ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 9, Issue 11 , November 2022

Obtaining of Potassium Sulfate from Flotation Potassium Chloride and Ammonium Sulfate

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ABSTRACT: The results of studies on the production of potassium sulfate by the conversion of flotation potassium chloride of the Tubegatan deposit with ammonium sulfate are presented. The effect of S:L on the formation of a double salt and potassium sulfate at a temperature of 25°C, the duration of the process of 60 minutes was studied. Optimal technological parameters for the separation of double salt and potassium sulfate have been established. The individuality and purity of the synthesized substances have been established by X-ray and scanning electron microscope methods.

I. INTRODUCTION

Recently, with the cultivation of vegetables by hydroponics and drip irrigation, the demand for chlorine-free potash fertilizers, which include potassium sulfate, potassium nitrate, potassium phosphates, potassium-magnesium concentrate, has greatly increased. One of the main and most effective forms of chlorine-free potash fertilizers is potassium sulfate, which is determined by the high content of the useful component in terms of K_2O (48-50%), as well as the presence of the SO_4^{2-} ion, which provides sulfur nutrition to plants. The use of potassium sulfate is useful due to a reduction in the consumption of sulfate-containing nitrogen and phosphorus fertilizers, displaced by more concentrated sulfate-free forms [1-3].

II. LITERATURE SURVEY

There are numerous ways to produce potassium sulfate using potassium chloride as a raw material, natural sulfate-type minerals, as well as various sulfate-containing chemical products [4-6].

Most often, potash sulfate fertilizers are obtained from natural raw materials – potash sulfate ores by the galurgies method. Another promising method for obtaining potassium sulfate is conversion – by the interaction of potassium chloride and a sulfate-containing reagent [7, 8].

Uzbekistan has large natural reserves of raw materials for the production of potassium sulfate, which can be used as potassium chloride of JSC "Dehkanabad Potash Plant", obtained from silvinite of the Tubegatan deposit, mirabilite of the Tumruk deposit, sodium or ammonium sulfates [8-11]. However, to date, the Republic has not developed acceptable, continuous technologies for obtaining potassium sulfate from the above local raw materials, while the Republic's need for chlorine-free potash fertilizers exceeds 100 thousand tons per year.

Proceeding from this, an urgent task for the Republic is the development of a continuous technology for obtaining potassium sulfate by conversion of potassium chloride with ammonium sulfate. The chemistry of the process consists in the exchange reaction of potassium chloride and ammonium sulfate to form a double salt

$$2KCl + 2(NH_4)_2SO_4 = K_2SO_4 \bullet (NH_4)_2SO_4 + 2NH_4Cl$$

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
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and the interaction of a double salt solution with potassium chloride

$$K_2SO_4{\bullet}(NH_4)_2SO_4 + 2KCl = 2K_2SO_4 + 2NH_4Cl$$

In connection with the above, science and producers of the republic face an urgent task - the development of a continuous, effective technology for producing potassium sulfate based on the available raw materials of Uzbekistan, the solution of which will meet the needs of the domestic market in chlorine-free potash fertilizers and increase the export potential of the republic.

The existing methods of obtaining potassium sulfate suffer from multi-stage, complexity of the technological scheme, high energy costs, the formation of by-products of little-used products and cause the high cost of the resulting products. The development of an optimal, cost-effective, waste-free, continuous technology for the production of potassium sulfate is an urgent problem for the republic.

The most acceptable way to obtain potassium sulfate for the conditions of the republic is the conversion method, since in this case potassium chloride from the Tubegatan deposit can be used, and sodium or ammonium sulfates, which are produced on an industrial scale, can be used as a sulfate component.

III. RESEARCH METHODS

Research on the conversion of potassium chloride with ammonium sulfate were carried out using flotation potassium chloride of JSC "Dehkanabad Potash Plant" composition (mass. %): KCl - 95.3; NaCl - 2.97; u.p. - 1.1; H_2O - 0.43 in a laboratory installation consisting of a glass reactor equipped with a stirrer and placed in a thermostat.

