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WHITE PAPER: MONITORING OF HCI

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

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ICAC acknowledges the contributions of the following individuals and companies:

- Dan Kietzer - Workgroup Leader, SICK Process Automation

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- Matt Swanson - CAI

- Ken Greaves, Keith Crabbe - CEMTEK

- Mike Hayes - Linde

- Peter Zemek - MKS

- Anand Mamidipudi - Thermo Fisher Scientific

Table of Contents

1.0 - Introduction

This publication provides an overview of the existing technologies available to measure HCl from combustion sources.

Chloride exists in varying levels in most combustion fuels. During the combustion process, most of the chloride in these fuels is converted to gaseous HCl. As there is little interaction with fly ash in the process unless the temperature falls below 140° F, most of the HCl in the flue gas is released to the atmosphere, even in the presence of a particulate control device. Conventional flue gas desulfurization (FGD) systems, either wet or dry, are highly effective at removing HCl emissions.

Regulatory Drivers

New environmental regulations have been promulgated in the Federal Register that require the installation of continuous Hydrogen Chloride monitoring systems (HCl CEMS) in the Electric Power Generation, Major Source Industrial, Commercial and Institutional Boilers, and Portland Cement manufacturing industries.

The Mercury and Air Toxics Standards (MATS) requires coal and oil (both solid and liquid) fired boilers used to generate electricity monitor HCl. The rule does allow for units that use either wet or dry flue gas desulfurization (FGD) to continuously monitor SO_2 as a surrogate for HCl. However, using SO_2 as a surrogate does place additional emissions restrictions on the unit, causing some facilities to choose to install HCl CEMS. The MATS rule also has exemptions from this monitoring requirement for units that meet the low emitting EGU (LEE) requirement listed in the rule. If neither of the above listed exemptions is met, then the unit must either install an HCl CEMS or perform quarterly stack testing for HCl to be compliant with the standards.

The National Emission Standards for Hazardous Air Pollutants for Major Sources: Industrial, Commercial, and Institutional Boilers and Process Heaters, aka the IBMACT or ICIMACT, posted as finalized in the Federal Register on March 21, 2011, re-proposed on December 23, 2011, and with a final version released on December 21, 2012, also has requirements for HCl monitoring. The IBMACT does allow for SO_2 CEMS as a surrogate for HCl, and in some instances allows for periodic fuel sampling.

The final version of the Portland Cement MACT (PCMACT), published in the Federal Register on September 9, 2010 (75 FR 54970), requires monitoring of HCl emissions from new and existing kilns located at major sources. These sources have two options for monitoring HCl emissions; install an HCl CEMS or install a parametric monitoring system. This requirement was modified in proposed changes to the PCMACT that were posted in the Federal Register on July 18, 2012 (77 FR 42368) and finalized and published in the Federal Register on February 12, 2013 (78 FR 10005). The final rule does allow for a third option for affected sources to demonstrate compliance and is limited in applicability to those sources that have installed either a wet or dry scrubber and have set an SO_2 limit equal to or lower than the average HCl level measured during required performance tests. This option allows for the facility to install an SO_2 monitor in lieu of the HCl CEMS. While this may decrease the number of HCl CEMS installed on kilns it is not anticipated that all facilities will follow this option.

2.0 - Process Conditions

HCl continuous emissions monitoring system (CEMS) applications have been around for several years –

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starting primarily in the waste or trash incineration processes. The chlorines in the plastics that are burned in trash incinerators will combine with the moisture in the trash to form HCl during the combustion process. HCl, in addition to other acid gases, has typically been controlled by post combustion clean up systems, such as acid gas scrubbers (either wet or dry). These systems will typically address several acid gases in addition to various air toxics. Exhaust levels of HCl downstream of the pollution control devices are typically low on most applications – single digit ppm levels or below 30 ppm typically.

Incinerators over the past 30 years have gradually had their allowable HCl limits reduced from 31 to 29 to 25 ppm and lower. Hospital Medical Infectious Waste Incinerators (HMIWI) have HCl limits of 100 ppm or 93% removal.

The long term health exposure threshold for HCl is typically 0.01 ppm for continuous exposure. This would represent the lower end of any required control or measurement of HCl emissions.

Control Options

Typical control of HCl for new or retrofit boilers consists of a sorbent injection into a spray dryer absorber (SDA), or circulating dry scrubber, and fabric filter bag house system to capture the lime and particulate. This type of system is effective at controlling SO_2, SO_3, HCL & HF emissions. Typical removal efficiencies are $\geq$ 90% for SO_2 and $\geq$ 95% for HCL, HF & SO_3. HCl typically has a stronger affinity to combine with sorbents or scrubber slurry then SO_2 and as such, HCl is typically removed at higher rates when back end pollution control equipment is employed.

Lime is used as the sorbent feedstock, which is then slaked into a calcium hydroxide $Ca(OH)_2$ slurry for use in the SDA. Other options to reduce HCl emissions are to switch fuels to a lower chlorine content fuel or inject a dry sorbent (DSI) to absorb HCl.

Current US EPA Limits

Several current or pending US EPA regulations will require reductions of HCl emissions from various stationary sources as well as monitoring. These regulations include: HCl Limits for Utility MATS (UMATS), Industrial, Commercial, and Institutional Boilers MACT, Cement MACT and Municipal Solid Waste (MSW) combustors. Some of these regulations allow periodic monitoring of HCl or annual compliance testing in lieu of continuous CEMS measurements, while others allow SO_2 measurement and control limits as a surrogate to monitoring HCl. These surrogate limits are typically coupled with a requirement to also install some type of acid gas scrubber on the affected boiler (wet or dry scrubber and/or lime/limestone injection). Most backend control technologies that reduce SO_2 emissions also tend to control HCl emissions.

1. Utility MAT limits for electric utility boilers (40CFRPart 63, Subpart UUUUU) – Compliance required by April 16, 2015 (With a possibility of a 1 year extension):

UMAT Limits	HCl		SO_2	
Existing Units	Lbs/mmBTU	PPM @ 3%O_2	Lbs/mmBTU	PPM @ 3%O_2

Coal>=8300 BTU	0.002	1.9	0.2	105.5
Coal <8300 btu	0.002	1.9	0.2	105.5
IGCC	0.005	4.9	N/A	N/A
Liquid Oil	0.002	2.0	N/A	N/A
Solid Oil (COKE)	0.005	4.6	0.3	158.3
NEW UNITS	**Lbs/GW-Hr**	**PPM @ 3%O$_2$**	**Lbs/MW-Hr**	**PPM @ 3%O$_2$**
Coal >=8300 btu	10	0.97	1.0	55.53
Coal <8300 btu	10	0.97	1.0	55.53
IGCC	2.0	0.19	0.4	22.21
Liquid Oil	0.4	0.04	N/A	N/A
Solid Oil (COKE)	0.4	0.04	1.0	55.53

Typical conditions in a coal fired utility boiler are as follows:

Temperature: 280°-310^oF (lower on wet scrubbed stacks – down to 110^oF)
Pressure: -10" to +20" WG
H$_2$O: 16 – 22% Vol. (wet stacks), 10-15% Vol. (Dry Stacks)

HCl Emissions (uncontrolled) from coal fired utility boilers will vary depending on coal type and the chlorine content of the fuel. Single digit levels of HCl are typically expected. The addition of wet scrubbers or sorbent injection systems will typically drop these levels well below the UMATS limits listed in the table above.

