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Abstract. Baby food can contain harmful components that are very dangerous to little consumers. One of the most common harmful factors is heavy metals, in particular lead. It is known that introducing one extra microelement into the body changes not only the concentration of this element, but also the concentration of other elements. Disturbing the physiological balance of microelements leads to changes in complex enzymatic processes, which in turn violates the structure of tissue cells of individual organs. Studies by Russian scientists (T. Suldina and others) have determined, in milk for newborns, the maximum levels of lead (0.02 mg/kg), of cadmium (0.02 mg/kg), of arsenic (0.05 mg/kg). While studying certain samples of baby food, the method for determining the content of lead and other heavy metals was improved. Depending on the lead concentration, characteristic lines of both the ultraviolet and the visible spectral regions can be used. Monitoring heavy metals in infant milk has shown that lead, copper, and zinc are the main contaminants of the product. The concentration of toxic agents in baby milk depends on the type of raw materials and on the environmental conditions of their manufacture. To detect lead in products quickly and accurately, a method was used based on the emission spectral analysis. To this end, spectrographs ISP-28 and ISP-30 widely employed in industry and laboratory studies were taken, but the detection limits were lowered compared to those in the methods that had been used previously. Besides, the field-proven method for determining lead is applicable to detecting zinc and copper, too. An excess of lead by 0.08 mg/kg, copper by 0.07 mg/kg, zinc by 0.45 mg/kg was observed in the baby milk "Malyatko Premium 2." In the milk "Bellakt 2," the excessive amount of copper was 0.05 mg/kg, of zinc 0.20 mg/kg, of lead 0.05 mg/kg. In the baby milk "Nitricia Malyuk Istrynsky," only zinc was found to exceed the normal level (by 0.1 mg/kg). The baby milks "Nitricia Milupa 2," "Nestle Nestogen 2," "HiPP Organic 2" do not contain excessive heavy metals, and thus, can be recommended as safe for consumption.

Key words: baby food, contamination, harmful elements, lead.

Introduction. Formulation of the problem

In living organisms, heavy metals have a dual role. In low concentrations, they are part of biologically active substances that regulate the normal course of life processes [1]. When concentrations of heavy metals increase due to technogenic pollution, it results in negative and even disastrous consequences for living organisms. The research conducted deals with the agro-ecological aspect of producing safe raw materials for baby food. In the successful development of production of high quality food for children, the most urgent problem is providing safe raw materials. Therefore, it is necessary to monitor toxic substances in the environment for many years and establish how they get into raw materials. Such substances include toxic substances, of them, first and foremost, such

microelements as heavy metals (mercury, cadmium, lead, arsenic). They have a negative effect on the health of people, especially infants [2].

Analysis of recent research and publications

Baby food is manufactured industrially. It undergoes multiple processing in the course of changing cow milk and turning it into enriched powder. Its composition meets the nutritional requirements of an infant's body, but besides it, baby food can also contain substances that are detrimental to children's development [3]. These include heavy metals, mycotoxins, aflatoxins, etc. Metal compounds, when they enter the body, interact with a number of enzymes, inhibiting their activity. Heavy metals,

especially copper, lead, and zinc, have a wide toxic effect [4].

In 1972, the Experts Committee was created to consider the problem of lead poisoning [5]. Once in the body cells, lead (like many other heavy metals) deactivates enzymes, slows down children's cognitive and intellectual development, increases the blood pressure, and causes cardiovascular disease. Lead can replace calcium in the bones, thus becoming a constant source of poisoning. An increased lead content in a child's body results in various disorders, causes nausea, vomiting, dizziness, etc. [6]. Lead, as a toxic substance, has been known for almost five thousand years to Greek and Arab scientists. Lead impedes one of the stages of haem biosynthesis, is considered to be a strongest neurotoxin, causes high aggressiveness. Chronic lead poisoning gradually leads to renal and nervous disorders, to anaemia [7]. Lead becomes more toxic with calcium and iron deficiency. When lead enters the body, it is distributed between the organs such as the brain, kidneys, liver, and bones [8]. In the body, lead is deposited in the teeth and bones, where it eventually accumulates. Typical signs of chronic lead poisoning are anaemia, intestinal colic, a black-blue "lead line" (Burton's line) along the margin of the gums. Subclinical lead poisoning manifest itself by nonspecific symptoms: first, by increased excitability and insomnia, later by fatigue and depression. Children can suffer brain damage resulting in blindness, deafness, or even death. Organic lead compounds are even more toxic [1-5].

