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KH_2PO_4 crystallisation from potassium chloride and ammonium dihydrogen phosphate

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Seeking to obtain bulk (NPK – nitrogen, phosphorus, potassium), chlorine-free fertilizers, the influence of interaction between potassium chloride and ammonium dihydrogen phosphate in aqueous solutions at temperature of 20, 40, 60 and 80°C has been investigated. Components of the solid phase have been identified by methods of chemical and instrumental analysis: radiography (X – ray), infra – red molecular absorption spectroscopy (IR) and scanning electron microscopy (SEM). It has been observed that the largest amount of solid state potassium dihydrogen phosphate was obtained at 60–80°C, when the potassium chloride and ammonium dihydrogen phosphate molar ratio is equal 0.8:0.2. Changing the molar ratio of 0.5:0.5 to 0.8:0.2, and with increasing temperature, various shaped crystals have developed in the remaining aqueous solutions with a morphology shifting from sharp needles to tetragonal prism.

Keywords: potassium dihydrophosphate, ammonium dihydrophosphate, molar ratio, crystallization, crystal.

INTRODUCTION

Potassium is an essential plant nutrient and is required in large amounts for proper growth and reproduction of plants. Potassium is considered second only to nitrogen, when it comes to nutrients needed by plants, and is commonly considered as the "quality nutrient." It affects the plant shape, size, color, taste and other measurements attributed to healthy produce. Plants absorb potassium in its ionic form, K^+.

Potassium is classified as macroelement, since plants require a large amount of this element. Potassium makes up about 2.3% of the Earth's crust, and 1.3% occurs in soil (solid state), yet, the larger part of the compounds is inaccessible to plants, and in most soils on the Earth, plants lack of the element. Compared to the overall amount, the low potassium levels in a form easily accessible to plants complicates the development of evaluation methods and criteria for optimal nutrition indicators of this element, especially the ones that are versatile and easily applied in practice[1].

The main, the cheapest and concentrated currently used fertilizer is potassium chloride. KCl is often used as 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 to use it 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].

About the crystalline structure and properties of this phosphate is only few information in the literature. The potassium dihydrophosphate is known as a crystal which shows the non linear optical properties in a laser fusion system[4]. Potassium dihydrophosphate is used in the aerobic composting process as a adsorbent of ammoniacal nitrogen[5]. KH_2PO_4 (KDP) is an ideal model system because of its high crystalline quality (no mosaic spread) and because it is a very interesting crystal both from a technological and a fundamental point of view. KDP crystals are the primary material used in devices controlling laser radiation, its modulation and frequency conversion. KDP crystals are manufactured in larger quantities than the total sum of all other crystals used in qantum Electronics[6].

The process of formation of solid solution material precipitating from a solution, melt or steam is called crystallisation. In this way, pure valuable materials or impurities are obtained, i.e. crystallisation is a method of material isolation and purification based on the limited solubility of solid materials. Based on the level of dissolved material, solutions are classified into supersaturated, saturated and unsaturated. Based on this method for the crystallization process can be chosen. The supersaturated solutions tend to be unstable – a slight shock, entered crystal or lowered temperature might lead to a crystallisation. The higher the level of supersaturation, the more solute will be discharged from solution under proper conditions. Crystallisation process evolves when the solution is metastable, and it is the most efficient when the solution is labile (Fig. 1).

The following main stages of the crystallisation process are distinguished: preparation of supersaturated solution, stimulation of the formation of crystallisation centres, crystal growth, crystal discharge from the solution, drying and further processing of the crystalline material. Crystal formation stage also consists of two stages: nucleation and

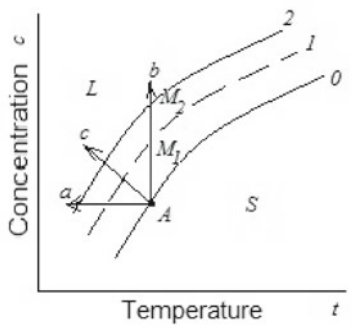

Figure 1. Diagram of state for solutions[7]
S – stable area; M1 and M2 – first and second metastable areas; L – labile area; O – solubility curve; 1 and 2 – limits of first and second metastable states

crystal growth. Crystal nucleation and growth processes can be accelerated or slowed down – duration of these processes effects the crystal size[7, 8].

Defects (dislocations) are common in crystal grating, and they interfere with regular repetition of elements forming the crystal. The outside shape of a crystal is determined by crystallisation conditions and admixtures[9].

Due to complex production processes and high costs, crystalline potassium phosphate (hydrophosphate and dihydrogen phosphate) production volumes are low. Other production methods are not developed for industrial application and pose numerous environmental issues, thus, they are not used in practice.

