Development of New Macroscopic Raman Spectrometer and Application to Quantitative Analysis

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1. Introduction

Sample preparation for Raman spectroscopy is generally considered to be much easier than that for infrared spectroscopy. In addition, there is an increasing need for the type of qualitative and quantitative information that Raman spectroscopy can provide. For routine measurements, it is important that highly accurate and reproducible results can be obtained in a convenient manner. In the case of microscopic Raman systems, the laser spot size is generally less than 1 μm, and the information obtained is extremely localized. In addition, it sometimes takes time and effort to focus on a sample.
In order to overcome these barriers, we have decided to develop the Macroscopic Raman Spectrometer, which is compact and easy to use. In this presentation, the details of this system are introduced, and real world application results are described.

2. Overview of Macroscopic Raman System

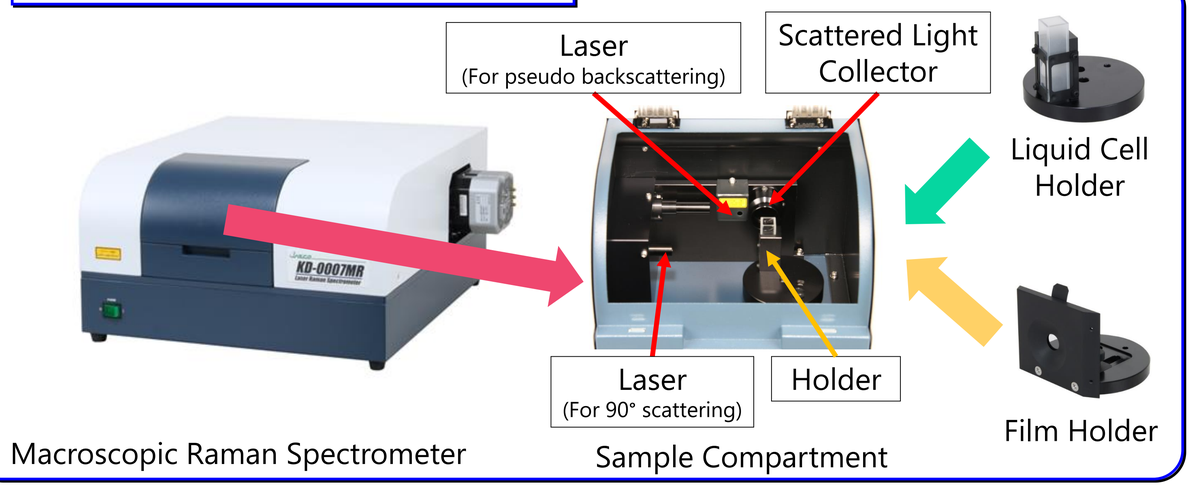
Features

- Desktop size
- Various sample holders (for liquid, films, etc.)
- 1064 nm excitation available

