Trace HCl measurements in coal-fired power plant emissions using Cavity Enhanced Laser Absorption Spectroscopy

Cavity Enhanced (laser) Absorption Spectroscopy CEAS) for continuous emission monitoring.

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Measurement made easy

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Cavity Enhanced (laser) Absorption Spectroscopy (CEAS) system

Introduction

Regulations recently promulgated by the Environmental Protection Agency (EPA) require qualifying power and cement plants to monitor and control hydrogen chloride (HCl) emissions. These regulations call for HCl concentrations to be below 1 ppm for power plants and 3 ppm for cement plants.

A few key factors can make these measurements challenging. HCl is highly soluble in water and suffers from adsorption and desorption effects with certain materials like PTFE, which is often used in sample tubing. Additionally, reactions with ammonia in the flue gas can form several salts. In the case of an extractive sampling system, if the temperature of the sample drops below the sublimation point of these salts, build-up occurs. Salt build-up on sample tubing can interfere with the measurement of HCl and other flue gas components.

Measurement techniques

Three approaches (see Figure 1) to overcome these challenges are:

- hot/wet extractive sampling
- integrated Path (IP) monitors
- dilution-extractive sampling

Hot/Wet extractive systems generally employ analyzers based on absorption spectroscopy. These analyzers use light sources that allow simultaneous measurement of multiple component concentrations. However, some analyzers are susceptible to interferences from other gases, most notably H_2O and CO_2, which can create difficulties in achieving the necessary sensitivity and accuracy. Additionally, maintaining a stable and sufficiently high temperature throughout hot/wet extractive sample systems requires careful planning and design to minimize the risk of cold spots. Installing a complete hot/wet system to measure only HCl is cost prohibitive in most cases, but can make sense if other component concentrations must also be measured. In fact, ABB pioneered the use of FTIR based CEMS over 20 years ago and has experience applying this technology successfully at over 1,600 plants worldwide.

Integrated Path (IP) monitors often use tunable coherent laser light sources. As a result, spectral interferences from other gases may be reduced significantly. However, these monitors are generally limited to measuring only one or two components. Since the flue gas remains in the stack, sample conditioning is not necessary, simplifying overall system design. However, the system must account for temperature and pressure variations within the stack. Also, any movement of the stack can affect optical alignment.

For these IP or 'cross stack' systems, the stack's internal diameter limits the optical path length and thus the measurement sensitivity according to the Beer-Lambert law. While these laser-based instruments generally do not require frequent calibration (three months or more), challenging the complete analyzer with zero and span gases can require dismounting from the process.

Dilution-extractive systems, commonly employed in continuous emission monitoring systems (CEMS) in the US power industry and on most Mercury CEMS, can overcome these challenges. Dilution ratios often range from 30:1 to 150:1. Dilution (for example, with clean dry air) lowers the dew point of the sample to avoid the salt build-up and condensation. However, the use of dilution requires analyzers with higher sensitivity.

