MULTIMODAL FIBER PROBE FOR SIMULTANEOUS MID-INFRARED AND RAMAN SPECTROSCOPY

A fiber probe has been developed that enables simultaneous acquisition of mid-infrared (MIR) and Raman spectra in the region of 3100–2600 cm^{-1}. Multimodal measurement is based on a proposed ZrO_2 crystal design at the tip of an attenuated total reflection (ATR) probe. The capability of combining MIR and Raman spectra in a single probe has been illustrated using liquid samples.

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Chemical analysis is becoming more instrumental with an increasing role of spectroscopic techniques. The joint use of two or more spectroscopic techniques can be more efficient than single-method approaches. For example, in the food and pharmaceutical industries, the use of complementary methods like IR absorption and Raman spectroscopy are highly desirable due to the compositional complexity of raw materials and products.

Compared to probes that use only one method, combination of two (or more) spectral methods in a single probe saves space and necessary sample volume, requires only a single connection port for an in-line measurement, can be manipulated with one hand, and demands less cleaning and maintenance effort. The most essential advantage of the multimodal probes is the possibility of simultaneous measurement at the same sample point.

Combining different spectroscopic techniques within the same probe is facilitated by the application of fiber optics. Advances in the development of chalcogenide (CIR) and polycrystalline infrared (PIR) fiber materials expand the analytical spectral range of modern probes towards MIR allowing to cover the entire wavelength range from 0.2 to 17 microns.

The present study investigates the feasibility of obtaining the Raman spectra through the silica fiber channels using a multimodal probe design.

MIR absorption bands generally exhibit higher intensity for anti-symmetric molecules vibrations than the respective Raman signals of the same functional group, and vice versa. In spite of the affinity of chemical information provided by these two methods, their joint use in analysis is technically complicated.

This study is aimed at obtaining a Raman spectrum through a ZrO_2 crystal head of the recently developed multimodal ATR probe with two built-in silica-fiber channels. Due to the expected optical losses in the fibers, the ATR-crystal, and the sample medium, the detection of the intrinsically weak Raman signal on any chemically informative spectral range is an experimental challenge. The proposed multimodal probe should be a useful tool accelerating the further development of complementary vibrational analysis.

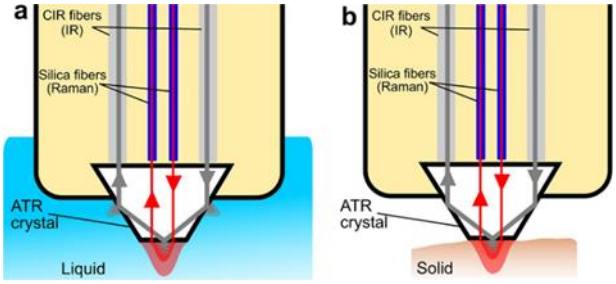

Fig 1. Multimodal IR and Raman probe design: (a) for liquid and (b) solid samples.

The probe's shaft is made of polyether ether ketone (PEEK) and has a diameter of 6.3 mm. The probe head has a crystal made of cubic zirconia ZrO_2, which enables ATR-measurements with triple reflections due to its frustum shape. Two CIR-fibers attached to the base of the crystal were responsible for conducting the MIR radiation to/from the sample. The incident MIR radiation is directed at an angle of 60° to the axis perpendicular to the ATR crystal surface. The same angles of incidence are observed for all reflections inside the ATR crystal (Fig. 1).

To enable multimodal measurements, the ATR probe was modified by adding a pair of fused silica fibers lying in a plane perpendicular to the ATR channels. The high-OH silica fibers having transmission in the broad 0.25–1.2 μm range were used for the Raman spectroscopy in this work.

A separate silica-fiber Raman probe specially designed by art photonics GmbH (Germany) for obtaining high-quality Raman spectra was used as a benchmark. It provides the possibility to collect Raman signals in the whole range of Raman shifts from 200 cm^{-1} to 4000 cm^{-1} using standard Raman spectrometers of this type with a working range of 800–950 nm. The excitation sources used were 680-nm and 785-nm lasers, packaged in a single unit (Innovative Photonics Solutions, USA). The FT-IR spectrometer Bruker Matrix-MF (Bruker Corporation, USA) was used to obtain MIR spectra. Raman spectra were recorded using the WP 785 Raman Spectrometer, model WP-785-C-SR-S (Wasatch Photonics, USA). Data

evaluation and visualization were performed using an on-line chemometrics software TPT-cloud (Global Modelling, Germany and Mestrelab Research, Spain). Distilled water, acetone (99.5%), ethanol (80%), and cyclohexane (99.9%) were chosen as non-fluorescent samples.
The optimal experimental conditions were chosen by adjusting the laser power and acquisition time.