In our[10] and other[11] works the details of potassium dihydrogen phosphate derivation from aqueous solutions of potassium chloride and ammonium dihydrogen phosphate were presented, and in order to determine the optimum conditions for derivation of these crystals, further investigation has been carried out.

The aim of this study is to examine the potential of potassium dihydrogen phosphate derivation from aqueous solutions of potassium chloride and ammonium dihydrogen phosphate by means of conversion, also determining optimal temperature and to investigate the chemical composition of the derived crystalline materials.

MATERIAL AND METHODS

The chemically pure substances of potassium chloride (KCl, 99−100% w/w Sigma − Aldrich) and ammonium dihydrophosphate ($NH_4H_2PO_4$, 99.0% w/w Fluka Analytical) were used in this work. The solid phase has been obtained when carrying out the conversion reaction between potassium chloride and ammonium dihydrogen phosphate:

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

at different temperatures: 20, 40, 60 and 80°C. Aqueous solutions of these salines have been prepared by dissolving the starting materials – potassium chloride, ammonium dihydrogen phosphate – at a molar ratio of 0.8:0.2. Total number of moles was 5.5 mol. The equilibrium, observed at measuring the refractive index, was steady after 5 hours under isothermal conditions. The resulting solid phase was filtered by a vacuum glass filter and dried to constant weight in an oven at 60°C. When exposed to 60 and 80°C temperature, solid phase could be only obtained having the solution cooled down to ambient temperature (20–22°C). In leftover liquid phase, in 3–5 days, when the temperature was gradually lowered to 18°C, crystals in various shapes occurred.

The chemical composition of crystallized solid phase 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 photocolorimetrical method[13]; concentration of potassium (K_2O) – by marginal solutions method[14], by use of flame photometer PFP – 7; concentration of chlorine (Cl^-) – by potentiometric method, with use of silver nitrate[15].

All samples were characterized by infrared spectroscopy (FTIR) and X – ray powder diffraction (XRD) analysis. Diffraction analysis of roentgen rays was performed with X – ray diffractometer "DRON – 6" with CuK_α radiation. Nickel filter was used. Movement step of 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 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 cm^{-1} to 4000 cm^{-1} [16].

Scanning electron microscopy (SEM) is characterised by high resolution and magnification rate from 10 to 500.000. In this analysis, FEI, Quanta 200 FEG was used[17].

RESULTS AND DISCUSSION

The conversion reaction between potassium chloride and ammonium dihydrogen phosphate has been examines by determining equilibrium between the liquid and solid phase, when the molar ratio of starting materials (based on previous studies) was equal to 0.8:0.2[10].

The solid phase obtained at conversion has been analysed using the chemical and instrumental methods of analysis. Chemical methods allowed investigating the chemical composition of the solid phase, Table 1.

The results indicate that the composition of the solid phase is not greatly influenced by temperature. With increased temperature, the solid phase composition varied as follows: nitrogen concentration increased from 1.69% to 1.89%, phosphorus – increased from 21.06 to 21.66%, potassium – increased from 27.14% to 33.40%, chlorine – decreased from 5.01% to 0.77%. The data in Table 1 shows that at 80°C, the chemical composition of the obtained solid phase is similar to that of pure potassium dihydrogen phosphate, since the major part is made up of potassium (28.67%) and phosphorus (22.79%), and there are only traces of nitrogen and

Table 1. The chemical composition of the solid phase obtained during conversion when the molar ratio of KCl and $NH_4H_2PO_4$ is equal 0.8:0.2

t, [°C]	Solid phase, [%]			
	N	P	K	Cl
20	1.69	21.06	27.14	5.01
40	1.82	21.50	31.96	1.87
60	1.89	21.66	32.27	1.21
80	0.58	20.19	33.40	0.77

chlorine remaining. High concentration of potassium and phosphorus, and low concentration of ammonium and chlorine in the solid phase also occurs at 20–60°C.

During a conversion reaction (at 80°C), regular shape crystal nuclei forming in the solid phase was observed. The solid phase obtained under such conditions consists of larger regular shaped crystals (Fig. 2) as opposed to small crystallites (powder).

It can be consequently stated that in order to obtain potassium dihydrogen phosphate, 80°C suits best, as the solid phase obtained in such temperature is the closest to the composition of potassium dihydrogen phosphate, and it contains less ammonium and chlorine.

On the basis of the data acquired by X – ray analysis (Fig. 3), it is safe to claim that, when molar ratio between potassium chloride and ammonium dihydrogen phosphate is 0.8:0.2, the composition of solid phase closest to that of potassium dihydrogen phosphate with increased conversion temperature is obtained at 80°C (Fig. 3, (e) curve). The below X – ray pictures show most of the peaks that are characteristic to potassium dihydrogen phosphate (d = interplanar spacings: 0.5309, 0.3383, 0.3055, 0.2639, 0.2369 nm).

