



Fiber optic probes add flexibility to Raman chemical analysis

Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy are non-destructive analytical techniques that rely on the interaction of electromagnetic radiation with molecular vibrations to provide information about the chemical composition and structure of a sample. Despite their similarities, there are some distinct differences between the two techniques. In principle, FTIR is based on the absorption of infrared radiation by molecules and measures changes in dipole moment during molecular vibrations. Raman spectroscopy, on the other hand, is based on the inelastic scattering of monochromatic light and measures changes in polarizability during molecular vibrations.

When applied to bulk chemical analysis, both FTIR and Raman spectroscopy can be used to analyze solids, liquids, and gases, but the nature of Raman spectroscopy lends some unique sampling advantages. Additionally, Raman often requires little to no sample preparation. Presented herein are application examples that highlight some of the sampling advantages of Raman spectroscopy. All the spectral data in this technical note were collected using a Thermo Scientific™ DXR3 Flex Raman Spectrometer equipped with a fiber optic probe. (Fiber optics are readily available for Raman spectroscopy because of the use of visible and NIR light and do not require the exotic materials associated with FTIR fiber optics.) Preliminary tests for all samples were carried out using both 532 nm and 785 nm excitations, and it was determined that the 785 nm laser set gave an overall better balance between fluorescence and Raman scattering efficiency.

Sampling through containers

Raman uses laser light for excitation, which allows for precise and localized analysis at the light beam's focal point. Raman spectroscopy is therefore well suited for the analysis of materials inside containers, through container walls, so long as the container is at least partially transparent to the laser light. There might be some contributions from the container walls in the total spectra, but subtracting out those contributions results in Raman spectra of the contents inside without the need to open the container. This can be particularly advantageous in applications such as toxic chemical identification, pharmaceutical counterfeit analysis, and illicit drug detection; keeping the analyte contained helps eliminate contamination, preserve evidence fidelity, and avoid accidental operator exposure to toxic chemicals or high potency drugs such as fentanyl.

Figure 1 shows the spectra determined from Raman analyses of chemicals, both in liquid and solid forms, in various types and sizes of glass containers. Glass is transparent to visible lasers used for Raman excitation, and it does not exhibit significant Raman scattering signals that would interfere with the analysis. In Figure 1, the relatively minor contributions from glass fluorescence were subtracted from all spectra, resulting in the Raman spectra with flat baselines and sharp features. The identities of the materials were confirmed by searching against libraries.

A similar application is the analysis of samples within packaging, such as the pharmaceutical products in blister packaging. Figure 2 demonstrates the direct analyses of two over-the-counter (OTC) pharmaceutical products, a solid tablet (Cinnarizine) and a soft gel, through the blister packaging. Blister packs are preformed plastic materials, but the packaging is relatively thin and does not contribute much to the observed Raman spectra.

