ARTICLES

PHYSICAL AND CHEMICAL ANALYSIS OF THE SYSTEM OF LANTHANUM NITRATE – NICOTINAMIDE – WATER 25 °C

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This article reflects the results of our systematic studies of the processes of complexation of rare-earth metal salts with nicotinic acid amide in order to obtain bioactive substances. Nicotinamide, in the molecule of which there are three coordination-active centers capable of forming bonds with metals – complexing agents, attracts the attention of inorganic chemists as a ligand. The scientific novelty lies in the fact that for the first time a physicochemical study of the interaction of nicotinamide with lanthanum nitrate in an aqueous solution at 25 °C by the solubility method was carried out. As a result of studying the ternary system, the formation of a new solid phase of the composition $La(NO_3)_3$ • 2C6H6N2O • 2H2O was established, which was isolated from a saturated aqueous solution in a crystalline form and identified by methods of physicochemical analysis. IR spectroscopic studies show that nicotinamide molecules are coordinated with lanthanum ions through the oxygen atoms of the carbonyl group. Analysis of the X-ray diffraction pattern of the complex confirms the individuality of the crystal lattice of the new compound and allows it to be attributed to the rhombic system. Based on the data of IR spectroscopic and X-ray phase analyzes, it was found that in the complex compound La(NO3) 3 • 2C6H6N2O • 2H2O, one molecule of the NO3 group is in the outer coordination sphere, and the other two molecules of the NO3 group, two molecules of water and two molecules nicotinamide form a coordination bond with a complexing agent – the La^{3+} ion.

Keywords: lanthanum nitrate, nicotinamide, physicochemical analysis, complexing agent, ligand coordination

The synthesis and study of the physicochemical properties of complex compounds of rare earth elements with heterocyclic compounds is a promising direction in the chemistry of coordination compounds [1, 2].

Earlier, we [3] performed work on the synthesis of complex compounds of chlorides of a number of lanthanides (Ln = La3 +, Nd3 +, Pr3 +, Sm3 +, Gd3 +, Dy3 +, Er3 +) with nicotinamide.

Experimental part

A physicochemical study of the interaction of lanthanum nitrate with nicotinamide was carried out in an aqueous medium by the isothermal solubility method at 25 °C. The concentration of lanthanum ions and the presence of nicotinamide nitrogen were determined by traditional methods [4, 5].

$La(NO_3)_3$-$C_6H_6N_2O$-H_2O system at 25 °C

According to the results of the experimental data of the study of the system lanthanum nitrate – nicotinamide – water, a solubility diagram was constructed (table 1, fig. 1), consisting of three crystallization branches.

The first branch of crystallization corresponds to the separation of lanthanum hexahydrate nitrate into the solid phase. The solubility of lanthanum nitrate at 25 °C is 58.78 %.

Upon reaching the concentration of lanthanum nitrate – 57.10 %, nicotinic acid amide – 14.23 %, water – 28.67 %, a new compound congruently soluble in water (the second crystallization branch) of the composition 1: 2: 2 ($La(NO_3)_3$:$C_6H_6N_2O$:H_2O). The next branch (the third branch) corresponds to the crystallization of pure nicotinamide.

By the nature of the diagram of the ternary system $La(NO_3)_3$-$C_6H_6N_2O$-H_2O at 25 °C, one can judge that complexation occurs between the reacting components, that is, the formation of one compound corresponding to the gross formula La (NO3) 3 • 2C6H6N2O • 2H2O.

To determine the pycnometric density of crystals of the obtained compound, the solubility of the complex in organic solvents has been studied.

From the obtained experimental data, it can be seen that the compound under study is soluble in alcohol, acetone, ether and practically insoluble in benzene. Using an indifferent liquid (benzene), the density of solid phases was determined by the pycnometric method (d = 1,46 g/см^3).

In order to identify a new compound, to clarify the nature of the chemical bond in the complex, IR absorption spectra of nicotinamide and its coordination compound with lanthanum nitrate in the range of 400-4000 cm-1 were investigated on a Nicolet-IR-1200 spectrometer in the form of tablets with potassium bromide (fig. 2, 3). The values of the characteristic frequencies in the IR absorption spectrum are given in table 2.

