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Krystyna HOFFMANN[1], Józef HOFFMANN[1]
and Filip DONIGIEWICZ[1]

INFLUENCE OF CONCENTRATION OF PHOSPHORIC ACID ON OBTAINED FODDER PHOSPHATE QUALITY

WPŁYW STĘŻENIA ZATĘŻONEGO EKSTRAKCYJNEGO KWASU FOSFOROWEGO NA JAKOŚĆ OTRZYMANYCH FOSFORANÓW PASZOWYCH

Abstract: Results of qualitative analysis of the fodder monocalcium phosphate product based on concentrated phosphoric acid obtained in the laboratory conditions were presented. Phosphoric acid was produced by wet method from apatite raw material. Phosphorus is essential, regarded as biogenic nutrient, in animal feeding. Moreover the form of its availability contained in fodder phosphates is of great significance. The aim of conducted research was to determine different forms of phosphorus in monocalcium phosphate and depict the relation between contents of phosphorus in the fodder phosphate and concentration of the phosphoric acid used for its production. Furthermore it was evaluated whether the product meets the requirements of the Polish Standard PN-R-64803 regarding contents of different forms of the phosphorus

Keywords: concentrated phosphoric acid, fodder phosphate, monocalcium phosphate, fodder additive

Phosphorus is one of the main nutrients present in the human and animals' body. It is included as an essential element into the composition of all cells of living organisms and it participates in transformations of energy and other nutrients. It is abundant in bones and blood.

Phosphorus is an integral part of organic compounds of both plants and animals. This element participates in energy and nutrients transformations such as: carbohydrates, proteins, lipids. It plays important role in the lipid transport system, in the phosphorylation process and absorption of carbohydrates and in the metabolism of nerve tissue. The molecules of phosphorus compounds are one of the fundamental building materials of the nucleic acids such as DNA and RNA and high energy compounds adenosine phosphates – ADP and ATP. The deficiency of this macronutrient in the food chain

[1] Institute of Inorganic Technology and Mineral Fertilizers, Wroclaw University of Technology, ul. M. Smoluchowskiego 25, 50–372 Wrocław, Poland, phone: +48 71 320 30 39, email: jozef.hoffmann@pwr.wroc.pl

causes serious complications, among other disturbances it affects negatively the functioning of living organisms, the process of ossification, hunger, and the intensity of metabolism. Supplying phosphorus in required quantity and appropriate, available form is essential for correct human and animal development. One of the most profitable ways of providing people with bioavailable phosphorus is the intake of meat of a proper quality. Supplying people with proper and sufficient level of phosphorus is dependent on the balanced diet of animals which are part of the elementary human food chain. Selecting an appropriate form and dosage of phosphorus in fodder mixtures fitted for the particular animal species and their age has a great importance within this range.

Fodder phosphates such as monosodium phosphate, monocalcium phosphate, magnaphoscal, disodium phosphate, calcium-sodium phosphate, dicalcium phosphate, trisodium phosphate and dimagnesium phosphate can be applied as the fodder supplements containing phosphorus in fodder mixtures products. Biological value of mono- and dicalcium phosphates reaches over 100 points according to the Günther scale what confirms their very good biological quality [1].

Examinations were carried out for the *monocalcium phosphate* (MCP) due to the highest bioavailability and the content of another biogenic component included within its composition which is calcium. MCP is a fodder supplement which constitutes one of the main sources of the phosphorus and calcium in concentrates for all kinds of farm animals.

Calcium is biologically-essential nutrient. It can be found mainly in the bones in the forms of calcium-phosphorus compounds – hydroxyapatite. It plays important role in human and animal body, *inter alia* it takes part in blood clotting and transmission of bioelectrical impulses. Furthermore calcium is one of the enzymes activators, and participates in skeletal muscle contractions and systoles.

$Ca(H_2PO_4)_2$ has also found the application in fertilizer industry. It constitutes one of the components of fertilizer mixtures based on the superphosphates [2, 3]. MCP is used for the manufacture of detergents and cosmetics as well as an agent enhancing nutritional properties.

Large amount of phosphorus is emitted along with animal excrements what causes the need to replenish it in the diet, however it has also harmful influence on the environment resulting in pollution by water eutrophication. It is believed that phosphorus from excrements gets into ground water or sewages, and then goes into a water basins where, as a biogenic nutrient cause significant enrichment of waters with nutrients, thus stimulating the growth of phytoplankton and cyanobacteria. Excessive and acute growth of microorganisms as a coat on the water surface causes oxygen depletion in the water and death of many organisms. For this reason it is important to reduce emissions of this element to the environment [4].

