Hydrogen Chloride as a Pollutant

Hydrogen Chloride (HCl) is a major atmospheric pollutant associated with the combustion of fossil fuels, such as coal and heavy oils, and also with a number of manufacturing processes, including cement production. HCl in the atmosphere has an adverse effect on both human health and the wider environment. The inhalation of even low concentrations of HCl can cause irritation of the respiratory tract in healthy individuals and exacerbate symptoms associated with conditions such as asthma and emphysema.

Dissolved HCl is a contributor to acid rain pollution, the results of which include damage to building materials and reduced crop yields. Atmospheric HCl pollution is also a factor in the production of photochemical smog. The economic impact makes the reduction of HCl pollution a priority for regulators and industry.

HCl is generated by multiple industrial processes, with combustion of coal and oil for household and industrial power generation as the primary source. Here, chlorides present in the fuel are converted to HCl in the combustion process and emitted with other by-products. In addition, industrial processes emit HCl as a result of chlorides present in raw materials that are converted to HCl during production. In cement production, for instance, raw materials, including calcium carbonate, silica, clays, and ferrous oxides, all contain chlorides, resulting in generation of HCl.

New EPA Regulations

Recent changes to EPA regulations will impose reduced limits on HCl emissions, depending on boiler output:

- Cement kilns: ~3 ppm
- Coal-fired utilities: ~1 ppm

Compliance with the new limits is generally effective in 2016, and industry preparations are under way. EPA and the Electric Power Research Institute (EPRI) have completed a series of trials to validate several candidate analytical techniques. Results show Tiger Optics’ Continuous-Wave Cavity Ring-Down Spectroscopy (CW-CRDS) leading the pack, demonstrating excellent sensitivity, measurement precision, and insusceptibility to interference from other compounds present in the stack gas.

Current Analytical Technologies

Current analytical methods for HCl CEM applications include GFC/NDIR, FTIR, and cross-stack TDLAS. These methods have, to date, been adequate to monitor HCl emissions, based on existing emissions limits. The detection limits for some of these techniques will not be sufficiently low, however, to meet the revised limits, and so alternative techniques will be necessary.

CW-CRDS offers the performance and range to cope with these regulations, delivering accurate measurements at levels far below the new limits in diluted stack gas.
**Cavity Ring-Down Spectroscopy for HCl CEM**

Tiger Optics’ T-I Max series—like its successful predecessor, the Tiger-i—has been developed for the measurement of trace level gases in samples at ambient pressure, using a vacuum pump to pull the sample through the analyzer. All Tiger Optics instruments are based on the CW-CRDS principle, shown in Figure 3.

CW-CRDS works by tuning laser light to a unique molecular fingerprint of the sample species. By measuring the time it takes the light to expire or “ring-down”, you receive an accurate molecular count in milliseconds. The time of light decay, in essence, provides an exact, non-contact, and rapid means to measure contaminants.

**Interference-Free HCl Measurement**

One specific advantage of the high spectral resolution of laser-based CW-CRDS is its excellent specificity to HCl. Flue gas from power plants contains large amounts of moisture, SO₂, and other species that can interfere with the HCl measurement. While many incumbent technologies frequently struggle with interference, CW-CRDS has proven to be interference-free at all HCl levels, as shown in Figure 4, a comparison between different HCl CEM technologies performed by UC Riverside in a test sponsored by EPRI.

Because of the many advantages of CW-CRDS, the National Institute of Standards and Technology (NIST) used Tiger Optics’ HCl analyzer to develop its HCl standards; Air Liquide and Airgas use Tiger instruments to produce their HCl calibration gases.

**CW-CRDS Sampling System and Operation**

Tiger Optics’ CW-CRDS analyzers bring significant benefits to CEM applications:

- Accuracy traceable to the world’s major national reference labs
- Freedom from interference
- No zero or span required; “fit” function allows adjustment to match EPA-mandated calibrations
- No periodic sensor replacement/maintenance
- Fast speed of response
- Wide dynamic range

Coupled with a suitable extractive dilution system – either a dedicated system or existing installation – the T-I Max CEM is capable of measuring HCl at concentrations in the raw sample gas from low ppb to high ppm. Dilution enables the use of non-heated transfer lines to deliver a clean, cool, dry gas with low particulate concentration to the analyzer. This simplifies the CEM system, improves transport of HCl from the stack to the measurement point, and negates the need for costly heated lines.

The maintenance-free nature of CW-CRDS also affords low cost of ownership and allows users to operate with confidence and ease in the field. And, despite the sophistication and performance associated with this technology, it remains extremely simple to use.

**Tiger Optics Overview**

Tiger Optics introduced the world’s first commercial CW-CRDS analyzer in 2001. Today, our instruments monitor thousands of critical points for industrial and scientific applications. They also serve the world’s national metrology institutes, where they function as transfer standards for the qualification of calibration and zero gases, as well as research tools for such critical issues as global warming and urban air quality.

CW-CRDS is ideally suited to the requirements of numerous environmental measurement applications, including CEM, where factors such as accuracy, sensitivity, freedom from interferences, low detection limits, speed of response, long-term stability, low maintenance, and low gas consumption are all essential.