Impact of active gas purge on FTIR measurements

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Thermo Scientific Nicolet iS50
FTIR Spectrometer.

Introduction

The throughput and multiplex advantage of Fourier transform infrared (FTIR) spectrometers have made them one of the most effective and popular analytical instruments to identify unknowns and analyze the molecular composition of materials. Spanning the entire infrared spectral range of the electromagnetic spectrum, modern FTIR systems are versatile instruments for a wide range of applications. One challenge in FTIR analysis arises from the presence of water vapor and carbon dioxide (CO_2) in the environment. Both water vapor and CO_2 are infrared (IR) active compounds that are ubiquitous in the atmosphere and can negatively impact FTIR analysis. When a single beam spectrum is acquired using an open sample compartment with no analyte present, the spectrum shows the clear presence of water vapor and CO_2; this can be seen in Figure 1. Both H_2O and CO_2 stretching/bending contribute significantly to the mid-IR spectral range (4000-400 cm^{-1}). In addition to their presence in the mid-IR, water vapor and CO_2 peaks are also present in the near- and far-IR regions. Addressing these contributions can be critical in both routine and high-sensitivity analyses. In this technical note, the impact of purging an instrument with nitrogen gas on FTIR measurements is evaluated.
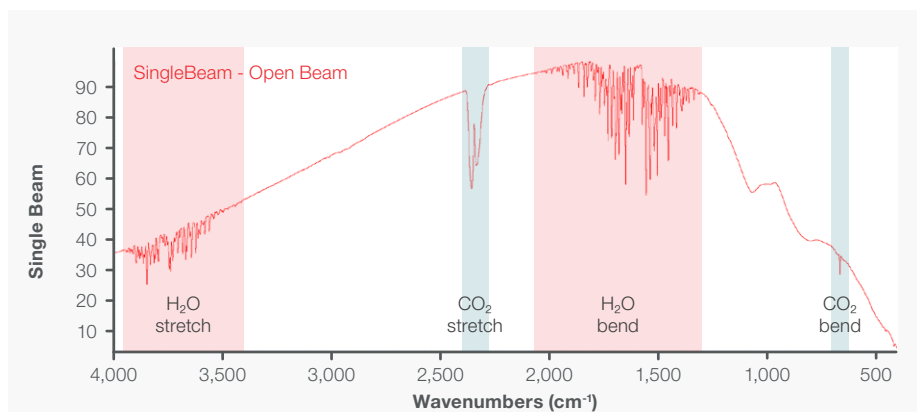

Figure 1. A single beam spectrum in the mid-IR spectral region showing the absorption bands of water vapor and CO_2.

Purge Performance

A Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer was connected to a nitrogen purge apparatus. Nitrogen flowed into the system at 30 SCFH, and the system was purged overnight prior to the experiments. Note that this overnight purge is not required for spectrometer operation nor necessary for routine use. An extended purge, however, is highly recommended prior to FTIR measurements that are sensitive to environmental water vapor/CO_2. For the experiments described herein, the spectrometer underwent a continuous purge, which was turned off only for unpurged samples as indicated in the text. Spectra were collected with a spectral resolution of 4 cm^{-1} and 32 scans. Single beam data was acquired at a resolution of 4 cm^{-1} with 4 scans averaged.

Most FTIR data is collected by ratioing the sample measurement to a background measurement. The background, taken without the sample in the beam path, captures the environmental contributions such as water vapor and CO_2. Ratioing sample and background measurements can remove most of the atmospheric contributions in the final spectrum, especially in a relatively stable environment. Analyses of bulk materials benefit greatly from this, resulting in high-quality spectra that yield excellent match values in spectral library searching. Figure 2 shows the process of ratioing measurements from a sample and a background single beam to generate a final spectrum in the % transmittance final format. A measurement of a 1.5-millimeter polystyrene film was taken with an open compartment without purge. Despite the presence of atmospheric water vapor and CO_2 in both the single beams and final spectrum, library searching of the final spectrum returns a strong match value of 99.30 for polystyrene. This example demonstrates how ratioing the sample and background can effectively address atmospheric contributions in bulk samples.

When atmospheric conditions fluctuate, there are two general approaches to mitigate water vapor and CO_2 contributions to IR spectra: spectral post-processing, and physically reducing/removing water vapor and CO_2 inside the spectrometer before data acquisition. Various spectral processing approaches have been developed, with new algorithms continuing to be researched[1,2]. For example, the Thermo Scientific™ OMNIC™ Paradigm software uses a library of high-resolution spectra as standards in a regression model. This model is applied to the sample spectrum, and the residual spectrum is calculated. Portions of the residual spectrum are then used to replace spectral regions commonly associated with water vapor and CO_2. The software approach can be a valuable option to address atmospheric contributions in many analyses. However, it is often not desired in applications where peaks of interest overlap with the water vapor/CO_2 bands, or when preserving the fidelity of the raw data is required. In these instances, users must rely on physically reducing/removing atmospheric contributions.