2. Industrial, Commercial, and Institutional Boilers (40 CFR Part 63, Subpart DDDDD)

ICI Boiler limits are categorized by new or existing source, by primary fuel type, and are limited to boilers with heat input capacity of greater than 10 million BTU per hour or greater.

Source Type	Subcategory	HCl limit lb/mmBtu Heat Input	Alternate HCL limit	
			lb/mmBtu Steam	lb/MWh
New:	Solid Fuels	0.022	0.025	0.28
	Liquid Fuels	0.00044	0.00048	0.0061
	Gas (other Gas 2)*	0.0017	0.0029	0.018
	Biomass	n/a	n/a	n/a
Existing	Solid Fuels	0.022	0.025	0.27
	Liquid Fuels	0.0011	0.0014	0.016
	Gas (other Gas 2)*	0.0017	0.0029	0.018

Biomass	n/a	n/a	n/a

* Gas 2 is considered to be "other Process Gases"

3. <u>Cement MACT HCl Limits for Portland cement kilns (40CFRPart60, Subpart F & part 63, Subpart LLL) – Compliance by Sept. 9, 2015:</u>

Both Existing and New Units: 3 ppmvd @ 7% O_2 (based on a 30 operating day rolling avg.).

4. <u>Municipal Solid Waste (MSW) combustors (Subpart Eb)</u>

MSW units normally represent a substantial source of HCl due to the chlorine in the plastics that are combusted from the municipal waste being burned. Typically these sources will have pollution control devices to reduce or eliminate acid gases like HCl from the exhaust gas stream.

New Source Performance Standards (NSPS) for large MSW combustors are listed in 40 CFR 60, Subpart Eb which applies to Large Municipal Waste Combustors

HCl Limits = 20 ppmvd emission standard

HCl is not a BACT pollutant. However, it must be limited together with SO_2 because they both comprise MWC-Acid Gases which has its own PSD threshold.

Applicable test methods: EPA Method 26 or 26A.

Typical stack conditions where HCl measurements are made for these applications:

Temperature: 280°-310° F

Pressure: -10 to +20 In. WG

H2O: 16 – 22% Vol. (wet stacks), 10-15% Vol. (Dry Stacks)

Measurements can be made in the duct work downstream of the pollution control equipment or in the exhaust stack (before or after the ID fan).

Typical HCl emissions downstream of a Spray Dryer Absorber (SDA) and bag house for MSW combustor = 16-25 ppm (typically a 95% removal from inlet HCl measurements to the SDA).

3.0 -HCl Measurement Technology Overview

3.1 - Sample Handling for Extractive System

Some of the issues typically encountered in measuring HCl emissions from source level applications are not in the analyzer, but with the sample extraction systems.

HCl is a reactive gas and is very water soluble – Thus easily lost in the sample transport system and the

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various sub-components (pumps, coolers, filters, etc.) of the sampling system. In order to avoid these issues, HCl can be measured either by:

- In-Situ (i.e. Not extracted)
- Dilution Extractive
- Hot, Wet Extractive (Sample kept hot, above the dew point – thus eliminating any moisture losses)

In-Situ

In-Situ, Latin for 'in position', monitors circumvent most problems associated with sample extraction by performing the measurement in the flue gas stream itself. These systems measure the flue gas in the stack or duct and are available in both "cross stack" and "probe" versions. Cross stack configurations, as the name suggests, measures across the stack and gives a representative concentration of the entire measurement location but require a flange and access to both sides of the stack. Probe versions measure in a fixed measurement cell at the end of a probe, which limits amount of the area measured while only requiring mounting from one side of the ductwork.

Dilution Extractive

Dilution extractive sampling involves diluting the extracted sample with clean, dry instrument air, typically at the probe (extraction point of stack or duct). This reduces the amount of sample gas that needs to be extracted, which reduces particulate build up and pluggage of the system. Dilution rates of 20 parts up to 250 parts of instrument air to 1 part sample are typical, with most systems designed for 100:1 or lower. The lower the dilution ratio the better is the system accuracy. But this must be balanced with the moisture content of the sample in order to avoid the sample falling below dew point during the transport process.

A dilution extractive CEMS typically consists of the following major components:

- Heated head probe with filter, purge, mixing orifice and educator for pulling sample from the process under vacuum
- Freeze protected sample umbilical with tubes and signal wires to conduct sample down to the analyzer
- Dilution probe control drawer – Flow meters, pressure regulators and vacuum gauges to control and monitor the sampling system
- Infrared analyzer for measuring HCl – Normally mounted in a rack at a remote location from the probe (for ease of access for maintenance)
- Zero air generator – To clean and dry instrument air and remove any interfering gases
- Controller – To monitor alarms, local control, collect data, and automate daily drift checks

Some key points to consider when designing a dilution extractive CEMS is the dilution ratio as compared to the HCl analyzer range and the HCl concentration in the process. Lower dilution ratios are most desirable. However, this needs to be balanced with the moisture content of the process gas and other acid gases present (typically SO_2 and SO_3).

Dilution extractive CEMS typically offer the following benefits:

1. Lower maintenance due to reduced probe pluggage and sampling system cleaning from particulate and/or moisture fouling
2. Lower cost sample umbilical (as compared to full strength extractive CEMS) due to the lower heater wattage requirements

3. Longer sample umbilical lengths increases flexibility of analyzer rack mounting location – Especially on very tall stacks (in excess of 200 feet)
4. No sample pump required – Reduced maintenance

Some potential drawbacks on a dilution extractive CEMS:

1. Reduced system sensitivity due to dilution of sample – May present problems in certification of system if extremely low ranges are required and higher dilution ratios are needed to mitigate dew point issues
2. Instrument air consumption to operate probe educator and dilution mixing orifice
3. Dessicants for Zero air generator – Typically changed 1-2 times per year

Hot / Wet Direct Extractive

As the name suggests, the hot/wet sample system involves the extraction, transport and measurement of the flue gas at temperatures above water and acid dew point. As HCl is water soluble and acidic, keeping the sample above dew point eliminates the fear of loss of the HCl to water or of acid formation.

