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Influence of the molar ratio of basic materials and temperature on production of potassium dihydrophosphate

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In this paper an interaction between potassium chloride and ammonium dihydrophosphate in water solutions at 20 and 40 °C temperature was studied in order to obtain non-chlorine fertilizers. After the analysis of the composition of liquid and solid phases in the balance state, it was determined that the composition of both phases depends more on the molar ratio of the starting substances and less depends on temperature. Components of the solid phase were identified by these analysis methods: X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The highest amount of potassium dihydrophosphate in the solid phase was obtained when the molar ratio of potassium chloride and ammonium dihydrophosphate is equal to 0.8 : 0.2.

Key words: potassium dihydrophosphate, potassium chloride, ammonium dihydrophosphate, conversion, molar ratio

INTRODUCTION

Potassium is one of the main nutrient materials of plants, in particular necessary for the development and growth. Potassium is responsible for very important physiological functions in the plants: it activates photosynthesis and synthesis of carbohydrates and vitamins, improves metabolism and access of water into cells, induces accumulation of proteins, and regulates relationship between non-protein nitrogen compounds and proteins. This element increases the amount of starch in the tubers of potatoes, improves the quality of seeds and increases the amount of grain in spica. Potassium increases the effect of turning to wood of cell walls of the spica plants and resistance to laying and fungous diseases, in addition to resistance of the plants to frost. When there is a lack of potassium, plants tend to accumulate larger amounts of inorganic nitrogen, the excess of which is harmful [1].

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The main and the cheapest currently used fertilizer is potassium chloride. Potassium chloride is a concentrated, commonly used potassium fertilizer. KCl is often a component of different compound fertilizers or mixes of fertilizers. It is suitable for fertilization of most plants, in particular cereal corn. On the other hand, a high concentration of chlorine (47.7%) does not allow its use for fertilization of sensitive plants: grapes, hops, tobacco, most vegetables and especially flowers. Potassium fertilizers without chlorine are used for these plants: potassium sulfate, more rarely – potassium nitrate, and even more rarely – potassium phosphates. Usage of potassium phosphates, in particular concentrated potassium and phosphorus fertilizers, is restricted by the high price of the product. Therefore it is mostly used for fertilization of greenhouse plants, as more expensive fertilizers do not make such a large part of their prime cost.

Potassium dihydrophosphate is a crystalline material, with 34.60% amount of potassium, recalculated into K_2O, and with 52.15% of phosphorus, recalculated into P_2O_5.

Under normal conditions, KH_2PO_4 is a stable, nontoxic and a nonflammable material. It can be used not only as a component of mineral fertilizer or compound fertilizers [2] but also in the food industry as an additive (emulsifier, humectant, sequestrant, stabilizer, thickener) [3]. Potassium dihydrophosphate is used in the aerobic composting process as an adsorbent of ammoniacal nitrogen [4]. As a crystal, potassium dihydrophosphate is noted for its non-linear optical properties in a laser fusion system [5]. Production of potassium phosphates is low because of the high price and complex production process. The known methods for obtaining of potassium phosphates are presented as follows:

1. Through neutralization of potassium alkali or potassium carbonate with phosphoric acid [6, 7].

2. By dissociating potassium chloride with orthophosphoric acid (with high excess) in approximately 250 °C temperature, and later by neutralization of the obtained solution with potassium carbonate or potassium alkali and drying in a hothouse [6, 8].

3. From potassium metaphosphate, at high pressure and under the influence of a water steam or nitric acid [9].

4. By affecting potassium chloride with sulphuric acid, and through reaction of the reaction products with calcium phosphate. Gypsum, which is formed during reaction, must be filtered.

5. From superphosphate, by affecting it with phosphoric acid and potassium sulfate [10].

The first production method is used more often, but it is expensive. Other production methods are not refined, cause a lot of ecological consideration and therefore, in fact, not used in practice.