Physical reduction/removal of atmospheric contributions involves the use of a desiccant or the application of an active purge. Using a desiccant provides the most simplistic means to reduce the amount of residual moisture in an FTIR system. This passive addition to the system works best in low-humidity or stable environments but might not be sufficient for analyzing challenging samples such as thin films or low concentration samples, or for analyzing analytes with absorptions in the H_2O and CO_2 regions. Samples can have weak attenuation of the IR energy due to low concentrations or thicknesses of the IR active analyte(s). The resulting spectra will present weak absorbances, which can be obscured under the atmospheric water vapor and CO_2 bands. For these situations, an active purge is often deployed.
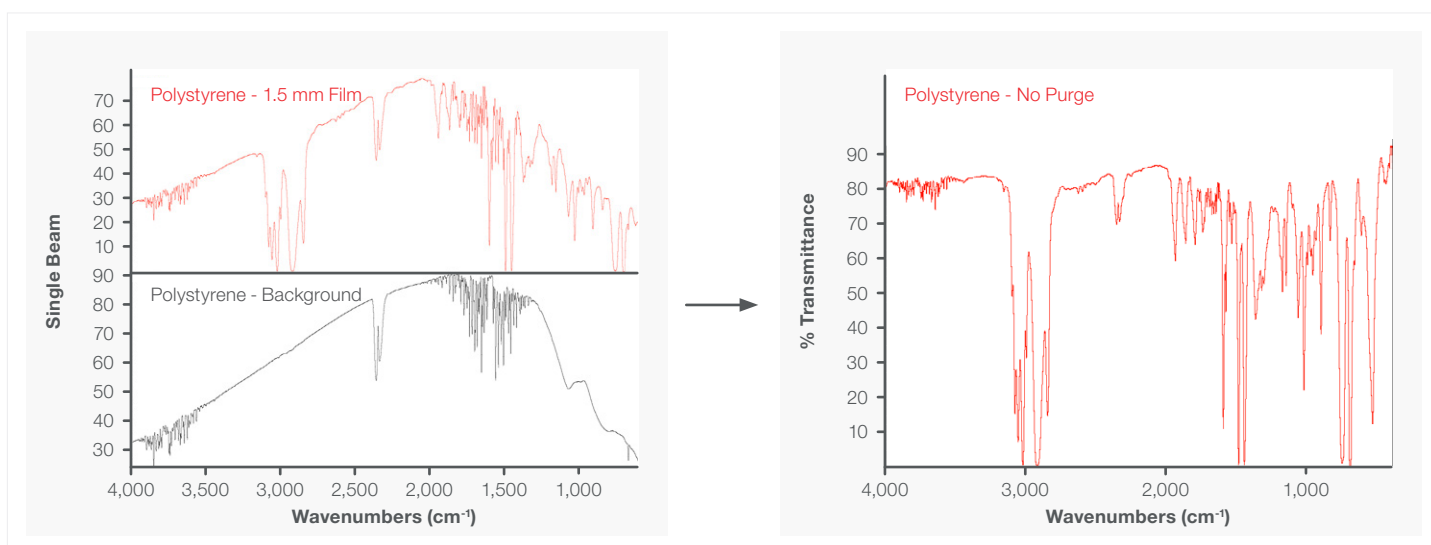

Figure 2. Single beam of a sample ratioed to background single beam for a spectrum displayed in % transmittance.

A purge gas system has a positive pressure of gas flow into the spectrometer, typically dry air or nitrogen; this creates a clean and dry environment throughout the beam path. A benefit of this active purge system is its simple implementation, requiring only tubing and flow control. Nitrogen or clean dry air lines feed into an adjustable flow controller which connects to the Nicolet iS50 spectrometer via quick-connect ports. The flow controller can be adjusted to open, close, or vary the flow rate of purge gas flowing into the spectrometer. Figure 3 depicts the efficiency in removing water vapor and CO_2 through purging with this simple setup. The peak areas for water (•) and CO_2 (♦) were plotted over the course of purging at 60-s intervals, where T-0 was measured with the sample compartment fully exposed to the environment. It is evident that most of the water vapor and CO_2 were effectively removed in the first 2 minutes of the purging.
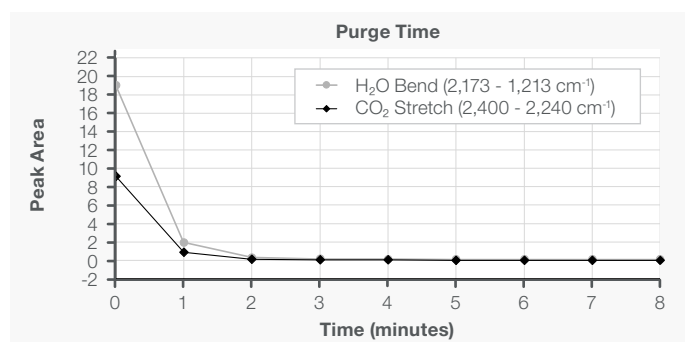
Figure 3. Peak area of H_2O bend and CO_2 stretch over 8 minutes of gas purge.

