APMP-APLAC joint PT (APLAC T109)

Measurement of Cadmium in Milk Powder

（Coordinated by National Institute of Metrology, China NIM）

Technical Protocol

Introduction

Cadmium is a toxic heavy metal which pollutes the environment and do the people's health harm. It enters into the human body through gastrointestinal tract and air inhalation and causes a toxic injury for kidneys, bones, reproductive system. As well, it can affect the children's growth and development, especially intelligence development and has an evident carcinogenicity. Powdered milks are one of the most essential dairy products needed by growing children. It contains both the basic and additional requirement needed by children especially during their developmental years. It is also one of the most popular dairy products due to long shelf life and its employment in the manufacture of many dairy products such as ice cream, cheese, evaporated milk, condensed milk and infant milk formula. Milk powder may be contaminated by cadmium at certain levels that may cause a potential health hazards for humans. It needs a rigorous monitoring program to prevent food contamination by cadmium and to ensure that its level did not exceed the legal limits for human consumption.

APMP and APLAC organized some comparisons and PT about cadmium in food matrix such as rice, herb, seafood and tomato paste, and some comparisons about essential elements in milk powder, such as iodine, potassium and cooper. However, there is no comparison or PT for cadmium in milk powder matrix. Therefore, NIM proposed the APMP-APLAC joint PT "Cadmium in Milk Powder" in the APMP-APLAC jiont meeting in Da Nang, Vietnam in November 2016.

Study Material

The source of milk powder sample was infant formula with quantitative addition of cadmium. The lower heavy metal element background infant formula milk powder was dissolved in pure water with a certain amount of cadmium. After stirring and

mixing, liquid milk was dry by a spray dryer. The sample was thoroughly homogenized and packed into vacuum-sealed-plastic/aluminum foil double-layer bags and each containing 20g of milk powder.

Measurand
The measurand of this study is cadmium in milk powder

Nominal value
The concentration of cadmium in the milk powder sample is in the range of (0.05 – 0.5) mg/kg.

Homogeneity
The homogeneity of cadmium in the milk powder sample was tested by IDMS method after microwave digestion of samples, and the sampling weight is about 0.5g. 12 units were selected randomly from 200 units, and two replicates from one unit. The data were treated with an analysis of variance. The obtained between-bottle homogeneity standard deviation of cadmium was less than 1.0%. No statistically significant heterogeneity was found based on F test. Neither the heterogeneity affects the performance evaluation, i.e. $Ss < 0.3\,\sigma$.

Stability
The stability study of samples was performed. Samples were stored at 37ºC for 1, 2, 4 and 6 weeks with two units being analyzed at each time point. This study was designed to test the material stability under transportation conditions and storage condition. Three replicates were taken from each unit and analyzed using the ICP-MS method. So far the instability of the material was insignificant at the study temperature over the study period. At last, it will be made sure that the difference arising from stability will not affect the performance evaluation, i.e.

$$|\bar{(x)} - \bar{y}| < 0.3\sigma$$

Study Guidelines
At least six determinations for each package of the milk powder sample should be performed (if applicable); an average value from all determinations should be reported with the individual values.

For the determinations, aliquots of 0.5g ~ 1.0g should be taken. Participants are free to use any suitable method but please include a full description of the method of analysis when reporting the results. A full uncertainty budget should also be included in the report with the results, as indicated below. Results regarding the milk powder sample should be reported on a dry-mass basis. Sampling for the analysis should be carried out in parallel with sampling for the dry-mass correction.   The recommended protocol for moisture determination is given below and for this part of the comparison participants are requested to adhere to the protocol to ensure consistent data between laboratories.

The moisture content of the milk powder sample should be determined from at least two separate aliquots of sample with a sample mass of 0.5g ~1.0g. Each aliquot should be heated at (80 ± 2) °C in an oven for 2 h. The aliquot should then be cooled down to room temperature in a desiccator and weighed. The procedure should be repeated with 2 h heating cycles until a constant mass is reached (difference between two consecutive values ≤ 0.0005 g). The overall drying time should be reported with the moisture content.

Reporting and Submission of Results

At the time of sample dispatch, a sample receipt form will be provided electronically to all participants and must be filled in and returned to the study coordinator on receipt of the shipments. The results reporting form will be provided to each participant and must be completed and returned to the study coordinator before the submission deadline.

A summary report table will be sent to the participants by email while the samples are dispatched. Participants should complete the result report table. The instructions on the manner of reporting test results are as follows:

➢ Units of measurement: Report the mass fractions of the analytes and associated uncertainties in mg/kg;

➢ Number of significant figures: Report the test results to 3 significant figures;

➢ Reporting basis: Report the test results on "dry-mass basis";

➢ The mean value of at least six independent measurements;

➢ Participants should provide information about methods of analysis.

