# WHITE PAPER:
# GUIDE TO FTIR TECHNOLOGY FOR COMPLIANCE TESTING, PERFORMANCE SPECIFICATION, AND CONTINUOUS EMISSIONS MONITORING (CEM) OF TARGET GASES

**INSTITUTE OF CLEAN AIR COMPANIES 2013**

The Institute's mission is to be the voice of the stationary source air pollution control and monitoring industry by providing technical information relevant to flexible clean air policies based on practical, achievable and measurable emissions limitations.

**Guide to FTIR Technology for Compliance Testing, Performance Specification, and Continuous Emissions Monitoring (CEM) of Target Gases**

The intention of this Whitepaper is to provide a general understanding to the reader about the technology and uses of Fourier Transform Infrared (FTIR) instrumentation for identifying and quantifying gases in near real time from a simple or complex gaseous matrix. The paper is collaboration from four different applications scientists from different FTIR manufacturers. Its intent is to present the various hardware and software used in FTIR instruments and software programs and allow the reader to understand the basic workings of FTIR as well as the subtle and great differences between manufacturers and approaches. In addition, it addresses the advantages that FTIR has over other technologies and parameters that need to be considered when deciding on whether to use FTIR over other technologies.

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ICAC acknowledges the contributions of the following individuals and companies:

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# Contents

# 1.    Introduction

Fourier Transform Infrared (FTIR) spectroscopy is a measurement technique for collecting all of the infrared spectral information simultaneously as opposed to a few frequencies at a time, as is typically done in non-FT spectrometers. Instead of selecting a specific wavelength or region within the entire infrared region selected, like non-FT IRs, the FTIR light source uses all the frequencies in the IR region selected simultaneously.

# 2.    Theory

The IR electromagnetic spectrum is comprised of broadband photons, each with its own discrete frequency that is a function of energy.   Higher frequencies mean that the photon has more potential and kinetic energy available.  In its simplest form, FTIR requires only a source of IR energy (glow bar), a sample that absorbs IR energy (solid, liquid, gas), a detector to measure the energy at all the discrete frequencies of interests, and an interferometer to modulate the photons meaning that the IR beam is halved by a beam splitter, take half of the IR beam out of phase, and then recombine the two beams again.

The interferometer is the piece of hardware that differentiates FTIR from other IR technologies. The interferometer is a tool for modulating the light from an IR source.  The interferometer takes the photons from the IR source and splits it approximately 50% into two beam paths.  Half of the photons go to a fixed mirror and half go to a moving mirror.  The two beams of photons are then recombined.  The moving mirror extends the path length that the photons must travel in the moving mirror path.  This optically retards the frequencies in the moving mirror path, and when a particular frequency is re-combined, it has the effect of a phase shift, otherwise known as an interference pattern with both constructive and destructive interferences.  By examining the fringes of the cosine curves of all of the frequencies of the recombined interference pattern and performing a mathematical transformation (fast Fourier transform, FFT) of that raw interference pattern, known as an interferogram, from the time domain (time it takes to move the mirror) to the frequency domain, the energy at every discrete frequency can be measured very accurately. The absorption, or loss, of energy at those discrete frequencies is a function of the molecular structure of molecules and their densities (concentration) in a sample cell.   From calibration spectra, the software algorithms may put fractions of each calibration spectrum together to recreate the sample spectrum.  Those factors are then used to quantitate the target compound concentration.

The IR beam is passed through a sample gas cell where the various target molecules of interest and all other IR reactive compounds, absorb the energy at various discrete frequencies.  The time domain raw data is interferogram.  An FFT is performed and a single beam spectrum is

generated which is a graphical representation of each discrete frequency energy as measured by the instrument detector simultaneously.  Usually, but not always depending on the algorithm used, the spectrum from the same sample cell filled with a non-IR absorbing gas such as N2 is ratioed point by point against the sample single beam spectrum to create a double beam transmission spectrum.  The transmission of light energy at each discrete frequency is now a non-linear function of the density of types of molecules in the sample.   An inverse log of each transmission data point frequency is then performed to create the linear absorbance spectrum.  Quantitative analysis is then performed using the Beer-Lambert law (Beer's law).

Only until the relatively recent advancement of computers over the last 2 decades has the FTIR instrument become and is still improving as a simple, yet powerful field test instrument.  Hardware and software improvements coupled with vast quantities of field test measurements on hundreds of applications that have been used to validate molecular reactions between species and the selection of FTIR regions to yield the most accurate and reproducible results, have "canned" methods (or calibrations) been utilized for specific applications like emissions from Portland Cement Kilns.  Canned methods eliminate the need for the user to select their own regions and calibration spectra to enable the reporting of accurate, precise data results.  The FTIR instrument has become a black box measurement tool that is customized for each application and validated and tested against dozens of source test data projects, so that simply following any PS18 procedures becomes academic and in the case of CEMs, completely automated.
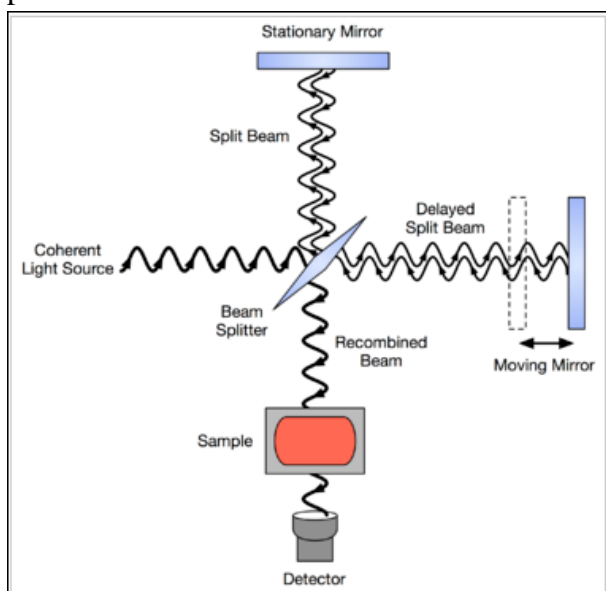


FTIR Schematic of an interferometer
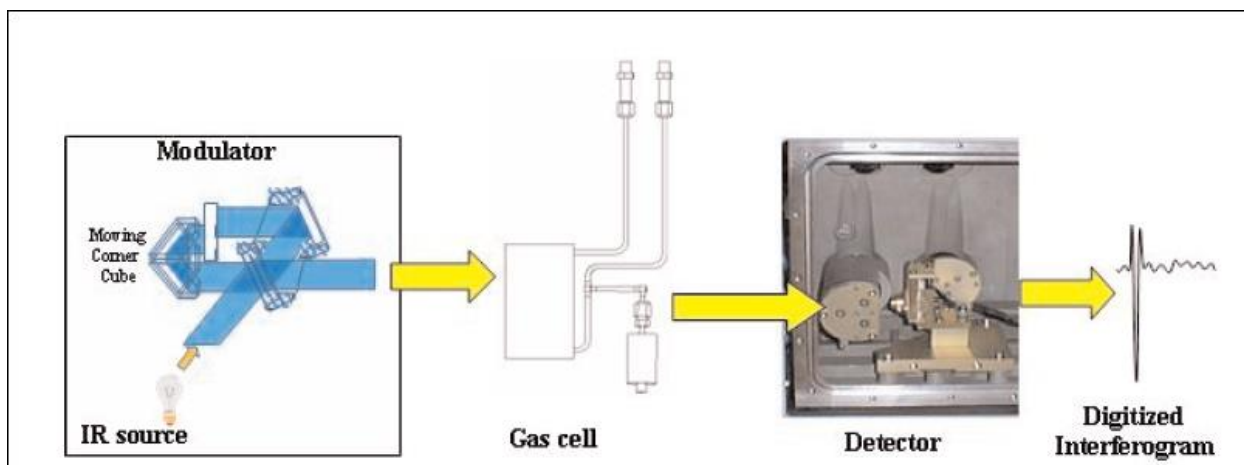
FTIR Schematic of interferometer (modulator) generation of an interferogram

The figure above shows a schematic of how the digitized raw signal (Interferogram) is converted to a frequency response signal by performing a mathematical Fast Fourier Transform (FFT). This frequency response signal is eventually converted to an Absorbance signal that is directly proportional to the concentration of each of the IR active molecules that are present during the time of sampling. In the process shown below, the Interferogram is converted via the FFT to a Single Beam spectrum which produces a signal that is easier to see all of the response of the IR active components within the gas sample as well as the response of the FTIR instrument. To remove the FTIR instrument background signal anomalies and obtain a baseline energy profile, a non-IR absorbing gas (typically $N_2$) is passed through the gas cell prior to analysis of sample gas. This background response is then used during the data retrieval process to remove the instrument response from the sample gas signal response. This is accomplished by taking a ratio of the gas sample Single Beam to the instrument background Single Beam. The result is then further processed by taking a negative log of that signal converting the response into the final Absorbance signal which contains all of the responses of compounds in the gas sample that are IR active. The Absorbance spectrum is used as any change in the height of any one of the peaks can be directly related to a change in that components concentration. In order to increase the long term stability of the signal that is produced, the background spectrum is typically replaced every 24 hours. By analogy in a conventional Non-Dispersive IR based system, this is the zero calibration and is performed daily.
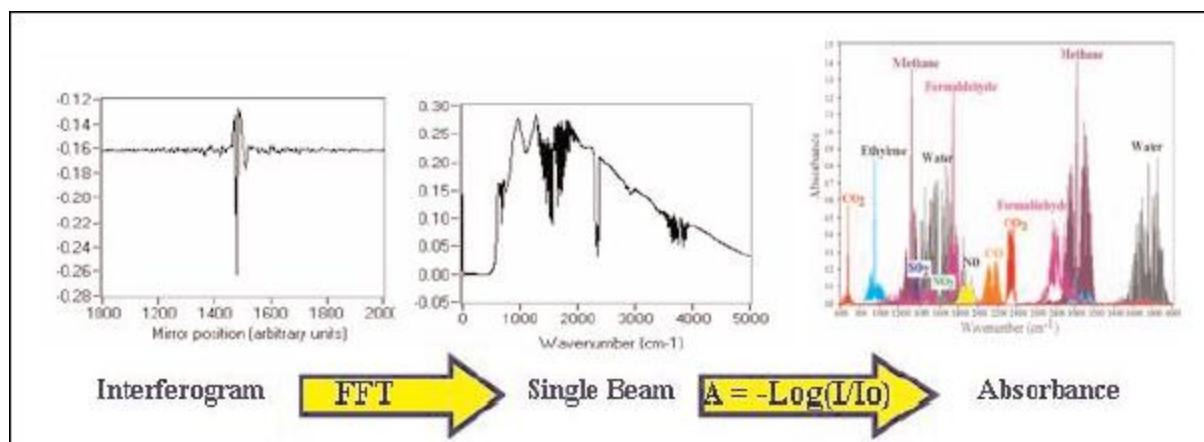
**Interferogram Conversion to Fast Fourier Transform**