A saturated (39.1%) solution of ammonium sulfate, a saturated solution of potassium chloride (26.8%) and a solution containing 10% potassium chloride were used to obtain potassium sulfate from the flotation potassium chloride of the Tubegatan deposit and ammonium sulfate by conversion. The conversion process was carried out at 25°C and the duration of the process was 40-60 minutes by introducing a saturated solution of ammonium sulfate into a saturated solution of potassium chloride to a molar ratio of components equal to 1:1. S:L at the conversion stage was supported by the introduction of an additional amount of potassium sulfate or saturated solution. After a predetermined time, the liquid and solid phases were separated by filtration.

To identify the phase composition of intermediates and finished products in addition to chemical [12-15] and physico-chemical (X-ray phase and scanning electron microscopic methods) analysis [16, 17].

X-ray images of the samples were taken on a computer-controlled XRD-6100 (Shimadzu, Japan) [16]. At the same time, CuKa radiation (β-filter, Ni, 1.54178 tube current and voltage mode 30 mA, 30 kV) and a constant detector rotation speed of 4 degrees/min with a step of 0.02 degrees were used. (ω/2θ-coupling), and the scanning angle varied from 4 to 80o.

The surface morphology and microstructure of the samples were studied using a scanning electron microscope SEM - EVO MA 10 (Carl Zeiss, Germany) with an X-ray spectrometer Aztec Energy Advanced X–Act-Oxford Instruments [17]. Experiments on a scanning electron microscope were carried out as follows. To carry out the sample preparation process, a holder made of a metal alloy was installed on the microscope slide table, on top of which an aluminum foil with a double-sided adhesive surface was glued. The test sample was applied to this foil. Next, the slide table was installed in the working chamber of the microscope, from which air was pumped out to create a vacuum. To carry out the measurement, an accelerating voltage of 12 kV was applied to the filament, with the working distance being 8.5 mm. The images were obtained at scales from 50 microns.

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IV. EXPERIMENTAL RESULTS

The technology for producing potassium sulfate consists of two stages. At the first stage, potassium chloride was converted with ammonium sulfate to obtain a double salt, and at the second stage, potassium sulfate was obtained by dissolving the double salt in water and introducing 10% potassium chloride, after filtration, 10-12% potassium sulfate solution was washed.
To obtain a double salt, crystalline potassium chloride was injected into the ammonium sulfate solution to a given molar ratio of $KCl:(NH_4)_2SO_4$. Separation of the solid and liquid phases was carried out on a filter unit at a discharge of 300 mm Hg. The area of the filter surface of the funnel is 0.005 m^2. The data obtained are shown in tables 1 and 2.

Table 1. Effect of S:L on the chemical composition of the solid phase of the conversion process of flotation potassium chloride with ammonium sulfate

S:L	Composition of the solid phase, wt. %			
	K_2O	NH_4^+	Cl^-	SO_4^{2-}
1:1,2	40,91	7,37	7,78	50,91
1:1,5	44,93	4,24	6,68	50,12
1:1,7	50,96	2,16	5,94	49,60
1:2,0	51,20	1,95	5,80	49,65

As can be seen from table 1, with an increase in the proportion of the liquid phase from 1:1.2 to 1:2, the K_2O content in the solid phase increases from 40.91 to 51.20%, and the remaining components decrease. Thus, the content of NH_4^+ decreases from 7.37 to 1.95%, chlorine from 7.78 to 5.80%, SO_4^{2-} from 50.91 to 49.65%.

Table 2. Effect of S:L on the chemical composition of the liquid phase of the conversion process of flotation potassium chloride with ammonium sulfate

S:L	Composition of the solid phase, wt. %			
	K_2O	NH_4^+	Cl^-	SO_4^{2-}
1:1,2	12,93	3,722	15,998	1,50
1:1,5	13,32	2,97	15,11	1,28
1:1,7	13,90	2,473	14,516	1,14
1:2,0	15,20	1,522	13,795	0,93

The resulting double salt $K_2SO_4 \bullet (NH_4)_2SO_4$ is contaminated with the initial components, as evidenced by the presence of ammonium and chlorine ions in the solid phase.

With an increase in S:L from 1.2 to 2:1, we can see that the composition of the liquid phase changes slightly, as shown in table 2. Thus, the K_2O content increases from 12.93 to 15.20%, the content of the remaining components decreases. The results obtained indicate that the technologically acceptable ratio S:L is 1:(1,2 to 2). The resulting double salt thus contains (wt. %): K_2O - 40.91-51.20; SO_4^{2-} - 50,10-49,65 ; NH_4^+ - 7,37-1,95 ; Cl^- - 7,78-5,8.