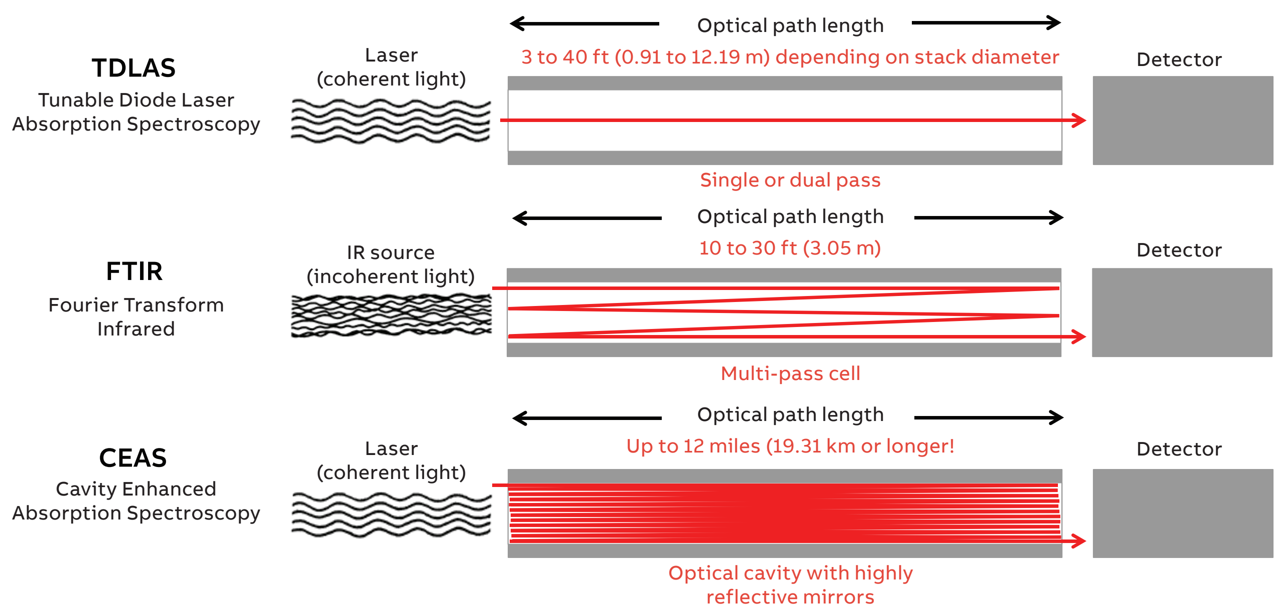

Figure 1 Comparison of HCl measuring technologies

High sensitivity analyzer

CEAS techniques provide extremely long optical path lengths (kilometers/miles) and thus significantly higher measurement sensitivity. Moreover, these analyzers employ tunable lasers and operate at reduced pressure. As a result, analyzers based on CEAS retain all of the benefits of traditional laser absorption spectroscopy, namely high selectivity, fast response, minimal calibration/consumables, robustness, and cost-effectiveness, plus they provide extremely high sensitivity. This high sensitivity permits accurate measurement of trace contaminants and weak optical absorbers, even in dilute samples.

A particularly effective variant of CEAS is Off-Axis Integrated Cavity Output Spectroscopy (Off-Axis ICOS) – a technology patented by Los Gatos Research, a member of the ABB Group since 2013. Off-Axis ICOS analyzers employ an optical cavity with highly reflective (greater than 99.9%) mirrors as the measurement cell. The laser beam passes through the first mirror and is then reflected between the mirrors to create a long effective optical length (many km) in a small package.

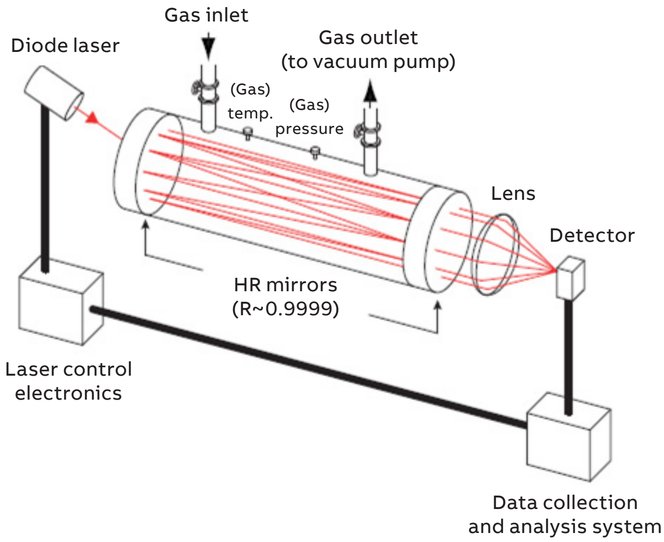

Figure 2 Off-Axis ICOS introduces the laser off-axis which negates the need for sub-nanometer alignment

In this case the laser is aligned off-axis with respect to the cavity as indicated in Figure 2. This arrangement prevents both optical interference within the cavity as well as optical feedback to the laser from the mirrors. The laser turns on, scans over selected absorption lines, and turns off, providing extremely short measuring times (1 to 10 milliseconds per sweep). The instrument analyzes the resulting absorption spectra to determine gas concentrations to less than1 ppb for some gases (HCl, HF, NH3). The health of the cavity mirrors is automatically monitored during the time the laser is off.

Unlike other cavity-based methods, in Off-Axis ICOS, the exact laser beam trajectory into the cavity is not critical, making the system immune to small changes in optical alignment from mechanical and thermal perturbations (for example, vibrations, shock, relative stack motion, etc). The mirrors use dielectric coatings that do not degrade with time or chemical contact. The sample gas is filtered (0.5 to 2 micron, typical) to prevent fouling of the mirrors during routine operation.