Analytically phosphorus in the samples can be determined by different methods. The most popular test is the spectrophotometric determination using the energy transition which takes place in the molecules by absorption of electromagnetic radiation in the ultraviolet, near-infrared or ultraviolet-visible 380–780 nm.

In order to analyze phosphorus content during performed research the absorption test of a colored vanadate-molybdate complex in the visible spectra at λ = 430 nm wavelength was used. Another method recommended in the Polish Standards, is gravimetric determination based on phosphate precipitation in the form of quinoline--phosphate-molybdate in an acidic environment. Both in fodders and fertilizers phosphorus content is expressed as P or P_2O_5 percentage by weight.

Analytic methods allow to determine the various forms of phosphorus such as available, water-soluble and total. These examinations provide very valuable information on the fodder's biological value. Having this knowledge it is possible to evaluate the quality of the sample and find the application which fits for it. Knowledge of the content of the various forms of phosphorus is especially important in animal nutrition because it helps to prepare the fodder mixtures with adequate phosphorus content, in order to stimulate normal animal growth.

Materials and methods

The investigation on the assessment of quality of the monocalcium phosphate were carried out for preparations obtained under laboratory conditions produced according to the following reaction:

$$CaHPO_4 + H_3PO_4 \longrightarrow Ca(H_2PO_4)_2$$

In frames of examinations 6 samples of the monocalcium phosphate produced by grinding dicalcium phosphate with phosphoric acid were prepared [4]. The industrial wet phosphoric acid was concentrated to various concentration levels: 48 %, 52 %, 56 %, 60 %, 64 % and 67 % P_2O_5 w/w. The total and water-soluble phosphorus as well as phosphorus soluble in hydrochloric acid contents were determined in samples. In these samples, phosphorus was determined spectrophotometrically in the form of P_2O_5 by the so-called yellow method utilizing yellow complex of phosphorus with vanadate--molyvdate reagent at wavelength of λ = 430 nm.

The examination of water-soluble phosphorus was carried out in accordance with Regulation of the Minister of Agriculture and Rural Development dated 27 June 2007 regarding methodology of analysis for determination of nutrients and fodder additives in fodder materials, premixes, fodder mixtures and therapeutic fodder and with PN-88/C-87015 Polish Standard [5–7].

Acid used for fodder phosphate samples production was prepared by concentration of wet phosphoric acid with an initial concentration of P_2O_5 about 24 % w/w.

The process of concentration was based on adding to 1500 cm^3 of industrial acid appropriate amount of CaO and SiO_2 to remove F^- and SO_4^{2-} ions, and subsequent heating up in a reactor equipped with two scrubbers in series connection to a concentration of P_2O_5 49.88 % w/w. Acid concentrated by this procedure was cooled, and then transferred to Imhoff funnels in order to separate sediment from acid. Separated acid was concentrated again under vacuum, to the P_2O_5 content assumed in the experiment. Laboratory-produced acid was applied to manufacture monocalcium phosphate by the reaction of concentrated phosphoric acid with dicalcium phosphate [8].

Elemental composition of the industrial acid used for manufacture of phosphoric acid of specified P_2O_5 content was determined using the ICP method. The results of the analysis were presented in Table 1.

Table 1

The results of ICP elemental analysis for concentrated wet phosphoric acid of P_2O_5 content 49.88 % w/w

Symbol of chemical element	Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Zn
Concentration [mg/kg]	2280	10	91	32	307	32	5340	0.0011	4230	347	0.67	352
Uncertainty ± [mg/kg]	460	2	14	5	46	5	800	0.0002	850	52	0.10	53

Methods of samples preparation for spectrophotometric analysis was different depending on determined form of phosphorus, and proceeded as follows:

Water-soluble phosphorus

Phosphate sample 1 g was added to 500 cm^3 flask. Then 400 cm^3 of water was poured and the flask was subsequently placed into the rotational set where it was shaken for 0.5 h at 45 rpm. Then a flask was filled up with water and components were carefully mixed. After precipitate sedimentation the solution was filtered through the dry filter into dry vessel.

Total phosphorus

Phosphate sample 1 g was added to 400 cm^3 beaker. Then 50 cm^3 of the nitric(V) and hydrochloric acid mixture at 3:1 ratio was introduced. The solution was boiled under the fume hood for 0.5 h. After this time 100 cm^3 of water was added and boiled again for 0.25 h. Then mixture was cooled and transferred to the 500 cm^3 flask quantitatively, carefully mixed and filtered rejecting about 50 cm^3 of first part of the filtrate. Sample of 1 cm^3 was collected for further analysis.

