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INVESTIGATION ON THE PHOSPHATE ROCK DISSOLUTION PROCESS BY PARTIAL ACIDULATION (PAPR METHOD) USING SULFURIC AND PHOSPHORIC ACID

BADANIA NAD CZĘŚCIOWYM ROZKŁADEM FOSFORYTU (METODĄ PAPR) Z ZASTOSOWANIEM KWASU SIARKOWEGO I FOSFOROWEGO

Abstract: The results of few factors on the each form of phosphates content in the PAPR-type fertilizer preparations were presented. Type of mineral acid, its concentration, amount and fineness were taken into account. Investigation was carried out with the recommendations enclosed in Regulation (EC) No 2003/2003 of the European Parliament and the Council on 13.10.2003 related to fertilizers, test methods for the phosphate content evaluation in fertilizers.

Keywords: partially acidulated phosphate rocks (PAPR), mineral acids, phosphate fertilizers, available P

One of the most popular fertilizers are phosphate fertilizers, mainly superphosphates – single and triple superphosphate which varies in the substrates used in the manufacture process. Traditional and main phosphorus source for phosphate fertilizers production process are phosphate rocks which differs in phosphorus compounds content expressed as a P_2O_5. Phosphate fertilizer manufacture process is based on treating grinded phosphate rocks (in the form of meal) with mineral acid. Main types of acids used in the manufacture process are sulfuric and phosphoric acid. As a result of phosphate raw material dissolution with phosphoric acid, triple superphosphate is being produced. When using sulfuric acid, single superphosphate is being produced. Main difference between triple and single superphosphate is phosphorus compounds content expressed as a P_2O_5. In triple superphosphate it is about three times higher than in the

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single superphosphate. Reason for this phenomenon is that phosphoric acid constitutes for additional phosphorus source in fertilizer. Depending on acid amount used in the fertilizer manufacture process, acidulation could be complete or partial. Complete acidulation takes place when the amount of acid used in the process is stoichiometric to calcium content in phosphate raw material. If the amount of acid is lower than stoichiometric to calcium content (usually 30–50 % amount of acid needed to complete dissolution) acidulation is partial [1]. Products manufactured with lower amount of acid are called PAPR fertilizer (PAPR – Partially Acidulated Phosphate Rock). Phosphate fertilizer production depends on raw material supply. One of the most important phosphate rocks suppliers, which supply main part of Polish market is Morocco and Tunisia. Rapid phosphate fertilizer market crash in 2008, caused prices increase of about 1000 % [2]. Fluctuations in the fertilizer market caused phosphate rocks output decrease and as a consequence fertilizer production decrease, which has caused fertilizer prices increase. As a result, buying possibility was limited to farmers. To avoid situation which has taken place in 2008, it is justified to search cost-effective, alternative fertilizers for conventional superphosphates, which can be used in the Polish climatic conditions. Recent trends in fertilizer market are focused on possibility of using partially acidulated phosphate rocks (PAPR – type fertilizers) as an alternative phosphorus source for crops in Poland. PAPR – type fertilizers are PAPR – partially acidulate phosphate rocks and preparations based on SSP or TSP – phosphate rocks mixtures, which differs in production process. PAPR are made by treating phosphate rock with less than the stoichiometric amount of acid needed for complete acidulation of apatite structure in the raw material [3]. Manufacture process of superphosphate – phosphate rock mixtures is based on mechanical blending of superphosphate and phosphate rock. Incomplete dissolution of apatite structure in both type of fertilizers makes them able to supply adequate dose of phosphorus in the whole plant growth cycle, because they contain both water soluble and insoluble phosphorus compounds. In the first phase of plant growth only water soluble compounds are available [4–6]. In the next phases, as a result of metabolic processes of microorganisms, water insoluble forms are becoming available for plants. There is a lack of data concerning PAPR – type fertilizers use in the modern climate of Central Europe, especially in Poland, whereas PAPR – type fertilizers are widely used in climate conditions of Australia, New Zealand where they show same agronomic effectiveness as conventional superphosphates [1, 7, 8].

