CCQM-K78.b

Non-polar analytes in organic solvent:

Methoxychlor and Trifluralin in Acetonitrile

OAWG Track A Comparison

Final Report

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SUMMARY

The CCQM-K78.b comparison was coordinated by the BIPM on behalf of the CCQM Organic Analysis Working Group (OAWG) for NMIs and DIs which provide measurement services in organic analysis under the CIPM MRA. The key comparison forms part of the current OAWG 10-year strategic plan of comparisons. CCQM-K78.b underpins capabilities for value assignment of calibration solutions consisting of low polarity/non-polar organic analytes in organic solvent. The model system selected was a two component pesticide solution in acetonitrile.

Participants were required to assign the mass fractions, expressed in units of μg/g, of methoxychlor (M) and trifluralin (T) in solution in acetonitrile (ACN). The content and analytical challenges of the selected analytes are representative of those for calibration solutions for non-polar organic analytes in solution.

Participation in CCQM-K78.b benchmarked capability for assigning the content of non-polar organic compounds ($pK_{ow} < -2$) in solution at a mass fraction range above 5 μg/g in an organic solvent. It also tested capabilities for the quantitative assignment of thermally labile compounds.

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ACRONYMS

ACN	Acetonitrile
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CIPM	International Committee of Weights and Measures
CMC:	Calibration and Measurement Capability (of an NMI/DI)
CRM	Certified Reference Material
DI	Designated Institute
GC-ECD	Gas Chromatography – Electron Capture Detection
GC-FID	Gas Chromatography – Flame Ionization Detection
GC-MS	Gas Chromatography – Mass Spectrometry

GC-MS/MS	Gas Chromatography – Mass Spectrometry/Mass Spectrometry
KCRU	Key Comparison Reference Value Uncertainty
KCRV	Key Comparison Reference Value
LC-UV	Liquid Chromatography – UV Spectroscopy
M	Methoxychlor
MRA	Mutual Recognition Arrangement (of the CIPM)
NMI	National Metrology Institute
OAWG	Organic Analysis Working Group of the CCQM
PAH	Polycyclic Aromatic Hydrocarbon
PRM	Primary Reference Material
T	Trifluralin

SYMBOLS

d_i	degree of equivalence: x_i - KCRV
$\%d_i$	percent relative degree of equivalence: $100 \cdot d_i/\text{KCRV}$
k	coverage factor: $U(x) = k \cdot u(x)$
n	number of quantity values in a series of quantity values
$u(x_i)$	standard uncertainty of quantity value x_i
$U(x_i)$	expanded uncertainty of quantity value x_i
$U_{95}(x_i)$	expanded uncertainty defined such that $x_i \pm U_{95}(x_i)$ is asserted to include the true value of the quantity with an approximate 95 % level of confidence
x	a quantity value
x_i	the i^{th} member of a series of quantity values
$\bar{x}$	mean of a series of quantity values: $\bar{x} = \sum_{i=1}^{n} x_i/n$

INTRODUCTION

The CCQM-K78.b key comparison was coordinated by the BIPM on behalf of the CCQM Organic Analysis Working Group (OAWG) for National Measurement Institutes (NMIs) and Designated Institutes (DIs) which provide measurement services in organic analysis under the CIPM MRA. Gravimetrically-prepared solutions having an assigned mass fraction of specified organic analytes are routinely used to calibrate measurements for the quantification of these analytes in matrix samples.

The ability to undertake assignments of the property value and associated uncertainty of the content of calibration solutions is critical for the provision of SI-traceable measurements and is thus a core competency for producers of reference materials as standard solutions and for providers of calibration and reference measurement services in organic analysis. Evidence of successful participation in formal, relevant international comparisons is needed to support calibration and measurement capability (CMC) claims for services in analytical organic chemistry made by national metrology institutes (NMIs) and designated institutes (DIs).

The OAWG Strategy for 2021-2030 the OAWG requires a comparison on the value assignment of non-polar organic compounds in an organic solvent. The aim of the CCQM-K78.b comparison is to permit NMIs or DIs to benchmark their procedures to assign the mass fraction content of single or multi-component non-polar organic analytes in organic standard solutions. All NMIs with ongoing programs in this area were encouraged to participate in the comparison and are required to do so if they wish to submit CMC claims for this class of measurement service. It allows NMIs and DIs to provide objective evidence that the procedures they use for the property value assignment of calibration solutions are suitable for their intended purpose. The subsequent application of primary calibrator standard solutions can be through their provision to external users as a Certified Reference Material (CRM) or internal use by the NMI to underpin the calibration hierarchy of a Reference Measurement Procedure.

Summary of Previous Studies

CCQM-P31a “Polycyclic Aromatic Hydrocarbons in Solution” conducted in 2004 investigated the mass fraction assignment of the components of a standard solution in toluene containing 35 polycyclic aromatic hydrocarbons (PAHs). This was followed in 2005 with key comparison CCQM-K38 “PAHs in Solution (Toluene)”, using a standard solution containing 10 PAHs. CCQM-K131 “PAHs in Acetonitrile”, was undertaken in 2015 to renew Key Comparison support for CMCs for the assignment of non-polar compounds in organic solution.

Key comparison CCQM-K78.a in 2017 required the mass fraction assignment of a multi-component amino acid system in aqueous solution and was a complementary study to benchmark capabilities for the value assignment of polar analytes in solution in an aqueous solvent.

TIMELINE

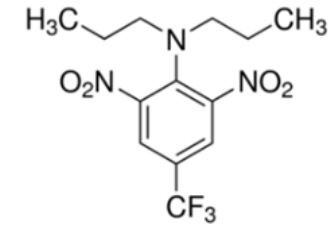
Date	Action
October 2018	Proposal to OAWG
April 2019	OAWG authorized CCQM-K78.b as a Track A Comparison
October 2021	Protocol approved by OAWG
February 2022	Call for participation to OAWG members
March 2022	Study samples shipped to participants
August 2022	Final deadline (after extensions) for result submission
February 2023	Result summary distributed to participants
March 2023	First participant result discussion (online)
April 2023	Comparison result summary presented to OAWG
May 2023	Second participant result discussion (online)
October 2023	KCRV proposal and survey form circulated to participants
January 2024	Comparison KCRV discussion presented to OAWG
April 2024	1st Draft B report circulated to OAWG

Table 1. Comparison timeline

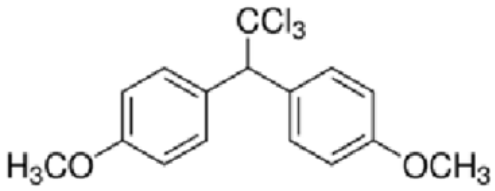
MEASURANDS

At the OAWG meeting at Chengdu in October 2018 the proposal for a comparison of the assignment of a standard solution containing methoxychlor (M) and trifluralin (T) in acetonitrile (ACN), to be coordinated by the BIPM, was accepted. The structures of methoxychlor and trifluralin are given in Figure 1.

The target levels of each analyte were to be in the range 5 to 10 µg/g, a level considered representative of the mass fraction content of non-polar organic analytes in a multicomponent solution in organic solvent intended for use as a primary calibrator for measurement procedures for the quantification of trace levels of organic analytes in matrix samples. A number of NMIs have CMC claims for the preparation of standard solutions at these levels.



Trifluralin (Herbicide)



Methoxychlor (OC Pesticide)

Figure 1 Structure of the analytes in CCQM-K78.b comparison

STUDY MATERIALS

The Primary Reference Materials (PRMs) used by the BIPM in the gravimetric preparation of the comparison solution were obtained from NMIA. Each material was a CRM produced under NMIA's ISO 17034 accreditation. Copies of the analysis certificate of each material are reproduced in Appendix A. The NMIA certified mass fraction content of each material was checked at the BIPM by qNMR measurements. The values used for subsequent gravimetric calculations were those provided by the NMIA in the material certification reports.

Gravimetric preparation of comparison stock solution

Samples of NMIA CRM P1305 (T, 8.848 mg) and NMIA CRM P1408 (M, 16.303 mg) were separately weighed using a Mettler XP2U balance reading to 0.1 µg. The masses of T and M used for gravimetric calculations were the product of the sample masses after applying a buoyancy correction for the mass of displaced air and the certified mass fraction content of each analyte in the solid powder.

Each solid sample was transferred quantitatively into a common 5 L capacity Erlenmeyer flask and taken up in 2 L of HPLC-grade ACN. The flask used to prepare the bulk solution had been acid-rinsed and dried immediately prior to use. The environmental temperature, pressure and relative humidity at the time of all weighing operations were noted. The final mass of the tared flask containing the solution, corresponding to the net mass of the bulk solution, was determined using a Mettler XP1002 laboratory balance. The net mass of the bulk candidate solution used for gravimetric calculations was corrected for the mass of air displaced by the solution.

Ampouling of comparison stock solution

Aliquots of the bulk stock solution (minimum volume 4 mL) were transferred into 10 mL ampoules and flame sealed under nitrogen. The integrity of each sealed ampoule was tested under vacuum. After removal of ampoules which failed the vacuum integrity test a batch of 273 ampoules, each containing a minimum of 4 mL of the bulk solution, remained. These were stored in the dark at 4 °C.

The content of each component with its associated uncertainty in the solution calculated from the certified mass fraction content of the source materials and the gravimetric operations used in the preparation of the solution are given in Table 2.

Component	Mass fraction (w, µg/g)	(u(w), µg/g)
Trifluralin	5.74	0.01
Methoxychlor	10.59	0.03

Table 2: Gravimetric mass fraction content of analytes in CCQM-K78.b solution

The uncertainty in each assigned gravimetric value is dominated by the uncertainty in the purity assignment of the NMIA CRM used as source material.

Homogeneity Assessment of the Study Material

Exploratory studies of GC-MS and GC-FID methods using difluorobenzene as an internal standard to quantify the T and M content of the solution were unable to achieve a satisfactory degree of precision. It was noted that measurement of the T/M ratio by GC-FID of a given sample was highly repeatable and an approach for homogeneity and stability testing of the material was adapted to use this parameter. The advantage of this approach is that losses of solvent due to evaporation from a sample in the course of the long injection sequence used for a homogeneity study should not impact the observed T/M ratio. Details of the GC method used to analyze sample are provided in Table 3.

Item	Description		
Column:	Phenomenex ZB-5 W, 5%Phenyl-95%Dimethylpolysiloxane, 30 m x 0.25 mm x 0.25 µm / OGGC.008		
Injector temperature:	250 °C		
Injection mode and volume:	Splitless – 1 µL		
Detector temperature:	FID – 250 °C		
Carier gas:	Helium 5.5		
	Rate (°C/min)	Value (°C)	Hold time (min)
		100	1
Temperature ramp:	25	250	0
	35	290	0
	35	300	4
			12.4 min (total)
Flow rate:	15.7 mL/min		

Table 3. GC-FID method for determination of T/M ratio

The homogeneity of the T/M ratio within the batch was tested using results obtained for individual sample by this method. The uncertainty contribution due to inhomogeneity of the sample values was evaluated by ANOVA. Ten units (ampoules 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 from the production batch filling sequence) were selected. Three replicate samples were prepared from each vial and these were analyzed in a randomized sequence to ensure trends in the bottling process were separated from trends from drift in the sample composition or detector response in the course of the analytical sequence.

