APPLICATION NOTE

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Metal Hydroxide Measurement Using Handheld and Portable Raman

Introduction

Metal hydroxides are chemical compounds consisting of a metal cation (Na^+, Mg^{2+}, K^+, Li^+, etc.) and a hydroxide anion (OH^-) [1].

Metal hydroxides have diverse industrial and medical applications. Among many uses, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are common caustic agents and are also used medically to remove dead/infected tissue [2]. Magnesium hydroxide ($Mg(OH)_2$) is a flame retardant additive for plastic [3] that can be used to treat occasional constipation [4]. Lithium hydroxide (LiOH) is used in manufacturing batteries [5].

Verification methods for metal hydroxides are available from USP as well as other institutes like CDC, and OSHA. These methods may differ depending on the detection purpose and sample types. However, these analytical procedures generally involve sample preparation and chemical testing, which is very cumbersome and inefficient when dealing with large quantities of samples. Raman spectroscopy can be a cost-effective, simple, and accurate alternative for identifying large quantities of metal hydroxides.

It is a common belief that identifying and differentiating different metal hydroxides is not viable with handheld Raman spectrometers. This study demonstrates that **B&W Tek's Handheld and Portable Raman** with a low wavenumber cutoff can identify commonly used metal hydroxides (NaOH, KOH, Mg(OH)2, and LiOH).

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Experiment setup

Metal Hydroxide Samples and Raman Instruments

NaOH (ACS reagent ≥ 97.0%), KOH (ACS reagent ≥ 85.0%), $Mg(OH)_2$ (reagent grade 95%) and LiOH (ACS reagent ≥ 97.0%) salts were acquired from Sigma-Aldrich.

Raman spectra were taken using a handheld **NanoRam-1064 (BWS456-1064)** with a **Point and Shoot Adaptor (NR2-PAS)** and a portable **i-Raman EX (BWS485III)** with a **lab grade fiber optic Raman probe (BAC102-1064-HT)** coupled to a standard **stainless-steel shaft (RSS100-1064)**. The portable system was controlled with **BWSpec** software and utilized a **Raman probe holder (BAC150B)** to hold the probe during measurements.

Raman Spectra Acquisition

Metal hydroxides were transferred to individual polyethylene sampling bags (Nasco Whirl-Pak bags) and then measured immediately using **NanoRam-1064** to minimize effects caused by adsorption of moisture from the atmosphere and other possible changes.

NanoRam-1064 allows users to develop and validate the method on the device, as well as detect spectral signals from as low as 176 cm^{-1}. The method was developed and validated as directed by the operating software for each sample using a spectral range of 176 – 1000 cm^{-1}. The specific spectral range is chosen to minimize the spectral signal from polyethylene sample bags. These methods were tested against a set of validation spectra from other pre-existing and enabled methods to prove its "specificity". The specificity is based on a calculated p-value, with a p-value cutoff of ≥ 0.05 for the "Pass" results.

Similarly, metal hydroxides were transferred to an individual aluminum weighing dish (Fisher) and then measured using the **i-Raman EX** The optimal working distance between the shaft and sample was established by adjusting the height of the neck of the probe holder. Table 1 summarizes the data collection method used for each measurement.

Table 1. Data collection methods used to measure NaOH, KOH, $Mg(OH)_2$ and LiOH using NanoRam-1064 – Method Validation; and i-Raman EX.

Samples	NanoRam-1064			i-Raman EX		
	Integration Time† (sec)	Laser Power	Average‡	Integration Time† (sec)	Laser Power	Average‡
NaOH	16	90%	1	15	100%	5
KOH	60	90%	1	20	100%	5
$Mg(OH)_2$	4	90%	1	25	100%	5
LiOH	7	90%	1	10	100%	5

† Optimal integration time is set by the software automatically; ‡ default setting.

Results

Raman profiles of tested metal hydroxides are summarized in Figure 1. Each sample had 2 – 3 Raman bands between 176 – 1000 cm^{-1}. NaOH had three Raman bands: a strong band at 207 cm^{-1}, a weak band at 295 cm^{-1}, and a broad band at 376 cm^{-1}.

