Measuring Chlorine in Chlor-Alkali

Applied Analytics Application Note No. AN-054

Application Summary

Analyte: **Chlorine (Cl_2)**

Detector: **OMA-300 Chlorine Process Analyzer**

Process Stream: **Chlorine Gas**

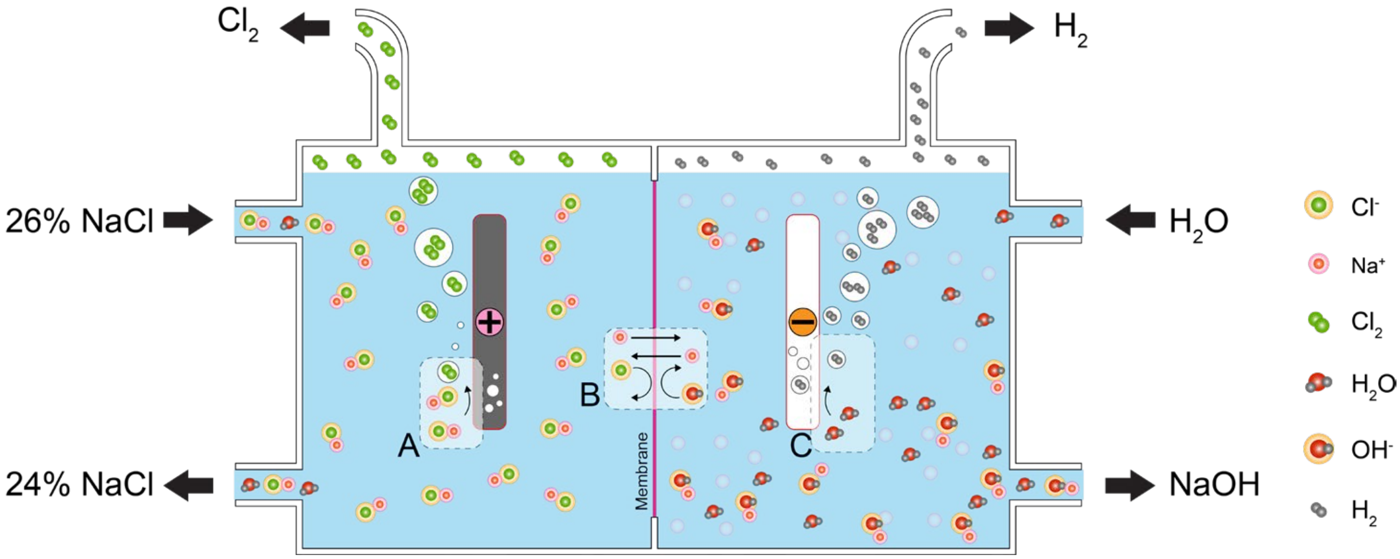
Typical Measurement Range: **0-100 ppm (±5 ppm) / 0-10,000 ppm (±2% full scale or 5 ppm)* / 0-100% (±2% full scale) [*whichever is larger]**

Introduction

Chlor-alkali refers to the production of Chlorine (Cl_2) sodium hydroxide/caustic soda (NaOH), and hydrogen gas (H_2) from the electrolysis of saltwater or brine. Both chlorine and hydrogen gases are used for a multitude of different operations in the chemical industry. Sodium hydroxide is also very common in the chemical and oil/gas industry for desulfurization and other areas.

