

# Studying the composition of complex mineral fertilizers and inorganic salts in accordance with international REACH requirements

**O Dormeshkin<sup>1,\*</sup>, A Hauryliuk<sup>1</sup>, N Muminov<sup>1,2</sup>, and B Khoshimov<sup>2</sup>**

<sup>1</sup>Belarusian State Technological University, Svyardlova, 13A, Minsk, 220006 Belarus

<sup>2</sup>Tashkent Chemical-Technological Institute, Navoi Road, 32, 100069, Uzbekistan

\*E-mail: [dormeshkin@yandex.ru](mailto:dormeshkin@yandex.ru)

**Abstract.** The qualitative and quantitative composition of chemical substances, entering in the complement of products of enterprise such as technical fluoride of aluminum, artificial technical cryolite, waterless sulfite of sodium, NPK-complex fertilizers of brands (10:19:25), (16:16:16), 7:16:31 (B), ammoniated superphosphate, ammophos, and also bulk blending fertilizers, containing ammonia nitrate as the nitrogen component, is defined. Chemical, phase, quantitative and mineralogical composition of products are set and specified, physical, structural-mechanical and physical-chemical properties of products are studied with the use of methods of X-ray analysis, IR spectroscopy, thermal, electronic-microscopic, grain-size, mass spectroscopic analyses and also calculations of balances on separate cations and anions taking into account their charges.

**Keywords.** Mineral fertilizers, GOST standard, chlorine, REACH, inorganic salts

## 1. Introduction

The quality of products manufactured at JSC "Gomel Chemical Plant", as well as at all other enterprises of mineral fertilizers most of the commonwealth of independent states (CIS) countries is regulated by the relevant regulatory documents - state standard (GOST), technical conditions (TU) [1]. The main indicators regulated by these documents are the content of the main nutrients, microelements and a number of impurities, for technical products - the content of the main components, as well as the physical properties of the product (particle size distribution, static strength, and friability) [2].

The importance of these indicators is due to the fact that the "free-field" logistics chain includes many intermediate stages of transportation, storage, reloading, etc [3]. In addition, the seasonality of the application of mineral fertilizers by agricultural consumers with the continuity (year-round) of the technological process of their production predetermines long periods of time. Storage of manufactured products varies from several months to six months [4]. The consequence of the above features of the use of mineral fertilizers is the observed deterioration in physical and mechanical properties, leading in some cases to the return of products to the manufacturer and significant financial sanctions [5].



A significant number of scientific papers and publications are devoted to the issue of improving the physical and mechanical properties of mineral fertilizers [6–10]. However, the main attention is paid to the consideration of chemical and physicochemical transformations occurring at individual stages of the technological process [2, 7], as well as to the issues of product conditioning, but not to the study of the ongoing processes during the storage of granules. There are a number of publications devoted to the study of the physical and mechanical properties of complex mineral fertilizers [1, 3-6, 8, 9], including during storage [10], but the emphasis in them is on describing changes in quantitative indicators of strength, caking, hygroscopicity, etc., as well as changes in the content of individual forms of phosphorus and chemical composition. In addition, methodologically, when conducting research, individual granules were considered as monoparticles having a uniform composition throughout the volume, and, accordingly, the average chemical composition of individual fertilizer samples was given [11].

To assess the change in the physical and mechanical properties of the final product due to the occurrence of chemical transformations, it is necessary to know the complete both qualitative and quantitative composition of the exported product [12]. Since a significant part of the production is export-oriented, including to the Baltic countries, Germany, Austria and other countries of the European Union, the issues of quality control of manufactured products and their compliance with world requirements are a priority.

According to the requirements in force on the territory of the countries of the European Economic Community (EU) [13], for products to enter the markets of these countries, products (substances) are subject to the “pre-registration” procedure, in accordance with the normative document of the REACH regulation [14]. The fundamental difference between the requirements of the REACH regulation and the requirements of the current regulatory documents is the need to indicate all the identification parameters of substances, including the complete chemical composition (including impurities and additives), the molecular and structural formula of single and multi-compound substances, the EU name and other identifiers of substances (for substances with variable composition) [15].

In this connection, at the request of specialized enterprises, the authors carried out a set of studies to clarify the chemical, phase, mineralogical compositions of products in accordance with the REACH requirements [16].

The purpose of the work, the results of which are presented in this article, was to determine the full salt composition of products manufactured by various enterprises for entering the European Union market. In particular, samples of products of JSC "Grodno Azot" were examined: anhydrous ammonia (in cylinders) and water technical; crystalline ammonium sulfate; crystalline caprolactam; methyl esters of fatty acids; crystalline hydroxylamine sulfate; technical methanol; urea; solution of urea and ammonium nitrate (UAN); nitric and sulfuric acids.

