

# HCl Monitoring in Stacks and Scrubbers

## Now Has a Dependable Solution

Due to its polluting effects, hydrogen chloride (HCl) levels in industrial exhausts are of growing concern. To ensure levels are within required limits, HCl monitoring equipment is installed on stacks and scrubbers where the gas is present. However, measuring the gas can be very challenging with commonly used technologies. In situ, probe-type analyzers using tunable diode laser spectroscopy offer a cost-effective, low maintenance and reliable alternative.

### The requirement for hydrogen chloride analysis

The most common non-sulfurous acid gas emitted from industrial processes is hydrogen chloride. It is a significant atmospheric pollutant which is harmful to human health and the environment. HCl contributes to acid rain and consequential damage to both infrastructure and agriculture. Common sources of HCl in industrial exhausts include waste incineration and ethylene dichloride production. These processes generate significant volumes of HCl which must be reduced to very low levels before off-gases can be released to the atmosphere.

HCl is a pungent gas with a low odor threshold of 0.26 ppmv and has an Immediately Dangerous to Life and Health concentration of 50 ppmv. It has a National Institute for Occupational Safety and Health and Occupational Safety and Health Administration Permissible Exposure Limit of just 5 ppmv. Due to these hazards HCl release from fixed emission sources are increasingly monitored and controlled, and legislative emission levels apply in many countries.



### The challenges of extractive measurement technologies

There are several emission monitoring system technologies available that can be considered for the measurement of HCl, including extractive techniques such as non-dispersive infrared, gas filter correlation, fourier transform infrared and cavity ring-down spectroscopy. Each of these has their relative merits but all

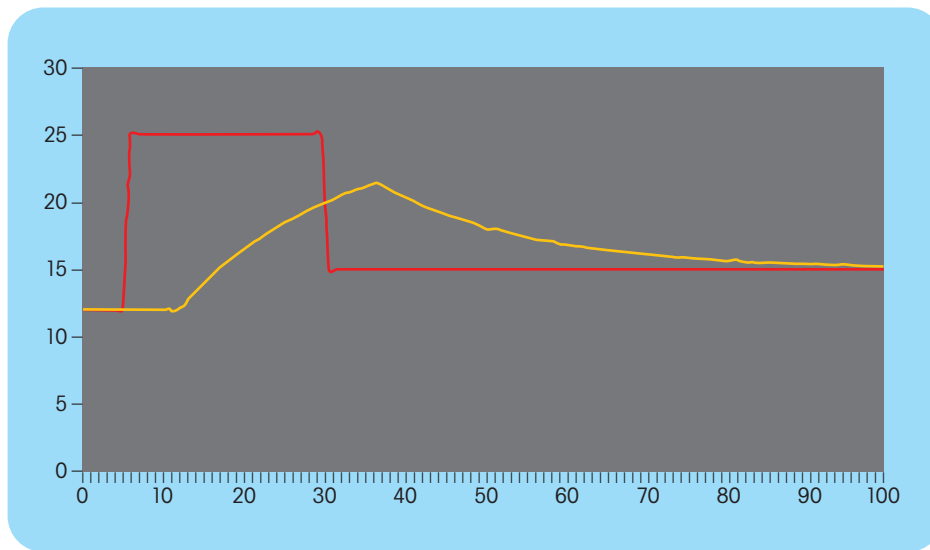


Figure 1: An example of reversible retention. The actual HCl concentration is shown in red with the analyzer response shown in yellow. It is clear that there is not only a significant response time delay, but in addition, the analyzer never reaches the true peak HCl reading.

share the same requirement: extraction and conditioning of a gas sample from the process to allow determination of HCl levels.

Consequently, one of the first challenges encountered when considering any of these methods is the provision of suitable sample extraction and conditioning equipment. Removing a gas sample containing HCl for analysis via off-line techniques can be problematic and expensive. This is largely due to the solubility and “sticky” nature of HCl gas, whereby any sample-wetted surfaces (pipes, regulators, rotameters, filters, etc.) will absorb and desorb the gas, a process often referred to as reversible retention, which can lead to delayed and inaccurate results (see Figure 1).