In the IR absorption spectrum of the nicotinamide complex of lanthanum nitrate, a shift of the stretching vibration ν (C = O) to the low-frequency region from 1682 cm-1 to 1656 cm-1 is observed, and the stretching vibrations of the displacement ring do not experience. The absorption bands related to stretching vibrations ν (C-N) are shifted towards higher frequencies from 1340 cm-1 to 1384 cm-1, which indicates an increase in the multiplicity of the C-N bond and a weakening of the C = O bond.

Table 1

Experimental data on solubility in the system $La(NO_3)_3$-$C_6H_6N_2O$-H_2O at 25 °C

№	Liquid phase, in mass %		Solid phase, in mass %		Crystallizing phase
	$La(NO_3)_3$	$C_6H_6N_2O$	$La(NO_3)_3$	$C_6H_6N_2O$	
1	58,78	-	75,05	-	$La(NO_3)_3 \cdot 6H_2O$
2	56,41	5,21	69,22	1,81	
3	56,17	8,83	70,01	2,32	
4	57,08	14,22	68,81	5,08	
5	57,10	14,23	77,75	15,85	$La(NO_3)_3 \cdot 6H_2O + La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$
6	57,10	14,23	54,45	34,45	$La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$
7	50,63	13,01	52,88	31,90	
8	45,11	12,17	50,95	30,93	
9	29,90	13,85	45,32	30,85	
10	24,20	17,49	44,38	33,18	
11	21,85	19,73	45,46	34,92	
12	19,31	23,22	46,72	36,75	
13	18,10	25,11	42,40	35,45	
14	17,02	27,65	40,90	35,91	
15	16,02	30,61	42,38	37,08	
16	14,10	44,98	44,93	39,90	
17	14,09	45,01	47,93	40,95	
18	14,07	45,01	42,01	53,01	$La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O + C_6H_6N_2O$
19	14,09	45,01	24,01	66,96	
20	14,08	45,35	4,24	82,91	$C_6H_6N_2O$
21	11,89	44,43	3,98	81,04	
22	7,93	43,81	2,21	83,95	
23	2,89	44,38	1,02	82,05	
24	-	45,65	-	-	

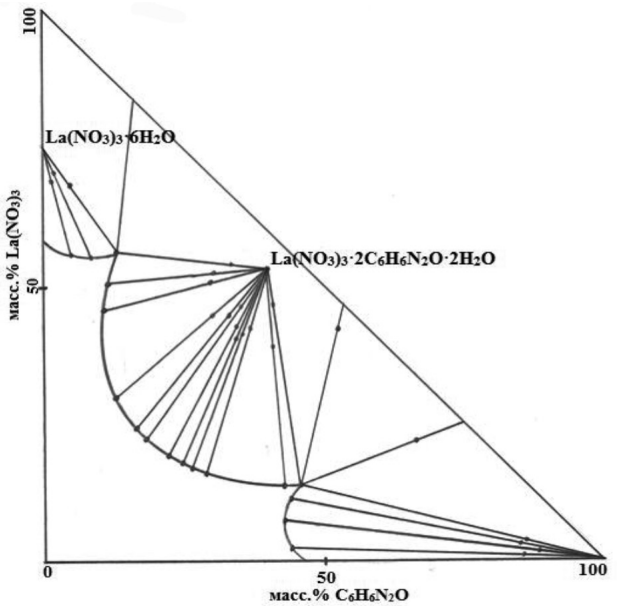

Fig. 1. Solubility isotherm of the $La(NO_3)_3$-$C_6H_6N_2O$-H_2O system at 25 °C

Table 2

Solubility of nicotinamide and a complex compound in organic solvents, wt %

Connections	In alcohol	in acetone	on air	in benzene	d (g/см³)
$C_6H_6N_2O$	21,43	14,61	1,62	н.р	1,38 ± 0,04
$La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$	14,77	8,12	1,96	н.р.	1,46 ± 0,03

The bands of bending vibrations of the δ (NH2) -group are slightly shifted towards low frequencies from 1619 cm-1 to 1615 cm-1, which is explained by the strengthening of the C-N bond. In the 1600-1700 cm-1 region, the δ (H2O) bands appear, overlapping with the intense ν (CO) and ν (NH) bands.

