

WHITEPAPER

FTIR Gas Analysis

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Introduction

FTIR (Fourier Transform InfraRed) spectroscopy is the most popular analytical technology for industrial applications requiring the continuous measurement of multiple parameters simultaneously. Typically, FTIR analyzers are employed for process control and emissions monitoring, however, due to the robustness and flexibility of this technique, it can also be applied in a wide variety of different applications, which will be discussed in greater detail below.

FTIR gas analyzers identify and measure gaseous compounds by their absorbance of infrared radiation. This is possible because every molecular structure has a unique combination of atoms, and therefore produces a unique spectrum when exposed to infrared light. Instrumental analysis of the spectrum (2 to 12 micrometer wavelength) enables the qualitative identification and quantitative analysis of the gaseous compounds in the sample gas.

Importantly, FTIR analyzers are able to simultaneously measure multiple analytes in complex gas matrices, detecting virtually all gas-phase species (both organic and inorganic, except diatomic elements N_2 , O_2 etc. and noble gases He, Ne, etc.). For example, the Gasmeter FTIR gas analyzer collects a complete infrared spectrum (a measurement of the infrared light absorbed by molecules inside the sample gas cell) 10 times per second. Multiple spectra are co-added together according to a selected measurement time (improving accuracy by raising the signal-to-noise ratio). The actual concentrations of gases are calculated from the resulting sample spectrum using a patented modified **Classical Least Squares analysis algorithm**.



FTIR – Common Questions

1. WHAT IS AN FTIR SPECTROMETER? AND HOW DOES IT WORK?

A FTIR spectrometer consists of the following key components:

- > A broadband IR source emitting all recorded wavelengths simultaneously
- > Beamsplitter which separates the IR beam into two equal parts
- > A moving/stationary mirror assembly where the two beams travel a distance which can be varied by moving one or more mirrors continuously back and forth
- > A reference laser source, which is used to track the position of the moving mirror
- > Focusing optics used to transfer the beam into the sample cell and from the sample cell into the detector
- > Sample cell filled with sample gas or test gas
- > IR detector which responds to the entire wavelength range of the spectrometer
- > Laser detector which responds to the wavelength of reference laser used

The beamsplitter and moving/stationary mirror assembly are collectively known as the interferometer and this is the heart of a FTIR spectrometer. Due to the motion of mirrors, the two beams produced by beamsplitter have a phase difference and when they recombine at the beamsplitter the produced IR intensity varies with mirror position. The interferometer can be considered an optical modulator and the modulation of the beam is the key to calculating intensity at each frequency from the signal recorded by IR detector.

The IR detector records a signal as a function of time (or mirror position, as the moving mirror has a constant speed) known as the interferogram. This signal is linked with the IR spectrum

by a Fourier transformation, a mathematical tool for converting time domain signal $I(t)$ to a frequency domain signal $I(f)$. By placing a sample cell between the interferometer and the detector, the spectrometer can be used to measure an absorption spectrum of the sample gas, and the identity and concentration of gases in the sample can be calculated from the absorption spectrum.

2. WHAT IS AN INFRARED SPECTRUM?

The infrared spectrum is a plot of infrared radiation related quantities as a function of wavelength or wavenumber. There are three commonly used quantities for an infrared spectrum:

- > **Intensity (I)**, is a measure of IR light falling on the detector, and this can have a unit of power per surface area but more commonly this is represented on a unitless scale of detector counts.
- > **Transmittance (T)**, is the ratio of Intensity measured with sample gas in the sample cell (sample spectrum) and Intensity measured with zero gas in the sample cell (background spectrum). Transmittance is a unitless number and is typically expressed as percentage (0 - 100%). The reason why Intensity is commonly represented by detector counts instead of SI units of power/area is that the same units are used for both I and I_0 when calculating transmittance and they cancel each other.
- > **Absorbance (A)**, is a logarithm of Transmittance with reversed sign. Absorbance is particularly useful for gas analysis because it is directly proportional to gas concentration unlike Transmittance or Intensity. The x-axis of an IR spectrum can be either wavelength in micrometers (microns) or more commonly wavenumber in reciprocal centimeter units. Wavenumbers are in common use as the spacing of spectral lines in IR spectrum is more constant in wavenumber than wavelength scale. The table below shows some common wavelengths and wavenumbers.

