



EVALUATION OF THE PERFORMANCE OF THE PARTICIPANT LABORATORIES IN PROFICIENCY TESTING SCHEMES ON pH 4,00 AND pH 6,86

Paulo Paschoal Borges, Isabel Cristina Sertá Fraga, Fabiano Barbieri Gonzaga, Júlio Cesar Dias

National Institute of Metrology, Standardization and Industrial Quality - Chemical Metrology Division - Electrochemistry Laboratory, Av. Nossa Senhora das Graças, 50, Xerém, CEP 22250-020, Duque de Caxias, RJ, Brazil. E-mail: ppborges@inmetro.gov.br

Abstract: Inmetro provides proficiency testing (PT) to Brazilian laboratories in order to guarantee the comparability and reliability of their measurement results. The continuous performance of the laboratories which participated in PT scheme for pH 4,00 and pH 6,86 measurements on three rounds is focused in this paper. A great number of laboratories has their pH measurement performance increased from 2008 to 2010. Therefore, it can be inferred that these laboratories have been providing pH measurements with good quality results for the consumers.

Key words: proficiency testing, pH, comparability.

1. INTRODUCTION

Inmetro, the Brazilian Metrology Institute, has provided proficiency testing schemes to the Brazilian laboratories in pH measurement since 2008, due to the importance that the pH measurements exert in the chemical analysis area. The participant laboratories from industry and diverse areas such as food, environmental, etc. in each exercise have the ability to compare their results based on metrological traceability of an assigned value of test item, providing comparability of PT results, and also on scoring PT results by taking into account uncertainties of the assigned value [1]. It is important to notice that the participation in a PT scheme is one of the requirements needed for the accredited laboratories to comply with the ABNT NBR ISO/IEC 17025 [2].

In this work, performance evaluation of the laboratories from three PT schemes for pH 4,00 and pH 6,86 measurements was analyzed based on the statistical test of z-score, and also in some rounds the En numbers were considered [3].

2. PURPOSE

This work aims at evaluating the performance results of the laboratories which have participated in the PT scheme provided by Inmetro for measurements of pH 4,00 and pH 6,86 from 2008 to 2010, since the participation in PT schemes is an adequate tool for the laboratories to demonstrate and evaluate the comparability and reliability of their measurement results.

3. MATERIALS AND METHOD

3.1. Proficiency Test Items

The test items for the PT schemes were made up of certified reference materials (CRMs) of pH 4,00 and pH 6,86, which were characterized by the Primary pH Measurement System from Inmetro [4] and certified according to ISO GUIDE 34 [5]. Specific report for each PT scheme can be downloaded from Inmetro's site [6]. In these reports, the procedures for the preparation of each test item and also the studies for its certification are presented.

3.2. Statistical Analysis

3.2.1. z-score

z-score (zeta score) was used as the statistical test to evaluate the performance of the participant laboratories (Equation 1) based on the ISO/IEC 17043 [3]. The reference value and the variability (s) related to the uncertainty of the CRM (the test item) for both the pH 4,00 or pH 6,86 were assigned by Inmetro.

$$z_i = \frac{y_i - y_{ref}}{s} \quad (1)$$

Where: y_{ref} is the reference value; y_i is the mean result of a specific laboratory i ; s is the combined standard uncertainty of the CRM. The performance of the laboratory was classified as satisfactory, unsatisfactory or questionable, presented as follows: $|z| \leq 2$, satisfactory result; $2 < |z| < 3$, questionable result and $|z| \geq 3$, unsatisfactory result.

3.2.2. En numbers

The En numbers [3] were considered from the second round of the PT schemes in order to evaluate the performance only of those laboratories which reported the uncertainty of their measurements. The En numbers are calculated using Equation 2.

$$En_i = \frac{y_i - y_{ref}}{\sqrt{U_i^2 + U_{ref}^2}} \quad (2)$$

Where: y_{ref} is the pH reference value assigned by Inmetro; y_i is the mean result of the pH measurement from one specific laboratory i ; U_{ref} is the expanded uncertainty value of the reference assigned by Inmetro; U_i is the uncertainty expanded value reported by the specific laboratory i . The

performance of the laboratories was considered satisfactory when $|En| \leq 1$ and unsatisfactory if $|En| > 1$.

