Comparative analysis of methods of photoelectric colorimetry and stripping voltammetry in assessing the content of arsenic in sea bass samples

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Abstract. The development of effective algorithms for optimizing the laboratory equipment base is one of the urgent tasks. Arsenic is classified as a toxicant of the highest hazard group; it is a highly toxic cumulative poison with a broad spectrum of action. The paper considers an assessment of the method for investigating the content of arsenic in sea bass. The research results (by the methods of photoelectric colorimetry and stripping voltammetry) on the operational control of the error using the method of additions and the assessment of the precision were found to be satisfactory. The monitoring results are presented, namely the results indicate that in the range from 0.02 to 0.05 mg of arsenic per 1 kg of sea bass, k prevails (28.1%) over other ranges. The least registered sample results (20.8%) with a range of obtained data are less than 0.02 mg/kg.

1. Introduction
The issues of the influence of nutrition on human health are discussed by many researchers [1-5], the level of exposure to xenobiotics entering the human body with food is constantly analyzed [6-9]. Research of food products and food raw materials for compliance with modern international quality standards is a component that determines the competitiveness of many laboratories [10-13]. The development of effective algorithms for optimizing the laboratory equipment base is one of the urgent tasks [12-18]. An important task is to ensure control of the quantitative content of heavy metals (including arsenic) [19-26].

This paper considers such a toxic element as arsenic, which is mandatory for control in fish and aquatic organisms, in accordance with the requirements of the Technical Regulations of the Customs Union 021/2011 (TR CU 021) "On food safety", as amended on August 8, 2019 (figure 1).
Arsenic 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).

A brief analysis of documents regulating the content of arsenic in different countries is presented. The national standard of the People's Republic of China GB 2762, in comparison with the requirements of TR CU 021, does not standardize the maximum levels of arsenic in the following types of products:
bakery products; biologically active food additives; food products for pregnant and lactating women; fruits and products from them; legumes and products from them. The national standard of the People's Republic of China GB 2762 rationing the maximum levels of arsenic is carried out by the allocation of total arsenic and inorganic arsenic. In the national standard of the People's Republic of China GB 2762, in comparison with the earlier version of the national standard, the maximum levels of arsenic were added for the following types of products: food products for special dietary purposes; canned complementary foods for infants and young children; drinks (packaged drinking water); seasonings; edible mushrooms and products from them. GB 2762 expanded the range of cereals and their products, milk and dairy products, aquatic animals and fish and their processed products. In the national standard of the People's Republic of China GB 2762-2012, compared with the earlier edition of the standard, there are no maximum levels of arsenic for eggs, liqueurs, fruits and fruit juices, juices with pulp.

The Codex Alimentarius standards set maximum arsenic levels (0.1 mg/kg) for various types of vegetable oils and animal fats: edible fats and oils; margarine; lard, rendered pork fat, oleostok and edible fat; olive oil, refined; extra virgin olive oil; extra virgin olive oil, vegetable oils, edible vegetable oils, unrefined. Also, the Codex Alimentarius standards set the maximum levels of arsenic for natural mineral waters (total As 0.01 mg/l) and food salt (0.5 mg/kg).

The maximum levels of arsenic in accordance with the national standard of the People's Republic of China GB 2762 and TR CU 021 meet the requirements of the Codex Alimentarius standards, unless there is no Codex standard. In comparison with the maximum permissible concentration of arsenic in food products regulated by the requirements of TR CU 021, the maximum levels of arsenic in accordance with the national standard of the People's Republic of China GB 2762 meet or below the requirements of TR CU 021, i.e. permissible levels of arsenic turned out to be stricter in TR CU 021.

The exception was the groups "Aquatic animals and products from them", "Sugar and sweeteners", "Seasonings", for which the maximum level of arsenic in accordance with GB 276 is lower than the requirements of TR CU 021.

2. Material and Methods

Determination of arsenic (standards and laboratory equipment used are shown in figure 3.

![Figure 3. Standards and applied laboratory equipment.](image)

The object of research is the samples of sea bass.

Equipment for research of cadmium content in food raw materials and food products is shown in figure 4.

