

## PORTUGUESE pH INTERLABORATORY COMPARISON

*M. João Nunes*<sup>1</sup>, *M. J. Guiomar Lito*<sup>2</sup>, *M. Filomena Camões*<sup>3</sup>, *Eduarda Filipe*<sup>1</sup>

<sup>1</sup>Instituto Português da Qualidade, 2829-513 Caparica, Portugal, [mjnunes@mail.ipq.pt](mailto:mjnunes@mail.ipq.pt)

<sup>2</sup>Faculdade de Farmácia da Universidade de Lisboa, 1649-019 Lisboa, Portugal, [mjglito@ff.ul.pt](mailto:mjglito@ff.ul.pt)

<sup>3</sup>Faculdade de Ciências da Universidade de Lisboa, DQB, 1749-016 Lisboa, Portugal, [fcamoes@fc.ul.pt](mailto:fcamoes@fc.ul.pt)

**Abstract** – The first interlaboratory comparison at national level for pH measurement of a primary standard phosphate buffer solution was carried out. The main aim of the exercise was to verify the way laboratories are planning and performing pH measurements and evaluates the performance of each laboratory. Seven laboratories have participated in this study.

Keywords: pH measurement, Uncertainty components.

### 1. INTRODUCTION

One of the most widespread measurements carried out by analytical laboratories is determination of pH. Similarly to experimental determination of other physical and chemical properties, pH measurement is affected by the limited accuracy process.

The comparability between the primary method at the top of the traceability chain (Fig.1) and the field method can be assessed through a traceability chain of a measured pH(X) value with target uncertainties [1].

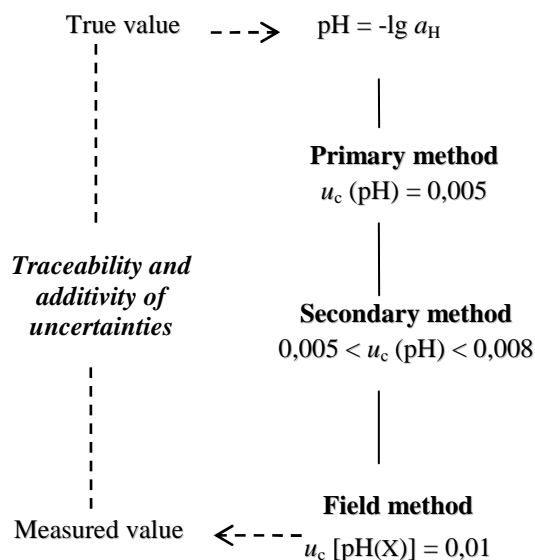


Fig. 1. Traceability chain of a measured pH(X) value with target uncertainties.

The pH primary laboratory conducted an interlaboratory comparison at a national level. Seven Portuguese

laboratories have participated in this study. The participants fields of working areas were ranged from health care, to environmental control, safety, process industry and among others.

The primary standard buffer solution for pH measurement was an equimolal phosphate buffer solution ( $0,025 \text{ mol kg}^{-1} \text{ KH}_2\text{PO}_4$  (potassium dihydrogen phosphate) +  $0,025 \text{ mol kg}^{-1} \text{ Na}_2\text{HPO}_4$  (disodium hydrogen phosphate)).

The incorporation of the uncertainty components [2] not only for at the primary level but also for at all subsequent measurements, permits the uncertainty for the whole procedure to be linked to the pH primary standard buffers by an unbroken chain of comparisons. The combined uncertainties estimated by the participant laboratories have been compared through calculation verified by the reference laboratory.

To assess the laboratory performance  $Z'$ -Scores and  $E_n$  numbers statistical methods have been used in proficiency tests [3, 4].

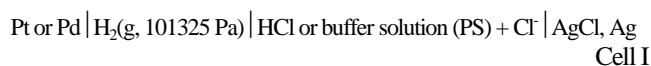
The work presented here deals with the assessment of the performance of the participating laboratories for the pH measurement of a primary standard solution and with the estimation of the respective results uncertainties.

