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Comparison of the results of pH measurements in a buffer solution

Abstract. As a result of the increasing need to study the choice of the assigned value during the inter-laboratory comparisons is becoming more and more relevant. Since the assigned value is a reference point when comparing the results of the participants of the qualification test. Frequently, qualification verification providers face a number of problems when choosing the assigned value. An incomplete analysis of the results of interlaboratory comparisons will lead to an inaccurate assessment of the competence of the laboratory, which contributes to the revocation of the certification of the accreditation of the laboratory participant.

This article attempts to provide a complete statistical analysis of the results of interlaboratory comparisons from the beginning to the end of the tour with the content of all statistical analyses recommended in GOST ISO/IEC 17043-2013.

The results of interlaboratory comparisons conducted in testing laboratories of Kazakhstan aimed at ensuring metrological traceability of pH measurements in a buffer solution are presented. The reference values of the buffer solution are determined in the state scientific metrological center.

Keywords: Traceability; reference laboratory; metrology; testing laboratory; interlaboratory comparison.

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Introduction

The relevance of the article. Participation in interlaboratory comparisons is one of the mandatory conditions for confirming the technical competence of the laboratory in accordance with GOST ISO/IEC 17025-2019, one of the forms of quality management of measurement results in laboratories (clause 7.7 of GOST ISO/IEC 17025-2019). [1]

Interlaboratory comparisons are a necessary and effective tool for ensuring the uniformity of measurements in the country and the quality of measurements in laboratories. Interlaboratory comparisons - organization, execution and evaluation of measurements or tests of the same or several similar samples by two or more laboratories in accordance with pre-established conditions. [2]

Research methods: alternative experimental methods and robust statistical methods.

The main part. The interlaboratory comparisons considered in this article were carried out according to the MLS schedule for 2020. [3]

The purpose of the work was to check the competence of the laboratory by means of interlaboratory comparisons. The subject of verification is the technological, informational and methodological support of the traceability of measurements in testing laboratories (IL).

The test was aimed at assessing the comparability of the results of laboratory measurements in sludge when determining the pH in a buffer solution.

10 IL were taken in interlaboratory comparisons.

The measurement results obtained during interlaboratory comparisons can be further used by laboratories for internal control of their performance indicators.

The article presents the specific results of the participants with a detailed statistical analysis in accordance with GOST ISO/IEC 17043-2013 and ST RK ISO 13528-2010.

The coordinator of the comparisons was RSE "KazInMetr". Certificate of accreditation no. KZ. C. 01. 1512 is valid for"05" August 2024. [4]

The comparison program "Determination of pH in buffer solution" involved 10 laboratories with different pH measurement technologies. It shows the level of acids and alkalis in the water, determining

what effect this can have on plants and fish. This indicator is an important indicator that affects a person's well-being. The deviation of this value from the norm indicates problems in the water supply, which should be paid attention to.

Description of samples for qualification testing

The sample of the qualification verification program was the state standard sample (GSO) pH of the reference buffer solution of the 2nd category of EBR2 7.41 pH, which is an aqueous solution of potassium dihydrophosphate and sodium monohydrophosphate. Extended uncertainty of the assigned value (k=2, P=95%) ±0.01 pH. The assigned value of the sample was established by an experimental calculation method according to the procedure for preparing GSO.

Traceability of the assigned value is ensured by using a standard sample of the 2nd category, an aqueous solution of sodium tetraborate 10-water; traceability to the standards of units of mass and volume is ensured by using verified scales, measuring flasks in accordance with State verification schemes for measuring mass and volume.

The samples were labeled, divided into portions with the indication of the sample code. In order to maintain confidentiality, the correspondence of the cipher of the sample and the participant of the comparisons was available only to one of the comparison coordinators.

The delivery of all samples was carried out simultaneously. All samples were tested for stability and uniformity before delivery. The results of uniformity and stability are presented in Tables 1, 2.