Figure 2 is the normalized plot of the T/M ratio observed for each replicate (30 in total) plotted in the sample injection sequence.

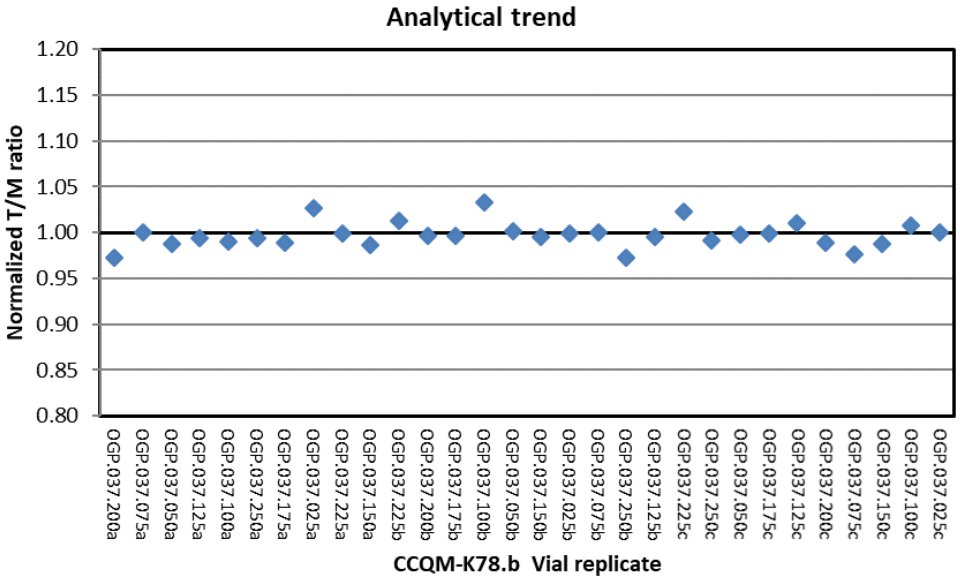


Figure 2: Normalized T/M ratio by sample in injection sequence

Figure 3 is a normalized plot of the mean value of the T/M ratio for the three replicates prepared from each ampoule tested in the sequence the individual units were ampouled.

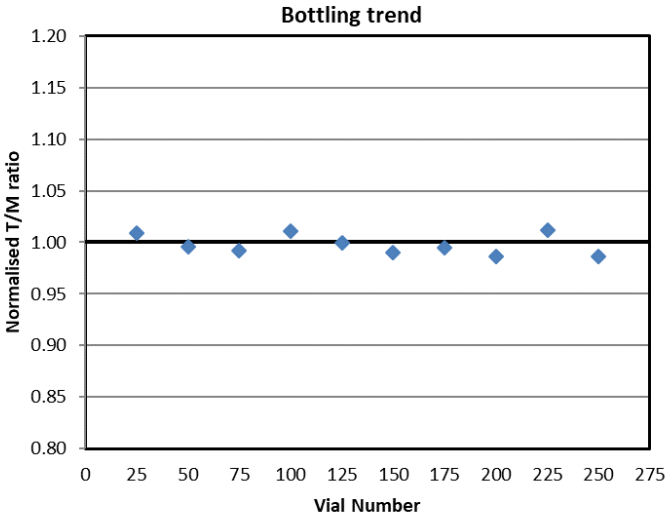


Figure 3: Mean T/M ratio by ampoule in bottling sequence

The results obtained indicated no statistically significant difference in the within- and between- vial levels of the analyte ratio of each component in the material. The upper limit for the uncertainty contribution due to inhomogeneity in all cases was considered sufficiently small to be unlikely to prevent the effective comparison of participant results.

Subsequent to the discussion of the participant results, further investigation of the sample homogeneity was undertaken using an additional set of vials to measure the absolute values for T and M content rather than content ratio of each analyte. The results of these supplementary studies are reported in the Discussion section of this report

Stability Assessment of the Study Material

An isochronous accelerated stability study of the analyte content was performed using as a reference storage in the dark at 4 °C and test storage temperatures of 22 °C (dark), 22 °C (ambient light) and 40 °C (dark). Assigned sample units were transferred from the study temperatures to the reference storage every two weeks over an eight week period. Units for testing were selected using a stratified sampling scheme from each quartile of the 278 units of candidate material. The study required two units stored throughout at the reference temperature to establish the reference stability values and twelve additional units for each of the study conditions.

The GC-FID method described in Table 3 was used to determine the T/M ratio in a sample.

The T/M ratio obtained for each replicate injection was normalised with respect to the results of two reference samples stored at 4° C for the length of the study. The results were plotted against increasing storage time for each test condition and the slopes of each plotline were used to test the significance at a 95 % confidence level of the observed data for evidence of instability of the T/M ratio in the solution under each storage condition.

No significant trends were observed in the stability of the ratio when stored at 22 °C in the dark. When exposed to ambient light at 22 °C, by inspection it was evident that the T/M ratio decreased relative to the reference sample by the final timepoint. Significant decrease in the T/M ratio when the solution was stored at 40 °C. The time plots for each storage condition are given in Figure 4.

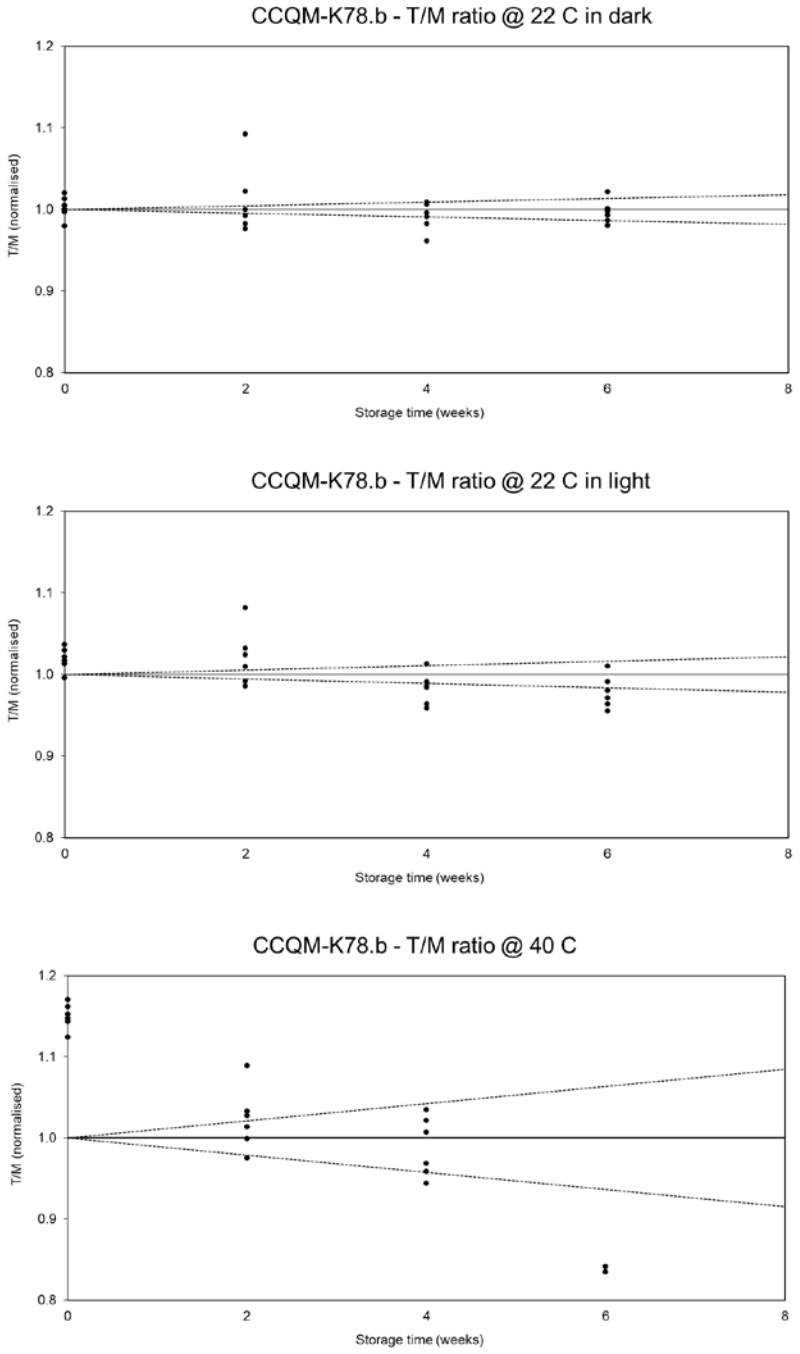


Figure 4: Stability of T/M ratio in CCQM-K78.b solution

The conclusion of the short term stability study was that the solution was suitable for use in the comparison provided it was not stored for extended periods at temperatures either in excess of ambient temperature or exposed to light.

PARTICIPANTS, SAMPLE DISTRIBUTION AND INSTRUCTIONS

The call for participation and study protocol was circulated in February 2022 with the intent to distribute samples starting in March 2022. The initial deadline to submit results by June 2022 was extended to August 2022. The combined results were collated and distributed to participants in January 2023. An online meeting of the comparison participants was convened in March 2023 to review the results. The results and actions arising from the participant meeting were discussed at the OAWG meeting in April 2023. The full comparison timeline is summarised in Table 1. Appendix B reproduces the Study Protocol.

Each participant was provided by the BIPM with four ampoules each containing at least 4 mL of the comparison solution containing T and M in ACN. One ampoule was provided for development purposes. Participants reported a value for the mass fraction content in units of μg/g for each analyte, using the reporting sheet provided with the samples. In addition to the quantitative results, participants were required to describe the basis of traceability for their results, provide an overview of their analytical methods, a summary of their approach to uncertainty estimation, and to list the Core Competencies claimed to have been demonstrated in this study. The twenty institutes listed in Table 4 submitted results for CCQM-K78.b.