This first interlaboratory comparison aims at understanding the state of the art in terms of pH measurements in Portugal and to the identification of training needs.

### 2. METHODS

#### 2.1. Primary procedure for pH assessment of the assigned value

The assigned value of the equimolal phosphate buffer was measured using the pH primary measurement method. This procedure is based on the measurement of the potential difference between a platinum-hydrogen electrode and a silver-silver chloride reference electrode of an electrochemical cell, known as the Harned cell [5, 6], without liquid junction, filled with a selected buffer solution, to which chloride ions, in the form of potassium or sodium chloride, were added enabling the use of the silver-silver chloride electrode, cell I,



with potential,  $E$ , defined by the Nernst equation:

$$E = E_{\text{Ag,AgCl}}^0 - \left[ k \ln \left( \frac{m_{\text{H}} \gamma_{\text{H}}}{m^0} \right) \left( \frac{m_{\text{Cl}} \gamma_{\text{Cl}}}{m^0} \right) \right] =$$

$$= E_{\text{Ag,AgCl}}^0 - k \lg(a_{\text{H}} m_{\text{Cl}} \gamma_{\text{Cl}}) \quad (1)$$

The potential,  $E$ , of cell (I) (corrected to 101325 Pa partial pressure of hydrogen gas) is the quantity to be measured,  $E_{\text{Ag,AgCl}}^0$  is the standard potential of the cell, which conventionally coincides with that of the silver-silver chloride electrode,  $m^0$  is the standard molality (1 mol kg<sup>-1</sup>) and  $\gamma_{\text{H}}$  and  $\gamma_{\text{Cl}}$  are the activity coefficients of the hydrogen ion and chloride ion at molalities (mol kg<sup>-1</sup>)  $m_{\text{H}}$  and  $m_{\text{Cl}}$  respectively; all subscripted ions are written without charges, for simplicity. The Nernstian slope,  $k$ , is given by:

$$k = \frac{RT}{F} \ln 10 \quad (2)$$

where  $R = 8,314492 \text{ J mol}^{-1} \text{ K}^{-1}$  is the molar gas constant,  $F = 96485,3415 \text{ C mol}^{-1}$  is the Faraday constant, and  $T$  is the temperature in K.

This conventional procedure is recommended by IUPAC [7] and is used by National Metrology Institutes. In the operation of the pH primary system measurement, five basic stages are required:

- determination of the standard potential of the Ag/AgCl electrode,  $E_{\text{Ag,AgCl}}^0$ ;
- determination of the potential of cell I at different concentrations of added chloride ion,  $m_{\text{Cl}}$  (0,005; 0,010; 0,015 mol kg<sup>-1</sup> of NaCl);
- extrapolation to zero chloride concentration through the linear regression of the acidity function,  $p(a_{\text{H}} \gamma_{\text{Cl}})$ ;
- calculation of the activity coefficient of the chloride ion,  $\gamma_{\text{Cl}}$ , using Bates-Guggenheim convention;
- calculation of hydrogen ion activity  $a_{\text{H}}$  and primary standard pH values.

The standard potential of the silver-silver chloride electrode,  $E^0$ , is determined from the potential,  $E(\text{HCl})$ , of a Harned cell filled with hydrochloric acid of fixed molality ( $m = 0,01 \text{ mol kg}^{-1}$ ), according to equation (3):

$$E_{\text{Ag,AgCl}}^0 = E(\text{HCl}) - 2k \lg(m_{\text{HCl}} / m^0) (\gamma_{\pm \text{HCl}}) \quad (3)$$

where  $\gamma_{\pm \text{HCl}}$  is the mean activity coefficient of the HCl.