In addition, the products of JSC "Gomel Chemical Plant" were examined, in particular: technical aluminum fluoride  $AlF_3$ ; artificial cryolite technical grade  $KP Na_3AlF_6$ ; anhydrous photographic sodium sulfite  $Na_2SO_3$ ; technical sodium pyrosulfite  $Na_2S_2O_5$ ; ammoniated superphosphate grades 9-30, 12-24, 16-20; nitrogen-phosphorus-potassium fertilizer 16-16-16, produced using both prilled and granular urea as nitrogen raw materials; nitrogen-phosphorus-potassium fertilizer 16-16-16-6 (S) and 10:19:25, produced using ammonium sulfate; nitrogen-phosphorus-potassium fertilizer 5-15-30, produced in the granulated ammophos workshop based on ammonium phosphates; nitrogen-phosphorus-potassium fertilizer 8-19-29, produced in the complex-mixed fertilizers workshop.

To establish the phase composition of these products, their X-ray phase and IR spectral analysis, liquid chromatography, gas chromatography-mass spectrometry, and nuclear magnetic resonance were performed. The determination of the quantitative content of individual phases was carried out according to the methodology developed by the authors by compiling balances for cations and anions, taking into account their charge and the intensity of reflections, based on the data of analysis of the chemical composition [17].

As a result of the research carried out, the structure and composition of chemical substances subject to registration as part of the products of JSC "Grodno Azot" was confirmed. In particular, the X-ray diffraction pattern of ammonium sulfate is consistent with the JCPDS reference sample [6, 9]. A partial redistribution of the intensities of some reflections is observed, caused by the presence of a predominant crystallographic orientation. The X-ray diffraction pattern of the investigated urea sample also corresponds to the reference sample. The relative intensity of the observed reflections, which are not characteristic of urea, is no more than 2%, which probably indicates the presence of impurities of biuret and triuret in an insignificant amount. The IR spectrum of the UAN sample under study contains absorption bands that are present in the IR spectra of urea and ammonium nitrate. The X-ray diffraction pattern of the hydroxylamine sulfate sample shows insignificant differences from the data available in the literature, a slight shift of the maximum reflex, redistribution of the intensities of some reflexes up to their practical disappearance [12].

The more complex chemical and mineral composition of the products of JSC "Gomel Chemical Plant", especially complex fertilizers, as well as the features of the technological scheme used at the enterprise, causes more significant differences in the phase composition of products and the distribution of components between individual phases as from the data specified in the factory technical documentation - shop regulations, and on the indicators, defined by regulatory documents. In particular, the phase composition of commercial sodium sulfite includes the following phases:  $\text{Na}_2\text{SO}_3$  (Sodium Sulfite),  $\text{NaCl}$  (Sodium chloride),  $\text{Na}_2\text{S}_2\text{O}_3$  (Sodium thiosulfate),  $\text{Na}_2\text{CO}_3$  (Sodium carbonate),  $\text{SiO}_2$ ,  $\text{FeSO}_3$  (Iron Sulfite).

## 2. Materials and methods

The following chemical products of JSC GSP were used as objects of study:

- Technical artificial cryolite (standard sample and sample from the technological process) – GOST 10561-80;
- Technical aluminum fluoride (standard sample and sample from the technological process) – GOST 19181-78;
- Anhydrous sodium sulfite – TU RB 400069905.031-2006;
- Ammoniated superphosphate (based on Khibiny and Kovdor apatites) – TU RB 400069905.023-2004;
- Ammophos (based on Khibiny and Kovdor apatites) – TU BY 400069905.030;
- fertilizer nitrogen-phosphorus-potassium complex complex-mixed (10:19:25, 7:15:31) (based on Khibiny apatite) – TU RB 400069905.022-2003;
- Fertilizer nitrogen-phosphorus-potassium complex complex-mixed (16:16:16) (based on Khibiny and Kovdor apatites) – TU RB 400069905.022-2003.

To establish the phase composition of these products, their X-ray phase and IR spectral analysis was performed. X-ray examination was carried out using a D8 Advance X-ray diffractometer manufactured by Bruker. IR spectroscopic studies were carried out on IR-Fourier spectrometer NEXUS Company NICOLET. IR spectra of sediments were recorded in the range of 300–4000  $\text{cm}^{-1}$ . When deciphering the data of X-ray phase analysis, the database [11] was used; the assignment of IR spectral bands was carried out using the reference literature [12, 13]. The determination of the quantitative content of individual phases was carried out according to the methodology developed by

the authors by compiling balances for cations and anions, taking into account their charge and intensity of reflections, based on the analysis of the chemical composition.

The study of the granulometric composition of fertilizer samples by fractions and the shape of granules was carried out on a particle analyzer with digital image processing CAMSIZER Studies of the uniformity of fertilizer granules and the elemental distribution of individual components in granules were carried out on a JEOL JSM-5610LV scanning electron microscope using a JED 22-01 electronic probe energy-dispersive X-ray fluorescence analysis system. Derivatographic studies of samples of complex fertilizers were carried out using a METTLER TOLEDO STAR<sup>®</sup> thermal analysis system (models TG-50 and DSC-30) with STARe software.