Since the optical alignment need not be precise, the mirrors can be removed, cleaned and replaced in the field in the event of a plant upset. This serviceability aspect further differentiates the Off-Axis ICOS technique from other long-path LAS technologies, including older, conventional cavity ringdown spectroscopy and multipass (Herriott, White) cell measurements.

CEMS trials using Off-Axis ICOS

The following describes three recent demonstration trials of the LGR Off-Axis ICOS technique under field and laboratory conditions.

Trial 1

An initial demonstration in a stack for a coal-fired plant in Maryland took advantage of an existing 35:1 dilution extractive sampling system for measuring mercury concentration in the flue gas. As shown in Figure 3, the mercury and HCl analyzers tie into accumulated flue gas from the stack that has been filtered, diluted, and conditioned by the extraction probe and associated converter.

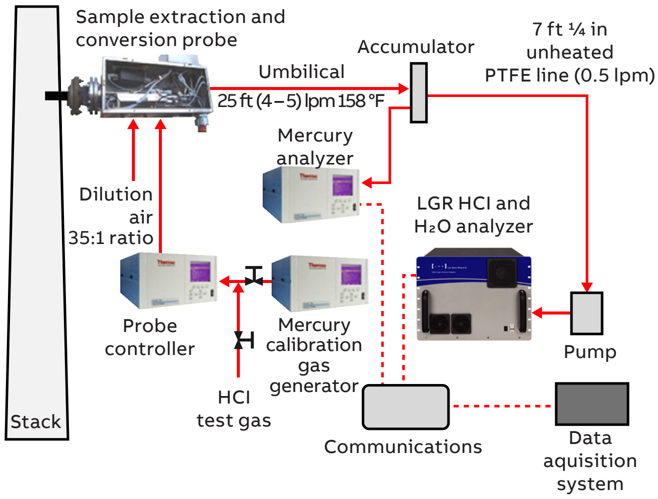

Figure 3 HCl analyzer trial at Maryland coal-fired plant

The probe converter extracts and returns the flue gas from the stack in a loop. While in this converter flow loop, the flue gas flows through a filter to remove particulates and through a venturi to measure its flow rate.

A portion of the flue gas from the filter moves through a critical orifice under known conditions to a dilution module. The orifice produces choked flow with a known velocity. The dilution module adds air to the flow at a ratio set in the probe controller. Key probe components reside in a heated enclosure to prevent condensation.

The probe converter can be altered to allow the sample gas and calibration gas to flow to both the mercury and the HCl analyzers. This setup gives plant technicians the ability to also handle calibration gases that check the zero and span concentration values of the HCl analyzer. Technicians operate the manual valves shown in the diagram, depending on which analyzer is undergoing calibration. This calibration process can also be automated using solenoid valves.

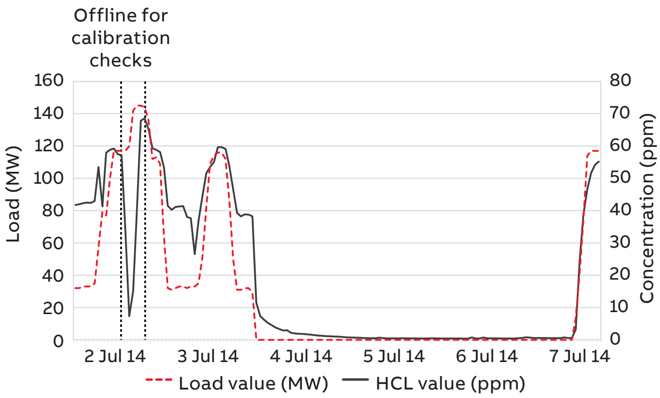

Figure 4 Analyzer trended well with plant load during short term trial

Results from this trial were limited because of unscheduled plant downtime. However, the trial did successfully demonstrate compatibility of the LGR analyzer with an existing stack monitoring system for mercury. The LGR analyzer shared the probe and sample line with the mercury measurement system. Analyzer data trended well with plant load and returned to zero when the plant was offline. HCl levels in the stack measured by the analyzer ranged from 20 to 60 ppm, so opportunities for demonstrating analyzer HCl sensitivity at 1 ppm or below were restricted.

Trial 2

A second demonstration of the LGR Off-Axis ICOS analyzer was managed by Spectrum Systems at a Southern Company coal-fired power plant in the southeast. Another analyzer based on conventional CRDS was run in parallel during testing. In this case both analyzers looked at stack sample lines from an extractive probe with 100:1 dilution. Figure 5 shows the setup for the LGR analyzer.

