

Effect of NaCl and HCl Concentrations on Primary pH Measurement for the Certification of Standard Materials

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ABSTRACT

pH is an important parameter to control the production of food, medicine, petrochemical products and others. Thus, standard reference materials used to calibrate pH meters are necessary to guarantee reliability of the measurements. The Chemical Metrology Division (Dquim) of the National Metrology Institute of Brazil (Inmetro) has as one of its missions the certification of standard reference materials. In the case of pH, it will be done by the pH primary measurement system of Inmetro, in operation at Dquim since 2003. The buffer solution of nominal pH value equal to 6.865 will be the first to be certified. The study of some measurement parameters has already been accomplished, and will lead to the improvement of the primary pH measurement. In this paper, the effect of NaCl and HCl concentrations on the primary pH measurement is discussed, based on the results obtained by Inmetro in the regional comparison SIM 8.11P.

Key words: Chemical metrology, primary pH, reference material

INTRODUCTION

Inmetro has a pH primary measurement system, so far the only one in South America, to fulfill the purpose of certification of buffer solutions, and consequently, supply certified reference materials to the measurement of pH (Souza et al., 2003). In order to obtain international recognition of its technical competence, Inmetro has participated in a regional comparison, organized in the sphere of the Interamerican Metrology System (SIM), the so-called SIM 8.11P, referring to the pH measurement of phosphate buffer solution. In this exercise, the importance of the optimization of the primary pH measurement system of Inmetro became evident to obtain more exact measurements. So, studies were performed

concerning the effect of some parameters on the correct measurement of pH. Among these parameters are the temperature control, the electrode potential, the extrapolation to zero of the concentration of the supporting electrolyte added to the buffer solution, the purity of the reagents and the concentration of the electrolytes.

The aim of this paper is to discuss the effect of the concentrations of sodium chloride (NaCl) and hydrochloric acid (HCl) to the measured value of pH and the estimation of its uncertainty. The discussion refers to the results obtained by Inmetro at the SIM 8.11P comparison.

This study will contribute to the certification of pH reference materials, based on the ISO Guides 30 to 35 and the ISO/IEC 17025 standard.

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MATERIALS AND METHODS

The primary pH measurement system of Inmetro has twelve electrochemical glass cells, known as Harned cells, in which the value of pH was determined by the measurement of the potential difference between two electrodes: the silver-silver chloride (Ag/AgCl) electrode and the standard hydrogen electrode (Harned and Owen, 1958). The cells were placed in high precision thermostatic baths (thermal stability of 0.003K), where temperature was monitored by resistance thermometers (Pt100). The cells were divided in four groups containing three Harned cells each. One group contained a 0.01 mol kg⁻¹ hydrochloric acid (HCl) solution. In the other three groups, the buffer solution to be measured - a 0.025 mol kg⁻¹ phosphate solution with a nominal pH value of 6.865 at 25°C - was analyzed. The difference among these three groups was the concentration of NaCl added to the buffer solution (0.005 mol·kg⁻¹, 0.010 mol·kg⁻¹ and 0.015 mol·kg⁻¹). pH values were calculated by using difference of potentials from all cells measured with a 8.5-digit multimeter. With the measurements of electrode potential accomplished in the cells containing HCl solution, the standard potential of the Ag/AgCl electrode (E°) was determined. This standard potential was also used in the calculation of the pH value. The result from the potential difference measurements in the cells containing the buffer solution was converted into a derived quantity (Inmetro, 2003) named acidity function (p_a). The latter was plotted as a function of the NaCl concentration and extrapolated to the zero concentration of NaCl. Finally, the extrapolated value of the acidity function was used to calculate the pH value (Buck et al., 2002). All calculations to obtain the pH value were described in detail elsewhere (Souza et al., 2003).

The sample for the pH determination, phosphate buffer solution, was supplied by Centro Nacional de Metrología (CENAM), the National Metrology Institute (NMI) from Mexico, that organized the SIM 8.11P comparison. The pH reference value

was the consensus value of the primary pH measurements performed by three traditional NMI: CENAM, the National Institute of Science and Technology (NIST, from USA) and the Physikalische-Technische Bundesanstalt (PTB, from Germany). The reference pH value was equal to (6.8656 ± 0.0030), at 25°C.

