Experimental quantification of measurement uncertainty and other verification criteria for analytical test methods

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Abstract. If the measurement produces a numerical result (or the stated result is based on a numerical result), then it is necessary to evaluate the uncertainty of these numerical results. If the test methodology does not provide for a rigorous, metrologically and statistically reliable estimate of measurement uncertainty, the test laboratory should attempt to reasonably assess the uncertainty of the measurement results. This is applicable in the case of test methods both rational and empirical. As well as in the laboratory activities, verification of test methods plays an important role in order to guarantee the competence of the laboratory by checking for the criteria of Kohren, Grabbs and others. In cases where test results are not numerically expressed or based on numerical data (e.g., fit/unsuitable or positive/negative, or based on visual or sensory perceptions or other forms of quality analysis), estimates of uncertainty or other variability of results are not required. Nevertheless, laboratories are advised to have an idea of the variability of the results, if possible. The importance of the uncertainty of qualitative test results is undeniable, as is the fact that the necessary statistical methodology (procedure) exists for the calculations. However, due to the complexity of the issue and the inconsistency in the approaches, it is not currently necessary for laboratories to assess the uncertainty of qualitative test results. However, this issue needs to be considered. The article discusses estimates of uncertainty of analytical measurements taking into account the requirements of regulatory documents. The criteria for verification of measurement methodology based on experimental works are also considered and analyzed.

1. Introduction

Verification object and investigation - O'z O'U 07.0682 "Method of measurement of mass concentration of ammonium ions in natural and standing waters by photometric method." The procedure is designed to determine the mass concentration of ammonium ions in natural and wastewater by photometric method in the range from 0.2 mg/dm³ to 2.0 mg/dm³.

Verification is carried out by analyzing samples by calculating verification criteria. Verification is considered successful when the eligibility criteria are met. Primary data (weights of canopies, etc.) are recorded in the working journals of analyst specialists. Electronic chromatogram files are attached to the protocol on the CD along with scans of work log pages. Analysts involved in verification should have experience in independent work in the laboratory for at least 12 months, study the analysis method,
first reproduce the analysis method, fulfilling the criteria for the suitability of the measurement method provided by the method [1].

2. Materials and methods
The procedure for performing measurements for determining the mass concentration of ammonium ions in natural and wastewater by photometric method in the range from 0.2 to 2.0 mg/dm$^3$ is described below.

The limiting measure of harm is toxic.

The maximum permissible concentration in water of reservoirs is 0.5 mg/dm$^3$. The essence of the method is based on the formation of Nessler-colored ammonium ions in a yellow-brown color.

The weight concentration of ammonium ions (C, mg/dm$^3$) in water is determined by the formula:

$$C = \frac{a \cdot V_1}{V},$$

(1)

where:
- $a$ - mass concentration of ammonium ions, found according to calibration diagram, mg/dm$^3$;
- $V$ - amount of sample taken for analysis, cm$^3$
- $V_1$ – volume to which the sample has been brought, cm$^3$.

3. Standard for monitoring accuracy of measurement results
The measurement result is taken as the arithmetic mean of two parallel observations, if the difference $D_1$ (convergence) between them, with a confidence probability $P = 0.95$, does not exceed the values indicated in table 1. The discrepancy between $D_2$ measurements (reproducibility) at confidence probability $P = 0.95$ shall not exceed the values specified in table 1 below.

| Mass concentration range, mg/dm$^3$ | Allowed variance, mg/dm$^3$ | Between parallel observations, $D_1$ | Between measurement results, $D_2$ |
|-----------------------------------|-----------------------------|--------------------------------------|-----------------------------------|
| 0.2 mg/dm$^3$ to 0.8 mg/dm$^3$    | 0.07                        | 0.08                                 |
| 0.8 mg/dm$^3$ to 1.2 mg/dm$^3$    | 0.11                        | 0.13                                 |
| 1.2 mg/dm$^3$ to 1.6 mg/dm$^3$    | 0.12                        | 0.14                                 |
| 1.6 mg/dm$^3$ to 3.0 mg/dm$^3$    | 0.13                        | 0.15                                 |

4. Results and discussion

4.1. Evaluation of repeatability of standard measurement method
Inside the laboratory 2, the personnel take measurements in parallel. Number of measurements $N = 10$. The results of the experiment are shown in table 1.

| Test part verification results |
|--------------------------------|
| Name defined characteristics (parameters) | Mass concentration of ammonium ions | |
| Date of testing | 23.09.2021 y. | 24.06.2021 y. |
| Test environment: Temperature (21±1)°C., Air humidity (51±1) % | |
| Personnel | Masharipov SH.M. | Sobirov O.K. |
| Number of test series: | |
| X1 test result,% | 2.59 | 2.595 |
| X2 test result,% | 2.575 | 2.575 |
| X3 test result,% | 2.61 | 2.61 |
| X4 test result,% | 2.585 | 2.585 |
X5 test result, % 2.605 2.615  
X6 test result, % 2.615 2.62  
X7 test result, % 2.635 2.63  
X8 test result, % 2.58 2.59  
X9 test result, % 2.605 2.6  
X10 test result, % 2.595 2.61  
Mean values, W, % 2.5995 2.603  
Reference values, W_T % 2.60125  

Repeatability standard deviation* (SD), % 0.0181 0.0170  
**Relative standard deviation (RSD), % (SD^100/W_T)= 0.0069 (SD^100/W_T)= 0.0065  
P=0.95, n=2, GOST 5900-2014, p.7.6. norm repeatability r 0.0812  

Meets the criteria. Meets the criteria.  

