Chemical and Physical Evaluations of Commercial Dicalcium Phosphates as Sources of Phosphorus in Animal Nutrition

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ABSTRACT Seven samples of commercial dicalcium phosphate, expected to contain variable amounts of monocalcium phosphate, from five established producers in Brazil and two in the United States, were evaluated and compared with a purified grade calcium phosphate dibasic dihydrate used as a reference standard. All samples were submitted to a wide range of tests at seven laboratories. Each determination was performed at least at two different laboratories, except for moisture, insoluble residue, loss on ignition, and x-ray diffraction assays, obtained from one single laboratory. All phosphate samples studied were in compliance with the manufacturer's levels of guarantee, except for three samples that were slightly out of specification (Ca, P, and F). Particle size patterns were variable, allowing for a classification of two products as "coarse", three as "fine", and three as "irregular". Phosphorus solubility in 2% citric acid ranged from 85.9 to 97.6%, pH from 3.2 to 6.1, and apparent density from 572 to 967 g/L. Atomic absorption or plasma emission spectrometry concentrations (average parts per million) for Al (3,200), As (10), B (14), Ba (165), Bi (< .1), Cd (6), Cr (57), Co (11), Cu (28), Fe (7,515), Hg (< .2), Mg (11,300), Mn (367), Mo (6), Ni (25), Pb (17), Se (< .5), Sb (1.3), Th (19), U (51), V (134), W (< 5), and Zn (152) were safe for all phosphates as compared to NRC standards. X-ray diffraction detected $CaCO_3$ and impurities for all commercial samples, dolomite for three phosphates. Monocalcium phosphate was found in four samples. Aluminum salts present were identified as the low solubility, low toxicity silicates, and phosphates.

(*Key words*: feed phosphates, chemical and physical analysis, composition, minerals, x-ray diffraction)

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INTRODUCTION

Dicalcium phosphate is commonly used as a source of supplemental phosphorus. Commercial dicalcium phosphate is an industrial product resulting from rock phosphate acidulation, frequently with sulfuric acid, yielding phosphoric acid that is neutralized, after purification, with calcium carbonate. Commercial dicalcium phosphate is not a chemically defined

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entity, but in fact a mixture of varying amounts of dicalcium and monocalcium phosphates, phosphoric acid, calcium carbonate, and impurities, depending on the origin of the raw material and procedures employed in its industrial production. In studies of P availability in different feed ingredients, commercial dicalcium phosphate is often utilized as standard reference product, and in commercial feed formulation, P from dicalcium phosphate is considered to be 100% available.

Considered to be a very safe source of P, dicalcium phosphate is largely used in animal feeds all over the world. Despite the enormous importance of this feed ingredient in animal feeding, scarce and scattered information is available in the literature regarding its chemical and physical characteristics, particularly concerning the levels of potentially toxic or harmful mineral elements, the proportions of monocalcium and dicalcium phosphates, the degree of hydration of the molecules, pH, particle size, and other parameters that are known to be relevant to P utilization by animals (Gillis *et al.*, 1962; NRC, 1980, 1994; Burnell *et al.*, 1990; McDowell, 1992; Sullivan *et al.*, 1994). Characteristics of dicalcium phosphates obtained from different manufacturers will vary according to the origin of the raw material (rock phosphate, phosphoric acid, limestone) and also according to variations in industrial processing methods and conditions. Essential mineral composition and potentially harmful or toxic element levels for 9 mono-dicalcium phosphates and 13 di-mono calcium phosphates were reported by Sullivan *et al.* (1994). Currently, there is no published information on the use of x-ray diffraction analysis to estimate monocalcium and dicalcium phosphates proportions in commercial feed phosphates. The purpose of this study was to evaluate chemical and physical characteristics of seven dicalcium phosphate products as compared with a purified grade calcium phosphate dibasic dihydrate ($CaHPO_4{\cdot}2H_2O$).

