## METABOLISM AND NUTRITION

# Laboratory Evaluations of Feed-Grade and Agricultural-Grade Phosphates[1]

F. R. LIMA,*,[2] J.I.M. FERNANDES,*,[3] E. OLIVEIRA,† G. C. FRONZAGLIA,‡ and H. KAHN‡

*Departamento de Nutrição e Produção Animal, Faculdade de Medicina Veterinária e Zootecnia, Universidade de São Paulo, Pirassununga, São Paulo, 13630-000, Brazil; †Instituto de Química, Universidade de São Paulo, São Paulo, São Paulo, 05508-900, Brazil; and ‡Laboratório de Caracterização Tecnológica, Departamento de Engenharia de Minas, Escola Politécnica, Universidade de São Paulo, São Paulo, São Paulo, 05508-900, Brazil

**ABSTRACT** Nine samples of pure, feed-grade (FP) and agricultural-grade (AP) phosphates were evaluated at seven laboratories (six in Brazil and one in the U.S.) for physical and chemical characteristics. Phosphates were one “standard” pure dicalcium phosphate; four FP, two dicalcium phosphates (FP-1 and FP-2) made in Brazil, one di-monocalcium phosphate (FP-3), and one defluorinated phosphate (FP-4) made in the U.S.; and four AP made in Brazil [single superphosphate (AP-1), triple superphosphate (AP-2) and monoammonium (AP-3), and thermomagnesium (AP-4) phosphates]. Average analytical values for FP and AP, respectively, were 3.3 and 6.3% moisture, 1.0 and 2.5% insoluble residue, 16.2 and 28.4% loss on ignition, 6.8 and 4.7 (pH), 1,028 and 1,023 g/L apparent density, 9.6 and 55.0% P solubility in water, 83.6 and 88.4% P solubility in 2% citric acid, and 85.2 and 97.0% P solubility in neutral ammonium citrate. Based on particle size, six products were classified as “fine,” and three were classified as “irregular.” Atomic absorption and plasma spectrometry determinations were performed for 31 essential and potentially harmful or radioactive minerals. The Na level was high in FP-4 (6.03%). Mineral concentrations were safe for all FP as compared with NRC standards. Levels in AP were toxic, exceeding the tolerance limits for F, Fe, Mg, and Ba, and were particularly high as compared with FP for S, Ti, and radioactive Th. The AP-1 was high in F, Ba, S, and Th; AP-2 and AP-3 were high in F and S; and AP-4 was high in F, Ba, Fe, Mg, Ti, and Th. X-ray diffraction assays detected impurities for all commercial samples and identified as major components $CaHPO_4 \cdot 2H_2O$ (standard phosphate), $CaCO_3$ and $CaHPO_4$ (FP-1, FP-2, and FP-3), $Ca(H_2PO_4)_2 \cdot H_2O$ (FP-3), $Na_2Ca_3Al_2(PO_4)_2(SiO_4)_2$ and $Ca_3(PO_4)_2$ (FP-4), $CaSO_4 \cdot nH_2O$ and $(NH_4)Fe_3P_6O_{20} \cdot (PO_4)_2$ (AP-1), $Ca(H_2PO_4)_2 \cdot H_2O$ and $KFe_3P_6O_{20} \cdot 10H_2O$ (AP-2), $(NH_4)H_2PO_4$ and $CaSO_4 \cdot nH_2O$ (AP-3), and no definite molecular structure for AP-4, an amorphous product. The biological consequences of feeding animals a mineral source with no definite molecular structure, an amorphous product, is not known. A biological evaluation of all phosphates included in this article is being published as a separate report (Fernandes *et al.*, 1999).

(*Key words*: feed phosphates, agricultural phosphates, chemical analysis, minerals, X-ray diffraction)

1999 Poultry Science 78:1717–1728

## INTRODUCTION

Phosphates are salts of phosphoric acid, and a wide variety of such products is commercially available. Among the various types of inorganic phosphates, biological value varies widely because of differences in chemical structure, crystallinity, particle size, pH, and concentration of contaminating elements. Phosphorus is not supplied as a pure chemical and many phosphates are ores that may have had little processing or purification, whereas others are by-products of some industrial process. These facts must be considered in estimating the quality of a mineral source (Ammerman *et al.*, 1977). Physical and chemical evaluations of sources of supplemental P, such as dicalcium and monocalcium phosphates, have been published by Gillis *et al.* (1962), Griffith and Schexnailder (1970), NRC (1980, 1994), Burnell *et al.* (1990), McDowell (1992), Sullivan *et al.* (1992, 1994), and Lima *et al.* (1995).

Dicalcium phosphate is commonly used as a source of supplemental P and is not a chemically defined entity. It is, 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 (Lima et al., 1995).

---

Received for publication November 19, 1998.
Accepted for publication July 1, 1999.

[1] Sponsored by FAPESP. Project Number 1995/2006-6.

[2] To whom correspondence should be addressed: frlima@usp.br

[3] Present address: UFPR - Campus Palotina. R.24 de Junho, 698. Palotina, Parana, 85950-000, Brazil.

**Abbreviation Key:** AP = agricultural-grade phosphate; FP = feed-grade phosphate.

Defluorinated phosphate is a feed-grade P supplement thermochemically produced by the reaction of phosphate rock concentrate and phosphoric acid in the presence of soda ash. The raw material is processed through a mixer and a kiln (1,300 to 1,500 C) so that fluorine is removed as hydrofluoric acid, a volatile compound. After cooling and screening, the final product is tricalcium phosphate [$Ca_3(PO_4)_2$] containing low F levels (0.17%) and a relatively high Na concentration (4.8 to 5.5%).

According to Sheve and Brink (1977), phosphate rock concentrate and sulfuric acid react to produce single superphosphate, a mixture of nearly equal amounts of monocalcium phosphate [$Ca(H_2PO_4)_2$] and calcium sulfate [$CaSO_4$]. The finely ground material is cured in large piles so that reaction may go to completion, a process that takes several weeks. Commercial superphosphate contains considerable amounts of unreacted phosphate rock and sulfuric acid. Triple superphosphate results from the reaction, at room temperature, of phosphate rock concentrate and phosphoric acid. Commercial triple superphosphate is a mixture of monocalcium phosphate [$Ca(H_2PO_4)_2$] and appreciable amounts of unreacted phosphate rock and phosphoric acid. Monoammonium and diammonium phosphates are obtained by reacting phosphoric acid and anhydrous ammonia (Cardoso, 1991). If purified phosphoric acid is used in the process, the products may be used safely to feed food-producing animals. Otherwise, toxicity and potencially toxic mineral residue in edible tissues may become a problem. Thermomagnesium phosphates are produced by very high temperature (1,600 C) fusion of rock phosphate concentrate blends in the presence of silica ($SiO_2$) and magnesium (MgO) sources (Cardoso, 1991).

When agricultural-grade phosphates (AP) are priced lower than feed-grade phosphates (FP), animal nutritionists become very much aware of the need for alternate dietary P sources. Safety, however, is a matter of concern. Agricultural-grade phosphates are not intended for use in animal diets because they are not routinely produced according to the strict manufacturing procedures necessary to guarantee the adequate degree of purity for feeding food-producing animals. Phosphorus in certain AP is present in chemical forms that are easily used by plants, but bioavailability for animals may be low. In addition, high levels of certain contaminating mineral elements are perfectly safe for soil and plants, but they may be toxic to the animal.

When rock phosphate is solubilized in the process to obtain phosphate fertilizers, little loss of contaminants takes place, and the final product undergoes no further purification (Cardoso, 1991).

The purpose of this study was to evaluate chemical and physical characteristics of one pure, four FP (two made in Brazil and two made in the U.S.), and four samples of AP made in Brazil.

