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FEATURE

The Acid Test: CRDS for HCl Continuous Emission Monitoring

By Lisa Bergson and Edward C. Burgher

Introduction

As the date nears for stringent limits on hydrogen chloride (HCl), among other toxic air pollutants, fossil fuel-fired electric utilities and portland cement plants are finding valuable allies among spectroscopic analyzer makers who seek to apply their advanced technology to Continuous Emission Monitoring Systems (CEMS) required by the U.S. Environmental Protection Agency (EPA). The irony is, adoption of these alternatives may be jeopardized by proposed EPA performance specifications and test procedures that, although well intentioned, are widely viewed as costly and overly cumbersome.

Tiger Optics, LLC, is among those innovative instrument makers working with government and industry to provide efficient and affordable stack gas analysis. In this article, Tiger recounts its experience in validating its dedicated HCl CEMS analyzer as it moved from the rarified environment of the US National Institute of Standards and Technology to the base of an unheated, 350-foot umbilical at a coal-fired plant in the Midwest. Along the way, Tiger demonstrated that new analytical technology truly helps these smokestack industries meet their commitments for a cleaner, safer environment.

Closing the "Toxic Loophole"

In past circumstances, a Continuous Wave Cavity Ring-down Spectroscopy (CW CRDS) analyzer for hydrogen chloride (HCl) would be an object of curiosity in the CEMS field, where longstanding instrumentation suppliers and well-grooved protocols dominate. But time is running short for coal- and oil-fired plants to comply with the Mercury and Air Toxics Standards (MATS) adopted by the EPA in February 2012. Under the rule, HCl emissions, as a surrogate for all acid gases, will be regulated for the first time.

Upheld by the D.C. Circuit Court of Appeals on April 15, 2014, the rule specifies that electric utility steam generating units must be in compliance by 2015, with additional-year extensions in some instances. That is barring a reversal by the U.S. Supreme Court, which recently agreed to hear arguments that the EPA should have considered the cost of compliance. In a separate regulatory action, the portland cement industry faces similar deadlines to reduce emissions of certain air toxics. The EPA expects its pertinent rule—as amended in December 2012—to slash that industry's HCl emissions by 96 percent when fully implemented. To comply, here too, continuous monitoring of HCl will be required.

Health advocates termed these actions long overdue. Indeed, the absence of such regulation was decried as a "toxic loophole" by Charles D. Connor, President and CEO of the American Lung Association from 2008 until 2012. He exhorted the EPA in early 2011 to "protect all Americans from the health risks imposed by these dangerous pollutants once and for all." HCl not only damages limestone buildings and crop yields in the form of acid rain, but also combines with particulate matter to cause and to exacerbate respiratory conditions, particularly in the young and the elderly. HCl, ammonia, mercury, sulfur dioxide, particulate and other related emissions bode ill for human health and the environment. "Power plant pollution kills people," Connor stated. "It threatens the brains and nervous system of children. It can cause cancer, heart attacks and strokes."

In drafting the MATS rule, the EPA estimated that coal-fired plants were responsible for total annual emissions of some 155,000 tons per year (TPY) HCl or nearly 82% of the total HCl emitted into the atmosphere by all stationary sources. The standards will limit releases to 0.002 lb/MMBTU (0.02 lb/MWh) for existing power plants and 0.0004 lb/MWh for new ones.

The EPA says that the implementation of MATS will have both health and economic payoffs. The agency predicts the avoidance of some 540,000 missed workdays, 130,000 cases of aggravated asthma, and between 4,200 to 11,000 premature deaths, among other related benefits, on an annual basis. The resultant dollar savings range between $30 billion and $90 billion, versus a $9.6 billion cost of implementation, according to EPA calculations.

But that $9.6 billion number suggests compliance—such as the measurement of the new MATS-specified HCl concentration limit of 1.3 parts per million (ppm) for regulated sources—will not be easy.