In Figure 3 one peak of low intensity (0.3149 nm) has been identified that can be related to potassium chloride. Identification of this one of the reacting materials supports the results of chemical analysis showing a small amount of Cl^- found in solid phase. In case of different temperatures (Fig. 3, curves (b), (c), (d)), identical compounds have been identified in the X – ray pictures, only with varying peak intensities.

IR spectra (Fig. 4) have been written in order to analyse the obtained solid phases in more detail. IR spectra in Figure 4 (a) – (d) show absorption band doublets within the portion of 3129.3–3251.76 cm^{-1} of the spectrum, and

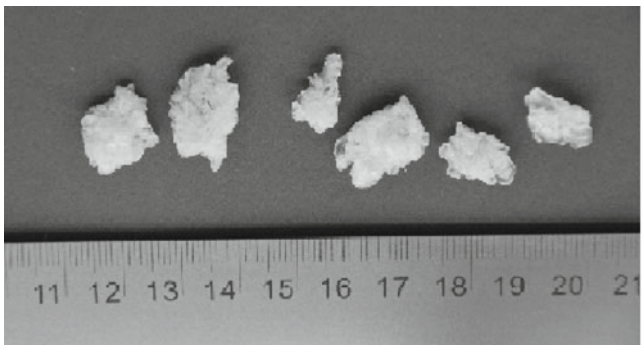

Figure 2. Photograph of grown crystals from a aqueous solutions, when the molar ratio of KCl and $NH_4H_2PO_4$ is equal as 0.8:0.2 and performed at 80°C temperature

these doublets can be related to valence vibrations of the NH_4^+ functional group[18], and confirm the presence of inorganic salines (e.g. NH_4Cl, $NH_4H_2PO_4$) in the obtained solid phase.

In accordance with data of Jegatheesan et al.[19], the vibrations in the spectrum part 1658.17–1718.90 cm^{-1} can be attributed to the – OH group. Considering the studies presented in the same paper, it can be stated that the peaks of absorption bands in the 1404.07–1453.89 cm^{-1} part is specific to valence vibrations of the NH_2 functional group.

Doublets of the absorption bands in the 909.54––1102.27 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 spectrum can be attributed to valence vibrations of tetrahedral form of PO_4^{3-} and this complies with the data published by Trinkūnaitė-Felsen et al.[20] As it can be seen, that in all cases the spicas of the absorption bands don't changed the location position.

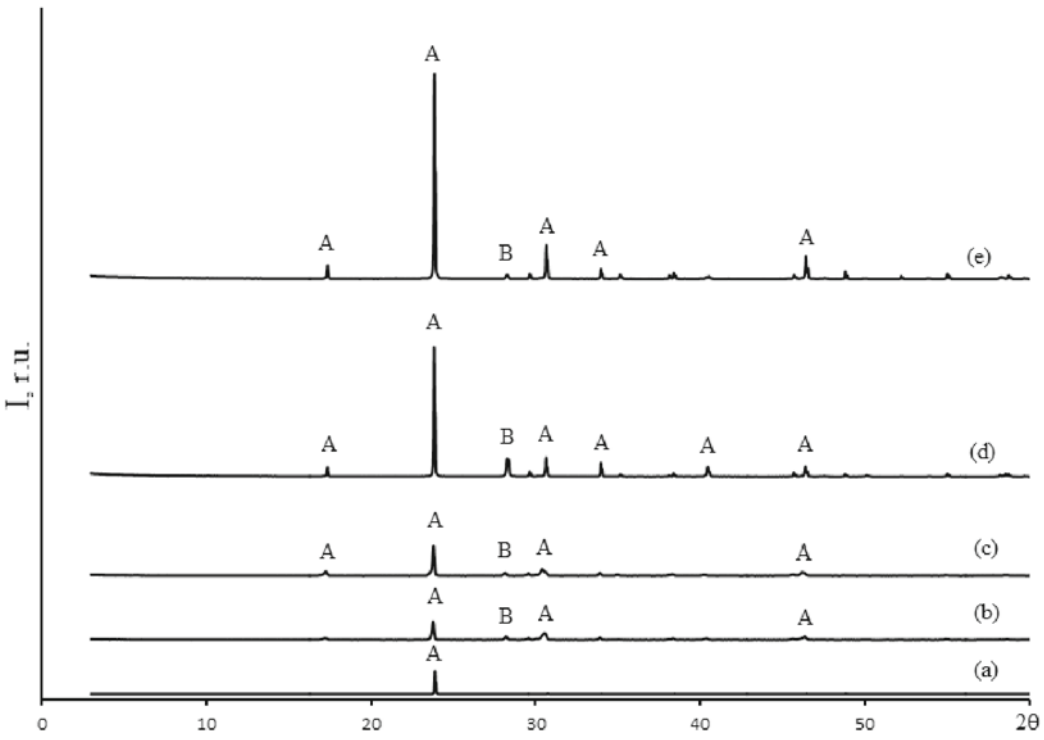

Figure 3. The XRD analysis curves of (a) – pure KH_2PO_4 and of the solid phase, when the molar ratio of KCl and $NH_4H_2PO_4$ is equal 0.8:0.2 performed at temperatures: (b) – 20°C; (c) – 40°C, (d) – 60°C; (e) – 80°C; A – KH_2PO_4, B – KCl

