Application Note AN-RS-048

Phosphates speciation with Raman spectroscopy

A simpler alternative to wet chemical analysis methods

Phosphates are integral to a wide range of industrial processes, from agriculture and food production to water treatment and pharmaceuticals. The ability to accurately identify and monitor the transformation of different phosphate species—such as phosphoric acid (H3PO4), dihydrogen phosphate (H2PO4−), hydrogen phosphate (HPO42−), and phosphate (PO43−)—is essential for optimizing these processes and ensuring compliance with regulatory standards. Each phosphate ion species exhibits unique chemical properties and behaviors, influencing their reactivity, solubility, response to excitation, and roles in industrial applications.

This Application Note demonstrates the ability of Metrohm's MIRA XTR handheld Raman instrument to speciate phosphate ions.

INTRODUCTION

Raman spectroscopy enables non-contact, real-time monitoring of complex chemical systems. Raman offers users exceptional sampling ease and accuracy, especially in harsh environments like strong acid testing. Its high specificity and sensitivity to small structural changes in a molecule make it an ideal sensitive tool for speciation. This application describes the use of handheld Raman to monitor phosphate species throughout an acid/base titration [1].

The transformation of phosphate species from phosphoric acid through its deprotonated forms to the simple phosphate ion can be monitored by Raman spectroscopy. The protonation state of H_3PO_4 significantly impacts industrial manufacturing processes and applications such as fertilizer application, wastewater treatment, and corrosion control [2].

$$H_3PO_4 \quad H_2PO_4^- + H^+ \; pK_{a1} = 2.14$$
$$H_2PO_4^- \quad HPO_4^{2-} + H^+ \; pK_{a2} = 7.20$$
$$HPO_4^{2-} \quad PO_4^{3-} + H^+ \; pK_{a3} = 12.37$$

Understanding and tracking these changes optimizes the use of phosphates, prevents unwanted side reactions, and maintains process stability.

METHOD

Raman spectroscopy was used to monitor phosphate species directly throughout the acid/base titration of phosphoric acid.

Sample preparation: A experimental solution of 2% phosphoric acid (v/v) was prepared from a 10% phosphoric acid stock solution (Sigma-Aldrich) with deionized water. The titrant was a 5 mol/L NaOH solution prepared by diluting 10 mol/L NaOH with deionized water.

Table 1. Titration and handheld Raman equipment and reagents.

Equipment
Titration 907 Titrando tiamo 2.5 software 801 stirrer 800 dosino (20 mL)
Raman MIRA XTR with XLWD attachment MIRA Cal DS software
Reagents 2% phosphoric acid 5 mol/L NaOH Deionized water

MEASUREMENT

A 907 Titrando automatic titrator (**Figure 1**) was used to titrate the 2% phosphoric acid against standardized 5 mol/L NaOH solutions. At each set point, the pH of the sample was measured, and the Raman spectrum was collected with MIRA XTR (**Figure 1**).

Raman data was collected from the top surface of the solution. Alternatively, Raman data can also be acquired directly from the solution using an immersion attachment or through the titration vessel's glass wall.

Figure 1. The 907 Titrando (top) and MIRA XTR (bottom) from Metrohm were used for simultaneous collection of pH and Raman data.

Table 2. MIRA XTR operational presets used for this study.

Parameter	Setting
Laser power	50 mW
Integration time	30 s
Averages	3
Raster	OFF

RESULTS

The first, second, and third midpoints of phosphoric acid occur at approximately pH 2, pH 7, and pH 12, respectively (**Figure 2a**). These correspond closely to the pK_a values for each deprotonation step of phosphoric acid. Likewise, the first and second equivalence points at approximately pH 4 and pH 9 are followed by complete deprotonation (**Figure 2a**). Raman spectra at the different equivalence points displayed distinct differences (**Figure 2b–d**).

Figure 2b shows the changes that occur between pH 1–5. The peak at 890 cm^{-1}, associated with the symmetric stretch ν_s(P(OH)$_3$) of H_3PO_4, shifts to 876 cm^{-1}, which corresponds to the symmetric stretch ν_s(P(OH)$_2$) of $H_2PO_4^-$. The peak at 1078 cm^{-1}, attributed to the symmetric stretching ν_s(PO$_2$), gradually increases [**1**].

As the titration progresses from pH 5 to 9 (**Figure 2c**), the peaks at 876 and 1078 cm^{-1} (associated with H_2PO_4) gradually decrease, and a new peak appears at 990 cm^{-1}, attributed to the symmetric stretch $v_s(PO_3)$ of HPO_4^{2-}. Finally, as the pH increases from 9 to 13 (**Figure 2d**), the 990 cm^{-1} peak gradually disappears, and a new peak at 937 cm^{-1} emerges, attributed to the symmetric stretching mode $v_1(PO_4)$.

These results demonstrate that Raman spectroscopy can effectively track changes in phosphate protonation states during titration reactions.