Table 1

Data for checking uniformity

Bottle number	Serving 1	Serving 2
3	7,413	7,416
8	7,417	7,415
6	7,409	7,416
11	7,416	7,413
14	7,407	7,404
20	7,41	7,414
27	7,408	7,411
26	7,412	7,409
38	7,406	7,412
41	7,408	7,404
General average		7,41100
SKO (S_x), standard deviation		0,00357
S_w, sample standard deviation for all samples		0,00288
S_s, standard deviation between samples		0,00293

Table 2

Data for checking stability

Bottle number	Serving 1	Serving 2
74	7,413	7,416
94	7,412	7,413
General average		7,4135
Deviation		0,0025

Table 3

Participants ' results

Laboratory code	pH value	Extended uncertainty, pH
Laboratory 1	7,36	0,06
Laboratory 2	7,15	0,1
Laboratory 3	7,5	0,2
Laboratory 4	7,42	0,04
Laboratory 5	7,4	0,1
Laboratory 6	7,4	0,08
Laboratory 7	7,43	0,1
Laboratory 8	7,42	0,06
Laboratory 9	7,38	0,08
Laboratory 10	7,32	0,1

Comparison of the assigned value with the robust average

In accordance with ST RK ISO 13528: if a standard sample is used as a sample for checking qualifications, then after the participants have made measurements, the robust average value of x*, estimated from the results of the participants ' measurements, should be compared with the assigned value of X. In this case, the inequality must be fulfilled:

$$|x^*\text{-}X| < 2\sqrt{\frac{(1{,}25s^*)^2}{p} + u_x^2}$$

x* - robust average value;

s* - robust standard deviation;

p – number of participants;

u_x- standard uncertainty of the assigned value X. [5]

The robust mean value and robust standard deviation are determined in accordance with the Annex to the ST RK ISO 13528-2010. The robust mean value is 7.40 pH, the robust standard deviation is 0.05 pH. [6]

The results of checking the inequality: the deviation from the assigned value with the uncertainty of the difference is 0,01<0,04.

The choice of statistics for evaluating the characteristics of functioning

In accordance with GOST ISO/IEC 17043 and ST RK ISO 13528, the performance characteristics of the participants are evaluated using the quantitative indicator z. The use of the z indicator is valid only if the conditions for limiting the uncertainty of the assigned value are met. If

$$u_x \leq 0{,}3\overline{\sigma}$$

then the uncertainty of the assigned value of $u_x$is insignificant, and there is no need to take it into account when interpreting the results of the qualification check. If the condition is not met, then the uncertainty of the assigned value should be taken into account when interpreting the test results using appropriate quantitative indicators.

The results of checking the condition for limiting the uncertainty of the assigned value are 0,005≤0,014. This means that the z indicator will be used to evaluate the functioning characteristics of the listed measured values, which does not take into account the amount of uncertainty of the assigned value.

The standard deviation for the qualification assessment was determined from the data obtained from the cycle of the qualification verification project, calculated using the robust analysis of Algorithm A in Appendix C given by ST RK ISO/IEC 13528-2010.

Table 4

Robust analysis

Laboratory code	Measuredvalue, pH	1-processing	2-processing
		δ =0,025 x*- δ=7,34 x*+ δ=7,46	δ =0,025 x*- δ=7,34 x*+ δ=7,46
Laboratory 1	7,36	7,36	7,36
Laboratory 2	7,15	7,34	7,34
Laboratory 3	7,5	7,46	7,46
Laboratory 4	7,42	7,42	7,42
Laboratory 5	7,4	7,4	7,4
Laboratory 6	7,4	7,4	7,4
Laboratory 7	7,43	7,43	7,43
Laboratory 8	7,42	7,42	7,42
Laboratory 9	7,38	7,38	7,38
Laboratory 10	7,32	7,34	7,34
Robust average value, x*	7,4	7,4	7,4
Robust standard deviation, s*	0,037	0,05	0,05

Evaluation of the functioning characteristics

Table 5

Evaluation of a quantitative indicator

Laboratory code	Meaning pH	Extended uncertainty, pH	z
Laboratory 1	7,36	0,06	-1,11
Laboratory 2	7,15	0,1	-5,76
Laboratory 3	7,5	0,2	1,99
Laboratory 4	7,42	0,04	0,22
Laboratory 5	7,4	0,1	-0,22
Laboratory 6	7,4	0,08	-0,22
Laboratory 7	7,43	0,1	0,44
Laboratory 8	7,42	0,06	0,22
Laboratory 9	7,38	0,08	-0,66
Laboratory 10	7,32	0,1	-1,99

The evaluation of the characteristics of the functioning of the laboratory was carried out according to the quantitative indicator z according to the formula:

$$z=(x-X)/\overline{\sigma}$$

x – measurement result of the participating laboratory,

X – assigned value.

