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Quality Assurance and Quality control of pH measurements for urban wastewater of a Nuclear and Radioactive Facility

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1. Introduction

In several research and development areas, pH measurements are critical to achieve the process optimal efficiency[1], [2], [3], [4]. A straightforward and simple measurement that reflects the hydrogen ion activity in solution is a frequent procedure in many academic and industrial laboratories. The correct pH measurement impacts directly on the wastewater treatment efficiency on metals, microorganisms, emerging contaminants removal[1], [2], regardless of the treatment step is primary(physical), secondary (chemical) or tertiary (advanced)[4]. With the accurate pH measurements, the correct treatment and amount of chemicals can be used. This is particularly true in a Nuclear and Radioactive Facility (NRF)[3] in a chemical or radiochemical laboratory. Many times, laboratories perform pH measurement without adequate calibration, or quality control measures. Rarely, reference material that provide metrological traceability is adopted[5]. Some laboratories also operate without the quality control and quality assurance protocol and without uncertainty estimates. With no metrological pH measurement assessment, the wastewater could be released with no regulation compliance [5], [6]. The present study assesses the main parameters that could affect the pH measurement in a wastewater laboratory, such as 1) instrument, 2) buffer solution, 3) range of values and 4) analysts. Accuracy was assessed by Certified Reference Material (CRM) and by two rounds of measurements under the scope of interlaboratory exercises. Long term stability assessment was performed to test the method robustness. The present study is particularly important while in service to a nuclear research institute, that requires optimal effluent monitoring and regulation compliance.

2. Methodology

2.1 Validation procedure

A total of 491 pH measurements were performed from November 2022 up to December 2023. The present study considered several sources of variability (See Figure 1), such as: 5 buffer solution, 5 analysts and 2 instruments. By this way, the range of values, repeatability, reproducibility, long term stability and other effects derived from solution preparation, instrumental variability and analyst experience/training could be assessed. The buffer solutions covered the full range of environmental samples analyzed in the laboratory (from pH 4.000 up to 10.014). The two selected instruments had same specification (PH2000, Gehaka) and

age, with different electrodes and applications. One as regularly used for rainwater and clean samples (IDT 86) and the second one was used to industrial effluent and saline matrices (IDT45). Five different analysts performed measurements at least once a week. All analysts were trained according to the Internal Standard Operational Procedure (ISOP), but some worked in laboratory from 5 to 20 years while others had just started laboratory activities (<1year). Because several buffer solutions were used, ΔpH was used (see eq.1) once the absolute deviation allow the comparison of all solutions by the same criteria. Factorial ANOVA was used to assess each factor variance over the measurement. Null hypothesis (H_o) considered that no effect was observed, and a two tailed alternative hypothesis (H_1) stated that effect was present and observed for the studied effects on a significance level of 0.05.

2.2 Precision and accuracy

A certified reference material of simulated rainwater (ERM®-CA408) for pH was used to access precision and accuracy, with 42 pH measurements on 26 distinct days, by 5 analysts. The certified reference value was 6.3±0.6 (k=2, 95%CI).

2.3 Interlaboratory results

The laboratory participated of two rounds of an interlaboratory exercise for pH. Rede Metrologica do Rio Grande do Sul was the interlaboratory provider, accredited on Quality Management (NBR/ISO9001) and as an interlaboratory provider (NBR/ISO17043)[7], [8]. The laboratory that performed the analysis has present satisfactory values for pH measurement since 2010.

$$\Delta pH = pH_{expected} - pH_{measured} \quad (1)$$

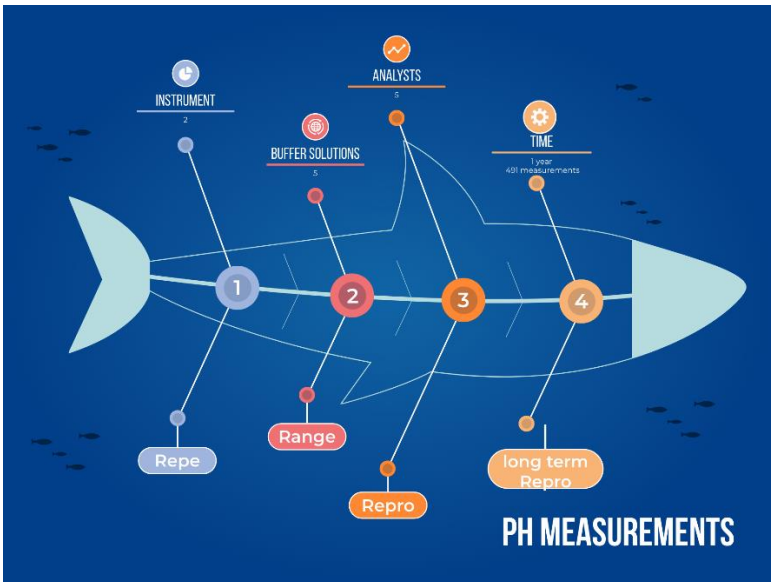

Figure 1: Ishikawa diagram with variability sources for pH measurement and uncertainty estimation steps.