MATERIALS AND METHODS

Seven commercial dicalcium phosphates, five made in Brazil and two in the United States, were studied along with a standard reference purified grade calcium phosphate dibasic dihydrate: $CaHPO_4{\cdot}2H_2O$ (Table 1). All commercial products were expected to be chemical mixtures of monocalcium and dicalcium phosphates. Phosphate 1 was the reference standard produced in Brazil, Phosphates 3 and 7 were made in the U.S., and all others were products of the Brazilian phosphate industry. Standard analytical methods recommended by the Association of Official Analytical Chemists (1984) were followed. All phosphates were analyzed for moisture, loss on ignition, insoluble residue, particle size, pH, P solubility in 2% citric acid. Mineral analysis included the essential Ca, P, Co, Cu, Fe, Mg, Mn, Mo, Se, Zn, and the potentially toxic elements F, Al,

TABLE 1. Analytical values guaranteed by manufacturers of the P sources studied

P Source	Origin	Guaranteed analytical values Ca (maximum)	 P (minimum)	 F (maximum)
		(%)		
1[1]	Brazil	23.3	18.0	. . .
2	Brazil	27.0	19.0	.19
3	U.S.	18.0	21.0	.21
4	Brazil	24.0	18.0	.18
5	Brazil	25.0	18.0	.18
6	Brazil	23.0	19.0	.19
7	U.S.	24.0	18.5	.19
8	Brazil	24.0	19.0	.19

[1] Standard calcium phosphate dibasic dihydrate purified grade.

Pb, Cd, Cr, As, Ni, Bo, Ba, V, Hg, Sb, W, Bi, and the radioactive U and Th. All samples were also evaluated by x-ray diffraction to identify chemical species present in each product. Analysis were performed at seven different laboratories in Brazil and in the United States.[7] Phosphorus analyses were averaged from the results obtained at six laboratories, Ca at five, F, pH, apparent density, particle size, As, Ba, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Se, Th, U, V, and Zn at two. The IMC-Agrico laboratory employed a segmented-flux analytical system for Ca and P determinations and an ion selective electrode for fluorine analysis. Atomic absorption (Perkin-Elmer model 5100[8]) was used for Al, Fe, and Mg. Trace elements were analyzed by plasma spectrometry (Perkin-Elmer Soiax Elan 500[8]) and moisture determinations were performed using a vacuum oven. At the Laboratório de Caracterização de Materiais (LACAM) laboratory, plasma spectrometry (ARL-ICP-AES, model 3410 sequential[9]) was used for analysis of 21 mineral elements. Values of pH were obtained from 5 g phosphate samples in 250-mL solutions (water pH = 7) using a potentiometer. Moisture was determined at 80 C, basically to quantify hygroscopicity of the products, because water of crystallization losses may occur with temperatures as low as 109 C. Loss on ignition was determined at 1,000 C in dry samples and represents losses in water of crystallization, carbon dioxide from carbonates, and volatile mineral elements such as As, Hg, and halogens. Insoluble residue in HCl followed by HNO_3 basically quantifies silica content. All x-ray diffraction assays were performed at the Laboratório de Caracterização Tecnológica (LCT) laboratory after mechanical grinding of the samples according to standard procedures to obtain particle size 80% < 400 mesh "Tyler" and 90% < 200 mesh. Analytical procedures employed equipment PHILLIPS-PW1880[10] with a PW1710 controller and PC-APD (automated powder diffraction) software. Operating conditions were standardized according to the following parameters: step-scan = .02°; time-step = .5 s, intervals of $2\Theta = 5$ to $70°$; radiation = copper ($K\alpha\ 1 = 1.5405981$ Å); tension = 40 Kv; current = 40 mA; spinner and monocromator. On peak-search, peak width was standardized as .05 and 1.0°, minimum and maximum, respectively, base width of 2.0° and relative significance of .5. A preliminary selection of possible phases present in the samples was made through software utilizing the identified peaks in an automated comparative process with the Phillips Plus 38 (CD-ROM - Total access diffraction database) databank based on JCPDS (Joint Committee on Powder Diffraction Standards) cards updated until 1988. Final identification of the chemical species present in the samples was obtained by comparison and superposition of the diffractogram and position and peak intensities of the species previously selected from the databank, according to Hanawalt procedures as described by Azároff (1968). Basic principles for x-ray diffraction assays have been previously published (Kaeble, 1967; Klug and Alexander, 1973; Cullity, 1978). All data, except for particle size and x-ray diffraction values, were statistically analyzed using the MEANS procedure of the SAS® software package (SAS Institute, 1985) for computation of mean and standard error of the mean values.

RESULTS AND DISCUSSION

Particle size data are presented in Table 2 and the moisture content, insoluble residue, loss on ignition, pH, apparent density, and P solubility in 2% citric acid values are presented in Table 3. The x-ray diffractogram interpretation is summa-

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TABLE 2. Particle size of commercial dicalcium phosphate

P Source	>2,00 mm	>1,00 mm	>0,84 mm	>0,30 mm	<0,30 mm
	(%)				
1	.0	.0	.0	.0	100.0
2	.0	.4	.5	3.8	96.2
3	.0	12.4	33.2	99.0	1.0
4	.1	1.3	2.4	5.9	94.1
5	.1	2.6	5.3	22.0	78.0
6	.0	4.2	7.4	24.2	75.8
7	.0	10.5	27.8	97.1	2.9
8	.4	18.5	23.6	55.4	44.6

rized in Table 4. Essential mineral composition is shown in Table 5. Levels of 16 potentially harmful or toxic mineral elements are presented in Tables 6 and 7.