![Figure 4. Research instrument base.](image)
The regulatory framework of standards for the determination of arsenic in these product studies is presented in figures 5 and 6.

**Figure 5.**
Photoelectric colorimetry of food and food raw materials.

**Figure 6.**
Stripping voltammetry on the analyzer "Pan-arsenic".

Arsenic volt-ampere curves (as one example) are shown in figure 7.

**Figure 7.** Arsenic current-voltage curves.

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 arsenic.
Under the conditions of in-laboratory precision, the analysis of samples with and without added arsenic was carried out. Operational control of the analysis procedure was carried out by the performer by comparing the result of a separate control procedure $K_c$ with the calculated control standard $K$ (figure 8).

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

**Figure 8.** Operational control of the analysis procedure.

### 3. Results and Discussion

In accordance with the requirements of the interstate standard GOST R ISO 5725-6, the acceptability of the results of determining arsenic in products was assessed. The critical range factor $f(n)$ for the five results is 3.9. Repeatability standard deviation $S_r$ for each measurement method:

- For "KFK-2MP": $(CR_{0.95}(5), \%) = f(5) \times S_r(\text{As}) = 3.9 \times 25 = 97.5 \%$
- For "Pan-arsenic": $(CR_{0.95}(5), \%) = f(5) \times S_r(\text{As}) = 3.9 \times 17 = 66.3 \%$

The absolute value of the critical range $CR_{0.95}(5)$ is calculated by the formula:

$$CR_{0.95}(5) = 0.01 \times (CR_{0.95}(5), \%) \times X_{cr}(5)$$

If the range between the maximum and minimum values of five analysis results ($X_{max} - X_{min}$) is equal to or less than the absolute value of the critical range $CR_{0.95}(5)$, then the results of the analysis performed under conditions of repeatability and intermediate precision are considered satisfactory. The research results are presented in table 1.

**Table 1.** Results of studies of sea perch for arsenic content.

| № | Pan-arsenic | KFK-2MP | Pan-arsenic | KFK-2MP | Pan-arsenic | KFK-2MP |
|---|-------------|---------|-------------|---------|-------------|---------|
|    |             |         |             |         |             |         |
| 1  | 0.78        | 0.64    | 1.16        | 0.95    | 1.26        | 0.97    |
| 2  | 0.73        | 0.63    | 1.11        | 1.03    | 1.31        | 1.15    |
| 3  | 0.71        | 0.57    | 1.21        | 1.05    | 1.12        | 1.11    |
| 4  | 0.75        | 0.68    | 1.04        | 0.96    | 1.19        | 1.03    |
| 5  | 0.69        | 0.65    | 1.14        | 0.97    | 1.24        | 0.98    |
| $X_{avr}$ | 0.732       | 0.634   | 1.132       | 0.992   | 1.224       | 1.048   |

Assessing the precision of results ($X_{max} - X_{min}$) ≤ $CR_{0.95}(5)$

| 0.09 < 0.49 | 0.11 < 0.63 | 0.17 < 0.75 | 0.10 < 0.97 | 0.19 < 0.81 | 0.18 < 1.02 |
3.1. Monitoring the stability of analysis results using the additive method
The operative control of the analysis procedure was carried out by the performer by comparing the result of a separate control procedure Kc with the calculated control standard K. The operative control of the procedure for testing sea bass for arsenic content provides for the operations approved in the standards for product testing.

The means of control were working samples of a stable composition of arsenic and the same samples with a known addition of arsenic determined by us during the operational control of the analysis procedure using a control procedure to assess the error using the addition method.

A diagram of the control process by the addition method is shown in figure 9.

![Diagram](image)

**Figure 9.** Procedure steps under conditions of intra-laboratory precision.

In accordance with the methods of analysis, the results of control measurements of the concentration of arsenic in the averaged working sample - \( X_{(n)} \) and in the averaged working sample with a known addition of arsenic - \( X_{(n)+a} \).