Phosphorus soluble in HCl 0.4 % w/w

Phosphate sample 1 g was added to 500 cm^3 flask. Then 400 cm^3 of 0.4 % w/w HCl was poured and the flask was subsequently placed into the rotational set where it was shaken for 0.5 h at 45 rpm. Then a flask was filled up with water and components were carefully mixed. After precipitate sedimentation the solution was filtered through the dry filter into dry vessel.

Spectrophotometric analysis

Samples of 1 cm^3 obtained by the methods mentioned above were introduced into the 100 cm^3 flask. Then the flask was filled with water up to 25 cm^3 capacity and 20 cm^3 of the yellow vanadate-molybdate complex was subsequently added. Solutions were left for 0.25 h at room temperature and then absorbance was measured at λ = 430 nm wavelength using spectrophotometer of the JASCO company. Contents of the phosphorus were found from the calibration curve which was prepared in earlier investigations.

Results and discussion

Results and parameters of manufacturing process referring to samples 1–6 were presented in the Table 2. Relation between the quantity of total, water-soluble, phosphorus soluble in 0.4 % w/w HCl and the concentration of phosphoric acid used in manufacturing process were depicted on Figs. 1–3.

Table 2

Dependence of contents of different forms of phosphorus contained in monocalcium phosphate on the phosphoric acid concentration used for samples production process [% P_2O_5 w/w]

Sample No.	Input concentration of phosphoric acid P_2O_5	Concentration of water-soluble P_2O_5	Concentration of P_2O_5 soluble in 0.4 % HCl	Concentration of total P_2O_5
1	48 % w/w	42.13 % w/w	43.31 % w/w	50.32 % w/w
2	52 % w/w	45.82 % w/w	46.51 % w/w	52.54 % w/w
3	56 % w/w	47.04 % w/w	49.54 % w/w	55.23 % w/w
4	60 % w/w	49.10 % w/w	50.89 % w/w	53.91 % w/w
5	64 % w/w	50.65 % w/w	51.74 % w/w	55.60 % w/w
6	67 % w/w	51.07 % w/w	52.78 % w/w	55.31 % w/w

The table shows the results of spectrophotometric measurements of all analyzed forms of phosphorus. The analysis of data collected in the table clearly shows that when the input concentration of phosphoric acid increases the concentration of all measured forms of phosphorus also elevates. All of the samples contained the highest amount of P_2O_5 in total form. Moreover it is shown that the content of P_2O_5 soluble in 0.4 % HCl is lower and the content of water soluble P_2O_5 is the lowest as all contents are compared. The difference between the content of water soluble P_2O_5 and P_2O_5 soluble in 0.4 % HCl is relatively low, which is an evidence of a high degree of bioavailability of phosphorus for animals.

The graph presents the relation between the amount of phosphorus water-soluble and concentration of acid used to prepare the sample. The analysis of the graph shows that with increasing concentration of the acid which the sample was prepared from, the increase in amount of water-soluble phosphorus i.e. bioavailable form of phosphorus for living organisms, is noticeable.

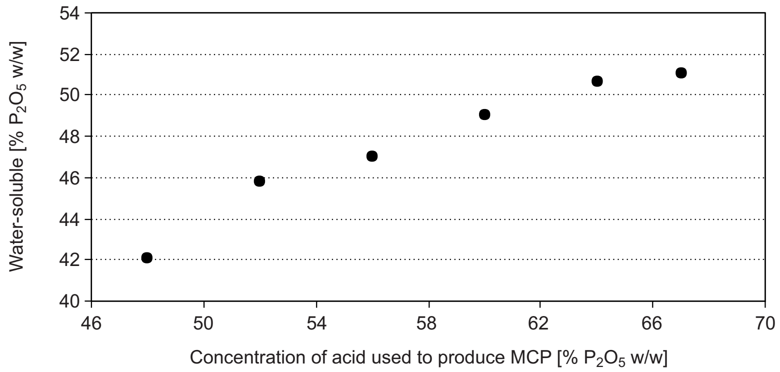

Fig. 1. Dependence of quantity of the water-soluble phosphorus on the acid concentration which the sample was produced from