Such changes in the positions of the bands "amide 1" and amide 2 "suggest the coordination of nicotinic acid amide to lanthanum ions through the oxygen atoms of the carbonyl group.

In the region of stretching vibrations ν (N-H), a broad spectrum is observed in the spectrum of the complex.

Band with indistinct maxima at 3349, 3077 cm-1, which is associated with overlapping valence bands ν (OH) and ν (N-H), indicating the hydration of the compound.

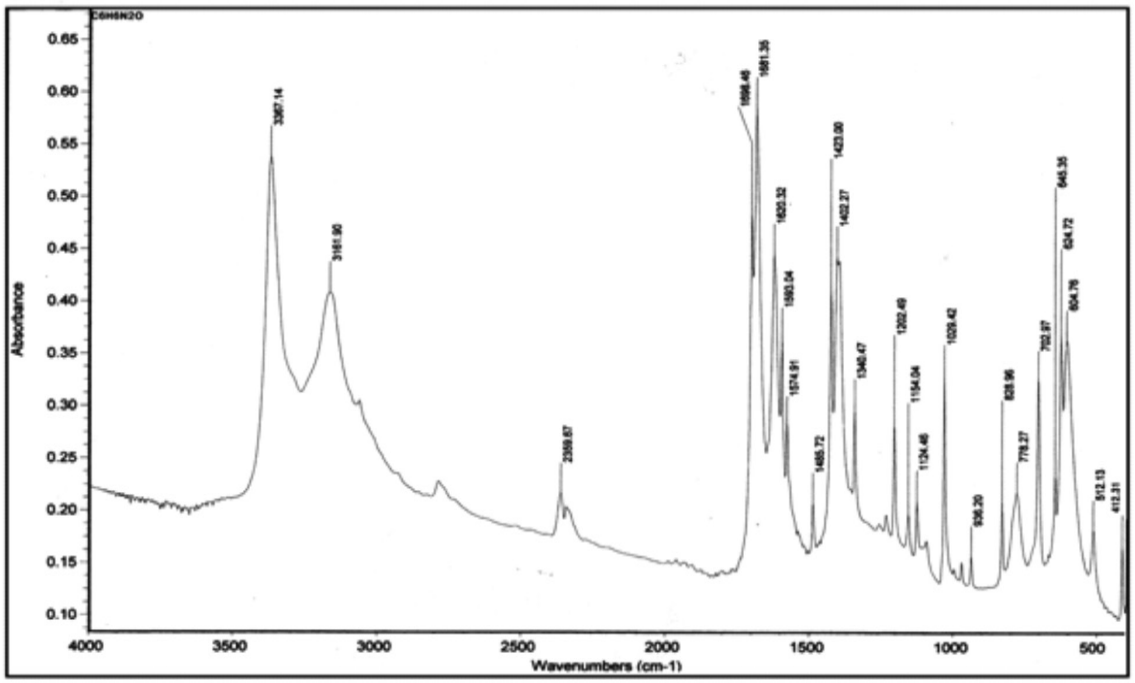

Fig. 2. IR absorption spectrum of nicotinamide

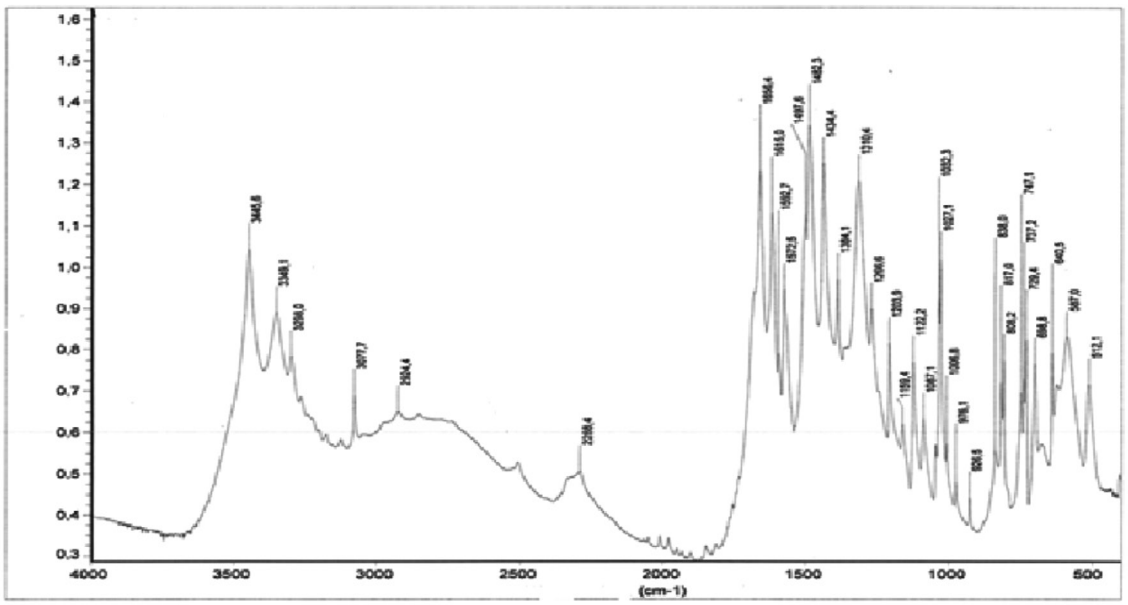

Fig. 3. IR absorption spectrum of the complex $La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$

Table 3

Experimentally obtained frequencies of stretching and bending vibrations of nicotinic acid amide and the newly obtained compound

Assignment	$C_6H_6N_2O$	$La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$
$\nu_{as}(NH_2)$, $\nu(OH^-)$	3367	3349
$\nu_s(NH_2)$	3164	3077
ν(C=O)	1682	1656
$\delta(NH_2)$, $\delta(H_2O)$	1619	1615
ν (pyridine ring)	1593 1574	1593 1572
ν(pyridine ring), δ (CCH)	1485	1482
