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

M B Rebezov1,2, Zh B Assirzhanova3, Assel Dautova3, M A Derkho4, G V Meshcheryakova4 and O A Gumenyuk4

1 V M Gorbatov Federal Research Center for Food Systems of Russian Academy of Sciences, 26 Talalikhina St., Moscow, 109316, Russian Federation
2 Prokhorov General Physics Institute of the Russian Academy of Science, 38 Vavilov st., Moscow, 119991, Russian Federation
3 Shakarim State University of Semey, 20a Glinka st., Semey, 071400, Republic of Kazakhstan
4 South-Ural State Agrarianl University, Gagarin st., 13 Troitsk, Chelyabinsk oblast, 454700, Russian Federation

E-mail: dr.rebezov.m@gmail.com

Abstract. The article presents the analysis of the study results of samples for lead content by their determination on the atomic absorption spectrometer "Kvant-2AT", taking into account the use of the microwave laboratory system PLP-01M and while the sample preparation in accordance with GOST 26929 "Raw materials and food product. Sample preparation. Mineralization to determine the content of toxic elements". 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 was created by a special generator-magnetron in the operating chamber of the furnace. According to the assessment results of the operational control of the measurement procedure applying samples for the lead control when the microwave laboratory system PLP-01M was introduced in the laboratory; the analysis procedure was found satisfactory.

1. Introduction

Studies of the heavy metals influence in ecosystems and technological methods for reducing the residual amounts of contaminants in products are one of the urgent issues [1-6]. Product testing for the content of xenobiotics requires constant improvement [7-16]. One of the important tasks of testing centers is to ensure reliability tests at minimal cost [17-21]. The relevance of the considered problem is confirmed by numerous studies of scientists from different countries [22-26].

Lead is classified as a toxicant of the highest hazard group.

A fundamentally new method of sample preparation is applied in the microwave laboratory system PLP-01M. The decomposition was carried out in a closed system, sealed fluoroplastic vessels under the influence of high temperature, pressure and microwave field. The microwave field was created by a special generator-magnetron in the operating chamber of the furnace.
The advantages of microwave decomposition of samples applying the PLP-01M over classical methods of the sample preparation are as follows:

- increase in the acid decomposition rate of inorganic and organic samples by 10-100 times;
- obtaining a sample of the improved quality;
- reproducibility of the research process;
- reduction in consumption of acids used for sample decomposition;
- realization of the ability to retain volatile components in the sample due to the closed vessels application;
- automation of the decomposition process of samples due to a microprocessor control unit.

2. Material and methods
The article presents the analysis of the study results of samples for lead content by their determination on the atomic absorption spectrometer "Kvant-2AT", taking into account the use of the microwave laboratory system PLP-01M and while the sample preparation in accordance with GOST 26929 "Raw materials and food product. Sample preparation. Mineralization to determine the content of toxic elements".

The sample mineralization by microwave decomposition using the microwave laboratory system PLP-01M was carried out by a general scheme in accordance with the instructions for the microwave laboratory oven from the TP Ural-Gefest.

The acid mineralization by the microwave laboratory system PLP-01M was realized according to the following scheme:

- sample weight of 2 g (0.5–2 g, depending on a type of a sample) was placed in a sealed fluoroplastic vessel;
- supplement of 8 cm³ of concentrated nitric acid was carried out, followed by sealing the vessel;
- in parallel, mineralization of the reagents supplemented to the sample weight was conducted to control their purity (control solution);
- carousel with fluoroplastic vessels was placed in the microwave laboratory system PLP-01M; the sample was decomposed in accordance with the program from the TP Ural-Gefest for this product group;
- vessels were cooled and opened in accordance with the instructions of the microwave laboratory oven from the TP Ural-Gefest when the decomposition was over.

The mineralization of samples based on an inorganic matrix was carried out in one stage (control samples (CS) analysis). The process was conducted with a gradual increase in pressure (maximum working pressure 1300 kPa) and the second stage of mineralization while the mineralization of samples with an organic matrix. For this, 2 cm³ of hydrogen peroxide was supplemented to the cooled sample. The vessel was hermetically closed and placed in the microwave laboratory system PLP-01M; the re-mineralization was carried out in accordance with the program from the TP Ural-Gefest.

