Highest available Signal-To-Noise performance, delivering superior sensitivity and analytical performance

Technical Overview

Advantage statement

The Agilent Cary 670/680 FTIR spectrometer delivers between three to four times more power at the sample focus than other competitive instruments, delivering superior sensitivity and analytical performance. Even with an attenuated total reflectance (ATR) accessory in place, which can attenuate the infrared energy throughput by up to 90%, Agilent's signal-to-noise performance rivals that of other research-grade spectrometers under commonly cited 'open beam' conditions.

Introduction

The signal-to-noise ratio (S/N) of an FTIR spectrometer can be considered to be a measure of its sensitivity and is often viewed as the primary specification for determining whether or not an instrument will meet the needs of intended use. At its simplest, S/N is the ratio of a peak height to the noise in an adjacent spectral region. However, in most cases the S/N ratio is determined with no sample or accessory in place. In this case, the signal becomes 100% and the noise is calculated, either p-p (peak-to-peak) or RMS (Root Mean Square) from a defined region, usually 2200–2100 cm^{-1}. This region is often chosen as it is near the maximum transmitted wavelength for most spectrometers. RMS noise is the standard deviation of all resolution elements across the chosen wavelength window whereas p-p noise is the difference between the highest and lowest points across the same region (Figure 1).

In recent years, the use of Attenuated Total Reflection (ATR) accessories has become commonplace. The accessory provides easy and accurate analysis of materials without time-consuming dilution in matrices such as Nujol or vacuum-pressed KBr discs. Materials for analysis, whether solid or liquid, are simply applied directly to the internal reflection element (IRE) and scanned. While the optical designs of ATR accessories provide for maximum IR energy throughput, the best ATR accessories on the market only have an overall transmission of about 30%. This significantly compromises the sensitivity and performance of the instrument when using the accessory. Longer scan times are often required to meet signal-to-noise requirements and the range of samples that can be measured, particularly those that are weakly absorbing, can be limited. To offset this accessory attenuation, a spectrometer with extremely high IR energy throughput is required.

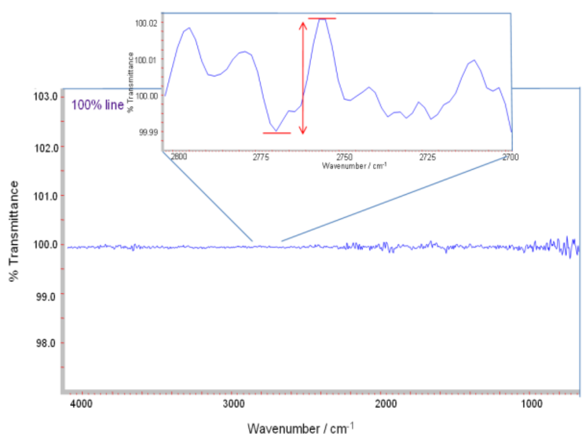

Figure 1. A 100% transmission line used in the calculation of the signal-to-noise ratio (S/N). Signal is 100% and noise is calculated, either p-p or RMS, from a defined spectral region, in this case 2800–2700 cm-1

In this study, the sensitivity of the Agilent Cary 670 FTIR spectrometer was measured in conjunction with a Pike MIRacle single bounce diamond ATR accessory. The S/N ratio of spectra, collected with the ATR in place with no sample, was used to define the sensitivity of this instrument/accessory combination. In this case, the signal is defined as 100% (Figure 1) but is attenuated significantly (~70%) by the ATR accessory (Figure 2). Even with this high level of attenuation, the S/N performance of the Cary 670 FTIR with ATR accessory was found to rival that of other FTIR spectrometers using traditional open beam measurements where there is no accessory in place. Similar results are achieved using an Agilent Cary 680 FTIR, the instrument being identical to the Cary 670 FTIR with the addition of step-scan capability.

