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Spray-Dried Monocalcium Phosphate Monohydrate for Soluble Phosphate Fertilizer

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ABSTRACT: Monocalcium phosphate monohydrate (MCPM) was obtained by water extraction of triple superphosphate. The solubility of MCPM is 783.1 g/L, and is entirely soluble. Saturated MCPM solution dissociates into free phosphoric acid and monetite (CaHPO_4), but evaporation to dryness by spray drying forms MCPM during crystallization. Complete characterization by infrared, X-ray diffraction, and scanning electron microscopies and NMR is reported for MCPM and the derived pyrophosphates.

1. INTRODUCTION

Calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, or monocalcium phosphate monohydrate, (MCPM), is an important calcium phosphate with a Ca/P ratio of 0.5.¹ Literature data claims repeatedly that MCPM has a low solubility, of the order of 1.8 g/100 mL.^{2–4} It has been found that MCPM decomposes in water solution and evolves to monetite (CaHPO_4) and free phosphoric acid. This may explain the low solubility reported by many authors. When recrystallized MCPM solution was partly evaporated from saturated solution to recover solids, monetite was the major product found. Further evaporation of the solution gave MCPM contaminated with excess phosphoric acid. Commercial products sold as MCPM declare 90% purity. This prompted us to investigate the formation of pure MCPM, verify the solubility in water, and report the IR, NMR, and X-ray diffraction spectra. Thermal analysis allowed determining the stability domain and following the dehydration reactions leading to the dihydrogen pyrophosphate and the polyphosphate form.

The aim of this work was to confirm the high solubility of pure monocalcium phosphate monohydrate, to show how the product dissociates in water, how it is possible to obtain the pure product by spray drying, and how it forms pyrophosphates during thermal treatments. The products were characterized, and the properties were listed.

2. EXPERIMENTAL DETAILS

Purified MCPM product was obtained by dissolving industrial TSP (triple superphosphate) from Tunisia in distilled water followed by filtration to remove insoluble fractions. The filtrate was then evaporated to dryness to give solid MCPM. Saturated solutions were made by dissolving 300 g of TSP per liter of

water. For spray drying, a GEA Niro Mobile Minor Spray Dryer was used operating between 160 and 67 °C. The solutions were prepared immediately before spray drying.

Elemental compositions were determined by ICP/OES using a Jobin Yvon spectrometer. Scanning electron microscopy (SEM) observations were made with an ESEM XL30 from Philips. IR spectra were recorded with a Nicolet Impact 410 spectrometer in the DRIFT mode with no sample preparation. Thermal analysis was investigated with a Q600 from TA Instruments. X-ray powder diffraction patterns were recorded with a Bruker D2 Phaser diffractometer. ^{31}P and ^1H NMR were obtained with a Bruker Advance 400 spectrometer. Calcium in solid phosphates was analyzed by precipitation as the oxalate followed by manganometric titration. P_2O_5 was analyzed by a gravimetric method involving molybdate precipitation. These methods are described in more detail in the standards used in industry.⁵

The solubility of MCPM was determined gravimetrically by dissolving recrystallized product in distilled water. After mixing for 10 min, the solid–water saturated suspension was equilibrated 10 min more then filtered on a number 4 glass frit under vacuum until no water dripped anymore. The solution was weighted and dried under air flow in an oven maintained at 60 °C for 48 h. Complete evaporation to dryness allowed determining the amount of water lost and the amount of solids recovered. A 10.0027 g sample of spray dried MCPM was mixed with 10.0753 mL of distilled water. After filtration,

and removal of the nondissolved slurry, the resulting solution was saturated and weighed a total of 11.0268 g. The following results were observed when drying the beaker: 4.8422 g of dry MCPM; 6.1846 g of evaporated water. Partial evaporation of an MCPM solution with a rotating evaporator operating at 185 mbar and 60 °C gave a solid identified as monetite containing small amounts of MCPM by XRD. However, the remaining solution gave MCPM following evaporation to dryness. pH titrations were carried out with a Metrohm titrator model 905 titrator using the tiamo software with standardized sodium hydroxide solutions. To analyze for phosphate, 1 g of MCPM dissolved in distilled water was passed through 50 mL of Dowex 50WX8 strong acid ion-exchange resin in the H⁺ form, and then rinsed with 100 mL of water. The eluate was titrated with standard base to determine the phosphate contents from the difference in moles of base between the first two inflection points observed. The calcium ions were found to be retained on the resin, and the phosphate ions were in the form of phosphoric acid. The chemical analysis of elements is presented in Table 1 for the different methods used.

