WHITE PAPER

FTIR Gas Analysis

> Know what's in the air.

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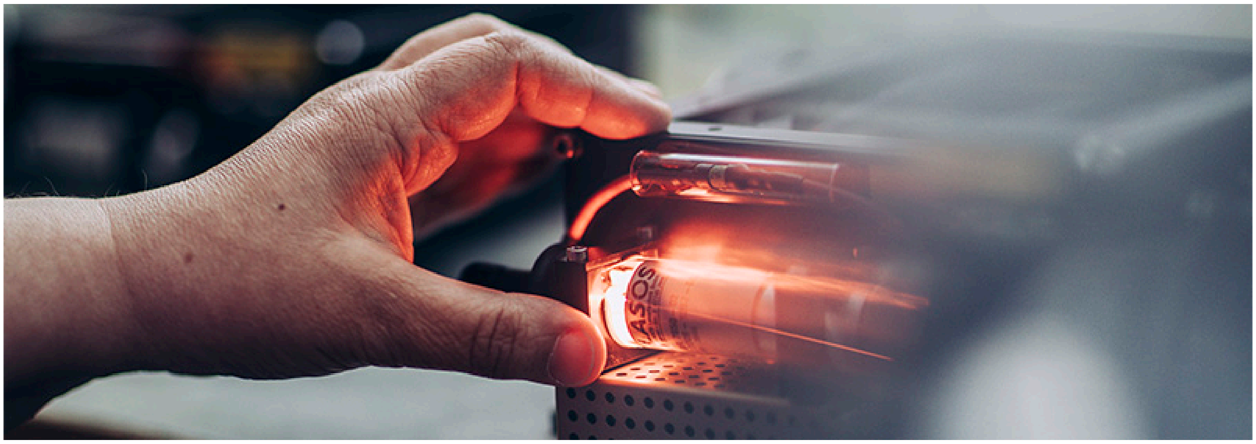
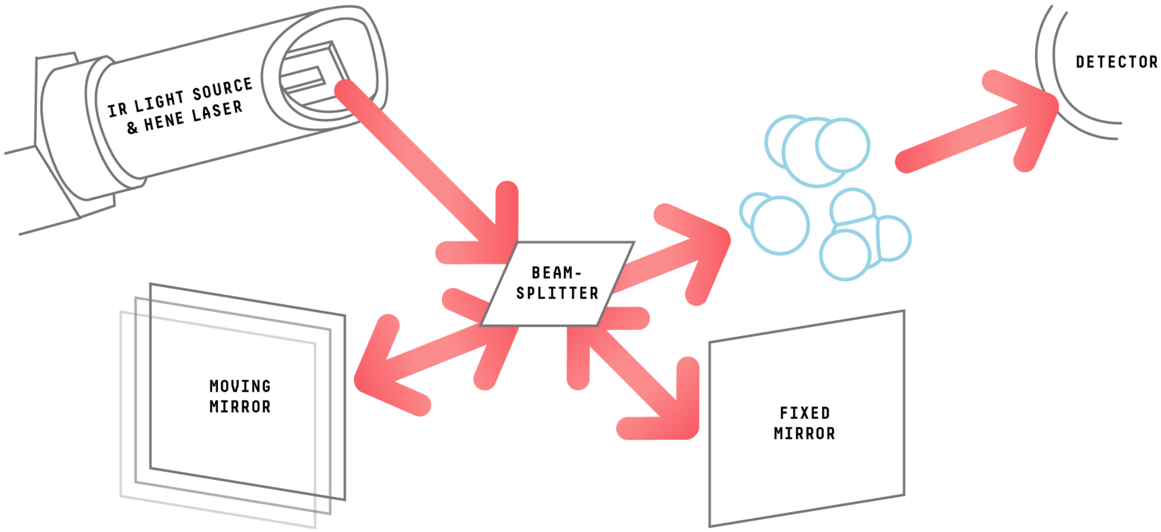


Introduction

FTIR (Fourier Transform InfraRed) spectroscopy is the most popular analytical technology for applications requiring 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.

FTIR gas analyzers identify and measure gaseous compounds by their absorbance of infrared radiation. This is possible because the combination of atoms and their arrangement is unique to every molecular structure, and therefore molecules produce a unique spectrum when exposed to infrared light. Instrumental analysis of the spectrum gathered from infrared with wavelength around 2-12 micrometers enables the qualitative identification and quantitative analysis of the gaseous compounds in the sample gas.