Table 1. Common wavelengths and wavenumbers

	WAVELENGTH	WAVENUMBER
Boundary of IR and Microwave scale	500 μm	20 cm^{-1}
Low end of Mid-IR scale	20 μm	500 cm^{-1}
High end of Mid-IR scale	2.5 μm	4000 cm^{-1}
Visible red	0.77 μm (770 nm)	13000 cm^{-1}
Typical Gasmet spectral range	12 μm to 2.5 μm	900 cm^{-1} to 4200 cm^{-1}

A typical infrared spectrum of HCl gas is shown below. The HCl molecules vibrate with a frequency that corresponds to the gap in the middle of the spectrum, and the individual lines are due to combinations of vibration and rotation of the molecules. This pattern is unique to HCl and each gas has a corresponding 'fingerprint' which is different to the spectra of other gases, forming the basis of identification. The peak heights in absorbance scale are also proportional to gas concentration, which is the basis of quantification of gases from the spectrum.

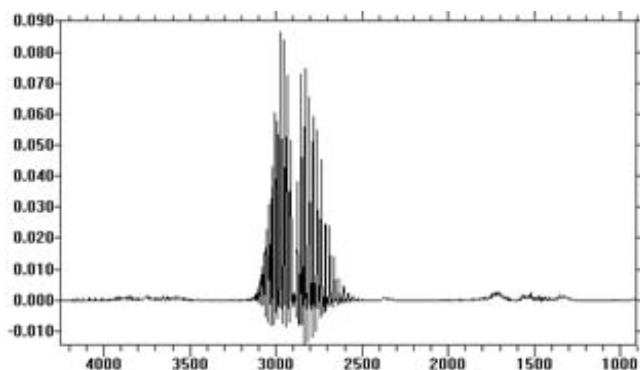


Figure 2. Infrared spectrum for HCL

3. HOW IS THE IR SPECTRUM USED FOR THE QUANTIFICATION OF GASES?

The amount of light passing through an absorbing medium decreases exponentially as the thickness of the absorber is increased (Figure 2). In the case of gas analysis, the absorber is the sample cell filled with IR absorbing gas. Absorbance at a given wavelength (λ) is a logarithm of transmittance, $A = \log_{10}(I/I_0)$, and is directly proportional to gas concentration (c), the distance travelled by the IR beam in the sample gas (b), and a gas specific constant (ϵ) known as molar absorptivity. The relation can be expressed as the LambertBeer law:

$$A(\lambda) = \epsilon(\lambda) \times b \times c$$

In this equation, the concentration c is the quantity to be determined, A is taken from the measured spectrum, ϵ from the reference spectrum (see below) and pathlength b is a known quantity of the FTIR gas analyzer. The actual quantification is achieved by building a model spectrum from the reference spectra and matching them against the sample spectrum over a wide range of wavelengths to determine concentrations of multiple gases simultaneously. The illustration below shows how light intensity drops when the beam passes through a thickness of IR absorbing sample gas.

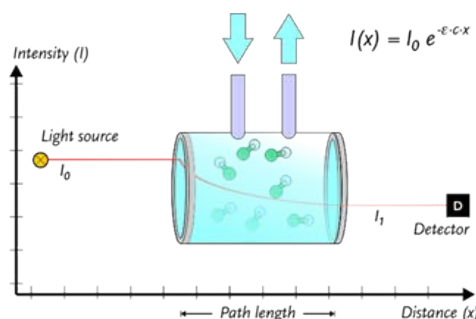


Figure 3. Lamber-Beer Law and Absorbance

4. WHAT IS A REFERENCE SPECTRUM?

A reference spectrum is a spectrum of known concentration of one IR absorbing gas diluted in nitrogen. Reference spectra are used to analyze measured sample spectra. The absorption peaks in a sample gas are compared with those of reference spectra to determine simultaneously the concentrations of multiple gas components of the sample. For instance, if the absorption due to Methane in the sample is 1.2 times that of a 10 ppm Methane reference spectrum, the concentration of Methane is 12 ppm.

