



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

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.

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.

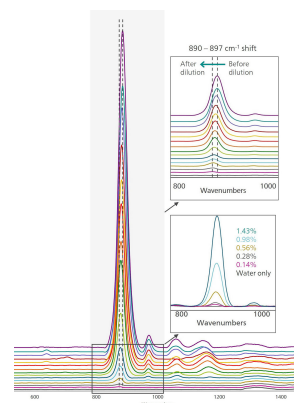


Figure 2. Overlaid, smoothed Raman spectra of phosphoric acid at varying concentrations. The Raman shift of the analyte peak is presented as a range due to its concentration dependence.

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).

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

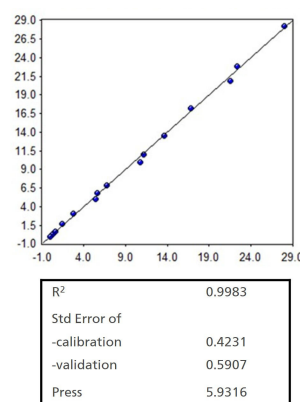


Figure 3. PLS calibration model of 0.0–28% dihydrogen phosphate samples and model statistics.

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 は、高出力 1064 nm システムに代わる装置です。高度な計算処理により、サンプルの蛍光発光からのラマンデータを抽出するのに、MIRA XTR は XTR アルコリズムと共により感度の高い 785 nm のレーザー光を使用します。MIRA XTR はまた、サンプルの包括域を拡張して結果の精度を高めるための軌道ラスタースキャン (Orbital Raster Scanning、ORS) を特徴としています。

Basic package は、MIRA XTR を操作するのに必要とされる基本コンポーネントを含むスターターパッケージです。Basic packageには、校正標準とインテリジェントなユニバーサルアタッチメントが含まれます。クラス 3B 操作。MIRA XTR は、Metrohm のハントヘルトラマンライフラインに対応しています。