Application Note AN-RS-007

使用拉曼光聚合物母料

Detecting dyes and additives in plastics with ease

Masterbatches play an essential role in polymer manufacturing. Some widespread additive masterbatches reinforce plastics or make them resistant to flame or UV radiation, for example. Masterbatches are not only added to change polymers' physical and chemical properties, they can also be used to color the polymer during the manufacturing process.

Measurement of masterbatches with handheld Raman spectroscopy requires no sample preparation and provides immediate results that easily distinguish between a polymer with different additives. Unique to Metrohm, the XTR® algorithm mitigates the inherent fluorescence of plastics and the background contribution from dyes; fluorescence mitigation is crucial for accurate library matching.

INTRODUCTION

785 nm Raman excitation is considered the ideal wavelength for a high spectral signal-to-noise ratio. However, approximately 10% of Raman-active materials fluoresce under interrogation with 785 nm Raman [**1**]. Fluorescence overwhelms the Raman signal and can prevent positive identification of the target substance. Even the Raman spectra of uncolored polymers exhibit some inherent fluorescence, as do many hydrocarbon-based materials. Nearly 100% of deeply colored materials—tablets, foodstuffs, art, and plastics—can be problematic for traditional Raman analysis. The ability of XTR to remove the fluorescent background and reveal a high-resolution spectrum of colored plastics is particularly impressive.

POLYPROPYLENE ADDITIVES

Polypropylene (PP) is widely used in manufacturing, with many different types including homopolymer and copolymer. It also comes in specialized variants like flame-retardant and reinforced PP. Homopolymer PP provides high strength, stiffness, and chemical resistance, while copolymer PP offers flexibility and impact resistance.

Raman spectroscopy ensures fast, precise on-site confirmation of PP types. **Figure 1** demonstrates the high specificity of Raman for very similar materials.

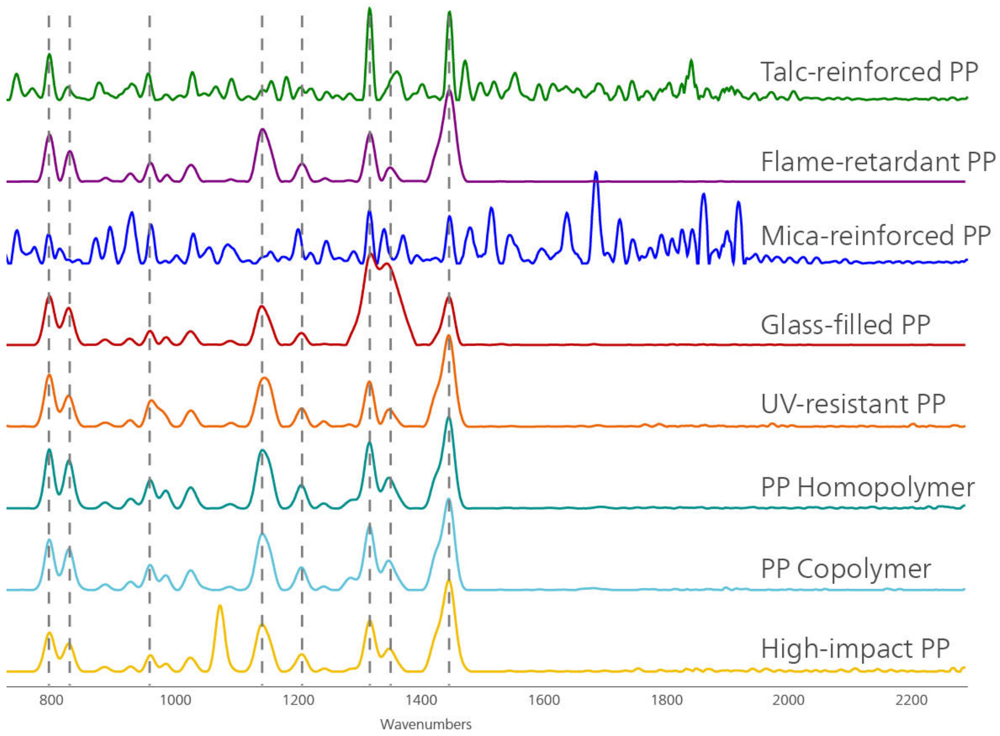

Figure 1. Overlaid spectra of different polypropylene variants, with dashed lines indicating the signature Raman peaks for polypropylene (PP). Spectral contributions from additives make for easily distinguishable spectra between polymer types.