The different stages in the calculation of primary pH value (PS), are combined in equation (4), which is derived from equation (1):

$$- \lg \left( \frac{a_{\text{H}} \gamma_{\text{Cl}}}{m^0} \right) = \frac{E - E_{\text{Ag,AgCl}}^0}{k} + \lg \left( \frac{m_{\text{Cl}}}{m^0} \right) \quad (4)$$

$$\text{pH} = \text{p}a_{\text{H}} = \text{p}(a_{\text{H}} \gamma_{\text{Cl}})^0 + \lg \gamma_{\text{Cl}} \quad (5)$$

where  $\lg \gamma_{\text{Cl}}$  is approximated by the Debye-Hückel model in which the Bates-Guggenheim convention for the ion size parameter has been introduced,  $Ba_i = 1,5$ ,  $A$  is the Debye-Hückel limiting slope and  $I$  the ionic strength of the solution in mol kg<sup>-1</sup>

$$\lg \gamma_i = - \frac{A I^{1/2}}{1 + Ba_i I^{1/2}} \quad (6)$$

The  $\text{p}a_{\text{H}}$  values thus obtained are conventionally adopted as reference values, pH (PS).

The method used for calculation of the uncertainties was that adopted by the ISO GUM [2] and the IUPAC 2002 recommendations [7].

## 2.2. Operation

The pH primary laboratory planned the various steps of the exercise operations. Seven Portuguese laboratories have participated in this study.

The pH primary laboratory prepared and certified the primary standard equimolar phosphate buffer solution. This primary phosphate buffer solution was certified for pH measurements at 15 °C, 25 °C and 37 °C.

A protocol has been prepared for pH measurement and reporting data, to be followed by all participant laboratories, once they have received the phosphate buffer sample.

The samples of primary buffer solution were sent out in 15 mL HDPE Nalgene® flasks. To allow for repeatability studies five replicate samples have been sent at the same time, together with the technical protocol.

## 2.3. Evaluation of performance

Proficiency testing by interlaboratory comparisons was used to assess the performance of individual laboratories for pH measurement of a reference solution of equimolar phosphate primary pH buffer. The criteria for performance evaluation was statistical determination for scores,  $Z'$ -scores and  $E_n$  numbers.

The performance evaluation using  $Z'$ -scores statistic method was done as defined by ISO 13528 [3]:

$$Z' = \frac{(X_{\text{Lab}} - X_{\text{Ref}})}{\sqrt{s^2 + u_{\text{Ref}}^2}} \quad (7)$$

where

$Z'$  is the  $Z'$ -score;

$X_{\text{Lab}}$  is the measured pH value by the participant laboratory;

$X_{\text{Ref}}$  is the pH assigned value measured by the reference laboratory;

$s$  is the standard deviation for proficiency assessment obtained from the results reported by the participants;

$u_{\text{Ref}}$  is the combined standard uncertainty of the pH assigned value determined by the reference laboratory.

The obtained results are considered to be satisfactory for “ $Z'$ -scores” values between  $-3$  e  $+3$ .

To assess the performance of the participant laboratories that estimate the uncertainty the proficiency test of  $E_n$  numbers [3, 4] has been used:

$$E_n = \frac{X_{\text{Lab}} - X_{\text{Ref}}}{\sqrt{U_{\text{Lab}}^2 + U_{\text{Ref}}^2}} \quad (8)$$

where

$X_{\text{Lab}}$  is the pH value measured by the participant laboratory;

$X_{\text{Ref}}$  is the pH value assigned by the reference laboratory;

$U_{Lab}$  is the expanded uncertainty of participant laboratory result;  
 $U_{Ref}$  is the expanded uncertainty of the reference laboratory value.

The obtained results for which  $|E_n| \leq 1$  are considered to be satisfactory and the ones with  $|E_n| > 1$  are considered to be unsatisfactory.

#### 2.4. Uncertainty in routine pH measurements

The basis for estimation of uncertainty is the "Guide to the expression of Uncertainty in Measurement" [2]. For pH routine measurements, several problems arise in practice due to influences that include:

- the reference solutions;
- the temperature;
- the pH electrode.