IR absorption positions on an x-axis are generally presented as either wavenumbers (cm$^{-1}$) or wavelengths (l). Most instruments using FTIR have a useable window in the mid-IR between 350-7000 cm$^{-1}$. IR is non-ionizing radiation, meaning that the photons (waves and/or particles of light) at these frequencies do not have enough energy to cleave (break) molecular bonds. The bonds only absorb the energy in the IR at specific frequencies depending on the structure of the molecule. This absorption of energy results in the molecular bonds, vibrating and translating while the molecule will begin to rotate faster. It is mostly the vibrational and somewhat the rotational energy absorbance that are measured by the FTIR detector at these discrete IR frequencies. The lower the resolution of the instrument, the more spectral data points may be plotted on the frequency x-axis and therefore, increase the resolving power of the instrument when interferences are present. This means that there are more non-interfered with absorption bands to utilize for quantification and there is more spectral information available to subtract (factor) out interferences obscuring target compound absorbance bands, so that they may be identified and quantified.

The definition of wavenumber is the number of waves per unit length. Wavenumbers are directly proportional to frequency, as well as the energy of the wave. The wavenumber unit (cm$^{-1}$) is a reciprocal centimeter and is commonly used in FTIR spectrometry.

We noted that when IR energy is absorbed by a molecule, the molecular bonds are excited, and vibrate faster, and we therefore call FTIR spectrometry, vibrational spectrometry. You may think of molecular bonds between atoms on a molecule as different size spheres connected by a spring. The difference in size between spheres and strength of the springs determine where absorbance's show up in the spectrum.

The combinations of vibrations and rotations from various functional groups and interactions of these functional groups with other atoms of the molecule and other molecules in a matrix result in unique, IR spectra for each IR active compound.

The following is a review of how an absorbance spectrum is generated to quantitate a sample spectrum for a specific target compound such as HCl.

1. A background spectrum is obtained by collecting an interferogram followed by processing by a Fast Fourier transform. This is a baseline energy curve of the spectrometer from the combined performance by the source, interferometer, and detector.

2. A sample single-beam spectrum is collected containing all absorption bands from the sample and the background baseline system energy.

3. A ratio of the two single-beam spectra is performed to produce a double-beam transmission spectrum of the sample.

To reduce the background absorption from water and carbon dioxide in the atmosphere, the optical bench is usually purged with an IR transparent gas (generally N2) or with dry, carbon dioxide free or scrubbed air from a commercially available FTIR purge gas generator or Zero Air generator.

## 3. Open Path Cross Stack (TDL) vs. Extractive systems

Presently, EPA is considering the use of Open-path cross stack TDL's to determine HCl emissions. There are pros and cons of using cross stack instruments. It is unknown if TDLs will be able to meet the required PS-18 requirements for several reasons. One reason for the disparity is that in cross stack technologies, it is near impossible to obtain a zero gas measurement to ensure that no part of the analytical system is contributing to HCl values or even biasing HCl values low by negative responses when non-detect or low concentrations of HCl is present. By removing the system from the stack or placing a zero cell in the laser path, it is no longer representative of the stack gas matrix.

There have been some issues with TDL that have come out of MCERTS testing. A summary of issues that were encountered are as follows:

1. Ambient vibrations causing a destructive interference in signal transmission
2. Spectral broadening of the sample gas absorption line when exposed to interferents
3. Miss-identification of HCl when exposed to methane – Also seen in Field tests
4. Loss of sensitivity in the presence of water vapor.
5. Molecules bound in complex compounds such as aerosols are not measured
6. Alignment of the optical beams is very important and sensitive to vibration

Additionally, a span and linearity would need to incorporate an extractive sample cell containing various concentrations of HCl placed into the original cross stack beam or somewhere outside the stack in-line with the laser typically by fiber optics. This completely changes the system integrity as well as the need to back out the native stack gas concentration that may be constantly changing. This is not representative of a check on the actual system less the stack contribution.

The third issue is that a dynamic spike would need to incorporate 90% stack gas matrix into an extractive cell to determine if any sample interaction is causing bias from the system. There does not appear to be an easy solution to this problem since complicated calculations would need to be performed as a slipstream of stack matrix must be flowed through the extractive sample cell and spike material added while subtracting out native stack gas concentrations. Additionally, since this is an extractive sample cell, additional QA/QC PS18 requirements would need to be performed separately on the extractive sample cell.

The advantages of the TDL vs. FTIR are:

1. Quick response
2. Lack of extractive sampling system bias (but no ability to determine component or matrix effects bias)
3. Less expensive capital cost

The disadvantages of TDL versus FTIR are:

1. Inability to perform a true zero, span, or dynamic spiking regimen while in the stack and not representative out of stack
2. Single component analysis requiring the need for additional lasers and increased cost for needed compounds such as $H_2O$ and possibly $CO_2$
3. Contamination of optics from dust, salts, and condensate requiring routine maintenance
4. High replacement/maintenance cost for consumable lasers and optics
5. Location on stack requiring logistics issues during maintenance or required PS-18 requirements
6. FTIR ability to analyze many other target compounds simultaneously with HCl
7. HCl aerosols loss in the TDL analysis that would be caught in extractive systems and re-volatilized representing true emissions and agreement with RATA reference method tests

## 4.     Types of Systems and Vendors

There are several FTIR manufacturers and their sales reps and integrators selling into the CEM industry.   Most of them are extractive in nature.  The differences between vendors are typically in the hardware and software used in the analysis.

The biggest difference between vendors is the use of detectors, resolution, and algorithms. Typically, there are 5 different types of detectors and 3 types of algorithms used in the analysis of HCl and are covered in other sections of this document.

Detectors: Listed in order of increasing sensitivity

1)  DTGS – Deuterated Tri-Glycine Sulfate
    a)  Room temperature – (CEM)
2)  MCT- Mercury Cadmium Telluride (different specified spectral ranges that determine sensitivity)
    a)  Thermo-Electrically Cooled (CEM)
    b)  Sterling Cooled (CEM)
    c)  Liquid Nitrogen Cooled
3)  "Sandwich" of all types
    a)  Liquid Nitrogen Cooled
4)  Indium Arsenide (InAs)
    a)  Thermo-electrically Cooled
5)  Indium Antimonide (InSb)
    a)  Liquid Nitrogen Cooled (typically)

Typically, there are many different resolutions that may be used to analyze HCl and most FTIRs may be set to lower resolutions from their maximum high resolution setting, but not vice versa. Generally, the scanning speed of an instrument is dictated by its detector type and its resolution. Certain detectors require longer scanning times to produce stable spectra and spectra with high signal to noise (S/N) ratios. Certain interferometers are designed so that they may only be able to produce lower resolution spectra meaning less data points per spectrum resulting in less information in the spectrum.  This result in faster scan rates and better signal to noise than a system with higher resolution, but the resolving power of the high resolution system relates to less interference issues, higher amplitudes of absorbance bands translating to better detection limits, and ability to subtract out interferences without compromising target compound accuracy or precision.  However, the inverse is also true, where low resolution systems have an extremely good single to noise ratio.  This allows for very good subtraction of interfering compounds and the trade-off is peak amplitude.   There are low resolution systems that are performing very well

in field trials and passing all EPA performance specification requirements anticipated to be used in new EPA emission standard QA/QC. The systems employed to measure HCl in CEMS range from 0.5 cm-1 to 8 cm-1. Combustion gas phase spectra are relatively complex in nature and should never be analyzed with a wavenumber higher than 8 cm$^{-1}$, but not as complex as some other applications. Low resolution instruments are quite capable of measuring combustion matrices as long as the detection limits are warranted. The lower the instruments wave number resolution, the higher the resolving power, but the higher resolving, the higher noise they produce, which can be compensated with more sophisticated detectors. Some systems are designed and work better at 0.5 cm-1; some others are designed and work better at 8cm-1. The resolution is an intrinsic feature of each FTIR manufacturer design leading to its own version of field deployed instrument, what's really important is the detection limit and the protection from interfering components.