## MATERIALS AND METHODS

Nine samples of phosphate sources were evaluated at seven different laboratories, six in Brazil and one in the U.S., for physical and chemical characteristics. Phosphate sources were four samples of FP [two dicalcium phosphates made in Brazil (FP-1 and FP-2) one di-monocalcium phosphate (FP-3), and one defluorinated phosphate (FP-4) made in the U.S.] and four samples of AP made in Brazil (AP-1, AP-2, AP-3, and AP-4). Analytical values estimated for all experimental phosphates are presented in Table 1.

Standard analytical methods recommended by the Association of Official Analytical Chemists (1984) were followed. All phosphates were analyzed for moisture, insoluble residue, loss on ignition, particle size, pH, P solubility in water, P solubility in 2% citric acid, P solubility in neutral ammonium citrate. Mineral analysis included the essencial Ca, P, Mg, Na, K, Co, Cu, Fe, Mn, Mo, S, Se, Zn, and the potencially toxic elements Al, F, As, B, Ba, Bi, Cd, Cr, Hg, Ni, Pb, Sb, Sn, Ti, V, W, and the radioactive U and Th. Analyses were performed at seven different laboratories in Brazil and in the U.S.[4] Phosphorus and Ca analyses were averaged from the results obtained at six laboratories; fluorine, pH, apparent density, and particle size analyses were based on the results from two labs. The IMC-Agrico laboratory employed a segmented-flux analytical system for Ca and P determinations and an ion selective electrode for flourine analysis. Atomic absorption (Perkin-Elmer model 5100[5]) was used for Al, Fe, and Mg. Trace elements were analyzed by plasma spectrometry (Perkin-Elmer Soiax Elan 500[5]), and moisture determinations were performed using a vacuum oven. At the Laboratory of Atomic Emission Spectrometry of the Institute of Chemistry (IQ-USP), plasma spectrometry (ICP-AES) 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 crystalization 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 crystalization, 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 using the methodology described by Lima *et al.* (1995) for identification of the chemical species present in the samples. Analytical procedures employed an X-ray diffractometer

---

[4] Laboratory 1: Departamento de Nutriçãoe Produção Animal, VNP-FMVZ-USP, Pirassununga, SP, Brazil; Laboratory 2: Multimix Ltda., Campinas, SP, Brazil; Laboratory 3: M. Cassab Ltda., S. Paulo, SP, Brazil; Laboratory 4: Socil S.A., Descalvado, SP, Brazil; Laboratory 5: Departamento de Quimica Analítica, IQ-USP, S. Paulo, SP, Brazil, Laboratory 6: IMC-Agrico, New Wales, Florida; Laboratory 7: LCT - Laboratório de Caracterização Tecnológica, Departamento de Engenharia de Minas, EP-USP, São Paulo, SP, Brazil.

[5] Perkin-Elmer, Norwalk, CT, 06859.

**TABLE 1. Analytical values guaranteed by manufacturers (FP; feed-grade phosphate) or estimated from the literature (AP; agricultural-grade phosphate) for the P sources studied**

| P source | Origin | Ca (maximum) | P (minimum) | F (maximum) |
|---|---|---|---|---|
| | | (%) | | |
| SP[1] | Dicalcium, Brazil | 24.0 | 18.0 | |
| FP-1 | Dicalcium, Brazil | 27.0 | 19.0 | 0.19 |
| FP-2 | Dicalcium, Brazil | 26.0 | 18.0 | 0.18 |
| FP-3 | Dicalcium, U.S. | 24.0 | 18.5 | 0.19 |
| FP-4 | Defluorinated, U.S. | 33.0 | 18.0 | 0.18 |
| AP-1 | Super single, Brazil | 20.0 | 7.8 | 0.90 |
| AP-2 | Super triple, Brazil | 14.0 | 17.9 | 0.50 |
| AP-3 | Monoammonium, Brazil | 1.0 | 21.0 | 0.30 |
| AP-4 | Thermomagnesium, Brazil | 20.0 | 7.5 | |

[1] Standard phosphate.

PHILLIPS-PW1880[6] with a PW1710 controller and PC-APD (automated powder diffraction) software.

## RESULTS AND DISCUSSION

The X-ray diffractogram interpretation is summarized in Table 2. Moisture content, insoluble residue, loss on ignition, pH, apparent density, P solubility in water, P solubility in 2% citric acid, and P solubility in neutral ammonium citrate values are presented in Table 3. Particle size data are shown in Table 4. Levels of 13 essential mineral elements are shown in Tables 5 and 6. Levels of 18 potentially harmful or toxic mineral and radioactive elements are presented in Tables 7 and 8.

### *Moisture, Insoluble Residue, Loss on Ignition, and pH*

Moisture levels (Table 3) were variable and averaged 3.3 and 6.3% for FP and AP, respectively. Particularly high moisture content for AP-1 (13.3%) and AP-2 (8.7%) seem to be primarily related to the industrial wet process used to obtain superphosphates, in which sulphuric acid is diluted in water to control product moisture conditioning the chemical reaction (Sheve and Brink, 1977). The low moisture (0.1%) detected for the thermochemically produced phosphate sources (FP-4 and AP-4) is in agreement with Sullivan *et al.* (1994), who reported that low moisture in such products may be explained by high temperatures (1,250 to 1,550 C) employed in industrial processing. Moisture was determined at a low temperature of 80 C, to quantify hygroscopicity of the products, as some hydration water losses may occur at temperatures as low as 109 C. Moisture values for FP in our study compare with those published by Potter (1988), Sullivan *et al.* (1994), and Lima *et al.* (1995). Insoluble residue levels (Table 3) were low, averaging 1.0% for FP and 2.5% for AP. Considerable variation, however, was observed among AP samples, ranging from 0% (AP-4) to a maximum of 9.2% (AP-1).

Insoluble residue in HCl followed by $HNO_3$ quantifies the silica content of the sample (Lima *et al.*, 1995). Single superphosphate is the product of reacting sulphuric acid and concentrate rock phosphate. Because no purification processes are applied whatsoever, all impurities present in rock phosphate, including silica, remain in the final product, which may very well explain the high insoluble residue value found for AP-1.

Loss on ignition levels (Table 3) were variable, with a minimum of 0% (FP-4 and AP-4) and a maximum of 53.5% (AP-3). Loss on ignition was determined at 1,000 C in dry samples and represents losses in water of crystalization, carbon dioxide from carbonates, and volatile mineral elements such as As, Hg, and halogens. Defluorinated rock phosphate (FP-4) and thermomagnesium phosphate (AP-4) are the products of high temperature (1,250 to 1,550 C) industrial processing that eliminates calcium carbonate, volatile mineral elements, as well as water of crystalization, which may explain the lack of detectable losses at 1,000 C observed for these samples. Loss on ignition values for commercial dicalcium phosphates (FP-1, 2, and 3) in this study are in agreement with data published by Lima *et al.* (1995) that reported, for seven

**TABLE 2. X-ray diffraction presence of chemical species in the P sources studied**

| P source | Chemical species present | |
|---|---|---|
| | Major | Minor |
| SP[1] | $CaHPO_4 \cdot 2H_2O$ | |
| FP-1 | $CaHPO_4$ | $CaCO_3$ |
| FP-2 | $CaHPO_4$ | $CaCO_3$<br>$CaSO_4 \cdot 2H_2O$ |
| FP-3 | $CaHPO_4$<br>$Ca(H_2PO_4)_2 \cdot H_2O$ | $CaCO_3$ |
| FP-4 | $Na_2Ca_3Al_2(PO_4)_2(SiO_4)_2$ | $Ca_3(PO_4)_2$ |
| AP-1 | $CaSO_4 \cdot nH_2O^2$ | $Ca(H_2PO_4)_2 \cdot H_2O$<br>$(NH_4)Fe_3P_6O_{20} \cdot (PO_4)_2$ |
| AP-2 | $Ca(H_2PO_4)_2 \cdot H_2O$ | $KFe_3P_6O_{20} \cdot 10H_2O$ |
| AP-3 | $(NH_4)H_2PO_4$ | $CaSO_4 \cdot nH_2O^2$ |
| AP-4 | amorphous | amorphous |

[1] SP = Standard phosphate; FP = feed-grade phosphate; AP = agricultural-grade phosphate.

