CCQM-K103
“MELAMINE IN MILK POWDER”

Final Report

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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 NIM and GLHK.

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1 Introduction

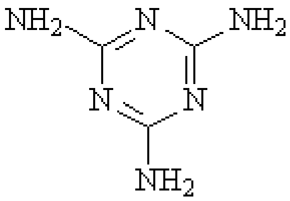
Melamine (1, 3, 5-triazine-2, 4, 6-triamine, or $C_3H_6N_6$) was first synthesized in 1834 and had later been found to have extensive uses in the industry. With high nitrogen content in the melamine molecule, the chemical could be unethically added to food products in order to increase the apparent protein content. Unfortunately, the melamine incidents that were due to tainted pet food in the United States in 2007 and tainted milk powder in China in 2008 have caused significant impact to the analytical chemistry world. After the crises, analysis of melamine becomes one of the routine measurements for food and laboratory testing.

In the OAWG meeting in Paris, France in April 2012, the OAWG defined Track C studies meant to support the assessment of measurement capabilities in emerging areas of global interest and importance within the scope of the OAWG Terms of Reference. One Track C study proposed in the OAWG meeting is CCQM-K103 “Melamine in Milk Powder”. The meeting agreed this to be a CCQM key comparison co-organized by NIM and GLHK. A CCQM pilot study (CCQM-P145) would be conducted in parallel with the proposed CCQM-K103 on melamine in milk powder (i.e., the same study material will be used in both studies).

2 Study measurand

The study measurand is melamine (1,3,5-triazine-2,4,6-triamine) .

Molecular Formula	$C_3H_6N_6$
Molar Mass	126.12 g·mol^{-1}
CAS Number	108-78-1
pK$_{ow}$	-0.382



The dry mass fraction (mg/kg) of melamine in milk powder was to be determined.

3 Study material

3.1 Preparation

The study samples were prepared by NIM from tainted milk powder. The tainted material was mixed with blank milk powder, and processed with spray drying equipment. The pooled material was milled and mixed to ensure its homogeneity. The final product was filled in 15 gram portions into amber glass bottles and stored at room temperature. A total of 300 bottles of material were prepared.

3.2 Homogeneity study

For the homogeneity study, 15 samples (with a sample size of about 1.0 g) were selected with a random stratified sample picking scheme and analysed for their melamine content by IDMS using LC-ESI-MS. Samples were measured in a random order and analyzed at least in duplicate to determine the sample inhomogeneity. 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 Table 1 and Figure1. The statistical results showed the calculated F-value was below the F-critical value which indicated that the inhomogeneity of the study material was insignificant.

Table 1 Summary of ANOVA for homogeneity test of melamine in the testing material

Source of variances	*SS*	*DF*	*MS*	*F*	$F_{Crit(0.05)}$
Between bottles	0.0018	14	0.000125	1.85	2.04
Within bottles	0.0020	30	0.0000676		

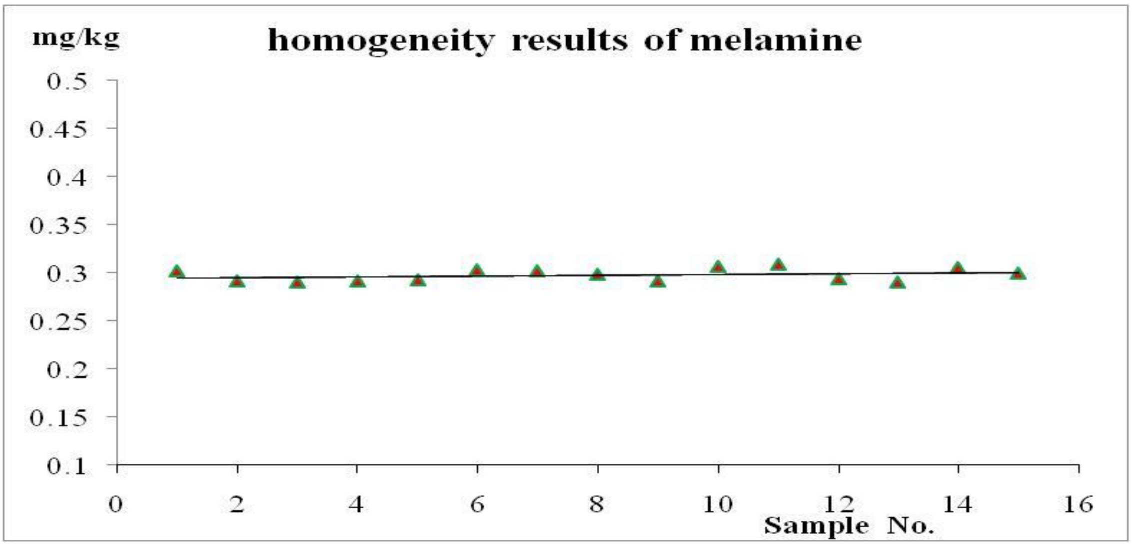


Figure 1 Graphical presentation of homogeneity results for melamine

3.3 Stability study

9 samples (with a sample size of about 1.0 g) were randomly chosen for the long-term stability study (18 months).The selected samples were stored at room temperature for one, three, six, nine, twelve and eighteen months. Their melamine contents were determined using the same analytical method and compared with the mean results of the samples which were stored at the reference temperature of 4°C over the whole stability study period.