Next, a 10% solution of potassium chloride was injected into the double salt solution, taken in an amount that provides S:L in the initial suspension (1,2÷2):1, was kept at a temperature of 25-30^{o}C for 30 minutes. The suspension was separated on a filter and the filtered solid phase was treated with a 10-12% solution of potassium sulfate and dried.

To check the obtained double salt and potassium sulfate, X-rays were taken (fig. 1 and 2). When removing the sample, a rotating camera was used, where the rotation speed is 30 vol./min. The transcription of X-ray was carried out using the database of the American card file "The American Mineralogist crystal structure database" and the radiometric

ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

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determinant of minerals by Mikheev. The X-ray image shows only diffraction maxima characteristic of a double salt ($K_2SO_4 \cdot (NH_4)_2SO_4$) with interplane distances of 4.33; 3.85; 3.12 Å $K_2SO_4 \cdot (NH_4)_2SO_4$.

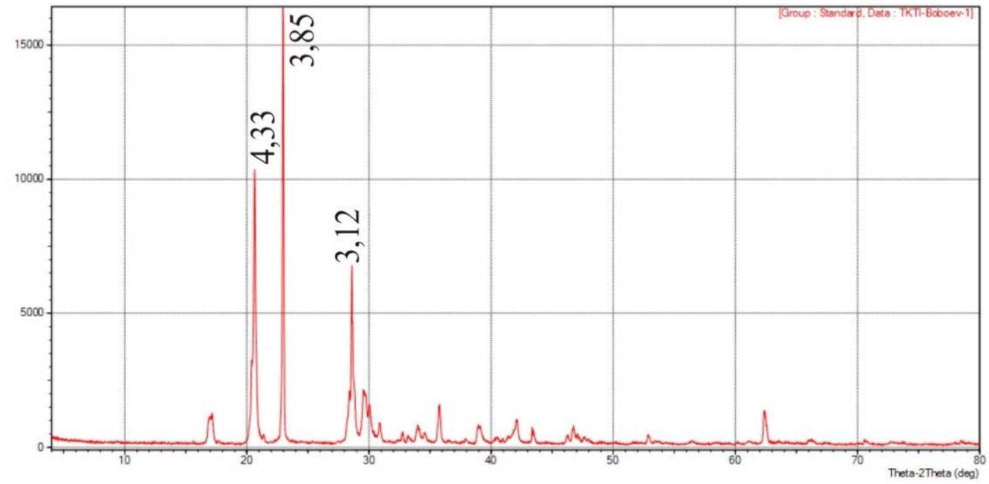

Fig. 1. X-ray of a double salt ($K_2SO_4 \cdot (NH_4)_2SO_4$) in the filtrate

The X-ray image shows only diffraction maxima characteristic of potassium sulfate with interplane distances of 3.14 Å K_2SO_4.

