

## Equilibrium, Thermoanalytical and Spectroscopic Studies to Characterize Phytic Acid Complexes with Mn(II) and Co(II)

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Estudos potenciométricos foram realizados para determinar o grau de ligação do ácido fítico com os íons Co(II) e o Mn(II), na ausência de dióxigênio. As constantes de equilíbrio para as principais espécies formadas são relatadas, e os resultados são representados na forma de diagramas de distribuição mostrando a concentração individual dos complexos como uma função do pH. Os valores das constantes de formação dos complexos foram elevados para as espécies em que o ligante encontra-se mais desprotonado. Os dados potenciométricos indicam que a espécie  $[\text{MH}_4\text{L}]^{6-}$ , encontra-se totalmente formada em pH 7,0 e a partir destes dados os complexos de Mn(II) e Co(II) com o ácido fítico foram sintetizados no estado sólido. Análises de infravermelho, termogravimetria e calorimetria exploratória diferencial foram utilizadas para caracterizar e investigar o comportamento térmico destes compostos. Os resultados conduziram a informações sobre composição, desidratação, estabilidade e decomposição térmica dos complexos.

Potentiometric studies were carried out to determine the binding degree of phytic acid with Co(II) and Mn(II) ions, in the absence of dioxygen. Equilibrium constants for all major complexes formed are reported, and the results are presented in the form of distribution diagrams showing the concentrations of individual complexes as a function of pH. The formation constants of the complexes show higher values for the species in which the ligand was more deprotonated. Potentiometric data indicates that the species  $[\text{MH}_4\text{L}]^{6-}$ , was totally formed at pH 7.0 and the complexes were synthesized from this data. A solid state complex of Mn(II) and Co(II) with phytic acid was synthesized. Thermogravimetry, differential scanning calorimetry, and infrared spectroscopy were used to investigate and characterize the thermal behavior of these compounds. The results led to information on the composition, dehydration, thermal stability and thermal decomposition of the isolated complexes.

**Keywords:** phytic acid, manganese (II) complexes, cobalt (II) complexes, equilibrium studies, thermal behavior

## Introduction

Phytic acid is a phosphorylated derivative, chemically named myo-inositol 1,2,3,4,5,6-hexakis(dihydrogen) phosphate, and known as  $\text{InsP}_6$ . The synthesis of  $\text{InsP}_6$  in vegetable derives from glucose 6-phosphate, that by syntase  $\text{Ins}(3)\text{P}_1$  enzyme action, goes on via phosphorylated derivative mono, di, tri, tetra, penta and hexa phosphate of cyclic alcohol myo-inositol.<sup>1</sup> This acid has important physiological functions in plant life cycles and the most

important is phosphorous storage. At seed maturity, 60% of phosphorous is related to the presence of phytate.<sup>2</sup> Phytic acid also exerts cellular metabolism effects due to its capacity to combine with multivalent cations, which control cellular processes.<sup>3</sup> Several experiments have shown the antioxidant effects of phytic acid. The effect of  $\text{InsP}_6$  on lipid peroxidation of meat products has been investigated and the antioxidant action is concentration and pH dependent.<sup>4,5</sup> The authors of this research suggested that the addition of small amounts of phytic acid may inhibit lipid peroxidation both by accelerating autoxidation of ferrous to ferric ion and by forming catalytically inactive iron chelates.

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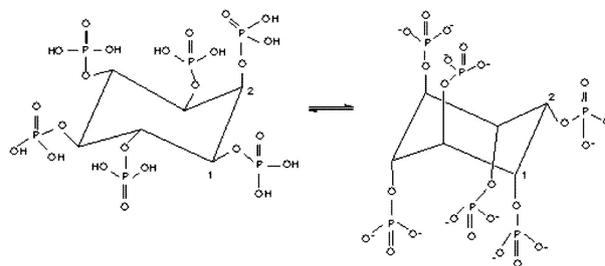
The capability of phytic acid to chelate metallic ions has led several investigators to evaluate the possibility of this acid being able to act in environmental accident control.<sup>6</sup> They studied the ability of phytic acid to immobilize PVP (poly-4-vinylpyridine) resin for subsequent use to adsorb heavy metals. The authors concluded that this compound showed high adsorption capacity for heavy metals at pH 6.5 and 25 °C. Another proposed use for phytic acid is as an inhibitor of copper corrosion in potable water, using Ca, Mg and Na salt derivative of phytic acid. These phytates were used in the simulation of domestic wastewater at pH 6.8, and the study demonstrated that the corrosion was delayed due to hydrolysis and the formation of insoluble copper chelates.<sup>7</sup> In a new study the phytic acid was used to build a modified platinum electrode and single-walled carbon nanotube. This electrode was tested for the selective determination of dopamine in the presence of ascorbic and uric acids. According to the authors the modified electrode demonstrated good enhancements of sensitivity and selectivity.<sup>8</sup>