A four weeks isochronous short-term stability study was performed to evaluate the stability of the sample during transport. The selected 9 samples in the study were stored at an elevated temperature of 40°C in an “*isochronous*” design approach, in which all measurements were carried out under repeatability conditions. The results of the samples stored at 40^{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 4°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 long-term statistical results shown in Table 2 indicated that no significant trend at 95% confidence level was detected as the absolute values of β_1 (i.e. slope of the regression line) were smaller than the critical values of β_1 which were the uncertainty associated with the slope of the regression line for the stability at room temperature for 18 months times the respective Student’s t-factor. Hence, the instability of the material was insignificant at the study temperature over the study period. To avoid any possible degradation, samples should be kept at or below 20 ºC. The short-term statistical results shown in Table 2 indicated that the instability of the material was insignificant at the study temperature (40°C) over 4 weeks. The sample is shipped with cooling elements or on dry ice to avoid any possible degradation.

Table 2 Summary of stability study results

Descriptions	*Long-term*	*Short-term*
Storing conditions	20±2ºC for 1,3,6,9,12,18months	40ºC for 7, 14, 28 days
Mean ($\bar{y}$)	0.298 mg/kg	0.300mg/kg
Slope of the regression line (β_1)	0.00053	0.00036
Intercept of the regression line (β_0)	0.296	0.295
Variance of the points (s^2)	0.000045	0.000012
Standard deviation of the points (s)	0.00672	0.003405
Uncertainty associated with slope [$s(\beta_1)$]	0.000638	0.000164
Student’s *t*-test ($t_{0.95, n-2}$)	2.78	4.30
Critical value of β_1 [$t_{0.95, n-2} \times s(\beta_1)$]	0.00178	0.00071

3.4 Participants instruction

Participants received two bottles of the study material, each bottle containing about 15 g of milk powder. Participants are requested to determine the mass fractions (in mg/kg) of melamine on a dry mass basis in one of the bottles using their preferred methods. The other bottle could be used for their method development. A minimum sample size of 1.0 g for testing is recommended.

For the dry mass correction, participants should follow the protocol for determination of moisture content:

i. A minimum of three separate portions (recommended size of 1 g each) of the sample should be taken.
ii. Place the portions over anhydrous calcium sulphate in a desiccator at room temperature for a minimum of 7 days.
iii. Weigh the samples until a constant mass is reached.
iv. Perform moisture determination at the same time as the test sample portions are to be analyzed.

4 Sample distribution and results submission

Seven NMIs/ DIs participated in CCQM-K103. Two bottles of sample each containing about 15 g of the milk powder with dry ice in a foam box were sent to each participant via couriers at 20 July 2012. Relevant documents, including Technical Protocol, Sample Receipt Form, Result Report Form and Type C 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 26 July 2012 except VNIIM which received the samples at 23 October 2012 due to the customs problems. The Table 3 showed the detailed information of the study schedule.

The participants were requested to report the following data in the Data Report Sheet provided to the organisers by email to lixq@nim.ac.cn. The detailed submission date can be seen in the Table 3.

1. For one bottle sample, the dry mass fraction of melamine in the milk powder in mg/kg as analyte content in milk powder and the overall, combined result for the bottle should be reported with the standard uncertainty, u_c, and the expanded uncertainty, U.

2. Outline of analytical method (including extraction methods, post-extraction clean-up method, transformation procedures, analytical instrumental details, measurement equation).
3. A full uncertainty budget.
4. For calibrant materials used: source(s), purity, information of who assigned the purity value and methods used to assess.
5. In addition, for this type C core competency key comparison, participants were also requested to analyze their competency underpinning the measurement and the completed type C competency template to the organizers.

Table 3 Study schedule

NMI/DI	Abbreviation	Sample Dispatching Date (2012)	Sample Receipt of Date (2012)	Result Submission Date (2012)
Chemical Metrology Laboratory General Chemical State Laboratory–Hellenic Metrology Institute, (Greece)	EXHM	20 July	26 July	19 October
State Research Institute Center for Physical Sciences and Technology (Lithuania)	FTMC	20 July	/	24 October
Government Laboratory Hong Kong	GLHK	20 July	25 July	20 October
National Metrology Institute of South Africa	NMISA	20 July	26 July	20 October
National Institute of Metrology (Thailand)	NIMT	20 July	26 July	20 October
National Institute of Metrology (China)	NIM	/	26 July	19 October
D.I. Mendeleyev Research Institute for Metrology (Russia)	VNIIM	20 July	23 October	31 October

5 Reference materials used by the participating laboratories

The calibration standards and the internal standards used by the participants are given in Table 4. EXHM, NMISA and NIM used the certified reference materials supplied by NIM as calibrant. GLHK, NIMT and VIINM assigned the purity of calibrant in-house. FTMC did not carry out any in-house assessment of the commercial calibrant which they used when they submitted the results. $^{13}C_3$-labeled melamine and $^{13}C_3$, $^{15}N_3$-labeled melamine were used as internal standard by participants.