[2] Several degrees of hydration molecules were detected for the chemical species.

---

[6] PHILLIPS, 7602 EA, Almelo, Holland.

**TABLE 3. Moisture, insoluble residue, loss on ignition, pH, apparent density, and P solubility of feed-grade phosphates (FP) and agricultural-grade phosphates (AP)**

| P source | Moisture | Insoluble residue | Loss on ignition | pH | Apparent density | Water solubility | Citric acid solubility | NAC solubility |
|---|---|---|---|---|---|---|---|---|
| | (%) | | | | (g/L) | (%) | | |
| SP[1] | 1.6 | 0.0 | 24.4 | 6.8 | 580 | 2.0 | 93.5 | 99.8 |
| FP-1 | 3.4 | 0.2 | 12.5 | 7.0 | 828 | 0.9 | 85.3 | 93.2 |
| FP-2 | 5.8 | 0.1 | 16.5 | 7.5 | 888 | 11.2 | 93.9 | na[2] |
| FP-3 | 3.8 | 1.8 | 19.5 | 4.4 | 966 | 25.6 | 86.8 | 97.0 |
| FP-4 | 0.1 | 1.9 | 0 | 8.2 | 1,429 | 0.8 | 68.4 | 65.3 |
| Mean | 3.3 | 1.0 | 16.2 | 6.8 | 1,028 | 9.6 | 83.6 | 85.2 |
| SE | 2.4 | 1.0 | 3.5 | 1.7 | 273 | 11.7 | 10.8 | 17.3 |
| AP-1 | 13.3 | 9.2 | 30.5 | 2.9 | 795 | 35.9 | 76.0 | 99.7 |
| AP-2 | 8.7 | 0.6 | 29.6 | 3.1 | 997 | 87.6 | 92.0 | 96.9 |
| AP-3 | 3.1 | 0.2 | 53.5 | 4.2 | 798 | 95.3 | 98.2 | 99.8 |
| AP-4 | 0.1 | 0 | 0 | 8.7 | 1,504 | 1.0 | 87.4 | 91.4 |
| Mean | 6.3 | 2.5 | 28.4 | 4.7 | 1,023 | 55.0 | 88.4 | 97.0 |
| SE | 5.9 | 4.5 | 21.9 | 2.7 | 334 | 44.6 | 9.4 | 3.9 |

[1] SP = Standard phosphate.

[2] na = Not available.

commercial dicalcium phosphates, loss on ignition values ranging from 13.7 to 23.9%.

Considering the X-ray diffraction data (Table 2) and comparing loss on ignition values presented in Table 3, the predominance of the dihydrate salt of calcium phosphate dibasic in SP 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 FP-1 (12.5%) and FP-2 (16.5%) seem to be primarily related to the presence of relatively high amounts of calcium carbonate (Table 2) in both samples. Loss at 1,000 C for FP-3 (19.5%) is probably the result of losses in water of crystalization from calcium phosphate monobasic monohydrate and carbon dioxide from calcium carbonate (Table 2). Regarding feed-grade dicalcium phosphates, higher values of loss on ignition may indicate a 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. A higher degree of hydration and higher proportions of the monocalcium salt are expected to contribute to increase P availability potential in commercial dicalcium phosphates (Sullivan *et al.*, 1994, Lima *et al.*, 1995). Considering the AP, the predominance of several hydrated forms of calcium sulphate and the monohydrate salt of calcium phosphate monobasic in AP-1 (Table 2) may explain the high loss at 1,000 C (30.5%) observed for that sample of single superphosphate. Loss at 1,000 C for AP-2 (29.6%) is probably the result of losses in water of crystalization from calcium phosphate monobasic monohydrate and other hydrated phosphate salts (Table 2). On the other hand, loss on ignition for AP-3 (53.5%) seems to be primarily related to volatile ammonia loss from the ammonium phosphate molecule (Table 2) at 1,000 C.

Values of pH (Table 3) were variable and averaged 6.8 and 4.7 for FP and AP, respectively, ranging from 2.9 (AP-1) to 8.7 (AP-4). Phosphate products containing higher proportions of monocalcium phosphate are expected to show lower pH values (Lima *et al.*, 1995). Our study has shown that, for FP, the lowest pH value (4.4) was obtained for the U.S.-made di-monocalcium phosphate FP-3 (Table 2), intermediate values (7.0 and 7.5) were assigned to the exclusively dicalcium phosphate (Table 2) containing products (FP-1 and FP-2), and the highest pH (8.2) was recorded for the tricalcium phosphate containing (Table 2) U.S.-made defluorinated rock phosphate (FP-4). Our data are in agreement with Potter (1988), who published pH values of 3.4 for monocalcium phosphate and values ranging from 4.4 to 7.4 for commercial dicalcium phosphate samples, and by Lima *et al.* (1995), who reported pH values ranging from 3.2 to 4.8 for four commercial dicalcium phosphates containing different proportions of monocalcium phosphate and pH = 5.7 to 6.1 for three products containing exclusively dicalcium phosphate. Regarding the AP, our interpretation of the pH data (Table 3) was reconfirmed by the X-ray diffraction assays (Table 2) that have detected levels of monocalcium phosphate inversely proportional to pH values in each product. The lowest pH values (2.9 and 3.1) were recorded for the monocalcium phosphate containing single (AP-1) and triple (AP-2) superphosphates and were slightly higher (4.2)

**TABLE 4. Particle size of feed-grade phosphates (FP) and agricultural-grade phosphates (AP)**

| P source | >1.00 mm | >0.30 mm | <0.30 mm |
|---|---|---|---|
| | (%) | | |
| SP[1] | 0 | 0 | 100.0 |
| FP-1 | 2.6 | 3.2 | 96.8 |
| FP-2 | 5.8 | 6.8 | 93.2 |
| FP-3 | 5.5 | 10.7 | 89.3 |
| FP-4 | 21.5 | 27.5 | 72.5 |
| AP-1 | 12.8 | 14.4 | 85.6 |
| AP-2 | 30.5 | 33.7 | 66.4 |
| AP-3 | 6.6 | 8.4 | 91.6 |
| AP-4 | 0 | 0 | 100.0 |

[1] SP = Standard phosphate.

**TABLE 5. Essential mineral element composition of feed-grade phosphates (FP) and agricultural-grade phosphates (AP): Ca, P, Mg, Na, and K**

| P source | Ca[1] | P | Mg | Na | K |
|---|---|---|---|---|---|
| | (%) | | | | |
| SP[2] | 24.5 | 18.0 | 0.02 | 0.13 | 0.008 |
| FP-1 | 26.2 | 19.2 | 0.45 | 0.21 | 0.03 |
| FP-2 | 25.4 | 18.1 | 0.91 | 0.31 | 0.05 |
| FP-3 | 21.1 | 18.1 | 0.78 | 0.31 | 0.09 |
| FP-4 | 31.9 | 17.8 | 0.35 | 6.03 | 0.09 |
| Mean | 26.2 | 18.3 | 0.62 | 1.72 | 0.07 |
| SE | 4.4 | 0.6 | 0.27 | 2.90 | 0.03 |
| AP-1 | 18.3 | 8.4 | 0.11 | 0.21 | 0.02 |
| AP-2 | 14.7 | 19.6 | 0.70 | 0.21 | 0.04 |
| AP-3 | 2.6 | 22.8 | 0.80 | 0.15 | 0.05 |
| AP-4 | 19.5 | 7.3 | 9.89 | 0.23 | 0.05 |
| Mean | 13.8 | 14.5 | 2.88 | 0.20 | 0.04 |
| SE | 7.7 | 7.8 | 4.68 | 0.03 | 0.01 |

[1] High variability on Ca results for phosphate AP-3 (1.2 and 4.1%).