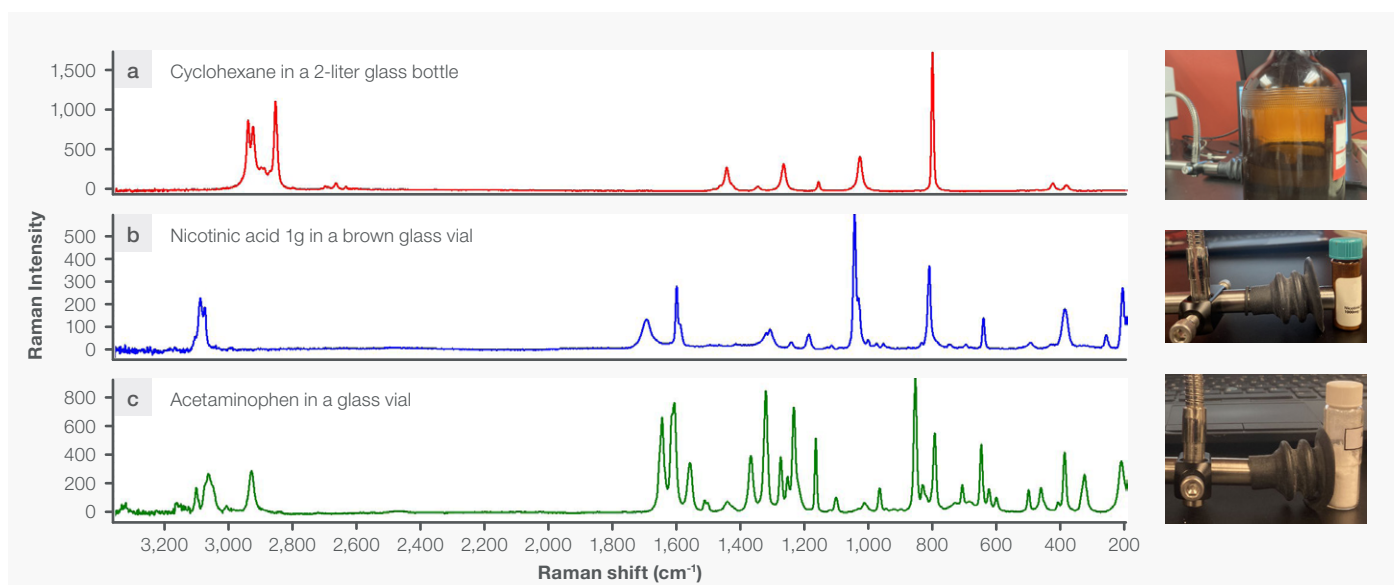


Figure 1. Raman spectra of chemicals stored in glass bottles. (a) Liquid in a large brown bottle; (b) solid in a small brown vial; and (c) solid in a small clear vial. Contributions from glass fluorescence have been subtracted.

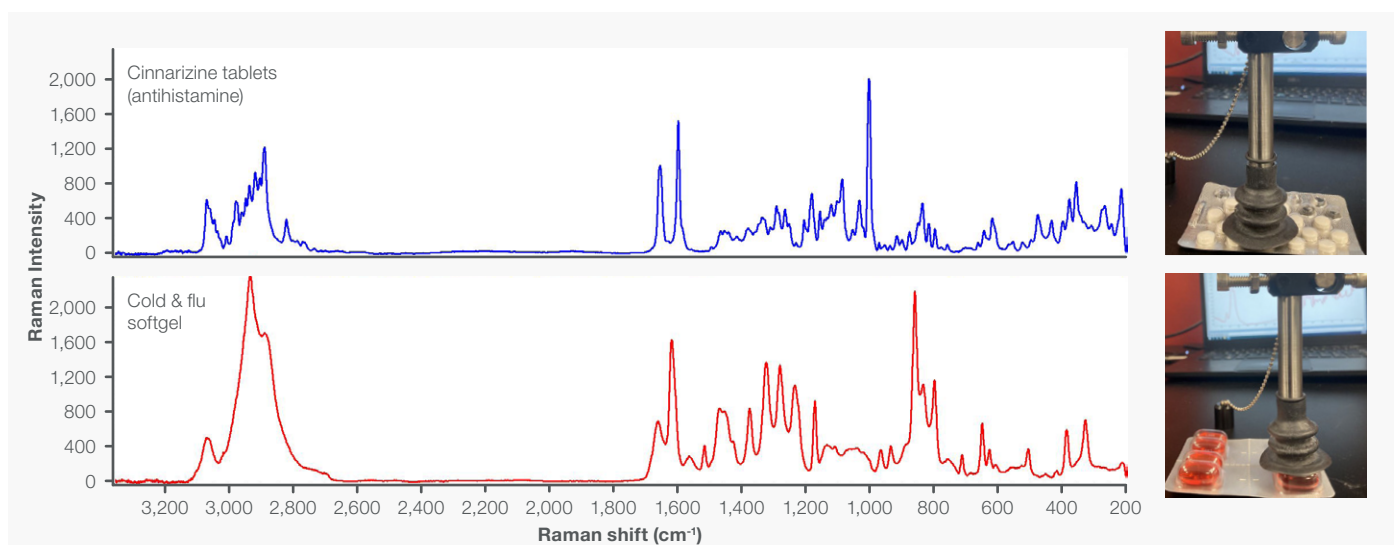


Figure 2. Raman spectra of two pharmaceutical products analyzed through blister packaging. The contributions from the packing were minor but have been subtracted from these spectra.