Experimental

The S/N performance was measured on a Cary 670 FTIR spectrometer with a Pike MIRacle single bounce diamond ATR (Figure 2) using the parameters listed in Table 1. The instrument and accessory were purged for five minutes before sampling. Measurement of open beam IR power was made using a Coherent-Fieldmaster power meter set to 4 µm at the sample focus of the instrument.

Table 1. Instrument parameters used in all collections

	Instrument Parameters	Settings
Detector	DLaTGS Speed (kHz)	5.0
Source	MIR	Normal
ATR	Pike Diamond MIRacle	
Cary 680 FTIR + Cary 610 FTIR	12500	7700
Collection	Sample scans Background scans Resolution (cm-1) Aperture (cm-1) Symmetry	4 16 4 4 sym
Computation	Apodisation type Zero filling factor UDR	BH4 2 2

Figure 2. The Pike MIRacle ATR used in this study. Energy limiting accessories such as the ATR require a high energy FTIR spectrometer to offset accessory attenuation

S/N – Agilent Cary 670 FTIR/Pike MIRacle ATR Measurements

The S/N ratio was determined with a Pike MIRacle ATR in place and no sample. A 5 second scan is collected, which is ratioed against a background to give a 100% transmission line (Figure 1). Noise is calculated in the region 2800–2700 cm^{-1}. This region is chosen for ATR measurements as it is outside the absorption region for diamond. The results presented in Table 2 represent an achievable range for two different source apertures.

Table 2. Measured range of S/N ratios (5 s collect) for the Agjlent Cary 670 FTIR spectrometer in conjunction with a Pike MIRacle ATR at open and 4 cm^{-1} source aperture

Source Aperture	S/N (p-p)	S/N (RMS)
Open	10-12,000:1	42-50,000:1
4 cm^{-1}	9–11,000:1	38–46,000:1

As shown in Figure 3, even with an ATR in place, the signal-to-noise performance of the Agilent Cary 670 FTIR rivals that of other spectrometers on the market, quoted under open beam conditions. It is common practice for vendors to quote the S/N performance of instruments under open beam conditions, that is, without an ATR in place. When considering such specifications it must be remembered that the performance of the instrument when used with an ATR will be significantly reduced. An ATR with a 25% throughput will reduce the S/N performance of the instrument by a corresponding amount. That is, an instrument achieving a S/N ratio of 10,000:1 under open beam conditions will achieve just 2,500:1 when used with an ATR accessory. Conversely, an instrument achieving 10,000:1 with an ATR in place can be extrapolated to 40,000:1 under open beam conditions. With this in mind, the S/N performance of the Agilent Cary 670 FTIR is far superior to any other spectrometer on the market, as proven by the S/N results in conjunction with an ATR.

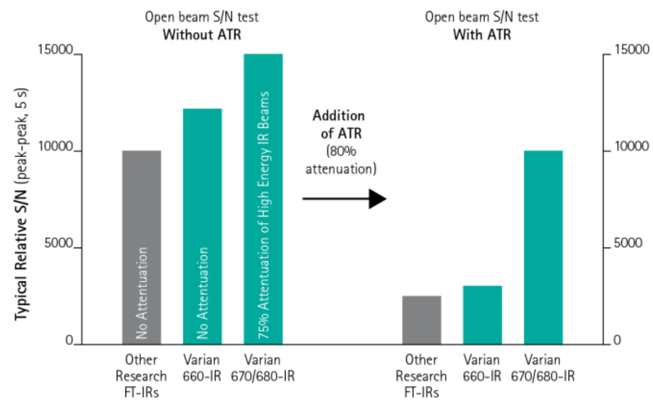

Figure 3. Left: Traditional S/N specification tests are performed without a sample or sampling accessory in the instrument, so they are effectively measuring air. Right: Agilent specifies S/N values under 'real-world conditions', giving a more true indication of what to expect when measuring samples

Even with an ATR in place, the S/N performance of the Agilent Cary 670 FTIR rivals that of other research grade spectrometers under commonly cited open beam conditions.

