Metrohm NIRSystems

Application Work AW Raman-US-003-122014

Rapid Determination of Purity of Acids using Handheld Raman

Branch

Chemical, Polymer Food, Electroplating; Fertilizer.

Keywords

Raman; Vial measurement; Point and Shoot; semi-quantitative; Qualitative; Organic acids, Mineral acids; Assay; branch 1; branch 7; branch 11; branch 6.

Summary

Raman spectroscopy, like infrared (IR), probes the fundamental vibrational motions of a molecule. In Raman spectroscopy, the shift in wavelength of scattered radiation provides chemical and structural information. Each peak in Raman spectrum is associated with a unique part of the molecule and can be used for identification and confirmation. These unique peaks are most relevant in the Raman shift range of 400 to 1800 cm^{-1}, giving rise to the nickname of the "finger print" region. This region of the spectrum is compared to library spectra for the proper identification and confirmation of chemical identity. The clarity of the Raman fingerprint makes it ideal for library matching. Extensive spectral detail dramatically increases the accuracy, reliability, and ease of identification and confirmation measurements.

The key advantage of Raman spectroscopy is that it requires little to no sample preparation. Samples can be analyzed through glass or clear packaging. Furthermore, water does not interfere with Raman spectra, giving Raman methods a distinct advantage over IR and near-IR. Beyond offering highest selectively for organic compounds, Raman is also suitable for polyatomic inorganic salts. In short Raman spectroscopy combines the selectivity of IR and simplicity of NIR making it a powerful tool for qualitative analysis.

This application work describes the rapid method to determine purity of polyatomic inorganic acids and organic acids by means of spectral correlation value using handheld Raman instrument.

Introduction

Phosphoric acid is one of the most widely known and used acid. This acid is also known as orthophosphoric acid and is a mineral acid. In industrial settings, phosphoric acid can be produced via two separate routes, known as the wet process and the thermal process. The vast majority of the worldwide production of phosphoric acid is used in the manufacture of fertilizers. The second most common application of phosphoric acid is in the food industry. Food grade phosphoric acid is used widely in beverages and in animal feeds. In addition to the two most common uses referred to above, phosphoric acid is used in a variety of niche applications, including rust removal and phosphatizing bath.

Sulfuric acid is one of the most important compounds made by the chemical industry. It is used to make, literally, hundreds of compounds needed by almost every industry. By far the largest amount of sulfuric acid is used to make phosphoric acid, used, in turn, to make the phosphate fertilizers. The process of refining crude oil requires the use of an acid as a catalyst and Sulfuric Acid is often used for this purpose. It is used in a SAAU or Sulfuric Acid Alkylation Unit. Nitric acid is a highly caustic and corrosive mineral acid. Used widely in fertilizer industry. Nitric acid's corrosive properties are explored in several ways, including as pickling stainless steel.

Acetic acid is one of the simplest carboxylic acids. It is an important chemical reagent and industrial chemical, used in the production of polyethylene terephthalate mainly used in soft drink bottles; cellulose acetate, mainly for photographic film; and polyvinyl acetate for wood glue, as well as synthetic fibers and fabrics. In households, diluted acetic acid is often used in descaling agents. In the food industry, acetic acid is used under the food additive code E260 as an acidity regulator and as a condiment.

Formic acid is an efficient and environmentally friendly organic acid for many applications. In leather processing, the acid is used in tanning and dye fixing and serves also as a neutralizing agent and pH adjuster in many steps of textile processing. In oil field applications it helps to dissolve calcium carbonate. Potassium formate, a salt of formic acid, also helps with well drilling and completion in the oil field industry. Furthermore, potassium formate is environment friendly and at the same time a highly efficient deicing agent for roads and airport runways. As it is readily biodegradable, it protects the environment. The pharmaceutical industry uses formic acid in the production of various active pharmaceutical ingredients.

