Application Note AN-RS-049

Determining phosphate concentration with Raman spectroscopy

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

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

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.

RESULTS

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.

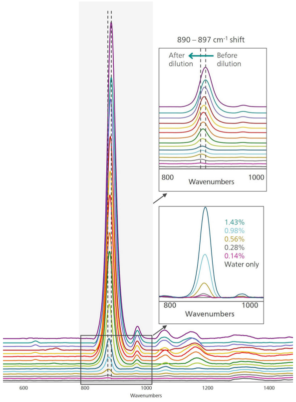
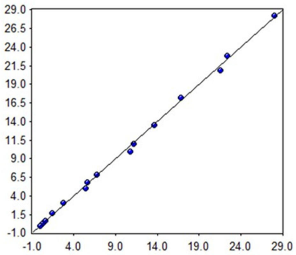


Figure 2. Overlaid, smoothed Raman spectra of phosphoric acid at varying concentrations. The Raman shift of the analyte peak is presented as a range due to its concentration dependence.

RESULTS

The Partial Least Squares (PLS) model developed from the sample set demonstrated a strong R2 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).



R^2	0.9983
Std Error of	
-calibration	0.4231
-validation	0.5907
Press	5.9316

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 是高功率 1064 nm 系的替代品。在先的算理的支持下,MIRA XTR 使用更敏的 785 nm 激光和 XTR 算法从品光中提取拉曼数据。MIRA XTR 配有道光栅描 (ORS) 技,可更好地覆盖品,从而提高果的准性。

Basic 套件是一个入套件,其中包含操作 MIRA XTR 所需的基本件。Basic 套件包括校正准件和智能通用附件。3B 操作。MIRA XTR 支持瑞士万通手持式拉曼功能。