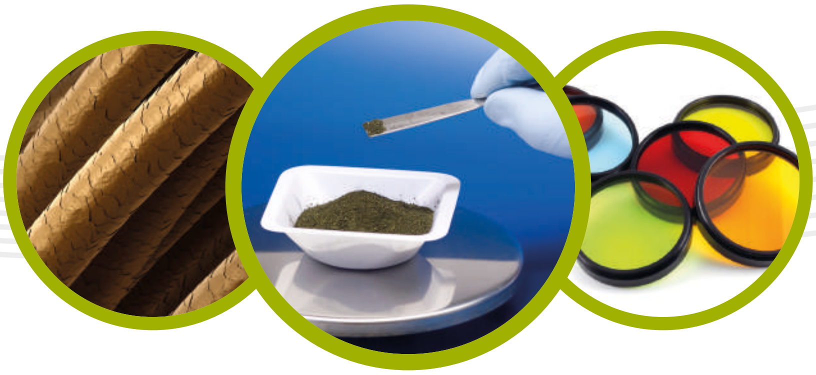
APPLICATION NOTE PA301

Widely scanning infrared lasers for photoacoustic detection of solids



Although superior results have been achieved with the combination of Fourier transform infrared (FTIR) spectrometers and cantilever-enhanced photoacoustic detection, some applications demand even higher sensitivity. This application note demonstrates the use of a broadly tunable external cavity quantum cascade laser (EC-QCL) source in place of a typical FTIR spectrometer in photoacoustic detection of solid samples. A superior signal-to-noise ratio (SNR) was achieved with the EC-QCL source. Further, the use of a modulated broadband source with infrared filters is discussed.

Introduction

The recent achievements in the field of QCLs have introduced vast opportunities in IR spectroscopy. More and more QCL chips are commercially available in wider range of wavelengths, also with more options in broadly tunable EC-QCL configuration. A single EC-QCL can offer a tunability of few hundred wavenumbers and multiple EC-QCLs can be combined to cover over thousand wavenumbers in mid-IR (800-1800 cm^{-1}), which is basically the whole fingerprint region used in materials identification. EC-QCLs enable multi-component infrared spectroscopy analysis, which has previously been limited to FTIR or dispersive spectrometers.

Advantages of EC-QCL sources against FTIR spectrometers

EC-QCLs bring several advantages in photoacoustic detection against FTIR or dispersive spectrometers. First obvious advantage is the higher output power: EC-QCLs can provide over hundred mW of optical power with a narrow line width, while the blackbody IR source of an FTIR typically produces notably less than one mW per wavenumber on average. The maximal resolution of EC-QCLs varies from <1 cm^{-1}, which is typical to pulsed mode lasers, to ultra-high resolution of continuous wave EC-QCLs, typically < 0.003 cm^{-1}. In practice, EC-QCL can yield up to five orders of magnitude better SNR compared to FTIR depending on the laser power and line width. Further, the EC-QCL beam can be narrowed down to a small spot without losses in throughput. The spectral radiance of an EC-QCL source can be even seven orders of magnitude higher than that of the FTIR source. Also, EC-QCLs can be modulated with a constant frequency over the full wavenumber range, which enables more sophisticated depth profiling experiments.

Fig 1. A PA301 photoacoustic detector (Gasera, Ltd) and a LaserTune EC-QCL source (Block Engineering, LLC).

Measurements

A PA301 (Gasera, Ltd.) photoacoustic detector for solid, semi-solid and liquid samples and a LaserTune (Block Engineering, LLC) EC-QCL source covering 970-1646 cm^{-1} with a maximum optical power of approximately 2 mW were used in the experiments. The EC-QCL was electrically amplitude modulated by altering the current of the QCL chip and the laser beam was guided to the detector with an adjustable plane mirror. A carbon black sample was used for normalization in all measurements and helium was used as a carrier gas inside the photoacoustic cell. A Bruker Tensor 37 FTIR spectrometer was used for comparison.