There is almost no data about a cheap and environment-friendly production method – abstraction of potassium dihydrophosphate by a conversion method from aqueous solutions of potassium chloride and ammonium dihydrophosphate according to the following reaction:

$$KCl_{(l)} + NH_4H_2PO_{4(l)} \leftrightarrow KH_2PO_{4(s)} + NH_4Cl_{(l)}.$$

Some data is presented from abstraction of potassium dihydrophosphate from aqueous solutions of potassium chloride and ammonium dihydrophosphate in the articles publicized in scientific literature, but in order to obtain more detailed analysis of samples, additional investigations were performed [11].

The purpose of this paper is to analyze the possibilities of producing potassium dihydrophosphate from aqueous solutions of potassium chloride and ammonium dihydrophosphate by a conversion method as well as to determine the optimal conversion conditions (proportion and temperature of starting substances). Also the chemical composition of the obtained balanced liquid and solid phases will be determined.

EXPERIMENTAL

The chemically pure substances of potassium chloride (KCl, 99–100.5% Sigma-Aldrich) and ammonium dihydrophosphate ($NH_4H_2PO_4$, 99.0% Fluka Analytical) were used in this work.

Conversion reaction potassium chloride and ammonium dihydrophosphate were analyzed by the determination of balance between liquid and solid phases in izomolar series solutions. Aqueous solutions of these salts were prepared by dissolving basic materials – potassium chloride and ammonium dihydrophosphate – in the following molar ratio: 1 : 0, 0.8 : 0.2, 0.6 : 0.4, 0.5 : 0.5, 0.4 : 0.6, 0.2 : 0.8, 0 : 1. The total amount of moles is equal to 5.5 mol. For the preparation of each solution 200 cm^3 of distilled water were used. The balance, that was observed during the measurement of the refractive index, under isothermal conditions had settling after 5 hours, when the chemical composition of solid and liquid phases ceased to change. The obtained solid phase was filtered with a vacuum glass filter and dried in a drying stove.

The chemical composition of liquid and crystallized solid phases were analyzed by chemical analysis methods: concentration of ammonium nitrogen (NH_4^+) – by the Kjeldahl method [12, 13]; concentration of phosphorus (P_2O_5) – by the photocolorimetrical method [12, 14, 15]; concentration of potassium (K_2O) – by the marginal solutions method [13–16], by the use of a flame photometer PFP-7; concentration of chlorine (Cl^-) – by the potentiometric method, with the use of silver nitrate [13, 17].

All samples were characterized by infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD) analysis. Diffraction analysis of roentgen rays was performed with an X-ray diffractometer DRON-6 with CuK_α radiation. A nickel filter was used. The movement step of a detector – 0.02°, duration of intensity measurement in the step – 0.5 s, voltage – 30 kV, power of current – 20 mA, rotation angle 2θ – from 3 to 70°. The substances were identified according to computer-based PDF-2 DATA data basis.

FTIR analysis was performed with a spectrometer Perkin Elmer FT-IR System. The tablet pressed in a press form was used for the analysis (1 mg of substance mixed with 200 mg KBr). The analysis was implemented in the main range of the IR spectrum from 400 to 4 000 cm^{-1} [18].

RESULTS AND DISCUSSION

The balance of potassium chloride and ammonium dihydrophosphate solid and liquid phases were analyzed under isothermal conditions, at 20 °C and 40 °C temperature. Phases were separated from each other by filtering through a Buchner filter and analyzed by chemical and instrumental analysis methods. The chemical composition of solid and liquid phases, determined by chemical methods, is presented in the Table.