[2] SP = Standard phosphate.

for the monoammonium phosphate product. A high pH value of 8.7 was recorded for the amorphous magnesium thermophosphate sample (AP-4).

## *Apparent Density, Particle Size, and Phosphorus Solubility*

Particle size patterns (Table 4) were variable, allowing for a classification of the products as “fine” (SP, FP-1, FP-2, and AP-4), “coarse” (FP-3 and AP-3), and “irregular” (FP-4, AP-1, and AP-2).

Apparent density (Table 3) values were higher (1,429 and 1,504 g/L) for thermochemically produced phosphates sources FP-4 and AP-4, respectively. For the remaining FP, density ranged from 828 and 888 g/L for the Brazilian “fine” products FP-1 and FP-2, respectively, to 966 g/L for the U.S.-made “coarse,” or granular, di-mono-calcium phosphate (FP-3). These results are in agreement with Potter (1988) and Lima *et al.* (1995), who reported higher density values for dicalcium phosphate samples classified as coarse according to their particle size pattern, as compared with finer products.

The defluorinated phosphate sample differed in appearance among the FP, showing wide variations in particle size (very coarse), in shape (from fine powder to scale-like particles), and in color (predominantely dark brown with scattered yellowish particles). Among AP, the thermomagnesium product markedly differed in appearance, showing homogeneity in particle size (very fine with tendency of particles to stay together but not to lump), and in color (dark brown). Considering the AP, the monoammonium product (AP-3) was a regular “coarse,” or granular, product (8.4% > 0.30 mm) with density equal to 798 g/L, whereas AP-1 and AP-2 were “lumpy” materials that tended to form objects 14.4 to 33.7% > 0.30 mm, with density ranging from 795 (AP-1) to 997 g/L (AP-2). These differences seem to be primarily related to the type of manufacturing procedures employed in the AP industry. Particle size and density are characteristics related to the miscibility of the product in conventional poultry diets

**TABLE 6. Essential mineral element composition of feed-grade phosphates (FP) and agricultural-grade phosphates (AP): Co, Cu, Fe, Mn, Mo, S, Se, and Zn**

| P Source | Co | Cu | Fe[1] | Mn | Mo | S | Se | Zn |
|---|---|---|---|---|---|---|---|---|
| | (ppm) | | | | | | | |
| SP[2] | 4 | 2 | 210 | 3 | <1 | 579 | <5 | 51 |
| FP-1 | 16 | 97 | 19,654 | 726 | 3 | 2,935 | <5 | 168 |
| FP-2 | 1 | 18 | 1,679 | 174 | 3 | 2,711 | <5 | 546 |
| FP-3 | 3 | 4 | 10,562 | 224 | 9 | 39 | <5 | 83 |
| FP-4 | 4 | 12 | 10,282 | 347 | 7 | 29 | <5 | 134 |
| Mean | 6 | 33 | 10,544 | 368 | 6 | 1,428 | <5 | 233 |
| SE | 6.8 | 43.2 | 7,340 | 250 | 3.0 | 1,613 | . . . | 212 |
| AP-1 | 4 | 10 | 5,848 | 370 | 1 | 122,054 | 25 | 172 |
| AP-2 | 6 | 16 | 8,533 | 284 | 3 | 18,090 | <5 | 66 |
| AP-3 | 6 | 11 | 10,154 | 338 | 1 | 15,825 | <5 | 70 |
| AP-4 | 26 | 55 | 67,147 | 2,010 | 6 | 168 | 35 | 473 |
| Mean | 10 | 23 | 22,920 | 750 | 3 | 39,034 | 16 | 195 |
| SE | 10.4 | 21.5 | 29,538 | 840 | 2.4 | 55,917 | 16 | 192 |

[1] High variability on Fe results for phosphate AP-1 (155 and 11,541 ppm).

[2] SP = Standard phosphate.

**TABLE 7. Potentially harmful mineral element levels of feed-grade phosphates (FP) and agricultural-grade phosphates (AP): Al, F, As, B, Ba, Bi, Cd, Cr, and Hg**

| P source | Al | F | As | B[1] | Ba[2] | Bi | Cd | Cr | Hg |
|---|---|---|---|---|---|---|---|---|---|
| | (%) | | (ppm) | | | | | | |
| SP[3] | 0.01 | 0.02 | 7 | <0.4 | 9 | <0.1 | <1 | 1 | <0.5 |
| FP-1 | 0.11 | 0.03 | 7 | <0.4 | 270 | <0.1 | 1 | 21 | <0.5 |
| FP-2 | 0.15 | 0.19 | 8 | 16 | 21 | <0.1 | 3 | 53 | <0.5 |
| FP-3 | 0.82 | 0.17 | 11 | 39 | 9 | <0.1 | 5 | 72 | <0.5 |
| FP-4 | 0.73 | 0.15 | 7 | 4 | 306 | <0.1 | <1 | 51 | <0.5 |
| Mean | 0.45 | 0.14 | 8 | 20 | 151 | <0.1 | 3 | 49 | <0.5 |
| SE | 0.37 | 0.07 | 2 | 18 | 158 | . . . | 2 | 21 | . . . |
| AP-1 | 0.16 | 1.11 | 9 | 62 | 18,494 | <0.1 | 1 | 11 | <0.5 |
| AP-2 | 0.14 | 0.66 | 10 | 12 | 643 | <0.1 | <1 | 2 | <0.5 |
| AP-3 | 0.15 | 0.38 | 8 | 7 | 333 | <0.1 | <1 | 3 | <0.5 |
| AP-4 | 0.61 | 0.95 | 11 | 9 | 32,206 | <0.1 | 1 | 661 | <0.5 |
| Mean | 0.27 | 0.78 | 10 | 22 | 12,919 | <0.1 | 0.8 | 169 | <0.5 |
| SE | 0.23 | 0.32 | 1.3 | 26 | 15,407 | . . . | 0.3 | 328 | . . . |

[1] High variability for phosphate AP-1 (non-detectable and 124 ppm).

[2] High variability for phosphate FP-1 (29 and 512 ppm), FP-4 (70 and 542 ppm), AP-1 (5,848 and 31,141 ppm), and AP-3 (11 and 655 ppm).

[3] SP = Standard phosphate.

based on ground cereal grain and oilseed meals. Larger particle size in phosphates was shown to improve P utilization, probably by increasing retention time of material in the gizzard of poultry (Griffith and Schexnailder, 1970; Potter, 1988; Burnell *et al.*, 1990), exposing food longer to the more acidic conditions of the upper digestive tract, which may solubilize P more completely (Burnell *et al.*, 1990). Very fine products are also difficult to handle at the feed mill, exposing mill workers to uncomfortable environmental conditions and increasing losses in exhaustion fans.