The FTIR gas analyzer performance in a real application depends on the overall design and performance of the unit. There are several factors affecting to this:
1. -detector (SNR and stability)
2. -optical throughput of the spectrometer / cell
3. -interferometer design (resolution, optical throughput, stability, scan rate)
4. -analytical algorithm applied

All these parameters are linked and cannot be looked at on an individual basis; for example lower resolution allows higher optical throughput improving SNR, certain detectors work better at higher resolutions, certain analytical algorithms work better in higher resolutions while others perform better at lower resolutions. Looking at separate parameters can easily end up to misleading conclusions. All instrument manufacturers are selecting design parameters as a whole, and what should be looked at is the overall resulting performance, not individual design parameters.

The difference in algorithms is of two typical classes, Classical Least Squares (CLS) and Partial Least Squares (PLS) but there are other techniques used occasionally. All have their pros and cons and are discussed in other sections of this document. There are variants of these two archetypical Chemometrics techniques that make analysis of extremely low levels of HCl possible. All FTIR systems tested by EPA are off the shelf models and readily available.

When considering the purchase of an FTIR instrument, the following criteria should be considered:

     a. a vetted QA/QC procedure on all system shipped
     b. customer service

c. Similar performance of each analyzer produced by the factory to enable replacement or maintenance of any necessary parts replacement or replacement of a system that performs identically to the one serviced or purchased

d. A proven track record of field analysis and word of mouth

e. A system that can meet required minimum detectable concentrations (MDC) to measure the required targets of interest to a level that both meets emissions levels and the ability to measure a difference in concentration when resulting lower levels of target compound are added to the native stack concentration during a dynamic spike

f. Has methods that are canned and transferrable between instruments to produce not-significantly different results

g. Has a highly accurate compound library to accurately determine target compound concentrations

h. Has software that enables the elimination of interfering species in the sample spectrum

i. Has hardware that is robust, stable, requires little maintenance, and is fast because speed means better signal to noise by co-addition of scans

j. Has a path length that meets detection limit requirements and has a low sample to path length volume

k. Is manufactured from materials that will not bias the sample, be damaged in a corrosive environment, and has a long time to maintenance interval

l. Has a good relationship with an integrator who has worked together on the needs of an HCl CEM

m. Has self-diagnostic software to alert the user of any problems with its performance or need of maintenance

## 5.    Spectral Range

Infrared sources used in FTIR spectrometers are typically inert solids electrically heated in the range of 1000 to 1800 °C. The three most common sources are Globars (SiC), Nernst Glowers, and Ni-Chrome Coils. The globar is the most common in the field due to its longevity, spectral range, and ability to perform well in a vacuum.  They all produce continuous blackbody radiation, but with slightly different radiation energy output profiles. Moreover the detector and window materials used also have an effect on the range of useable light in the system (as mentioned in other sections). Typical FTIR units will provide strong signal from 4300cm-1 to 600 cm-1.

FTIR is capable of measuring hundreds of different compounds and dozens simultaneously. Many of these compounds are both organic and inorganic in nature but that doesn't mean they cannot be measured simultaneously.   The most powerful attribute of FTIR is that it is a multi-

component analyzer.   Many CEM analyzers may be replaced with one FTIR and a single set of QA/QC parameters performed on only one of the target compounds depending on the regulation.

An example of just one of these target compounds is HCl.  In this example, HCl absorption bands are present from 2500 to 3200 cm-1 as shown in the Figure below. The following Figure shows a series of HCl calibration (reference) spectra at various concentrations.
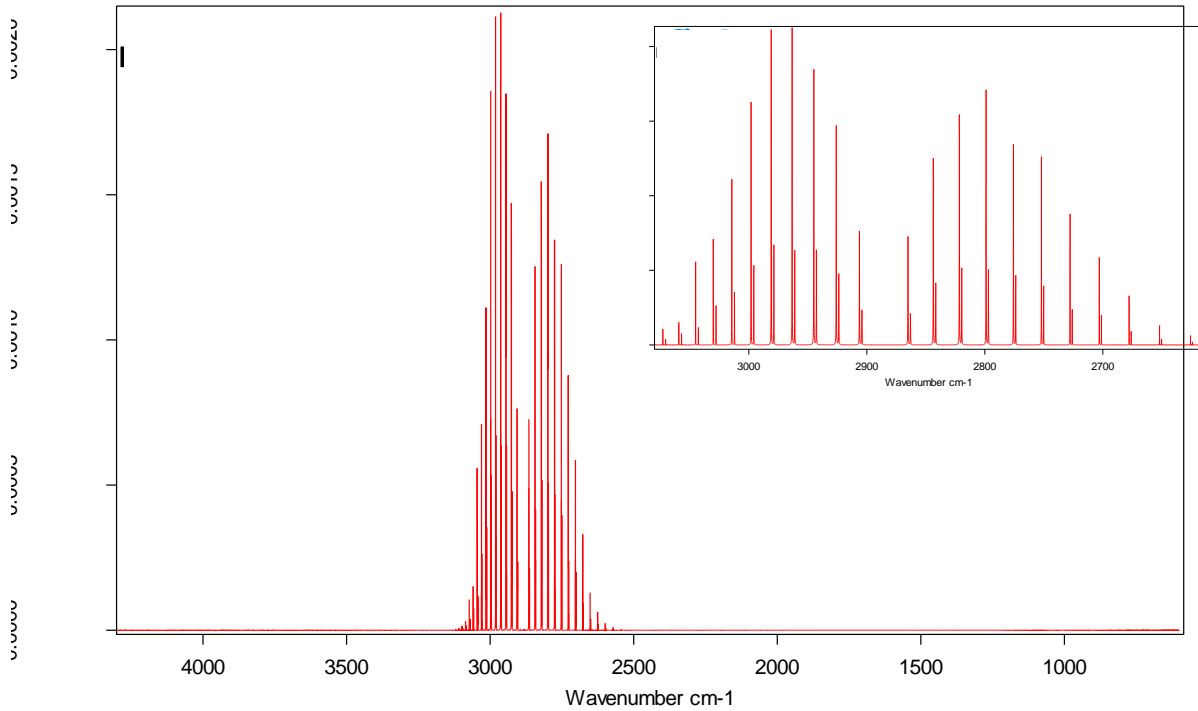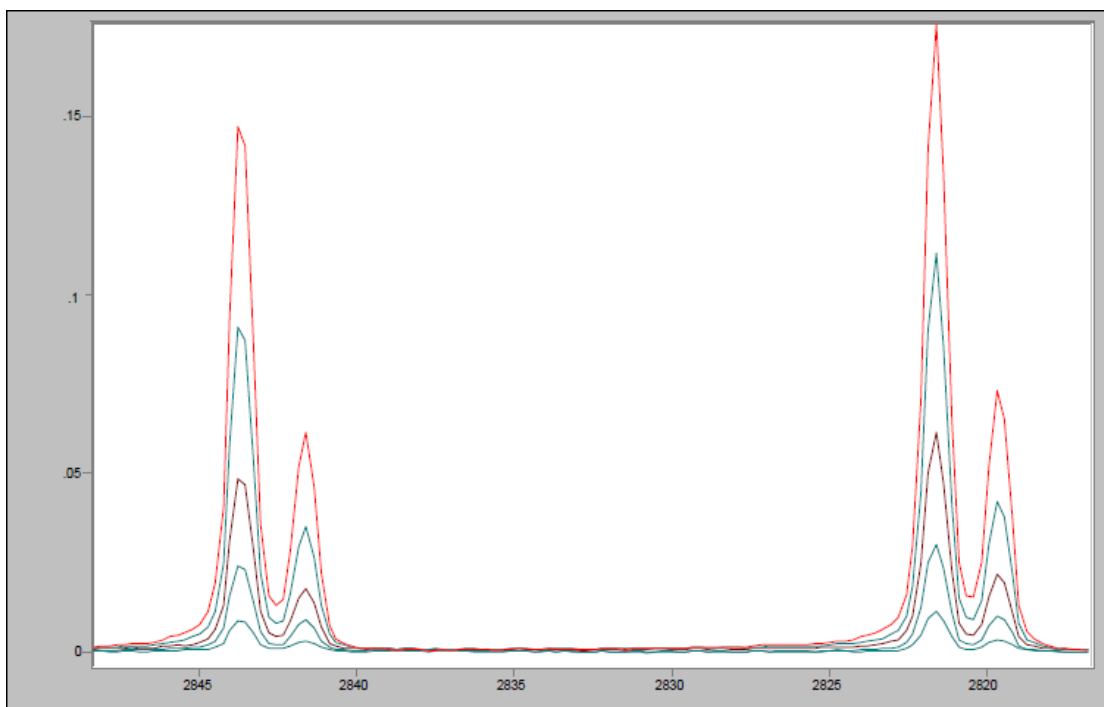
Spectral interferents also play a role in HCl measurement and many times, other target compounds have interferents. Interferents are compounds that have absorption bands that overlap with the analyte of interest. The common interferents for this example HCl measurement include water, formaldehyde, methane, high nitrogen dioxide, hydrogen cyanide, and compounds with a C-H bond such as propane and other straight chain alkanes. Other organic compounds also have the potential to act as interferents.
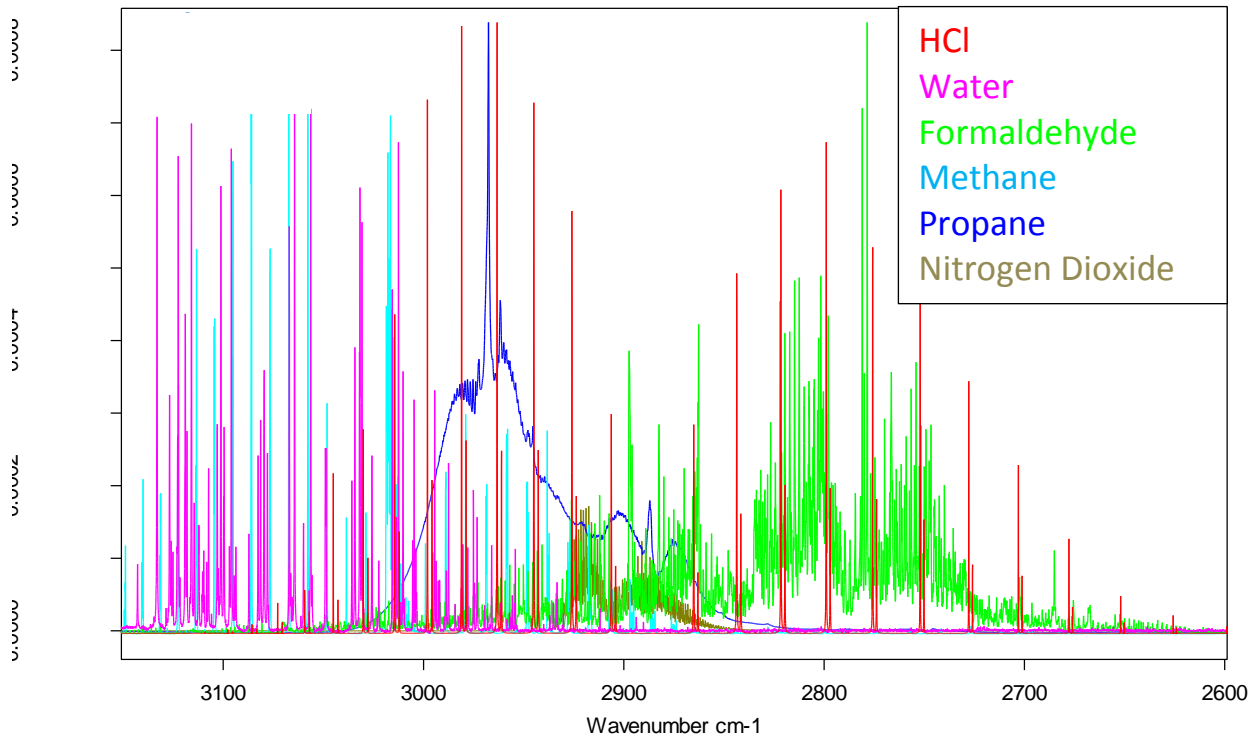
Interferents can be accounted for either by sampling, compensation or by quantification method development. As can be seen in the Figure above, there are many HCl absorption bands that may be used for quantification as would be present for any other target compounds needed to be measured. Any or all of them are acceptable provided they pass the QA/QC requirements of the regulatory performance specification or QA/QC document.

