

RAMAN SPECTROSCOPY

BRAVO – Handheld Raman Spectroscopy

For Art and Cultural Heritage Analysis

Innovation with Integrity

The analysis of artworks and other objects of cultural value can be very challenging. Many times, objects of interest are of complex material composition. Additionally, in nearly all cases, non-destructive analysis is required, and furthermore, the transfer of the object into an analytical laboratory would be highly undesirable. This is related to different factors, like dimensions as in the case of large sculptures and wall paintings, insurance management, or patron popularity in the case of famous artwork.

Handheld or portable Raman spectrometers enable a contact free analysis of various organic and inorganic compounds and are next to portable XRF and FT-IR spectrometers the most commonly applied spectroscopic techniques for the non-invasive surface analysis of objects. These instruments work very well for material characterization (pigments, fillers, waxes, varnishes, and many others), by determining elemental (XRF) and molecular content (IR and Raman)^[1]. With the Raman spectrometer BRAVO, Bruker offers a handheld instrument with unique performance of particular value for art and conservation studies^[2].

Advantages

- Patented fluorescence mitigation SSE™.
- DuoLaser™ excitation makes a large spectral range accessible (170 – 3200 cm⁻¹) and provides highest sensitivity.
- Unmatched wavenumber accuracy achieved of typically +/-1 cm⁻¹ in the fingerprint region.
- Reduced risk of material alteration or damage because of a low laser output power of typically < 100 mW and an optimized focus shape.
- Laser Class 1 in all operating modes.
- BRAVO can be remote controlled by a computer (via WiFi or Ethernet).
- Tripod mount available.
- Comprehensive software suite for advanced data evaluation included.

The performance of a benchtop instrument in a handheld format

One of the main limitations of Raman spectroscopy is fluorescence interference which can sometimes be overcome by changing the laser excitation wavelength to 1064 nm, which unfortunately significantly reduces the sensitivity. Two predominant factors limit the sensitivity at 1064 nm; first the scattering efficiency falls off as a fourth power as the wavelength is increased and second, detectors are more sensitive in the visible than in the near infrared.

Because detectors in the near infrared have fixed noise (unlike shot noise limited detectors in the visible), benchtop instruments can benefit from the high throughput of a FT-spectrometer and optimized sensitivity using a liquid nitrogen cooled Germanium detector. This is not easily accomplished with small handheld instruments, where 1064 nm excitation based units can only compensate for the reduced sensitivity by applying a higher laser output power. For materials with an even modest absorption, which is the case for many colored materials, this can lead to transient heating and sample alteration or damage. The signal from sample heating can be large thereby obscuring the desired Raman signal.

BRAVO challenges the above mentioned limitations providing ultimate sensitivity over the whole spectral range even including the CH-stretching region using DuoLaser™ excitation. This combined with a powerful fluorescence mitigation based on a Bruker's patented SSE™ shifted excitation technique. The high quality optics and resulting excellent sensitivity enable the collection of high quality Raman spectra with a fairly low laser output power reducing the risk of sample alteration.

Fluorescence mitigation SSE™

Many materials of interest in the field of art and conservation emit intense fluorescence signals as a consequence of the laser excitation. Such fluorescence signals can easily dominate a Raman spectrum as shown in Figure 1 (red spectrum). With sequentially shifted excitation (SSE™) fluorescence signals are mitigated (blue spectrum) and the generated result is comparable to a spectrum measured at a benchtop FT-Raman system using 1064 nm excitation^[3].

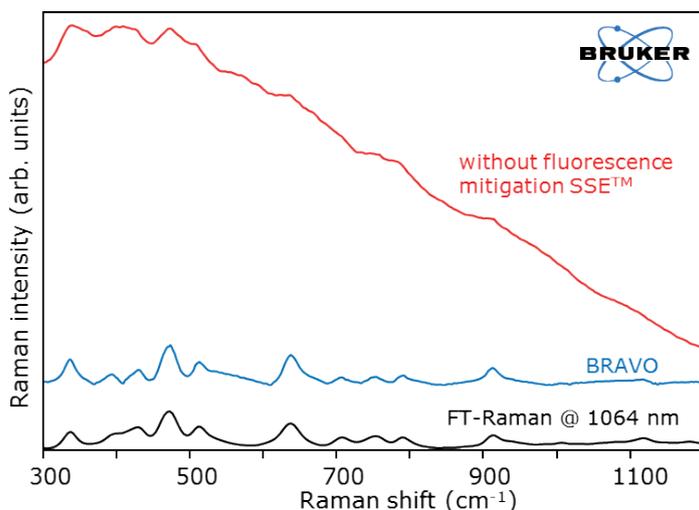


Fig. 1
Raman spectra of Kaolin (KREMER 5825) measured with BRAVO (red and blue) and the FT-Raman spectrometer MultiRAM (black).

Recently, it has been demonstrated on real world samples that the BRAVO is able to mitigate fluorescence without reducing sensitivity, while maintaining unmatched wavenumber accuracy. This is critical for successful library searching and automatic compound identification^[1].

Advanced data acquisition and evaluation

Usually handheld instruments are operated via keypads and/or touch screen displays and have user friendly workflows on the device targeting routine applications. BRAVO additionally offers remote control functionality such that measurement parameters can be set manually and the data collection executed from the computer. This is of particular value if the system is mounted on a tripod^[4]. With our growing expertise in the field of art and conservation, a spectral database including most common pigments, fillers, binders and waxes is available, which can be used for the identification of the unknown materials (see Figure 2).

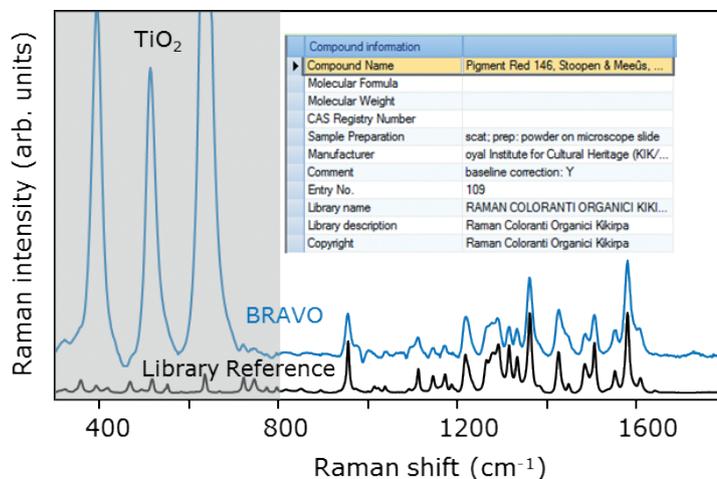


Fig. 2
Identification of the composition of paint using the library SEARCH functionality of OPUS.

References

- [1] Conti et al., Analyst 141, 4599 (2016)
- [2] Vagnini et al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 176, 174 (2017)
- [3] Bruker Product Note T29 12/15, Efficient mitigation of fluorescence in Raman spectroscopy using SSE™
- [4] Bruker Product Note R34 05/16, Advanced Data Acquisition and Evaluation in Handheld Raman Spectroscopy

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