

FT-IR Sampling Parameters for Exhaust Gas Measurements

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The Clean Air Act of 1990 sets stringent new limits for engine exhaust emissions levels. Emissions limits for traditionally regulated components such as CO, NO_x, and THC have been tightened. Additionally, highly reactive compounds in engine exhaust such as benzene and formaldehyde are now being carefully monitored. To meet the new standards, measurement techniques must be devised to analyze the additional species. The instrumental methods used to analyze these compounds are often expensive, imprecise, and require frequent recalibration.

Fourier transform infrared (FT-IR) spectroscopy is a useful solution to the analytical problems of exhaust measurement. While traditional on-line analyzers require exhaust to be diluted and cooled before sampling, FT-IR can measure the raw exhaust directly. Many highly reactive species in exhaust can be measured by FT-IR down to low part-per-million levels (see Table 1). A single FT-IR may be used to replace 5-6 discrete analyzers. Finally, an FT-IR's response is quite stable relative to other analyzers and requires only infrequent recalibration.

TABLE 1: REGA 7000 COMPONENTS

Water	CO
CO ₂	NO
NO ₂	N ₂ O
Ammonia	Methane
Ethane	Propane
Total Hydrocarbons	Ethene
Propene	1,3-Butadiene
Isobutadiene	Formaldehyde
Acetaldehyde	Total Aldehydes
Methanol	Ethanol
Aromatic Hydrocarbons	

Accurate measurement of exhaust gases requires reproducible sample handling techniques, optimized optical bench settings, and carefully defined quantitative methods of analysis. This technical note describes the sampling parameters which must be controlled for accurate, reproducible results from the FT-IR analysis.

OPTICAL BENCH PARAMETERS

Resolution

The FT-IR should be set to 0.5 cm⁻¹ resolution for exhaust gas measurements. At lower resolutions (1 cm⁻¹, 2 cm⁻¹), water's absorbance bands may create interference problems which affect the detection limits of many compounds. Setting the FT-IR to higher resolutions (.25 cm⁻¹, .125 cm⁻¹) will resolve water interferences more completely, but at the costs of added noise, spectral file size, and scanning time.

Detector

An MCT detector is recommended for the highest performance. The MCT detector responds very quickly and is extremely sensitive to weak infrared signals. As such, it is used to measure transient emissions levels down to low part-per-million concentrations. However, there are disadvantages in using an MCT detector. It requires liquid nitrogen to cool down to its working temperature (typically about 1 liter per day). Also, because the MCT's response is quite non-linear with concentration, calibration curves must be developed for many gases (including CO, CO₂, and NO_x).

A DTGS detector may also be used for exhaust gas measurements although its performance does not match that of an MCT. A DTGS detector operates at room temperature and has a quite linear response curve. It is also less expensive than an MCT. However, its response is less sensitive to the infrared signal, so detection limits are typically 3-10x higher. For example, the detection limits for NO may rise from 1-2 ppm with an MCT up to 10-15 ppm using the DTGS. Another disadvantage is the slow response of a DTGS which limits its use to steady-state engine measurements.

Gas Cell

The pathlength of the gas cell should be matched to the concentration levels of the exhaust. A longer pathlength helps the sensitivity of the FT-IR for compounds at low concentration levels. Gas cells with pathlengths of 10-20 meters are typically

used for diluted exhaust. Shorter pathlength cells (1-4 meters) have lower volumes and are useful for measuring transient emissions in raw exhaust. A wide variety of gas cells are available from Nicolet to meet different sampling conditions, including the patented gas cell for the highest sensitivity.

Measurement Time

The signal-to-noise ratio of an FT-IR measurement increases with scanning time. A one minute measurement will show higher sensitivity than a five second measurement. This is due to signal averaging which minimizes background noise and produces a quieter signal at the detector. MCT detectors, with high sensitivity and rapid response, can show useful values every few seconds. In contrast, a DTGS detector can only be used for steady state measurements due to its relatively slow response and lower sensitivity.

SAMPLE HANDLING CONSIDERATIONS

Temperature

Because the density of the exhaust is dependent on temperature, all samples should be run at a controlled temperature. Measurement temperatures of 80-150°C prevent water or heavier hydrocarbons from condensing and giving inaccurate results. The temperature should be controlled throughout the entire sample line from the engine to the FT-IR.

