Chlorine is one of the most common substances produced and processed in the chemicals industry. It is also a real challenge for gas analysts and safety engineers. Find out how you can increase the reliability and efficiency of chlorine detection.

Detect chlorine gas more efficiently and safely

Expert tips for practical application
Detect chlorine gas more efficiently and safely

The long path to the sensor
In the technical jargon, ‘adsorption’ (from the Latin adsorbere, to attract to itself) describes the state if a gas (or a liquid) is adhered to the surface of another substance – and this is frequently precisely the case for chlorine. Their high reactivity means that chlorine molecules are looking to link with other elements, even if they then diffuse in the direction of a Cl sensor.

An omnipresent all-rounder
Its typical odour revives childhood memories of swimming floats, headers off the 10-metre dive board and water slides, but this same odour puts an employee or safety engineer in the industry on alert. We are referring to chlorine, Cl for short.

In the periodic table of chemical elements, chlorine can be found under atomic number 17 in the 7th main group with the halogens. ‘Chlorós‘ (Greek) means ‘light green, fresh‘ – a reference to the colour of the gaseous substance at room temperature.

The most prominent property of chlorine is its reactivity: it links with many elements, even at normal temperature, frequently explosively. Chlorine is present in numerous organic and inorganic compounds, from harmless chlorides, such as sodium chloride (table salt) through to highly toxic dioxin, a chlorocarbon.

Chlorine gas itself is an everyday and fundamentally controllable risk in the industry if its presence is reliably detected. But this is not that easy...

The global production capacity for chlorine amounts to 58 million tonnes.

In the periodic table of chemical elements, chlorine can be found under atomic number 17 in the 7th main group with the halogens. ‘Chlorós‘ (Greek) means ‘light green, fresh‘ – a reference to the colour of the gaseous substance at room temperature.

The most prominent property of chlorine is its reactivity: it links with many elements, even at normal temperature, frequently explosively. Chlorine is present in numerous organic and inorganic compounds, from harmless chlorides, such as sodium chloride (table salt) through to highly toxic dioxin, a chlorocarbon.

Chlorine gas itself is an everyday and fundamentally controllable risk in the industry if its presence is reliably detected. But this is not that easy...

0.02 – 0.05 ppm Odour threshold
0.5 ppm Workplace threshold (AGW, NIOSH)
1.0 ppm Application tolerance value (ETW)
3.0 ppm Long-term activity intolerable
20 ppm Unconsciousness after a short period
50 ppm Death in less than 100 minutes

More info on chlorine and other hazardous substances can be found in the Dräger VOICE hazardous substances database at www.draeger.com/VOICE
The problem with chlorine gas is that it quickly gets caught on device surfaces, on the diaphragm of a gas detector for example, on the bump test adapter or in the valves of a calibration station, explains Ulf Ostermann, Sensor Expert at Dräger. The consequence: it simply takes much longer for the gas molecules to reach the sensor, regardless of whether a personal gas detector, clearance measurement or a functional test is used. In particular, chlorine molecules like to accumulate on the insides of hoses. As a result, many devices are not approved for chlorine clearance measurements.

A reason for the accumulation is contamination on the devices or hoses. Anyone working in the industry knows: a mobile gas detector is never completely clean, says Ostermann. Slight to severe contamination is impossible to avoid, depending on the environment in which it is used. Deposits are formed by particles, vapours or even just the skin of the user. Chlorine molecules immediately get caught if a surface displays traces of grease. Chlorine also particularly likes to accumulate on soot particles.

Bump test cost factor
The design of test stations marketed by most manufacturers does not allow chlorine gas tests, as the path that the test gas has to travel to the sensor is too long. As a result, in many operations, the devices are exposed to gas manually. But this is error-prone, time-consuming and expensive. The molecules often get caught in the device's fittings, reports Ulf Ostermann. For a test gas cylinder with 5 ppm chlorine, three litres of gas first have to be pumped through so that it functions in the first place. If the test gas is then fed through additional hoses to the gassing module, the number of surfaces to which chlorine can become stuck increases even further. A tedious procedure, especially if several devices have to be tested. And, from a commercial perspective, the workload as well as the test gas consumption have a significant impact.

Wouldn’t better cleanliness solve the problem of accumulation? This is a question that we are often asked in practice, says Ostermann. But you must not forget: we are talking about molecules.
Detect chlorine gas more efficiently and safely

of exposure to H2S. But how important is the sensor speed for chlorine? Ulf Ostermann explains: ››H2S is obviously a special case because it is impossible to smell in dangerous concentrations. In contrast, chlorine can be directly identified by its odour in all concentrations. This means that, in the event of unexpected exposure, e.g. due to a leak, your own nose would provide a warning even if the sensor did not respond. But: the odour alone does not indicate whether a concentration is within the workplace threshold range or 20 times over this limit. And this makes a significant difference after a few breaths. Let's not forget: this is about the health and safety of employees.‹‹

And sensor speed is also an economic issue. The quicker the response time, the shorter the test duration, the lower the working time and the test gas consumption. ››In everyday practice there is a huge difference between whether a chlorine sensor takes 30 seconds to respond during a bump test, or two minutes‹‹, stresses Ostermann. ››Every industry specialist can easily calculate what this one-and-a-half-minute shorter response time means for their equipment and frequency of use over a year.‹‹

Even a device that is fastidiously wiped down with a moist cloth still displays minuscule deposits with which the chlorine molecules would react. Even the extensive use of cleaning agents does not improve the situation.«

The smart solution

Countering the ›inertia‹ of chlorine gas during detection with a rapid sensor is much more effective. Chlorine sensors have significant differences in their response times, the products available on the market range from 30 to 120 seconds and more. The expert Ostermann explains the practical implication of a sensor that is 4 times faster than another: sensor speed is a safety issue for safety engineers and gas analysts in a plant environment: faster response times means more time to react, more reliability when deciding on the safety precautions and, in an emergency, naturally also: fewer or less-seriously injured people and a smaller amount of damage.

