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DETERMINATION OF LEAD, MERCURY AND ARSENIC IN FEEDING PHOSPHATES

O. SYNEK, S. ZIMA, M. ŠUCMANOVÁ, E. ŠUCMAN

Department of Chemistry, Physics and Biochemistry, University of Veterinary Science, 612 42 Brno

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Abstract

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Elaborated was the method of determination of lead, mercury and arsenic in feeding phosphates by means of atomic absorption spectrophotometry. Five different types of foreign and Czechoslovak phosphates commonly used for the preparation of feed mixtures were analyzed. The content of lead, mercury and arsenic ranged from 0.72 to 6.89 mg kg^{-1}, 0.09 to 0.37 mg kg^{-1} and from 0.75 to 69.77 mg kg^{-1}, respectively. With regard to the content of all the three elements studies it was found that the relatively purest was dinatriumphosphate (Fosfa, n. p.), while the highest amount of admixtures was found in monocalciumphosphate (Reymesholm) and dicalciumphosphate (CKF).

Microelements, atomic absorption spectrophotometry, feed mixtures.

The ever increasing industrialization and intensification of agricultural large-scale production necessitates investigations of new aspects in the nutrition of farm animals, aspects that had not been important before. One of the problems discussed has recently become the content of some microelements in feeds and feed mixtures; the intense development of instrumentation techniques over the past years has enabled these investigations to be carried out. The most important of these microelements are lead, cadmium, mercury and arsenic, indicated as „toxical civilization elements". The importance of uptake of these elements by farm animals should be judged from two aspects, i. e. from the point of view of the health condition of animals (possible intoxication, etc.), and because feed is the first link of the food chain which ends in man. Whereas the final links of this chain (raw materials for the preparation of foodstuffs, finished products, etc.) have already been studied, are being discussed, or there already exist standards for the admissible contents, in the field of feeds not many studies of this kind exist. These studies are aimed namely at lead of which namely the increased content in conventional feeds is closely associated with civilization. The intoxication of farm animals with lead in the industrial regions and in the vicinity of main roads with heavy traffic is becoming an ever increasing problem (Matyáš 1975).

The most important mineral components of feed mixtures include various types of phosphates, representing 1—10 % of the total composition of feed mixtures. With regard to the initial raw materials and the industrial character of the production of these substances the present study deals with the determination of lead, mercury and arsenic in the most frequently used types of feeding phosphates of both foreign and Czechoslovak origin.

Materials and Methods

Samples of dicalcium phosphate (DCP) and monocalciumphosphate (MCP) imported to Czechoslovakia in 1975—1977 as mineral feed admixtures were analyzed as for the content of lead, mercury and arsenic. The other phosphates studied (dinatriumphosphate, pyrophosphate and hexametaphosphate) were produced in Fosfa n. p. in Poštorná.

Determination of the content of lead, mercury and arsenic in phosphates was performed using the method of atomic absorption spectrophotometry (AAS) with the Varian Techtron Model

1000 apparatus. Absorbance signals were recorded using a Varian-Aerograph A-25 recorder.

Samples to be used for the determinations were dissolved in the following way: for arsenic determination a phosphate sample (1—2 g) was shaken for 3 hours with 25 ml of concentrated HCl. Next, about 30 ml of deionized water was added and the solution was heated (one hour) so that its temperature would not exceed 80°C. After cooling down to room temperature the volume was refilled in a volumetric flask to 100 ml. For the determination of lead and mercury the method was the same, only that a mixture of 10 ml of concentrated HNO_3 and 15 ml of concentrated HCl was used.

Table 1

Basic parameters of apparatus of determinations of lead, mercury and arsenic

Parameter Element	Wave length (nm)	Slot (nm)	Lamp current* (mA)
Pb	283.3	0.2	8
Hg	253.7	0.2	3
As	193.7	0.2	10

* For the determination of all elements hollow cathode lamps were used.

By an optimation of analytical conditions the methods were elaborated of determinations of the elements given in a certain material. Tab. 1 gives the basic parametres of the apparatus for the individual elements.

The content of lead was determined using flameless atomization; for this purpose the basic apparatus was supplied with the CRA device, Model 63, of the firm Varian. For the dosing of the samples analyzed we used an Eppendorf micropipette of a volume of 5 μl.

Mercury was determined using the cold vapour technique after reduction with tin dichloride in the equipment of the firm Varian, Model 64 (Hatch, Ott 1968; Hoower et al. 1971; Šucmanová et al. 1976). A constant volume (20 ml) of the standard solution or sample was dosed into the reaction vessel. After adding 1 ml of 20 % $SnCl_2$ in concentrated HCl the solution was intensively mixed with an electromagnetic stirer and after 90 s the mercury vapours were carried into an absorption measuring cell with a stream of argon.