The assay of mineral and organic acids are determined usually by time consuming manual or potentiometric titration. Samples are transferred to the analytical lab after sampling from the receiving area or from production location to determine the assay value. Some cases an online titration instrument is also used. Spectroscopic methods are direct with results obtained in real-time and thus can be used minimal lag time. However, because these organic or mineral acids has water, typical spectroscopic absorption techniques, UV, IR or NIR are of little to no utility. Raman Spectroscopy is best suitable for measuring organic acids and mineral acids in aqueous matrices. Raman measurement is faster and takes less than a second and offers an alternative method for quick quality control check these acids as the raw materials, manufacturing process monitoring.

Building and using a library for a specific acid of different concentration, handheld Raman could be deployed as a quick screening to tool determine the purity of acid in less than a second. The analytical capability and the speed of analysis is unparalleled to any wet chemistry and spectroscopy techniques.

Raman Instrumentation

Lab-based spectroscopy techniques, whether it is FT-IR or Raman, require the same traditional workflow of sampling, labeling and transportation of the sample to the analytical lab. Traditional lab based Raman instruments are very expensive and are primarily used for research and development by spectroscopists. Handheld and portable Raman system bring a new analytical technique into main stream applications.

The majority of the available portable and handheld systems use closely related sampling designs, which make the identification and qualification of samples difficult in most field applications. The Metrohm Instant Raman Analyzer (Mira) has overcome this limitation through the use of Orbital Raster Scan (ORS) sampling with its handheld systems.

Implementing the handheld Raman, Mira, can significantly streamline quality control measurements because it requires no sample pre-treatment, no direct contact with the sample, and has the unique capability of being able to test a sample in few seconds directly through a transparent packing material like glass or plastic bags. This reduces or eliminates the errors due to the sampling and sample preparation. Interpreting a Raman spectrum is simple for the operator through the on-board automatic matching software. MIRA uses the correlation algorithm and comes with built-in system intelligence and search techniques that allows the user to focus on results. Operators with no formal scientific education can operate the analyzer and understand the results.

Mira M-1 Basic package with the vial holder is the only handheld Raman instrument in the market with laser class I safety feature. Closing the cover prevents laser radiation from emerging. The covering also contains a safety feature which stops the measurement and turns off the laser if it is opened. Ideal for customers who want to implement handheld Raman, but has concern about laser safety. With class I laser safety and with additional safety build in in Mira, measurements can be done without laser safety goggles.

Mira M-1 basic package can be upgraded with two point-and-shoot adapters that enable the measurement of these acids in clear or colored glass containers. These sampling accessories maintain the precise optical alignment necessary to ensure high-quality spectral acquisition, and accommodate a number of sample types for material identification and verification applications.

Mira spectrometers give the option of capturing spectra of customers own samples and using them to generate a complete library. This open library structure affords the user the maximum flexibility and allows the customer to build and use their own libraries. The amount of library storage space is large—over 400,000 samples can be accommodated. The fast scan capability of Mira ensures that the library development is accomplished in shortest possible time without the need for additional software. It is recommended to do reference spectrum collection with the same sample container in which the samples will be tested on routine basis, with an appropriate sampling accessory. This will ensure the sample container influences are also included into the library. Once the instrument is loaded with a library of the materials to be identified, MIRA can perform a confident identification of the samples in the library within in seconds, making it the ideal choice for incoming raw materials confirmation, or the in process samples verification. Instrument operation steps is simple, requiring no formal chemistry education to use the instrument on a routine basis. The MIRA analyzer brings the measurement to the sample, eliminating the need to transfer samples to an analytical laboratory for measurement.

Sample

- 85 % phosphoric acid

Experiment

85 % pure phosphoric acid is diluted gravimetrically, and lower concentration of 76.58 %, 63.78 %, 59.52 %, 51.68 %, 38.21 %, 20.07 % and 12 % are prepared. Samples were transferred to the glass vial and inserted into the vial holder. Default measurement time of 0.5 seconds is used for the measurement. Reference spectra of each of the diluted phosphoric acid is measured and the specific library is developed.