Copper compounds are a group of substances that play an important role in biochemical processes in the human body. The main function of copper is stimulating tissue respiration and haematopoiesis. Copper (Lat. *cuprum*) is the only element that increases haemoglobin formation and the number of erythrocytes in the presence of iron (Lat. *ferrum*), and promotes the transfer of ferric ions to the bone marrow. Copper deficiency in the body leads to hair loss, depigmentation of the hair and skin, frequent infectious diseases, skin rash, nausea, depressive conditions, anaemia, etc. However, a high copper concentration in the body has a negative effect, too: it causes rapid aging, insomnia, epilepsy, mental retardation, and developmental delay in children [8].

Zinc is a physiological heavy metal, but is a vital element for humans and animals, plants and microorganisms. Zinc, in the form of a divalent element, is a part of more than 20 enzymes. Very often, zinc is found in proteins that are transcription factors. The function of the immune system depends on the presence of zinc. But an excess of zinc in the body can lead to general intoxication and DNA mutations, and can also unbalance the metabolic balance of other metals. Zinc/copper imbalance is the main causal factor in the development of coronary heart disease. Excessive consumption of zinc salts can lead to acute intestinal poisoning accompanied by nausea. Zinc poisoning promotes irritability, dull muscular aches,

nausea. It affects the lungs and eye mucosa, and causes taste disturbance [3-8].

In 1996 in the United States, apple and plum juices *Heinz* for babies were withdrawn from sale because they contained lead that exceeded the normal level [11]. In 1997, 2,141,880 product units of carrot-containing baby food by the *Gerber Company* were withdrawn from shops because of an increased arsenic content [12]. In 1998, 25,760 items manufactured by *Heinz* and intended for feeding infants were removed from the market due to an increased lead concentration [13]. In 2000, after a long disregard for local sanitary services' directives, *HiPP* withdrew its infant food *HAI* [14]. The catastrophic excess of heavy metals in the food already sold led to lawsuits brought against the company by several dozen parents whose young children had become disabled with the kidney disease. Some cases of foodstuff contamination with toxic metals are due to toxic substances released into the atmosphere from various industrial enterprises [2,8-10].

Reading the literature has shown that, though there are a number of works on the production of quality baby food by domestic and foreign authors (C. Yang, J. Brussard, S. Morozova, V. Tutelyan), there are relatively few studies of the quality of baby milk. In addition, they contain conflicting data [3-15].

N. Zabashta's, N. Kulopina's, O. Polezhaeva's works present experimental data of the long-term monitoring of heavy metals accumulation in the soil-food chain. The goal of these studies was the development of high quality raw materials for baby food production. It has been studied how to prevent the accumulation of heavy metals by adding a mineral fertilizer with a known heavy metals content, by selecting the species and varieties of food crops resistant to accumulating heavy metals [3].

S. Tiutikov's work presents an analysis of the distribution of heavy metals in biological objects and in the environment, and the ways of reducing the access of heavy metals from soil to the plant. The relationship between the increase in the soil pH and the reduction of biogenic accumulation of chemical elements has been studied, as well as the use of immune correctors [16].

Yu. Potatueva, N. Sidorenko, E. Prishchep studied how important admixtures of heavy metals are as components of fertilizers. The interaction of zinc and cadmium was studied. This interaction is of additive character, i. e. the presence of one element reduces the amount of the other [17].

T. Kuznetsova, A. Glazov, N. Kulpina and others studied soils with a low content of mobile forms of cadmium (<0,05 mg/kg). The obtained quantities of heavy metals accumulated did not exceed the maximum acceptable concentrations (MAC) of Cd – 2 mg/kg, Hg – 0,01 mg/kg, As – 0,5 mg/kg [18].

C. Yang and with co-authors conducted studies to detect cadmium-activated processes of cross oxidation of lipids in the fibroblast culture of the lungs, with antioxidant enzymes inhibiting this activation [4].

It is impossible to prevent completely chemicals from getting into the environment. The inevitability of this phenomenon, on the one hand, and the obvious adverse effect of almost all such factors on children require measures that limit the content of toxic substances in the environment. Today, the maximum acceptable concentrations of a substance are understood as concentrations that can cause a disease or harm to the health of today's and future generations [15].

The novelty of the subject:

1. The content of lead, copper, and zinc in infant milk by certain manufacturers have been studied.
2. The most common toxic agents and the degree of their accumulation have been established.
3. A new method of studying heavy metals has been tested.