The content of heavy metals in product samples was determined according to the “Methodology for measuring the content of arsenic, cadmium, chromium, cobalt, copper, lead, nickel, selenium, antimony, vanadium, manganese, tin, molybdenum, zinc, iron in aqueous and solid matrices using the atomic absorption spectroscopy” (MVL.MN 1137-99). The analysis of the prepared samples was carried out on GBC Avanta GM and Saturn-3-P1 spectrometers with electrothermal sample atomization.

### 3. Results and discussion

The results obtained showed that the phase composition of the products and the distribution of components between the individual phases differ both from the data specified in the factory technical documentation - workshop regulations, and from the indicators defined by regulatory documents (GOSTs and TUs). The processes of exchange interaction between the components of the systems with the production of double salts and adducts in the production of complex fertilizers, which have a significant impact on the physical and physico-chemical properties of the products, have been proven.

According to GOST 10561-80, technical cryolite is a double salt of sodium fluoride and aluminum fluoride with the chemical formula  $\text{AlF}_3\text{NaF}$ . An important indicator of quality is the cryolite module, which is the ratio of the number of NaF molecules to the number of  $\text{AlF}_3$  molecules. With a module of 1.5-1.7, cryolite was obtained that meets the requirements of GOST. The results of the chemical analysis of the composition of the standard sample of cryolite from JSC GCP are given in Table 1.

**Table 1.** Chemical composition of cryolite (standard).

Substances	Content, mass.vol. %
F	52.50±0.55
SiO <sub>2</sub>	1.28±0.08
Al	18.97±0.24
Na	20.46±0.36
H <sub>2</sub> O	0.630
P <sub>2</sub> O <sub>5</sub>	0.190
Fe <sub>2</sub> O <sub>3</sub>	0.057

Comparative analysis of the data on the phase composition and quantitative content of individual phases that make up the cryolite, provided by the JSC GCP, as well as the data obtained by the authors as a result of research (Table 2), led to the conclusion that the phase composition of the cryolite produced at the enterprise is practically all the main components does not correspond to the known literature data, as well as the data given in the regulatory documentation.

**Table 2.** Comparative qualitative and quantitative composition of artificial technical cryolite.

Product name	Chemicals contained in the product, including impurities $\geq 1\%$ (according to the plant data)	Content in the product, %	Chemicals contained in the product, including impurities $\geq 1\%$ (research results)	Content in the product, %
--------------	---	---------------------------	--	---------------------------

Cryolite (artificial technical)	trisodium hexafluoroaluminate – $\text{AlF}_3 \cdot 1.5\text{NaF}$	87	cryolite- $\text{Na}_3\text{AlF}_6$	14
			chiolite - $\text{Na}_5\text{Al}_3\text{F}_{14}$	65
			hydroxoaluminum fluoride - $\text{Al}(\text{OH},\text{F})_3$	16
			aluminum silicofluoride - $\text{Al}_2(\text{SiF}_6)_3$	3.4
			water - $\text{H}_2\text{O}$	0.6
	aluminum phosphate - $\text{AlPO}_4$	< 1	aluminum phosphate - $\text{AlPO}_4$	< 1
	iron phosphate - $\text{FePO}_4$	< 1	iron phosphate - $\text{FePO}_4$	< 1
	silicon oxide - $\text{SiO}_2$	1.5	silicon oxide - $\text{SiO}_2$	< 1
	aluminum sulfate - $\text{Al}_2(\text{SO}_4)_3$	< 1	aluminum sulfate - $\text{Al}_2(\text{SO}_4)_3$	< 1
	ferrous sulfate - $\text{Fe}_2(\text{SO}_4)_3$	< 1	ferrous sulfate - $\text{Fe}_2(\text{SO}_4)_3$	< 1

The presence of chiolite in the composition of the product with a modulus above 1.5 is confirmed by literature data [14]. The presence of aluminum silicofluoride in the composition of the product is confirmed by chemical analysis data ( $\text{SiO}_2$  content is 1.28%) presented in table 1. The presence of hydroxoaluminum fluoride in the product is also confirmed by the data of IR spectral analysis. In particular, the absorption band at  $3650\text{ cm}^{-1}$  corresponds to the stretching vibrations of the OH group (Figure 1). In addition, the possibility of the formation of this compound in this system was noted by Rodin and Zaitsev [15]. The product contains a certain amount of phosphorus and iron compounds (Table 1), however, since their content does not exceed 0.1–0.2%, the corresponding compounds cannot be identified by physicochemical methods, but are indicated by the gross formula based on balance sheets.

The phase composition of commercial aluminum fluoride, determined on the basis of chemical and X-ray fluorescence analyzes, includes the following *main phases*:

- beta  $\text{AlF}_3$  – beta aluminum fluoride;
- gamma  $\text{AlF}_3$  – gamma aluminium fluoride,

*additional phases*:

- $\text{Al}_2(\text{SiF}_6)_3$  – aluminium silicon fluoride;
- $\text{Al}_2\text{O}_3$  – aluminium oxide.

