Studies about Ammonium Phosphates Fertilizers with Boron Added as Boric Acid

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Boron, an important micronutrient for plants, is mainly applied mixed with basic fertilizers. Ammonium phosphates fertilizers with boron were obtained by neutralization of phosphoric acid with ammonia solution. Boric acid, as boron source, was added to the reaction mass at a NH3:H3PO4 molar ratio of 1.5. Fertilizers were prepared with addition of variable quantities of boric acid, in order to obtain products containing 0.1-1% boron. A standard sample without boric acid addition was prepared. In order to determine the influence of boric acid on the properties of the obtained fertilizers, the fertilizers without and with variable boron content have been subjected to a complex study, including chemical analysis, thermal analysis, X-ray diffractometry and FT-IR spectroscopy.

Keywords: ammonium phosphates, boric acid, complex fertilizers, micronutrient

The micronutrients are applied in small quantities. Boron, more than other micronutrients, presents a narrow range between deficiency and excess. These are the reasons why a strictly controlled application of fertilizers with boron is required [1-7]. Boron can be applied as a primary fertilizer, but also mixed with alkaline fertilizers [1]. In order to have a strict control on the boron content, the application of boron compounds mixed with basic fertilizers is highly recommended. In our work, ammonium phosphates fertilizers containing boron as microelement were obtained. Boron has been added as crystalline boric acid to the reaction mass, at a NH3:H3PO4 molar ratio of 1.5, in order to obtain some thermal stable fertilizers, with a minimum loss of ammonium nitrogen [8]. Variable quantities of boric acid were introduced, and the obtained products, dried at 60°C, have been subjected to a complex study: chemical analysis, thermal analysis, X rays diffractometry, FT-IR spectroscopy.

Experimental part

All reagents were of analytical grade. The ammonium phosphates fertilizers were obtained through neutralization of determined volumes (50 mL) of phosphoric acid 43.5% P2O5 (Merck, with a minimum purity of 99%) with ammonia solution 25% ('Reactivul' – București, with a minimum purity of 99%), through continuous stirring, up to a pH about 8.8. Crystalline boric acid (Merck, min. 99.8% H3BO3) was added in variable quantities to the reaction mass at a 1.5 NH3:H3PO4 molar ratio. The pH measurements were carried out on a Denver Instruments 250 pH-meter.

P2O5 content of the fertilizers was determined through gravimetric analysis [9], using magnesium mixture as precipitation reagent (55g MgCl2 + 70g NH4Cl dissolved in 250 cm3 of 10% ammonia solution) and a Denver analytical balance, with a maximum capacity of 110 g and a sensibility of 0.1 mg. The ammonia nitrogen was determined by spectrophotometric analysis with carmine acid reagent (λ = 630 nm) [11, 12]. A Cary 50 spectrophotometer was used to record the absorbance spectra.

The TG and DTG curves have been recorded in the temperature range 20-1000°C at a heating rate of 10°C min–1, on a computer controlled NETZSCH TG 209 apparatus with a K (NiCr-Ni) thermocouple, in Al2O3 crucibles.

X-ray powder diffraction patterns were taken on a Bruker D8 Advance diffractometer, in Bragg-Brentano geometry, with graphite monochromatized CuKα radiation of a 1.5148 Å characteristic wavelength.

The FT-IR spectra in KBr matrix were recorded to a Jasko 410 spectrophotometer in the region 4000 - 400 cm–1.

Results and discussions

As a result of the neutralization process of phosphoric acid with ammonia, without and with boric acid addition to the reaction mass, the following four samples were obtained:

– sample A, without boron
– sample B, with 0.1 % boron
– sample C, with 0.5 % boron
– sample D, with 1% boron

The boron content of the samples was given as boron mass (grams) in 100 g diammonium hydrogen phosphate.