$\overline{\sigma}$ – standard deviation for the qualification assessment.

The performance characteristic is evaluated as follows:

at $|z| \leq 2$ -the quality of the test results is recognized as satisfactory;

at $2 < |z| \leq 3$ -the quality of the test results is considered doubtful and subject to additional verification;

at $|z| > 3$-the quality of the test results is considered unsatisfactory.

Conclusion

The analysis of the measurement results presented by the laboratories participating in the comparisons showed that the majority of the participants in the comparisons successfully coped with the task of measuring the controlled indicators.

The conducted interlaboratory comparison to ensure the reliability of measurements can be considered as a metrological certification of a standard sample. Such a model will allow laboratories to participate in interlaboratory comparisons without a certified standard sample, which significantly affects the absence of a standard sample in medical laboratories.

The values of the z indicators except for Laboratory 2 did not exceed the limits of the permissible values ($|z| \leq 2$), which corresponds to satisfactory performance of the work, and Laboratory 2 exceeded the limits of the permissible values ($|z| > 3$), which corresponds to unsatisfactory performance of the work in the field of pH determination.

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Буферлік ерітіндідегі pH өлшеу нәтижелерін салыстыру

Аңдатпа. Қажеттіліктің өсуінің нәтижесінде зертханааралық салыстыру өткізу кезінде тірек мәнін таңдауды зерделеу маңызы бар және одан да астам өзекті болып келеді. Берілген мән біліктілікті тексеруге қатысушылардың нәтижелерін салыстыру кезінде тірек нүктесі болып табылады. Жиі біліктілікті тексеру провайдерлері тағайындалған мәнді таңдау кезінде бірқатар проблемаларға тап болады. Зертханааралық салыстыру нәтижелерін толық талдау зертхананың құзыреттілігін дәл емес бағалауға әкеледі, бұл қатысушы-зертхананың аккредиттеу аттестациясын қайтарып алуға ықпал етеді.

Бұл мақалада ГОСТ ISO/IEC 17043-2013 ұсынған барлық статистикалық талдаулардың мазмұнымен турдың басынан аяғына дейін зертханааралық салыстыру нәтижелерін толық статистикалық талдауды ұсынуға әрекет жасалды.

Буферлік ерітіндідегі pH өлшемдерінің метрологиялық бақылануын қамтамасыз етуге бағытталған Қазақстанның сынақ зертханаларында жүргізілген зертханааралық салыстырулардың нәтижелері ұсынылған. Буферлік ерітіндінің тірек мәндері мемлекеттік ғылыми метрологиялық орталықта анықталған.

Түйін сөздер: қадағалануы; референттік зертхана; метрология; сынақ зертханасы; зертханааралық салыстыру.

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Сличение результатов измерений pH в буферном растворе

Аннотация. Возрастает необходимость изучения выбора приписанного значения при проведении межлабораторных сличений, что становится все более актуальным вопросом, поскольку приписанное значение является опорной точкой при сравнении результатов участников квалификационного теста. Зачастую провайдеры проверки квалификации сталкиваются с рядом проблем при выборе приписанного значения. Неполный анализ результатов межлабораторных сличений приводит к неточной оценке компетентности лаборатории, что способствует аннулированию сертификата аттестации участника-лаборатории.

В данной статье предпринята попытка предоставления полного статистического анализа результатов межлабораторных сличений с начала до завершения тура с содержанием всех статистических анализов, рекомендованных в ГОСТ ISO/IEC 17043-2013.

Представлены результаты межлабораторных сличений, проведенных в испытательных лабораториях Казахстана, которые направлены на обеспечение метрологической прослеживаемости измерений pH в буферном растворе. Эталонные значения буферного раствора определены в государственным научном метрологическом центре.

Ключевые слова: прослеживаемость, референтная лаборатория, метрология, испытательная лаборатория, межлабораторное сличение.

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