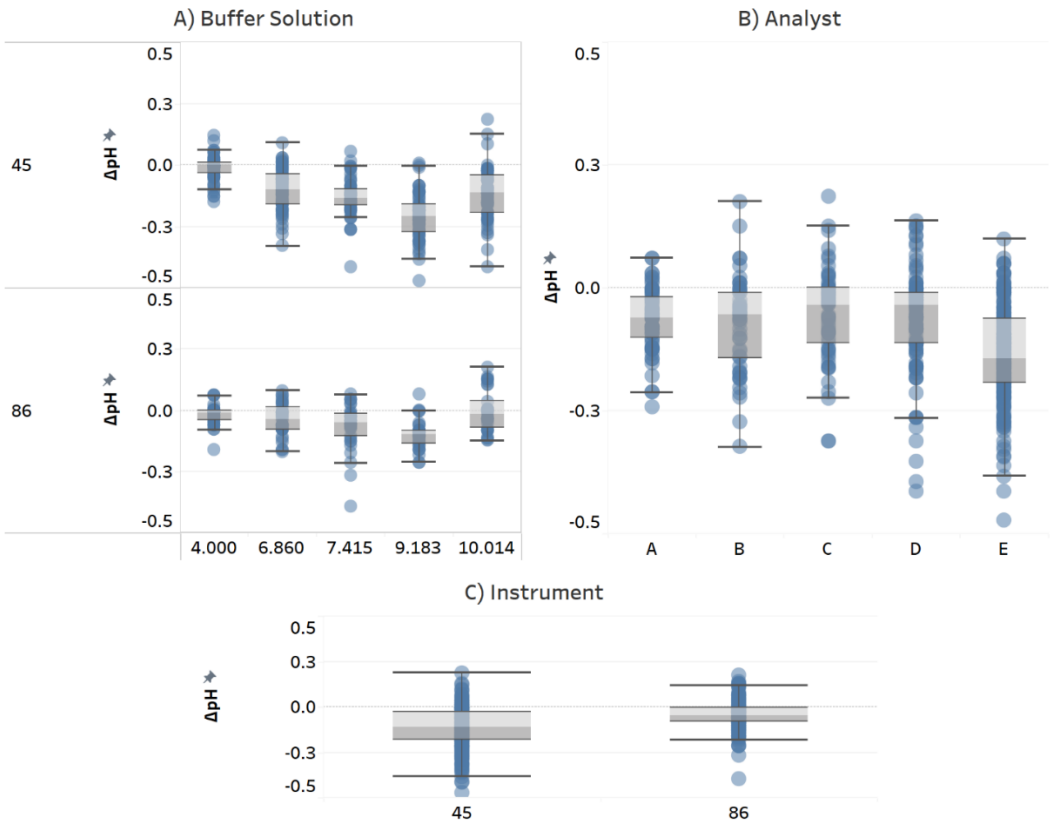

Figure 2: Box plot of ΔpH values considering the source of variability (A) Buffer solution, (B) Analyst and (C) instrument.

Table I: basic statistical assessment of pH validation.

Feature	All factors	Instruments	Analysts	Buffer solutions
Average	-0.10	-0.05	-0.15	-0.30
s.d.	0.30	0.03	0.05	0.15
minimum	-0.41	-	-	-
maximum	0.19	-	-	-
Estimated bias	-	-0.10	-0.40	-0.30

3. Results and Discussion

In all 491 measurements, two outliers were observed with ΔpH values over 0.5 pH unities. These outliers were removed from the dataset. The remainder data was tested and considered normally distributed ($p<0.001$). While considering all variability sources the ΔpH was -0.09±0.30 (average ±3sd). As presented in Figure 1. Analyst E was the least experienced and the one with larger measurement variability. All others presented equal average and standard deviation while performing the analysis.

Instruments identified as IDT 45 and 86 presented with different performances, with IDT 45 exhibiting a larger negative bias (-0.10). The buffer solution with value 9.183 presented the larger ΔpH, that will be further investigated. In two rounds of interlaboratory exercises, the laboratory presented satisfactory results within ±1 robust coefficient of variance (0.30 pH unities) among all participant laboratories [7]. All combined effects presented a larger combined uncertainty of ±0.50 (U, k=2), which is adequate for environmental purposes and to comply with Brazilian regulations.

4. Conclusions

During the validation process, it was possible to observe that the most important factor affecting pH results was the analyst training. An untrained analyst could increase the uncertainty of pH measurements up to 0.2 pH unities. While other analysts with different training experience (> 1 year) presented similar performances with no statistical differences among them. The selected instrument presented a statistically significant effect. However, that was solely observed due to the large number of measurements performed at the pH validation. The instrument accounted for less than half the effect exhibited by the untrained analyst. Temperature, buffer solution did not present statistically significant differences over the pH measurement over time.

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