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PHYSICO-CHEMICAL EVALUATION OF FEED PHOSPHATES AS A CRITERION OF THEIR CLASSIFICATION

PROSJEČNA TOPIVOST MONONATRIJEVIH FOSFATA FIZIKALNO--KEMIJSKA PROCJENA FOSFATA KRMIVA KAO KRITERIJ ZA NJIHOVU KLASIFIKACIJU

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SUMMARY

Chemical composition of 341 charges – samples of fodder phosphates, their physico-chemical properties (solubility in different solvents), harmful elements content, phase composition and thermal analysis of 150 selected samples of phosphates were determined. Average solubility of monocalcium phosphates (% P₂O₅ in relation to total P₂O₅) (in%) amounted to: in water 74.8 - 82.1; in 2% citric acid from 96.6 to 98.3; in 0.4% HCl 94.8 - 98.8 and in neutral ammonium citrate 93.6 - 97.1. Solubility of dicalcium phosphates amounted to (in %): in water from 1.4 to 7.4; in 2% citric acid 50.9 - 98.5; in 0.4% HCl 78.7 - 92.3 and in neutral ammonium citrate 70.3-85.1. Average solubility of monosodium phosphates amounted to (in %): in water 0.1-89.6; in 2% citric acid 25.0 – 90.0; in 0.4% HCl 26.9 – 47.7 and in neutral ammonium citrate 27.7 - 90.2. Solubility of the remaining groups of phosphates (tricalcium, calcium-magnesium and sodium-calcium phosphates) amounted to (in %): in water from 0.1 to 25.8; in 2% citric acid from 25.1 to 95.7; in 0.4% HCI from 26.9 to 56.2 and in neutral ammonium citrate from 23.1 to 79.3. Hydrated monocalcium phosphates with admixture of both hydrated and dehydrated dicalcium phosphate were characterized by the highest solubility in water. In the group of dicalcium phosphates the lowest solubility in 0.4% HCl was stated for dehydrated forms, while the highest solubility was observed in hydrated phosphates. Solubility in water or in 0.4% hydrochloric acid together with the roentgenographical and thermogravimetrical investigations as well as solubility in 2% citric acid and in neutral ammonium citrate are good and cheap methods for identifying by precise the quality of phosphates.

Keywords: feed phosphates, physico-chemical quality

INTRODUCTION

The recognition of the real requirement of animals for the phosphorus and the precise balancing of it in the concentrate mixtures and diets Dorota Jamroz, Agnieszka Gajda-Janiak, Wrocław University of Environmental and Life Sciences; Department of Animal Nutrition and Feed Quality; Zbigniew Wzorek, Zygmunt Kowalski, Cracow University of Technology; Institute of Inorganic Chemistry and Technology, Poland.

with considering the availability of different forms of phosphorus from the raw feed components and mineral compounds has been the subject of numerous investigations (Gillis et al.1954, Baruach et al. 1958, Sullivan et al., 1992, Coffey et al., 1994, Duarte et al., 2003). The low degree of P-phytate utilization from the vegetable feeds requires in animal nutrition of the use mineral sources of this element – fodder phosphates. The great diversification of origin, chemical composition and availability of phosphorus can lead to serious mistakes in supplying animal' organism with this ingredient, important for metabolic processes.

The availability of phosphorus from phosphates for animals depends on numerous factors – P-contents, Ca:P ratio, pH of solvents, hydration level, size of particles, solubility of these chemical bonds and presence of harmful elements (Burnell et al.,1990, Jamroz, 1994, Fernandez et al.,1999, Rame, 2003, Rodehutscord, 2009). Special importance also has the chemical structure of different kinds of phosphates (Table 1).

Table 1. Chemical structure of feed phosphates
Tablica 1. Kemijska struktura fosfata krmiva

MATERIAL AND METHODS

The wide research on the evaluation of the chemical, physico-chemical value of the fodder phosphates available on the feedstuffs market was carried out. The results were treated as basic data for evaluation of the criterion of their usefulness in the animal nutrition. In the first part of investigations the wide range of changes of chemical composition and degree of phosphorus releasing (P_2O_5) from the fodder phosphates was estimated using different solvents. The samples of fodder phosphates were collected at the 2-year period; 351 samples (charges) were taken from the Polish fodder factories and from 9 phosphates manufacturers, including some European factories.

The greatest number of phosphate samples of monocalcium phosphates resulted from common use of this mineral compound in feed industry.

In completed samples evaluations were executed on the basis of methods described by European Chemical Industry Council, Brussels, Inorganic feed phosphates quality (Cefic, 2006). The analysies was

Kind of phosphates - Vrsta fosfata	Chemical formula - Kemijska formula			
Hydrated monocalcium dihydrophosphate	Ca(H ₂ PO ₄) ₂ x H ₂ O			
Dehydrated monocalcium dihydrophosphate	Ca(H ₂ PO ₄) ₂			
Hydrated dicalcium hydrophosphate	CaHPO ₄ x 2H ₂ O			
Dehydrated dicalcium hydrophosphate	CaHPO ₄			
Dehydrated tricalcium dihydrophosphate	Ca ₃ (HPO ₄) ₂			
Dehydrated monosodium dihydrophosphate	NaH ₂ PO ₄			
Monoammonium dihydrophosphate	NH ₄ H ₂ PO ₄			
Hydrated monomagnesium hydrophosphate	MgHPO ₄ x H ₂ O			

The purpose of conducted studies was to determine the quality of different kinds of phosphates in aspect of potential availability of phosphorus from these chemical bonds for animals, estimated in presented investigations on chickens as an model.

carried out in the laboratory of Department of Animal Nutrition and Feed Quality of Wrocław University of Environmental and Life Sciences and in the laboratory of Cracow University of Technology; Institute of Inorganic Chemistry and Technology.