Phosphorus solubility in water, in 2% citric acid, and in neutral ammonium citrate (Table 3) was variable and averaged, respectively, 9.6, 83.6, and 85.2% for FP and 55.0, 88.4, and 97.0% for AP. Water solubility of P was high for AP-2 (87.6%) and AP-3 (95.3%), which is in agreement with the work of Sheve and Brink (1977), who reported P from monocalcium and monoammonium phosphate sources to be highly soluble in water. Compared with triple superphosphate (AP-2), single superphosphate (AP-1) was found to contain higher levels of Ca, which is present in the product largely as nonwater soluble compounds, and may explain the low water solubility of P in AP-1 (35.9%). Phosphorus solubility of defluorinated phosphate (FP-4) was low in water (0.8%), in 2% citric acid (68.4%), and in neutral ammonium citrate (65.3%). Phosphorus was found to be highly soluble (all values in excess of 85%) in 2% citric acid and in neutral ammonium citrate for all phosphate samples studied, except for the defluorinated sample and for the citric acid solubility for AP-1 (76%). Our results are in general accordance with Potter (1988), Sullivan *et al.* (1992), and Lima *et al.* (1995), who reported P solubility in 2% citric acid greater than 90% for FP samples. The work of Sullivan *et al.* (1992) has shown that P solubility of feed phosphates in HCl or neutral ammonium citrate was positively correlated with the bioavailability of P, and this is of great interest to the phosphate industry and to nutritionists. However, other researchers (Gillis *et al.*, 1948; Day *et al.*, 1973) found little or no agreement between bioavailability

**TABLE 8. Potentially harmful and radioactive mineral element levels of feed-grade phosphates (FP) and agricultural-grade phosphates (AP): Ni, Pb, Sb, Sn, Ti, V, W, Th, and U**

| P source | Ni | Pb | Sb | Sn | Ti | V | W | Th | U |
|---|---|---|---|---|---|---|---|---|---|
| | (ppm) | | | | | | | | |
| SP[1] | 2 | <1 | <1 | 5 | <0.6 | 1 | <5 | 5 | 1 |
| FP-1 | 44 | 21 | <1 | 11 | 519 | 32 | <5 | 9 | 142 |
| FP-2 | 15 | 16 | 1 | 8 | 37 | 81 | <5 | 6 | 114 |
| FP-3 | 16 | 24 | 3 | 12 | 122 | 139 | <5 | 10 | 149 |
| FP-4 | 21 | 26 | 1 | 13 | 398 | 129 | <5 | 13 | 126 |
| Mean | 24 | 22 | 1 | 11 | 269 | 95 | <5 | 10 | 133 |
| SE | 14 | 4 | 1 | 2 | 227 | 49 | . . . | 3 | 16 |
| AP-1 | 22 | 39 | <1 | 12 | 339 | 33 | <5 | 139 | 9 |
| AP-2 | 9 | 18 | <1 | 9 | 146 | 101 | <5 | 46 | 6 |
| AP-3 | 7 | 4 | <1 | 52 | 225 | 122 | <5 | 43 | 8 |
| AP-4 | 258 | 95 | <1 | 27 | 2,010 | 111 | <5 | 237 | 14 |
| Mean | 74 | 39 | <1 | 25 | 680 | 92 | <5 | 116 | 9 |
| SE | 123 | 40 | . . . | 20 | 890 | 40 | . . . | 92 | 3 |

[1] SP = Standard phosphate.

of P of the FP and their solubility in dilute acid solutions and suggested that the *in vitro* tests could be useful only to identify and eliminate insoluble compounds.

## Essential Mineral Composition

Levels of Ca and P were determined at six laboratories; Mg at four laboratories; Na, K, Co, Cu, Fe, Mn, Mo, Se, and Zn at two laboratories; and S at one laboratory (Tables 5 and 6).

**Calcium.** Levels of Ca (Table 5) were variable, ranging from 21.1 (FP-3) to 31.9% (FP-4), with an average of 26.2% in FP. The average Ca content in AP was lower than that in FP, averaging 13.8%, ranging from 2.6 (AP-3) to 19.5% (AP-4). All samples were in compliance with the limits of label guarantees (Table 1), not exceeding the maximum Ca allowed, except for a deviation detected in sample AP-3 (2.6 *vs* 1.0%).

**Phosphorus.** Levels of P (Table 5) were not very variable in FP, ranging from 17.8 (FP-4) to 19.2% (FP-1), with an average of 18.3%. The P content in AP was lower than that in FP, averaging 14.5%, ranging from 7.3 (AP-4) to 22.8% (AP-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.

**Magnesium.** Magnesium levels (Table 5) were variable, averaging 0.62%, and ranging from 0.35 (FP-4) to 0.91% (FP-2) in FP sources. Magnesium in AP was higher than that in FP, averaging 2.88% and ranging from 0.11 (AP-1) to 9.89% (AP-4). High content of Mg in AP-4 was due to large amounts of this element added in the manufacturing procedure used to obtain magnesium thermophosphates. This high level of Mg (9.89%), *per se*, would not be toxic for poultry because the maximum tolerable Mg level (NRC, 1980) for poultry is 0.3% in the complete diet or 15% in a P source used at a dietary level of 2%, as proposed by Lima *et al.* (1995). However, many other factors must be considered in Mg toxicity, such as chemical form in which Mg is present in the product and the metabolic relationship of Mg and other mineral elements. High levels of Mg are known to interfere with the metabolism of several mineral elements and to increase the incidence of wet litter. In addition, to provide an equal amount of P as obtained from FP (18% P), 2.4 times as much AP-4 is needed so that 8.89% Mg in that product would be equivalent to 21.3% Mg, a value that exceeds by 42% the maximum tolerable level of Mg (NRC, 1980) for poultry. It should be emphasized that, according to our X-ray diffraction assays (Table 2), AP-4 is an amorphous product, showing no regular molecular structure. Consequences of feeding animals high levels (or any level) of Mg in a nonregular molecular structure form is unknown, as no references can be found in the literature regarding such a situation. A biological evaluation for all samples studied in this experiment was performed at our laboratory (Fernandes *et al.*, 1999), and signs of toxicity were evident for the AP-4 sample, with great depression in growth, low bone ash, and low bone strength.

**Sodium.** Levels of Na (Table 5) were very variable, ranging from 0.21 (FP-1) to 6.03% (FP-4), with an average of 1.72% in FP sources. The Na content in AP was lower than that in FP, averaging 0.20% and ranging from 0.15 (AP-3) to 0.23% (AP-4). High content of Na in FP-4 is due to the addition of $Na_2CO_3$ in the industrial processing methods used to obtain defluorinated phosphates (Association of Florida Phosphate Chemists, 1991). Levels of Na in FP may be of little or no consequence in poultry feed formulation; nevertheless, Sullivan *et al.* (1992) reported difficulty in managing poultry litter and facilities because of increased water consumption when excess Na diets were fed. The use of defluorinated phosphates as a P supplement for poultry may require adjustments in the level of salt in the diet. The maximum tolerable Na level (NRC, 1980) for poultry is 2% in the complete diet.

**Potassium.** Levels of K (Table 5) were low, averaging 0.07% and ranging from 0.03 (FP-1) to 0.09% (FP-3 and FP-4) in FP sources. The K content in AP averaged 0.04%, ranging from 0.02 (AP-1) to 0.05% (AP-3 and AP-4). These levels may be of little or no consequence in poultry feed formulation because of the abundance of this element in feedstuffs. The maximum tolerable K level (NRC, 1980) for poultry is 3% of the complete diet.

**Cobalt.** Levels of Co (Table 6) were low, ranging from 1 (FP-2) to 16 ppm (FP-1), with an average of 6 ppm in FP sources. The Co content in AP averaged 10 ppm, ranging from 4 (AP-1) to 26 ppm (AP-4). 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.** Levels of Cu (Table 6) were low, ranging from 4 (FP-3) to 97 ppm (FP-1), with an average of 33 ppm in FP sources. The Cu content in AP averaged 23 ppm, ranging from 10 (AP-1) to 55 ppm (AP-4). 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 FP or AP tested would be negligible.