The electrolyte added to the buffer solution was Merck NaCl of 99.5% purity. The HCl solution was prepared from Merck reagent for analysis and Milli-Q water. The concentration of this solution was determined by coulometric titration (Borges et al., 2004) and its value was (0.00990800 ± 0.00000030) mol·kg⁻¹.

The preparation of the electrodes was performed using Merck reagent for analysis and Milli-Q water. The purity of the hydrogen gas was 99.999%. Prior to the activation of the platinum electrodes with hydrogen gas, which took approximately two hours, an inert atmosphere was created inside the cells by passing argon (99.99% purity), during 30 minutes.

The estimation of the uncertainty of the measured pH was done considering the following sources of uncertainty: extrapolation of the acidity function to zero concentration of NaCl, the temperature measurement, the standard potential of Ag/AgCl electrode determination, the potential measurements in the cells, the hydrogen gas pressure, the universal constant of ideal gases and the Faraday constant. All uncertainties were calculated according to the Guide to the Expression of Uncertainty in Measurement (ABNT, 2003).

RESULTS

Table 1 shows the mean values of potential difference measured in the HCl solution and in the buffer solution containing three different concentrations of NaCl.

Table 1 - Mean values of potential difference.

Solution	Potential difference (V)
HCl ~ 0.01 mol·kg ⁻¹	0.4636259 ± 0.0000029
Buffer + 0.005 mol·kg ⁻¹ NaCl	0.7409896 ± 0.0000036
Buffer + 0.010 mol·kg ⁻¹ NaCl	0.7515557 ± 0.0000036
Buffer + 0.015 mol·kg ⁻¹ NaCl	0.7409896 ± 0.0000036

Using the potential difference measurements shown in Table 1 and considering the nominal values of HCl ($0.01 \text{ mol}\cdot\text{kg}^{-1}$) and NaCl ($0.005 \text{ mol}\cdot\text{kg}^{-1}$, $0.010 \text{ mol}\cdot\text{kg}^{-1}$ and $0.015 \text{ mol}\cdot\text{kg}^{-1}$) concentrations, results for the calculation of the acidity function (p_a) in relation to the

concentration of NaCl were obtained (Fig. 1). A straight line was adjusted by linear regression. The extrapolation of this line to zero concentration of NaCl resulted in a p_a value of 6.9523 ± 0.0034 . The pH value calculated from this result was equal to 6.8427 ± 0.0034 .

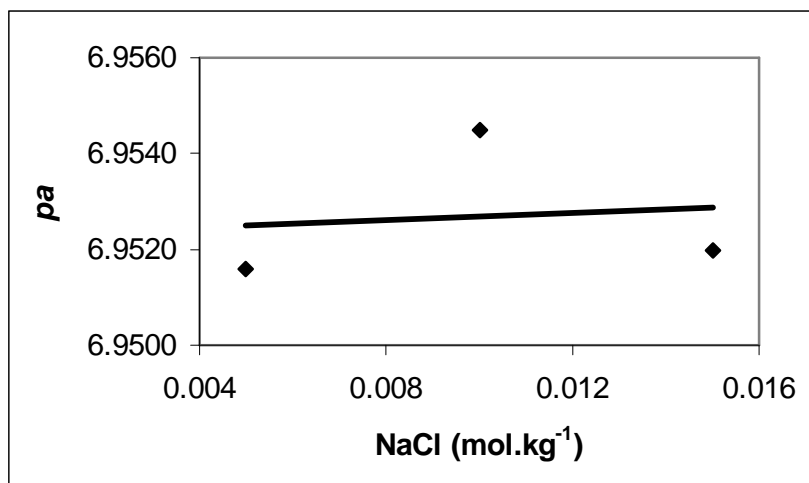


Figure 1 - Acidity function (p_a) values as a function of NaCl concentration using nominal values for NaCl and HCl concentrations.

Fig. 2 presents the results of the calculation of p_a considering the experimental values of the concentrations of NaCl and HCl. These values can be seen in Table 2. The straight line (a) shown in Fig. 2 corresponds to the linear regression of the results of p_a calculated as function of the experimental values of NaCl concentration (Table

2), applying the nominal value of $0.01 \text{ mol}\cdot\text{kg}^{-1}$ as the concentration of HCl. The straight line (b) indicates the linear regression of the results of p_a , in this case, calculated using the experimental concentration values of both electrolytes, NaCl and HCl (Table 2).

