Analyzing Vapor Phase Samples with the Nicolet iS50 Multi Range Spectrometer

Key Words

ABX Automated Beamsplitter Exchanger, Gas Phase Research, Multi-spectral Range, Quality Control Applications

Figure 1

Fourier transform spectroscopy was initially developed by molecular physicists to provide a way to observe the high resolution structure in the infrared spectral region of gas phase molecules. Instruments were designed to measure not only chemicals in the atmosphere but also at infrared emissions throughout the universe. Infrared spectroscopy has been used extensively in physical chemistry to characterize gas phase molecules and as a routine analytical technique to determine the concentrations of specific compounds in commercial products and processes, as well as environmental monitoring. A major benefit of infrared spectroscopy is that both oxygen and nitrogen are transparent in the mid-infrared region, resulting in very low detection limits for trace chemicals that are infrared active. However, both water and carbon dioxide can be interferences, particularly in combustion analysis, where they are major reaction products. In many applications, infrared spectroscopy can routinely detect parts per billion (ppb) levels of specific chemicals.

In this application note, several examples are described where the Thermo Scientific Nicolet iS50 spectrometer has proven valuable in characterizing gas phase samples. Major areas of interest are:

- Physical chemistry and molecular characterization
- Quality assurance/quality control (QA/QC) and contaminant detection
- Combustion and catalyst research
- Environmental and air monitoring

We will also describe spectra showing the expanded spectral range capability of the Nicolet™ iS™50 spectrometer into the far-infrared and visible regions of the spectrum.

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Experimental

All spectra reported in this paper were acquired on a Nicolet iS50 spectrometer using various pathlength gas cells from 5 centimeters to 10 meters. Spectral resolution and scan times were optimized for each application. The specific instrument used in this work was configured with all-aluminum optics for operation in the visible spectral region and the iS50 ABX automated beamsplitter exchanger containing KBr (7000–400 cm^{-1}), solid substrate (700–100 cm^{-1}) and Quartz (25,000–5000 cm^{-1}) beamsplitters. The combination of the three beamsplitters, the three software-selectable detectors (visible, mid-IR and far-IR) and two sources (visible and infrared) provides a fully integrated, high resolution spectrometer that can automatically cover the spectrum from 25,000–100 cm^{-1}. Figure 1 shows the Nicolet iS50 spectrometer with 10 meter gas cell sample compartment however many different gas cells can be precisely mounted in the sample compartment.

Some users dedicate an instrument to gas analysis while most users in analytical, or QC laboratories, deal with multiple samples including liquids and solids. One of the greatest benefits of the Nicolet iS50 is flexibility and the ability to rapidly switch between sampling options. Figure 1 also shows a Nicolet iS50 configured with the ABX automatic beamsplitter exchanger which provides the rapid and precise switching of the optical components required for different spectral ranges. The 10 meter gas cell can be mounted in the sample compartment and easily swapped with other accessories including the iS50 Raman module. All Nicolet iS50 spectrometer systems are validated with a CO sample during final test. Figure 2 shows a spectrum acquired with the 5 cm CO standard cell with a full width at half height of better than 0.1 cm^{-1}.