Institute	Code	Country	Contact
Bureau International des Poids et Mesures	BIPM	France	Steven Westwood
Instituto Boliviano de Metrologia,	IBMETRO	Bolivia	Evelyn Mendoza
Instituto Nacional de Metrologia	INMETRO	Brazil	Eliane do Rego
National Research Council of Canada	NRC	Canada	Jennifer Bates
National Institute of Metrology, China	NIM	China	Fuhai Su
Laboratoire National de Métrologie et d'Essais	LNE	France	Fanny Gantois
Physikalisch-Technische Bundesanstalt	PTB	Germany	Christian Piechotta
National Chemical Metrology Laboratory	EXHM	Greece	Elias Kakoulides
Government Laboratory of Hong Kong	GLHK	Hong Kong	Chi-Kin Koo
National Metrology Institute of Japan	NMIJ	Japan	Miho Kuroe
CENAM	CENAM	Mexico	Marco Calderón
Saudi Standards, Metrology and Quality Org.	SASO	Saudi Arabia	M. Alrashed
Health Sciences Authority	HSA	Singapore	Tang Lin Teo
National Metrology Institute of South Africa	NMISA	South Africa	Laura Quinn
Korea Research Institute of Standards and Science	KRISS	South Korea	Seonghee Ahn
National Institute of Metrology (Thailand)	NIMT	Thailand	Thitiphan Chaiphet
INRAP	INRAP	Tunisia	Hanen Klich
National Metrology Institute of Turkey	UME	Turkey	Mine Bilsel
LGC Limited	LGC	UK	Chris Hopley
LATU	LATU	Uruguay	Florencia Almiron

Table 4: Participants in CCQM-K78.b

SOURCE OF METROLOGICAL TRACEABILITY

All participants anchored the metrological traceability of their results through a Primary Reference Material (PRM) which was used to prepare a primary calibrator solution for each analyte by a gravimetric procedure. The majority of participants used the NMIA CRM P1305 for trifluralin and CRM P1408 for methoxychlor as the PRM for their preparation of a primary calibrator. Fifteen NMIs used the certified value for mass fraction content provided by NMIA for the materials. EXHM undertook an internal value assignment by qNMR of the NMIA materials and used this value.

Four NMIs undertook an internal mass fraction value assignment of a commercially-sourced high purity materials. Table 5 lists the source material and the traceability claim for the value assignment of the PRMs for methoxychlor and trifluralin used by each participant.

Participant	Source of Traceability	Basis of Traceability Claim
BAM, BIPM, GLHK, HSA, IBMETRO, INRAP, KRISS, LATU, LGC, LNE, NIMT, NMIJ, NMISA, NRC, SASO	NMIA CRM P1305 (T) ; NMIA CRM P1408 (M)	NMI CRM produced under ISO 17034 accreditation
EXHM	qNMR purity assignment	qNMR assignment of NMIA CRMs P1305 (T) and P1408 (M) via an SI- traceable internal standard
NIM	NIM GBW 060877 (T); Mass balance and qNMR purity assignment (M)	For T: NIM CRM For M: qNMR and mass balance assignment of material from Ehrenstorfer
CENAM	Mass balance purity assignment	Application of mass balance method
INMETRO	qNMR purity assignment	Application of qNMR method via an SI- traceable internal standard
UME	qNMR purity assignment	Application of qNMR method via an SI- traceable internal standard

Table 5. Source of traceability for measurements in CCQM-K78.b.

RESULTS

Participants reported values for the mass fraction content of T and M in the CCQM-K78.b solution in units of μg/g. In addition to the quantitative results participants were required to describe the basis of traceability for their results and to provide an overview of their analytical methods and of their measurement uncertainty budget. Values for the content of CCQM-K78.b and summary plots of the participant results are shown below for trifluralin (Table 6) and methoxychlor (Table 7).[1]

Participant	Trifluralin (μg/g)	u (μg/g)	U_{95} (μg/g)
BAM	5.52	0.072	0.14
BIPM	5.74	0.051	0.10
CENAM	5.59	0.140	0.29
EXHM*	5.55	0.073	0.15
GLHK	5.78	0.130	0.25
HSA	5.53	0.091	0.18
IBMETRO	5.10	0.129	0.27
INMETRO	5.61	0.18	0.35
INRAP	5.26	0.016	0.032
KRISS*	5.67	0.067	0.16
LATU*	5.32	0.087	0.18
LGC	5.69	0.070	0.14
LNE	5.36	0.100	0.20
NIM	5.63	0.060	0.12
NIMT	5.49	0.090	0.18
NMIJ	5.66	0.020	0.04
NMISA	5.36	0.090	0.18
NRC	5.68	0.060	0.12
SASO	6.48	0.150	0.30
UME*	5.42	0.085	0.17

Table 6: Trifluralin values reported for CCQM-K78.b

[1] Results listed with an asterix (*) in Table 6 were recalculated subsequent to initial submission to exclude data from ampoules which were shown to have potential stability problems

Participant	Methoxychlor (µg/g)	u (µg/g)	U_{95} (µg/g)
BAM	10.37	0.06	0.124
BIPM	10.59	0.07	0.132
CENAM	10.39	0.31	0.630
EXHM	10.55	0.11	0.220
GLHK	10.57	0.21	0.430
HSA	10.38	0.17	0.350
IBMETRO	9.94	0.25	0.518
INMETRO	10.10	0.22	0.43
INRAP	9.49	0.05	0.095
KRISS	10.60	0.09	0.200
LATU	10.04	0.22	0.450
LGC	10.65	0.10	0.200
LNE	10.44	0.21	0.420
NIM	10.57	0.06	0.120
NIMT	10.26	0.18	0.360
NMIJ	10.51	0.04	0.080
NMISA	10.29	0.09	0.180
NRC	10.54	0.13	0.260
SASO	9.55	0.27	0.560
UME	10.52	0.16	0.320

Table 7: Methoxychlor values reported for CCQM-K78.b

A summary of the analysis procedure used for the value assignment, confirmation methods (where used) and the calibration strategy applied by each participant is provided in Table 8.

Table 8: Analytical Methods and Calibration Strategy used by Participants

NMI	Assignment	Calibration	Confirmation
BAM	GC-MS/MS	multi-point	
BIPM	GC-FID	bracketing	
CENAM	GC-MS & LC-UV	multi-point	
EXHM	LC-UV	single-point	GC-FID
GLHK	GC-IDMS	exact matching IDMS	LC-MS/MS
HSA	GC-IDMS	exact matching IDMS	GC-MS
IBMETRO	GC-ECD	multi-point	
INMETRO	GC-MS	multi-point	
INRAP	GC-ECD	multi-point	
KRISS	GC-IDMS	exact matching IDMS	GC-MS/MS (2nd MRM)
LATU	GC-ECD (M) GC-FID (T)	multi-point	
LGC	GC-IDMS	exact matching IDMS	
LNE	GC-IDMS	multi-point	
NIM	LC-UV	exact matching	GC-FID
NIMT	GC-IDMS	exact matching IDMS	
NMIJ	LC-UV & GC-FID	single point	
NMISA	GC-MS/MS	bracketing	
NRC	GC-FID	bracketing	GC-IDMS
SASO	GC-MS/MS	multi-point	
UME	LC-UV	multi-point	GC-MS

Methods based on GC-MS/MS using exact matching IDMS were used by six participants. Two participants used a multipoint calibration GC-MS/MS approach. Other methods used to obtain either the sole or a contributing result were based on LC-UV, GC-FID, GC-ECD and direct GC-MS.

The NMIJ reported result is the combination of independent values obtained using both LC-UV and GC-FID methods. The CENAM result combines values from LC-UV and GC-MS methods.

NMIJ and LGC both reported in their result submission that they obtained outlier results with a significantly lower value for trifluralin for one of the vials they examined, compared with the values obtained for the other ampoules received, and that they excluded this data from their reported result. Anomalous values were obtained for ampoule 248 by NMIJ and for ampoule 245 for LGC. Further evidence of instability of the trifluralin value in ampoules prepared in the later stages (above ampoule 240) of the production batch are discussed in the next section of this report.

DISCUSSION

Circulation of Result Summary and Initial Participant Discussion

A summary of the combined comparison results was circulated to the participants in February 2023. The combined result plots for the two analytes are given in Figures 5 and 6 for trifluralin and in Figures 7 and 8 for methoxychlor. The method-linked plots in Figures 6 for T and Figure 8 for M do not indicate a significant correlation of a specific method to magnitude of reported value apart from results based on GC-ECD which appear biased low for both analytes.

There is a set of participant results in agreement with the gravimetric values for both T and M content along with a gradation of other results below the gravimetric value for each analyte.

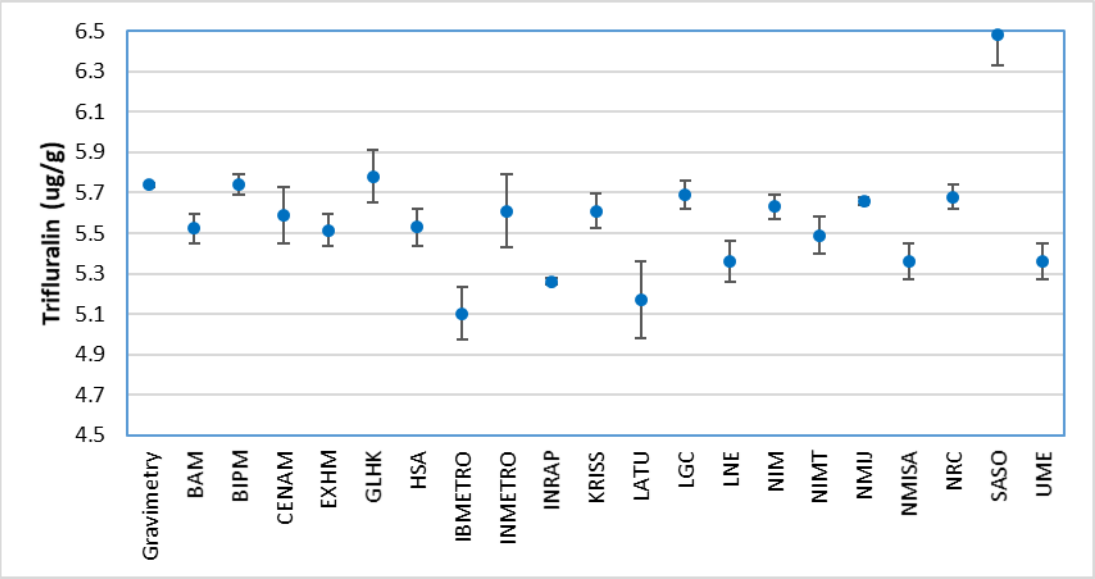


Figure 5 Trifluralin result plot for CCQM-K78.b (± *u*, *k* = 1)

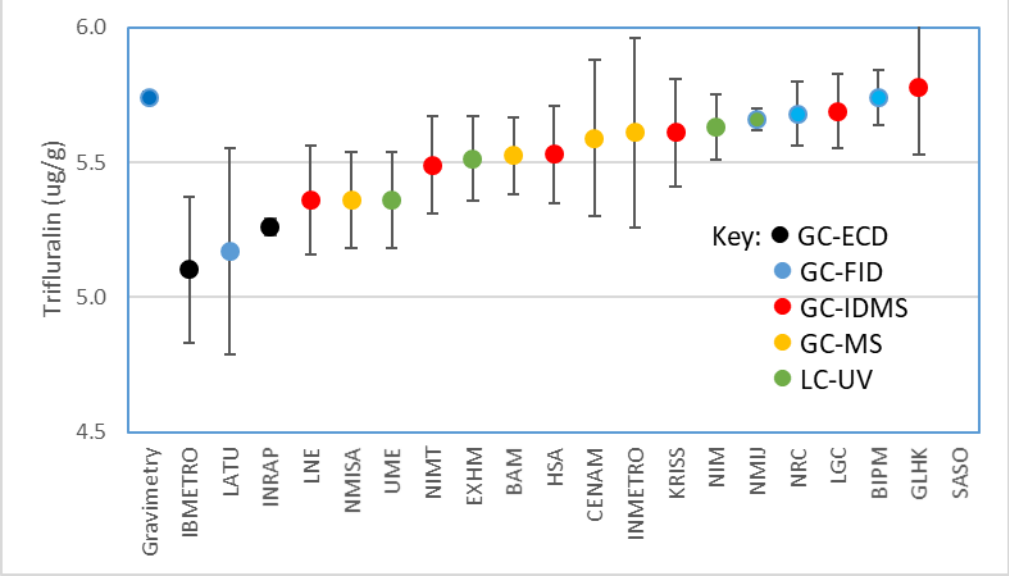


Figure 6: Trifluralin content by method (± $U_{95\%}$)