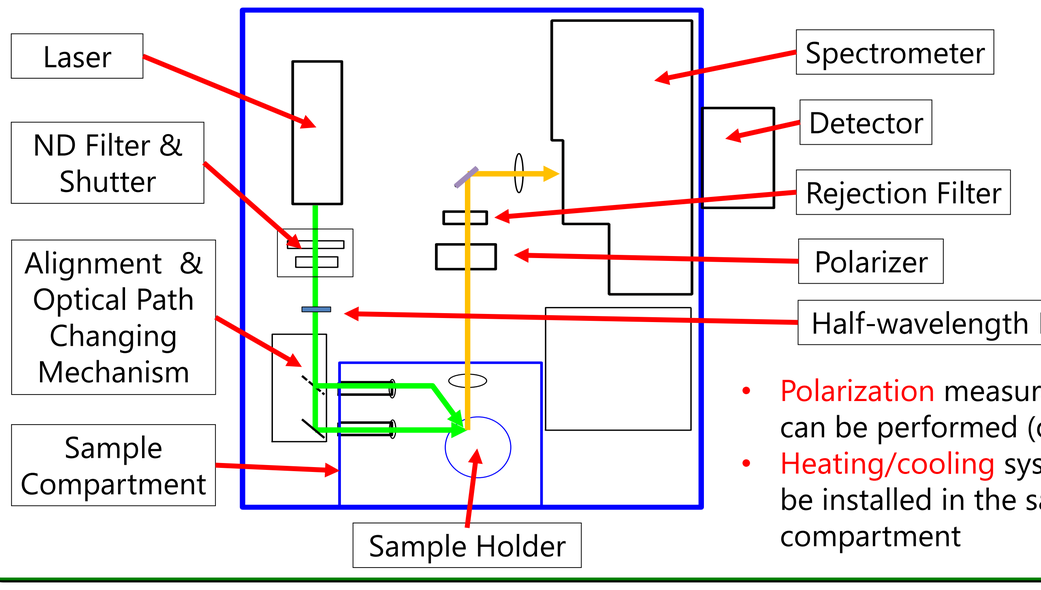
Specifications

- Dimensions: W520 mm x D620 mm x H300 mm
- Measurement spot size: 50-100 μm
- Measurement method: 90° scattering and pseudo backscattering
- Example mountable laser wavelengths: 405, 457, 532, 633, 785 and 1064 nm
- Lowest measurable Raman shift: 50 cm^{-1}
- Laser safety: Interlock system is standard
- Connection with PC: USB

System Image and Accessories



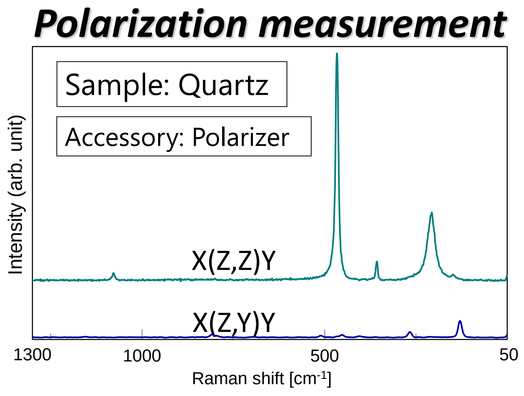
Block Diagram of Macroscopic Raman Spectrometer



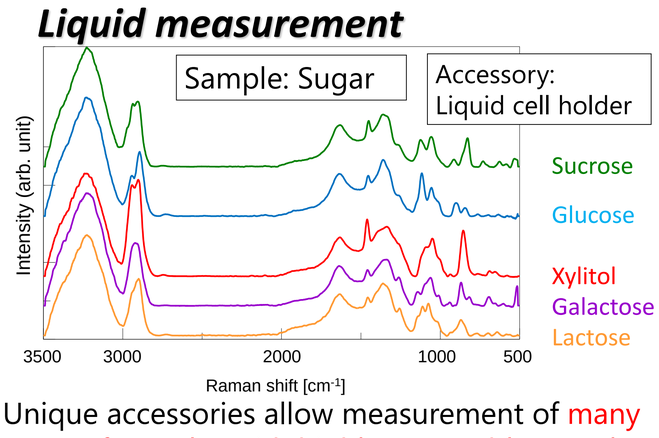
- Polarization measurements can be performed (optional)
- Heating/cooling system can be installed in the sample compartment