The reference spectrum is recorded using a long measurement time to eliminate noise from the spectrum and the instrument is carefully purged to eliminate traces of moisture and carbon dioxide (the two main atmospheric IR absorbing gases) from the spectrum. In order to model moisture and carbon dioxide in the sample, reference spectra of these gases are used.

5. WHICH GASES CAN BE MEASURED BY THE GASMET™ FTIR GAS ANALYZERS?

IR absorption spectroscopy such as FTIR detects those gases that absorb infrared radiation in internal motion (vibration) of the molecule. The absorption strength of a gas depends on the change of dipole moment (separation of electric charge) caused by the vibration. A molecule with strongly varying dipole moment absorbs radiation strongly whereas a molecule with no net change of dipole moment is transparent to IR radiation. Most molecules absorb IR light and are therefore measurable. However, some molecules (N_2 , O_2 , H_2 , Cl_2 , ...) and all single-atom gases (He, Ne, Ar, Hg, ...) do not change dipole moment and therefore they do not have an IR absorption spectrum. These gases, especially Nitrogen, can be used as a zero gas for recording a background spectrum (I_0). The gases measured by FTIR include:

- > Inorganic gases: Water, CO_2 , CO, NO, NO_2 , N_2O , NH_3 , SO_2 , HCl, HF, ...
- > Volatile organic compounds: hydrocarbons, alcohols, aldehydes, ketones, freons, ...
- > The main exceptions are:
 - > noble gases (He, Ar, ...)

- > metals (Hg)
- > molecules with just two atoms of the same element (N_2 , O_2 , H_2 , Cl_2)
- > molecules with very small dipole moment change (H_2S)
- > low volatility organics (high boiling point or room temperature solid)
- > particulate matter or aerosols (not a gas)

6. WHAT IS THE TYPICAL PERFORMANCE OF GASMET™ FTIR GAS ANALYZERS IN EMISSIONS MONITORING APPLICATIONS?

Gasmet FTIR analyzers meet the performance requirements laid down in EN 15267-3 (Europe) and PS 15 (U.S). Linearity deviations are less than 2% of full scale and crossinterference effects due to stack emissions gas (H_2O up to 40 vol-%) are less than 4% of full scale for certified gases. Measurement accuracy is typically expressed in terms of expanded measurement uncertainty (U_c), a combination of uncertainty sources such as:

- > nonlinearity (lack of fit)
- > cross-interference
- > zero and span drift
- > temperature
- > flow rate
- > pressure
- > mains voltage

Measurement uncertainty for specific gases (CO , NO , NO_2 , SO_2 , HCl , HF , ...) has a limit value proportional to emission limit value in the EU Industrial Emissions Directive, and the Gasmet system typically has measurement uncertainties smaller than one half the maximum uncertainty allowed for a certified (**EN 15267-3, TÜV, MCERTS**) emissions monitoring system. This ensures that Gasmet gas analyzers are capable of monitoring not only today's emission limits but also lower limit values that may be introduced in the future.

7. HOW ARE NEW GASES ADDED TO THE LIBRARY?

New gases can be either measured with the instrument in question or imported from a generic library. The best method depends on the application; if traceability is required, instrument specific calibration is the best option, otherwise generic spectra may be used. Instrument specific calibration can be performed by the user or by the Gasmet calibration laboratory.