ν (CN)	1340	1384
δ (CCH)	1202	1204
ν (pyridine ring)	1029	1027
ν(CC), δ (CCC)	829	838
δ (CCN), δ(CO)	703	699

Based on the data obtained, the complex compound of lanthanum with nicotinic acid amide can be assigned the following structure:

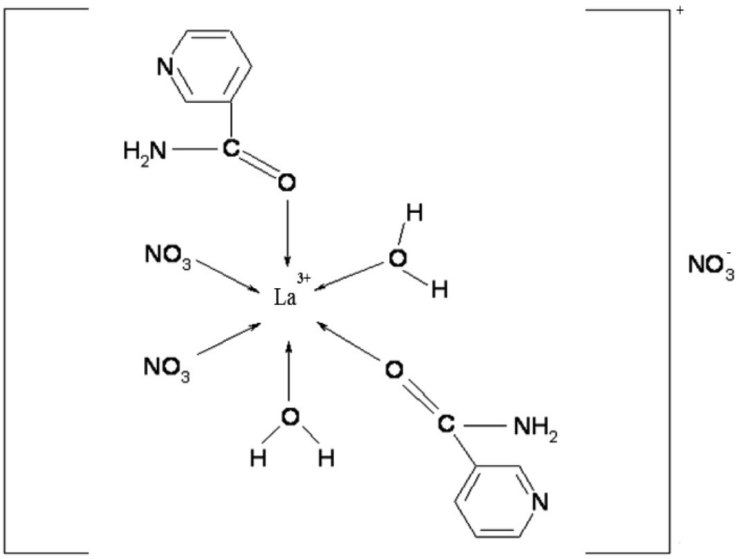

Fig. 4. Scheme of the structure of the complex compound $La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$

Thus, the analysis of the IR spectra of nicotinamide and the new complex compound showed that the nicotinamide molecules in this complex act as a monodentate ligand, coordinating through the oxygen atoms of the carbonyl group of nicotinic acid amide.

In order to obtain information about the crystal structure of the obtained complex, an X-ray study of the compound of lanthanum with nicotinic acid amide was carried out on a DRON-3.0 diffractometer (CoK_α radiation, with a filter). The results are shown in Fig. 5, 6, tabl. 4, 5.

The X-ray diffraction pattern of the complex contains new lines characteristic of the compound, and the lines of the initial components are absent.