➢ Each laboratory should make an assessment of the experimental uncertainty according to ISO principles (Guide to the Expression of Uncertainty in Measurement, ISO). The expanded uncertainty of the mean value and the coverage factor (which gives a level of confidence of approximately 95 %) should be reported. Each variable contributing to the uncertainty of the result should be identified and quantified in order to be included in the combined standard uncertainty of the result. A full uncertainty budget must be included in the report. Contributions to the overall uncertainty will arise from the repeatability of the sample preparation, the repeatability of instrumental determination, determination of masses and volumes, concentration of primary and internal standards, and any other parameter specific to each method of analysis chosen by the participant.

Evaluation of Results

The performance of the participating laboratories will be assessed using z-score, which is calculated as follows:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}}$$

Where x_i : the participant's result

x_{pt} : the assigned value*

σ_{pt} : the standard deviation for proficiency assessment estimated from the Horwitz equation

* Note: The IDMS method result from NIM be used as the assigned values for evaluating the performance of participants of this PT based on the CMCs claimed on Cadmium in Milk Powder. This is in accordance with the ISO/IEC 17043 recommendations on the determination of assigned values for proficiency testing schemes.

z-score is commonly interpreted as:
  (i) $|z| \leqslant 2.0$ Satisfactory
  (ii) $2.0 < |z| < 3.0$ Questionable
  (iii) $|z| \geqslant 3.0$ Unsatisfactory

Laboratories having a $|z|$ score equal to or larger than 3.0 shall thoroughly investigate their results for the discrepancy and those having a z-score in the range $2.0 < |z| < 3.0$ are also encouraged to review their results.

For reference purpose, the performance of the participating laboratories will be assessed using zeta-score (ζ), which is calculated as follows:

$$\zeta_i = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}}$$

Where x_i:the participant's result
        x_{pt}:the assigned value (KCRV)
        $u_{(xi)}$:the participant's own estimate of the standard uncertainty of its result x_i.
        $u_{(xpt)}$:the standard uncertainty of the assigned value x_{pt}

ζ-scores are interpreted as in the same way as z-scores using the same critical values of 2.0 and 3.0. ζ-scores may be used in conjunction with z-scores, as an aid for improving the performance of laboratories as follows. If a laboratory obtains $|z|$ scores that exceed 3.0, they may find it of value to examine their test procedure step by step and derive an uncertainty budget for that procedure. The uncertainty budget will identify the steps in the procedure where the largest uncertainties arise, so that the laboratory can see where to expend effort to achieve an improvement. If their $|\zeta|$ scores also exceed the critical value of 3.0, it implies that their uncertainty budget does not include all significant sources of uncertainty. Laboratories are encouraged to review their uncertainty budget.

Confidentiality
The proficiency testing programme is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of the proficiency testing programme.

The concerned parties (APMP, APLAC and NIM) strive to maintain strict confidentiality with respect to composition of the proficiency test samples distributed and the performance of all participating laboratories. To preserve the confidentiality, participants receive report(s) giving all results for assessment but without identifying individual laboratories.

In general, all information on participant performance shall not be disclosed to any third party unless prior agreement with the concerned participants has been obtained or applicable laws or regulations stipulate such disclosure. NIM, the proficiency testing provider for this proficiency testing programme, shall also take into consideration local regulatory requirements for the disclosure of confidential information. NIM may disclose any relevant information to China National Accreditation Service for accreditation purposes, with the consent/agreement obtained from participating laboratories through completion of the Registration Form/Sample Receipt Form / Result Table for this proficiency testing programme.

Invitation and selection of participants

APLAC members and APMP Developing Economies' Committee (APMP DEC) members will be invited to participate in this program. Once this proposal is approved by the APLAC Proficiency Testing Committee, invitations will be sent to all APLAC members through their accreditation bodies, and to APMP DEC members by both APMP DEC and TCQM Chairs.

Total number of participants for this Joint PT programme will be 100.
Laboratories nominated by the APMP DEC are about 15.
Laboratories nominated by APLAC accreditation bodies and non-APLAC accreditation bodies are about 85.

Time schedule
- Calling for participation: March 2018
- Deadline for registration: 30th April 2018
- Sample distribution from NIM: June 2018
- Deadline for reporting August 1, 2018
- Discussing the result: APMP-APLAC Meeting, 2018
- The draft final report: March 2019

Contact information
The APMP-APLAC joint PT coordinated by National Institute of Metrology, China

For enquiries, participants may wish to make contacts as follows:

WEI Chao, NIM, weichao@nim.ac.cn

Li Xiao, NIM, lixiao@nim.ac.cn