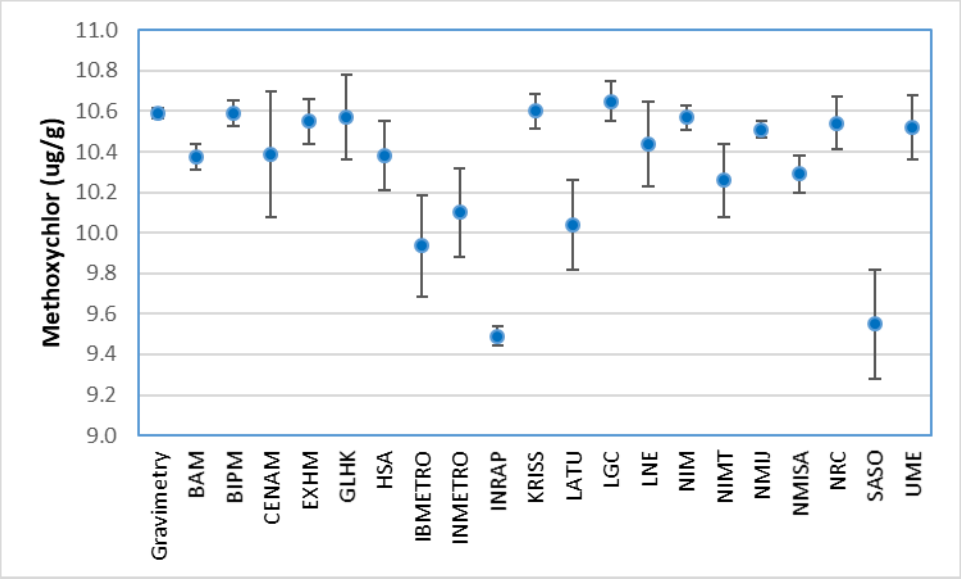


Figure 7 Methoxychlor result plot for CCQM-K78.b (± *u*, *k* = 1)

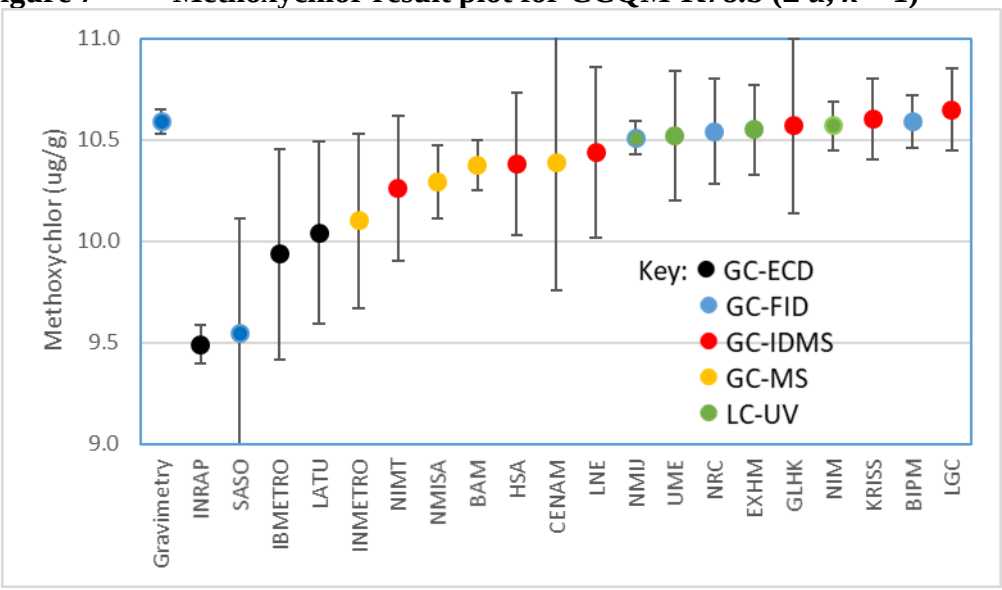


Figure 8: Methoxychlor content by method (± $U_{95\%}$)

It is noted that the set of results consistent with both gravimetric values only used either single point or bracketing calibration strategies whereas results obtained using multipoint calibration showed a wider range.

An illustration of the relative performance is provided by the "x-y" plot of the results reported for M (x-axis, ± $U_{95\%}$) and T (y-axis, ± $U_{95\%}$) by each participant in Figure 9.

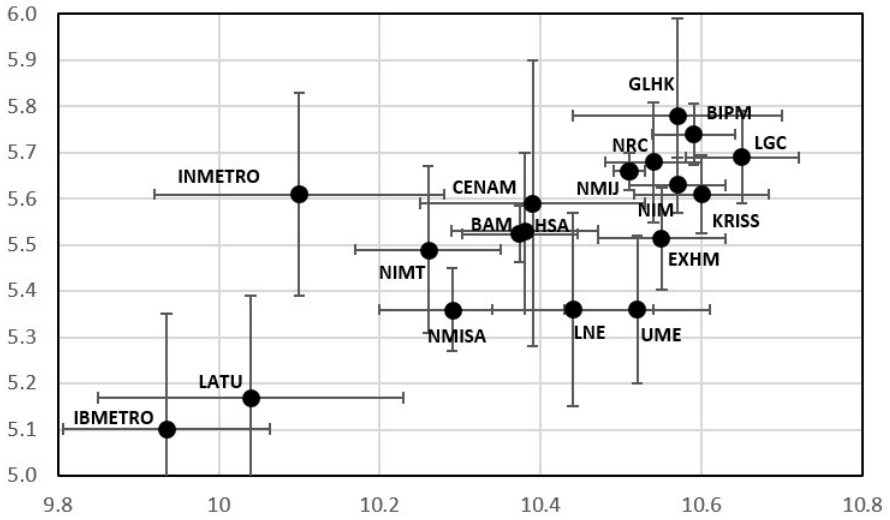


Figure 9: Methoxychlor content (x-axis) v. Trifluralin content (y-axis) in CCQM-K78.b

A two-session online meeting was hosted by the coordinating laboratory in March 2023 to discuss the key comparison results and measurement issues arising from the study. Each participant submitted a short presentation outlining aspects of their sample preparation, calibration strategy and analysis approach and these videos were made available in advance of the meeting to all participants. During the meeting four participants provided in-depth presentations of their methods. These were selected for their application of specific methods - GC-FID, LC-UV, GC-IDMS and GC-ECD respectively - for the value assignment of the CCQM-K78.b material.

A correlation in the deviation of reported values from the gravimetric value for both analytes is evident for some participants. Participants noted that thermal instability of the analytes was a challenge and potential source of bias when GC methods using heated sample injection were used.

Several participants commented that in their experience single point or bracketed calibration is advisable when an organic solvent is used. If multi-point calibration is used in this case there is potential for the introduction of bias due to solvent evaporation effects.

It was observed by the coordinating laboratory and confirmed by other participants that results based on MS detection for quantification exhibited larger variability for these analytes compared with detection using FID or UV absorbance.

Additional Homogeneity studies

The coordinating laboratory was requested to investigate further the homogeneity of the solution and to obtain additional information on the instability in the trifluralin content in vials from the latter stage of the production batch.

Each participant was asked to submit their results for each individual vial from the set of ampoules supplied to them. These results are shown as a T v. M plot in Appendix D. The results for the majority of participants were internally consistent for M content (agreement within their assigned uncertainty regardless of unit number). The results for T content were also internally consistent for ampoules below unit 230 of the batch but results for ampoule 235 or later were uniformly lower than the results for the earlier ampoules.

The coordinating laboratory reexamined the homogeneity of the material using quantification of T and M values rather than the T/M ratio data. The quantification data was obtained from three independent measurements each using three ampoules of the comparison material. T and M content of triplicate samples prepared from each vial were quantified using the GC-FID method with bracketing calibration. Figure 10 shows the T v. M plot of results for each of the 27 samples analyzed. The three data points obtained for the replicates prepared from vial 265 are significantly lower for T content compared to the dispersion of the 24 results obtained from the other eight vials. By contrast the results for M content of the three samples from vial 265 were all consistent with the observed variation of the grouped data.

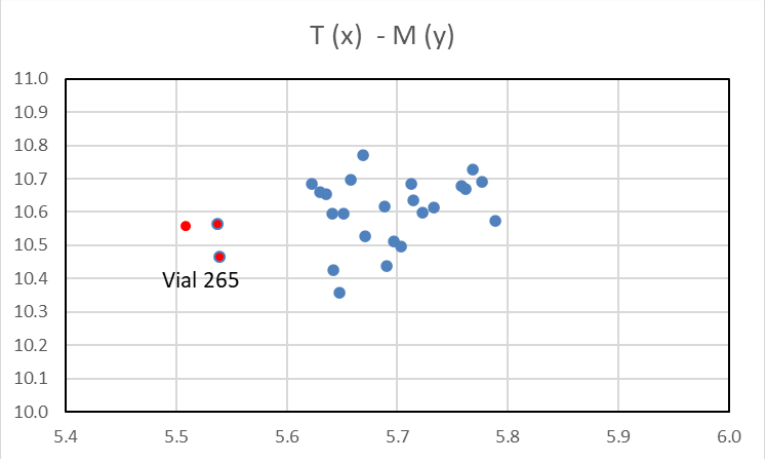


Figure 10: Combined plot of Trifluralin content (x-axis) v. Methoxychlor content (y-axis) for nine vials in triplicate by the coordinating laboratory

It was concluded from these two additional sources that there was no convincing evidence of significant inhomogeneity in the methoxychlor content of the full batch or in the trifluralin content for ampoules below unit 240 in the comparison material.

It was agreed that four participants – EXHM, KRISS, LATU and UME - who had incorporated in their original result for T content data from one unit from a later portion of the production batch (> unit 240) should be allowed to recalculate their result removing the contribution from the non-conforming vial. The trifluralin results for these participants reported in Table 6 and in subsequent data plots are their corrected values.

The following overall observations were made:

- the analytes are challenging for GC analysis with factors such as thermal decomposition on injection, liner effects and choice of temperature program potentially significant;
- evidence for decomposition of trifluralin relative to the gravimetric value in the later ampoules (units 240 to 276) of the production batch;
- the homogeneity of methoxychlor content in the whole batch and trifluralin content up to ampoules 240 of the comparison material appears satisfactory and is unlikely to be the source of the observed variation in results relative to the gravimetric value;
- in several cases methods based on quantification via MS detection provided results with low levels of precision compared with those obtained using other quantification methods.