**Iron.** Levels of Fe (Table 6) were variable, ranging from 1,679 (FP-2) to 19,654 ppm (FP-1), with an average of 10,544 ppm in FP sources. The Fe content in AP was higher than that in FP, averaging 22,920 ppm and ranging from 5,848 (AP-1) to 67,147 ppm (AP-4). The highest Fe level was observed for AP-4 (67,147 ppm), and this level may 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%. A biological evaluation for all samples studied in this experiment was performed at our laboratory (Fernandes *et al.,* 1999), and signs of toxicity were evident for the AP-4 sample, with a strong depression in growth, low bone ash, and low bone strength. Our observations are in agreement with Sooncharerying and Edwards Jr.

(1990), who reported low body weights, low bone ash, and signs of rickets in birds fed diets containing 1,000 ppm Fe. Rock phosphates are frequently high in Fe and Al, forming insoluble iron-aluminum-phosphate complexes (Ammerman *et al.* 1977).

***Manganese.*** Levels of Mn (Table 6) were variable, ranging from 174 (FP-2) to 726 ppm (FP-1), with an average of 368 ppm in FP sources. The Mn content in AP was higher than that in FP, averaging 750 ppm, ranging from 284 (AP-2) to 2,010 ppm (AP-4). These levels of Mn 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 neglegible.

***Molybdenum.*** Levels of Mo (Table 6) were low, averaging 6 and 3 ppm for FP and AP sources, respectively. 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%.

***Sulfur.*** Levels of S (Table 6) were variable, ranging from 29 (FP-4) to 2,935 ppm (FP-1), with an average of 1,428 ppm in FP sources. The S content in AP was higher than that in FP, averaging 39,034 ppm and ranging from 168 (AP-4) to 122,054 ppm (AP-1). High content of S in AP-1 is due to the presence of large amounts of calcium sulphate in the product as detected by X-ray diffraction (Table 2). Consequences of these levels for poultry feed formulation are unknown because the maximum tolerable S level has not yet been established (NRC, 1980) for any animal species.

***Selenium.*** Levels of Se (Table 6) were undetectable (<5 ppm) in all FP sources and in two AP sources. The maximum tolerable Se 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%. The poultry requirement for this mineral is 150 ppb (NRC, 1994).

***Zinc.*** Levels of Zn (Table 6) were variable, ranging from 83 (FP-3) to 546 ppm (FP-2), with an average of 233 ppm in FP sources. The Zn content in AP averaged 195 ppm, ranging from 66 (AP-2) to 473 ppm (AP-4). These levels of Zn may be of little or no consequence in poultry feed formulation because 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 phosphate products tested would be neglegible.

## *Potentialy Harmful and Radioactive Minerals*

Levels of Al, F, As, B, Ba, Cd, Cr, Hg, Ni, Pb, Sn, V, and W were determined at two laboratories, and Bi, Sb, Ti, Th, and U were determined at one laboratory (Tables 7 and 8).

***Aluminum.*** Levels of Al (Table 7) were variable, ranging from 0.11 (FP-1) to 0.82% (FP-3), with an average of 0.45% in FP sources. The Al content in AP averaged 0.27%, ranging from 0.14 (AP-2) to 0.61% (AP-4). The highest Al levels were observed for FP-3 and FP-4 (0.82 and 0.73%, respectively) and were produced from sedimentary rock phosphate. These results are in agreement with Lima *et al.* (1995), who published higher values of Al for phosphates produced from rocks of sedimentary origin. Sedimentary phosphate deposits contain higher levels of Al than rock phosphates from igneous origin. These levels may be of little or no consequence in poultry feed formulation because 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%. Higher levels of less soluble forms can be tolerated (NRC, 1980). According to Cakir *et al.* (1978), poultry can tolerate 300 to 400 ppm. 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 FP-4, which is in agreement with previous work from our laboratory (Lima *et al.*, 1995) that reported the presence of low solubility Al salts in all seven commercial FP studied.

***Fluorine.*** Levels of F (Table 7) ranged from 0.03 (FP-1) to 0.19% (FP-2), with an average of 0.14% in FP sources. The F content in AP was higher, averaging 0.78%, ranging from 0.38 (AP-3) to 1.11% (AP-1). All samples of FP were in compliance with the limits of label garantees (Table 1) for each product, not exceeding the maximum F allowed. On the other hand, all samples of AP contained excessive F, as compared with a recommendation of the AAFCO (1973), that feed phosphate supplements should contain no more than 1 part F to 100 parts P. The proportions of F to 100 parts of P determined were 13.2, 3.4, 1.7, and 13.0 for AP-1, AP-2, AP-3, and AP-4, respectively, unacceptable under the AAFCO (1973) recommendation, which was exceeded by 1,210, 240, 70, and 1,200%, respectively, in those products.

***Arsenic.*** Levels of As (Table 7) were very low, averaging 8 and 10 ppm for FP and AP sources, respectively. That level would be of little or no consequence in poultry feed formulation because 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.*** Levels of B (Table 7) were variable, ranging from undetectable (<0.4 ppm) in FP-1 to 39 ppm (FP-3), with an average of 20 ppm in FP sources. The B content in AP was equally low, averaging 22 ppm and ranging from 7 (AP-3) to 62 ppm (AP-1). That level would be of little or no consequence in poultry feed formulation because 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.*** Levels of Ba (Table 7) were variable, ranging from 9 (FP-3) to 306 ppm (FP-4), with an average of 151 ppm in FP sources. The Ba content in AP was markedly higher than that in FP, averaging 12,919 ppm, ranging from 333 ppm (AP-3) to 18,494 (AP-1) and 32,206 ppm (AP-4). The higher Ba levels observed for AP-1 and AP-4 may be toxic to poultry because 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%. There is little information in the literature concerning Ba toxicosis in food-producing animals. According to the NRC (1980), Ba is a highly toxic mineral when absorbed. Despite the information that Ba tends to accumulate in bone tissue, there are no reports describing pathological bone disorders that can be accounted for by the ingestion of high Ba diets (NRC, 1980).

***Bismuth.*** Levels of Bi (Table 7) were undetectable (<0.1 ppm) in all samples evaluated. 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.*** Levels of Cd (Table 7) were very low in all samples, ranging from undetectable (<0.1 ppm) in three experimental phosphates to 5 ppm (FP-3), with averages of 2.4 ppm for FP sources and 0.8 ppm for AP. That level would be of little or no consequence in poultry feed formulation because the maximum tolerable Cd level (NRC, 1980) for poultry is 0.5 ppm in the complete diet or 25 ppm in a P source used at a dietary level of 2%.

***Chromium.*** Levels of Cr (Table 7) were variable, ranging from 21 (FP-1) to 72 ppm (FP-3), with an average of 49 ppm in FP sources. The Cr content in AP was higher than that in FP, averaging 169 ppm and ranging from 2 (AP-2) to 661 ppm (AP-4). That amount would be of little or no consequence in poultry feed formulation because 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.*** Levels of Hg (Table 7) were undetectable (<0.5 ppm) in all samples evaluated. The level would be inconsequential in poultry feed formulation because 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.*** Levels of Ni (Table 8) were low, ranging from 16 (FP-3) to 44 ppm (FP-1), with an average of 24 ppm in FP sources. The Ni content in AP was higher than that in FP, averaging 74 ppm and ranging from 7 (AP-3) to 258 ppm (AP-4). This level would be of little or no consequence in poultry feed formulation because 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.*** Levels of Pb (Table 8) were very low in all samples, with averages of 22 ppm for FP sources and 39 ppm for AP. This amount would be of little or no consequence in poultry feed formulation because 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%.

***Antimony.*** Levels of Sb (Table 8) were very low, found to be undetectable (<1 ppm) in most samples. Dietary levels of Sb may be of no consequence in poultry feed formulation because the maximum tolerable Sb level has not been established (NRC, 1980) for poultry.