Particle Size, Apparent Density, pH, and P Solubility

Particle size values are presented in Table 2 and apparent density, pH, and P solubility in Table 3. Particle size patterns were variable, allowing for a classification of the products as "fine" (phosphates 1, 2 and 4), "coarse" (phosphates 3 and 7), and "irregular" (phosphates 5, 6, and 8). Apparent density values were variable, ranging from 556 g/L (phosphate 1) to 967 g/L (phosphate 3). The highest density values were recorded for samples 3 (967 g/L) and 7 (920 g/L), the two products classified as coarse according to their particle size pattern. Similar results were observed by Potter (1988) for coarse phosphates (967 and 988 g/L) in contrast to a fine product (610 g/L). Particle size and density are characteristics related to the miscibility of the product in conventional poultry diets based on ground cereal grain and oilseed meals (American Feed Manufacturers Association, 1976). Very fine or very coarse product may not disperse homogeneously in the feed, preventing poultry from receiving on a regular basis available P in the amounts specified by the animal nutritionist and this may impair performance of birds. Very fine products are also difficult to handle at the feed mill, exposing mill workers to uncomfortable, if not hazardous, environmental conditions and increasing losses in exhaustion fans. Phosphorus from larger particle size phosphates were shown to be more biologically available to poultry (Griffith and Schexnailder, 1970; Potter, 1988; Burnell *et al.*, 1990), probably due to being retained longer in the gizzard under more acidic conditions that may solubilize P

TABLE 3. Moisture, insoluble residue, loss on ignition, pH, apparent density, and P solubility of commercial dicalcium phosphate

P Source	Moisture	Insoluble residue	Loss on ignition	pH	Apparent density	P Solubility
	(%)				(g/L)	(%)
1	.15	.77	24.1	5.8	556	97.6
2	1.58	1.57	13.7	6.1	840	94.8
3	1.34	1.82	23.9	3.2	967	92.4
4	.96	1.35	17.1	5.8	849	90.4
5	.99	5.14	16.3	4.8	814	96.5
6	1.31	2.84	16.0	5.7	572	94.9
7	2.17	2.88	21.4	3.5	920	85.9
8	1.80	2.50	22.6	3.9	844	94.6
Means	1.29	2.36	19.4	4.8	795	93.4
SE	.61	1.35	4.1	1.2	151	3.8

TABLE 4. X-ray diffraction–presence of chemical species in decreasing order of occurrence[1,2]

	Phosphate source							
Chemical species	1	2	3	4	5	6	7	8
$CaHPO_4$	3	1	1	1	1	1	2	2
$CaHPO_4 \cdot 2H_2O$	1+2	3	. . .	3+4	. . .	4	. . .	8
$Ca(H_2PO_4)_2 \cdot H_2O$	. . .	. . .	2	. . .	4	. . .	3	3
$CaCO_3$	. . .	2	3	2	2	2	1	1
$(CaMg)CO_3$	. . .	. . .	. . .	PP	3	3	. . .	. . .
$MgHPO_4 \cdot 3H_2O$	. . .	4	5	5	7	7	5	5
$CaMnPO_4 \cdot H_2O$	5	PP	4	PP	PP	5	4	4
$KCaPO_4$	4	5	. . .	. . .	6	6	. . .	. . .
$K_2CaP_2O_7 \cdot 4H_2O$	. . .	6	7	. . .	. . .	. . .	. . .	. . .
$K_4P_2O_7$	. . .	. . .	. . .	. . .	. . .	PP	. . .	. . .
$NaCa(PO_4)$	. . .	PP	. . .	. . .	. . .	. . .	. . .	. . .
Ca_2SiO_4	PP	. . .	. . .	. . .	. . .	. . .	. . .	. . .
$Ca_5(PO_4)_2SiO_4$	. . .	. . .	. . .	. . .	. . .	. . .	. . .	9
$NH_4CaHP_2O_7$	. . .	. . .	9	. . .	. . .	. . .	. . .	. . .
$(NH_4)Fe_3P_6O_{20} \cdot 10H_2O$	. . .	. . .	10	. . .	. . .	. . .	7	6
$AlPO_4 \cdot 2H_2O$	. . .	PP	. . .	. . .	5+PP	PP	8	7
$KAlP_2O_5$	. . .	. . .	. . .	6	. . .	. . .	. . .	. . .
Ca_2AlSiO_7	. . .	. . .	6	. . .	. . .	. . .	6	. . .
$CaAl_2(Si_2Al_2)O_{10} \cdot (OH)_2$	. . .	. . .	8	. . .	. . .	. . .	9	. . .