Also, any contamination in the sample conditioning system can contribute significantly to the retention of HCl (dirt in the regulators or tubing is a typical example). Indeed, a dirty sample transport line can result in T90 response times of 30 minutes or more. Such a delay in analysis is, of course, impractical and therefore, in an attempt to address the issue, conditioning systems require very careful material selection and design to reduce the internal surface area and minimize the effects of reversible retention.

Various techniques can be used to decrease response times, including running high concentrations of HCl through the system to passivate surfaces, followed by reduction in concentration and

regular cleaning of any in-line filters which could be sites of HCl retention. Moist HCl passivation gas can also be effective. In addition, it is essential to maintain the sample system at a high temperature (typically 180 °C or greater) when measuring low level HCl to prevent loss of sample through the system which would lead to false low readings. Therefore, what is termed a “hot/wet” system is normally required.

The key components of a hot/wet sample system are:

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

All of the above mentioned constraints add additional expense to the purchase of the HCl measurement system, and ongoing operational servicing and frequent maintenance required on such equipment can be very costly. Problems in sustaining reliable HCl measurements can ultimately reduce confidence in the analysis itself.

In addition to the requirement for monitoring pollutants from fixed emission sources, as part of the mitigation process to reduce HCl levels some processes use gas scrubbers to wash HCl from the carrier gas stream.

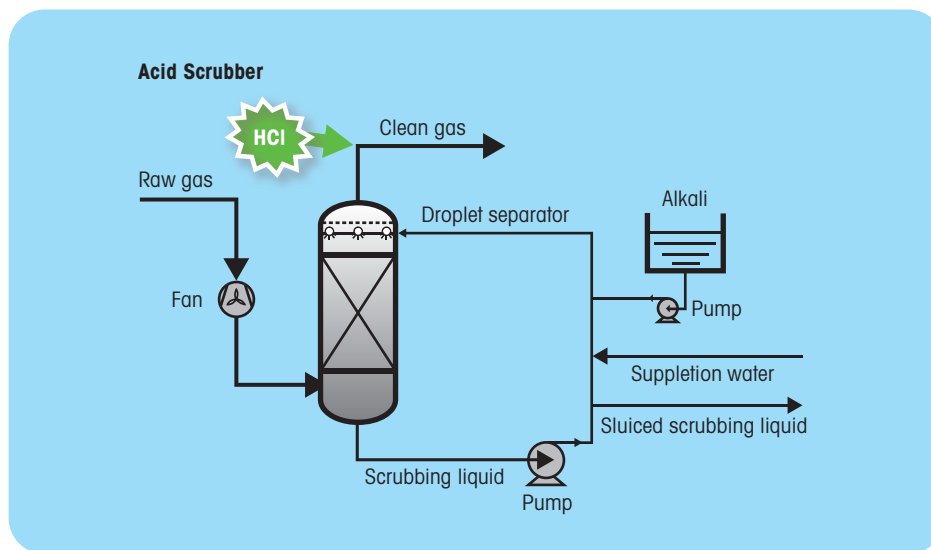


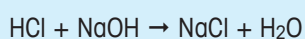
Figure 2: With sufficient height in the tower, HCl scrubbers can have efficiencies as high as 99.9%.

### Wet gas scrubbers

Many industrial and chemical processes create large quantities of waste gas. Some of these waste gas streams are acidic in nature and require treatment to neutralize the acid prior to further treatment. This prevents downstream damage to plant infrastructure or processes and ultimately reduces plant emissions. To achieve this neutralization, wet scrubbing towers (or columns) are used. Inside these towers, water or liquid chemicals are typically sprayed in a counter-flow to the waste gas stream to chemically absorb (scrub) the acidic components from the gas (Figure 2). HCl is one such acidic gas and can be present for example in raw and clean gas streams from thermal oxidizers, pulp and paper mills, and cement plants.

To control efficiency in these scrubbers HCl is monitored at the scrubber outlet to detect breakthrough (sometimes inlet HCl levels may also be monitored). These measurements are typically considered as a process control measurement and are not directly subject to legislative controls.

Plain recycled water may be used to absorb the HCl in scrubbers, resulting in wastewater comprising a weak hydrochloric acid solution (hydrochloric acid is formed when HCl gas is in contact with water), which may be a valuable by-product for use elsewhere on the plant. However, as HCl is highly acidic, scrubber efficiency is significantly improved if a strongly alkali scrubbing medium is used, such as sodium hydroxide (NaOH). The resulting by-product in this case is sodium chloride (NaCl).