The resulting solution was filtered through a paper filter, transferred quantitatively into a 25 cm³ volumetric flask; the volume was brought to the mark with a background solution of nitric acid, and thoroughly mixed.

The independent measurement results were obtained by the same method on identical test objects, in the same laboratory, by one operator, using the same equipment, an atomic absorption spectrometer "Kvant-2AT", within a short period of time, i.e. the repeatability conditions were met.

3. Results and discussion
Intervals were identified and control samples (CS<sub>Pb</sub>/CS<sub>Cd</sub>) with a certified lead value 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 operating samples of food products (table 1).

**Table 1.** Intervals and control samples of the determined lead.

| intervals, mg/dm³ | CS_{Pb}, mg/dm³ |
|-------------------|-----------------|
| 0.01–0.03         | 0.015           |
| 0.03–0.05         | 0.04            |
| 0.05–0.10         | 0.085           |
| 0.1–1.0           | 0.55            |

The standard samples of the solution composition of lead ions were applied for the research purposes, presented in figure 1.

![Figure 1. Characteristics of a standard sample of the solution composition of lead ions.](image)

The studies were carried out to check the reproducibility of the results by different operators using the same equipment on different days, i.e. conditions of intermediate (in-laboratory) precision were met. The data accumulation and processing were conducted within three days. The sample preparation and analysis of two parallels were carried out during the first day, the average values for each parallel was calculated and the average research result for a day was found.

All the obtained values were entered into the table in the appropriate columns (tables 2-5).

**Table 2.** Results of studies for the lead concentration control for 0.015 mg / dm³.

| C_{CS_{Pb}=0.015} mg/dm³ | X₁ | X₂ | X_{av} | X_{av} per day |
|---------------------------|----|----|--------|----------------|
| PLP-01M                   |    |    |        |                |
| I day                     | 0.01464 | 0.01453 | 0.014585 | 0.01456 |
|                           | 0.01451 | 0.01456 | 0.014535 |
|                           | 0.01461 | 0.01466 | 0.014635 |
|                           | 0.01402 | 0.01423 | 0.014125 |
|                           | 0.01386 | 0.01411 | 0.013985 |
|                           | 0.01445 | 0.01428 | 0.014365 |
| Accepted result           |    |    |        | 0.014372 |
| GOST26929                 |    |    |        |                |
| I day                     | 0.01364 | 0.01353 | 0.013585 | 0.013568 |
|                           | 0.01351 | 0.01359 | 0.01355 |
|                           | 0.01401 | 0.01416 | 0.014085 |
|                           | 0.01405 | 0.01417 | 0.01411 |
|                           | 0.01296 | 0.01311 | 0.013035 |
|                           | 0.01315 | 0.01327 | 0.01321 |
| Accepted result           |    |    |        | 0.013596 |
A sample of lead control with a concentration of 0.015 mg/dm$^3$ analyzed taking into account the microwave laboratory system PLP-01M application, is defined as 0.0144 mg/dm$^3$; in the case of sample preparation in accordance with GOST 26929 it is 0.0136 mg/dm$^3$.

Table 3. Results of studies for the lead concentration control for 0.04 mg/dm$^3$.

| $C_{CSPb}$=0.04 mg/dm$^3$ | $X_1$ | $X_2$ | $X_{av}$ | $X_{av}$ per day |
|---------------------------|-------|-------|----------|-----------------|
| PLP-01M                   |       |       |          |                 |
| I day                     | 0.04011 | 0.03870 | 0.039405 | 0.038595        |
|                            | 0.03772 | 0.03785 | 0.037785 |                 |
| II day                    | 0.04031 | 0.04011 | 0.04021  | 0.03976         |
|                            | 0.03915 | 0.03947 | 0.03931  |                 |
| III day                   | 0.03686 | 0.03629 | 0.036575 | 0.036333        |
|                            | 0.03615 | 0.03603 | 0.03609  |                 |
| Accepted result           |       |       |          | 0.038229        |
| GOST 26929                |       |       |          |                 |
| I день                    | 0.03641 | 0.03553 | 0.03597  | 0.03551         |
|                            | 0.03551 | 0.03459 | 0.03505  |                 |
| II day                    | 0.03492 | 0.03564 | 0.03528  | 0.035           |
|                            | 0.03511 | 0.03433 | 0.03472  |                 |
| III day                   | 0.03657 | 0.03618 | 0.036375 | 0.036215        |
|                            | 0.03614 | 0.03597 | 0.036055 |                 |
| Accepted result           |       |       |          | 0.035575        |