Table 2

Analytical characteristics of the process of lead, mercury and arsenic determinations

	Sr (%)	Sensitivity g/1%	Concentration range	Correlation coefficient
Pb	5.3	$5 . 10^{-12}$g	0.1 – 1.0 μg/ml 0.01 – 0.08 μg/ml	0.9819
Hg	5.0	$2.5 . 10^{-11}$g	10 – 100 ngHg 0.5 – 5(10) ngHg/ml	0.9986
As	4.5	$6 . 10^{-9}$g	0.02 – 0.4 μg 0.05 – 0.6 μg	0.9994

For the determination of arsenic we used the method of hydride development after reduction with sodium borohydride (5 ml of 5 % $NaBH_4$) in the Model 64 device of the firm Varian. A nitrogen-entrained air-hydrogen flame served as absorption medium. A constant volume (20 ml) of standard solution or sample was dosed into the reaction vessel.

Tab. 2 shows the analytical characteristics of processes elaborated for the determination of the individual elements. The results measured were statistically elaborated in the common way.

Table 3

Lead content in feed phosphates analyzed (mg kg^{-1})

Sample	Producer	n	$\bar{x}$	95 % CI
Dicalciumphosphate	Kuhlman (France)	14	3.71	3.18 – 4.23
Dicalciumphosphate	CKF (FRG)	13	6.89	6.37 – 7.40
Dicalciumphosphate	Viktor (FRG)	10	3.98	3.82 – 4.15
Dicalciumphosphate^{a}	Windmill (Holland)	10	1.12	1.02 – 1.23
Dicalciumphosphate^{b}	Windmill (Holland)	6	1.15	1.01 – 1.29
Dicalciumphosphate	Sojuzchimexport (USSR)	10	2.20	1.96 – 2.44
Monocalciumphosphate	Reymesholm (Sweden)	10	4.35	3.08 – 5.26
Dinatriumphosphate	Fosfa, n. p. (ČSSR)	6	0.72	0.58 – 0.85
Pyrophosphate	Fosfa, n. p. (ČSSR)	6	0.88	0.74 – 1.02
Hexametaphosphate	Fosfa, n. p. (ČSSR)	6	1.40	1.34 – 1.46

n – number of samples elaborated
$\bar{x}$ – average value
95% CI – a 95% confidence interval for lead content found
a – sample imported in 1976
b – sample imported in 1977

Table 4

Mercury content in feed phosphates analyzed (mg kg^{-1})

Sample	Producer	n	$\bar{x}$	95 % CI
Dicalciumphosphate	Kuhlman (France)	8	0.14	0.08 – 0.20
Dicalciumphosphate	CKF (FRG)	8	0.23	0.14 – 0.31
Dicalciumphosphate^{b}	Windmill (Holland)	6	0.13	0.12 – 0.15
Monocalciumphosphate	Reymesholm (Sweden)	6	0.29	0.25 – 0.32
Dinatriumphosphate	Fosfa, n. p. (ČSSR)	10	0.37	0.29 – 0.44
Pyrophosphate	Fosfa, n. p. (ČSSR)	10	0.20	0.14 – 0.25
Hexametaphosphate	Fosfa, n. p.	10	0.09	0.07 – 0.11

Table 5

Arsenic content in feed phosphates analyzed (mg kg^{-1})

Sample	Producer	n	$\bar{x}$	95 % CI
Dicalciumphosphate	Kuhlman (France)	10	1.10	0.85 – 1.35
Dicalciumphosphate	CKF (FRG)	10	69.77	65.81 – 73.72
Dicalciumphosphate	Viktor (FRG)	10	5.17	4.75 – 5.59
Dicalciumphosphate^{a}	Windmill (Holland)	10	6.90	6.62 – 7.19
Dicalciumphosphate^{b}	Windmill (Holland)	6	17.00	14.61 – 19.39
Dicalciumphosphate	Sojuzchimexport (USSR)	10	10.23	9.57 – 10.89
Monocalciumphosphate	Reymesholm (Sweden)	6	20.70	19.98 – 21.43
Dinatriumphosphate	Fosfa, n. p. (ČSSR)	4	0.75	0.70 – 0.80
Pyrophosphate	Fosfa, n. p. (ČSSR)	4	2.94	2.88 – 3.00
Hexametaphosphate	Fosfa, n. p. (ČSSR)	4	3.50	3.20 – 3.80

Results

Tables 3, 4 and 5 give the contents of lead, mercury and arsenic found in the feeding phosphates analyzed.

The minimum content of lead determined in dinatriumphosphate was 0.72 mg kg^{-1}. Of the DCP imported the lowest content (1.12 mg kg^{-1}) was found in the sample of the firm Windmill, whilst the maximum content (6.89 mg kg^{-1}) was found in DCP of the firm CKF. In total, the contents of lead in the samples analyzed ranged within one order.

The amounts of mercury found in phosphates were relatively low. The content of mercury did not exceed 0.5 mg kg^{-1} in any of the samples analyzed.

However, the arsenic contents ranged within two orders. The highest content of arsenic was found in DCP of the firm CKF and the lowest in dinatriumphosphate, i. e. 69.77 mg kg^{-1} and 0.75 mg kg^{-1}, resp. From the point of view of all the elements studied the relatively purest was considered to be dinatriumphosphate, the impurest were DCP of the firm CKF and MCP of the firm Reymesholm.