It is essential that all components of the sample system remain above a minimum temperature. For low levels of HCl, this is 185° C. Key components of the hot/wet sample system are:

- Sample probe (depending on flue gas temperature)
- Sample probe filter
- Sample line
- Heated head pump
- Fittings
- Measurement cell

The advantage of the hot/wet sample system is that it is simplistic and low maintenance. It does not require the additional components such as mixing orifices and zero air generators. They can be used with either a heated pump, or an educator as with dilution systems, with the maintenance on the pump higher than for the educator. Additionally, they do require more expensive sample lines as they need to be able to handle the higher temperatures.

3.2 - Calibration

Overview of Proposed Performance Spec 18

The EPA HCl CEM Performance Specification (PS-18) presently titled, *"PERFORMANCE SPECIFICATION 18 - PERFORMANCE SPECIFICATIONS AND TEST PROCEDURES FOR HCl CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES"* is in draft format and has been circulated to the Institute for Clean Air Companies (ICAC) hydrochloric acid (HCl) stakeholder's workgroup members for comments that will be delivered to EPA.

The PS-18 specification covers all HCl Continuous Emissions Monitoring Systems (CEMS) self-validation procedures and requirements that must be met during the initial CEM installation. After the initial performance evaluation test, additional criteria may be required for a time period, yet to be established, after

installation.

PS-18 is anticipated to be released, still as a draft, in January 2013 for final comment period. It will include provisions for the following:

    a.   CEM measurement location specifications
    b.   Data reduction procedures
    c.   Instrument linearity
    d.   Interference tests
    e.   Limit of Detection (LOD) determination
    f.   Calculations to determine an accurate Minimum Detectable Concentration (MDC)
    g.   Response time test
    h.   Calibration error test
    i.   Calibration drift test
    j.   Stratification test
    k.   Use of Relative Accuracy Test (RATA) and/or Dynamic Spiking Test (DST) for total system bias
    l.   Calibration cylinder source stability and reproducibility
    m.   Appropriate use of dry and/or wet gas calibration and check gas sources
    n.   Proper zero gas procedures

PS-18 will be applicable for evaluating the acceptability of Hydrogen Chloride (HCl) continuous emission monitoring systems (CEMS) at the time of installation or soon after and whenever specified in the source category regulations.

However, as per the draft PS-18 document, "the specification is not designed to evaluate ongoing CEMS performance nor does it identify specific calibration techniques and auxiliary procedures to assess CEM performance over an extended period of time. The source owner or operator will be responsible to calibrate, maintain, and operate the CEMS properly according to manufacturer instructions. When the initial PS-18 criteria are completed, it does not necessarily mean that the CEM validation is completed for the life of the analyzer. The Administrator may require the operator under Section 114 of the Clean Air Act, to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance." See 40 CFR Part 60, §60.13(c) and §63.8(e)(1). This essentially means that the implementation of periodic additional QA/QC procedures such as completion of Relative Accuracy Tests (RATA) by comparison to a reference test method may be required. Reference test methods may include EPA Methods 320, 321, or ASTM D6348-12 as a substitute for the other EPA methods. These are all FTIR methods

Other reference methods such as the manual isokinetic testing EPA Method 26A impinger train method is also valid, but NOT on Portland Cement Kilns. EPA Method 26A may encounter bias from other compounds in the sample matrix. However, because the NESHAP emissions standard was determined with data from many EPA Method 26A source test reports, precedence exists for its continued use on plants other than Portland cement due to the high loading of alkaline particulate that accumulate on the front half filter that may interfere with HCl measurements.

It may be required that HCl CEMS report concentrations in the units of the existing standard and other CEMS components (e.g., oxygen, temperature, stack gas flow, and pressure) will be necessary to convert the units

reported by the HCl CEMS to the units of the standard. In almost all cases, the additional use of an oxygen monitor will be necessary to determine dilution and excess air rates. Several vendors' instruments provide for CO_2 and other compounds of interest.

The performance specification test results are intended to be valid for the life of the system and standard Part 60, and appropriate Part 60 Appendixes, shall apply.

One of the major parameters presently being discussed for acceptability in the PS-18 document is the use of wet versus dry calibration gases. Dry gases present three issues that must be addressed before the PS-18 document is promulgated. The first issue is that the stated values HCl cylinders obtained by gas vendors may be affected by dirty pressure regulators or incompatible materials in the sample systems. This results in the HCl stated value and the instrument measured value not within specifications.

The second issue is that cylinders which contain less than approximately 100 ppm HCl in a balance of nitrogen (N_2) may not be stable over time unless there is a concerted effort in QA/QC cylinder programs where cylinders are checked for contamination and only released when concentrations in the cylinder reach a steady-state over time.

Presently, cylinder standard vendors are looking into the two issues mentioned above and testing is on-going. The current status of testing shows long term stability of HCl/N_2 mixtures down to 1—ppm contained in passivated Luxfer aluminum cylinders. Stability has been shown in mixtures down to 25ppm HCl in N_2 using nickel plated steel cylinders. Tests conducted on lower levels of HCl/N_2 mixtures (2ppm, 5ppm and 9ppm) over the second half of 2012 show stability when tested by a cavity ringdown spectrometer (CRDS). The overarching issue, however, is that industry does not, as of this writing, have any reference material from NIST or VLS from which to claim traceability. At the end of the day, audit gases must be made available for the implementation of PS-18.

The third issue is that dry HCl is difficult to transport through a sampling system to the analyzer.

These effects result in reversible retention of HCl in the sampling system and relatively long times to reach 90% of the representative HCl concentration value (t90). Times in excess of 30 minutes may not be uncommon for long sample lines >100 ft (>30 meters). However, there are many parameters that will affect the t90 times including materials, sample cell volume, etc., but most importantly regulators, temperature, and flow rate.

Additionally, it may likely take relatively long times to purge any span gas (likely 10 ppm HCl) from any indirect measurements when purging with dry zero gas. There are techniques for significantly improving results that include the use of humidified calibration gas or humidified N_2 to improve t90 "up and down" results, use of various materials of construction, passivation of the system by initial high HCl concentration flows initially and then reducing concentrations and/or flow rates before performing any necessary dynamic spiking or span procedures, and/or 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 4-8% 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

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small amounts of 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 (and should) be allowed. Another suggested solution, would be to place dry cylinders close to the analyzers to reduce the response time of daily span checks, and build in a monthly "line loss" test similar to that in Method 15 and 16 for TRS and H_2S.