Table 4 Summary of reference standards, purity assessments and internal standards materials used by the participants

NMI/DI	Source of calibrant	Purity %	Methods used for purity assessment	Internal standard
EXHM (Greece)	NIM GBW 10058	99.6 ± 0.5 (k=2)	/	$^{13}C_3$-labeled melamine and $^{13}C_3$,$^{15}N_3$-labeled melamine
FTMC (Lithuania)	Merck	>99	Not provided	$^{13}C_3$,$^{15}N_3$-labeled melamine
GLHK (Hong Kong)	Purity assessed by in house purity assessment by GLHK.	99.8 ± 0.5	HPLC, KFT, Headspace GC/MS, ICP-MS	$^{13}C_3$ $^{15}N_3$-labeled melamine
NMISA (South Africa)	NIM GBW 10058	99.6 ± 0.5 (k=2)	/	$^{13}C_3$ $^{15}N_3$-labeled melamine
NIMT (Thailand)	Accu Standard, Inc., USA	99.55 ± 0.065	HPLC-UV, TGA, KFT	$^{13}C_3$ $^{15}N_3$-labeled melamine
NIM (China)	NIM GBW 10058	99.6 ± 0.5 (k=2)	/	$^{13}C_3$-labeled melamine
VIINM (Russia)	Melamine obtained from BASF	99.8±0.5	LC-UV, GC/MS, LC/MS, KFT, GC/MS with thermodesorbtion ,ICP-MS	$^{13}C_3$ $^{15}N_3$-labeled melamine

6 Methods used by the participating laboratories

The participating laboratories were encouraged to use methods of their own choice. The details of sample preparation and measurement are summarized in Table 5 and Table 6, respectively. The full method reported by participants is given in Appendix I. All laboratories used IDMS (isotope dilution mass spectrometry) technique with $^{13}C_3$-labeled melamine and $^{13}C_3$,$^{15}N_3$-labeled melamine as internal standard. Different sample preparation techniques were applied. Extraction solvents were mainly the different combination of acetonitrile, water, 0.04 N HCl solution, diethylamine, formic acid, trichloroacetic acid. Melamine was extracted by vortex, sonication, shaking and centrifugation and the duration was from 10 minutes to 5 hours. For clean-up procedures, all laboratories applied cationic solid phase extraction (SPE). EXHM, NMISA, NIM, GLHK, NIMT, VIINM and FTMC used the LC/MSMS technique; all of them used positive electrospray as ionization technique. FTMC used the GC-HRMS technique, also in the positive ion mode. NIM and VIINM applied single-point calibration in their quantification and the others quantified the level of melamine by using bracketing calibration. All of the participants followed the suggested protocol for moisture determination.

Table 5 Summary of sample preparation methods used by the participants

NMI/DI	**m_{Sample}**	**Extraction Solvent(s)**	**Extraction method(s)**	**Clean-up method(s)**
EXHM (Greece)	1 g	Hydrochloric acid (HCl) 0.04 N solution	vortexed, sonicated, the mixing procedure was repeated once more, Centrifuged	SPE (Supelco Discovery DSC SCX, 500 mg/6 mL) eluted with 5 mL 5% NH_3 in MeOH
FTMC (Lithuania)	0.5 g	Water/formic acid (99:1, v/v)	sonicated, shaked, centrifuged	SPE (ISOLUTE SCX) eluates dried under nitrogen stream; dried extracts were dissolved and derivatised to the tris-TMS derivatives with 100μL MSTFA/TMCS (99/1, v/v) for 15 min at 80°C.
GLHK (Hong Kong)	1 g	Diethylamine/ acetonitrile/water mixture (10:40:50 v/v)	vortexed , sonicated , shaked	SPE (MCX) eluted with 5 mL of 4% (v/v) ammoniacal methanol
NMISA (South Africa)	1.0 g	Acetonitrile/water (50:50, v/v)	shaked, centrifuged	SPE (MCX（6cc,150mg）) eluted with 4 mL 2% diethylamine in acetonitrile
NIMT (Thailand)	1 g	Acetonitrile/ water(50:50, v/v) /2.5 % formic acid (4:4:0.5, v/v)	shaked, centrifuged, perform the second extraction with 8 mL of 50 % acetonitrile and shaked, centrifuged;	SPE (Oasis MCX (6cc, 150 mg)) eluted with 8 mL of 4 % NH_4OH in methanol
NIM (China)	1 g	5%trichloroacetic acid/acetonitrile（70:30, v/v）	vortexed，sonicated，shaked . centrifuged	SPE (MCX（6cc, 150mg）) eluted with 5 mL of 5% ammoniacal methanol
VIINM (Russia)	1 g	Water/acetonitrile (50:50)	sonicated	SPE SCX