Fig 2 shows the spectra of a same polyethylene sample measured with EC-QCL and FTIR setups. The spectra are similar, only difference being the SNR. The SNR of the polyethylene sample measured with the EC-QCL setup is almost ten times higher, which corresponds to 100 times longer measurement time with the FTIR setup to achieve the same SNR. The difference in the noise level is also clearly visible in the spectra, especially when investigating the spectral range between 1000 and 1100 cm^{-1}. Fig 3 shows the measured spectra of a same single 8 mm piece of hair measured with the EC-QCL and FTIR setups. A fiber holder accessory was used to hold the hair fiber in place and also for an enhanced signal in both setups. While the FTIR spectrum shows mainly noise with some possible broad features buried under the noise floor, clear peaks are visible in the EC-QCL spectrum of the hair sample. Further, all the spectral peaks in the EC-QCL spectrum can also be identified and assigned to certain vibrational states.

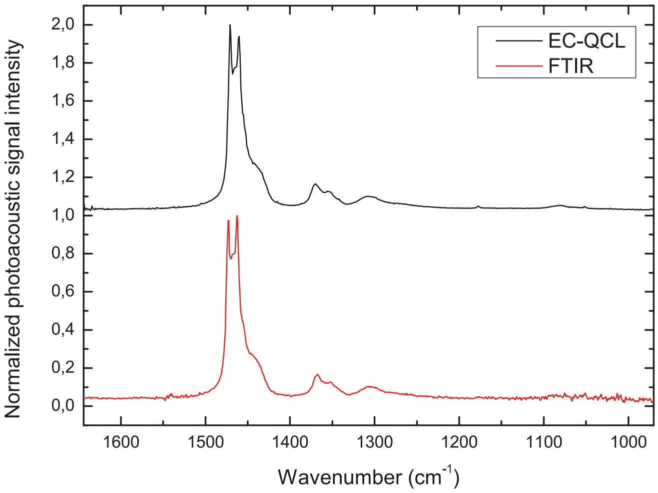


Fig. 2. A polyethylene disk (1 cm in diameter, 2 mm thick) measured with EC-QCL and FTIR setups.

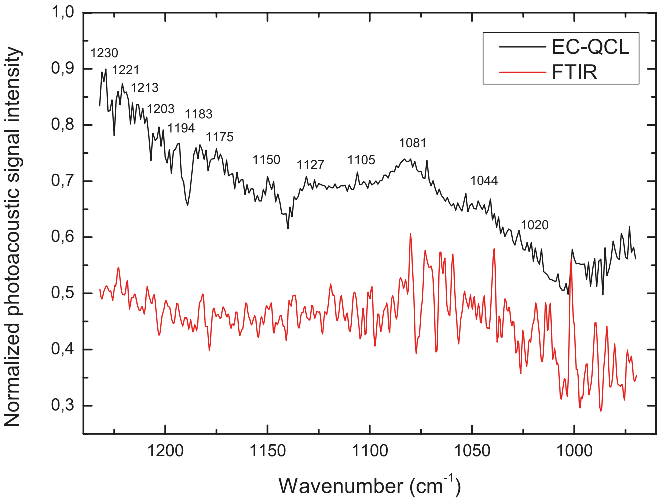


Fig. 3. A single hair fiber (8 mm long, 50 µm thick) measured with EC-QCL and FTIR setups.

Broadband source with infrared bandpass filters for cost-efficient monitoring

Another alternative for the use of FTIR in photoacoustic detection of solids is to use a broadband source with infrared bandpass filters. Infrared filters offer a cost-effective solution for specific applications, in which only certain infrared peaks, or ratios of certain peaks, have to be monitored. One clear application is the monitoring of the polymerization level, for example the ratio of CH_3 and CH_2 vibration peaks in polyethylene. Possible applications fields include, for example, manufacturing process control and quality control. Standard infrared filters are available in various center wavelengths with a narrow bandpass to cover the desired spectral features. Further, tunable filters are available for more detailed analysis.

Conclusions

EC-QCLs can bring clear advantages in photoacoustic detection of solid samples. EC-QCL-PAS would bring advantage especially in cases that involve samples, which require high resolution, are too small for conventional FTIR with a reasonable SNR or where high SNR is required from low absorbance samples. Of course, the case could be a combination of all these attributes. This experiment proves that photoacoustic spectroscopy of solids does not necessarily require an FTIR spectrometer, although the price of an EC-QCL is relatively high and the scanning ranges are limited.