EPA will likely be addressing the use of either wet and/or dry HCl calibration 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. There has been push-back from industry as to the ease of use and availability of these humidified calibration gas generators. One of them is a common instrument manufactured by IAS, Inc. and named a "Hovacal." However, these humidified (or non-humidified) calibration gas generators are quick to set-up and stabilize, easy to transport, accurate, NIST traceable with aqueous solutions and standards readily available from several vendors, and their prices have been reducing as they become more accessible. 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. These systems will, however, be required to meet certain traceability standards.

The field testing already performed and additional testing scheduled to be performed by EPA and their open-door transparent policies used in developing this performance specification have greatly improved the CEM techniques and procedures to measure HCl in the field.   Other improvements gleaned from EPA's use of field and pilot generated data have produced improvements to the sampling techniques for HCl other than moisturized calibration gas.   Among these are the use of high density polyethylene (HDPE) un-heated lines for transportation of dry or non-condensing moisture laden HCl calibration and span gas to the sampling probe of CEM systems to aid in HCl transport. The use of HDPE for cold, dry calibration lines has significantly reduced dry gas transport t90 times.

EPA is presently struggling to determine if insitu analyzers will be able to demonstrate compliance with the self-validating techniques of the new PS. These instruments are designed differently than extractive systems and therefore may fall under a different set of rules to demonstrate compliance with the necessary parameters of the PS. The greatest challenge is how to determine a true zero on the instrument when it is installed in the stack. There does not appear to be a correct way unless certain assumptions are made that cannot be easily verified. Additionally, span and dynamic spiking would also be a challenge.   The dynamic spike is a strong self-validation technique that determines bias from the components of the sampling system, instrument, and interaction with a representative sample of the stack gas matrix. Presently vendors of cross stack instrumentation want to be able to put gas cells in-line with existing hardware filled with zero gas, span gas, or various concentrations of HCl as a spike gas. This may not represent the true self-validating techniques that the PS is devised to address. The intent of a dynamic spike is to not ONLY determine the bias of a sampling system, but to determine the effect of the sample matrix and its components such as moisture, oxygen, particulate loading and sizing, and other compounds present that would react with HCl such as NH3. Other stack matrix compounds may also interact in the presence of spike gas that may also react with HCl due to the complex chemistry in the duct. There is no way to measure these effects by experimental design if spike gas and stack gas are isolated by the use of a "spike/span/zero" temporarily installed sample cell into an open-path measurement.

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It is likely that the EPA will allow certain procedures to be employed by TDL users as long as a RATA is performed on the TDL instrument using a reference method such as EPA Method 321, ASTM D6348-12, or EPA Method 26A (M26A is not acceptable for the Portland Cement Industry).

No one outside those EPA personnel assigned to develop the PS18 knows what will be in the final document. However, the PS-18 document will address the topics listed above and based on the results from December pilot plant testing; it may or may not change markedly from its present draft form.

3.3 - FTIR Measurement Technology

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.

Detection Technique

The IR electromagnetic spectrum is comprised of broadband photons, each with its own discreet 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 discreet 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.
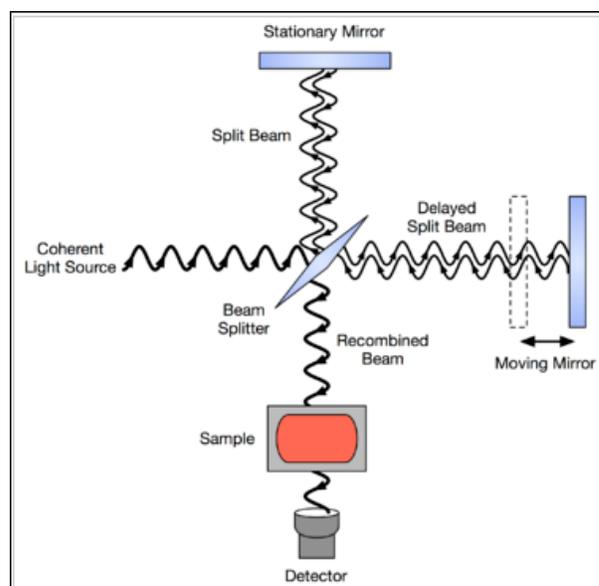
The interferometer is the piece of hardware that differentiates FTIR from other IR technologies. The interferometer is a tool for modulating the light from an IR source. The interferometer takes the photons from the IR source and splits it approximately 50% into two beam paths. Half of the photons go 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 discreet frequency can be measured very accurately. The absorption, or loss, of energy at those discreet 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 discreet frequencies. The time domain raw data is an interferogram. An FFT is performed and a single beam spectrum is generated which is a graphical representation of each discreet frequency energy as measured by the instrument detector simultaneously. The transmission of light energy at each discreet 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.
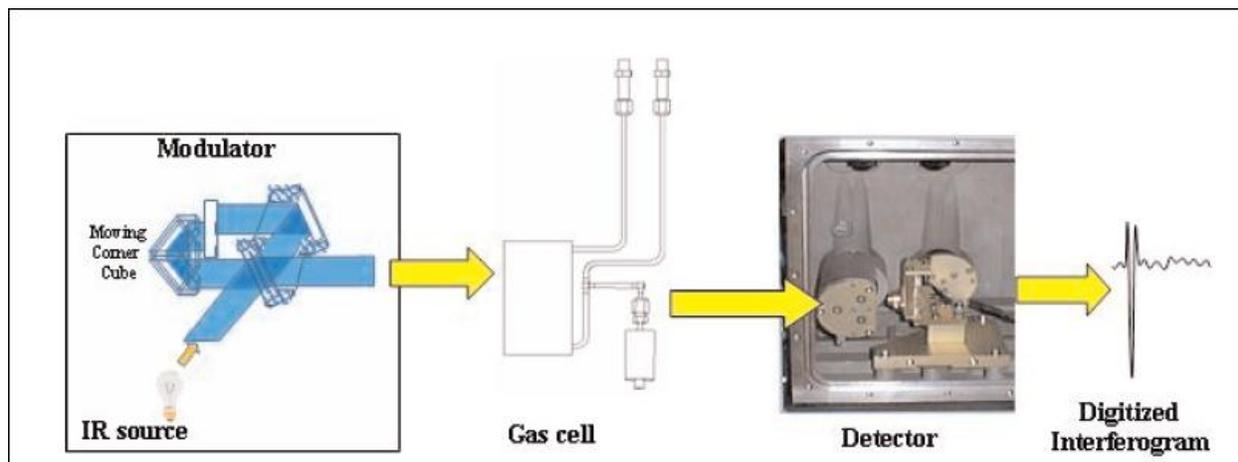
Detection Limits

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.