8. WHEN SHOULD GASMET™ FTIR GAS ANALYZERS BE RECALIBRATED?

FTIR gas analyzers do not require periodic recalibration. A daily background spectrum measurement with zero gas is enough to preserve measurement accuracy. Instead of periodic

span calibrations, reference spectra for analyzed gases are measured at the factory when the instrument is made and these do not drift. Calibration of an FTIR instrument relies on:

- > reference spectra recorded on a computer
- > daily background spectrum measurement with zero gas (N_2) which compensates for any variation in the IR source, sample cell, etc.
- > continuous internal reference of wavelength scale with a reference laser

For the above reasons the response of an FTIR instrument does not drift and separate zero and span adjustments of each measured gas are not required. FTIR measures low ppm concentrations of pollutants in hot/wet gases up to 40 vol-% (400 000 ppm) water, so the reference spectra of H_2O are measured again after a service operation (involving the optical components) to preserve highest accuracy.

9. WHY IS THE QUALITY OF THE INTERFEROMETER CRUCIAL?

The Gasmet GICCOR (Genzel Interferometer with Cube Corner Retroreflectors)

interferometer is specially designed for maximum optical throughput and maximum signal-to-noise ratio at a resolution of 7.72 cm^{-1} providing unparalleled stability with respect to vibration and temperature changes. It can be used in a temperature range of 0 to 40 °C (short term) and also in a person-portable analyzer while the user is moving with the instrument. The use of cube corner mirrors, a highly symmetric mirror layout and a patented moving mechanism removes temperature and vibration influence and the use of non-hygroscopic optical material removes the need for dry air or nitrogen purging of the interferometer

10. WHY IS THE QUALITY OF THE SAMPLE CELL IMPORTANT?

The Gasmet sample cells have mirror surfaces machined directly to the cell end plates, eliminating a source of drift and uncertainty associated with adjustable mirror gas cells. The cell surfaces are coated with a proprietary combination of materials including Rhodium and Gold selected for their corrosion resistance against reactive gases and high IR reflectance (in the case of Gold). Sample cells are available in a very wide range of path lengths from 1 cm to 980 cm, and long path lengths are achieved in a small cell volume (450ml in the case of 980 cm path). The cells are heated optionally up to 180 °C to allow hot/wet sampling of gases with high concentrations of H_2O , SO_2 , etc.

11. DO ACIDIC GASES SUCH AS HCL AND HF DAMAGE THE SAMPLE CELL?

The multiple layer coatings on the sample cell and elevated cell temperatures make the cell remarkably resistant to the corrosive effects of acid gases even when the water content of the gas is high. However, if the sample is allowed to cool down and condense inside the cell

or the acid gas dew point exceeds cell temperature, damage to the cell is possible. For this reason the Gasmet sampling system design prevents the sample pump from pulling wet gas into a cell under the temperature set-point. If the temperature of any heated part falls below the set-point, or the system loses power, the cell is flushed with dry air or nitrogen before condensation can take place. As long as condensation is avoided the cell is not damaged by moderately high levels HCl or HF.

The corrosion resistance of the sample cell depends on the prevention of condensation inside the cell. The cell temperature should exceed the dew point of the sample gas by a safety margin. For this reason Gasmet analyzers have different temperature set points as shown in the table below:

Table 2. Temperature set points of Gasmet gas analyzer

	TEMPERATURE	USED FOR
CX4015 and DX4015	50 °C	ambient temperature samples
CX4000 and DX4000	180 °C	stack emissions monitoring
In-Situ	variable, typ. 20°C above process temp.	stack emissions monitoring

12. HOW IS PRESSURE COMPENSATION ACHIEVED?

All Gasmet FTIR gas analyzers have a pressure sensor for measuring atmospheric air pressure. In the preferred sampling technique the outlet of the cell is open to atmosphere, ensuring that the pressure in the cell is equal to the measured air pressure thereby simplifying pressure measurement. Optionally, the gas cell can be fitted with a pressure sensor or an analog input signal from an external pressure sensor can be used to measure process pressure if the outlet of the gas cell cannot be vented into atmospheric pressure.

The reference spectra used to interpret the sample spectrum contain pressure and temperature values from the time that they were recorded. These are scaled to match sample gas pressure and temperature and the comparison is always performed on the actual conditions inside the sample cell during measurement.