The total phosphorus content, expressed in P_2O_5 (Regulation 2003/EC, method 3.2 Cefic, 2006) was determined using quinoline phosphomolybdate gravimetric method (dissolving samples in mixed 1:3 hydrochloric acid (HCl) 1.19 Mol/dcm³ and nitric acid (HNO₃) (1.4 Mol/dcm³) at boiling temperature.

The Calcium content in phosphate samples after dissolving in nitric acid turned out to be compexometric with disodium versenate (2.02 Mol/dcm³) by indicator fluorexone with thymolofthaleine determined (Polish standard PN-R-64803, 1997, phosphates).

The availability of phosphorus from inorganic phosphates was analyzed according to the methods recommended by Regulation No. 2003/2003 and European Chemical Industry Council (Inorganic feed phosphates quality, Brussels, Belgium,2003) (Cefic, 2006). The following features were examined:

- solubility in water,
- solubility in 2 % citric acid (Regulation 2003/2003/EC, method 3.1.3), (temp. 20 C, 35-40 min. P-content determined according to the gravimetric quinoline phosphomolybdate method),
 - solubility in 0.5 % HCl,
- solubility in ammonium citrate (pH 7) (Regulation 2003/2003/EC, method 3.1.5) (temp. 65 C, alkaline citrate from bi-ammonium citrate, pH 9.4-9.7, 30 min, + 60 min using gravimetric quinoline phosphomolybdate method).

In 20 samples of phosphates selected for biological tests and in 12 samples characteristic for particular groups of the mono-, di- and tricalcium and calcium-magnesium phosphates the harmful chemical elements contents were determined: Cd, Pb, Hg, As, F. These investigations were executed in the Chemical Laboratory of the Multi-element Analysis of the Technical University of Wrocław. Analyses of As, Cd, Pb were carried out with the plasma spectrometer with mass detection ICP-MS managed by the computer aggregated with the analytical system UltraMass 700 (Varian). The analysis of Hg content was executed using the analyser AMA - 254, spectrometer of atomic absorption used for direct estimation of the mercury content in solid and liquid samples with accuracy of 0.1 ppb of mercury in the studied sample. The fluorides content (F) was estimated by ionometric method using the apparatus ORION RESEARCH type EA -940.

The phase composition of fodder phosphates allows to identify the true composition and purity of phosphates. Analysis of the diffraction picture of the Roentgen irradiation (X-rays) of evaluated cristalline phases of phosphates allows to separate the different forms of phosphates and to evaluate their degree of crystallization. With this method it is also possible to identify the introductory compounds used for phosphate production that should not be present in the final product. The phase composition of phosphates was estimated by X-rays method using Phillips X'Pert diffractometer equipped with the graphite monochromator PW 1752/00 with the CuK_a radiation at the angle range of 2Θ 10-60° at the Institute of Chemistry and Inorganic Technology of Cracow University of Technology.

In the carried out experiment the X-rays diffraction by the dust method of Debye - Scherer – Hull was used. This method depends on the irradiation with X-rays of polycrystallic sample made from the crystals placed in the accidental ways but fulfilling the condition of Bragg's interference. X rays irradiation is induced with the help from properly chosen lamp depending on the predicted composition of examined sample. Anthicathode must be made from the material which dos not induce the fluorescent X-ray radiance in the atoms of the analysed secondary material.

The thermal analysis of fodder phosphates is the most precise method to determine the real crystalline content phases - the percentage share of the hydrated and unhydrated phases as well as unprocessed materials. By this method it is possible to determine the changes occuring in the sample as a temperature function. This is the possibility of simultaneous registration of the changes of sample weight (the TG and dTG) as well as its energy (the DTA) in the temperature/time function. The result of measurement - the termogram, contains the graph of the dependence of the sample weight on the (TG) as well as its first derivative (dTG) as well as the DTA curve. The thermal differential analysis of phosphates has been conducted at the Institute of Chemistry and Inorganic Technology of Cracow University of Technology using the SDT 2960 Simultaneous DTA - DTG apparatus of the TA Instruments in the air atmosphere. The measurements were made in the temperature range of 20-1000 °C (1773K), with the constant speed of temperature rise by 20 °C/min. There the 150 samples of fodder

phosphates were analysed. Collected data were classified according to the composition of the crystalline phases. Among the monocalcium phosphates 6 and among of dicalcium phosphates 5 groups that were characterized by different share of particular phases, were identified. The most characteristic fodder phosphates and the X-ray photographs as well as the results of thermal analysis are presented.

RESULTS

The calcium content in analysed phosphates amounted in monocalcium to about 17 %, in dicalcium phosphates in mean 25 % and in other kinds of analyzed bonds to 35 % (tricalcium phosphates). Concentration of total phosphorus (in P_2O_5) varied between 32 and 54 % (Table 2).

The best solubility – releasing of phosphorus from monocalcium in water (28-48 %) – and Na-Caphosphates (45-52 %) were determined. By using 2 % citric acid and 0.4 % hydrochloric acid as solvents the differences were similar. Almost the same, but a little higher solubility was noted by using neutral ammonium citrate. For other chemical forms of phosphates very low degrees of solubility were determined, specially by using water as a medium. The lowest indices in this field were obtained for diand tri-Ca-phosphates.