Calibration Requirements

FTIR analyzers can be calibrated via a certified cal standard injected into the system at the probe, which allows for a full check of the entire sample system, or at the analyzer which saves on cal gas costs. Additionally, many IR systems are available with internal filter calibrations, which eliminate the need for gas bottles.

Maintenance Requirements

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. All vendors selling into the CEM market are not 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 in use are the DTGS and the TE-Cooled MCT.

3.4 - NDIR – Gas Filter Correlation

The use of NDIR analyzers for monitoring HCl is a well established technique. The key aspect to a successful design utilizing these measurement techniques is the proper design of the sample system. Due to the highly reactive nature of HCl in terms of both acid formation and water solubility, the sample system will make or break a successful monitoring program.

Detection Techniques

NDIR multi-component type systems use infrared (IR) light absorption to determine the concentration of the HCl gas. A big advantage is that it is able to measure multiple components (up to 12) in addition to HCl, limiting the cost of procurement. Additionally, their benefits typically lie in the CEM application, where HCl can be easily added to a system already including other regulated gases such as SO_2, NOx, CO, etc.

Infrared (IR)

Multi-component NDIR systems utilize both the "Dual Wavelength" and "Gas Filter Correlation" techniques to measure gas components. For HCl, GFC is the technique of choice. In this case, the gas filter is swung into the light path, and eliminates the HCl spectrum. See example to the right. A reference signal is then obtained as a background at the selected wavelength. By comparing the sample and reference absorption, we can eliminate cross interference as they will be present in both signal types.
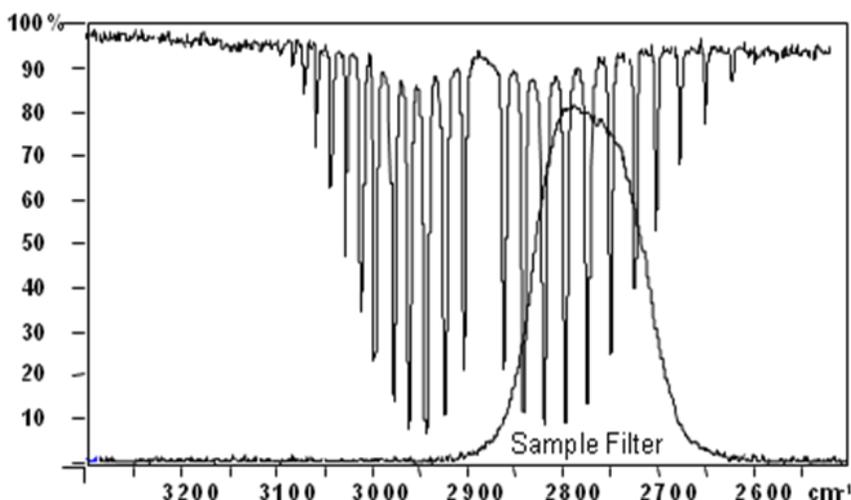
Typical NDIR GFC system consist of a light source, a chopper motor, a measurement cell, a filter wheel (for

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isolation of various measurement components) and a detector. Below is a typical GFC configuration for

Light Source Cell Lens

Detector

VW

Chopper Filter Wheels
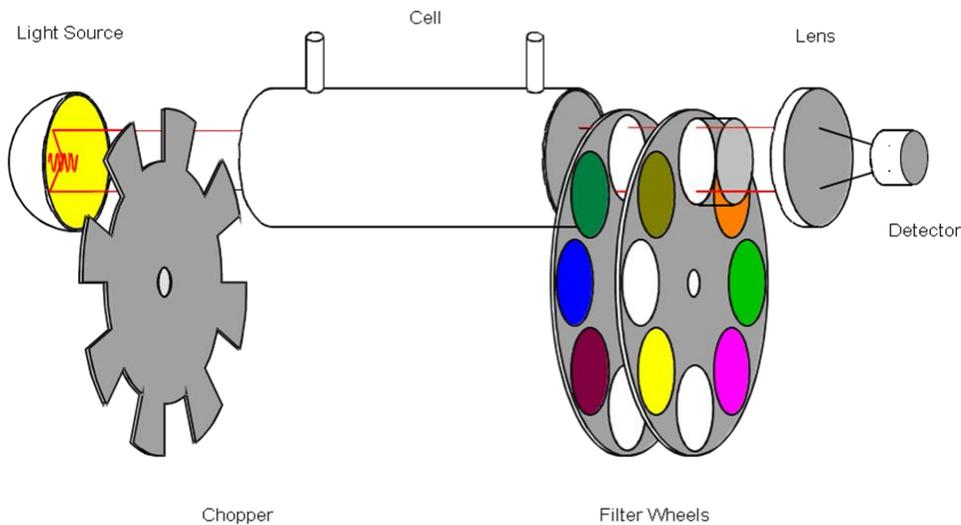
review.

Cross Interference

The gas filter correlation (GFC) is quite resistant to cross interference issues. Due to their multi-component properties, these devices are able to measure and compensate for most cross interference issues directly leading to a more accurate and reliable measurement. This is particularly true regarding H_2O which is a particularly broad interferent in the IR range.

Minimum Detection Limits

IR analyzers have a typical minimum range in the area of 0-10 ppmd, with a detection limit of 2% of full scale

Calibration Requirements

NDIR analyzers can be calibrated via a certified cal standard injected into the system at the probe, which allows for a full check of the entire sample system, or at the analyzer which saves on cal gas costs. Additionally, many IR systems are available with internal filter calibrations, which eliminate the need for gas bottles.

Maintenance Requirements

Typical maintenance procedures for extractive sample systems apply. This includes maintenance on the pumps, filters, sample probe, etc.

Maintenance on the instrument is minimal. Yearly checks of the instrument with a calibration device, specifically for water interference, are recommended. Additionally, as the mirrors in the measurement cell age, the amount of light they can transmit is reduced, necessitating the replacement of these mirrors. The time frame these need to be replaced depends highly on the corrosive nature of the flue gas being sampled, but lifetimes of greater than 10-15 years can be expected.

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3.5 – Tunable Diode Laser

Measurement Technology

Tunable Diode Lasers (TDL's) have special properties based upon small crystals (about 0.1 mm2) made of a mixture of elements such as gallium, arsenic, antimony and phosphorus. The proper selection and proportion of these elements the crystal can be made to emit at wavelengths where the target gas, which is HCl in this application, absorbs radiation of a particular energy. Changing either the temperature or current through the laser permits the wavelength to be tuned over the selected absorption feature of the target molecule. When an electric current is passed through these crystals they emit very pure laser light in the near-infrared spectral region. The temperature of the laser, which is stabilized with a thermoelectric cooler, will roughly establish the wavelength near the target gas' absorption feature. The laser current is then simultaneously modulated in the kilohertz region so that phase sensitive detection techniques may be used to improve sensitivity.