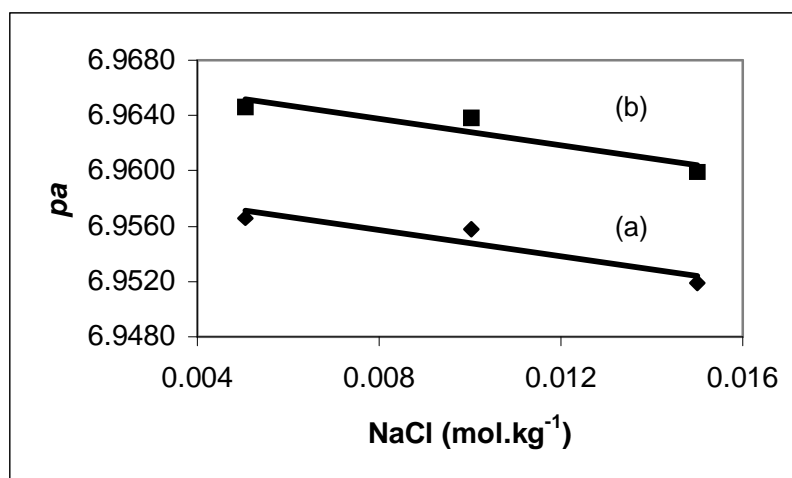


Figure 2 - Acidity function (p_a) values as a function of NaCl concentration using (a) the nominal value for HCl concentration and experimental values for NaCl concentrations; and (b) the experimental values for both electrolytes, HCl and NaCl.

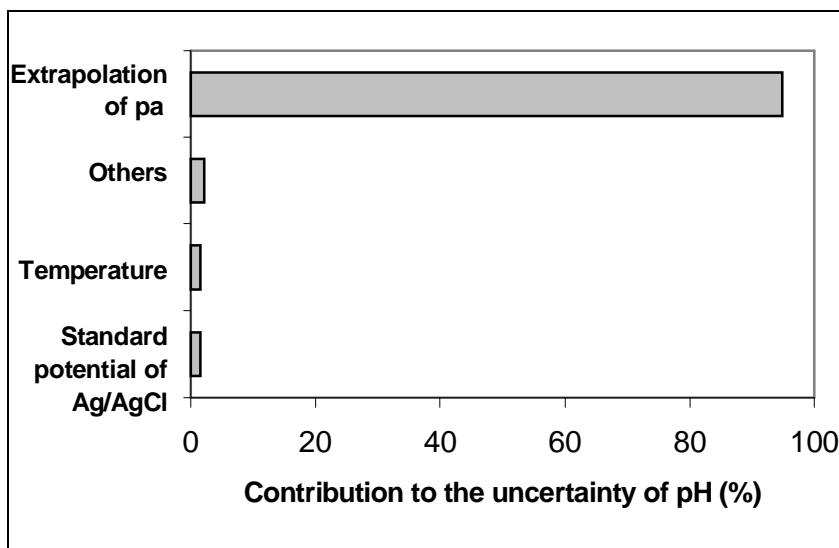
Table 2 - Nominal and experimental values of HCl and NaCl concentrations.

Solution	Concentration (mol·kg ⁻¹)	
	Nominal value	Experimental value
HCl	0.010	0.0099080 ± 0.0000003
NaCl	0.005	0.005058 ± 0.000012
NaCl	0.010	0.010030 ± 0.000013
NaCl	0.015	0.014997 ± 0.000014

Table 3 shows the p_a values for the zero concentration of NaCl, the values of pH calculated from these p_a values, and the respective experimental errors in relation to the reference value of pH of 6.8656 ± 0.0030 at 25°C.

The relative contribution of the measurement parameters for the estimation of the uncertainty of pH is shown in Figs. 3 and 4. In Fig. 3, the results were calculated by considering the nominal values of the concentrations of HCl and NaCl. On the

other hand, in Fig. 4, the indicated relative uncertainties were obtained considering the experimental values of the concentrations of both electrolytes, HCl and NaCl. When the nominal value of HCl concentration and the experimental values of NaCl concentrations were considered, the relative contributions to the uncertainty estimation of pH were alike that shown in Fig. 4.

**Figure 3** - Effect of the uncertainty sources on the pH uncertainty, considering the nominal values of HCl and NaCl concentrations.**Table 3** - Effect of HCl and NaCl concentrations on the pH determination.