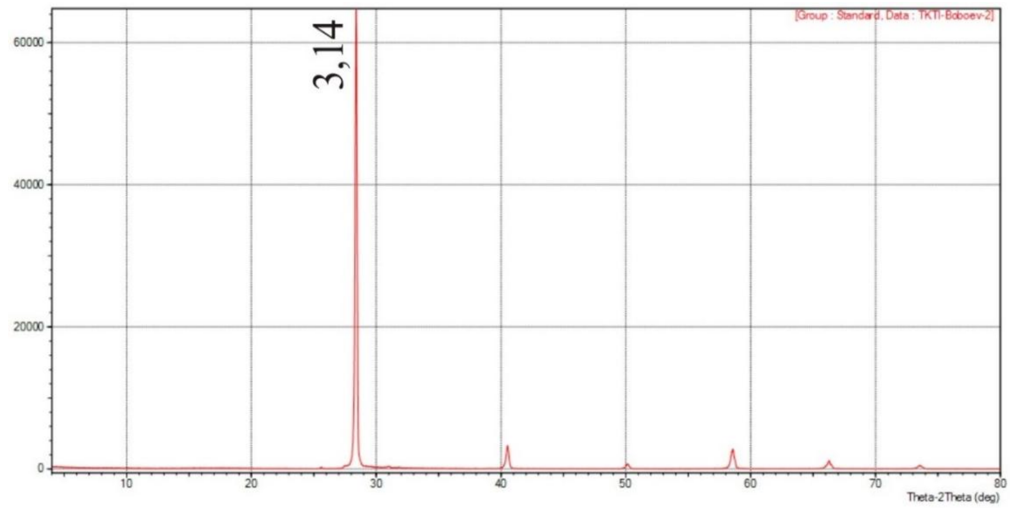

Fig. 2. X-ray of potassium sulfate washing

Electron microscopic analysis of the double salt ($K_2SO_4 \cdot (NH_4)_2SO_4$), the results of elemental chemical analysis are shown in figure 3. Energy dispersion analysis of the double salt showed the following element content: N-1.25%; O-37.13%, S-18.60%; Cl-0.68%; K-42.34%.

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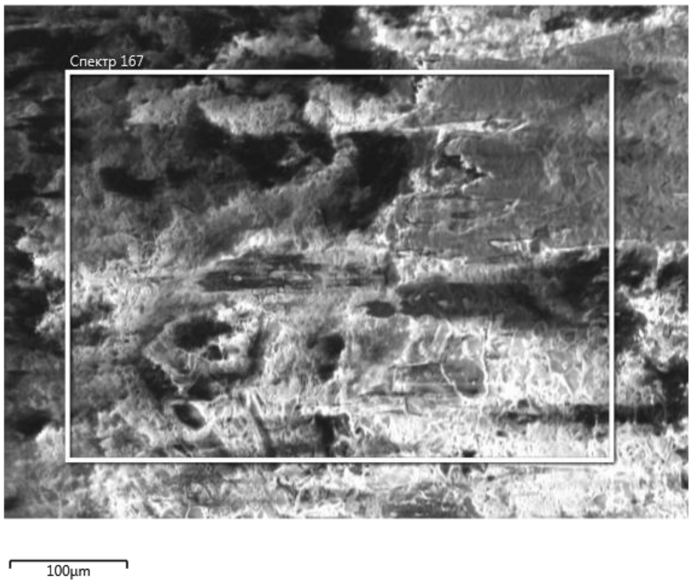
Электронное изображение 233



Element	Weight.%	Sigma Weight.%
N	1.25	0.54
O	37.13	0.24
S	18.60	0.18
Cl	0.68	0.08
K	42.34	0.26
The amount:	100.00	

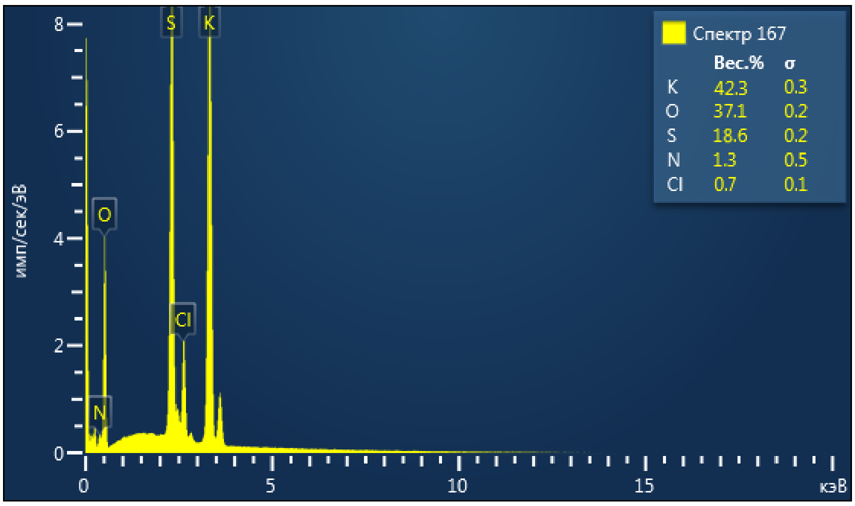


Fig. 3 - Energy dispersion spectrum and quantitative composition of double salt elements on a scanning electron microscope

