

APPLICATION NOTE

Analysis of Highly Fluorescent Chemical Materials

Comparison between traditional and eXTRaction fluorescence-reducing Raman technologies

Use of handheld Raman analyzers for industrial applications is limited by the fluorescent properties of the sample materials. Although fluorescence reduction is achieved with 1064 nm Raman, the higher laser power and longer integration time come with the risk of sample damage or ignition.

The ideal Raman solution minimizes measurement time and laser power while also providing a well-defined signal. Additionally, the ability to measure through containers and from a distance is required to reduce human interaction with hazardous samples.

This application note compares intelligent spectra eXTRaction Raman technology with conventional 785 nm and 1064 nm Raman devices for the analysis of chemicals that are difficult to measure due to their known fluorescent properties. Additional experiments were made to compare signal-to-noise ratios and to demonstrate analysis from a distance.

EXPERIMENTAL EQUIPMENT

Samples were aliquoted into glass vials, the vials placed in dedicated vial-holder attachments and spectra collected with three different Raman approaches. To collect the highest data quality, software was used to automatically optimize laser power, integration time, and spectral averaging.

Table 1. Equipment overview

Equipment	Experimental Use
TacticID 1064	Traditional 1064 nm Raman
MIRA XTR	Traditional 785 nm Raman with normal processing
MIRA XTR	785 nm Raman with XTR extraction processing

RESULTS OF SPECTRAL COMPARISON

Spectral analysis of polyphenyl isocyanate (PMDI or PAPI) from all three devices was overlaid to generate a comparison. Figure 1 shows the traditional 785 nm Raman approach gives a spectrum that is dominated by fluorescence and does not give a reliable analysis. The 1064 nm spectrum shows several distinct Raman peaks, making identification unambiguous; however, this requires 10x the laser power and 5x the measurement time. Analysis using the MIRA XTR with eXTRaction processing separates Raman data from a Raman-fluorescence data mixture. The result is six distinct peaks at 641 cm^{-1} , 800 cm^{-1} , 1102 cm^{-1} , 1443 cm^{-1} , 1529 cm^{-1} , and 1610 cm^{-1} , which match peaks collected by 1064 nm analyzer.

The mathematical extraction process in the MIRA XTR provides a superior way to analyze highly fluorescent materials compared to conventional 785 nm and 1064 nm Raman analyzers.

RESULTS OF SIGNAL TO NOISE ANALYSIS

The signal-to-noise ratio (SNR) is a good predictor of Raman analytical performance. A higher SNR indicates more useful signal and less interfering data for the instrument algorithms to use.

We evaluated the SNR of traditionally processed 1064 nm and 785 nm data and compared those results with XTR processed data. We used folic acid as the test system, which

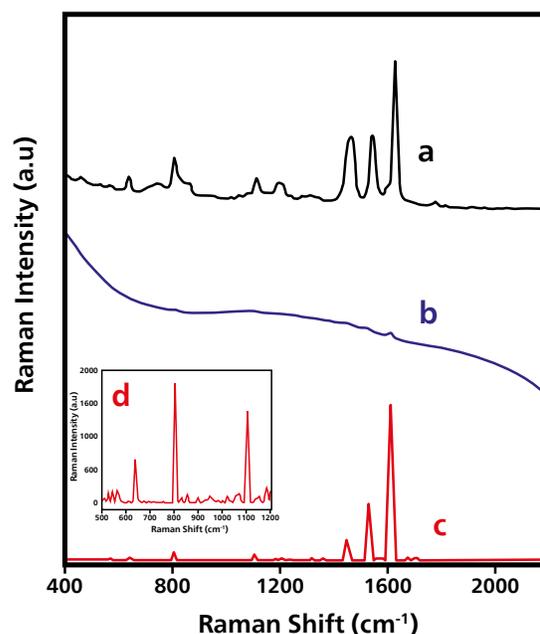


Figure 1. PMDI spectra overlay a.) traditional 1064 nm Raman (black), b.) traditional 785 nm Raman (blue), c.) 785 nm Raman with XTR extraction processing (red), d.) inset of spectrum (c) showing three small peaks at 641 cm^{-1} , 800 cm^{-1} , 1102 cm^{-1} .

