Agilent linearized MCT detectors for superior photometric accuracy and sensitivity

Technical Overview

Advantage statement

Agilent's linearized mercury cadmium telluride (MCT) detector technology delivers substantial advantages for quantitative measurements. It extends the linear range of the detector versus energy flux relationship by about a factor of ten above the range that can be obtained with a standard MCT detector, while still maintaining high photometric accuracy. The result is a wider concentration range when performing quantitative measurements, so you can avoid time-consuming dilutions, providing greater productivity and lower running costs for your laboratory.

Introduction

MCT detectors have been widely used for qualitative applications in Fourier transform infrared (FTIR) spectroscopy due to their ability to provide high quality infrared spectra. These detectors have proved to be particularly useful to infrared spectroscopists for measurements in conditions where the energy flux incident on the detector is limited by the sample or an accessory (that is, when using an ATR accessory or highly absorbing sample). However, MCT detectors have a limited applicability for quantitative measurements in real-world situations, as they exhibit a non-linear response with regard to energy flux in cases of high incident energy, leading to errors in photometric measurements. This is demonstrated in Figure 1, which shows a typical response curve for an MCT detector versus energy flux (solid line). Consequently, to maintain photometric accuracy, spectroscopists traditionally only use the data from the limited range of energy flux where MCT detectors exhibit linear behavior.

Agilent Technologies

Agilent is able to extend the linear response range of MCT detectors by approximately one order of magnitude over non-linearized detectors. These modified MCT detectors result in spectra with higher photometric accuracy and better sensitivity than those obtained from non-linearized detectors. This paper discusses the quantitative errors in spectral measurements caused by detector non-linearity, describes a mechanism to correct MCT detectors for this behavior, and provides a demonstration of the improvements in quantitative results and sensitivity that can be achieved by using Agilents's linearized MCT detectors.

Experimental

All spectra were collected on an Agilent Cary 660 FTIR spectrometer by co-adding 16 symmetric interferograms in transmission mode, computing to single-beam spectra using a medium Norton-Beer apodization function, and ratioing to open-beam background spectra collected and computed under the same conditions.

Traditional MCT response curves

MCT detectors respond linearly to increasing incident energy only for low energy flux, beyond which the response starts to deviate below the ideal linear response. When measuring the spectra of actual samples, this will result in spectral distortions that produce artifacts in the wavenumber regions where the detectors are non-linear, as shown in Figure 1.

To maintain photometric accuracy, a spectroscopist must limit the energy flux of the spectrometer to the energy flux corresponding to the overlap of the dashed and solid lines. Some accessories naturally limit the energy flux, but if the energy is too high, additional attenuation may be required.

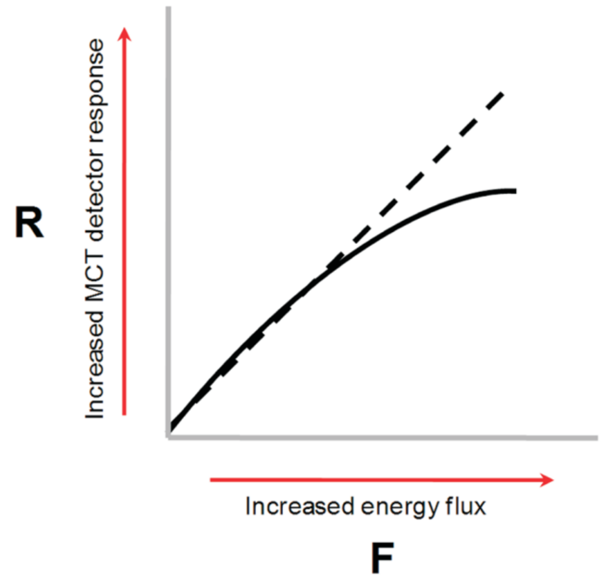

Figure 1. MCT detector response (R) versus incident energy flux (F) for a typical MCT detector (solid line). Linear response is indicated by the dashed line

Non-linear response can be observed spectroscopically by examining a single-beam spectrum generated by an MCT detector, as displayed in Figure 2. The single-beam spectrum was collected with a high-sensitivity (narrow band) MCT detector with a standard pre-amplifier as an open-beam spectrum with just sufficient attenuation to prevent A/D overflow. The spectrum in Figure 2 shows a region of non-physical energy below the detector cutoff at 600 cm^{-1}, indicating detector saturation. This region of the spectrum should return to 0 response units if the detector is exhibiting linear behavior. A detector is said to be saturated when its incident energy is high enough to cause non-linear response. As a general 'rule of thumb', the amount of detector saturation should be less than 5% (the response of the non-physical energy ratioed to the apex of the single-beam spectrum) to maintain photometric accuracy, but the lower this ratio the better. In Figure 2, the saturation level is 8%, which is too high for measurements to be quantitatively accurate.

