Monitoring the stability of the results of studies of chilled river fish for cadmium content using the method of additions

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Abstract. The results obtained indicate that in the range of less than 0.01 mg of cadmium per 1 kg of river fish prevails (43.3%) over other ranges. The least registered sample results (4.3%) with the range of obtained data - 0.1-1.0 mg/kg. The relevance of the problem under consideration is due to the need to encompass a broad spectrum in the determination of cadmium in river fish in hardware. The primary and important task remains to ensure control of the quantitative content of cadmium, the introduction and application of fast and reliable methods of their research. The analysis of the data obtained shows that all the results on the study of chilled river fish for the content of cadmium, obtained by the methods of stripping voltammetry and atomic absorption spectrometry, to assess the precision and operational control of the error using the method of additions are satisfactory. The implementation of the methods of stripping voltammetry and atomic absorption spectrometry achieves the best precision of research results in the testing laboratory, both under repeatability conditions and under conditions of intermediate precision.

1. Introduction
In the scientific literature, enough attention is paid to the study of the effect of nutrition on human health, information on contaminants, their types and effects on the body as a whole, routes of intake of toxicants and preventive measures to reduce the level of food contamination with toxic substances, as well as technological methods of reducing residues are presented in detail. contaminants in food products [1-6]. The processes of updating the laboratory base in modern conditions of development of scientific and technological progress are objectively necessary [7-14]. Testing laboratories monitoring food safety indicators are equipped with equipment for photometric, atomic absorption, chromatographic analysis. The development of effective algorithms for optimizing the laboratory base of equipment, as well as the search for a solution that will allow laboratories to provide reliable test results at minimal cost in the shortest possible time, is an important and urgent task [15-19]. The relevance of the problem under
consideration is due to the need for hardware to cover a wide range in the determination of toxic elements. The primary and important task remains to ensure the control of the quantitative content of toxic elements, the introduction and application of fast and reliable methods of their analysis [20-25]. Implementation of quality management systems is of great importance [26-27].

This paper considers such a toxic element as cadmium, which is mandatory for control in food, in accordance with the requirements of the Technical Regulations of the Customs Union 021/2011 (TR CU 021) “On food safety” (figure 1).

Cadmium is classified as a toxicant of the highest hazard group; it is a highly toxic cumulative poison with a broad spectrum of action (figure 2).
2. Material and methods
The development and approbation in the laboratory of modified test methods of the conformity confirmation method is an important and urgent task.

Conducting comparative tests with these methods in order to ensure control of cadmium in food products, analyzing the accuracy, precision, repeatability of the results obtained allows us to judge the effectiveness of these methods, and also allows for a comparative analysis of the results. An analysis was carried out in order to optimize the methods used and to develop the most economical and effective option for optimizing the equipment used in the testing laboratory while maintaining the metrological characteristics of the accuracy of the results obtained.

The methodological basis is the standards for research methods, test methods, operating manuals and instructions for the use of equipment.

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Quality control of the analysis results during the implementation of the technique in the laboratory provides for the control of the stability of the analysis results.

The object of research is samples of chilled river fish.

Equipment for research of cadmium content in food raw materials and food products is shown in figure 3.

![Equipment for research](image)

**Figure 3.** Research instrument base.

During the research, the standard deviation (RMS) of the intralaboratory repeatability of $S_r$ and the intermediate precision $S_R$ of atomic absorption analysis and stripping voltammetry were estimated.

For research purposes, we used standard samples of the composition of a solution of cadmium ions (1.0 mg/cm$^3$). The main document of the research procedure is the test facility quality manual.

The control by the method of additions during the implementation of various methods in this work was carried out according to the approved research scheme.

During the operational control of the analysis procedure using the control procedure to control the error using the method of additions, the control means were working samples of a stable composition and the same samples with a known addition of cadmium.

Under the conditions of in-laboratory precision, samples were analyzed with and without added cadmium.