Overall it appeared that agreement with the gravimetric value was generally obtained using:

- LC- rather than GC-based methods;
- exact matching or bracketing rather than multipoint calibration;
- procedures to control for solvent volatility.

KCRV

The OAWG document CCQM-OAWG/92 *Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence*, describes options for the choice of appropriate estimators for the KCRV, depending on the nature of the results and the degree of agreement. ISO Standard 6142:2015 *Gas Analysis – Preparation of calibration mixtures* describes an alternative approach to the assignment of reference values based on gravimetric data.

A second online discussion by the comparison participants in May 2023 discussed the follow-up studies arising from the March 2023 meeting and reviewed options for the KCRV for the study results. A KCRV proposal was circulated to the participants in November 2023 and a survey form was used to obtain feedback.

Estimators for the KCRV for methoxychlor are listed in Table 9. For methoxychlor the Hierarchical Bayes REM value was calculated via the NIST Consensus Builder application (https://consensus.nist.gov) using ten participant results that were consistent with the gravimetric value within their stated uncertainty as the input data set. For trifluralin the Hierarchical Bayes value used eight results which are internally consistent within their reported standard uncertainty.

	Methoxychlor (ug/g)				Trifluralin (µg/g)			
Estimator	X	$u(X)$	$U_{95}(X)$	$U_{rel}(\%)$	X	$u(X)$	$U_{95}(X)$	$U_{rel}(\%)$
Gravimetry	10.59	0.027	0.054	0.51	5.74	0.009	0.018	0.31
Heirarchical Bayes REM	10.57	0.035	0.070	0.61	**5.68**	**0.031**	**0.062**	**1.06**
Gravimetry + analytical verification (ISO 6142)	**10.59**	**0.066**	**0.132**	**1.25**	5.74	0.051	0.102	1.78

Table 9: Estimators for analyte content in the CCQM-K78.b material
The proposed KCRVs for each component are highlighted in bold

KCRV for Methoxychlor

It was agreed for methoxychlor to follow the ISO 6142:2015 approach for value assignment of calibration gas mixtures prepared gravimetrically. In this case the KCRV for methoxychlor is the gravimetric value. The KCRU includes the uncertainty in the gravimetric value but expanded with a component for uncertainty in the analytical verification of the value by the coordinating laboratory.
The alternative approach of using the gravimetric value alone or the Bayes REM value calculated using the ten participant results consistent with the gravimetric value within their stated uncertainty were considered to give unrealistically small values for the KCRU.

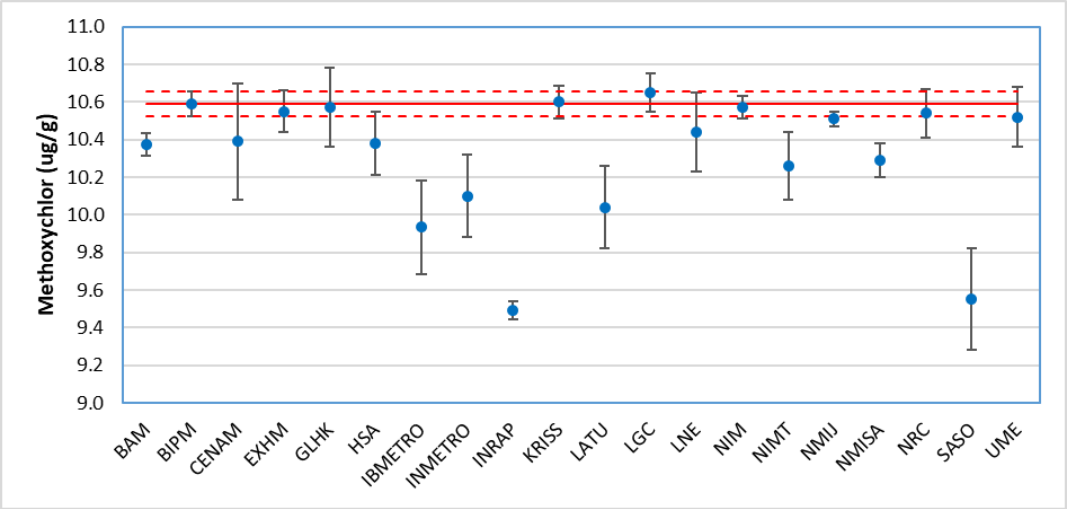


Figure 11: Methoxychlor results and KCRV with KCRU limits (red lines), all $k = 1$

KCRV for Trifluralin

It was established that decomposition in the trifluralin content relative to the gravimetric value occurred in ampoules from the latter portion (> vial 240) of the production batch. Although the evidence for significant reduction in the trifluralin content only applied to these late units of the production batch it was not considered to be justified in this case to base the KCRV primarily on the gravimetric value, given the possibility that some decomposition earlier in the production process could not be ruled out.

For trifluralin the KCRV was assigned using a group of eight results which are internally consistent within their reported standard uncertainty. In this case the recommendations of the OAWG KCRV Guidance document (CCQM-OAWG/92) were followed and the Hierarchical Bayes Gaussian REM value calculated using the NIST Consensus Builder was assigned as the KCRV and KCRU.

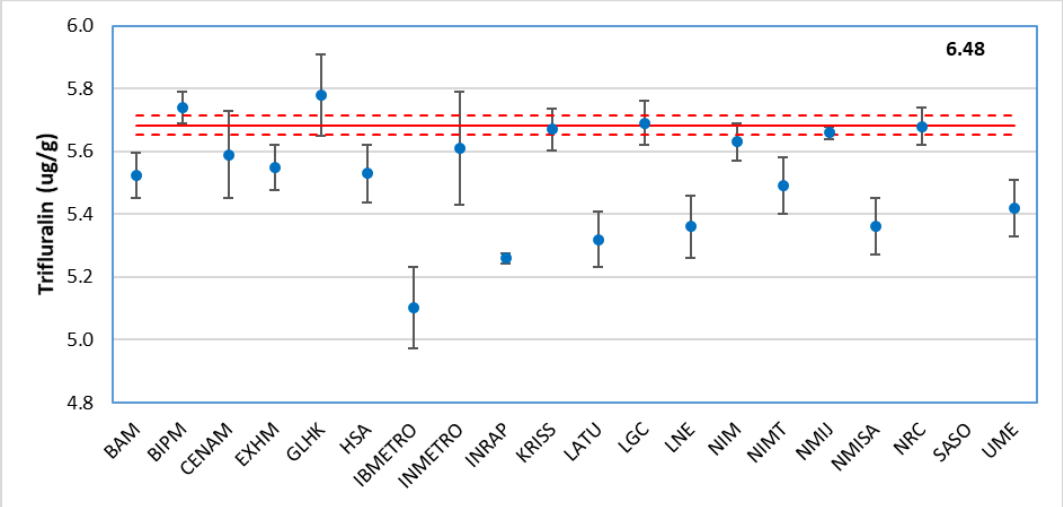


Figure 12: Trifluralin results and KCRV and KCRU (red lines), all $k = 1$

DEGREES of EQUIVALENCE

The absolute degrees of equivalence of each result for analyte content reported by the participants in CCQM-K78.b were estimated as the difference between the value and the KCRV: $d_i = x_i$ – KCRV.

The nominal $k = 2$ expanded uncertainty on the d_i, $U_{k=2}(d_i)$, was estimated as twice the square root of the sum of the squares of the standard uncertainties of the two components:

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

The d_i and $U_{k=2}(d_i)$ were calculated as percentages relative to the KCRV:

$\%d_i = 100 \cdot d_i/\text{KCRV}$ and $U_{k=2}(\%d_i) = 100 \cdot U_{k=2}(d_i)/\text{KCRV}$.

Table 10 lists the numeric values of d_i, $U_{95}(d_i)$, $\%d_i$, and $U_{95}(\%d_i)$ for each analyte for each participant.

Table 10: Degrees of Equivalence with KCRV

	Methoxychlor (µg/g)				**Trifluralin (µg/g)**			
NMI	d	$U_{k=2}(d)$	$\%\ d$	$\%U_{k=2}(d)$	d	$U_{k=2}(d)$	$\%\ d$	$\%U_{k=2}(d)$
BAM	-0.22	0.18	-2.04%	1.71%	-0.16	0.16	-2.81%	2.74%
BIPM	0.00	0.19	0.00%	1.76%	0.06	0.12	0.99%	2.08%
CENAM	-0.20	0.63	-1.89%	5.99%	-0.09	0.29	-1.65%	5.04%
EXHM	-0.04	0.26	-0.38%	2.42%	-0.14	0.16	-2.38%	2.78%
GLHK	-0.02	0.44	-0.19%	4.16%	0.10	0.27	1.69%	4.69%
HSA	-0.21	0.36	-1.98%	3.44%	-0.15	0.19	-2.71%	3.37%
IBMETRO	-0.65	0.51	-6.19%	4.85%	-0.58	0.26	-10.24%	4.66%
INMETRO	-0.49	0.46	-4.63%	4.34%	-0.07	0.36	-1.30%	6.42%
INRAP	-1.10	0.16	-10.39%	1.54%	-0.42	0.07	-7.46%	1.20%
KRISS	0.01	0.22	0.09%	2.03%	-0.01	0.15	-0.25%	2.58%
LATU	-0.55	0.46	-5.19%	4.34%	-0.36	0.18	-6.40%	3.24%
LGC	0.06	0.24	0.57%	2.26%	0.01	0.15	0.11%	2.68%
LNE	-0.15	0.44	-1.42%	4.16%	-0.32	0.21	-5.70%	3.67%
NIM	-0.02	0.18	-0.19%	1.68%	-0.05	0.13	-0.95%	2.36%
NIMT	-0.33	0.38	-3.12%	3.62%	-0.19	0.19	-3.41%	3.34%
NMIJ	-0.08	0.15	-0.76%	1.46%	-0.02	0.07	-0.42%	1.27%
NMISA	-0.30	0.22	-2.83%	2.11%	-0.32	0.19	-5.70%	3.34%
NRC	-0.05	0.29	-0.47%	2.75%	0.00	0.13	-0.07%	2.36%
SASO	-1.04	0.56	-9.82%	5.25%	0.80	0.31	14.00%	5.38%
UME	-0.07	0.35	-0.66%	3.27%	-0.26	0.19	-4.64%	3.34%

The DoE results are plotted in Figure 13 for methoxychlor and in Figure 14 for trifluralin.

