Journal of the Serbian Chemical Society

Synthesis and characterization of ammonium phosphate fertilizers with boron

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Abstract: The concentration of boron, an essential micronutrient for plants, presents a narrow range between deficiency and toxicity. In order to provide the boron requirement for plants, and to avoid toxicity problems, boron compounds are mixed with basic fertilizers. Sodium borate pentahydrate was used as a boron source. Ammonium orthophosphates fertilizers with boron were prepared by neutralizing phosphoric acid with ammonia and addition of variable amounts of sodium tetraborate pentahydrate to the reaction mixture at a $NH_3:H_3PO_4$ molar ratio of 1.5. The fertilizers obtained with boron contents ranging from 0.05 to 1 % (w/w) were fully characterized by chemical analysis, thermal analysis, X-ray diffraction and infrared spectrophotometry. The studies showed that up to 500 °C, regardless of the boron content, no significant changes concerning thermal stability and nutritional properties occurred. Above 500 °C, an increase of thermal stability with an increase of the boron content was observed. X-Ray diffraction of a heat-treated sample containing 5 % (w/w) boron indicated the appearance of boron orthophosphate, BPO_4, as a new crystalline phase, and the disappearance of the previous structures above 500 °C, which explains the increase in thermal stability.

Keywords: sodium borate pentahydrate; fertilizer; micronutrient; diammonium hydrogen phosphate; ammonium dihydrogen phosphate; boron orthophosphate.

INTRODUCTION

Boron is an essential micronutrient for all vascular plants. Boron deficiency causes rapid biochemical, physiological and anatomical aberrations. It is very important to maintain a continuous supply of boron for efficient agricultural production.[1–5] Boron has restricted mobility in many plants and is freely mobile in others. In the majority of plant species, the boron distribution between plant or-

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gans indicates a restricted transport of boron. Thus, symptoms of boron deficiency occur mainly in the growing organs of plants. On the other hand, boron is highly mobile in some plants.[6] For example, under similar soil conditions, pistachio contains the highest boron concentration in the leaves and the lowest in fruit and seeds (leaf 130, hull 33, shell 2 and kernel 1 ppm/dry product). This indicates that boron is not transported from the leaves to the fruit and seeds. Unlike pistachio, apple trees grown under same conditions have the highest boron concentrations in the hull (51 ppm/dry product) and fruit (54 ppm/dry product), and lower boron concentration in the leaves (41 ppm/dry product) and shell (34 ppm/dry product).

The concentration of boron in leaves of different ages on the same plant provides evidence of boron mobility in plants. Thus, a higher boron concentration in older (basal) leaves than younger (apical) leaves indicates a restricted transport of boron. For example in tomato, the boron concentration (ppm/dry product) is 721 in basal leaves, 318 in middle and 94 in apical leaves. In contrast, higher boron concentration in younger leaves indicates boron mobility. For example in apple trees, boron concentration (ppm/dry product) in basal leaves is 50, middle leaves 56 and apical leaves 70.

Correction of boron deficiency is affected by boron mobility or immobility in plants. Boron is applied directly to developing tissues, such as flowers, in order to ensure an adequate boron supply during the time of their development. On the other hand, foliar sprays can be applied to boron-mobile species at any time when functional leaves are present. The applied boron corrects current deficiencies, and assures boron supply to future developing flowers and fruit tissues.[7]

Boron is required in small amounts. In order to maintain the recommended application rate, boron compounds are mixed with a basic fertilizer.[3,8] A very efficient boron-containing fertilizer, boron phosphate, BPO_4, when incorporated into soil, slowly releases soluble boron over a period of time corresponding at least to the critical uptake period of the usual crop. BPO_4 is not soluble in water; hence, there is no possibility of rainfall washing it from the soil.[9]

In the present study, ammonium phosphates with a variable boron content ranging from 0.1 to 1 % (w/w) were prepared by neutralizing phosphoric acid with ammonia and introducing sodium borate pentahydrate in variable amounts into the reaction mixture. In connection with a previous report,[10] in order to obtain heat-resistant fertilizers which undergo a minimum loss of ammonia, sodium borate was added to the reaction mixture at 1.5 NH_3:H_3PO_4 molar ratio. The pH of the reaction mixture was proved to be the controlling parameter of the neutralization process.[10,11] Thus, the dependence of pH on the NH_3:H_3PO_4 molar ratio was monitored. In addition, a boron free sample was prepared under the same conditions.