Table 6 Summary of analytical methods used by the participants

NMI/DI	**Instrument(s)**	**Column(s)**	**Quantitative method**	**Type of calibration**
EXHM (Greece)	TSQ Quantum Ultra AM Mass Spectrometer (Finnigan)	Ascentis Express HILIC (100 x 2.1 mm, 2.7 μm)	**LC-IDMS** melamine,127→85,68,43 ; $^{13}C_3$ melamine, 130→87, 70, 44; $^{13}C_3$, $^{15}N_3$ melamine, 133→89, 72, 45	Bracketing
FTMC (Lithuania)	Agilent GC6890N with Waters/ Micromass Autospec Premier HRMS	Agilent DB_5-MS (30m x 0.25 mm x 0.25 μm)	**GC-IDMS** (in SIR mode) m/z 342 melamine-tris-TMS; m/z 348 ^{13}C-^{15}N- melamine-tris-TMS	Bracketing
GLHK (Hong Kong)	LC/MS/MS(API 4000 QTRAP)	Supelcosil LC-NH2, (250 x 3mm,. 5μm)	**LC-IDMS** melamine,127 → 85, 68, 43; $^{13}C_3{}^{15}N_3$melamine, 133 → 89, 71, 45	Bracketing
NMISA (South Africa)	Waters Acquity UPLC with Quattro Premier XE MS/MS	Acquity UPLC® BEH HILIC (1.7 μm, 2.1 x 100 mm)	**LC-IDMS** melamine,126.9→ 84.8, $^{13}C_3{}^{15}N_3$ melamine,132.95→88.9, 45.0	Bracketing
NIMT (Thailand)	Shimadzu LC with ABI 4000 MS/MS	SeQuant ZIC_HILIC (3.5 μ m, 200A, 100x2.1 mm)	**LC-IDMS** melamine, 127.1 → 85.1, 68.1; $^{13}C_3{}^{15}N_3$ melamine, 133.1→89.1, 71.1	Bracketing
NIM (China)	Applied Biosystems series 5000 LC-MS/MS	Capcell PAK CR (2.0*150mm, 5 μ m)	**LC-IDMS** melamine, 127→85, 68; $^{13}C_3$melamine, 130→ 87, 7	Single-point
VIINM (Russia)	LC-MS/MS Agilent Triple Quard 6460	Eclipce Plus C18 (2.1 x 100mm, 3.5μm)	**LC-IDMS** melamine, 127 → 85 , 68, 43; $^{13}C_3{}^{15}N_3$ melamine, 133→89, 72, 45	Single-point

7 Results reported by participating laboratories

The results reported by participating laboratories are summarized in Table 7 and the summary plots are given in Figures 2. For K103, seven results spread from 0.173 mg/kg to 0.315 mg/kg and only one of the results is below 0.2 mg/kg.

Table 7 Summary of K103 results

NMI/DI	Mass fraction (mg/kg) (on dry mass basis)	Combined standard uncertainty (mg/kg)	Coverage factor (*k*)	Expanded uncertainty (mg/kg)	Moisture Content (%, w/w)	sample No.
EXHM (Greece)	0.284	0.005	2.31	0.012	2.01	SA155
FTMC (Lithuania)	0.173	0.016	2	0.032	2.14	SA200
GLHK (Hong Kong)	0.302	0.012	2	0.023	2.35	SA159
NMISA (South Africa)	0.266	0.0085	2	0.017	1.5	SA130
NIMT (Thailand)	0.273	0.0071	2.08	0.015	1.87	SA107
NIM (China)	0.287	0.010	2	0.020	2.50	SA127
VNIIM (Russia)	0.315	0.009	2	0.018	1.22	SA150

8 Approaches to uncertainty estimation

The relative standard uncertainties of the results and the major contributions in the uncertainty budgets are summarized in Table 8. The full uncertainty evaluation reported by participants is given in Appendix II.

Table 8 Summary of relative standard uncertainty of participants and the factors contributed in their uncertainty budget

NMI/DI	Standard uncertainty u	*k*	Expanded uncertainty U	Considered contributions to measurement uncertainty budget
EXHM (Greece)	1.8% 0.005mg/kg	2.31	4.2% 0.012mg/kg	(i) Method precision (ii) Mass fraction of melamine in the calibration solution (iii) Sample moisture content (iv) Mass of ^{13}C3-melamine solution added to sample blend (v) Mass of test material in sample blend (vi) Mass of melamine solution added to calibration blend (vii) Mass of ^{13}C3-melamine solution added to calibration blend (viii) Measured peak area ratio of the selected ions in the sample blend (ix) Measured peak area ratio of the selected ions in the calibration blend
FTMC (Lithuania)	9.2% 0.016mg/kg	2	18.5% 0.032mg/kg	(i) The preparation and purity of the two reference solutions and the bias of the mass determinations (ii) The determination of the intermediate precision.

NMISA (South Africa)	3.2% 0.0085mg/kg	2	6.4% 0.017mg/kg	(i) MEL_{CRM} solution added to calibration blend (ii) Mass MEL_{CRM} solution added to calibration blend (iii) Mass of melamine isotope solution added to sample blend (iv) Mass of melamine isotope solution added to calibration blend (v) Mass of milk powder sample (vi) Ratio of peaks areas of MEL/ISO MEL in the sample blends (vii) Ratio of peaks areas of MEL CRM/ ISO MEL in the calibration blends (viii) ESDM of independent repeat measurements (n=8)
NIMT （Thailand)	2.6% 0.0071mg/kg	2.08	5.5% 0.015mg/kg	(i) The mass fraction of analyte in the calibration (ii) The masses (iii) The precision factor (iv) The interference effect (v) The extraction efficiency factor (vi) The dry mass correction factor
NIM (China)	3.5% 0.010mg/kg	2	7.0% 0.020mg/kg	(i) Method Precision (ii) Calibrant solution (iii) Weight of sample taken for analysis (iv) Weight of $^{13}C_3$- melamine solution spiked into sample taken for analysis (v) Moisture Content
GLHK (Hong Kong)	3.9% 0.012mg/kg	2	7.7% 0.023mg/kg	(i) Precision (ii) Method recovery (iii) Sample Recovery (iv) Purity of calibrant (v) Moisture Content (vi) R: isotope amount ratio
VIINM (Russia)	2.8% 0.009 mg/kg	2	5.7% 0.018 mg/kg	(i) Mass of sample (m) (ii) Mass of internal standard added to sample before extraction (m IS) (iii) Response factor (F) (iv) RSD of results, %