Instrument & Parameters

MIRA M-1 Advanced Package	2.923.0020
Sampling	Vial Holder
Collection time	0.5 sec; Constant

Results & Discussion

The overlay of the mineral acid and acetic acid spectra are shown in the appendix, Figure 2.

Overlay of phosphoric acid from 85 % to 12% purity is shown in Figure 3. The peak near 900 cm^{-1} is due to the phosphate component from the phosphoric acid. The peak height decreases proportionately with respect to phosphoric acid concentration. Table 1 shows the plot of correlation values for all eight solutions against each other. All eight phosphoric acid samples of varying concentrations samples passes with correlation value greater than 0.999, when their respective spectrum is compared against their library spectra. Each samples fails with correlation value less than 0.96 when their respective spectrum is compared against other sample's spectra in the library. In this case each sample is identified as phosphoric acid of specific % purity. For example if the sample is 12 % pure, then it is identified as 12 % Phosphoric acid with spectral correlation value greater than 0.999. If the acid is only 10 % pure, still it is identified as 12 % phosphoric acid, with correlation value lower than 0.99. As more number of samples of covering the expected concentration range are added into the library, the prediction accuracy improves. This clearly proves that the Mira could be used for rapid determination of phosphoric acid purity apart from identification.

Similarly to the phosphoric acid example, specific libraries could be developed for the other acids, covering the expected concentration range. With the library covering the expected concentration range from low to high, samples could be analyzed for the purity in less than a second. The portability of Mira could be deployed to production area or receiving area and can be used as a powerful **identification** and **confirmation tool** for monitoring the quality of individual acids. This method is not suitable for mixture of acids at the moment, as Mira doesn't have the quantitative analysis capability. This is a quick qualitative way of checking the purity of Raman active acids with constant integration time.

Conclusion

MIRA measurements are quick and confirmative compared to the traditional wet chemical techniques. MIRA could be used as Identification tool to check the quality of the incoming polyatomic mineral acids and organic acids. Instead of bringing the samples to the analytical lab, MIRA could be deployed to the production & sampling locations and can be used for quick assay determination of various mineral and organic acids.

Date

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APPENDIX

Figure 1: Mira M-1 Basic Package: Vial holder – Operator friendly and Laser Safe – Insert the sample vial and start measuring. The integrated safety system will start the measurement only when the vial holder is closed.