Materials and methods

Research on the partial acidulation of Tunisia phosphate rock and the influence of acid type, amount and concentration, raw material fineness and also alterations in the phosphorus content in time for each product were presented. PAPR – type fertilizes were made using Atlas Syrris apparatus equipped with hotplate, teflon vessel and aluminium coating allowing to control temperature, stirring intensity and time of the process. Fertilizers were obtained using Tunisia phosphate rock, containing about 28.5 % P_2O_5. Phosphorus content in each product was being analyzed in the day of its manufacture and after 2, 4, 7, 10, 14 days. The influence of fineness on partial acidulation process was investigated by sampling two following fractions: 125–160 and 250–500 μm. Phosphoric and sulfuric acids were taken into consideration in examination of acid type influence on phosphorus compound content in products. Three values of degree of PAPR stoichiometric norm (η_{PAPR}) were taken into consideration: 0.3; 0.5; 0.7. Degree of PAPR stoichiometric norm determines amount of acid used in the process in proportion to acid required for complete acidulation of apatite structure of phosphate rock. Examination of the acid concentration influence on phosphorus compounds content was carried out using two values of concentration for each acid. For sulfuric acid it was 65 and 75 mass percent and for phosphoric acid it was 62 and 69 mass percent Manufactured PAPR type fertilizers were compared with fully acidulated reference samples (η_{PAPR} = 1). Analyzes of phosphorus content in fertilizers were carried out with the recommendations enclosed in Regulation (EC) No. 2003/2003 of the European Parliament and the Council on 13.10.2003 related to fertilizers, test methods for the phosphate content evaluation in fertilizers [9].

Results and discussion

Table 1 presents PAPR – type fertilizers manufacture process parameters in lab-scale. Results of the analysis of water soluble and available phosphorus compound in ratio to total phosphorus content of selected fertilizers were presented.

Table 1

Fertilizers manufacture process parameters

Fineness [μm]	Acid conc. [% w/w]	Acid type	Product number and η_{PAPR}
125–160	75	sulfuric	P1(η_{PAPR} = 0.7), P2(η_{PAPR} = 0.5), P3(η_{PAPR} = 0.3)
125–160	65	sulfuric	P4(η_{PAPR} = 0.7), P5(η_{PAPR} = 0.5), P6(η_{PAPR} = 0.3)
250–500	75	sulfuric	P7(η_{PAPR} = 0.7), P8(η_{PAPR} = 0.5), P9(η_{PAPR} = 0.3)
250–500	65	sulfuric	P10(η_{PAPR} = 0.7), P11(η_{PAPR} = 0.5), P12(η_{PAPR} = 0.3)
125–160	69	phosphoric	P13(η_{PAPR} = 0.7), P14(η_{PAPR} = 0.5), P15(η_{PAPR} = 0.3)
125–160	62	phosphoric	P16(η_{PAPR} = 0.7), P17(η_{PAPR} = 0.5), P18(η_{PAPR} = 0.3)
250–500	69	phosphoric	P19(η_{PAPR} = 0.7), P20(η_{PAPR} = 0.5), P21(η_{PAPR} = 0.3)
250–500	62	phosphoric	P22(η_{PAPR} = 0.7), P23(η_{PAPR} = 0.5), P24(η_{PAPR} = 0.3)
125–160	75	sulfuric	P29(η_{PAPR} = 1)
125–160	65	sulfuric	P30(η_{PAPR} = 1)
250–500	75	sulfuric	P31(η_{PAPR} = 1)
250– 500	65	sulfuric	P32(η_{PAPR} = 1)
125–160	69	phosphoric	P25(η_{PAPR} = 1)
125–160	62	phosphoric	P26(η_{PAPR} = 1)
250–500	69	phosphoric	P27(η_{PAPR} = 1)
250–500	62	phosphoric	P28(η_{PAPR} = 1)

In the picture from 1 to 8 changes in the phosphorus water soluble and 2 % citric acid soluble compounds in ratio to total phosphorus compounds content were presented.