Thick plastic containers bring varying extents of contributions to the Raman spectra, depending on material type, thickness, and compositional complexity. Figure 3 shows an example where the container is polyethylene (PE) with titanium dioxide (TiO₂) as a pigment. As can be seen in Figure 3b, the container itself has noticeable Raman features. By subtracting the spectrum of the container (Figure 3b) from the total spectrum (Figure 3a), a high-quality Raman spectrum of the content inside (Figure 3c) was obtained notwithstanding a fairly opaque container. The identity of the content was confirmed to be acetaminophen through library searching.

Analysis of aqueous solutions

Water has a strong dipole moment and thus absorbs strongly in the mid-infrared region, often interfering with the sample spectra in FTIR analysis. Conversely, water is a relatively weak Raman scatterer, allowing Raman to be more effective in aqueous environments.

Figure 4 shows spectra from the Raman analysis of an energy drink in a vial. The energy drink is a mixture of multiple components including 0.4% (0.004 g/ml) caffeine. As shown in Figure 4b, water produces relatively weak and broad Raman peaks. After subtracting out the water contributions (Figure 4b) from the total spectrum (Figure 4a), the resulting spectrum (Figure 4c) reveals the presence of some of the expected components (caffeine, L-phenylalanine, and potassium sorbate).

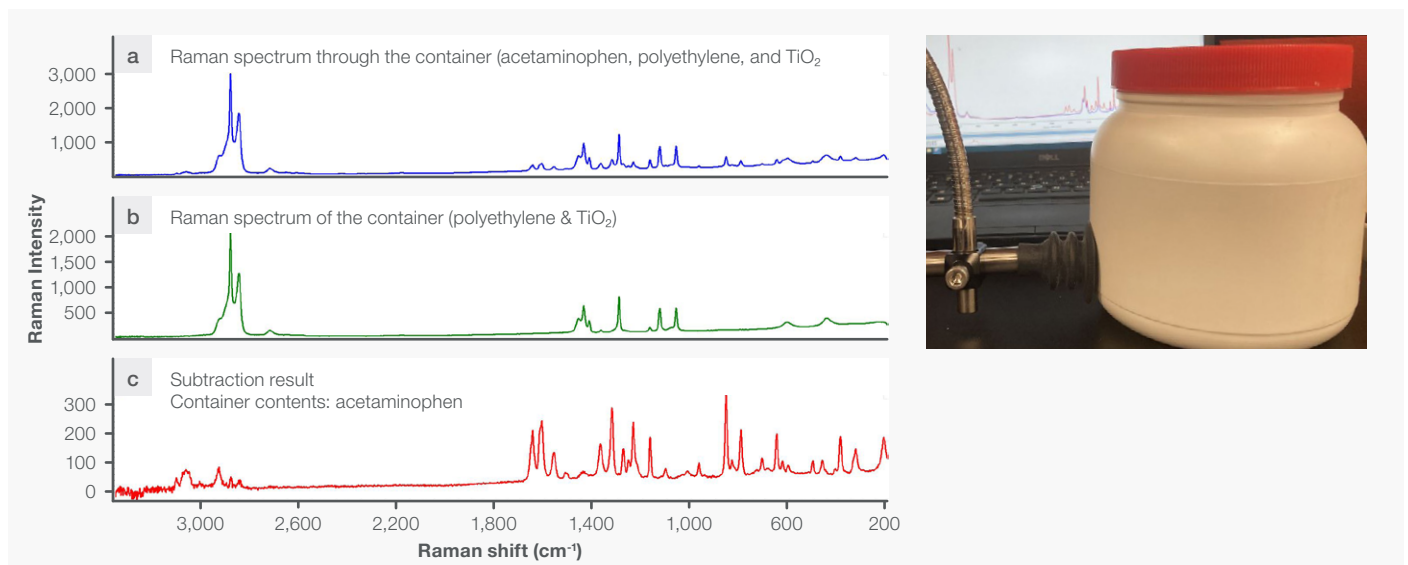


Figure 3. Raman spectra from the analysis of acetaminophen inside a white container. (a) Spectrum obtained through the container, (b) Spectrum of the container, (c) Spectrum of acetaminophen inside the container (subtraction result). Components were identified by searching against libraries.