[1] Two values in a single cell indicates the presence of two crystalline forms of the same chemical entity.

[2] PP indicates possible presence.

TABLE 5. Essential mineral composition of commercial dicalcium phosphate

P Source	Ca	P	Mg	Co	Cu	Fe	Mn	Mo	Se	Zn
	(%)			(ppm)						
1	24.9	18.6	.001	1	4	20	4	<1	<.5	16
2	25.7	19.3	.98	13	24	8,100	424	3	<.5	398
3	16.5	21.2	.75	14	20	11,100	365	16	<.5	127
4	24.3	18.4	2.42	12	15	6,300	763	1	<.5	20
5	24.5	17.4	1.67	7	48	5,200	273	6	<.5	260
6	23.8	19.5	1.49	13	19	8,500	373	1	<.5	38
7	21.6	18.8	.79	12	17	9,900	303	11	<.5	111
8	20.6	19.4	.92	17	73	11,000	430	7	<.5	247
Means	22.7	19.1	1.13	11	28	7,515	367	6	<.5	152
SE	3.0	1.1	.73	4.9	22	3,684	210	5.6	. . .	138

TABLE 6. Potentially harmful mineral element levels of commercial dicalcium phosphate: Al, F, As, B, Ba, Bi, Cd, and Cr

P Source	Al	F	As	B	Ba	Bi	Cd	Cr
	(%)		(ppm)					
1	.003	.007	1	6	8	<.1	<.1	1
2	.15	.16	9	10	226	<.1	7	75
3	.92	.14	15	36	12	<.1	5	82
4	.15	.14	3	7	569	<.1	<.1	6
5	.21	.12	13	15	174	<.1	14	131
6	.11	.15	9	4	135	<.1	<.1	6
7	.80	.14	12	27	16	<.1	6	89
8	.24	.21	16	8	179	<.1	17	67
Means	.32	.13	10	14	165	<.1	6	57
SE	.34	.06	5.4	11.5	184	. . .	6.5	47.6

TABLE 7. Potentially harmful and radioactive mineral element levels of commercial dicalcium phosphate: Hg, Ni, Pb, V, W, Sb, Th, and U

P Source	Hg	Ni	Pb	V	W	Sb	Th	U
	(ppm)							
1	<.2	11	1	2	<5	<1	<5	<1
2	<.2	28	2	160	<5	<1	18	41
3	<.2	21	30	195	<5	3	13	178
4	<.2	12	3	110	<5	<1	13	1
5	<.2	44	2	168	<5	2	20	63
6	<.2	17	1	159	<5	<1	28	10
7	<.2	23	77	185	<5	<1	9	62
8	<.2	42	19	91	<5	3	45	51
Means	<.2	25	17	134	<5	1.3	19	51
SE	. . .	13	26	64	. . .	1.2	13	58

more completely (Burnell *et al.*, 1990). Values of pH were variable, ranging from 3.2 (phosphate 3) to 6.1 (phosphate 2). Industrial processing affects pH values: products containing higher proportions of monocalcium phosphate are expected to show lower pH values. Potter (1988) observed pH = 3.4 for monocalcium phosphate and values ranging from 4.4 to 7.4 for commercial dicalcium phosphate samples. Our interpretation of the pH data was reconfirmed by the x-ray diffraction assays, which have detected levels of monocalcium phosphate inversely proportional to pH values in each product. Phosphorus solubility in 2% citric acid values were high, ranging from 85.9% (phosphate 7) to 97.6% (phosphate 1). These values are in agreement with the results of Sullivan *et al.* (1992), which found P solubility in 2% citric acid greater than 90% for most of 13 dicalcium phosphate samples analyzed. Our results also compare with the observations of Potter (1988) that reported, for commercial phosphates, values of 94.2, 95.5, and 98.6% for one monocalcium and two dicalcium phosphate samples, respectively.