Scientific and practical value:

1. The lead research method tested can be used to investigate other heavy metals.
2. The formulae studied can be recommended for use.

The purpose of the work is monitoring the content of heavy metals in infant milk.

The objectives:

1. Detect the content of heavy metals in infant milk by certain manufacturers.
2. Determine the anthropogenic factors that influence the accumulation of heavy metals in food raw materials.
3. Try a new method of studying heavy metals in infant milk.

Research materials and methods

For the study, milk No. 2 (for infants aged 6 months to 1 year) was used. As the range of such products is considerable, only some brands have been covered. The dry milk formulae tested were those developed in Ukraine (*Malyatko Premium 2*, Khorol Baby Food Factory), in Belarus (*Bellakt 2*, Volkovysk OJSC *Bellakt*), two baby formulae from Poland (*Malyuk Istrynsky 2* and *Milupa 2*, *Nutricia*), two brands from Switzerland (*NAN Optipro 2* and *Nestogen 2*, *Nestle*) and one from Germany (*Hipp organic 2*, *HiPP*), 7 samples altogether.

To detect lead in products quickly and accurately, a method was used based on the emission spectral analysis. To this end, spectrographs ISP-28 and ISP-30 widely employed in industry and laboratory studies were taken, but the detection limits were lowered compared to those in the methods that had been used previously [7].

From the milk to be analysed for a lead content, 100–200 g portions were taken and burned (GOST

26929-86). The methods were developed and tested using the samples in which lead was practically absent. Plumbic (II) acetate was added to the ash. The residues were diluted and evaluated photometrically.

This method can also be used to determine the amount of copper and zinc.

Microelements in the milk was determined by the method of atomic absorption spectroscopy using a *Saturn-2* spectrophotometer.

The method is based on spraying a solution of the mineralized sample under study in air-acetylene flame. Metals in the solution, when in the flame, go to the atomized state. The absorption of light with a wavelength corresponding to the resonance line is proportional to the metal concentration in the sample under analysis. The content of the elements in the solutions was determined by the calibration curve method. The curve was based on the values of atomic absorption of solutions with given concentrations.

The mixtures and samples were prepared in a porcelain dish using a porcelain pestle or spatula to avoid contact with lead usually contained in glass.

From the ash of the mixture without lead, the following samples were prepared: No. 1 – with the amount of lead $C_x+0.001\%$ (used as the sample with an unknown concentration to test the method); No. 2, No. 3, No. 4 – containing lead $(C_x+0.01)\%$, $(C_x+0.1)\%$, $(C_x+1)\%$, respectively. The obtained samples were burned in an AC arc (~ 5 A), with the carbon electrodes spectrally pure, with the spectral photographic plates of type I.

The lines of lead were distinguished, with the wavelengths $\lambda = 283.31$ nm and $\lambda = 405.78$ nm, and next to them, the lines of the ash of the mixture, with $\lambda = 282.4$ nm and $\lambda = 408.0$ nm, and a doublet with $\lambda = 404.4$ nm and $\lambda = 404.6$ nm. The mixture ash line with 282.4 nm serves for comparison (as a reference line), or is homologous to the lead line ($\lambda = 283.31$ nm). This area is very convenient to work with, as there are no other bands that complicate the photometry. However, if the lead concentration in the ash sample is lower than 0.001%, it is better to work in the visible region and use $\lambda = 405.78$ nm for this substance, and $\lambda = 408.0$ nm or $\lambda = 404.4$ nm as the comparison lines. In this region, there are carbon lines and bands of CN groups. However, against their background, the studied bands are clearly visible.

Results of the research and their discussion

Using an MF-2 microphotometer, the blackening of the S bands has been determined. A graph (Fig. 1) has been constructed showing how the difference in blackening ($\Delta S = S_{\text{black}} - S_{\text{Pb}}$) of the reference line S_{black} and the lead line depends on the logarithm of its concentration ($\lg C$).