New Challenges Call for New Technology

In the case of HCl, industry leaders and instrument makers cite four major hurdles to MATS compliance:

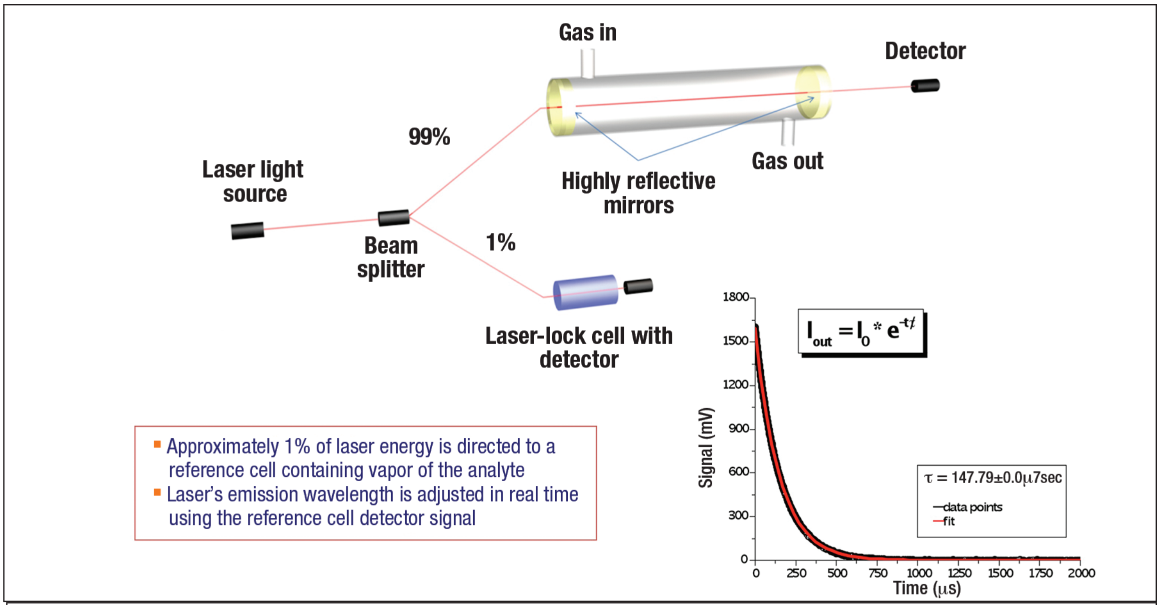


Figure 1. How Tiger Optics CW CRDS Works

A. Laser light attuned to target molecule is beamed into cavity with highly reflective mirrors on each end, allowing the light to travel for 30 kilometers in less than a millisecond. This accounts for the analyzer's great sensitivity.

B. The light builds to a predetermined threshold at which point the laser cuts off, and the Tiger detector measures the time taken for the light to extinguish or "ring-down."

C. The ring-down time, which is defined by a single exponential, is directly proportional to the presence of the target molecule in the sample.

the extreme solubility of trace HCl in water, potential sampling system losses due to reactivity, susceptibility to interference from other constituents found in flue gas and the lack of stable, low-level EPA-certified calibration gases. Sources or industries emitting HCl and affected by the new EPA rules may use SO_2 continuous emissions data as an indicator of HCl, but that has its own set of issues. Faced with these obstacles, the Electric Power Research Institute (EPRI) and the federal government, along with a broad cross-section of researchers, instrument companies, gas standards makers and other stakeholders began a series of studies, evaluating a few promising alternatives.

To that end, Franklin R. Guenther, group leader of Gas Sensing Metrology at the National Institute of Standards and Technology in Gaithersburg, Maryland, purchased Tiger's basic HCl analyzer. With an undiluted measurement range of 1 part per billion (ppb) to 4 parts per million (ppm), the analyzer was used to develop the new HCl Research Grade Material (RGM) to meet anticipated requirements. "The EPA pushed us," Guenther recalled. "They were saying, 'It's coming; it's coming.'"

