The Advantages of High Resolution FTIR Spectrometry in CEMS Applications

Fourier Transform Infrared (FTIR) spectrometry is becoming an increasingly popular analytical technique for use in Continuous Emissions Monitoring Systems (CEMS). A single instrument can monitor all of the main combustion gas components in real time, with direct analysis of the hot, wet effluent stream, avoiding the need for sample conditioning and any resulting sample modification. Unlike conventional "dispersive" IR spectrometry which uses filters to sequentially isolate individual wavelengths of light, FTIR simultaneously uses all wavelengths of light, instantaneously, from a broadband IR source, to give a shorter scan-time and greatly enhanced signal-to-noise performance. A further benefit of FTIR-based CEMS over those based on a series of gas-specific analysers, is that their configuration parameters can be modified to monitor additional gaseous species, therefore addressing evolving requirements for CEM applications in years to come. As a result, these systems are now being used in an increasing number of mainstream applications, including the monitoring of municipal and industrial waste incinerators, cement plants, coal, oil and natural gas fired power stations and other stationary emission sources.

> *"There are many instrument design and operational factors that affect the analytical performance of an FTIR-based CEMS, including the sampling system, internal optics and the system's ability to regulate and maintain a stable sample temperature and pressure."*

Fig 1 High resolution MultiGas™ 2030 FTIR spectrometer plus extractive sampling components – Courtesy of MKS Instruments, Inc.

Commercial FTIR-based CEMS use an extractive sampling system to transport the effluent gas from the stack to the instrument for analysis. Extractive sampling components typically include a sample probe with integral particle filter, a heated line to transport the sample to the FTIR analyser and a heated pump to facilitate the flow of sample through the system. All "wetted parts" in the sampling system are maintained at an elevated temperature (typically >150°C) to ensure that combustion species remain in the gas phase and that no sample condensation occurs. The materials used in the construction of these parts are carefully selected to ensure that sample integrity is maintained and that no selective adsorption of gas components takes place during the sample extraction and monitoring.

The core FTIR spectrometer includes a "modulator" assembly, which is generally based on a Michelson interferometer. A broadband beam of infrared radiation (typically from a silicon carbide "Globar") is introduced to the Michelson interferometer, which consists of a beam splitter and two mirror assemblies, one fixed and one moving, as shown in Fig 2.

In the interferometer, the beam splitter reflects approximately half of the IR light to the moving mirror and transmits approximately half to the fixed mirror. The light reflected by the two mirrors then recombines at the beam splitter, where wave interference occurs. The action of the moving mirror leads to the sequential constructive and destructive interference of each of the different wavelengths of light in the combined beam and the creation of an interferogram (as shown in Fig 3).

The peak at the centre of the interferogram (also known as the "centre burst") is where the maximum constructive interference occurs. This is where the maximum amount of light is able to pass through the interferometer and onto the detector and occurs when the distance between the beam splitter and the fixed and moving mirrors is the same (i.e. zero path difference position). The continuous modulation of the IR light takes place at different rates and encodes each wavelength with a new frequency.

