Control by the accuracy of the results of studies for the cadmium content in samples applying the microwave laboratory system PLP-01M

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Abstract. The article states that in order to compare the results obtained while operating on the atomic absorption spectrometer "Kvant-2AT" applying the microwave laboratory system PLP-01M and during the sample preparation in accordance with GOST 26929 "Raw materials and food products. Sample preparation. Mineralization to determine the content of toxic elements", on operating samples, the products were selected that most fully cover the range of results obtained during the research. Some research results and data analysis were carried out within 30 operating days. The data were obtained while working on the Kvant-2AT atomic absorption spectrometer, taking into account the application of the PLP-01M microwave laboratory system and while the sample preparation in accordance with GOST 26929. The average values obtained under repeatability conditions were put in the table. The analyte cadmium was supplemented to assess the accuracy of the obtained values. The implementation of sample preparation methods taking into account the microwave decomposition of the sample in the case of using the microwave laboratory system PLP-01M and while sample preparation in accordance with GOST 26929-94 achieves the precision of the analysis results both under conditions of repeatability and under conditions of intermediate precision.

1. Introduction
The investigation of the heavy metals influence in ecosystems and technological methods for reducing the residual amounts of contaminants in products is one of the topical issues [1-8].

Ensuring product testing for the content of xenobiotics requires constant improvement [9-18].

The permissible levels of cadmium in products are shown in figure 1.
Figure 1. Permissible levels of cadmium in flour, cereals and bakery products according to the requirements of technical regulations, mg/kg, not more.

One of the important tasks of testing centers is to ensure the reliability of tests at minimal cost [19-23]. The relevance of the problem under consideration is confirmed by numerous studies of scientists from different countries [24-29].

A fundamentally new method of the sample preparation is used in the microwave laboratory system PLP-01M. The decomposition was carried out in a closed system, i.e. sealed fluoroplastic vessels under the influence of high temperature, pressure and microwave field. The microwave field in the operating chamber of the furnace was created by a special generator-magnetron.

The advantages of microwave decomposition of samples applying the PLP-01M over classical methods of the sample preparation are undeniable.

2. Material and methods

The article considers and analyzes the results of examining samples for cadmium content by determining them on a Kvant-2AT atomic absorption spectrometer. It takes into account the use of the PLP-01M microwave laboratory system and while the sample preparation in accordance with GOST 26929 "Raw materials and food products. Sample preparation. Mineralization to determine the content of toxic elements”.

Sample mineralization by microwave decomposition applying the microwave laboratory system PLP-01M was carried out according to the general scheme in accordance with the instructions for the microwave laboratory oven from the TP Ural-Gefest.

The intervals were identified and control samples (CS\textsubscript{Pb}/CS\textsubscript{Cd}) with a certified value of the determined toxic element, cadmium, were selected for these intervals to cover the entire range of results obtained during research and thereby simulate the obtaining of values of various concentrations in the analysis of working samples of food products (table 1).

| Intervals, mg/dm\(^3\) | CS\textsubscript{Cd}, mg/dm\(^3\) |
|------------------------|------------------|
| 0.001–0.005            | 0.0035           |
| 0.005–0.010            | 0.0075           |
| 0.01–0.05              | 0.0              |
Standard samples of the cadmium ions solution composition were applied for research purposes (figure 2).

3. Results and discussion
The products were selected on the operating samples; they cover the range of results obtained during the research. They were selected to compare the results obtained while operating on the atomic absorption spectrometer "Kvant-2AT" taking into account the application of the microwave laboratory system PLP-01M and while the sample preparation in accordance with GOST 26929 "Raw materials and food products. Sample preparation. Mineralization to determine the content of toxic elements".

The data were obtained while working on the Kvant-2AT atomic absorption spectrometer, taking into account the application of the PLP-01M microwave laboratory system and while sample preparation in accordance with GOST 26929. The average values obtained under repeatability conditions were recorded in the table. The analyte cadmium was supplemented to assess the accuracy of the obtained values.

As a result, five average values were obtained under conditions of intermediate precision.

The preparation of the selected samples of wheat bread was carried out in accordance with GOST 26929 and in accordance with the instructions for a microwave laboratory oven PLP-01M from TP Ural-Gefest, the volume of the sample taken for analysis is given in table 1.

### Table 2. Weight of the sample in g.

| Sample preparation in accordance with GOST 26929 | Microwave decomposition on PLP-01M |
|-------------------------------------------------|-----------------------------------|
| 15                                              | 2                                 |

The results are summarized in table 3.