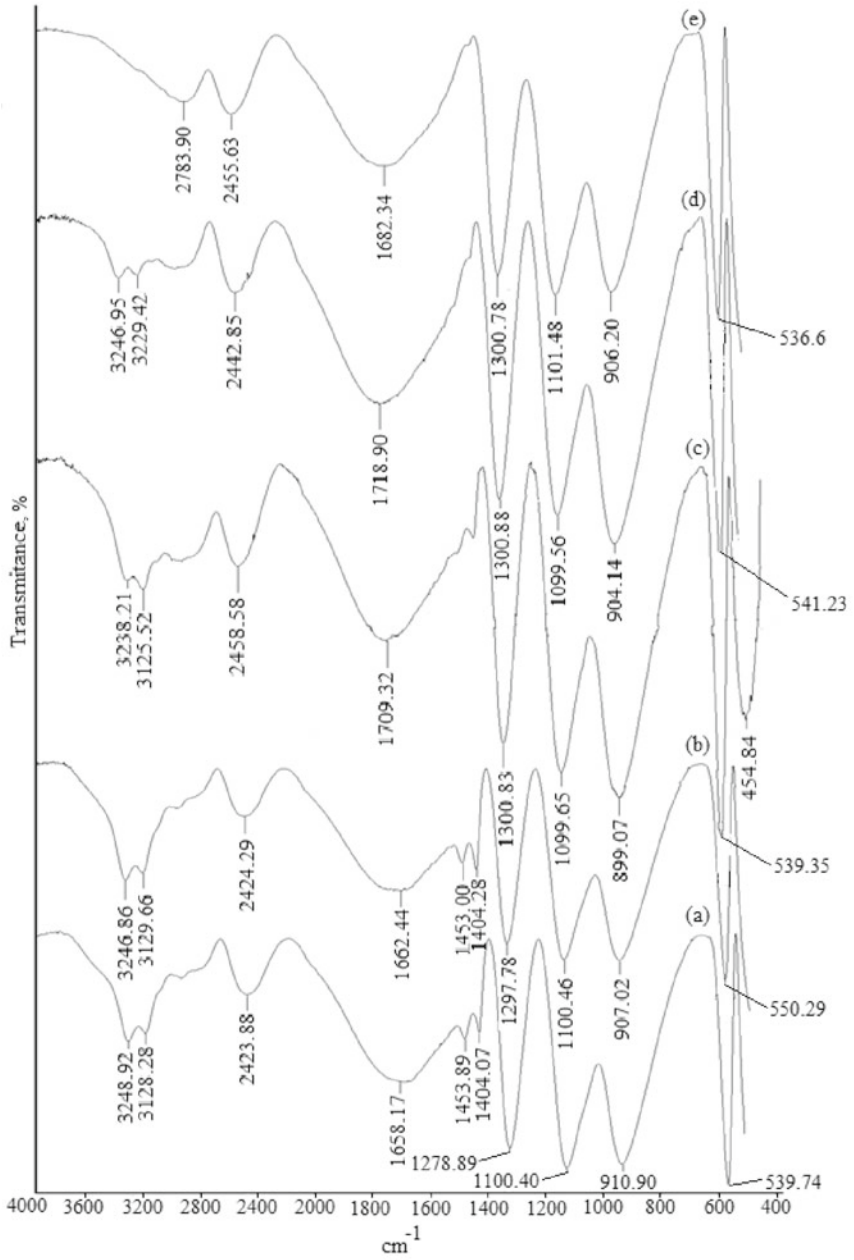

Figure 4. IR spectrums of (e) – pure KH_2PO_4 and of the solid phase obtained during conversion, when the molar ratio of KCl and $NH_4H_2PO_4$ is equal 0.8:0.2 performed at temperatures: (a) – 20°C; (b) – 40°C; (c) – 60°C; (d) – 80°C

Subject to these vibrations, it can be stated that there are inorganic salts (KH_2PO_4, K_2HPO_4) in the obtained solid phases.

The difference between the spectra of solid phase obtained during conversion and presented in Figure 4 and the IR spectrum of pure potassium dihydrogen phosphate (Fig. 4 (e) curve) is not significant. More significant differences have been observed between the (a)–(d) and (e) curves at lower temperature.

SEM of the solid phase has been performed (Fig. 5).