3. Spectra Measured Using Various Accessories

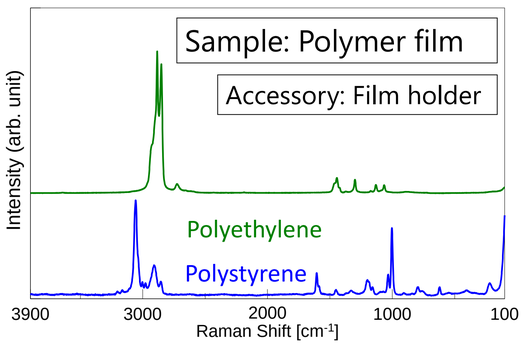
Polarization measurement



Liquid measurement

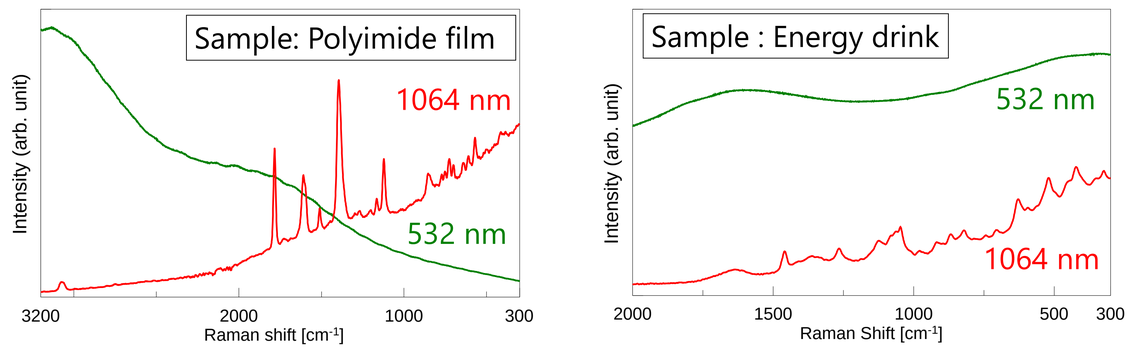


Film measurement



- Unique accessories allow measurement of many types of samples with highly repeatable sample placement.
- Crystal orientation can be analyzed using a polarizer.
- Many kinds of liquids can be identified using a liquid cell holder.
- Polymer films can be easily measured using a film holder. In addition, by measuring a polystyrene film, the instrument can be validated in compliance with standards such as JP (Japan Pharmacopoeia).

4. Measurement of Samples Exhibiting Strong Fluorescence Using 1064 nm Laser Excitation

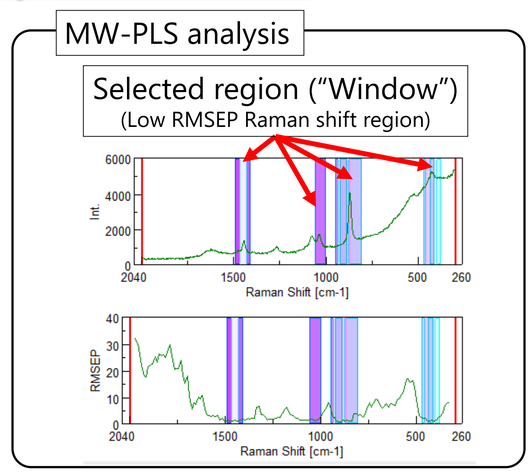


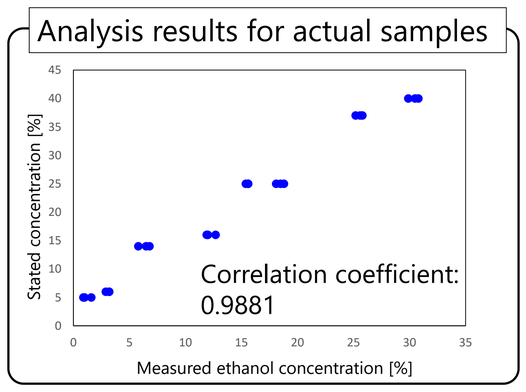
- Spectra of a polyimide film and an energy drink were measured using 532 nm and 1064 nm laser excitation.
- For 532 nm excitation, strong fluorescence interferes with the Raman signal.
- A normal spectrum of polyimide can be measured under 1064 nm excitation (left).
- A spectrum of the fructose additive in the energy drink can be measured under 1064 nm excitation. (right)

5. Quantitative Analysis of Liquid Content

We performed a quantitative analysis of the ethanol content of different drinks. When drinks such as beer and whisky are measured under 532 nm excitation, strong fluorescence can make the analysis difficult. Therefore, the measurements were performed using a 1064 nm laser.

To produce a calibration model using different-concentration ethanol solutions, we applied the partial least squares (PLS) method to avoid the loss of precision due to interfering peaks that occurs with conventional quantification methods. Due to high repeatability of sample placement, the model showed a high correlation coefficient (0.9992).
We then applied the moving-window PLS (MW-PLS) method, which automatically finds calculation regions with a low RMSEP by continuously scanning the entire wavenumber range. Using this method, the correlation coefficient increased to 0.9996. Therefore, the combination of the Macroscopic Raman System and MW-PLS is a powerful tool for quantitative analysis of additives in liquids.





A quantitative analysis of the ethanol content of actual samples was then performed. The samples used were beer (stated alc. 5%), Korean makgeolli (6%), white wine (14%), Japanese sake (17%), Japanese spirits (25%), Korean spirits "JINRO" (25%), whisky (37%) and brandy (40%).
As seen in the figure on the left, a high correlation was found between the measured and stated concentration, although the correlation for the calibration model is higher.
We are therefore considering methods for further improving the accuracy for actual samples.

6. Summary

- The Macroscopic Raman Spectrometer is compact and designed to excel at general-purpose and routine analysis because of its ease of operation.
- The excitation wavelength range can be extended to match high-end models, and optimized holders for different types of samples are available with this system. Even a near-infrared laser (1064 nm) can be installed.
- Polarization and temperature-dependent measurements are also available.
- This system can also be used for quantitative analysis due to the high repeatability of sample placement.
- In this presentation, this system was combined with the MW-PLS method to quantify the alcohol content in drinks.