A series of strongly colored plastic marker casings were directly tested at the surface with a 785 nm handheld Raman spectrometer equipped with the XTR algorithm. Similarly to Sequentially Shifted Excitation (SSE), XTR uses multiple shifted spectra that are generated by internal algorithms during the experiment to distinguish the Raman shift from fixed fluorescence, permitting the fluorescence component to be isolated and extracted. The Raman data is optimized through an iterative process in a secondary automated process in real time. After identification and elimination of the fluorescence component, only a pure, unobstructed Raman spectrum remains.

The ability of XTR to return baselined spectra containing the signature Raman fingerprint peaks for a given substance is demonstrated across a spectrum of colors in **Figure 2**.

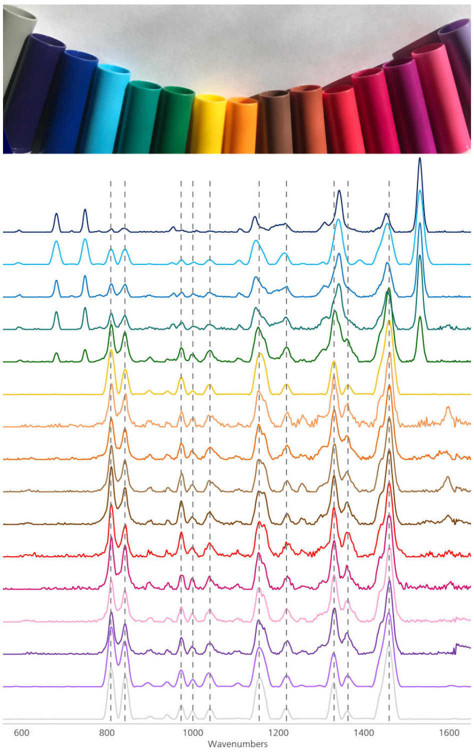

Figure 2. The color of the XTR spectra shown here coordinates with the color of the polypropylene tested (at top). The signature Raman peaks for polypropylene are indicated by dashed lines.

PHTHALOCYANINE BLUE

Only very saturated blue colors containing a cyan pigment showed strong spectral contribution from the dye (**Figure 2**). Indeed, most strongly blue-colored polymers are dyed with masterbatches featuring phthalocyanine chemistry [**2**].

Interestingly, the cyan signal was the main spectral contributor for only the very dark blue polypropylene (**Figure 3**). The resulting spectrum is an obvious blend of both polymer and dye masterbatch [**3**].

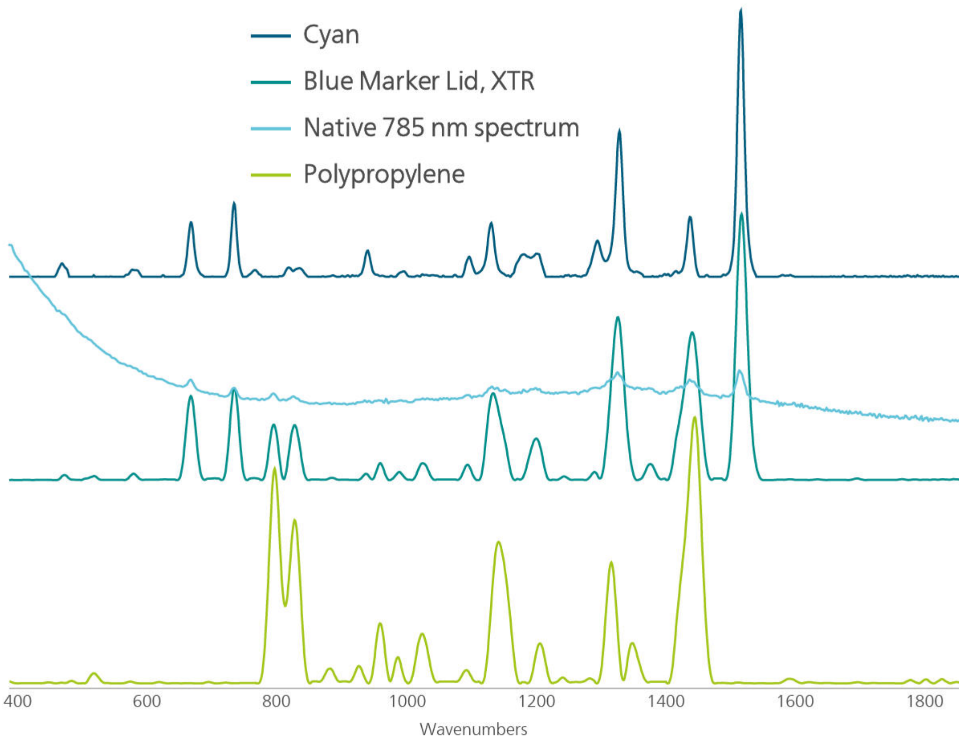

Figure 3. Despite significant spectral contribution from cyan pigment, XTR produces a baselined, high-resolution spectrum that is obviously a mixture of both dye and material. The native 785 nm spectrum reveals the striking benefits of XTR.