Figure 4 shows the impact of purge on the FTIR measurements of a dilute solution. A 10 µL aliquot of 100 ppm caffeine solution in ethanol was deposited onto a KBr window and allowed to dry, leaving roughly 1 µg of caffeine deposited on the window. The unpurged spectrum in Figure 4A is dominated by the spectral bands from water and CO_2. Small features from caffeine, such as those around 3000 cm^{-1} and 1000 cm^{-1}, are discernable, but largely overwhelmed by the water vapor bands. A library search for this unpurged measurement provides a weak match to water, due to the significant H_2O stretching and bending present in the spectrum. The purged spectrum in Figure 4B was acquired by providing a 4-min purge prior to data acquisition. Figure 4B shows virtually no contribution from water vapor/CO_2 and the spectral features associated with caffeine are readily seen, particularly those in the H_2O bending region. A library search of this purged sample provides reasonable matching for caffeine, with a match value of >78.
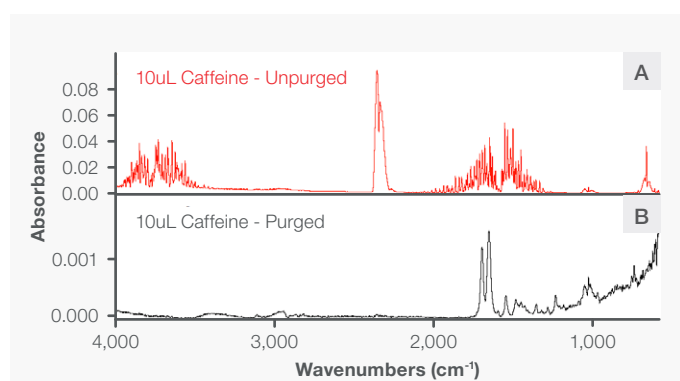
Figure 4. Mid-IR spectra of 10uL of 100ppm Caffeine in A) unpurged and B) purged system.

The far-IR spectral range can also be significantly impacted by water vapor. Water vapor has substantial features in the far-IR region, such that even bulk samples analyses may be hindered by the residual water vapor contributions. Figure 5 shows the impact of purge on a bulk analysis of PTFE film in the far-IR region. Figure 5A shows the PTFE film analyzed with the sample compartment closed and a 4-min purge, whereas Figure 5B shows the same film analyzed in an open compartment without purge. Without purge, water bands completely overwhelm the PTFE feature around 200 cm^{-1}. A purge may become a necessity for far-IR analyses, as demonstrated by Figure 5.
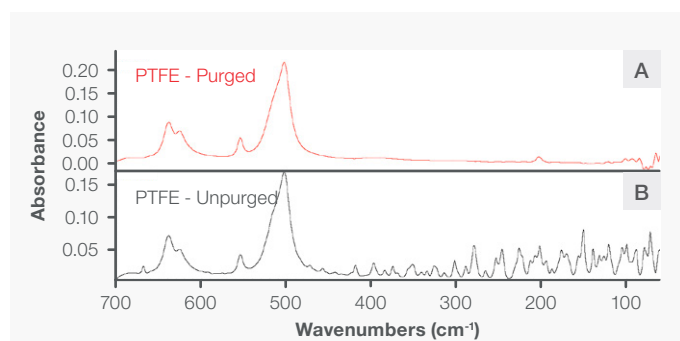
Figure 5. Far-IR analysis of a PTFE film A) analyzed with the sample compartment closed and the spectrometer purged and B) with no purge and an open sample compartment.

Conclusion

In this technical note, the impact of active gas purge on FTIR measurements is described using the analyses of a dilute caffeine solution in the mid-IR region and a thin PTFE film in the far-IR region. In both cases, the critical features are inundated by water vapor/CO_2 bands if there is no purge, but are readily detected for positive identification after an active gas purge. The results unequivocally demonstrate that gas purge is a simple yet highly effective and efficient method to remove water vapor and CO_2 from FTIR spectrometers. A gas purge helps to minimize or remove atmospheric contributions in FTIR spectra and improves the ensuing library search. Furthermore, the implementation of a gas purge is easy, and the purge stabilizes within a few minutes after sample loading, thus minimizing the acquisition time needed for analysis.

References

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