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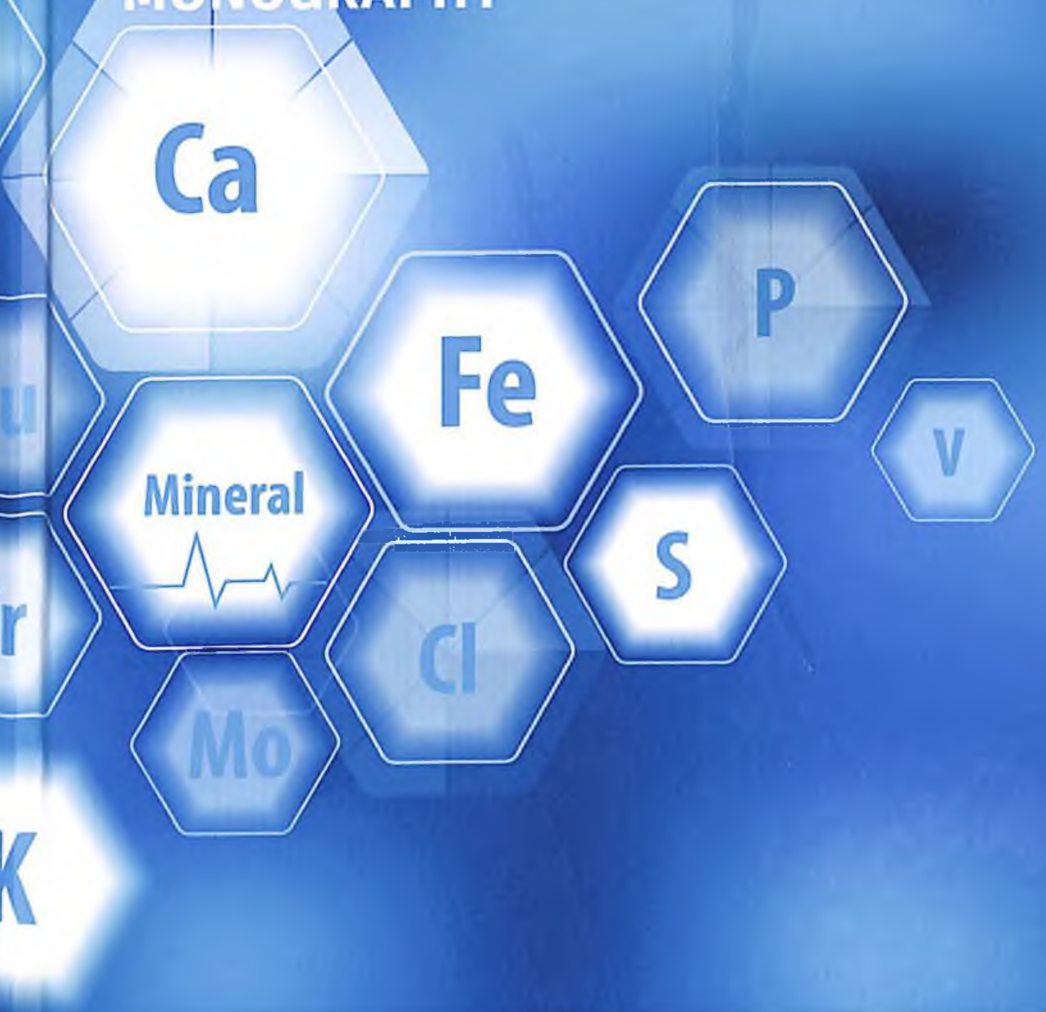

MINISTRY OF HEALTH OF THE
REPUBLIC OF UZBEKISTAN

SAMARKAND STATE MEDICAL UNIVERSITY

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Annotatsiya

The identification of the biological and physico–chemical bases of the migration, concentration, and function of metal ions in living organisms in phylo - and ontogenesis is a problem that attracts the attention of various branches of modern science, including biochemistry, biogeochemistry, bioorganic and bio–nonorganic chemistry, biotechnology, and other areas of physico-chemical biology. In this regard, it is of considerable interest to study the chemical interaction of specific ligand centers of biomolecules with metal ions, which underlies their metabolism and reactions on the interaction of environmental factors.

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INTRODUCTION

The identification of the biological and physico–chemical bases of the migration, concentration, and function of metal ions in living organisms in phylo - and ontogenesis is a problem that attracts the attention of various branches of modern science, including biochemistry, biogeochemistry, bioorganic and bio–nonorganic chemistry, biotechnology, and other areas of physico-chemical biology. In this regard, it is of considerable interest to study the chemical interaction of specific ligand centers of biomolecules with metal ions, which underlies their metabolism and reactions on the interaction of environmental factors.

It is pertinent to review and clarify the norms of mineral nutrition of humans and animals, find new and effective sources of mineral additives, improve the technology of their feeding, along with the studying of the biochemical and physiological laws of the state and direction of the animals' productivity.

This is due to the transition to industrial forms of raising and feeding of farm animals, their intensive use, changes in the technology of feed production and cultivation. Shifts in mineral metabolism often occur as a result of using wastes of food and light industry, animal feces, as well as samples grown under conditions of geochemical and man-made environmental pollution as food, which can lead to an excess of toxic elements entering the body, reducing their productivity and various types of toxicosis. In the conditions of Uzbekistan, such elements can be fluorine, lead, mercury, arsenic, chromium, antimony, and others. It should also be borne in mind that in the natural and economic conditions of Uzbekistan, territories, where people and animals are deficient in such vital elements as copper, zinc, manganese, iodine, and according to some sources, cobalt, are widespread. In this regard, the use of mineral additives should be based on knowledge of the biogeochemical situation, the study of the needs of organisms in specific macro – and microelements. Otherwise, the inclusion of particular chemical elements in the diet may not only be ineffective, but also cause direct damage to human health and animal productivity.

The successful conduction of biogeochemical studies requires the development of non-destructive methods for obtaining objective information about the mineral metabolism of animals and humans, reflecting their physiological state, the influence of environmental factors and the level of nutrition. In this aspect, the most promising and practically significant test objects are hair and wool, which are easily available for analysis and contain increased concentrations of all chemical elements present in the body. To answer the question of the suitability of epidermal structures as bioindicators, it was necessary first of all to find out the dependence of the behavior of more than 40 chemical elements found in the hair. From its main organic components, pigments and proteins, to develop new and modify existing chemical-analytical methods for determining the levels of elements in these materials and to use the obtained data for the purposes of biogeochemical zoning and assessment of the anthropogenic load of the environment.

Wool and hair as indicators of environmental pollution by technogenic and geochemical sources.

The concentration of trace elements in the body of animals is regulated and controlled very subtly. This control is carried out by certain proteins, hormones and depositing systems (bone tissue, hair, cornea, etc.). On the other hand, the correlation between metal ions and the substances that are broken down to them is so close that changes in the state of the animal's body can be the result of both an increased and a reduced content of metal ions compared to the norm. The study of tissues and body fluids on the content of elements is therefore a very important diagnostic test.

The human body weighing 70 kg contains 1050 g Ca, 245 K, 105 g Na, 35 g Mg, 700 P, 175 g S, 100 g of Cl, 3 g. of Fe, Zn 2.5 g, 1.2 g, Rb, 100mg Si, 20 mg Mn, 5 mg Co, 5-6 mg vanadium, tin, chromium, ~ mg Ni, Rb, Se, F, Si, J, etc. Some of the elements, such as Cs, Rb, Sr, Ni, are relatively non-toxic. Others are highly toxic-Sb, As, Ba, Be, Cd, Pb, Hg, Ag, Te, Th.

The toxicity is strongly influenced by the form in which the metal ion is located. The formation of fat-soluble complexes with organic ligands increases toxicity. A classic example is Minimata disease, which is caused by the transformation of inorganic mercury from wastewater to methylmercury under the action of vitamin B12 contained in microorganisms, which then enters the body together with food or water.

Background concentrations of heavy metals in the organism of animals.

When assessing man-made impacts on the animal body, various tests can be used, including the analysis of the chemical composition of organs, tissues and secretions, the activity of certain enzymes, the state of health and productivity of animals. The first two groups of tests used in biological monitoring of the impact of environmental pollution have been most widely used. For most natural products, human organs and tissues, the maximum possible concentrations of a significant number of chemical elements have been established, and methods for sampling and analyzing samples have been developed. As for animals, there are currently no uniform standards for them, and before judging the changes in the chemical composition of their body under the influence of external influences, it is necessary to carefully study the background contents of chemical elements in the conditions of specific natural and economic conditions of this region. It is important for biological monitoring to choose the analyzed indicator or so-called "critical" organ. It should meet some general requirements, that is, be easily accessible, objectively reflect the level of exposure and the body's supply of trace elements. According to a number of authors, wool meets these requirements (25, 37). However, a number of authors/ 14,17 / dispute the suitability of wool as an indicator of the content of certain heavy metals in the body.

In connection with the foregoing, we studied the possibility of using this test in the natural and economic conditions of this region. At the same time, we, first of all, faced two tasks: to find out the background concentrations of microelements in the absence of pollution and to establish how objectively wool reflects the microelement status of animals under the studied conditions /15/.

For the purposes of these purposes, sheep and cattle removed from the sources of man-made damage were studied. Organs and tissues that most fully reflect the microelement status of organs were found in twenty 6-7-year-old Karakul sheep and twenty cows of the Red Steppe breed, culled by age. During sampling, organs and tissues were obtained from animals that most fully reflect the microelement status of the body.

Background content of copper in the brain, components in Karakul sheep. Average 4.7 mg/kg fresh tissue. According to statistical data, the content of copper in the brain under physiological conditions is 54.1 mg/kg/29/. Anke et al. We give the figure 18.0±7.1 mg/kg of dry matter. In terms of fresh tissue, this is 4.5±1.8 mg/kg/2/.

The content of copper in the liver of healthy adults is 78.0 mg/kg of fresh tissue /29/, 74-430 /27/, 220 mg/kg /2/ of dry matter, which, in terms of fresh tissue, corresponds to 22-130 and 67 mg/kg, respectively.

In Karakul sheep, the content of copper in the wool ranges from 8-9 mg/kg /2, 29/. Our data, as can be seen from table 1.1, correspond to the figures given above.

The level of zinc in the body of animals most fully reflects the bone, muscles and, to a lesser extent, the liver. Detailed studies of the content of zinc and copper in the organs and tissues of Karakul sheep were carried out by M.A. Rish et al. /29/, which are found in healthy adult animals in tubular bones 81.5±1.4; in the liver - 28.0±0.4; in muscles - 38.0±2.9 and in wool - 80.7±6.5 mg/kg of this metal.

Table 1.1

The content of trace elements in the organs and tissues of Karakul sheep and cows in the conditions of physiological norm. mg / kg of fresh tissue

	Sheep				Cows			
Bone	1,6±0,6	2,4±0,3	1,6±0,4	79,2±1,2	1,3±0,1	3,0±1,0	1,4±1,1	97,7±1,3
The brain	4,7±0,4	1,2±0,1	0,19±0,02	14,8±0,3	3,1±0,2	0,5±0,1	0,12±0,01	8,9±0,1
Whole blood	1,1±0,04	0,44±0,01	0,12±0,03	3,3±0,1	1,2±0,08	1,09±0,01	0,14±0,03	3,5±0,1
Wool	7,2±1,2	7,0±0,6	2,0±0,9	104,3±2,9	12,4±1,1	8,7±1,4	1,1±0,2	114±4,0

№	The bodies of the elements	Liver	Kidneys	Lungs	Muscles
1	**Copper**	73,3±2,5	3,3±0,2	2,9±0,2	0,7±0,07
2	**Manganese**	3,8±0,1	1,9±0,1	0,76±0,2	0,24±0,06
3	**Lead**	0,31±0,15	0,2±0,14	0,12±0,09	0,18±0,03
4	**Zinc**	30,4±1,2	22,2±3,5	22,1±3,5	44,3±2,9
1	**Copper**	30,0±2,1	5,1±0,3	1,8±0,3	1,1±0,04
2	**Manganese**	3,1±0,3	1,4±0,3	0,66±0,11	0,19±0,03
3	**Lead**	0,21±0,09	0,16±0,1	0,18±0,02	0,08±0,03
4	**Zinc**	34,2±1,3	13,9±1,1	13,2±1,6	30,1±0,7

The figures obtained by us correspond to the results given and can be considered as a physiological norm (background).

Data on the content of manganese in the organs and tissues of Karakul sheep are not available in the literature available to us. In this regard, our results have to be compared with the figures obtained for sheep of other breeds. In particular, /I8/, was found in healthy adult sheep in average in the liver II, 0±2.2, in wool - 9.4±5.6, kidneys - 4.9±1.6, brain - 2.7±1.1, ribs - 5.5±0.7 mg of manganese per kg of dry matter. In terms of fresh matter, this is 3,4±0,7, 1,3±0,4, 0,68±0,3 and 3.1±0.4 mg / kg of manganese, which is slightly different from the background values obtained for Karakul sheep in our studies.

The lead content in the body of Karakul sheep has also not been studied. Sheep of other breeds it likewise / I8 / equal in blood to 0,09±0,05, in the liver-0,72±0,52 and kidney - 0,72±0,58 mg/kg dry matter, respectively, which is in terms of fresh tissue is 0.23±0.18 in the liver and 0,18±0,85 mg/kg in kidneys. Detailed information on the level of lead in the body of sheep normally and with additional giving of this element is made in GDR / I7/. According to their data, the content of this element in animals that did not receive its compounds with food was 1.1±0.69 in wool, 1.4±0.45 in the liver, 2.5±0.89 in the ribs, 3.2±2.2 in the femur, 1.1±0.43 in the kidneys, and 0.57±0.40 mg/kg in the brain. This data is about twice as high as our results, which is probably due to higher levels of lead in the environment where the animals were kept (mountain Yen).

In human organs and tissues from areas not contaminated with lead /17/, the content of this element is: hair-6.6-39.6 mg / kg, liver-0.28-1.84, kidneys-0.24-1.23, lungs-0.20-0.45, brain - 0.16-0.46, muscles-0.05-0.33 mg / kg in fresh matter.

The content of elements in homologous organs and tissues of different ruminant species differs slightly. Differences are observed only in particular cases. Thus, the copper content in the liver of cows is two times lower than in sheep and is according to Risch and co. / 29 / 27 mg / kg, according to Anka /2 / 33 mg/kg of fresh tissue. The zinc content in the kidneys and lungs of sheep is 1.4 times higher than in cows. Similar differences in these two animal species are also found /29/ (15.8±1.4 and 15.0±0.9 mg / kg of fresh tissue, respectively). The content of manganese in the conditions of the physiological norm in the wool of cows varies between 4.5 and 13 mg / kg / 180/, and less concentrations are found in white wool, and higher (2-3 times) in pigmented wool. The content of this element is significantly influenced by the origin of the animal. Thus, in the descendants of two different breeding bulls, the concentrations of this element averaged 6.1 and 9.4 mg/kg /2/.

The concentration of manganese in the liver of cattle varies under normal conditions in the range of 5.5-6.8 mg / kg of dry weight /190/, which in terms of fresh tissue is 1.8-2.2 mg/kg. These data closely correspond to the values obtained in our studies.

From Table 1.2 it is evident that the copper content in the liver, brain, in other words, organs and tissues that reflect the most objectively copper status of the body, shows a close correlation with the level of this element in the wool. There was also a link between the copper content in whole blood wool.

For zinc, the highest positive correlation is observed between the content of the element in wool and bone, and to a lesser extent with the level of this element in the brain and liver. In terms of lead, wool correlates well with bone, and in terms of manganese, it correlates well with the kidneys, liver, and brain.

In cows, unlike sheep, the highest correlation in copper content is observed between wool and liver, and in zinc content-between wool and brain. For lead, in both cases, the closest relationship was found between the hair on the one hand and the kidneys, liver, and brain on the other.

Heavy metals in the organs and tissues of sheep and cows under conditions of technogenic province.

Twenty red steppe cows and twenty Karakul sheep located in the impact zone of the factory were selected to study the impact of emissions from the Samarkand factory on the microelement status of farm animals in the slaughterhouse.

The animals received coarse feed prepared on the territory of the technogenic province. When slaughtering animals, the same organs and tissues were obtained as when studying the background concentrations of trace elements. As can be seen from the results of the analysis given in Table 1.3, the level of copper in the liver of sheep grazed on the territory of the technogenic province is 2.5 times lower than the stock ones, in wool-2.3 times, in the brain-2.2 times, and in whole blood - 2 times. Copper content in the kidneys, lungs, and muscles. And the bones are preserved at the level of the physiological norm. According to Anke et co.,/ 2 / in sheep grazed in an industrial area with intensive emissions of sulfur dioxide compounds the copper content in the liver was 17 times lower than the background values, and in the brain – 5 times. In the kidneys, as in our studies, the differences were insignificant.

Table 1.2

Correlation between the content of trace elements in organs and tissues and in the wool of Karakul sheep and cows in the conditions of physiological norm

Bone	**Sheep**	0,32	0,88	0,66	0,42	**Cows**	0,51	0,78	0,56	0,36
The brain		0,98	0,71	0,44	0,61		0,84	0,77	0,22	0,67
Whole blood		0,73	0,75	0,32	0,23		0,77	0,69	0,39	0,17
Muscles		0,57	0,69	0,21	0,51		0,44	0,57	0,33	0,41
Lungs		0,37	0,33	0,49	0,47		0,29	0,37	0,53	0,33
Kidneys		0,54	0,41	0,33	0,68		0,57	0,32	0,27	0,77
Liver		0,74	0,68	0,3	0,61		0,93	0,61	0,37	0,74
The bodies of the elements		**Copper**	**Manganese**	**Lead**	**Zinc**		**Copper**	**Manganese**	**Lead**	**Zinc**
№		**1**	**2**	**3**	**4**		**1**	**2**	**3**	**4**

In the conditions of the Golodnostep biogeochemical province of copper deficiency in sheep, the copper content in the liver drops 41 times, in the brain 3 times, and in the blood 2 times lower than the background values /29/. In other organs and tissues, there were no differences in the copper content compared to the norm.

Based on the data we have obtained, we can thus conclude that, first, animals in the area of exposure to chemical plant emissions experience a moderate copper deficiency, apparently associated with the intake of excessive amounts of sulfur compounds into their bodies. These compounds, being reduced to sulfides in the contents of the rumen and liver, bind copper to the sulfide of this metal, which is inaccessible to the body, and cause secondary copper deficiency in animals. /19/.

4.4, 6, 6.6, and 8.8 times, respectively. It has been shown /15/ that if sheep are daily given during 584 days 50 mg of lead per kg of feed, the content of this element increases in the kidney 25, rib – 46, in the femur in 28 liver in 9 in hair – 8 and in the brain in 7 times relatively to the control. From this work, as well as from our data, it is evident that the accumulation of lead mainly occurs in the kidneys, hair and bones.

The content of manganese in the organs and tissues of sheep grazed on the territory of the technogenic province does not differ from the control.

The copper content in the body of cows from the technogenic province is significantly reduced. Very noticeable differences (2 times) were found for the liver, brain and hair. In the rest of the studied tissues, these differences range from 5-7%. Thus, the decrease in the level of copper in the body, noted above in sheep, is also observed in cattle and is explained by the same reason – the action of sulfur compounds on animals. As for another factor leading to a decrease in the level of copper in the body of animals, cadmium and silver released into the atmosphere by industrial enterprises are indicated / 2, 15/. However, in our conditions, the pollution of the environment with these elements is small and the main cause of copper metabolism disorders should be recognized as sulfur dioxide.

Table 1.3

The content of trace elements in the organs and tissues of Karakul sheep and cows under conditions of the technogenic province of the Samarkand chemical plant.

№	The bodies of the elements	Liver	Kidneys	Lungs	Muscles	Wool	Whole blood	The brain	Bone
	Sheep								
1	**Copper**	29,6±0,7	3,5±0,3	2,3±0,1	1,2±0,02	2,9±1,1	0,54±0,01	1,62±0,3	1,6±0,6
2	**Manganese**	3,6±0,11	0,8±0,04	0,81±0,04	0,2±0,01	11,7±0,28	0,03±0,01	1,4±0,1	2,4±0,3
3	**Lead**	0,5±0,05	0,9±0,2	0,2±0,02	0,2±0,03	12,0±1,9	0,14±0,03	1,3±0,06	1,6±0,4
4	**Zinc**	21,4±0,9	16,2±0,6	18,1±0,5	19,4±0,07	86,7±1,3	2,3±0,3	11,9±0,3	79,2±1,2
	Cows								
1	**Copper**	18,3±0,8	4,3±0,6	1,4±0,2	0,7±0,09	5,4±0,2	0,7±0,03	1,8±0,3	1,1±0,3
2	**Manganese**	3,5±1,2	1,2±0,4	0,8±0,1	0,2±0,03	9,8±1,0	0,09±0,01	0,44±0,02	9,1±0,4
3	**Lead**	0,27±0,02	0,22±0,4	0,23±0,02	0,08±0,02	3,3±1,1	0,17±0,01	0,16±0,07	2,3±0,2
4	**Zinc**	26,6±2,2	11,6±1,6	9,7±1,0	18,7±0,9	77,6±3,3	2,4±0,1	7,6±1,2	58,3±2,8

Our observations correspond well to the data of other authors. Thus, in cattle under the influence of sulfur compounds, the concentration of copper in the liver was 15, in the brain – 5.2, in blood serum – 0.73 and in wool-6.0 mg/kg of dry matter. In terms of fresh matter, this corresponds to 4.8 mg/kg in the liver and 1.3 mg / kg in the brain. /2 / also indicate that the lower limits of the physiological norm for cattle are 6.0 mg/kg of copper in the brain, 15-for the liver, 0.60-for blood serum and 5.0 - for black wool (based on fresh matter). Thus, the copper content in the wool and brain of cows grazed in the vicinity of the chemical plant falls below the physiological norm and can affect their health and productivity.

The most significant differences in the concentrations of zinc in the organs and tissues of cows of their technogenic province compared to the control are observed in bone, muscle, wool and blood. In them, the difference is 30-40% compared to the background.

According to the level of manganese, there were no significant deviations from the normal contents in the organs and tissues of cows. The most significant deviations do not exceed 12-17% and are found in the lungs, kidneys and brain. In contrast to copper and zinc, the lead content in the wool of animals from the technogenic province increases more than 7.5 times compared to the control. Significant concentrations of this element are also observed in the bone, kidneys, brain, liver, and lungs. Their lead content is higher than that of control animals by 39, 27, 25, 23 and 22%, respectively. Experimental feeding of cattle with lead is described, as a result of which the concentration of this element increases in average in the liver to 26.4, in the kidneys to 50.3 and in the blood to 0.8 mg/kg of fresh substance.

The correlation between the content of trace elements in wool and other tissues is shown in Table 1.4. It is evident that the closest relationship in terms of copper content in cows grazed in the action area of the chemical factory is observed between the wool and the brain, as in control animals, the closest correlation is found between the liver and wool. This observation is probably due to the fact that in the technogenic province, part of the copper in the liver is present in the form of hardly soluble sulfide and does not reflect the availability of this element in the body. A similar phenomenon occurs when copper exchange is disrupted by an excess of molybdenum and sulfates. The correlation coefficients between hair and blood were also reduced, compared to the control. A significant relationship (L < 0.05) is observed for the copper content in wool and kidneys, muscles and bone.

According to the level of zinc and lead, the closest correlation is found between wool and bone both in animals from the technogenic province and in the control. According to the content of manganese in cows, the correlation in both cases is highest between the wool on the one hand and the liver and kidneys on the other.

Trace elements in the organs and tissues of yellow gophers

To identify the impact of chemical factory emissions on the microelement status of yellow gophers, 14 animals were captured in the territory of the technogenic province and 11 in the control zone. The results of the determination of trace elements in the organs and tissues of gophers are presented in Table 1.5.

In the literature available to us, we did not find data on the content of trace elements in the organs and tissues of rodents living in natural conditions. All available data relates to laboratory (boiled) animals. According to the table, the copper content in the organs and tissues of animals of the technogenic province is significantly lower than the background values. The greatest differences (by 2 times or more) were noted for the brain, hair and liver. In other organs and tissues, these differences range from 10-38% and are not always statistically significant.

Thus, the depletion of the body of copper under the influence of emissions of phosphate production, noted above for ruminants, is fully observed in rodents and is not associated with the peculiarities of the structure of the digestive tract.

It is interesting that gophers' liver, unlike ruminants and humans, are much richer in copper content. Such a picture is observed both in the conditions of the physiological norm and in the technogenic province. A similar situation is observed in rats, in which the copper content in the kidneys reaches 22 mg / kg, with 7.6 mg/kg of fresh liver tissue. This phenomenon is associated with the increased ability of the rat body to synthesize metallothioneins. Metallothioneins are low-molecular-weight proteins that do not have enzymatic activity, contain a significant amount of sulfhydryl groups, and have a very high affinity for certain metalloions (zinc, cadmium, copper, lead, mercury, gold, and bismuth).

As in ruminants, gophers from the technogenic biogeochemical province have a significantly reduced content of zinc in organs and tissues.

Table 1.4

Correlation between the content of trace elements in the organs and tissues of Karakul sheep and cows under the conditions of the technogenic province.