Comparison of curves obtained for products with different raw material particle size (P13 Fig. 1 and P19 Fig. 2) and identical other parameters allows to conclude that the impact of raw material particle size is greater in the case of preparations obtained by using sulfuric acid. The reason of this phenomenon might be the formation of phosphogypsum in the first stage of the dissolution with sulfuric acid. As a result

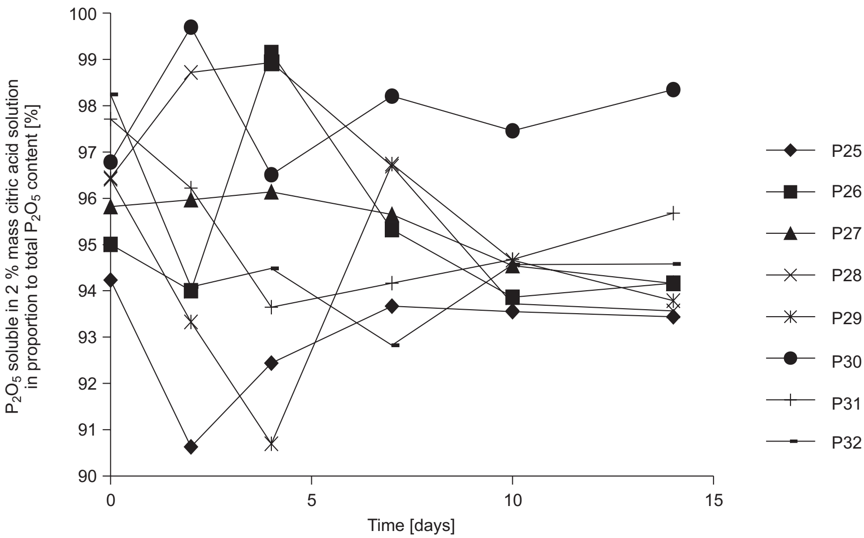

Fig. 1. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 1 to 8

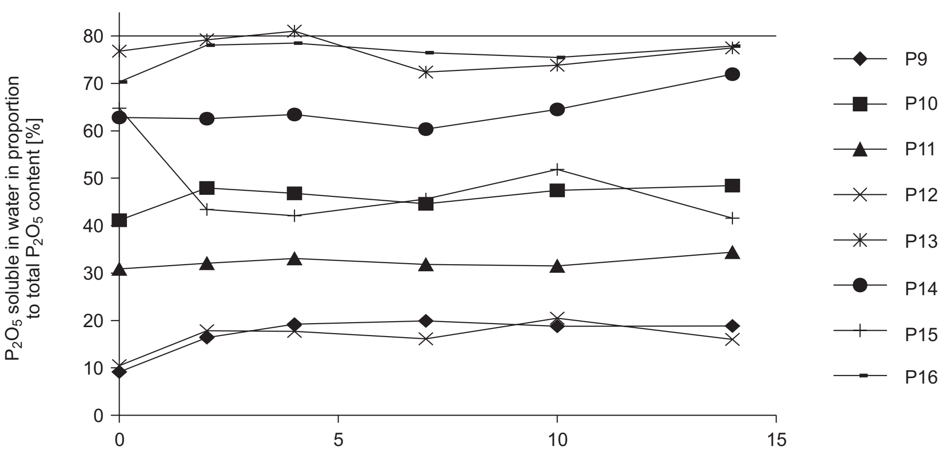

Fig. 2. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 9 to 16

phosphogypsum coats grains surface of raw material and stops further dissolution. In case of products which differ from each other by fineness and received on the basis of sulfuric acid it is clearly visible, that the differences in contents of various forms of phosphates are significant (P1 Fig. 1 and P10 Fig. 2). Influence of acid concentration on

