A. Photoacoustic Detector

FTIR photoacoustic detector accessories are currently manufactured by Bio-Rad (Cambridge, MA USA) and MTEC Photoacoustics (Ames, IA USA) for use with FTIR spectrometers. This discussion will be limited to the MTEC model 200 unit because it is available from distributors and all major FTIR companies throughout the world. Figure 3 isa photograph of the MTEC unit which mounts directly in the sample compartment of the FTIR's optical bench.


Fig. 3. MTEC Model 200 photoacoustic detector mounted on a Nicolet sample compartment baseplate.

The spectral range of a photoacoustic detector depends only on the transparency of the sample chamber window. With suitable windows a detector can operate from the UV to the far-infrared. The most common window material is KBr (UV through mid-infrared), but quartz (UV through near-infrared), CsI (UV - 200 $cm^{-1}$), ZnSe (near-infrared - 560 $cm^{-1}$), and polyethylene (far-infrared) are also frequently used.

The maximum MTEC sample holder dimensions are 10.7 mm in diameter by 9.0 mm deep. Most analyses require a much smaller sample volume. Sample holder inserts are provided to displace unused gas volume and boost the signal level which is proportional to the reciprocal of the gas volume.

Only the central region of the MTEC sample chamber is irradiated by the infrared beam because the photoacoustic detector's mirror causes a factor of two diameter reduction in the FTIR beam focal-spot diameter, this size is reduced to a 5 mm diameter inside the detector sample holder at the focal plane position which is approximately 1.0 mm to 1.5 mm below the detector window. Consequently, the sample volume that is actually analyzed is approximated by the focal area times the sampling depth, L, which depends on the modulation frequency.

When helium is used in the sample chamber, the modulation frequency range of the MTEC model 200 extends from below 1 Hz to nearly 10 kHz. The use of air results in a high frequency cut-off at approximately 3 kHz. Measurements at higher frequencies in air are difficult due to a substantial loss in sensitivity after the detector goes through its first Helmholtz resonance.13 This type of resonance is due to gas oscillations in the tube

between the sample and microphone chambers. Acoustic resonances in the sample chamber itself do not occur because the chamber dimensions are too small when a sample is in place.

Helium purging of the sample and microphone volumes enhances sensitivity by a factor of 2 to 3, allows higher frequency operation, and removes moisture and $CO_2$. Moisture and $CO_2$ cause spectral interference as well as photoacoustic signal generation interference. The latter interference is caused by a phase difference between photoacoustic signals generated by absorption in gases or vapors versus solids. The phase shift of gas or vapor signals leads to increased noise in spectra.

Many samples such as coal evolve water vapor after being sealed in the sample chamber. In such cases, a cup of desiccant is placed in the sample holder beneath the sample cup. Magnesium perchlorate is an excellent desiccant for this purpose and typically can be used for a day of operation without renewal.

It is important to note that moisture and $CO_2$ bands in spectra can be due to the presence of vapor and gas in both the FTIR optical path and the photoacoustic detector. The source location can be identified by recognizing that contamination in the FTIR causes negatively pointing (transmission-like) moisture and $CO_2$ bands in FTIR-PAS spectra, whereas bands are positively pointing (absorbance-like) if contamination is in the detector itself. These observations should be used as a guide in purge and desiccant operations.

A final instrumental consideration is provision for normalizing spectra to account for spectral variations in the FTIR source and optics, and for any sensitivity changes that may occur from day to day due to changes in source intensity or optical alignment. Normalization is performed by computing the ratio of the sample spectrum to a carbon black spectrum. The latter spectrum is best obtained with a MTEC reference standard consisting of an absorber element with a stable carbon black coating that is permanently mounted and protected in a dedicated sample holder. Loose carbon black is not a good standard for general use because its signal intensity varies as the powder settles and it is easily spilled or blown out of the sample cup. In some instances, a glassy carbon or graphite standard is desirable (See Section V.E.).

Many FTIR data systems erroneously label the normalized PAS spectrum as a "transmittance" spectrum rather than an absorbance spectrum. The FTIR data system should be commanded to change the label to absorbance prior to processing the data because many computer processing routines will either not operate or will produce incorrect results if a spectral file carries the wrong ordinate axis designation.

The signal-to-noise ratio of FTIR-PAS measurements depends on the FTIR spectrometer's performance level as well as the detector sensitivity and noise level, and signal generation efficiency of the sample. Low FTIR mirror velocities produce low modulation frequencies and more efficient signal generation due to the slow thermal response of samples. Low modulation frequencies yield higher signal-to-noise spectra for a FTIR's mirror servo-control system. A high infrared beam intensity is also beneficial and requires a large source aperture, high source intensity, and low f number optics. All commercial FTIR systems provide combinations of these beneficial features to an extent that good FTIR-PAS measurements can be performed assuming that the FTIR is in good operating condition.