3. Results and discussion
Atomic absorption spectrometry is widely used in the determination of heavy metals (toxic elements) in various branches of science and industry.
Voltammetric analyzers, as a rule, have their own electrodes, software and methodological support. The voltammetric analyzer can have one electrochemical cell or several. Examples of voltammetric analyzers: with one electrochemical cell - "ABS-1.1", "IVA-5", "Ecotest-VA", "AVA 3", "AKV-07MK", "Pan-arsenic", "PU-1"; with three electrochemical cells - "TA-4", "TA-07" and others.

Maximum levels of cadmium in accordance with the national standard of the People’s Republic of China (PRC) GB 2762-2012 meet the requirements of the Codex Alimentarius standards, unless there is no Codex standard. The maximum levels of cadmium in accordance with the requirements of TR CU 021 comply with, and for some types of products are more stringent, the requirements of the Codex Alimentarius standards, except in cases where there is no Codex standard. In comparison with the maximum permissible concentration (MPC) of cadmium in food products regulated by the requirements of TR CU 021, the maximum levels of cadmium in accordance with the national standard of the PRC GB 2762-2012 meet or below the requirements of TR CU 021, i.e. MPCs for cadmium for some types of products were stricter in TR CU 021.

It should be noted changes in the national standard of the PRC GB 2762-2012 in the direction of expanding the range of product groups for which standard cadmium indicators have been established, compared to GB 2762-2005. In the national standard GB 2762-2005, only maximum levels of cadmium were presented for the following types of products: cereals (rice, soybeans, peanuts, flour, corn, millet, sorghum); potatoes; animal meat; liver and kidneys of animals; fruit; stem vegetables (other than celery); leafy vegetables; celery; edible mushrooms; other vegetables; fish; fresh egg.

3.1. Intermediate precision control
Under conditions of repeatability and intermediate precision, five average measurement results were obtained for a chilled river fish sample.

The acceptability of the determination results was assessed in accordance with GOST R ISO 5725-6 "Accuracy (correctness and precision) of methods and measurement results". The range between the maximum and minimum values of all five analysis results \(X_{\text{max}} - X_{\text{min}}\) was compared with the absolute value of the critical range for five analysis results \(CR_{0.95}(5)\).

The critical range factor \(f(n)\) for the five results is 3.9.

The analyzer is controlled by pressing the control buttons displayed on the display of the test equipment.

The permissible discrepancy between two parallel results obtained in the same laboratory in one series of measurements (convergence r) depends on the mass fraction of cadmium in chilled river fish and, at a confidence level of \(P = 0.95\), does not exceed the established values of regulatory documents.

The analyzer is controlled by the software of the testing process at all stages of measurements. The widespread use of computer software significantly expands the capabilities of the devices, allows more reliable isolation of the analytical signal, reduce the measurement error to 2-5%, automate statistical processing and calculation of analysis results: for the Kvant-2AT spectrometer, when determining cadmium = 46.8%. For the analyzer "TA-4" in the determination of cadmium = 50.7%. The analysis of the obtained research results, presented in table 1, found that the condition \(X_{\text{max}} - X_{\text{min}}\) \(\leq\) \(CR_{0.95}(5)\) is satisfied for all measurement results.

**Table 1.** Results of studies of chilled river fish for cadmium content (standardized level of permissible concentration 0.2 mg/kg).

| №  | TA-4  | Kvant-2AT | TA-4  | Kvant-2AT | TA-4  | Kvant-2AT |
|----|-------|-----------|-------|-----------|-------|-----------|
|    | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) |
| 1  | 0.044 | 0.046 | 0.094 | 0.089 | 0.097 | 0.096 |
| 2  | 0.042 | 0.051 | 0.086 | 0.094 | 0.093 | 0.088 |
| 3  | 0.045 | 0.048 | 0.083 | 0.096 | 0.091 | 0.092 |
| 4  | 0.058 | 0.047 | 0.089 | 0.095 | 0.088 | 0.097 |
| 5  | 0.054 | 0.051 | 0.095 | 0.087 | 0.094 | 0.095 |
| \(X_{\text{avg}}\) | 0.0486 | 0.0486 | 0.0894 | 0.0922 | 0.0926 | 0.0936 |
Assessment of the precision of research results \((X_{\text{max}}-X_{\text{min}}) \leq CR_{0.05}(5)\)

\[
0.016<0.025 \quad 0.005<0.023 \quad 0.012<0.045 \quad 0.009<0.043 \quad 0.009<0.047 \quad 0.009<0.044
\]