Values used in the calculation of pH for the HCl and NaCl concentrations	Figure	p_a	pH	Experimental error ^a
Nominal values for both electrolytes	1	6.9523 ± 0.0034	6.8427 ± 0.0034	0.33%
Experimental values for NaCl and nominal values for HCl	2 (a)	6.9595 ± 0.0020	6.8500 ± 0.0022	0.23%
Experimental values for both electrolytes	2 (b)	6.9675 ± 0.0020	6.8580 ± 0.0022	0.11%

^aReference value: 6.8656 ± 0.0030 at 25 °C.

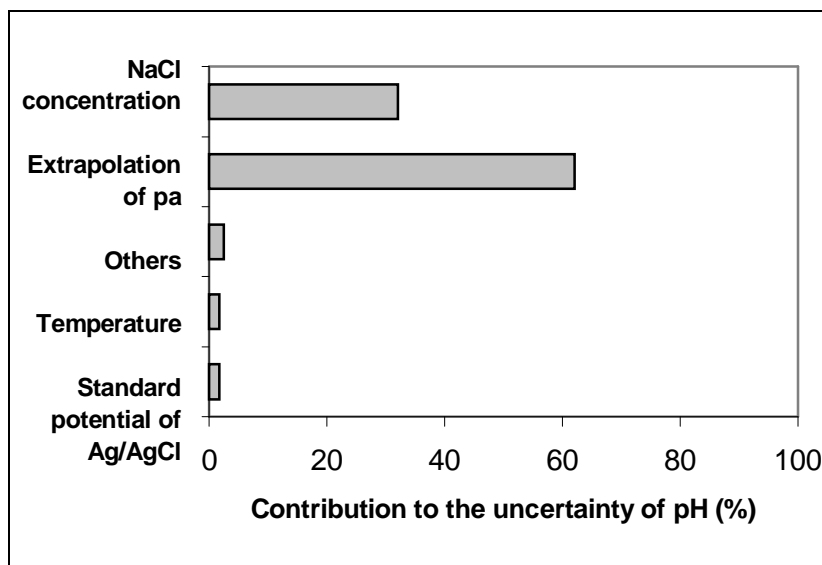


Figure 4 - Effect of the uncertainty sources on the pH uncertainty, considering the experimental values of HCl and NaCl concentrations.

DISCUSSION

One of the important effects on pH buffer solution determination by the primary measurement system is due to the purity of the used reagents and the knowledge of the exact concentration of the species in the samples. In Fig. 1, the results were calculated considering the nominal values of HCl and NaCl concentrations in solutions. As can be seen in Table 3, in this case, the pH value showed the highest experimental error, 0.33% in comparison to the reference value.

With regard to Fig. 1, there is a significant dispersion of p_a values around the straight line. The correlation coefficient obtained for this linear regression was 0.015, reflecting the poor adjustment of the line. Consequently, the uncertainty due to p_a extrapolation for zero NaCl concentration was considerable and lead to the major contribution to the pH uncertainty estimation, as can be seen in Fig. 3. In fact, this contribution represented 95% of the pH uncertainty estimation, whereas 1.5% of the contribution was due to the temperature measurement; 1.5%, due to the determination of the Ag/AgCl standard potential; and an additional 2%, due to the sum of the contributions from cell potential measurement, hydrogen gas pressure, the universal constant of ideal gases and the Faraday constant. The pH uncertainty contribution due to HCl and NaCl concentrations was not considered

in this case, because nominal concentration values of both electrolytes were used in the calculation.

On the other hand, lower dispersions of the points around their respective regression straight lines can be observed in Fig. 2, showing clearly the linear behavior of p_a as a function of the experimental concentrations of the HCl and NaCl electrolytes. The correlation coefficient in both cases was around 0.873.