## 6.    Temp and Press Effects

Most FTIR CEMS utilize the hot-wet extraction method to measure the sample. The sample is drawn from the flue gas into the CEM system via a heated sample probe and heated filter. The sample is then transported through a hot sample line to the analyzer for measurement. Since this process does not remove the moisture from the sample, it is very important to ensure that the entire sample stream from the probe to the gas cell is heated to the appropriate temperature to avoid condensation or chemical deposition of reactive components (e.g. $NH_3$ and HCl).

The dew point of HCl can be determined by the following equation:

$$1000/T = 3.7368 - 0.1591 \log_e (P_{H2O}) - 0.0326 \log_e (P_{HCl}) + 0.00269 \log_e (P_{H2O}) \log_e (P_{HCl})$$

Where T = the acid dew point temperature (K) and P= Partial pressure (mm Hg)

This equation shows the relationship between the dew point and the partial pressure of the sample constituent and water vapor. A higher moisture or higher HCl concentration means that the dew point will be higher. Therefore, it is desirable to maintain the sample at high temperatures (typically ≥ 180°C) to ensure that the sample is well above the dew point. The sample is analyzed inside the spectrometer at a high temperature and correction factors need to be applied in order to ensure that an accurate comparison is made with any reference methods used during Relative Accuracy Test Audits. (I.e. concentrations are typically reported with corrections to 1 ATM pressure at 25 °C). The Ideal Gas Law is used PV=nRT; and the factors (T1/T2) $^o$R and (P2/P1).

The pressure in the gas cell can also impact resolution and sensitivity. A higher pressure will increase the sensitivity of measurement, but may consequently cause absorption line broadening, which can make it difficult to separate spectra of interferents. Cell pressure is monitored and correction factors are applied in the software. Measuring cell pressure is important when the sampling pump is located downstream the sample cell, then the cell pressure is typically lower than ambient atmospheric pressure. Sample pumps may be placed before or after the sample cell. It is generally best to have the sample cell post sample cell because the sample cell must then be constructed of wetted materials that will not bias any of the sample target compound concentrations and be heated to an appropriate temperature. Typically the sampling system and pump are heated to the same temperature as the sample cell to avoid condensing any sample matrix components with lower dew points on optical surfaces. If the sample point is under positive pressure or near ambient pressure, eliminating the pump or placing the pump post cell is preferred. Typically a pump is placed pre-cell only when measuring high vacuum applications or applications there are high particulate loadings, where pre-sample cell filters way produce continuously falling pressures in the sample cell until a filter back-purge or change is warranted. The use of heated head pumps of SS and Teflon wetted materials or other non-corrosive materials used before the FTIR sample cell will always enable a pressure inside the sample cell to be approximately 1 ATM or whatever the pressure the calibration (reference) spectra were collected. The dynamic spiking tests will determine if there is any bias from all components such as pumps and valves prior to any analysis by the FTIR instrumentation. All wetted components need to be at a temperature ≥ 180°C to allow good recovery of HCl. Sometimes, higher temperatures greater than180°C have been shown to increase the HCl recovery during certain field trials. Some of these reasons may be because 1) heavy molecular weight, high boiling point HC or 2) prevention of certain salt formation that sublime at higher temperatures. Some manufacturers have software that have correction factors that will go an added step and model the empirical pressure broadening effect from both pressure and molecular interactions at high concentrations that may occur from high CO, CO2, H2O effects in the sample matrix and make corrections in the final reported concentration. This is a source of error that should be addressed in the software algorithm if high errors are encountered.

## 7.    Resolution

It is possible to achieve accurate reporting of HCl emissions at multiple instrumental resolution settings.   Typically, the design of the interferometer will determine the maximum resolution that may be achieved and usually results in higher initial capital costs.  The spectral fingerprints of HCl are clearly distinguished between 2500 cm$^{-1}$ and 3200 cm$^{-1}$ and can be separated from potential interferents like water vapor using multiple scans and strong compensation algorithms and apodization functions that are not discussed in this paper, but automatically built into all software algorithms.  The scope of this paper does not go into spectral signal processing.

However, high resolution systems do allow for more efficient quantification models and usually better detection limits.  For example, if 4 cm$^{-1}$ resolution is selected, spectra will be obtained at intervals of approximately 2 cm$^{-1}$, where 0.5 cm$^{-1}$ resolution will result in a data point will be obtained every 0.25 cm$^{-1}$.  The following Figures depict the spectral information that is obtained by the same instrument set to different resolutions.

| Resolution | 16 | 8 | 4 | 2 | 1 | 0.5 |
|---|---|---|---|---|---|---|
| Optical Path Difference | 0.075 | 0.125 | 0.25 | 0.5 | 1 | 2 |
| Number of Data Points | 2048 | 4096 | 8192 | 16384 | 32768 | 65536 |
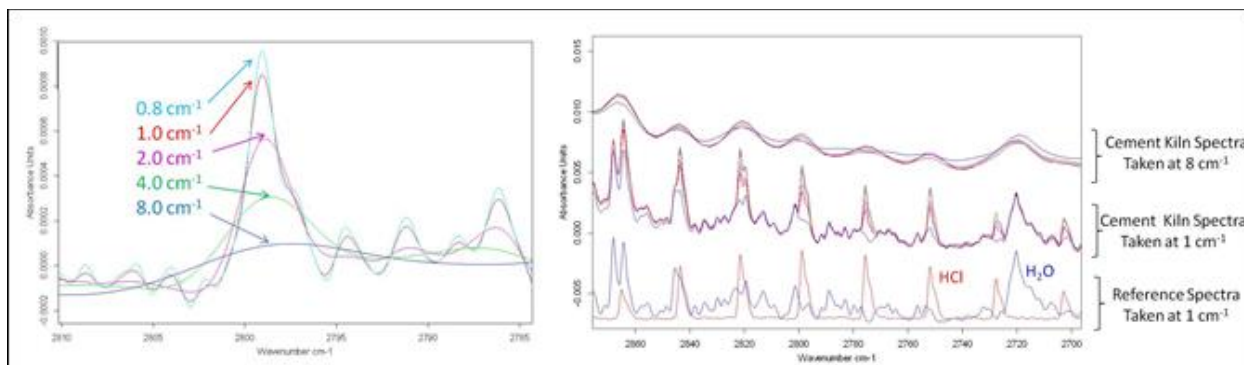


In the Figure above, one of the HCl absorbance bands is shown for at 5 different resolutions.  It is apparent that as the resolution increases (wavenumber decreases), the information gleaned from the spectrum is diminished.  The second graph to the right above demonstrates why this is important for any HCl interferents such as H2O. With some vendors, there's may be a tradeoff between resolution and long term stability of instruments.  It is important to look at a vendors drift test results for a target compound.

- High spectral resolution is more difficult to achieve and the interferometer is more sensitive to environmental effects than at lower resolution

- Because Lambert-Beer law applies more closely to high resolution instruments, the spectral lines reach saturation at lower concentrations which generally results in low dynamic ranges
- Even if high resolution does not enhance the detection limits, it does make spectral identification easier
- Some low resolution instruments are typically less sensitive to vibrations or environmental changes and may offer better signal to noise ratio's that allow comparable detection limits to some high resolution systems and protection against interferences compared to some higher resolution instruments.