***Tin.*** Levels of Sn (Table 8) were very low in all samples, with averages of 11 ppm for FP sources and 25 ppm for AP. This level may be of no consequence in poultry feed formulation because the maximum tolerable Sn level has not been established (NRC, 1980) for poultry.

***Titanium.*** Levels of Ti (Table 8) were variable, ranging from 37 (FP-2) to 519 ppm (FP-1), with an average of 269 ppm in FP sources. The Ti content in AP was markedly higher than that in FP, averaging 680 ppm and ranging from 146 (AP-2) to 2,010 ppm (AP-4). Dietary levels of Ti may be of no consequence in poultry feed formulation because the maximum tolerable Ti level has not been established (NRC, 1980) for poultry.

***Vanadium.*** Levels of V (Table 8) were variable, ranging from 32 (FP-1) to 139 ppm (FP-3), with an average of 95 ppm in FP sources. The V content in AP averaged 92 ppm, ranging from 33 (AP-1) to 122 ppm (AP-3). This amount would be of little or no consequence in poultry feed formulation because 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.*** Levels of W (Table 8) were undetectable (<5 ppm) in all samples and that would be inconsequential in poultry feed formulation because 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%.

***Thorium.*** Levels of Th (Table 8) were variable, ranging from 6 (FP-2) to 13 ppm (FP-4), with an average of 10 ppm in FP sources. The Th content in AP was higher than that in FP, averaging 116 ppm and ranging from 43 (AP-3) to 237 ppm (AP-4). This level may be of no consequence in poultry feed formulation because the maximum tolerable Th level has not been established (NRC, 1980) for poultry.

***Uranium.*** Levels of U (Table 8) were variable, ranging from 114 (FP-2) to 149 ppm (FP-3) with an average of 133 ppm in FP sources. The U content in AP was lower than that in FP, averaging 10 ppm, ranging from 6 ppm (AP-2) to 14 ppm (AP 4). This amount may be of no consequence in poultry feed formulation because the maximum tolerable U level has not been established (NRC, 1980) for poultry.

## *X-Ray Diffraction Analysis*

The diffractograms generated by X-ray diffraction analysis were interpreted, and the results are summarized in Table 2.

The predominant chemical substances present in all commercial FP 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.

Among the FP, monocalcium phosphate was found only in FP-3. The anhydrous salt of dicalcium phosphate was identified as the most predominant substance present in FP-1, FP-2, and FP-3. Calcitic limestone was found in large proportions in all three comercial dicalcium phosphate products and may be the result of excess calcium carbonate added to neutralize phosphoric acid during industrial processing.

These results are in agreement with a previous publication from our laboratory (Lima *et al.*, 1995) that reported X-ray diffraction evaluations for one pure and seven commercial dicalcium phosphates and found that monocalcium phosphate was present in only four commercial products. According to that report, the most predominant chemical species present in all commercial dicalcium phosphates were calcium carbonate and anhydrous dicalcium phosphate.

The U.S.-made defluorinated phosphate was found to contain tricalcium phosphate, predominantely in the form of a sodium calcium aluminum silica phosphate, and this is in agreement with Na analysis of this product that has shown comparatively higher Na values (6.03%) than other FP samples (0.21 to 0.31%). These results are consistent with the pH values obtained, showing the lowest value for FP-3 (pH = 4.4), intermediate values for samples FP-1 (pH = 7.0) and FP-2 (pH = 7.5), and the highest value for FP-4 (pH = 8.2).

Considering the AP, the most predominant chemical substances present in single superphosphate (AP-1) were one anhydrous and two hydrated forms of calcium sulphate, followed by smaller amounts of monocalcium phosphate, plus an ammonium and iron salt of P. The triple superphosphate product (AP-2) was found to contain monocalcium phosphate as the major chemical species, and a potassium and iron salt of P as a minor component. Monoammonium phosphate was found to be the major component in the commercial monoammonium phosphate sample (AP-3). Surprisingly, no crystaline structure was identified by X-ray diffraction in the thermomagnesium phosphate (AP-4). Apparently, the high temperature used in industrial processing of rocks to obtain AP-4 produces an amorphous product with no definite crystaline structure. There is no information in the literature regarding the biological consequences to animals of feeding a product in which P is not present in a regular molecular form.

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 concentrations in feed ingredients are generally more desirable, so that high P and Ca phosphate sources will add flexibility to the 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 phosphates are inconsequential. However, supplementing diets with defluorinated phosphate can make a meaningful contribution to the requirement of the animal for Na (Miles and Henry, 1997). Considering the defluorinated phosphate sample evaluated in this study (FP-4), the relatively high Na level observed (6.03%) may require adjustment on salt addition to the diet under certain practical feed formulation conditions.

A comparison of the maximum tolerable level of several mineral elements for domestic animals, as suggested by the NRC (1980), with values observed in this study indicates no toxicity risks for the use of any of the feed 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. A comparison of the average results for three dicalcium phosphate samples obtained in this study with the levels reported for 19 mineral elements by Sullivan *et al.* (1994) in 13 di-monocalcium phosphates shows comparable values for F (0.14 *vs* 0.17%), Cd (3 *vs* 8 ppm), and V (84 *vs* 96 ppm), indicating that no serious problems should be expected when using any of the dicalcium phosphates studied in animal feeds. Higher average values were obtained for Fe (10,631 *vs* 6,468 ppm) and Pb (21 *vs* 4 ppm), and comparable levels were obtained for Ca, P, Mg, Na, K, Cu, Mn, Se, Zn, Al, As, Cr, Hg, and Ni. The paper published by Sullivan *et al.* (1994) also includes analytical results for 14 defluorinated phosphates. Values obtained in this study for the defluorinated sample were comparable with those reported by Sullivan *et al.* (1994) for F (0.15 *vs* 0.14%), Cd (non detectable), and V (129 *vs* 94 ppm), indicating that no serious problems should be expected when using the defluorinated product studied in animal feeds. Higher average values were obtained for Fe (10,282 *vs* 6,520 ppm) and Pb (26 ppm *vs* nondetectable), lower value was observed for Cr (51 *vs* 110 ppm), and comparable levels were obtained for Ca, P, Mg, Na, K, Cu, Mn, Se, Zn, Al, As, Hg, and Ni. 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, S, Sb, Sn, Ti, Th, and U. As far as the reference standard, calcium phosphate dibasic dihydrate, is concerned, all of the analytical mineral levels obtained in this study were comparable or lower than the values reported for the same reference standard by Sullivan *et al.* (1994).

Previous publication from our laboratory (Lima *et al.*, 1995) reported analytical values for 26 mineral elements in one pure dicalcium phosphate and in seven commercial dicalcium phosphates. A comparison of the average results for three dicalcium phosphate samples obtained in this study with the levels reported by Lima *et al.* (1995) shows comparable values for F (0.14 *vs* 0.13%), Cd (3 *vs* 6 ppm), and V (84 *vs* 134 ppm). Higher average values were obtained for Fe (10,631 *vs* 7,515 ppm) and U (135 *vs* 51 ppm), lower value was observed for Mg (0.17 *vs* 1.13%), and comparable levels were obtained for Ca, P, Co, Cu, Mn, Mo, Se, Zn, Al, As, B, Ba, Bi, Cr, Hg, Ni, Pb, Sb, W, and Th. Mineral element analyses performed in this study that were not included in the paper published by Lima *et al.* (1995) are Na, K, S, Sn, and Ti. As far as the reference standard, calcium phosphate dibasic dihydrate, is concerned, all of the analytical mineral levels obtained in this study were comparable with the values reported for the same reference standard by Lima *et al.* (1995).

Nutritionally essential element concentrations in common macromineral supplements have been reported by the NRC (1994). Levels of Fe, Cu, Mg, Mn, and Zn generally compare very well with values obtained in this study.