Moisture, Insoluble Residue, and Loss on Ignition

Moisture, insoluble residue and loss on ignition are presented in Table 3. Moisture levels were low and variable, ranging from .15% (phosphate 1) to 2.17% (phosphate 7) and averaging 1.29%. Moisture was determined at a low temperature of 80 C, basically to quantify hygroscopicity of the products, as some hydration water losses may occur at temperatures as low as 109 C. Moisture values in this study are in agreement with data published by Potter (1988) and by Sullivan *et al.* (1994). Insoluble residue levels were low and variable, with a maximum of 5.14% (phosphate 5) and other values ranging from .77% (phosphate 1) to 2:88% (phosphate 7). Insoluble residue in HCl followed by HNO_3 basically quantifies silica content of the sample. Loss on ignition levels was variable, ranging from 13.7% (phosphate 2) to 24.1% (phosphate 1). Loss on ignition was determined at 1,000 C in dry samples and represents losses in water of crystallization, carbon dioxide from carbonates, and volatile mineral elements such as As, Hg, and halogens. Considering the x-ray diffraction data (Table 4) and comparing loss on ignition values presented in Table 3, the predominance of the dihydrate salt of calcium phosphate dibasic in phosphate 1 may very well explain the relatively high loss at 1,000 C (24.1%) observed for that product. On the other hand, losses on ignition for phosphate 7 (21.4%) and phosphate 8 (22.6%) seem to be primarily related to the presence of calcium carbonate as the most predominant chemical species in both samples. Loss at 1,000 C for phosphate 3 (23.9%) is probably the result of both losses in water of crystallization from calcium phosphate monobasic monohydrate and carbon dioxide from calcium carbonate, the second and third most predominant chemical species, respectively, in the sample analyzed. Higher values of loss on ignition may indicate higher degree of hydration on the calcium phosphate molecule, suggesting superior P availability potential. Lower values for loss on ignition, on the other hand, may be due to variations in processing that influence the degree of hydration and the proportion of mono to dibasic calcium phosphate. Higher degree of hydration and higher proportions of the monocalcium salt are expected to contribute to higher P availability potential.

Calcium

Calcium levels (Table 5) were variable, ranging from 16.5% (phosphate 3) to 25.7% (phosphate 2) with an average of 22.7%. All samples were in compliance with the limits of label guarantees (Table 1) for each product, not exceeding the maximum Ca allowed, except for small deviations detected in samples 4 and 6 that would be of little or no consequence in poultry feed formulation.

Phosphorus

Phosphorus levels (Table 5) were variable, averaging 19.1%, ranging from 17.4% (phosphate 5) to 21.2% (phosphate 3). All samples were in compliance with the limits of label guarantees (Table 1) for each product, not showing values below the minimum P allowed, except for small deviation detected in sample 5 that would be of little or no consequence in poultry feed formulation.

Magnesium

Magnesium levels (Table 5) were variable, ranging from .001% (phosphate 1) to 2.42% (phosphate 4) with an average of 1.13%. The highest Mg levels were observed for phosphates 4, 5, and 6 (24,200, 16,700, and 14,900 ppm, respectively), products in which the x-ray diffraction assays detected the presence of dolomite. These levels would not be toxic for poultry, as the maximum tolerable Mg level (NRC, 1980) for poultry is 3,000 ppm in the complete diet, or 150,000 ppm in a P source used at a dietary level of 2%. However, if available biologically, these levels could furnish considerable proportion of the bird's requirement of Mg, which was estimated by the NRC (1994) to be 600 ppm in a complete diet.

Cobalt

Cobalt levels (Table 5) were low, averaging 11 ppm and ranging from 1 ppm (phosphate 1) to 17 ppm (phosphate 8). These levels may be of little or no consequence in poultry feed formulation, because the maximum tolerable Co level (NRC, 1980) for poultry is 10 ppm in the complete diet, or 500 ppm in a P source used at a dietary level of 2%.

Copper

Copper levels (Table 5) were low, averaging 28 ppm and ranging from 4 ppm (phosphate 1) to 73 ppm (phosphate 8). These levels may be of little or no consequence in poultry feed formulation, because the maximum tolerable Cu level (NRC, 1980) for poultry is 300 ppm in the complete diet, or 15,000 ppm in a P source used at a dietary level of 2%. Considering the poultry requirement for Cu (8 ppm in a complete diet) as estimated by the NRC (1994), any possible contribution to Cu nutrition by the commercial phosphate products tested would be negligible.

Iron

Iron levels (Table 5) were variable, ranging from 20 ppm (phosphate 1) to 11,100 ppm (phosphate 3), and averaging 7,515 ppm. The highest Fe levels were observed for phosphates 3, 7, and 8 (11,100, 9,900, and 11,000 ppm) and these levels would not be toxic for poultry, because the maximum tolerable Fe level (NRC, 1980) for poultry is 1,000 ppm in the complete diet, or 50,000 ppm in a P source used at a dietary level of 2%. However, if available biologically, these levels could furnish the bird's requirements of Fe, estimated to be 80 ppm in a complete diet by the NRC (1994).