## 8.    Sample Cell

The IR beam passes through the sample gas cell where a portion of the signal is absorbed by molecules of the sample gas. The distance the beam travels through the gas cell before impinging upon the detector is known as the fixed optical path length.  The longer the path length, the more molecules are impacted by the IR beam, and therefore results in stronger absorption signals at a given concentration of gas at a given wavenumber. This follows the Beer-Lambert law, which relates the absorbance of light to the distance traveled by the light through the medium (in this case, the sample gas), as show below.

$$A = \varepsilon \, l \, c$$

Where $\varepsilon$ is the molar absorptivity, l is the path length and c is the concentration.

Compared to solid and liquid samples, infrared measurements of gaseous samples have to take into account the lower density of IR absorbing molecules and the fact that the bulk constituents of air, Nitrogen and Oxygen, do not absorb infrared light. For this reason the optical density or absorption per unit length of optical beam is always much lower in gas samples than in solids and liquids. For this reason, long path length sample cell designs need to be used where the beam is folded with the aid of mirrors.

The increased path length is achieved by a signal entering a corner of the gas cell and bouncing back and forth among multiple mirrors until it hits an exit window where the signal is directed to the detector. An increased path length would improve the signal-to-noise ratio of the response up to a certain point, when the loss of signal strength through the reflecting mirrors may offset gains in signal absorbance.

The best known folded-path gas sample cell design is the White cell developed by J. U. White (1942). In the White cell there are three spherical mirrors, as shown in Figure 5.
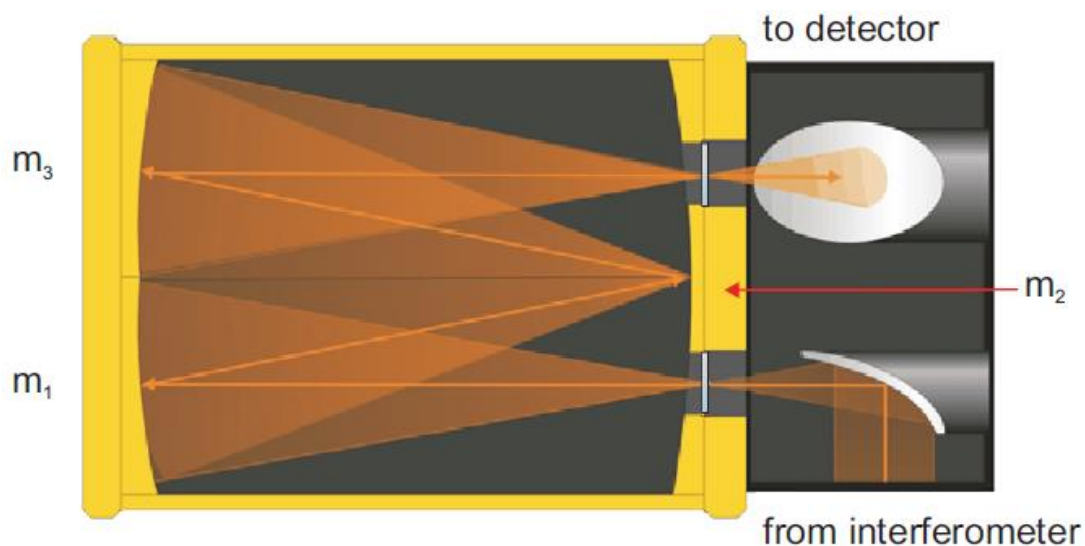
Fig 5. Schematic drawing of a White cell with folded beam path. $m_1$, $m_2$, and $m_3$ are spherical mirrors. Outside the cell the focusing mirrors are used to guide the beam from interferometer to the cell and from the cell to detector.

The beam from the interferometer is focused into an image at the entrance window of the cell, which is located in an opening on mirror m2. The beam is collected at the opposite wall of the cell by mirror m1, which refocuses the beam onto the mirror m2 between the entrance and exit windows. From the mirror m2 the beam diverges onto the third mirror m3, from where the beam returns to a different spot on the mirror m2 than in the first pass. Different optical paths can be achieved by selecting the radius of curvature and its origin for the three mirrors, and depending on the cell geometry the beam makes a certain number of passes back and forth before focusing on the exit window on mirror m2, from where the beam is directed on to the detector.

In addition to the original White cell design, other variations of the same principle with more complex geometry have been developed, e.g. the Hanst and Herriott cell designs. In current sample cell designs, long optical paths are routinely achieved in a relatively low volume of <0.5 liters. Depending on the gas and its infrared absorptivity, concentrations down to 100 ppb or less can be measured. The cell mirrors are typically coated with gold as it is a material with excellent IR reflectivity and it is resistant to most chemicals. The windows in such cells are selected so that they do not absorb the wavelengths of light being measured and they are resistant to the gases present in the sample. This precludes the use of hygroscopic materials otherwise in widespread use in FTIR instruments, with Zinc Selenide (ZnSe) and Barium Fluoride (BaF2) being common choices.

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## 9.    Algorithms used with FTIR Gas Analyzers

After the interferogram has been recorded with the spectrometer as explained above, it must be converted into an absorption spectrum with the Fourier transform algorithm and associated signal processing steps (truncation, zero filling, filtering). The resulting spectrum must also be interpreted in order to perform either *qualitative* analysis (identification) or *quantitative* analysis (determination of concentration). This interpretation is typically performed with a computer. It is also possible to split the computation into two steps, so that the interferogram is converted into an IR spectrum with dedicated electronics inside the analyser while the spectral interpretation is carried out in an external computer. The following paragraphs deal solely with the analysis of the IR spectrum, and a good review of the Fourier Transform can be found for instance in Griffiths (2008).

Qualitative Analysis (Identification)

Identification of a gas from its IR spectrum involves comparing the spectrum of the unknown sample with a library of spectra for known gases using one of several available library search routines. The sample spectrum is typically corrected for baseline slope and shift before conducting the library search, and the spectrum may be screened so that those parts of the spectrum with very strong $H_2O$ and $CO_2$ absorptions are avoided.

In its simplest form the library search consists of calculating the correlation between sample and each of the library spectra after absorption peak heights are normalized. The library spectrum with the highest correlation is the most likely identification for the unknown. This approach works well for samples containing only one IR active component, which is found in the library. In the case of gases not found in the library or samples containing mixtures this procedure may fail, and the highest correlation found in the search would be lower than in the case of a successful search, which can be used as a Quality Control (QC) parameter.

This basic library search routine has several variants such as correlation of first derivatives instead of absorbance spectra, calculation of Euclidean distance of sample spectrum against library spectra, or other algorithms that make comparisons between the sample spectrum and library spectra. Some spectral search enable subtraction of the best fitting library spectra from the sample spectrum, so that the process can be repeated for the next unknown in the mixture and so on. This type of analysis can identify several unknown gases from a mixture in one run but at the cost of somewhat longer searches. For most CEM type applications, qualitative analysis has already been done by the vendor and only quantitative analysis of what is found is required.

Quantitative Analysis

The use of an FTIR spectrometer as a gas analyzer relies on the integration of spectrometry with chemometric or multivariate techniques. These techniques extract such information from the

measured spectrum that can be linked directly or indirectly to the concentrations of infrared light absorbing gases in the sample. The term multivariate analysis highlights the fact that the absorption at multiple wavelengths is obtained in a single measurement (simultaneously) and the complete spectrum is used as the input data, which is in contrast with non-dispersive infrared (NDIR) and gas filter correlation infrared (GFC) methods.

Chemometrics is the science of extracting useful information by the application of statistical methods to large data sets. This includes calibration techniques that correlate measured quantities like the absorption of infrared radiation with properties of the system. These processes are often referred to as algorithms, quantification methods, or simply calibrations. In FTIR this describes the process of applying statistics to an absorption spectrum of a gas sample to produce a prediction of the multiple components present in the sample. The two most common methods currently used in FTIR quantitative analysis are classical least squares (CLS) and partial least squares (PLS).

**Classical least squares (CLS)**
Classical least squares starts with the Beer-Lambert Law:
Absorbance (A) = Absorptivity Constant ( Ɛ )* Pathlength (l)* Concentration (C)
This equation is then expanded to include wavelength range ($\lambda$) and gases that are being accounted for:

$$\begin{pmatrix} A(\lambda_1, gas_1) \dots A(\lambda_x, gas_1) \\ . \qquad\qquad . \\ A(\lambda_1, gas_y) \dots A(\lambda_x, gas_y) \end{pmatrix}$$
$$= \begin{pmatrix} K(\lambda_1, gas_1) \dots K(\lambda_x, gas_1) \\ . \qquad\qquad . \\ K(\lambda_1, gas_y) \dots K(\lambda_x, gas_y) \end{pmatrix} \begin{pmatrix} C(\lambda_1, gas_1) \dots C(\lambda_x, gas_1) \\ . \qquad\qquad . \\ C(\lambda_1, gas_y) \dots C(\lambda_x, gas_y) \end{pmatrix} + E$$

A is the spectral data. K is a constant determined from the calibration spectra. C is the concentration that will be computed. This equation is then solved for C by determining the lowest residual spectrum E.