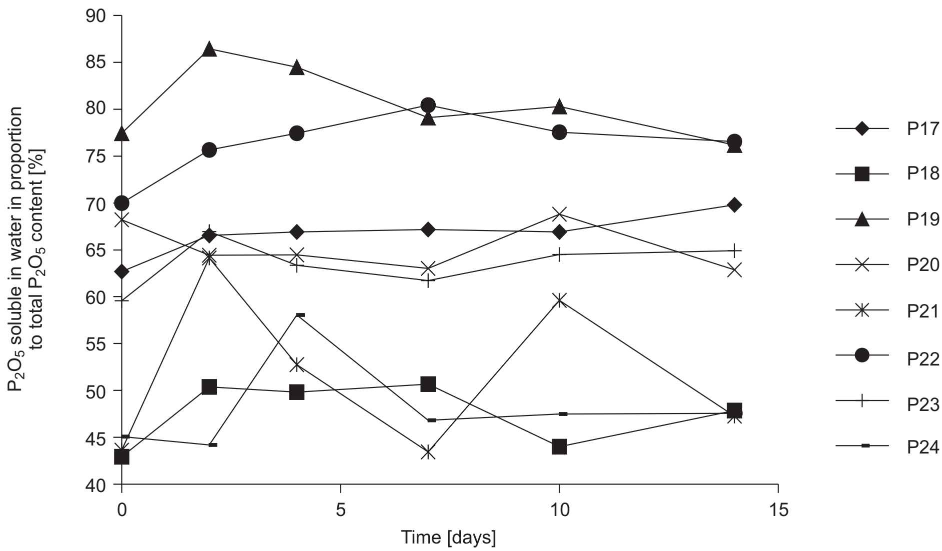

Fig. 3. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 17 to 24

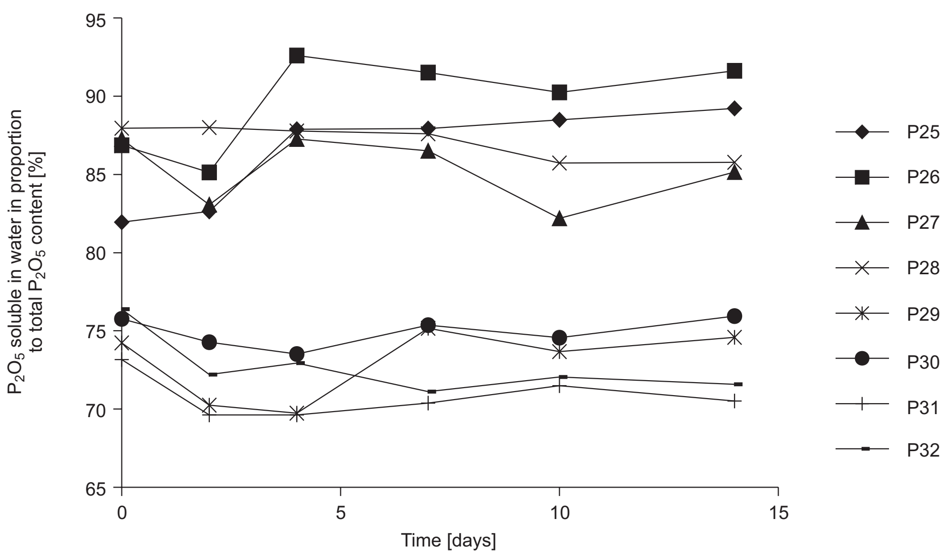

Fig. 4. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 25 to 32

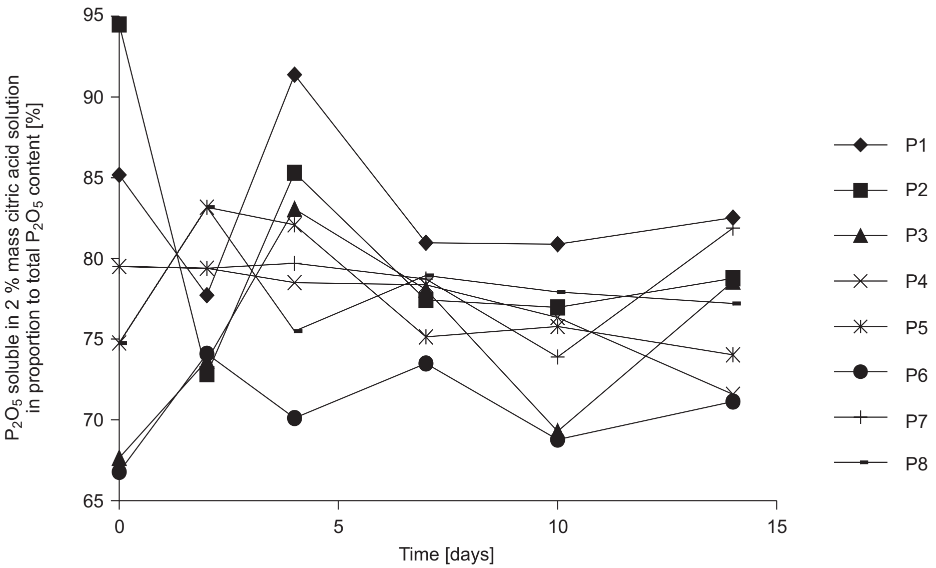

Fig. 5. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 1 to 8

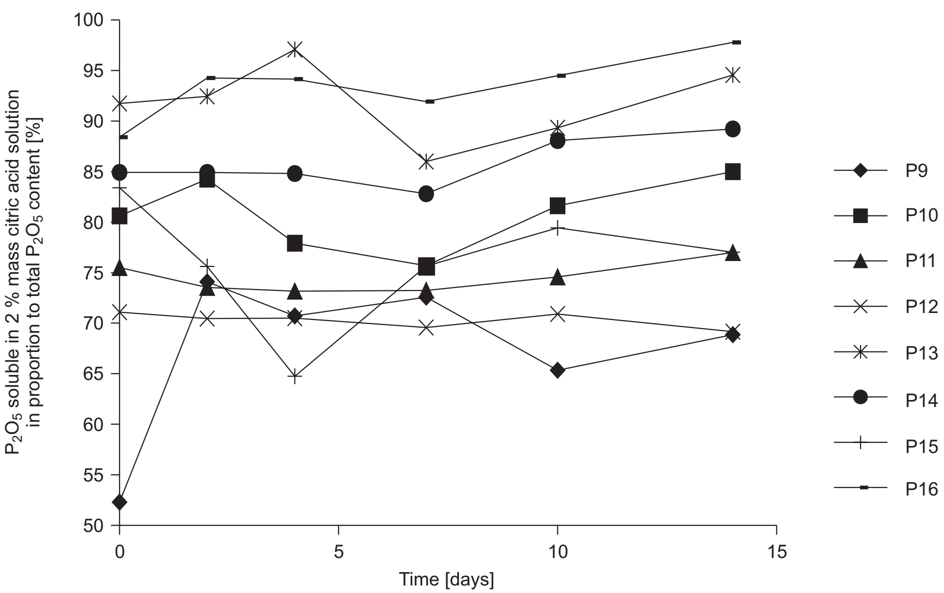

Fig. 6. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 9 to 16

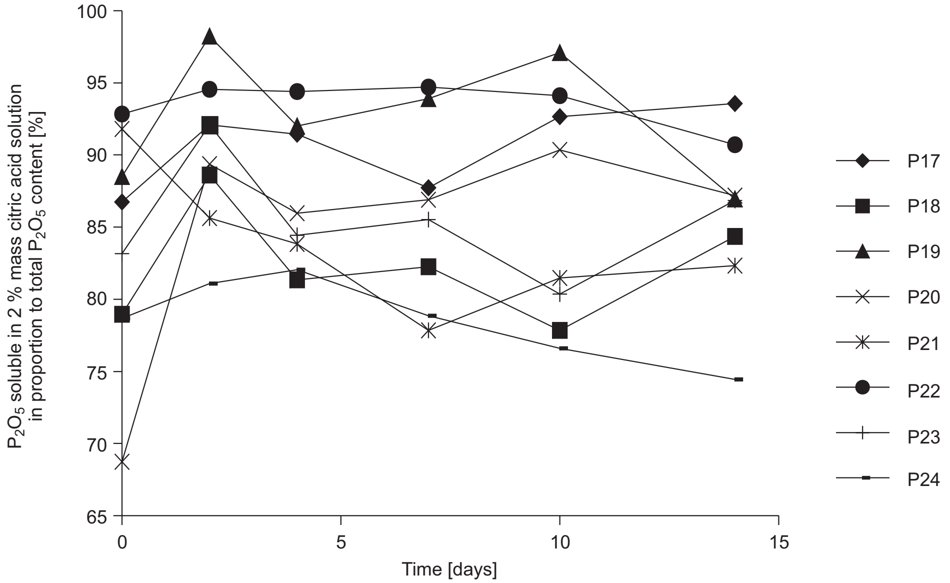

Fig. 7. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 17 to 24

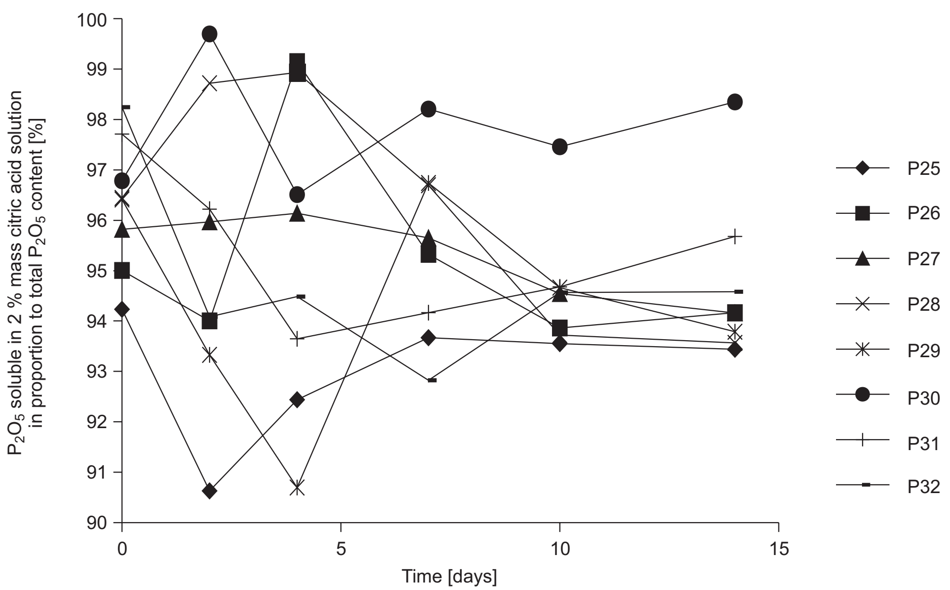

Fig. 8. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 25 to 32

phosphorus compound content is minimal. Change of acid concentration in the range used during the trials, does not cause major changes in the content of individual forms of phosphates (P7 Fig. 1 and P10 Fig. 2).

Conclusions

1. PAPR type fertilizer samples manufactured by using phosphoric acid were specified by higher phosphates content (about 45 %) than manufactured with use of sulfuric acid.