Table 4. Results of studies for the lead concentration control for 0.085 mg/dm$^3$.

| $C_{CSPb}$=0.085 mg/dm$^3$ | $X_1$ | $X_2$ | $X_{av}$ | $X_{av}$ per day |
|-----------------------------|-------|-------|----------|-----------------|
| PLP-01M                     |       |       |          |                 |
| I day                       | 0.08411 | 0.08471 | 0.08441  | 0.080528        |
|                            | 0.07775 | 0.07554 | 0.076645 |                 |
| II day                      | 0.08513 | 0.08507 | 0.0851   | 0.084958        |
|                            | 0.08476 | 0.08487 | 0.084815 |                 |
| III day                     | 0.08362 | 0.08347 | 0.083545 | 0.083763        |
|                            | 0.08411 | 0.08385 | 0.08398  |                 |
| Accepted result             |       |       |          | 0.083083        |
| GOST 26929                  |       |       |          |                 |
| I день                      | 0.08231 | 0.08314 | 0.082725 | 0.082043        |
|                            | 0.08125 | 0.08147 | 0.08136  |                 |
| II day                      | 0.07684 | 0.07567 | 0.076255 | 0.077323        |
|                            | 0.07814 | 0.07864 | 0.07839  |                 |
| III day                     | 0.07947 | 0.07873 | 0.07910  | 0.080033        |
|                            | 0.08062 | 0.08131 | 0.080965 |                 |
| Accepted result             |       |       |          | 0.079799        |
Table 5. Results of studies for the lead concentration control for 0.55 mg/dm$^3$.

| $C_{CS Pb}$=0.055 mg/dm$^3$ | $X_1$ | $X_2$ | $X_{av}$ | $X_{av}$ per day |
|-----------------------------|------|------|----------|-----------------|
|                             |      |      |          |                 |
| PLP - 01M                   |      |      |          |                 |
| I day                       | 0.55002 | 0.55141 | 0.550715 | 0.549753       |
| II day                      | 0.54982 | 0.54776 | 0.54879  | 0.54547        |
| III day                     | 0.54837 | 0.54374 | 0.54311  | 0.543545       |
| Accepted result             |      |      |          | 0.545957       |
| GOST 26929                  |      |      |          |                 |
| I day                       | 0.52423 | 0.52371 | 0.52397  | 0.526323       |
| II day                      | 0.52974 | 0.52761 | 0.528675 | 0.510383       |
| III day                     | 0.51134 | 0.51334 | 0.51234  | 0.511038       |
| Accepted result             |      |      |          | 0.515914       |

A sample of lead control with a concentration of 0.55 mg/dm$^3$ analyzed taking into account the use of the microwave laboratory system PLP-01M, is defined as 0.546 m/dm$^3$; in the case of sample preparation in accordance with GOST 26929 it is 0.516 mg/dm$^3$.

As a control sample (CS), standard samples were applied that were adequate to the analyzed samples (possible differences in the composition of the CS and the analyzed samples do not introduce an additional systematically significant error into the analysis results). The error of the certified CS value does not exceed one third of the error characteristics of the analysis results.

The results of the CS analysis were obtained under the conditions of repeatability and intra-laboratory precision.

The result of the control $C_k$ procedure was calculated by the formula:

$$C_k = X_{av} - C, \text{ mg/kg}$$

where $C$ is a certified concentration value of the determined element in the CS, mg/kg;

$X_{av}$ is a result of the control concentration measurement of the determined element in the CS, mg/kg.

The control standard $C$ was calculated according to the formula:

$$C = \Delta l$$

where $\pm \Delta l$ is the characteristic of the error of the control measurement results corresponding to the certified CS value.

The $\Delta l$ value is calculated by the formula:

$$\Delta l = 0.01 \times \delta l \times C, \text{ mg/kg}$$

$\pm \delta l$ is the relative value of the characteristics of the error of the analysis results established during the implementation of the technique in the laboratory and provided by the control of the stability of the analysis results:

$$\Delta l = 0.84 \times \delta, \%$$

$\pm \delta$ is relative value of the method accuracy indicator, %.

$$\delta = 1.96 \times \sigma R$
The standard deviation of reproducibility in the analysis of food samples for lead and cadmium $\sigma_R$ is 17%, therefore

$$\delta = 1.96 \times 17\% = 33\%$$

The analysis procedure was considered satisfactory if the following condition was met:

$$|C_k| \leq C$$

If this condition is not met, the control procedure is repeated. If the conditions are not met again, the reasons leading to unsatisfactory results are found out, and measures are taken to eliminate them.