\(C-a\) - is the concentration of the certified mixture of the element, from which the additive is made to the analyzed sample

3.2. *Monitoring the stability of analysis results using the addition method*

Operational control of the analysis procedure was carried out by the performer by comparing the result of a separate control procedure \(K_k\) with the calculated control standard \(K\) (figure 4).

![Figure 4. Operational control of the analysis procedure.](image)

In accordance with the methods of analysis, the results of control measurements of the concentration of cadmium in the averaged working sample of river fish were obtained – \(X_{(n)}\) and in the averaged working sample with a known addition of cadmium – \(X_{(n)+a}\).

The results of the operational control of the analysis procedure using the control procedure to control the error using the addition method are presented in table 2.

**Table 2.** The results of the operational control of the analysis procedure using the method of additions (examination of samples for the content of cadmium).

| № | sample preparation | stage addition | measurements |
|---|-------------------|----------------|--------------|
|    | TA-4              | Kvant-2AT      | TA-4         | Kvant-2AT    |
|    | Kk                | K              | Kk           | K            |
| 1  | -0.0092           | 0.01111        | -0.0066      | 0.01051      | -0.006       | 0.01142      | -0.005       | 0.010631    |
| 2  | -0.007            | 0.00747        | -0.007       | 0.00715      | 0.0046      | 0.008676     | 0.0036       | 0.008162    |
| 3  | -0.002            | 0.00203        | -0.0017      | 0.00187      | -0.00118    | 0.00211      | -0.00082     | 0.001951    |
| 4  | -0.0082           | 0.00878        | -0.0062      | 0.00837      | -0.007      | 0.008904     | -0.0036      | 0.008615    |

Analyzing the obtained research results presented in table 2, we came to the conclusion that the condition \(|K_k| \leq K\) is satisfied, the analysis procedure is recognized as satisfactory.

In order to control the stability of the analysis results obtained by different methods, operational control of the error was carried out using the method of additions. The results of the operational control
of the test procedure for chilled river fish using the control procedure to control the error using the addition method are presented in table 3.

Table 3. Research results of chilled river fish for cadmium content.

| Kvant-2AT | TA-4 | Kvant-2AT | TA-4 | Kvant-2AT | TA-4 |
|-----------|------|-----------|------|-----------|------|
| X(5)avr   | 0.0486 | 0.0486 | 0.0922 | 0.0894 | 0.0936 | 0.0926 |
| Xavr      | 0.0486 | 0.0908 | 0.0931 |

Assessment of the precision of research results

| 0 % < 17 % | 1.5 % < 17 % | 0.54 % < 17 % |
|------------|--------------|--------------|
| K          | Kk           | K            |
| 0.01470674 | -0.0078      | 0.01499711   |

The research results (table 3) are considered satisfactory.

3.3. Research results monitoring

We monitored the results of studies on the content of cadmium in river fish from January 2019 to October 2020. We assessed the distribution of research results depending on the concentration of cadmium in river fish (figure 5).

Figure 5. Distribution of test results depending on the concentration (mg / kg) of cadmium in river fish samples, %.

The obtained results indicate that in the range of less than 0.01 mg of cadmium per 1 kg of river fish prevail (43.3%) over other ranges. The least registered sample results (4.3%) with the range of obtained data - 0.1-1.0 mg/kg.
4. Conclusion
The analysis of the obtained data results shows that all the results on the study of the cadmium content in the chilled river fish by assessing the precision and operational control of the error using the method of additions are satisfactory.

The implementation of the methods of stripping voltammetry and atomic absorption spectrometry achieves the best precision of the results of studies of cadmium in the testing laboratory, both under conditions of intermediate precision and under conditions of repeatability.

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