Nutritionally, phytic acid is important because it interacts with metallic bivalent ions forming stable complexes.<sup>9-11</sup> Phytic acid has been found to inhibit the oxidative damage caused to DNA through the chelating action with metals, inhibiting the generation of highly reactive species, such as free radicals. Phytic acid is expected to effectively inhibit oxidative DNA damage by chelating Cu(II) as well as Fe(II) and Fe(III). Thus, phytic acid may inhibit the generation of highly reactive species from H<sub>2</sub>O<sub>2</sub> by chelating transition-metal ions, resulting in chemoprevention of cancer.<sup>12</sup> This review assesses the potential of InsP<sub>6</sub> being a wide-ranging regulator of many important cellular functions.<sup>13</sup> While another review will give a general overview of the structure and function of phytic acid and phytases, phytic acid as a component of food and animal feed, industrial applications, and medicinal qualities in order to better understand the complete phytic acid system.<sup>14</sup> This article shows new evidence in that the consumption of phytate reveals several positive effects on human health as well. The authors reported that dietary phytate prevents kidney stone formation, protects against diabetes mellitus, caries, atherosclerosis and coronary heart disease as well as against a variety of cancers.<sup>15</sup>

The present study examined the inhibitory effects of pyrophosphate, etidronate, and phytate on bovine pericardium calcification *in vitro*. The data indicated that phytate was the most potent inhibitor of calcification, and the effects of this agent were apparent at levels as low as 0.25 mg L<sup>-1</sup>.<sup>16</sup> Excessive iron can induce oxidative stress subsequently causing degradation of nigral dopaminergic neurons in Parkinson's disease (PD) this research showed

the protective effect of a naturally occurring iron chelator, phytic acid (IP<sub>6</sub>), on 1-methyl-4-phenylpyridinium induced cell death in immortalized rat mesencephalic/dopaminergic cells. The results demonstrated a significant neuroprotective effect of phytate in a cell culture model of PD.<sup>17</sup>

To define the structural aspect of myo-inositol phosphate, <sup>13</sup>C NMR, <sup>31</sup>P NMR techniques and RAMAN spectroscopy were used. Results showed that the action of phytic acid is dependent on pH. Thus, at pH values below 9.0, one phosphate is in the axial form and five are in the equatorial form (1ax/5eq), as shown in Scheme 1. It is believed that the presence of four or more equatorial phosphates in the inositol ring results in the conformation change from 1ax/5eq to 5ax/1eq at high pH.<sup>18-20</sup>



**Scheme 1.** Phytic acid conformation according pH.

Several minerals and trace elements present in food form soluble and non-soluble complexes with phytic acid in the human small intestine. The interaction of phytic acid with trace elements, depending on the amount in the organism, affects the absorption of these minerals.<sup>21</sup> The interaction mechanism is related to the phytic acid structure.<sup>22</sup> Since phytic acid coordinates through phosphate groups, the resulting structure is a chelate compound. *In vitro* studies indicate that phosphate hexakisdi-hydrogen, InsP<sub>6</sub> and its derivatives InsP<sub>5</sub>, InsP<sub>4</sub>, and InsP<sub>3</sub>, are bound to metallic ions at similar pH values to that of the duodenum. Thus, researchers have concluded that the binding capacity of phosphate inositol to metallic ions is dependent on the quantity of deprotonated phosphate groups.<sup>23</sup>

Studies concerning phytic acid in aqueous solution showed that only 10 of 12 hydrogens of its molecule are substituted. In addition, they revealed that phytate ion protonation is dependent on both the ionic medium and ionic strength.<sup>24</sup> In another study, researchers determined phytic acid protonation enthalpies and entropies and concluded that entropic values for each protonation constant are significantly higher than the corresponding enthalpy changes.<sup>25</sup> This ligand has also been used in interesting applications, such as in multilayer films with titanium dioxide for hemoglobin adsorption.<sup>26</sup> It has also been used to prevent metal pipe