Thus, the data of X-ray phase analysis confirmed the presence of aluminum fluoride in several modifications as the main phase. The presence of free  $\text{Al}_2\text{O}_3$  oxide is indirectly confirmed by an X-ray diffraction pattern, and the indication of its content in GOST (up to 4%) and chemical analysis data (3.73%) is due to the method of the analysis itself, according to which aluminum oxide must be calculated. According to the data of chemical analysis, the product contains a certain amount of phosphates, chlorides and compounds of iron, zinc, however, since their content does not exceed 0.2%, the corresponding compounds cannot be identified by physicochemical methods, but are indicated by the gross formula based on balance equations.

The results of studies of NPK fertilizer samples confirmed the above assumption that the phase composition of products and the distribution of components between individual phases differs both from the data specified in the factory technical documentation - the regulations of the corresponding shops, and from the data given in the technical literature.

The phase composition of commercial aluminum fluoride, determined on the basis of chemical and X-ray fluorescence analyzes, includes the following *main phases*:

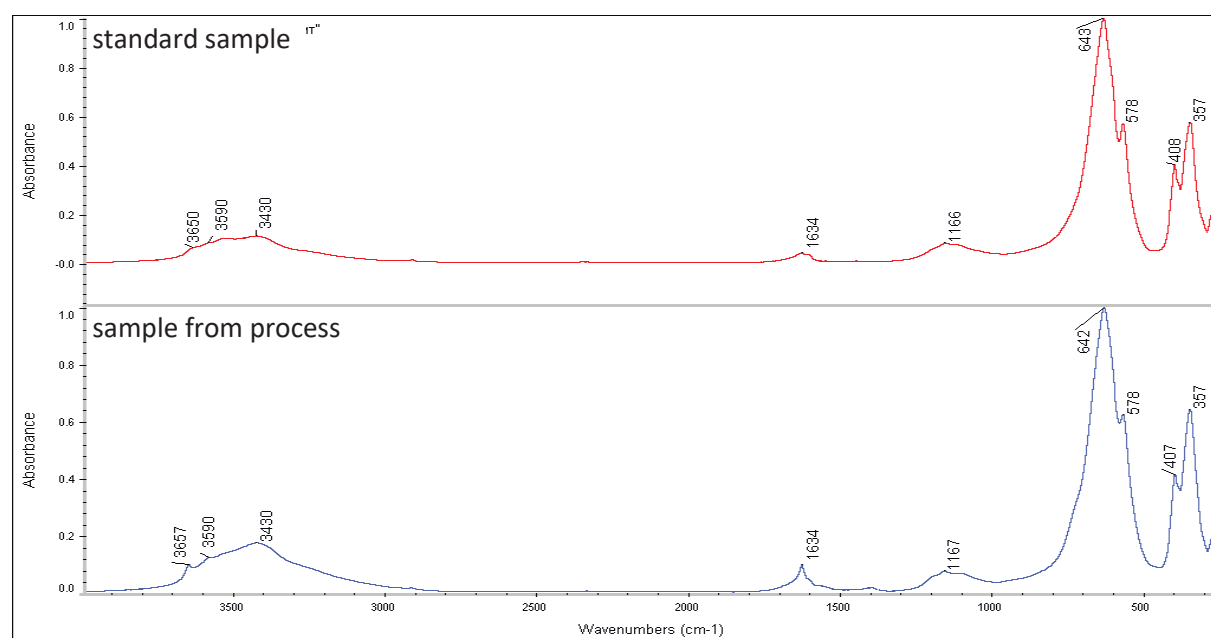
- beta  $\text{AlF}_3$  – beta aluminum fluoride;
- gamma  $\text{AlF}_3$  – gamma aluminium fluoride,

*additional phases*:

- $\text{Al}_2(\text{SiF}_6)_3$  – aluminium silicon fluoride;
- $\text{Al}_2\text{O}_3$  – aluminium oxide.

Thus, the data of X-ray phase analysis confirmed the presence of aluminum fluoride in several modifications as the main phase. The presence of free  $\text{Al}_2\text{O}_3$  oxide is indirectly confirmed by an X-ray diffraction pattern, and the indication of its content in GOST (up to 4%) and chemical analysis data (3.73%) is due to the method of the analysis itself, according to which aluminum oxide must be calculated. According to the data of chemical analysis, the product contains a certain amount of phosphates, chlorides and compounds of iron, zinc, however, since their content does not exceed 0.2%, the corresponding compounds cannot be identified by physicochemical methods, but are indicated by the gross formula based on balance equations.

The results of studies of NPK fertilizer samples confirmed the above assumption that the phase composition of products and the distribution of components between individual phases differs both from the data specified in the factory technical documentation - the regulations of the corresponding shops, and from the data given in the technical literature.