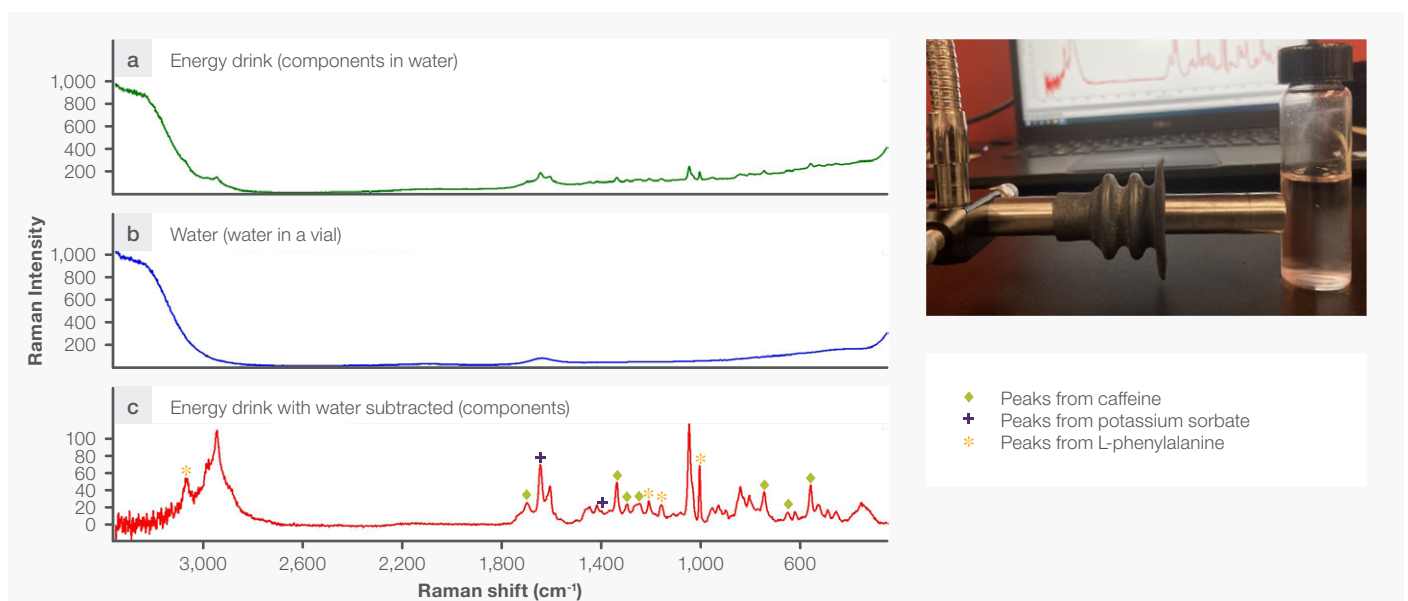


Figure 4. Raman spectra from the analyses of an energy drink and water. (a) The spectrum of an energy drink with multiple components. (b) The spectrum of water. (c) The result of the subtraction of the water spectrum from the energy drink spectrum. Peaks associated with caffeine, potassium sorbate and L-phenylalanine are marked in the spectrum.

Analysis of inorganic samples

Both FTIR and Raman can be used to analyze inorganic samples such as minerals, but there are challenges associated with the common sampling techniques in FTIR. Preparing samples for transmission FTIR measurements can be time consuming. FTIR reflection measurements can be complicated by a mix of diffuse and specular reflection. Attenuated Total Reflection (ATR) depends on the differences in refractive index (RI) between the ATR crystal and the sample, but inorganic material can have higher RI. In contrast, sampling with Raman spectroscopy simply requires focusing the excitation laser on the surface. Raman spectroscopy provides easy access to low frequency vibrations often associated with inorganic materials and often displays narrow and well-defined peaks that are particularly sensitive to molecular symmetry, making it well-suited for detecting variations in crystal structures including differentiating polymorphs.

Figure 5 shows the Raman analysis of three geological samples. The spectra were searched against libraries for identification. Figure 5a represents the bulk mineral analysis by Raman whereas Figures 5b and 5c exemplify the Raman analysis of multi-component mineral samples with small deposits on the surface. Figure 5b shows the identification of hematite (Fe_2O_3) in an agglomeration of different minerals, whereas Figure 5c demonstrates the identification of cerussite (PbCO_3) on the surface of galena (PbS), likely resulting from the weathering of PbS .