Given the company's extensive experience with HCl in the semiconductor field and elsewhere, Tiger had addressed the special materials considerations that monitoring this particular acid gas entails. "The Tiger instrument has been very stable and robust," Guenther said. (See Figures 1 and 2.)

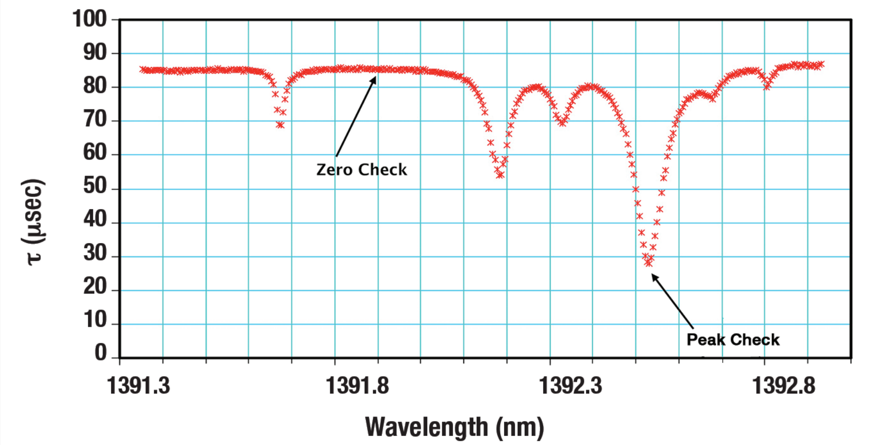


Figure 2. Ringdown time vs. Wavelength

The graph depicts the Zero Check achieved by adjusting the laser light to a wavelength region where there is NO absorption of the target molecule. This internal zero is constantly monitored by the analyzer. Peak Check assures that the laser is free of drift by continuously referring to the Laser-lock Cell shown in Figure 1. The cell contains a tiny amoount of the target molecule, akin to having your own built-in generator.

NOTE: *The measurement is the difference between the Zero and Peak Checks.*

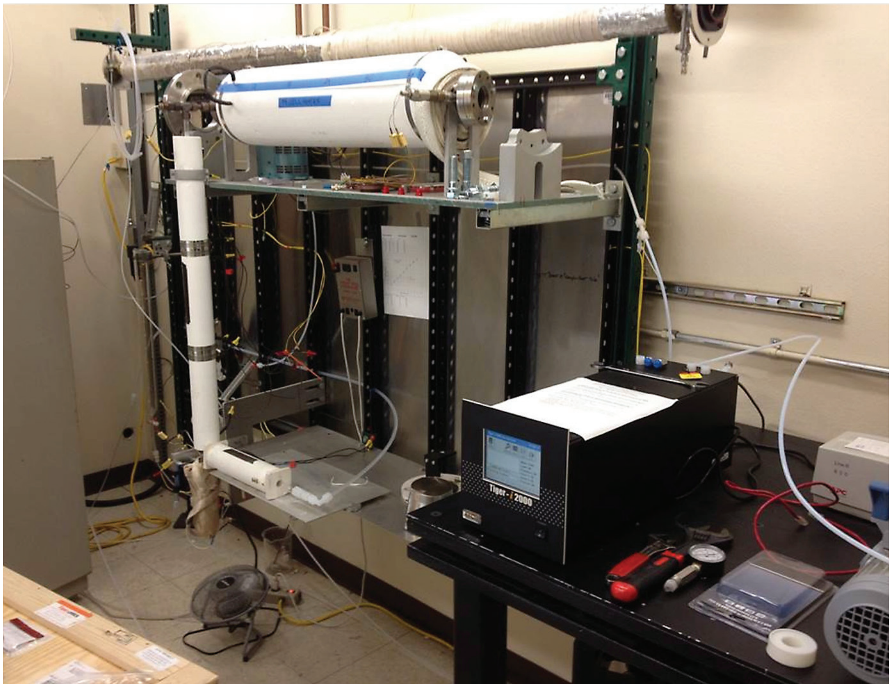


Figure 3. EPRI test set-up at UC Riverside; Tiger-i analyzer, with sample pump and Teflon® line connected to sampling manifold (sample cell upper left)