9 Key comparison reference value (KCRV) calculation

The criteria of OAWG to cover the results in the calculation of the KCRV included the use of a method that had been verified as appropriate for the measurand and of higher metrological order, and the use of a primary standard with a metrological traceable assigned purity – that means, either a Certified Reference Material from an NMI or Di with demonstrated capability or a material the purity of which has been suitably assessed by the reporting participant. For melamine, the seven results spread from 0.173 mg/kg to 0.315 mg/kg. Seven results were principally available for the KCRV calculation. Data from FTMC were not included since the laboratory did not provide metrological traceable results (lack of reference material characterization). As a result, six sets of valid results were used for the estimation of the KCRV for melamine (Table 9).

Table 9 Results of provisional KCRV and the associated uncertainties calculated by different approaches.

KCRV-1	***Arithmetic Mean***	**0.288 mg/kg**
	Standard deviation (SD)	0.018 mg/kg
	Standard uncertainty(u) ($= \frac{\mathbf{SD}}{\sqrt{\mathbf{N}}}$)	0.0074 mg/kg
KCRV-2	***Median***	**0.286 mg/kg**
	MADe	0.021 mg/kg
	Standard uncertainty($= 1.25 \times \frac{\mathbf{MADe}}{\sqrt{\mathbf{N}}}$)	0.011 mg/kg

No. of data used (N=6)

Considering no significant difference among the calculated KCRV results from the two different approaches, the piloting institutes, NIM and GLHK 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 KCRV calculated as the median of the six remaining values was 0.286 mg/kg, the standard uncertainty of the median as 0.011 mg/kg (3.8 %). The k-factor for the estimation of the expanded uncertainty was chosen as k = 2.57 (t (0.05;5)), since the very limited number of employable results (results of six laboratories, i.e. degrees of freedom=5) and their distribution should be considered adequately. Thus the expanded uncertainty of the KCRV is 0.028 mg/kg (9.8%).

The participants data (see table 7) and the values of KCRV and the standard uncertainty of the KCRV are summarized in Figure 2 (blue lines denoting the KCRV and KCRV ± KCRV standard uncertainty values).

