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pH MEASUREMENT CAPABILITY THROUGH THE PRIMARY pH MEASUREMENT OF CARBONATE BUFFER SOLUTION

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Abstract: The Chemical Metrology Division (Dquim) from National Institute of Metrology, Standardization and Industrial Quality – Inmetro established in 2003 the primary system of pH measurement. The main use of this system is to provide reliability and traceability to the pH measurements in Brazil since its measurement is one of the most important analyses carried out in many laboratories all over the country. In order to show comparability and capability in primary pH measurement, Inmetro participated in both the key-comparisons CCQM-K18 and in the supplementary comparison that followed, named CCQM-K18.1, to measure the pH in a carbonate buffer solution of nominal value of pH 10. Both exercises were organized by Consultative Committee for Amount of Substance (CCQM) of the International Bureau of Weights and Measures (BIPM). This work aimed at showing the development and optimization of the primary pH system from Inmetro in order to participate in the supplementary key-comparison. Inmetro´s results in that supplementary comparison have shown its capability in primary measurement of pH 10.

Keywords: primary pH measurements, key-comparison, carbonate buffer.

1. INTRODUCTION

pH measurement is one of the most used techniques carried out in laboratories all over the world. Its accurate determination is very important to different fields, such as health, food, environmental and biotechnology as well as to control of diverse industrial process. The measurement is based on physical-chemistry principles and it is carried out by potentiometric technique. The potentiometric method is very simple, precise and it is used in measurements in third (glass electrode), secondary (potentiometric cell with liquid junction) and primary level (Harned cells). The National Institute of Metrology, Standardization and Industrial Quality – Inmetro by its Chemistry Metrology Division – Dquim, established in 2003 the primary system of pH measurement in the Electrochemistry Laboratory – Label [1]. The aim of the primary system is to certify reference material and provide the traceability in pH measurements for the country. The technique used in pH measurements is in accordance with the IUPAC [2].

In 2007, Inmetro participated in a key-comparison, CCQM-K18.1 (pH of carbonate buffer) [3] supplementary to the previous one called CCQM-K18, for institutes which could not take part in the comparison at that time or did not consider their results representative for their capabilities. This exercise was coordinated by National Institute of Metrology (NMI) from Slovakia – SMU, in order to evaluate the equivalence among the National Institutes and to show the competence in primary measurement in pH 10. In this comparison participated 8 NIMs (CENAM-Mexico, DFM-Denmark, Inmetro-Brazil, INPL-Israel, LNE-France, NIM-China, PTB-Germany and SMU-Slovakia).

2. PURPOSE

The objective of this work is to present the results of a key comparison CCQM-K18.1 (pH of carbonate buffer) and the capability of Inmetro in the primary measurement of pH 10, whose measurement is considered demanding, because of the decomposition of carbonate buffer solution into CO_2 during the measurement.

3. METHODS

Potential measurements related to the silver-silver chloride and hidrogen electrodes and pH determination were evaluated by using twelve Harned cells [2] and two thermostatic baths. The cells were divided into two groups of six cells and each group was immersed in one different thermostatic bath. The first group of six Harned cells was filled with a carbonate buffer solution to which six different concentrations of sodium chloride [4] in $mol.kg^{-1}$ (varying from 0.005 to 0.02) [2] were added in each cell and the other group of six Harned cells was filled with hydrochloric acid solution (nominal molality of 0.01), which the exact value was determined by primary system of coulometry from Inmetro [5]. During the time of the measurement, the system was scanned while the potential difference between the two electrodes (Ag-AgCl/Pt platinized/H_2) was being measured in each cell and registered electronically, while hydrogen gas

(99.999% purity) was passed through the solution. The flow of hydrogen gas used was 7.5 mL/min. Each scan took about 10 min for all the 12 cells to be scanned. The system attained its steady state when the slope of the three last measurements of each cell potential was below 1.5 μV/min and the difference from the last potential to the first one at a specific time was 10 μV/min. The total time of the primary pH measurement was 4 h 40 min.

4. RESULTS

Table 1 shows the results of acidity function (AF) [3] and its uncertainty measurements for each NMI which participated in the CCQM-K18.1 comparison. As it can be seen, Inmetro´s results were very close to the coordinating laboratory (SMU).