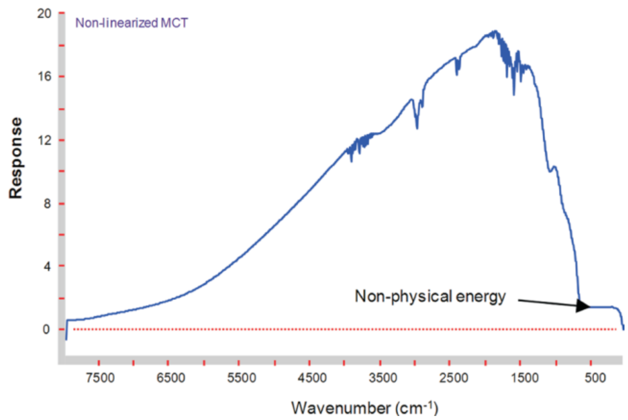

Figure 2. Single-beam spectrum of a saturated (non-linear) narrow band MCT detector. The non-physical energy below the detector cutoff at 600 cm^{-1} (indicated by the non-zero response on the y-axis below 600 cm^{-1}) is indicative of detector saturation

A saturated MCT detector can be brought into linear response by further attenuating the beam. The red single-beam spectrum in Figure 3 was obtained as a result of reducing the energy flux by an additional factor of 8 by inserting three 50% attenuating screens into the infrared beam. The saturation of the detector has been reduced to 1%, at which level spectra with good photometric accuracy should be produced.

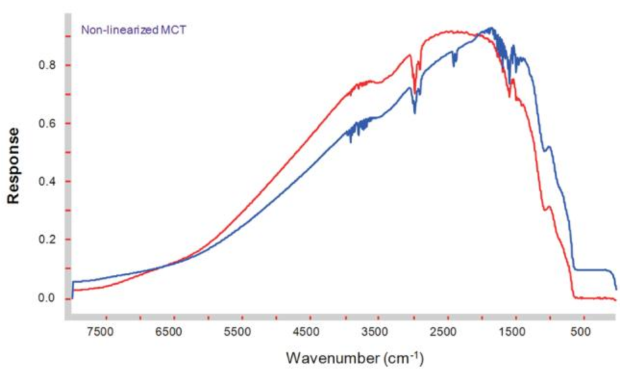

Figure 3. Overlay of a single-beam spectrum obtained from a non-linearized MCT detector with adequate attenuation to prevent detector saturation (red), and the single-beam spectrum from Figure 2 (blue). With additional attenuation, the non-physical energy below the detector cutoff has been reduced to ~ 0

Spectra of a polystyrene film recorded with the non-linearized MCT detector at the two attenuation levels of Figure 3 are displayed in Figure 4. The absorbance intensities in the spectrum recorded at lower attenuation (with 8% saturation) are lower by as much as an absorbance of 0.6 compared to the spectrum recorded at higher attenuation (1% saturation). Absorbance intensities are lower for a saturated detector since, its response is less than it would be for a linear detector. Errors in absorbance intensities are higher for strong absorbance bands.

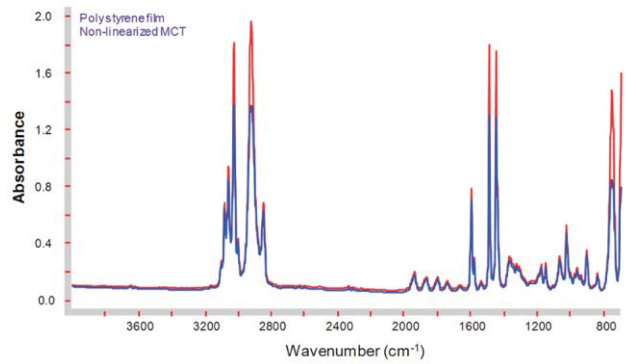

Figure 4. Spectra recorded from a polystyrene film with the same attenuation levels in Figure 3. The spectrum recorded with 8 times more attenuation (red) exhibits better photometric accuracy (as indicated by higher absorbance intensities) compared to the spectrum with only enough attenuation to prevent A/D overflow (blue)