№		The bodies of the elements	Liver	Kidneys	Lungs	Muscles	Whole blood	The brain	Bone
1	Sheep	Copper	0,7	0,50	0,25	0,52	0,70	0,96	0,22
2		Zinc	0,65	0,33	0,20	0,66	0,68	0,68	0,84
3		Lead	0,28	0,29	0,43	0,20	0,31	0,36	0,69
4		Manganese	0,56	0,6	0,41	0,47	0,29	0,57	0,40
1	Cows	Copper	0,74	0,50	0,32	0,46	0,71	0,79	0,53
2		Zinc	0,51	0,35	0,31	0,53	0,57	0,62	0,83
3		Lead	0,23	0,26	0,58	0,28	0,30	0,20	0,62
4		Manganese	0,63	0,59	0,27	0,23	0,26	0,45	0,49

Table 1.5

The content of trace elements in the organs and tissues of yellow gophers

№	The bodies of the elements	Liver	Kidneys	Lungs	Muscles	Wool	The brain	Bone
Background (economy) (n=11)								
1	Copper	6,7±0,68	14,8±4,16	1,8±0,4	1,3±0,2	5,3±1,1	9,4±2,72	0,9±0,3
2	Zinc	16,3±1,23	13,6±0,7	11,7±2,3	12,2±3,2	39,6±2,7	19,3±2,4	24,7±4,1
3	Manganese	3,5±0,3	1,7±0,6	0,3±0,03	0,1±0,03	4,8±0,7	0,3±0,07	1,3±0,2
4	Lead	0,2±0,06	0,2±0,08	0,1±0,6	0,1±0,11	1,3±0,4	0,1±0,09	1,5±0,4
Technogenic province (n=14)								
1	Copper	3,9±0,3	10,4±1,2	1,5±0,3	0,8±0,2	2,4±0,4	3,7±1,4	1,0±0,2
2	Zinc	11,7±1,1	9,8±0,7	9,6±1,1	7,9±1,4	26,4±1,2	15,6±2,2	13,1±2,3
3	Manganese	3,3±0,1	1,6±0,7	0,2±0,04	0,1±0,02	5,2±0,6	0,3±0,02	1,6±0,3
4	Lead	0,4±0,09	0,4±0,08	0,1±0,04	0,2±0,06	6,2±1,1	0,2±0,22	3,3±0,7

The greatest differences are observed in the content of this element for bone and wool, and less significant, but statistically significant differences - for the liver and kidneys. The level of zinc in other studies of organs and tissues also shows a downward trend, which, however, does not reach the first statistical threshold of significance.

The coat of gophers, like other animals, objectively reflects the level of copper and zinc in their body, as evidenced by the elements in the coat and indicator organs (Table 1.6).

In terms of the manganese content, there are no noticeable differences between the animals from the technogenic province and the control, while in terms of the lead level, these differences are very significant. They are especially noticeable for wool, in which the level of this element exceeds the control by almost 5 times and for bone, liver and kidneys (by 2 times). In other organs and tissues studied, a similar trend is observed, but the observed differences are not statistically significant.

A similar increase in the lead content was observed in the body of rats that received 20 mg of lead per kilogram of live weight for 14 days. The concentration of this element in the liver increased by 3.3 times, in the kidneys-by 2.5 times, in the brain-2 times, while reducing the level of copper and zinc in these organs. Thus, the level of copper and zinc in the body of animals from the technogenic province is influenced, apparently, not only by sulfur compounds, but also by lead. It is interesting to note that the important role of lead in the occurrence of the phenomenon of copper deficiency was pointed out by V. V. Kovalsky, who notes that, obviously, the malfunction of copper metabolism in animals can be caused not only by a lack of copper, but also by a high content of lead in soils, "sick' pastures. Data on the antagonism of lead and copper are also given by N. V. Badanin, Nekhotyaev et al. and G. N. Gireev, who note that the action of lead is cumulative and it accumulates in the body over time.

The content of trace elements in the hair of children

To determine the background concentrations of trace elements, we selected samples of black hair from 16 girls and 16 boys aged 7-12 years, studying at the school of the village of Sazagan. The hair of children reflects the microelement status of the body better than that of an adult, since it is less exposed to various cosmetics.

The results of the analysis of the hair of children from the control zone closely correspond to the data given in the literature. So, Anke et al.

Table 1.6

Correlation between the content of trace elements in the organs and tissues of yellow gophers

№	The bodies of the elements	Liver	Kidneys	Lungs	Muscles	The brain	Bone
Background (economy)							
1	**Copper**	0,74	0,37	0,34	0,30	0,73	0,48
2	**Zinc**	0,54	0,35	0,29	0,41	0,63	0,70
3	**Lead**	0,29	0,31	0,48	0,36	0,26	0,61
4	**Manganese**	0,71	0,65	0,30	0,26	0,47	0,35
Technogenic province							
1	**Copper**	0,71	0,42	0,27	0,21	0,68	0,30
2	**Zinc**	0,44	0,39	0,22	0,32	0,65	0,72
3	**Lead**	0,17	0,33	0,37	0,21	0,19	0,59
4	**Manganese**	0,67	0,61	0,20	0,19	0,31	0,33

It is indicated that the copper content in the hair of girls from the zone not exposed to industrial emissions at the age of 6-10 years makes up 21, and boys – 24 mg/kg. It is interesting to note that in women's hair, the copper content in 11-12 years of age is 15, and in men – more than twice as much – 37 mg/kg. In our studies, the background level of copper in the hair of boys was also higher than in girls, but the differences were not so significant. According to Anke and co. The zinc content in the hair of girls is 9% higher than that of boys, which is confirmed by our data. We also observed higher levels of lead and manganese in girls ' hair than in boys. We did not find any differences in the level of arsenic in the hair of children of different sexes. In terms of the level of manganese, our data correspond to the figures given by Anke and co. (1.0 mg / kg for girls, 1.1 mg/kg for boys). Data on the concentration of lead in the hair of children living in a non-industrial zone cover a wide range of fluctuations – from 10.7 to 112.3 mg / kg.

Our results correspond to the average values given for the human hair on the aforementioned elements, which are for copper-19, zinc-220, manganese-0.25 – 5.7, lead-3-70, arsenic-0.60-3.7 mg / kg. Unfortunately, the author does not provide sex and age differences in the microelement composition of human hair, which makes it difficult to use them for biological monitoring.

As can be seen from Table 1.7, the level of copper and zinc in the hair of children of 7-12 years of age – schoolchildren, in the zone of exposure to chemical factories' emissions-is lower than in children from the control zone. According to the content of these elements in the hair, the same pattern is observed as in the wool of farm animals and yellow gophers, as well as smoothing out the sex differences in the concentration of these elements. There were no significant differences in the content of manganese in the hair. The hair of children from the technogenic province is enriched with lead in comparison with the control more than 3 times and arsenic-4 times.

Thus, the hair cover of various animals and humans can be considered as an indicator of the content of a number of important elements in the body. The levels of the elements depend on the condition and age of the animal, as well as on the chemical effects of various environmental factors.

Table 1.7

The content of trace elements in the hair of children from the technogenic province

Elements Selection location, gender	Copper	Zinc	Lead	Manganese	Arsenic
Technogenic province (n=32)	23	190	8,8	1,3	1,2
Girls(n=16)	22,5±1,2	182±11	9,2±0,4	1,3±0,1	1,3±0,2
Boys (n=16)	23,5±1,5	198±8	8,4±0,2	1,3±0,1	1,1±0,1
Background (n=32)					
Girls(n=16)	25,0±0,7	232±6	2,3±0,1	1,3±0,1	0,3±0,1
Boys (n=16)	29,0±1,0	208±10	2,1±0,1	1,1±0,2	0,3±0,1

Microelement composition of goat hair in the conditions of mountain pastures of Uzbekistan.

In the Republics of Central Asia, goat breeding is a traditional branch of animal husbandry, which makes it possible to include in the economic turnover the sparse stony pastures of the mountains and foothills, just as karakul farming makes available for economic use the pasture lands of deserts and semi-deserts. The arid climate, high soil pH, widespread in the Western spurs of the Tian Shan metal ore manifestations determine the identity of the mineral composition of pasture forage, not always meeting the needs of animals in the vital macro - and micronutrients, and often containing excessive number of them. In this regard, the study of the conditions of mineral nutrition of goats as an important reserve for increasing their productivity and viability becomes of some importance.

To study the chemical composition of goat hair, the livestock of the farm located in the southern spurs of the Nurata Mountains was chosen. In this farm, on the basis of crossing local goats with goats-producers of wool breed, as well as purebred breeding, a herd of highly productive animals of wool and down directions with a number of 12.5 thousand heads was created. There are also a significant number of crossbreeds of different generations in the herd.

The wool of goats of the wool breed belongs to the Angora type (mohair) with a predominance (up to 95%) of transitional hair. Black down goats are distinguished by the fact that their coat is divided into a roughly shiny awn (35%) and a thin longer matte down (65%). The color of the coat varies depending on the season. In winter, when the down protrudes above the awn, the coat is dark gray or light gray, and in summer, when the down is combed, the goats are covered with awn hair of a dark or dark brown color. Black downy goats were bred as a result of crossing black local goats with white Angora goats (when crossing crossbreeds of 1 and 2 generations).

In the literature available to us, there is only limited data on the content of trace elements in goat hair. The results of the determination of manganese, copper and zinc in the wool of white goats, respectively, are presented in the studies. 2,4+1,74; 2+1,4; 126+23. The authors note that manganese and copper in goat hair do not show sexual differences, but the zinc content in goat hair is lower than in goats and is 113±18 mg/kg.

The same author notes age differences in the content of copper in goats. Thus, in the wool of adult animals, the content of this element is 3.0±1.4 and in goats-5.5±2.4 mg/kg, in goat hair, with their insufficient content in the diet,it contains: manganese – 1.1±0.6; copper - 2.3± I, 0; zinc - 108 ± 10 mg/kg.

The results of determining the listed elements in the white wool of Altynsay goats are shown in Table 1.8.

Table 1.8

The content of manganese, copper and zinc in a white goat hair "of Altunsa»

Indicator	Ash content, in %	Manganese	Copper	Zinc
X±Sx	0,8±0.04	2,1±0.22	4,37±0,19	71,6±1,95

A comparison of our results and data shows an almost complete coincidence of the figures for manganese and copper, and not only the arithmetic mean, but also the values of the square deviation. A little bit smaller values of the latter, found by us, are explained by the fact that the number of samples of the finger subjected to analysis was higher than that of the above-mentioned author.

As for zinc, the values obtained by us are lower than the figures given, even for goats experiencing a pronounced deficiency of this element. Whether this is evidence of an insufficient supply of goats grazed in Altynsay, Kazakhstan, is difficult to say, since no experimental verification of this assumption has been carried out. But there are data on the existence in the conditions of loess foothills of endemic parakeratosis in cattle caused by a deficiency of pink and vitamin A, and data on the positive effect of zinc on the reproductive function of sheep grazed on similar pastures. Our results indicate the need for experimental testing of the role of zinc additives in the diet of Altynsai goats.

If for white wool we have literature data for a limited range of trace elements, then for pigmented wool such information is not available in the literature available to us. The results of the study of the trace element composition of pigmented wool are shown in Table 1.9.

Table 1.9

The content of trace elements in pigmented wool of goats "of Altunsa"

The color and figure	The Ash Content Of	Manganese	Copper	Zinc
Black (n=16)				
X±Sx	1,9±0,04	8,9±0,5	6,23±0,3	90,5±4,0
Dark gray (n=22)				
X±Sx	1,6 ±0,03	9,2±0,36	5,6± 0,2	88,5±42,5

The table shows that in terms of ash content and manganese, there are significant differences between pigmented and white wool by 2 and 4 times, respectively. This is in good agreement with our earlier observations on the relationship between the ash content and the manganese content in wool on the one hand and its pigmentation/ 20 / Brochard data.

The content of copper and zinc in pigmented wool is also higher (α>0.05) than in white wool, but these differences reach only 22-30% and are caused rather by breed characteristics, since pigmented wool belongs to downy goats, and white wool belongs to woolly goats. Comparing the obtained figures with the data on the content of these elements in the wool of other ruminants, it can be noted that the level of copper and manganese in downy Altynsay goats meets the standards adopted for black wool of sheep and cattle, and is 120 mg/kg. The wool of downy goats that we subjected to chemical analysis consists, as already noted, mainly of two functions-awn and down, and therefore it was of some interest to find out the difference in the trace element composition of these fractions in order to assess the contribution of each of them to the results of the analysis. Winter dark gray wool was studied (Table 5. 10) in which the down fraction was 63±10 %.

The table shows that downy hair is richer in zinc and manganese and poorer in copper (α>0.05), and thus, a large proportion of down in the composition of goat hair leads to higher figures for the first two elements and to lower results for the third.

Cobalt, chromium, and possibly nickel are among the trace elements whose vital necessity is explained by their presence in the composition of the molecules of vitamins, hormones, and enzymes. In human hair, their concentration is 0.2-1.0; 0.13-3.6 and 0.2-6.5 mg / kg, respectively.

Table 1.10

The content of trace elements in individual fractions of dark gray goat hair

Indicator, fraction	The Ash Content Of	Manganese	Copper	Zinc
Guard hair				
X±Sx	1,6±0,05	7,2±0,78	5,6±0,51	74,0±6,9
Fluff				
X±Sx	1,4±0,09	8,9±0,73	4,3±0,3	94,0±4,0

The content of these elements is significantly influenced by the sex and age of animals, their physiological state, for example, the nickel content in the hair of men is four times lower than in women (0.87±0.15 mg / kg), and the chromium content in the hair of women who gave birth and nulliparous women was 0.75 and 0.22 mg/kg, respectively. In newborns, the chromium content in the hair is higher than in 2-3-year-old children (0.9 and 0.44 mg / kg, respectively).

The results of studying the content of these elements in the wool of 2-5-year-old goats, obtained by emission spectral analysis, are shown in Table 1. II, From the figures given, it follows that the content of the trace elements listed in the table in goat wool is closer to the lower limit of the values set for human hair. The concentration of cobalt and chromium in the black wool of downy goats is about the same, and nickel is twice as high.

Table 1.11

The content of cobalt, chromium and nickel in the wool of Altynsay goats

Color	Cobalt	Chrome	Nickel
Black, n	5	9	13
X±Sx	0,41±0,09	0,39±0,03	0,8±0,09
White, n			
X±Sx	0,47±0,09	0,27±0,03	0,7±0,16

White and black wool did not differ in the content of cobalt and nickel, as we noted earlier when studying the wool of Karakul lambs, this is due to the greater ability of nickel and cobalt to form complexes with ligands containing sulfur and nitrogen (i.e., with wool keratin) than with ligands containing charged oxygen and nitrogen (i.e., with wool melanin). The determination of cobalt by emission spectral analysis gave lower values than according to neutron activation analysis (0.2 mg / kg), but this method also did not show any differences between the cobalt content in white and pigmented wool, As for chromium, the concentration of this element seems to be related to the content of melanin in wool ($\alpha<0.05$), With the parallel determination of chromium by neutron activation, we obtained slightly higher results, amounting to 0.65±0.02 for black wool and 0.02 for white wool. - 0.42±0.04 mg / kg, and in this case, the correlation between the pigmentation of the hair and the content of the element was preserved.

On the basis of obtained data it is impossible to decide whether goats need in these elements, but because of the livestock farm is not marked signs of acobaltosis and the need for chromium and Nickel of goats does not exceed 50 mg per head per day, it can be assumed that the obtained numbers are close to the physiological norm. In addition to the vital elements for the animal body, we also studied the content of some "toxic" elements in wool - arsenic, antimony, mercury (Table 1.12).

The mercury content in goat hair is close to the figures given for human hair, which are 0.83 - 4.4 mg/kg. The arsenic content in the hair of people who do not have contact with the compounds of this element is usually below 1 mg/kg and is usually 0.3-0.5 mg/kg. Our figures are close to the lower limit of this interval, interestingly, the arsenic content in the hair of men is almost twice as high as in women and is 0.62 and 0.37 mg/kg, respectively.

Table 1.12

The content of arsenic, antimony and mercury in the wool of Altynsay goats

The color parameters	Arsenic,	Antimony	Mercury
Black, n	10	8	8
X±Sx	0.37± 0.03	0.29± 0.04	4.9± 1.0
White, n	7	33	27
X±Sx	0.24± 0.05	0.27± 0.04	3.4±0.75

From our data, it follows that white goat hair is poorer in this element than black, and the antimony content in the wool of Altynsay goats is close to that of arsenic. Comparison of our results with the data for normal human hair, amounting to 0.34 mg / kg, allows us to assume that the values obtained by us also do not go beyond the norm, By the method of neutron activation analysis used in our studies, it is possible, along with the elements described above, to determine with sufficient accuracy gold, bromine and samarium, the content of which in goat hair is given in Table 1.13.

Table 1.13

The content of gold, bromine and samarium in the wool of Altynsay goats

Color parameters:	Gold	Bromine	Samari
Black, n	12	6	4
X±Sx	0,0152±0,001	0,55±0,03	1,0±0,12
White, n	9	6	6
X±Sx	0,0102±0,004	0,37±0,08	0,45±0,09
Human Hair	0,0017-1,8	0,65-53	0,23

In addition, we also determined the concentration of lanthanum in goat hair, which is 0.09-0.125 mg / kg, which is lower than in human hair, for which the values of 0.15 -0.65 mg/kg were obtained, while the content of samarium, on the contrary, is higher. For the other elements, the results obtained by us are close to the data for the human hair. The concentration of bromine and under these conditions of special veterinary and hygienic studies,

Antimony in the wool of farm animals of the upper Zarafshan.

The concentration of antimony in the earth's crust is very small and is 4.10^-5%, but it is one of the available elements, due to the presence of ores and minerals with a high content of it. In addition, antimony is found in the form of impurities in the ores of many metals, during the processing of which it is isolated as a by-product.

The largest explored reserves of antimony raw materials are located in the republics of Central Asia, the Krasnoyarsk Territory, Kazakhstan and the Caucasus, in Central Asia, antimony reserves are concentrated in the Upper Reaches of Zarafshan and Southern Ferghana.

Due to the fact that antimony is a highly toxic element, it is of great interest to study the content of this element in various objects of the biosphere - soils, plants, natural waters and living organisms, especially in areas where it is possible to assume an increase in the level of antimony in natural environments, as is the case in Upper Zarafshan./20, 15, 28, 29, 25, 29/ and they showed the relevance of these studies from the point of view of regional medicine and veterinary medicine.

For chemical studies, samples of soil and plants growing on them (20 samples each), 18 water samples and 234 wool samples (112 cattle, 55 sheep and goats, 12 camels) were selected. Analysis of antimony was carried out by atomic absorption and neutron activation analysis.

In the literature available to us, there are no reliable data on the content of antimony in animal hair. In this regard, the task was set to determine the content of antimony in the feathers of farm animals and to find out the factors that affect the level of this element in the wool - its color, location on the body, the type and age of animals, natural and economic conditions.

The antimony content in the wool of various types of farm animals is shown in Table 1.14.

Table 1.14

Antimony content in the wool of farm animals

Parameter	Cattle	Camels	Sheep	Goats
(n)	112	12	23	16
X±Sx	0,27±0,046	0,25±0,024	0,56±0,074	0,25±0,033

Judging by the data given in the table, animals do not differ much in their content of antimony in wool, and the significant differences between sheep and animals of other species are rather related to the geochemical background. In other animal species, both the lower and upper limits of fluctuations are practically the same, and there is no statistically significant difference between them in this indicator. This gives reason to believe that the species differences in the level of antimony in wool, if any, are relatively small, and the main influence on this indicator is posed by other factors.

Location on the body. The concentration of antimony in the wool of cows cut from different parts of the body (tail, side) is shown in Table 1.15, which shows that the behavior of antimony differs from that of manganese and zinc, the content of which in the wool from the side and tail significantly differ.

Table 1.15

The antimony content in the hair of cattle from various parts of the body

Parameter	Side	Tail
(n)	31	70
X±Sx	0.31±0.03	0.25±0.02

Coloring. The content of antimony in wool of various colors is given in Table 1.16, from which it follows that the color it does not significantly affect the content of antimony in wool, as it was noted for other chalcophilic elements, in particular, for copper and zinc, and no differences were found in the content of antimony between down and awn hair, the age of animals. To clarify the influence of animal age on the content of studied elements the wool of 2-3 day Karakul lambs, 1-2 year and 3-4 year sheep was sampled (table 1.17). The table shows that despite the significant fluctuation of numbers, lower values are found in young, large - in adult animals. This suggests that with age, the concentration of antimony in the fur of animals shows a tendency to increase.

Table 1.16

Antimony content in the wool of cattle and goats of various colors

Parameter	Cattle			Goats	
	Black	White	Red	Black	White
(n)	25	5	66	9	8
X±Sx	0,24±0,025	0,28±0,06	0,28±0,02	0,29±0,04	0,27±0,04

Table 1.17

Effect of age of sheep on the content of antimony in hair.

Parameter	2-3-day	1-2-year-old	3-4-year-old	
	Mutton Nurata	Sheep Concoc	Sheep Concoc	Sheep Jam
(n)	24	10	13	10
X±Sx	0,17	0,80	0,79	0,27

in young animals, large - in adult animals. This suggests that with age, the concentration of antimony in the fur of animals shows a tendency to increase.

Geochemical factors. To determine the influence of geochemical factors on the level of antimony in wool, we took samples in I5 different points of the Upper and Middle Zarafshan. Samples of soils, wild and cultivated plants were also taken here, and the wool of sheep and goats grazed under these conditions showed an increased antimony content (10-15 times higher than the background values), for example, in sheep grazed near the antimony deposits in the Konchoch basin, the content of this element in wool was 1.23±0.15 mg/kg in I980 with fluctuations of 0.3-2, 1 and in 1981 - 0.8±0.1 with fluctuations of 0.3-1.3. Even higher concentrations were found in the feathers of sheep and goats grazed in the valleys of the Shinka and Magiyana rivers - 2.1±0.23 mg / kg with fluctuations of 0.3 - 7.2. The studied animals can be divided into groups with normal (0.3 - 0.5 mg/kg) and increased (above 0.5) antimony content in wool. This depends, apparently, on whether the grazing areas are located in the zone of halos of scattered ore deposits of antimony or not,

The wool of sheep and goats grazed on the pastures of the foothills (Jam, Altynsay) is 2-3 times poorer in antimony, and cattle of the middle Zarafshan contain 0.067-0.165 mg/kg of this element, the difference is due to the presence of most of the studied cows in the stable, and sheep and goats in the pasture content, at which their body receives more minerals with ingested soil particles. Due to the fact that the food of stable animals is more homogeneous, the fluctuations in the concentration of antimony in their wool are less significant than during grazing.

Antimony in soils and plants

Antimony in soils near deposits of this element is contained in the amount of 162-496 mg / kg with a background content in the soils of the Middle Zarafshan equal to 0.4+0.02 mg/kg, plants growing on antimony-rich soil (Konchoch) are 5-10 times richer in this element than plants from moderately antimony-rich areas (Sarytag) (Table 1.19), Juniper, wormwood and tobacco accumulate antimony more than others. Similar observations were made in the antimony biogeochemical provinces of Southern Ferghana. It should be noted that the intake of antimony in plants is difficult and the coefficient of its biological accumulation is only 10-2-10-3 % against 0.4-0.2 in copper and zinc. Apparently, plants have a barrier mechanism that restricts the entry of antimony into them. A significant amount of antimony migrates with water (Table 1,20). The table shows that the rivers of the upper Zarafshan contain 0.05-0.08 micrograms / ml of antimony, and a stable concentration of this element is established downstream equal to 0.02 mg/ml. Sharp increase in the content of antimony in water Zarafshan river connected with the activities of Anzob mining and processing plant, waste water, bypassing the settlers, often dumped into the river and are I0-I00 multiple quantity of that item. The waters of Zarafshan, which are polluted by sewage, are used for watering tobacco, alfalfa and other crops, enriching them with antimony, and some other elements. With an average annual flow of 4.3 km^3, Zarafshan brings 80-90 tons of antimony to the plain per year Due to the fact that the Zarafshan River basin is a closed geochemical system, antimony and other elements carried out by its waters for thousands of years accumulate in the alluvium of the river, in the soils fed by the Zarafshan irrigation network and its dry delta.

Animal wool of the Zarafshan valley is poorer in antimony than in the mountainous part in I,5-2 times and contains 0.07-0.165 mg / kg of this element, Animals from farms located in the foothills (Jam, Altynsay) have a higher content of antimony in wool than animals from the river valley, and the content in wool is not increased here.