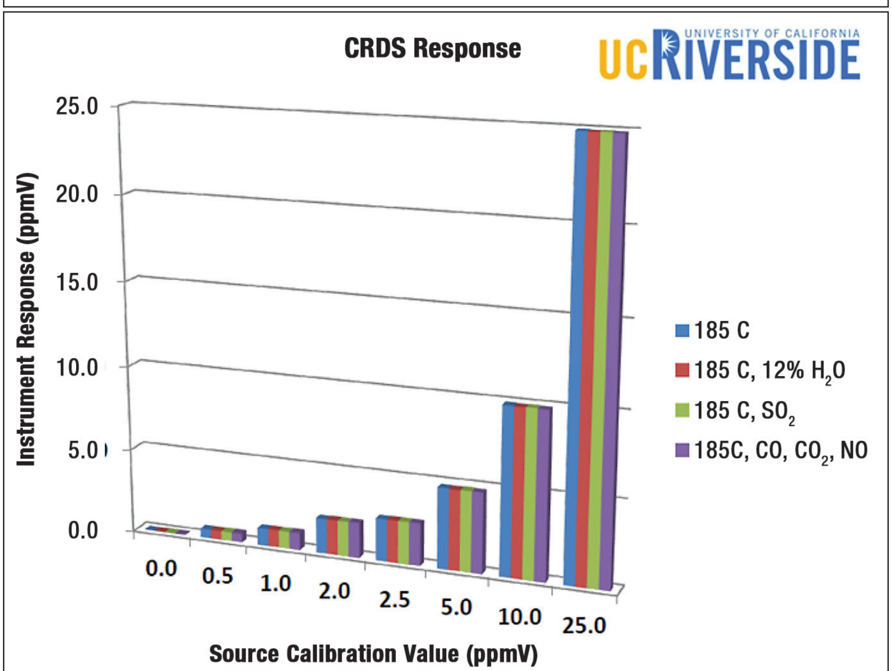


Figure 4. In simulated stack emissions at UC Riverside, Tiger-i proved free of flue gas interferences. Graph shows system response of all 185° (365° F) tests, including baseline at 0% H_2O, 12% SO_2 interference and CO, CO_2 and NO matrix

Subsequently, Airgas and Air Liquide bought the same analyzer to help develop their trace HCl Standard Reference Materials (SRMs). At this point, however, such materials have yet to be certified by NIST, since that requires close consistency from cylinder to cylinder and long-term validation of stability. Given such unknowns, even the newly minted NIST RGMs are only certified for one year and intended for use under "lab conditions."

The biggest hurdle that potential users face, in Guenther's estimation, is the need for proper sampling systems. Because HCl is highly reactive, uncoated stainless steel cannot be used for regulators, tubing, probes and any facets of the sampling system. "All surfaces must be treated or they will act as a permanent or temporary reservoir for HCl, and slow response," he said, adding, "It's stable in the cylinder, but you need to be very careful with sampling and to follow EPA recommendations to the letter."

Parallel work to qualify the Tiger-i CEM HCl and other analyzers for the prospective HCl CEMS regulations began at the EPA's simulated burner facility operated by the Air Pollution Technology Branch of the National Risk Management Research Laboratory and the University of California (UC), Riverside. (See Figure 3.) At the latter, EPRI contracted a study entitled "Continuous Emission Monitor Evaluation of Three Spectroscopic Techniques for Hydrochloric Acid," to compare detection limits and response to gas constituents that threaten to interfere with measurements at the very low levels (below 5 parts per million) of HCl that EPRI stated is typically found in those power plants continuing to operate.