The size of particles of phosphates influenced the solubility of phosphates but the greater crumbling of phosphates had no positive effect on the release of P from these chemical substances.

The share of soluble P_2O_5 in total P_2O_5 amounted to 89-98 % by using citric acid,

Table 2. The range of the chemical composition of phosphatesTablica 2. Opseg kemijskog sastava fosfata

				P cont	ents expresse	d in % of solul	ole P ₂ O ₅	
Particle size of the phosphate Veličina čestice fosfata (mm)	n	P-P ₂ O ₅ total, %	Ca %	P sadržaj izražen u % topivog P ₂ O ₅				
				in water u vodi	in 2% citric acid	in 0,4% HCl	in ammonium citrate	
1-Ca 1.0-0.5 or after crumbling 0.1-0.01	114	52.0-54.0	16.1-17.9	38.7-48.9	47.9-53.3	49.5-53.7	41.4-53.8	
1-Ca 0.5-0.2 or after crumbling 0.1-0.01	106	49.3-54.5	15.1-18.8	28.7-47.4	42.5-53.8	45.6-55.6	24.9-58.0	
1-Ca 0.2-0.1 or after crumbling 0.1-0.01	8	49.0-52.4	15.7-22.4	28.7-47.4	48.5-52.2	30.8-52.0	48.3-51.7	
2-Ca 0.5-0.1 or after crumbling 0.1-0.01	17	39.0-54.8	23.2-26.6	0.0-25.3	31.9-49.0	36.4-46.1	18.9-47.0	
2-Ca 0.1-0.01 or after crumbling 0.1-0.01	72	38.7-46.6	22.8-28.2	0.0-25.3	31.9-48.0	29.3-42.6	22.8-46.6	
3-Ca 0.1-0.01 or after crumbling 0.1-0.01	13	41.4-43.4	34.1-35.6	0.2-1.3	15.7-24.2	10.0-20.9	1.4-13.1	
Ca-Mg 1.0-0.2 or after crumbling 0.1-0.01	7	32.2-35.1	0.9-1.1	2.9-10.4	21.1-33.1	10.6-24.4	19.4-33.0	
1-Na 1.0-0.2 or after crumbling 0.1-0.01	9	53.5-57.4	0.1-0.9	45.3-52.2	47.2-52.7	47.2-56.0	43.6-56.1	
Na-Ca 1.0-0.01 or after crumbling 0.1-0.01	5	42.8-43.8	31.0-31.8	0.0-0.1	10.6-22.7	8.7-21.2	8.6-17.5	

ammonium citrate or HCl as solvents (Table 3). The highest values for analysed parameters were obtained for monocalcium phosphates and mono-Na-Ca-phosphates.

The harmful contents radicals in analyzed phosphates were below the standards, only in the mono-Ca-Mg-phosphates samples they exceeded the permissible levels (Table 4).

Table 3. The range of changes of the chemical composition of natural and crumbled phosphates Tablica 3. Opseg promjena kemijskog sastava prirodnih i mrvljenih fosfata

Size of the phosphate particles	Soluble P ₂ O ₅ (%) in total P ₂ O ₅ (%)					
(mm)	water	2% citric acid	0,4% HCI	ammonium citrate pH 7		
1-Ca 1.0-0.5 or after crumbling 0.1-0.01	80.7-82.1	96.9-98.3	98.5-98.7			
1-Ca 0.5-0.2 or after crumbling 0.1-0.01	74.8-77.4	96.6-97.6	97.6-98.9	93.6-97.1		
1-Ca 0.2-0.1 or after crumbling 0.1-0.01	77.2-77.6	98.0-98.1	94.8-97.7			
2-Ca 0.5-0.1or after crumbling 0.1-0.01	6.4-7.4	98.4-98.5	78.7-81.6	70.0.05.4		
2-Ca 0.1-0.01 or after crumbling 0.1-0.01	1.4-1.5	50.9-60.0	92.2-92.4	70.3-85.1		
3-Ca 0.1-0.01 or after crumbling 0.1-0.01	1.3-1.2	50.6-50.4	44.1-44.3	23.1-28.3		
Ca-Mg 1.0-0.2 or after crumbling 0.1-0.01	13.0-25.8	73.6-95.7	41.8-56.2	79.3-79.1		
1-Na 1.0-0.2 or after crumbling 0.1-0.01	86.9-89.6	89.9-90.9	47.7-47.3	90.2-90.0		
Na-Ca 1.0-0.01 or after crumbling 0.1-0.01	0.1-0.2	25.1-49.8	26.9-26.7	27.7-27.5		

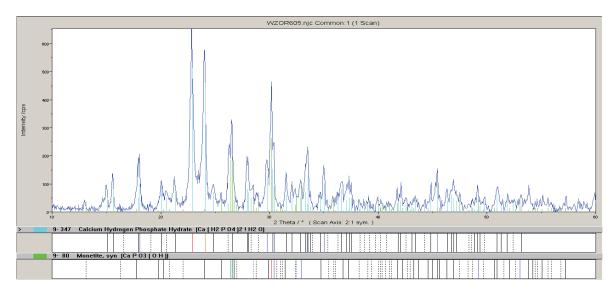
Table 4. The range of diversification of harmful mineral radicals in analyzed phosphates (x, ±SD)

Tablica 4. Opseg raznolikosti štetnih mineralnih radikala u analiziranim fosfatima (x, ±SD)