Chemical composition

The data regarding the chemical composition of the samples are presented in table 1. The N/P2O5 molar ratio which takes values between 0.37 and 0.41 is not significantly influenced by boron content. Regardless the amount of boric acid added to the reaction mass, in accordance with literature data [13 - 15], a mixture of diammonium hydrogen phosphate (NH4)2HPO4 and ammonium dihydrogen phosphate NH4H2PO4 was obtained. Boron content of the samples lies in the limits of the initial chosen values.
Thermal studies
The results of the thermogravimetric analysis of samples A-D, expressed by the TG curves and their derivatives DTG, are presented in figures 1-4.

Table 1
CHEMICAL COMPOSITION OF THE OBTAINED FERTILIZERS

<table>
<thead>
<tr>
<th>Sample</th>
<th>P₂O₅/ %</th>
<th>N-NH₄/ %</th>
<th>Massic ratio N/P₂O₅</th>
<th>Boron/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50.9</td>
<td>19</td>
<td>0.37</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>51.1</td>
<td>21.1</td>
<td>0.41</td>
<td>0.1</td>
</tr>
<tr>
<td>C</td>
<td>51.9</td>
<td>20.1</td>
<td>0.39</td>
<td>0.5</td>
</tr>
<tr>
<td>D</td>
<td>49.4</td>
<td>19.1</td>
<td>0.39</td>
<td>0.9</td>
</tr>
</tbody>
</table>

From figure 1 one can observe that at a heating rate of 10°C min⁻¹ sample A is stable up to 65°C. Above 65°C, the DTG curve shows three processes associated with mass loss. The first process takes place in two steps, in the temperature range 65-490°C. In the first step, the mass loss which occurs in the range 65-175°C, with a maximum rate at 145°C is attributed to the decomposition of diammonium hydrogen phosphate to ammonium dihydrogen phosphate with ammonia evolution (1). In the second step, between 175 and 490°C, thermal decomposition processes of ammonium dihydrogen phosphate take place (2-4). Ammonium dihydrogen phosphate decomposes to ammonium pyrophosphate (2), which in turn is transformed to ammonium metaphosphate (3). Ammonium metaphosphate decomposes to P₂O₅ (4) with ammonia and water evolution [16-18].

\[
\text{(NH}_4\text{)}_2\text{HPO}_4 \rightarrow \text{NH}_4\text{H}_2\text{PO}_4 + \text{NH}_3 (g) \quad (1)
\]

\[
2\text{NH}_4\text{H}_2\text{PO}_4 \rightarrow (\text{NH}_4\text{)}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} (g) \quad (2)
\]

\[
(\text{NH}_4\text{)}_2\text{H}_2\text{P}_2\text{O}_7 \rightarrow 2\text{NH}_4\text{PO}_3 + \text{H}_2\text{O} (g) \quad (3)
\]

\[
2\text{NH}_4\text{PO}_3 \rightarrow \text{P}_2\text{O}_5(g) + 2\text{NH}_3(g) + \text{H}_2\text{O} (g) \quad (4)
\]

The TG curve shows a constant mass loss up to 490°C, so the reactions 2-4 take place in a very complex manner and can not be separated as individual reactions [18].

The second process occurs between 490 and 700°C, and the mass loss is attributed to the sublimation of P₂O₅ with a maximum rate at 625°C. Between 700°C and 750°C the mass of the sample remains constant.

The third process occurs in the temperature range 750-850°C; the decomposition of the sample continues with a maximum rate at 780°C.
The first process of the thermal decomposition of samples B, C and D (figs. 2-4) is overlapped with the thermal decomposition of boric acid with water release [19]. The mass losses and the temperature ranges corresponding to the thermal decomposition of the samples are presented in table 2.