Table 1.19

Antimony content in plants of the Upper Zarafshan

Name of the plant	Place of selection	Antimony content
	Concoc	
Barberry	Adit 41	2,2
Barberry	Adit 41	2,8
Barberry	Adit 47	1,6
Christmas tree	Adit 41	2,2
Christmas tree	Adit 44	7,7

Christmas tree	Adit 47	1,1
Tobacco	Konchoch village	4,0
Tarragon	The slope of the mountain	0,6
Wormwood	Adit 44 Konchoch	7,2
Hay wiki	village	0,4
Ephedra	Adit 47	2,1
Alfalfa	Sarath	0,4
Barberry	Sarath	0,4
Juniper 1	Sarath	1,2
Juniper 2	Sarath	0,2
Wormwood 1	Sarath	0,3
Wormwood 2	Sarath	1,0
Ephedra	Sarath	0,5
Alfalfa	The site near AGOK	2,0
Tobacco	Near the mountains	1,5

Table 1.20

Antimony content in the river water of the Upper Zarafshan

№	Sampling location	Content
1	The source of Iskander-darya	0,069
2	Konchoch River	0,047
3	Spring in a birch grove	0,043
4	Kanok-SAI	0,229
5	Conchos, mine rock	0,229
6	Konchoch adit 41	0,161
7	Konchoch adit 44	2,060
8	Konchoch Adit 47	2,060
9	Konchoch tap water	2,080
10	Ruzi obnox	0,085
11	River Matches	0,050
12	Fandarya, mining and processing plant	0,0150
13	Fandarya, after resetting the AGOK	3,0
14	Fandarya 1 km down	0,17
15	Zarafshan at the bridge 30 km down	0,070
16	Zarafshan at the bridge 50 km down	0,020
17	Zarafshan at the bridge 70 km down	0,020
18	Zarafshan dam	0,060

The fluctuations in the content of this element in stable animals do not exceed two times, while in animals mainly grazing, for example, in

Altynsay goats, differences reaching 63 times (0.27 and 17.0 mg/kg) were noted. It is also possible that the level of antimony in the finger is influenced by genetic factors.

Our studies indicate that the average antimony content in the wool of farm animals ranges from 0.025-0.165 mg / kg and does not depend much on its color, location on the body and type of animals, but increases with age. In areas of ore deposits, the level of antimony in animal feathers can increase by 70-100 times and reach 27 mg/kg. Given that, while on pasture, sheep and goats collect food from a large area, the analysis of their wool can provide valuable information about the ore occurrences of antimony and the metals in paragenesis with which it occurs.

Gold in the wool of farm animals

Data on the content of gold in the wool of farm animals are not available in the literature available to us. In human hair, the gold content varies by a thousand times - from 1.7 micrograms to 1.8 mg per kg / 17/. According to other authors, the gold content in human hair ranges from 1.5-5 micrograms/kg. In our studies, similar figures were obtained in about 15% of farm animals, but in most samples we found significantly larger values. In the wool of sheep from farms remote from gold ore occurrences (Kasan, Payaryk, Nurabad districts), the content of this element is on average about 12-15 micrograms / kg with extreme values of 1-30 micrograms/kg. When grazing animals in gold-mining areas (Farish, "Marjanbulak", Gall-Aral and" Kukcha " Gijduvan districts), the average gold content in wool is twice as high-30-35 micrograms/kg, and in individual animals reaches 50-80 micrograms/kg (Table 1.21).

Similar results were obtained for cattle, in which the gold content in most samples of gold (57 or 73) does not exceed 30 micrograms/kg and only in some cases reaches 40-70 micrograms/kg, These cases were noted in the middle course of the Zarafshan River, known for its gold content. The studies conducted allow us to believe that animal gold to a certain extent reflects the geochemical situation of the territory in relation to gold and can serve as an additional zoo-indication criterion in the search for this element.

The hair of horses and the bristle of pigs differ little in gold content from the wool of sheep and cattle. It should be noted, however, that in the hair of horses, the concentration of gold is in average slightly lower, and in pigs - slightly higher than in ruminants.

Uranium in the fur of farm animals

Data on the content of uranium in the epidermal formations are very limited. In the literature available to us, the figure for the content of uranium in human hair is equal to 0.13 micrograms/kg. In the wool of an agricultural animal of Uzbekistan, significantly higher concentrations of uranium were found, ranging from 0.4 to 60 micrograms/kg, i.e. Almost 160 times. In 46 % of the studied animals (27 out of 62), the concentration of uranium in the wool is in the range of 1-10 micrograms/kg. Another 37 % of the results for a concentration of 11-30 micrograms / kg, a content of more than 30 micrograms/kg are found less than in 1/5 of the studied samples (Table 1.21). In some cases, high concentrations of uranium in animal hair can be associated with grazing near deposits of this element, in others-a high concentration of uranium (over 60 micrograms/kg) is found in the wool of animals grazed away from known ore occurrences of this metal. The average content of uranium in the wool of sheep is 11.3±6.8; cattle -22.6±2.7; pigs-18.8±4.4 and horses-9.3±2.5. From these data, however, it cannot be concluded that there are significant differences in the content of uranium in wool between the studied species of farm animals, since they are not statistically confirmed. But there were no differences in the content of uranium in the coat and depending on its color and location on the body. Since we did not have data on the content of uranium in the fur of animals from other regions, it is difficult to assess whether our results are typical or deviate from the norm in one direction or another. If we judge by the ratio of gold to uranium in human hair equal to about 1:10, then in the wool of the studied animals it is higher by an order of magnitude and is 1:1 and animal hair, thus much richer in uranium than human hair. Given that uranium and calcium have close ionic radii and that the biogeochemical background of Uzbekistan and other Central Asian republics is characterized by an increased level of calcium, it can be assumed that the increased content of uranium in animal hair that we have noted is a specific feature of this region. However, this assumption can only be proved by conducting broader comparative studies.

Table 1.21

Gold content of farm animal wool

Classes	Karakul sheep						Cattle			Pig	Horse
	Nurabad district	Gallaaral district	Ksani district	Farish district	Payarik district	Gijduvan district	Bulungur district	Akdarya district	Kasansky district	Bulungur district	Istinski district
1-10	4	-	3	-	2	1	4	4	4	2	8
11-20	1	6	5	-	5	3	2	18	2	5	2
21-30	2	9	-	9	2	1	1	10	2	1	-
31-40	1	6	-	8	-	2	3	-	1	1	-
41-50	-	1	-	5	-	2	-	-	-	1	-
51-60	-	-	-	2	-	1	-	2	-	-	-
61-70	-	-	-	-	-	-	-	1	-	-	-
71-80	-	2	-	-	-	-	-	-	-	-	-
X	16.6	29.6	12,5	34,6	16,3	29,0	19,2	20,9	14,6	20,7	8,0
Sx	3.8	3.5	1,2	2,6	1,7	5,0	4,0	3,5	2,5	4,0	1,6

The use of diphenylcarbazone in combination with atomic absorption analysis for the determination of trace elements in natural objects

Extraction concentration

Extraction concentration is the method most often combined with atomic absorption. For extraction concentration in atomic absorption, extraction within complex compounds is used. Many papers have been published that describe methods for determining more than 60 elements. Extensive material has been accumulated on the reagents used for extraction in atomic absorption. The selectivity of atomic absorption makes it possible to widely use group reagents, such as diethyl-and pyrrolidindio-carbamates, ditizone, oxy-quinoline, etc.

A common reagent is sodium diethyldithiocarbamate (sodium DDA), which interacts with more than 40 elements. Its use is hindered by the instability of the reagent in acidic environments. The rate of decomposition of dithiocarbamic acid is proportional to the concentration of hydrogen ions. In addition, complexation occurs in a fairly narrow pH range, which makes it difficult to separate the elements that interfere with joint extraction.

More commonly, ammonium pyrrolidine dithiocarbamate (CDCA) is used for extraction concentration in atomic absorption. This reagent also interacts with many metals, and in solutions it is more stable than sodium DDK. However, the MPC is difficult to access and quite expensive. There are attempts to use analogues of diethyl - and pyrrolidinedithiocarbamate.

Diphenyl diticarbazone, otherwise known as ditizone, is one of the most commonly used reagents in atomic absorption. The properties of ditizone and the conditions for the formation of metal ditizonates are sufficiently fully described in the works. The solubility of the reagent in hydrocarbons is very small, much greater solubility of ditizone and ditizonates have in chloroform and carbon tetrachloride, solvents that form toxic products during combustion and pyrrolysis. The disadvantages of ditizon can also be attributed to the decomposition of its solutions under the influence of strong oxidizing agents, light and heat. The disadvantage of 8-oxy-quinoline, one of the most versatile reagents that interact with more than 50 elements, is the high pH of the formation of many oxy-quinolates. In addition, chloroform is usually used for the extraction of oxy-quinolinates. For the extraction-atomic-absorption determination, acetylacetone (AA), a reagent from the group of β-diketones, 1-(2 – pyridylazo) - 2 naphthol and aromatic diamine are also used.

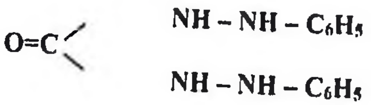
The solvents used for the atomic absorption with a pulsed atomization, should, in the main, meet the requirements of the chemistry of the extraction, i.e., should have a high solubility of the reagent and of the complexes in the solvent, the low solubility of solvent in water and water in solvent, etc.

These requirements are not fully met often used in atomic absorption methyl isobutyl ketone (MIBK). It has a high solubility in water (1.9 percent), in addition, MIBC seems to be prone to the formation of emulsions in the aqueous phase, which requires centrifugation of the phases to separate them.

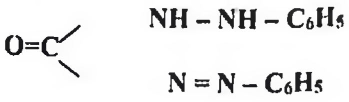
In our studies, we paid attention to diphenylcarbazone. Used as an extraction-photometric reagent for the determination of traces of metals in animal organs and tissues. The reagent interacts with a large number of transition metals, has sufficiently high values of the distribution constants of diphenylcarbazonate in the extraction of the distribution constants of diphenylcarbazonates in the extraction of toluene and pyrimidine. An important advantage of diphenylcarbazone is its prevalence and availability.

Properties of diphenylcarbazone and its metal complexes

Diphenylcarbazone-C13H12ON4-is a needle-like crystal of orange color. The commonly used diphenylcarbazone (DFC) is the oxidation product of diphenylcarbazide.



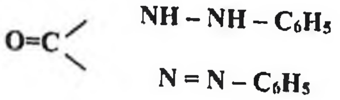
$$O{=}C\begin{matrix} \diagup\ NH-NH-C_6H_5 \\ \diagdown\ NH-NH-C_6H_5 \end{matrix}$$



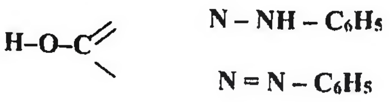
$$O{=}C\begin{matrix} \diagup\ NH-NH-C_6H_5 \\ \diagdown\ N=N-C_6H_5 \end{matrix}$$

Diphenylcarbazide Diphenylcarbazone

As a weak monobasic acid, diphenylcarbazone exists in organic solvents in two forms – ketone and enol:



$$O{=}C\begin{matrix} \diagup\ NH-NH-C_6H_5 \\ \diagdown\ N=N-C_6H_5 \end{matrix}$$



$$H{-}O{-}C\begin{matrix} /\!\!/\ N-NH-C_6H_5 \\ \diagdown\ N=N-C_6H_5 \end{matrix}$$

Ketone form of DFC enol form of DFC

The dissociation constant of diphenylcarbazone, determined at μ = 0.1, is (2.9 ± 0.3) 10-9, its solubility in water is very insignificant-1.8. 10-4 mol/l. DFC has a relatively higher solubility in some organic solvents: benzene, toluene, alcohols, ketones, etc. (table 1.21).

Table 1.22

Distribution constants and solubility of diphenylcarbazone in some organic solvents

Solvent	S mol/l	Lg PMA	References
Toluene	1.10^{-2}	1,59	
Carbon tetrachloride	$2,75.10^{-3}$	0,88	
Benzene	-	1,0	
Methyl isobutyl ketone	-	2,61	

The nature of the absorption spectra of diphenylcarbazone depends on the nature of the solvent (Table 1.23).

Table 1.23

Maximum absorption and molar extraction coefficients of diphenylcarbazone

Solvent	λnm	E
Toluene	289	$(10,8 \pm 0,1).\ 10^3$
Carbon tetrachloride	467	$(1,21 \pm 0,5).\ 10^3$
	565	$(0,17 \pm 0,01).\ 10^3$
	288 465	$(1,25 \pm 0,5).\ 10^3$
	555	$(3,04 \pm 0,05).\ 10^3$
		$(0,91 \pm 0,06).\ 10^3$

Diphenylcarbazone interacts with many metals to form intracomplex compounds extracted by benzene and other organic solvents. With many metals, the reactions are sensitive and quite specific, so the reagent is quite widely used in photometric analysis. DFC is used to open copper. The optimal reaction conditions are within the pH range of 4-6. Copper is extracted with benzene or toluene. In a slightly acidic medium, pH 5-6, indium interacts with diphenylcarbazone to form purple-colored complexes. DFC is used for the spectrophotometric determination of mercury (P). Mercury complexes with DFC formed at pH b, 5-8, 0 are extracted with benzene.

Some diphenylcarbazone extraction with toluene was studied by Baltic and van Dalena. They calculated extraction constants and the constants were determined diphenylcarbazone distribution of cadmium (II), cobalt (N), copper (P), copper (P), iron (P), iron (III), mercury (I), manganese (P), lead (P), pewter (P), pink (P). Method isomolar series the composition of the complexes is determined. The data obtained by the authors are presented in Table 1.24.

Diphenylcarbazone, in which the metal can bind both by oxygen and nitrogen atoms, has a high reactivity, covering part of the transition metals, whose ions have partially filled and filled α-levels. The shaded cells in Table 2.4 show elements that interact with diphenylcarbazone under certain conditions. The table is compiled according to the above literature data. Due to the similarity between the chemical structures of diphenylene area and dithizone with DFK react with many elements of the group decision. The total number of elements interacting with diphenylcarbazlnlm is slightly higher than the number of elements reacting with ditizone. This makes diphenylcarbazone a very convenient group-action reagent.

Table 1.24

Extraction of some diphenylcarbazonates with toluene

Complex	Logarithms and extraction constants	Logarithms and distribution Constants
Cadmium	-8,15	0,04
Cobalt	-7,0	1
Copper	4,13	2,52
Copper	1,27	2,94
Iron	-4,7	3
Iron	1,05	2,45
Mercury	5,26	3
Manganese	-11,54	-0,3
Nickel	-6,1	-0,1
Lead	-5,5	1,18
Tin	-2,06	2,3
Zinc	-6,76	0,11

Extraction diphenylcarbazone mixtures of solvents.

The coordination unsaturation and hydrophilicity of a number of diphenylcarbazone complexes is one of the reasons that the extraction constants of these complexes have low values when they are extracted with nonpolar or weakly polar solvents.

Table 1.25

Elements of the periodic table of D. I. Mendellev interacting with diphenylcarbazone

H																	He
Id	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Xe
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	Kr
Cs	Ba	La	Hf	Ta	W	Re	Cs	Jr	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ak	Ku														
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Kr	Tm	Yb	Lm	
			Th	Pa	U	Np	Pu	Am	Cm	Rk	Cf	Rs	Fm	Md	No	Er	

The extraction of such hydrated intra-complex compounds can be provided by the addition of active solvents. The solvent most commonly used with DFC is toluene-convenient for extraction-atomic-absorption methods /129/. The extractability of metals forming coordination unsaturated complexes with DFC can be increased by adding donor-active additives. Thus, the study of synergistic extraction in the Me-DFC - tributylphosphate - benzene /137 / system showed that there is a significant increase in the distribution coefficients during the extraction of some of the above elements. A similar synergy is shown when using the DOK-pyridine-toluene system in the extraction of zinc and copper /131/.

Extraction of cadmium, cobalt, copper, manganese, nickel, lead and zinc with a solution of diphenylcar-basone with pyridine in toluene

In the toluene-pyridine-water triple system, pyridine is a component that is completely miscible with both water and toluene. Changing the ratio between the components changes the compositions of the phases after extraction. This, in turn, can affect the extraction of intra-complex compounds, especially when the ratio between the volumes of the phases - water and organic-changes. In addition, in the presence of pyridine, which is a polar solvent, it is possible to change the solubility of diphenylcarbazone in toluene.

Therefore, we studied the distribution of pyridine in the water-pyridine-toluene system and determined the solubility of diphenylcarbazone in the toluene-pyridine mixture. For this purpose, we have constructed a diagram in triangular coordinates (pmo.2.1). The diagram defines the boundary conditions of the heterogeneity of the system and shows that even at very high pyridine concentrations, in the system, for example, 5 M and the ratio between the volumes of the phases V/V0-10, the amount of water in the extractant is insignificant (does not exceed 2 %). That is, the range of use of the system for extraction concentration is very wide.

Pyridine

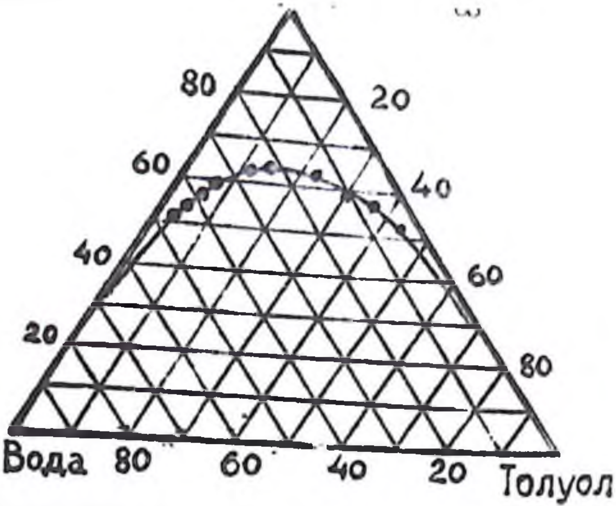
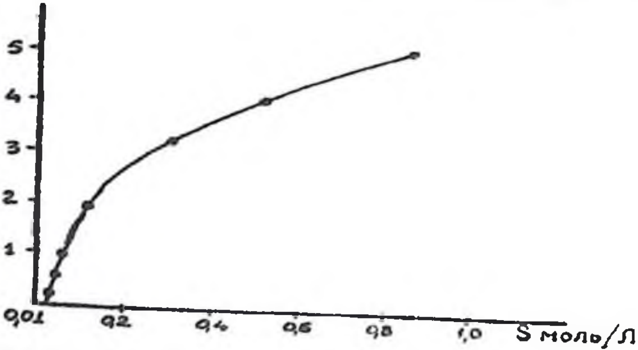


Figure 2.1 Solubility curve for the triple toluene-water-pyridine system



Rice.2. 2 solubility of diphenylcarbazone in a pyridine-toluene mixture depending on the pyridine concentration

The pyridine distribution coefficient has a numerical value, R = 0.98 ± 0.03, which for the convenience of calculations can be considered equal to 1. Data on the solubility of DFC in a mixture of toluene-pyridine solvents at different pyridine concentrations are shown in Fig.2.2, from which it follows that the solubility of diphenylcarbazone in this mixture is functionally dependent on the concentration of pyridine in toluene S = f (with rut). And since at Y = 1

SRUT = SRUV = VRU / VT + VB + VPU

SRUT is the concentration of pyridine in toluene;

SRUV - pyridine concentration in the aqueous phase;

VT, VB, VPU are the volumes of each of the components, then the maximum concentration of diphenylcarbaeon in the extractant should not exceed the following value on the solubility curve

[DFC] ≤ S = f (VT / VT + VB + VP))

Otherwise, DFC will precipitate in the extract (Table 1.26). The use of the diphenylcarbazone-pyridine-toluene system for the development of extraction-atomic absorption methods requires knowledge of the effect of pH on the extraction of metals, the composition of complexes, the distribution constants and the extraction constants of the extracted compounds.

Table 1.26

Study of the solubility of MLC in a mixture of toluene and pyridine at different concentrations of pyridine

[Ru]	Initial DFC weight, g	Weight of DFC after evaporation, g	S mol/l
-	64,0	23,8	10^{-2}
0,1	71,0	27,3	1,125. 10^{-2}
0,2	78,0	29,5	1,125. 10^{-2}
0,5	90,0	33,6	1,400. 10^{-2}
1,0	182,0	66,0	2,75. 10^{-2}
2,0	630,0	236,1	9,837. 10^{-2}
3,0	620,0^{x}	293,0	2,441. 10^{-1}
4,0	1260,0^{xx}	565,2	4,710. 10^{-1}
5,0	2500,0^{xx}	1117,4	9,312. 10^{-1}

x-Was dissolved in 25 ml when heated,
IC ml was taken at 20°C, and evaporated
xx-Was dissolved in 10 ml, 5 ml was taken.

Effect of pH on extraction. Previously, the dependence of the extraction of elements on the phase contact time was found. It was found that at the phase contact time of 2 minutes, the distribution coefficients for all the elements we studied, both without pyridine in the extractant and with pyridine, take a constant value.

The results of studies of the pH effect on the extraction of elements in the Me-DFC-toluene system are presented in Figures 2.3, 2.4. Graphically, the dependence of the pH effect on the degree of metal extraction is described by S - shaped curves. The extraction of diphenyl carbazonates proceeds in a more acidic environment if the pH was set with an acetate buffer, in the case of a citrate-phosphate buffer, the extraction pH is higher for extractants of the same composition. At pH > 9, the degree of recovery of the studied metals decreases, most likely, as a result of hydrolysis.The maximum recovery rate, as shown in Figures 2.3 and 2.4, is small and amounts to 52 percent for cadmium, 96.6 percent for cobalt, 99 percent for copper, 41.3 percent for manganese, 47.1 percent for nickel, and 94 percent for lead. One of the reasons for this may be the coordination unsaturation of the complexes

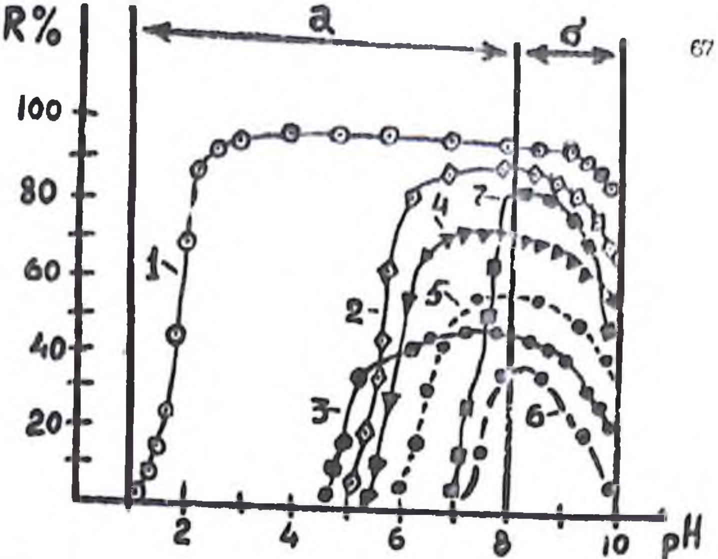


Fig. 2. 3 Effect of pH on some metals extraction of definylcarbazone in toluene

a-0.1 m acetate buffer, b-0.1 m alkaline buffer. (DFC)-5×10-3 M.
1-Cu, 2-Co, 3-Ni, 4-Zn, 5-Cd, 6-Mn, 7-Pb

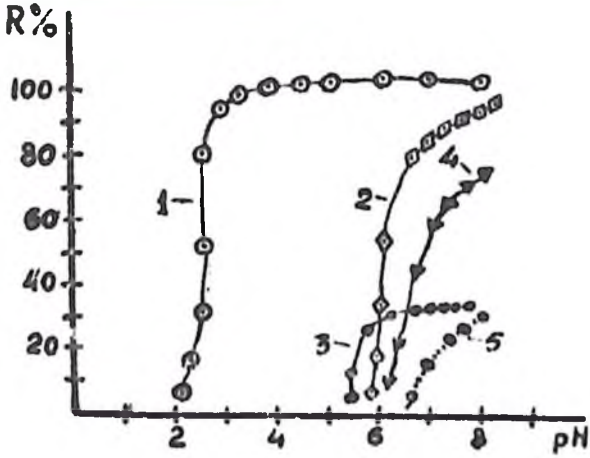


Figure 2. 4 Effect of pH on the extraction of some metals by diphenicarbase in tolula

0.1 M citrate-phosphate buffer, (DFC)-$5 \cdot 10^{-3}$ M.

0.2 **1-Cu, 2-Co, 3-Ni, 4-Zn, 5-Cd**

When pyridine is added to the extractant, the dependence of the degree of metal extraction on the pH is also described by S-shaped curves (Fig.2.5, 2.6). At pH > 9, the degree of extraction of the elements decreases. More favorable for extraction is the acetate buffer (in the case of lead - boron-alkaline) than the citrate-phosphate buffer, which, among other things, masks manganese and lead.

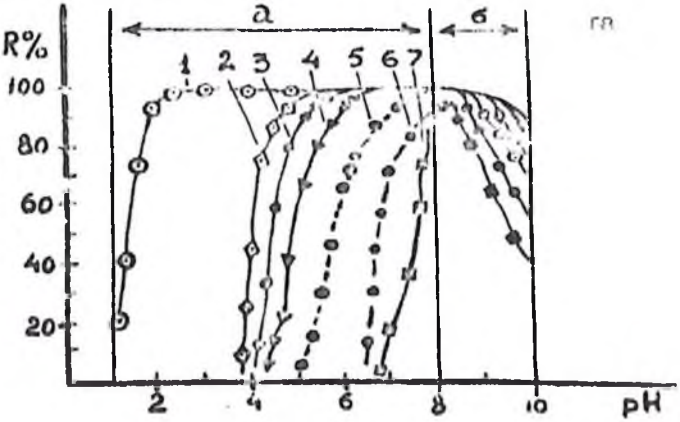


Figure 2. 5 Effect of pH on the extraction of certain metals by diphenylcarbazone with pyridine in toluene.

a-0.1 M acetate buffer; b-0.1 M boron-alkaline buffer. (DFC)-5×10-3 M, 9Ru)-0.1 M, when extracting copper (Ru)- 0.01 M.