Table 2 also shows the high S/N performance of the ATR to be maintained at 4 cm^{-1} source aperture. This is particularly important as the majority of users perform their scans at 4 cm^{-1} in order to achieve an acceptable resolution.

The high sensitivity of the Cary 670 FTIR spectrometer is attributable to a number of design features, which have been incorporated into the design of the instrument.

These features combine to yield a high power IR beam at the sample focus, between three to four times higher than any bench top spectrometer on the market (Figure 4).

- 57 mm clear aperture optics throughout, (twice that of most other FTIR instruments).
- 60° interferometer configuration providing for a greater solid angle.
- Highly efficient source collection optics with retro-reflector.
- Customized aspheric mirrors.

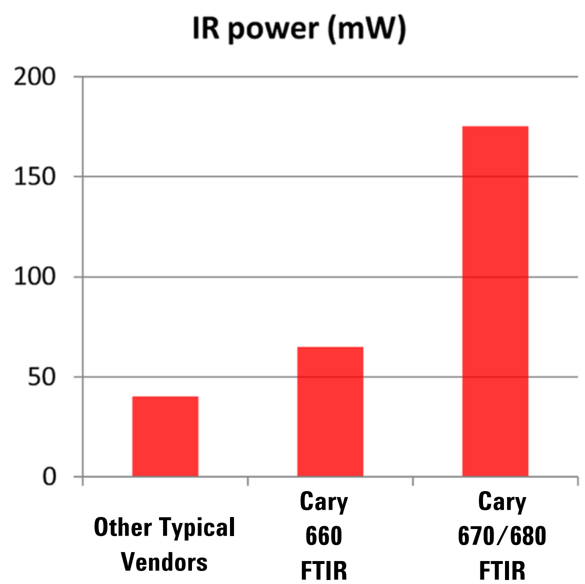

Figure 4. Typical IR power measured at the sample focus for the Agilent Cary 600 FTIR series of spectrometers, compared with other FTIR spectrometers on the market

The high power of the Agilent Cary 670 FTIR spectrometer provides excellent signal-to-noise performance, especially in conjunction with low throughput accessories such as ATR. It also permits the measurement of weakly absorbing samples that may be undetectable using less sensitive instruments. To further demonstrate the superior performance of the Agilent Cary 670 FTIR with an ATR accessory, a limit of detection of 0.04% v/v EtOH/H_2O was measured[1].

> The Agilent Cary 670/680 FTIR spectrometers deliver unrivalled energy throughput, essential for highly absorbing samples or low throughput accessories such as ATR, diffuse reflectance and photoacoustic accessories or microscopes.

S/N – Agilent Cary 670 FTIR, Open Beam Measurements

Comparison of S/N performance under open beam conditions is difficult, as the higher energy throughout of spectrometers such as the Agilent Cary 670 FTIR and 680 FTIR will saturate most DLaTGS detectors. When measuring the S/N performance of these spectrometers, the high energy IR beam must be artificially attenuated using attenuation screens (Figure 5). Just like using an ATR accessory, this has the effect of reducing the S/N performance of the spectrometer. All other lower energy spectrometers do not require attenuation under open beam conditions, making comparisons between Agilent air-bearing spectrometers and all other spectrometers using open beam results invalid.

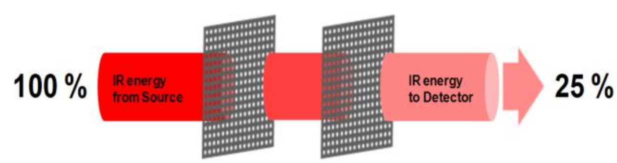

Figure 5. Under open beam conditions the high energy IR beam of the Agilent Cary 670 FTIR must be artificially attenuated by 75% using a semi-permeable mesh screen to avoid saturating the DLaTGS detector

The 5 second S/N performance of the Agilent Cary 670 FTIR spectrometer under open beam conditions with 75% beam attenuation was measured, with results presented in Table 3. Also presented are measured S/N performance values for the Agilent Cary 660 FTIR. This instrument, like most spectrometers in its class, does not require attenuation for an open beam measurement. The degree of attenuation is given alongside the spectrometer model, and other collection conditions are identical to those supplied in Table 1. Noise was calculated in the region 2200–2100 cm^{-1}.