The results of the operational control of the analysis procedure applying the procedure to control the error using the supplement technique are presented in table 6.

**Table 6.** Assessment of the operational control results of the measurement procedure applying samples for the lead control during the implementation of the microwave laboratory system PLP-01M in the laboratory.

| Introduced value Pb, mg/dm³ | Result of the control determination, mg/dm³ | Result of the control measurement | Result of the control procedure | Control standard | Assessment of the results acceptability $|C_k| < C_n$ |
|-----------------------------|-------------------------------------------|----------------------------------|-------------------------------|-----------------|------------------------------------------------|
| 0.015                       | 0.01456                                   | 0.01438                          | 0.014175                      | -               | 0.00062833 < 0.004158 satisfactory                |
| 0.015                       | 0.0135675                                 | 0.0140975                        | 0.0131225                     | -               | 0.00140417 < 0.004158 satisfactory                |
| 0.04                        | 0.038595                                 | 0.03976                          | 0.0363325                     | -               | 0.00177083 < 0.011088 satisfactory                |
| 0.04                        | 0.03551                                  | 0.035                             | 0.036215                      | -               | 0.004425 < 0.011088 satisfactory                 |
| 0.085                       | 0.0805275                                | 0.0849575                        | 0.0837625                     | -               | 0.0019175 < 0.023562 satisfactory                |
| 0.085                       | 0.0820425                                | 0.0773225                        | 0.0800325                     | -               | 0.00520083 < 0.023562 satisfactory               |
| 0.55                        | 0.5497525                                | 0.5445725                        | 0.543545                      | -               | 0.00404333 < 0.15246 satisfactory               |
| 0.55                        | 0.5263225                                | 0.5103825                        | 0.5110375                     | -               | 0.03408583 < 0.15246 satisfactory              |

4. Conclusion
The analysis procedure was recognized as satisfactory based on the results of the assessment of the operational control of the measurement procedure applying control samples for lead during the implementation of the microwave laboratory system PLP-01M in the laboratory.

Acknowledgements
The authors would like to express special gratitude to the AM Chuprakova, an engineer who conducted multi-stage tests of the designated products for compliance with the requirements of regulatory documents.
References

[1] Macleod C and Coughanowr C 2019 Heavy metal pollution in the derwent estuary: history, science and management Regional Studies in Marine Science 32 100866

[2] Ali M M et al. 2019 Heavy metal concentrations in commercially valuable fishes with health hazard inference from Karnaphuli river, Bangladesh. Human and Ecological Risk Assessment An Int J 1-17

[3] Kaushik A, Kansal A, Santosh M, Kumari S and Kaushik C P 2009 Heavy metal contamination of river Yamuna, Haryana, India: assessment by metal enrichment factor of the sediments Journal of Hazardous Materials 164(1) 265-70

[4] Cherif A, Abdoum S and Gaci O 2014 Food survey: levels and potential health risks of chromium, lead, zinc and copper content in fruits and vegetables consumed in Algeria Food and Chemical Toxicology 70 48-53

[5] Mansour S A 2014 Monitoring and health risk assessment of heavy metal contamination in food Practical Food Safety: Contemporary Issues and Future Directions 235-55

[6] Mourya A, Mazumdar B and Sinha S K 2019 Determination and quantification of the heavy metal ion by electrochemical method Journal of Environmental Chemical Engineering 7(6) 103459

[7] Ivanova-Petroplous V et al. 2015 Determination of Pb and Cd in Macedonian wines by electrotetro-atomic absorption spectrometry (ETAAS) Food Analytical Methods 8(8) 1947-52

[8] Kataoka Y et al. 2015 Development of ICP-OES, ICP-MS and GF-AAS methods for simultaneous quantification of lead, total arsenic and cadmium in soft drinks Food Hygiene and Safety Science 56(3) 88-95

[9] Li N et al. 2009 Determination of arsenic in foods by flow injection on-line sorption pre-concentration with hydride generation atomic fluorescence spectrometry Food Additives and Contaminants 26(6) 839-46