has a strong signal intensity, moderate intrinsic fluorescence, many spectral bands, and no Raman features after 1700 cm^{-1} . Unprocessed representative spectra in Figure 2 demonstrate these features with both 785 nm and 1064 nm excitation. SNR was computed by taking the baseline corrected peak height of the strongest Raman band at 1610 cm^{-1} , which is related to the NH_2 and $\text{C}=\text{N}$ stretches of the pteridine ring¹ and dividing it by the RMS noise of the background signal between 1700 and 2100 cm^{-1} .

Table 2 shows the results of the SNR computations as a function of laser power, integration time, and processing. 1064 nm excitation yielded both lower SNR and longer integration times than the MIRA except at the highest laser power setting. XTR processing of the MIRA data resulted in a higher SNR than standard processing due to the eXTRaction algorithm's separation of low and high frequency components from the signal.

The longer measurement times of the 1064 nm systems increase the potential for inaccurate measurements due to changes in sample contact, while the high laser powers increase the risk of sample damage.

Based on these SNR results, we expect the MIRA XTR to perform as well as or better than a 1064 nm Raman system for identification of fluorescent materials.

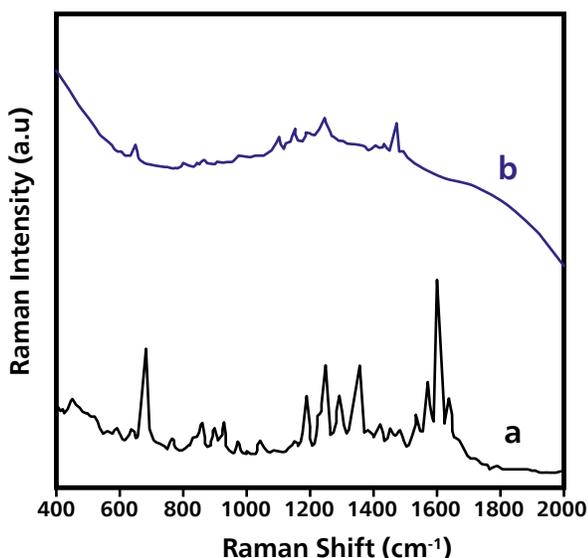


Figure 2. Folic acid Raman spectra without baseline correction or extraction. a.) 1064 nm Raman (black), b.) 785 nm Raman (blue).

RESULTS OF MATERIAL IDENTIFICATION

Material identification for industrial applications is difficult because chemicals exhibit different levels of fluorescence which interfere with the Raman signal. This presents a challenge for the laboratory or plant looking for a single device for their Raman applications. A device with a high SNR provides more useful signal with less unwanted data. A lower laser power is desired due to safety concerns.

We tested four chemicals with different spectral and fluorescent properties, comparing the Hit Quality Index (HQI) between 1064 nm Raman and the MIRA XTR with both standard and XTR processing. HQI is a metric that determines how well a collected spectrum matches a reference spectrum and is used in many Raman instruments. Use of HQI as computed by the two test instruments allows us to compare how well these instruments perform as used.

Shown by the confusion matrix in Figure 3; as fluorescent properties increase the MIRA XTR demonstrates excellent matching (0.99 HQI) for all four chemicals and is able to deliver comparable (if not better) results in comparison to the 1064 nm analyzer. The 785 nm Raman system with standard processing shows the expected reduced analytical performance due to fluorescence interference.

RESULTS OF ANALYSIS FROM A DISTANCE

Accurate identification of fluorescent chemicals without having to physically load them into the analyzer provides added safety for the analyst. This is done by directly scanning the chemicals through a site-glass or through the opening of a drum. Having already proven the MIRA XTR's ability to provide high quality spectra with low laser power while accurately identifying a variety of fluorescent chemicals, the next step is to see if this performance is still observed when measuring from a distance.