The images showed that the crystals of synthesised material at 20°C and 40°C (Fig. 5 (b)–(e)) slightly resemble the crystals of pure potassium dihydrogen phosphate by their surface and shape (Fig. 5 (a)). Meanwhile, the solid phase obtained during the conversion reaction between potassium chloride and ammonium phosphate at 60°C to 80°C (Fig. 5 (d) and (e)) is very similar to pure potassium phosphate by the surface and particle shape.

In order to obtain more information about the composition of the investigated materials, using the SEM method, their element schemes have been drawn (Fig. 6).

The presented images show that the largest part in the composition of the analysed material consists of potassium, phosphorus and oxygen, and the presence of chlorine and ammonium is very low.

In some time, crystals of various shapes have developed in the leftover aqueous solutions after separation of the solid phase after the conversion reaction between KCl and $NH_4H_2PO_4$ (Fig. 7).

As it can be seen in Figure 7, the change of the molar ratio from 0.5:0.5 to 0.8:0.2 (Fig. 7 (a)–(e)) and temperature from 20°C to 60°C, the crystal morphology shifts from sharp needles to tetragonal prisms. Meanwhile in the publications of Srinivasan et al.[21] the morphology of the crystals changes from tetragonal prism to needles when the concentration of either of the components approaches that of the other. With increasing amount of potassium chloride, and decreasing amount of am-