Fig. 4 presents the contributions to the estimation of the pH uncertainty, including those due to the determination of HCl and NaCl concentrations. The contribution due to the exact knowledge of the NaCl concentration represented 32% of the pH uncertainty, whereas the contribution due to the extrapolation of p_a corresponded to 62%. The remaining sources were the temperature measurement (2%), the Ag/AgCl standard potential determination (2%) and others (2%), regarding to the cell potential measurement, the hydrogen gas pressure, the universal constant of the ideal gases and the Faraday constant. For the uncertainty calculation of the Ag/AgCl standard potential, the uncertainty of the determination of the HCl concentration was considered, but its contribution was negligible because of the employed method for the determination of this concentration, which was coulometric titration. As indicated in Table 2, the uncertainty provided by the method was around $10^{-8} \text{ mol}\cdot\text{kg}^{-1}$, which resulted in an increase of only 0.5% of the relative

contribution due to the Ag/AgCl standard potential determination on the pH uncertainty estimation. This statement can be confirmed when one compares the Ag/AgCl standard potential contribution in Fig. 4 with the same in Fig. 3.

The results discussed show the importance of the electrolytes concentration in the determination of pH by a primary method. It can be stated that the reliability of the pH determination depends strongly on the knowledge of the exact concentration of HCl and NaCl. In fact, when the experimental values of the NaCl concentrations were used to determine the pH (Table 3), an experimental error of 0.22% in comparison to the reference value was achieved, less than that when the concentrations were the nominal values (0.33%). Moreover, the exact determination of the HCl concentration could improve this result, which presented an error of only 0.11%. In this case, the coulometric titration has shown its considerable importance on the HCl concentration determination (Borges et al., 2004).

It is worthwhile to point out that the concentration of NaCl was obtained by the gravimetric addition of the salt to the buffer solution (Máriássy et al., 2000), taking into account the purity of the salt, its molecular mass (Lide, 2000) and the water mass fraction of the buffer. The latter is important for the correct calculation of the electrolyte concentration, in $\text{mol}\cdot\text{kg}^{-1}$, according to the molality definition (Galster, 1991).

When the experimental values of the electrolytes were considered, not only an improvement in the determination of pH was achieved, but also a reduction in the uncertainty of the pH value was brought about. As it can be seen in Table 3, the uncertainty of pH decreased from 0.034 to 0.022 units of pH, when the nominal values of the concentrations of HCl and NaCl were changed by the experimental values of the same quantities.

CONCLUSIONS

The primary pH measurement system of Inmetro was capable of presenting good results in the determination of pH 6.865 using the buffer solution studied in the SIM 8.11P comparison. In this paper, the effect of the electrolyte concentrations added to the buffer solution and the determination of HCl concentration showed to be of major importance in the exact determination of

pH, decreasing its experimental error from 0.33% to 0.11% in comparison to the reference value, when the nominal and experimental values of the electrolytes were employed, respectively.

As a consequence, the use of adequate methodologies to determine the concentrations of HCl and NaCl resulted in a reliable primary pH measurement.

Consequently, this study contributed to the optimization of the pH primary measurement system of Inmetro, allowing the certification of buffer solution of pH 6.865 with higher reliability. In doing so, Inmetro fulfills one of its missions, which is guaranteeing the traceability of pH measurements by producing and certifying primary reference materials.

ACKNOWLEDGEMENTS

To FINEP (Convênio Inmetro/FINEP CT Verde Amarelo n^o 22.02.0465.00 e convênio 01.03.0383.00) and to CNPq for the financial support.

RESUMO

O pH é um importante parâmetro para o controle do processo de produção de inúmeros insumos e produtos finais da indústria alimentícia, farmacêutica, petroquímica, entre outras. Assim, o uso de soluções tampão certificadas na calibração de medidores de pH é necessário para conferir confiabilidade às medições. Uma das missões da Divisão de Metrologia Química (Dquim) do Inmetro é a certificação de materiais de referência, no caso do pH, soluções tampão, utilizando o sistema primário de medições de pH implantado em 2003. A solução tampão de fosfato com valor nominal de pH igual a 6,865 será a primeira solução a ser certificada, sendo importante para isso o estudo de determinados parâmetros de medição, tais como: concentração de HCl e NaCl, potencial padrão do eletrodo de Ag/AgCl e temperatura. Neste trabalho, a influência de alguns parâmetros na medição exata da grandeza pH é discutida, valendo-se dos resultados obtidos pelo Inmetro com amostras da comparação SIM 8.11P, utilizando o sistema primário de medição de pH. Observou-se que a influência dos valores nominais e experimentais das concentrações de NaCl e HCl

afetam o valor de pH em 0,33% e 0,11%, respectivamente, em comparação ao valor de consenso da comparação, utilizado como valor de referência.

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Received: July 29, 2005;
Revised: September 05, 2005;
Accepted: November 22, 2005.

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