The objective of the present study was to examine to what extent the thermal and nutritive properties of boron-containing fertilizers are affected by changing the amount of sodium borate pentahydrate added to the reaction mixture. Consequently, the dried products were fully characterized by chemical analysis, thermal analysis, X-ray diffraction analysis and infrared spectroscopy. Another objective of the study was to investigate the possible formation of new chemical compounds of boron with phosphates from the system. With this end in view, an additional product containing a larger amount of boron (5 % w/w) was prepared.

EXPERIMENTAL

All employed reagents were of analytical grade. Volumes of 50 mL phosphoric acid, 43.5 % P_2O_5 (obtained from Merck phosphoric acid, 64.47 % w/w P_2O_5, with a minimum purity of 99 % w/w) were neutralized with a 25 % ammonia solution ("Reactivul" – Bucureşti, with a minimum purity of 99 %) under continuous stirring at 20 °C up to a pH of about 8.0. Crystalline sodium tetraborate pentahydrate (Merck, with a minimum purity of 99.8 % $Na_2B_4O_7$) was added in variable quantities to the reaction mixture at a 1.5 NH_3:H_3PO_4 molar ratio. The fertilizers obtained were dried at 60 °C. During the neutralization process with the addition of sodium tetraborate pentahydrate, the dependence of the pH of the reaction mass on the molar ratio NH_3:H_3PO_4 was measured using a Denver instrument 250 pH-meter.

The P_2O_5 content in the dried products was determined by gravimetric analysis.[12] The gravimetric determination of phosphorus was accomplished by its precipitation as magnesium ammonium phosphate hexahydrate $MgNH_4PO_4.6H_2O$ using a magnesium mixture as the precipitation reagent (55 g $MgCl_2$ + 70 g NH_4Cl dissolved in 250 cm^3 of a 10 % ammonia solution). The precipitate was converted by calcination at 1000 °C into magnesium pyrophosphate $Mg_2P_2O_7$ and weighed in that form. The nitrogen in the ammonia was determined by spectrophotometric analysis in the presence of Nessler reagent ($\lambda = 425$ nm)[13] and the boron content was determined by spectrophotometric analysis with Carmine Acid reagent ($\lambda = 630$ nm).[14,15] UV–Vis Spectra were recorded on a Cary 50 spectrophotometer.

Thermogravimetric, TG, and differential TG, DTG, curves were obtained on a computer controlled Netzsch TG 209 apparatus with a K(NiCr–Ni) thermocouple, in an platinum crucible, at a linear heating rate of 10 °C min^{-1}, in the temperature range 20–990 °C, under a dynamic atmosphere (nitrogen, 5 mL min^{-1}), on samples of about 10 mg.

X-Ray powder diffraction patterns were recorded on a Bruker D8 Advance diffractometer, in Bragg–Brentano geometry, with graphite monochromatized CuK-α ($\lambda = 1.5418$ Å) radiation.

The infrared spectra in KBr matrix were run on a Jasko 410 spectrophotometer in the wave number range 4000–400 cm^{-1}.

The sample containing 5 % boron was calcined for 2 h at 500 °C in a Nabertherm oven with a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The following samples were obtained through the neutralization of phosphoric acid with ammonia solution and sodium tetraborate pentahydrate addition to the reaction system:

– sample 1, with 0.05 % boron;
– sample 2, with 0.1 % boron;

– sample 3, with 0.5 % boron;
– sample 4, with 1 % boron;
– sample 5, with 5% boron and
– sample 6, without boron.

The boron content was expressed as g boron/100 g diammonium hydrogen phosphate.