The procedure for estimating the uncertainty essentially consists of recognizing the individual effects that contribute to the uncertainty, and determining their size. To evaluate the declared uncertainty, the participant laboratories were asked to declare the standard uncertainties, the sensitivity coefficients, the uncertainty contributions, the degrees of freedom and the expanded uncertainty. Finally the reference laboratory calculated the combined uncertainties of the results supplied by all participant laboratories.

### 3. RESULTS AND DISCUSSION

The results for pH measurement at the top of the traceability chain are presented in Table 1.

Fig. 2 shows the results of pH measurement at 25 °C, both by the reference laboratory and by the participant laboratories. The horizontal solid line indicates the pH value measured by the reference laboratory and the dotted lines represent the corresponding expanded uncertainty. Five laboratories indicate the result with expanded uncertainty, represented by vertical bars. Two laboratories reported only the measured pH value; although the uncertainties are not reported, proximity to the reference value is noticeable. From these experimental results one may conclude that only one result (L5) is not comparable to the reference value.

Table 1. Reference pH values measured by the primary method ( $pH_{Ref}$ ).

$t / ^\circ C$	$pH_{Ref}$	$U$
15,0	6,9130	0,0073
25,0	6,8682	0,0063
37,0	6,8449	0,0089

The performance of each participant laboratory has been evaluated using the statistical methods of the proficiency tests [3, 4].  $Z'$ -scores statistical method has been applied to all the laboratories and the results are given in Fig. 3.  $E_n$  numbers statistical method has been applied only to the five laboratories that have estimated the uncertainty. Fig. 4 presents the performance of laboratories assessed by  $E_n$  numbers method.

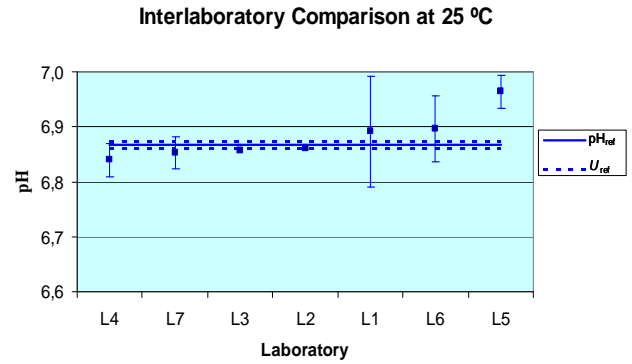


Fig. 2. Results of pH measurements at 25 °C. The vertical bars indicate the reported expanded uncertainties. The horizontal lines indicate the laboratory reference pH value and its corresponding expanded uncertainty.

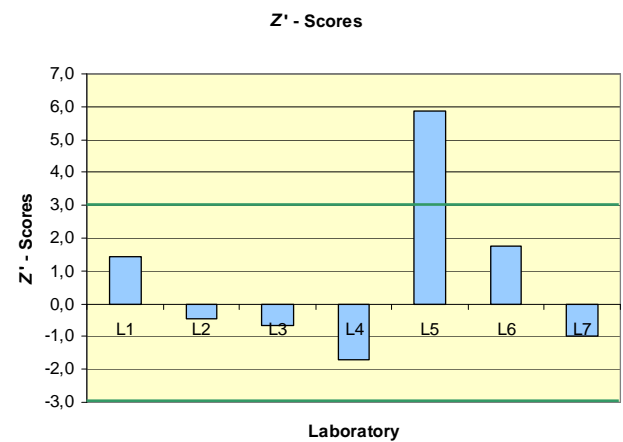


Fig. 3. Performance of laboratories by  $Z'$ -Scores method.