Besides the Tiger-i CEM HCl extractive dilute analyzer, the study included a Unisearch Associates Inc. TDL (Tunable Diode Laser) single-pass cross-stack analyzer and an Industrial Monitor and Control Corporation FTIR (Fourier Transform Infrared) spectrometer. Up until now, FTIR has been the specified method for HCl monitoring in accordance with the EPA's Performance Specification 15 of 2014. Like the FTIR, the Tiger-i CEM HCl relies upon "extractive" measurement, pulling the sample from the stack.

This instrument has high sensitivity, allowing for 100:1 dilution, thereby lessening exposure to contamination and particulates, while still achieving sub-ppm detection. Of its dilution-extractive method, the UC Riverside study found that, "Overall the tests do not seem to be biased by gas through the dilution as average percent difference values were 3.2% direct and 2.6% through the dilution system." Since dilution-extractive systems are commonly used for CEMS analysis of sulfur dioxide (SO_2), oxides of nitrogen (NOx) and mercury, the CRDS analyzer is easy

Analyzer	Min. Detection Limit (ppmV) at 25, 100, 185°C	Drift	Avg. Precision
Tiger-i CEM HCl	.06–.08	0.88%	2.5%

Table 1. EPRI evaluation of Tiger-i CEM HCl conducted at UC Riverside

to integrate into existing installations.

At UC Riverside, the three devices were subjected to a comprehensive, highly systematic, carefully controlled and uniform series of tests. With one frontrunner, all fared well and were found to be sufficiently impervious to multiple interfering species, including SO_2 at 2,050 ppmv; a matrix of CO, CO_2 and NO, with 201 ppm propane; and 12% moisture, at concentrations ranging from ambient to those representative of flue gas. Assessing the Tiger device, the report said, "It is clear from these tests that the other gases at concentrations typical to flue gases in coal-fired plants do not interfere with CRDS HCl measurements, as there was no observed effect in the system response." (See Figure 4.) Beyond that, the instrument proved very reliable when it came to linearity, precision, detection limit and stability, with zero drift reported. (See Table 1.)

EPRI Field Evaluation

What the researchers and the industry did not know was how well—if at all—the three different technologies under consideration for HCl CEMS could withstand exposure to the moist, corrosive and particle-laden atmosphere often found in emissions from coal-fired boilers. Tiger's CRDS technology operates in Persian Gulf syngas production facilities, and is deemed safe for Safety Integrity Level 1 nuclear plants; it has been used for many years to manufacture aggressive gases, including HCl, ammonia and hydrogen bromide in semi-enclosed instrument sheds.

Therefore, its instrument was selected to participate in a six-month evaluation study sponsored by EPRI and coordinated by RMB Consulting & Research Inc. EPRI sought to apply a pre-determined sequence of manual tests, generally used for Relative Accuracy Test Audits (RATAs), to assess the viability of the different HCl CEMS technologies, as well as to determine their maintenance requirements and to observe long-term operation in a real-world setting.