Table 1. Chemical Analysis of Air Dried MCPM by Different Methods

analysis of Ca[H ₂ PO ₄] ₂ ·H ₂ O	wet industrial	ICP	potentiometric	atomic absorption
%CaO expt.	20.83			
%CaO theor.	22.22			
%P ₂ O ₅ expt.	55.27			
%P ₂ O ₅ theor.	56.33			
%Ca expt.		15.88		15.20
%Ca theor.		15.90		15.90
%PO ₄ expt.		75.45	75.25	
%PO ₄ theor.		75.37	75.37	

3. RESULTS AND DISCUSSION

Solid MCPM was often off white to greenish yellow in color and could be purified by washing with absolute ethanol if excess phosphoric acid was present. Elemental analysis results were close to the theoretical values for calcium dihydrogen phosphate monohydrate, but some samples had a little more water than expected explaining the smaller values in phosphate and calcium. The dissolution experiments showed that 4.8427 g of MCPM were dissolved in 6.1841 mL of water. The statistical result on six trials gave the solubility as 78.31 g/100 mL ± 0.07. The solid product obtained by recrystallization was identified as MCPM by XRD. The dissolution was rapid. Starting TSP gave 60 g of MCPM and 40 g of insoluble solids when dissolved in water. Thus, MCPM has higher solubility in water than TSP, and could be used in hydroponics to prevent adding insoluble compounds to the culture media.

The examination of literature data is misleading concerning MCPM, and many reports describe MCPM as a sparingly soluble calcium salt.² Dorozhshkin gives a value of 18 g/L at 25° similar to the value given by The Handbook of Chemistry and Physics for 30 °C.^{3,4} These values are quite different from the solubility measured experimentally at 293 K and found to be 783.1 g/L. We feel this discrepancy is related to the fact that MCPM dissociates to monetite and phosphoric acid in solution, and the monetite has low solubility (less than 0.05 g/L). The purity of MCPM can be essayed by pH titration as described above or by XRD. When the compound is

contaminated by excess phosphoric acid, it can be purified by washing with ethanol. The ethanol rinsed product shows a pure MCPM XRD pattern, as no water of crystallization is removed by ethanol washing.

The spray-dried products were obtained starting with solutions made by dissolving 300 g of TSP in 1 L of water, which were filtered immediately before drying. An amount of 300 g TSP yielded 184 g of MCPM. Thermogravimetric analysis revealed spray-dried MCPM contained 5.8% by weight of surface sorbed water, which could be removed by heating to 60 °C. Further heating resulted in the formation of anhydrous MCPA above 120 °C, followed by calcium dihydrogen pyrophosphate [CaH₂P₂O₇] formed at 200 °C. Further weight loss from 200 to 600 °C yielded calcium pyrophosphate Ca(PO₃)₂ which melted above 780 °C to give a transparent glassy polymeric metaphosphate compound. Upon being cooled the melted glass became opaque and solid. The thermal weight losses and corresponding thermal events are illustrated in Figure 1 where the phase transitions are also observed, at

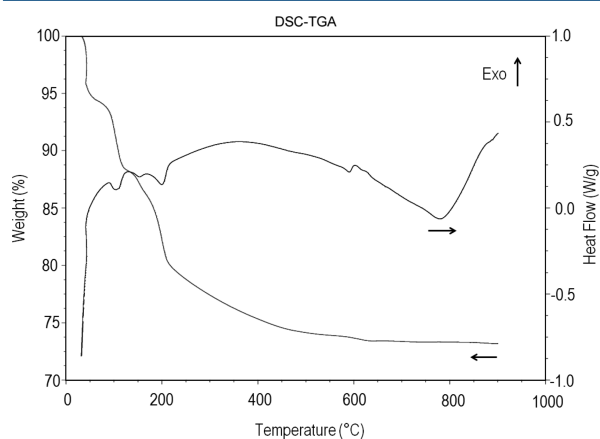


Figure 1. Thermogram of spray-dried MCPM; left scale shows weight loss, right scale shows heat flow.