4. RESULTS

Table 1 shows the reference value and its expanded uncertainty for each test item which was used in the PT schemes for pH measurements since 2008.

Table 1. Reference values with the expanded uncertainties at 25 °C assigned for each round of the PT schemes.

Round	Year	pH	Expanded Uncertainty ($k=2$; 95%)
First	2008	4,006	0,012
		6,883	0,014
Second	2009	4,001	0,026
Third	2010	6,853	0,026

The evolution of the number of the participant laboratories in the PT schemes for pH measurement provided by Inmetro from 2008 to 2010 is represented in Fig. 1. It can be seen that the participation of the laboratories represents an ascendant curve.

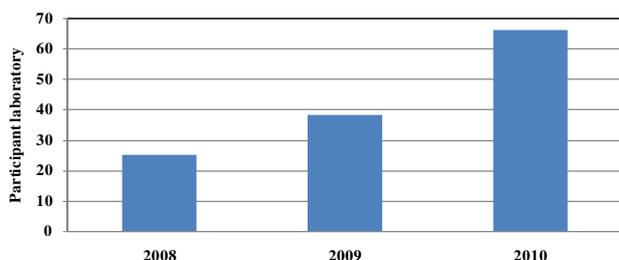


Fig. 1. Evolution of the number of participant laboratories in PT.

The performance of the laboratories for pH measurement on pH 4,00 and pH 6,86 obtained in all PT schemes provided by Inmetro is shown from Fig. 2 to 4. In these figures the performance was obtained on both z-score (Figs. 2 and 3) and En numbers (Fig.4).

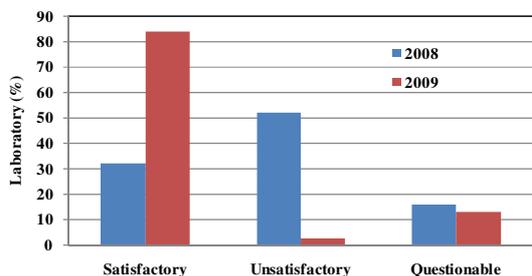


Fig.2. Laboratories' performance in PT for pH 4,00 by z-score.

Fig. 2 shows that there was an increase in the satisfactory results for pH 4,00 from 2008 to 2009. The same occurred in the results for pH 6,00 from 2008 to 2010 (Fig.3).

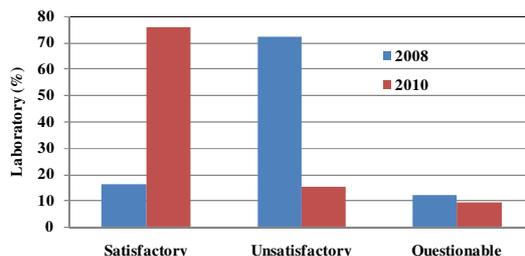


Fig.3. Laboratories' performance in PT for pH 6,86 by z-score.

Taking into account the En numbers (Fig. 4), the PT schemes from 2009 to 2010 showed that a great number of the laboratories presented satisfactory results as well as comparable uncertainty estimations.

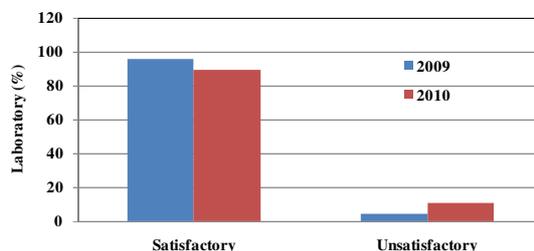


Fig.4. Laboratories' performance in PT for pH 4,00 (2009) and pH 6,86 (2010) according to En numbers.