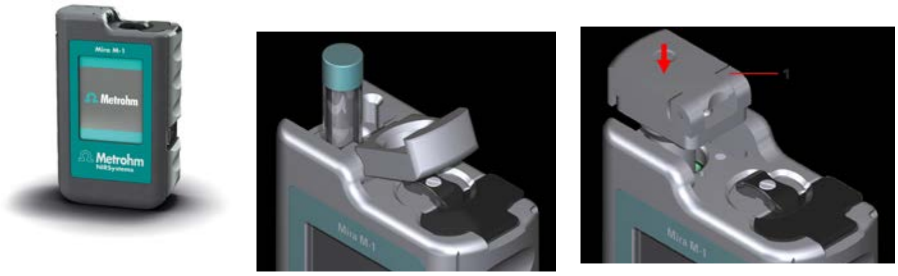

Figure 2: Overlay of common mineral acid and acetic acid

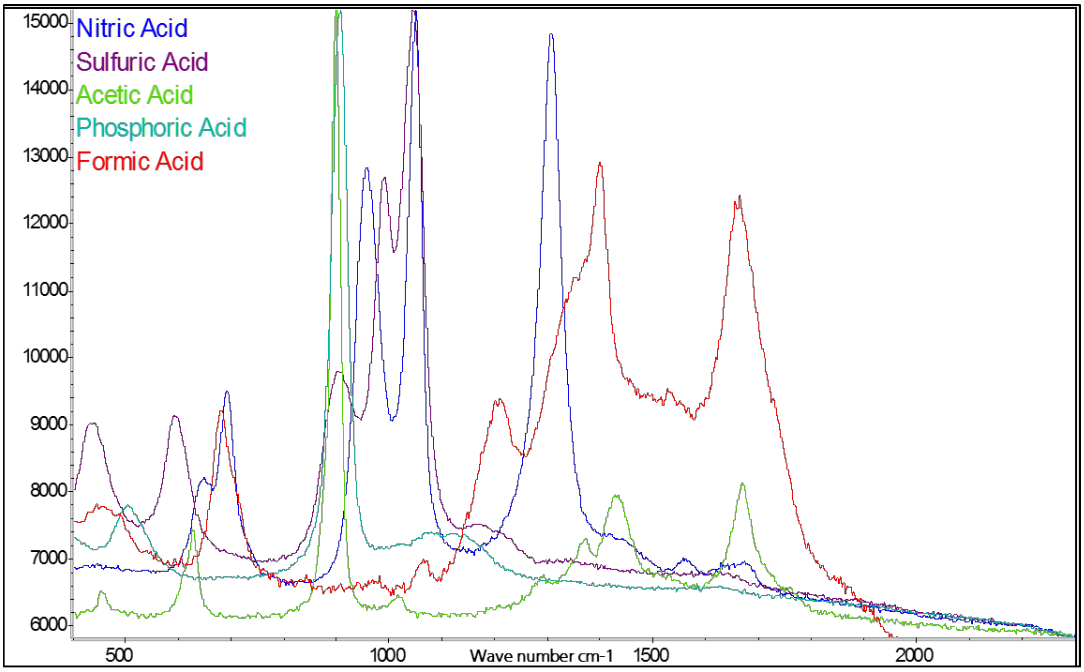

Figure 3: Overlay of phosphoric acid of varying concentration from 12 % to 85 %

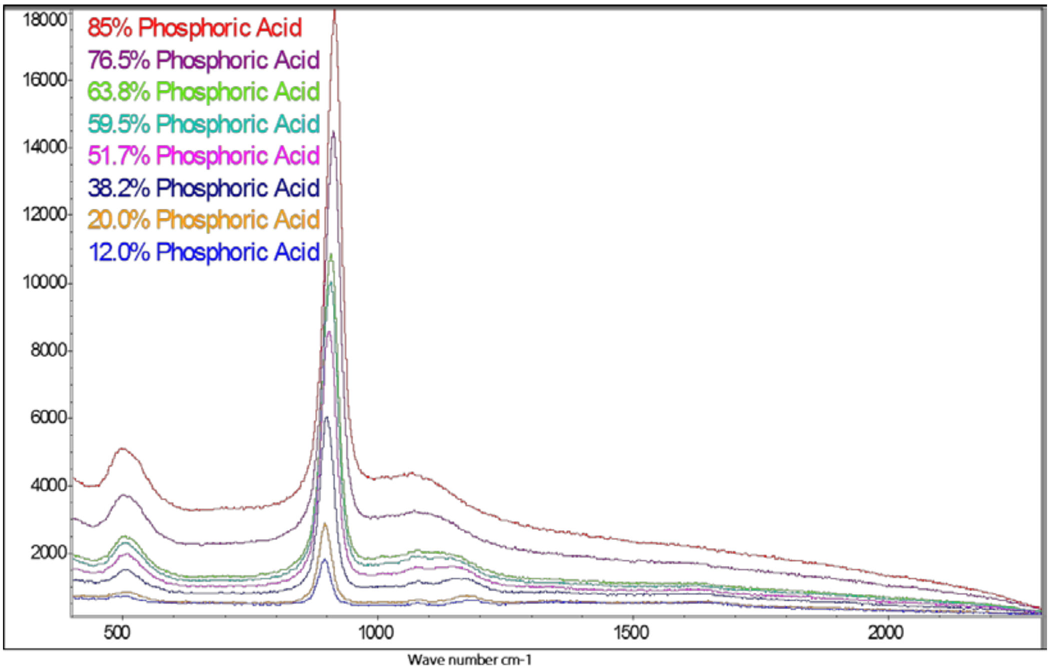

Figure 3: Zoomed part of spectra off phosphoric acid of varying concentration from 12% to 85%. Respective spectral correlation values of each phosphoric acid sample when compared against 85% pure is shown in the table

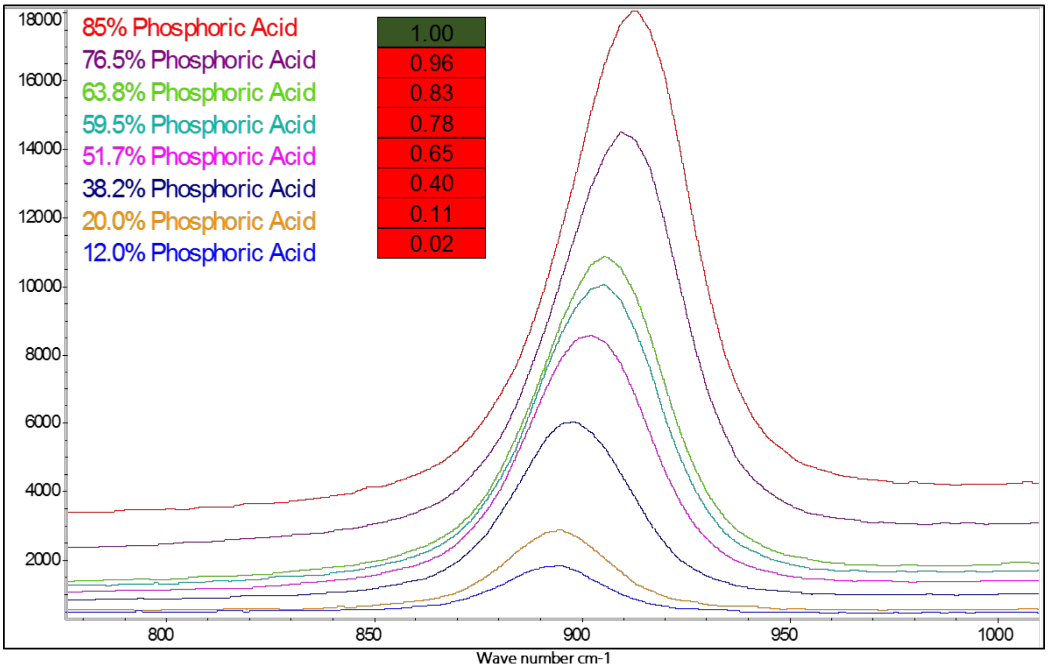

Table 1: Spectral Correlation value results for varying phosphoric acid concentration samples

Library \ Sample	85.00	76.50	63.70	59.50	51.70	38.20	20.00	12.00
85.00	1.00	0.96	0.83	0.78	0.65	0.39	0.11	0.02
76.50	0.96	1.00	0.92	0.88	0.78	0.54	0.24	0.14
63.70	0.83	0.92	1.00	0.98	0.95	0.78	0.50	0.38
59.50	0.78	0.88	0.98	1.00	0.96	0.83	0.56	0.43
51.70	0.65	0.78	0.95	0.96	1.00	0.91	0.69	0.55
38.20	0.40	0.54	0.78	0.83	0.91	1.00	0.85	0.73
20.00	0.11	0.24	0.50	0.56	0.69	0.85	1.00	0.79
12.00	0.02	0.14	0.38	0.43	0.55	0.73	0.79	1.00

Figure 4: Overlay of varying concentration of Acetic Acid