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[1]L V de Santana, [1]J E S Sarkis, [1]J C Ulrich and [1]M A Hortellani.

[1] Institute of energy and nuclear research-National (IPEN/CNEN-SP), Av. Professor Lineu Prestes 2242 05508-000 São Paulo, SP, Brazil

E-mail: santana-luciana@ig.com.br

Abstract: A proficiency-testing scheme concerning total mercury determination in fish tissue involved 10 laboratories as participants, who used their regular in-house analytical methods, and the assigned value and the standard deviation used in proficiency testing program was derived from calibration against the certified reference values of the CRMs. The majority of participants obtained satisfactory Z-scores, and laboratories that need to revise their procedures were singled out. The objective these exercises were makes a useful contribution towards the production of proficiency test in Brazil. The uncertainty expanded calculated for the reference material was 22%.

1. Introduction

Proficiency tests are inter-laboratory exercises and the results of the particular laboratory are compared with reference value or with the results obtained by other laboratories. A proficiency item test is required for the effective execution of these tests and it can be a sample product or device, reference material, equipment, a standard set of data or other information [1].

The statistical treatment data produced during an inter-laboratory exercise is the most useful for population analysis data and adds information on its statistical properties technical scrutiny enables discussion of the possible sources of disagreement between laboratories [1].

Nowadays there are not proficiency providers essay in Brazil for toxic metals such as mercury in fishes tissues. Furthermore, the production of the RM was explored by gamma irradiation process to maximize the shelf life of it. In additional it was examined the homogeneity and stability by atomic absorption spectrometry with hydride generation.

A proficiency pilot test quality assurance program was also successfully performed using this material. The developed RM candidate in this study has demonstrated its suitability for quality assurance in the analysis of the total arsenic in fish tissue [1, 2].

2. Methodology

The preparation of the reference material used in the proficiency test for determination of mercury in fish tissues followed the recommendations of ISO Guide 35: 2012 [3].

2.1. Study of homogeneity and stability
For the study of homogeneity were randomly assigned to ten sachets temperature of 23 ± 0.2 ° C. The statistical tool ANOVA was used to evaluate the possible heterogeneity of the sachets and the sachets inside, as described in ISO Guide 35 [3].
The stability study was performed with 16 randomly selected sachets for a period of 0, 7, 15, 30 and 45 days in 4 different temperatures ranges 5 ° C, 23 ° C, 40 ° C and 60 ° C using model isochronous. The evaluation results of the stability study of the material were performed by linear regression analysis [3].

3. Results and discussions

3.1 Homogeneity study and stability study and uncertainty of the assigned value
The characterization of a reference material is defined as the complete set of measurements, which establishes, as such, the property values, not necessarily their uncertainties. In this work the characterization results were obtained from a method of measuring single (FIA-CV-AAS) where each parameter was calculated by Excel spreadsheet, developed in the laboratory for the determination of mercury in fish (test accredited in CGCRE / INMETRO second ABNT: ISO / IEC 17025: 2005) [4, 5].
The homogeneity study was conducted within the sachet or between sachets to assess possible differences of concentration which can be displayed during the production stage [1, 2]. The Shapiro-Wilk test (W) was used to verify the results showed normal behavior at a significance level of 5%. (Wcalc.= 0.78 Wcrit.(0.05;5) = 0.762).
The ANOVA evaluates the value of the result $F_{critical}$ and $F_{calculated}$ for a confidence level of 95%,
The stability study was performed in different temperature ranges (5-60 °C) for a period of 0-45 days using an isochronous model. The results were submitted to Grubbs test for the presence of outliers and were then submitted to linear regression analysis and significance testing.
The significance of the linear regression slope was evaluated using the "regression analysis" implemented in MS Excel ® at a level of 95% [2, 3, 5].
The expanded uncertainty U_{pt} is obtained by multiplying the combined standard uncertainty, u_{char} = uncertainty for characterization, u_{bbr} = uncertainty for homogeneity, and u_{sts} = uncertainty for stability by a coverage factor k (k= 2), the result was expressed by equation 1. [2, 3, 5].

$$U_{pt} = k\sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2} \quad (1)$$

The reference results obtained for total mercury was 0.69 ± 0.15 μg g^{-1} (table 1).
The value proficiency assigned samples presented were calculated by calibration against the certified reference values of the CRMs (DORM-2 - "Dogfish" – National ReserchConciul of Canada); the process is recommended by ISO/IEC 13528:2015[2].

Table 1. Estimation of uncertainties in μg g^{-1} for the element Hg-total determined by FIA-CV-AAS (wet basis).

Element Hg	(μg g^{-1})	%
u_{char}	0.074	10.6
u_{bb}	0.0002	0.03
u_{sts}	0.003	0.43
[a]Average ± U_{pt}	0.69 ± 0.15	

[a]Average-obtained in the characterization, represents the average of 45 replicates of each material

3.3 Proficiency test pilot

The proficiency testing was relied on the ten participation governmental and private laboratories. The reference material for proficiency testing was prepared according to the recommendations of the ISO/IEC 17043:2010 [1].