Figure 1A

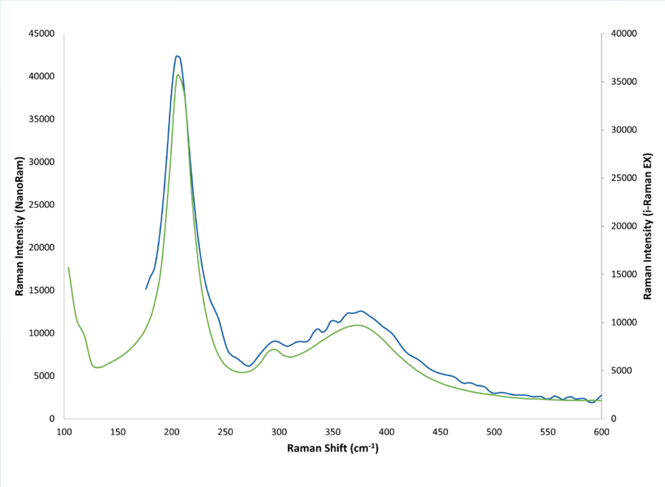

Figure 1B

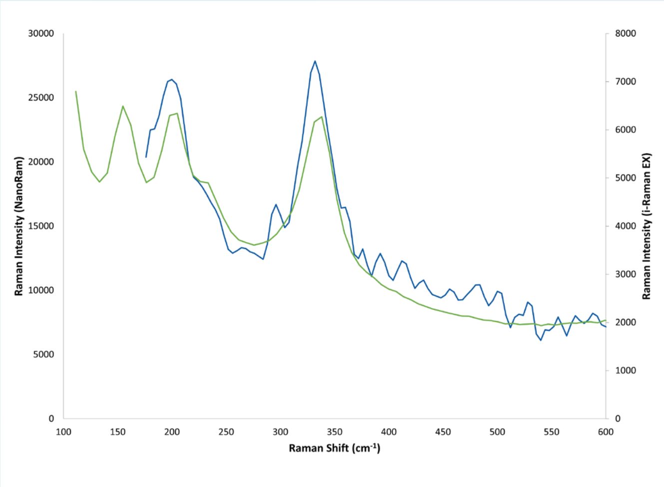

Figure 1C

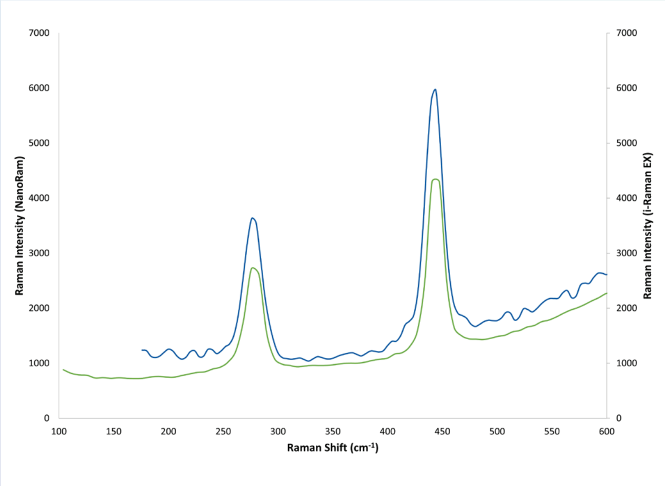

Figure 1D

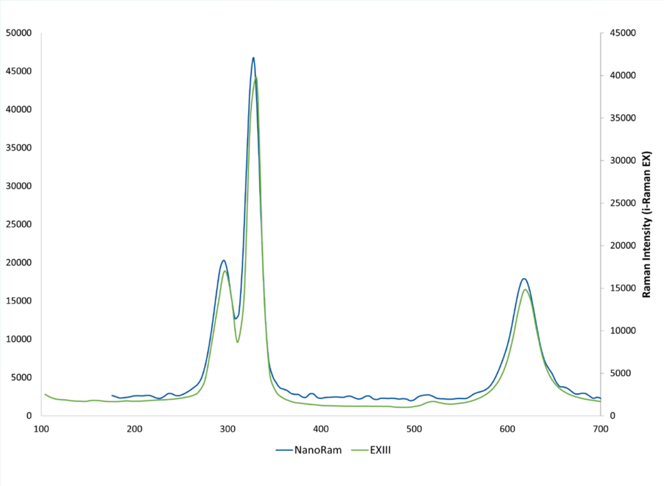

***Figure 1** Raman spectra of NaOH (a), KOH (b), $Mg(OH)_2$ (c) and LiOH (d) collected using a **NanoRam 1064 (Blue line)** and **i-Raman EX (Green line)**. The lower limit of Raman spectral range is 176 cm^{-1} for **NanoRam 1064** and 100 cm^{-1} for **i-Raman EX**.*

KOH had the weakest Raman response among samples, requiring longer integration time than others. It had two Raman bands at 199 cm^{-1} and 335 cm^{-1}, with similar intensities. In contrast, LiOH had the strongest Raman response among tested samples, with three prominent Raman bands at 296 cm^{-1}, 328 cm^{-1}, and 618 cm^{-1}, comparable to a previous study [6].

$Mg(OH)_2$ has a two Raman bands, 278 cm^{-1} and 443 cm^{-1}, corresponding well to that of a Brucite – a mineral form of $Mg(OH)_2$ [7]. The peak intensity could be improved using longer integration time, although this led to saturation of absorbance band beyond 1000 cm^{-1}.

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Results cont'd

Table 2. Specificity matrix for NaOH, KOH, $Mg(OH)_2$ and LiOH built using NanoRam 1064

	METHOD			
Samples	**NaOH**	**KOH**	**$Mg(OH)_2$**	**LiOH**
NaOH	**Pass (0.97)**	Fail (0.00)	Fail (0.00)	Fail (0.00)
KOH	Fail (0.00)	**Pass (0.99)**	Fail (0.00)	Fail (0.01)
$Mg(OH)_2$	Fail (0.00)	Fail (0.00)	**Pass (1.00)**	Fail (0.00)
LiOH	Fail (0.00)	Fail (0.01)	Fail (0.00)	**Pass (0.99)**

Methods developed for individual metal hydroxides had high specificity, as shown in the specificity matrix (Table 2), and could distinguish individual samples with high accuracy.

The major Raman band identified by the **i-Raman EX** was comparable to those from the **NanoRam-1064**. In addition, the **i-Raman EX** can detect the additional Raman band from KOH at 156 cm^{-1}, because the lower limit of Raman spectral range is 100 cm^{-1}.

It's worth noting that the physical form of the metal hydroxides affected the data acquisition. For example, a KOH pellet of > 0.5 mm diameter had a stronger Raman signal than KOH from the same batch ground into a powder (data not shown).

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Keyword Tags

NanoRam 1064 | i-Raman EX | Metal Hydroxides | Chemical Compounds | Industrial | Medical Applications | Sodium Hydroxides | Potassium Hydroxides | Magnesium Hydroxides | Lithium Hydroxides | Caustic Agents | Raman Spectroscopy | Qualitative Analysis | Quantitative Analysis