Pressure

Many applications can be run at atmospheric pressures. However, variations in pressure will change the gas density and give less accurate results. A pressure control gauge set to slightly below atmospheric pressure (600-650 mmHg) increases the sampling reproducibility for more precise experiments.

Sampling Line

The transfer line between the engine and the FT-IR should be heated to prevent condensation. A heated particulate trap is recommended to stop soot particles from

coating onto the gas cell mirrors. Finally, a vacuum pump is required to pull the exhaust through the sampling system. Diaphragm pumps are recommended over oil pumps due to the high water levels in exhaust which can mix into the oil and cause the pump to seize.

Water condensers are used with many on-line analyzers to minimize interferences. However, many compounds of interest in the exhaust, such as form aldehyde and SO₂, will also condense with the water. By correct definition of the quantitative method on the computer, water interferences can be minimized in the software without use of a condenser.

QUANTITATIVE ANALYSIS PARAMETERS

Quantitative analysis methods are based on Beers Law, which states that spectral absorbance is proportional to a compound's concentration. Thus, if the concentration of a gas doubles, its infrared absorbance will double. In practice, the FT-IR analysis is limited at low levels (<.01 AU) by baseline noise, and at high levels (>1.0 AU) by non-linear response and excessive interference from water. Ideally, the spectral bands chosen for each compound should be in the .1-.7 AU absorbance range for its expected concentration in the exhaust and be free of interferences from water.

Infrared regions

Table 2 lists the spectral regions typically used for commonly-measured compounds. Measurement of CO₂ is very straightforward. Carbon monoxide levels vary greatly with different applications, which requires the careful selection of infrared absorbance bands to stay

within the desired absorbance range. The measurement of NO_x is complicated because it is not a single compound, but rather the sum of two separate compounds NO and NO₂. The FT-IR measures NO and NO₂ separately and adds them together to reach a NO_x-equivalent value. Also, both NO and NO₂ absorb only in regions with very high levels of water interference, as well as CO and CO₂ interferences. Nicolet's classic-least-squares (CLS) software uses multiple spectral "windows" within these regions to specify individual NO or NO₂ bands between the water bands.

Total Hydrocarbons (THC)

FT-IR measures hydrocarbons differently from the flame ionization detector (FID) typically used in exhaust measurements. FT-IR can measure 15-20 hydrocarbons individually in exhaust, whereas the FID measures all hydrocarbons together in a single bulk reading. By weighting the calculated levels of individual hydrocarbon species with their carbon numbers, the FT-IR values can be combined into an FID-equivalent reading.

Quantitative Software

Nicolet's CLS II software is designed specifically for gas phase calculations. With CLS II, interferences from water or other compounds may be minimized by careful selection of "windows" which blank out the interfering bands. A further advantage is the "+/- fit error" calculation with each reported concentration (see

TABLE 3: ANALYSIS OF DIESEL EXHAUST USING CNG FUEL

Component	Conc (ppm)	Error (+/-)
H ₂ O	53038.79	4437.73
CO	496.9	9.3
CO ₂	25292	487.7
NO	94.12	3.83
NO ₂	0.74	1.36
N ₂ O	1.93	9.22
Ammonia	0.0	0.31
Methane	1087.97	9.68
Acetylene	4.27	3.69
Ethene	10.67	0.4
Ethane	6.12	10.68
Propene	2.97	1.31
Propane	43.67	7.85
Methanol	2.31	0.68
Formaldehyde	27.35	3.23

Table 3). This provides the user a confidence level for each value, and is useful to diagnose optical bench problems or unexpected spectral interferences. These important features are available only with Nicolet's CLS II software.

SUMMARY

Engine exhaust emissions can be successfully analyzed by FT-IR, including species such as formaldehyde, methane, and sulfur dioxide. FT-IR's advantages over other measurement techniques include direct sampling of raw exhaust, measurement of many compounds with one analyzer and highly-stable calibrations. Important parameters for exhaust sampling, optical bench setup, and quantitative method development are reviewed. Careful control of these parameters is required for accurate results. Finally, the Nicolet CLS II software has unique capabilities to provide the greatest accuracy and minimize calculation errors.

TABLE 2: INFRARED ANALYSIS REGIONS

Compound	Conc Range (ppm)	Spectral Range (cm ⁻¹)
CO (high)	1000-5%	2000-2050
CO (low)	1-1000	2150-2225
CO ₂	2-20%	725-765
NO	5-5000	1850-1950
NO ₂	5-500	1580-1650
CH ₄	1-5000	2800-3000