Dependency of the pH of the reaction system on the NH_3:H_3PO_4 molar ratio

The pH of the reaction mixture was measured during the preparation of samples 1–4. The dependency of the pH of the reaction mixture on the NH_3:H_3PO_4 molar ratio is shown in Fig. 1.
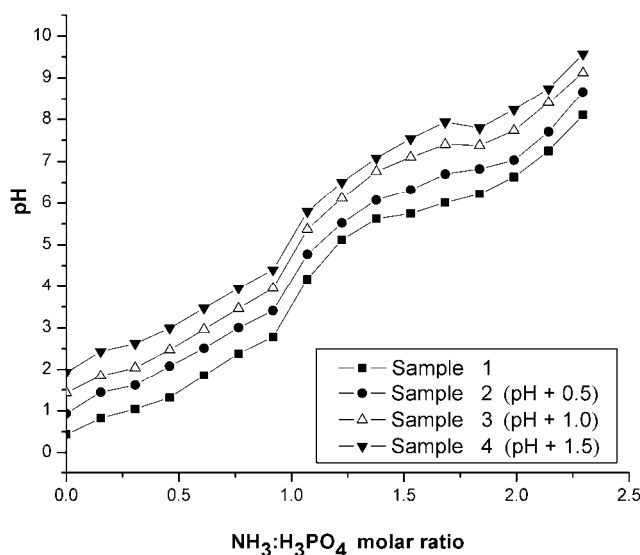

Fig. 1. Dependency of the pH on the NH_3:H_3PO_4 molar ratio during the synthesis of samples 1–4.

The curves shown in Fig. 1 have similar profiles. The pH values corresponding to similar NH_3:H_3PO_4 molar ratios were very similar for the 4 samples. In order to distinguish the curves and to obtain a higher accuracy of the figure, the experimental pH values corresponding to samples 2–4 were offset 0.5, 1, and 1.5 pH-units, respectively. Each curve has two inflection points corresponding to completion of ammonium dihydrogen phosphate (ADP), and diammonium hydrogen phosphate (DHP) formation. The experimental pH values and the NH_3::H_3PO_4 molar ratio corresponding to the inflections points are given in Table I.

The pH value and the NH_3:H_3PO_4 molar ratio corresponding to the first inflection point are similar for each neutralization curve. This was also the case for the second inflection point. Consequently, up to a limit of 1 % B in the final

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product, the neutralization process was not significantly influenced by the addition of sodium tetraborate pentahydrate to the reaction mixture.

TABLE I. NH_3:H_3PO_4 molar ratio and pH values at the inflection points of the pH *vs.* NH_3:H_3PO_4 molar ratio curves during the synthesis of samples 1–4

Sample	Inflection point 1		Inflection point 2	
	NH_3:H_3PO_4 molar ratio	pH	NH_3:H_3PO_4 molar ratio	pH
1	1	3.56	1.84	6.40
2	1	3.66	1.84	6.40
3	1	3.67	1.82	6.33
4	1	3.68	1.85	6.53

Chemical composition

The chemical composition of samples 1–4 are given in Table II.

The N:P_2O_5 mass ratio, corresponding to the samples 1–4, ranges from 0.38 to 0.39. Thus, in accordance with literature data,[10,11,16] a DHP and ADP mixture is obtained. The addition of sodium tetraborate up to a limit of 1% (w/w) boron in the final product did not significantly change the content of macronutrients N and P in the products obtained.

TABLE II. The chemical composition of samples 1–4

Sample	P_2O_5 Content, %	N–NH_4 Content, %	Mass ratio N:P_2O_5	Boron content, %
1	52.3	20	0.38	0.07
2	50.5	19.9	0.39	0.1
3	50.3	19	0.38	0.5
4	49.4	19.1	0.38	0.9

Thermal analysis

The thermogravimetric curves (TG and DTG) obtained by heating samples 1–4 from 20 to 990 °C at a heating rate of 10 °C min^{-1} are shown in Figs. 2–5, respectively.

TG and DTG analysis showed that the thermal decomposition of sample 2–4 began at 30 °C and proceeded up to about 990 °C. The DTG curves showed four processes associated with mass loss. Sample 1 was relatively stable up to 65 °C. Above this temperature, thermal decomposition proceeded up to about 900 °C. The mass losses of samples 1–4 and the corresponding temperature ranges are shown in Table III in comparison to similar data obtained by heating sample 6 (ammonium phosphate without boron) in the same temperature range.[11]