13. HOW IS OXYGEN COMPENSATION UNDERTAKEN?

Oxygen compensation is undertaken automatically with readings from a hot/wet Zirconium Oxide oxygen sensor. In portable emissions monitoring analyzers this sensor is built into the sampling unit and in continuous emissions monitoring systems the O₂ analyzer is in separate 19" rack housing. The compensation formula below uses the dry O₂ reading, and the H₂O

concentration measured by the FTIR is used in the dry gas conversion calculation.

$$c_{\text{norm}} = c_{\text{dry}} \times \frac{21\text{vol}\% - c(\text{O}_2)_{\text{ref}}}{21\text{vol}\% - c(\text{O}_2)_{\text{dry}}}$$

$$c_{\text{dry}} = c_{\text{wet}} \times \frac{100\text{vol}\%}{100\text{vol}\% - c(\text{H}_2\text{O})}$$

$c(\text{O}_2)_{\text{ref}}$ is the reference oxygen concentration and it is defined for different fuel types to represent typical oxygen concentrations. Some typical values include 11% for waste incineration, 6% for solid fuels and 3% for liquid or gaseous fuels.

14. HOW LONG DOES IT TAKE TO LEARN HOW TO USE A GASMET™ FTIR GAS ANALYZER?

Initial training during commissioning typically consists of one day, which is sufficient for carrying out measurements and preventive maintenance tasks with a pre-defined application library. Additional training is available from Gasmeter and their distributors worldwide for users wishing to develop their own application libraries and for other advanced tasks.

15. WHAT ARE THE MAIN FEATURES OF CALCMET™ SOFTWARE?

Gasmeter Calcmeter software is used for all tasks on both portable emissions analyzers and continuous emissions monitoring systems:

- > data acquisition from the FTIR spectrometer
- > quantitative analysis of spectra
- > visualization of spectra, results, and time trend views
- > wide range of I/O functions (4-20 mA, 0-10 V, MODBUS, digital and relay I/O)
- > sampling system control including automatic calibration and drift checks, and probe back-flushing

In '**Calcmeter Professional**' software the following features are also enabled:

- > identification of unknowns with the Advanced Library Search tool, which works even for mixtures of unknowns
- > support for NIST/EPA vapor phase library with 5000+ qualitative references
- > calculation of maximum and minimum absorbance, integrated absorbance, RMS noise absorbance...
- > calculation of FMU and MAU as defined in US EPA test method 320

- > combinations of alarm and status signals using Boolean logic
- > AK protocol communications for automotive applications
- > peak marking, spectrum smoothing, spectrum deconvolution

16. WHAT ARE THE DETECTION LIMITS FOR COMMONLY MEASURED GASES?

The Gasmet FTIR gas analyzers can measure from low ppm levels up to vol-% with sub-ppm detection limits for almost all gases. Exact detection limits depend on the type of sample cell and detector used. Please contact Gasmet or one of its Distributors for performance data on your list of target gases.

17. WHAT IS THE REFERENCE LIBRARY COLLECTION?

The Gasmet reference library collection contains IR spectra and concentration information for over 250 gas species measured at Gasmet Technologies, enabling library searches and the use of non-instrument specific references. To complement this collection of spectra, the NIST/EPA vapor phase IR library is also available in a form compatible with Gasmet IR spectra and this allows the identification of an additional 5000+ gases.

18. WHAT EFFECT IS THERE FROM THE USE OF A REFERENCE SPECTRUM FROM A DIFFERENT ANALYZER?

An instrument-specific reference spectrum is one that is measured with the same instrument as the sample spectra, whereas a non-instrument-specific reference is one transferred from another instrument or a generic reference library. As the FTIR instruments are very stable and the wavelength scale does not drift due to the use of internal wavelength scale calibration with Helium-Neon laser, the accuracy of both methods is comparable. The main difference is that an instrument-specific reference spectrum is traceable back to calibration gas certificates and thereby to primary standards, whereas the non-specific references are not traceable.