Table 1 – Results of acidity function and its expanded uncertainty from the CCQM-K18.1 comparison.

Institute	Acidity function, AF	$U_{AF°}$ (k=2)
LNE	10.0857	0.0068
NIM	10.0861	0.0036
INMETRO	10.1032	0.0032
PTB	10.1048	0.0029
DFM	10.1076	0.0012
CENAM	10.1092	0.0037
INPL	10.1409	0.0067
SMU	10.1033	0.0030

The equivalence among the NMIs which participated in the CCQM-K18.1 exercise [3] is presented in the Figure 1.

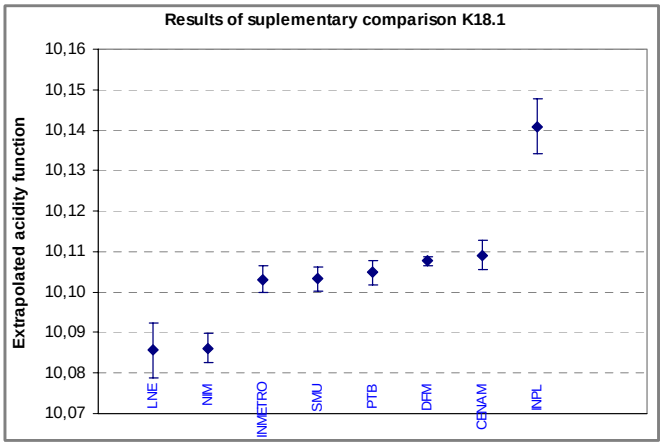

Figure 1 – Results of the key-comparison CCQM-K18.1.

The degree of equivalence of the participants of the supplementary comparison relative to the original CCQM-K18 comparison was calculated based on the assumption that the deviation of the coordinating laboratory's result from the reference value is constant. In Figure 2, the degrees of equivalence are shown together with the results of the first key comparison, CCQM-K18. The degree of equivalence obtained by Inmetro in this key comparison was 0,0009 [3], which demonstrates a very good comparability in the measurements.

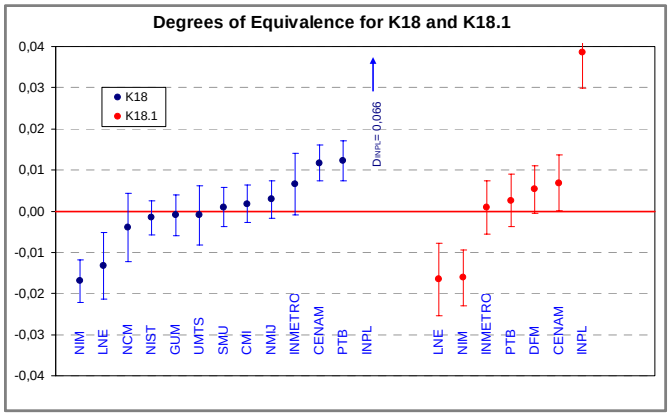

Figure 2 – Degrees of equivalence between the two comparisons.

5.DISCUSSION

In the key comparison CCQM-K18.1, Inmetro used six different concentrations of sodium chloride added to the sample of carbonate buffer and the accurate determination of hydrochloric acid was made by coulometry. This new approach, different from the way it was previously used [1] showed that the measurements of pH value were improved as well as its uncertainty of measurement, as shown in Table 1 and Figure 1. In addition, these improvements have also contributed to the optimization of the primary system of pH from Inmetro, as showed by the two participations of Inmetro in the key comparisons (Figure 3), making it possible to certify buffer solution of pH 10 as well as guarantee the quality of the measurement results, since the measurement of pH 10 is tough, due to the decomposition of carbonate buffer solution into CO_2 during the measurement time.

6. CONCLUSIONS

Inmetro carries out one of its mission which is to participate in key-comparisons in order to compare its measurements with other national metrology institutes. The results of Inmetro demonstrated its competence in the measurements of the carbonate pH 10 buffer solutions, confirming the guarantee of the quality of its results. Consequently, Inmetro will be able to claim its calibration and measurement capability (CMC) in this measurement and, thus, provide the traceability and reliability of the measurement results in pH 10 to the chemical laboratories in Brazil.

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