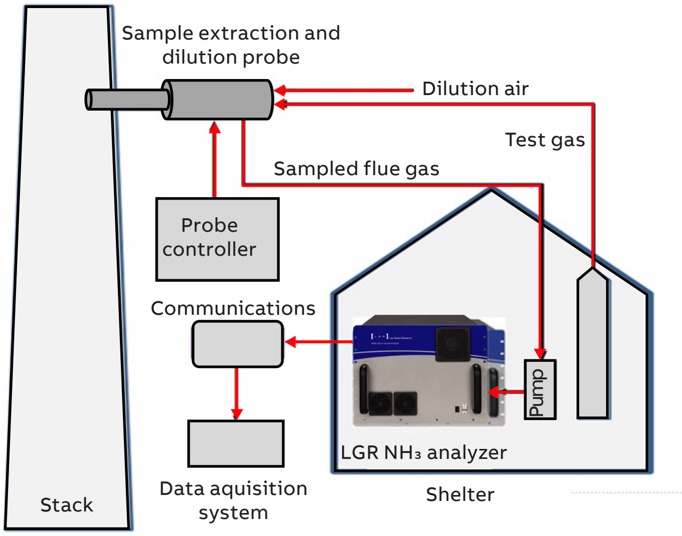

Figure 5 Setup for trial at Southern Company coal-fired plant in southeast

The plant tested the analyzers with the goal of using them for process monitoring rather than compliance. Online measurements would be used to adjust the dosing of chemicals in a wet scrubber that controls contaminants before they reach the stack. The idea is to avoid over-dosing and wasting expensive chemicals, but also ensuring continuous compliance with emission limits.

As the probe exits the stack the flue gas encounters a ceramic filter. After the filter, the sample is diluted and flows through 100 feet of chemically resistant tubing to the analyzer. Spectrum attempted calibrations of the system using instrument air for zero and with 9.6 ppm HCl (in N_2) span gas. Since the calibration gas was housed in the shelter with the analyzer, it flowed through a total of 200 ft (60.96 m) of tubing to the dilution probe and back to reach the analyzer.

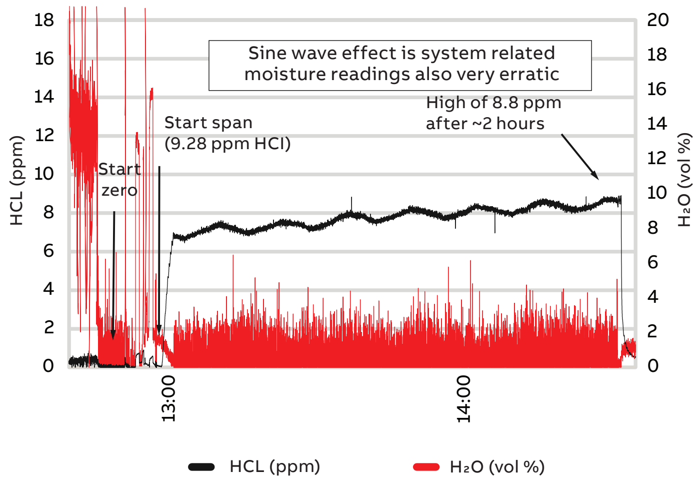

Figure 6 H_2O **measurement proved extremely valuable in diagnosing sampling system setup issues**

Initial response times for both analyzers to see step changes from zero to the HCl span level and back were too slow to comply with the expected QA/QC requirements in EPA's Performance Specification 18 (PS-18) – Procedure 6. Fortunately, the measurements of H_2O provided by the LGR analyzer (in addition to HCl) enabled determination of a problem in the sampling system setup – eductor malfunction. Subsequent installation of a sampling pump on the eductor bypass dramatically improved measurement response times of the entire system, as shown in Figure 7.

Note. CR coated filter from previous HCl trial installed before testing started.