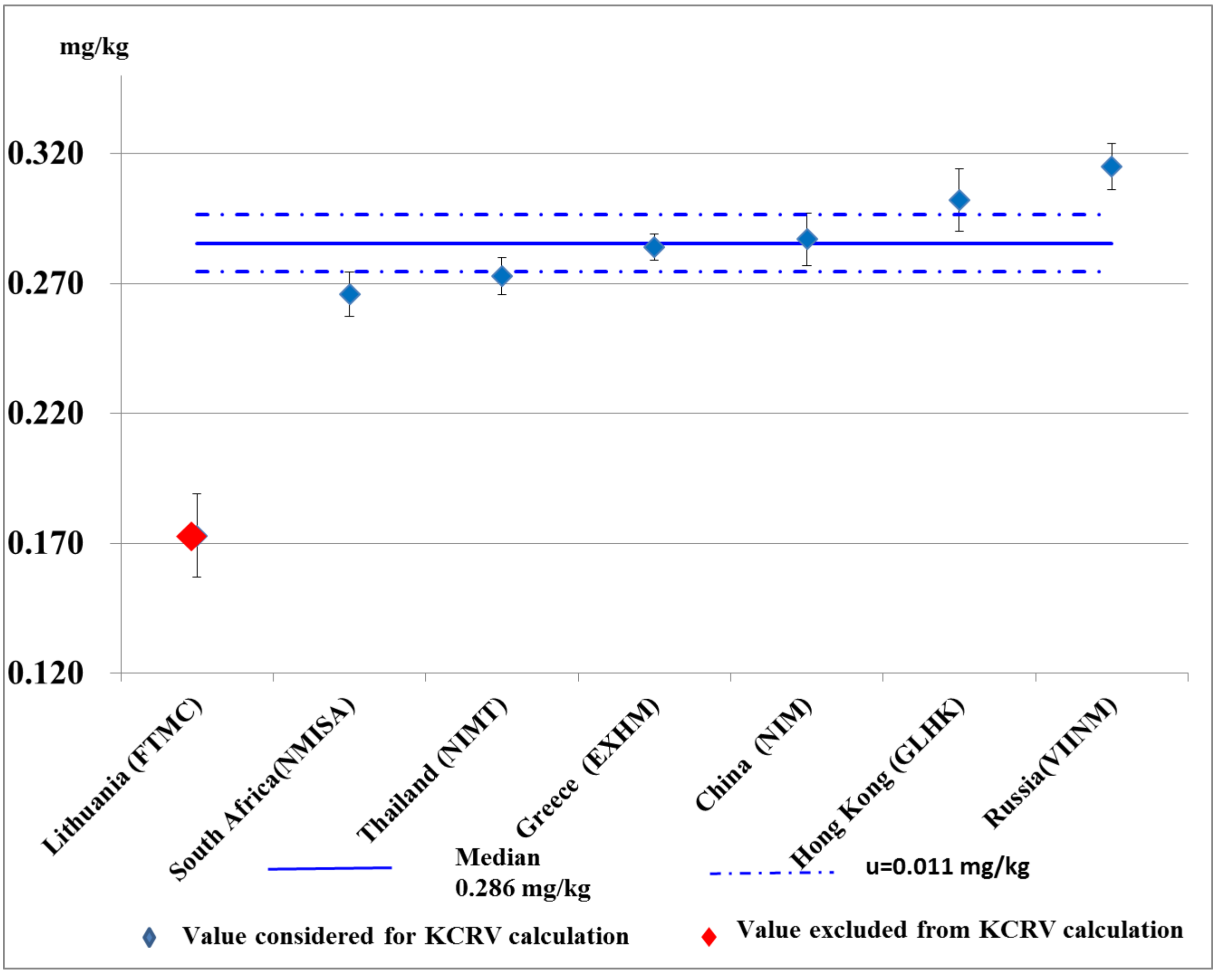


Figure 2 CCQM-K103: KCRV for melamine and its standard uncertainty with participants' results and the associated reported standard uncertainties.

10 Degree of equivalence (DoE) calculation

The DoE for NMIs has a value component and an uncertainty component. The DoE and its uncertainty between an NMI result and the KCRV has been calculated within CCQM according to the following equations:

i. The value component is $D_i = X_i - X_{ref}$

Where,

D_i is the degree of equivalence between the NMI result $\mathrm{X_i}$ and the KCRV $\mathrm{X_{ref}}$.

The best possible D_i is zero, when the result is identical to $\mathrm{X_{ref}}$.

$\mathrm{X_i}$ is the reported result of participant i; $\mathrm{X_{ref}}$ is the proposed KCRV value.

ii. The expanded uncertainty component is $U(D_i) = k * \mathrm{u}(Di)$

Where,

The expanded uncertainty $U(D_i)$ is calculated by combining the expanded uncertainties $k_i\mathrm{u_i}$ of X_i and $k_{ref}\,\mathrm{u_{ref}}$ of X_i as $U(D_i) = [(k_i^2\mathrm{u_i}^2 + k_{ref}^2\,\mathrm{u_{ref}}^2)]^{1/2}$,

k_{ref}, $\mathrm{u_{ref}}$ was under point 9 as described (k_{ref} = 2.57, $\mathrm{u_{ref}}$ = 0.011mg/kg) and k_i, $\mathrm{u_i}$ as reported by the participating laboratories.

Table 10, Figures 3a and 3b gives the absolute D_i and the relative D_i with uncertainty ranges (with the corresponding uncertainty U_i calculated as described above).

Table 10 Degrees of equivalence [D_i] and their expanded uncertainties [$U(D_i)$]

	melamine				
	D_i		$U(D_i)$		$\frac{D_i}{U(D_i)}$
laboratory	**(mg/kg)**	**(%)**	**(mg/kg)**	**(%)**	
Greece (EXHM)	-0.002	-0.7	0.021	7.4	-0.10
Lithuania (FTMC)	-0.113	-39.5	0.037	12.8	-3.09
Hong Kong (GLHK)	0.016	5.6	0.030	10.4	0.54
South Africa(NMISA)	-0.02	-7.0	0.024	8.6	-0.82
Thailand (NIMT)	-0.013	-4.5	0.023	8.0	-0.57
China (NIM)	0.001	0.3	0.027	9.3	0.04
Russia(VNIIM)	0.029	10.1	0.025	8.8	1.15