corrosion, as the phytic acid and its salts showed very high performance when compared with some traditional and environmentally toxic inhibitors.<sup>27</sup> Studies showed that phytic acid interacts through phosphate groups with different metallic ions, to form heterometallic complexes of Zn(II) and Mn(II).<sup>28</sup> The complexation of Zn(II) and Mn(II) by the phosphate groups of IP<sub>6</sub> is demonstrated by the NMR and X-ray photoelectron spectroscopy (XPS) results. The <sup>13</sup>C NMR data showed a conformation for IP<sub>6</sub> consisting of five equatorial phosphate groups and one axial group showing only one chemical environment for Zn(II) and two for Mn(II). Studies highlight the interaction of phytic acid with multivalent cations, such as Fe(III), Hg(II), Cd(II), Ca(II), Mg(II) and Cu(II).<sup>29-33</sup> Results indicated a high stability constant for Fe(III), corresponding to complexes with highly deprotonated InsP<sub>6</sub> species. Phytic acid also showed very good sequestering ability toward Hg(II), even in the presence of considerable excesses of chloride ions, another ligand that interacts strongly with mercury. Recent work reported on the data of interaction between Sr<sup>2+</sup> and Ba<sup>2+</sup> with phytic acid, which behaved similarly to Mg<sup>2+</sup> and Ca<sup>2+</sup>, but giving even less soluble systems.<sup>34</sup> It also described phytic acid interactions with Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> in a non-interacting medium: these depended strongly on cation charge but only weakly on ionic radius within each series.

A study gathered and analyzed information about the formation and stability of phytate complexes in solution.<sup>35</sup> According to the authors regarding to the thermodynamic data on phytate complexes in solution, some are lacking, while some others exhibit large discrepancies between different authors. The review aimed at identifying the most accurate data on phytate coordination in solution. Crea *et al.*<sup>36</sup> investigated thermodynamic parameter for zinc(II) sequestration at different ionic strengths and temperatures. The sequestering ability of phytate toward zinc(II) was quantified in various conditions, and the dependence of these parameters on temperature, pH, and ionic strength was modeled by simple empirical equations. These equations allow the determination of zinc(II) sequestration by phytate in a very wide range of conditions of environmental and biological interest.

This paper describes the equilibrium association of the metal ions Mn(II) and Co(II) with phytic acid through equilibrium, thermal and spectroscopy studies.

## Experimental

### Materials

Phytic acid in form of dipotassium salt (C<sub>6</sub>H<sub>16</sub>O<sub>24</sub>P<sub>6</sub>K<sub>2</sub>), potassium chloride (supporting electrolyte), manganese(II)

chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O), cobalt(II) chloride hexahydrate, (CoCl<sub>2</sub>·6H<sub>2</sub>O), ethylenediaminetetraacetic acid (EDTA) and potassium acid phthalate were reagent-grade materials, from Sigma and Merck, and were used without further purification. The stock solutions of Mn(II) and Co(II) were standardized by titration according to methods in the literature.<sup>37</sup> A carbonate-free solution of 0.100 mol L<sup>-1</sup> KOH was prepared from Baker Diluit-It ampoules and was standardized by titration with standard potassium phthalate.

### Potentiometric equilibrium measurements

Potentiometric studies of phytic acid in the absence and presence of manganese(II) and cobalt(II) were carried out with a Micronal model B474 research pH meter fitted with blue-glass and Ag/AgCl reference electrodes. The potentiometric apparatus was calibrated with standard HCl and KOH solutions to read  $-\log [H^+]$  directly,<sup>38</sup> and the pK<sub>w</sub> for water at  $\mu = 0.100$  mol L<sup>-1</sup> was 13.70 at 36.0 °C. Samples of about 0.100 mmol of phytic acid were diluted with 60 mL of distilled water (KMnO<sub>4</sub>) in a sealed thermostated vessel at 36.0 ± 0.1 °C. The experimental solution of phytic acid alone, adjusted to 0.100 mol L<sup>-1</sup> ionic medium with KCl, was titrated with 0.100 mol L<sup>-1</sup> standard CO<sub>2</sub>-free KOH until the pH reached about 11, providing 108 points. Solutions containing phytic acid plus Co(II) and phytic acid plus Mn(II) were studied potentiometrically at molar ratios of 2:1, with 0.200 mmol of phytic acid, 0.100 mmol of Co(II), and 0.100 mmol Mn(II). The solutions containing phytic acid and Co(II) or Mn(II) were then titrated with standard KOH solution until the pH was around 10.5, providing 98 points. All systems were studied under anaerobic conditions, purged with purified argon using two 0.100 mol L<sup>-1</sup> KOH solutions. Computations of the triplicates were all carried out with the BEST-7 program, and the species diagrams were obtained with SPE and SPEPLOT programs.<sup>38</sup> All equilibria, as well as hydrolysis of the metal ion, were considered in the calculation of the constants.<sup>39</sup>

### Synthesis of complexes: $K_6[Mn(C_6H_{10}O_{24}P_6)]$ and $K_6[Co(C_6H_{10}O_{24}P_6)]$

Complexes of phytic acid with bivalent manganese and cobalt ions have been synthesized using species distribution curves with pH 7.0. Thus, the synthesis of the complexes was carried out by adding 0.2 mmol of phytic acid in 5 mL of distilled water to 0.1 mmol of the respective metal-ion solutions; the pH was adjusted with 1.0 mol L<sup>-1</sup> potassium hydroxide solution with continuous stirring for 2 h. The

resulting solutions were kept at room temperature and after 14 days a glass-like solid for the manganese complex and a blue solid for the cobalt complex were obtained. These complexes were kept over silica gel in desiccators for 1 week.