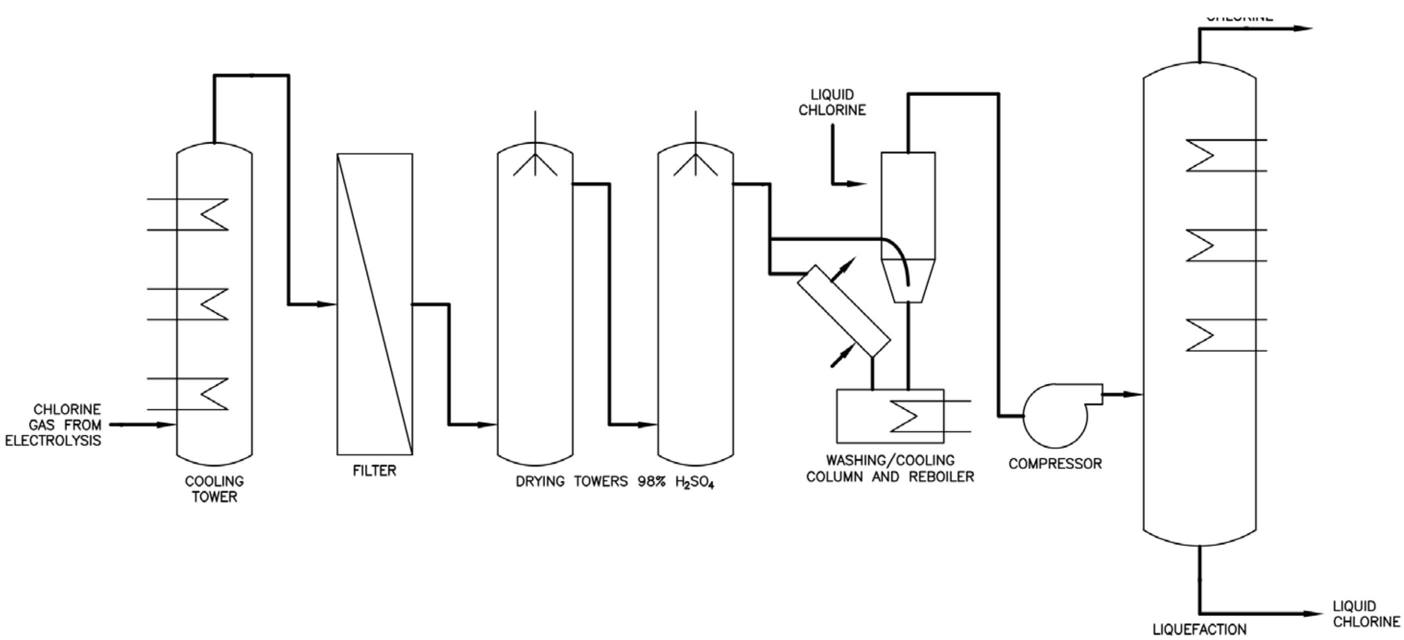
Electrolysis is a technique used to break bonds and reformulate molecules using redox (reduction-oxidation) reactions. Salt (NaCl) and water (H_2O) are fed into a vessel. Inside the vessel are two electrically conductive leads, with a DC power source at the top. When powered, one of the leads serves as the anode (negatively charged) and one serves as the cathode (positively charged).

NaCl is an electrolyte, so the Na^+ and Cl^- ions are floating freely in the H2O. When the leads are powered, the hydrogen bonds in the H_2O molecule break, which leads to hydrogen and oxygen now floating freely as well. When this happens, new molecules form—the Cl^- ions attach to the cathode and Cl_2 forms, flowing up to the top of the vessel. Likewise, H_2 molecules form at the anode and release in gaseous phase at the top. What is left in the solution in liquid form is NaOH—sodium hydroxide, also known as caustic soda.



Chlor-Alkali

Hereafter, the chlorine gas goes through a purification and liquefaction process:



Chlorine Gas Goes Through a Purification and Liquefaction Process

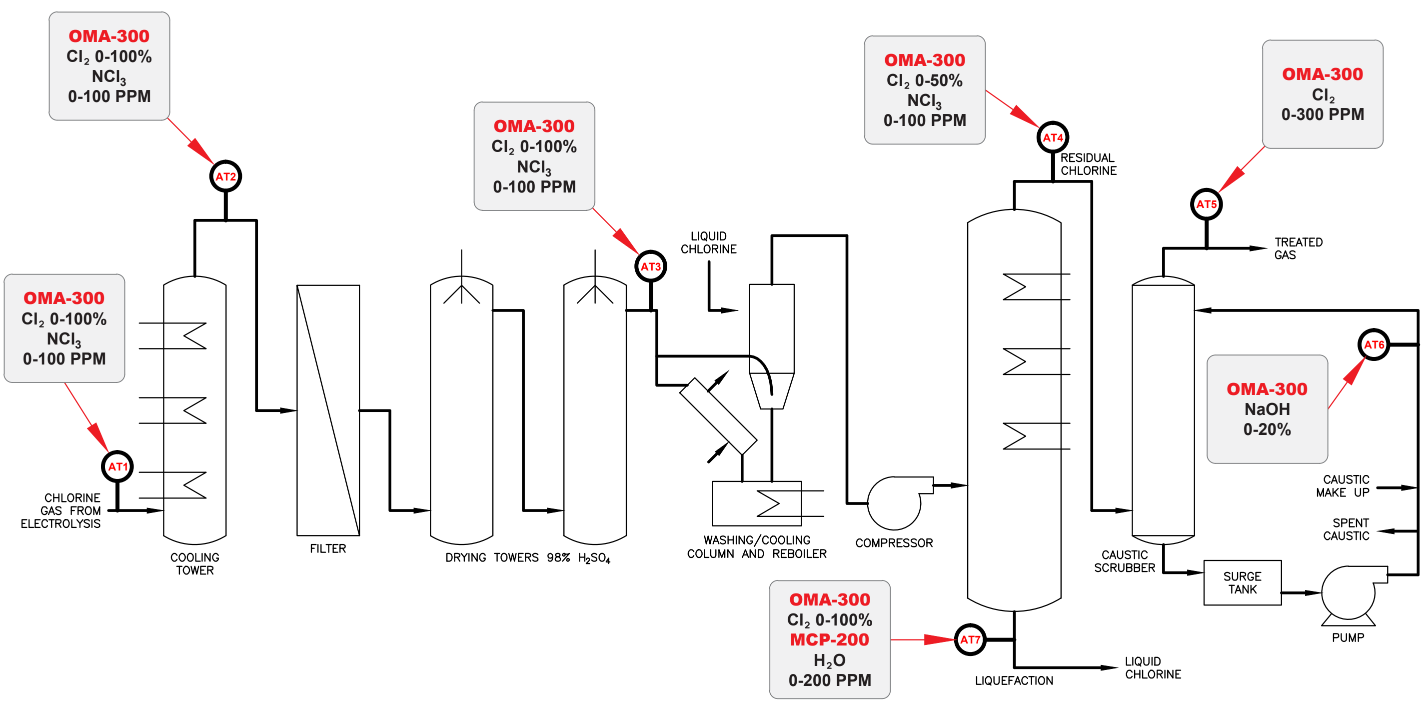
As the chlorine gas (wet chlorine) from electrolysis enters the cooling tower, it separates the chlorine from any impurities (brine mist, N_2, H_2, O_2, CO_2, & chlorinated hydrocarbons) in the gas sample. By using a cooling tower, the moisture/impurities will cool from vapor into liquid phase and travel to the bottom of the tower, whereas chlorine gas, with a much lower boiling point, will stay in the gas phase and travel up the column/cooling tower. As the chlorine gas rises, it may still contain up to 3% moisture.