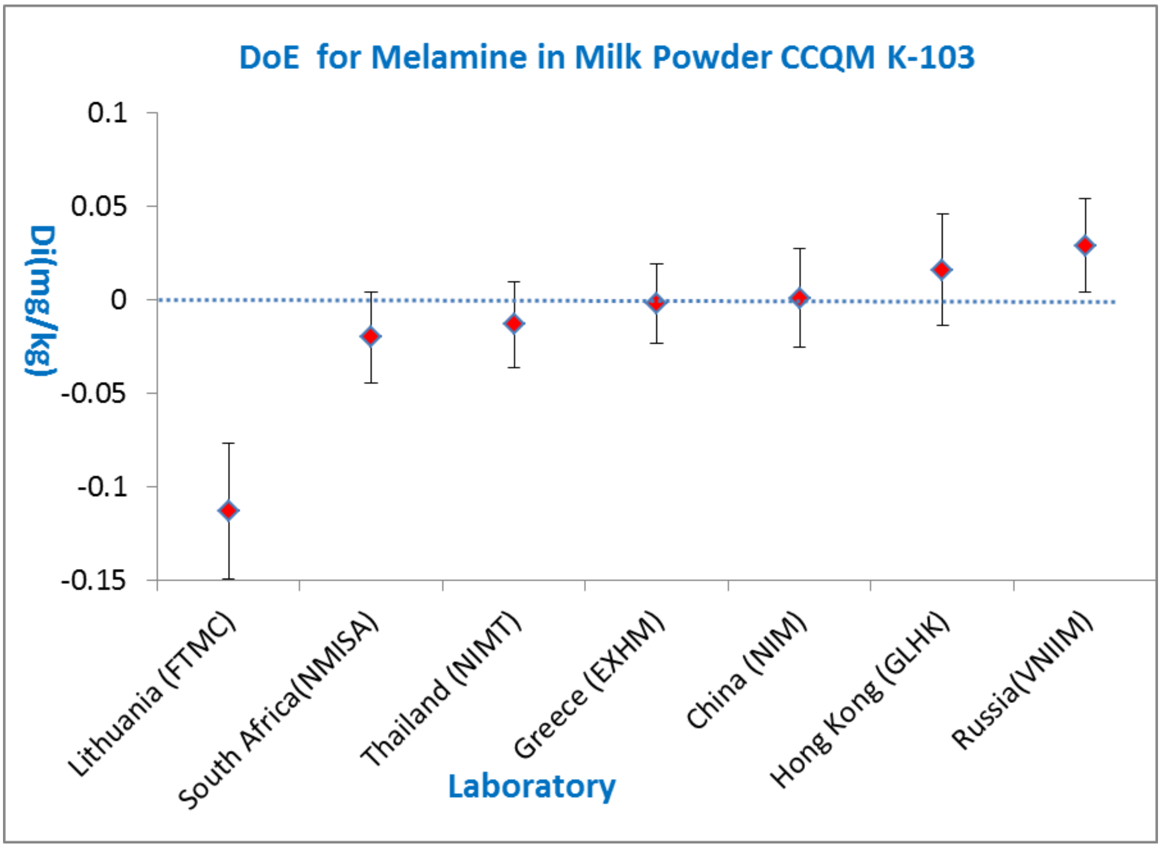


Figure 3a CCQM-K103: Plot of degrees of equivalence [D_i] (mg/kg) of melamine using the median as KCRV and their expanded uncertainties [$U(D_i)$].

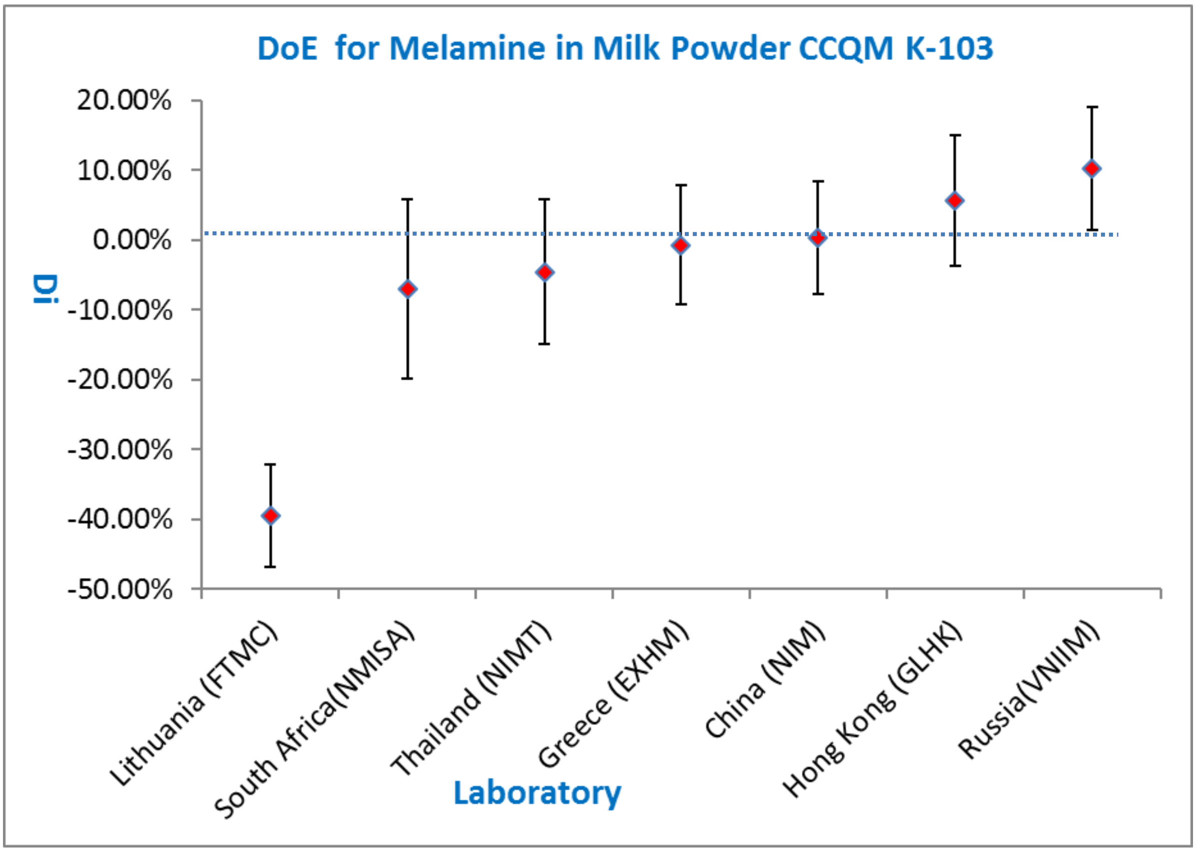


Figure 3b CCQM-K103: Plot of degrees of equivalence [D_i] (%) of melamine using the median as KCRV and their expanded uncertainties [$U(D_i)$].