[10] Katsnelson B et al. 2014 Some considerations concerning the theory of combined toxicity: a case study of subchronic experimental intoxication with cadmium and lead Food and Chemical Toxicology 64 144-56

[11] Kim B-M et al. 2013 Influence of squid liver powder on accumulation of cadmium in serum, kidney and liver of mice Preventive Nutrition and Food Science 18(1) 1-10

[12] Ma W, Zhao B and Ma J 2019 Comparison of heavy metal accumulation ability in rainwater by 10 sponge city plant species Environmental Science and Pollution Research 26(26) 26733-47

[13] Alaqouri H A A et al. 2020 The possibility of using scots pine needles as biomonitor in determination of heavy metal accumulation Environmental Science and Pollution Research 26(1) 1-22

[14] Šrut M, Menke S, Sommer S and Höckner M 2019 Earthworms and cadmium – heavy metal resistant gut bacteria as indicators for heavy metal pollution in soils? Ecotoxicology and Environmental Safety 171 843-53

[15] Rahimi G, Kolahchi Z and Bayat S 2019 Heavy metals’ bio-accumulation and transfer in lemon balm (melissa officinalis l) irrigated with industrial wastewater International Journal of Environment and Waste Management 23(3) 238-56

[16] Singh BR et al. 2011 Safety of food crops on land contaminated with trace elements J Sci Food Agric 91(8) 1349-66

[17] Sizonts O V, Sizonts O A, Bibartseva E V and Osipova E A 2019 Comparative analysis of heavy metal sorption characteristics on laboratory animal models Research Journal of Pharmaceutical, Biological and Chemical Sciences 10(1) 1313-6

[18] Tumanyan A F, Tusaint F, Shcherbakova N A, Seliverstova A P and Tyutyuma N V 2019 Heavy metal contents in soils and vegetables of Southern Russia Chemistry and Technology of Fuels and Oils 54(6) 766-70

[19] Barsova N, Yakimenko O, Tolpeshta I and Motuzova G 2019 Current state and dynamics of heavy metal soil pollution in Russian Federation Environmental Pollution 249 200-07
[20] Kuramshina N, Rebezov M, Kuramshin E, Tretyak L, Topuria G, Kulikov D, Evtushenko A, Harlap S and Okuskhanova E 2019 Heavy metals content in meat and milk of Orenburg region of Russia International Journal of Pharmaceutical Research 11(1) 1301-5 DOI: 10.21668/health.risk/2019.2.04.eng

[21] Kuramshina N, Rebezov M, Kuramshin E, Krasnogorskaya N, Tretyak L, Somova Yu, Dolmatova I, Zaitseva T, Grigoryeva I and Bakirova L 2018 Heavy Metals Contamination of Soil in Urban Areas of Southern Ural Region of Russia International Journal of Engineering and Technology (UAE) 7(4.42) 14-8 DOI: 10.14419/ijet.v7i4.25536

[22] Zykova I, Maksimuk N, Rebezov M, Kuznetsova E, Derkho M, Sereda T, Kazhibayeva G, Somova Yu and Zaitseva T 2019 Interaction between heavy metals and microorganisms during wastewater treatment by activated sludge Journal of Engineering and Applied Sciences 14(11) 2139-45

[23] Assenova B, Okuskhanova E, Rebezov M, Korzhikenova N, Yessimbekov Zh and Dragoev S 2016 Trace and toxic elements in meat of maral (red deer) grazing in Kazakhstan Research Journal of Pharmaceutical, Biological and Chemical Sciences 7(1) 1425-33

[24] Barbosa J T P, Korn M G A, Santos C M M, Flores E M M, Peralva V N, Korn M and Nóbrega J A 2015 Microwave-assisted diluted acid digestion for trace element analysis of edible soybean products Food Chemistry 175 212-7

[25] Yang Z Y 2005 To study the activity of palladium used as modifier under microwave decomposition and atomic absorption spectrometry with graphite furnace for the determination of trace elements in food products Chinese Journal of Spectroscopy Laboratory 22(3) 607-17

[26] Rebezov M et al. 2020 Improvement of Laboratory Services When using Sample Preparation in Microwave System International Journal of Current Research and Review 12(16) 29-33 doi:10.31782/IJCRR.2020.12167