Electron microscopic analysis of potassium sulfate washing using a 10-12% solution of potassium sulfate, the results of elemental chemical analysis are shown in figure 4. The energy dispersion analysis of potassium sulfate showed the

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
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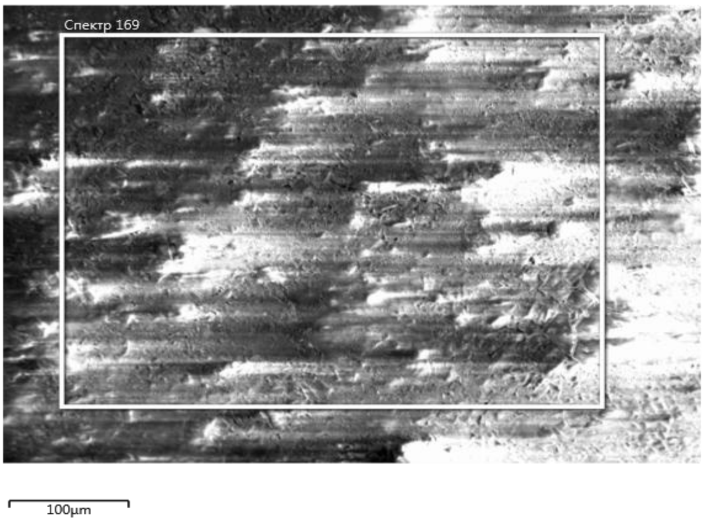
following content of elements: N-0.08%; O-36.72%, S-18.33%; Cl-0.18%; K-44.69%, which corresponds to the requirement for potassium sulfate.

Электронное изображение 235



Element	Weight.%	Sigma Weight.%
N	0.08	0.06
O	36.72	0.26
S	18.33	0.17
Cl	0.18	0.09
K	44.69	0.23
The amount:	100.00	

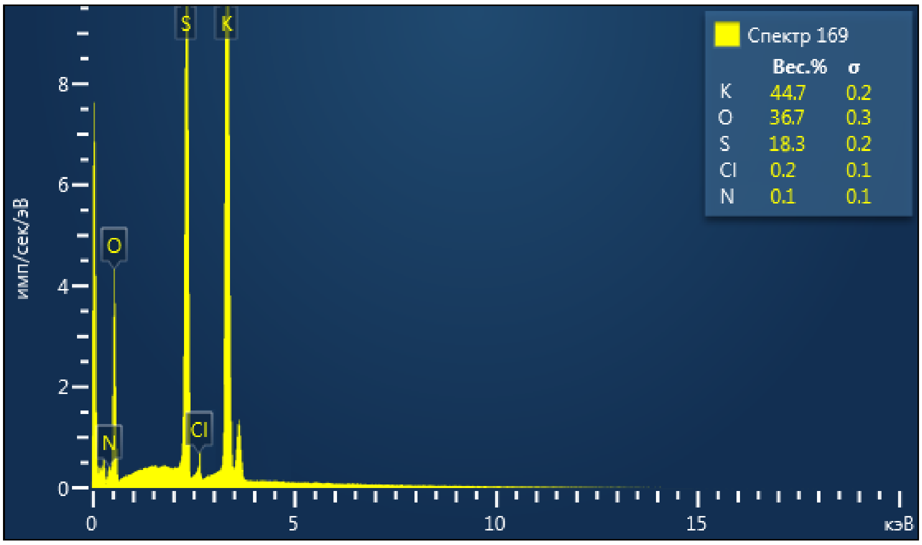


Fig. 4 - Energy dispersion spectrum and quantitative composition of potassium sulfate elements on a scanning electron microscope

Thus, the possibility of obtaining potassium sulfate has been experimentally established, optimal parameters of all stages of the process have been determined, and its physico-chemical properties have been clarified.

V. CONCLUSION

Thus, the conducted studies have shown the possibility of obtaining potassium sulfate from the flotation potassium chloride of the Tubegatan deposit by conversion with ammonium sulfate. To do this, a saturated solution of ammonium sulfate is injected into purified, saturated solutions of potassium chloride to a molar ratio of components equal to 1:1 at a temperature of 25°C, stirred for 60 minutes, the double salt $K_2SO_4{\cdot}(NH_4)_2SO_4$ is separated and dissolved in a 10% solution of potassium chloride at a temperature of S:L = 1:1. The precipitate of potassium sulfate is filtered and dried. The suspension was separated on a filter and the solid phase was washed with a 10-12% solution of potassium sulfate and dried. The physicochemical characteristics of the double salt and potassium sulfate were studied by methods of physico-chemical analysis using X-ray and scanning electron microscopy.