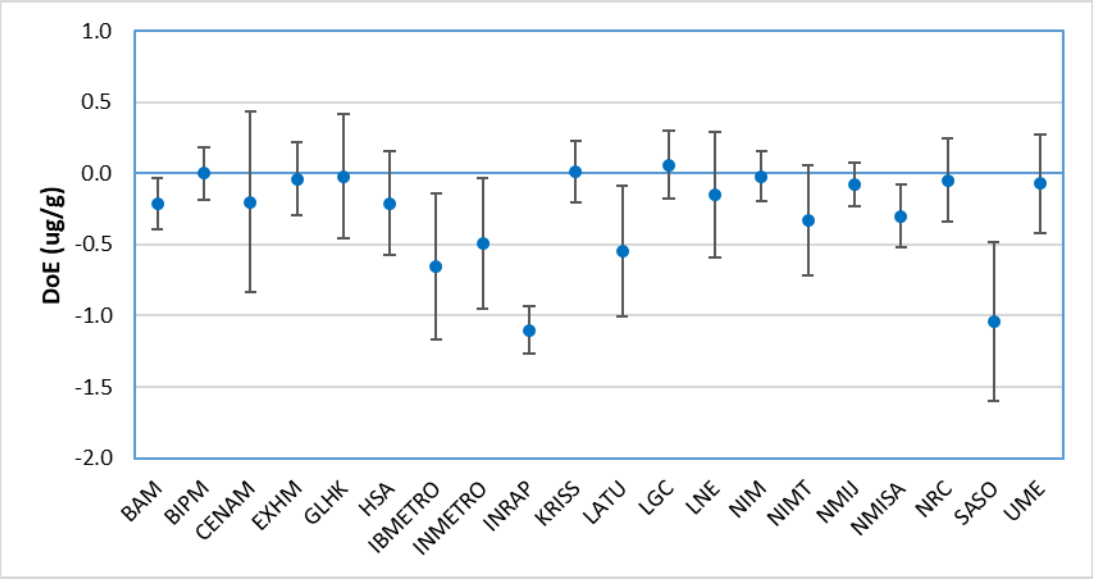


Figure 13: DoE plot for Methoxychlor results in CCQM-K78.b

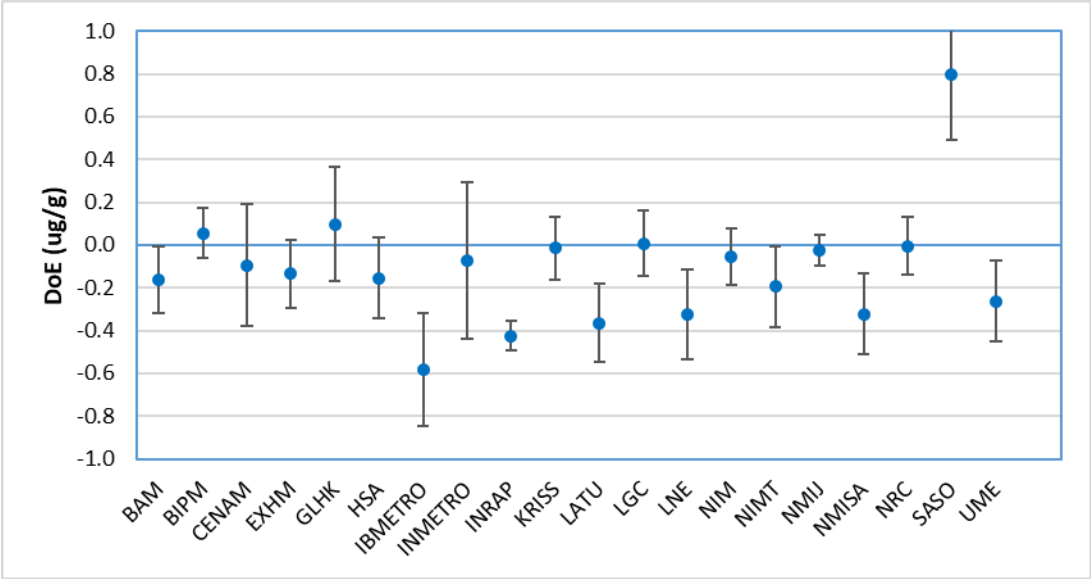


Figure 14: DoE plot for trifluralin results in CCQM-K78.b

USE OF CCQM-K78.b IN SUPPORT OF CMC CLAIMS

"How Far The Light Shines" Statement for CCQM-K78.b

CCQM K78.b tests measurement capabilities for the content of non-polar organic compounds in a multicomponent organic calibration solution in the mass fraction range 5 – 10 μg/g and where:

- analyte molar masses are in the range 100 g/mol to 500 g/mol
- analyte $pK_{ow} < -2$

Participants in this comparison may use their result to underpin CMC claims for mass fraction assignment of non-polar analytes, single or multiple, in a calibration solution, in an appropriate organic solvent, at mass fractions > 5 μg/g and having molar masses in the range 100 to 500 g/mol;

CONCLUSIONS

This proved to be a more challenging set of analytes than those provided for the CCQM-K78.a comparison. Challenges included the thermal stability of the analytes under selected analytical techniques, controlling for the volatility of the solvent and a relatively large variation in some results using MS-based quantification.

Where these challenges were addressed the level of performance was consistent with that obtained in earlier comparisons of quantification of non-polar analytes in solution, provides additional support for existing CMC claims for the assignment of organic analyte standard solutions and can be used to support future claims for standard solutions of non-polar analytes in organic solvent.

The comparison demonstrated that care must be taken with the choice of calibration strategy when volatile solvents are used. Alternatives to a traditional multi-point calibration approach should at least be considered if highest levels of precision are desired.

It was also recommended that an advisory group be established from within the OAWG to provide a written guidance on how to use performance in this comparison to assess CMC claims.

APPENDIX A: NMIA CRM CERTIFICATES

Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

NATA

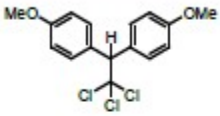
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA P1305: Methoxychlor

Report ID: P1305.2013.02

Chemical Formula: $C_{16}H_{15}Cl_3O_2$

Molecular Weight: 345.6 g/mol



Certified value

Batch No.	CAS No.	Purity (mass fraction)
96/024237	72-43-5	99.7 ± 0.5%

The uncertainty has been calculated according to ISO Guide 35 and is stated at the 95% confidence limit (k = 2).

IUPAC name: 1,1'-(2,2,2-Trichloro-1,1-ethanediyl)bis(4-methoxybenzene)

Expiration of certification: The property values are valid till 29 November 2027, i.e. ten years from the date of re-certification provided the **unopened** material is handled and stored in accordance with the recommendations below. The material as issued in the unopened container and stored as recommended below should be suitable for use beyond this date, subject to confirmation of batch stability from the issuing body. The expiry date/shelf life does not apply to sample bottles that have been opened. In such cases it is recommended that the end-user conduct their own in-house stability trials.

Description: White crystal sourced from an external supplier, and certified for identity and purity by NMIA. Packaged in amber glass bottles with a septum and crimped aluminium cap or screw top cap.

Intended use: This certified reference material is suitable for use as a primary calibrator.

Instructions for use: Equilibrate the bottled material to room temperature before opening.

Recommended storage: When not in use this material should be stored at or below 4 °C in a closed container in a dry, dark area.

Metrological traceability: The certified purity value is traceable to the SI unit for mass (kg) through Australian national standards via balance calibration. In the mass balance approach all impurities are quantified as a mass fraction and subtracted from 100%. Quantitative NMR provides an independent direct measure of the mass fraction of the analyte of interest, calibrated with an internal standard certified for purity (mass fraction).

Stability: This material has demonstrated stability over a minimum period of five years. The measurement uncertainty at the 95% confidence interval includes a stability component which has been estimated from annual stability trials. The long-term stability of the compound in solution has not been examined.

Homogeneity assessment: The homogeneity of the material was assessed using purity assay by GC-FID on five randomly selected 1-2 mg sub samples of the material. The material was judged to be sufficiently homogeneous at this level of sampling as the variation in analysis results between samples was not significantly different at a 95% confidence level from that observed on repeat analysis of the same sample.

Safety: Treat as a hazardous substance. Use appropriate work practices when handling to avoid skin or eye contact, ingestion or inhalation of dust. Refer to the provided safety data sheet.

Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

NATA

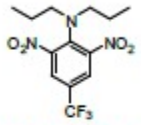
CERTIFIED REFERENCE MATERIAL CERTIFICATE OF ANALYSIS

NMIA P1408: Trifluralin

Report ID: P1408.2019.01

Chemical Formula: $C_{13}H_{16}F_3N_3O_4$

Molecular Weight: 335.3 g/mol



Certified value

Batch No.	CAS No.	Purity (mass fraction)
97-000046	1582-09-8	99.9 ± 0.3%

The uncertainty has been calculated according to ISO Guide 35 and is stated at the 95% confidence limit (k = 2).

IUPAC name: 2,6-Dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)aniline

Expiration of certification: The property values are valid till 27 March 2029, i.e. ten years from the date of re-certification provided the **unopened** material is handled and stored in accordance with the recommendations below. The material as issued in the unopened container and stored as recommended below should be suitable for use beyond this date, subject to confirmation of batch stability from the issuing body. The expiry date/shelf life does not apply to sample bottles that have been opened. In such cases it is recommended that the end-user conduct their own in-house stability trials.

Description: Orange crystalline solid sourced from an external supplier, and certified for identity and purity by NMIA. Packaged in amber glass bottles with a septum and crimped aluminium cap or screw top cap.

Intended use: This certified reference material is suitable for use as a primary calibrator.

Instructions for use: Equilibrate the bottled material to room temperature before opening.

Recommended storage: When not in use this material should be stored at or below 4 ºC in a closed container in a dry, dark area.

Metrological traceability: The certified purity value is traceable to the SI unit for mass (kg) through Australian national standards via balance calibration. In the mass balance approach all impurities are quantified as a mass fraction and subtracted from 100%. Quantitative NMR provides an independent direct measure of the mass fraction of the analyte of interest, calibrated with an internal standard certified for purity (mass fraction).

Stability: This material has demonstrated stability over a minimum period of ten years. The measurement uncertainty at the 95% confidence interval includes a stability component which has been estimated from annual stability trials. The long-term stability of the compound in solution has not been examined.

Homogeneity assessment: The homogeneity of the material was assessed using purity assay by GC-FID on ten randomly selected 1-2 mg sub samples of the material. The material was judged to be sufficiently homogeneous at this level of sampling as the variation in analysis results between samples was not significantly different at a 95% confidence level from that observed on repeat analysis of the same sample.

Safety: Treat as a hazardous substance. Use appropriate work practices when handling to avoid skin or eye contact, ingestion or inhalation of dust. Refer to the provided safety data sheet.

APPENDIX B: STUDY PROTOCOL
CCQM-K78.b
Non-polar Analytes in a Multi-component Organic Solution:
Mass Fraction of Non-polar Pesticides in Acetonitrile

Track A Key Comparison

Study Protocol

February 2022

Steven Westwood

BIPM

Pavillon de Breteuil, Sèvres, France

Introduction

The OAWG Strategy Document for 2021-2030 includes a planned Track A key comparison, CCQM-K78.b, to be conducted in 2022 on the value assignment of the mass fraction content of non-polar analytes in a standard solution of organic solvent. This comparison compliments CCQM-K78.a, completed in 2017, which examined the same measurement for polar organic analytes present in aqueous solution.