590° for the calcium pyrophosphate structure transition, and at 780° for melting. Comparable results were reported previously by Elliot.⁶

XRD showed the diffraction pattern known for MCPM, with a strong line at the two theta value of 7.5° and smaller lines at 23° and 24° and corresponding to the Joint Committee for Powder Diffraction Data Standards (JCPDS) reference (File Card No, 00-009-0347).⁷ The XRD patterns were modified as a function of the drying method used. The spray dried solid showed a typical pattern, but otherwise, the patterns presented small differences in the intensities of the first peak at 7.5° compared to the intensities of the peaks at 23° and 24°. The XRD patterns also varied according to crystallinity, and heated samples showed a collapse of the pattern and the appearance of a broad band typical of amorphous solids. The evolution of the XRD patterns is presented in Figure 2. An amorphous phase formed above 200° and remained until acid pyrophosphate crystallized.

Infrared spectra of all solid samples of MCPM were similar regardless of their mode of drying. However, the bands were modified following water loss and formation of acid pyrophosphate or polyphosphate. The spectra are presented in Figure 3 and correspond to the phosphate band assignments given in the literature.^{8,9} The IR spectra show the typical bands

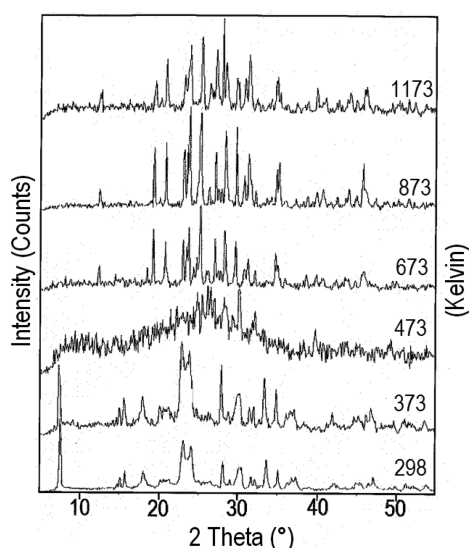


Figure 2. X-ray diffraction (XRD) patterns of spray-dried MCPM heated at different temperatures (temperatures are in Kelvin).

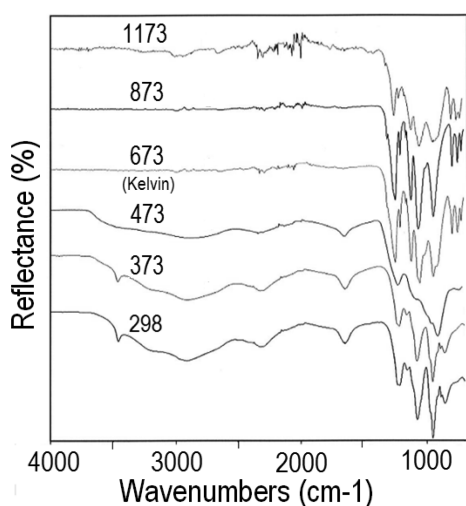


Figure 3. Infrared (IR) spectra of spray-dried MCPM heated at different temperatures (temperatures are in Kelvin).

for orthophosphate groups, with major absorptions at 1000 cm^{-1} corresponding to the PO stretching frequencies and the deformation bands of the tetrahedral PO_4 groups located at lower frequencies below 1000 cm^{-1} . These results are similar to those reported by Desai et al. and others.^{10–12}

SEM observations illustrate the formation of spherical particles following spray drying, with some particle aggregation and visible hollows inside the spheres (see Figure 4).