Table 3. Measured signal-to noise ratios (p-p) for the Agilent Cary 670 FTIR, and 660 FTIR spectrometers under open beam conditions. Degree of attenuation as indicated

FTIR spectrometer	S/N (p-p) 5 s
Cary 670/680 FTIR 75% attenuation	12,000:1
Cary 670/680 FTIR Extrapolated value No attenuation*	48,000:1
Cary 660 FTIR No attenuation	10,000:1

*Value extrapolated from S/N at 75% attenuation. This measurement cannot be made on a Cary 670/680 FTIR with no attenuation, as the high energy IR beam will saturate the DLaTGS detector.

Measured S/N ratio values for the Agilent 670 FTIR are comparable with those for the Agilent Cary 660 FTIR despite the instrument delivering over three times more IR power at the sample focus (Figure 4). This is because, when performing an open beam measurement on the Agilent Cary 670 FTIR, the beam must be artificially attenuated to avoid saturating the DLaTGS detector. This is accomplished with a software-controlled attenuation screen, which attenuates the IR beam by 75%, reducing the measured S/N performance of the spectrometer by the same amount (Figure 6).

Furthermore, another point to note is that the Agilent Cary 660 FTIR, although primed in the mid-range region of the market, has a S/N comparable to that of high-end research FTIR spectrometers.

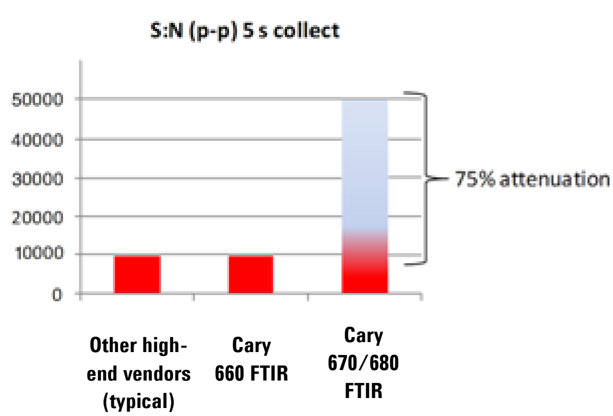

Figure 6. Measured S/Nperformance (p-p, 5 s collect) of the Agilent Cary 600 FTIR series of spectrometers. Typical values quoted by other vendors included for comparison

Higher powered instruments such as the Agilent Cary 670/680 FTIR require significant attenuation of the high energy IR beam to avoid saturating the detector. Comparison of S/N performance using traditional open beam measurements is therefore invalid.

Conclusion

The Agilent Cary 670 FTIR spectrometer delivers between three to four times more power at the sample focus than most competitive products, translating to superior sensitivity and performance. In conjunction with an ATR, the instrument achieves 9-12,000:1 p-p S/N for just a 5 s collection time, comparable with most other spectrometers under open beam conditions. The performance of these spectrometers can be expected to be reduced by up to 80% with the introduction of an ATR. The extraordinary energy throughput of the Agilent Cary 670 FTIR and 680 FTIR spectrometers is attributable to a number of design features including a retro-reflected source, a 60° interferometer and 57 mm optics throughout. The high energy throughput of the Agilent Cary 670/680 FTIR makes it ideal for use with low throughput accessories such as ATR, diffuse reflectance and photoacoustic accessories, and microscopes, and permits the measurement of weakly absorbing samples, which may be undetectable with less sensitive instruments.

References

1. Boyd S. and Kirkwood J. *Quantitative Analysis using ATR-FTIR Spectroscopy*, Application Note SI-01374

www.agilent.com/chem

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