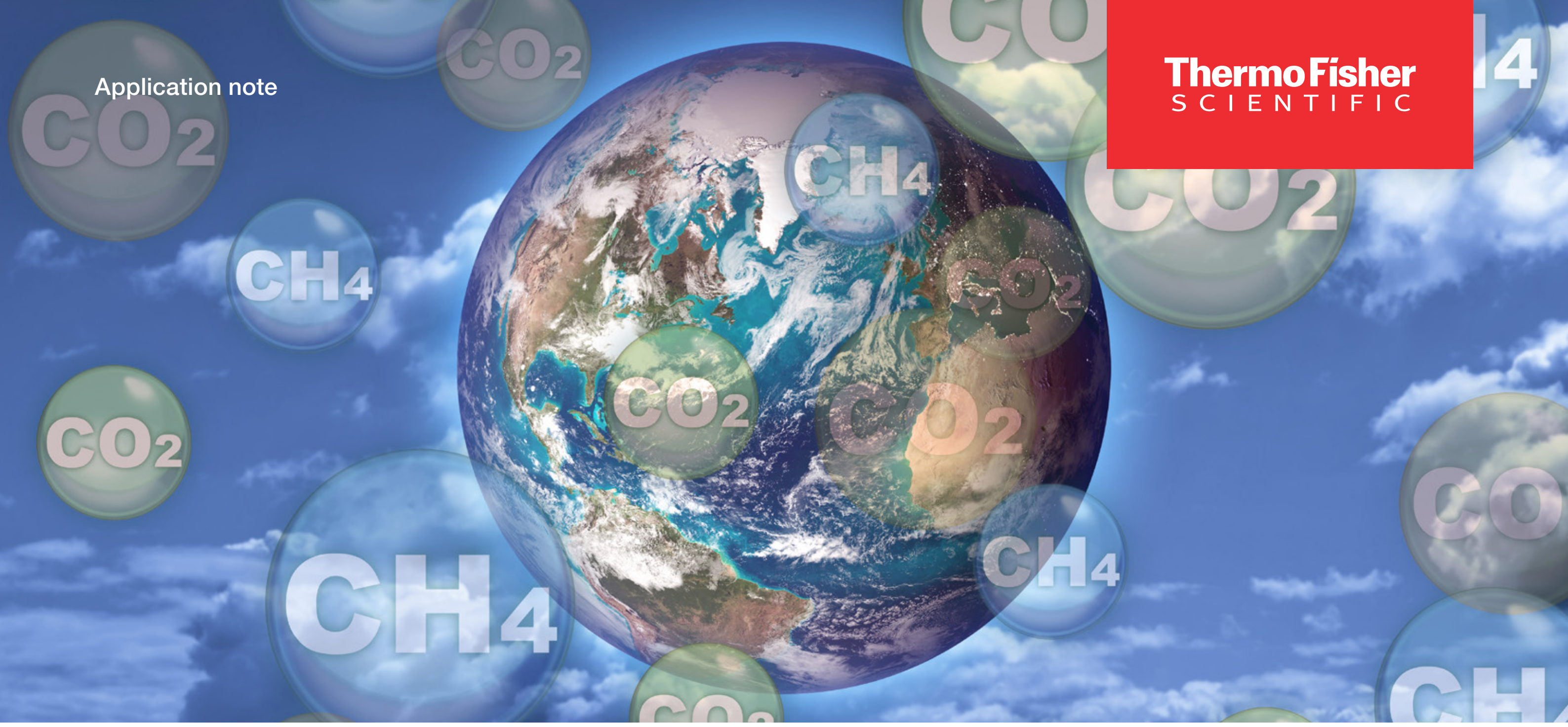
Application note



Thermoelectrically cooled MCT detectors enable high speed and high sensitivity gas analysis by FTIR

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Overview of FTIR Gas Analysis

Fourier transform infrared spectroscopy (FTIR) is a powerful and versatile analytical technique for qualitative and quantitative gas analysis. By measuring the absorption of infrared light, gases present in a sample can be identified through library matching. Multivariate data reduction algorithms, most commonly Classical Least Squares (CLS), are often employed for the quantitative analysis and allow for the analysis of complex mixtures of gases, up to 30 components, from processes such as combustion.