NMR results showed the presence of two different phosphate environments for the spray-dried product, in accordance with previous studies.¹³ As the phosphate loses water and forms pyrophosphates, the number of protons decreases and the CP NMR spectra show loss in the intensities of the ^{31}P peaks. At high temperatures, several P atoms exist in different environments including an amorphous phase with a broader absorption peak.¹⁴ The ^1H and ^{31}P NMR spectra are illustrated in Figures 5 and 6.

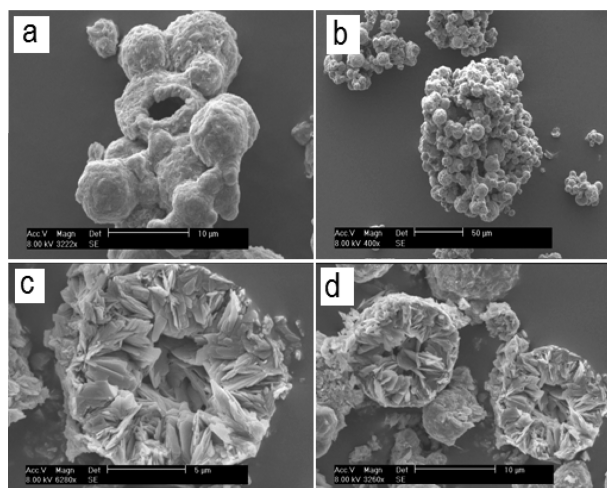


Figure 4. Scanning electron microscopy (SEM) images of spray-dried MCPM. The scales are indicated by the bars. The images c and d represent cut samples.

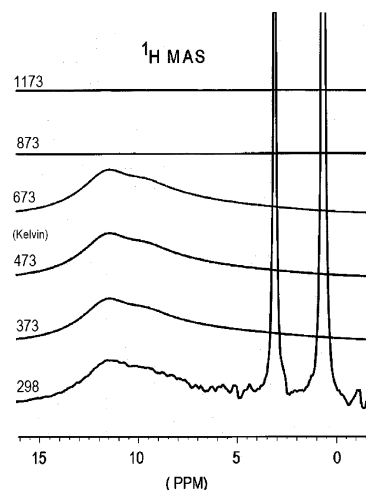


Figure 5. ^1H nuclear magnetic resonance (NMR) spectra of spray-dried MCPM heated at different temperatures (temperatures are in Kelvin).

MCPM is used in biomedical applications such as calcium phosphate cement for orthopedic use. It serves as an acid salt reacting with other components such as tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$), to form other salts close to dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) in compositions that solidify in a hydraulic process in vivo to fill bone voids. The reactivity of such calcium phosphate cements is often difficult to master because the starting MCPM is not available as a standardized reproducible product with constant particle sizes and stoichiometry. The pH profiles and final pH values of these cements vary depending on composition and presence of impurities.¹⁵ To check for excess phosphoric acid contamination on MCPM, two titration methods can confirm the purity. An absolute ethanol rinse can be titrated to reveal any acid present, or a sample of MCPM can be dissolved in water and titrated against base. The stoichiometric product gives a titration curve starting at the first inflection point of phosphoric acid, whereas contaminated product shows a titration curve starting before the first inflection point. The amount of

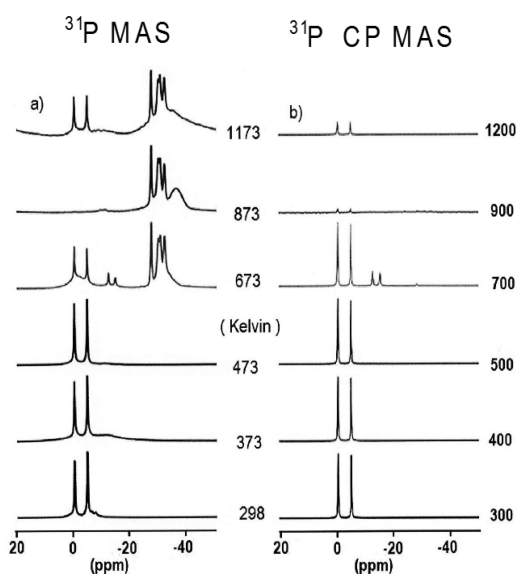


Figure 6. ^{31}P nuclear magnetic resonance (NMR) spectra of spray-dried MCPM heated at different temperatures (temperatures are in Kelvin): (a) ^{31}P MAS; (b) ^{31}P CP MAS.

phosphoric acid can be calculated from the amount of base needed to go from the first to the second inflection points in the titration curve. A typical titration curve is shown in Figure 7.