REFERENCES

[1]. Dormeshkin O.B., Novik D.M., Shatilo V.I. Universal technology for producing chlorine-free, water-soluble complex fertilizers based on technical products. Minsk, 2018, no. 4. pp. 163-172.

[2]. Vorobev N.Ch., Dormeshkin O.B., Shatilo V.I. Obtaining chlorine-free, water-soluble NPK fertilizers by conversion method. News of the National Academy of Sciences Belarus. 2004. no. 1. pp. 96-101.

[3]. Grabovenko V.A. Manufacture of chlorine-free potash fertilizers. Leningrad: Chemistry, 1980. 256 p.

[4]. Boboev A.H., Samadiy M.A., Usmanov I.I., Mirzakulov Kh.Ch. Research of the process of processing glazerite for potassium sulfate. // Universum: Technical Sciences: electron. scientific. Journal 2019, no. 1 (58). URL:http://7universum.com/ru/tech/ archive/item/6834.

[5]. Patent. 2235065 (RF). A method for obtaining potassium sulfate from potash and sodium sulfate. Kurt Holdengraber. Publ. 2004. Bul. no. 24.

[6]. Patent. 102005045055 (Germany). A method for producing potassium sulfate from potassium chloride and sulfuric acid without the formation of hydrogen chloride. You Jurgen, Kaps Stephan, Schtrzberg Heinz. Vol. 2007.

[7]. Patent. 2205795 (RF). Method of obtaining potassium sulfate. Yu.S. Safrygin, G.V. Osipov, V.I. Timofeev, A.V. Balakhnichev. Publ. 2003. Bul. no. 28.

[8]. Bobokulova O.S., Usmanov I.I., Mirzakulov Kh.Ch. Salts of lakes Karaumbet and Barsakelmes - raw materials for the obtaining of magnesium salts. Journal "Chemistry and Chemical Technology". Tashkent, 2014, no. 1. pp. 11-17.

[9]. Patent. IAP 04526. A method for processing natural brines containing sodium and magnesium chlorides and sulfates / Turobjonov S.M., Mirzakulov Kh.Ch., Asamov D.D., Khalmuminov S.A., Kuznetsova Zh.N., Bardin S.V., Tojiev R.R., Bobokulova O.S., Juraeva G.Kh. Publ. 2012. Bul. no. 7.

[10]. Patent. IAP 05794. Method for obtaining sodium sulfate. Mirzakulov Kh.Ch., Usmanov I.I., Bobokulova O.S., Melikulova G.E., Shamshidinov I.T. Publ. 2019. Bul. no. 4.

[11]. Bobokulova O.S. Development of technology for processing raw materials of lakes Karaumbet and Barsakelmes for hydroxide, magnesium oxide and sodium sulfate. Diss. ... Candidate of Technical Sciences, Tashkent, 2018. 113 p.

[12]. Burriel - Marty F., Ramirez - Munoz X. Flame photometry. - M.: "Mir", 1972, 520 p.

[13]. Methods for the analysis of brines and salts / Under. ed. Morachevsky Yu.V. and Petrova E.M. - M.: Chemistry. 1965. 404 p.

[14]. Kreshkov A.P. Fundamentals of analytical chemistry. V.2. Quantitative analysis. - M.: Chemistry, 1965. - 376 p.

[15]. Kelman F.N., Brutskus E.B., Osherovich R.I. Methods of analysis in the control of production of sulfuric acid and phosphate fertilizers. - M.: Goshimizdat, 1982. 352 p.

[16]. Miller F.A., Mayo D.W. Course notes on the interpretation of infrared and Raman spectra. - Hoboken, New Jersey: John Wiley, 2003. 567 p.

[17]. Kalmykov K.B., Dmitrieva N.E. Scanning electron microscopy and X-ray spectral analysis of inorganic materials // Moscow, 2017. 52 p.