Polyphenyl isocyanate was measured at distances from 0.25-1.5 meters using laser power of 30mW, which is below the Class 1 Division 2 operational limit (<35mW). While acquisition time increased with distance, the material was accurately identified within 10 seconds at all measured distances (Table 3).

In the case of drum inspection, the exact distance from the bung hole to the sample is not known. An analyzer too sensitive to sample distance. To mimic how MIRA XTR handles data collection with an out-of-focus lens, the polyphenol isocyanate was measured from 0.4-0.6 meters with the lens focused at 0.5 meters. Increased measurement times were observed at 0.4 meters and 0.6 meters but the sample was accurately identified (Table 4).

Table 2. SNR comparison at different laser powers and integration times. 785 nm excitation results in higher or comparable SNR than 1064 nm excitation. XTR processing increases SNR compared to traditional Raman processing methods

Equipment	Baseline Correction	Laser Power (mW)	Integration Time (s)	Signal-to-Noise Ratio (SNR)
MIRA XTR	Standard	51.5	1.90	932,000
MIRA XTR	XTR	51.5	1.90	856
1064 Raman	Standard	40.7	10.00	51,300
1064 Raman	Standard	204	10.00	38,500
1064 Raman	Standard	365	7.90	916,000

		Actual Sample			
		4,4'-Methylenebisphenyl isocyanate	Bisphenol A diglycidyl ether Br	Microcrystalline cellulose	Polyphenyl isocyanate
Reference Spectra	4,4'-Methylenebisphenyl isocyanate	Mira XTR HQI = 0.95	Fail	Fail	Fail
		785 nm HQI = 0.99			
		1064 nm HQI = 0.96			
	Bisphenol A diglycidyl ether Br	Fail	Mira XTR HQI = 0.99	Fail	Fail
			785 nm HQI = 0.84		
			1064 nm HQI = 0.99		
	Microcrystalline cellulose	Fail	Fail	Mira XTR HQI = 0.99	Fail
				785 nm HQI = 0.78	
				1064 nm HQI = 0.98	
	Polyphenyl isocyanate	Fail	Fail	Fail	Mira XTR HQI = 0.99
					785 nm = No Match
					1064 nm HQI = 0.97

Increasing Fluorescence

Figure 3. Confusion matrix showing ability of MIRA XTR to identify samples of increasing fluorescence compared to traditional 785 nm and 1064 nm Raman analyzers.



Figure 4. Setup of identifying polyphenyl isocyanate through sealed glass container at 0.5 meters using the manual standoff.

Table 3. Comparison of MIRA XTR measurements of polyphenyl isocyanate at different distances.

Standoff (meters)	Acquisition time (sec)	HQI
0.25	1.34 ±0.08	0.99
0.50	1.80 ±0.02	0.99
1.0	6.72 ±0.27	0.99
1.5	10 ±0.00	0.97

Table 4. Comparison of out-of-focus measurements performed on the MIRA XTR of polyphenyl isocyanate with standoff set at 0.5 m.

Standoff (meters)	Acquisition time (sec)	HQI
0.40	4.69±0.07	0.99
0.50	1.78 ±0.02	0.99
0.60	3.26 ±0.34	0.98

SUMMARY

Raman spectroscopy can safely and accurately be used to analyze industrial chemicals with ranging fluorescent properties. With the MIRA XTR's Raman extraction technology, a safer, lower-powered laser can be used without compromising signal-to-noise analytical performance. Additionally, these measurements are possible from up to two meters away.

REFERENCES

- 1) Castilla, J.J., et al. Adsorption and Vibrational Study of Folic Acid on Gold Nanopillar Structures Using Surface-Enhanced Raman Scattering Spectroscopy. *Nanomaterials and Nanotechnology*. 2015; 5. doi:10.5772/61606