Application Note AN #94

Photoacoustic Spectroscopy

Introduction

The photoacoustic (PA) effect is based on the absorption of infrared radiation by the sample which is heated up and the absorbed heat is transferred into the surrounding gas. Because the FT-IR measurement signal is modulated by the interferometer scanner pressure waves are created in the surrounding gas which are detected by a sensitive microphone and converted into an electrical signal. So the sample itself together with the PA cell becomes the detection system. The measurement is non-destructive, the signal is not degraded by the sample morphology and typically no sample preparation will be required.

History

The PA effect was detected in the 19th century and explored for its spectroscopic usability in the visible spectral range ca. 80 years ago. With the availability of FT-IR spectrometers it became applicable in the infrared spectral range as well. We are proud to note that the first FT-IR PA spectrum was published in 1978 using a Bruker IFS113v FT-IR spectrometer [1]. The principles of the photoacoustic measurement cell is shown in figure 1.

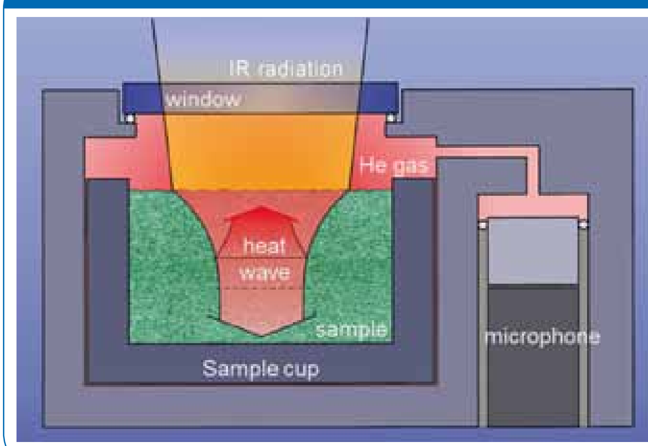

Figure 1: Principle of photoacoustic measurement cell.

Although PA spectroscopy (PAS) has advantages compared to diffuse reflectance spectroscopy (DRIFTS) and the attenuated total reflectance (ATR) measurement technique, it was not widely used in the past. It was applied to such types of samples for which the standard measurement accessories failed or were difficult to use. The major reason was the lack of the required sensitivity.

New PA Cell

Now, with the new microphone design comprising a MEMS cantilever coupled with a laser readout interferometer the measurement sensitivity and especially the PA signal detection speed were significantly enhanced. The new PA cell A560-K/Q is based on the product from the company Gasera [2] and was adapted mechanically and electrically to the Bruker TENSOR and VERTEX FT-IR spectrometer QuickLock™ sample compartment mechanism and DigiTect™ technology. In figures 2 and 3 the Bruker VERTEX 70 FT-IR spectrometer with the A560-K/Q placed inside the sample compartment is shown. The impressive mid Infrared signal-to-noise ratio achieved with such an instrument combination is demonstrated in figure 4.

Figure 2: Overview picture of the VERTEX 70 FT-IR spectrometer with the photoacoustic measurement cell placed inside the sample compartment of the VERTEX 70 and control electronics

Figure 3: Detailed look at the PAS cell mounted inside the spectrometer sample compartment showing the inserted sample carrier.

PA Application

A detailed look at the PA cell with its opening for the sample carriers together with available sample carriers is shown in figure 5. The spectra show PA application examples of black polymer foam in the mid IR (see figure 6) and Aspirin™ tablet in the far IR (see figure 7) which are typically difficult to measure with standard IR measurement techniques and accessories. The second spectrum is of

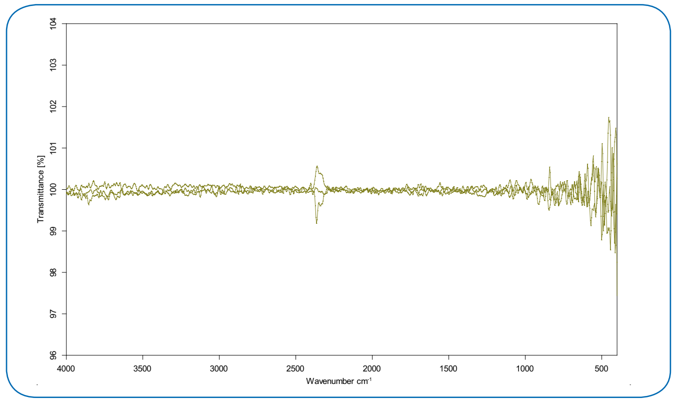

Fig. 4: The 100% lines show the achieved signal to-noise-ratio using pressed carbon black powder which is typically used for reference purposes. A noise level of less than 0.1%T at 2000 cm^{-1} using the standard internal IR source and KBr beamsplitter at 8 cm^{-1} spectral resolution and less than 20 sec measurement time will be achieved with the VERTEX and TENSOR FT-IR spectrometer series.

particular interest because it was impossible to get reasonable far IR spectra within an acceptable measurement time with previously used PA cells due to their comparatively low measurement sensitivity.