2. Decrease in the acid amount used in the manufacture process caused decrease in the phosphorus content soluble in 2 % citric acid solution and in water, however drop in the water soluble phosphorus content is higher.

3. There was no significant influence of phosphate rock fineness on phosphates content in manufactured samples.

4. Small change in acid concentration (in the range used in industry) did not cause significant changes in phosphates content in samples.

5. When degree of PAPR stoichiometric norm (η_{PAPR}) was smaller *eg* 0.3–0.7 samples contained less moisture because water amount used in manufacture process was smaller than samples which were completely acidulated.

6. Samples manufactured with use of sulfuric acid contained more phosphates soluble in mineral acid than reference samples.

7. PAPR manufacture technology has few benefits from economical point of view, because it allows to reduce raw material and technological solution costs. It is important factor in fertilizer manufacturing based on phosphoric acid because it account for major raw material costs (even about 80 %). It is not so important in production of fertilizers based on sulfuric acid.

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BADANIA NAD CZĘŚCIOWYM ROZKŁADEM FOSFORYTU (METODĄ PAPR) Z ZASTOSOWANIEM KWASU SIARKOWEGO I FOSFOROWEGO

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Abstrakt: Przedstawiono wyniki badań nad wpływem różnych czynników przy częściowym rozkładzie surowca fosforowego na zawartość związków fosforu w produkcie nawozowym. Uwzględniono wpływ rodzaju, stężenia i ilości kwasu mineralnego oraz uziarnienia surowca na zawartość poszczególnych form fosforanów oznaczonych zgodnie z dyrektywą Unii Europejskiej (EC) No. 2003/2003 dotyczącą metod badań zawartości fosforanów w nawozach sztucznych.

Słowa kluczowe: fosforyty częściowo rozłożone (PAPR), kwasy mineralne, nawozy fosforowe, fosforany przyswajalne