Figure 6 shows the Raman analysis of two different paints (white and yellow) on a painting. The white pigment was identified as the rutile form of titanium dioxide (TiO_2). Rutile and anatase are the two most stable crystalline forms of TiO_2 . Raman spectroscopy is sensitive to crystal symmetry, making it useful for identifying crystal phases and polymorphs. The yellow pigment was identified as chrome yellow (lead chromate, PbCrO_4). The analyzed section appears to contain a hint of titanium dioxide.

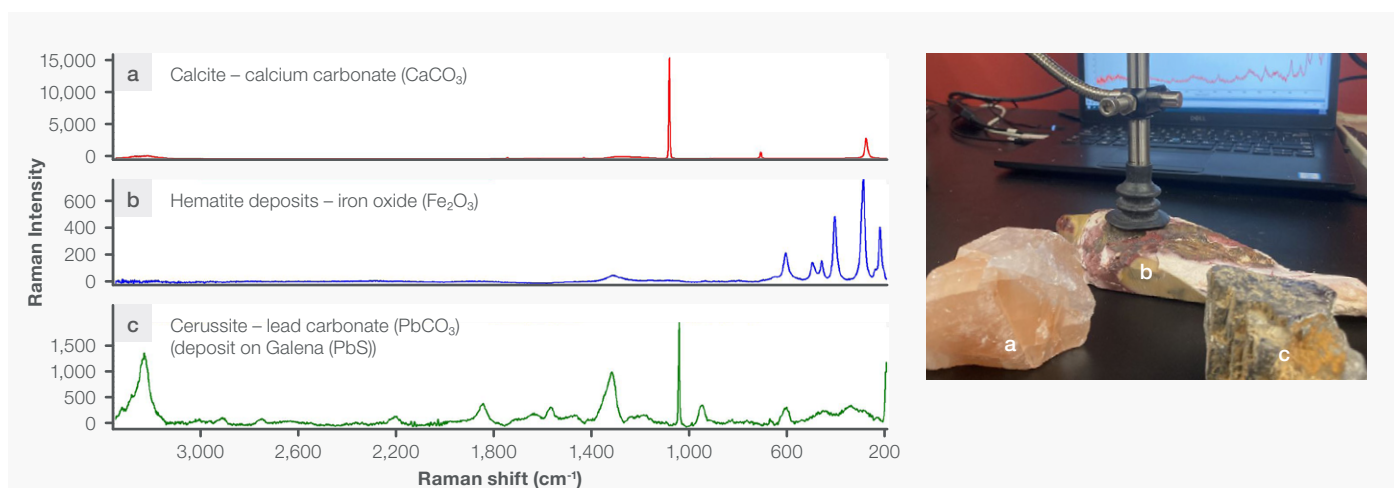


Figure 5. Analysis of three large geological samples: (a) calcite; (b) hematite deposits; and (c) cerussite deposits. Spectra were baseline corrected.