The first process with mass loss (samples 2–4), observed within the temperature range 30–65 °C was assigned to the partial dehydration of sodium borate pentahydrate; the mass loss increased with increasing boron content. No ammonia was released; hence the nutritional properties of the obtained fertilizers were not affected. Sample **1** was stable up to 65°C.
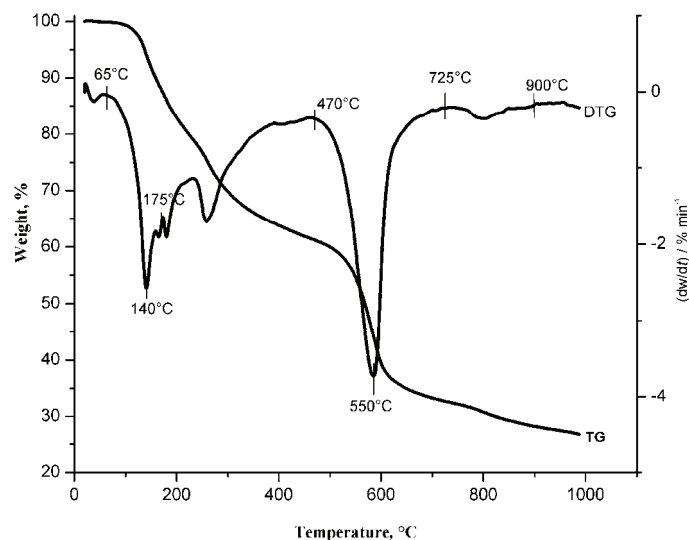
Fig. 2. Thermal gravimetric curves (TG and DTG) of sample 1.
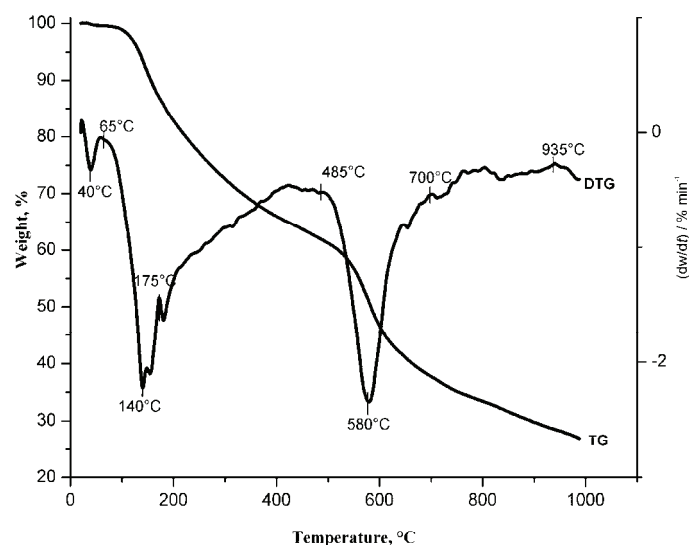

Fig. 3. Thermal gravimetric curves (TG and DTG) of sample 2.

The second process with mass loss (samples 1–4) occurred from 65 °C up to around 500 °C and developed in two stages. In the first stage, the mass loss was assigned to DHP decomposition with ammonia release and ADP formation (reaction (1)). In the second stage, the mass loss was assigned to the decomposition of ADP to ammonium metaphosphate, according to equations 2 and 3, which is in agreement with literature data,[17,18] and to the liberation of constitution water during polycondensation processes.[19,20] The TG curves showed continuous mass

loss; thus, the processes occurred in a very complex manner, which could not be separated into individual reactions:
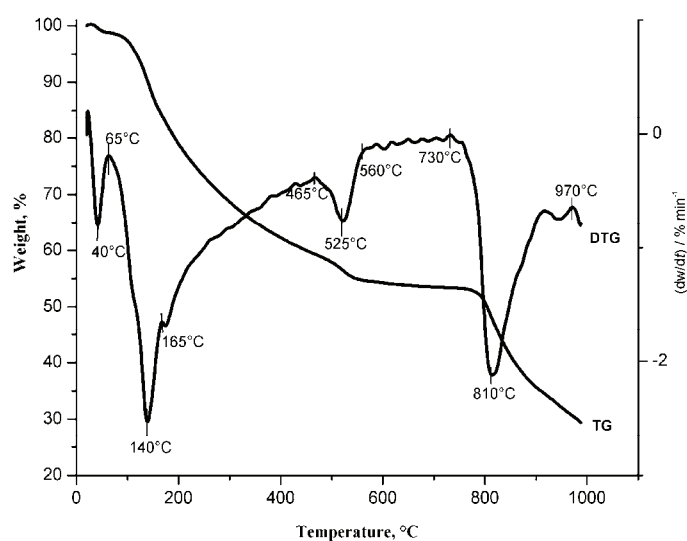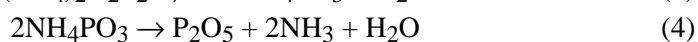
$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3 \qquad (1)$$