5. DISCUSSION

All the reference values with their uncertainties assigned on the rounds of the PT scheme for measuring the pH is presented in Table 1. It is important to realize that in the PT schemes all the test items were certified reference materials (CRMs) which were developed and provided by Inmetro. Thus, it can be possible to compare the results with metrological traceability [1,3].

In Fig. 1, the number of the laboratories increased from 25 to 66 participants which means that there was an increase higher than 160% on the participation of the laboratories in PT schemes from 2008 to 2010. This increase can justify how important a PT scheme is in terms of an appropriate tool for monitoring the quality control of the measurement results just as the pH measurements are to chemical laboratories.

In the PT scheme for pH 4,00 measurement, the laboratories' performance increased from the first round (25 participant laboratories) to the second round (38 participant laboratories) as shown in Fig.2. At the first round (2008), about 30% of the laboratories obtained satisfactory results. On the other hand, at the second round (2009), the same scoring was acquired by more than 80% of the laboratories. Similar performance was shown in Fig. 3 in the PT scheme for pH 6,86 measurement (66 participant laboratories). Satisfactory pH measurement results were carried out by almost 75% of the laboratories in 2010 in comparison to the

weak performance obtained in 2008, when only about 15% acquired such scoring.

According to the performance of the En numbers, from PT scheme of the second round in pH 4,00 measurement, in 2009, 24 out of 25 participants presented satisfactory results (representing a total of 96%). On the other hand, from 56 participant laboratories in the PT scheme for pH 6,86 measurement, in 2010, satisfactory results were reported by 50 laboratories (representing a total of 89,3% of the participant laboratories).

As shown in Fig. 4, a great number of laboratories which estimated their uncertainty according to ISO GUM [7] obtained satisfactory results. Therefore, it can be inferred that most of the laboratories have competently estimated their uncertainties which is a quality parameter on pH measurement results.

6. CONCLUSIONS

There was an evolution from 2008 to 2010 in the number of chemical laboratories from industry and diverse areas such as food, environmental, etc. which has been participating in the PT schemes for pH measurement provided for Inmetro.

The laboratories which participated in the PT schemes for pH measurements of pH 4,00 (two rounds) and pH 6,86 from 2008 to 2010 have shown a significant increase in their performance, demonstrating ability to deliver accurate pH measurement results as well as estimating the uncertainty budget consistently with ISO GUM.

ACKNOWLEDGMENTS

The authors thank Inmetro for supporting this research.

REFERENCES

- [1] Kuselman, I., Fajgelj, A., "IUPAC/CITAC Guide: Selection and use of proficiency test schemes for a limited number of participants-chemical analytical laboratories (IUPAC Technical Report)", *Pure Appl. Chem.*, Vol.82, n^o. 5, pp. 1099-1135, 2010.
- [2] ABNT NBR ISO/IEC 17025:2005, Requisitos Gerais para a Competência dos Laboratórios de Ensaio e de Calibração.
- [3] ISO/IEC 17043:2010(E), Conformity assessment – General requirements for proficiency testing.
- [4] Souza, V., Ordine, A. P.; Fraga, I. C. S., Getrouw, M. A., Borges, P. P., Damasceno, J. C., Couto, P. R. G. "Effect of NaCl and HCl concentrations on primary pH measurement for the certification of standard materials", *Braz. arch. biol. technol.*, Vol. 49, pp. 79-85, 2006. Available in <http://www.scielo.br/pdf/babt/v49nspe/28423.pdf>
- [5] ISO GUIDE 34:2009(e), General requirements for the competence of reference material producers.
- [6] www.inmetro.gov.br/metcientifica/profiPH.asp, accessed in 17.03.2011.
- [7] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (2008), Evaluation of measurement data — Guide to the expression of uncertainty in measurement, first edition, GUM:1995 with minor corrections.