Next, the chlorine gas goes through a filter to further remove water droplets and brine impurities from electrolysis that made it through the cooling tower. At this point the chlorine gas is clean enough to be sent to a hydrochloric acid plant. Otherwise, the sample is sent to a sulfuric acid drying tower. Sulfuric acid (H_2SO_4) is very hygroscopic, meaning that it has a large affinity to absorb water. Here, any residual water not filtered out gets absorbed by the sulfuric acid. The remaining chlorine gas (dry chlorine) exits the drying tower and faces washing/cooling, wherein water is flushed back through the chlorine and then re-cooled, to eliminate any final impurities. Also, re-boiling boils off any chlorine that may exist in the residual water from washing. Some of these final impurities include nitrogen trichloride (NCl_3) which forms in the electrolytic cell if the brine contains ammonium ions or organic nitrogen.

When it is finally clean, the chlorine gas can either be sent to a VCM plant for processing or sent to a compressor for liquefaction and eventual storage. Any residual chlorine that does not liquefy will vaporize and exit through the top of the column and is either sent to a gas scrubber or used to make HCl or EDC.

Applications

Cl_2 is a toxic and corrosive gas. It is also the final product of the chlor-alkali process. Therefore, it is essential to measure the Cl_2 content at several points throughout the chlor-alkali process. This can be accomplished using the OMA-300 Chlorine Process Analyzer.



AAI Analyzers in a Chlor-alkali Plant

1. The first measurement point for the Cl_2 is after electrolysis and before the cooling tower. This gas is typically referred to as Wet Chlorine. The Cl_2 concentration at this measurement point should be close to 90%, with moisture and some impurities completing the balance. It is important to monitor the chlorine concentration here, since it reflects the efficiency of the electrolysis. The OMA-300 Chlorine Process Analyzer can measure Cl_2 in the 0-100% concentration range via UV absorbance spectroscopy. The chlorine does have percent level water at this location, however, this does not affect the accuracy of the Cl_2 measurement, since moisture is transparent in the ultraviolet wavelength region and thus has no absorbance spectra.

2. The second measurement point for the Cl_2 is after the cooling tower, but before the filter. Although some moisture was removed in the cooling tower, this gas is still typically referred to as Wet Chlorine because it contains more than 30 ppm moisture, making the gas much more corrosive. The Cl_2 concentration at this measurement point should be closer to 100%. It is important to monitor the chlorine concentration here, since it reflects the proper function of the cooling tower. As mentioned previously, the OMA-300 Chlorine Process Analyzer can measure Cl_2 in the 0-100% concentration range via UV absorbance spectroscopy.

3. The third measurement point for the Cl_2 is after the sulfuric acid drying tower. This gas is typically referred to as dry chlorine. Again, the Cl_2 concentration will be close to 100%. The Cl_2 is monitored at this location to confirm proper function of the sulfuric acid drying tower.