1-Cu, 2-Co, 3-Ni, 4-Zn, 5-Cd, 6-Mn, 7-Pb

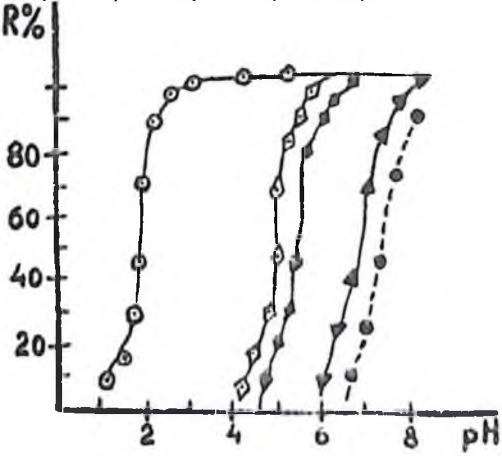


Fig.2.6 Influence of pH on the extraction of some metals by diphenylcarbazone with pyridine in toluene.

0.1 M citrate-phosphate buffer (DPA) - 5·10-3 M,
(Ru) - 0.1 M, with copper extraction (Ru) - 0.01 M.

1-Cu, 2-Co, 3-Ni, 4-Zn, 5-Cd

The recovery rate for all elements except lead in the acidic region increases. Its maximum value exceeds 99 percent. This indicates that in the presence of pyridine, synergistic extraction takes place and, in all likelihood, sour cream complexes are formed.

Determination of the stoichiometric ratio Me: DFC Extraction of diphenylcarbazonates with toluene can be represented by the equation:

Mp+ + n [NA]0 ↔ [mAn]o + pN+ (1)

with extraction constant

Keh = [MAn]0 [H+]n [Mn+]-1 [NAo]-n (2)

or

Kex = E [HA]-n0 [H+]n (3)

In logarithmic form, equation 3 will have the form:

lgE = lg Kex + n lg [HA]0 + n pH (4)

If the effect of pH on the extraction of diphenylcarbaeonates is represented in the lgE - pH coordinates, then, as follows from Figure 2.7, the rectilinear section of the dependence has a slope equal to 2. This is a confirmation that the extracted complexes have the composition Me DFC2 .

For the formation of mixed complexes in the presence of pyridine, the equation of the extraction reaction can be written as follows:

Men+ + n [HA]0 + m[S] ↔ [MeAnSm]0 + nH (5)
with extraction constant
Kexs = [MeAnSm]0 [H+]n [Men+]-1 [HA]0-n [s]-m (6)
or
Kexs = E [H+] [HA]-n0 [S]m (7)
or in logarithmic form
lg E = lg Kexs + n pH + n lg [HA]0 + m lg [S] (8)

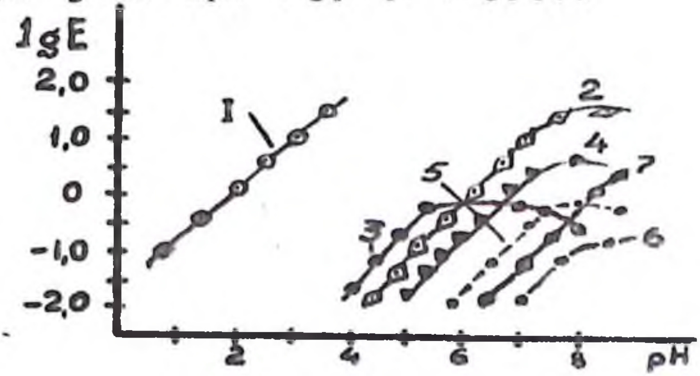


Fig. 2. 7 Effect of pH on the extraction of certain metals by diphenylcarbazone in toluene. DFC - 5×10-3 M, 11-Cu, 2-Co, 3-Ni, 4-Zn, 5-Cd, 6-Mn, 7-Pb

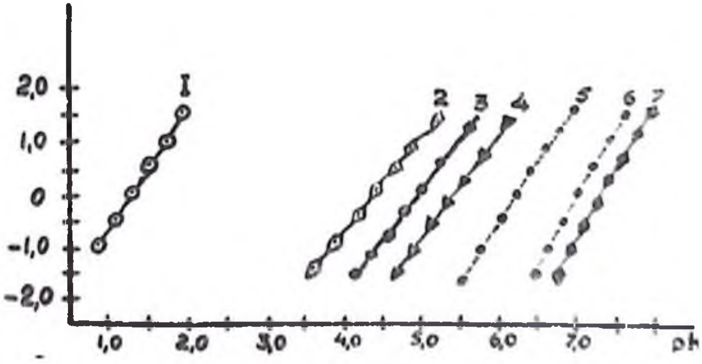


Figure 2. 8 Effect of pH on the extraction of certain metals by diphenylcarbazone with pyridine in toluene. 0.1 M acetate buffer DFC-5×10-3 M; Ru-0.1 M, for copper extraction Ru-0.01 M.

1-Cu, 2-Co, 3-Ni, 4-Zn, 5-Cd, 6-Mn, 7-Pb

The coefficient of n in equation (8) is equal to 2, so the slope of the linear part of the dependence of lg E of pH equal to 2 (Fig. 2.8).

To determine the composition extragenomic mixed chelate compounds used equation (8), from which it follows that if at constant pH and constant concentration of one of the reagents change the concentration of the other, then the graph of lg E lg [HA]0 or Lg E lg [S] is a straight line with a slope of n or m, respectively.

Based on the study of the relationship between the distribution coefficients of the complexes of each of the metals and the concentration of the reagent [NA]0 (the concentration of pyridine is constant, the optimal pH was chosen to determine the composition of the complexes of each of the metals), straight lines were constructed in the coordinates lg E-lg [HA]0. The slope tangent of the straight lines is close to 2 (Fig. 2. 9, 2.10). The constancy of the extraction coefficients (DFC = 10-2 M) shows that the anionic form of the complexes is not formed.

The study of the dependence of the distribution coefficients of the extracted compounds on the pyridine concentration at constant pH and the concentration of DFC for each case showed that the straight lines constructed in the coordinates lg E-lg [S] have a slope tangent equal to 1 (Fig. 2. 11, 2.12). Thus, the metal complexes extracted in the DFC - Ru - toluene system have the composition Me (DFC)2Ru

The change in the pyridine concentration to 10-1 M had no effect on the extraction of lead, so it can be assumed that the resulting complexes in the system of P - DFC - Ru - toluene have the composition of P (DFC) 2.

Determination of extraction constants. Based on equation (4), the extraction constants of metal complexes in the Me - DFC - toluene system were determined. To determine the extraction constants of mixed complexes, the formula (8) was used. The data on the extraction constants Kexs and Kex allowed us to calculate the constants of the formation of adducts in the organic phase.

MeA20 + Py0 + □ MA2 Py0 (9)

βs = [MeA2Py]0 [MeA2]-1 [ru]0-1 = Kexs Kex-1 (10) It should be noted that the extraction constants of diphenylcarbazonates P in the presence of pyridine in the extractant, and without it, do not have a significant difference.

Determination of the constants of the distribution of complexes. It is known that the distribution constant is equal to the largest value of the distribution coefficients. Preliminary studies have shown that the anionic form of the complexes is not extracted, and therefore the concentration of diphenylcarbazone in the extractant is maximal for a given pyridine concentration in the system. The pyridine concentration varied for each individual case. The pH value did not exceed the limits at which the extraction constants were determined.

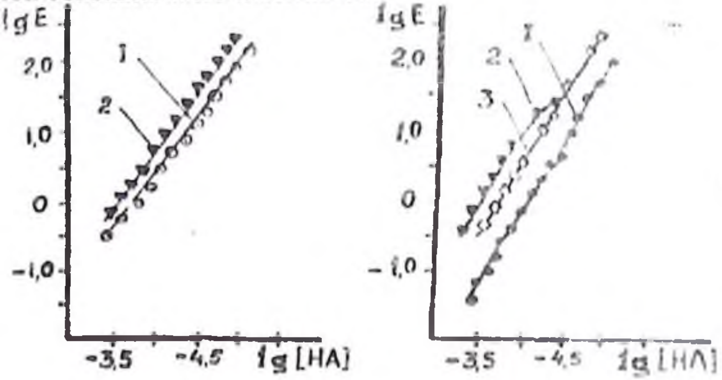


Figure 2.9 Dependence of the extraction of Zn, Cu, Co, Mn, Pb on the concentration of diphenylcarbazone. Ru-10-2 M, 1-Zn (pH 6.75). 2-Cu (pH 2.15), 3-Co (pH 6.10), 4-Mn (pH 7.5), 5-Pb (pH 6.5)

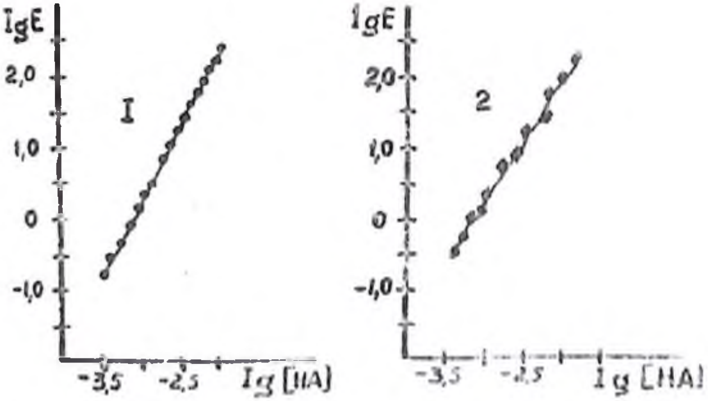


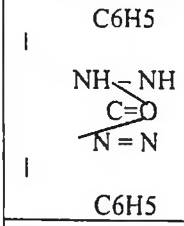
Figure 2. 10 Dependence of the extraction of cadmium and nickel on the concentration of diphenylcarbazone. 1-Cd pH 7/3; Ru-2.5×10-2 M; 3-Ni pH 6.15; Ru-10-2 M.

Structure of diphenylcarbazone

The IR spectra of diphenylcarbazone have absorption bands characteristic of all its bonds and groups (Table 1.27).

(Table 1.27).

Characteristic absorption frequencies of various groups of atoms in the IR region of diphenylcarbazone and its complexes with metals

Connection	Frequency, cm-1	Intensity	Group of atoms
	1713	C	C=0
	1662	CP	N= N
	1650	CP	NH
	1550	CP	N = N
	1500	C	C = A
Diphenylcarbazone cadmium	3200-3400	C широкая	OH AH ROH H_2O

A strong absorption band characteristic of the C = 0 group valence oscillations is observed in the region of 1713 cm -1. The band at 1662 cm-1 is caused by the valence vibrations of the N = N bond, and the band at 1650 cm-1

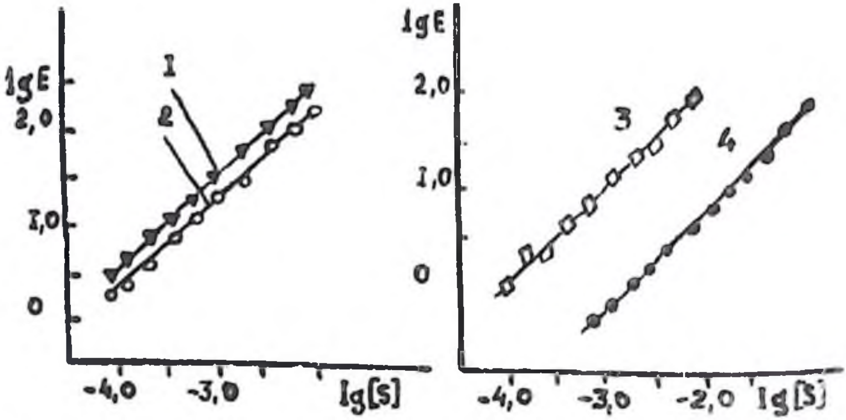


Figure 2.11 Extraction dependence of Co, Cu, Mn, Zn, on the concentrations of pyridine. DFC-10-2 M; The 1 - Zn (pH 6.75); 2-Cu (pH 2.65); 3-Co (pH 6.10); 4 - Mn (pH7.9)

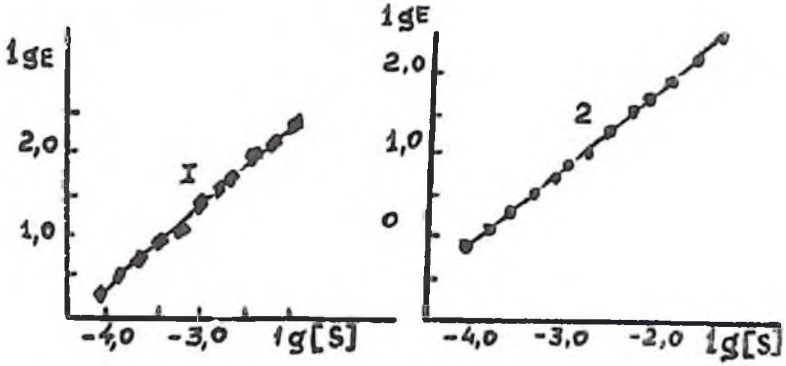
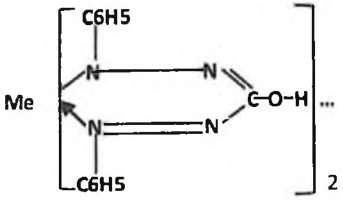


Figure 2. 12 Dependence of Ni and Cd extraction on pyridine concentration. DFC-10-2 M; 1-Ni (pH 6.75); 2-Cd (pH 7.3)

The spectra of diphenylcarbazonates do not have the absorption band characteristic of the C = 0 group. The absorption band caused by the N = N bond oscillations is shifted to the low-frequency region by 112 cm-1 and is manifested at 1550 cm-1. In this case, a new C = N bond occurs in the diphenylcarbazonates in the region of 1500 cm-1 .In all IR spectra of the complexes, a strong broad signal appears in the region of 3200-3400 cm-1, indicating the presence of a hydroxyl group in the associated state. All this indicates that the metal atom in the formation of diphenylcarbazonates takes the place of a single proton. At the same time, the second proton shifts to the carbonyl group, forming the enol form of diphenylcarbazone. It is known that two forms of diphenylcarbazone are in equilibrium in the solution (see page 57). This equilibrium can be shifted in the direction of the enol form in the interaction of diphenylcarbazone with metals. Moreover, the greatest reactivity of a proton bound to a nitrogen atom will be manifested in the case of the association of hydroxyl groups by means of a hydrogen bond:



Confirmation of the conclusion that the substitution of the proton associated with the nitrogen atom to the metal complexation obtained by comparison of proton NMR spectra of the source diphenylcarbazone and its complex with copper (Fig.2.13, 2.14). Their study showed that in the spectrum of diphenylcarbazone observed signals from 2 protons while the 5.8 - -6,2 M. D. protons of aromatic rings in the field of 6,8-8,2 M. D.

Odnorodnye the multiplets 8.2 and 7.8 M. D. shifted more downfield relative to other signals of the phenyl radicals, obviously due to the effect of the C = 0 group in diphenylcarbazone.

The absence of the last signals in the NMR spectrum of the diphenylcarbazone cadmium complex, along with the presence of only one active hydrogen signal at 5.7 m.d., confirms our assumption that the tautomeric equilibrium is shifted towards the enol form. In addition, during complexation, both phenyl radicals become almost equal (4-proton signal at 6.7 - 6.95 m. d. and 6-multiplet at 7-7. 2 m. d.), which is explained by partial aromatization of chelate cycles.

The EPR spectrum consists of characteristic signals of copper atoms (p.2. 15) qw = 2,117 and splitting of the hyperfine interaction of copper atoms with nitrogen atoms CTBN = 12.5 gs. From this it follows that the complex is formed by means of nitrogen-metal bonds, where the nitrogen atoms are located unequally relative to the copper atom, two of the four nitrogen atoms are located closer.

Thus, the enol form of the reagent interacts with the metal to form metal - nitrogen bonds and partially aromatize the chelate cycle.

The absorption spectra of IR, EPR and NMR to solid diphenylbuta - Saratov and diphenylcarbazone pyridine completely identical. At the same time, the study of the stoichiometry of the complexes in the extracts made it possible to identify MDFC and Ru in the composition. Apparently, pyridine is part of the complexes only in solutions. Diphenylcarbazone in solutions gidratirovana and coordination unsaturated. The donor-active additive displaces hydrates, contributing to the improvement of extraction characteristics. The electronic absorption spectra indicate that pyridine in solutions is a part of the complexes. For diphenylcarbazonates of cadmium and nickel in the presence of pyridine, a bathochrochromic shift of the absorption maximum and an increase in extinction are observed (139).

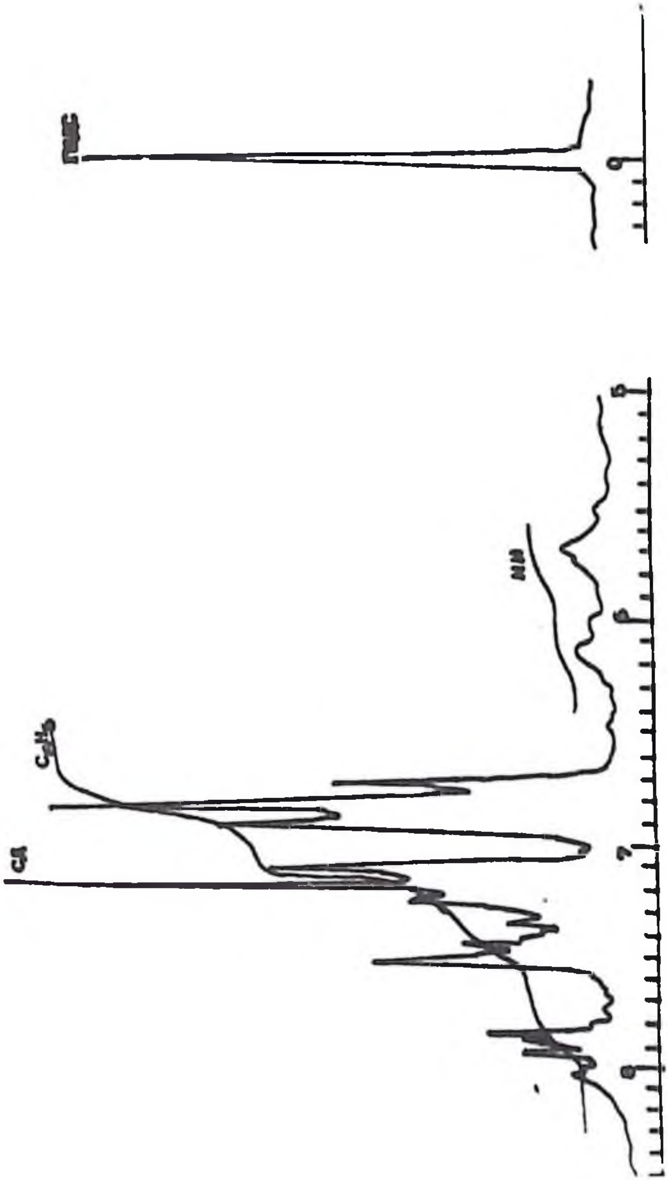


Figure 2. 13 Proton NMR spectrum of copper diphenylcarbazonate

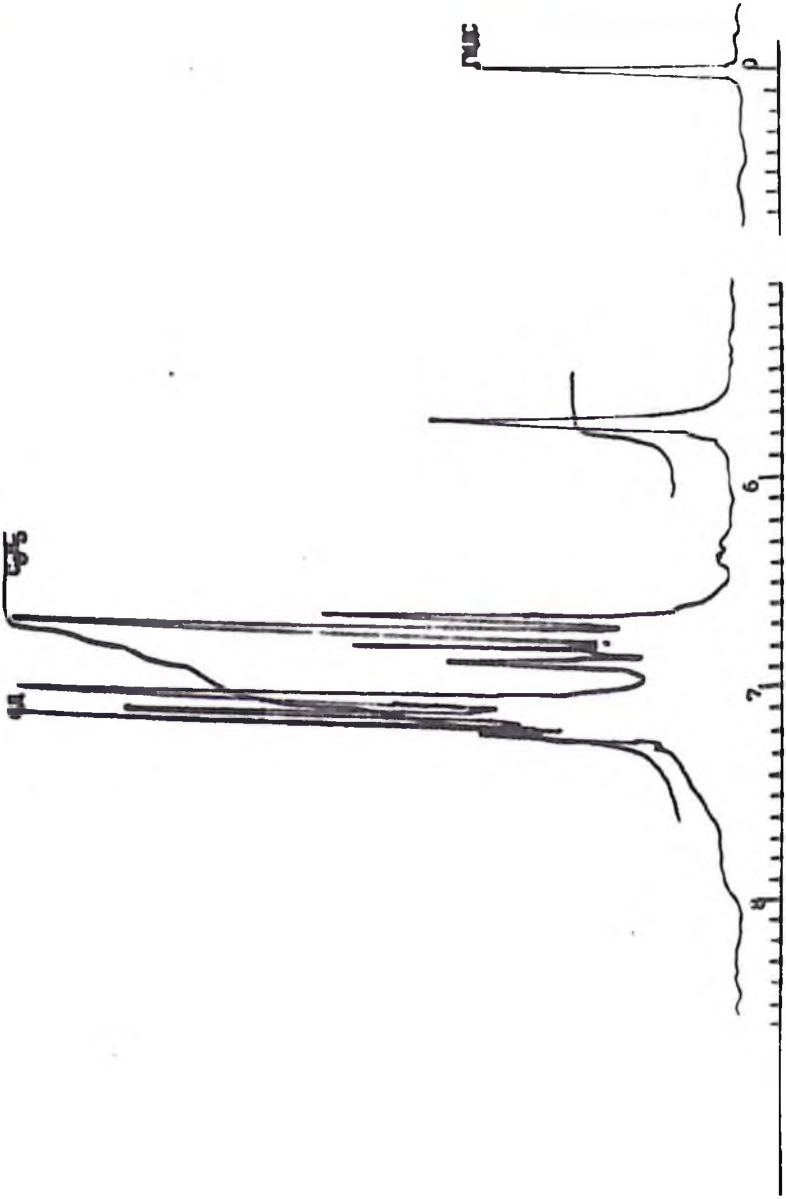


Figure 2. 14 Proton NMR spectrum of cadmium diphenylcarbazonat

Masking effect of pyridine. Copper, cobalt, zinc, cadmium and other elements are capable of forming water - soluble intra - complex compounds with pyridine /138/, so it is possible that at certain concentrations of pyridine in the Me - DFC-pyridine-toluene system, the distribution coefficients of some of the metals will decrease as a result of their competing reactions with pyridine in the aqueous phase. In this regard, we have studied the extraction of elements at different concentrations of pyridine. The results of the studies are presented in Table 2.7. If the elements are arranged in rows in descending order of their corresponding distribution coefficients, then at a given pyridine concentration in the system, the order of the elements is determined by the extraction conditions and the properties of the extracted complexes. Thus, in the absence of pyridine in the system ([DFC] - 1.5. 10-3M), zinc is in second place after copper, followed by cobalt, and at [DFC] ≤ 2.5. 10 -3 M, zinc is after cobalt. This is caused by the fact that the constant extraction of zinc diphenylcarbazone above Kekh diphenylcarbazone cobalt, and the constant distribution below. Table 2.7 shows that in the absence of pyridine in the system, it is possible to separate copper, cobalt and zinc from cadmium and manganese. Indeed, the extraction constant of zinc complexes is more than two orders of magnitude higher than the extraction constants of cadmium and manganese complexes.

When 0.05 M of pyridine is added to the system, the elements are reversed. This change is determined by synergistic extraction. Mixed complexes are formed with other higher values of the constants of the extraction and distribution.

A further increase in the pyridine concentration in the system has an ambiguous effect on the extraction of elements. The distribution coefficients of the cobalt and nickel complexes increase, the cadmium, zinc and manganese complexes first increase to [Ru] in the system of 1.25 M, then decrease. The same thing happens with Pb complexes (up to [Ru] in the 0.5 M system). The distribution coefficients of copper complexes tend to decrease, and with pyridine conpeitrepia in the 2.5 M system, copper is almost completely masked and stands in the last place in the series of elements.

The closest values of the distribution coefficients of the intracomplex compounds of cadmium, cobalt, copper, nickel and zinc are taken at a pyridine concentration in the system of 1.25 M. It is under these conditions that the group extraction of the above elements is possible. At a pyridine concentration in the system of 2.5 M, the difference between the distribution coefficients of nickel and zinc complexes is maximal. Under these conditions, it is possible to separate cobalt and nickel from copper.