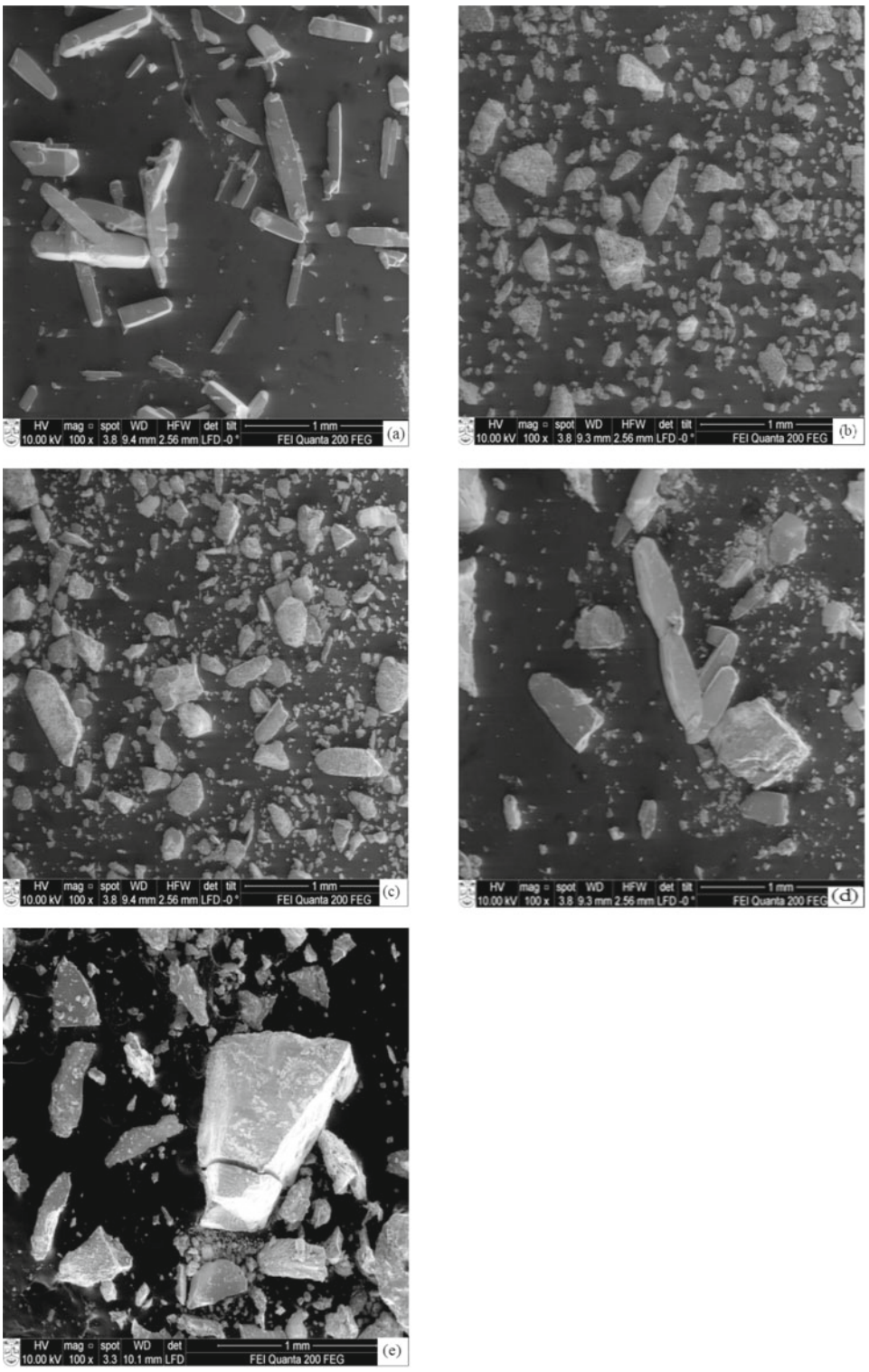

Figure 5. SEM of (a) – pure KH_2PO_4 and of the solid phase, when the molar ratio of KCl and $NH_4H_2PO_4$ is equal 0.8:0.2 performed at temperatures: (b) – 20°C; (c) – 40°C; (d) – 60°C; (e) – 80°C

monium dihydrogen phosphate, more regular prismatic shaped crystals are formed as opposed to sharp needles.

When the molar ratio between starting materials is 0.8:0.2, even at the temperature of 20°C, crystals of shapes similar to regular tetragonal shape crystals are formed (Fig. 7, (c)). The images show that, with increasing temperature, the regularity of the formed crystal shape is increased (Fig. 7, (d) and (e)). Needle shaped crystals are formed at higher concentration of the $NH_4H_2PO_4$ in the aqueous solutions after the separation of the solid phase (Fig. 7, (a) and (b)).

The acquired data suggests that potassium dihydrogen phosphate has formed in the solid phase, when carrying out the potassium chloride and ammonium phosphate conversion at temperatures of 20, 40, 60 and 80°C (with molar ratio between starting materials of 0.8:0.2). The data of this study can be used as theoretical assumptions at derivation of compound fertilizers.