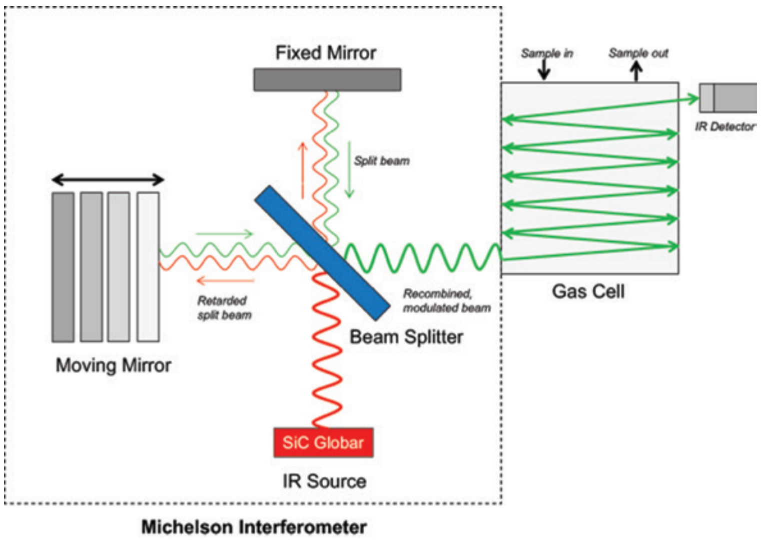

Fig 2 Michelson Interferometer

Author/Contact Details:
Ian Clarke
MKS Instruments UK Ltd
2 Cowley Way
Crewe
Cheshire
CW1 6AE
Tel: +44 (0)1270 253 400
Email: ian_clarke@mksinst.com
Web: www.mksinst.com

Gas Cell and Detector

The modulated beam of broadband IR light enters a gas cell containing continuously flowing sample gas. Gas cells generally incorporate a pair of mirrors which reflect the IR light back and forth between them to create a long effective path length – typically in the order of several metres. In accordance with Beer's law, this increases the opportunity for sample compounds to absorb certain wavelengths of IR light as different molecules undergo their characteristic vibrations (stretching, rocking, wagging, twisting and scissoring). Having passed through the gas cell, the light intensity is measured using an infrared detector, which is generally based on a thermoelectrically-cooled Hg/Cd/Te (MCT) device. Although lower temperature liquid nitrogen-cooled detectors would provide superior analytical performance, the requirement to keep the detector filled with liquid nitrogen is not practical for use in long term continuous emissions monitoring applications.

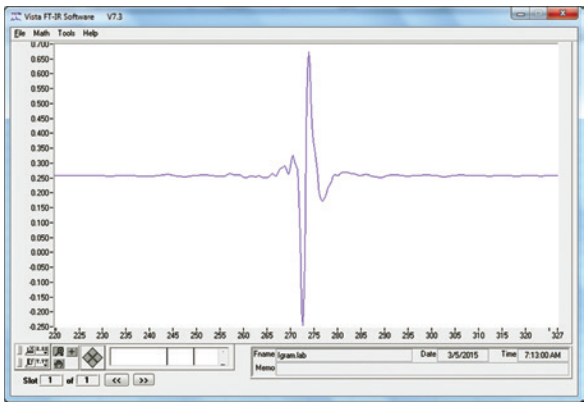

Fig 3 FTIR interferogram displaying the "centre burst" position: x-axis is in the time or distance domain

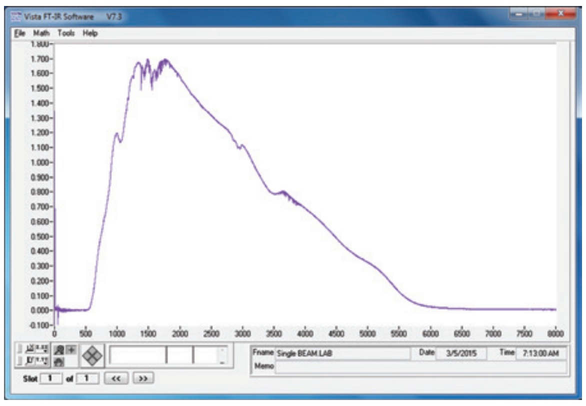

Fig 4 Single beam spectrum: produced by applying a Fourier Transform to the interferogram in Fig 3

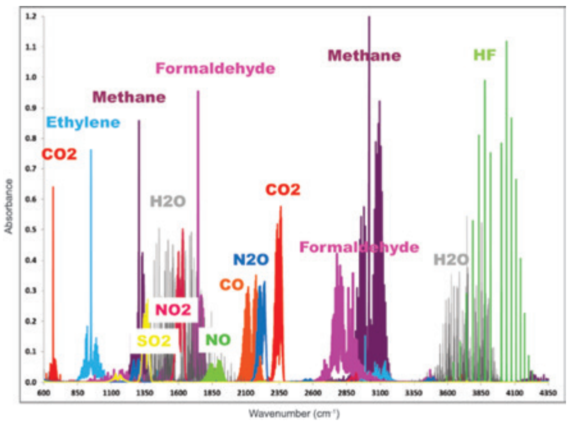

Fig 5 Absorption spectrum: produced from the ratio of the background single beam spectrum to the sample single beam spectrum