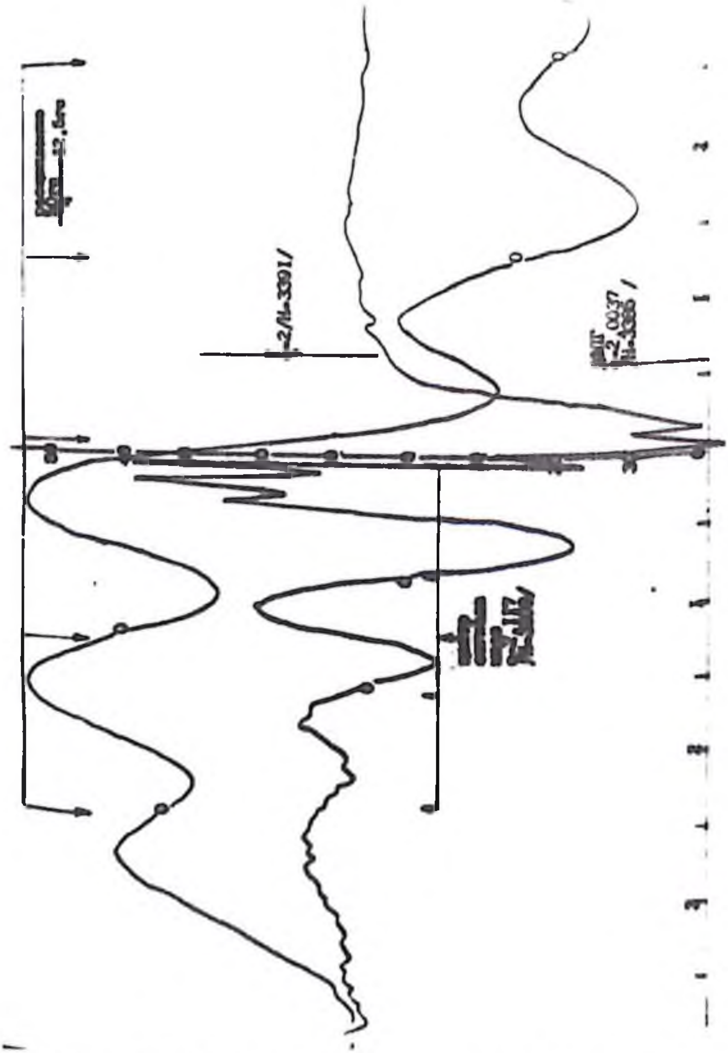


Fig. 2. 15 EPR spectrum of copper diphenylcarbazonate

Group extraction, separation of elements and their extraction concentration

In many biological objects, the concentration of copper and zinc is 2-3 orders of magnitude higher than the concentration of cobalt, cadmium, manganese and nickel. That is, copper and zinc in relation to the other elements can be an extractable macro component. In addition, in the analysis of biological materials, the extraction of trace elements is carried out against the background of high concentrations of the base elements-sodium, potassium, calcium, magnesium and iron. The concentrations of cobalt, nickel, cadmium, and manganese in many biological materials are well below the detection limit of the atomic absorption method, and their determination is often impossible without sufficiently effective extraction concentration. It should be noted that in serial analyses, the duration of preservation of extracts is very important.

In this regard, the extraction of trace elements in the presence of base elements has been studied, the conditions for group extraction of some elements have been identified, and some issues related to the duration of storage of extracts have been studied.

Extraction of trace elements in the presence of base elements. We studied the effect of 10,000 micrograms / ml of potassium and sodium, 500 micrograms/ml of calcium, magnesium and iron on extraction (0.2-0.5). 10-5g-ion/l of cadmium, cobalt, copper, manganese, nickel, lead and zinc.

Studies have shown that in the presence of base elements, the distribution coefficients of metal complexes do not change. The extraction remains unchanged even at different ionic strengths of the buffer solutions-0.2 M; 0.5 M; I M of the acetate buffer-and regardless of the pyridine concentration in the system.

Special attention should be paid to the absence of interfering influence from the iron. Pe (P), Pe (W) are known to be extracted by diphenylcarbazone in toluene. It is shown (135,136) that the extraction of iron is greatly influenced by pH. At pH 1,2-1,6, both Fe(II) and Fe(III) complexes are formed with diphenylcarbazone) The extraction time at which the distribution coefficients take a constant value is one minute. With an increase in pH, Fe(III) stops reacting with diphenylcarbazone, and the extraction time of diphenylcarbazonates formed by Fe (II) increases. At a pH of 3.9-4.2, it is already 3.5 minutes. The reason for all this is the hydrolysis of iron. Thus, the optimal conditions for the extraction of the metals we studied (pH 6.0-7.8; phase contact time-2 min) are unfavorable for the extraction of iron. When pyridine is added to the system, in addition to hydrolysis, iron complexation occurs with the participation of pyridine / 138/, which, apparently, also negatively affects the extraction of iron complexes.

Influence of the extracted macro component. One of the conditions for the separation of elements and the complete extraction of metals (Me) in the presence of an extractable macro component (Me2) is a difference in the extraction constants of at least two orders of magnitude. That is, the elements are separated if Kex < < Kex2.

The elements can be arranged in the following rows in descending order of the extraction constants in the compounds they form-k Me(DFC)2 Ru (2):

1 copper > zinc >- nickel > cobalt > cadmium > manganese

2 copper > cobalt > nickel > zinc > cadmium > manganese

Thus, if the concentration of copper and zinc in the analyzed solution is such that they bind a significant part of the reagent, then it is possible to reduce the extraction of cobalt, nickel, and especially cadmium and manganese.

We have studied the effect of copper and zinc, whose concentration is 50-300 times higher than the concentration of other elements, on the extraction of cadmium, cobalt, manganese and nickel (the concentration of pyridine in the system is 1.25 M). The results obtained are shown in Table 1.29.

Studies show that group extraction of elements with R ≥ 97 percent is possible if their total concentration in the organic phase is ≈ 7 times lower than the concentration of the reagent (other favorable conditions). Otherwise, the distribution coefficients of the metals decrease in the order determined by their extraction constants. To extract the manganese together with the other elements, the excess of the reagent must be even greater. Therefore, it is more convenient to perform group extraction of cadmium, cobalt, nickel and zinc. It should be noted that the I degree of extraction of copper complexes does not significantly differ from the I degree of extraction of cobalt, nickel and zinc. The method of group extraction of the above elements I can be used to separate the analyzed elements from the base elements at the phase ratio V / Vo = 1 and only in some cases extraction concentration V / V0 = is possible. Thus, the limitation of the method of group extraction = 2: elements in the determination of trace elements in biological objects is the impossibility of conducting a sufficiently effective concentration. For the concentration of elements such as cobalt, nickel, cadmium and manganese, it is necessary to exclude the interfering influence of copper and zinc.

Table 1.29 shows that at a pyridine concentration in the system of 2.5 M, copper and partially zinc are masked by pyridine. This also reduces the distribution coefficients of cadmium and manganese. The extraction of cobalt and nickel remains unchanged. Studies have shown that at a pyridine concentration in the system of 2.5 M ([DFC]0 - 3.10-5 M; pH = 6.5; 7.0; 7.5); copper and zinc contained in the analyzed solution (4.10-4 g-ion/l, 1.5. 10-3 g-ion/l

accordingly), do not interfere with the extraction of cobalt and nickel 0.5 .. 10-5 g-ion/l. More than 99 percent of cobalt and nickel passes into the organic phase, with the ratio between the volumes of the phases I) V / Vo = 5 ; 2) V / Vo = 10. Copper and zinc are not fully extracted. In the first case, the degree of extraction of copper is 31%, zinc-66% , in the second - copper-12%, zinc-31%. Comparison of the extraction constants of copper, zinc, cadmium, and manganese complexes shows that it is possible to separate copper and zinc from cadmium and manganese if extraction is carried out with a solution of diphenylcarbazone in toluene.

Copper and zinc diphenylcarbazone in toluene ([DFC]-2.5.10-3 m, V=V0) were extracted from the analyzed pH 6.3 solution (0.1 M acetate buffer) containing zinc 1.510 - 3 g-ion/l, copper - 4.10 g - ion/l, cadmium-0.2.10-3 g - ion/l, and manganese - -0.4.10-5 g-ion/l. At the same time, copper is extracted completely, zinc - by 19%. When re-extracted with an extractant of the same composition, 31% of the remaining zinc passes into the organic phase, after the third - 45% and after the fourth-76%. In the aqueous phase, zinc - 1,11.10-4g-ioi/l remains, and cadmium and manganese, containing 10-5g-ion/l, almost completely remain in the aqueous phase. The loss of cadmium does not exceed 2%. The remaining elements were extracted with diphenylcarbazone (2.5. .10 -2 M) and pyridine (1.25 M in the system) in toluene at the ratio between the phases - V / V0 = 5 and 10. The equilibrium pH increases due to the redistribution of pyridine to 7.8. Cadmium and manganese completely pass into the organic phase: cadmium-96%, manganese - - 97%.

The number of preliminary extractions associated with the removal of copper and zinc from the analyzed solution depends on the concentration of all elements in it. The more copper and zinc in the sample and the less cadmium and manganese, the more completely the analyzed solution should be purified from copper and zinc.

The stability of the extracts during storage. Over time, the extracts are discolored. Moreover, the atomic adsorption analysis of the discolored extracts showed the absence of metals in them.

We investigated the relationship between the concentration of diphenyl carbazone in the extractant and the preservation time of the extracts. The results of the studies show that the higher the concentration of diphenylcarbazone in the extracts (the case of group extraction was considered) the longer the intra-complex metal compounds remain in them. Intra-complex connections begin to unlearn at the same time.

Re-extraction of diphenylcarbazonates

Preliminary studies have shown that the atomic absorption analysis of metal extracts with the "furnace-flame" atomizer is impossible. Prior to atomization, the thermal destruction of diphenylcarbazone and diphenylcarbazonates present in the extract produces gaseous compounds that promote the sublimation of the metal, as a result of which a significant part of the analyzed element is lost. If you combine the process of mineralization and atomization, that is, introduce the boat directly into the flame with an unsalted extract and pass a current through it, then there is such a high non-selective absorption that it is not possible to isolate the signal responsible for atomic absorption from it. Thus, in the extraction-atomic-absorption determination of elements with the "furnace-flame" atomizer, the extraction must be completed by an operation that leads to the destruction of the complexes, transferring the metals to an aqueous solution. To do this, the extract is mineralized with the addition of acids, or the metal is extracted into the aqueous phase.

And in that and in other cases it is possible that an additional concentration of the elements.

The effect of pH on the extraction and re-extraction of metals. For the convenience of calculations, we used the equality of volumes between the phases. The distribution coefficient of diphenylcarbazone is sufficiently large, which allowed us to consider the initial concentration of the reagent equal to the equilibrium and to neglect the loss of DFC during extraction. The constant concentration of pyridine was achieved by its additional introduction into the re-extract phase. The study of the effect of pH on the extraction and re-extraction of cadmium, cobalt, copper, manganese, nickel and zinc showed that in both cases, for each of the metals, the dependence of the degree of extraction on pH is described by S - shaped curves that overlap each other. This "uniformity" is observed for different concentrations of diphenylcarbazone and pyridine (Fig. 2. 16). The phase contact time does not exceed 2 minutes. This indicates the equilibrium of extraction and re-extraction.

The process of extraction and reextraction in our case can be described by one equation

$Men+ + n[NA]o + m[Ru] \leftrightarrow [MeAp\ Sm) + nH$ (1)

with an extraction constant

$Kexs = [Me\ An\ Sm]\ [H]+\ [Men+]-1\ [HA]-n\ [S]-m$ (2)

Thus, the constants that characterize the extraction can be used to quantify the reextraction. This allows us to calculate the pH of the re-extraction, at which no more than 0.01 percent of the metal remains in the organic phase. The calculated data are presented in Table 1.30.

The effect of diphenylcarbazone and pyridine. The prevalence constant of diphenylcarbazone between the aqueous phase and toluene is PH= 40. This implies a small loss of the reagent during extraction and re-extraction as a result of its transition to the aqueous phase. Rewrite the equation

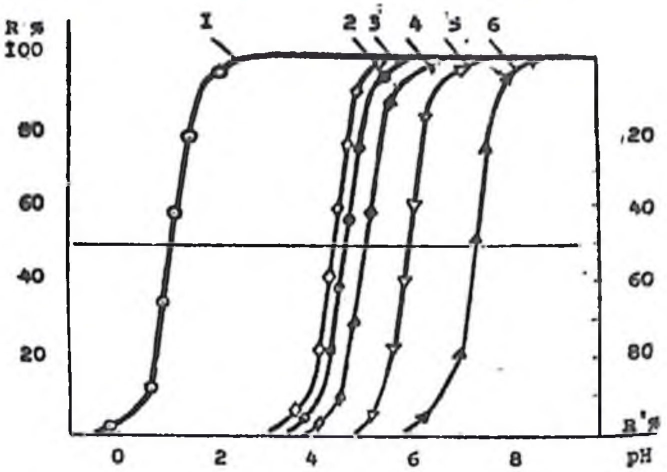


Fig. 2. 16. Effect of pH on extractions in metal re-extraction (a solution of diphencacarbazone with pyridine in toluene was used as an extraction reagent).

(DFC)-5×10-3 M; for copper extraction-0.01 M;
1-Cu, 2-Co, 3-Ni, 4-Zn, 6-Mn,
R-percentage of extraction; R 1-percentage of re-extraction

Table 1.28.

Reextraction pH, which ensures the transition of 99% (Vb/V0 = 1) of the metal from the organic phase to the aqueous phase*

Complexes	LG Kexs	*lg Rt* S	pH
DFC2Ru	-6,75	2,63	3,37
DFC2Ru	-3,65	2,80	1,82
DFC2Ru	3,02	3,44	-1.0
DFC2Ru	-8,99	2,40	4,49
DFC2Ru	-3,93	2,78	1,96
DFC2Ru	-4,93	2,59	2,46

* SDFC for Si = 10-3 M , for other metals SDFC = 10-2 M. Kexs - extraction constant, Pms-distribution constant of mixed complexes.

(2) in logarithmic form,
lg Kexs = lg E - n lg [HA]0 - m lg [S] (3) we present it as:
pH = 1/n (lg E * lg Kex – m lg [S] – lg [HA]0) (4)

From equation (4) implies that when the concentration of the reagent (other conditions constant) each point of the curve lg E pH will shift to a more acidic region, as well as the processes of extraction and re-extraction equilibrium, the increase in the concentration of DFK will be to shift the pH of the Stripping. With an increase in the concentration of diphenylcarbazone by an order of magnitude, the pH of the re-extraction of this point of the curve will shift to the acidic region by one. Thus, diphenylcarbazone must have a concentration that ensures the extraction of the analyzed and co - extracted elements. In this case, the excess of diphenyl carbazone, providing a more complete extraction of the analyzed element, especially in the presence of co-extractable metals, shifts the optimum pH to a more acidic region, which makes it difficult to achieve boundary conditions. The results of the studies (Table.1.31) allow you to select such a concentration of the reagent in the analysis of each of the elements, which provides the most complete transition of the metal from one phase to another with double concentration. They also allow you to choose the most favorable ratio between the volumes of the aqueous phase and the extract and re-extract phase.

This is not the case with pyridine. The study of the effect of pyridine on extraction at constant pH and DFA concentration showed (Table 1.32) that pyridine leads to synergistic extraction and an increase in the distribution coefficients. With an increase in the pyridine concentration, the distribution coefficients take constant values, then decrease. The decrease in the distribution coefficients can be explained by competing reactions of metals in the aqueous phase with the participation of pyridine. The ranges of pyridine concentrations for which the maximum values of the distribution coefficients are observed are ambiguous for individual elements. For cobalt and nickel, they are unchanged in the range of 0.1-2.5 M of pyridine in the system, for manganese 0.8-1.3 M, copper-0.01-0.1 M, cadmium-0.8-1.3 M, zinc-0.2-1.3 M. In addition, the pyridine present in the extractant or extract is distributed between the phases during mixing, resulting in an increase in the equilibrium pH both during extraction and re-extraction. If in the case of extraction, the increase in pH is positive, then in the case of re-extraction, the achievement of boundary conditions meetscertaindifficulties.

Table 1.29.

Dependence of the distribution coefficients of diphenylcarbazonates on the pyridine concentration in the system*

C_{py} в сис' теме (M)	: E					
	: *Cu.*	*Co*	*Ni*	*Zn*	*Cd*	*Mn.*
0,05	2,0	1,75	1,63	0,96	-0,43	-
0,10	2,0	2,0	1,97	1,35	-0.21	-
0,50	1,69	2,0	1,96	1,91	0,21	*-1,95*
1,25	0,55	2,0	1,97	1,85.	0,31	*-1,65*
2,5	-1,71	2,0	2,0	0,85	0,09	-1,85

* - SDFC 1.5. 10-3 M, Ph = 6.6, the shaded cells show the minimum concentration (Ru) in the system at which the distribution coefficients remain constant.

To optimize the reextraction process, we investigated the relationship between the pyridine concentration in the extract and the pH of the aqueous phase, which was used as HCl solutions of different molarity. The volume ratios of the organic and water phases were 1:1, 5:1, 10:1 (table.1.33). The larger the volume of the organic phase relative to the aqueous phase and the higher the initial concentration of pyridine in the extract, the more noticeable the pH shift. Using the data given in the table, it is possible to select the pyridine concentration, which provides the most favorable course of extraction and re-extraction of elements.

When copper is extracted with diphenylcarbaeon (DFC =10-3M), the optimum pH is due to the concentration of pyridine in the system, which is 0.05 M (Table 1.34). Under these conditions, copper is extracted quite selectively. A significant excess of zinc, cadmium, manganese, cobalt, and nickel does not affect the extraction process. To transfer 99.9 % of copper to the re - extract phase at a pyridine concentration in the extract of 0.05 M, the pH of the aqueous phase should be equal to - 1, which is practically unattainable. As a result of the redistribution of pyridine, the pH of the re-extract, which is 5 mHCl. , ranges from 0.8 to 0.7, depending on the phase volume ratio. However, the total metal loss at a concentration of 1: 100 does not exceed 3%

Effect of diphenylcarbazone on group extraction and re-extraction

The conditions for the extraction and re-extraction of cobalt and nickel are the same. The concentration of DFK, providing a transition 97-98% of cobalt and Nickel in the organic phase is 6.5.10-3 M, PY - 0.1 M and pH 7.5, and the relationship between the volumes of the phases V0 /V = 10. Zinc, copper, manganese, concentrations more than an order of magnitude higher than the concentration of cobalt and Nickel, do not reduce the degree of extraction of these elements, due to the significant excess of DFK in relation to the total concentration of all coextrusion elements. In addition, for the extraction of zinc and manganese, a larger amount of pyridine is needed, and at the same time, copper is partially masked by pyridine at its concentration in a system equal to 0.1 M. With the re-extraction of cobalt and nickel of 5 MnCl and the ratio between the volumes of the extract and re-extract phases equal to Yu, cobalt and nickel almost completely pass into the aqueous phase. The total loss of cobalt and nickel at double concentration does not exceed 7% by a factor of 100.

At an equal pH of b,0 , (DFC) - 10-2 M, Ru - 0.5 M and the ratio between the volumes of the phases V0/ V= 10, the degree of zinc recovery is 95%. A significant excess of zinc, cadmium, manganese, cobalt, and nickel does not affect the extraction process. To transfer 99.9 % of copper to the re - extract phase at a pyridine concentration in the extract of 0.05 M, the pH of the aqueous phase should be equal to - 1, which is practically unattainable. As a result of pyridine redistribution, the pH of the re-extract, which is 5 mHCl., ranges from 0.8 to 0.7, depending on the ratio of the phase volumes.

However, the total metal loss at a concentration of 1:100 does not exceed 3%

The conditions for the extraction and re-extraction of cobalt and nickel are the same. The concentration of DFK, providing transition - 97-98% of cobalt and Nickel in the organic phase is 6.5.10-3 M, PY - 0.1 M and pH 7.5, and the relationship between the volumes of the phases Vo /V = 10. Zinc, copper, manganese, concentrations more than an order of magnitude higher than the concentration of cobalt and Nickel, do not reduce the degree of extraction of these elements, due to the significant excess of DFK in relation to the total concentration of all coextrusion elements. In addition, for the extraction of zinc and

manganese, a larger amount of pyridine is needed, and at the same time, copper is partially masked by pyridine at its concentration in the system equal to 0.1 M. With the re-extraction of cobalt and nickel of 5 MnCl and the ratio between the volumes of the extract and re-extract phases equal to 10, cobalt and nickel almost completely pass into the aqueous phase. The total loss of cobalt and nickel at double concentration does not exceed 7% by a factor of 100.

At an equal pH of b,0 , (DFC) - 10-2 M, Ru - 0.5 M and the ratio between the volumes of the phases V0/ V= 10, the degree of zinc recovery is 95%. Due to the fact that the concentration of zinc in natural objects, as a rule, is higher than the concentration of other elements co-extracted with it, their influence on the degree of zinc extraction is insignificant. The total concentration of elements is an order of magnitude lower than the concentration of DFC. When the kick is re-extracted, 5 mHCl. in the ratio between the volumes of the phases V0 /V = 10, about 95% of zinc passes into the re-extract phase. The pH of the reextraction resulting from the pyridine redistribution is 3.1, which exceeds the minimum pH that ensures the complete transition of zinc to the reextraction (pH-2.46). When the ratio between the volumes of the phases Vo / V =5, the pH of the aqueous phase as a result of re-extraction becomes equal to 1.1. In this case, almost all of the zinc passes into the re-extract. The loss of the element when it is concentrated in 50 times does not exceed 5%.

The degree of extraction of cadmium at pH 8.5, (DFC) - 10-2 M, Ru-1.0 M and V0 / V =5 is ≈ 95%. Simultaneously with cadmium, copper, zinc, cobalt, nickel and partially manganese are extracted. At the same time, if the total concentration of the elements is 50 times less than the concentration of the reagent, there is no interfering effect of the co-extractable elements on the extraction of cadmium. Cadmium re-extraction can be carried out in 5 mHCl with the ratio between the volumes of the phases V0/VP = 10, the water phase passes ≈ 94% of cadmium. The total loss of cadmium during extraction (V0/VP = I: 5) and re-extraction (V0/VP = 10) does not exceed 10% , and the concentration of elements is 50 times achieved.

The optimal conditions for manganese extraction are pH-9; da-10-2 M; Ru-1.25 M. At V0/V = 5, the manganese recovery rate is 95%. Zinc, cadmium, nickel, cobalt, and partially copper are co-extracted with manganese under these conditions. If the total concentration of all elements is 50 times less than the concentration of the reagent, then there are no matrix effects. Extrac - tion increases the possibility of concentration of manganese. Almost the entire element passes into the re-extract phase, which is 5 mHCl. The total loss of manganese at double concentration does not exceed 7%.

The conducted research was the basis for the development of extraction-atomic-absorption methods for the determination of cadmium, cobalt, copper, manganese, nickel and zinc in some natural objects.

The biological role of trace elements and their content in epidermal formations.

Mineral exchange of wool and hair

Epidermal formations, like any other animal tissues, reflect the state of the environment and the functional features of this type of tissue in ontogenesis in terms of their mineral composition and the distribution of trace element levels.

A systematic study of the effect of nutrition on the concentration of chemical elements in the fur of domestic animals was started relatively long ago (2,3). The concentration of other substances in the hair, such as vitamins, urea, proteins, glycosides, etc., was also studied (4,5).

From the very beginning, it was noted that hair and wool have the following advantages as an object of chemical analysis as an indicator of the mineral status of animals: a) during its growth, the hair accumulates changes occurring in the internal environment of the body, which can be used to obtain information about previous nutrition. For this reason, hair analysis is a method traditionally used in forensic medicine; b) the hair is well processed, easily accessible, and chemically stable.

The possibilities of chemical analysis of hair were periodically "rediscovered", especially in the United States, where the level of environmental pollution was studied using the analysis of human hair. Over the past 20 years, about 250 scientific articles have been published on the chemical composition of hair and wool, but American researchers apparently did not suspect the existence of such a large number of works in this field.

Opinions about the ability of the hair to reflect the nature of previous human and animal nutrition or toxicological data range from extreme optimism to complete denial. In our opinion, there are three reasons for such differences: a) limited knowledge about the origin and methods of including its components in the hair; b) too simplistic idea of possible links between the excess or lack of chemical components of the diet and their content in the hair; c) a lack of understanding of the physiological functional unity that exists between the hair follicle and the two associated glands – the sebaceous and sweat glands.

It is now well known that keratin binds many organic substances (such as dyes), but it is less well known that it is also able to fix mineral compounds. It is shown, for example, that black hair is richer in calcium and phosphorus than white hair (3). On the same black phenotype of animals (43 head of Frisian cattle) (6), it was found that the content of melanin varies from one animal to another and there is a close correlation between the concentration of melanin and calcium in the hair (r=+0.79), magnesium (r=+0.79) and phosphorus (r=+0.64). The content of sodium and potassium is not related to the concentration of melanin.

The concentration of manganese, cobalt, selenium, and molybdenum also correlates with the content of melanin, while copper and zinc do not show a similar correlation (2). The fixation of divalent cations by melanin is explained by its ability to cation exchange. In 1957, Broshar found that the ash content of black cattle wool is higher than the ash content of white wool.

From the above data, it follows that information about the content of chemical elements in wool that depend on the presence of melanin should be attributed to the concentration of this pigment before judging the influence of environmental factors on their content.

The concentration of melanin is determined colorimetrically after its isolation by 4 n. hydrochloric acid and dissolution in alkali. The content of trace elements in wool that correlate with melanin can be correlated with the content of calcium, which, as noted above, is closely related to the content of melanin. It should not be overlooked, however, that the intake of calcium from the feed affects the concentration of this element in the wool.

For a long time, it was assumed that the intake of minerals into the hair comes from the blood capillaries, which are provided with hair follicles and epithelial layers of the skin. Attempts were made to establish a positive correlation between the content of mineral and organic substances in the blood and in wool.