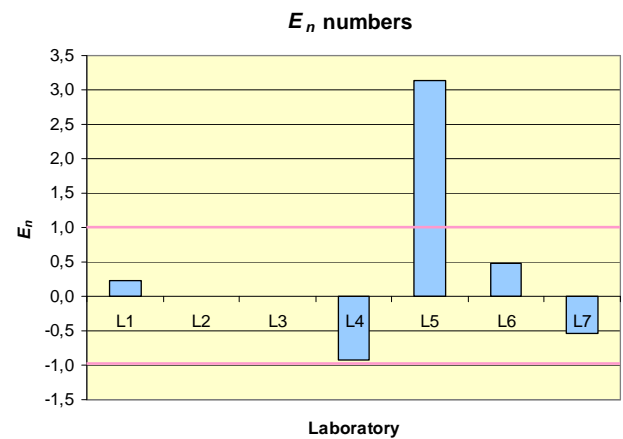


Fig. 4. Performance of laboratories by  $E_n$  numbers method.

Results indicated in Figs. 3 and 4 shows that six laboratories present a satisfactory performance and one laboratory presents an unsatisfactory performance, L5. This result indicates that laboratory L5 should revise its analytical procedure.

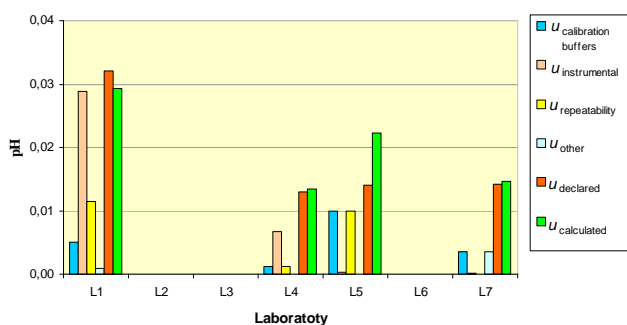


Fig. 5. Components of standard measurement uncertainty and combined standard uncertainty declared by each laboratory and calculated by the reference laboratory.

In order to assess consistency in the estimation of the uncertainty, the reference laboratory has calculated the combined standard uncertainty of each laboratory and compared the calculated result with the one declared by the laboratory. These results are presented in Fig.5. It may be observed that laboratories do not consider the same sources for uncertainty calculation. Also some differences in the calculations were observed from the declared combined uncertainties and the ones calculated by the reference laboratory. This proves there is need for a common protocol for estimating the contribution and calculation of the combined uncertainty.

#### 4. CONCLUSIONS

A high degree of agreement of measurement pH results of the participant laboratories is evident. Only one laboratory presented an unsatisfactory performance. These

results lead to conclude that there exist comparability results from the primary method and those from the field method in the pH measurement of a primary standard buffer solution of equimolar phosphate.

The results presented in this study come from the first interlaboratorial comparison and show clearly the necessity of a technical protocol for the evaluation of uncertainty contributions to the combined uncertainty. Future actions should aim at the discussion of uncertainty estimation. This work should also be extended to more participant laboratories.

#### REFERENCES

- [1] M.J. Lito, M.F. Camões and C.M. Viçoso, "Improving the quality of potentiometric pH measurements", *Accred Qual Assur.*, vol. 12, pp. 447–453, 2007.
- [2] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML, 1995, *Guide to the expression of uncertainty in measurement*, 2<sup>nd</sup> ed. (Genève: International Organization for Standardization).
- [3] ISO 13528, 2005, *Statistical methods for use in proficiency testing by interlaboratory comparisons*.
- [4] ISO/IEC 43-1,1997 *Proficiency testing by interlaboratory comparisons*.
- [5] R.G. Bates, *Determination of pH – Theory and Practice*, 2<sup>nd</sup> edn. Wiley, New York, 1973.
- [6] A.K. Covington, R.G. Bates and R.A. Durst, "Definition of pH Scales, Standard Reference Values, Measurement of pH and Related Terminology", *Pure Appl. Chem.*, vol. 57, pp. 531–542, 1985.
- [7] R.P. Buck, S. Rondinini, A.K. Covington, F.G. Baucke, C.M. Brett, M.F. Camões, M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer and G.S. Wilson, "Measurement of pH. Definition, Standards, and Procedures IUPAC Recommendations 2002", *Pure Appl. Chem.*, vol. 74, n°. 11, pp. 2169–2200, 2002.