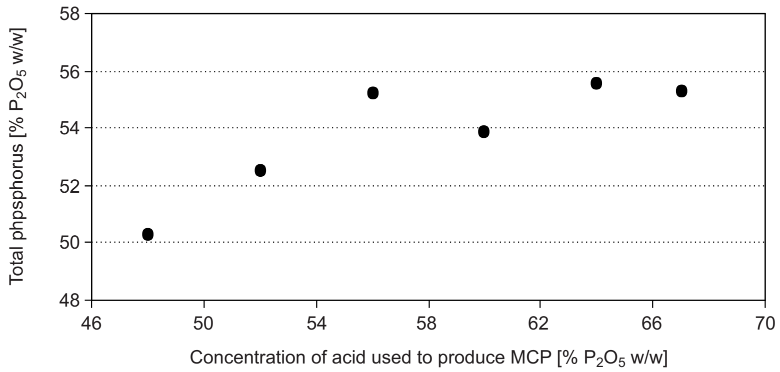

Fig. 2. Dependence of quantity of total form of phosphorus on the acid concentration which the sample was produced from

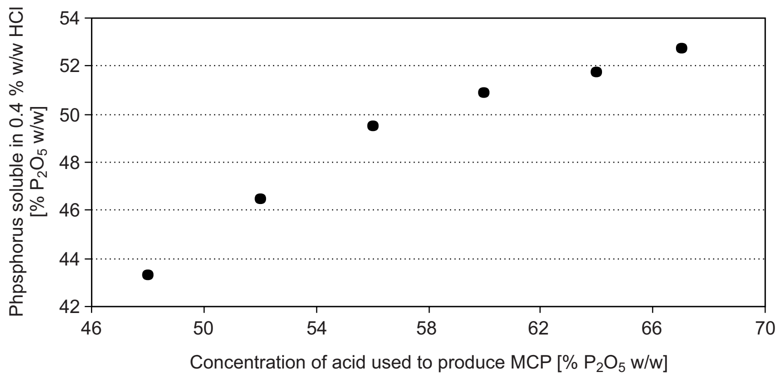

Fig. 3. Dependence of quantity of the phosphorus soluble in 0.4 % w/w HCl on the acid concentration which the sample was produced from

According to Polish Standard PN-R-64803 contents of total phosphorus in the monocalcium fodder phosphate should not be less than 50.41 % w/w of P_2O_5. Samples 2–6 found to meet this requirement, content of phosphorus in the sample no. 1 is not corresponding with the standard. The clear correlation between the increase in acid concentration which the samples were prepared from and the growth of total concentration of P_2O_5 in the product can be spotted in this graph similarly like in the former one.

According to Polish Standard PN-R-64803 contents of the phosphorus soluble in 0.4 % w/w HCl in the monocalcium fodder phosphate should not be less than 54.83 % w/w of P_2O_5. Samples 2–6 found to meet this requirement, contents of phosphorus in the sample no. 1 is not corresponding with the standard. The amount of P_2O_5 soluble in 0.4 % HCl increases as the concentration of the phosphoric acid used to prepare a sample grows, similar relation was shown in the former graphs.

Conclusions

All samples represent high contents of the water-soluble and phosphorus soluble in 0.4 % w/w HCl in relation to the total phosphorus. Such relation is very profitable by taking into consideration the fact that the large quantity of the phosphorus occurs in the sample in the available form.

Dependence of quantity of the various forms of P_2O_5 from the acid concentration which the sample was produced from is in all cases approximately linear function. This fact is caused by decreasing the humidity of the sample with the increase in the acid concentration.

The most profitable ratio of the available to total phosphorus content presents a sample produced from acid of the highest concentration (67 % w/w P_2O_5).

Sample no. 1 does not meet the standards requirement regarding contents of the both total and phosphorus soluble in 0.4 % w/w HCl.

Most preferred results of the analysis were revealed for the samples of fodder phosphates manufactured from concentrated dicalcium phosphate and phosphoric acid at a concentration above 60 % w/w of P_2O_5.

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Instytut Technologii Nieorganicznej i Nawozów Mineralnych
Politechnika Wrocławska

Abstrakt: Przedstawiono wyniki oceny jakościowej jednowapniowego fosforanu paszowego otrzymanego z zatężonego, w warunkach laboratoryjnych, ekstrakcyjnego kwasu fosforowego wytworzonego z surowca apatytowego. Fosfor należy do koniecznych tzw. biogennych pierwiastków w żywieniu zwierząt. Duże znaczenie ma również forma jego występowania w dodatku paszowym. Niniejsze badania miały na celu oznaczenie różnych form fosforu w fosforanie jednowapniowym, oraz przedstawienie zależności między zawartością fosforu w fosforanie paszowym, a stężeniem przemysłowego kwasu fosforowego z jakiego został otrzymany. Sprawdzono również, czy produkt spełnia warunki Polskiej Normy PN-R-64803 dotyczące zawartości różnych form fosforu.

Słowa kluczowe: zatężony kwas fosforowy, fosforan paszowy, fosforan jednowapniowy, dodatek paszowy