Methods of linearizing MCT response

The response of MCT detectors to incoming energy flux can be expressed as:

$$dR/dF$$

where dR is the incremental change of detector response and dF is the incremental change in energy flux. When the detector behaves in a non-linear mode, as shown in Figure 1, dR/dF will not be a constant. The MCT detector response can be linearized with a detector pre-amplifier that generates non-linear gain:

$$dG/dR$$

such that the product:

$$dG/dR * dR/dF$$

is constant over a wide range of energy flux (F). This simply means that a factor is applied at different points to remove the non-linearity and adjust the response of the MCT detector to follow the linear response line (dashed), as shown in Figure 1. The pre-amplifier must be designed so that it does not introduce noise beyond that of the MCT element, and since each MCT detector element has a different response to energy flux, the pre-amplifier must be individually calibrated to each MCT detector.

Many schemes have been proposed to correct the non-linearity of MCT detectors through both software and electronics. The use of software to process the detector's signal is fundamentally flawed, as it alone cannot compensate for detector saturation. An appropriately designed spectrometer acquisition system will electronically filter the detector's output to avoid spectral aliasing. This alters the detector signal so that the precise behavior of the detector's output versus time is unrecoverable. In practice, there is no way of knowing exactly what optical signals actually fall on the MCT detector, so a software program cannot be used to effectively linearize its response.

Several hardware correction schemes have been developed, primarily based on products devised from 'off the shelf' non-linear circuits. Unfortunately, these schemes suffer from two major problems. First, the non-linear circuit elements internally generate noise levels that are considerably higher than those of an MCT. The resultant detector is therefore not MCT noise-limited and produces spectra with degraded signal-to-noise performance. Second, they allow too few degrees of freedom to accurately correct for the non-linear MCT response and provide a less precise correction.

Agilent has a ten-stage non-linear pre-amplifier network consisting of gradually activated circuit elements that are heavily overlapped, to achieve the objective of low composite noise while producing a smooth monotonic correction to the non-linear MCT response. This method of correcting non-linear MCT response does not increase the noise level in the detector signal.

The pre-amplifier is statically calibrated over its entire radiometric range of use. Since the correction stage has many degrees of freedom, it can conform to very high order shapes in the radiometric response curve. This makes it potentially complex to calibrate. However, the calibration process has been reduced to a series of simple static measurements of the uncorrected detector to develop a computer model of the detector's response to a stepped range of intensity inputs. A mathematical computation processes this raw data and results in a predicted response function to an array of linearly stepped optical inputs. Given this model, the intricate pre-amplifier can be calibrated for a given detector 'on the bench' using only a computer and a waveform generator. The multiple degree of freedom pre-amplifier can hence be trimmed rapidly and to high precision. However, it is noteworthy that the electrical bandwidth of this compensation allows for operation up to 80 KHz in collecting IR spectra, and this potentially limits its applicability for high speed kinetics measurements.

Performance of Agilent's linearized MCT detector

The same MCT detector used to generate the spectra shown in Figures 2 to 4 was fitted with a Agilent non-linear MCT pre-amplifier. Figure 5 displays the single-beam spectrum of this modified detector (green) at the same incident energy flux as that used in Figure 2, overlaid with the original single-beam spectrum from Figure 2 (blue).