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



FTIR – Common Questions

1. What is an FTIR spectrometer and how does it work?

An FTIR spectrometer consists of the following key components:

> Broadband IR source emitting all recorded wavelengths simultaneously
> Beamsplitter, which separates the IR beam into two equal parts
> 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
> 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 the mirrors, the two beams produced by the beamsplitter have a phase difference and when they recombine at the beamsplitter, the produced IR intensity varies with the 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.

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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)*. This conversion gives us the signal as a function of frequency of the infrared light. 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, which is commonly used in IR spectroscopy. Wavenumber is the inversion of wavelength, and in practice tells us the number of waves per unit of distance. Wavenumber is also directly proportional to the energy of the wave. 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 (I_0) in the sample cell (background spectrum). Transmittance is a unitless number and is typically expressed as percentage (0 - 100%). This is also the reason why intensity is commonly represented by unitless detector counts instead of SI units of power/area. As intensity is mainly used to calculate transmittance, its unit would disappear in the division and is thus irrelevant.
> **Absorbance (A)**, is a negative logarithm of transmittance. 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, because 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 in Figure1. 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. Another example is the infrared spectrum of Ethanol, showing more complex molecule in Figure 2. The peak heights in absorbance scale are also proportional to gas concentration, which is the basis of quantification of gases from the spectrum.

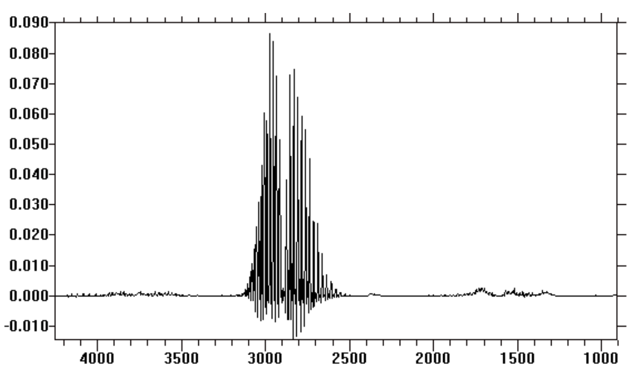

Figure 1. Infrared spectrum for HCl

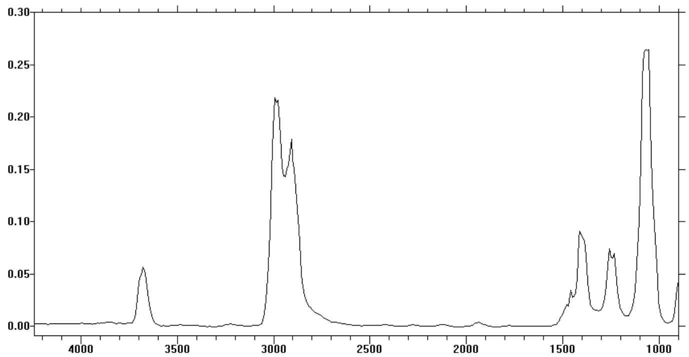

Figure 2. Infared spectrum from Ethanol

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 3). 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 negative 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 Beer-Lambert law :

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

In this equation, the concentration c is the quantity to be determined, A is taken from the measured spectrum, *ε* is calculated 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.

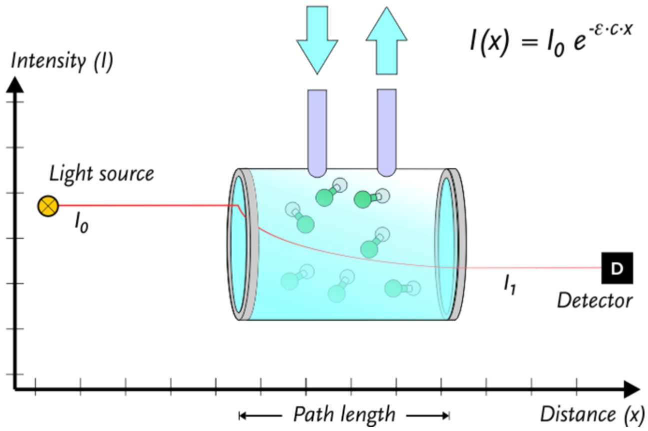

Figure 3. Beer-Lambert Law and Absorbance

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, see Figure 4. 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.

