HCL MONITORING

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CEMTEK
HCL MONITORING

Applications
Existing Measurement Technologies
New Technologies
Calibration and issues
CEMENT:
- Fuel type: coal, biomass, gas.
- MACT Limit – 3ppmvd@7%O2
- Requires CEMS

UTILITY:
- Fuel type: Coal
- Proposed MACT Limit – 0.2 lbs/MMBtu
- Will Require CEMS

WASTE INCINERATION:
- Fuel Type: Biomass
- SIP Emission Limit – 29ppmvd@7%O2 (for affected facilities)
- May require CEMS, based on source.
WET SAMPLING:
Most applications and measurement methods require the use of wet sampling to avoid any issues that may compromise the sample

- When measuring a hot wet sample it prevents errors due to absorption, desorption effects from HCl on the wetted parts.
- Keep the entire sample train hot/insulated to prevent cold spots – Conventional Hot/wet systems require sample components be kept at a minimum of 185°C to prevent cold spots.
- Low pressure sample systems should be kept above 50°C.
- Standard hot/wet systems sample at high temperature and high flow rate. –This shortens the time the sample is in contact with the system components, minimizing memory effects.
- Low pressure sample systems require no sample conditioning or moisture removal.
Problems associated with Acid Gases:

- The sample has to be maintained above acid dew point (normally 140-150 °C)
- Chlorides not removed in the particulate filter can cause interference problems.
- NH3 can cause interference.
- Biggest problem with stability is keeping moisture from reaching the gas.
- N2 purge on the pressure side is recommended to insure that ambient H2O does not mix with the gas.
MEASUREMENT TECHNIQUES

FTIR: Fourier Transform IR

NDIR: Non Dispersive IR

TDL: Tunable Diode Laser - Cross Duct

Extractive Type - Optical Feedback Laser
FTIR: Fourier Transform IR Technique utilizes a moving mirror in an interferometer to generate an “interferogram” of the sample absorption spectrum

- Performing a mathematical Fourier transform on the “interferogram” generates a single beam spectrum.
- The single beam spectrum must be routinely ratioed against a zero gas single beam spectrum to compensate for drift & linearize instrumental response.
- FTIR can generate multi-component measurement results, including HCl.
- Hot wet sample system
- Internal gas cell available.
- Typical minimum range for HCl: 0-10ppm
What is Fourier Transform Infrared Spectroscopy (FTIR)?

- Measurement technique collects all of the infrared spectral data at once.
- A broadband IR light is sent through the interferometer (modulator) which modulates all of the light wavelengths at once.
- Once modulated, the signal is passed through the gas cell where various molecules absorb some of the light.
- The measured signal is demodulated, using the Fourier Transform process, which converts the mirror position into a frequency response that is directly related to the molecules present in the gas sample.
**Fourier Transform Infrared (FTIR) Data Analysis**

- The demodulated signal (interferogram) is converted via the Fast Fourier Transform (FFT) to a single beam spectrum.
- To remove the FTIR instrument response, a non-IR absorbing gas is passed through the gas cell prior to flowing the sample. This instrument response is removed from the sample signal during the sample process.
- A logarithmic ratio of the sample beam to the background beam produces the final Absorbance signal over the IR spectrum and contains the response of all compounds that are IR active.
- The height of the Absorbance peak is directly related to the concentration.
**NDIR:**

- Non-dispersive or filter-based IR systems utilize either the “Dual Wavelength / Filter” or “Gas Filter Correlation (GFC)”, Cross Flow Modulation techniques to measure gas components. For HCL, GFC is the technique of choice for some CEMS suppliers.
- Both sample and reference filters are swung into the light path. In the case of the reference filter, typically nitrogen, or some other gas with no absorbance in the IR region, is passed through the gas cell, leaving a baseline background for comparison. Then the sample gas is run through the gas cell and the sample filter is swung into the light path allowing only a narrow band of light at a specific wavelength region to pass through to the detector, measuring the absorption of the gas that is specific for that filter in question. The background interference is eliminated by ratioing the sample absorbance to that of the reference (N2) absorbance, as they are present in both spectrum.
- The NDIR can monitor additional gases such as NO, NO2, CO2, CO, SO2 and others by the application of multiple filters tuned to those compounds, providing a more versatile analysis instrument.
NDIR GAS FILTER CORRELATION

Typical GFC configuration

- Light Source
- Chopper
- Cell
- Filter Wheels
- Lens
- Detector
HOT WET SAMPLING

Sick MCS-100.

HCl module can be added to existing systems. Similar to other NDIR systems.
Are there other options?

- Yes there are!
Can We Do Better?

- We don’t believe that existing FTIR & NDIR analyzer systems are able to accurately measure the low levels HCl that the rules will require.
- What other options are available?
- Can these newer analyzers be more accurate, require less maintenance and still be cost effective?
- Accurate analyzers are needed to maximize effectiveness of scrubbing systems and reduce the amount of scrubber media required.
What are the options?