Data Treatment

As shown in Fig 3, the x-axis of the interferogram recorded by the spectrometer is displayed in the distance domain and corresponds to the distance of the timed pull of the moving mirror. Applying a Fourier Transform to the interferogram converts the data from the distance/time domain to the frequency domain to produce a "Single Beam" spectrum (see Fig 4), where the x-axis now represents wavenumbers (cm^{-1}). Applying a zero air or nitrogen background spectrum ratio to the Single Beam spectrum and then multiplying by the inverse log of each point, results in the creation of a linearised "Absorption Spectrum" (see Fig 5). In CEM applications, instruments are normally configured to collect a background spectrum every 24 hours so that any instrument-related drift may be zeroed out.

Gas composition data is derived from the Absorption Spectrum by using a preconfigured measurement "method", in combination with a series of reference calibration spectra. The method defines which spectral peaks are to be used for the quantification of each gas component and which calibration spectra and concentration ranges should be referenced. Some commercial FTIR analyser designs have the inherent unit-to-unit reproducibility required to enable all units to use standard methods and a universal library of calibration spectra. This ability illustrates a further benefit of FTIR-based CEMS in that they are able to function on a day-to-day basis without the need for time consuming recalibration routines requiring expensive span gas mixtures.

Spectrometer Resolution

The spectral resolution of an FTIR-based CEMS is an important factor in its ability to accurately measure the composition of a specific gas in the presence of another potentially interfering component absorbing at or near the same frequency as the target compound. Resolution is determined by the maximum distance travelled by the moving mirror inside the interferometer and is specified in units of "wavenumbers" (designated as cm^{-1}). It is calculated from the reciprocal of the optical path difference between the fixed and moving mirrors and an instrument with a high resolution of 0.5 cm^{-1}, typically requires the moving mirror to travel a distance in excess of 1 cm in a perfectly straight line. This presents significant mechanical challenges which have been addressed by manufacturers through the use of special mirrors called "corner-cubes", which ensure that incident and reflected IR light paths are parallel, irrespective of the orientation of the mirror to the incoming light beam.

In CEM applications where water may be present at levels of up to 40%, water interference becomes a particular concern for components such as nitric oxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and hydrogen fluoride (HF) as their characteristic infrared absorption spectra coincide with the regions of infrared absorption represented by the much larger water peaks. This situation is exacerbated by the fact that these compounds have relatively low emission limit values (ELVs) and therefore require monitoring at low concentration ranges (e.g. the ELV for HF is 1 mg/m^3). A further example of coinciding IR absorption regions occurs between nitrous oxide (N_2O) and carbon monoxide (CO). In these circumstances, a high instrument resolution and the careful selection of interference-free or minimally interfering regions for monitoring minor components, combined with the masking of high interference regions, are important factors in ensuring that cross-interference effects are minimised.

To illustrate the importance of collecting high resolution spectra for identifying and selecting interference-free regions to monitor in FTIR "methods", Fig 6 and Fig 7 show IR absorption spectra for NO (135ppm) in the presence of water (1%).
In the case of NO monitoring, Fig 6 illustrates the somewhat limited NO spectral regions available at 2.0 cm^{-1} resolution that have low interference from water peaks. However, Fig 7 shows a considerable number of interference-free peak options that are revealed when spectra are collected at the higher resolution of 0.5 cm^{-1}.

High resolution is also of benefit when monitoring infrared absorbers like SO_2 where, although it is not possible to identify peaks that are entirely free of interference from water, the higher resolution enables the selection and tracking of spectral regions which have relatively low water interference. In circumstances where water interference is unavoidable in the regions where the composition of a component is being quantified, a custom water calibration performed on each instrument allows accuracy for the component to be maximised by reducing any bias due to the mismatch of the water peaks.