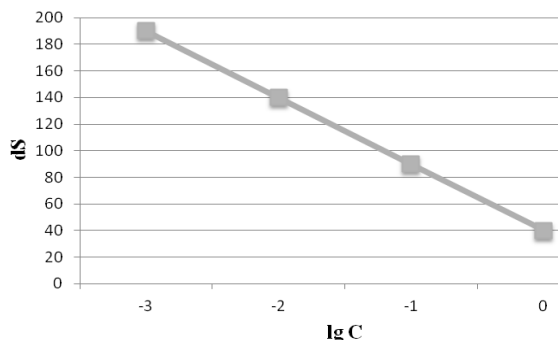


Fig. 1. Dependence of the difference in blackening (dS) of the reference line $\lambda = 285.5$ nm and the analysed lead line ($\lambda = 283.31$ nm) on the logarithm of the lead concentration in the ash of the milk formula

In the region of normal blackenings, when $40 < S < 200$, a direct proportional dependence of ΔS on $\lg C$ is observed.

An analysis of the triangles in Fig. 1 has allowed developing the formula for finding the unknown concentration of C_x by two known concentrations of lead added to the test sample – $C_1 = 0.01\%$, $C_2 = 0.1\%$:

$$\lg C_x = \frac{(\Delta S_x - \Delta S_2) \lg C_1 - (\Delta S_x - \Delta S_1) \lg C_2}{\Delta S_1 - \Delta S_2} \quad (1)$$

Where: $\Delta S_1 = S_{\text{black}} - S_1$, $\Delta S_2 = S_{\text{black}} - S_2$ – the differences of blackening between the reference line and the lead line of the samples containing lead at concentrations $(C_x + C_1)\%$, $(C_x + C_2)\%$, respectively.

In the example considered, the reference line always had more blackening when compared to the lead line, so we checked the cases ($C_x = 1\%$), when S_{black} was less intense than the blackening of the lead line $\Delta S = S_{\text{Pb}} - S_{\text{ref}}$ and when ($C_x = 0.05\%$) was comparable in intensity to S_{Pb} . Then ΔS acquired both positive and negative values. The suggested formula appears to be valid in all cases, and to establish the concentration of C_x , it is enough to prepare two samples with known additional lead concentrations, i. e. $(C_x + C_1)\%$, $(C_x + C_2)\%$.

To see the concentration of C in the product, recalculation is done: $C = (C_x \cdot m_1) / m_2$ (%), where m_1 is the mass of ash, m_2 is the mass of the product.

The time spent to determine the lead concentration in one product, starting with weighing the ash and adding the specified concentrations, does not exceed 2–3 hours, i. e. is 2–3 times less than that allowed by GOST (State Standard) 26932-86.

The results of studying the content of heavy metals in the tested formulae are shown in Tables 1–7.

Table 1 – The content of microelements in the baby milk *Malyatko Premium 2*

Chemical element	MAC, mg/kg	The content of the microelement, mg/kg	Excess of the microelement content, mg/kg
Copper (Cu)	0.5	0.57	0.07
Zinc (Zn)	5	5.45	0.45
Lead (Pb)	0.05	0.13	0.08

Table 2 – The content of microelements in the baby milk *Bellakt 2*

Chemical element	MAC, mg/kg	The content of the microelement in the baby food, mg/kg	Excess of the microelement content, mg/kg
Copper (Cu)	0.5	0.55	0.05
Zinc (Zn)	5	5.20	0.20
Lead (Pb)	0.05	0.1	0.05

Table 3 – The content of microelements in the baby milk *Nutricia Malyuk Istrynsky 2*

Chemical element	MAC, mg/kg	The content of the microelement in the baby food, mg/kg	Excess of the microelement content, mg/kg
Copper (Cu)	0.5	0.5	0.0
Zinc (Zn)	5	5.1	0.1
Lead (Pb)	0.05	0.05	0.00

Table 4 – The content of microelements in the baby milk *Nutricia Milupa 2*

Chemical element	MAC, mg/kg	The content of the microelement in the baby food, mg/kg	Excess of the microelement content, mg/kg
Copper (Cu)	0.5	0.49	- 0.01
Zinc (Zn)	5	4.9	- 0.1
Lead (Pb)	0.05	0.05	0.00

Table 5 – The content of microelements in the baby milk *Nestle NAN Optipro 2*

Chemical element	MAC, mg/kg	The content of the microelement in the baby food, mg/kg	Excess of the microelement content, mg/kg
Copper (Cu)	0.5	0.5	0.0
Zinc (Zn)	5	5	0.0
Lead (Pb)	0.05	0.05	0.00

Table 6 – The content of microelements in the baby milk *Nestle Nestogen 2*

Chemical element	MAC, mg/kg	The content of the microelement in the baby food, mg/kg	Excess of the microelement content, mg /kg
Copper (Cu)	0.5	0.5	0.0
Zinc (Zn)	5	4.95	- 0.05
Lead (Pb)	0.05	0.049	- 0.001