An attractive feature of CLS analysis is that each row of the K matrix represents the spectrum of a pure gas in the library. If new gases are added to the library, there will simply be another column in the K matrix, which does not affect other elements of the matrix. This means that a CLS method is easy to expand with the addition of more gases, as long as it is ensured that there are more absorption data points (rows in A) than there are unknown gases (columns in K and C). In practice the CLS method can be applied to 25 or more gases simultaneously when the entire spectrum is recorded from e.g. 900 cm-1 to 4000 cm-1 and the underlying assumptions about additive absorbance do not cause significant errors in analysis. One of the main limitations is that all gases absorbing in the wavelengths, A must be included in the method. If an unknown gas is present, then the CLS regression will fail, but these results, in the spectrum of the unknown,

being shown in the residual. That residual can trigger an automatic alarm to tell the user that an unknown is present and can be used as a starting point for further investigation. In other words, residual spectra from the CLS routine act as built in QC feature.  Alternatively, the wavelengths, A, used for analysis, may be selected so that only the gases of interest, and a limited number of overlapping or interfering gases are included in the model.

A thorough knowledge of the application sample matrix and accounting for possible interferences typically eliminate any issues with CLS.

**CLS Advantages**
      a. Calculations are relatively fast.
      b. Can be used for complex mixtures and combustion matrices
      c. Calibrations do not necessarily require wavelength selection. As long as the number of wavelengths exceeds the number of constituents, any number (up to the entire spectrum) can be used.
      d. Using a large number of wavelengths tends to give an averaging effect to the solution, making it less susceptible to noise in the spectra
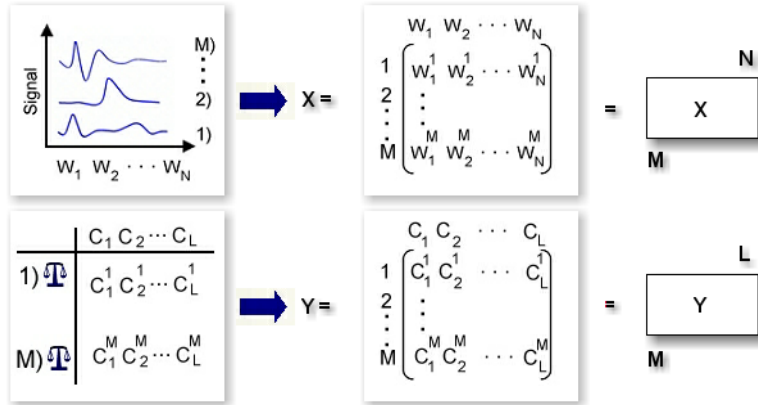
**CLS Disadvantages**
      a. Requires knowing the components that may interfere with the target compound data retrieval (components may be unknown)
      b. Not useful for matrices with constituents that interact on the molecular level by causing peak broadening or instrument line shape (ILS) changes
      c. Very susceptible to baseline effects since equations assume the response at a wavelength is due entirely to the calibrated constituents and a baseline correction should be used in the algorithm procedures

**Partial least squares (PLS)**
Partial least squares (PLS) correlates considerably more spectral information using larger spectral ranges with the reference values of the calibration set. In order to conveniently handle the data, the spectral data and the concentration data are written in the form of matrices, where each row in the spectral data matrix represents a sample spectrum. The concentration data matrix contains the corresponding concentration values of the samples. The matrices will be broken down into their Eigenvectors which are called factors or principal components. The advantage of this approach is that not all of the principal components are necessary to describe the relevant spectral features; for example some of these vectors simply represent the spectral noise of the measurement. Only the relevant principal components will then be used instead of the original spectral data, thus leading to a considerable reduction of the amount of data. A PLS regression

algorithm will be deployed to find the best correlation function between spectral and concentration data matrix.



## PLS Advantages

    a. Combines the full spectral coverage of CLS with partial composition regression of ILS

    b. Single step decomposition and regression; eigenvectors are directly related to constituents of interest rather than largest common spectral variations

    c. Calibrations are generally more robust provided that calibration set accurately reflects range of variability expected in unknown samples.

    d. Can be used for very complex mixtures since only knowledge of constituents of interest is required

    e. Can sometimes be used to predict samples with constituents (contaminants) not present in the original calibration mixtures

## PLS Disadvantages

    a. Calculations are slower that most Classical methods

    b. Models are more abstract, thus more difficult to understand and interpret

    c. Generally, a large number of samples are required for accurate calibration

    d. Collecting calibration samples can be difficult; must avoid collinear constituent concentrations

    e. Must have very similar instrument performance if the same PLS calibration is used between instruments

## 10.    Calibrations- Wet and Dry

The difference between "wet" and "dry" calibration gases is that "dry" gases are typically delivered via a compressed cylinder containing the target gas of interest in a balance gas that is typically nitrogen gas or various grades of clean, dry, THC free air.   Cylinders may be made of

aluminum, nickel coated aluminum, steel, or nickel.  However, syringe injection systems and permeation tubes are also a good source of dry calibration gas.

The dry gas cylinders are typically certified by the vendor to a pre-determined accuracy.  Spike material may also be blended with the target gas as a dilution tracer gas, to a concentration that when diluted is easily quantified by an analyzer in addition to the target gas. The tracer gas is typically an inert compound or compound with high vapor pressure that has a strong IR absorptivity (strong IR absorber/steep calibration slope) and is easily measured on a standard type FTIR instrument, so that there is no bias on the compound when it travels through the sampling system.  The tracer should be non-reactive, have very few absorbance bands that are not interfering with or are interfered with the target compounds absorbance bands of interest. They also should be easily measured to very low concentrations since they will be diluted along with the spike material by the stack gas matrix.  However, $CO_2$ and $H_2O$ are good tracer gases if used as an internal stack gas tracer.

Dry HCl calibration gas is typically provided in a steel cylinder due to its reactivity and certified to a +-5% only due to its instability in a cylinder at low concentrations.   However, nickel coated or glass lines cylinders will be less reactive to HCl.  Higher concentrations greater than 100 ppm HCl in balance nitrogen gas are more stable than lower HCl concentrations contained in a cylinder of appropriate material.

An additional issue encountered with "dry" HCl gas in a compressed cylinder is that the gas pressure must be reduced by a regulator that may have a significant effect on the bias of the HCl concentration.   Regulators that are made of incompatible materials with HCl, are not dried by purging with dry nitrogen gas, contain organic or inorganic contaminants that will react with HCl.  The influence of material of construction and cleanliness of materials is a significant factor in recovery of accurate HCl gas concentrations from a cylinder.

Because of the stability and transport issues associated with dry HCl calibration gas, as mentioned above, there have been several complaints and enough data from source testers in the field using EPA method 321, 320, and the ASTM D6348-12 methods to determine that low concentrations of HCl in dry gas cylinders is problematic.  However, if higher HCl concentrations are used, stability and transport is greatly improved, but there will be some error associated with the dilution of the initial cylinder concentrations to concentration levels that may be used to demonstrate linearity, dynamic spiking, and multi-day drift testing compliance. EPA is considering the use of a direct measurement of the cylinder by the instrument without traveling through the sampling system or being exposed to any stack gas matrix, and using that number as the new cylinder tag value.  This does involve making the assumption that the instrument is fully calibrated prior to transport to the field or calibrated correctly in the filed by some other means.

Linearity tests, dynamic spiking, and drift testing may then be accomplished with dry gas cylinders.

One of the major parameters being discussed presently is the use of dry versus wet calibration gases. Dry gases present two issues that must be addressed before the PS-18 document is promulgated. The first issue is that HCl cylinders obtained by gas vendors are not stable at low levels and therefore, the HCl gas concentration in the cylinder, or from the exit of the regulator, does not represent the cylinder tag value.   Additionally, the cylinders that seem to be less than 100 ppm HCl (writer's opinion) in a balance of nitrogen (N2) are not stable over time. The second issue is that dry HCl is difficult to transport through a sampling system to the analyzer. These effects result in retention of HCl in the sampling system and long times to reach 90% of the representative HCl concentration value ($t_{90}$). Times in excess of 20 minutes may not be uncommon for very long sample lines.  However, there are many parameters that will affect the $t_{90}$ times including temperature, flowrate, materials, sample cell volume, etc.  Additionally, it will likely take time to remove any span gas from any indirect measurements.  There are techniques for improving results that include the use of humidified calibration gas or N2 to improve $t_{90}$ up and down results, use of various materials of construction, passivation of the system by initial high HCl concentration flows initially and then performing any necessary dynamic spiking or span procedures, periodic back-purging of filters to remove the formation of filter cakes that tend to retain HCl.

Stack gas from coal combustion will typically have from 4-6% moisture present, unless a wet scrubber is part of the control process, in which case moisture values may be as high as 40%.   It has been demonstrated that a little moisture, in association with HCl, significantly decreases the t90 times.  Therefore, the use of humidified calibration gas for spans and other necessary performance specification tests, will likely be allowed.  This paper is not designed to go into the detail as to why this phenomenon occurs.

EPA will likely be addressing the use of either wet and/or dry HCl gas to demonstrate the PS-18 requirements.  Wet calibration gas generators are commercially available and have been used by several vendors to generate accurate, stable, precise, and transportable wet calibration gas as well as compare the empirical data obtained with these devices to the deterministic models of HCl frequency and optical densities from the HITRAN database. HITRAN is an acronym for High-Resolution Transmission Molecular Absorption database. HITRAN is a compilation of spectroscopic parameters that may be used to predict and simulate the transmission and emission of light in the atmosphere. The database is a long-running project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 1960's in response to the need for detailed knowledge of the infrared properties of the atmosphere. The HITRAN database, and its sister database HITEMP (High-Temperature spectroscopic absorption parameters that are more deterministic for predicting IR molecular adsorption in stacks and process ducts), are now being

developed at the Atomic and Molecular Physics Division, Harvard-Smithsonian Center for Astrophysics.

