Application Note AN-RS-054

# Monitoring phosphate reactions in real time with Raman spectroscopy

## Improving product quality in fertilizer production

Phosphorus and nitrogen are essential inorganic nutrients required for plant growth. While nitrogen is primarily sourced from the atmosphere via fixation processes, phosphorus is obtained by mining phosphate rock. Phosphorus supplements are vital to overcome diminishing crop yields as soil reserves deplete over time [1].

Phosphate fertilizer is produced via a wet chemical process in which phosphate rock is reacted with sulfuric acid to yield phosphoric acid and calcium sulfate dihydrate (gypsum) [2]. Traditional analytical methods—titration for acid and phosphate quantification, and gravimetric analysis for gypsum—are time consuming, require hazardous reagents, and provide delayed feedback. These limitations hinder real-time process optimization [3].

Raman spectroscopy provides a non-invasive, reagent-free alternative for real-time analysis. It can simultaneously detect phosphate and sulfate species in solution, enabling tighter process control and improved fertilizer product quality.

## CURRENT METHODES FOR REACTION ANALYSIS

Titration is highly effective for quantifying phosphate and sulfate species to determine reaction completion and final product composition in fertilizers. Gravimetric analysis is used to quantify insoluble byproducts like gypsum (CaSO4·2H2O). Both techniques require sample collection, hazardous reagents, and manual processing – all of which introduce time delays and incur costs with every measurement. This Application Note describes how Raman spectroscopy was used as an alternative method to monitor a simplified phosphate fertilizer production process under laboratory conditions.

## METHOD

Raman spectroscopy is well suited to monitor phosphate species due to its high selectivity and nondestructive nature. Furthermore, it can simultaneously detect sulfate ions, enabling real-time analysis of multi-component reaction systems.

In this study, dicalcium phosphate (CaHPO4, hereafter referred to as DCP) is used as a model compound for phosphate rock. In a 100 mL beaker, 500 mg of DCP was dissolved in 10 mL of 0.5 mol/L hydrochloric acid (HCl) (Equation 1). To simulate industrial reaction conditions and introduce sulfate ions, 0.25 mL of 1.0 mol/L sulfuric acid (H2SO4) was then added. The use of low-concentration HCl ensures safe handling and facilitates clear identification of the sulfate (SO42–) Raman peak.

$$CaHPO_{4(s)} + HCl_{(aq)} \rightarrow Ca^{2+} + H_2PO_4^{-} + Cl^{-}$$

**Equation 1**

The resulting acidic mixture was titrated with 1 mol/L sodium hydroxide (NaOH) in 0.25 mL increments while Raman spectra were acquired with 1064 nm Raman (SpecSuite software; 100% laser power, 30 s integration, 1 average). Continuous monitoring of pH using a Metrohm 913 pH meter with Electrode Plus (6.0262.100) permitted correlation of chemical speciation with spectral changes. Maintaining pH below 4 prevents precipitation of brushite (CaHPO4·2H2O) and other calcium salts from HPO42– and Ca2+ (Equations 2–3).

$$H_2PO_4^{-} \rightleftharpoons HPO_4^{2-} + H^{+}$$

**Equation 2**

$$Ca^{2+} + HPO_4^{2-} + 2H_2O \rightarrow CaHPO_4{\cdot}2H_2O_{(s)}$$

**Equation 3**

## RESULTS

The Raman spectrum of DCP powder (**Figure 1**) exhibited characteristic peaks consistent with previously reported values [**4**]. Upon dissolution in 0.5 mol/L HCl, the solution displayed Raman peaks at 889 and 1189 cm−1 corresponding to fully protonated phosphoric acid (H3PO4) and a peak at 1076 cm−1 from the dihydrogen phosphate ion (H2PO4−). These features closely matched those of a reference H3PO4 solution, confirming the successful dissolution of DCP and the coexistence of multiple phosphate species under strongly acidic conditions.

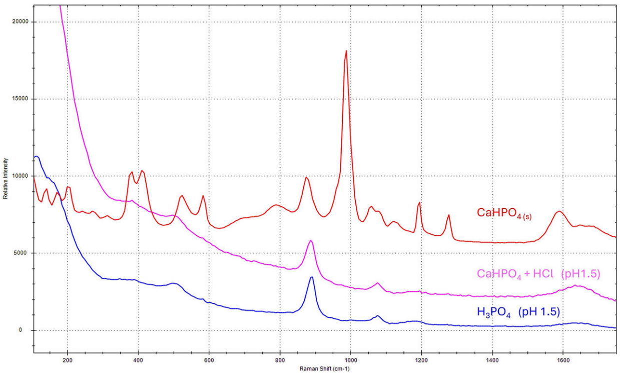

**Figure 1.** Raman spectra of DCP powder (red), DCP dissolved in HCl (pink), and reference phosphoric acid solution (blue).

After adding sulfuric acid, a distinct Raman peak corresponding to SO42− appeared at 983 cm−1. In aqueous solution, sulfuric acid dissociates in two steps (**Equation 4**), SO42− being the predominant species under conditions of low pH and dilution (**Figure 2**).