By indicating the main parameters of the diffractogram, we obtained the following unit cell parameters: a = 8.805; b = 8.980; c = 11.279 and we assume that the crystal lattice of the test sample is assigned to the rhombic system.

Table 4

X-ray analysis of nicotinamide $C_6H_6N_2O$

2θ	H	Θ	I%	d(A^0)	H	k	L	Syngonia
16,80	132	8,40	94	6,1274	0	0	1	Monoclinic a = 7,051 b = 11,338 c= 6,551 β = 110^0
22,72	68	11,36	48,5	4,5443	0	2	1	
25,53	140	12,76	100	4,0527	0	2	1	
27,40	17	13,70	12	3,7794	0	3	0	
28,70	33	14,35	23	3,6116	1	1	1	
29,80	101	14,90	72	3,4811	1	1	1	
31,50	89	15,75	63	3,2976	2	0	0	
34,90	31	17,45	22	2,9849	0	4	0	
37,75	12	18,87	8	2,7676	0	2	2	
39	23	19,50	16	2,6815	0	4	1	
39,85	27	19,92	19	2,6272	0	4	1	
41,55	22	20,77	16	2,5341	2	1	1	
42,93	62	21,46	44	2,4466	2	1	1	
44,95	36	22,47	26	2,3420	1	1	2	
47,70	26,5	23,85	19	2,21372	1	2	2	
55,65	17	27,82	12	2,01796	0	0	3	
59,28	19	29,64	13	1,80994	3	0	1	

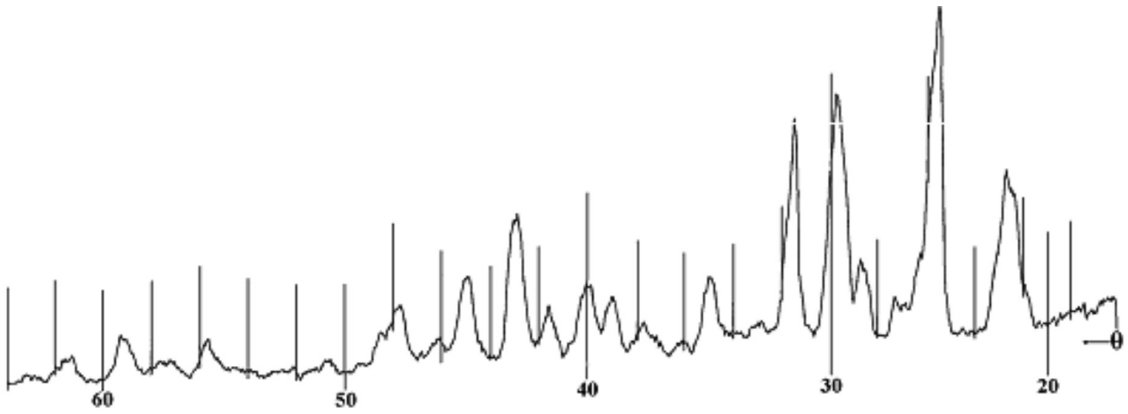

Fig 5. X-ray of nicotinamide $C_6H_6N_2O$

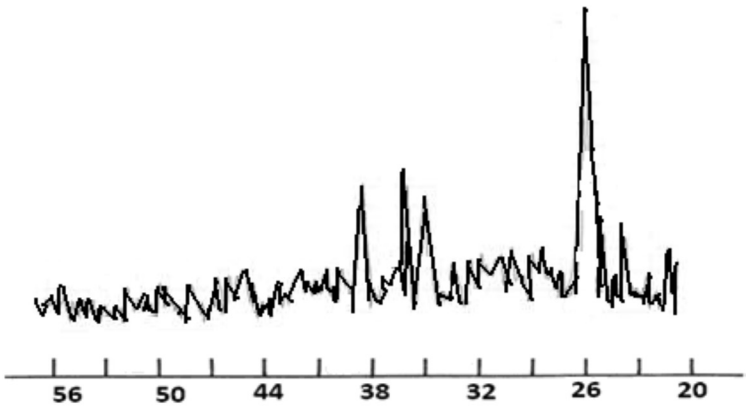

Fig. 6. X-ray diffraction pattern of a complex compound $La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$