When comparing the responses of blood plasma and hair of rats to change the composition of food was established (5) that the plasma responds quickly to changes in the diet of magnesium and potassium, slowly – on the phosphorus content and does not respond to changes in the level of sodium and calcium (this is due to the precise homeostatic regulation of the concentrations of these elements in the blood). At the same time, it reacts quickly to changes in sodium content, slowly to changes in calcium, magnesium, and phosphorus, and very slowly to changes in potassium concentration.

The reaction of the hair to changes in the composition of food is thus specific and is associated, first of all, with changes in the composition of the secretion of the sebaceous and sweat glands, which is reflected in the chemical composition of the hair (Fig. 1.1).

Some of the components of the secret of these glands are easily washed out of the wool. Urea 5 is completely washed, and sodium and potassium are largely removed during washing. To a lesser extent, calcium, phosphorus and magnesium are washed out, while the copper content does not change. The leaching of components associated with melanin is inversely proportional to its content in the hair.

The presence of sodium, potassium, lactic acid and other substances in sweat has been known for a long time. Interestingly, sweat also contains all the mineral elements, including trace elements, and that their secretion increases with increased intake from the feed.

Hair fixation of mineral substances released by sweat and sebaceous glands was tested in this way (5): in cattle, a small area of skin was shaved, then a month later, when the hair grew back, half of the area was re-shaved, and at the end of the second month, the upper part of the hair of the unshaven area was cut off. This upper part corresponded to the hair shaved off in the first month. It was shown that between the first and second months, the content of potassium in the hair increases by 9, sodium – by 132, calcium – by 42 and magnesium-by 128%.

This observation explains the increase in the concentration of calcium and phosphorus from the base to the top of the hair and the reason why, in the absence of a lack or excess of individual feed elements, the concentration of chemical elements of the hair does not remain constant

The accumulation of mineral components in the hair increases if the hair follicle is at rest for a certain period of time. This can explain a number of changes in the mineral composition of the hair, namely: an increased content of calcium, phosphorus, which characterizes the wool of yal cows with low milk yield (3). It is associated with a delay in hair regrowth due to stress, chronic infection, and insufficient nitrogen and phosphorus content in the diet. This also explains the annual cycle of changes in the concentration of calcium in the hair (7), with a maximum in winter and a minimum in spring. In the spring, when the new hair grows, she does not have time to accumulate a sufficient amount of mineral substances. The change in the concentration of calcium and phosphorus, which is associated with pregnancy (the maximum concentration is observed at the end of pregnancy) is the result of a slow activity of the hair follicles during pregnancy.

Little is known about the role of sweat and sebaceous glands in the absorption of mineral components by the hair. The sebaceous glands cover the hair with a lipid layer that prevents the intake of minerals dissolved in sweat. This assumption is confirmed by a negative correlation between the content of lipids and minerals in the hair in cattle (7), ($r=-0.66$).

The amount of lipids depends on the level of nutrition and gender (8). A low level of nutrition leads to a decrease in the amount of lipids in the wool of bulls, but increases it in the wool of cows. These differences are caused by hormonal factors. Poor feeding inhibits the secretion of both male and female sex hormones. However, testosterone increases the secretion of the sebaceous glands, while estrogen has the opposite effect on them.

As most studies show, the mineral composition of hair and wool reflects the excess or lack of chemical elements in the diet of animals. However, it is necessary to take into account the length of the hair regrowth. In cattle, the hair grows on average by one cm per month. The faster the wool grows, the less mineral substances it contains, and vice versa. In this regard, the hair of sick animals that grows more slowly than that of healthy animals may contain an increased amount of trace elements. A similar phenomenon is possible with the deterioration of the protein nutrition of animals.

At the same time, it became obvious that the relationship between the mineral composition of epidermal formations and the body's supply of trace elements is not always direct, but is influenced by a number of external and internal influences that make it difficult to use the mineral composition of wool as an indicator of the macro - and microelement status of the body.

It is also shown that the body's supply of iron and cobalt is characterized by the level of hemoglobin in the blood and vitamin B12 in milk and blood plasma is much better than the content of these elements in the outer integument. The greatest amount of data on the ability of individual mineral components to serve as an indicator of the microelement status of the body was obtained in relation to copper, manganese, zinc, selenium, molybdenum, iodine and potassium. Somewhat less is known about the indicative ability of the content of elements such as mercury and lead in wool, although it is not disputed. As for chromium, fluorine, tin, vanadium, silicon, nickel, antimony, and arsenic, data on these elements are very scarce, mainly due to analytical difficulties. At the same time, these elements are of particular importance in the conditions of Central Asia, where the largest biogeochemical provinces are located, enriched with antimony, mercury, arsenic, lead, zinc, and other rare and scattered elements, and where biogeochemical provinces of iodine, copper, and zinc deficiency are widespread, the rapid diagnosis of which can have a significant economic effect.

The trace elements, the vital necessity of which for the animal body was proved before the 70s (the so-called 'classic' trace elements), include iron, iodine, copper, zinc, cobalt, molybdenum, selenium and chromium. Since then, 5 more elements have been added to them – vanadium, tin, silicon, nickel, arsenic and lead, and according to (9) and (10) more and cadmium ("new" trace elements). The state of knowledge of the biological role of these elements and the indicative value of their content in wool is convenient to consider for each individual.

Manganese

The vital need for manganese in animals was established 80 years ago by scientists at the University of Wisconsin (11,12). The lack of this element in ruminants leads to a weak manifestation of signs of hunting while maintaining the normal process of ovulation and an increased number of abortions and resorption of fetuses. The offspring of mothers who are deficient in manganese have a lower live weight and reduced viability at birth.

Manganese is necessary for the biosynthesis of mucopolysaccharides and lipids, and therefore its lack causes a violation of the formation of mucus and cartilage, especially in the prenatal period. Mothers who are deficient in manganese produce more male offspring, which is probably due to the predominant fertilization of the egg by more mobile sperm carrying the y chromosome.

The external manifestation of manganese deficiency is the thickening and deformation of the tubular bones and the violation of osteogenesis in general. These lesions are especially noticeable in mammals on the hock joints, which experience the greatest load, during the milk period. With the transition to a more manganese-rich feed, the growth of cartilage is normalized. In the offspring of mothers who are deficient in manganese, the nervous system is often affected, which is expressed in paralysis during the first 10 days of life, which can be treated with manganese. In poultry, a lack of manganese leads to the disease perozom (slipping tendon), which can be cured by feeding this element.

The presence of its physiological antagonists in the feed, the most important of which is iron, has a significant impact on the animals ' need for manganese. The requirement of cattle, horses, sheep, goats and poultry for manganese is usually 60 mg/kg of feed. 30 mg/kg is enough for pigs. However, with a high concentration of iron, even 100 mg of manganese per kg of feed may be insufficient.

The determination of manganese in wool requires careful cleaning, as dust, excrement, and soil tend to contain more manganese than the wool itself. These impurities are retained by the lipid film surrounding the hair, and therefore it is necessary to first remove the grease, preferably by extraction with sulfur ether or acetone, followed by washing with bidistilled water.

Comparison of the indicative capacity of various organs and tissues in goats (2) shows that manganese deficiency is most noticeable in the content of this element in the liver. It is followed by a white coat, kidneys, heart muscle and ovary, while other organs and tissues, such as bone, plasma, blood, lungs, due to better homeostatic control, respond much less strongly to manganese deficiency. Thus, the analysis of wool is quite suitable for determining the availability of this element in the body.

This is also evidenced by experiments with radioactive manganese (Mn52). Its inclusion in the composition of the wool occurs within a few hours after giving through the mouth, and two days later the radioactivity of the wool disappears again. This indicates that wool, like any other body tissue, is actively involved in the exchange of manganese.

The plumage of the bird is also actively involved in the exchange of manganese and can serve for a short time as a depot of this element. 9 hours after giving Mn52 through the mouth, 18% of the absorbed manganese is present in the plumage, from which it moves to other organs (skeleton, ovaries, liver) over the next few hours.

The content of manganese in wool reflects not only its deficiency in the body, but also its normal level and excess.

Hair from different parts of the body reflects the level of manganese in the body in different ways. So, the hair on the bangs is usually 1.5 times poorer than the manganese of the hair growing on the side, and therefore the latter is more suitable for characterizing the manganese status of the body. Along with topographical differences, the content of manganese in the coat depends on a number of physiological features, including the age and color of the coat, the state of health of the animal, pregnancy, lactation, and the height of the sample cut.

Thus, the coat on the withers is usually richer in manganese than the coat on the side, and the light coat is usually poorer in this element than the dark one, and the coat and hair of brown and red colors are usually the most rich in manganese. Thus, it was shown that in humans, light hair contains 1.6 mg / kg and red hair-3.2 mg/kg (13).

As a result of periodic molting, the animal's coat is heterogeneous. Before molting, the flow of nutrients to the hair follicle is reduced. The hair gradually separates from the follicle and dies, remaining, however, depending on the circumstances, for a long time in the hair vagina. Next to the dead one, a young hair appears. During the summer, the cover hair ages, and with the onset of autumn, animals also have a young downy hair in addition to the cover. Accordingly, the content of trace elements in the hair undergoes periodic changes. At the same time, the highest content of manganese was observed in the integumentary hair in the spring during the molting period and the lowest in the autumn (14). Dead hair is always richer in manganese than living cover hair, since the manganese it absorbs is excluded from the metabolism. In this regard, it is not recommended to take wool samples to assess the body's supply of manganese during the molting period. In sick or emaciated animals that do not have a shift As a rule, the amount of manganese in the hair also exceeds the physiological norm.

There were no statistically significant differences in the level of manganese in wool associated with age in animals (15,16). The influence of age is rather indirect due to the fact that young animals on a dairy diet, poor in this element, contain less manganese in their wool than adults. With depigmentation of the hair, the content of manganese in it also decreases.

Another factor influencing the level of manganese in wool is the origin of the animals, as has been demonstrated in cattle (2) and in pigs. It is also shown that the peripheral part of the hair differs from the basal part by the high content of this element. In pigs, these differences are statistically significant. It follows that the hair for the analysis should be cut, if possible, closer to the skin.

The threshold concentration of manganese, which characterizes the provision of the animal body with this element, should be considered its content in the liver, 8 mg/kg and in black wool, equal to 6 mg/kg. There is a statistically significant relationship between these two values ($L<0.05$), characterized by a correlation coefficient – $r=0.83$ and a regression equation – $y=2.45+0.64$ x.A positive relationship was also noted between the content of manganese in the liver, kidneys and brain.

A significant correlation was also established between the content of manganese in cow hair and red clover growing on soils of various geological origins. The highest concentrations of the element are found in wool and clover on soils formed by the weathering products of syenites, granites and porphyry, and the lowest - on loess and limestone soils. The manganese content in the red clover of the prosperous territories ranged from 57-71 mg/kg of dry weight, and in the unfavorable territories – from 22-34 mg/kg. These values corresponded to the level of manganese in wool, which was 15-19 and 4-5 mg/kg, respectively. Among animals with low levels of manganese in their fur, a large number of cases of manganese deficiency were found. The cattle that were kept on pasture were usually superior to the animals kept in the stall in terms of the content of manganese in the wool, which corresponded well to the higher concentration of this element in green feed (17, 18, 19, 20, 21). As for sheep, there is much less data for this type of animal, since their wool is difficult to clean, especially in fine-wooled sheep, and in coarse-wooled sheep and goats, the analysis results are significantly affected by the ratio of down and awn hair in the rune, which varies greatly with age and season, as well as depending on the method of sampling. In these conditions, it is especially important to adhere to the standard conditions for sampling wool. Such requirements are met, for example, by the wool of one-to two-month-old Karakul lambs (22).

The phenomena of manganese deficiency, expressed by disorders of reproductive function and skeletal development, were observed, as a rule, in animals with a liver content of less than 8 mg / kg and in wool-less than 5 mg/kg of manganese (2). The ability of sheep wool to reflect the level of manganese in the diet is also noted by New Zealand (23,24) and Hungarian authors.

A similar relationship was found in wild ruminants, minks, and humans (2). In men and women, the content of 5.5-7.5 mg/kg in the liver and 1-2 mg/kg in the hair of manganese corresponds to the physiological norm. Age and gender do not significantly affect the metal content in the hair, unlike its level in other organs and tissues.

With insufficient protein nutrition, the level of manganese in the hair also increases due to its slow growth. The inclusion of protein in the diet leads to a rapid normalization of the level of manganese in the hair – 4.4-1.4 mg / kg, respectively (25).

Copper

The vital necessity of copper was shown in 1928 by the same group of students of the University of Wisconsin (26). The widespread occurrence of copper deficiency among farm animals caused great interest in the biological role of this element in the animal body (27).

Initially, it was shown that copper is necessary for the normal process of hematopoiesis. Further, it was found that copper deficiency causes endemic ataxia of newborns, causing great damage to sheep and goat breeding in large areas around the world. This disease is caused by myelin aplasia in the central nervous system. The effect of copper deficiency on reproductive function is expressed by increased embryonic mortality in ruminants with impaired function of copper-containing cytochrome oxidase, a terminal electron carrier in the respiratory chain.

In sheep and cows, an elongation of the sexual cycle was observed, returning to normal after giving copper. Another characteristic sign of copper deficiency is damage to the connective tissue of the vascular walls and bone collagen. These phenomena are caused by a decrease in the activity of specific lysyl oxidases containing copper and necessary for the formation of desmosin and isodesmosin-amino acids involved in the maturation of elastin and collagen and determining their strength. Vascular and cardiac wall lesions lead to sudden deaths in cattle, pigs, and poultry (27).

A sensitive indicator of copper deficiency in rabbits and sheep, which occurs earlier than anemia, is depigmentation of dark wool. As early as 2 days after the occurrence of copper deficiency, the conversion of tyrosine to melanin is disrupted in dark-colored fine-wool sheep, and pigment-free keratin is formed [27]. Similar phenomena were observed in Karakul sheep [28]. Cattle wool reacts to copper deficiency to a lesser extent than sheep wool. It is important to note that the brown color of the coat in black-and-white cattle may not be the result of copper deficiency, but the result of crossing it with Jerseys.

Copper is also necessary for the synthesis of keratin. In sheep that are deficient in this element, the wool grows more slowly, showing a weak tortuosity and refined areas. It also increases the content of a number of amino acids such as glycine, alanine, serine, and glutamic acid.

Recently, it has been shown that there is a genetic disease in humans and mice associated with a violation of the transport of copper by metallothioneine through the intestinal wall, called Menkes ' disease.

To determine the body's need for copper, the analysis of feed is of subordinate importance, since the exchange of this element is influenced by a large number of physiological antagonists (sulfur, calcium, cadmium, silver, molybdenum, zinc, iron).

The brain better than other organs and tissues reflects the body's supply of copper and surpasses even the liver in this respect. The fact is that with copper insufficiency caused by an excess of cadmium, the synthesis of metallothionein increases in the liver, which accumulates along with cadmium also copper, zinc and mercury, which, thus, are excluded from the metabolism.

Other organs and tissues that reflect the copper status of the body are, after the liver, the plasma (serum) of the blood, the guard hair and the heart muscle (in the given sequence).

The copper content in goat hair reflects the deficiency of this element in the feed (<2 mg / kg) only 2 months after the transfer of animals to a copper-poor diet. In females, the level of copper in the coat decreases faster than in males, which is probably due to the influence of pregnancy, which causes an additional decrease in copper reserves.

Additional giving of copper to adult animals is reflected in the content of this element in the wool. However, as long as the liver copes with the function of depositing this element, wool reflects an increase in the copper content in the diet only within limited limits.

In the case of an inverse relationship between the content of copper in the internal organs, as well as in pasture plants, and its level in wool, work indicates (23). These observations are also confirmed in the work of Nazarov (1968), where it was found that the hair cover of 15-20 day-old Karakul lambs experiencing pronounced copper deficiency in the prenatal period contains an increased amount of copper compared to lambs from the reference province. The author explains this phenomenon by the increased release of copper from the body under the influence of increased consumption of molybdenum and sulfates by animals, and the inclusion of copper in wool is considered as one of the ways to remove it from the body.

Copper differs from manganese in its relation to the color of the hair. The dependence of the copper level in wool on the melanin content has not been established [29]. The indications for such a relationship, in particular, for a higher copper content in black wool compared to white wool [30], seem to be based on analytical errors. On the other hand, there may be linear and pedigree differences in the copper content of white and black animals. In particular, the coat of albinos and albinoids is always poorer in copper than the coat of normally pigmented animals. At the same time, in the piebald animal, the wool samples from the black and white areas do not differ in the content of this element. It can be assumed that copper, preferring sulfur-containing ligands, is significantly more bound by keratin than nitrogen and oxygen-containing ligands of melanin [22].

The differences in the copper content between black and red wool in cattle seem to be related not so much to the color as to the type of wool. For example, the copper-rich wool of the German mountain motley cattle is coarser and longer, and also richer in ash components, than the shorter and finer wool of the black-and-white cattle.

In Hungarian red-spotted cattle, it was found that the amount of copper increases from light yellow to dark red [31]. In the normal copper status of the body, it contains 5 mg/kg of copper. The weak effect of color on the copper content is also shown on human hair (2).

Sexual differences have little effect on the copper content in wool and hair and become noticeable only in conditions of deficiency of this element. At the same time, smaller values were found in female individuals, which spend an additional amount of copper on the reproduction of offspring. The available sex differences are 4-4, 3 in goat hair and 13-14 and 15-18 mg/kg in human hair, respectively. In the bristles of pigs, there were no sex differences in the copper content (13 mg / kg).

In wild geese, on the contrary, the feather of the females is richer in copper than the feather of the males. Thus, in other habitats, 14-27 mg/kg of copper was found in goose feathers, and 10-18 mg / kg of copper in geese [32]. As a norm for people of both sexes, you can take the copper content in the hair equal to 15 mg/kg.

In cattle, seasonality has virtually no effect on the copper content in wool, which varies by no more than 1 mg/kg. On the basis of these data, it is possible to ignore seasonality when taking wool samples to determine the copper status of animals, although the molting period should still be considered unfavorable for this purpose.

The age of the animals does not affect the level of copper in the coat. Thus,in calves of one line, it ranged from 10-10. 7 mg/kg for 2 to 45 weeks, and in the other-from 9.8 to 11.0 mg/kg. There were no significant fluctuations in the level of copper in adult cows from 3 to 10 years of life. In Karakul lambs, the coat at birth is richer in copper than in adult sheep, however, from the age of one year to 6 years, there are no statistically significant changes in the copper content in them [33]. In

humans, the copper content in the hair shows a certain age dynamics. The greatest amount of this element is found in the hair of girls aged 6-10 years (21 + 14 mg / kg) and adolescents aged 11-10 years (37+23 mg/kg). In the future, the level of copper in the hair fluctuates around the value of 15 mg / kg, which can be taken as a conditional physiological norm (34).

In poultry, age also has a noticeable effect on the level of copper in the plumage. So in chickens the content of this metal at hatching from the egg was 24 mg/kg and decreased to 70 day life is more than 3 times (7,3 mg/kg) and age did not change (35).

As evidenced by most of the above studies, the level of copper in the outer integument of young animals is usually higher than in adults, in which it remains more or less constant level, reflecting species-specific.

The copper content in wool is under genetic control. Thus, it was shown in (2) that the offspring of one breeding bull had on average 45% more copper in the wool (8 mg/kg) than the offspring of 11 other bulls (4.8-6.0 mg/kg). Linear differences in the content of copper in the blood and liver were also found for sheep, in which, unfortunately, the level of this element in the wool was not analyzed [36]. These observations suggest that differences in analytical results may depend on genetic causes.

Breed differences in the concentration of copper found in the hooves of pigs, where the contents of this element ranged from 6.9 in pigs breed Cornwall to 15 animals breed Duroc and 16 mg/kg of rocks Herceghalom (37).

Pregnancy of cows affects the level of copper in their hair only in the last month of pregnancy (approximately 1.3 mg/kg). In earlier periods and in the second month of lactation, the content of this metal in the wool does not differ from the norm. In this regard, the wool of cows at the end of pregnancy and in the first month of lactation is less suitable for indicative studies (2).

The limited material obtained in humans shows that the level of copper in the hair varies with various diseases. It is reduced in Menkes ' disease (38.39) and increased in infectious hepatitis (46 + 29 mg / kg) and hyperthyroidism (43+12 mg/kg) (40).

In cattle, the norm should be taken as the content of copper in the brain (better indicator of copper status), equal to 9 mg/kg. With this amount of copper, the content of this element in the liver is 35 mg / kg, the content in the blood serum is 0.65 mg/l and in the black guard hair – 6.0 mg/kg. With a higher level of copper in the brain, the other listed tissues are enriched with this element, with a highly reliable correlation coefficient (r) of 0.91, 0.84 and 0.80, respectively. The kidneys and skeleton show no such correlation with the brain.

If the copper content in the brain is in the range of 6-9, in the liver – 15-35 mg / kg, in serum-0.6-0.65 mg / l and black hair-5-6 mg / kg, then we can expect a delay in the growth of young animals. When the copper content falls below 6 mg/kg in the brain, clinical phenomena of copper insufficiency are observed.

In contrast to manganese, the correlation between the level of copper in wool and red clover could not be established, since the copper content in the animal body is greatly influenced by various physiological antagonists of this element of man-made origin, such as sulfur dioxide, molybdenum and cadmium, especially in the vicinity of industrial enterprises. At the same time, there was a good correlation between the number of samples of wool with a low level of copper and its content in clover in each province studied.

The largest number of samples of copper-poor wool was found in cows from provinces with swampy and sandy soils (6.4 and 7 mg / kg), where there was also a reduced copper content in red clover. In areas not polluted by industrial emissions, a better match was found between the level of copper in wool and red clover.

In areas polluted by industrial emissions, there is usually a decrease in the copper content in the wool of cattle by 16-29% (41).

The existence of a relationship between the level of copper in the wool of cattle and its availability of this element is noted by many researchers (42, 43, 44, 45, 46, 47, 48, 49). The

wool of sheep can also serve as an indicator of their copper nutrition. For this type of animal, as well as for cattle, the presence of a correlation between the copper content in the brain, liver, blood serum and wool was found [2].

Critical values for this element should be considered its content in the brain less than 4 mg / kg, in which the liver contains 7, blood serum 0.3, and wool 3.7 mg/kg of this element. These figures were obtained in adult sheep from biogeochemical provinces where clinical trials were observed. signs of copper deficiency – endemic ataxia of lambs. Under normal copper nutrition conditions, the following dry tissue was found in the body of sheep: brain 18+7.1; liver 220+25.1; blood serum 0.84+0.46; wool 10+8.2; kidneys 15+5 mg / kg.

The copper content in the brain is equal to 6.0-9.0; in the liver-16, in the blood serum – 0.66 and in wool – 5.2 mg / kg should be considered close to the lower threshold (29, 2). Similar concentrations were observed in the wool of one-year-old sheep in Hungary-4.2-5.4 mg/kg – The results obtained in the USA (50),- 25-147 and in New Zealand (23,24) – 22-81 mg/kg differ from the above data. The reason for this discrepancy is unclear. Contamination of wool with copper is not excluded.

In wild artiodactyls-mouflons, deer, elk-similar copper content in wool was found – 6.6, 7.1, 12 mg / kg, respectively. In moose in Alaska, the given value corresponded to a good copper status. With a copper deficiency, only 5.2 mg/kg of this element was found in their wool (51).

The copper content in the mink covert hair is 8+1.4 (2), and in rabbits it is 9.1+3.2 mg/kg. In the conditions of copper deficiency in these animals, the copper content in the wool is also significantly reduced and is 5.6+2.3 mg/kg.

In pigs, the copper content in the bristles is 10-14 mg / kg on different diets. When copper is included in the diet in the amount of 250 mg/kg of feed, the content of this element in the bristles increases only 2-3 times, reaching 33+9.1 (grain ration) and 32+71 mg/kg (root vegetables) on different diets. At the same time, the copper content in the liver increases almost 20 times. Thus, the copper content in the bristles, as well as in the wool of ruminants, reflects the level of this element in the body only within certain limits, since the liver, accumulating this element within a wide range, performs a buffer function in relation to it [25].

Normally, the hair of a person over 20 years old contains 15 mg/kg of copper, regardless of gender. Such figures were obtained in the cities of Freiberg and Jena in the GDR (2). Similar values (18 mg/kg) were found in 204 adult New Yorkers (34). In bushmen, the copper content in the hair was 10 mg/kg, and in lactating women, the level of this element decreased to 8 mg/kg (53). The same authors found 9.9 mg / kg of copper in the hair of nursing Bantu women, which is also significantly inferior to the data found in Europeans. The authors note that these values are apparently not associated with copper deficiency in the body of the examined people, since they did not have the anemic conditions characteristic of copper deficiency.

In hair of adult residents of Chandigarh (India) found even lower copper content was 7.1 mg/kg, whereas in Thailand and Denver (USA) have comparable persons discovered on 13 and 14 mg/kg (25).

Workers engaged in the smelting and refining of nonferrous metals, without exception, contain high concentrations of copper in the hair, which exceeds the norm in several professions 4-10 times.

Zinc

Zinc-the third element, the need for which for the animal body was discovered by a group of scientists at the University of Wisconsin under the leadership of its rector-Todt. Since then, research on the biological role of this element has been intensively developing, and now it has left behind all other trace elements in terms of the number of publications. One of the indicators of the biological role is the detection of more than 200 enzymes of all known classes, in which zinc is found.