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \qquad HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

**Equation 4**

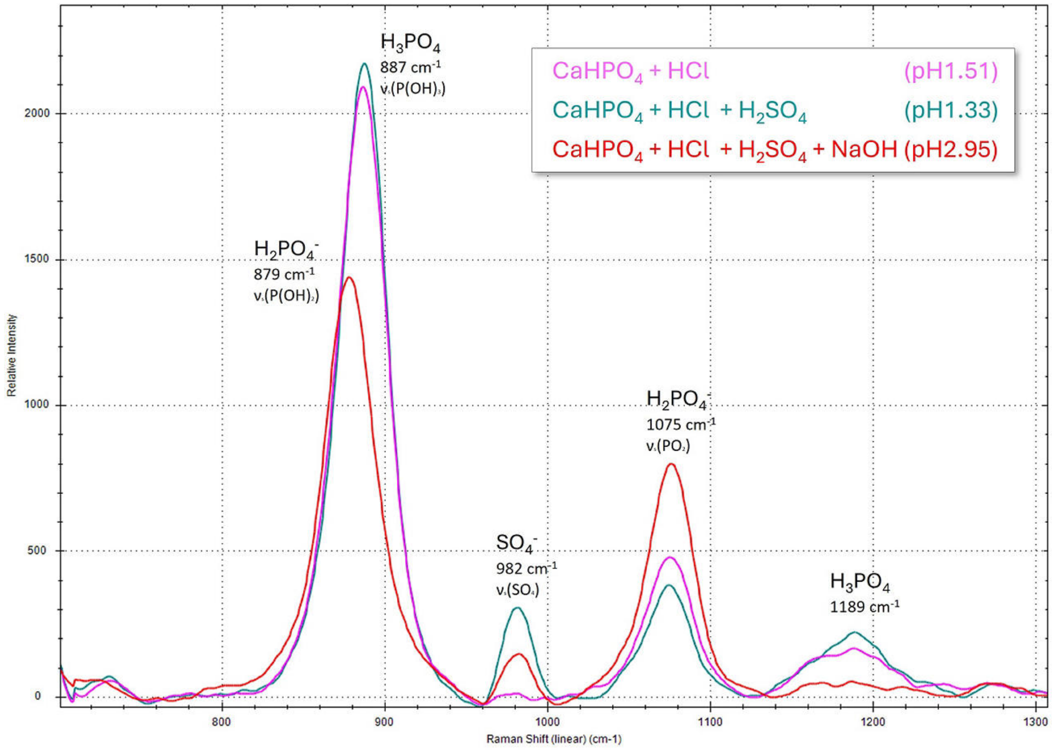

**Figure 2.** Raman spectra of DCP in HCl (pink), after addition of sulfuric acid (green), and after neutralization to pH 2.95 (red).

Phosphate peak intensities changed after H2SO4 addition, indicating protonation of H2PO4– to H3PO4 (Equation 5) and increased ionic strength. These results demonstrate Raman spectroscopy's ability to detect phosphates and sulfates simultaneously, and its sensitivity to protonation state changes, consistent with prior findings.

Stepwise addition of 1.0 mol/L NaOH raised the pH, leading to visible precipitation. At pH 2.95, the 889 cm–1 peak shifted to 879 cm–1, the 1189 cm–1 peak dropped to baseline, and the 1076 cm–1 peak increased—confirming H3PO4 deprotonation (Figure 2). Concurrently, SO42– intensity fell by 52%, well above the expected 16%, suggesting sulfate removal via precipitation (likely as gypsum, Equation 6), a known step in phosphorus fertilizer production to eliminate excess $Ca^{2+}$ and SO42– [4].

$$H_2PO_4^{-} + H^{+} \rightarrow H_3PO_4$$

**Equation 5**

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O_{(s)}$$

**Equation 6**

To verify this, the solid precipitate was isolated, washed, dried, and analyzed with Raman spectroscopy (Figure 3). The dried sample exhibited a dominant Raman peak at 1001 cm−1, slightly downshifted from the 1008 cm−1 peak typical of pure gypsum (Figure 4). This shift may reflect the co-precipitation of gypsum, brushite, and ardealite (Ca2(HPO4)(SO4)·4H2O) [5]. Ardealite exhibits a SO42− peak near 1001 cm−1. These mixed precipitates may be the result of elevated local pH (3.5–4) as NaOH makes contact with the reaction mix.

**Figure 3.** Precipitate recovered from the reaction and mounted on a BAC151B probe holder for Raman analysis.

These results underscore the utility of Raman spectroscopy as a selective tool for monitoring reaction progress and product composition in real time. It has potential applications in both process optimization and quality assurance.

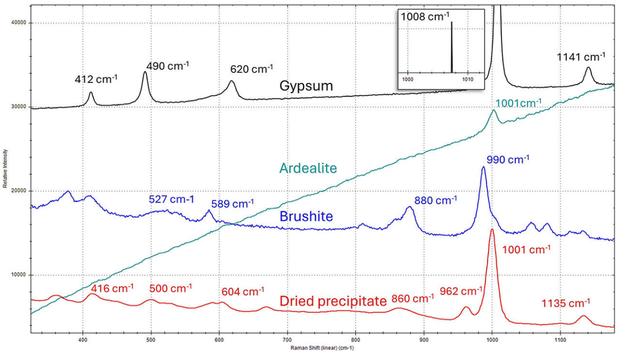

**Figure 4.** Raman spectra of dried precipitate compared with reference spectra of gypsum, brushite, and ardealite. Spectra are vertically offset for clarity.

## CONCLUSION

Raman spectroscopy proved to be an effective tool for monitoring a phosphate fertilizer production process, providing clear insights into phosphate speciation, sulfate concentration, and precipitation dynamics. Raman spectral changes revealed transitions in phosphate protonation states and the formation of calcium-based precipitates. These capabilities support enhanced process control and product quality in phosphate fertilizer manufacturing.

## REFERENCE

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