### Table 3. Analysis of bread samples for cadmium content.

| Days | GOST | PLP-01M | GOST | PLP-01M |
|------|------|---------|------|---------|
|      |      |         | Cs=0.015 |         |
| 1    | 0.033| 0.037   | 0.041 | 0.055   |
| 2    | 0.035| 0.035   | 0.039 | 0.054   |
| 3    | 0.029| 0.044   | 0.045 | 0.051   |
| 4    | 0.036| 0.043   | 0.046 | 0.048   |
| 5    | 0.038| 0.041   | 0.048 | 0.056   |
| Xav  | 0.0342| 0.04 | 0.0438 | 0.0528 |

Assessing the precision of results \( (X_{\text{max}} - X_{\text{min}}) \leq C R_{0.05}(5) \)

|                 | 0.009<0.016 | 0.009<0.019 | 0.009<0.020 | 0.008<0.025 |
|-----------------|-------------|-------------|-------------|-------------|

Figure 2. Characteristics of a standard sample composition of cadmium ion solution.
The data analysis in table 3 showed that the condition \((X_{\text{max}}-X_{\text{min}}) \leq CR_{0.95}(5)\) is satisfied for all measurement results.

3.1 Monitoring the stability of the results applying the supplement technique

The control tools were operating samples of a stable composition and the same samples with a known supplement of the analyte, carrying out operational control of the analysis procedure using the control procedure for error control (CPEC) applying the supplement technique.

The control while the implementation of various types of the sample preparation by the supplement technique was carried out according to the following scheme.

The sample was taken in a double size; the analyzed sample was divided into two parts. One part remained unchanged; the second one was supplemented with the determined element \(C_s\). The supplementation was carried out at the stage of sample preparation; the analysis of samples was carried out with the added additive of the determined element and without a supplement in conditions of intralaboratory precision.

The control measurements result of the determined element concentration in the averaged working sample \(X_{(n)}\) and in the averaged operating sample with a known addition of the determined element \(X_{(n)+a}\) were obtained in accordance with the analysis methods, taking into account various types of sample preparation.

As the results of control measurements of the determined element concentration in the sample and in the sample with a supplement, the simple average of two results of a single analysis were applied. The discrepancy between them does not exceed the repeatability limit.

The result of the control procedure \(C_c\) and the control standard \(C\) were calculated according to the approved methods. The comparison condition was also checked.

The results of the operational control of the analysis procedure applying the procedure to control the error using the supplement technique are summarized in table 4.

| Table 4. Results of the operational control of the analysis procedure applying the supplement technique. |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| GOST 26929                                      | PLP-01M         |
| \(C_c\)                                         | \(C\)           | \(C_c\)         | \(C\)           |
| -0.0016                                         | 0.0085954       | 0.0004          | 0.0098494       |
| -0.0054                                         | 0.0056015       | -0.0022         | 0.0066771       |
| -0.0018                                         | 0.0018943       | -0.001728       | 0.0021763       |
| -0.0044                                         | 0.006834        | -0.0032         | 0.0082083       |

The analysis of the obtained research results showed that the condition \(|C_c| \leq C\) is fulfilled for all measurement results.

3.2 The precision assessment of the analysis obtained results taking into account the application of two different types of the sample preparation

The analysis procedure was considered satisfactory if a condition 3.12 was fulfilled. The evaluating precision results of the results obtained taking into account the use of different types of sample preparation are summarized in table 5. The operational control of the error was carried out by the supplement technique to control the stability of the analysis results obtained taking into account the application of different types of sample preparation. The operational control results of the analysis procedure applying the control procedure for the error control applying the supplement technique are summarized in table 5.
Table 5. Analysis of wheat bread samples for cadmium content.

| GOST | PLP-01M | GOST | PLP-01M |
|------|---------|------|---------|
| -    | Cs=0.05 | 0.04 | 0.0528  |
| X(5)av | 0.0342 | 0.0438 |
| Xav | 0.0371 | 0.0483 |

Evaluation of the results precision obtained by different sample preparations:

|  | 9.3 % < 17 % | 7.8 % < 17 % |
|---|-------------|-------------|
| X | Cc | C |
| | -0.0038 | 0.00869709 |

The analysis of the obtained data concludes that the results for the assessment of the precision and operational error control applying the supplement technique are satisfactory.

4. Conclusion
The results of analyzes carried out under conditions of repeatability and intermediate precision are considered satisfactory. The results for the assessment according to the precision and operational control of the error applying the method of additions are satisfactory.

The implementation of sample preparation methods taking into account the microwave decomposition of the sample in the case of using the PLP-01M microwave laboratory system and while the sample preparation in accordance with GOST 26929-94 achieves of the analysis results precision both under conditions of repeatability and under conditions of intermediate precision.

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