc.*	**Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea**
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from NIMT and NMIA*
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 spec ion ratios.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*LC fractionation*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	*GC-µECD , GC-MS*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*IDMS with single-point calibration (EI mode)*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*IDMS using CI mode*
Other	N/A	

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.

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

CCQM-K95	*GLHK*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Calibration solution from NIST.*
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 spec ion ratios, HRMS accurate mass measurement.*
Extraction of analyte(s) of interest from matrix	✓	*Soxhlet*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE, LC fractionation*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	*GC-MS, GC-HRMS*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*IDMS with 7-point calibration curve and IDMS with bracketing.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*HSA*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from NMIA*
Identity verification of analyte(s) in calibration material.[#]	✓	*GC-HRMS*
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, HRMS accurate mass measurement.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid, ASE.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*IDMS with single-point calibration*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*INMETRO*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Dr. Ehrenstorfer and Fluka.*
Identity verification of analyte(s) in calibration material.[#]	✓	*GC-MS, GC-MS/MS*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).[#]	✓	*qNMR cross-checked by mass balance (GC-FID)*
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 spec ion ratios.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*IDMS and internal standard, with 6-point calibration curve*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*INTI*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*a) Pure materials from* Dr. Ehrenstorfer GmbH *b) Calibration solutions from NIST*
Identity verification of analyte(s) in calibration material.[#]	✓	*CG-MSD and CG- µECD*
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).[#]	✓	*Calibration against external standards*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time, mass spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*LC fractionation*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	*GC-MS, GC-µECD*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*External standards with single point calibration and calibration curve verification.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*GC-µECD*
Other	N/A	

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.

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

CCQM-K95	*KRISS*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Dr. Ehrenstorfer*
Identity verification of analyte(s) in calibration material.#	✓	*GC/MS*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass Balance(GC/FID, TGA, Karl-Fisher titmetry)*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time, HRMS accurate mass measurement.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid extraction*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*IDMS with single-point calibration*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*LGC*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from NMIA*
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 spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*Soxhlet, ASE.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*IDMS with bracketing*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*NIM*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Dr. Ehrenstorfer GmbH*
Identity verification of analyte(s) in calibration material.#	✓	*Mass spectrometry*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass balance (GC-FID, GC-MS, Karl-Fischer coulometry)*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time, HRMS accurate mass measurement.*
Extraction of analyte(s) of interest from matrix	✓	*Soxhlet*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE, GPC.*
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	✓	*IDMS with single-point calibration*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*NIST*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Calibration solutions from NIST.*
Identity verification of analyte(s) in calibration material.[#]	✓	*DSC, GC and EI-MS*
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).[#]	✓	*GC-FID against external standard*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time, mass spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*Sonication, Soxhlet, ASE.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*Internal standard with bracketing*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*NMIA*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from NMIA.*
Identity verification of analyte(s) in calibration material.#	✓	*1H NMR, 13C NMR, GC-MS, HS-GC-MS, IR, microanalysis*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass balance (GC-FID, HPLC, thermogravimetric analysis, Karl Fischer analysis), qNMR.*
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 spec ion ratios.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/liquid, ASE.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*QuEChERS - Dispersive clean- up with primary secondary amine (PSA) resin and carbon (GCB) sorbents*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	*GC-MS, GC-MS/MS.*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*IDMS with bracketing and single-point calibration*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*Comparison of results using independent extraction (liquid/liquid and ASE) and detection (GCMSMS, GCMS/NCI) techniques*
Other	N/A	

Instructions:

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- 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.

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

CCQM-K95	*NMIJ*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Wako.*
Identity verification of analyte(s) in calibration material.#	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass balance (GC-FID, HPLC-UV and Karl-Fischer Coulometry)*
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 spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/solid*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*SPE*
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	✓	*IDMS with single-point calibration*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*NRC*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Sigma-Aldrich*
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).#	✓	*qNMR*
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 spec ion ratios.*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/solid, sonication.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*QuEChERS*
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	✓	*IDMS with matching*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*UME*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Pure materials from Fluka-Sigma and Aldrich.*
Identity verification of analyte(s) in calibration material.#	✓	*q-NMR, GC-ECD*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass balance (GC-ECD, TGA, Karl Fisher, Headspace-GC-MS), qNMR*
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 spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*ASE*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*LC fractionation*
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 with 6-point calibration curve*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.

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

CCQM-K95	*VNIIM*	Mid-Polarity Analytes in Food Matrix: Mid-Polarity Pesticides in Tea
Scope of Measurement: Mass fraction in the range from 100 to 1000 µg/kg of analytes with the molecular weight range 100–500 and having polarity $pK_{ow} < -2$ in low fat, low protein plant matrices.		
Competency	**Tick, cross, 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?		*Calibration solutions from Cambridge Isotope Laboratories*
Identity verification of analyte(s) in calibration material.[#]	✓	*GC-MS*
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).[#]	✓	*Calibration against external standards*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time, mass spec ion ratios*
Extraction of analyte(s) of interest from matrix	✓	*Liquid/Solid sonication.*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*LC fractionation.*
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	✓	*IDMS with single-point calibration.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

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.