To ensure efficiency, the internal structure of the scrubbers are designed to provide the maximum contact area between the waste gas and the scrubbing medium, and designs integrate a variety of gas/liquid contacting methods, including spray chambers, water jets and packed beds. Depending on the levels of HCl, in some scrubbers mist removal systems are required to prevent acid mist formation at the exit of the unit.

Measurement of HCl on the scrubber tower outlet using extractive technologies has very similar requirements and constraints to stack emissions as discussed above, therefore extraction and conditioning equipment, with its inherent high maintenance and ongoing operation costs, remains a constraint.

### HCl measurement directly in the process

A better solution to the problems of extracting and conditioning gas samples for HCl measurement was found in tunable diode laser (TDL) spectroscopy. This technology uses a laser beam that is of the same frequency as the absorption frequency of the gas to be measured. The laser source is mounted directly in the gas stream and a detector is installed directly opposite. As the laser beam passes through the gas, some of the light is absorbed by the target gas and analysis of the quantity of light received at the detector specifies the level of the target gas in the stream.

As TDL analyzers are installed in situ, sample extraction and conditioning equipment is not required. This also means that measurements are almost instantaneous. Because of these and other advantages TDL solutions for measuring O<sub>2</sub>, CO<sub>2</sub>, CO, HCl, moisture and other gases are becoming the standard measurement technology in many chemical and petrochemical processes.

Commonly, TDL analyzers are of a cross-stack configuration as described above, i.e. separate laser source and detector installed on opposite sides of the stack, pipe or vessel. Such an arrangement requires the mounting of a flange on both sides of the stack and careful alignment of laser source and detector, plus there must be access to the two flanges.

Unfortunately, this “line of sight” configuration can have its issues. When the stack walls flex due to thermal expansion and contraction, the laser source and detector can become misaligned and in extreme cases the entire signal can be lost. The solution is to realign the beam or move the installation to a point where thermal conditions are less severe, but perhaps to a location where the gas stream is less representative of the target gas. In addition, high consumption of purge gas is required to keep the optical windows free of dust, particles and “sticky” hydrocarbons.

**Alignment-free TDLs are the solution**

The answer to these concerns is TDLs such as METTLER TOLEDO’s GPro® 500 series, that do not require alignment. These analyzers contain both laser source and detector in one unit. The probe attached to the analyzer head has a corner cube (retroreflector) at the far end which directs the laser beam from the source back up the probe to the detector. This means mounting in only one side of the stack or vessel is required, and even if high process temperatures warp the stack/vessel the corner cube will still direct the laser beam to the detector. The design of the probe is such that purge gas consumption is much lower than with cross-stack TDLs, and as the GPro 500 has no moving parts, maintenance is very low, amounting only to annual verification and periodic cleaning of the optics.

The absence of alignment issues, compact dimensions of probe and detector/analyzer head unit, plus a range of process interfaces ensure that the GPro 500 can be installed precisely where the measurement is required, even in tight spaces, without the compromises that often have to be made when operating with bulky cross-stack designs.

GPro 500 analyzers provide all the benefits of in situ analysis but without the alignment and purge gas consumption concerns of the majority of cross-stack TDLs. This makes the GPro 500 HCl analyzer a highly suited and economical solution to monitoring stack emissions and gas scrubber outlets.

**Conclusion**

To help minimize pollution, hydrogen chloride levels in industrial waste gases must be curtailed, but the practicalities of measuring HCl using extractive technologies can be very cumbersome and costly.

Tunable diode laser analyzers are at the forefront of gas analysis and are increasingly the first choice for a growing number of applications which were once the province of extractive gas analyzers. The measurement precision, lower cost of installation and operation, minimal maintenance, fast response times and reliability of TDLs has cemented their reputation as a technology of choice.



A new generation of probe-type TDLs takes the core benefits of the technology, but overcomes earlier drawbacks of alignment difficulties and the requirement for significant optical process purge gas, to provide a truly flexible, easy to install, compact and reliable solution for HCl measurement.

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