4. The final point where Cl_2 is typically measured is in the Tail Gas or Sniff Gas. This is the gas that is not liquefied during the liquefaction process. The concentration of Cl_2 in this gas is related to efficiency of the liquefaction process. This can range anywhere from ~45% with a 95% liquefaction efficiency to ~1.5% with a 99.9% liquefaction efficiency. There are a few reasons to measure this gas. The first is to understand the efficiency of the liquefaction process. The second will depend on what is being done with the gas downstream. If the sniff gas is going to be sent to the caustic scrubber, then it is important to know the concentration of Cl_2, so that an operator will know how much NaOH to add to the scrubber solution. If the sniff gas is going to be used for HCL or EDC production, it is important for the operator to know the concentration because this will now become the new feed for the next stage of processing.

5. Nitrogen Trichloride (NCl_3) is an impurity found in the Cl_2. It is formed in the electrolytic cell if ammonium ions or organic nitrogen is present in the original brine. Only 1 ppm of NH3 in the brine is enough to create greater than 50 ppm NCl_3 in liquid Cl_2. This is dangerous. NCl_3 is very unstable and has been shown to be capable of accelerated decomposition at concentrations greater than 3%. This reaction is strongly exothermic and has caused several explosions in various chlor-alkali processes. Since NCl_3 has a higher boiling point than Cl_2, any NCl_3 present in the chlorine gas will concentrate in the liquid phase during liquefaction. Therefore, the NCl3 should be monitored in the dry Cl_2 gas prior to liquefaction for safety. The OMA-300 Chlorine Process Analyzer is capable of measuring the NCl_3 and the Cl_2 concentrations simultaneously.

6. Lastly, if a Cl_2 scrubber is used on the tail gas, then the vent gas after scrubbing that is released to the atmosphere needs to be measured. Typically, the Cl_2 measurement should be very low, since it is being removed from the gas by the scrubber. However, the Cl_2 content needs to be measured for EPA reporting and to confirm proper operation of the scrubber. The OMA-300 Chlorine Analyzer can measure the Cl_2 content in this vent gas.

OMA-300 Benefits

- Using the OMA-300 Chlorine Process Analyzer to monitor a chlor-alkali process has many advantages such as:
- Continuously measures Cl_2 concentration using UV-Vis absorbance spectroscopy
- Totally solid-state build with no moving parts — modern design for low maintenance
- Ultra-safe fiber optic design with dedicated sample flow cell — no toxic/corrosive sample fluid in analyzer enclosure
- Additional software benches available for additional measured chemicals (up to 4 total)
- Excellent dynamic range due to photodiode array — no error due to absorbance saturation
- Decades of field-proven performance in industrial and environmental applications

Examples of OMA-300 Chlorine Process Analyzers

The systems pictured below were built to monitor the concentration of Cl_2.

OMA-300 Chlorine Analyzer used for the measurment of Cl_2 with the concentration range of 0-30%.

OMA-300 Chlorine Analyzer used for the measurment of Cl_2 with the concentration range of 0-800 ppm.

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The specifications below represent performance/build of the OMA-300 Chlorine Process Analyzer in a typical Cl_2 application.

For technical details about the OMA-300 Chlorine Process Analyzer, visit our site at:

https://aai.solutions/oma-chlorine-analyzer

All performance specifications are subject to the assumption that the sample conditioning system and unit installation are approved by Applied Analytics. For any other arrangement, please inquire directly with Sales.

Application Data		
Performance Specifications		
Accuracy	*Custom measurement ranges available; example ranges below. Accuracy specifications represent headspace gas sample analysis validated with span gas.*	
	OMA-300 **(UV-Vis)**	Cl_2: 0-100 ppm (±5 ppm) 0-10,000 ppm (±2% full scale or 5 ppm*) 0-100% (±2% full scale)
		*Whichever is larger.

Further Reading

Subject	Location
OMA-300 Chlorine Process Analyzer Web page	https://aai.solutions/oma-chlorine-analyzer
OMA-300 Process Analyzer Data sheet	https://aai.solutions/documents/AA_DS001A_OMA300.pdf
Analysis in Vinyl Chloride (VCM) Production Process Application Note	https://aai.solutions/application-notes/analysis-in-vinyl-chloride-vcm-production-process
Measuring $TiCl_4$ and Vanadium in TiO_2 Pigment Production Application Note	https://aai.solutions/application-notes/measuring-TiCl4-and-vanadium-in-TiO2-pigment-production
Measuring Vanadium Oxytrichloride Application Note	https://aai.solutions/application-notes/measuring-vanadium-oxytrichloride
Features Product Features	https://aai.solutions/oma-chlorine-analyzer-features
Features Product Features	https://aai.solutions/oma-chlorine-analyzer-technology

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