DOI 10.5162/SMSI2023/P47

Portable Raman sensor systems for life sciences and agri-photonics – from light sources to field measurements –

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Raman spectroscopy is a well-established non-invasive label-free optical measurement technique for the analysis of numerous substances in various application fields, e.g., process control, food safety and quality control, the detection of hazardous compounds, e.g., explosives, and narcotics, and the analysis of minerals. Finally, also the application in medicine, e.g., for point-of-care diagnostics, is promising.

Nevertheless, in several fields, when disturbing signals like fluorescence from the sample itself occurs or background light from the sun or artificial light sources cannot be avoided, the weak Raman signals are obscured. Beside mathematical techniques to simulate the disturbing signals and subtract the obtained background spectra from the measured signals, physical approaches have the advantage of a direct separation of desired and interfering spectral contributions. Here, beside the selection of the excitation wavelength or the utilization of the different temporal behavior of fluorescence and Raman signals, several methods using multiple laser wavelengths within a narrow spectral range for the excitation of the Raman effect can be implemented. The underlying effect in this case is that the Raman signals follow the change in the excitation wavelength whereas the background signals remain mainly constant.

Shifted excitation Raman difference spectroscopy (SERDS) uses two excitation lines typically with a spectral distance of about the full-width at half-maximum of the Raman signals under study. For solids and liquids this value amounts to 10 cm^{-1} and it corresponds to a spectral distance of 0.25 nm at a commonly used excitation wavelength like 488 nm, whereas the value at 785 nm excitation is 0.60 nm. Lasers based on atomic transitions like the Argon-ion laser cannot be tuned over such spectral distances and solid-state lasers with a broader gain profile like Ti:sapphire lasers require moving mechanical parts to adjust the respective wavelengths. Here, diode lasers and diode laser based light sources with implemented wavelength stabilization and the option for spectral tuning provide a compact and robust solution, e.g. with respect to portable instruments for field deployment.

In this contribution, compact dual-wavelength diode lasers and diode laser based light sources developed for SERDS will be presented together with their implementation into portable Raman sensor systems widely usable from measurements on agricultural fields to applications in hospital environments, e.g., for point-of-care measurements or therapy monitoring.

The light sources used for SERDS in the red and near-infrared spectral range are based on monolithic dual-wavelength diode lasers. The dual-wavelength operation is realized using two implanted Bragg gratings and respective ridge waveguide (RW) branches which were coupled using a Y-branch coupler followed by a common output section. The switching between the two wavelengths can be performed directly by applying an injection current to the respective RW-section. Herewith, a fast switching up to the kHz-range is easily possible. The spectral distances between the two wavelengths can be adjusted by implemented resistor heaters located above the gratings. Using this concept, one-chip diode lasers with emission wavelengths of 671 nm and 785 nm were realized with output powers up to 200 mW.

Devices for the green and blue spectral range are developed based on frequency doubling of the laser emission of distributed feedback or distributed Bragg reflector RW-lasers. Here, light sources at 488 nm, 515 nm, and 532 nm with output powers up to 50 mW were realized. Due to the fact, that the temperature-related spectral tuning of the grating wavelength and the phase-matching wavelength of typically used Li:NbO$_3$-crystals are comparable, the tuning can be performed by changing the temperature of the whole device.

The above-described laser devices were implemented into in-house developed and manufactured turn-key-systems, that provide the necessary heat removal, temperature control, and injection and heater currents for laser operation. The emitted laser radiation can be transmitted into the Raman setup either by using free space optics or fiber coupling. The control of the whole system is realized via a standard USB interface and a graphical user interface based on in-house developed software.

Such a turn-key-system equipped with a 785 nm dual-wavelength Y-branch DBR-RW-laser was implemented into a measurement system inside a rugged housing dedicated for Raman measurements on soils in the field. Via a fiber coupler, the light was transferred into a commercial transfer optic from InPhotonics (Raman probe II^{TM}), which is designed for a 180° backscattering geometry. The probe contains the necessary optical filters for the suppression of spontaneous emission from the diode laser and the Anti-Stokes shifted Raman photons as well as Rayleigh scattered light. The Stokes-shifted Raman photons are coupled into a 300 µm optical fiber and transferred to a compact Raman spectrometer. All assemblies are supplied by means of a rechargeable battery with a nominal voltage of 12 V and a capacity of 20 Ah. With this system, successful measurement campaigns on agricultural fields were performed showing the potential to detect carbonates and soil organic matter.

A similar system was manufactured to measure carotenoids using resonance Raman enhancement at an excitation wavelength of 488 nm. Here, the target was to monitor the antioxidant level of human skin in vivo to gain data on human health status and provide diagnostic information during medical treatments and accompanying medical therapies. Again, the light source was implemented into a turn-key-system and the light was fiber coupled into an in-house developed optical transfer system. A calibration procedure using skin phantoms containing varying ß-carotene levels demonstrated a limit of detection of 0.03 nmol g^{-1}, which is well-below the typical concentration of carotenes in skin.

Beside the technical description, examples for field and clinical measurements will be presented. An outlook will be given with respect to other targets and applications and the potential to simplify the setup by implementing a filter-based detection concept.

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Acknowledgment:

This work was realized within the projects I4S-RaMBo (031A564C, 031B0513C), the projects Exasens (13N13858), Freshscan (16SV2334), and iCampus (16ES1132) funded by the Federal Ministry of Education and Research (BMBF) and it was supported by the Einstein Stiftung, Berlin, in the project Hautscan (A-2011-88). This work was also partly funded by the BMBF under the project reference number 16FMD02 (Research Fab Microelectronics Germany - FMD). Moreover, the work was supported by the European Commission in the project MIB (667933-2) and USER-PA (FKZ 2812ERA039).