Table. **The chemical composition of liquid and solid phases, obtained during conversion**

t, °C	KCl, mol. r.	$NH_4H_2PO_4$, mol. r.	Elements in the solid phase, %				Elements in the liquid phase, %			
			N	P	K	Cl	N	P	K	Cl
20	1.0		0	0	50.20	47.65	0	0	13.69	13.60
	0.8	0.2	1.69	21.06	27.14	5.01	1.19	1.11	13.29	13.52
	0.6	0.4	2.60	23.08	28.19	3.53	2.50	2.09	7.61	11.07
	0.5	0.5	4.05	29.59	24.37	3.26	2.82	3.09	4.89	8.60
	0.4	0.6	6.38	33.19	13.63	2.71	3.01	4.19	4.29	7.05
	0.2	0.8	11.10	34.52	4.31	0.77	3.15	5.92	2.71	3.96
	0	1.0	12.07	26.72	0	0	3.30	7.31	0	0
40	1.0	0	0	0	52.30	47.65	0	0	23.12	13.42
	0.8	0.2	1.82	21.50	31.96	1.87	1.25	0.46	22.04	13.39
	0.6	0.4	1.96	21.48	53.84	3.25	2.57	0.85	12.18	10.37
	0.5	0.5	3.86	22.59	31.76	2.05	2.96	1.48	12.23	8,31
	0.4	0.6	6.39	24.05	22.34	1.69	2.97	1.89	7.39	6.05
	0.2	0.8	10.29	25.99	7.83	0.85	2.98	2.83	4.76	3.62
	0	1.0	12.07	26.72	0	0	3.51	7.82	0	0

As shown in the Table, the results of the balance composition of both phases are very different depending on the molar ratio of the basic materials. At 20 °C temperature and when the ratio of basic materials is changed, the composition of the solid phase (after elimination of crystallization of pure materials) is changing in the following way: the concentration of nitrogen increases from 1.69% to 11.1%, the concentration of phosphorus increases from 21.06% to 34.52%, the concentration of potassium decreases from 28.19% to 4.31%, and the concentration of chlorine decreases from 5.01% to 0.77%. In the liquid phase at 20 °C temperature, the concentration of nitrogen increases from 1.19% to 3.15%, the concentration of phosphorus increases from 1.11% to 5.92%, the concentration of potassium decreases from 13.29% to 2.71%, and the concentration of chlorine also decreases from 13.52% to 3.96%. The composition of the solid phase at 40 °C temperature also changes in a very similar way.

The experiments found that the concentration of nitrogen in the solid phase at 40 °C temperature increased from 1.82% to 10.29%, the concentration of phosphorus increased from 21.50% to 25.99%, the concentration of potassium decreased from 31.96% to 2.83%, and the concentration of chlorine decreased from 3.25% to 0.85%. At this temperature, when the molar ratio of the basic materials is 0.6 : 0.4, the concentration of potassium is higher than in the case when the molar ratio of basic materials is 0.8 : 0.2 as more potassium chloride is obtained.

The composition of the liquid phase at 40 °C temperature is changing in the following way: the concentration of nitrogen increases from 1.25% to 3.51%, the concentration of phosphorus increases from 0.46% to 7.82%, the concentration of potassium decreases from 22.04% to 4.76%, and the concentration of chlorine also decreases from 13.39% to 3.62%. It can be stated that under these conditions the conversion of primary materials produces the best results. As shown in the Table, the results when the molar ratio of potassium chloride and ammonium dihydrophosphate is 0.8 : 0.2 (both at 20 °C and 40 °C temperature), the chemical composition of the obtained solid phase is corresponding to the composition of pure potassium dihydrophosphate (K – 28.67%, P – 22.79%).

High concentrations of potassium and phosphorus are obtained in the solid substance, and concentrations of nitrogen and chlorine are low. Therefore it can be stated that in order to obtain potassium dihydrophosphate, this molar ratio could be the most suitable as it corresponds to stecheometric ratio, according to which the exchange reaction between potassium chloride and ammonium dihydrophosphate is taking place.

Data of the roentgenographic analysis (Fig. 1) allow to state that irrespective of temperature of the conversion (both at 20 °C and 40 °C temperatures), the composition corresponding to that of potassium dihydrophosphate of the solid phase is obtained when the molar proportion of potassium chloride and ammonium dihydrophosphate is equal 0.8 : 0.2 (Fig. 1, a, b, curve 1).