There has been push-back from industry and vendors as to the ease of use and availability of these humidified calibration gas generators. However, they are quick to set-up and stabilize, easy to transport, accurate, solutions are accurate and readily available from several vendors, stable, and their prices have been reducing as they become more accessible. Some CEM vendors are starting to look at them for incorporation into their CEMs as on-board calibration gas generators. Critical parts of the system are available for vendors to obtain to develop their own OEM systems.

FTIR permanent calibrations are made on the initial instruments (they can be provided by the instrument manufacturer directly). The assumption is that below 1 ppm the system response will be linear. The system performance can be periodically checked by running a certified gas standard at the analyzer ensuring that the system is still performing accurately. During a Relative Accuracy Test Audit (RATA) performance test, both FTIRs (CEM and RATA test Instrument) are validated via a certified calibration gas standard spike injected into the system at the probe, which allows for a full check of the entire sample system. The method can be validated by running a sample of the calibration gas at the inlet of the FTIR.

## 11.     Materials of Construction - mirrors/cells/windows

Any part of the analyzer that comes in contact with the gaseous sample has to be able to withstand the corrosive and reactive effects of the sample as well as high temperature (>180º-190 ºC). In a typical FTIR, this includes the cell body, mirrors, windows, and seals.   Cell body is typically Nickel plated aluminum or electroplated stainless steel 316, or Dursan coated SS. Cell mirrors are typically composed of the same material as the cell then either plated or vapor deposited with gold. Gold is used since it has the highest reflectivity in the IR region. It is also very chemically inert. Some mirrors and windows are also protected by an overcoat material such as $MgF_2$ or SiO. Windows are used to pass IR light into and out of the cell, while maintaining a leak tight seal between the sample and electronics compartments. Windows do absorb a portion of the signal and each type has it pros and cons. See table below:

| | Spectral Cut off | Cost | Frequency of replacement | Water Soluble |
|---|---|---|---|---|
| KBr | $400\ cm^{-1}$ | $ | High | Yes |
| KBr w/humidity protection | $400\ cm^{-1}$ | $$ | Mid | Slightly |
| ZnSe | $600\ cm^{-1}$ | $$$ | Low | No |
| $CaF_2$ | $1100\ cm^{-1}$ | $ | Low | No |

| BaF$_2$ | 690 cm$^{-1}$ | $ | Low | No |
|---|---|---|---|---|

KBr is a very common window material due the broad spectral range and low cost. However they need to be replaced periodically due to water damage and while they are commonly used in lab environments, KBr is typically not recommended to use in process instruments. ZnSe with a broadband anti-reflection coating has a slight compromise on spectral range but is not water soluble and chemically mostly inert and do not need to be changed frequently. However ZnSe tends to be the most expensive of the window materials. CaF$_2$ is very robust and cost effective but it has a very poor spectral range. BaF2 is a very good material that has good IR throughput, does not significantly adsorb moisture, and is inert. Any of these window materials may be used for the measurement of HCl. Sealing the various parts to the cell gets difficult at high temperatures. There are 3 elastomers that are often used: Viton© is the most common but may become brittle at high temperatures and cannot be re-used. Others such as Kalrez© (Chemrez©) and Parafluor© are more robust but they are more costly.

## 12.    Detectors

After the sample absorbs a portion of the IR radiation, the rest of the signal is focused onto a detector element. The detector element produces an electrical signal proportional to energy hitting it although in different forms.

Detectors come in two basic forms: those that detect the heat of the infrared signal, called thermal detectors, and those that use the signal to disturb the electrons in the detector element material, called quantum detectors.

Thermal detectors — Thermal detectors respond to changes in the temperature of the detector element material caused by the infrared signal. The benefits of using thermal detectors include low cost, low operating temperatures with no cooling required and response to a wide range of wavelengths. These detectors have limited sensitivity and relatively slow response time to changes in the infrared beam. Deuterated Tri-glycine Sulphate (DTGS) is the most common thermal detector. They are typically an order of magnitude less sensitive and slower than their quantum detector counterparts.

Quantum detectors — Quantum detectors use the energy in the light signal to excite the electrons in the detector material, boosting them into higher energy levels. Because the electrical properties of materials change depending on their electron levels, an electrical signal passing through the semiconductor material will change in response to a change in the energy striking them. These detectors require cooling well below room temperature. At room temperatures, the detectors can be noisy as they respond to even small changes in energy. This can be addressed by cooling the detectors to neutralize room temperature effects and their own IR signature. A cooled

quantum detector, typically using liquid Nitrogen, can produce a highly sensitive response. However, more sensitive quantum detectors may be susceptible to non-linear responses due to optical saturation. Manufacturers have to take that into consideration when designing their instrument and must solve them because field tests are required to demonstrate detector linearity.

The most commonly used chip type quantum detector is manufactured from mercury cadmium telluride (MCT). These detectors are both very sensitive and respond to a wide range of infrared wavelengths. Quantum detectors can also be produced from other materials. Lead selenide (PbSe), indium antimonide (InSb), and indium arsenide (InAs) for example, are also used for mid/near-IR analysis.

Instruments using MCT detectors have figured out how to linearize them either electronically or mechanically by eliminating photons to produce a linear output. Additionally, MCT detectors may be cooled with Sterling type closed loop coolers that are relatively significantly more expensive and maintenance intensive or by Peltier type thermoelectrically cooled (TE). The advancement of 3 and 4 stage TE coolers has allowed the use of TE-MCTs that have S/N ratios close to that of liquid nitrogen detectors, but with slightly diminished spectral range. This is critical if an FTIR is installed in a CEM type application where the use of LN2 is prohibitively cumbersome and expensive but the speed and sensitivity of an MCT detector is warranted.

## 13.    Maintenance

The maintenance on an FTIR instrument is significantly less than the maintenance on the sampling system. Sampling system maintenance involves replacing filters periodically, depending on the particulate loading in the sample matrix and whether it may be removed efficiently with filter back purging. Other system maintenance would involve any mechanical pumps and any HVAC that may need check-ups periodically. Typical FTIR instrument maintenance includes cleaning or replacing the windows and mirrors on the gas sample cell, if the light throughput decreases. However, this will depend on the filtering capability of the sampling system as a function of surface area and porosity of the filters. FTIR Infrared sources will require periodic IR light source replacement that usually will last the life of the instrument but usually longer than 5 years.

HeNe lasers are used to determine highly accurate frequency measurements. They require a laser light source replacement on a 3-4 year time basis, and are relatively inexpensive. Some analyzers incorporate diode lasers that typically last 20+ years. However, there are trade-offs with using solid state diode type IR light sources.

Room temperature detectors and thermo-electrically cooled detectors require no service. Most vendors selling into the CEM market are <u>not</u> using liquid nitrogen cooled detectors as they will

need re-filling and will require pumping out as the ambient moisture leaks into the high vacuum part of the detector over an average 2 year period   and are either room temperature or thermo-electrically cooled. The most common detectors used for continuous operation are the DTGS and the TE-Cooled MCT.

## 14.    Accuracy and Detection Limits

Presently, the accepted minimum detection limits are confusing to most users of FTIR and cover a plethora of calculations and acronyms (MAU, OCU, MDC#1, #2, #3, etc.).   It is hopeful that there will be a more defined equation, definition, and/or document to reference to ensure that all types of technologies used to determine the target compound detection limit are using the same equations and procedures.  The 2 most common documents are the EPA Method 320 and the ASTM D6348-13 documents annexes that define the acceptable practices for detection limits. Most users and usually regulators seem to be leaning toward the minimum detectable concentration (MDC) equations in the ASTM D6348-12 document.  While it has some errors associated with the document, it does have 2 good calculation techniques.

During the last check, the spread of detection limits for HCl on 1 instrument using 5 different detection limit techniques had good agreement between techniques, but ~2x higher using a different document calculation.  Reported concentrations were as follows:

| Gas Calibration Name | Conc | MDC3 | MDC2 | MDC1 | MDC3% | MDC2% | MAU | FMU*R | OCU |
|---|---|---|---|---|---|---|---|---|---|
| HCL PPM (100) 191C | 2.67 | 0.15 | 0.14 | 0.14 | 5.6% | 5.1% | 0.25 | 0.27 | 0.27 |

However, on a different instrument, where precision was very good, but different parts of the HCl region were used due to a different detector and a different algorithm for the calculation, the MDC difference between reported calculation techniques was varied for both documents.

| Gas Calibration Name | Conc | MDC3 | MDC2 | MDC1 | MDC3% | MDC2% | MAU | FMU*R | OCU |
|---|---|---|---|---|---|---|---|---|---|
| HCL 1-8X COS-FZ 191C-ACTUA | 2.59 | 0.06 | 0.05 | 0.25 | 2.3% | 2.0% | 0.35 | 0.09 | 0.35 |

Software exists to automatically calculate all of the different MDC and M320 calculations from spectra collected on the instrument employed in the testing:

1. Zero line spectrum – Zero $N_2$ spectrum collected after collection of a clean background

2. Seven different Moisture level spectra that include levels above and below expected sample matrix moisture concentrations.  No HCl is present in the spectra.

3. An actual sample spectrum containing both a low HCl concentration less than 3 ppmv and its interference spectrum, $H_2O$

4. The actual method/recipe used in the quantitative analysis of HCl containing all target compounds reported in the final method

The most reasonable technique for an accurate detection limit based upon empirical field data and many combined years of source test experience, is MDC #3.

MDC #1 is basically only a zero gas noise based measurement.

MDC #2 is a precision based measurement of 3 times the square root of the standard deviation from 7 different concentrations of an interfering compound. MDC #2 is only a measure of instrument precision and underestimates the true target compound detection limit. Although the precision of the instrument may be exceptional, that does not translate into overall system performance.