Manganese

Manganese levels (Table 5) were variable, averaging 367 ppm and ranging from 4 ppm (phosphate 1) to 763 ppm (phosphate 4). These levels may be of little or no consequence in poultry feed formulation, because the maximum tolerable Mn level (NRC, 1980) for poultry is 2,000 ppm in the complete diet, or 100,000 ppm in a P source used at a dietary level of 2%. Considering the poultry requirement for Mn (60 ppm in a complete diet), as estimated by the NRC (1994), any possible contribution to Mn nutrition by the commercial phosphate products tested would be negligible.

Molybdenum

Molybdenum levels (Table 5) were low and averaged 6 ppm, ranging from undetectable, < 1 ppm (phosphate 1) to 16 ppm (phosphate 3). These levels may be of little or no consequence in poultry feed formulation, because the maximum tolerable Mo level (NRC, 1980) for poultry is 2,000 ppm in the complete diet, or 100,000 ppm in a P source used at a dietary level of 2%.

Selenium

Selenium (Table 5) was undetectable, < .5 ppm, in all phosphate samples and this will be inconsequential in poultry feed formulation. The maximum tolerable Se level (NRC, 1980) for poultry is 300 ppm in the complete diet, or 15,000 ppm in a P source used at a dietary level of 2%. The poultry requirement for this mineral is 150 ppb (NRC, 1994).

Zinc

Zinc levels (Table 5) were variable, ranging from 16 ppm (phosphate 1) to 398 ppm (phosphate 2), averaging 152 ppm. These levels may be of little or no consequence in poultry feed formulation, as the maximum tolerable Zn level (NRC, 1980) for poultry is 1,000 ppm in the complete diet, or 50,000 ppm in a P source used at a dietary level of 2%. The poultry requirement for Zn is 40 ppm (NRC, 1994), so that any possible contribution to Zn nutrition by the commercial phosphate products tested would be negligible.

Aluminum

Aluminum levels (Table 6) were variable, averaging .32% and ranging from .003% (phosphate 1) to .92% ppm (phosphate 3). The highest Al levels were observed for phosphates 3 and 7 (9,200 and 8,000 ppm, respectively), produced from sedimentary rock phosphate and for that reason expected to present higher values of Al. These levels may be of little or no consequence in poultry feed formulation, as the maximum tolerable Al level, from soluble salts of high bioavailability (NRC, 1980), for poultry is 200 ppm in the complete diet, or 10,000 ppm in a P source used at a dietary level of 2%. The NRC (1980) stresses the fact that higher levels of less-soluble forms can be tolerated. In our studies, the x-ray diffraction assays detected the presence of Al in the form of the highly unsoluble (low toxicity) silicates and phosphates in all commercial samples. Therefore, Al levels found in phosphate samples in this study would not be a problem.

Fluorine

Fluorine levels (Table 6) were variable (average of .13%), ranging from .007% (phosphate 1) to .21% (phosphate 8). All samples were in compliance with the limits of label guarantees (Table 1) for each product, not exceeding the maximum F allowed, except for a small deviation detected in sample 8 (2,100 ppm) that would be of little or no consequence in poultry feed formulation. It is generally accepted, based on a AAFCO (1973) recommendation, that feed phosphate supplements should contain no more than 1 part F to 100 parts P.

Arsenic

Arsenic levels (Table 6) were very low, averaging 10 ppm and ranging from 1 ppm (phosphate 1) to 16 ppm (phosphate 8). That would be of little or no consequence in poultry feed formulation, as the maximum tolerable As level (NRC, 1980) for poultry is 100 ppm in the complete diet, or 5,000 ppm in a P source used at a dietary level of 2%.

Boron

Boron levels (Table 6) were very low, ranging from 4 ppm (phosphate 6) to 36 ppm (phosphate 3), with an average of 14 ppm. That would be of little or no consequence in poultry feed formulation, as the maximum tolerable B level (NRC, 1980) for poultry is 150 ppm in the complete diet, or 7,500 ppm in a P source used at a dietary level of 2%.

Barium

Barium levels (Table 6) were variable, averaging 165 ppm and ranging from 8 ppm (phosphate 1) to 569 ppm (phosphate 4). That would be of little or no consequence in poultry feed formulation, as the maximum tolerable Ba level (NRC, 1980) for poultry is 20 ppm in the complete diet, or 1,000 ppm in a P source used at a dietary level of 2%.