Most peaks that are typical to potassium dihydrophosphate can be seen in these radiographs (XRD pictures) (0.5309, 0.3383, 0.3055, 0.2639, 0.2369, 0.1877 nm). In addition, the identification of two low intensity peaks (0.3149, 0.2227 nm) can be attributed to potassium chloride. Identification of this single reacting substance confirms the results of chemical analysis, stating that a small amount of Cl^- is found in the solid phase. In the case of other molar ratio of the basic materials (Fig. 1, a, curves 2–5), double potassium and ammonium dihydrophosphates and also potassium chloride are obtained. Chemical compounds of the solid phase, obtained at 40 °C temperature (when the molar ratios of potassium chloride and ammonium dihydrophosphate are as follows: 0.8 : 0.2; 0.6 : 0.4; 0.5 : 0.5; 0.4 : 0.6; 0.2 : 0.8), hardly differ from the compounds, identified in the solid phase that was obtained at 20 °C temperature, meanwhile the peaks of spikes intensity are different.

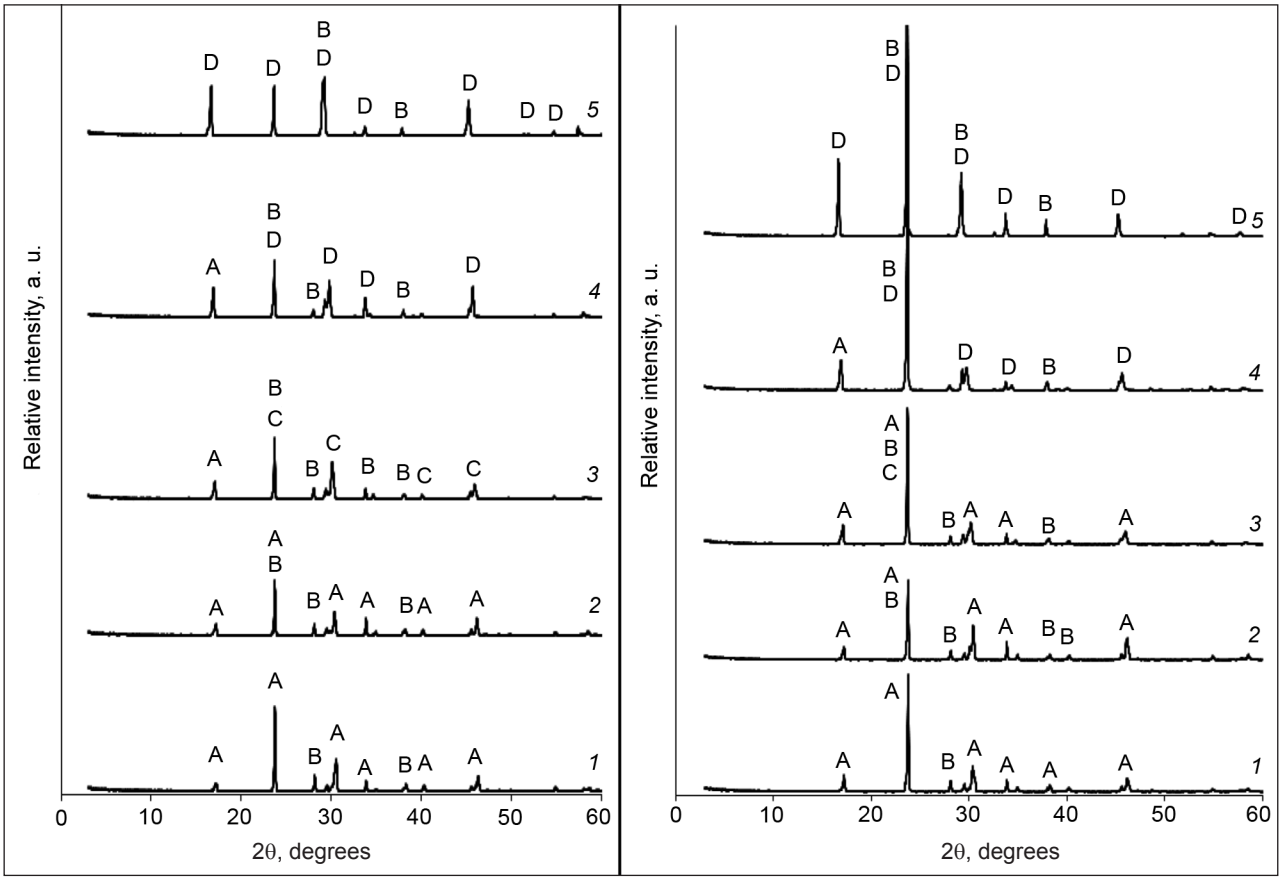

Fig. 1. The XRD analysis curves of the solid phase obtained during conversion, performed at 20 °C (*a*) and 40 °C (*b*) temperatures, when the molar ratios of KCl and $NH_4H_2PO_4$ are the following: *1* – 0.8 : 0.2; *2* – 0.6 : 0.4; *3* – 0.5 : 0.5; *4* – 0.4 : 0.6; *5* – 0.2 : 0.8; A – KH_2PO_4, B – KCl, C – K_2HPO_4, D – $NH_4H_2PO_4$

In order to analyze the obtained materials in more detail, the structure of solid phases was characterized and confirmed by FTIR spectroscopic data (Fig. 2). Doublets of the absorption band in 3 129.3–3 251.76 cm^{-1} in the 1–4 IR spectrums (when the molar ratio of the basic materials is equal to 0.8 : 0.2) of Fig. 2 are characteristic of the valence vibrations of the NH_4^+ functional group. When the basic materials have a lot of KCl (0.8), then this double absorption band has low intensity (curve 1). When KCl is less (0.4), then double absorption bands intensity is higher (curve 4).

