DIRECT MERCURY DETERMINATION: A "TOOL" TO THOROUGHLY INVESTIGATE THE HOMOGENEITY OF PROFICIENCY TEST MATERIALS

M. Ciprotti, A. Colabucci, A.C. Turco, M. Di Gregorio, A. Sorbo, M. D'Amato, G. Fornari Luswergh and L. Ciaralli

European Union Reference Laboratory for Chemical Elements in Food of Animal Origin (EURL-CEFAO),
Dept. of Food Safety, Nutrition and Veterinary Public Health, Istituto Superiore di Sanità, Rome, Italy

maria.ciprotti@iss.it

INTRODUCTION

Homogeneity of Proficiency Testing (PT) items is one of the fundamental requirements that a PT provider cannot disregard. In fact, inhomogeneity of samples can lead to false warnings to be avoided in order to guarantee that the performances of participants are not affected by the quality of the PT samples. The minimum amount of sample on which the homogeneity tests have to be carried out should be consistent with the physical form (fresh/frozen or freeze-dried) and representative of the entire PT material.

MATERIALS AND METHODS

The direct mercury determination (DMD) is a sensitive technique not requiring any sample pre-treatment and using very small sample intakes. An in-house validated method based on this technique was employed to demonstrate the homogeneity of EURL-CEFAO PTs leftover materials with sample amounts as small as 10 mg for freeze-dried samples and 50 mg for fresh/frozen ones.
The PT materials were either incurred, spiked with standard solutions or mix of different samples of the same matrix.
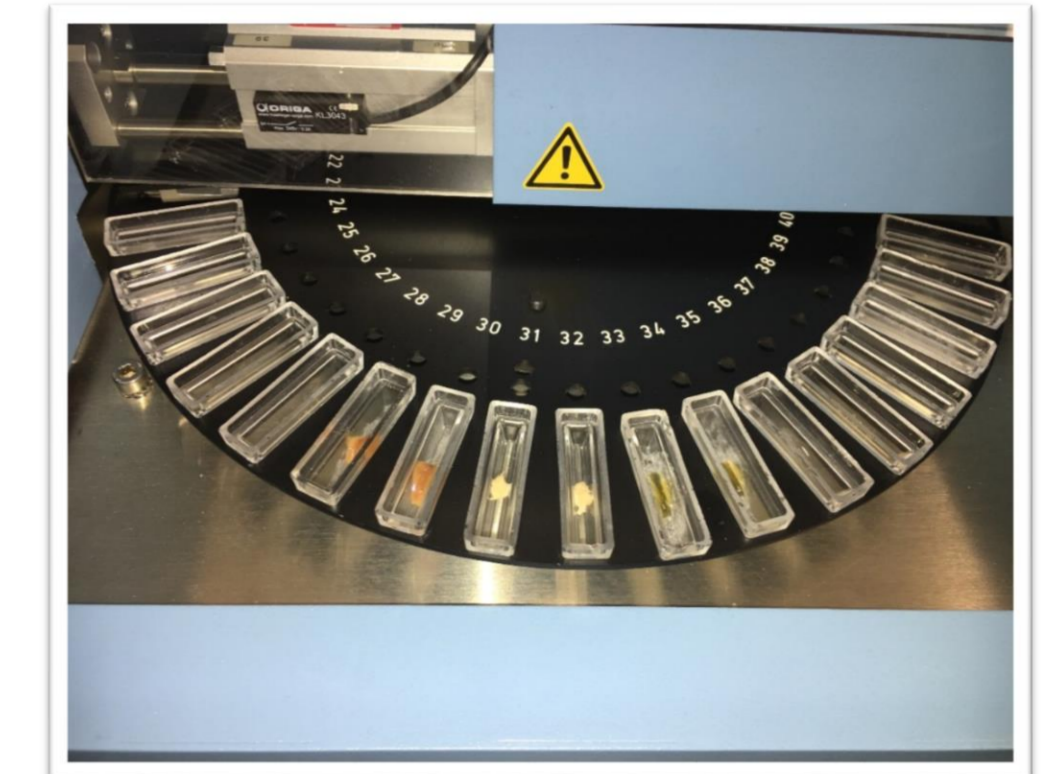
HOMOGENEITY EVALUATION

For all samples (tab 1), the homogeneity was estimated by analysing 10 samples in duplicate and evaluated through the σ_{pt} based on the equations developed by the EURL-CEFAO. The criterion on the precision of the analytical method was fulfilled as the ratio between the analytical standard deviation (s_{an}) and the σ_{pt} were lower than 0.5 ($s_{an}/\sigma_{pt} < 0.5$) meaning that the analytical method used had a repeatability adequate to detect any significant inhomogeneity at the applied σ_{pt}. In addition, the sampling variance satisfied the relation $s^2_{sam} < c$ where c is the critical value for the statistical test and depends both on the allowed sampling variance and the analytical variance.

Table 1. Results of the test for sufficient homogeneity: grand mean is in µg/kg, σ_{pt} is the standard deviation for proficiency assessment based on the EURL-CEFAO equation in µg/kg, s^2_{an} is the analytical variance, s^2_{sam} is the sampling variance and c is the critical value for the test.

	11th PT	14th PT	18h PT	20h PT	21st PT	23rd PT	24th PT	26th PT	27th PT
Matrix	Hake and swordfish	Pangasius and swordfish	Spiked Veal meat	Spiked veal kidney	Incurred Mussels	Pangasius and swordfish	Wildflower honey	Spiked Veal meat	Spiked Infant formula
Physical form	Freeze-dried	Frozen	Frozen	Frozen	Freeze-dried	Freeze-dried	Liquid	Freeze-dried	Freeze-dried
Grand Mean	753	222	9.3	22	33	439	14.4	12.2	5.7
σ_{pt}	79	24	1.1	2.7	5.5	46	1.9	2.2	1.00
s^2_{an}	101	61	0.1	0.2	1.2	103	0.2	0.5	0.14
s_{an}/σ_{pt}	0.13	0.33	0.28	0.18	0.2	0.22	0.25	0.31	0.36
$s_{an}/\sigma_{pt} < 0.5$	YES	YES	YES	YES	YES	YES	YES	YES	YES
s^2_{sam}	0[a]	0[a]	0[a]	0.09	0.03	0[a]	0.10	0.21	0[a]
c	1158	157	0.3	1.4	6.3	466	0.8	1.3	0.32
$s^2_{sam} < c$	YES	YES	YES	YES	YES	YES	YES	YES	YES

[a] According to the International Harmonized Protocol, s^2_{sam} is assumed to be equal to zero if its estimate from the equation is negative.

RESULTS AND CONCLUSIONS

Leftover materials of EURL-CEFAO PTs were analyzed to verify their homogeneity even when small amounts are concerned. To this aim, mercury was used as clue element employing the DMD technique. The results of all the matrices investigated (meat, offal, infant formula, fish and honey) show that the sufficient homogeneity of incurred as well as mixed and/or spiked EURL-CEFAO PT samples can be still demonstrated when 10 mg for freeze-dried samples and 50 mg for fresh/frozen ones are considered.
This is particularly remarkable, considering that the standard deviations for proficiency assessment used by the EURL to assess homogeneity are well below those derived from the Horwitz-Thompson equation commonly considered in food sector.

9th Workshop on Proficiency Testing in Analytical Chemistry, Microbiology and Laboratory Medicine - Portorož, Slovenia 9 – 12 October 2017

www.iss.it/lcdr