Table 7 – The content of microelements in the baby milk *Hipp organic 2*

Chemical element	MAC, mg/kg	The content of the microelement in the baby food, mg/kg	Excess of the microelement content, mg /kg
Copper (Cu)	0.5	0.5	0.0
Zinc (Zn)	5	5	0.0
Lead (Pb)	0.05	0.05	0.00

Monitoring heavy metals in infant milk has shown that lead, copper, and zinc are the main contaminants of the products. The level of concentration of the toxic agents in baby milk depends on the type of raw materials and the environmental conditions of their manufacture. A new method for determination of lead, which is also suitable to determine zinc and copper, has been tested. An excessive content of lead (0.08 mg/kg), copper (0.07 mg/kg), zinc (0.45 mg/kg) was observed in the milk *Malyatko Premium 2*. Besides, in the milk *Bellakt 2*, the excess of copper was 0.05 mg/kg, of zinc 0.20 mg/kg, of lead 0.05 mg/kg. In the milk *Nutricia Malyuk Istrynsky 2*, only zinc was excessive (0.1 mg/kg). In the milks *Nutricia Milupa 2*, *Nestle Nestogen 2*, *Hipp organic 2*, there is no excess of heavy metals, which allows recommending these formulae as safe.

Conclusion

Contamination of biosphere objects, including plant and animal raw materials, with salts of different metals, can have a number of important consequences

for people. So, it is clear how necessary environmental monitoring of food products and food raw materials is in developing methods of preventing low-quality and dangerous food from entering the market. According to the results of the research, it has been found that in infant milk from different manufacturers, the content of heavy metals is not very different from the normal level, with the exception of the dry milk formula *Malyatko Premium 2*. An important element in providing people with safe food is developing a system of monitoring the quality of raw materials and the distribution of certain toxic compounds by the regions of the country. Food raw materials of plant and animal origin and food products are a sort of environments that provide information on the level of contamination and distribution of heavy metals in the biospheres. To improve the food quality, it is necessary to include in the system of regional monitoring the control of the content of heavy metals in food raw materials of plant and animal origin.

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ВАЖКІ МЕТАЛИ У ДИТЯЧИХ МОЛОЧНИХ СУМІШАХ

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Анотація. Дитяче харчування може містити шкідливі компоненти, які становлять велику небезпеку для маленьких споживачів. Одними з найпоширеніших чинників є важкі метали, зокрема свинець. Відомо, що додаткове введення в організм одного мікроелемента змінює не лише концентрацію даного елемента, але й концентрацію інших. Порушення фізіологічної рівноваги мікроелементів призводить до змін складних ферментативних процесів, що у свою чергу порушує структуру тканинних клітин окремих органів. При проведенні досліджень певних зразків дитячого харчування поліпшено метод визначення в них вмісту свинцю та інших важких металів. У залежності від концентрації свинцю, можна використовувати характеристичні лінії як ультрафіолетової, так і видимої області спектру. Моніторинг важких металів в дитячих молочних сумішах показав, що основними забруднювачами продуктів є свинець, мідь, цинк. Рівень концентрації токсикантів в молочних сумішах залежить від виду сировини та екологічних умов їхнього виробництва. Для швидкого визначення свинцю у продуктах без зниження точності було використано метод, в основу якого було покладено емісійний спектральний аналіз за допомогою широко застосовуваних у промисловості та лабораторних дослідженнях спектрографів ІСП-28 та ІСП-30, але межі виявлення понижено порівняно з методикою, яка застосовувалася раніше. При цьому апробований метод визначення свинцю також придатний для визначення цинку та міді. встановлено, що надлишок вмісту свинцю на 0,08 мг/кг, міді на 0,07 мг/кг, цинку на 0,45 мг/кг спостерігався у молочній суміші «Малютко Premium 2». У суміші «Беллакт 2» надлишок міді становив 0,05 мг/кг, цинку 0,20 мг/кг, свинцю – 0,05 мг/кг. У молочній суміші «Nitricia Малюк Істринський 2» було встановлено тільки надлишок цинку – 0,1 мг/кг. У молочних сумішах «Nitricia Милура 2», «Nestle Nestogen 2», «HiPP Organic 2» надлишок важких металів відсутній, що дозволяє рекомендувати їх як безпечні до споживання.

Ключові слова: дитяче харчування, забруднення, шкідливі елементи, свинець.

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