When the molar ratio of the basic materials is 0.2 : 0.8 in the IR spectrum (Fig. 2, curve 5), a broad absorption band is to the spectrum part 2 800–3 300 cm^{-1}. This absorption band can also be attributed to valence vibrations of the NH_4^+ functional group. Subject to it, we can state that there are inorganic salts (for example: NH_4Cl, $NH_4H_2PO_4$) in the obtained solid phases. The absorption band at 2 300–2 450 cm^{-1} indicates the presence of potassium bromide, which is used for sample preparation [19].

In accordance with data in the publications of Jegatheesan, Muruman et al. in scientific literature, in our opinion, vibrations in the spectrum part 1 600–1 700 m^{-1} can be attributed to the –OH group [5]. Considering the studies presented in the same scientific paper, it can be stated that the peaks of absorption bands in the 1 401.61–1 454.17 cm^{-1} part are specific to valence vibrations of the NH_2 functional group. When the basic materials have a small amount of $NH_4H_2PO_4$ (0.2), then the NH_2 absorption band has very low intensity (curve 1). In curve 4 we can see that in this case, when the $NH_4H_2PO_4$ is more (0.6), the absorption band intensity is very high.

Doublets of the absorption bands in the 901.54–1 102.27 cm^{-1} part of all spectrums can be attributed to valence vibrations of the PO_4^{3-} functional group. In addition, peaks of absorption bands beside the 539.74–663.82 cm^{-1} part of the spectrum can be attributed to valence vibrations of the tetrahedral form of PO_4^{3-} and this complies with the data published in the scientific paper of J. Trinkūnaitė-Felsen, A. Žalga et al. [20]. As it can be seen, in all cases the spicas of the absorption bands do not change the location position. Subject to these vibrations, it can be stated that there are inorganic salts (KH_2PO_4, K_2HPO_4) in the obtained solid phases.

Spectrums of the solid substance obtained during conversion, as presented in Fig. 2, marginally differ from the IR spectrum of pure potassium dihydrophosphate. Differences occur when the ratio of basic materials are changed, i. e. when the amount of ammonium dihydrophosphate is increased.