CCQM-K78.b will allow National Measurement Institutes (NMIs) to demonstrate and benchmark the validity of their procedures for this class of assignment and to support relevant CMC claims under the CIPM MRA.

Related key comparisons for the mass fraction content assignment of non-polar analytes in solution completed recently were CCQM-K131: Low Polarity Analytes in a Multi-component Organic Solution (2015), CCQM-K154.a: Zearalenone in acetonitrile (2018) and CCQM-K154.b: Aflatoxin B_1 in acetonitrile (2021).

Timeline

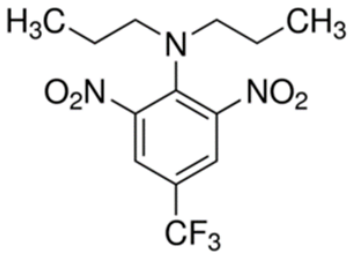
The timeline for the comparison is given in Table 1:

Date	**Activity**
15 February 2022	Call for participation to OAWG members
15 March 2022	Sample distribution completed
1 July 2022	Data due to coordinator
1 August 2022	Summary of results/Initial Draft A report distributed to participants
1 September 2022	Participant result discussion by video conference
15 October 2022	OAWG VC to include discussion of results and KCRV proposals

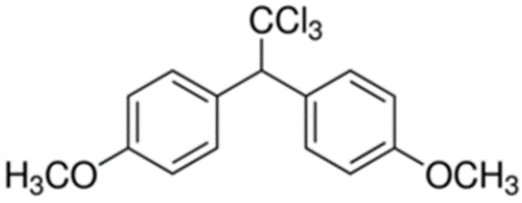
Table 1: Comparison schedule

Measurands

The comparison will require the assignment of the mass fraction content of two non-polar pesticides, trifluralin and methoxychlor, provided in a standard solution in acetonitrile. The structure of the two pesticides are shown in Figure 1 below.



Trifluralin



Methoxychlor

Preparation of the Comparison Material

BIPM prepared gravimetrically a bulk standard solution of trifluralin and methoxychlor in acetonitrile and sub-divided aliquots from this solution into a batch of flame-sealed ampoules. BIPM has verified the mass fraction values assigned by gravimetry for both analytes using an independent analytical technique. The mass fraction content levels of each pesticide are intended to be representative of the mass fraction content of non-polar analytes in a typical multi-component pesticide calibration solution.
Each ampoule contains 4 ml of the pesticide solution.

Each participant will receive four ampoules. Three ampoules will be required for analysis to obtain the comparison result and an additional ampoule is available as a back-up in case of breakage or for use in preliminary method development. The ampoules should be stored at 4 °C in the dark prior to opening.

Homogeneity Assessment of the Comparison Material

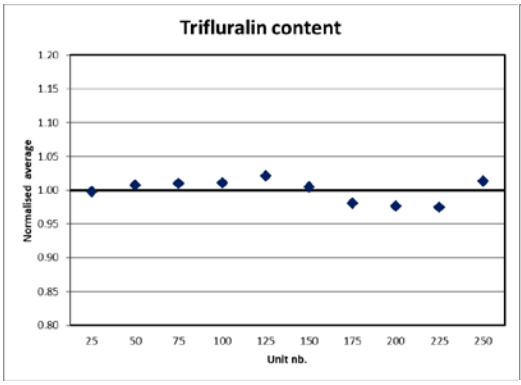
The homogeneity of the batches was tested using a GC-FID method with the analytes quantified against an internal standard and the uncertainty contribution due to inhomogeneity of the assigned values was evaluated by ANOVA. Ten vials were selected at regular intervals from the filling sequence to ensure that the results would indicate any trend in the filling process. Each ampoule was analyzed in a random order to ensure any trends in the bottling process were separated from possible trends resulting from the analytical sequence.

The results obtained indicated no statistically significant difference in the within- and between- ampoule levels of the mass fraction of each component in the solution. Please note that the relatively high within-ampoule variance of the results compared to the between-ampoule variance reflects the performance limits of the GC-FID method used rather than being a true indication of inhomogeneity of the analyte within each ampoule. The potential contribution due to the upper limit for uncertainty due to inhomogeneity in any case is sufficiently small as to be unlikely to influence the effective comparison of participant results. A summary of the observed within- and between-sample variability for each analyte is shown in Table 2:

	Trifluralin	**Methoxychlor**
Within-ampoule, CV_{wth}:	2.48 %	3.2 %
Between-ampoule, CV_{btw}:	1.04 %	3.1%
Upper limit of relative uncertainty contribution due to inhomogeneity:	1.13 %	1.37 %
Probability of falsely rejecting the hypothesis that all samples have the same concentration:	< 5%	< 5 %

Table 2

A plot of the normalized GC-FID response area ratio for each pesticide obtained for the homogeneity assessment of trifluralin and methoxychlor content is plotted by filling sequence. The data for trifluralin in Figure 2.a and for methoxychlor in Figure 2.b The normalized average of repeat measurements from three aliquots taken from each individual vial are plotted.



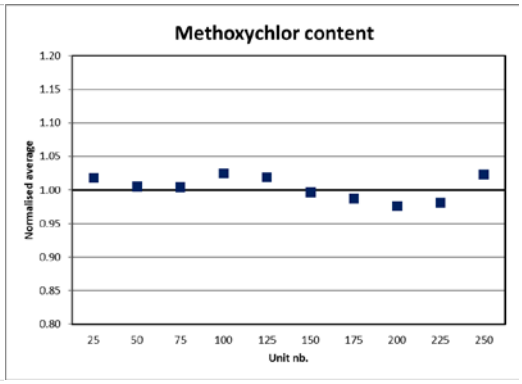


Figure 2a: Trifluralin homogeneity data **Figure 2b: Methoxychlor homogeneity data**

Stability Assessment of the Comparison Material

An isochronous stability study was undertaken for each analyte on storage at 22 °C in the dark, at 22 °C exposed to light and at 40 °C. The material is sufficiently stable, within the proposed time scale of the comparison, when stored at 4 °C and can be exposed to ambient temperature for short periods of time without significant decomposition. The analytes were not stable in solution at 40 °C. Precautions will be taken to monitor if the comparison material is exposed to extremes of temperature during shipment.

The ratio of the response of the two components stored at 22 °C in the dark is shown in Figure 3.

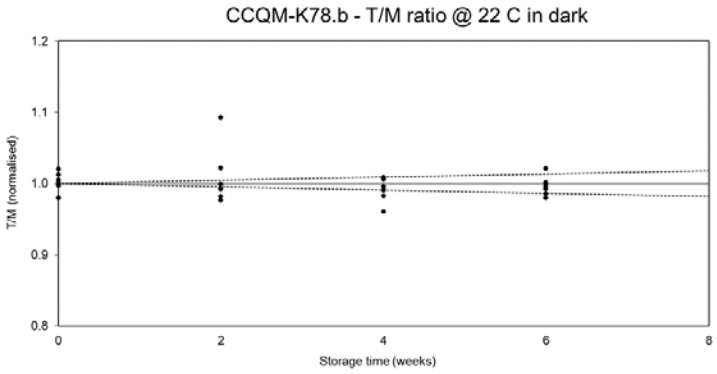


Figure 3: Stability of T/M ratio against storage time at 22 °C in the dark

A summary of the stability results is reported in OAWG document CCQM-OAWG/2021-007

Primary Calibrator Materials

To undertake the value assignment each participant will need to source and, where necessary, characterize a primary calibrator for both trifluralin and methoxychlor. Please consult the section "Metrological Traceability Requirements of Comparison Calibrator Materials" in the OAWG Guidance Document CCQM-OAWG/075 if further information is required.

CRMs for trifluralin and methoxychlor are available from NMI Australia or their distributors

Sample handling

Gravimetric operations involving aliquots of the solution taken from opened ampoules should be undertaken as soon as possible after opening the vial to minimize change in the analyte content due to solvent evaporation.

RESULTS

Participants are required to assign the mass fraction in the solution of both trifluralin and methoxychlor. The result should be based on combined values obtained by the measurement of at least one aliquot from each of three of the ampoules supplied (i.e. at least three independent replicates). Participants can use multiple aliquots per ampoule if they so choose.

There is no restriction on the use of methods to obtain data to assign the mass fraction content of trifluralin and methoxychlor in the solution, but only one overall result can be submitted by each participant.

Submission of Results

Each participant must provide results using the reporting sheet provided with the samples and also provide a completed Core Competency table. The results are to be sent via e-mail to the study coordinator (steven.westwood@bipm.org) prior to the submission deadline. In compliance with the general Submitted results are final and no corrections or adjustments of analytical data will be accepted unless approved by the OAWG.

For each reported value the associated uncertainties shall be reported along with a description of the uncertainty budget. A description of the analytical procedure (eg GC or LC column; chromatographic conditions, quantification approach, calibration standards used, sample chromatogram) should be provided.

Participation

All NMIs with measurement capabilities for the analysis of non-polar organic compounds are expected to participate in CCQM-K78.b. It constitutes a “Track A” Key Comparison and is used to demonstrate an NMI’s Core Competencies for the delivery of Measurement Services to their customers and stakeholders.

The ability to perform fit-for-purpose value assignment of the mass fraction content of an organic analyte in a calibration solution, either for internal use or to be made available to external users, is a critical technical competency for NMIs claiming metrological traceability for the results of organic analysis measurement services disseminated from their institute.

Failure to participate in the comparison could result in delays in the review and approval of existing or future CMC claims by an NMI in this measurement field.

USE OF CCQM-K78.b IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

"How Far The Light Shines" Statements for CCQM-K78.b

CCQM-K78.b tests measurement capabilities for determining the content of non-polar organic compounds in a multicomponent organic calibration solution present in the mass fraction range 5 mg/kg – 10 mg/kg and where:

- molar masses of analytes are in the range 100 g/mol to 500 g/mol
- pK_{ow} of analytes < -2

Participants successful in this comparison may use their result to:

a) underpin CMC claims for mass fraction assignment of non-polar analytes, single or multiple, in a calibration solution, in any appropriate organic solvent, at mass fractions > 5 mg/kg and having molar masses in the range 100 g/mol to 500 g/mol;

b) underpin CMCs for mass fraction solution assignments at levels below 5 mg/kg if a method that required dilution of the comparison solution prior to analysis was used. In this case, if desired, the mass fraction of the solution at the level it is analyzed after dilution can be claimed as the lower limit of a CMC for mass fraction assignment in a calibration solution. The dilution details and results obtained must be reported with the results submission.

Participants who carry out in-house purity assignment of a material to use as their primary calibrator can use successful participation as supporting evidence for existing or future broad-scope CMC claims for the value assignment of high purity non-polar organic materials.

Please note that demonstration of a fit-for-purpose purity assignment capability in this comparison cannot be used as the primary evidence in support of a broad-scope CMC claim. It can be used as supporting evidence for a claim underpinned directly by participation in relevant OAWG Track A purity key comparisons.

Reporting of Results

An electronic data submission form will be supplied as an EXCEL document.