Unlike a solid or liquid, gas molecules can freely rotate many times before colliding with another molecule, giving rise to fine, rotational features centered around the vibrational mode, as shown in Figure 1(a). In order to resolve these fine structures, gas analysis by FTIR is generally performed with a higher spectral resolution, ranging from 0.5 cm^{-1} to 2 cm^{-1}, than those for solid and liquid analysis. The high spectral resolution also enables the analyses of the gas of interest even in the presence of heavy spectral interferences, such as those from water, carbon dioxide, and methane produced in combustion processes. Figure 1(b) shows the FTIR spectra of gaseous NO and H_2O. Each gas has its distinct peak patterns, but the H_2O bands have much higher intensity that could overwhelm the NO bands when overlapping. Due to the high spectral resolution, 0.5 cm^{-1} in this case, there are regions where the NO peaks are free from the H_2O interference, allowing for accurate identification and quantification of NO.

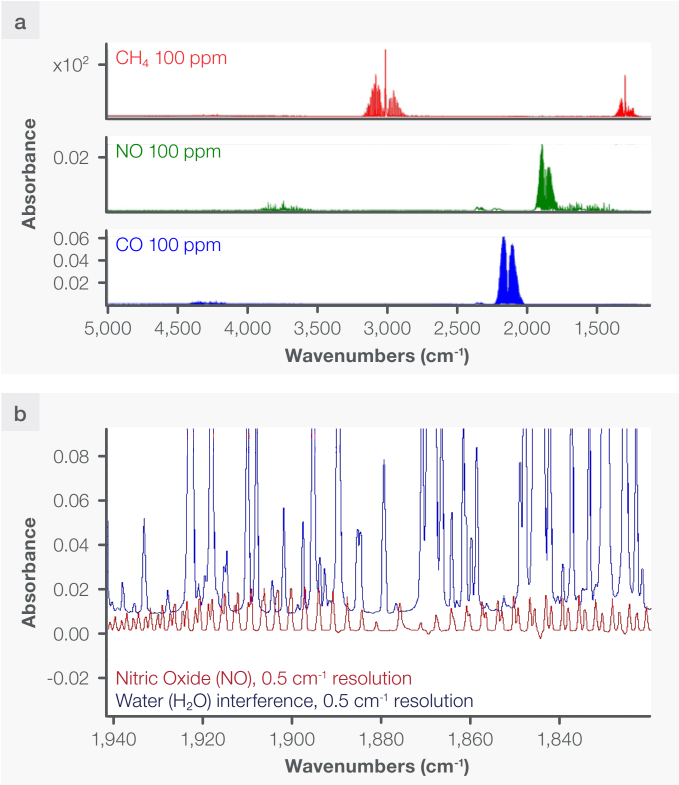

Figure 1. (a) FTIR spectra of gaseous CH_4, CO, and NO with 0.5 cm^{-1} resolution; and (b) An overlay of the FTIR spectra for NO and H_2O with 0.5 cm^{-1} resolution.

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The advantages of using FTIR for gas analysis are summarized in Table 1. In short, FTIR can provide accurate identification and quantification of multiple gases simultaneously, real-time monitoring capabilities, and the ability to quantify complex gas mixtures with advanced algorithms. One notable application is the tracking of catalytic processes, such as the reduction of NOx emissions from diesel engines, to optimize engine efficiency and minimize environmental impact in real time. FTIR also finds its extensive use in the semiconductor manufacturing, particularly in monitoring the concentrations of reactive gases involved in the doping and etching processes of silicon chips. The SEMATECH publication, "Protocol for FTIR MMTs of Fluorinated Compounds in Semi Process Tool Exhaust," provides valuable insights into the use of FTIR for monitoring these gases during semiconductor manufacturing.