### Infrared and thermal analysis

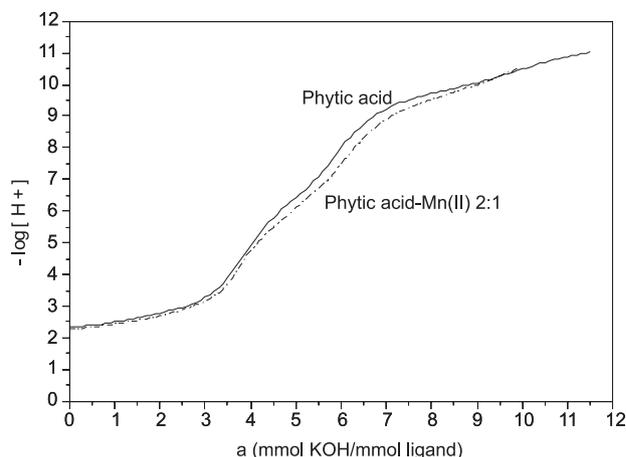
Infrared spectra were recorded on a Spectrum 8400 FT-IR Shimadzu spectrophotometer. Samples were prepared as KBr pellets. For the thermal analysis TG/DTG and DSC curves were obtained with two Shimadzu thermal analysis systems, model TG-60 and DSC-60, and the purge gas was an air flow of 50 mL min<sup>-1</sup>. A heating rate of 20 °C min<sup>-1</sup> was adopted, with samples weighing about 12 mg (TG) and 7 mg (DSC). Alumina and aluminum crucibles, the latter with covers, were used for the TG and DSC, respectively.

## Results and Discussion

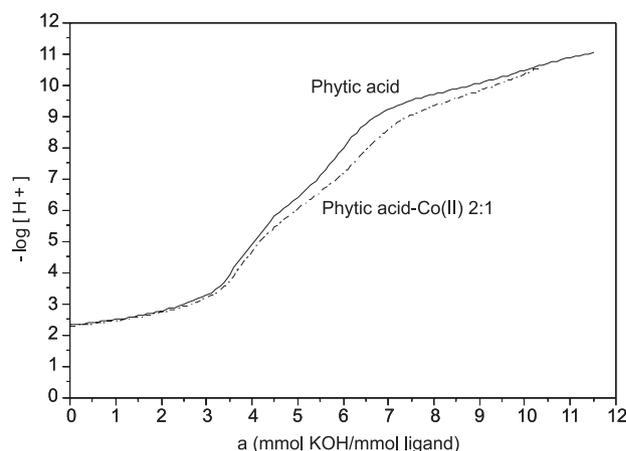
### Equilibrium studies

The potentiometric equilibrium curves are illustrated in Figures 1 and 2 where each curve represents a separate experiment. The shapes of the curves give qualitative information of solution stoichiometry and suggest possible species that could be present. The upper curve in Figure 1 reveals that phytic acid gives rise to three buffer regions; one around pH 2.3-3.8, another in the pH range 6.0-7.5 and the last at pH 9.2-11. The two inflections of the curve at pH 3.8-6.0 and 7.5-9.2 indicate that protonation does not occur in this pH range, and that six protons of the phytic acid had been neutralized. The other four protons of the ligand were neutralized at pH values above 9.2. The neutralization of the ligand occurred in the pH range from 2.3 to 11, and so all of the protonation constants could be calculated from the potentiometric data. The protonation constants of the phytic acid were all considered for the calculation of the systems stability constants with manganese(II) and cobalt(II) ions.<sup>40</sup>

The curve for phytic acid-Mn(II) in a 2:1 molar ratio is below that of phytic acid alone at pH values above 4.5, and this decrease becomes more evident from pH 5.5 up to 9.5 (Figure 1). The curve ends at pH near 10.5. The curve shown in Figure 2 for Co(II) and the ligand, also in a 2:1 molar ratio, is below that of phytic acid at pH values above 3.5, and again the decrease is more evident between pH 5.5 and 10.0. Such observations indicate that the phytic acid interacted with both Mn(II) and Co(II) ions forming different species in solution.



**Figure 1.** Potentiometric pH profiles for solutions containing  $1.00 \times 10^{-3}$  mol L<sup>-1</sup> phytic acid alone;  $1.00 \times 10^{-3}$  mol L<sup>-1</sup> ligand and  $0.50 \times 10^{-3}$  mol L<sup>-1</sup> Mn(II) in the absence of dioxygen; at  $36.0 \pm 0.1$  °C and ionic strength 0.100 mol L<sup>-1</sup> (KCl).