One advantage of the TDL technology is that the presence of the measured component in the gas stream can be used as a reference point for the laser itself. This function is called "line locking" and consists of the absorption peak of the HCl being used to keep the laser at the desired frequency. However, in the absence of the measurement component, during bypass or scheduled shutdowns, the laser can drift, and be outside calibration when the measurement component returns. To avoid this drift, many TDLs are supplied with a sealed internal reference cell, which contains a known amount of the gas to be measured. The use of the reference cells allows for not only line locking of the analyzer, but also the ability to continuously monitor the instrument's calibration.

A typical system configuration consists of the Analyzer unit in either stand alone or 19" rack mount configuration, which contains the TDL and associated electronics for signal transmittal and signal analysis. The Optical heads which contain the Launch and Receive components are mounted on the duct or stack and connected to the Analyzer via Fiber Optic/Coax cabling. This permits the analyzer to be placed in any suitable location, such as the CEM shelter or control room of the plant where it is not subjected to harsh environments and where it can be readily serviced as required. The optical signal is conveyed from the instrument to the measurement location by fiber optics and the return detected signal transported to the instrument by a separate coaxial cable. Thus, for example, continuous measurements can be made of the emissions in stacks and ducts which can be as much as 1500 feet (with a Photo Detector Amplifier or PDA) away from the instrument.

1) Single-Pass Stack Configuration

2) Dual-Stack

Pass

Configuration
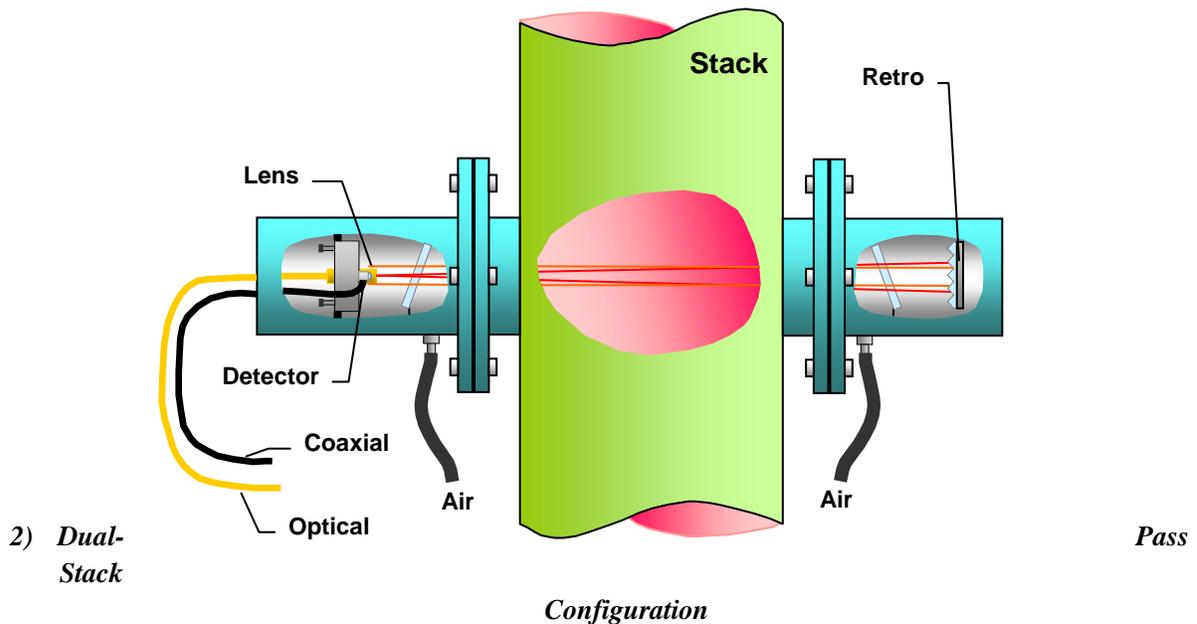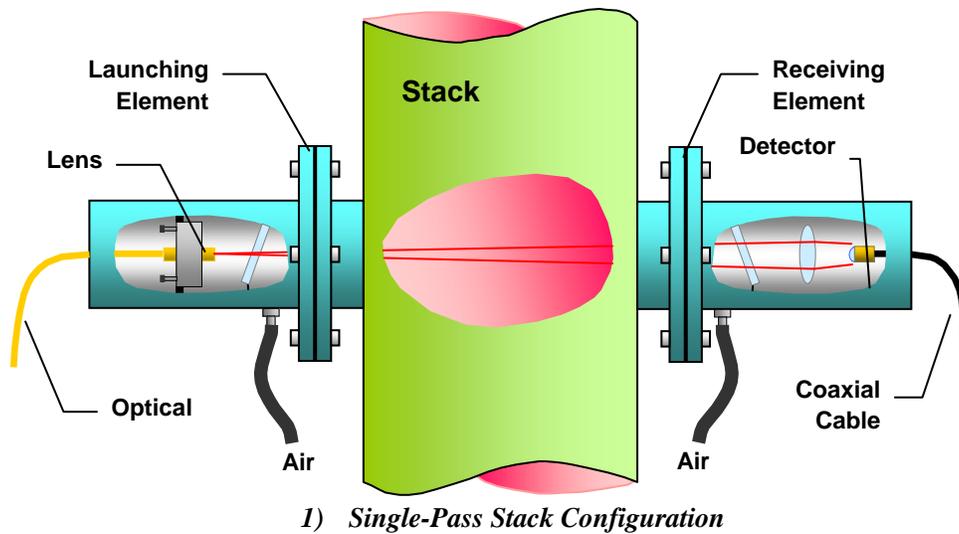
Multi-point array monitoring systems are also available with these systems allowing for a number of locations to be monitored from a single analyzer. The laser light signal is either multiplexed to prevent the loss of light intensity or passed through a beam splitter which will reduce the power of the laser. Each method will determine the number of locations that can be monitored by a single analyzer for various applications. This allows for an array of detectors to be mounted on the stack or duct for measurement in a turbulent area. Moreover, the use of optical multiplexing techniques offers a cost effective method for multi-point monitoring.