19. HOW IS AN FTIR ANALYZER MAINTAINED?

Preventive maintenance includes the measurement of background spectrum with zero gas before measuring sample spectra, flushing the analyzer with dry air or zero gas after measuring sample spectra and ensuring that sample gases are vented away from the analyzer outlet without a flow obstruction. In the case of sample gases with above ambient dew point temperature, it is also important to eliminate cold spots from the sampling system connections.

20. HOW MANY GASES CAN BE MEASURED AND ANALYZED AT THE SAME TIME?

Typically up to 40 or 50 gases can be analyzed from a sample spectrum. The exact number of gases depends on the availability of non-saturated absorption peaks in the spectrum (areas of spectrum with absorbance stronger than 0.8 absorbance units should be avoided) and in samples with strong absorbance across the spectrum the number of gases may be lower.

21. WHAT IS THE TYPICAL RESPONSE TIME?

The response time of the Gasmet FTIR analyzers depends on the sample cell volume, pump flow rate and the length of heated line. Typical response times are as follows:

- > less than 120 seconds for a CEMS with 20 meter heated line for all gases except NH₃, HCl, HF
- > less than 180 seconds for a CEMS with 20 meter heated line for NH₃, HCl, HF
- > less than 30 seconds for a DX4015 or DX4040 analyzer with built-in pump and short unheated sample line
- > 1-2 seconds for an Engine Emissions Monitoring system with high flow rate pump and small volume sample cell

22. WHAT CERTIFICATIONS DOES GASMET HAVE?

- > TÜV / German Type Approval for Gasmet CEMS II e, Gasmet CEMS II ef, Gasmet CMM
- > MCERTS Certified products
 - > Continuous Emissions Monitoring System (CEMS)
 - > Continuous Mercury Monitoring System (CMM)
 - > Gasmet DX4000 has the MCERTS certification for stack emissions monitoring. There is also VDI 3862 standard for measuring formaldehyde emissions from biogas plants in Germany
- > Gasmet DX4000 gas analyzer GOST certificate (Russia)

Summary

FTIR analyzers offer the ability to monitor multiple gases simultaneously, reliably and accurately in a wide variety of applications. Gasmet emissions monitoring analyzers comply with international performance standards and can even measure the components of hot, wet aggressive gas mixtures.

Comprehensive certification provides regulated processes with the assurance that monitoring data from Gasmet FTIR analyzers will meet or exceed all regulatory requirements across an expanded range of compounds. Furthermore, the experience of Gasmet customers all over the world provides confidence that these analyzers will provide long-term, reliable, trouble free monitoring.

As the developer and manufacturer of FTIR analyzers and associated software, Gasmet is able to offer the highest levels of technical support both before and after sales, either directly or through a world-wide network of subsidiaries and highly trained distributors. One of the most important features of Gasmet FTIR analyzers is their flexibility. If users need to monitor new gases; no extra hardware is necessary because the addition of new compounds to the list of measured species is a relatively simple procedure. This means that the monitoring equipment is future-proof. In addition, Calcmeter Professional software enables users to retrospectively analyze recorded spectra, which means that it is possible to measure compounds in previous data, that were not originally of interest. Many users have found this to be an extremely useful tool in the identification of process related problems.

The portable versions of the Gasmet analyzers offer a range of unique advantages. For example, many stack monitoring locations can be difficult to access so small lightweight equipment is preferred. The Gasmet DX4000 is therefore the instrument of choice for stack testers with multiple monitoring locations.

A non-heated, ambient version of the portable FTIR analyzer (DX4040) is supplied with a convenient backpack and can be operated wirelessly from a PDA with Bluetooth. This enables users to move freely, analyzing multiple compounds simultaneously. As a result, this instrument is popular in a wide variety of field/site monitoring applications.

In conclusion, FTIR is a powerful but flexible monitoring technology; able to provide comprehensive monitoring data in an enormous variety of monitoring applications. For help and advice on how FTIR can be employed in your application, please visit www.gasmet.com or contact your local Gasmet subsidiary or distributor.

> Know what's in the air.

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