**Figure 2.** Potentiometric pH profiles for solutions containing  $1.00 \times 10^{-3}$  mol L<sup>-1</sup> phytic acid alone;  $1.00 \times 10^{-3}$  mol L<sup>-1</sup> ligand and  $0.50 \times 10^{-3}$  mol L<sup>-1</sup> Co(II) in the absence of dioxygen; at  $36.0 \pm 0.1$  °C and ionic strength 0.100 mol L<sup>-1</sup> (KCl).

### Formation constants of the complexes

Table 1 shows the values of log K of the complexes of phytic acid and the cations Mn(II) and Co(II). It is verified that for the ML specie of phytic acid-Mn(II) complex log K 10.85 is presented and for MHL specie a similar value is revealed, log K is 10.42. For the subsequent di, tri, tetra, penta, hexa and heptaprotonated species, the force of interaction between the metal and the ligand reduced as the ligand became more protonated. For the phytic acid-Co(II) complexes the species MH<sub>2</sub>L, MH<sub>3</sub>L, MH<sub>4</sub>L, MH<sub>5</sub>L, MH<sub>6</sub>L and MH<sub>7</sub>L showed a decrease in the log K values with the phytic acid becoming more protonated.

### Species distribution curves

Figure 3 shows the species distribution curves for

**Table 1.** Logarithms of the stability constants of Mn(II) and Co(II) complexes of phytic acid at  $36.0 \pm 0.1$  °C and ionic strength  $0.100 \text{ mol L}^{-1}$  (KCl), measured under argon

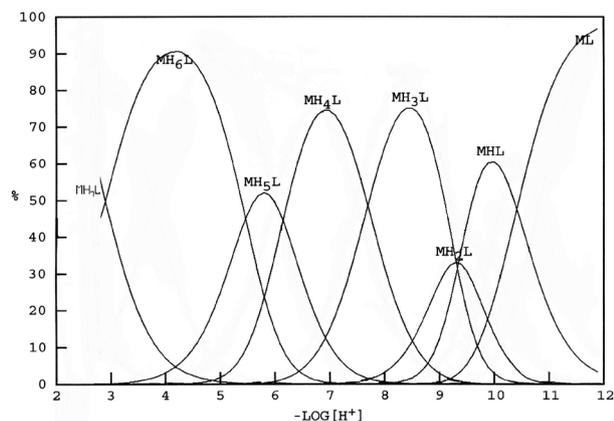
Equilibrium expression	log K Mn(II)	log K Co(II)
$[\text{ML}]/[\text{L}][\text{M}]$	10.85 (3)	9.73 (3)
$[\text{MHL}]/[\text{ML}][\text{H}^+]$	10.42 (3)	9.73 (3)
$[\text{MH}_2\text{L}]/[\text{MHL}][\text{H}^+]$	9.35 (3)	9.21 (3)
$[\text{MH}_3\text{L}]/[\text{MH}_2\text{L}][\text{H}^+]$	9.32 (2)	8.84 (2)
$[\text{MH}_4\text{L}]/[\text{MH}_3\text{L}][\text{H}^+]$	7.70 (3)	7.31 (3)
$[\text{MH}_5\text{L}]/[\text{MH}_4\text{L}][\text{H}^+]$	6.15 (2)	6.22 (2)
$[\text{MH}_6\text{L}]/[\text{MH}_5\text{L}][\text{H}^+]$	5.47 (3)	5.51(2)
$[\text{MH}_7\text{L}]/[\text{MH}_6\text{L}][\text{H}^+]$	2.90 (2)	3.34 (2)

The average deviation standard for the phytic acid-Mn(II) system is  $\sigma\text{-fit} = 0.009938$  and phytic acid-Co(II) system is  $\sigma = 0.007083$ .  $\sigma\text{-fit}$  is the deviation computed from calculated pH values relative to those observed.<sup>38</sup>