Bismuth

Bismuth (Table 6) was undetectable, < .1 ppm, in all phosphate samples and that would be inconsequential in poultry feed formulation. The maximum tolerable Bi level (NRC, 1980) for poultry is 400 ppm in the complete diet, or 20,000 ppm in a P source used at a dietary level of 2%.

Cadmium

Cadmium levels (Table 6) were variable, averaging 6 ppm and ranging from undetectable, < .1 ppm (phosphate 1, 4 and 6) to 17 ppm (phosphate 8). That would be of little or no consequence in poultry feed formulation, as the maximum tolerable Cd level (NRC, 1980) for poultry is .5 ppm in the complete diet, or 25 ppm in a P source used at a dietary level of 2%.

Chromium

Chromium levels (Table 6) were very low, ranging from 1 ppm (phosphate 1) to 131 ppm (phosphate 5), with an average of 57 ppm. That would be of little or no consequence in poultry feed formulation, as the maximum tolerable Cr level (NRC, 1980) for poultry is 3,000 ppm in the complete diet, or 150,000 ppm in a P source used at a dietary level of 2%.

Mercury

Mercury (Table 7) was undetectable, < .2 ppm, in all phosphate samples and that would be inconsequential in poultry feed formulation, as the maximum tolerable Hg level (NRC, 1980) for poultry is 2 ppm in the complete diet, or 100 ppm in a P source used at a dietary level of 2%.

Nickel

Nickel levels (Table 7) were very low, averaging 25 ppm and ranging from 11 ppm (phosphate 1) to 44 ppm (phosphate 5). That would be of little or no consequence in poultry feed formulation, as the maximum tolerable Ni level (NRC, 1980) for poultry is 300 ppm in the complete diet, or 15,000 ppm in a P source used at a dietary level of 2%.

Lead

Lead levels (Table 7) were very low, averaging 17 ppm and ranging from 1 ppm (phosphate 1, 6 and 8) to 77 ppm (phosphate 7). That would be of little or no consequence in poultry feed formulation, as the maximum tolerable Pb level (NRC, 1980) for poultry is 30 ppm in the complete diet, or 1,500 ppm in a P source used at a dietary level of 2%.

Vanadium

Vanadium levels (Table 7) were variable, ranging from 2 ppm (phosphate 1) to 195 ppm (phosphate 3), with an average of 134 ppm. That would be of little or no consequence in poultry feed formulation, as the maximum tolerable V level (NRC, 1980) for poultry is 10 ppm in the complete diet, or 500 ppm in a P source used at a dietary level of 2%.

Tungsten

Tungsten (Table 7) was undetectable, < 5 ppm, in all phosphate samples and that would be inconsequential in poultry feed formulation, as the maximum tolerable W level (NRC, 1980) for poultry is 20 ppm in the complete diet, or 1,000 ppm in a P source used at a dietary level of 2%.

Antimony

Antimony levels (Table 7) ranged from undetectable, < 1 ppm to 3 ppm. The consequences of these amounts in poultry feed formulation are unknown, as the maximum tolerable Sb level has not yet been established (NRC, 1980) for poultry.

Thorium

Thorium levels (Table 7) ranged from undetectable, < 5 ppm (phosphate 1) to 45 ppm (phosphate 8), with an average of 19 ppm. Consequences of these levels for poultry feed formulation are unknown, as the maximum tolerable Th level has not yet been established (NRC, 1980) for poultry.

Uranium

Uranium levels (Table 7) ranged from undetectable, < 1 ppm (phosphate 1) to 178 ppm (phosphate 3), averaging 51 ppm. Consequences of this much U in poultry feed formulation are unknown, as the maximum tolerable U level has not yet been established (NRC, 1980) for poultry.

X-Ray Diffraction Analysis

The diffractograms generated by x-ray diffraction analysis were interpreted and the results summarized in Table 4. Within a phosphate source, the chemical species detected were listed in decreasing order of occurrence so that number 1 indicates a chemical species that was present in highest concentration in the sample, number 2 indicates a lower concentration than number 1, number 3 lower than 2, and so on. Two numbers in a single cell of Table 4 indicates the presence of two crystalline forms of the same chemical species and PP indicates possible presence. The most predominant chemical substances present in all commercial products were calcium phosphates and calcium carbonates. For the reference standard, calcium phosphate dibasic dihydrated purified grade, two forms of calcium phosphate dibasic dihydrated were found to be the most predominant products present, followed by smaller proportion of an anhydrous form of the same salt. Very small proportions of other calcium phosphates (Mn and K) were also detected, as well as the possible presence of a calcium silicate. Surprisingly, monocalcium phosphate was found in only four commercial products (samples 3, 5, 7, and 8).