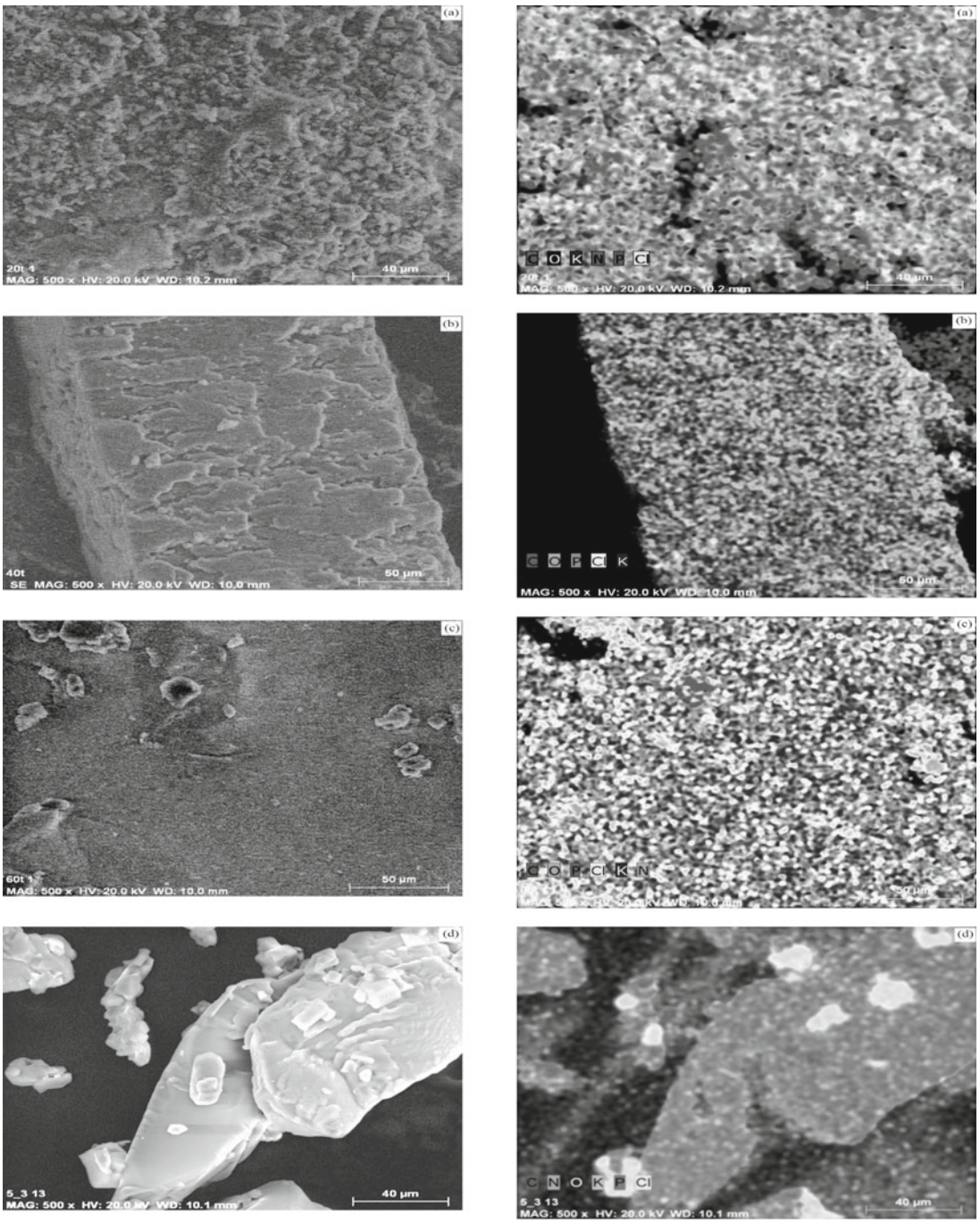

Figure 6. SEM pictures (schemes of the elements) of the solid phase, when the molar ratio of KCl and $NH_4H_2PO_4$ is equal 0.8:0.2 and performed at temperatures: (a) – 20°C; (b) – 40°C; (c) – 60°C; (d) – 80°C

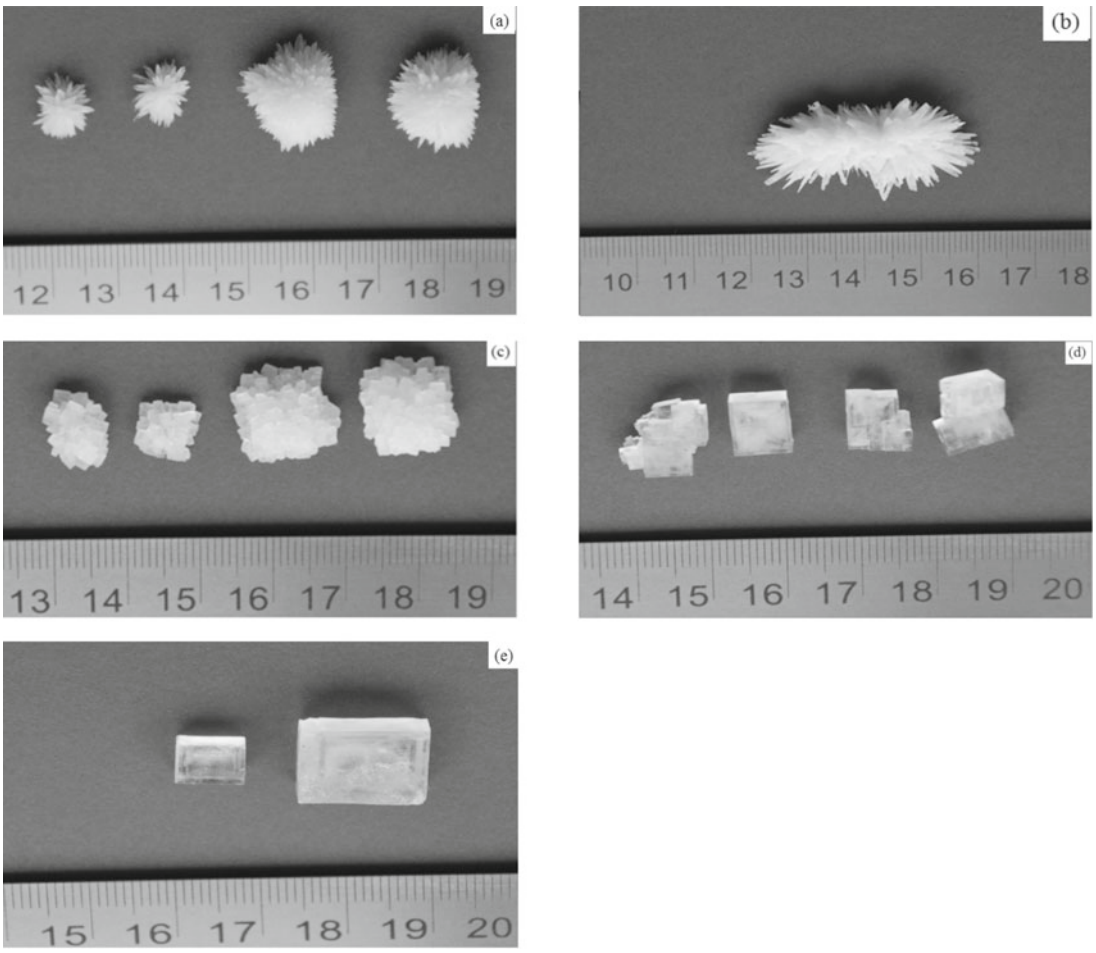

Figure 7. Photograph of grown crystals, when the molar ratio of KCl and $NH_4H_2PO_4$ is different and performed at different temperatures: (a) – 0.5:0.5 and 20°C; (b) – 0.5:0.5 and 40°C; (c) – 0.8:0.2 and 20°C; (d) – 0.8:0.2 and 40°C; (e) – 0.8:0.2 and 60°C

CONCLUSIONS

It has been established that the highest yield of KH_2PO_4 when carrying out a conversion reaction is achieved at the temperature of 60–80°C. The results of chemical analysis have been supported by the data of the IR, XRD and SEM instrumental analysis. Changing the molar ratio of 0.5:0.5 to 0.8:0.2, and with increasing temperature, various shaped crystals have developed in the remaining aqueous solutions with a morphology shifting from sharp needles to tetragonal prism. Crystalline material can be obtained by conversion method and it by the degree of purity can be used to obtain the fertilizers. Crystals can be obtained by selecting the appropriate conditions and they can be used in the other areas.