- Option 1:
  - Cross Duct TDL’s
  - Utilize existing TDL technology used for NH3 and other gasses to measure HCl.
  - Several successful installations measuring less than 2ppm HCl.
- How do they work?
Measurement method

Very accurate method for measuring emissions of HCL. Several different configurations offer flexibility depending on application.

- Across Stack Analyzer: non contact sampling, measures flue gas in its natural condition
- Purge air or blowers to keep optics clean.
- Shorter path lengths required in high particulate applications.
- No Zero Drift. Built in Span Calibration Cell.
How do Tunable Diode Lasers (TDL) Operate?

- Laser center wavelength depends on composition of crystal

- Laser wavelength can be changed over narrow range by changing current or over a wider range by changing laser operating temperature

- By temperature controlling the laser, changing the electric current permits scanning over entire absorption feature

- By scanning the entire absorption feature, interference from dust is eliminated as the laser signal power is continuously measured.
Fiber-optic & coax cables

Analyzer
CALIBRATION

Internal Calibration Cells
Calibration Capabilities:

Daily Calibration:
- Calibration check using Internal Cal Cell.
- Checks Zero by analyzing background signal.
- Span Cal value typically 20ppm.
- Timing controlled by Analyzer.

Additional Calibration Verification Option:
- Calibration using Inline Flow – Thru’ Cell.
- Zero Air purge for cell to ensure no false indication, Zero check as per daily cal check.
- Span gas flow thru’ (approx 8 minutes, 3 for stabilization, 5 for detection).
- Optical Feedback Cavity Enhanced Absorption Spectroscopy.
- The challenge was developing a sampling method that would allow this technology to be used in almost any application.
- This lead to Patented Low Pressure Sampling Technology being used from probe to analyzer.
- No sample conditioning required.
- No interference from other gasses or moisture.
CEMTEK OFL-CEM for HCl
Extractive OFL-CEM Analyzer

- Utilizing the latest advancements in Scanning Laser Analyzer technology. Optical Feedback improves analytical performances in terms of accuracy, stability & sensitivity.
- Up to 20 KM path length allows for PPM, PPB & in some cases PPT measurements.
- Optical Feedback stabilizes the spectrometer by monitoring & compensating for source variations in the optical system & monitoring in real time (10Hz) the output signal of the spectrometer to automatically correct for any drift.
OFL-CEM Analyzer

- Optical Feedback improves laser accuracy 100x, reducing noise & interference & increases sensitivity by 1,000 x over standard metric gas cells by increasing path length a thousand fold.
- Low pressure sampling in the gas cell narrows the absorption bands to a point where no spectral overlapping occurs.
- Range of 0-3ppm with 30 ppb accuracy
Low pressure sampling probe

3-9 L/hr.
0.11 - 0.33 scfh
1-2 Bar

PM2.5 Filter

50-100 mBar
Optical Feedback Cavity Enhanced Absorption Spectroscopy + Low Pressure Sampling for HCl\(_{(g)}\) Measurement

A Scanning TDL or QCL
B Hyper-Reflective Gas Cell
C Detector - high speed
D Beam splitter
E Detector
F Sampling Probe
G Vacuum Pump

- 200 data points spectra @ 1 picometer resolution
- up to 20km path length equivalent
- (100 msec. scan) High MTBF
- Rugged, non-hygroscopic optics
- high MTBF
- low flow rate, low fouling sonic nozzle
- cost effective, low maintenance
1 Laser - Multiple Gases (50 mbar – 45°C – 10 km)

50-100 mbar Patented LPS sampling

No Spectral Overlapping (@ 50-100 mbar) = No Possible Cross Response / Interference

Can be used to measure H2O, NO, CO, CO2, H2S, NH3, SO3, CH4, N2O, CO3, O3, Methanol's etc.
Lowering the pressure of a gas sample therefore also reduces the dew point of all chemicals present.

A flow rate of 3 l/h results in extremely low fouling – est. 4g deposit over a 12 month period.

Because H2O remains in gas phase there is no spectrally overlapping, unlike in most FTIR’s where spectral overlapping can occur.

Additional particulate filters ensure that the gas cell remains clean.
Self-referencing spectrometer – No zero gas required

Zero Reference Information is contained in the signal itself.

Calibration Method: Beer-Lambert’s Law

Can be verified with calibration gas at the probe tip or directly into the analyzer.

N.I.S.T Traceable direct measurement.
Calibration Gas Requirements:

- Keep Calibration gas cylinders and associated hardware dry.
- Cylinders should have nickel coating on the walls.
- Pressure regulators must be nickel lined stainless steel.
- No protocol gas at present. EPA & manufacturers in discussion on this.
- Cylinders available in the range of 10ppm and higher.
- Keep all moisture out of regulator & cal lines.
Calibration Gas Issues:

- Biggest issue is moisture in the sample and sample line. Sample temperature should be maintained above 180°C for FTIR & NDIR Systems.
- Should be kept above 50°C for OFL-CEM Systems.
- Keep Calibration gas cylinders and associated hardware dry.
- The OF-CEAS analyzer system eliminates the typical calibration issues of instability.
- Recommend using silica coated probes and silica coated stainless steel tubes for sample & calibration gas.
QUESTIONS?

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