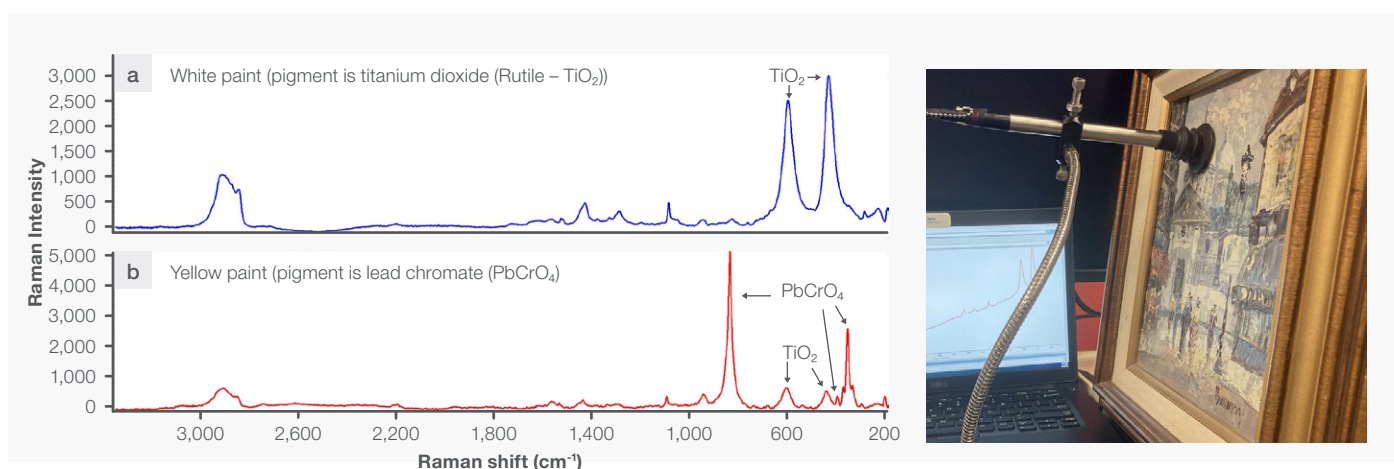


Figure 6. (a) Raman spectrum of the white paint on the painting; and (b) Raman spectrum of the yellow paint on the painting. Both spectra are baseline corrected. Components were identified by searching against libraries.

Flexibility of fiber optic probe for Raman sampling

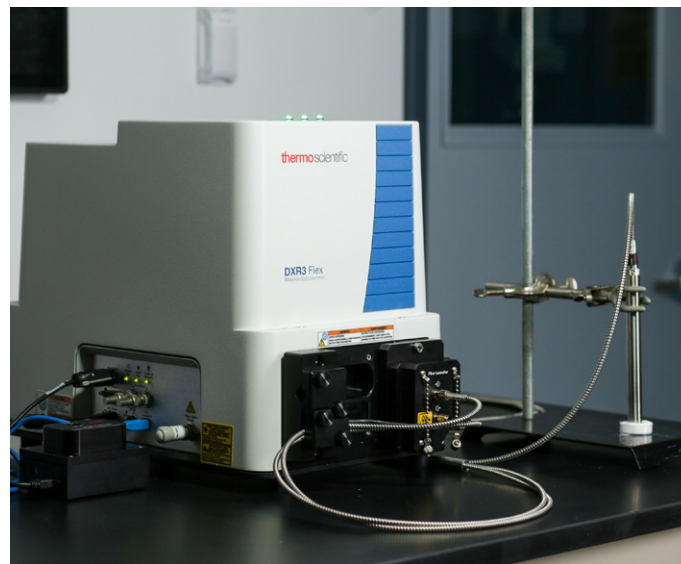
Fiber optic probes provide flexibility and ease of maneuverability. This is advantageous when analyzing samples that are difficult to access or manipulate, such as the 2-L glass bottle shown in Figures 1a, the large plastic container shown in Figure 3, the geological samples shown in Figure 5, and the painting example shown in Figure 6. All these samples are too big to fit into the sample compartments of most commercial Raman instruments. The use of a fiber optic probe allows for direct and facile analysis of these samples without the need to either transfer the material into smaller containers or damage the samples.

Summary

In this technical note, the analyses of a variety of samples by Raman spectroscopy are demonstrated. All samples were analyzed without sample preparation.

- Precise and localized analysis at the focal point of the Raman-exciting laser allows sampling through glass bottles, blister packaging and plastic containers, which eliminates possible cross contamination and analyst exposure to hazardous materials. The contributions from the packaging and containers depend on the type of container material, the container thickness, and the materials' chemical compositional complexity, but these contributions can be readily subtracted out when needed.
- Water is a weak Raman scatterer. Raman therefore has reduced water sensitivity, making it a preferred technique for aqueous solution analysis over FTIR. As demonstrated in the analysis of an energy drink, the Raman bands from water can be subtracted from the spectrum of the aqueous solution, leading to the identification of the components of the solution.
- Raman spectroscopy is well suited for the analysis of inorganic materials, especially in identifying the crystal phases and polymorphs, as demonstrated by the analyses of minerals and pigments in a painting.
- Fiber optic probes provide flexibility and ease of maneuverability. This is particularly advantageous when analyzing samples that are difficult to access or manipulate, such as large containers, geological samples and paintings.

The DXR3 Flex has multiple sampling options available. A properly configured fiber-optic probe is arguably the most versatile accessory for the analysis of bulk solids and liquids. The advantages, both from those inherent to Raman spectroscopy and those resulting from the use of fiber optic probe, provide opportunities for a wide variety of different applications when using the DXR3 Flex Raman Spectrometer.



Thermo Scientific DXR3 Flex Raman Spectrometer.

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