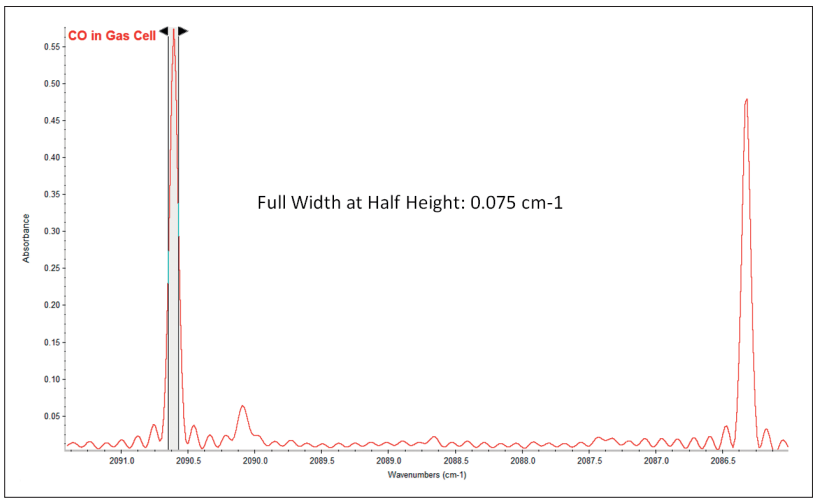


Figure 2

Physical Chemistry and Molecular Studies

The infrared spectra of gas phase molecules are often a very complex set of peaks corresponding not only to vibrational transitions but also the quantized rotational transitions of the molecule. These peaks often provide valuable information about the chemical bonds and structure of the molecule. This unique combination of vibrational and rotational transitions also provides the spectral specificity that makes multicomponent gas analysis possible. A good example that demonstrates the capability of the Nicolet iS50 spectrometer is a traditional physical chemistry laboratory experiment involving the visible spectrum of iodine vapor. While iodine is a solid at room temperature, it easily sublimates and an excellent spectrum can be obtained by placing iodine crystals in the bottom of a 10 cm gas cell. Although iodine has no allowed infrared vibrational modes, it has a multitude of spin-forbidden transitions between the vibrational levels of the ground state and levels in the excited triplet states. The result is a unique high resolution spectrum from 20,000–17,000 cm^{-1} as shown in Figure 3.

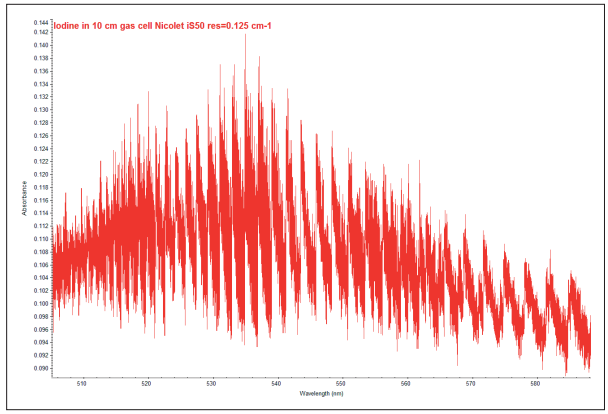


Figure 3

A second example used in physical chemistry is the mid-infrared spectrum of ammonia. The spectrum was acquired in a 10 cm cell at 0.125 cm^{-1} spectral resolution with the Nicolet iS50 as shown in Figure 4. The doubling of the Q-branch due to inversion is clearly seen, as are the multiple high resolution bands for rotations.

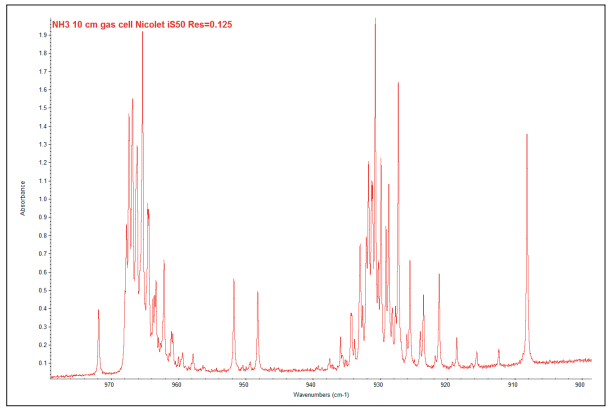


Figure 4

Far-infrared spectroscopy has also been used extensively to characterize gas phase molecules. The high-resolution spectrum shown in Figure 5 was collected in a single-button-push on the Nicolet iS50, switching the beamsplitter from the visible spectral region to the far-infrared.

QA/QC and Air Purity

A very important U.S. QA/QC application of infrared gas analysis is screening for trace contamination in Aviator's Breathing Oxygen (ABO). Both the Air Force and the Navy have systems stationed throughout the world to verify that no dangerous contaminants are present in the oxygen. Figure 6 lists the 20 components analyzed with this method.