Specification	As	Cd	Hg	Pb	F
эреспісаціон		g/kg			
Monocalcium phosphates	4.7-9.8	0.39-8.60	0.0019-0.0080	0.27-8.25	1.47-2.28
Dicalcium phosphates	2.4-7.8	<0.01-0.55	0.0019-0.0090	1.10-6.30	1.06-2.08
Calcium-magnesium phospahtes	3.10	0.24	0.0024	17.00	1.00
Tricalcium phosphates	5.80	0.01	0.0016	6.50	1.17
Permissible amounts in materials (12 % H ₂ O), mg/kg	4-10	<10.0	<0.5	<30	<2.0

Both a roentgenographic study and a thermogravimetric analysis were carried out of all the 150 samples; a few exemplary results of this analysis are presented in Figures 1-9. The roentgenogrammes and thermogravimetric analyses show that the

different kinds of phosphates were not pure substances. They contained admixtures of other chemical compounds. Some typical examples of monocalcium phosphates analyses are presented in Figures 1, 2, and 3.



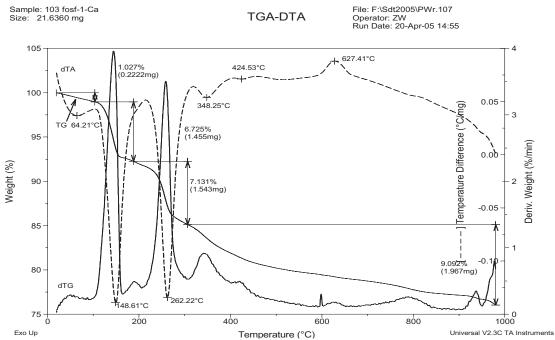


Fig. 1. Rentgenogramme and the thermogravimetric analysis of hydrated dihydrogen monocalcium phosphate with monetite

Graf. 1. Rendgenogram i termogravimetrijska analiza hidratnog dihidrogenog monokalcijevog fosfat s monetitom

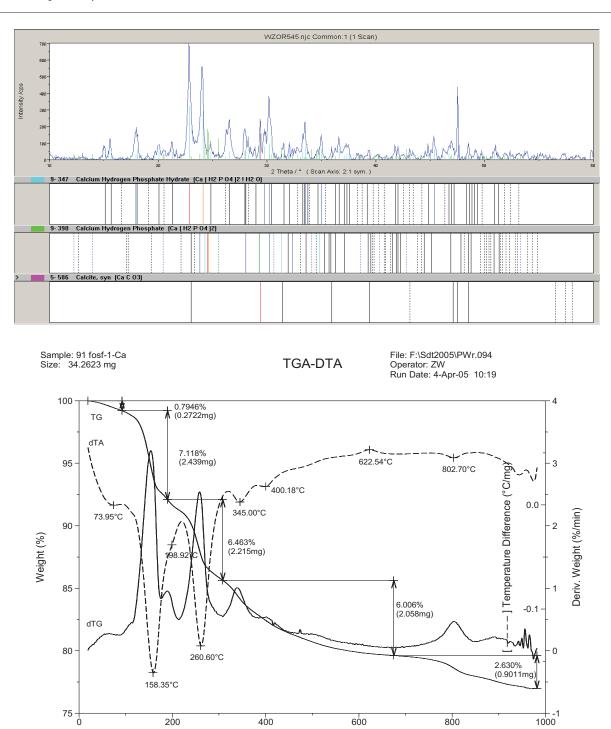


Fig. 2. Rentgenogramme and the thermogravimetric analysis of hydrated dihydrogen monocalcium phosphate and calcite

Temperature (°C)

Universal V2.3C TA Instruments

Graf 2. Rendgenogram i termogravimetrijska analiza hidratnog dihidrogenog monokalcijevog fosfata i kalcita

Hydrated monocalcium phosphate $Ca(H_2PO_4)_2 \times H_2O$ contained admixture of dehydrated dicalcium phosphate – monetite (DCP – CaHPO₄) (Fig. 1). The $Ca(H_2PO_4)_2 \times H_2O$ contents amounted to approx. 94.0 % as measured at humidity of 0.6 %. The $Ca(H_2PO_4)_2 \times H_2O$ can contain DCP and calcite, too (degradation in 800 °C), (Fig. 2). Some of this kind of

MCP can contain just to 10 % of DCP without calcite (CaCO₃). The $Ca(H_2PO_4)_2 \times H_2O$ was the main substance and there the presence of amorphic fractions, excluding $CaCO_3$, was determined. This MCP contained both hydrated and dehydrated forms of DCP (Fig. 3).

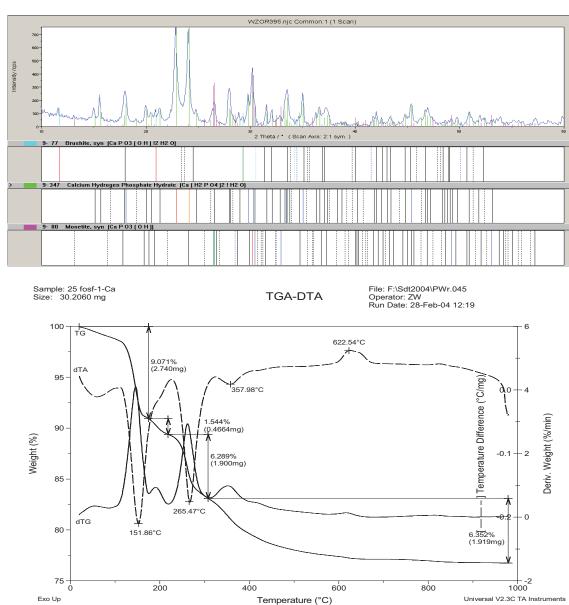


Fig. 3. Rentgenogramme and the thermogravimetric analysis of hydrated dihydrogen monocalcium phosphate with monetite and other compounds