The importance of zinc for animal husbandry practice was revealed in 1955, when it was shown that its deficiency is the cause of parakeratosis in pigs and giving them zinc cures this disease. After a few days of consuming a diet poor in zinc, the animals lose their appetite and reduce their food intake. Giving zinc restores your appetite again within a few hours. The decline in taste (hypogeusia) - specific disease, treatable zinc salts.

Another typical, though non-specific sign of zinc deficiency is growth retardation, which is caused by both a decrease in feed intake and a violation of the processes of protein synthesis. Zinc-deficient ruminants release more sulfur and nitrogen in their urine, indicating that the body has a poorer use of nutrients.

Especially rich in zinc are the epithelial cells of the prostate, its juice and seminal fluid. Zinc deficiency, especially in the prenatal period, can lead to a decrease in the gonads in males and irreversible atrophy of the germ epithelium. Prolonged deficiency of this element reduces sexual function, although it does not reduce the sexual instinct, leads to a decrease in sperm production in goats.

In the Middle East, cases of hypogonadism and underdevelopment of secondary sexual characteristics in young men, cured by giving zinc salts, have been repeatedly described.

Intrauterine zinc deficiency causes deformities in the fetus and can lead to miscarriage or difficult delivery. Goats that experience a lack of zinc in the embryonic period are born with signs of parakeratosis. The milk of all animal species is rich in zinc and, as a rule, contributes to the cure of the phenomena of zinc deficiency in the offspring.

Violation of the outer integument with a lack of zinc is also noted in ruminants and rodents. First of all, damage occurs on the skin, esophagus and genitals. In poultry, zinc deficiency causes ack of plumage and dermatitis. In sheep, it leads to a violation of the tortuosity of the wool, baldness, a decrease in wool productivity, the appearance of brittle coarse, dry hair, a violation of the growth of horns and epithelium.

The positive effect of zinc on wound healing was known in ancient times and described in 1953. A number of authors question these observations, while others confirm them. One of the manifestations of zinc deficiency in ruminants and humans may be dwarf growth associated with delayed growth of tubular bones, impaired ossification of the skull and other parts of the skeleton, also noted in rodents. The biochemical mechanisms of zinc's action on skeletal formation remain unclear.

Lack of zinc in the last third of intrauterine development in rodents reduces the size of the brain in the offspring and worsens its ability to learn. These results were confirmed in experiments on pigs and monkeys.

In animals and humans, genetic defects leading to zinc deficiency are known. In Danish Frisian cattle, such a defect is described under the name of Adem's disease, after the name of the bull in whose offspring it was found. In humans, the input condition known as enteropeptidase of macroderma. This disease is autosomal recessive in nature and appears after weaning from the breast. It is characterized by lesions of the epithelium of the skin, close areas of the mucous membrane and intestines, hair and nails. At first, purely empirically, this disease was treated with drugs that form complex compounds with zinc and promote its absorption through the intestinal wall, for example, orthooxyquinoline derivatives. Then zinc compounds were used with complete success. Then, with complete success, zinc compounds were used to cure all the symptoms of the disease and restore normal hair growth,

The damage to the intestinal tract observed in this disease has a close similarity to another human disease - celiac disease (Giherter - Geibner disease), in which the level of zinc in the blood serum is reduced, especially in forms resistant to a gluten - free diet (0.37+_0,075 versus 0.96+_0,125 mg/l of zinc in the norm). Giving sick children zinc was also effective in this disease.

Zinc plays a crucial role in the parenteral nutrition of a person, often accompanied by the phenomena of zinc deficiency associated with enteropathic acrodermatitis. Thus, in 37 adults who received parenteral nutrition and fell ill with signs of zinc deficiency, a complete cure and restoration of hair growth was achieved by the use of zinc preparations. It turned out that with parenteral nutrition, the excretion of zinc in the urine increases, resulting in a deficiency of this element in the body.

According to a number of studies [60, 61], the level of zinc in the body also decreases in a hereditary disease known as sickle cell anemia, accompanied by the phenomena of zinc deficiency. The level of zinc in the hair of people affected by this disease is significantly reduced. These findings, however, have not been confirmed by other researchers.

Mice and humans were found to have inherited elevated levels of zinc in the blood serum. The mice were resistant to zinc deficiency and survived in conditions where the death of mice of other lines was inevitable. The stable line was called supermysh; in humans, the high level of zinc in the blood serum (3.15 mg/l) corresponded to the normal content of this element in the hair (189 mg/kg). This hereditary feature has no negative consequences for health.

Given the numerous effects on the level of zinc in the body of its physiological antagonists and various components of the feed, as well as genetic factors, it should be recognized that the development of a reliable test that characterizes the zinc status of the body is of particular importance for this element.

The preparation of wool for the determination of zinc in it does not differ from that for copper. The level of zinc in the body is more subject to homeostatic regulation than the level of copper or manganese [64]. To a lesser extent, this control extends to the ribs, testes, guard hair, liver, heart muscle, and abortions, and they are therefore more likely to perform an indicator function in relation to this element than blood plasma.

In goats that died from a lack of zinc, its content in these organs and tissues decreased only by 16-28%. (from 113-134 to 102 - 122 mg / kg), while in plasma its concentration changed only slightly. On the day of death, the zinc content in the goat's guard hair was 21% lower than normal. Such small fluctuations in the level of zinc require great care in working with this element and special analytical accuracy.

A statistically significant decrease in the zinc content in the guard hair of growing non-lactating goats was also observed only after a long-term deficiency of this element in the feed (4-5 mg/kg), lasting at least 2-4 months [2,67].

The content of lactating cows for 2 months on the diet, poor circus (6 mg / kg) caused a decrease in the content of this element in blood serum, bones and guard hair by 40%. Strict homeostatic control of the level of zinc in the body of animals complicates the occurrence of primary zinc deficiency, and the observed cases seem to be associated not only with a deficiency of this element in the feed, but with the action of a number of other factors that inhibit the exchange of zinc, such as hypovitaminosis A [68,69]. Similar results were obtained in rabbits. Which ones the zinc content in wool decreased from 321 +_40 to 280+_44 mg/kg and in thigh muscles from 116+33 to 102 +_20 mg/kg when fed a diet containing 7 mg / kg of zinc for 56 days. The additional supply of zinc also does not cause rapid shifts in the content of this element in animal hair. It was found that giving 50 mg of zinc for 60 days increased its content in the hair of girls by 22, and boys - only by 4% (from 208±32 to 284±65 and from 180±30 to 187±46 mg/kg, respectively).

When using the analysis of epidermal structures in order to indicate the zinc status of animals and humans, it should therefore be borne in mind that even small changes in the content of zinc in them, amounting to 20%, indicate significant shifts in the exchange of this element.

The level of zinc in the hair and in the coat does not depend much on their color. Thus, the differences between black and white wool in terms of zinc content were 119±12 and 112±8 mg/kg for wool from the shoulder blade and 141±13 and 111±9 mg/kg for wool from the forehead and tail. In the first case, this difference was statistically unreliable, and in the second - it met the 0.01% criterion. There is evidence that red and brown wool seem to have a higher zinc content than black and white wool. For example, in winter, Hungarian variegated cattle have a higher zinc content in dark red wool than in yellow-colored wool. (129,117 mg

/ kg, respectively); these differences, however, were less pronounced in summer wool (107 and 96 mg/kg, respectively).

From Karakul lambs are not found differences in zinc concentration between black and white wool, but the wool of the sheep painting sur and the camera was on average 23% richer in zinc than in sheep black, white and gray colors, and the coat darker variants Groundhog was attended by more zinc than the light. The kind of hair is also affected by the concentration of zinc.

This was noted above in cattle, and was also found for the hair of women, whose head hair is richer in zinc than hair from other parts of the body (143 and 110 mg/kg, respectively). Differences in the zinc content between down and poultry feathers (211±51±20 mg/kg, respectively) were found.

The zinc content in the epidermal structures shows no more, but the sex differences are quite distinct, averaging about 10%. These differences are not always statistically significant, but they always attract attention. They are quite consistent with the results of the analysis of other organs and tissues, for example, bone tissue in humans. Thus, the data obtained on goats indicate that the wool of females is richer in zinc than the wool of males (125±23 and 113±18 mg / kg, respectively).

Human hair, studied in detail in this regard in the GDR and Iran, is also richer in zinc in women than in men, and this difference persists from 6 to 90 years of age. The values found for the two cities of the GDR are 271±67 and 213±54 for women and 262±40 and 198±43 mg / kg for men, while in Iran these differences were 268±59 and 181±36 mg/kg, respectively. These studies allow us to accept as the norm the zinc content in the hair of Europeans -215 mg/kg in women and 200 mg/kg in men.

It is shown that in young animals of both sexes, the level of inca in the coat is slightly higher than that of adult animals.

Similar results were obtained for the wool of Karakul sheep. In lambs, the zinc content in the wool exceeded that of adult sheep, in which it practically did not change with age. In piglets, according to some authors, the bristles are also richer in zinc than in adult animals (at the age of 42 days -218 and in suckling sows - 194 mg/kg). Other authors do not find such a difference (202 and 198-211, respectively).

In the human hair, a well-defined dynamics of zinc is established. Regardless of gender, the hair of 3-5-year-olds contains less of this element than in later age (185±43; 15 years - 234±57; 11-25 years-237±64; 65 years-239 mg / kg).

Slightly different results were obtained for children from Central America; the lowest zinc content in their hair was found at the age of 6-10 years, that is, in older children than in Europe and the United States. There was also a statistically significant correlation between the level of zinc in blood plasma and hair, which was r=0.55 in girls and r=0.66 in boys.

The results obtained for European residents were confirmed in studies performed on 338 residents of Denver (USA). It was shown that the highest concentration of zinc is present in the hair of infants (180 mg / kg), in children after weaning and up to one year of age, it reaches the minimum values, falling to 70 mg/kg. At the age of 1 to 4 years, it ranges between 90-100 mg / kg, then at 4-5 years of age it increases rapidly, reaching 120-140 mg/kg, after which it gradually increases to 180 mg/kg by 13-17 years of age and remains at this level for the rest of life.

When assessing the availability of zinc in humans and animals, it should be borne in mind that in children and young animals, the content of zinc in the epidermal structures is lower than in adults.

In animals, there are apparently genetic differences in the level of zinc in their bodies. In pigs from 5 of the considered families, one was characterized by a 37% reduced content of zinc in the bristles (185 mg / kg) at a rate of 200-251 mg/kg. In one of the eight litters studied, the zinc content in the piglets ' bristles averaged 159, while in the other flights it ranged from 200-224 mg/kg.

A significant decrease in the zinc content in the body was observed in Adema disease associated with the lethal A 46 gene and in enteropathic acrodermatitis in humans. In the hair of a two-year-old child with this disease, almost half as much zinc was found as in the normal (100 mg/kg). After a month of treatment with zinc, its content in the hair approached the norm and amounted to 168 mg/kg. Giving zinc leads not only to the normalization of the content of this of the element in the hair of patients with acrodermatitis, but also to restore the growth and color of the hair.

An even more dramatic decrease in the level of zinc in the hair was found in 4-16-year-old children from Denver (USA) suffering from loss of appetite and impaired taste sensations, in which the concentration of zinc fell below 70 mg / kg with a minimum value of 10-18 mg/kg.

Most of the pathological conditions of the body are not reflected in the level of zinc in the hair, except for the genetic defects described above. It is necessary, however, to mention the human hypogonadism syndrome described in the Middle East. Adolescents suffering from this disease and characterized by delayed growth and sexual development, contained only 54 mg/kg of zinc in their hair, the amount of which after treatment with its drugs reached 125 mg/kg.

In Iran, in areas where rural residents often dwarfed, women's hair contained 114 and men's hair contained 139 mg / kg of zinc. In the urban population, among which there were no cases of dwarfism, the zinc content was 268 and 181 mg/kg, respectively.

According to available data, zinc is distributed along the length of the hair relatively evenly. In an environment rich in zinc, there is a tendency for its accumulation in the upper part of the hair, as, for example, in pigs (the base is 163±36 in sows and 154±21 in wild boars and the tip is 198±43 and 197±38, respectively). This phenomenon is due to the absorption of zinc from the external environment and the fact that the top of the hair participates in the exchange of zinc less actively than its base. In cattle, such differences are not noted. In humans, there is also a weak tendency of zinc accumulation in the peripheral part of the hair, which is 3% (men 231±84 and 237±89 and women 232±40 and 240±41) and is not statistically confirmed. This trend was noted in the works of a number of other authors.

The ability of wool to characterize the zinc status of the body in comparison with other organs and tissues was studied in the most detailed way on the example of cattle in the GDR. The data from these studies are presented below. As follows from the table, the highest content of zinc is found in the body of calves, which is explained by the favorable conditions of zinc nutrition of animals during the suckling period. From the table, however, it also follows that the animal hair does not reflect these differences.

Table 1.30

The content of zinc in the body of cattle

Organ tissue	*Suckling calves n=24*	*Heifers n=39*	*Steers n=75*	*Cows n=468*
Edge	98±24	75±7	68±12	64±16
Wool	127±22	123±19	122±17	126±28
Blood serum, mg/l	2,1±0,4	1,2±0,5	1,3±0,6	1,5±0,5
Liver	287±225	120±41	129±27	135±61
The brain	77±25	52±5	54±10	53±9
Kidneys	124±61	87±21	88±16	98±22

The best way to reflect the body's supply of zinc is its content in the rib, which is the most reliable indicator organ for this element. As the lower limit of the norm for cattle, the zinc content in the rib is equal to 40 mg/kg, in pigmented wool - 120 mg/kg and in blood serum-0.6 mg/kg. In this species, a significant correlation was established between the level of zinc in the coat and the rib (r 0.99). Similar correlations were found between the rib and liver (r=0.96) and the brain (r = 0.86).

At the same time, Kirchgessner and Schwartz could not find any connection between the levels of zinc in the blood serum, wool and rib of cows. This observation is difficult to explain. It can be assumed that prolonged starvation of animals before slaughter caused them to increase the level of zinc in the blood plasma, as evidenced by the value given by these authors-I, 5 mg/kg of zinc, which is significantly higher than the usual content of this element.

The above comparison suggests that the wool of cattle can serve as an indicator of the level of zinc in feed and other environmental objects. A number of other researchers come to a similar conclusion.

The zinc content in the organs and tissues of sheep is close to that of cattle, with the exception of the ribs, which are about 40% richer in zinc and contain it 89±21 and 81±17 mg/kg in old and young animals, respectively. The blood serum contains 1.0±0.5 and 1.2±4 mg / l, the liver 136±42 and 128±46; the brain 53±10 and 56±9; the kidneys 104±31 and 103±39 mg / kg of this element. Sheep's wool contains approximately the same amount of zinc as cow's wool-133±24 and 147±32 mg / kg, these data were obtained on 101 and 43 sheep, respectively, and they can be considered as a physiological norm.

There is a highly reliable correlation between the zinc content in the rib and coat, blood serum, and even the brain, indicating the ability of these tissues to reflect the zinc status of the body. So, in the pair edge: wool, the correlation coefficient (r) was 0.94 with the regression equation in 97.6+0.37 x; in the pair edge: blood serum r=0.96, y=0.52+0.02 x and in the pair edge: brain-r+0.97, y=39.6+0.14 x; the reliability of the values given in all cases was < 0.01.

The zinc content in sheep wool has been studied many times. In the wool of sheep from Austria and the United States, an average of II5 mg/kg of this element was found [I05]. In the rune of New Zealand sheep, 113 mg/kg of zinc was found with fluctuation limits from 89 to 169 mg/kg. I0I-III mg/kg of this element was found in the wool of Hungarian sheep.

The coarse wool of Karakul sheep is poorer in zinc than that of the fine-wooled sheep discussed above. In the autumn wool of Karakul sheep from various farms in Uzbekistan, 83-99 mg/kg of zinc was found, and in the spring wool-53-62 mg/kg. It is also possible that such a low level of zinc in the wool of Karakul sheep indicates insufficient provision of their body with this element.

The content of zinc in the wool of wild ruminants is similar to that of cattle, sheep and goats, and in rodents it is much richer in this element (mink 200±22.5, rabbit 32I±40 mg / kg). In the wool of rats, a number of researchers found 200-400 mg/kg.

Zinc deficiency affects the coat of rats in the same way as it affects the coat of ruminants. With the content of this element in the feed in the amount of 2 mg / kg, the level of zinc in the wool decreases sharply (from 188 to 131 mg/kg) and growth is delayed, and the inclusion of tyrosine and arginine in the wool decreases and the amount of proline increases.

The zinc content in the coat of rats is significantly affected by various components of the feed-vitamins, proteins, carbohydrates. This effect seems to be related to the different growth rates of the wool fiber, although it is possible that there are other still unknown causes that change the zinc content in wool. Attention is drawn to the sharp decrease in the level of zinc in wool with a lack of vitamins A and D (from 309±15 to 122±29 mg / kg) and with a high content of sugar in the diet (from 342±7 to 96±11 mg/kg). These findings are consistent with observations in chickens and cattle that low levels of vitamin A in the diet make it difficult for the body to absorb zinc.

In pigs, the normal zinc content in the bristles ranges from 150-200 mg / kg, below which you can expect the disease of animals with parakeratosis. The zinc content in the bristles decreases under the influence of calcium, cadmium and copper, as well as substances that inhibit the activity of the thyroid gland. The zinc content in the horn of nails and hooves also has indicative properties. In sheep and pigs, it is normally 88 and 92 mg / kg, respectively, and differs in piglets of different breeds. Human nails contain about the same amount of zinc (61-152 mg / kg). The content of pink in the hair of primates has been studied repeatedly. Thus, in Rhesus monkeys, the concentration of this element in the summer coat was 197 mg / kg, which exactly coincides with the level of this element in the male head hair. In Europe and Canada, the normal amount of zinc in the hair of people of both sexes can be taken as 200 mg/kg. Concentrations of less than 150 mg/kg were found in Irena and Egypt. In India, Thailand and the United States, the zinc content in the head hair ranges from 140-180 mg / kg. In persons engaged in the smelting and processing of zinc, its content in the hair is significantly increased and exceeds the norm in certain professions by Z-10 times, reaching 596-1979 mg/kg. The analysis of the hair allows, thus, to obtain information about the level of zinc contamination of the workplace.

Summarizing the data on the level of zinc in the epidermal structures, it should be said that as a result of pronounced homeostatic regulation, its level in wool, hair and feather fluctuates only within limited limits and reflects the zinc status of the body more slowly than its content in the blood serum. Human hair reflects well the pollution of the external environment with zinc. The zinc content in wool and feathers does not depend on their color, but varies depending on the type of wool fiber or plumage. The hair of male individuals is 10% poorer in zinc than that of female individuals. Young hair is somewhat richer in zinc than old hair. Especially rich in zinc in the hair of cubs with dairy nutrition.

Lead

The analysis of wool and hair has been repeatedly used, as already noted, in conducting toxicological studies. Especially many works are known on the study of the content of lead in hair and wool.

The results of these studies are shown in table I. 2.

Gender and age do not affect the lead content in wool and hair, but there is less lead in the lower part of the hair than in the upper part. The lead content in the hair increases as a result of its contamination from external sources, as shown in Table 1.2, the lead content in non-polluted hair does not exceed 10 mg/kg.Such a concentration of lead is found in rural areas with its minor lead pollution from transport and industrial emissions. It follows that the lead content in the head hair, which did not exceed I0 mg/kg, indicates a low pollution of the environment with this element. In the urban population, not associated with the processing of lead, its content in the head hair reaches Z2-2I7 mg/kg. Similar results were also obtained for small mammals (rats) in rural and urban habitats and is 11 and 133 mg / kg, respectively.

Table 1.31

Lead content in human head hair

Country, gender, location	χ	б
Ireland, children, countryside	3,1	-
India, men, countryside	5,0	4,3
USA, rural area	7,6	5,0
Canada, rural area	9,1	-
India, students	9,4	7,4
United States, women, men	11,0	3,0
USA, printers	15,0	12,0
USA, young women	20,0	-
USA, men contact with lead	32,0	29,0
Canada, men, lead contact	45,0	-
USA, children, lead contact	217,0	213,0

In healthy dogs, the concentration of lead in the coat ranges from 10 to 30 mg / kg, and in dogs poisoned with lead - from 30 to 180 mg/kg. In the wool of elk from Alaska, 0.5-26 mg/kg of lead was found [116], and in the wool of sheep - 9 mg/kg [50]. In cattle from areas with low levels of lead, its content ranged from I-4 mg/kg, and from areas contaminated with this element-in the range of 60-96 mg/kg [99].

From the above data, it clearly follows that the lead content in hair and wool well reflects the level of this element in the body and in the environment.

Mercury

The mercury content in human hair and animal hair has also been studied repeatedly. The results of the studies are shown in table I.3. In countries with low industrial development and in rural areas, the mercury content in human head hair and animal hair is insignificant and does not exceed I mg/kg of this element. The same low content of this element is found in the hair of the inhabitants of India, who eat exclusively plant food. In the population of countries with developed industry, the mercury content in the hair ranges from I-5 mg / kg. With mercury poisoning (Minimat's disease), the concentration of this element in the hair reaches 25 or more mg / kg.

Studies of the ability of hair and wool to reflect the content of trace elements in the body of animals and in the environment can be presented in the form of the following summary (Table I.4), from which it follows that under certain conditions of sampling hair and wool, their analysis is quite suitable for assessing the microelement status of the body. At the same time, it should be borne in mind that the capabilities of this test are in feedback with the power of homeostatic control of the exchange of trace elements. Thus, the content of zinc in the body, subject to good regulation in a wide range of its concentrations in the body and the environment, decreases with the death of animals from a deficiency of this element by only 20%.

Under similar conditions, the level of copper decreased by 35, manganese – by 50, selenium – by 60 and iodine-by 65%. The analysis of the content of molybdenum, cadmium, lead and mercury can be used to assess the pollution of the environment with these elements. This test also reflects the excess in the medium of manganese, copper and zinc.

Data on the content of other elements in wool and hair will be given below in the relevant sections.

Table 1.31

The content of mercury in hair head of a man

Country	*Women*	*Men*	*Note*
India-nepal	0,48±0,46	0,16±0,19	
India	-	0,83±0,85	*Vegetarians*
Japan	1,6±1,0	2,0±1,3	
Italy	-	1,8±0,3	
Japan	2,0±0,61	2,1±0,92	*Non-vegetarians*
India J	-	2,1±2,2	
apan	3,2±2,0	4,4±2,4	
USA	59	2,4	
Italy	-	4,0±0,8	*Miners*
Japan	22	24	
Italy	-	25±6,1	

Table 1.32

The ability of wool and hair to reflect the microelement status of the body

Displayed increased	Mn	Cu	Zn	Se	Mo	J	Cd	Pb	Hg
Content in the environment	++	++	+	+++	+++	+++	+++	++	++
Paint job	+++	-	-	-	+++	-	+	-	-
Paul	-	-	+	-	-	-	+	-	-
Aging hair	+++	+	+	-	-	+	+	-	-
Genetic features	++	++	++	-	-	-	-	-	-
Pregnancy	-	++	-	-	-	-	-	-	-

+ - weak, ++ - medium, + + + - good display ability

Nickel

Divalent nickel ions are necessary for the existence of animals. In a diet deficient in nickel in animal cells, mitochondrial swelling, expansion of the perinuclear space, and a number of other phenomena associated with impaired membrane functions are found. The toxicity of nickel is very low and there are homeostatic mechanisms in the body that regulate its concentration levels. 0The usual content of this element in tissues is 1-5 micrograms/kg. Famous macroglobulin in the blood, which is the carrier of Nickel-nickelplated. In the blood serum, it is also found in low-molecular-weight complexes and compounds with serum albumin. Due to the ubiquity of nickel (soil, plants, etc.), it is difficult to make a diet in which this element is completely absent, which forms the active center of a very important enzyme - urease, which cleaves urea to form two molecules NH3, and CO2. This enzyme with M. V. 105000 contains two nickel atoms. It is possible that this ion plays the role of a biological Lewis acid (similar to Zn), although it is possible that an forms a strong complex with ammonia, the product of urea cleavage. It is possible that this ion is part of the enzyme systems of glutamine metabolism, in particular, catalyzing its hydrolysis to form ammonia.

Arsenic

Despite the well-known toxic properties of this element and its compounds, there is reliable evidence that a lack of arsenic leads to inhibition of the growth of rats, pigs and goats and a decrease in the birth rate. The addition of sodium arsenite to food led to an increase in the growth rate. Arsenite AsO2 is similar to phosphate in chemical properties such as the size of the molecule, structure, and ability to enter into biochemical reactions. But the esters of arsenic acid are very unstable, if they are formed on the surface of the enzyme, then they are immediately hydrolyzed during cleavage. This circumstance explains the high toxicity of arsenates.

Arsenate can replace phosphate in all photolytically reactions. In the presence of arsenate, the oxidation of glyceraldehyde-3-phosphate does not stop, but the synthesis of ATP does not occur, because I-arseno-3-phosphoglycerate is formed. In other words, arsenate separates the oxidative phosphorylation process.

Arsenite AsO2 is able to interact energetically with dithiols, for example, with lipoic acid and cysteine residues in S-H groups (accumulation in wool). By blocking oxidative enzymes, it promotes the accumulation of pyruvate and other L-keto acids.

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The use of bentonite from the Azkamar deposit for balancing the mineral nutrition of farm animals.