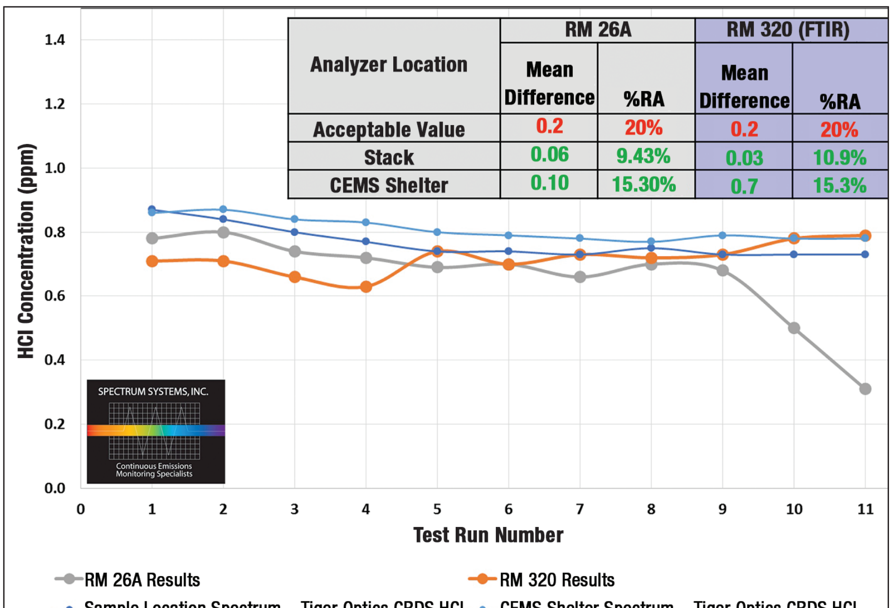
Conducted at the AMEREN Rush Island facility, a sub-bituminous (PRB) coal-burning plant in Festus, Missouri, the Tiger-i CEM HCl CRDS dilution-extractive analyzer was compared to Thermo Fisher Scientific's FTIR CEMS and two TDL analyzers: the Unisearch dual-pass cross-stack analyzer and an Oasis Emission Consultants Inc. single-pass cross-stack analyzer. The TDL devices measure light absorption in situ across the stack, where they are typically positioned several hundred feet up to detect absorption from the stack gas.

Weighing in at 33 lb, with a half 19" rack-mount footprint (8.75" X 8.5" X 23.6"), the Tiger-i CEM HCl was the most compact of the instruments. But none of the four competitors experienced anything like the comfort and cleanliness of the lab. "Dust everywhere," Tiger's applications engineer, Chris Stokes, reported, adding, "I would guess the annulus that we are working in is 115-120° F, with a good breeze coming through. I'm going to drink a gallon of water now."

Imagine when the power to Tiger's air-conditioned enclosure cut off in early September, and the temperature inside the unit spiked. That and other mishaps, such as a temporary four-day power loss to the air compressor affecting all analyzers, were among the not unexpected setbacks faced in the course of the study. Nonetheless, the Tiger-i CEM HCl recovered and chugged along with minimal on-site maintenance.

By the last RATA on January 23, our service engineer, Josh Paugh, reported that, "Tiger pretty much nailed the reference FTIR, and our readings were so consistent, that it looks more like the reference bounces around our reading than the other way around." In fact, results presented by EPRI at the 2014 Mega Symposium in Baltimore showed the CRDS Tiger-i CEM HCl and the Thermo FTIR tracking closely between October 2013 and January 2014. The absolute average difference between the two over 1,769 hours (~10 weeks) was approximately 0.1 ppmw. (See Figure 5.) For the same period, the two TDL-based instruments had an average absolute difference of ~0.4 ppmw, which improved to ~0.2 ppmw after Unisearch implemented a moisture correction in December.

The final report showed that the little Tiger demonstrated the greatest stability and emerged as the only contender to ace all categories, with a "green" score across the board. This impressive performance was a tribute to the company's highly experienced partners, CEMS integrator Spectrum Systems, Inc. of Pensacola, Florida, and M&C TechGroup



Analyzer Location	RM 26A		RM 320 (FTIR)	
	Mean Difference	%RA	Mean Difference	%RA
Acceptable Value	0.2	20%	0.2	20%
Stack	0.06	9.43%	0.03	10.9%
CEMS Shelter	0.10	15.30%	0.7	15.3%

Figure 5. Two Tiger-i CEM HCl analyzers compared to wet chemistry method (RM 26A) and FTIR (RM 320); data from EPRI HCl CEMS field evaluation