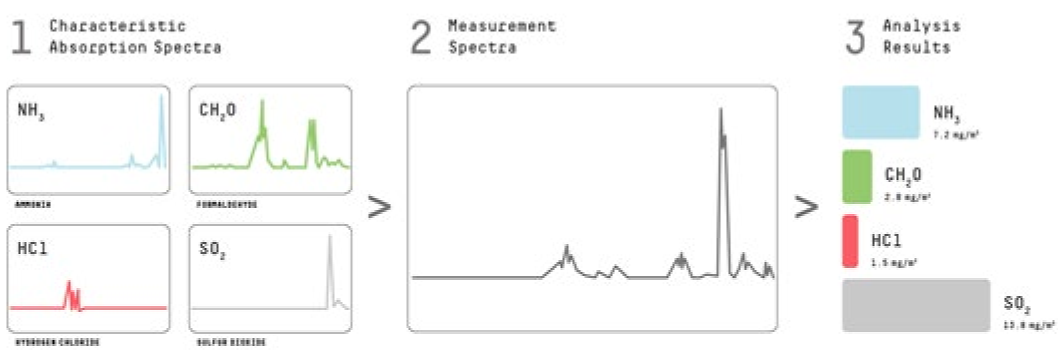

Figure 4. FTIR analysis

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 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. 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 cross-interference 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 (Uc), 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 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 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 point as shown in the table below:

Table 2. Temperature set point of Gasmet gas analyzer

	Temperature	**Used for**
CX4015 and DX4015	50 °C	ambient temperature samples

		with high moisture content
CX4000 and DX4000	180 °C	stack emissions monitoring
GT5000 Terra	Ambient (-5 – 40 °C)	ambient temperature samples

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 a 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.

$$c_{norm} = c_{dry} \times \frac{21\text{ vol-\%} - c(O_2)_{ref}}{21\text{ vol-\%} - c(O_2)_{dry}}$$

$$c_{dry} = c_{wet} \times \frac{100\text{ vol-\%}}{100\text{ vol-\%} - c(H_2O)}$$

$c(O_2)_{ref}$ 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 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 Gasmet 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?

Gasmet Calcmet 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

Calcmet comes in different versions, depending on the product you are using and depth of analysis you need. Calcmet Easy and Calcmet Expert can be used only with GT5000 Terra. Other Gasmet FTIR products work with Calcmet Standard and Calcmet Professional.

Calcmet Easy:

- Designed for accessible on-field work, touch screen friendly
- Simple to use, with one-click measurements and instructions
- Switch between different views
- Settings and options for everyday use

Calcmet Expert:

- Full analysis settings
- Post analysis tools (simulation tool and identification tool)
- Identification of unknowns with the Identification tool, which works even for mixtures of unknowns
- Full communication configurations (I/O signals)

Calcmet Standard:

- Full analysis settings

Calcmet Professional:

- Full communication settings for advanced use
- 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
- Additional math functions, lika calculation of maximum and minimum absorbance, integrated absorbance
- calculation of FMU and MAU as defined in US EPA test method 320
- combinations of alarm and status signals using Boolean logic

Full list of Calcmet features can be found on technical datasheets from Gasmet's website.

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 your local 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 600+ 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 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.

20. 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 NH_3, HCl, HF
- less than 180 seconds for a CEMS with 20-meter heated line for NH_3, HCl, HF
- less than 30 seconds for a DX4015 or GT5000 Terra 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

21. 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.

22. What certifications does Gasmet have?

- TÜV / German Type Approval for products:
  - Continuous Emissions Monitoring System (CEMS II e)
  - Continuous Emissions Monitoring System (CEMS II ef)
  - Continuous Mercury Monitoring System (CMM AutoQAL)
  - Continuous Mercury Monitoring System (CMM)
- MCERTS Certified products:

- Continuous Emissions Monitoring System (CEMS)
- Continuous Mercury Monitoring System (CMM AutoQAL)
- Continuous Mercury Monitoring System (CMM)
- Dioxin Monitoring System (GT90 Dioxin+)
- 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 and gas analyzer GOST certificate in Russia.

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Summary

FTIR analyzers offer the ability to monitor multiple gases simultaneously, reliably and accurately in a wide variety of applications. The experiences 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 simple procedure. In addition, Calcmet software enables users to retrospectively analyze recoded 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.

Gasmet's portable FTIR solutions are designed for field use. They are easy-to-carry, lightweight and yet powerful solutions providing laboratory quality results in the field. The unique capability to measure multiple compounds simultaneously makes these analyzers suitable for a wide variety of 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.

Gasmet Technologies is a company providing world-class gas monitoring solutions for industrial, environmental and safety markets. Worldwide, the company's customers include, but are not limited to, power plants, waste incinerators, first responders and universities.

Our mission is to provide solutions that help improve air quality, protect the environment, mitigate climate change and promote occupational safety. In the field of gas analysis, Gasmet has established a global reputation for innovative, customer-driven and reliable solutions, with a heavy emphasis on high levels of technical support.

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