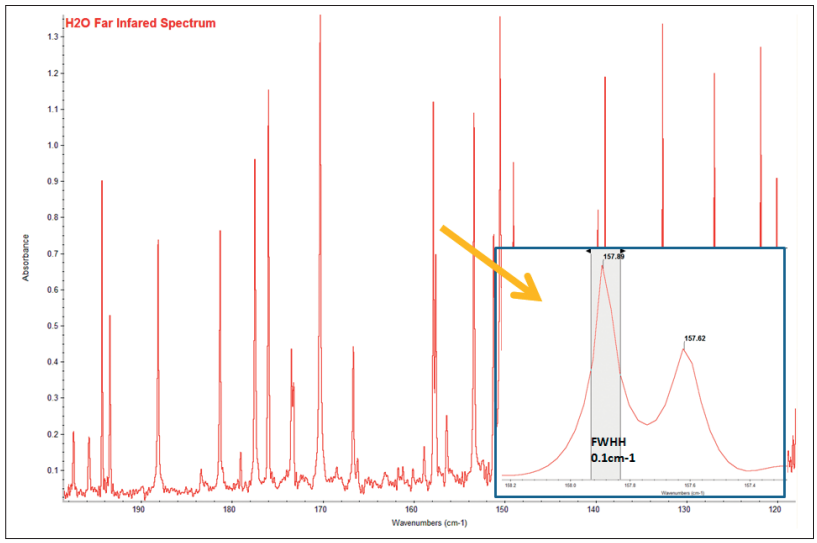


Figure 5

Aviator's Breathing Oxygen Method and Calibration

The Aviator's Breathing Oxygen (ABO) method is designed to detect impurities in ABO gas according to the U.S. Air Force military standard 1564A. This method is used with the 10 meter gas cell. Detection limits assume a collection time of 2 minutes with a room-temperature DTGS detector.

	Type of Calibration	Calibration Range	Notes
Acetylene	One point calibration from a cylinder	0.5 – 10 ppm	
Carbon dioxide	One point calibration from a cylinder	1 – 20 ppm	
Carbon monoxide	One point calibration from a cylinder	0.1 – 10 ppm	
CFC 11	One point calibration from a cylinder	0.5 – 10 ppm	
CFC 113	One point calibration from a cylinder	0.5 – 10 ppm	
CFC 12	One point calibration from a cylinder	0.5 – 10 ppm	
CFC 13	One point calibration from a cylinder	0.5 – 10 ppm	
CFC 141b	One point calibration from a cylinder	0.5 – 10 ppm	
CFC 22	One point calibration from a cylinder	0.5 – 10 ppm	
CFC 225	One point calibration from a cylinder	0.5 – 10 ppm	
Ethane	One point calibration from a cylinder	0.5 – 10 ppm	
Ethylene	One point calibration from a cylinder	0.5 – 20 ppm	
Methane	One point calibration from a cylinder	0.5 – 50 ppm	
Nitrous oxide	One point calibration from a cylinder	0.5 – 10 ppm	
Propane	One point calibration from a cylinder	0.5 – 10 ppm	
Propylene	One point calibration from a cylinder	0.5 – 10 ppm	
Sulfur hexafluoride	One point calibration from a cylinder	0.5 – 10 ppm	
1,1,1-Trichloroethane	One point calibration from a cylinder	0.5 – 10 ppm	
Trichloroethylene	One point calibration from a cylinder	0.5 – 10 ppm	
Water	Factory calibrated (Room temp – 60°C)	5 – 100 ppm	1

NOTES: 1. Use ZnSe if greater than 3% water. Do not use ZnSe if more than a few hundred ppm of halogens (e.g.: HF, HCl, HBr) or % level acidic gases, such as NO.

Figure 6

In this example, spectra were acquired in a 10 meter gas cell on the Nicolet iS50 from gas standards and verification samples used to calibrate the Air Force method. Spectra were acquired from each cylinder with a one minute scan time at 1 cm^{-1} resolution as shown in Figure 7. A validation sample containing 10 ppm levels of these components was provided by the U.S. Navy as part of this project.