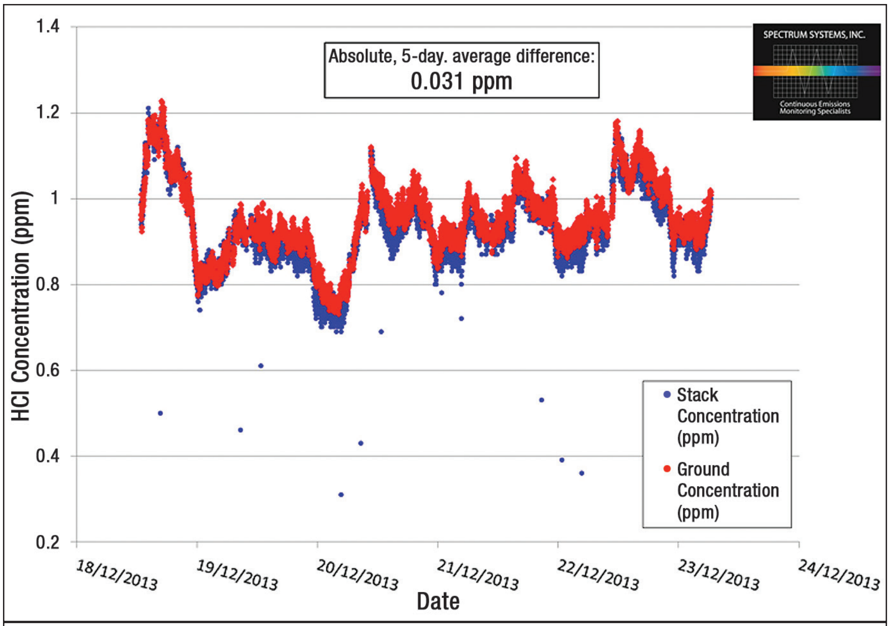


Figure 6. Results for Tiger-i CEM HCl monitors track closely on stack and ground; data from EPRi HCl CEMS field evaluation

Germany, a maker of robust, sophisticated dilution probes and other CEMS equipment.

The real test was yet to come, however.

CRDS is Plug 'n Play for Existing Dilutive CEMS

It was a long way from the +/- one degree temperature controlled lab at NIST to the Rush Island instrument shelter at the base of a 350-foot unheated umbilical, conveying sample gas from a sample probe in the stack to a second Tiger-i CEM HCl monitor in mid-January. Through the project coordinator, RMB, the company accepted an invitation to run that dilution-extractive monitor in parallel with the one up the stack. The two matched each other with very satisfying uniformity, within an absolute 5-day average of 0.031 ppm, while measuring between .8 and 1.2 ppm HCl. (See Figure 6.)

Based on this performance, Chuck Dene, Project Manager of Continuous Emission Monitoring at EPRI, described CRDS as, "plug 'n play for existing dilutive HCl CEM systems." making it convenient to integrate and to operate. For, although the TDL cross-stack analyzers perform in situ, measuring directly in the stack, CEMS applications are best addressed in ground-level instrument shelters. In addition to routine maintenance, CEMS analyzers are subject to frequent, even daily, calibration checks and other performance tests, which are much more convenient to conduct on the ground. Stack conditions are often harsh, with wind, cold and stifling heat afflicting technicians and stack testers; while, in some locations, only managers may go up the stack since union contracts keep members from so doing.

Generally, FTIRs also are installed on the ground. But, the operation of such devices is known to be complex and time-consuming, requiring a practiced, highly trained technician. By contrast, CRDS analyzers are virtually "plug 'n play," with no special expertise entailed. Moreover, because the analyzer is all solid-state and highly robust, users never need bother with mirror change-outs or the purchase and storage of spare parts. The only consumable: calibration gases required for quality assurance checks. Between the low maintenance costs and ease of use, CRDS analyzers actually save sources money, while helping to solve compliance headaches.

In summarizing the overall EPRI evaluation, Dene reported that all five HCl CEMS systems "performed very well." achieving the minimum requirement of 0.1 ppmw on average over the final weeks of the demonstration project. Perhaps understandably, both Tiger and Thermo crowed that they were "ready for 2015" at the annual EPRI CEMS User Group Conference in Denver this past May.