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O \qquad (2)$$

$$(NH_4)_2H_2P_2O_7 \rightarrow 2NH_4PO_3 + H_2O \qquad (3)$$

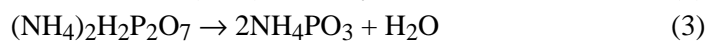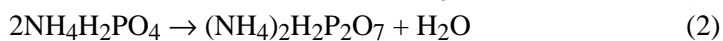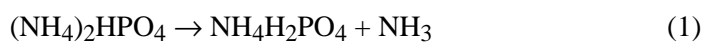$$2NH_4PO_3 \rightarrow P_2O_5 + 2NH_3 + H_2O \qquad (4)$$

Fig. 4. Thermal gravimetric curves (TG and DTG) of sample 3.

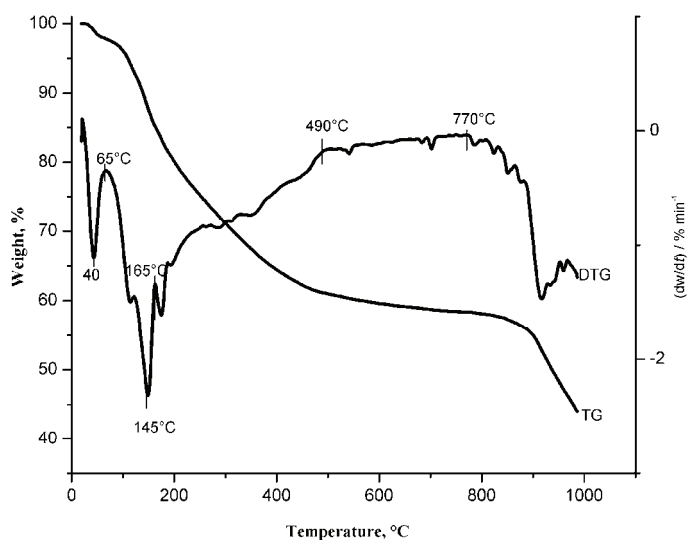Fig. 5. Thermal gravimetric curves (TG and DTG) of sample **4**.

TABLE 3. Mass losses on heating for samples 1–4, 6

Sample	Temp. range °C	Mass loss %	Temp. range °C	Mass loss %	Temp. range °C	Mass loss %	Temp. range °C	Mass loss %	Final residue %
1	30–65	–	65–470	39	470–725	28	725–900	4.7	27
2	30–65	0.13	65–485	38	485–700	24.5	700–935	8.5	27
3	30–65	0.44	65–465	40	465–560	4.2	730–970	22.7	29.5
4	30–65	0.87	65–490	37	490–770	–	770–990	14	44
6	30–65	–	65–490	37	490–700	43	750–850	5	12.5

On the DTG curve of sample 1 (Fig. 2), an endothermic peak at about 250 °C appears, which could be assigned to the mass loss described by reaction (2), which was particularly separated from the other processes.

Up to about 500 °C, the thermal behavior of samples 1–4 was not influenced by the addition of sodium tetraborate. The boron-containing samples underwent similar mass losses (ammonia nitrogen) within similar temperature ranges as those for the boron-free sample 6.

Consequently, on processing the obtained fertilizers up to 500 °C, their nutritional properties were not affected by the addition of boron, in comparison with the ammonium phosphates without boron.

The third process with mass loss occurred in the temperature interval from around 500 up to around 700 °C. The mass loss, assigned to sublimation of P_2O_5, decreased with increasing content of boron. The mass loss of the boron-free sample 6 within 490 and 700 °C was 43 %. Sample 1 lost 28 % mass between 470 and 725 °C, the mass loss of sample 2 within the temperature range 485–700 °C was 24.5 %. Sample 3 lost only 4.2 % mass between 465 and 560 °C, while between 560 and 730 °C no mass loss was registered. Sample 4 was stable within 490 and 770 °C, the decomposition processes were shifted towards higher temperatures.