Graf 3. Rendgenogram i ternogravimetrijska analiza hidratnog dihidrogenog monokalcijevog fosfata s monetitom i i drugim spojevima

The rentgenogrammes and deryvatogrammes – thermogravimetric analysis of dicalcium phosphates show another composition of these chemical bonds. In Figure 4 characterizing the pure dicalcium phospahte – exclusively $\text{Ca}(\text{H}_2\text{PO}_4)_2 \times \text{H}_2\text{O}$ is presented. The mixture of hydrated and dehydrated $\text{Ca}(\text{H}_2\text{PO}_4)_2 \times \text{H}_2\text{O}$ and CaHPO_4 in ratio 1:1, which it is not visible in RTG spctrum because of the great reflex by angle of 12° (Figure 5). Some of DCP are relatively pure substances. They contain the dehydrated DCP contaminated with ca. 3 % of

calcite only (Fig. 6), another DCP had a complicated composition: dehydrated CaHPO $_4$ (about 80 %), unprocessed calcite (about 10 %) by about 3 % of hydrated form and higroscopic water (Fig. 7). Tricalcium phosphate was the main component of mixture presented in Figure 8. The small losses of mass in temperature of about 670 °C may be an effect of trace amount of calcite. The ratio of calcium phosphate and sodium phosphate in mixed product can not be determined by the used analytical methods (Fig. 9).

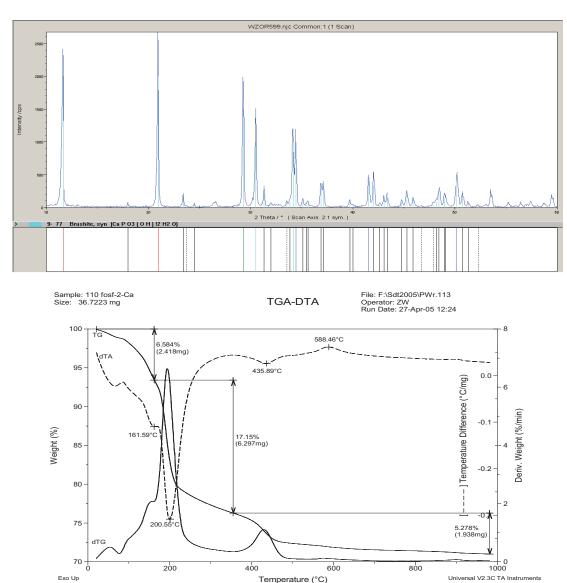
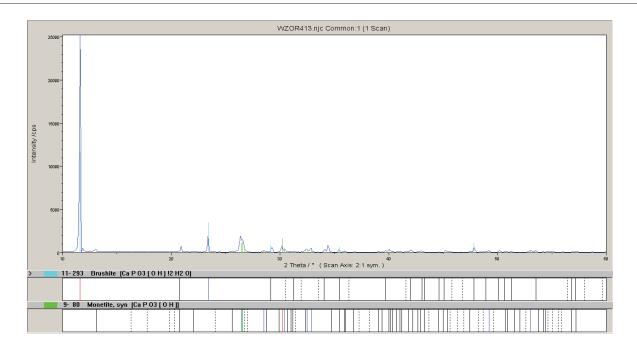


Fig. 4. Rentgenogramme and the thermogravimetric analysis of dicalcium phosphate Graf. 4. Rendgenogram i termogravimetrijska analiza dikalcijevog fosfata



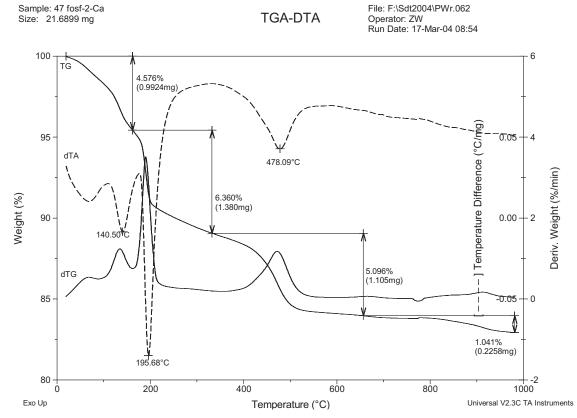


Fig. 5. Rentgenogramme and the thermogravimetric analysis of dicalcium phosphate with monetite Graf. 5. Rentgenogram i termogravimetrijska analiza dikalcijvog fosfata s monetitom