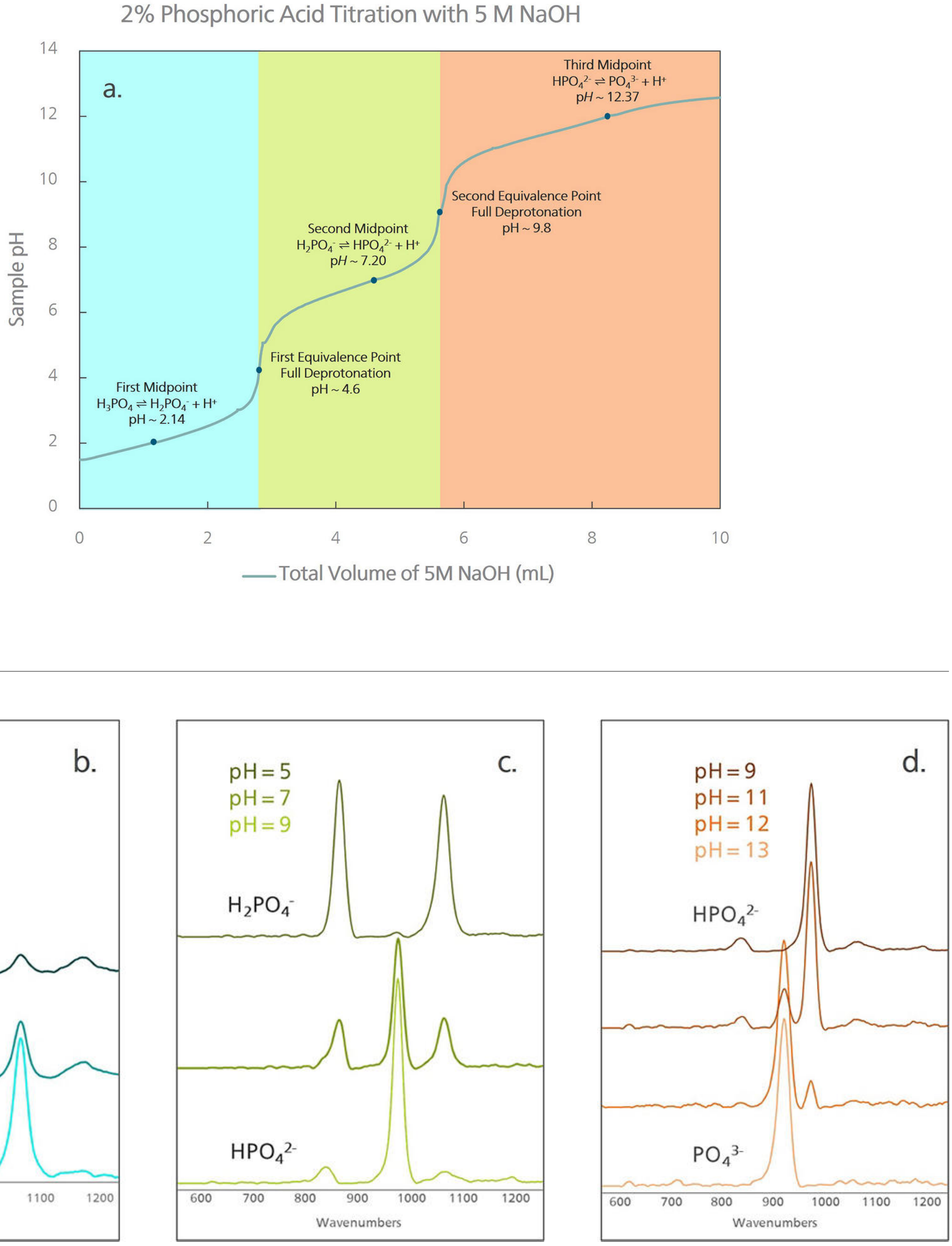

Figure 2. a) Titration curve of the 2% phosphoric acid against 5 mol/L NaOH solution. Raman spectra of the titration at the full range of b) pH 1–5, c) pH 5–9, and d) pH 9–13 showing the spectra of different species at different deprotonation points.

CONCLUSION

Raman spectroscopy provides real-time analysis of the analyte species present in solution, permitting precise identification of phosphate ions as they transition with pH changes. A small handheld Raman system like MIRA XTR achieves fast and direct confirmation of wet chemical techniques like titration with no need for reagents or complex sample preparation. Additionally, it enables continuous monitoring of dynamic systems, providing detailed and accurate insight into the speciation process and reducing the potential for error in measurements.

REFERENCES

1. Lackey, H. E.; Nelson, G. L.; Lines, A. M.; et al. Reimagining PH Measurement: Utilizing Raman Spectroscopy for Enhanced Accuracy in Phosphoric Acid Systems. *Anal. Chem.* **2020**, *92* (8), 5882–5889. DOI:10.1021/acs.analchem.9b05708
2. *Determination of phosphoric acid with sodium hydroxide*. https://www.metrohm.com/en/applications/application-notes/aa-t-001-100/an-t-237.html (accessed 2025-02-03).

CONTACT

メトロームジャパン株式会社
143-0006 東京都大田区平和島6-1-1
null 東京流通センター アネックス9階

metrohm.jp@metrohm.jp

CONFIGURATION

MIRA XTR Advanced

MIRA XTRは、高出力1064 nm システムに代わる装置てす。高度な計算処理により、サンフルの蛍光発光からのラマンテータを抽出するために、MIRA XTR は XTR アルコリスムと共により感度の高い785 nm のレーサー光を使用します。MIRA XTR はまた、サンフ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。

MIRA XTR Advanced package には、校正標準、インテリシェントなユニハーサルアタッチメント、ライトアンクルアタッチメント、ハイアルアタッチメント、MIRA SERS アタッチメントか含まれています。あらゆるタイフの分析に対応する完全なハッケーシてす。クラス3B操作。MIRA XTR は、Metrohm のハントヘルトラマンライフラリに対応しています。