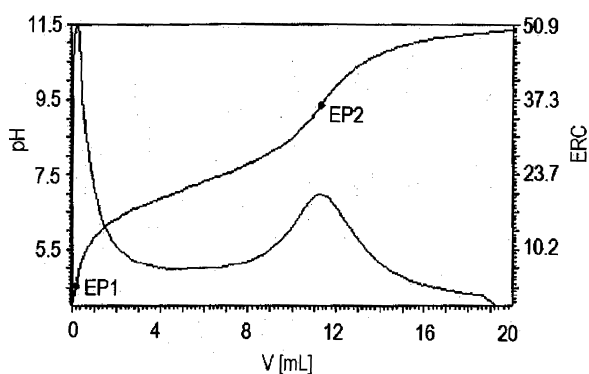


Figure 7. Titration curve showing the two inflection points (EP1 and EP2) used to determine acid concentration. The right scale shows ERC (Equivalence point Recognition Criterion), which is obtained from the derivative of the pH titration curve. V[mL] is the volume of 0.1 M NaOH.

Pyrophosphate bands appear when MCPM is heated, giving IR bands centered at 750 and 1200 cm^{-1} . These bands have been previously described by Destainville et al. and de Waal et al.^{16,17}

The NMR spectra also confirm the loss of protons during pyrophosphate formation, by loss of intensity of the CP spectra for ^{31}P . The MAS ^{31}P spectra reveal the formation of new phases at high temperatures, with several types of P atoms coexisting with different chemical shifts. Such data are in agreement with the results in the literature.^{18–21}

An important observation is that heating solution to evaporate water leads to MCPM dissociation. When the saturated solution is filtered to isolate the solids in the

suspension, monetite is obtained. However, evaporating to dryness converts this monetite to MCPM because the monetite reacts with the previously dissociated phosphoric acid to reform MCPM; thus recrystallization of MCPM should not be performed by partial evaporation. Spray drying seems to be the best option to form a stoichiometric product. The SEM observations show the formation of hollow spheres of approximately 5 μm diameter consisting of crystalline platelets arranged in a hollow core system. Similar images were found by Marc Bohner.¹ This product is stable in air atmosphere and entirely soluble in water. There are few reports on the spray drying of calcium phosphates. Starting with sol-gel derived precipitates, amorphous nanostructured hydroxyapatite particles were obtained by spray drying to retain their original highly reactive surfaces.²² Although no details were given on the temperatures used for spray drying, it was claimed that the spray drying technique could be used for preparing a range of calcium phosphate phases with minimum impurities. Our results show that pure MCPM (over 95% purity) can be obtained by this technique, but further studies would be needed to investigate the morphologies resulting from different flow rates and temperatures.

4. CONCLUSION

MCPM is a water-soluble calcium phosphate resulting in an acidic pH solution. The MCPM solution is unstable and tends to dissociate into monetite and free phosphoric acid in a reversible fashion. Evaporation of an MCPM solution will recover MCPM if evaporated completely to dryness, for example by spray drying. Thermal treatment of MCPM leads to an amorphous product near 200 $^{\circ}\text{C}$ that transforms into a crystalline dihydrogen pyrophosphate $[\text{CaH}_2\text{P}_2\text{O}_7]$ and finally, above 400 $^{\circ}\text{C}$, into a metaphosphate solid of composition $[\text{Ca}(\text{PO}_3)_2]_n$. The pyrophosphates are slightly soluble in water and could be used to control the availability of phosphate in engineered phosphate fertilizers of a more complex formulation.

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Notes

The authors declare no competing financial interest.

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