The fourth process with mass loss occurred on further heating of samples 1–4 up to 990 °C. An increase of mass loss with increasing boron content was observed. The mass loss was assigned to the decomposition of the polycondensation products.[19,20] The completion of the decomposition process was shifted towards higher temperatures from sample 1 to sample 3. The decomposition of sample 4 was not completed at 990 °C.

Increasing the boron content resulted in an increase of the thermal stability of the obtained fertilizers at temperatures above 500 °C.

X-Ray diffraction

The X-ray diffraction patterns of samples 1, 3 and 4 together with that of sample 6 (ammonium phosphate without boron)[11] for comparison are given in Fig. 6.
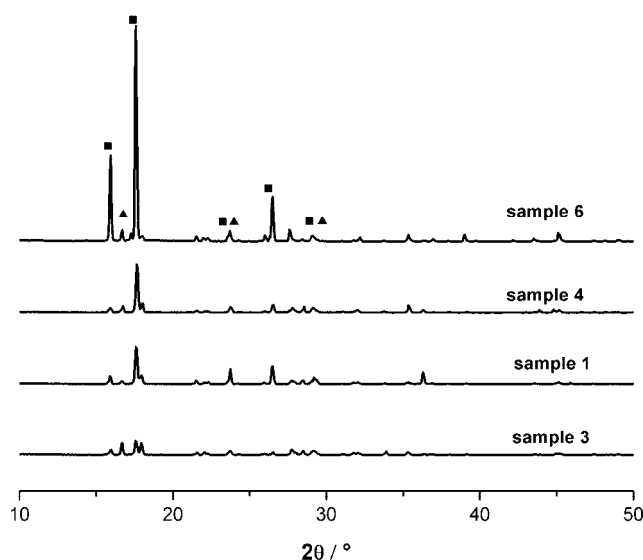
Fig. 6. X-Ray diffraction pattern of samples 1, 3, 4 and 6; ■ – $(NH_4)_2HPO_4$; ▲ – $NH_4H_2PO_4$.

Two crystalline phases were detected in all the three boron-containing samples: monoclynic diammonium hydrogen phosphate[21] and tetragonal ammonium dihydrogen phosphate.[22]

Regardless of the boron content, no new crystalline phases could be detected by X-ray diffraction in any of the three samples. Therefore, ammonium phosphate with boron concentration of up to 1 % (w/w) may be utilized as fertilizers, without any structural changes in comparison to the fertilizers without boron.

FTIR Analysis

The infrared spectrum of sample 4, having the maximum boron content in the series, was compared with the spectrum of boron-free ammonium phosphates (sample 6). The spectra are shown in Fig. 7.

According to literature data,[23–25] the following four bands are observed in the infrared spectrum of BPO_4: 1085, 925, 615 and 550 cm^{-1}. The IR spectrum of sample 4 showed three absorption bands at 1080, 950 and 550 cm^{-1}, which eventually could be assigned to the B–O–P link, present in boron orthophosphate, BPO_4. However, as can be seen, the IR spectrum of sample 4 was almost the same as the IR spectrum of sample **6**. This could be explained by the low concentration of boron and by overlapping with the IR bands assigned to ammonium phosphate. The difference spectrum between sample **6** and sample **4** was recorded in order to emphasize the boron presence (spectrum 4, Fig. 7). Although a weak band at around 933 cm^{-1} appeared, the other three bands (1085, 615 and 550 cm^{-1}) were not observed, which confirms the overlapping of the bands. In conclusion,