**Figure 1.** IR spectrum of a “standard” cryolite sample.

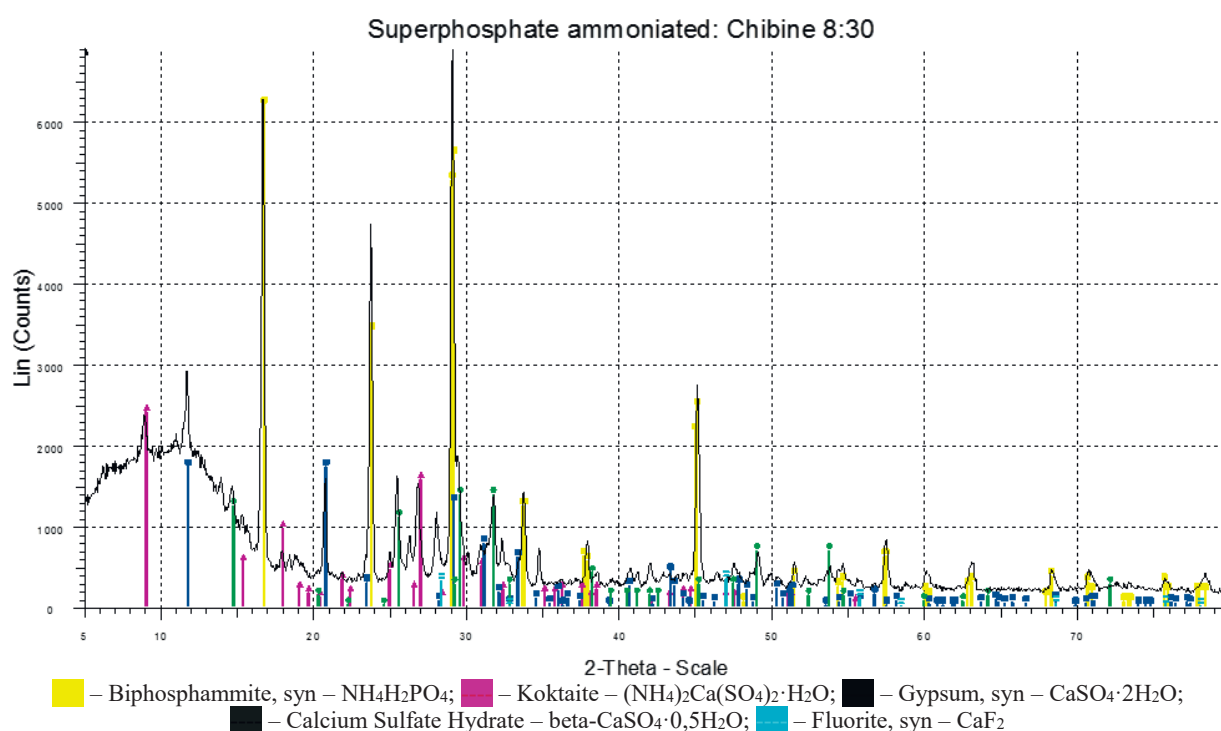
To establish the phase and mineralogical composition of complex fertilizers, X-ray phase and IR spectral analysis of samples provided by the Plant's Central Laboratory was performed. The main phases of ammoniated superphosphate grades 8:30, 8:33 are ammonium dihydrogen phosphate, hydrated calcium sulfate (Table 3).

**Table 3.** Qualitative and quantitative composition of ammoniated superphosphate from Khibiny apatite grade 8:30.

All chemicals included in the product (including impurities $\geq 1\%$ )	Content in the product, %
$\text{NH}_4\text{H}_2\text{PO}_4$ – ammonium dihydrogen phosphate	45.1
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – gypsum	7.4
$\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$ – calcium sulfate hemihydrate	17.0
$(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ – coctaite	24.2
$\text{CaF}_2$ – calcium fluoride	3.5

$\text{AlPO}_4$ – aluminum phosphate	1.0
$\text{FePO}_4$ – iron phosphate	1.8
$(\text{NH}_4)_2\text{SO}_4$ – ammonium sulfate	-
$\text{CaHPO}_4$ – calcium hydrogen phosphate	-

The presence of phosphorus in the product in the composition of ammonium phosphates fundamentally distinguishes the ammoniated superphosphate produced at JSC GCP from traditional grades of superphosphates, in which phosphorus is present in the form of calcium dihydro- and hydrophosphates. This difference is due to the peculiarity of the technological process developed with the participation of the authors of the article, and providing for the use of unfiltered phosphoric acid suspension, which is formed at the extraction stage in the production of extractive phosphoric acid, as the initial phosphorus-containing raw material. The total content of sesquioxides, according to chemical analysis, reaches 3%; therefore, the X-ray diffraction pattern contains reflections characteristic of medium iron and aluminum phosphates (Figure 2). Note the absence of reflections characteristic of ammonium sulfate (within the sensitivity of the method), which is unexpected, since it is traditionally considered one of the main impurities in the composition of ammoniated superphosphate. At the same time, there are clear reflections characteristic of calcium-ammonium double salts, in particular, coctaite  $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . In our opinion, this is due to the following reasons.