Feature	Benefit
Wide spectral range	Ability to analyze multiple gases in a single measurement without the need for multiple gas sensors
Broad dynamic range	Ability to monitor percent concentration down to sub-part per million level in a single measurement
Simple sampling requirements	No time-consuming chemical extractions or derivatives are required —simply maintain temperature and gas cell pressure for accurate results
Real-time continuous monitoring	Can sample a flowing stream of gas through the cell with second-by-second measurements

Table 1. Advantages of gas analysis by FTIR.

The Choice of Detectors for FTIR Gas Analysis

FTIR spectrometers are often configured with two main types of detectors: DTGS (deuterated L-alanine doped triglycine sulphate) and MCT (Mercury Cadmium Telluride). DTGS detectors are based on a pyroelectric effect where incoming IR radiation heats and expands the detector material. DTGS detectors offer high sensitivity and excellent linearity, and work particularly well under room temperature conditions, but with relatively slow scan speeds. For example, a single scan at 0.5 cm^{-1} may take 4-5 seconds. When multiple scans are co-added to improve the signal-to-noise (S/N) ratio, collection times for a single high-resolution gas spectrum may add up to 2-4 minutes. While this scan speed might suffice for single gas samples or monitoring slow industrial processes, it is not adequate for tracking high-speed catalytic processes second-by-second.

MCT detectors, on the other hand, are based on an internal photoelectric effect where incoming IR radiation excites electrons into the conduction band, but the excitation can also be triggered by thermal processes. To suppress thermally induced noise, it is necessary to cool MCT detectors using liquid nitrogen (LN2). LN2 cooled MCT (LN2-MCT) detectors offer significantly better S/N ratios and exhibit much faster response times than DTGS detectors. However, their applications can be limited by the use of LN2. The refilling of the nitrogen during prolonged use and subsequent cooling down takes time and incurs additional costs. In certain industrial settings, LN2 may not be readily available or even prohibited.

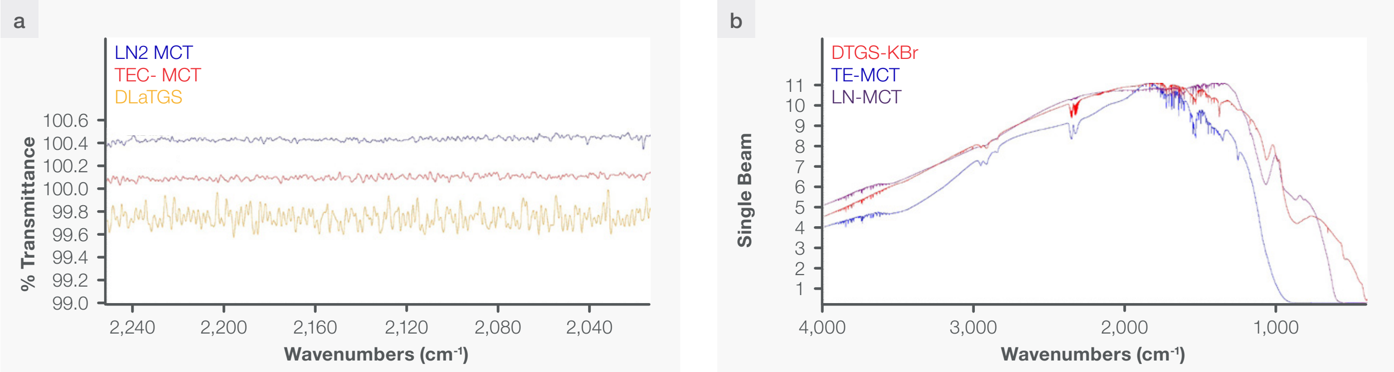

Figure 2. Comparison of LN2-MCT, DTGS, and TEC-MCT detectors: (a) overlay of the detector noise between 2,250 and 2,000 cm^{-1}; and (b) the single beam spectra showing the detector response cutoff.