no B–O–P or B–P bonds that could eventually affect the assimilation boron by plants were detected in the infrared spectrum of sample 4.
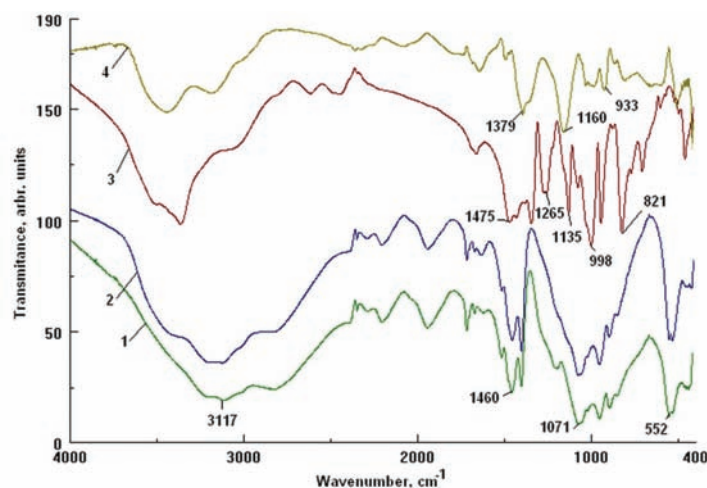

Fig. 7. Infrared spectra: 1) sample 6; 2) sample 4; 3) sodium tetraborate; 4) sample 4 minus sample 6.

X-Ray diffraction and infrared spectrum of heat treated fertilizer

A possible explanation of the increase in thermal stability above 500 °C with increasing boron content was the formation of a new chemical combination of boron with the phosphates present in the system. In order to investigate the new structure, product **5** with a higher boron content (5 %) was calcined at 500 °C. The calcined product was investigated by X-ray diffraction and infrared spectroscopy. The X-ray patterns are shown in Fig. 8.

The X-ray pattern after calcination at 500 °C indicated the disappearance of the previous structures and the appearance of BPO_4, boron orthophosphate,[26] which explains the increase of thermal stability with increasing boron content.[24] In addition, the formation of BPO_4 induced an improvement in the efficiency the fertilizer.[9,27]

The infrared spectrum of product 5 is shown in Fig. 9.

The IR spectrum of sample 5 showed all the bands assigned to boron phosphate, slightly shifted towards higher frequencies, which confirms the XRD data. In addition, some bands appeared, assigned as γ_{as} PO_2 (1276 cm^{-1}),[28] γ_s P–O–P (766 cm^{-1})[29] and δ PO_2 (511 cm^{-1})[29] vibrations, characteristic of polyphosphates.

In conclusion, in addition to the already studied methods,[9,23,24] boron orthophosphate may be obtained by calcination at 500 °C of the neutralization products of phosphoric acid with ammonia and addition of boron tetraborate to the reaction system.
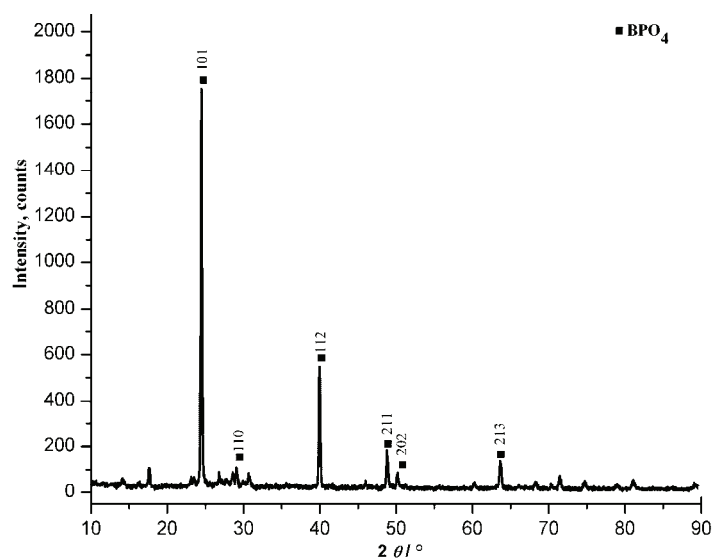
Fig. 8. X-Ray diffraction pattern of the sample calcined at 500 °C; ● – BPO$_4$.
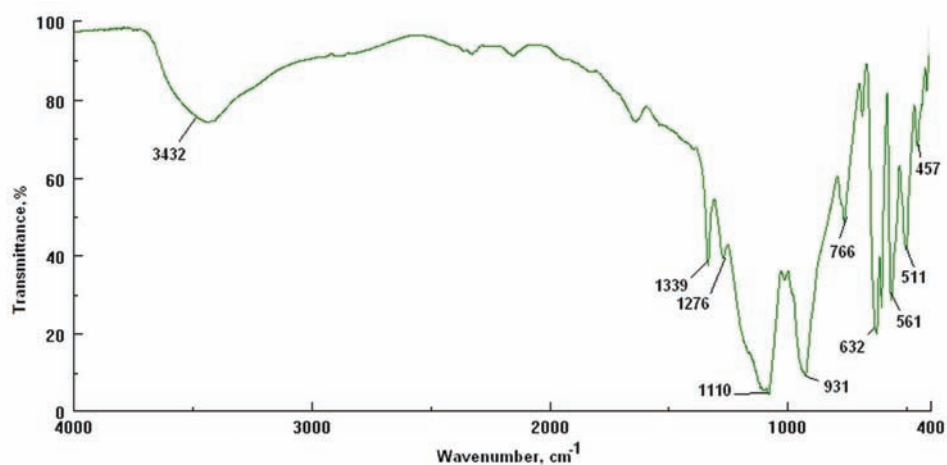