From figures 1-4 and table 2 one notice that the presence of boric acid does not modify the thermal behaviour of the samples up to 500°C: the samples undergo similar mass losses in the same temperature ranges. Above 500°C, up to a temperature of about 760°C, one can observe a decrease of mass loss at samples B, C and D, compared to sample A. At further heating, the decomposition process of sample A is completed at a lower temperature than the decomposition of samples B and C. Sample D is relatively stable at temperatures above 715°C and its decomposition process is not completed up to 1000°C. In conclusion, at temperatures above 500°C, the thermal stability of the products increases with the increase of boron content.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature range/ °C</th>
<th>Mass loss/%</th>
<th>Temperature range/ °C</th>
<th>Mass loss/%</th>
<th>Temperature range/ °C</th>
<th>Mass loss/%</th>
<th>Final residue/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65-490</td>
<td>37</td>
<td>490-700</td>
<td>43</td>
<td>750-850</td>
<td>5</td>
<td>12.5</td>
</tr>
<tr>
<td>B</td>
<td>65-515</td>
<td>39.5</td>
<td>515-690</td>
<td>31</td>
<td>740-930</td>
<td>10.3</td>
<td>16.3</td>
</tr>
<tr>
<td>C</td>
<td>65-490</td>
<td>36.9</td>
<td>490-760</td>
<td>25.2</td>
<td>760-950</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>D</td>
<td>65-480</td>
<td>36.1</td>
<td>480-715</td>
<td>28.9</td>
<td>715-950</td>
<td>4</td>
<td>29.5</td>
</tr>
</tbody>
</table>

X-ray powder diffraction

The X-ray powder diffraction pattern of samples A, C, D are shown in figures 5-7.

Sample A (fig. 5) has the highest degree of crystallinity in the series. Sample C (fig. 6) has a lower degree of crystallinity than sample A (fig. 5), while sample D (fig. 7) has the lowest degree of crystallinity in the series. Two crystalline phases were detected in all the three samples of the series: diammonium hydrogen phosphate (NH₄)₂HPO₄ (tetragonal) [20] and ammonium dihydrogen phosphate NH₄H₂PO₄ (monoclinic) [21]. The presence of boric acid doesn’t modify the crystalline phases of the obtained products, but the degree of crystallinity decreases with the increase of boron content. No crystalline phases corresponding to some possible new chemical combinations of boron, which could affect its assimilation by plants, were detected.

FT-IR spectroscopy

Samples A and D, respectively boric acid were subjected to the infrared spectroscopy analysis. The spectra are shown in figure 8.
As expected, because of the low value of boron content, the spectrum of sample D has the same profile as the spectrum of sample A. The IR spectrum of sample D shows three absorption bands at 1080, 950 and 550 cm⁻¹. These three bands could be assigned to the B-O-P group present in boron orthophosphate BPO₄. According to literature data the IR spectrum of BPO₄ presents four characteristic intense bands at 1085, 925, 615 and 550 cm⁻¹ [22-24]. The possible presence of boron phosphate would not affect the quality of the obtained fertilizers, because BPO₄ itself is known as an efficient boron source used in agriculture [25, 26]. However, it doesn’ necessary mean that the three bands in the IR spectrum of the sample D belong to a new formed system, because overlapping with the characteristic frequencies assigned to ammonium phosphates is possible. Besides, the band at 615 cm⁻¹ was not observed. In order to emphasise the differences between the spectra of samples A and D, the substraction of the two spectra were recorded (spectrum 4, fig. 8). Although a weak band around 620 cm⁻¹ was observed, the other three bands does not appear any more, which confirms the possibility of bands overlapping. In conclusion, neither infrared spectral analysis nor X-ray diffractometry confirmed the formation of new chemical combinations between boric acid and ammonium phosphates.

Conclusions

In order to obtain ammonium phosphates fertilizers containing boron as micronutrient, variable quantities of boric acid were added to the reaction mixture at the NH₃:H₃PO₄ molar ratio of 1.5. Regardless boron content, a mixture of diammonium hydrogen phosphate and ammonium dihydrogen phosphate was obtained.

At temperatures which do not exceed 500°C, boric acid addition does not affect the thermal behaviour of the obtained products. At temperatures above 500°C, the thermal stability of the obtained fertilizers increases with the increase of boron content. Neither X-ray diffractrometry nor IR spectroscopy confirm any possible chemical combinations of boron with ammonium phosphates, which could affect its assimilation by plants. In conclusion, ammonium phosphates with addition of boric acid, processed at temperatures lower than 500°C, may be used as fertilizers with a boron content up to 1%, with no changes concerning thermal stability, nutritive elements content and boron assimilation by plants in comparison with boron free fertilizer.

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