The participating laboratories received one samples of 15 g (recommended size to be about 1 g each). They were analyzed in three different days in order to check the robustness of their results. The laboratories were instructed to proceed with the test item following the same procedure used in their routine analysis. They were allowed to use any suitable method(s) of measurement. The analytical techniques were used absorption spectrometry atomic- AAS (CV-AAS, HG-AAS, GF-AAS, TDA-AAS), Hg analysis Thermal decomposition mass spectrometry (ICP-MS) and spectroscopy optical (ICPOES).

All results were statistically evaluated using procedures based on standard ISO/IEC 17043:2010 (Table 2) [1].

Table 2. Results reported by participants

Laboratories	Average ± *U* (μg g^{-1})
1	0.50 ± 0.09
2	X
3	0.65 ± 0.10
4	0.82 ± 0.02
5	0.84 ± 0.04
6	0.69 ± 0.02
7	**0.23 ± 0.02**
8	**4.03 ± 0.06**
9	0.56 ± 0.04
10	**0.18 ± 0.02**

X = result not reported.

The assigned value and the standard deviation used in proficiency testing program was derived from calibration against the certified reference values of the CRMs. A good agreement was observed among the values calculated and results obteined by (Table 3).

Table 3. Estimate for the assigned values and standard deviation, in μg g^{-1} for the results of pilot proficiency testing (wet basis)

Element	Assigned values (μg g^{-1}) %
Hg	0.693 ± 0.15

The analytical performances were evaluated by calculating the Z-score values characterizing individual laboratories [1], which is the most conventional way of performance evaluating a laboratory participating in a PT scheme [1, 2].
These values were calculated by using as assigned value (X_{ref}) the corresponding standard deviation unit (s) according to the following formula:

$$Z\text{-}score = \frac{\left(X_{lab} - X_{ref}\right)}{s} \tag{2}$$

Where: X_{lab} = average result of the laboratory, X_{ref} = reference value, and s = standard deviation for proficiency testing.
The z-score, helps identify outlying results as z-scores are standardized values that give it a score note for each result on the others in the group. Thus, a Z value close to zero means that the findings are consistent with those of other participants. A disperse value in proficiency testing is any results that present an absolute value of z-score greater than three.
The Z-score classifies laboratory performance as follows:

$|Z| \leq 2$ is ''satisfactory''

$2 < |Z| \leq 3$ is ''acceptable''

$|Z| > 3$ is ''unsatisfactory''.

The evaluated laboratory performance is summarized in the Figure 1. Considering the results obtained to date, the majority laboratories obtained a satisfactory z-score.
The laboratory 7, 8 and 10 showed result for z-score considered unsatisfactory, because were above 3 and -3. The z-score for laboratory 8 was 9.04, in this case, the graph was presented with open bar and axis to -5 and 5 for better visualization.

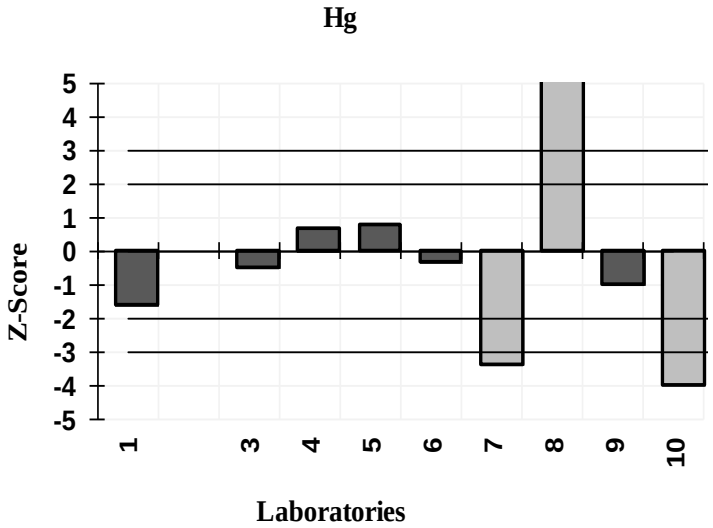

Figure 1: shows the results of z-scores for each participating laboratory proficiency test pilot program for mercury in fish tissue

4. Conclusions

The studies of homogeneity and stability at 23 °C indicated no significant variations that could affect the intended use of this material. Thus, the produced sample is suitable to be used in a program of proficiency testing of laboratories. Therefore, there is no need for freezing during transport.

The results obtained by the collaborating laboratories were in agreement with the results determined by the producer laboratory using the homogeneity test. Each participant sent along with the concentrations found information on the analytical methods used by the analyzes.

Laboratories with unsatisfactory results had informed by proficiency completion testing meeting that they had sent the wrong results of the sample analysis moreover just one laboratory does not report the result. Laboratories with unsatisfactory results had informed by proficiency completion testing meeting that they had sent the wrong results of the sample analysis moreover just one laboratory does not report the result. In addition laboratories that have sent the correct data, there are no inferences or deviation from the reference value, z-score ≤ 2.

In the first analysis the number of laboratories was small and for this reason we have considered this comparison pilot study safety for proficiency testing development in the future program with larger group laboratories.

5. Aknowledgements

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6. References

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