Algorithms for conducting experiments on evaluation of repeatability, reproducibility, intermediate precision indicators, correctness indicators (characteristics of systematic error) of methods and measurement results are recommended to be introduced through experimental metrological studies of accuracy indicators (error characteristics) of measurement results performed according to the developed methodology, and (or) through programs for monitoring accuracy indicators of the applied methodology [2-3].

Figure 1. Evaluation of "measurement repeatability" of the first personnel.
4.2. Evaluation of reproducibility of standard measurement method

The method does not specify the reproducibility limit [4-5]. The reproducibility limit, if not specified in the test procedure, can be calculated according to the formula (2-5)

\[ S_R = \sqrt{S_X^2 + S_r^2 \left( \frac{n-1}{n} \right)} \] (2)

\[ S_r = \sqrt{\frac{\sum_{i=1}^{p} S_i^2}{p}} = \sqrt{\frac{S_1^2 + S_2^2 + S_3^2 + \ldots + S_k^2}{p}} \] (3)

\[ S_X = \sqrt{\frac{\sum_{i=1}^{p} d_i^2}{p-1}} = \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots + d_k^2}{p-1}} \] (4)

\[ R = 2.8 \cdot S_R \] (5)

Figure 2. Evaluation of "measurement repeatability" of the second personnel.

Figure 3. Evaluation of "reproducibility of measurements" when two laboratories participate (according to the test method).
4.3. Measurement Uncertainty Assessment
According to [6], the total uncertainty of measurements is calculated using this formula 6:

\[ U(1)_{SUMM} = C(1) \cdot \sqrt{\left( \frac{U(a)}{a} \right)^2 + \left( \frac{U(V_i)}{V_i} \right)^2 + \left( \frac{U(V)}{V} \right)^2} = 0.0068 \text{ mg/dm}^3 \]  

(6)

\[ U(2)_{SUMM} = C(2) \cdot \sqrt{\left( \frac{U(a)}{a} \right)^2 + \left( \frac{U(V_i)}{V_i} \right)^2 + \left( \frac{U(V)}{V} \right)^2} = 0.0065 \text{ mg/dm}^3 \]  

(7)

4.4. Now we define the extended uncertainty of measurements

\[ U(1)_{EXTENDED} = k \cdot U(1) = 2 \cdot 0.0068 \text{ mg/dm}^3 = 0.0136 \text{ mg/dm}^3 \]  

(8)

\[ U(2)_{EXTENDED} = k \cdot U(2) = 2 \cdot 0.0065 \text{ mg/dm}^3 = 0.0130 \text{ mg/dm}^3 \]  

(9)

To assess the acceptability of measurements, we use the En factor calculated by formula 10 [6,7,8].

\[ E_n = \frac{x - X}{\sqrt{u_{lab}^2 + U_{ref}^2}} \]  

(10)

where \( U_{lab} \) - extended uncertainty associated with the participant's outcome; \( U_{ref} \) - extended uncertainty of the attributed value obtained in the reference laboratory.

The quality of our experiments meets the criteria \( En=0.185<1 \).

5. Conclusions
Between results of parallel observations < 0.13 mg/dm\(^3\), discrepancies between measurement results < 0.15 mg/dm\(^3\). The difference in results (\( X_{max} - X_{min} \)) obtained under repeatability conditions will not exceed from the corresponding repeatability limits (\( r \)) at \( P=0.95 \) (probability of coverage). The requirements of the used method of verifying the acceptability of measurement results obtained under repeatability conditions have been met and meet the established criteria.

The difference in the inter-laboratory results obtained under reproducibility conditions will not exceed from the corresponding tolerance limits at \( P = 0.95 \) (probability of coverage). The requirements of the method used to verify the acceptability of the results of measurements obtained under reproducibility conditions have been met and meet the established criteria.

The results of qualification tests often need to be converted into performance statistics in order to interpret them and be able to compare them with established goals. The objective is to measure the deviation from the assigned value in a way that allows comparison with performance evaluation criteria. It is possible to use both simple statistical methods that do not require processing, and complex methods with statistical transformations. The quality of our experiments meets the criteria \( En=0.185<1 \).

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