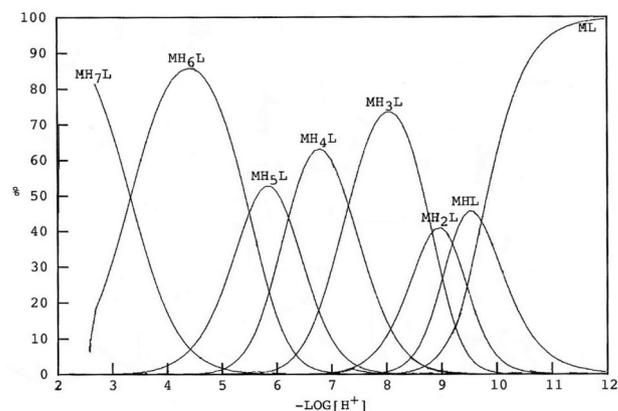
the phytic acid-Mn(II) system. The ML species reached a maximum formation of 96.7% at pH 11.9, which decreased at lower pH values, leading to the formation of monoprotonated species, MHL, which reached a maximum formation of 60.4% at pH 10. The other species:  $\text{MH}_2\text{L}$ ,  $\text{MH}_3\text{L}$ ,  $\text{MH}_4\text{L}$ ,  $\text{MH}_5\text{L}$ ,  $\text{MH}_6\text{L}$  and  $\text{MH}_7\text{L}$  are the di, tri, tetra, penta, hexa and heptaprotated ones, respectively, and they reached their maximum formations in the pH range of 2.6 to 9.3.

Figure 4 shows the species distribution curves for phytic acid-Co(II) system, the ML species is 99.3% formed at pH 11.9. At lower pH values the concentration of ML species decreased and the concentration of MHL species increased, reaching a maximum formation of 45.4% at pH 9.5. The mono, di, tri, tetra, penta, hexa and heptaprotated species reached maximum formations in the pH range of 2.0 to 9.0.

From Figures 3 and 4, the major species which predominated at pH 7.0-7.5 can be seen. There are two



**Figure 3.** Species distribution curves for a solution containing  $1.00 \times 10^{-3} \text{ mol L}^{-1}$  phytic acid (L) and  $0.5 \times 10^{-3} \text{ mol L}^{-1}$  Mn(II) (M) under anaerobic conditions in aqueous solution at  $36.0 \pm 0.1$  °C and ionic strength  $0.100 \text{ mol L}^{-1}$  (KCl).

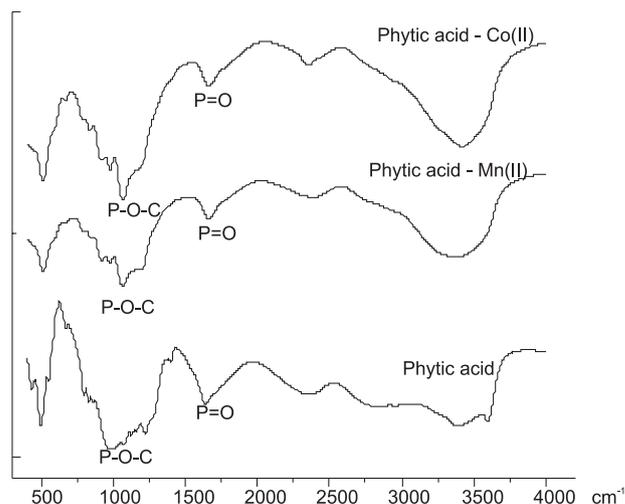


**Figure 4.** Species distribution curves for a solution containing  $1.00 \times 10^{-3} \text{ mol L}^{-1}$  phytic acid (L) and  $0.5 \times 10^{-3} \text{ mol L}^{-1}$  Co(II) (M) under anaerobic conditions in aqueous solution at  $36.0 \pm 0.1$  °C and ionic strength  $0.100 \text{ mol L}^{-1}$  (KCl).

major species:  $\text{MH}_4\text{L}$  and  $\text{MH}_3\text{L}$ , for both metal systems. Thus, the species  $[\text{MH}_4\text{L}]^{6-}$  for the two metallic ion systems was synthesized in the pH range 7.0-7.5.

#### Spectroscopic studies

The infrared spectroscopic data on the dipotassium salt of phytic acid and its compounds with Mn(II) and Co(II) are shown in Figure 5. In the phytic acid dipotassium salt, a medium band at  $1647 \text{ cm}^{-1}$  is attributed to the stretching frequencies of the P=O groups. A strong band at  $1070 \text{ cm}^{-1}$  and a medium one at  $996 \text{ cm}^{-1}$  are attributed to the anti-symmetrical and symmetrical frequencies of the P-O-C groups, respectively.<sup>41</sup> For these complexes the stretching frequencies of the P=O groups, as well as the anti-symmetrical and symmetrical frequencies of P-O-C groups, shift to lower or higher frequencies, suggesting interactions between phytic acid and metal ions.



**Figure 5.** Infrared spectra of the phytic acid, phytic acid Mn(II) and Co(II) complex, specie  $[\text{MH}_4\text{L}]^{6-}$ .