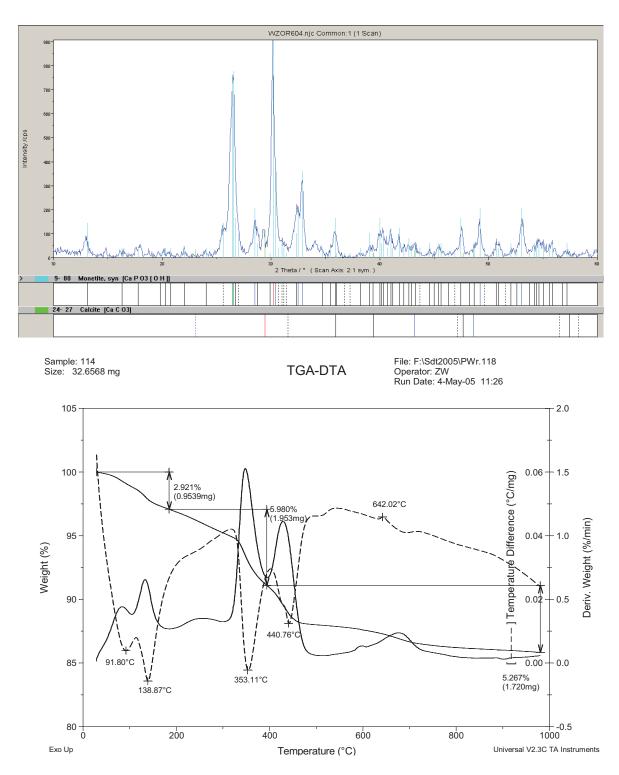


Fig. 6. Rentgenogramme and the thermogravimetric analysis of dicalcium phosphate Graf. 6. Rendgenogram i gtermogravimetrijska analiza dikalcijevog fosfata

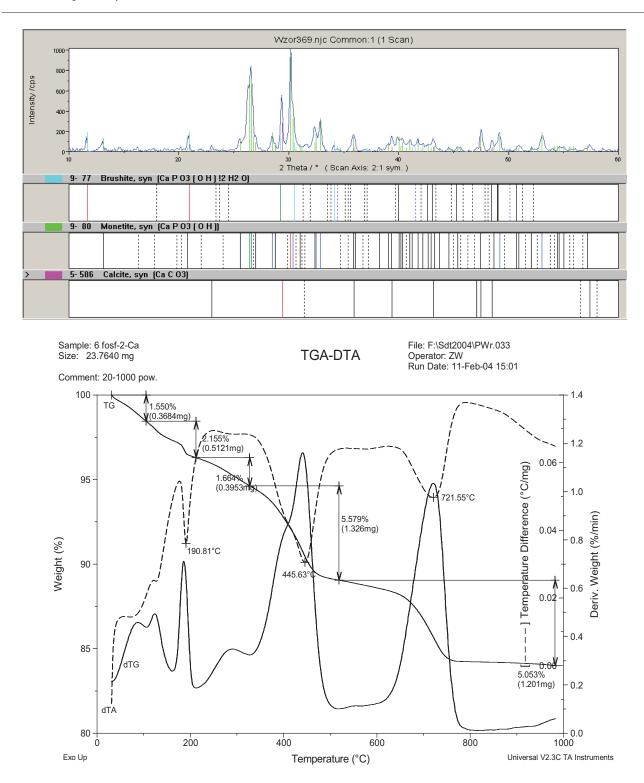
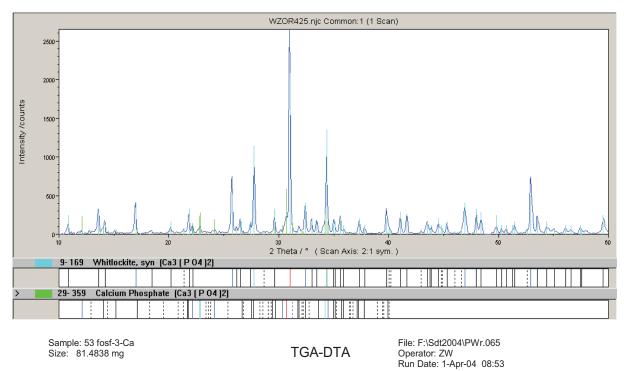


Fig. 7. Rentgenogramme and the thermogravimetric analysis of dicalcium phosphate with other compounds Graf. 7. Rendgenogram i termogravimetrijska analiza dikalcijevog fosfata s drugim spojevima



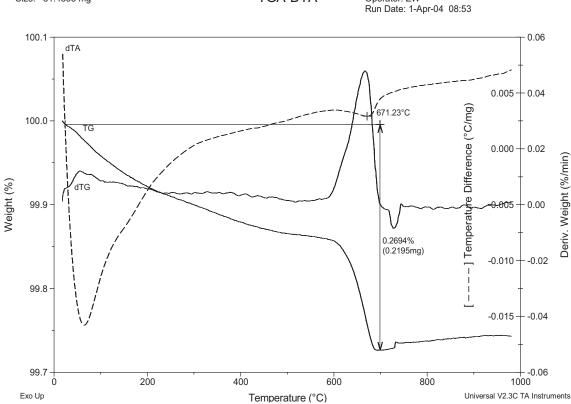


Fig. 8. Rentgenogramme and the thermogravimetric analysis of dicalcium phosphate Graf. 8. Rendgenogram i termogravimetrijska analiza dikalcijevog fosfata