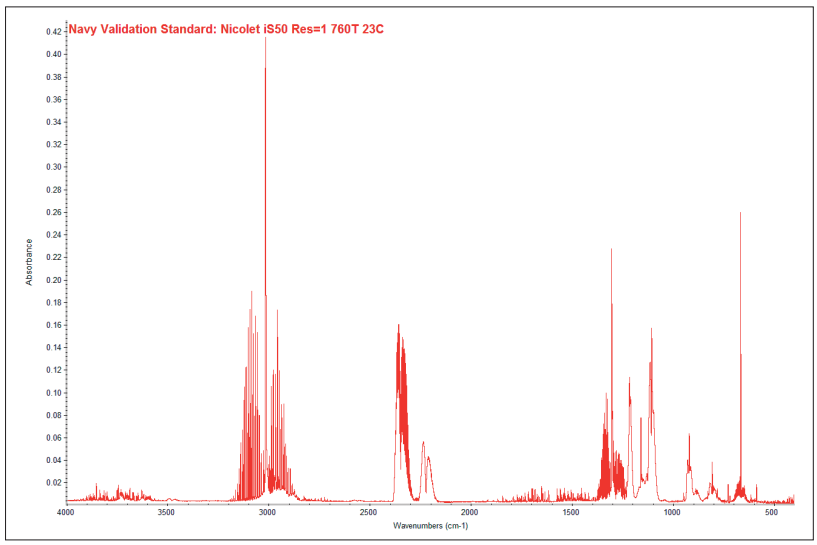
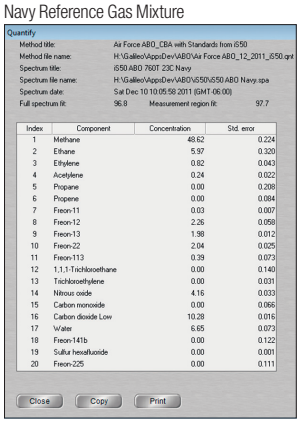


Figure 7

A Thermo Scientific TQ Analyst software method was calibrated with spectra obtained from gas standards purchased from Scott Specialties Gases® and tested on a spectrum of the Navy test gas. The method was also applied to a spectrum obtained from a nitrogen zero gas. The results are shown in Figure 8.

Navy Reference Gas Mixture



Nitrogen Zero Gas

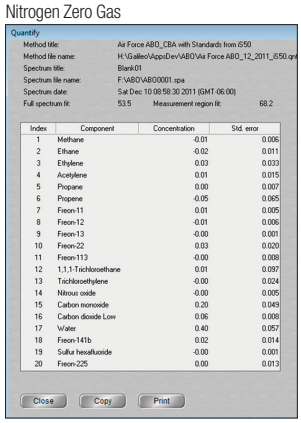


Figure 8

These results are reported as ppm and show a standard error of less than 100 ppb for most of the 20 components. The standard errors are even lower for the results with zero gas with the calculated vales for all components below 1 ppm and many below 100 ppb.

Similar methods have been used in many industries to detect trace contamination and moisture. Many producers of specialty gases use infrared spectroscopy as a key analysis technique in their QA/QC laboratories.

Environmental and Air Monitoring

Infrared spectroscopy has been used extensively to detect volatile organic species and other pollutants in the air. These hazardous compounds may result from a manufacturing process, land fill off-gas, vehicle exhaust or a chemical spill. A major challenge in measuring pollutants in the air is the strong infrared absorbance for both water and CO_2 which block out many of the spectral regions. A spectral resolution of 0.5 cm^{-1} is often necessary to create analysis windows between the water and CO_2 peaks as shown in Figure 9.

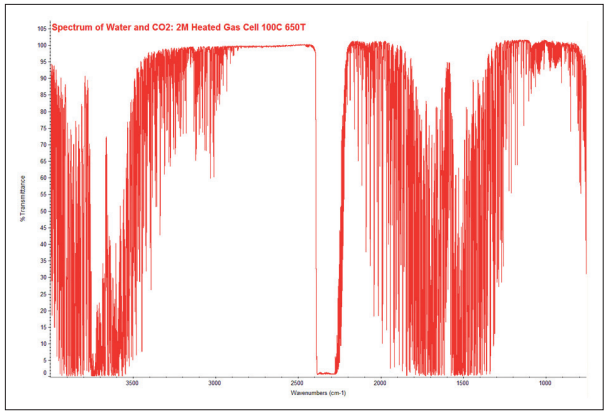


Figure 9

In many applications, continuous extractive sampling, Summa canisters or Tedlar bags are used to collect samples which can be pulled into the same 10 meter gas cell described previously. In high humidity situations the gas cell may be heated above 100 °C to ensure that water does not condense in the gas cell.

Conclusion

In this article, we have presented an overview of various gas analysis application areas where infrared spectroscopy has proven valuable. The Nicolet iS50 is designed with flexibility to analyze a variety of sample types with ease. The combination of high sensitivity and a full suite of software features, specifically designed for gas analysis, creates a world class solution to a broad range of applications.

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