MDC #3 takes into account the residual noise left over after all of the interfering compounds have been factored out (subtracted out) of the spectrum and the residual noise ratioed to a very low calibration (reference) target compound spectrum

As you can see from the above examples, the MDC #3 calculation for HCl could easily be used to measure dynamic spiking levels from a source where the emission limit for HCl was 0.3 ppmv.

FTIR instruments have distinct advantages over other spectrometers that enable them to have very high accuracy on the order of +-2% of span and superior signal to noise ratios to produce very low detection limits. An example is "where spectra are collected under identical conditions (spectra collected in the same measurement time, at the same resolution, and with the same source, detector, optical throughput, and optical efficiency) on dispersive and FT-IR spectrometers, the signal-to-noise ratio of the FT-IR spectrum will be greater than that of the dispersive IR spectrum by a factor of $\sqrt{M}$, where $\sqrt{M}$ is the number of resolution elements. This means that a 2 cm$^{-1}$ resolution 800 - 8000 cm$^{-1}$ spectrum measured in 30 minutes on a dispersive spectrometer would be collected at equal S/N on an FT-IR spectrometer in 1 second, provided all other parameters are equal" (Newport Corporation Website).

The ability to use FTIR measurements to measure low concentrations of HCl and other target compounds is the following:

- Felgett advantage - speed and sensitivity is improved over dispersive IR instruments because a complete spectrum can be obtained with a single scan of the interferometer moving mirror because the detector measures all frequencies at exactly the same time.
- FTIR instruments scan extremely fast with systems typically in the range of 1 scan/second to as fast as 14 Hz (14 scans/second) with an MCT detector for lower resolution systems. Low resolution systems scan faster because the moving mirror has a stroke difference that is inversely proportional to the resolution number (peak width at ½ base-height). All of these scan times is significantly faster than a dispersive IR

instrument that results in a S/N ratio significantly greater because the S/N is proportional to the square root of the total number of scans.  The fast scanning of the MCT FTIR instrument results in greatly improved sensitivity by co-adding many spectra.  Co-adding spectra results in the averaging out of random noise.

- Jaquinot advantage is due to a very high optical throughput (signal).  There are no slits or filtering that waste energy (signal) and more energy is available to the detector to measure. This is a major advantage for analytical instrumentation that is signal limited.

- Connes advantage is where a helium neon (HeNe) laser is used as an internal reference in FTIR systems to provide an accuracy of better than 0.01 cm–1 x-axis accuracy.  The laser is monochromatic light that can be used to measure the number of x-axis cross-overs to determine exact mirror distance as the moving mirror strokes back and forth creating a highly accurate frequency measurement.  The wavelength of the monochromatic He-Ne laser is very stable at 632.99 nanometers, or 15798.04 cm-1.  This very high degree of accuracy allows the FTIR to record peak positions with great reliability, which is critical when doing multi-component quantitative analysis.  External peak position calibration is not necessary with the FTIR due to the utilization of the He-Ne laser.

- Simple mechanical design has only one moving part, the moving mirror, resulting in maintenance and improved reliability.

- Because the interferometer is responsible for modulating the light energy in a non-open-path configuration, elimination of stray light (un-modulated) and atmospheric emission contributions are not accounted for in the spectrum generated.  Stray light is minimized.

For FTIR analyzers, the minimum detection limits are based on the actual system configuration. FTIRs main influence on detection limits are typically detector type, optics materials and coatings, path length, time of scanning, tuning/alignment, accuracy of x-axis, algorithms, instrument stability from scan to scan, ability to compensate or eliminate interfering species, cell temperature and pressure used during analysis, and electronic noise.  FTIRs have a typical minimum detection range for HCl in the area of 10 ppb to 2 ppmv depending on the variables listed above and therefore, the manufacturer.  Span ranges for HCl applications are typically 0-10 ppmv with an accuracy of +-2% of full scale.  The longer the path length, the higher the absorption (optical density) and the lower the detection limit. Therefore, longer path length gas cells result in better detectability of low concentrations but may be compensated, sometimes to a larger degree, by the use of more sensitive detectors and instruments with greater precision. The FTIR is also capable of providing accurate measurement spanning concentrations ranging from ppbv (parts per billion – volume) up to percent for most of the typical components present in a CEM stack using the same system.

Dust loading in the effluent stream needs to be filtered out within the heated extractive sampling system prior to entering the gas cell of the FTIR. Very fine particulate, smaller than the heated filter used to remove it, eventually does penetrate to the gas cell mirror reducing the overall light

energy that reaches the detector. The use of extremely fine filters is of diminishing returns due to pressure drop and the need for more frequent back-purging.  Because the FTIR uses a reference background to remove system changes in signal day to day from any loss of signal or any other changes in the system it is able to tolerate up to a 40% loss in the overall signal without affecting the accuracy of the measurement.  The instruments are extremely robust and will tolerate a great deal of abuse and contamination before any changes in performance and accuracy is observable. The systems have been demonstrated during several decades in service analyzing hundreds of different applications globally, including the analysis of HCl.  There is no other technology that will provide the simultaneous analysis of dozens of different species, both organic and inorganic in nature to extremely low detection limits in conjunction with reporting percent levels of other species while not requiring any more than a one-time calibration.

During a preventive maintenance schedule the gas cell as well as the mirrors can be easily removed, cleaned and reinstalled by the end user without requiring the system to be realigned. Water vapor is particularly active in the IR spectral region and it must be taken into consideration when creating a method for the analysis in FTIR techniques. FTIR interference from the water vapor signal has been reduced by the development of algorithms that remove this interference by spectrophotometric techniques, or use its resolving power (resolution of the instrument) to choose any of numerous different target compound absorbance peaks that have no interference associated with them.

Note: The resolution of an instrument is inversely proportional to the length of moving mirror travel in the interferometer (*Example* 0.5 cm$^{-1}$ resolution has a mirror travel of 2 cm whereas 2.0 cm$^{-1}$ resolution has a mirror travel of 0.5 cm).

Detection limits that are based on 2 or 3 standard deviations (depending on data quality objectives - DQO) about the mean value when $N_2$ is flowing through the gas cell for HCl measurements on coal fired Portland Cement Kilns are achievable at the 0.2 ppmv level by several manufacturers.

Because the FTIR signal can be acquired in the presence of high moisture levels, gas conditioning is not required that would always bias HCl concentrations passing through them, and the amount of HCl in the effluent gas stream can be obtained directly both hot and wet.


## 15.    Summary

FTIR technology has advantages when used to measure HCl in combustion matrices.  Among the largest advantages of the FTIR instrument technology is the following.

- FTIR instrumentation is calibrated once and does not need to be re-calibrated unless replacement of a major component results in a different response. However, that is due to instrument design and not a function of FTIR technology. Regulations do require that the user check the calibration periodically as required.

- No Drift or re-calibration required. On several instruments, a span function is available for any calibration gas bottle changes that do not match previous calibration gas bottle accuracy.

- Low maintenance period or parts replacement. Systems have been proven to run 24/7 for many years with no servicing, repair or re-calibration.

- Maintenance on order of 2-4 years for replacement of laser/laser power supply and source. All parts warranted for 1 year parts and labor. Additional warranty available for cost.

- Multiple compounds can be reported with same instrument at different orders of magnitude. Each reported concentration also comes with a standard error calculation (SEC) that provides a confidence interval with the reported concentration.

- Both organic and inorganic compounds can be reported simultaneously such as $H_2O$, $CO_2$, $CO$, $CH_4$, $HCl$, $HF$, $HBr$, $HCN$, $CH_2O$, $NO$, $NO_2$, $SO_2$, $N_2O$, $H_2SO_4$ and hundreds of other compounds with the same instrument.

- Calibrations are canned for a specific sample matrix such as coal or natural gas combustion, stack, diesel, etc. No region selection is needed by the user.

- Calibrations are good for up to 40% moisture by volume.

- Samples come in Hot and Wet without any conditioning

- High accuracy on order of +-2% of span. Precision is very high.

- Powerful algorithms to calculate and subtract or compensate for any interfering compounds.

- Ability to use single absorbance peaks or multiples or series of absorption bands to get highest accuracy, linearity, and precision and also eliminate need to subtract interferences.

- Software ability to drive complex sampling system as usually found in CEMS.

- Individual compound or simultaneous CEM software strip charts directly printable of concentration trends over time.

- Ability to view and report individual compound calibration curves.

- Use of highly sensitive linearized detectors using software algorithms.

- Instrument Line Shape (ILS) modeling for increased accuracy in combustion sources.

- Choice of detectors without the need for liquid nitrogen cooling

- Rugged 316 stainless steel, Ni-coated Al, Ni-Free SS, Dursan sample cells path lengths that optimize the application with a choice of optical materials including ZnSe, CaF2, BaF2 and anti-reflective coatings to provide for corrosion resistant mirrors

- Pressure transducer and cell temperature readings directly into the software for pressure and temperature compensation

- Software alarms for low, med, and high users selectable alarms through digital and/or analog outputs or e-mail.

- Software self-diagnostics checking and alarms

- Traceable calibration for all target compounds of interest (Note: No NIST standard are currently available for HCl in the US, but anticipated, but there are some HCl traceable standard in Europe)

- Low sample cell volumes

- Complete internal heat traced sample paths in and out of instrument with all corrosion resistant materials

- No pressure drop across sample cell

- Advantages over conventional CEMS and other analyzers are very high signal to noise and throughput, zero drift and no need for periodic calibrations, extremely accurate frequency determinations, ability to deal with interfering species, and ability to measure multiple compounds over differing orders of magnitude with one method

- Ability to quickly modify methods to deal with any unknowns encountered.

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