Measurement Location

For process control, the measurement is normally made at the inlet and outlet of the pollution control device. If the measurement is being made for stack emissions monitoring or HCl CEMS, it is on the stack or at another

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location that would be considered representative of stack emissions. The measurement sensitivity is dependent upon the measuring path length (Beer–Lambert law) and the opaqueness (particulate matter density) of the gas stream. The path length distance between the light source and the detector can vary depending upon the sample stream's particulate concentration. Monitoring locations that have conditions such as a fully saturated or condensing stack or duct that has a similar effect as high dust loading, which would extinguish the laser light, should be avoided. Therefore when choosing the measurement location, these factors along with the turbulence and stratification issues that arise must be considered. The measurements are usually made in-situ across the stack or duct. Various configurations can be chosen to define the process interface by the choice of flange sizes, materials, purging modes and purging media in order to adapt the sensors for process engineering measurements. In some cases, the optical path can be inside a probe. However, this will limit the path length. Alignment of the optical heads are of significant importance, and therefore the sight tubes to which the optics are attached to, are required to be aligned to specific tolerance typically within 1 degree and must be maintained at relative high temperatures. The optical heads must have the capability to adjust for any small misalignment errors. Another component that must be taken into account is the "thermal growth" of the duct or stack and material aging. Several engineered solutions are available to counteract this issue.

Two methods are employed for measurements across stacks or ducts: 1) single-pass where the laser radiation is transmitted across the stack to the detector on the other side, and 2) dual-pass where the laser radiation is transmitted across the stack to a reflector and then back to the detector on the same side as the transmitter. In typical installations, instrument air is used at each of the optical lenses to keep them clear of flue gas contaminants. In special situations where long spool pieces or lagging is employed, especially in the prescience of negative pressure stacks or ducts, blowers are required to prevent the migration of HCl in the spool pieces. Such migration would cause a variable and inconsistent concentration of HCl in the laser path resulting in inconsistent and inaccurate measurements. Thus, applying a positive pressure of ambient air to the spool pieces will assure that no stack gas HCl is migrating into the spool pieces. Particular attention must also be paid to the location of the measurement tools to limit the accumulation of particulate matter which can not only cause loss of signal due to light scattering but also can result in physical changes in the alignment of the laser light requiring realignment after cleaning.

Sensitivity and Detection Limit

The sensitivity and minimum detection limit of an absorption device are path length dependent. The longer the path length, the higher the absorption and the lower the sensitivity and detection limit. Therefore, longer path lengths result in better detect ability of low concentrations.

Dust loading in the effluent stream has the effect of blocking and scattering the laser radiation such that the detection limit will be compromised, leading to a much higher minimum detection value, due to lower power levels of the laser radiation reaching the detector. While particulate matter affects the detection limit, most systems can tolerate laser radiation power reductions of up to 90% without affecting the accuracy of the measurement. Nevertheless, there is a trade off in path length considerations between detect ability and reliability of the measurement. A single pass system with a PDA is recommended for high dust applications. Water vapor is also active in the near-IR spectral region, and some diode laser based analyzers have a significant sensitivity to water vapor as well as HCl. The HCl absorption line used by the particular instrument determines the degree of interference from water vapor. The interference from the water vapor signal is reduced by the development of algorithms used to address this interference. Typical sensitivity and detection

limits on coal fired sources dependent on the above criteria would be ±1 ppm$_v$ with a detection limit of 0.2 part per million by volume (ppm$_v$) respectively.

Calibration Requirements

Prior to initial usage, the instrument must be calibrated for HCl using a gas standard. After the initial calibration is performed, system validation is performed on a regular basis as defined by the governing body. A flow-though gas cell permanently in the optical path that allows for introduction of cylinder gases to be injected to check the analyzer response as an additive or dynamic spike should be part of the analyzer. After use the cell would be purged with dry air or nitrogen.

Maintenance Requirements

Daily checking for alarms or status signals of the following items will indicate proper running of the instrument:

- Laser Power

- Signal strength

- Peak Signal

- Laser Temperature

To ensure that the air purging system is still in good operating condition, monthly checks should be performed on the filters, pressure supply, optical purge line as well as making sure the optics in the stack are being kept clean. Finally, a verification of the optical alignment in the stack should be done on a quarterly basis.

3.6 - Cavity Ringdown Spectroscopy

Based on absorption spectroscopy, Cavity Ringdown Spectroscopy (CRDS) works by attuning light rays from a Continuous Wave (CW) laser to a wavelength within the IR spectrum where a contaminant absorption peak occurs (Figure 1-3). By measuring the time it takes for the light to fade, or "ringdown," an accurate molecular count is calculated that is not pressure sensitive. The time of light decay, in essence, provides an exact, non-*in*vasive, and rapid means to detect contaminants in gases.

Light Source   Light Detector
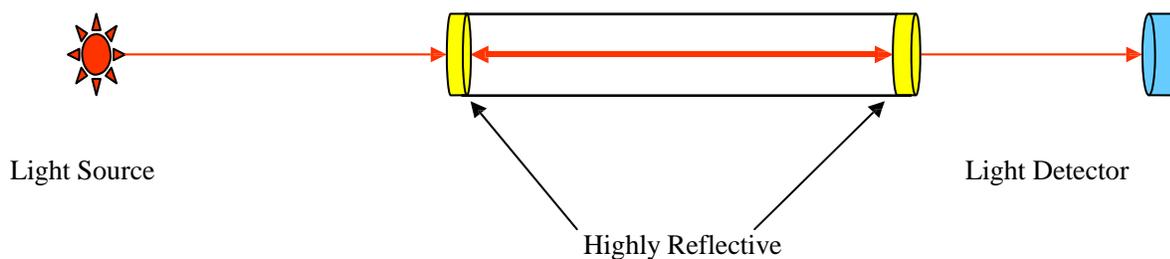
Highly Reflective

- A Continuous Wave (CW) diode laser emits a directed beam of light energy through an ultra-high

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reflective mirror into the absorption cell (cavity).

- The light reflects back and forth between two ultra-high reflective mirrors multiple times
- On each successive pass, a small amount of light or ringdown signal emits through the second mirror and is sensed by the light detector
- Once the photodiode detector "sees" a preset level of light energy, the light source is shuttered, or diverted from the cavity (time ~ 0 μsec)
- Once the light decays, or "rings down", the detector achieves a point of zero light energy in microseconds, and the measurement is complete (time ~ 160μsec)