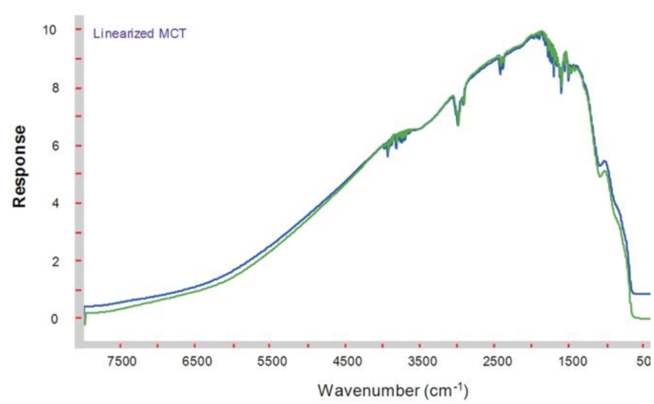

Figure 5. Open beam spectra of the same MCT detector at the same incident energy flux with a non-linear (green) and standard (blue) pre-amplifier. The absence of non-physical energy below the detector cutoff for the non-linear pre-amplifier highlights that photometric accuracy is maintained

The single-beam spectrum from the non-linear pre-amplifier (generating a linear response for the MCT/pre-amplifier combination) shows none of the non-physical energy that is observed with a standard pre-amplifier. Figure 6 displays a spectrum of a polystyrene film recorded with the linearized detector at the same energy flux as the spectrum in Figure 2, overlaid with the spectrum recorded at the same energy flux with the same detector with a standard pre-amplifier.

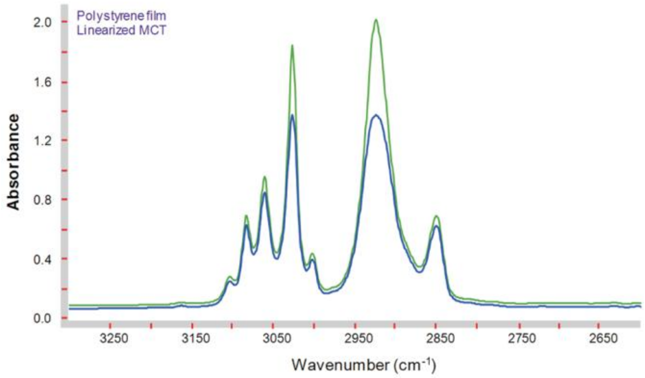

Figure 6. Spectra recorded from a polystyrene film with the same attenuation levels in Figure 3, expanded around the CH stretching region. The spectrum recorded with the non-linear pre-amplifier (green) exhibits better photometric accuracy than the one recorded with a standard pre-amplifier (blue)

The spectrum of the linearized detector (fitted with the non-linear pre-amplifier) shows better photometric accuracy, as demonstrated by the higher intensities of the strong absorbance bands. In addition, this spectrum shows even better photometric accuracy than the one recorded with the standard pre-amplifier at 8 times higher attenuation, as illustrated in Figure 7.

The photometric accuracy of the linearized MCT can be further tested against that of a deuterated L-alanine doped triglycene sulphate (DLaTGS) detector. The DLaTGS detector is generally considered to set the standard for photometric accuracy in FTIR spectrometers, because a pyroelectric detector's output is directly related to the incident energy flux.

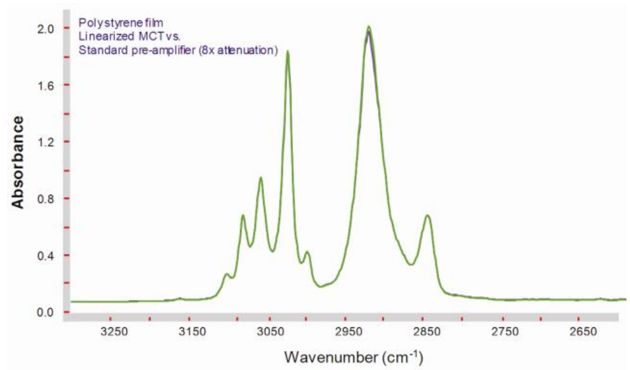

Figure 7. Spectra recorded from a polystyrene film with the non-linear pre-amplifier (green) at the same attenuation levels of Figure 3, overlaid with the spectrum recorded with the standard pre-amplifier (purple) at 8 times higher attenuation

Single-beam spectra of a DLaTGS detector (with no attenuation) and the linearized narrow band MCT (with only enough attenuation to prevent A/D overflow) are presented in Figure 8, and their corresponding polystyrene spectra in the CH stretching range are displayed in Figure 9. The absence of non-physical energy below the detector cutoffs for both spectra in Figure 8 indicates linear detector response. This is further supported by the complete overlap of the polystyrene absorbance bands in Figure 9.