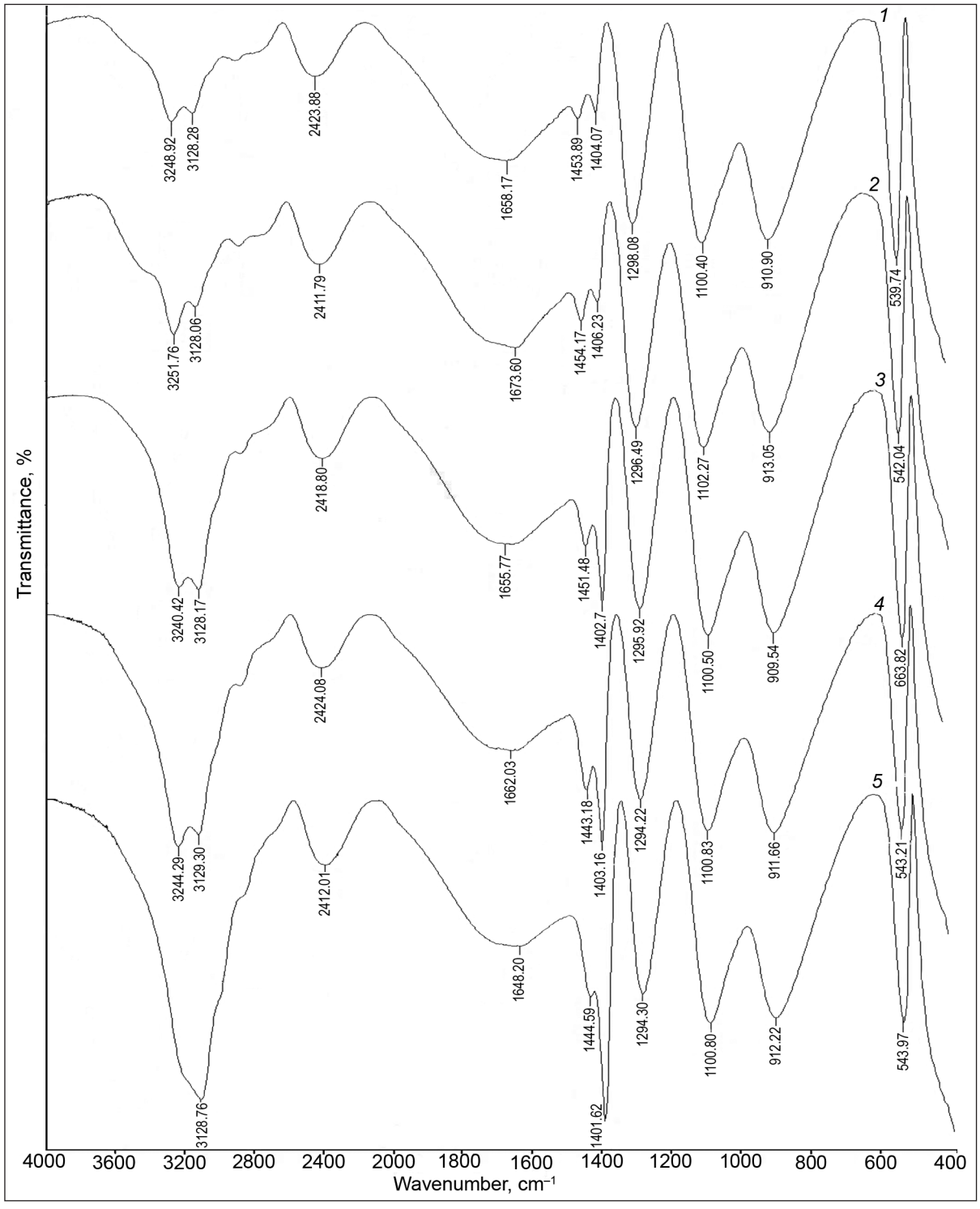

Fig. 2. IR spectrums of the solid phase obtained during conversion, performed at 20 °C temperature, when the molar ratios of KCl and $NH_4H_2PO_4$ are the following: *1* – 0.8 : 0.2; *2* – 0.6 : 0.4; *3* – 0.5 : 0.5; *4* – 0.4 : 0.6; *5* – 0.2 : 0.8