**Table 2.** Calculated and experimental mass loss and residual mass of the thermal decomposition of the phytic acid – Mn(II) complex, specie  $K_6[MnH_4L]$ 

Group or molecules lost	Mass percentage (%)		Temperature range (°C)
	Calculated	Experimental	
One lattice $H_2O$ molecules	2.33	2.18	30 - 172
Five $H_2O$ molecules of constitution	11.65	11.71	173 - 350
Six atoms of carbon	9.31	9.51	351 - 680

**Table 3.** Calculated and experimental mass loss and residual mass of the thermal decomposition of the phytic acid – Co(II) complex, specie  $K_6[CoH_4L]$ 

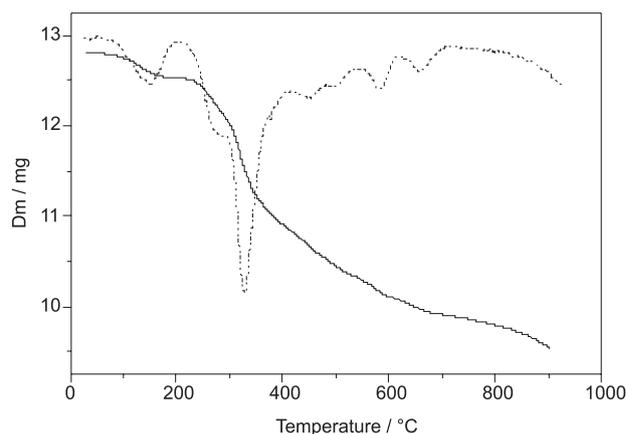
Group or molecules lost	Mass percentage (%)		Temperature range (°C)
	Calculated	Experimental	
2.5 $H_2O$ lattice molecules	4.53	5.60	30 - 180
Five $H_2O$ molecules of constitution	11.32	11.04	181 - 400
Six atoms of carbon	9.06	8.58	401 - 700

### Thermogravimetric measurements

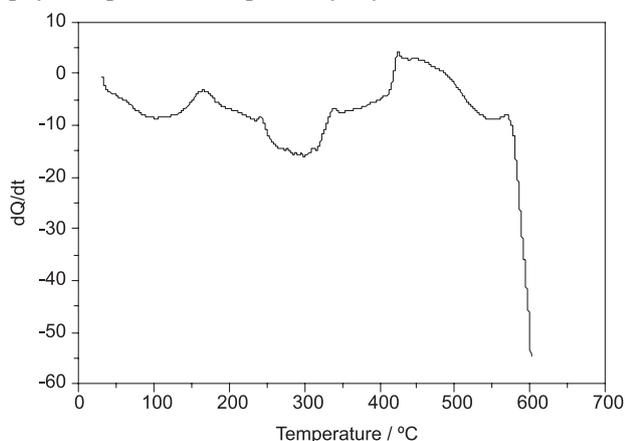
The TG/DTG and DSC curves of the compounds are shown in Figures 6-9. These curves show mass losses in steps and thermal events corresponding to these losses. In both TG curves the first mass loss corresponding to the endothermic peak is attributed to dehydration. These curves also show that mass losses can be observed up to 900 °C with formation of a mixture of pyro and metaphosphate.

For the manganese phytate complex the TG curve in Figure 6 shows mass losses in four steps between 30 and 900 °C. The first step, up to 170 °C, is due to the dehydration with a loss of  $1H_2O$  (calculated 2.33%; TG 2.18%). The anhydrous compound was stable up to 220 °C, and above this temperature the thermal decomposition occurred in three overlapping steps, although the DTG curve shows a large number of consecutive and/or simultaneous steps occurring through a more complex pathway than that observed from the TG curve. The step observed between 220-350 °C, which occurred through a fast process, is attributed to the loss of constitution water corresponding to  $5H_2O$  (calculated 11.65%; TG 11.71%), with formation of double potassium and manganese pyrophosphate and potassium metaphosphate. The mass loss that occurred between 350-680 °C is ascribed to the oxidation of organic matter (calculated 9.31%; TG 9.51%). From 680 °C up to 900 °C a mass loss is still observed, which is attributed to the loss of potassium metaphosphate. The DSC curve for the manganese phytate complex is shown in Figure 7. This curve shows endothermic peaks at 100 and 200 °C attributed to losses of hydration and constitution waters, respectively, and in agreement with the first and second steps of the TG curve. The exotherm between 400 and 550 °C, with a peak at 425 °C, is ascribed to the oxidation of the organic matter, corresponding to the third step of