No references can be found in the literature concerning the proportion of mono and dicalcium phosphates in commercial dicalcium phosphate products. Phosphates 3 and 7 were found to contain at least equal amounts of mono and dicalcium phosphates. The other two products were identified as containing less monocalcium than dicalcium phosphates (phosphate 8 about 30% and phosphate 5 not more than 10%). These results are consistent with the pH values obtained, showing the lowest values for phosphates 3 (pH = 3.2) and 7 (pH = 3.5), and intermediate values for phosphates 8 (pH = 3.9) and 5 (pH = 4.8).

Calcitic limestone was found in large proportions in all commercial products and may be the result of excess calcium carbonate added to neutralize phosphoric acid during industrial processing. Considerable amount of dolomitic limestone was detected in samples 5 and 6 and a smaller amount was detected in sample 4. These results are consistent with Mg analysis of these products that have shown comparatively higher Mg values than other samples.

The presence of ammonium salts in samples 3 and 7 can be explained by the known sedimentary origin of the precursor rocks utilized in phosphoric acid production. In sample 8, the presence of ammonium salts may suggest the use of phosphoric acid originated from sedimentary phosphate rock reserves. Aluminum salts were present in all commercial phosphates. All of the Al salts identified in the difractograms were low solubility, low biological availability phosphates and silicates (NRC, 1980). Other impurities found were phosphates and silicates of Ca, Mg, Mn, K, and Na that may be inconsequential in poultry feed formulation.

In routine feed formulation for poultry and swine, phosphate supplements are largely used at levels not to exceed the 2% limit in conventional diets. Higher nutrient concentration in feed ingredients are generally more desirable, so that high P and Ca phosphate sources will add flexibility to formulation of high performance animal ration. Considering the poultry requirements for minerals according to the NRC (1994), Cu, Mg, Mn, Se, and Zn levels present in feed dicalcium phosphates are inconsequential.

A comparison of the maximum tolerable level of several mineral elements for domestic animals, as suggested by the NRC (1980), to values observed in this study, indicates no toxicity risks for the use of any of the dicalcium phosphates studied in normal diets for poultry. According to the findings of Sullivan *et al.* (1994), F, Cd, and V are potentially toxic elements of greatest concern in feed phosphates. However, average values obtained in this study were lower than levels reported by those authors for F (.13 vs .24%) and Cd (6.0 vs 10.6 ppm), indicating that no serious problems should be expected when using in animal feeds any of the phosphates studied. Vanadium mean levels were comparable (134 vs 139 ppm) but the maximum value obtained was 195 ppm in this study, much lower than the maximum level (796 ppm) reported by Sullivan *et al.* (1994). A comparison of the results obtained in this study to the levels reported by Sullivan *et al.* (1994) shows lower values also for Zn (152 vs 228 ppm), Al (.32 vs .52%), and Cr (57 vs 132 ppm). Higher average values were obtained for Ca (22.7 vs 19.3 %), Mg (1.13 vs .55%), Cu (28 vs 14 ppm), Mn (367 vs 242 ppm), As (10 vs 5.2 ppm), Ni (25 vs 19 ppm), and Pb (17 vs 5 ppm), and comparable levels were obtained for Fe (7515 vs 7424 ppm), Se (undetectable), and Hg (undetectable).

Mineral element analyses performed in this study that were not included in the paper published by Sullivan *et al.* (1994) are Co, Mo, B, Ba, Bi, W, Sb, Th, and U. As far as the reference standard, calcium phosphate dibasic dihydrate, is concerned, all of the analytical mineral levels but P and Ni, obtained in this study were lower than the values reported for the same reference standard by Sullivan *et al.* (1994). Nutritionally essential element concentrations in common macromineral supplements has been reported by the NRC (1994). Levels of Fe, Cu, Mn, and Zn generally compare very well to values obtained in this study. Although inconsequential relative to animal nutrition, Mg levels were higher in the phosphate sources studied as compared with the values reported by the NRC (1994).

Analytical values obtained for the phosphorus sources studied were all in compliance with the manufacturers levels of guarantee. The results obtained from x-ray diffraction assays were encouraging, indicating that this analytical tool may be more completely developed in its applications to feed phosphate evaluation. No mineral element was found in any of the phosphate supplements studied at levels that would represent a toxicological problem considering the use of the products in normal animal diets.

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