Because the penetration depth of the IR radiation depends on the modulation frequencies and thus from the interferometer mirror scanning speed it is possible to measure depth profiles from the investigated sample. Publications made more than 10 years ago were already [3]. The VERTEX series instruments with its optional step san and slow scan functionalities are the ideal measurement tools for such demanding and sophisticated depth profile application examples.

Operation of the A560-K/Q PA Cell

The PA cell provides a sample space for a maximum sample size of 10 mm diameter and 9 mm height. The supplied sample cups are shown in figure 8. It is recommended to purge the sampling volume with a small flow of He gas in order to achieve the best spectrum quality. But due to the

Figure 5: Photoacoustic cell mounted on the QuickLock sample compartment base plate showing the opening for insertion of the sample carrier together with different types of the sample carriers

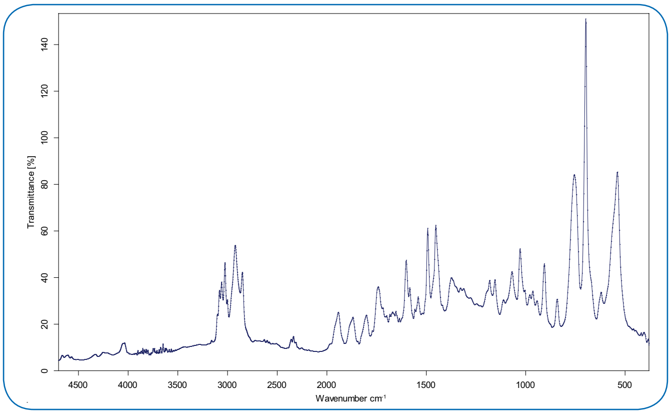

Fig. 6: The spectrum shows a typical photoacoustic (PA) spectrum of a dark Polystyrene foam measured with 4 cm^{-1} spectral resolution and 4.5 min data acquisition time using the standard IR source and beamsplitter.

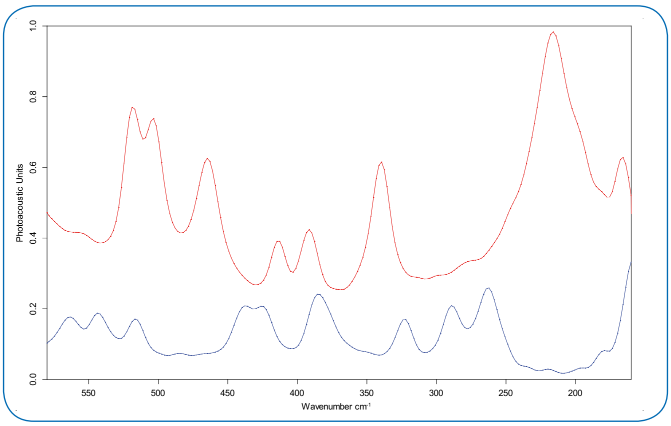

Fig. 7: Photoacoustic (PA) far IR spectra of an Aspirin™ tablet (red) and the pharmaceutical active agent Paracetamol (blue) (spectra are off-set for clarity) measured on the VERTEX 70 with the PA cell A560-K/Q under He gas purge and ca. 3 min. data acquisition time. The sample has been measured without prior preparation and treatment and no contact to the measured surface was applied.

high sensitivity of the novel cantilever sensor, the A560-K/Q can be used with dry air or dry nitrogen purge or even without purge as well. By extending the data acquisition time comparable signal-to-noise-ratios are achievable.

A560-K/Q Package:

- PA cell including QuickLock sample compartment mount
- DigiTect electronics and electrical connection cable
- Power supply unit
- Adaptor and tools for He gas purge
- Accessory box containing sample cups, sample holders, reference carbon black, tweezers, etc.
- Storage case

Usefulness of PA:

- High IR light absorbing samples
- Pharmaceutical active agents and fillers
- Carbon filled rubber and dark elastomers
- Polymer pellets and foams
- Paper and wood
- Tissue and hair samples
- Difficult to prepare samples
- Cosmetics and pastes
- Paint pigments
- Surface analysis and depth profiling

Figure 8: The picture shows the supplied three different sample mounts together with the available sample cups

Outlook:

The described new photoacoustic spectroscopy (PAS) accessory provides significantly enhanced sensitivity and measurement speed compared to earlier used PA cells. These advantages will cause a renaissance for this very interesting measurement technique and will open the doors for its use in a much wider range of FT-IR application. In particular it will make difficult to prepare samples applicable and demanding research application more easily possible.

References:

[1] G. Busse et al; Infrared Phys. 18, 631 (1978)
[2] J. Kaupinnen et al; Appl. Spectroscopy 57, 1087 (2003)
[3] R. Palmer et al; Bruker Application Note #48 (1998)

www.brukeroptics.com

Bruker Optics Inc.
Billerica, MA · USA
Phone +1 (978) 439-9899
Fax +1 (978) 663-9177
info@brukeroptics.com

Bruker Optik GmbH
Ettlingen · Deutschland
Phone +49 (7243) 504-2000
Fax +49 (7243) 504-2050
info@brukeroptics.de

Bruker Optik Asia Pacific Ltd.
Hong Kong
Phone +852 2796-6100
Fax +852 2796-6109
asiapacific@brukeroptics.com.hk