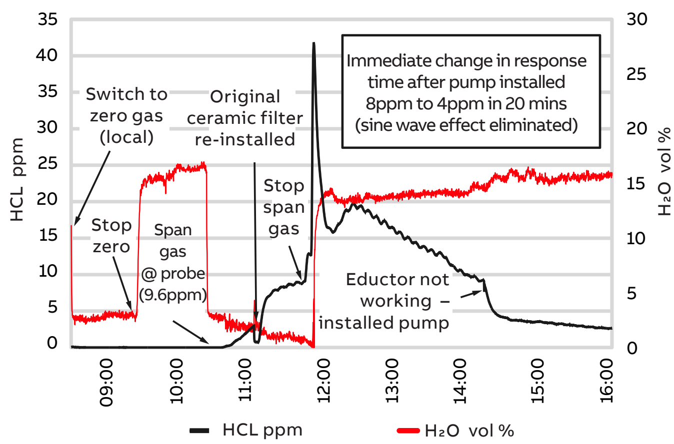

Figure 7 System response time improved dramatically once eductor failure diagnosed and pump installed

...CEMS trials using Off-Axis ICOS

In the opinion of Doug Baer, President of Los Gatos Research, "the sensitivity of the Off-Axis ICOS analyzer enabled the customer to quickly identify a problem in the sample handling. Slower, less sensitive and less capable instruments would have difficulty reaching these conclusions (with a dilution setup)."

This trial also employed a HovaQuick vapor generator to provide a humidified HCl calibration gas. This device vaporizes liquid HCl to develop a span gas with a known HCl concentration. Measurement response times in this case indicated that calibrations could take place within 15 minutes, demonstrating one method for compliance with Procedure 6. While time limitations did not allow injection of dry span gas after the sampling system issues were resolved, a separate trial using an FTIR system on a US cement plant has demonstrated that this can be achieved within the allotted 15 minutes by pre-saturating the sampling system with a higher concentration of HCl (for example, 200 ppm).

Figure 8 shows measurements of actual flue gas from the stack at the coal-fired plant over 24 hours. The data shows that the stack gas contained stable concentrations of HCl and H_2O at 1 ppm and 15 vol % respectively. Since the dilution ratio is 100:1, the analyzer is actually measuring HCl with a sensitivity of better than 10 ppb. The data spikes shown are thought to have resulted from steam cleaning operations.

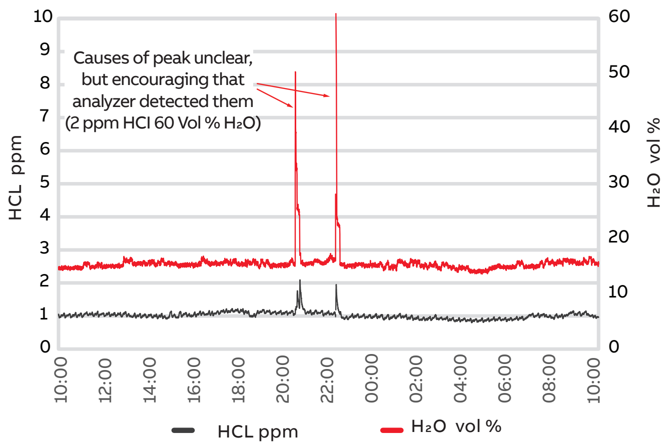

Figure 8 Data from coal-fired stack gas over 24 hours shows measurement of 1 ppm HCl and 15 vol % H_2O

Plant personnel's appreciation of the ABB/LGR Off-Axis ICOS analyzer's performance during this trial were relayed by Reggie Davis, President of Spectrum Systems, when he said "our client was very upbeat about how well it is doing and getting the moisture channel appears to be a huge plus. They all rave about the instrument and I have little doubt the LGR instrument will be the one they order." That turned out to be the case with the system due to be commissioned towards the end of 2015.

Trial 3

System integrator Cemtek Environmental at its offices in Santa Ana, CA conducted a third demonstration of the LGR Off-Axis ICOS analyzer for measuring HCl in power plant stack gases. These in-house tests were aimed at optimizing system design and response times as well as checking for interferences with other stack gas contaminants in accordance with PS-18. In this case technicians plumbed the LGR analyzer in association with a Thermo Fast Loop probe and Mercury Freedom system. Cemtek set the dilution ratio at 40:1, consistent with the standard design of the system.

The studies concluded that the two measurement systems could use the same extractive probe, filter, and dilution mechanism. However, it could not be determined whether each should have its own sample line since the standard sample flow rate for the mercury system was insufficient for the LGR analyzer if they shared the same pump. One suggestion, although this was not tested, was to relocate the critical orifice close to the mercury CEMS.

The tests also indicated that the sample line material wasn't critical over lengths less than 30 ft (9.14 m) Longer lines of conventional materials, such as PTFE, slowed measurement response times. However, this may be related to a lack of conditioning which is a known issue when measuring 'sticky' gases such as HCl. Once installed measuring stack emissions for some hours, sampling system materials become conditioned and reach a point of equilibrium, after which point hang ups of HCl become less critical.