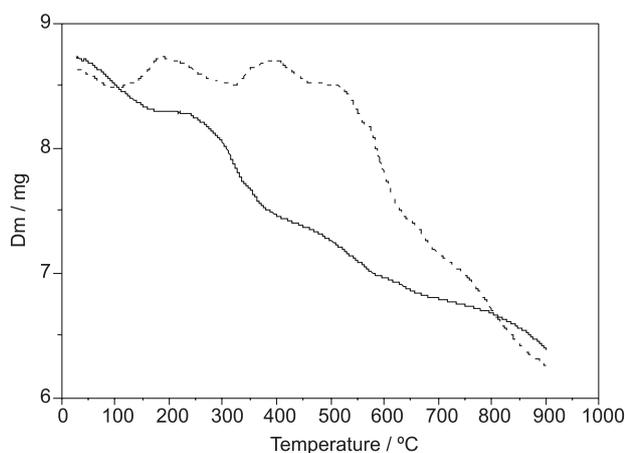
the TG curve. The final residue presented a violet color. For the cobalt phytate complex, the TG curve in Figure 8 also shows mass loss in four steps, between 30 and 900 °C with mass loss still observed. The first step up to 180 °C is attributed to the loss of 2.5  $H_2O$  (calculated 4.53%; TG 5.60%). The anhydrous compound was stable up to 220 °C and between 220-400 °C the mass loss is ascribed to the elimination of the constitution water, corresponding to  $5H_2O$  (calculated 11.32%; TG 11.04%) with formation of double potassium and cobalt pyrophosphate and potassium metaphosphate. The mass loss between 400 and 700 °C is ascribed to the oxidation of the organic matter (calculated 9.06%; TG 8.58%). The mass loss above 700 °C is attributed to the elimination of potassium metaphosphate. The DSC curve of the cobalt complex, Figure 9, shows endothermic peaks at 130 and 325 °C attributed to dehydration and loss of constitution water, respectively. The broad exothermic peak at 500 °C

**Figure 6.** TG and DTG curves for phytic acid-Mn(II) complex, species  $[MH_4L]^{6-}$ , obtained in a dynamic synthetic air atmosphere, 50 mL  $min^{-1}$  flow, room temperature to 900 °C, 20 °C  $min^{-1}$  heating rate,  $\alpha-Al_2O_3$  support.

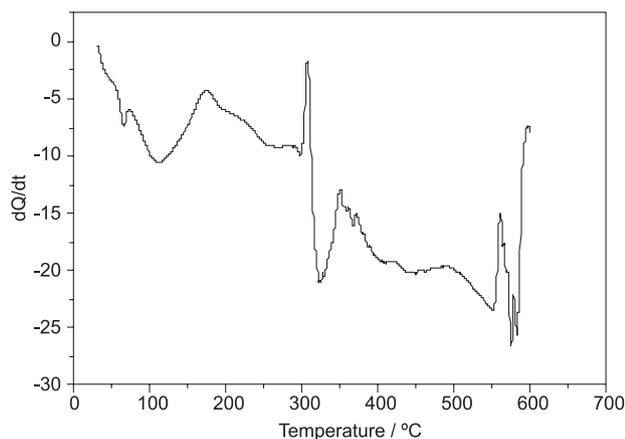
is ascribed to the oxidation of the organic matter and sharp exothermic peaks at 310 and 560 °C are attributed to the physical phenomena, probably crystalline transitions. At



**Figure 7.** DSC curve for phytic acid-Mn(II) complex, obtained in dynamic synthetic air atmosphere with 50 mLmin<sup>-1</sup> flow, room temperature to 600 °C, 20 °C min<sup>-1</sup> heating rate,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.



**Figure 8.** TG and DTG curves for phytic acid-Co(II) complex, species [MH<sub>4</sub>L]<sup>6-</sup>, obtained in dynamic synthetic air atmosphere, 50 mL min<sup>-1</sup> flow, room temperature to 900 °C, 20 °C min<sup>-1</sup> heating rate,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.



**Figure 9.** DSC curve for phytic acid-Co(II) complex, obtained in dynamic synthetic air atmosphere, 50 mL min<sup>-1</sup> flow, room temperature to 600 °C, 20 °C min<sup>-1</sup> heating rate,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.

the end of the thermal analysis, the residue in the crucible had a blue color indicating that the oxidation state is not modified and that the formation of metaphosphate Co(II) is probable.

## Conclusions

The potentiometric study of two systems allows the accurate verification of pH at which the phytic acid coordinates with the metallic ions. Results provide evidence of strong chelating action of phytic acid in relation to the Mn(II) and Co(II) ions. The species distribution curves of these systems were determined and they will be used to choose the appropriate pH values at which synthesis will be performed. The infrared spectroscopic data suggests interactions between phytic acid and bivalent manganese and cobalt. The TG/DTG and DSC curves provided information on the thermal stability and thermal decomposition of the complexes. The TG curves also showed that mass losses were still observed up to 900 °C, with formation of pyro and metaphosphate. The DSC obtained from phytic acid-Co(II) complex, showed a physical phenomena that was not observed from phytic acid-Mn(II) complex. The residue obtained from thermal analysis, indicated that the Co(II) oxidation state was not modified, with probable formation of metaphosphate Co(II).

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