In contrast to the safety demonstrated for FP in supplementing animal diets, this was not found to be true for the AP tested. The AP may represent considerable risk of toxicity for use in animal diets, considering their levels of F, Fe, Mg, S, Ba, Ti, and Th. According to a recommendation of the AAFCO (1973), phosphate sources for use in animal feeds should not contain more than 1 part F to 100 parts P, and, according to the NRC (1980), the maximum tolerable levels for poultry in phosphate sources used at a dietary level of 2% are 1,000 ppm for Ba, 50,000 ppm for Fe, and 15% for Mg. The maximum tolerable levels for S, Ti, and Th have not yet been established (NRC, 1980) for any animal species. Single superphosphate (AP-1) was found to contain 1,210% excess F, 1,750% excess Ba, and (compared with the average content in FP) 8,550% excess S (122,054 vs 1,428 ppm). The radioactive Th level found in the AP-1 source was particularly high as compared with the FP, exceeding by 1,300% the average Th content detected for FP (139 *vs* 10 ppm). Triple superphosphate (AP-2) level of F exceeded the tolerance limit by 240%, and S content was in excess of 1,270% as compared with the average S content in FP (18,090 *vs* 1,428 ppm). Monoammonium phosphate F level was found to exceed by 70% the tolerance limit, and an excess of 1,110% S was observed as compared with FP (15,825 *vs* 1,428 ppm).

Concerning the thermomagnesium phosphate (AP-4), a product identified by X-ray diffraction as amorphous with no definite crystalline structure, there is no information in the literature on the consequences of feeding animals such products in which mineral elements are not present in an organized, well-defined molecular fashion. Mineral analysis revealed that AP-4 exceeded the tolerance levels by 1,200% for F, 3,120% for Ba, and 34% for Fe. Magnesium level was particularly high (9.89%), exceeding by 1,500% the average Mg content for FP (0,62%). The amorphous product was also found to contain an excess of 650% Ti compared with an FP average Ti content (2,010 *vs* 269 ppm). The radioactive Th level found in the AP-4 source was particularly high compared with the FP, exceeding by 2,300% the average Th content detected for FP (237 *vs* 10 ppm).

Scarce information can be found in the literature concerning micromineral composition of AP. Ammerman *et al.* (1977) reported that a level of 1,100 ppm V was found in a sample of monoammonium phosphate originating from a localized area.

Analytical values obtained for the four FP sources studied were all in compliance with the manufacturers' levels of guarantee, and no mineral element was found at levels that would represent a toxicological problem considering the use of the products in normal animal diets. X-ray diffraction assays were found to be a useful analytical tool for application, combined with chemical and physical analysis, in the evaluation of phosphates for use in animal feeds. Considering that no purification procedures are applied in industrial production of AP, all impurities present in the precursory rocks remain in the product, and levels of contaminating mineral elements will be variable, according to the origin of the rock phosphate. Analytical evaluations of the four AP sources studied revealed that these products can be toxic to animals.

## ACKNOWLEDGMENTS

The authors are grateful to IMC-Agrico, Mundelein, IL, 60060; Multimix Ltda., Campinas, SP, 13082-380, Brazil; M. Cassab Ltda., São Paulo, SP, 04728-000, Brazil; and Socil S.A., Descalvado, SP, 13690-000, Brazil for laboratory analysis. The assistance of Mitsui S.A., São Paulo, SP, 01311-940, Brazil, and Fosfértil, Uberaba, MG, 38102-970 in obtaining some phosphate source samples is acknowledged. This material is based on work supported in part by the Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP, under project number 1995/2005-0 and 1995/2006-6.

## REFERENCES

Ammerman, C. B., S. M. Miller, K. R. Fick, and S. L. Hansard, 1977. Contaminating elements in mineral supplements and their potential toxicity: A review. J. Anim. Sci. 44:485–508.

Association of American Feed Control Officials, 1973. Page 62 *in*: Official Publication. Association of American Feed Control Officials, Charleston, WV.

Association of Florida Phosphate Chemists, 1991. Page 131 *in*: Methods Used and Adopted. 7th ed. Association of Florida Phosphate Chemists, Bartow, FL.

Association of Official Analytical Chemists, 1984. Methods of Analysis, 14th ed. Association of Official Analytical Chemists, Washington, DC.

Burnell, T. W., G. L. Cromwell, and T. S. Stahly, 1990. Effects of particle size on the biological availability of calcium and P in defluorinated phosphate for chicks. Poultry Sci. 69:1110–1117.

Cakir, A., T. W., Sullivan, and F. B. Mather, 1978. Alleviation of fluorine toxicity in starting turkeys and chicks with aluminum. Poultry Sci. 57:498.

Cardoso, J.L.A., 1991. Produção, processamento e perspectivas do fosfato na alimentação animal. Pages 35–52 *in*: Anais do Mini Simpósio do Colégio Brasileiro de Nutrição Animal. Colégio Brasileiro de Nutrição Animal, Campinas, SP, Brazil.

Day, E. J., J. McNaughton, and B. C. Dilworth, 1973. Chemical versus chick bioassay for P availability of feed grade sources. Poultry Sci. 52:393–395.

Fernandes, J.I.M., F. R. Lima, C. X. Mendonça, Jr., I. Mabe, R. Albuquerque, and P. M. Leal, 1999. Relative bioavailability of phosphorus in feed- and agricultural-grade phosphates for poultry. Poultry Sci. 78:1729–1736.

Gillis, M. B., H. M. Edwards, Jr., and R. J. Young, 1962. Studies on the availability of calcium orthophosphates for chickens and turkeys. J. Nutr. 78:155–162.

Gillis, M. B., L. C. Norris, and F. G. Heuser, 1948. The utilization by the chick of P from different sources. J. Nutr. 35:195–207.

Griffith, M., and R. Schexnailder, 1970. The relation of dietary particle size to P availability in purified diets. Poultry Sci. 49:1271–1274.

Lima, F. R., C. X. Mendonça, Jr., J. C. Alvarez, G. Ratti, S.L.R. Lenharo, H. Kahn, and J.M.F. Garzillo, 1995. Chemical and physical evaluations of commercial dicalcium phosphates as sources of P in animal nutrition. Poultry Sci. 74:1659–1670.

McDowell, L. R., 1992. Minerals in Animal and Human Nutrition. 1st ed. Academic Press, Inc., New York, NY.

Miles, R. D., and P. R. Henry, 1997. Defluorinated phosphates may provide advantages. Feedstuffs June 1:12–15.

National Research Council, 1980. Mineral Tolerance of Domestic Animals. National Academy Press, Washington, DC.

National Research Council, 1994. Nutrient Requirements of Poultry. 9th ed. National Academy Press, Washington, DC.

Potter, L. M., 1988. Bioavailability of P from various phosphates based on body weight and toe ash measurements. Poultry Sci. 67:96–102.

Sheve, R. N., and J. A. Brink, Jr., 1977. P Industries. 7th ed. R. N. Sheve and J. A. Brink, Jr., ed. Chemical Process Industries, Tokyo, Japan.

Sooncharernying, S., and H. M. Edwards, Jr., 1990. Aluminium and iron in poultry rations. In: Georgia Nutrition Conference. University of Georgia, Athens, GA.

Sullivan, T. W., J. H. Douglas, and N. J. Gonzales, 1994. Levels of various elements of concern in feed phosphates of domestic and foreign origin. Poultry Sci. 73:520–528.

Sullivan, T. W., J. H. Douglas, N. J. Gonzales, and P. L. Bond, Jr., 1992. Correlation of biological value of feed phosphates with their solubility in water, dilute hydrogen chloride, dilute citric acid, and neutral ammonium citrate. Poultry Sci. 71:2065–2074.