The analysis procedure is considered satisfactory if the following conditions are met:

\[
|K_c| \leq K
\]

The results of the operational control of the analysis procedure using the control procedure to control the error using the addition method are summarized in tables 2 and 3.

| Table 2. | Results of investigations of samples for arsenic content using the addition method (addition of arsenic at the stage of sample preparation). |
| --- | --- |
| KFK-2MP | Pan-arsenic |
| \( K_c \) | K | \( K_c \) | K |
| -0.142 | 0.1858 | -0.1 | 0.24723 |
| -0.0104 | 0.01865 | -0.0074 | 0.01372 |
| -0.0044 | 0.00538 | -0.0042 | 0.00595 |
| -0.0206 | 0.0247 | -0.0168 | 0.01868 |

| Table 3. | The results of testing samples for arsenic content using the additive method (additive at the stage of measurements). |
| --- | --- |
| KFK-2MP | Pan-arsenic |
| \( K_c \) | K | \( K_c \) | K |
| -0.086 | 0.257219 | -0.008 | 0.3411 |
| -0.0046 | 0.019748 | -0.0028 | 0.01431 |
| -0.0004 | 0.006216 | -0.003 | 0.00611 |
| -0.0036 | 0.028146 | -0.0066 | 0.02007 |

The condition \( |K_c| \leq K \) is fulfilled for all measurement results.
The evaluation of the precision of the results obtained by different methods is carried out by calculating the relative error, which reflects the measurement accuracy, and comparing it with the standard deviation of the reproducibility of the result when implementing different research methods.

The analysis procedure is considered satisfactory if the following conditions are met: \( \sigma \leq \sigma_R \)

Table 4 shows the study of assessing the precision of product test results for arsenic content, obtained by photoelectric colorimetry and stripping voltammetry, by calculating the relative error and comparing it with the standard deviation of the reproducibility of the results.

Also, the stability of the results of testing products for arsenic content, obtained by photoelectric colorimetry and stripping voltammetry, was monitored, and operational control of the error was carried out using the additive method.

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

The values of \( X_{av(n)} \) and \( X_{av(n)+d} \) were taken as the average values of the averaged results of five measurements obtained by different methods, in samples without an additive and in samples with an additive.

| Table 4. Results of studies of sea bass for arsenic content. |
|-------------------------------------------------------------|
| Pan arsenic | KFK-2MP | Pan arsenic | KFK-2MP | Pan arsenic | KFK-2MP |
|--------------|---------|-------------|---------|-------------|---------|
| \( X(5)_{av} \) | 0.732 | 0.634 | 1.132 | 0.992 | 1.224 | 1.048 |
| \( X_{av(n)} \) | 0.683 | 1.062 | 1.136 |  |
| Evaluation of the precision of results obtained by different methods | \( 7.2 \% < 22 \% \) | \( 6.6 \% < 22 \% \) | \( 7.7 \% < 22 \% \) |
| Kk | K | Kk | K |
| -0.121 | 0.23334123 | -0.047 | 0.24495482 |

The results of investigations (by the methods of photoelectric colorimetry and stripping voltammetry) on the operational control of the error using the method of additions and the assessment of precision were recognized as satisfactory.

3.2. Research results monitoring
We monitored the results of studies for the content of arsenic in sea bass from January 2019 to October 2020. We evaluated the distribution of research results depending on the concentration of arsenic in sea bass (figure 10).

![Figure 10. Distribution of test results depending on the concentration (mg/kg) of arsenic in sea fish samples, %](image)
The obtained monitoring results indicate that, in the range from 0.02 to 0.05 mg of arsenic per 1 kg of sea bass, k prevails (28.1%) over other ranges. The least registered sample results (20.8%) with a range of data obtained - less than 0.02 mg/kg.

4. Conclusion
The analysis of the obtained data results shows that all the results on the study of the content of arsenic in the sea bass by assessing the precision and operational control of the error using the method of additions are satisfactory.

A comparative analysis of two methods of photoelectric colorimetry and stripping voltammetry in assessing the content of arsenic in sea bass samples showed their relevance in the context of the development of laboratory practice.

Acknowledgements
The authors would like to express special gratitude to the engineer A M Chuprakova who carried out multi-stage tests of the designated products for compliance with the requirements of regulatory documents.

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