The recently emerged thermal-electrically cooled-MCT (TEC-MCT) detectors offer a highly desirable balance between performance and maintenance requirements. Albeit the slightly lower S/N ratios than the LN2-MCT, TEC-MCT eliminates the use of LN2. Compared to the other cryogen-free DTGS detectors, they offer superior sensitivity and higher scanning speed. Figure 2(a) shows the noise comparison between three detectors in the region between 2,250 and 2,000 cm^{-1}. The LN2-MCT detector (top) exhibits the lowest noise level whereas the DTGS (bottom) has the highest (bottom). The TE-MCT detector noise level is situated between the two.

Another important difference between the DTGS and MCT detectors lies in their spectral range. As shown in Figure 2(b), the spectral response of DTGS detectors cut off around 400 cm^{-1} and the LN2-MCT detectors cuts off around 650 cm^{-1}. The TEC-MCT has a low-end cutoff around 1,100 cm^{-1}. When selecting detectors, it's critically important to ensure a balance between sensitivity, scan speed, spectral range, and maintenance requirements to meet application needs. The TEC-MCT detectors readily lend themselves for gas analysis that requires fast data acquisition and high sensitivity, such as catalysis/kinetics studies, particularly in laboratories without access to liquid nitrogen.

Examples of Gas Analysis by FTIR Using a TEC-MCT Detector

A Thermo Scientific™ Nicolet™ Apex FTIR Spectrometer (Figure 3), configured with a TEC-MCT detector was used in the experiments. Time series functionality of Thermo Scientific™ OMNIC™ Paradigm software was used for data collection. All spectra were collected at 2 cm^{-1} resolution and collected at 1-5 s intervals. Spectra were processed with Happ Genzel apodization and backgrounds collected for 1 minute. Gas samples that consist of methane (CH_4), nitric oxide (NO) and carbon monoxide (CO), with their concentration ranging from 10-100 ppm, were analyzed using a Nicolet 2 m pathlength gas cell. The temperature was maintained at 50 °C and the sample pressure was set at 650 mmHg.

Figure 3. Photo of a Thermo Scientific Nicolet Apex FTIR Spectrometer equipped with a TEC-MCT detector. The 2-m gas cell is in the main sample compartment. The iZ10 module is configured with a smart iTX ATR and DTGS-KBr detector. The setup allows for easy switching between accessories and detectors.

Figure 4(a) shows the three peak area profiles of the gaseous $CO/CH_4/NO$ over a span of 600 seconds. The gases were serially measured, represented by the rise and fall of their respective profile. Figure 4(b) is the FTIR spectrum at 175 s (where the red line indicates) that demonstrates the simultaneous detection of three gases. The spectrum consists of contributions from all three gases: features centered around 3,000 cm^{-1} and 1,300 cm^{-1} from CH_4, features around 2,140 cm^{-1} from CO, and features around 1,900 cm^{-1} from NO.