Fig. 9. Infrared spectrum of the sample calcined at 500 °C.

CONCLUSIONS

The pH of the reaction mixture represents a control parameter which enables the proper management of the neutralization process of phosphoric acid with ammonia in presence of sodium tetraborate pentahydrate. Up to a concentration of 1 % boron in the final product, the addition of sodium tetraborate did not significantly influence the neutralization process.

Chemical analysis of the products obtained showed that the addition of sodium tetraborate up to a content of 1 % boron in the final product did not signi-

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ficantly change the nutritional properties of the fertilizers in respect to the content of nitrogen and phosphorus.

Thermal analysis showed that up to 500 °C, regardless of boron content, no significant differences in thermal behavior of the boron-containing fertilizers in comparison with the boron free-fertilizer were observed. The thermal stability of the products obtained during their processing up to 500 °C was not changed. Moreover, the products underwent similar mass losses (ammonia nitrogen); hence their nutrition qualities were not altered. Above 500 °C, the thermal stability of fertilizers increased with increasing boron content.

X-Ray diffraction analysis showed that no structural changes of the obtained products occurred with increasing content of boron, compared with boron-free ammonium phosphates.

The infrared spectra did not positively confirm the formation of new chemical compounds of boron with the phosphates present in the system.

In conclusion, the addition of sodium tetraborate pentahydrate to the reaction mass of phosphoric acid with ammonia at a $NH_3:H_3PO_4$ molar ratio equal to 5, up to a limit of 1 % boron in the final products, did not result in any changes of structure and nutritional properties of the obtained products compared with boron-free ammonium phosphates.

On calcination at 500 °C of a 5 % boron-containing fertilizer, boron phosphate, which is a quality fertilizer with high contents of boron and phosphorus and a slow release of boron, was obtained.

ИЗВОД

СИНТЕЗА И КАРАКТЕРИСАЊЕ АМОНИЈУМ-ФОСФАТНОГ ЂУБРИВА
СА ДОДАТКОМ БОРА

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Бор је један од основних микро-нутрицијената биљака, али је према концентрацији узан опсег између дефицитарности и токсичности. Да би се обезбедила потреба биљака за бором и избегао проблем токсичности, једињења бора се мешају са основним ђубривом. У овом раду је као извор бора коришћен натријум-борат пентахидрат; у реакциону смешу са молским односом $NH_3:H_3PO_4$ 1,5 за добијање амонијум-ортофосфатног ђубрива неутрализацијом фосфорне киселине амонијаком, додаване су променљиве количине натријум-тетраборат пентахидрата. Ђубриво које садржи 0,05–1 % w/w бора потпуно је окарактерисано хемијском анализом, термичком анализом, дифракцијом X-зрака и инфрацрвеном спектрофотометријом. Испитивања су показала да до температуре 500 °C, без обзира на садржај бора, не долази до значајних промена термичке стабилности и нутрификационих својстава, а изнад ње повећава се термичка стабилност са повећањем садржаја бора. Дифракција X-зрака термички третираних узорака који садрже 5 % w/w бора, указала је на присуство бор-ортофосфата, BPO_4, као

нове кристалне фазе и нестајање претходних структура изнад температуре 500 °C, што објашњава повећање термичке стабилности.

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