As shown in Table 1, interferences with other possible stack gases did not affect HCl measurements by the LGR analyzer to a degree that would violate standards expected in EPA

Interference gas or gas combination	HCl concentration (ppmv)	HCl concentration with interference gas (ppmv)	Absolute difference (ppmv)	Average absolute difference (ppmv)
10.9 % CO_2, 276 ppm SO_2	0.16	0.17	0.01	0.01
	0.16	0.17	0.01	
	0.16	0.17	0.01	
135 ppm CO	0.16	0.17	0.01	0.01
	0.16	0.17	0.01	
	0.17	0.17	0.00	
445 ppm NOx	0.19	0.20	0.01	0.01
	0.18	0.20	0.01	
	0.19	0.19	0.01	
89.74 ppm CH_4	0.16	0.27	0.10	0.10
	0.17	0.27	0.10	
	0.16	0.27	0.11	
11.5 ppm NH_3	0.13	0.12	0.01	0.01
	0.11	0.10	0.01	
	0.10	0.09	0.01	
445 ppm NOx	0.09	0.09	0.00	0.00
	0.09	0.09	0.00	
	0.09	0.09	0.00	
18.7 ppm CH_2O	0.18	0.18	0.00	0.01
	0.14	0.13	0.02	
	0.10	0.09	0.01	
			Sum of responses	0.14
			% of calibration span	1.44

Table 1 The ABB/LGR HCl analyzer showed very little interference when challenged with PS-18 listed gases

Conclusions

Trials continue to optimize the sampling systems to ensure that HCl CEMS measurements will meet EPA specifications, but the LGR Off-Axis ICOS analyzer itself passes all tests. System integrators like Spectrum Systems and Cemtek Environmental are confident they can develop a system that will meet PS-18 and satisfy coal-fired power plants and further field trials are planned to confirm this.

In summary, the online trials demonstrate the LGR Off-Axis ICOS analyzer:
- can measure less than 1 ppm HCl in stacks
- is compatible with 100:1 dilution-extractive sampling systems, as well as those of mercury continuous emission monitoring systems
- responds to a 95 % step change in HCl in less than 15 minutes using vaporized liquid standards, when integrated with an extractive sampling system
- can successfully integrate with a mercury CEMS

The trials have also confirmed the high importance of measurements of H_2O and HCl simultaneously to validate the integrity of the sampling systems and the HCl readings.

Measurements with the LGR Off-Axis ICOS analyzer in conjunction with mercury CEMS systems can make use of a common sample probe, filters, and dilution mechanisms, but may require separate sampling lines for each analyzer or a relocation of the critical orifice.

Lastly, lab tests have demonstrated the LGR Off-Axis ICOS analyzer exceeds the requirements in EPA Performance Specification 18 (less than 0.15 ppm) for combined interferences with stack gases. In fact, this is well within the PS-18 limit of 0.5 ppmv for a calibration span of 5 to 10 ppm. Recent improvements in measurement strategy will significantly reduce interferences further.

Further field trials are planned on longer sample line lengths and will evaluate whether daily validation can be done in accordance with Procedure 6. The final promulgated PS-18 and Procedure 6 allows the use of a dynamic spiking (DS) procedure for the daily mid-level calibration drift (CD) test and this is expected to greatly simplify compliance with the ongoing QC requirements.

In summary, the LGR Off-Axis ICOS technology is extremely powerful and shows a great deal of promise for continuous measurement of HCl emissions below 1ppm. The fact that it is compatible with dilution-extractive systems with ratios up to 100:1, and possibly even higher, makes this a very attractive solution, particularly for the coal/oil fired power industry where dilution-extractive CEMS are most common.

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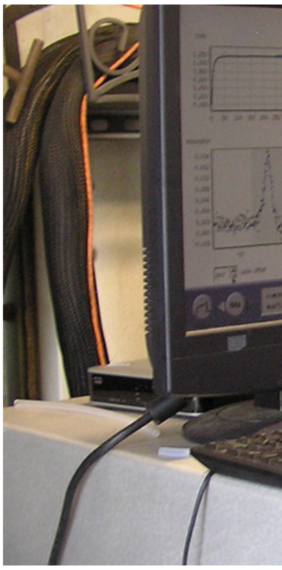

WP/ANALYTICAL/001-EN Rev. B 12.2018