Despite significant contribution from both the dye and high levels of fluorescence, XTR permitted identification of both material and colorant (**Figure 4**). Note the very high Hit Quality Index (HQI = 0.99) values, indicating a high correlation between the sample and reference spectra.

PHTHALOCYANINE BLUE

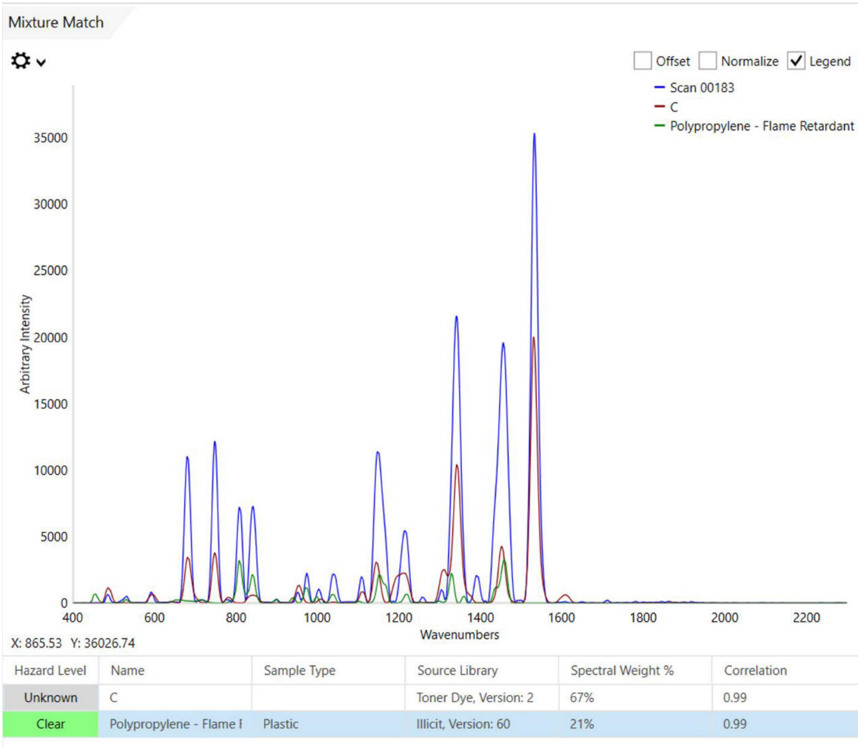

Figure 4. Despite significant contribution from both the dye and high levels of fluorescence, XTR permitted identification of both material and colorant.

CONCLUSION

This study demonstrates Raman's ability to unambiguously identify polymers, even with spectral contribution from various masterbatches. The XTR algorithm, Metrohm's unique fluorescence-rejection technique, extends the usefulness of Raman in the analysis of colored plastics. Raman spectroscopy provides polymer manufacturers with a fast and efficient, nondestructive method to investigate the quality and consistency of materials.

REFERENCES

1. *Handheld dual-wavelength Raman instrument for the detection of chemical agents and explosives*. https://www.spiedigitallibrary.org/journals/optical-engineering/volume-55/issue-7/074103/Handheld-dual-wavelength-Raman-instrument-for-the-detection-of-chemical/10.1117/1.OE.55.7.074103.short (accessed 2025-01-30).
2. Christensen, I. *Developments in Colorants for Plastics*; iSmithers Rapra Publishing, 2003.
3. Balakhnina, I. A.; Chikishev, A. Yu.; Brandt, N. N. Raman Spectroscopy of Thermo- and Laser-Induced Transformations of Gouache Paint Layer of Copper Phthalocyanine Blue. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2024**, *318*, 124430. DOI:10.1016/j.saa.2024.124430

CONTACT

Metrohm AG
Ionenstrasse
9100 Herisau
info@metrohm.com

CONFIGURATION

MIRA XTR Basic

MIRA XTR 1064 nm ,MIRA XTR 785 nm XTR
MIRA XTR (ORS) ,,
Basic , MIRA XTR Basic 3B MIRA XTR