In Fig. 3 the IR spectrums are presented that were recorded during conversion in the same ratio of basic materials, but at higher temperatures, i. e. 40 °C. When decoding these IR spectrums, the same vibrations can be seen, meaning that the same compounds can be identified. Difference can be noticed only in Fig. 3, curve 5, when the molar ratio of basic materials is 0.2 : 0.8, as a doublet is obtained in the 2 800–3 300 cm^{-1} part of the absorption band, which is typical to the NH_4^+ group.

The results show that potassium dihydrophosphate was produced in the solid phase during conversion of potassium chloride and ammonium dihydrophosphate at 20 °C and 40 °C temperatures, when the molar ratio of basic materials was 0.8 : 0.2. Data of the research can be used as theoretical

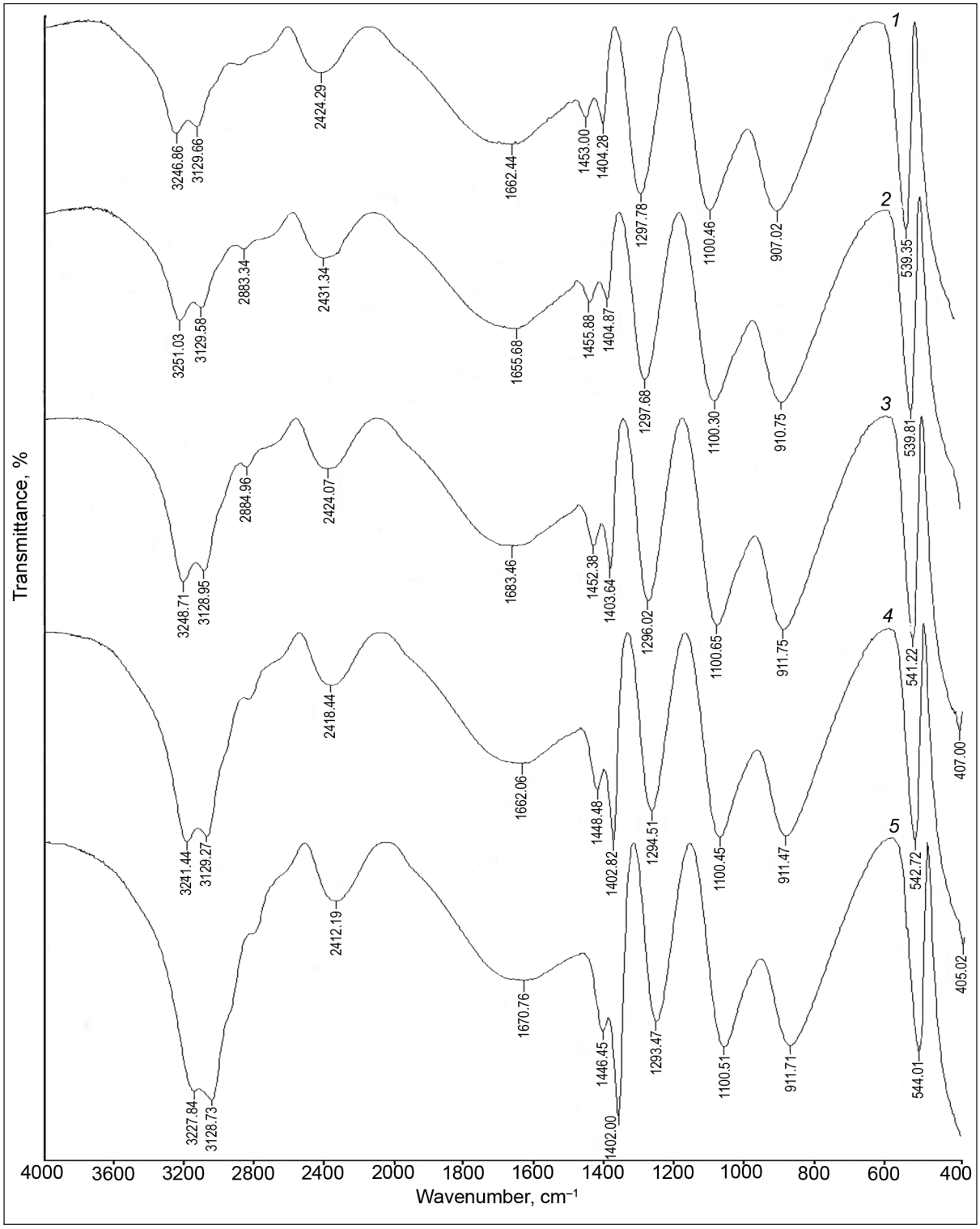

Fig. 3. IR spectrums of the solid phase obtained during conversion, performed at 40 °C temperature, when the molar ratios of KCl and $NH_4H_2PO_4$ are the following: *1* – 0.8 : 0.2; *2* – 0.6 : 0.4; *3* – 0.5 : 0.5; *4* – 0.4 : 0.6; *5* – 0.2 : 0.8

presumptions of the abstraction of complex fertilizers. Additionally, usage of the liquid phase for abstraction of liquid fertilizers should be analyzed.

CONCLUSIONS

1. It was determined that in the solid phase of aqueous solutions, when the molar ratio of potassium chloride and ammonium dihydrophosphate is equal to 0.8 : 0.2,

a solid phase is obtained, with the composition (K – 28.19%, P – 21.06% at 20 °C, and K – 31.96%, P – 21.50% at 40 °C) according to the composition of pure potassium dihydrophosphate (K – 28.67%, P – 22.79%).