The ringdown decay is exponential, and is described by the equation listed below.
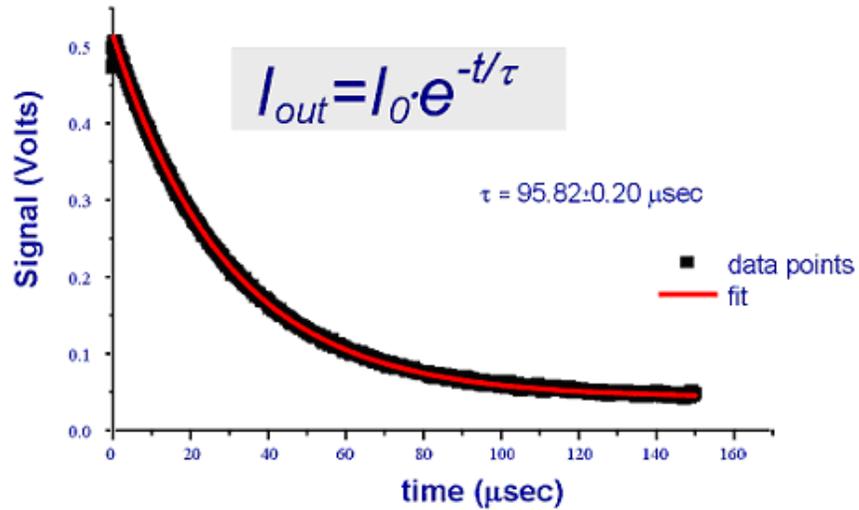
Ringdown Time

The computer-controlled system tunes the laser off the absorption peak for the sample species to determine the "tau zero" value, equivalent to a zero baseline.
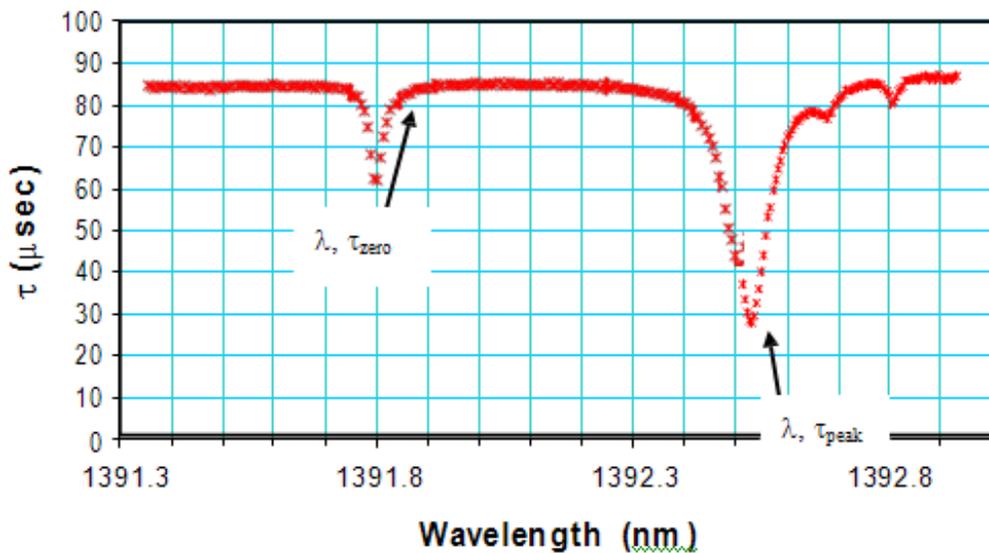
- The concentration of the sample species is calculated below by comparing this "tau zero" value to the "tau measured" ringdown time.

- These calculations are based on first principles and follow the Beer-Lambert Law.

$$\tau_{zero} = \frac{d}{c(1-R)}$$

$$\tau(v) = \frac{d}{c((1-R)+\sigma(v)Nd)}$$

$$N = \frac{1}{c\sigma(v)}\left(\frac{1}{\tau(v)} - \frac{1}{\tau_{zero}}\right)$$

c = Speed of Light
Section d = Cell Length
R = Reflectivity of the Mirror
N = Molecular Density (concentration)

σ = Absorption Cross
$\tau(v)$ = Ringdown Time
v = Laser Frequency

Concentration (N) Calculation

Detection Limit and Sensitivity

The cavity ringdown analyzer is very sensitive and designed to measure in the ppb range. The lowest detectable limit is 1ppb, with a sensitivity of 0.5ppb. For a range of 0-5ppm the accuracy would be +/- 1ppb.

Measurement Location

For stack emissions monitoring or HCl CEMS, it is on the stack or at another location that would be considered representative of stack emissions. The measurement sensitivity is dependent upon the gas stream conditions; since the analyzer has the ability to measure in the ppb range then it is highly suited to a dilution extractive CEMS configuration. This allows flexibility for process monitoring since variance in moisture and particulate concentrations can be handled by this method.

Dilution Extractive Measurement

The sample steam is conditioned at the sampling location by diluting the sample with an ultra-clean air supply with very low dewpoint temperature better than -40F. The dilution ratio can vary depending on the

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concentration expected, but typically 100-200:1. This diluted sample is then presented to the analyzer at some remote location in a controlled environment for analysis. This method is used extensively in coal fired boilers for other pollutant measurements.

Calibration Requirements

Cavity ringdown methodology is an "absolute" method, unlike techniques such as Tunable Diode Laser Absorption Spectroscopy (TDLAS). These analyzers have a built-in spectroscopic reference standard based on fundamental molecular characteristics as published in the High-resolution Transmission Molecular Absorption (HITRAN) database. This measurement technique is based on an absolute principle, the Beer-Lamberts law and used extensively by NIST as the standard for specific gases. Therefore in theory once the analyzer has been calibrated to the gas of interest then no further calibration is required. However, since each application may have different conditions and using the analyzer with dilution extractive systems means a way is required to determine the accuracy of the system. Also, if used for EPA compliance then certain criteria must be met for daily calibrations of any system.

Prior to initial usage the instrument is calibrated for HCl using a gas standard. After the initial calibration is performed, system validation is performed on a regular basis as defined by the governing body. Also the analyzer provides several internal checks to ensure it remains "on peak", and that the zero is absolute. The procedure to verify the unit's zero baseline using this reference standard is called "Tuning". This can be initiated at set intervals. Also the analyzer has a built in HCL reference cell for wavelength calibration (not for gas concentration calibration), which ensures that the analyzer is always measuring at the absorption wavelength for the target gas.

In order to comply with calibration requirements for compliance purposes, the dilution extractive system provides the ability to flow calibration gas via the probe and sampling system to the analyzer to check both low end and high end of the span range of the analyzer.

Maintenance Requirements

As with any Dilution Extractive sampling system there will be a general maintenance routine, ensuring the sampling system and components are in peak condition. Daily checking for alarms or status signals with respect to analyzer drift and system temperatures etc. is normally defined in the maintenance manual for the system.

4.0 - Conclusion

While there is still some uncertainty regarding the Performance Specification and regulations surrounding the measurement of HCl in US industry, it should be clear that the technology and understanding needed to make the measurement continuously is well developed. HCl monitoring has been done continuously for over 30 years, utilizing the techniques mentioned in this paper; Fourier Transform Infrared, Gas Filter Correction, Tunable Diode Laser and Cavity Ringdown. Based on the sites specific technical requirements, there are monitors available to meet the plant and regulatory requirements.