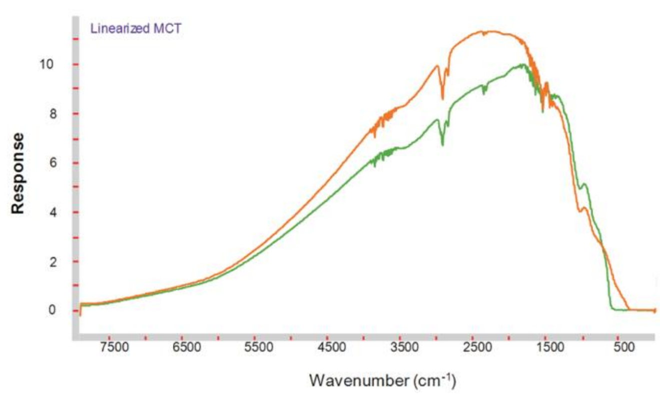

Figure 8. Single-beam spectra of the linearized MCT detector (green) with enough attenuation to prevent A/D overload, and DLaTGS detector (orange) with no attenuation

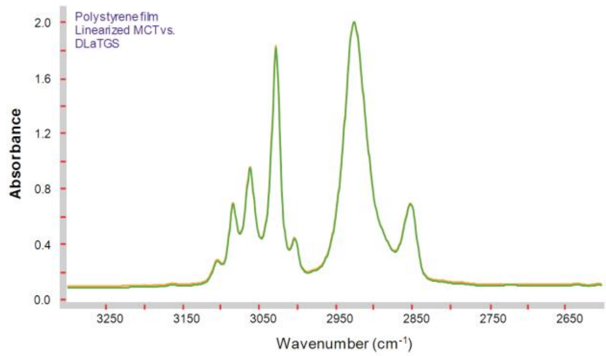

Figure 9. Absorbance spectra of a polystyrene film collected in transmission using a linearized MCT detector (green) with enough attenuation to prevent A/D overflow, and using a DLaTGS detector (orange) with no attenuation

Sensitivity improvements of Agilent's linearized MCT detector

The major benefit of using an MCT detector in regions of higher energy flux is to obtain an improvement in sensitivity, or signal-to-noise (S/N). The S/N improvement of the linearized MCT detector over the non-linearized detector is demonstrated in Figure 10, where a spectrum showing a weak polystyrene absorbance band from the linearized MCT detector is overlaid with that obtained from the non-linearized MCT. The photometric accuracy of the two spectra is equivalent (as demonstrated in Figure 7), but the S/N of the linearized detector is approximately one decade higher, thereby producing higher quality data.

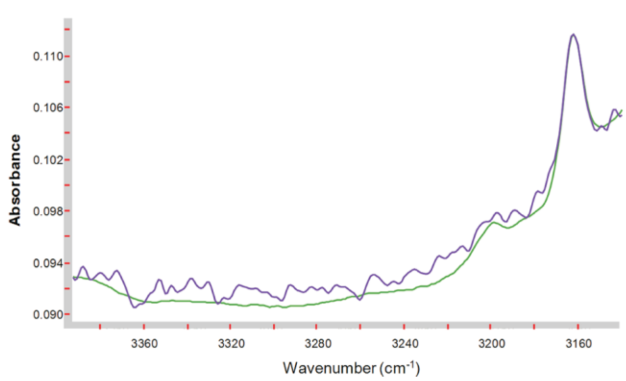

Figure 10. Absorbance spectrum of a polystyrene film collected in transmission using a linearized MCT detector (green) with enough attenuation to prevent A/D overflow, overlaid with a spectrum of the same film recorded using the non-linearized detector (purple) at 8 times higher attenuation to obtain linear response

Summary

Agilent has a technique to linearize an MCT detector. This technology brings substantial advantages for quantitative measurements. It extends the linear range of the detector versus energy flux relationship by about a factor of ten above the range that can be obtained with a standard MCT detector, while still maintaining high photometric accuracy. This provides a wider concentration range when performing quantitative measurements.

The linearized MCT detector matches the photometric accuracy of a DLaTGS detector (which is the standard for photometric accuracy in FTIR spectrometers), and it provides better quality data in situations where the energy flux incident on the detector is limited by a sample or an accessory. The extension of the linearized MCT detector into regions of higher energy flux results in a potential ten-fold improvement in S/N ratio.

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