2. The composition of the solid phase mostly depends on the molar ratio of basic materials; temperature has little impact on the composition in the analyzed range of temperatures (20 °C and 40 °C).

3. The XRD and FTIR data confirmed that different molar ratios of the initial reagents resulted in a different content of the solid phase (K_2HPO_4, KH_2PO_4, $NH_4H_2PO_4$ and KCl detected). Instrumental analysis methods also confirmed that the molar ratio of KCl and $NH_4H_2PO_4$ of 0.8 : 0.2 resulted in relatively pure potassium dihydrophosphate.

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PRADINIŲ MEDŽIAGŲ SANTYKIO IR TEMPERATŪROS ĮTAKA KALIO DIHIDROFOSFATO SUSIDARYMUI

S a n t r a u k a

Nustatyta, kad vandeninių tirpalų kietojoje fazėje, kai kalio chlorido ir amonio dihidrofosfato molinis santykis 0,8 : 0,2, gaunama kietoji fazė, kuri sudėtimi (K – 28,19 %, P – 21,06 % esant 20 °C; K – 31,96 %, P – 21,50 % esant 40 °C) yra artimiausia gryno kalio dihidrofosfato sudėčiai (K – 28,67 % ir P – 22,79 %). Kietosios fazės cheminė sudėtis labiausiai priklauso nuo pradinių medžiagų molinio santykio ir tirtame temperatūrų intervale (20 °C ir 40 °C) mažai priklauso nuo temperatūros. Rentgeno spindulių difrakcinės ir infraraudonųjų spindulių molekulinės absorbcinės spektrinės analizės tyrimai patvirtino, kad esant skirtingam pradinių medžiagų moliniam santykiui kietojoje fazėje buvo identifikuoti tokie junginiai: KCl, K_2HPO_4, KH_2PO_4, $NH_4H_2PO_4$. Instrumentinės analizės duomenys taip pat patvirtina, kad tuo atveju, kai molinis KCl ir $NH_4H_2PO_4$ santykis tirpale buvo 0,8 : 0,2, kietojoje fazėje susidarė druska, kuri savo sudėtimi yra artimiausia gryno kalio dihidrofosfato sudėčiai.