



Application Note AN-RS-049

Determining phosphate concentration with Raman spectroscopy

A rapid and reagent-free alternative to chromatography and other wet chemical methods

SUMMARY

Phosphates are vital inorganic compounds found extensively in nature and created by industrial processes. They play a crucial role in biological systems and are essential for life. In agriculture, phosphates are a primary component of fertilizers, enhancing soil fertility and increasing crop yields. Industrially, they are used in detergents, food additives, and as corrosion inhibitors.

Raman spectroscopy, combined with PLS (Partial Least

Squares) modeling, rapidly and quantitatively determines total phosphate concentration. Compared to other techniques like thermometric titration, Raman requires minimal sample preparation and accurately determines phosphate concentration over several orders of magnitude. Furthermore, Raman analysis is accomplished in a few minutes, compared to the longer analysis time required for chromatography and other wet chemical methods

CURRENT METHODS FOR PHOSPHATE ANALYSIS

Phosphate content is traditionally analyzed by wet chemical colorimetric methods. In colorimetry, a color-forming reagent reacts with phosphates in solution to form a reaction product with a measurable color change. Ion chromatography is also used for quantitative analysis of phosphate ions, especially at low concentrations. While effective, both methods

require extensive and time-consuming sample preparation. Ion chromatography is quite sensitive but requires several minutes to complete a determination. Additionally, these methods can generate waste that can damage the environment and are expensive to dispose of properly.

PHOSPHATE ANALYSIS WITH RAMAN

Raman spectroscopy can be used for both speciation analysis and quantification using the unique spectral fingerprint of phosphoric acid's protonation states. It is sensitive and nondestructive, making it ideal for the analysis of fast, in-process measurements. This Application Note demonstrates Raman's ability to determine phosphate concentration over a wide range.

Sample preparation: A 68% phosphoric acid production sample was obtained directly from a phosphate manufacturer (Figure 1). Phosphoric acid samples were prepared by serial dilution of the concentrated solution to obtain samples with concentrations ranging from 0.14% to 28%.



Figure 1. Phosphoric acid sample provided by the manufacturer.

MEASUREMENT

A 1 mL aliquot of each dilution was dispensed into glass vials and then placed into the Vial Holder Attachment on a MIRA XTR handheld Raman spectrometer. Samples were measured using 785 nm laser excitation at 50 mW power. Each sample was measured for 6 seconds, and 5 consecutive measurements were averaged to obtain the Raman

spectrum.

Data analysis: Raman data was imported into Vision software to build the PLS model used for speciation and quantification. The intensity of the Raman peak is proportional to the concentration of total phosphate in a sample.

The principal Raman band for phosphate ions, observed between 850 to 950 cm^{-1} [1], changes with the protonation state of the molecule. Deprotonation occurs as a function of concentration and the phosphate peak ranges from 890 to 897 cm^{-1} , with lower sample concentrations shifting to lower wavenumbers and intensities (Figure 2). This band was used for quantitative analysis of total phosphate ion concentration.

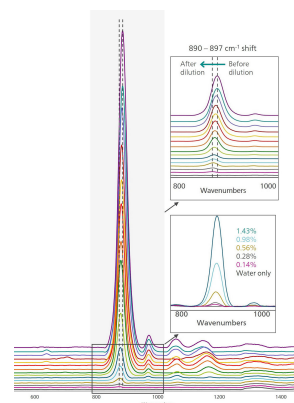


Figure 2. Overlaid, smoothed Raman spectra of phosphoric acid at varying concentrations. The Raman shift of the analyte peak is presented as a range due to its concentration dependence.

The Partial Least Squares (PLS) model developed from the sample set demonstrated a strong R^2 value and low standard error, indicating that Raman spectroscopy can be used for routine or real-time quantification (Figure 3). The lowest phosphate ion concentration examined in this feasibility and suitability study was 0.14%. Further improvements to the limit of detection (LOD) and limit of quantification (LOQ) can be made by modifying data collection parameters (increasing integration time, averaging), or changing the sampling method (e.g., using an immersion probe for higher laser power delivery).

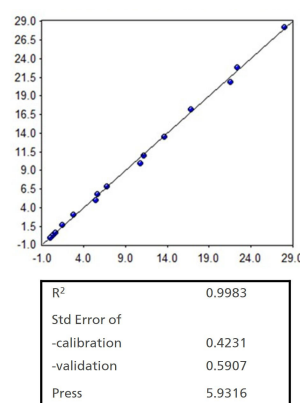


Figure 3. PLS calibration model of 0.0–28% dihydrogen phosphate samples and model statistics.

Five phosphoric acid samples were prepared from the production solution to validate the calibration model. The predicted concentrations versus the actual sample concentrations (from dilution) are shown in

Table 1. The model's high predictive accuracy shows its ability to determine the phosphoric acid concentration in a sample.

Table 1. Validation of the calibration model.

Sample	Conc. (%)	Prediction (%)	% Error
1	5.4	5.45	0.9
2	10.8	10.67	1.2
3	21.6	21.59	0.45
4	6.8	6.96	2.35
5	13.6	13.49	0.8

CONCLUSION

Raman spectroscopy offers a reliable and efficient method for quantitative analysis of total phosphates in solution. Its advantages include minimal sample preparation, nondestructive analysis, and high accuracy over a broad concentration range. This

technique is particularly valuable for industrial applications where rapid and accurate phosphate determination is crucial for quality control and regulatory compliance.

REFERENCE

1. Reimagining pH Measurement: Utilizing Raman Spectroscopy for Enhanced Accuracy in Phosphoric Acid Systems | Analytical Chemistry. <https://pubs.acs.org/doi/10.1021/acs.analchem.9b05708> (accessed 2025-05-22).

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CONFIGURATION



MIRA XTR Basic

MIRA XTR is an alternative for high power 1064 nm systems. Powered by advanced computational processing, MIRA XTR uses a more sensitive 785 nm laser light along with XTR algorithms to eXTRACT the Raman data from the sample fluorescence. MIRA XTR also features Orbital Raster Scanning (ORS) to provide better coverage of the sample increasing the accuracy of the results.

The Basic package is a starter package that contains the basic components required for operating the MIRA XTR. The Basic package includes a Calibration Standard and Intelligent Universal Attachment. Class 3B operation. MIRA XTR supports Metrohm handheld Raman libraries.