All data should be entered as individual values and NOT include formulas

Worksheet headings within the data submission form for this comparison are:

- Participant details
- Comparison Result
    - mass fraction content of trifluralin and methoxychlor in the comparison solution (in mg/kg) with the associated combined standard uncertainty of the result and the expanded uncertainty at a 95% confidence range.
- Analytical Method
    - summary of technique, instrumentation and chromatography conditions
- Calibration
    - details of the calibrants used and their traceability with the basis for compliance with CIPM traceability requirements noted;
    - discussion of issues with the traceability of the calibrants or outline the technique used to carry out an in-house assessment, if undertaken;
    - outline of the calibration protocol used to quantify trifluralin and methoxychlor in the comparison solution.
- Sample analysis
    - summary of sample preparation procedure for analysis;
    - measurement equation and uncertainty calculations for each assignment;
    - main components of the uncertainty budget for each assignment.
- Confirmation method (if used)
    - brief description of any confirmatory or check methods
- Value assignment
    - results obtained for each method used to obtain the comparison result;
    - measurement equation and uncertainty budget if the results of two or more methods are combined to give the overall comparison result;
    - if dilution of the solution is undertaken as part of the analysis method, mass fraction content of trifluralin and methoxychlor in the diluted solution with the associated combined standard uncertainty of the result and the expanded uncertainty at a 95% confidence range

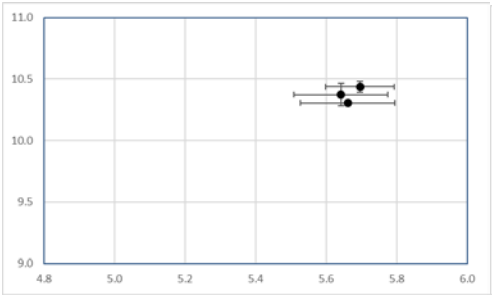
Safety and Handling

Suitable precautions should be used to manage the risk of exposure to acetonitrile when opening and handling individual ampoules.

The content organic analytes in the comparison solution is so low that no health risks arise due solely to exposure to these compounds from contact with the solution.

APPENDIX C: PARTICIPANT RESULTS FOR TRIFLURALIN (X-AXIS) and METHOXYCHLOR (Y-AXIS) BY VIAL

BAM



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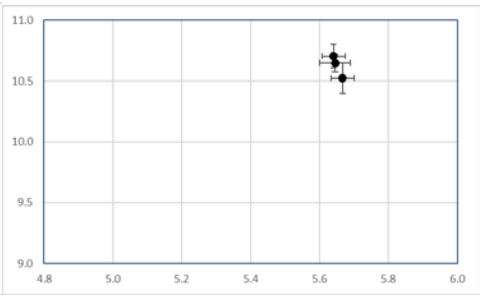

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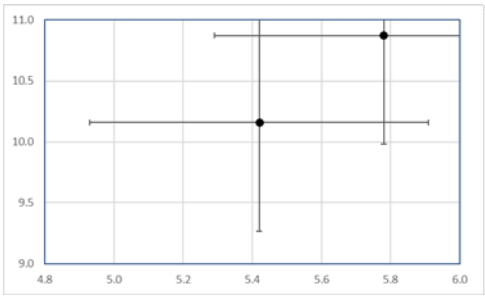

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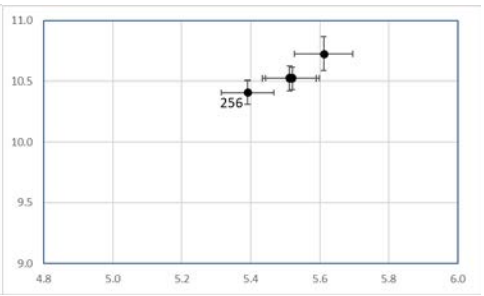

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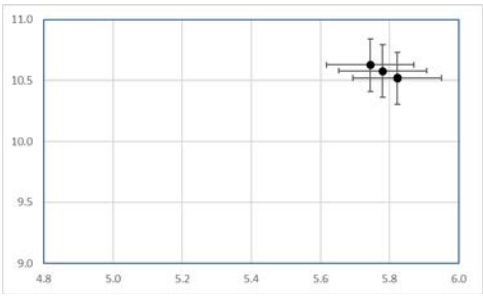

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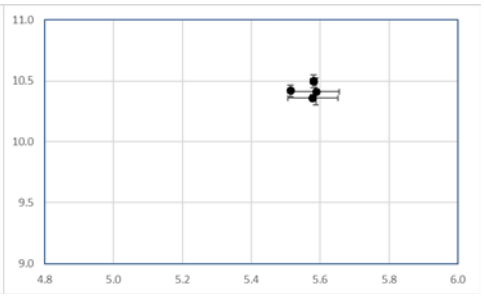

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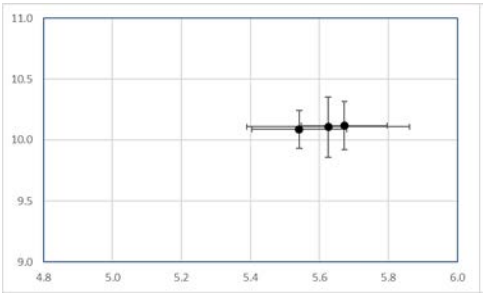

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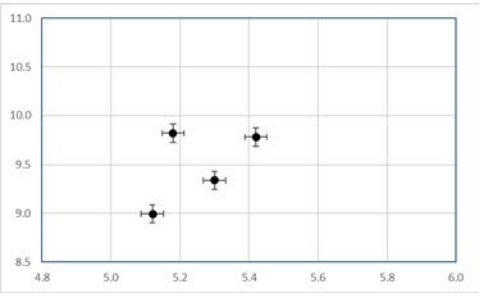

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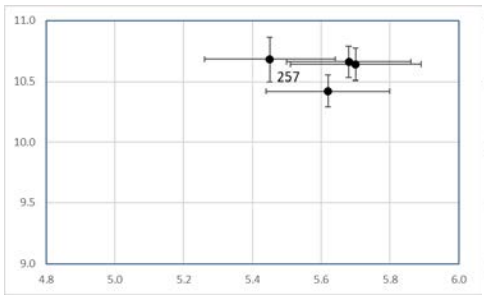

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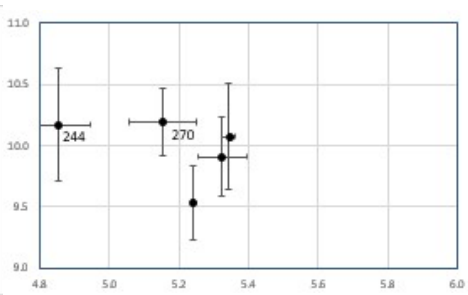

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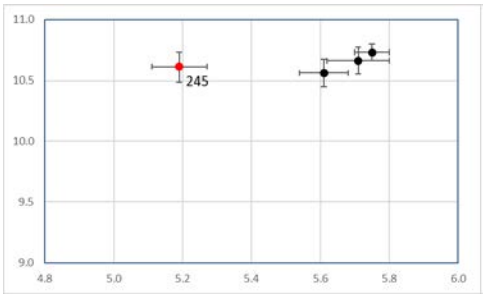

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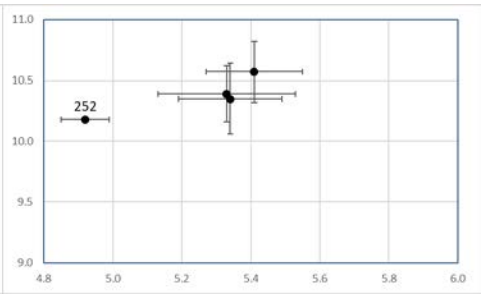

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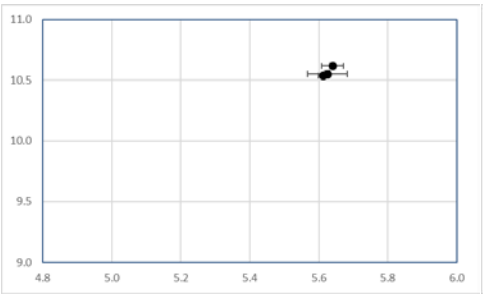

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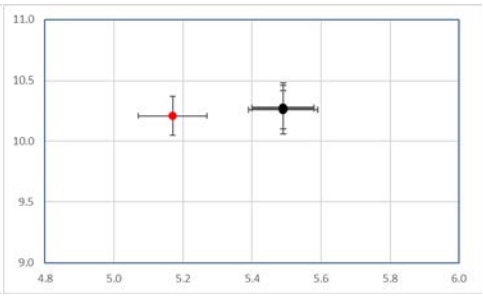

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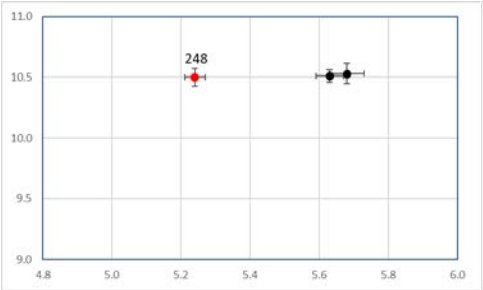

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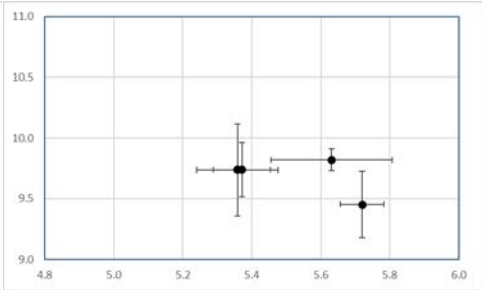

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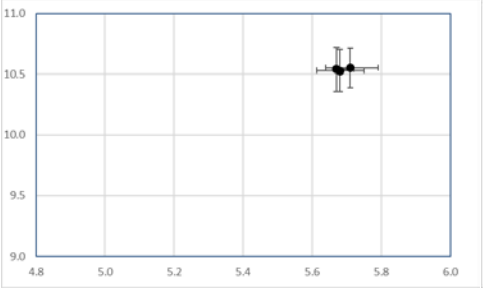

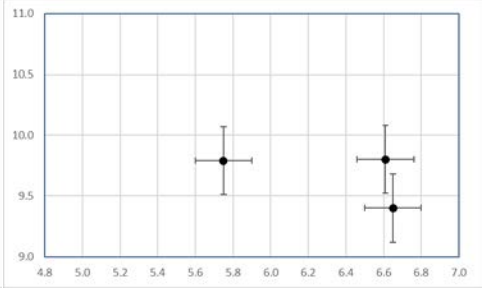

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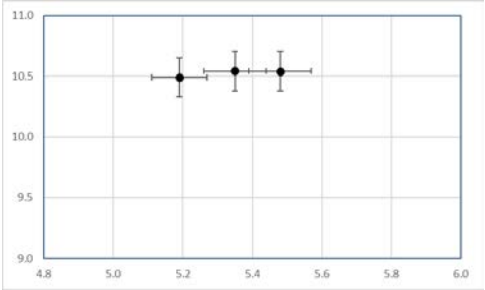
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