**Figure 2.** X-ray pattern of ammoniated superphosphate from Khibiny apatite grade 8:30.

The ammonium calcium double salt is incongruently soluble in water and in the process of dissolution only one of the salts, ammonium sulfate, passes into the solution, which is identified by chemical analysis methods. At the same time, calcium sulfate, as a sparingly soluble compound, remains in the solid phase. The presence in the composition of ammoniated superphosphate, as well as complex NPK fertilizers based on it, of double ammonium calcium salts was established by the authors earlier and described in detail in publications [16, 17]. The results of studies of samples of

NPK fertilizer grade 10:19:25 are presented in Table 4 (in brackets the content of components according to factory data is indicated).

**Table 4.** Qualitative and quantitative composition of the “standard” sample of SSMU brand 10:19:25

All chemicals included in the product (including impurities $\geq 1\%$ )	Content in the product, %
$\text{NH}_4\text{H}_2\text{PO}_4$ – ammonium dihydrogen phosphate	16.9 (42)
KCl – potassium chloride	33.7
$(\text{NH}_4)_2\text{HPO}_4$ – diammonium hydrogen phosphate	13.7 (12)
$[\text{K}_{0.5}(\text{NH}_4)_{1.5}]_2\text{SO}_4$ – arcanite	26.1
$\text{NH}_4\text{Cl}$ – ammonium chloride	4.9
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ – calcium sulfate semi-hydrate	0.5 (2)
$\text{CaHPO}_4$ – calcium hydrogen phosphate	0.4
$\text{CaF}_2$ – calcium fluoride	0.8
$\text{AlPO}_4$ – aluminum phosphate	1.0
$\text{FePO}_4$ – iron phosphate	1.1
$(\text{NH}_4)_2\text{SO}_4$ – ammonium sulfate	footprints (38)

The main phases in a sample of nitrogen-phosphorus-potassium fertilizer grade 8-19-29, made using one stripped off extraction phosphoric acid, sulfuric acid, ammonia, potassium chloride and gypsum, are ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), potassium chloride (KCl) and ammonium arcanite ( $[\text{K}_{0.5}(\text{NH}_4)_{0.5}]_2\text{SO}_4$ ), additional phases – silicon oxide ( $\text{SiO}_2$ ), magnesium sulfate dihydrate ( $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ ), iron phosphate ( $\text{FePO}_4$ ), aluminum phosphate ( $\text{AlPO}_4$ ), calcium fluoride ( $\text{CaF}_2$ ) and calcium sulfate hydrate ( $\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$ ). The last four phases are calculated based on the performed chemical analysis. On the X-ray diffraction patterns of the sample, due to their small number, their peaks merge with the background and cannot be identified.

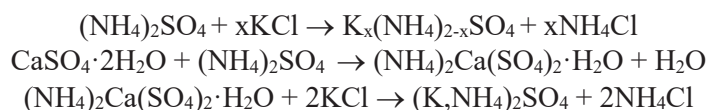
The presence of reflexes corresponding to ammonium chloride confirms the progress of the conversion process also in the case of the introduction of potassium chloride together with re-tour into the ammonizing granulator. The formation of diammonium hydrogen phosphate is confirmed by the pH value of the aqueous extract equal to 7. The IR spectral analysis data confirm the absence of absorption bands characteristic of ammonium sulfate, as well as the presence of vibrations characteristic of the  $\text{HPO}_4^{2-}$  group.

It was also established that the processes of exchange interaction between potassium chloride introduced into the technological process during the production of complex fertilizers through the dry return path of the granulation stage, and other components of systems leading to the formation of a number of double salts, as well as ammonium chloride and its adduct with urea.

The formation of double salts of koktaite, ammonium arcanite, as well as the adduct of tetracarbamide ammonium sulfate, which have a significantly lower solubility in water, makes it possible to classify the studied brands of complex fertilizers as fertilizers with prolonged action.

Note the absence of reflexes characteristic of ammonium sulfate, as in the case of ammoniated superphosphate. At the same time, there are clear reflections characteristic of potassium-ammonium double salts, in particular, ammonium arkanite -  $(\text{KNH}_4)_2\text{SO}_4$ . The authors previously described the possibility of formation of these compounds in the system [16]. The formation of these double salts indicates the course of the process of conversion of potassium chloride with ammonium sulfate formed at the stage of ammonization according to the following scheme:





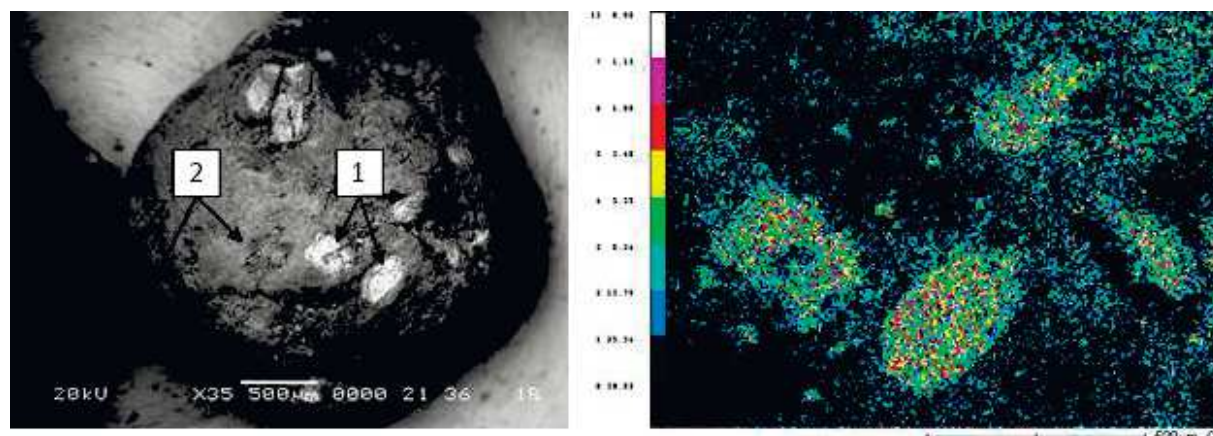
The presence of reflections corresponding to ammonium chloride confirms the course of the conversion process in the case of introducing potassium chloride together with returning into the ammonizer-granulator. The formation of diammonium hydrophosphate is confirmed by the pH value of the aqueous extract, equal to seven. The data of IR spectral analysis confirm the absence of absorption bands characteristic of ammonium sulfate, as well as the presence of fluctuations characteristic of the  $\text{HPO}_4^{2-}$  group.

The main phases of the 16:16:16 brand fertilizer are:  $\text{NH}_4\text{H}_2\text{PO}_4$  - ammonium dihydrogen phosphate (25.1%);  $\text{K}_{0.5}(\text{NH}_4)_{0.5}]_2\text{SO}_4$  - ammonium arkanite (35.3%); KCl - potassium chloride (9.0%);  $\text{CO}(\text{NH}_2)_2$  - urea (8.8%);  $\text{NH}_4\text{Cl}$  - ammonium chloride (8.0%); and,  $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$  - adduct of urea with ammonium chloride (9.2%).

The data obtained confirm the course of conversion processes between potassium chloride and other components of the system, leading to the formation of a number of double salts, as well as ammonium chloride and its adduct with urea. The technology underlying the production of the studied grades of complex-mixed mineral fertilizers involves the introduction of potassium chloride through the recycle tract at the stage of granulation and drying. Therefore, until now it was believed that in this case, the conversion processes do not actually occur, and all the introduction of potassium is in the product in the form of potassium chloride. Thus, because of the completed complex of studies, results were obtained that have practical significance and scientific novelty.

The results of electron microscopic studies of samples of granulated complex fertilizers made it possible to obtain data on the features of the granulation process, the quality of the product granules and give practical recommendations for its improvement.

The micrograph of complex-mixed mineral fertilizers brand 10:19:25 (Figure 3a) clearly shows inclusions, as well as zones of varying intensity. Analysis of the elemental distribution of individual components in granules SSMU grade 10:19:25 (Figure 3b) confirmed the fact of significant heterogeneity of the composition of the granules, the uneven distribution of the main elements - phosphorus, potassium, nitrogen, and made it possible to establish its cause. The highest content of chlorine and potassium is noted in the places of inclusions (zone 1), while in some zones (zone 2) chlorine and potassium are practically absent (Figure 3b). Studies of the quantitative elemental composition of the 10:19:25 grade SSMU granule in zones 1 and 2, performed using the JED 22-01 electronic probe energy-dispersive X-ray fluorescence analysis system, showed that the composition of the granule in zone 1 fully corresponds to potassium chloride. The composition of the granules in the zone 2 differs significantly in the content of the main elements. This confirms the previously made conclusions about the uneven distribution of potassium chloride in the composition of the granules, which is a consequence of the shortcomings of the granulation stage, due to the existing technology for introducing potassium chloride into the technological process. The homogeneity of the surface of the granules observed in the micrographs of SSMU grade 16:16:16 and ammoniated superphosphate is confirmed by the data of their elemental composition. In particular, the composition of granules SSMU brand 16:16:16 in different zones has slight differences within the measurement error, which indicates a good flow of rolling granules.



**Figure 3.** Micrograph (a) and quantitative distribution of chlorine on the surface (b) of SSMU grade 10:19:25 granules

Atomic absorption spectroscopy data indicate that the content of impurity elements of heavy, radioactive and other environmentally harmful elements in the company's products do not pose any danger and comply with sanitary standards.