After the baseline subtraction (Fig. 2), spectra of liquid samples obtained using a multimodal probe in the studied region look very similar to those obtained with the standard Raman probe. It confirms the principal feasibility of Raman measurements using the multimodal probe.

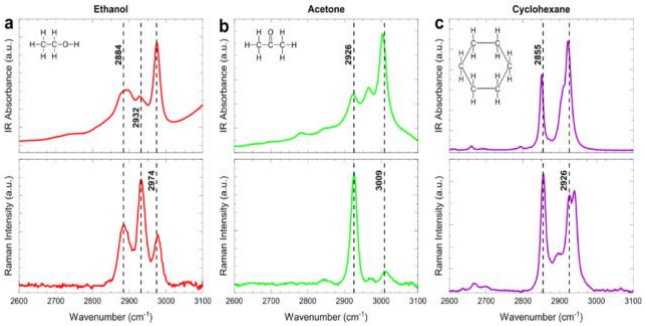

Fig 2. MIR and Raman spectra of (a) ethanol, (b) acetone and (c) cyclohexane obtained using the multimodal probe and plotted using the same frequency axis.

The main interest in terms of the complementary MIR and Raman multimodal analysis presents in our case the region of high wavenumbers and particularly the interval 2600–3100 cm^{-1}. It is available for spectral observations by both methods using the multimodal probe. The MIR and Raman spectra of organic solvents in the region 2600–3100 cm^{-1} acquired using the multimodal probe are plotted in Fig. 2. Raman spectra were preprocessed to eliminate strong background effects. Spectral quality in both cases is good and suitable for the data analysis. Although the spectra obtained with the multimodal probe are observed in a technically limited spectral region, combining them in one measurement produces a synergistic effect.
Further evaluation of the multimodal probe was performed using extra virgin olive oil and refined rapeseed oils. The corresponding Raman and MIR spectra are presented in Fig. 3. After applying spectral subtraction and baseline correction both probes produce Raman spectra of comparable quality for both studied oils.
In practice it can be necessary to recognize the product adulteration, when an expensive product is diluted or replaced by a low-cost substitute. For example, cheap rapeseed oil and high-quality olive oil. The presented MIR and Raman spectra of vegetable oils are similar, which is explained by their close chemical similarity. The fluorescence signal in this case represents an additional source of chemical information that can be used along with vibrational spectra to clearly discriminate two vegetable oils from each other. In this way depending on the sample we can focus on either the fluorescence or on the Raman signal applying appropriate mathematical processing to the data. Depending on the sample nature and the analytical problem being solved, various pairwise combinations of methods, and in some cases their triple combination, can result in a synergistic improvement.

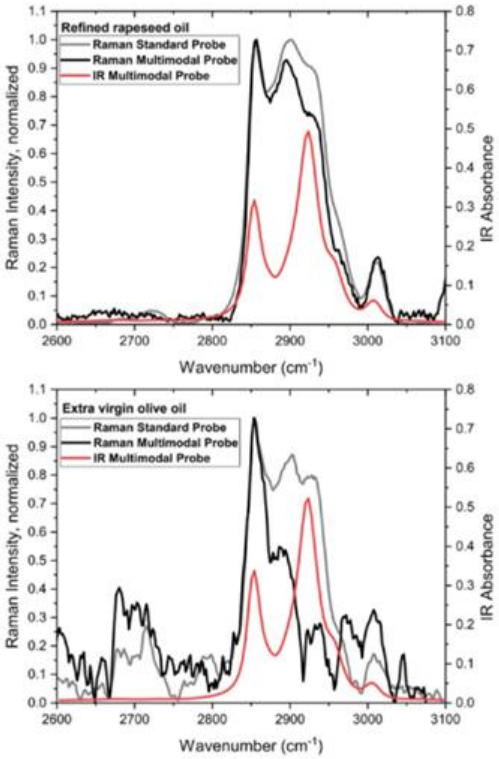

Fig 3. Raman and MIR spectra of the refined rapeseed oil after baseline correction of Raman spectra; and the extra virgin olive oil after baseline correction of Raman spectra.

The multimodal fiber optic probe proposed and tested in this work helps to reveal the advantages of simultaneous MIR and Raman spectroscopy, which is traditionally complicated by significant technical and methodical differences between these methods. The probe allows focusing the measurements at the same point and synchronizing them in time. This is very important for the analysis of processes and heterogeneous samples.
It was possible to obtain a good quality spectrum in the region 2600–3100 cm^{-1} after simple mathematical data processing. This spectral region is particularly valuable for the complementary MIR and Raman analysis, because it reflects a lot of information about the C–H stretching vibrations of aliphatic hydrocarbons. The possibility of simultaneous acquisition of MIR and Raman spectra can significantly increase the analytical importance of this region.