11 Core competency and how far does the light shine?

This study was intended to demonstrate the capability of NMIs/DIs to analyse traces of melamine in milk and milk powder at concentration levels resulting from legal requirements for food safety. Additionally the quality of this kind of analysis with respect to compliance with legal requirements for food control methods and the international comparability of measurements should be evaluated.

More generally, participants have described the details of the competencies underpinned for the measurand based on their specific approach/techniques, which are listed in the Type C Competency Template. The complete core competency tables reported by participants are given in Appendix III.

Comments on “How far does the light shine?”

The OAWG key comparison for this measurement will assist in ensuring the comparability of reference measurement procedures, as well as to support the CMC claims of NMIs/DIs in this measurement field.

Participation in this key comparison can demonstrate the capability to apply IDMS in determining mass fractions in the range from 0.1 to 5.0 mg/kg of analytes with low molar mass (range 50-300 Da) with high polarity (pK_{ow} > -2.0) in milk and milk products. Extension to other analytes and matrices should be applied with care since there is a close linkage to other relevant parameters as e.g. sample preparation procedures (liquid/liquid extraction, SPE clean-up) and analytical separation techniques (e.g., GC-MS, LC-MS/MS etc).

The AOAC food-matrix triangle is shown in Figure 4 for reference. This milk powder matrix would be expected to fall into segment “6” as a high protein relatively low fat material.

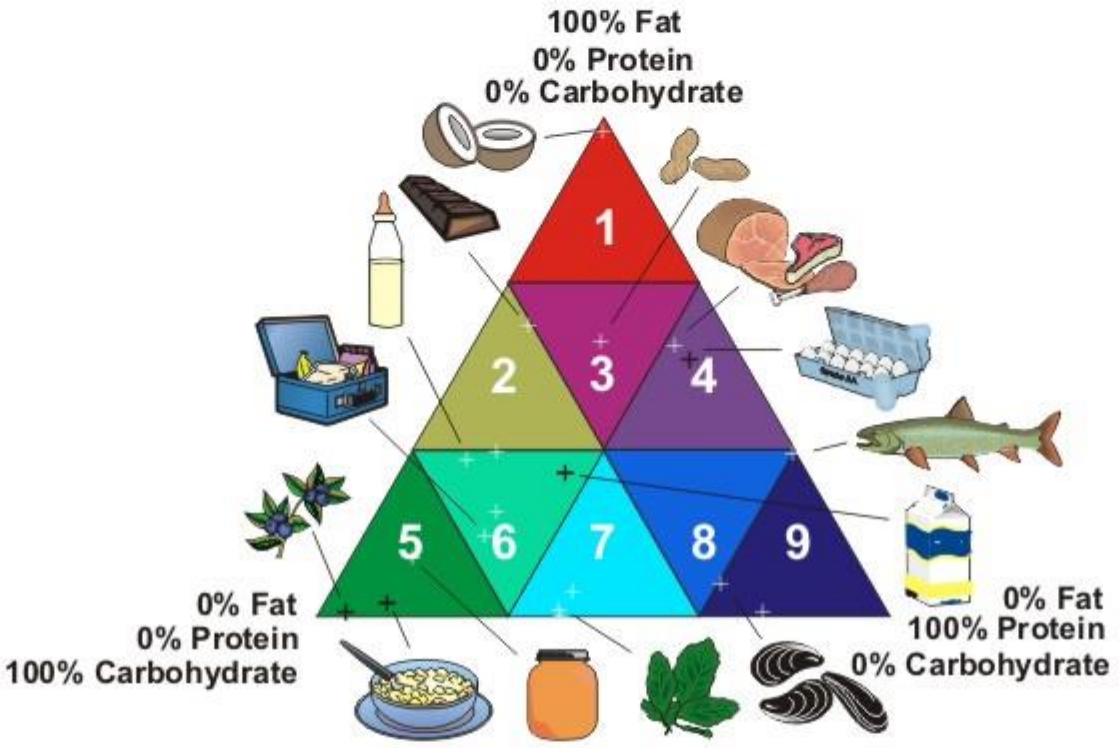


Figure 4 AOAC Food-matrix Triangle (by courtesy of NIST)

12 Summary and conclusions

Most of participants were able to quantitatively determine melamine residue levels around 0.28 mg/kg in milk powder. Although different sample preparation techniques (different pre-treatments, deproteinized steps, solvents) as well as different analytical techniques (LC-MSMS, GC-MS, different instruments, columns, eluents) were applied to detect melamine at a low concentration, a KCRV of 0.286 mg/kg with an expanded uncertainty of 0.028 mg/kg (k =2.57) were calculated. The result of the key comparison proved the capabilities of the participating laboratories could fulfill the legal requirements of quantitative methods for residue control in food, with highest precision and provided calibration and measurement services to residue control laboratories.

References:

[1] OAWG 10/10: CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version 6, 2010-03-01

[2] Draft CCRVDF Guidelines for the development of performance characteristics for multiresidue analysis of veterinary drug residues, March 2011; draft of electronic working group, 19th Session of CCVRDF, Burlington Vermont, USA, August 2010.

[3] CCQM KCRV WG: Data Evaluation Principles for CCQM Key Comparisons, 19 March 2008.

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