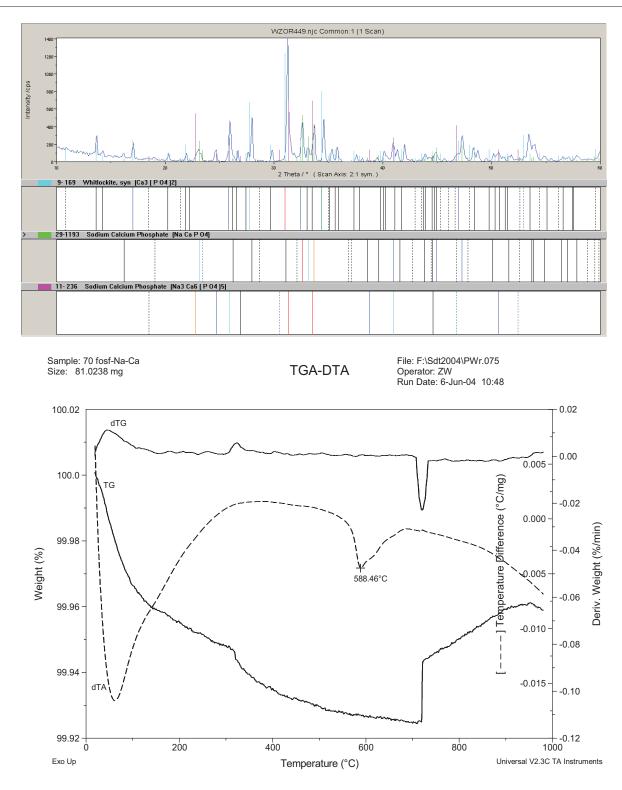


Fig. 9. Rentgenogramme and the thermogravimetric analysis of Ca-Na-phosphate Graf. 9. Rendgenogram i termogravimetrijska analiza Ca-Na-fosfata

DISCUSSION

The bioavailability of phosphorus from inorganic bonds is an important factor in animal nutrition (Gillis et al., 1954, Coffey et al., 1994, De Groote a. Huyghebaert, 1997, Kinal et al., 2004). The biological evaluation of P availability in animals is connected with great expences and a long-lasting estimation period, however chemical methods create the possibility of fast determination of phosphates quality (Baruah et al., 1958, Caswell, 1987, Lima et al., 1999, Duarte et al., 2003, Hemme et al., 2004).

The rational application of feed phosphates has a significant relevance for metabolic processes in animal organism, for good utilization of phosphorus and reduction of P-excretion into environment (Underwood, 1971, Jamroz, 1997, Jamroz, Kubizna, 2001, Craig,, Manangi, 2006). The completed investigations show the great diversification of phosphates present on the commercial market. The great differences appeared in the phosphorus, content but more of them – in chemical purity and solubility of these chemical bonds. These data are specially important for their application in animal nutrition.

According to Sullivan et al. (1992), the very low correlation between indices of solubility in water and biological value of phosphates was determined. It may indicate that this method is not useful and can not be accepted for evaluating of phosphates quality. Ammonium citrate (pH 7) and HCl as solvents are the mediums similar to the gastrointestinal juice in animal. Therefore, obtained characteristic of phosphates can be useful for their qualification (Gajda-Janiak et al.,2005). Observed differences in solubility of mono- and dicalcium phosphates were observed when ammonium citrate was used as a solvent.

In the commercial turnover (tranactions) the composition, solubility and phase composition of fodder phosphates are usually unknown for purchasers, but should be carefully recognized by them. Most of the available and examined monocalcium fodder phosphates contained mainly the hydrated calcium dihydrophosphate Ca(H₂PO₄)·H₂O with a small amount of dehydrated hydrophosphate CaHPO₄. The high monocalcium phosphate content may improve the solubility and in the same way the absorption of the commercial products. Among the dicalcium phosphates the occurence of three groups of products was found. These are: preparations

containing only hydrated calcium hydrophosphates CaHPO₄·2H₂O, mixture of both hydrated and dehydrated calcium hydrophosphates and finally the mixture of dehydrated calcium hydrophosphate and unprocessed calcium carbonate. The high dehydrated form, content especially unprocessed calcium carbonate, can decrease the solubility of fodder phosphates and in consequence decline the commercial fodder phosphates utilization.

As a continuation of presented studies, the biological evaluations of typical kinds of phosphates were conducted with growing chickens used as a model monogastric animals.

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LITERATURE

- Baruah, J. N., Reid, B. L., Couch, J. R. (1958): A comparison of methods for estimating phosphorus availability. Poult. Sci., Abstr., 37,1183.
- Burnell, T. W., Cromwell, G. L., Stahly, T. S. (1990): Effects of particle size on the biological availability of calcium and phosphorus in defluorinated phosphate. Poultry Sci. 69,1110-1117.
- Caswell, L. F. (1987): Feed phosphates. Relating laborative solubility to turkey nutrition. Feed Management 9,8-12.
- Coffey, R. D., Mooney, K. W., Cromwell, G. L., Aaron, D. K. (1994): Biological availability of phosphorus in defluorinated phosphates with different phosphorus solubilities in neutral ammonium citrate for chicks and pigs. J. Anim. Sci. 72 (10), 2653 – 2660.
- Craig, N. C., Manangi, M. K. (2006): Phosphorus utilization and environmental concerns. Mid-Atlantic Nutrition Conference, Maryland (USA), 29-30, March.
- CEFIC, European Chemical Industry Council, Inorganic Feed Phosphates Quality, Brussels, Belgium, http://feedphosphates.org/guide/test method.html.2006
- De Groote, G., Huyghebaert, G. (1997): The bioavailability of phosphorus from feed phosphates for broilers as influenced by bio-assay method, dietary Ca-level and feed form. Anim. Feed Sci. and Techn. 69, 329-340.