Derivatographic studies of samples of complex fertilizers led to the conclusion about their good thermal stability. In the temperature range up to 150-160°C, the weight loss does not exceed 2-3%. For samples of the complex fertilizer grade 16:16:16, a noticeable weight loss begins in the temperature range above 120°C, which is due to the process of decomposition of the initial urea.

#### 4. Conclusions

The refined data obtained as a result of research on the chemical and mineralogical composition of complex mineral fertilizers and industrial salts produced at specialized enterprises of the CIS countries made it possible to obtain new information both on their composition and chemical processes that occur between the individual ingredients of the system at various technological stages, and also contributed to successful entry of these products into the European market.

Confirmation of the reliability of the results obtained by the authors was the absence of claims from European customers and European institutions that ensure quality control and compliance of the supplied chemical products. Because of the completed complex of studies, the composition of the main and impurity components of the products of JSC GCP was established. The results obtained allowed us to conclude that the phase composition of the products and the distribution of components between the individual phases differ both from the data indicated in the factory technical documentation - the regulations of the respective workshops, and from the data given in the technical literature. The processes of exchange interaction between potassium chloride were introduced into the technological process during the production of complex fertilizers. The dry path of the granulation stage and other components of the systems leads to the formation of a number of double salts, as well as ammonium chloride and its adduct with carbamide, which have a significant effect on product properties.

Using the methods of derivatographic, electron microscopic, using the system of electron probe energy-dispersive X-ray fluorescence analysis, granulometric, mass spectroscopic analyzes, the physical, structural-mechanical and physico-chemical properties of the product were studied and recommendations were issued to improve its quality.

#### References

- [1] Gorbovskiy K, Norov A, Malyavin A, Pagaleshkin D, Mikhaylichenko A and Ksenofontov D 2014 Study of the hygroscopic properties of complex NPK fertilizers based on carbamide, ammonium phosphates and potassium chloride *Proceedings of NIUIF 1919-2014* 141-146

- [2] Brizitskaja N, Kazak V, Maljavin A and Lamp V 2004 Monitoring of salt content of the compounds formed in the nitrophosphate production process *Proceedings of NIUIF 1919-2004* 221-225
- [3] Zaytsev P, Davydenko V, Syrchenkov A and Litusova N 2009 Study of dustiness and caking of complex mineral fertilizers *Proceedings of NIUIF 1919-2009* 80-88
- [4] Grishaev I and Grinevich V 2009 Investigation of the influence of operating parameters of the unit tubular reactor - ammoniaizer-granulator on the granulometric composition of ammonium phosphates *Proceedings of NIUIF 1919-2009* 95-99
- [5] Gorbovskiy K, Norov A, Malyavin A and Mikhaylichenko 2014 Physical and chemical properties of complex balanced grades of NPK fertilizers using urea *Proceedings of NIUIF 1919-2014* 152-157
- [6] Andriyanova E, Matveeyeva R, Sokolov V and Gribkov A 2014 Dependence of the physical and mechanical properties of granulated ammonium phosphates on the conditions for their preparation *Proceedings of NIUIF 1919-2014* 158-160
- [7] Bushuev N, Norov A and Borisov D 2014 Features of the phase composition of the mineral fertilizer diammonium phosphate *Proceedings of NIUIF 1919-2014* 161-168
- [8] Norov A, Ovchinnikova K, Malyavin K and Razmakhnina G 2014 Properties of carboammophoska and ways to improve them *Proceedings of NIUIF 1919-2014* 106-109
- [9] Syrchenkov A, Tihonovich Z, Grishaev I, Korshuk A and Sobolev N 2004 Research of physical & mechanical properties of DAP fertilizing *Proceedings of NIUIF 1919-2004* 389-394
- [10] Kolpakov B 2019 Comparative analysis of the properties of granulated NPK fertilizers obtained by various methods *Proceedings of NIUIF: on the 100th anniversary of the founding of the institute: in 2 volumes. Vologda: Antiquities of the North* 2 191-199
- [11] JCPDS International Centre for Diffraction Data 2021
- [12] Zharskiy I M 1996 Properties and methods of identification of substances in inorganic technology *Fund foundation research, Minsk* 372
- [13] Grigorov A and Teterin M 1966 Infrared spectra of inorganic coordination compounds *Mir Press, Moscow* 290
- [14] Information and Technical Guide to Best Available Techniques 2019 ITS 11-2019 Aluminum production. Moscow. Bureau of NTD 2019
- [15] Zaytsev V A 1982 Production of fluoride compounds in the processing of phosphate raw materials *Khimiya Press, Moscow* 248
- [16] Dormeshkin O B 2007 Low-waste technology for obtaining new types of sulfur-containing complex NPKS fertilizers *Chemistry and Inorganic Tech.* 3-8
- [17] Dormeshkin O B 2008 Resource-saving technologies for obtaining complex fertilizers based on multicomponent water-salt systems *DSc dissertation – Belorussian State Technological University, Minsk* 398