Discusion

It was Lebeda and Přikrylová (1976) who drew attention to the importance of investigating the content of microelements in feeds as well as in commercially produced feed mixtures. Also Matyáš (1976) considers investigations of microelements in feeds to be an important aspect in the prevention of intoxication and also of the good quality of foodstuffs.

The ever more frequent cases of intoxication of farm animals with lead necessitated investigations of the content of lead in feeds. Oelschläger (1974) determined that the content of lead in green fodder from different regions without developed industry and traffic ranged from 0.6 to 3.9 mg kg^{-1}. Many authors (Hapke 1975; Horák et al. 1977; Auermann et al. 1976) dealt with determinations of the lead content in plants near to roads with heavy traffic; the results acquired are in accordance and range from 10 to 300 mg kg^{-1} (in extreme cases even more) with regard to the distance of the place of sampling from the road and to some other factors. Mineral feeding phosphates can be considered to be a further potential source of lead with regard to the initial raw materials and technology of production. However, data on the content of lead are not very frequent in literature. Oelschläger (1974) found an average of 6.8 mg kg^{-1} in the mineral additive for cattle and 11.0 mg kg^{-1} in the mineral additive for pigs which was of the same order as our results. Fox et al. (1978) analyzed the commercially prepared mineral additives of feed mixtures for laboratory animals and found that the lead content ranged from 0.1 to 3,600 mg kg^{-1}. The value for monocalciumphosphate was 23.2 mg kg^{-1}. Crössmann (1977) determined that the average lead content in a number of various types of commercial feed mixtures for cattle, pigs, horses and poultry ranged from 0.65 to 7.77 mg kg^{-1}. He stated that the content of lead in the mineral feeding additives themselves (not specified in greater detail) ranged from 0.42 to 21.7 mg kg^{-1}.

Very dangerous for farm animals are — from the point of view of mercury poisoning — especially fungicides on the basis of mercury compounds, to a lesser extent water. The contents of mercury in feeding phosphates analyzed found by the authors of this study are relatively low. This fact is in accordance with data of Crössmann (1977) who found that the content of mercury in mineral feeding additives ranged from 0.01 to 0.36 mg kg^{-1}. The average mercury contents in the finished feed mixtures were always found to be lower than 0.1 mg kg^{-1}; in about 69 % its content was below the limit of detection, i. e. lower than 0.01 mg kg^{-1}.

The common source of arsenic are mostly pesticides on the basis of arsenic (III) compounds. Arsenic in low concentrations is considered to be essential (Schwarz 1977). Arsenic poisoning is not very frequent and as stated by Selby et al. (1977) it afflicts mostly cattle and also dogs. Recently, investigations of the content of arsenic in foodstuffs have been carried out. Jelinek and Corneliussen (1977) state that in meat and fish the range was 0.020 to 0.180 mg kg^{-1}. The values of arsenic contents in feeding phosphates given in the present study are relatively high, especially for DCP of the firm CKF (69.77 mg kg^{-1}) and for MCP (20.70 mg kg^{-1}). This fact could play a certain role in long-term feeding with regard to the cummulative properties of arsenic in the animal organism.

Stanovení obsahu olova, rtuti a arzénu v krmných fosfátech

Byly vypracovány postupy stanovení olova, rtuti a arzénu v krmných fosfátech pomocí atomové absorpční spektrofotometrie. Bylo analyzováno pět různých typů zahraničních i tuzemských fosfátů běžně používaných pro přípravu krmných směsí. Byly nalezeny obsahy olova v intervalu 0,72—6,89 mg kg^{-1}, rtuti v intervalu 0,09—0,37 mg kg^{-1} a arzénu v intervalu 0,75—69,77 mg kg^{-1}. S ohledem na obsah všech tří sledovaných prvků se jako relativně nejčistší jeví dinatriumfosfát (Fosfa, n. p.), zatímco největší množství byla zjištěna u monokalciumfosfátu (Reymesholm) a dikalciumfosfátu (CKF).

Определение содержания свинца, ртути и мышьяка в кормовых фосфатах

Разрабатывались методические приемы определения свинца, ртути и мышъяка в кормовых фосфатах с помощью атомно абсорбционной спектрофотометрии. Проводились анализы пяти разных типов зарубежных и отечественных фосфатов, используемых на практике для подготовки кормовых смесей. Было найдено содержание свинца в интервале 0,70—6,89 мг кг$^{-1}$, ртути в интервале 0,09—0,37 мг кг$^{-1}$ и мышьяка в интервале 0,75—69,77 мг кг$^{-1}$. Принимая во внимание содержание всех трех исследуемых элементов, относительно самым чистым выходит динатрийфосфат (Фосфа, национальное предприятие), между тем как самое большое количество было установлено в монокальцийфосфате (Реимесгольм) и дикальцийфосфате (ЦКФ).

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