Bentonites are called, regardless of their origin, fine-dispersed clays consisting of at least 50-80% of the minerals of the montmorillonite or beidellite group, having a high binding capacity, absorption and catalytic activity /239/. Many bentonite clays were formed as products of the decomposition of volcanic ash, which settled mainly in marine basins and are characterized by relative homogeneity, endurance along the strike over a large area, and the absence of extraneous material in them. Such a valuable varieties include bentonite clay Azkamar field. Montmorillonites are electroneutral aluminosilicates formed by crystalline three-layer packages of two sheets composed of silicon-oxygen tetrahedra separated by a sheet of aluminum-oxygen octahedra. The vertices of the tetrahedra occupied by oxygen ions are part of the intermediate "hydrargillite" sheet, and the vertices occupied by hydroxyl ions face the adjacent flat three-layer package. The average composition of montmorillonite can be expressed by the formula: $M_{x+} Si_8[Al_{4-x}(Fe^{2+}, Mg)]^{0}20(OH)_4 \cdot {}_nH_20$;

where x varies in a fairly wide range from-0.1 to 0.6. M-interlayer cations of the Na+, Ca2+, Mg2+, etc. A characteristic feature of montmorillonite is that the negative charge is concentrated in the octahedra and is caused by the substitution of a part of the Al 3+ cations for divalent cations. The negative charge of the layers is compensated by M cations (Na, Ca, Mg, etc.) located in the interlayer gaps.

There is a very weak bond between the hydroxyl ions of neighboring packages and they are able to hold a large amount of water and other polar liquids, including organic ones, which enter the inter-package spaces and cause the lattice to swell. The high absorption capacity of montmorillonite is widely used in industry, where they are known as bleaching clays, bentonites, bentonite clays, humbrin, ascangglina, nalchikite, bentobiotics, Fuller's earth, etc.

Another very important property of the minerals of the montmorillonite group is their strong ability to cation exchange like zeolites and permutites. Per 100 g of the substance, they contain 60-100 ig-eq. Exchange of cations, mainly calcium, potassium or sodium, which are located on the surface of the particles and in the spaces between the layered packages, balancing their negative charges

The third property of bentonites is their catalytic activity in a number of chemical reactions-the production of unsaturated hydrocarbons, the synthesis of pyrimidine bases from ammonia, aldehydes and ketones, the production of nitriles from ammonia and carboxylic acids, the cyclization of olefins, etc., the formation of peptide bonds. They are able to protect amino acids from the action of the rumen microflora, which leads to their more efficient use by the body.

Bentonite clays have been used in medicine for many centuries as adsorbents to combat irritants of the gastrointestinal tract. It is believed that clay has the ability to adsorb poisons, toxins and bacteria, to envelop the inflamed mucous membranes of the digestive tract. They are also used in pharmacy as a binder in the manufacture of medicines, feed pellets. It is interesting that the population of the Middle East systematically accepts clay during pregnancy and childhood. This phenomenon, described in detail under the name "geography", is also widespread in the republics of Central Asia.

Since the 1940s, the scientific literature has indicated the possibility of using bentonite clays as stimulators of the productivity of farm animals and poultry. A positive effect was achieved in pigs, ruminants, in which bentonite contributed to a decrease in the acidity of the contents of the rumen with an acidogenic diet, a decrease in the level of ammonia, and normalization of mineral metabolism. The positive effect of bentonites is noted in poultry farming. In Bulgaria and Czechoslovakia, bentonites are also used for the prevention and treatment of diseases of the digestive tract of cattle, sheep and pigs.

The mechanisms of action of bentonite clays are associated not only with their ability to preserve amino acids, but also with their adsorption of digestive juices, which increases the surface of their contact with food. An important role in this case is played, apparently, by the property of clays to reversibly adsorb ammonia and some other components of the chyme, which ensures their uniform use by the animal's body. According to others bentonites contain unidentified growth factor, normalizes peristalsis of the intestine and functioning of the rumen in stressful situations. Under the influence of bentonite, the processes of parietal digestion, which uses the absorption properties of these clays, are enhanced. At the same time, it occurs in the departments of the digestive tract, which are not normally characterized by these processes. In addition to the adsorption properties, the surface surface of bentonites, as well as the content of macro and microelements in them, which can make up for their deficiency in the diet or limit the negative impact of their excess on the body by ion exchange, is of significant importance.

Clays added to animal feed should not contain an increased amount of lead, arsenic and other toxic components. However, these elements are often found in bentonite as part of the exchange cations and the crystal lattice, and therefore the clays of each deposit must be carefully analyzed before they can be recommended for use as feed additives.

We have studied some physical and chemical properties of bentonite clays from three deposits in order to use them as a stimulator of dairy productivity of cattle in the conditions of Uzbekistan

Physico-chemical properties of Azkamar bentonite.

Medium samples were taken from horizons operated three fields - Cooperating, Opanlynka and Azkamar - strictly across the formation. The content of trace elements was determined by the methods of emission and atomic absorption spectral analysis, the content of the fine fraction was determined by the sedimentation method. The chemical composition of the bentonites of the three studied deposits is shown in Table 1.1.

At present, the vital necessity of all 11 trace elements listed in the table has been proven, so that the presence of small amounts of vanadium, chromium, lead, nickel, arsenic and tin in the feed also it is necessary, as well as the "classic" trace elements-manganese, cobalt, nickel, zinc, copper and molybdenum.

It follows from the table that the most favorable set and ratio of trace elements has bentonite of the Azkamar deposit, which contains more manganese, cobalt and copper with a ratio of the latter to molybdenum as 10:1, which is considered favorable for the animal body. Vanadium and chromium in this clay are less than in the clays of other deposits, lead is 4 times less than in the Oglanlin clay, and arsenic is 8 times less than in the Chupanatinskaya clay.

Table 1.2

The content of trace elements in bentonite clays of three deposits, mg / kg

Elements	*Chupanata*	*Oglanly*	*Of Azkamar*
Manganese	208,3		262,5
Nickel	51,7	112,9	41,9
Cobalt	9,0	41,4	18,2
Molybdenum	7,6	8,3	5,0
Copper	31,7	5,0	47,5
Zinc	70,0	27,1	65,6
Vanadium	400,0	50,0	200,0
Chrome	225,0	258,0	85,0
Lead	6,8	150,0	7,8
Arsenic	130,0	32,8	15,0
Tin	Not detected	Not detected 5,2	3,0

Since there is no data on the maximum permissible concentrations of these elements in clays, it is possible to judge the suitability of these clays as feed additives based on their comparison with the chemical composition of the soil, which animals in free grazing swallow in an amount of 10 - 12% of the dry weight of the eaten feed. If we take the content of these elements in the soil as conditionally normative indicators, then the data obtained for the Azkamar bentonite quite fit into the regional soil clarks. As for Caponatina clay, they are superior to Clark at the concentration of arsenic and Ullanlinna clay – for lead content.

Thus, the content of trace elements allows us to give preference to the bentonite of the Azkamar deposit, which also has fairly large well-explored clay reserves (as of 1980, about 16 million tons), conveniently located and a small amount of overburden work, which allows for widespread use of these clays in animal husbandry. The light green (gray) bentonite of the Azkamar deposit bears obvious traces of volcanic origin, contains 31% water and 73% fine-dispersed colloidal fraction of montmorillonite, as well as Oglanlin clays. Cooperatista clays contain only 25% of montmorillonite and much of ballarina than the previous one. Another feature of the Azkamar bentonites is their alkaline character - the predominance of sodium and magnesium among the exchange cations and the "hydrargillite" structure, which allows them to be attributed to the magnesium-sodium type, while the most well – studied (reference) bentonite - humbrine-is dominated by calcium ions (Table 1.2)

Table 1.2

Structure of montmorillonites from bentonites of some deposits

Bentonite	Formula
Escaparse grey Quantisci grey Ogulinski tight Humpin	Na0,48 K10 Ca0,07 (Mg0,35 Fe0,17 Al1,31) [Al0,15 Si3,85 O10] (OH)2 * H2O Na0,13 K0,22 Ca2,13 (Mg0,21 Fe0,30 Al1,16) [Si4,1 O10] (OH)2 * 1,26H2O Na00,9 K0,01 Ca0,02 (Mg0,18 Fe3+0,10Al1,22) [Si4,4 O10] (OH)2 * 1,77H2O Na0,07 K0,03 Ca0,14 (Mg0,40 Fe0,12 Al1,52) [Al0,08 Si3,92 O10] (OH)2 * 3H2O

The prevalence of sodium among exchange cations Azkamar montmorillonite is of some value, especially in Uzbekistan, where the feed usually fortified with calcium, which inhibits the absorption of phosphorus and some trace elements, especially copper, manganese, zinc. Given that in a number of activities, calcium follows far behind sodium, it can be expected that as a result of cation exchange, it will be sorbed by bentonite, and instead of it, sodium ions will be released into the surrounding liquid, which will lead to a balancing of the mineral composition of the chyme. This property of Azkamar montmorillonite makes it unnecessary to convert it to a sodium form, as is practiced by a number of researchers who used bentonite for livestock feed /253/.

From other physical and chemical properties of the studied bentonites, the following characteristics can also be brought (Table 1.3.)

Table 1.3

Some physico – chemical characteristics Azkamar and Oglanlin clay

Bentonite	Oil capacity, %	Carbonate content, %	Salinity%	Exchange capacity, mg-eq/1000	Swelling according to GOST-3226-46
Azkamar	**18,1**	**3,6**	**0,28**	**58,8**	**552**
Oglanlin	**16,1**	**0,82**	**0,32**	**64,5**	**900**

The table shows that the Azkamar clays have an increased carbonate content, are moderately saline and have average indicators of exchange capacity and swelling for clays of this kind. The macronutrient composition of Azkamar bentonite clays in comparison with Askangel is shown in Table 1.4.

Based on the data on the study of bentonite clays from three deposits, we stopped in animal experiments on Azkamar bentonites.

Influence of Azkamar bentonite on milk productivity of cows.

The experiments were carried out on dairy farms of the Krupskaya collective farm in the Urgut district of the Samarkand region (I experience) and the Kh. Alimjan state farm in the Oktyabrsky district of the Jizzakh region (II experience). Per day, watering-from car watering machines, milking-machine, in the morning and in the evening. The average live weight of cows in the experimental group was 405.4 kg at the beginning of the experiment and 410.6 kg at the end, and in the control group 406, 9 and 405.7 kg responsibly. When setting up the experiment, 5 cows in both groups were recently inseminated, 3 others were calved in January and February and inseminated in the second half of April during the experiment. 4 cows were pregnant at 2-3 months.

Rectal studies conducted at the end of the experiment showed that all the cows in the experimental group were pregnant, and in the control group three remained sluggish. Milk productivity was taken into account on the basis of control milkings carried out every 10 days. Milk yield for the period between control milks was calculated by multiplying the amount of milk received on the control day by the number of days in the period.

When forming pairs, the main studied feature - milk yield-was taken into account. At the same time, in case of a mismatch, animals with a high milk yield were placed in the control group. In this regard, the milk yield of cows in the first month of the experiment in the control group was slightly higher than in the experimental group. This was especially noticeable according to the data of the first control milking (Table 1.5). On the 20th and 30th days of the experiment, both groups were equal in milk yield, and on the 40th day, the animals receiving bentonite exceeded the control by an average of 0.4 kg of milk per day.

By the 50th day, this difference was 0.5 kg and then remained with some fluctuations until the end of the experiment.

The milk yield of cows calculated by the months of the experiment is presented in Table 1.6. From Tables 1.5 and 1.6, it can be calculated that at the end of the experiment, the milk yield of cows in the experimental group exceeded the control by an average of 7.2 kg per day (7%, $\alpha<0.05$), and for the entire third month by - 170 kg (5.5%, $\alpha<0.01$).

The first experiment was conducted from April 17 to July 16, 1985. Under the experiment there were 24 cows of the red steppe breed, divided into 12 heads each. Ten cows in each group were born in 1973 and 2 cows were born in 1989. Cows of the first group received bentonite in the composition of granules containing 70% wheat straw, 25% clay and 5% grass flour in an amount of 1.5 kg per day.

The animals of the second group (control) received the same amount of grass flour and straw, but without bentonite. The economic ration of cows in March-April consisted of haylage, silage, chatterbox from concentrates with trace elements, bards; in May-from mixed feed, green mass of alfalfa and chatterbox from end feeds, a total of 10.4 feed units. per head per day. The content of the cows of the stable-walking. Feeding – 5 times the gradual increase in milk yield, which is explained, first of all, by the improvement of their feeding conditions in the spring and summer period. Such factors as pregnancy, lactation period and age of animals in our experience did not have a significant impact on milk productivity. The addition of bentonite had a more noticeable effect on animals with low milk yields, which rose during the experiment from 5.5-7.2 to 7.2 - 8.2 kg / day, while in the control of such animals they increased less significantly - from 5-6.5 to 6.5 - 7.5 kg / day. The milk yield of animals with higher productivity varied to a lesser extent from 8-9.5 to 10.5 - 11.6 kg/day in the experimental group and from 9.0 - 9.4 to 9.5 – 11.2 in the control group. As a result, the animals of the experimental group by the end of the experiment were aligned with the milk yield, while in the control the difference between individual milk yields reached 4-5 kg per day. This is evidenced by the results of statistical processing. So, the square deviation of the average values of the control milk yields varied in the experimental group in the range of 1.0 – 1.3, and in the control group - in the range of 1, 3 - 2.1 kg.

The second production experiment was conducted at the state farm named after Kh. Alimdzhan of the Oktyabrsky district of the Jizzakh region for 7 months from 4.1 Y to 26. X-1985. For the experiment, 20 dairy cows of the Schwyz breed were selected, divided into 2 groups of 10 heads each, of which one - the experimental one received 400 g of crushed bentonite per head per day as part of concentrates. In both groups, at the beginning of the experiment, there was one yalova, two recently calved, two recently inseminated cows, and one cow at 2,3,4 and 5 months of pregnancy. All animals were born in 1979. births with an average live weight at the beginning of the experiment of 385-415 kg and at the end of the experiment-386 - 416 kg in the experimental and 394 - 415 kg control groups. During the experiment, 3 cows in each group brought calves. The feeding and maintenance of the animals were similar to the conditions of the first one (10.1 feed units).per head per day)

The results of control milking increased in both groups until mid-September, after which they began to decline slightly (Table 1.7). As in the first experiment, giving bentonite during the first 20 days did not significantly affect milk yield, and only after a month this indicator reached statistically significant differences - 0.4 kg on average between the groups.

After another 20 days, the differences reached 0.7 kg per day and remained at this level with some fluctuations throughout June. In July, the difference between the control milks averaged 0.9 - 1.1 kg per cow, and in August 1.1-1.3 and in September, when the highest milk yields were achieved-1.2-2-5 kg. At the end of October, the milk yield and the differences between the groups for this indicator decreased slightly by 1.0-1.1 kg.

During the experiment period, 3 calves were born in each group, and cows treated with bentonite brought calves with a slightly higher live weight than in the control (28.1 vs. 25.8 kg), which, however, soon almost leveled off and amounted to 41 and 39 kg, respectively, by day 60. In the second month, the milk yield of cows in the experimental group was higher than in the control group by 170l (7.4%, $\alpha < 0.01$), in the third month-by 240l (10%, $\alpha < 0.001$), in the fourth – by 264l (10%, $\alpha < 0.01$). In the 5th, 6th and 7th months, the difference was 200, 526 and 374 kg, respectively. The difference was also influenced by the different start-up times of the cows in the experimental and control groups. As in the first experiment, the effect of bentonite appeared primarily on cows with less high productivity and to a lesser extent affected high-yielding animals (Table 1.8). This pattern allows us to believe that bentonite does not so much stimulate the process of lactopoiesis itself, as it helps to improve the digestive processes.

It should be noted that the animals used in the experiments do not fully meet the genetic potential of their breeds, both in terms of live weight and milk productivity, although they have milk yields that are considered good for the specific conditions of their farms - 2.5 - 3.3 thousand per lactation. The lower milk yield in 1 experiment is partly due to the fact that some of the cows used are subject to age-related culling. In households where the experiments were carried out, still a significant barrenness, duration of service period is 200 days or more. In cows treated with bentonite, the duration of the service period significantly decreased, but still amounted to 120-160 days with a normal period of 85 days.

Influence of bentonite on dairy productivity of cows (II experiment)

Giving bentonite had a positive effect on the fertilization of cows. But since these observations were made on a limited number of animals, they need further verification.

Thus, in specific conditions of feeding and keeping animals, on dairy farms where experiments were conducted, the inclusion of bentonite in the diet of cows contributed to an increase in their milk productivity by 6-10%, primarily in low-yielding animals. Feeding bentonite was equally effective both in the form of pellets containing 25% bentonite, and in the form of ground clay added to the feed.

Changes in the mineral composition of bentonite during digestion.

The chemical transformations of bentonite during digestion were studied by comparing its composition before and after passing through the digestive tract. Bentonite was obtained from ground feces, by thawing in distilled water, after removing undigested organic residues (from 100 g of feces, 3.2 g of bentonite was obtained). Determination of the exchange capacity of bentonite isolated from feces showed that it decreased by about 40% (45 vs. 72 mg-eq per 100 g of clay) due to strongly adsorbed organic components of chyme (based on the mineral part of the clay). After salinization of bentonite isolated from feces, its exchange capacity increases by 1.5 orders of magnitude (from 45 to

600). This indicates the presence of a significant amount of organic components in the soil of natural bentonite, which are removed during the process of greening.

The content of exchange cations was determined by the AAS method after ozonation and decomposition of the silicate base with hydrofluoric and sulfuric acids in platinum cups and the transfer of the mineral residue to the solution. The experiment was carried out in threefold repetition. At the same time, a blank sample was set up with a strict standardization of the amount of added acids. The results of the analysis are shown in Table 1.9.

The table shows that when passing through the digestive tract, bentonite is 2 times enriched with potassium, 5-6 times with calcium and magnesium, while maintaining the same sodium level. At the same time, there is a significant enrichment of copper (5.2 times), manganese (6.2 times) and especially zinc (16 times). Since 130 g of bentonite is released per day with feces, 513 g of potassium, 158.6 g of calcium and 319.2 g of magnesium, 8.7 mg of copper, 97.5 g of zinc and 57.8 g of manganese are removed from the body, which is about 50% of the total amount of elements present in the feed.

Table 1.9

Changes in the mineral composition of bentonite during digestion, mg / kg

Element	Before feeding	After the feeding	enrichment	Removed with bentonite
Calcium	280	1500	5,36	158,6
Magnesium	5450	30000	5,50	319,2
Sodium	650	700	-	-
Potassium	4350	8300	1,91	513,5
Copper	16	83	5,19	8,7
Zinc	50	800	16,0	97,5
Manganese	85	530	6,24	57,8

Discussion of the results.

During the milk period (from 50-60 days to 4-6 months), a significant restructuring of the digestive organs is carried out, thanks to which the animals develop the ability to absorb the nutrients of plant feeds. This period is characterized by the restructuring of metabolic processes, increased protein, mineral and water metabolism in the body, intensive growth of organs and tissues. Moreover, the feed factor during this period is decisive in the formation of the animal, in creating prerequisites for a more complete manifestation of the genetic potential of the organism. The level, completeness and organization of feeding have a decisive influence on the intensity of raising and fattening livestock. A low level of feeding delays the growth of muscle and fat tissue.

During this period, natural sorbents that can balance the ionic composition of the feed and the microflora of the rumen, such as bentonite clays, are of particular importance.

Bentonite of the Azkamar deposit has a set and ratio of trace elements that are favorable for the animal body. In addition, it has a fairly large well-explored reserves, a convenient location and a small amount of uncovered work, which makes it possible to widely use these clays in animal husbandry. The use of bentonite as part of the main diet has a positive effect on the development of young cattle at 2-3 months of age.

Bentonite, apparently, contributes to the better absorption of carotene and a number of mineral components of the feed from the gastrointestinal tract. The stable consumption of bentonite clay by animals allows it to be used as a carrier of trace elements and medicines instead of scarce concentrates and combined feeds.

Our research shows that bentonite has a significant effect on the balance of macro - and microelements. If the removal of potassium, calcium and manganese has a beneficial effect, reducing their excess in the body of animals, the adsorption of trace elements, on the contrary, can have undesirable consequences. In this regard, the feeding of bentonite should be carried out on a sufficiently high trace element background of the diet. Our experiments are quite consistent with the observation that people who have been eating clay for a long time may experience zinc deficiency, which is prevented by increased doses of this element. Thus, bentonite has a twofold effect on the body, normalizing the level of trace elements in the digestive tract, it, at the same time, can lead to a deficiency of trace elements, which should be taken into account when using it for a long time.

Our data directly contradict the opinion of the authors, who believe that bentonite can be considered as a source of trace elements in the feeding of farm animals. Not by accident, apparently. When feeding bentonite, its dosage plays such an important role. The most favorable dose is considered to be its content in the feed in an amount of 2-3%. Exceeding this dose negates the stimulating effect of bentonite, and even more increased doses lead to negative consequences.

Conclusions

The content of copper, manganese, zinc, and lead in the wool of sheep and cattle objectively characterizes the microelement status of animals. Copper content the most close correlation is established with the liver and the brain, on zinc with muscles and skeleton, the manganese – kidney and liver and in the lead – with a skeleton. In this regard, the analysis of animal hair allows us to assess the conditions of their mineral nutrition and use it in conjunction with other indicators in biogeochemical studies and the assessment of environmental pollution with heavy metals. For the accuracy of the assessment, it is necessary to compare the results of the analysis of wool of the same color taken on a certain area of the body in healthy animals in the periods preceding the molt.

The content of manganese, chromium, arsenic, and samarium in the black wool of downy goats is significantly higher than in the white wool of the Angora type, while the level of copper, zinc, nickel, bromine, antimony, and gold does not depend much on the color. The wool of goats grazed in the areas of mercury-antimony ore occurrences of the Upper Zarafshan contains an increased amount of arsenic, antimony and mercury, indicating that the analysis of wool can be used as a zooindication method for searching for ore deposits. The study of the effect of pyridine and diphenylcarbazone concentrations on the extraction and re-extraction of the elements revealed the optimum concentrations of the reagent and adduct, which provide the maximum value of the distribution coefficients during extraction and complete re-extraction of the analyzed elements. Double concentration reduced the detection limits of the analyzed elements by two orders of magnitude.

In relation to biological and natural–economic objects of the work carried out, the method of multi–element neutron activation analysis was applied and significantly modified. When analyzing hair and wool, radionuclides of three groups appear: with a half-life of up to three hours, from 3 hours. Up to 120 hours. And more than 3 days. Methods for the determination of zinc, scandium, cobalt, iron, antimony, caesium, lead, europium, sodium, potassium, bromine, arsenic, gold, uranium, mercury, beryllium, chlorine, manganese, and others have been developed and correlated with the photo peaks of radionuclides.

The content of copper, manganese, zinc, and lead in the wool of sheep and cattle objectively characterizes the microelement status of animals. Copper content the most strong correlation is established with the liver and the brain, on zinc with muscles and skeleton, the manganese – kidney and liver and in the lead – with a skeleton. In this regard, the analysis of animal hair allows us to assess the conditions of their mineral nutrition and use them in combination with other indicators in biogeochemical studies and assessment of environmental pollution with heavy metals. For the accuracy of the assessment, it is necessary to compare the results of the analysis of wool of the same color taken on a certain area of the body in healthy animals in the periods preceding the molt.

Zinc deficiency is most widespread among cattle, found in 58 percent of all animals surveyed. Manganese deficiency is observed in 34 percent and copper-in 30 percent of the examined animals. Copper deficiency is most pronounced in the territory composed of limestone weathering products, in the conditions of soil salinization with calcium and magnesium carbon dioxide salts, as well as in the washed sandy–gravelly soils of the Zarafshan River floodplain. On the basis of biogeochemical zoning, differentiated norms of mineral nutrition of animals are proposed. Zinc deficiency was found in almost all animal studies(98%), copper-in almost 90% of animals, and low levels of manganese in 81% of animals. In the farms of the lowland part of the region, animals are deficient, first of all, in copper and zinc, and in the mountain – foothill part – in zinc and manganese. The analysis of organs and tissues and the study of the balance of trace elements revealed a deficiency in the body of animals of manganese, diagnosed by the content of this element in the wool. The lack of manganese is caused by the low level of this element in the feed of local production, the excess of iron in the diet, and the increased acidity of the feed. Manganese deficiency causes a specific pathology of the musculoskeletal system, enhanced by the state of hypodynamics in animals. Recommended measures to prevent the observed pathology.

Based on the analysis of trace elements in environmental objects and the wool of sheep, cattle, goats, etc., characteristic clinical signs in the territory of Uzbekistan identified subregions of the biosphere, endemic disorders of mineral metabolism in farm animals – endemic goiter in sheep and goats, parakeets and osteochondrodystrophy cattle, copper deficiency in sheep and proposed evidence – based recommendations for their prevention.

For balanced mineral nutrition of animals, the use of bentonite from the Azkamar deposit is proposed. Its physical and chemical properties have been studied. Bentonite is characterized by a suspended content of sodium, copper, manganese, and zinc with a low level of lead, etc. toxic elements. The high content of sodium contributes to its ion exchange of calcium, the excess of which in the feed of Uzbekistan reduces the availability of trace elements for the animal body. Research and production experiments on the use of bentonite in an amount of 3-4 % of the diet showed its positive effect on productivity, growth, and development.

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