But that week, everything changed.

The Law of Unintended Consequences

To expand the use of innovative, robust solutions and to give sources more flexibility regarding analytical methods for HCl CEMS, the EPA proposed a new rule in the spring of 2014, allowing performance-based, "technology neutral" options for HCl CEMS analyzers and procedures. Slated for adoption by February 2015, Performance Specification 18 (PS 18) and Procedure 6 (which outlines quality assurance procedures) would serve to open up opportunities for newer methods, such as CRDS and TDL.

But, as drafted, the rules provide highly controversial criteria for assessing instrument accuracy and stability, along with guidelines to guarantee the quality and consistency of the resultant data. "The requirements of Performance Specification 18 and Procedure 6 are overly complicated and unnecessarily burdensome," ReginaldA. Davis, president of Spectrum Systems, wrote in response to the EPA's call for comments. His position was widely echoed across the industry. Indeed, the cost and complexity of the procedures threaten to make the use of alternative techniques, like CRDS and TDL, prohibitive for sources and stack testers alike, thereby defeating the stated goal.

Long subject to a complex and vast set of emissions regulations, coal-fired plants and other emission sources have grown accustomed to performing or paying for batteries of quarterly and even daily tests designed to maintain a continuous loop of quality assessment and control. But PS 18 and Procedure 6 comprise a whole new regimen of frequent field-based tests, involving detailed and elaborate level of detection (LOD), linearity and interference validations for each HCl CEMS installation.

Further complicating matters, the new procedures would require that all testing, either at the source or the instrument maker, be conducted on a set-up identical to that in field use. In drafting these new rules, the EPA did not take cost into account, which could lead to unintended consequences. On one hand, those wishing to implement PS 18 may elect to standardize sampling systems and analyzers to the extent possible, thus limiting opportunities for competition and innovation. Alternately, the mandate, combined with the considerable challenge of performing on-site interference tests in HCl, may simply lead folks to stick with PS 15 or comply by taking the risk of opting for three one-hour tests per quarter.

"Clean coal is a beautiful thing"

Tiger CEMS Business Manager Phil McMaster expresses a view shared by much of the industry in stating, "Clean coal is a beautiful thing." To that end, Tiger is grateful to serve the many power and paper companies that have already purchased Tiger-i CEM HCl analyzers in preparation for MATS. This technology has come to the fore, based on its multiple advantages of great sensitivity, high resolution, savvy materials selection, low cost-of-ownership and ease of installation and operation

As documented, the Tiger-i CEM HCl is the first advanced spectroscopic analyzer to not only ace all categories at the EPRI trial, but also match its performance up the stack with its results on the ground. As such, it will undoubtedly inspire other makers of both extractive and cross-stack HCl monitors to develop effective models, giving the industry a host of viable choices. In this way, new technology will help to promote clean, affordable energy; preserve and expand employment, as well as boost profits by reducing the need for maintenance, parts and consumables.

Uncertainty Equals Dollars

Still, the near-term implementation and enforcement of PS 18 or even its predecessor, PS 15, is far from certain. The countervailing forces of politics, industry lawsuits and lobbyists aside, significant technical hurdles remain. "We are not ready," as NIST's Frank Guenther has warned. The avalanche of complex procedures proposed in PS 18 comes on top of basic issues like availability of stable, consistent calibration gases and the adoption of appropriate sampling systems.

That said, if the United States continues to make acid gas reduction a priority, the work currently underway should prove foundational. It will ultimately inform advances in Europe and help to mitigate major emissions sources in China and India. To promote HCl CEMS in the service of cleaner coal, Guenther has a suggestion: "What really tightens the analytical scheme is when they start to have credit," he stated, referring to a cap-and-trade scheme for acids. "Then uncertainty equals dollars." G&I

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