›Faster means safer‹ – this equation would be emphasized for a hazardous substance such as hydrogen sulphide. Ultimately, a few seconds can be the difference between life and death in the event of exposure to H2S. But how important is the sensor speed for chlorine? Ulf Ostermann explains: ››H2S is obviously a special case because it is impossible to smell in dangerous concentrations. In contrast, chlorine can be directly identified by its odour in all concentrations. This means that, in the event of unexpected exposure, e.g. due to a leak, your own nose would provide a warning even if the sensor did not respond. But: the odour alone does not indicate whether a concentration is within the workplace threshold range or 20 times over this limit. And this makes a significant difference after a few breaths. Let's not forget: this is about the health and safety of employees.«
A FASTER SENSOR PAYS OFF

The higher the number of units and the more frequently the chlorine detectors are used, the more important the consideration of operating costs becomes. Test gas is expensive and consumption increases with every second that the sensor needs to reliably detect the gas concentration during a function test. We have calculated the total difference that this can make in a year using the example of a sensor with a 30 second response time and one with a much longer response time of 120 seconds.

Basic assumptions:
A company uses 20 mobile gas detectors for chlorine detection, which each perform 230 bump tests per annum, a total of 4,600 tests every year. The cost of a cylinder of test gas (58 litres) is 342 euros. The costs for a working hour is calculated as 40 euros/h.

<table>
<thead>
<tr>
<th>Technical data for device</th>
<th>Device 1</th>
<th>Device 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of the bump test (s)</td>
<td>40</td>
<td>120</td>
</tr>
<tr>
<td>Duration of the flushing time</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Gas consumption (ml/min)</td>
<td>300</td>
<td>300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Working hour costs</th>
<th>4,600 bump tests with flushing time of 55 s (40 s bump test + 15 s flushing time) =</th>
<th>4,600 bump tests with flushing time of 135 s (120 s bump test + 15 s flushing time) =</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>253,000 s = 70.28 h</td>
<td>621,000 s = 172.5 h</td>
</tr>
<tr>
<td></td>
<td>70.28 h x 40 euros = 2,811.11 euros</td>
<td>172.5 h x 40 euros = 6,900 euros</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Costs of the test gas</th>
<th>4,600 bump tests at 40 s =</th>
<th>4,600 bump tests at 120 s =</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>184,000 s = 3,066.67 min</td>
<td>552,000 s = 9,200 min</td>
</tr>
<tr>
<td></td>
<td>3,066.67 min x 300 ml/min = 920,000 ml</td>
<td>9,200 min x 300 ml/min = 2,760,000 ml</td>
</tr>
<tr>
<td></td>
<td>9,200 ml x 5.90 euros/l = <strong>5,428 euros</strong></td>
<td>2,760,000 ml x 5.90 euros/l = <strong>16,284 euros</strong></td>
</tr>
</tbody>
</table>

Result: The working time expense and the consumption of calibration gas is significantly higher for the slower sensor: in total, the costs for both items amount to **23,184 euros**. By comparison: the expenses for device 1 only amount to about **8,239 euros**.

14,945 € can be saved per annum by a fast sensor.
Detect chlorine gas more efficiently and safely

Measure chlorine efficiently and safely – the easy way
From the bump test to the clearance measurement: sensor expert Ulf Ostermann knows what is important.

Chlorine is difficult to detect due to its high reactivity. What problems arise in practice, and what solutions does Dräger provide?

The main problem is that chlorine molecules quickly and easily accumulate on device surfaces and it takes a long time for a contaminated atmosphere to diffuse adequate molecules through to the sensor. In this case, the use of a highly sensitive sensor is extremely beneficial. Our DrägerSensor® XXS for chlorine, for example, has a t-90 time of 30 seconds, 4 times faster than many other chlorine sensors.

Another critical point often relates to cross-sensitivities...

Correct, such as with hydrogen sulphide. There are devices on the market for which the sensor responds to 10 ppm H₂S in the atmosphere with a chlorine alarm and displays 30 ppm, which can obviously lead to a large number of unwanted alarms, especially in petrochemical plants. Our sensor is much more robust in this respect: 10 ppm H₂S results in a reading of less than 0.5 ppm chlorine.

The more difficult a hazardous substance is to measure, the more important it is that a device operates with absolute reliability. It was previously difficult to test the correct functioning of chlorine sensors. Has anything changed?

The Dräger X-dock® provides a convenient and stationary method for testing chlorine sensors. For one thing, the X-dock has relatively short paths. Another benefit is that we have developed and introduced a stainless steel valve specifically for exposure to chlorine. This makes the bump test even faster. And cheaper: for example, our system lets you test a Dräger device with chlorine sensor every day for a whole year using only a 58 litre cylinder of test gas.

At the same time, the X-dock can also test the response time of a chlorine sensor. If a device does not respond after 60 seconds in the station this means: bump test failed! This is helpful, for example, to identify slower response times due to contaminated surfaces on the devices.

Clearance measurements for containers or confined spaces are also problematic. What needs to be considered here?

Conventional hoses that are used in pumping operations do not allow chlorine to pass through, or only very slowly. As a result, in practice, the devices themselves are often lowered into the confined space or container on a strap, rod or the like. The problem: you can't read the values.

That's why we developed a new hose that now also lets you conveniently perform clearance measurements for chlorine with pumping devices.

SOURCE:
www.worldchlorine.org