Table 5

X-ray analysis $La(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$

№	2Θ	H	Θ	I(%)	D(Å)	h	k	l	Syngonia
1	9,1	41	4,55	100	11,2791	0	0	1	Rhombic
2	11,43	34	5,72	82	8,9859	0	1	0	a = 8,805
3	11,66	20	5,83	48	8,8091	1	0	0	b = 8,980
4	14,66	30	7,33	73	7,0141	1	1	1	c = 11,279
5	15,13	36	7,57	87,8	6,7983	0	0	2	
6	16,80	14	8,40	34,14	6,1259	0	2	0	
7	16,96	14	8,48	34,14	6,0698	2	0	0	
8	17,63	9	8,82	21,95	5,8401	2	2	2	
9	18,16	8	9,08	19,50	5,6717	2	3	1	
10	19,91	10	9,96	24,39	5,1779	0	0	3	
11	21,61	11	10,81	26,82	4,7746	3	0	3	
12	22,10	13	11,05	31,70	4,6699	3	0	0	
13	22,41	8	11,21	19,50	4,6063	3	3	3	
14	23,55	7	11,78	17,07	4,3862	3	1	2	
15	23,83	12	11,92	29,26	4,3352	0	0	4	
16	24,16	10	12,08	24,39	4,2762	0	4	0	
17	25,83	8	12,92	19,50	4,0045	4	0	0	
18	26,66	11	13,33	26,82	3,8820	4	4	4	
19	27,16	10	13,58	24,39	3,8118	4	0	4	
20	27,100	23	13,55	56,09	3,8199	4	1	2	
21	29,16	15	14,58	36,58	3,5551	4	3	2	
22	30,100	12	15,05	29,26	3,4469	0	0	5	
23	31,16	12	15,58	29.26	3,3321	5	0	5	
24	31,80	9	15,90	21,95	3,2670	5	0	0	
25	33,25	4	16,63	9,75	3,1283	0	5	0	
26	33,58	5	16,79	12,19	3,0985	5	5	5	
27	33,100	10	16,55	24,39	3,1420	1	2	3	
28	35,83	5	17,92	12,19	2,9096	4	4	4	
29	36,33	7	18,17	17,07	2,8709	5	3	4	
30	37,50	6	18,75	14,63	2,7843	0	0	6	
31	37,83	5	18,92	12,19	2,7610	0	6	0	
32	38,50	6	19,25	14,63	2,7146	6	0	0	
33	39,30	6	19,65	14,63	2,6617	6	1	6	
34	39,60	5	19,80	12,19	2,6421	6	2	3	
35	41,16	6	20,58	14,63	2,5462	6	0	6	

Conclusions

1. When studying a water-salt system containing nicotinamide and lanthanum nitrate, one complex compound La $(NO_3)_3 \cdot 2C_6H_6N_2O \cdot 2H_2O$ was obtained.

2. The novelty of the synthesized compound was proved by pycnometry, IR spectroscopy and X-ray analysis.

3. It was found that nicotinamide in a complex with lanthanum nitrate is coordinated monodentately through the oxygen atom of the carbonyl group, and the structure of the complex is proposed.

References

1. Kiselev Yu.M. Chemistry of coordination compounds / Yu.M. Kiselev., N.A. Dobrynina M.: Academy, 2007. P. 320–323.

2. Kindu M.F. Synthesis and study of the coordination compounds of REE (III) with some nitrogen-containing ligands and salicylic acid: author. dis. ... Cand. chemical sciences: 02.00.01 / M.F. Kindu. Moscow, 2012. 21 p.

3. Osmonova S.S. On the method of coordination of nicotinamide molecules in the complexes of rare earth elements / S.S. Osmonova, K.S. Sulaimankulov, T.B. Baydinov, N.O. Orozbaeva // Science and new technologies. 2013. № 4. P. 131–134.

4. Ivanov, V.M. Application of sodium ethylenediaminetetraacetate in chemical analysis / V.M. Ivanov, T.F. Rudometkina; Moscow. state un-t them. M.V. Lomonosov. Moscow, 2019. P. 19–21.

5. Sauer E.A. Modern analyzers for the determination of nitrogen by the Kjeldahl method / E.A. Sauer // Analytics and control. 2019. T. 23. № 2. P. 168–192.