- Duarte, H. C., Graca, D. S., Borges, F. M. O. (2003): Comparison between "in vitro" methods to determine the bioavauilability of phosphorus. Arq. Bras. Med. Vet. Zoot. 55,1,80-84.
- Fernandes, J. I. M., Lima, F. R., Mendoca, C. X., J. R., Mabe, I., Albuquerque, R., Leal, P. M. (1999): Relative bioavailability of phosphorus in feed and agricultural phosphates for poultry. Poult. Sci. 78, 1729-1736.
- Gajda-Janiak, A., Jamroz, D., Wzorek, Z. (2005): Physicochemical properties of phosphates applied in animal feeding. Pol. J. of Chem. Tech. 7, 20-23.
- 11. Gillis, M. B., Norris, L. C., Heuser, G. F. (1954): Studies on the biological value of inorganic phosphates. J. Nutr. 52, 115-125.
- Hemme, A., Spark, M., Wolf, P., Paschertz, H., Kamphues, J. (2004): Effects of different phosphorus sources in the diet on bone composition and stability (breaking strength) in broilers. J. Anim. Physiol. and Anim. Nutr. 89, 129-133.
- Jamroz, D. (1994): Poultry requirement for minerals. Proceed. Sci. Conf. Minerals in animal nutrition, AR Poznań, 299-309 (in Polish).
- 14. Jamroz, D. (1997): Nutritional ways to reduce of excretion of nitrogen, phosphorus and other elements into environment by the poultry. Proceed. Conf. Nutritional ways to reduce of excretion of nitrogen, phosphorus and other elements into environment by the farm animals. Balice, 17-18.11., 85-105. (in Polish).
- Jamroz, D., Kubizna, J. (2001): Reducing the environment pollution through modification of performed animals nutrition. Krmiva 43, 195-209.
- 16. Kinal, S., Preś, J., Bodarski, R. (2004): Current view on the phosphorus metabolism in cattle and swine.

- Research Works, AE in Wrocławiu, 1017, 257-273 (in Polish).
- Lima, F. R., Fernandes, J. I. M., Oliveira, E., Fronzaglia, G. C., Kahn, H. (1999): Laboratory evaluations of feed-grade and agricultural-grade phosphates. Poult. Sci. 78, 1717-1728.
- Rama Rao, S. V, Ramasubba Reddy, V. (2003): Relative bio-availability and utilisation of phosphatic fertilisers as sources of phosphorus in broilers and layers. Br. Poult. Sci. 44, 1, 96-103.
- Regulation No. 2003/2003/EC, of the European Parliament and of the Council of 13. Oktober, 2003 relating to fertilizers, method 3.2., 3.1.3, 3.1.5.
- 20. Rodehutscord, M. (2009): Approaches and challenges for evaluating phosphorus sources for poultry. Proceed. 17th Europ. Symp. Poult. Nutrit., Edinburgh, Scotland, 2-6.
- Sullivan, T. W., Douglas, J. H., Gonzalez, N. J., Bond, P. L., JR. (1992): Correlation of biological value of feed phosphates with their solubility in water, dilute hydrogen chloride, dilute citric acid, and ammonium citrate. Poult. Sci., 71, 2065-2074.
- 22. Underwood, S. J. (1971): Mineral nutrition of animals. PWRiL,Warszawa,54-91 (in Polish).
- Upton, E. (2003): Using analytical results in order to choose the appropriate inorganic feed phosphate products. Mat.inf. Kemira-Grow-How.
- 24. Wzorek, Z., Kowalski, Z. (1995): Thermal methods of feed phosphates production using of phosphorus salt. Chem. Industr. 74, 12, 463-466 (in Polish).
- 25. Wzorek, Z., Kowalski, Z., Milewska, A. (1996): Investigations on the production of dicalcium phosphate. Prace Naukowe Inst. Techn. Nieorg. i Naw. Miner., Polit. Wrocł. 45, 26, 203-214.

SAŽETAK

Određen je kemijski sastav 341 uzorka fosfata krmiva, njihova fizikalno-kemijska svojstva (topivost u raznim otopinama), sadržaj štetnih elemenata, fazni sastav i termalna analiza 150 odabranih uzoraka fosfata. Prosječna topivost monokalcijevih fosfata (%P2O5 u odnosu na ukupno P2O5) (%) iznosila je u vodi 74,8 - 82,1; u 2% limunskoj kiselini od 96,6 do 98,3; u 0,4% HCl 94,8 - 98,8 i u neutralnom amonijevom citratu 93,6 - 97,1. Topivost dikalcijevih fosfata iznosila je (u %) u vodi od 1,4 do 98,5; u O 4% HCl 78,7 -92,3 i u neutralnom amonijevom citratu 70,3 - 85,1. Prosječna topivost mononatrijevih fosfata iznosila je (u %) u vodi 0,1 do 89,6; 2% limunskoj kiselini 25,0 do 90,0; u 0,4% HCl 26,9 do 47,7 i u neutralnom amonijevom citratu 27,7 do 90,2. Topivost ostalih skupina fosfata (trikalcij,

kalcijev magnezij i natrijevi-kalcijevi fosfati) iznosila je (u %) u vodi od 0,1 do 25,8; u 2% limunskoj kiselini od 25,1 do 95,7; u 0,4% HCl od 26,9 do 56,2 i u neutralnom amonijevom citratu od 23,1 do 79,3. Hidratni monokalcijevi fosfati s primjesom hidratog i dehidratnog dikalcijevog fosfata obilježila je najviša topivost u vodi. U skupini dikalcijevih fosfata najniža topivost u 0,4% HCl ustanovljena je za dehidrirane oblike, ali je najviša topivost primijećena u hidratnim fosfatima. Topivost u vodi ili u 0,4% hidroklornoj kiselini zajedno s rendgenografskim i termogravimetrijskim ispitivanjima kao i topivost u 2% limunskoj kiselini i neutralnom amonijevom citratu dobre su i jeftine metode za precizno identificiranje kakvoće fosfata.

Ključne riječi: krmni fosfati, fizikalno-kemijska kakvoća

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