Importance of High Resolution in Product Certification Testing

To be qualified for use in continuous emissions monitoring in Europe, the entire Automated Monitoring System (AMS) must achieve certification in accordance with the DIN EN 15267-3 standard. This standard is intended to assess the suitability of an AMS for the measurement of emissions from stationary sources and involves a series of laboratory tests followed by an endurance field test at a working industrial facility (e.g. a waste incinerator plant). The initial laboratory phase involves a series of challenging tests which assess all aspects of performance including response time, repeatability, linearity and drift, as well as the influence of external factors including ambient temperature, sample flow and pressure, variations in supply voltage and vibration. However, generally considered to be the most challenging part of the laboratory phase is the series of cross-sensitivity tests, where the influence of potentially interfering components, simultaneously present in the effluent sample, is assessed. Each gas in the list of components to be certified is measured initially without an interferent and then in the presence of a series of different interferents. Any positive or negative deviations in the measured values of each component are recorded and summed, before strictly defined "pass/fail" criteria are applied. For reasons outlined earlier, instrument resolution is a key factor in the successful completion of these tests.

The results of the rigorous testing required to achieve the DIN EN 15267-3 standard are summarised in a product certificate. This certificate confirms details of the CEMS configuration tested and lists the official composition ranges successfully addressed by the system for each gas component. The overall "analytical performance" of the system may be judged by reviewing the "relative total expanded uncertainty" results achieved for each gas component. These are derived from the combined results of the various certification tests, including the cross-sensitivity test results.

Summary

There are many instrument design and operational factors that affect the analytical performance of an FTIR-based CEMS, including the sampling system, internal optics and the system's ability to regulate and maintain a stable sample temperature and pressure. However, it is clear that instrument resolution and its impact on the interference-free quantification of gas composition, is a key factor in achieving the best overall results. It affects the concentration ranges that may be addressed for the various certified gas components and contributes to the overall uncertainty performance achieved for each component. Furthermore, high resolution applied in conjunction with a suitable data processing algorithm, is a key factor in achieving optimum low-level gas detection performance.

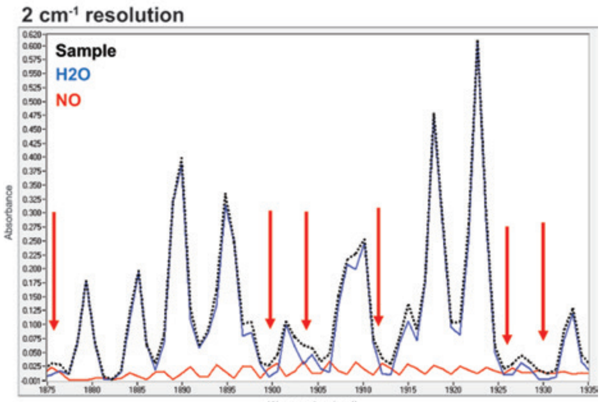

Fig 6 Coinciding IR absorption spectra at 2 cm^{-1} resolution of NO (135ppm) in the presence of water (1%) have limited low interference regions for monitoring NO as shown by the arrows

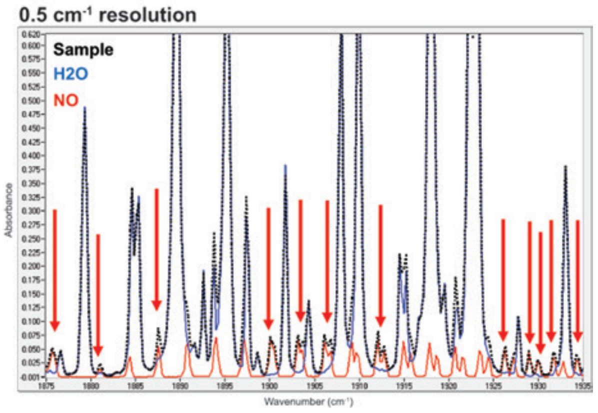

Fig 7 Coinciding IR absorption spectra at 0.5 cm^{-1} of NO (135ppm) in the presence of water (1%) reveals a number of interference-free sites for monitoring NO as shown by the arrows