LITERATURE CITED

1. Retrieved December 10, 2014, from http://www.asu.lt/nm/l--projektas/DirvozemioIstekliu/5.html.
2. Sviklas, A.M., Paleckienė, R. & Šlinkšienė, R. (2008). *Compound fertilizers*, Vilnius.
3. *CODEXalimentarius*. Retrieved September 6, 2014 from http: //www. codexalimentarius. net/gsfaonline /additives/ details.
4. Hu, T.J., Zeng, G.M., Huanga, D.L. & Yu, H.Y., et al. (2007). Use of potassium dihydrogen phosphate and sawdust as adsorbents of ammoniacal nitrogen in aerobic composting process. *Journal of Hazardous Materials*, 141 (3). 736–744. DOI: 10.1016/j.jhazmat.2006.07.027.
5. Pritula, I., Kosinova, A. & Kolybayeva, M., et al. (2008). Optical, structural and microhardness properties of KDP crystals grown from urea – doped solutions. *Materials Research Bulletin*, 43 (10). 202–205. DOI: 10.1016/j.materresbull.2007.10.040.
6. De Vries, S.A., Goedtkind, P., Huisman, W.J., Zwanenburg & M.J., et al. (1999). X–ray diffraction studies of potassium dihydrogen phosphate (KDP) crystal surfaces. *Journal of Crystal Growth*, 205 (1–2). 2778–2782. DOI: 10.1016/S0022-0248(99)00249-3.
7. Retrieved November 15, 2014 from www.agrolink.ru/.../Лекция%2017.%20Кристализация.
8. Beckmann, W. (2013). *Crystallization*: *Basic Concepts and Industrial Applications*. Retrieved September 21, 2014 from: http://ebooks.ulb.tu-darmstadt.de/2274. DOI: 10.1002/9783527650323
9. Mullin, J.W., (2001). *Crystallization*, Butterworth Heinemann, 600.
10. Jančaitienė, K. & Šlinkšienė, R. (2014). Influence of the molar ratio of the basic materials and the temperature on the production of potassium dihydrophosphate. *Chemistry*, 2 (25), 89.
11. Tatariškinaitė, L. & Sviklas, A.M. (2002). Potassium phosphate production by conversion reaction. *Chemical technology*, 4 (25), 32.
12. Standards Association of Lithuania. (2009). Lithuanian standard: Fertilizers – Determination of ammoniacal nitrogen. EN15475 – 2009.
13. The Fertilizers (Sampling and Analysis) regulations // Agriculture. Statutory Instruments, London (1991).
14. Standards Association of Lithuania. (2009). Lithuanian standard: Fertilizers – Determination of the water-soluble potassium content. EN15477 – 2009.
15. Alov, N.V. & Garmas, A.V., et al. (2002). *Fundamentals of Analytical Chemistry* (Book 2) (pp. 147–150).
16. Šiaučiūnas, R., Baltakys, K. & Baltušnikas A. (2007). *Instrumental analysis of the silicate materials*, Kaunas.

17. *Scanning Electron Microscope*. Retrieved November 6, 2014 from http://www.purdue. edu/rem /rs/ sem. htm.
18. Jegatheesan, A., Murugan, J., Neelakantaprasad, B. & Rajarajan, G. (2012). FTIR, XRD, SEM, TGA Investigations of Ammonium Dihydrogen Phosphate (ADP) Single Crystal. *International Journal of Computer Applications*, 53 (4), 15–20. DOI: 10.5120/8408–2040.
19. Nakamoto, N. (1991). *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York.
20. Trinkūnaitė–Felsen, J., Žalga, A. & Kareiva, A. (2012). Characterization of naturally derived calcium compounds used in food industry. *Chemistry*, 2 (23), 76.
21. Srinivasan, K., Ramasamy, P., Cantoni, A. & Bocelli, G. (1998). Mixed crystals of $NH_4H_2PO_4$–KH_2PO_4: compositional dependence of morphology, microhardness and optical transmittance. *Materials Science&Engineering B*, 52 (2–3). 129–134. DOI: 10.1016/S0921-5107(97)00286-9.