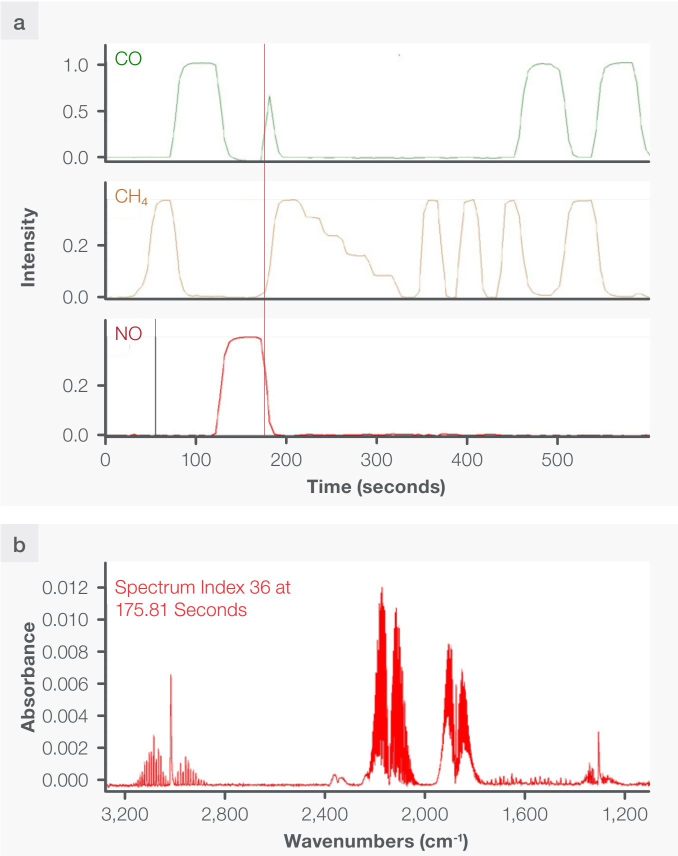

Figure 4. (a) The peak area profiles showing the serial FTIR measurement of gaseous $CO/CH_4/NO$. (b) FTIR spectrum at 175 s that shows the simultaneous detection of three gases.

Figure 5(a) shows the CO profile that depicts a serial dilution of CO. The last plateau represents the CO concentration of 10 ppm. Figure 5(b) shows the FTIR spectrum at 475 s, corresponding to approximately 5 ppm CO. The IR spectrum consists of a series of regularly spaced peaks, typical for simple heteronuclear diatomic molecules, with the P-branch on the left of the gap near 2,140 cm^{-1}, and the R-branch on the right. Even at 5 ppm, the spectrum shows $S/N > 3$ demonstrating the superior S/N performance of the TE-MCT detector.

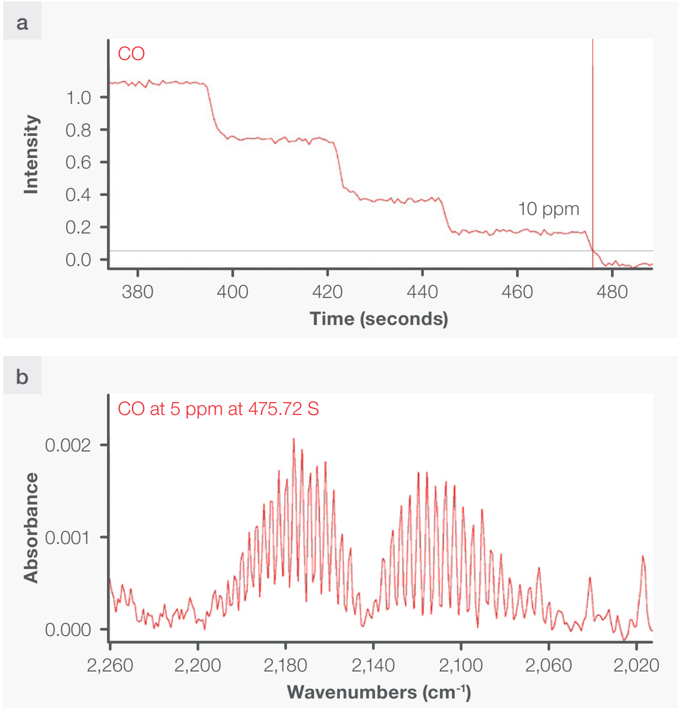

Figure 5. (a) The peak area profile showing the serial dilution of gaseous CO. (b) FTIR spectrum of CO at 475 s, corresponding to the CO concentration of approximately 5 ppm.

Summary

Fourier transform infrared spectroscopy (FTIR) is a powerful analytical technique for gas analysis, offering accurate identification and quantification of gases, real-time monitoring capabilities, and the ability to analyze complex spectra with advanced algorithms. By optimizing data collection at high spectral resolution and employing multivariate data reduction algorithms, FTIR enables the quantitative analysis of multiple components in a single sample. While FTIR spectrometers traditionally employ either DTGS or LN2-MCT detectors, the Nicolet Apex with TEC-MCT detectors offers a highly sought-after balance between S/N performance and maintenance requirements and is well suited for gas analysis, combining high scanning speed and superior sensitivity without the need for liquid nitrogen.

Additional resources

1. Sematech
2. Gas analysis with iS10
3. Gas Phase Spectroscopy Brochure
4. 10 Meter and 2 Meter Gas Cells

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