Monitoring Nitrogen Trichloride in Chlorine Manufacture

Applied Analytics Application Note No. AN-005

Application Summary

Analytes: NCl_3 (nitrogen trichloride)

Detector: OMA-300 Process Analyzer

Process Stream: headspace gas above saturated CCl_4 solvent

Typical Measurement Range: 0-20,000 ppm

Introduction

Most of the production of chlorine and caustic soda (NaOH) is done by electrolysis of sodium chloride brine. The brine is produced by dissolving salt (from seawater or mines) or by pumping water into underground salt veins. There are 3 types of electrolytic processes used to produce chlorine, each of which involves a salt solution electrolyzed by direct electric current that converts chloride ions to elemental chlorine:

$$NaCl + H_2O \longrightarrow NaOH + {}^1/_2H_2 + {}^1/_2Cl_2$$

The chlorine is produced at the cathode, while NaOH and hydrogen are produced at the anode. After cooling in heat exchangers, the gases undergo additional processing, including chlorine liquefaction, hydrocholoric acid production, and/or hypochlorite production.

The chlorine scrubbing and cooling process is used to purify the chlorine product from contamintants like chlorinated organic compounds, bromine, and **nitrogen trichloride** (NCl_3). The nitrogen derivatives which lead to NCl_3 formation may come from additives like calcium ferrocyanide, an anti-caking agent.

An extremely dangerous explosive and a tear gas, NCl_3 needs to be carefully controlled. The concentration should be controlled well below 1%, the lower explosive limit of NCl_3.

The NCl_3 scrubbing process uses the difference in boiling point between NCl_3 (+74 °C) and Cl_2 (-34 °C). When chlorine gas is mixed with liquid chlorine, the liquid vaporizes; the impurities like NCl_3 remain in the liquid, which gets sent to the decomposer. In the decomposer, the cold liquid chlorine encounters heated CCl_4 solvent, which forces the chlorine to vaporize while the impurities get dissolved into the CCl_4. NCl_3 undergoes thermal decomposition in this solvent.

As the CCl_4 solvent becomes saturated with broken down NCl_3, it begins to lose efficiency. Controlled replacement of the solvent is critical for healthy process operation.

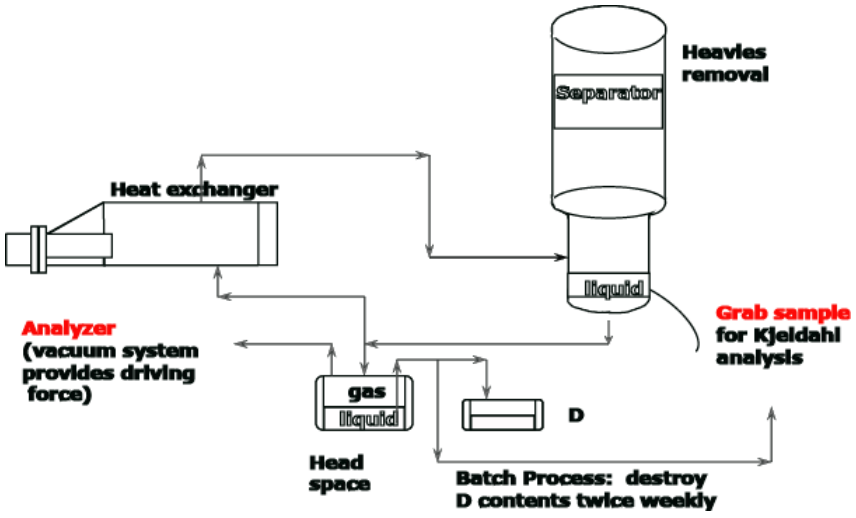
Traditional Method

The traditional method of analysis is Kjeldahl analysis performed offline on grab samples. This method is slow, expensive, and time-consuming. It was developed in 1883 and requires heat, catalysts, and consumables.

The modern solution for this measurement need is the OMA-300 Process Analyzer, a totally solid state instrument which provides continuous analysis at the process site. This system has enormous advantages of Kjeldahl analysis, including:

- Increased safety as the NCl_3-containing sample never needs to be extracted further than the sample flow cell
- Ability to easily differentiate between NCl_3 and other nitrogen compounds in the sample
- Fast, continuous response for tight solvent control and rich trend data
- Modern design with no moving parts and reduced maintenance

The schematic below illustrates the analysis points for the OMA and Kjeldahl sample grabbing:



Headspace Measurement

The OMA's analysis is typically performed in the headspace gas above the CCl_4 solvent (illustrated above) because it is easier to transmit a light signal through the gas.

In the context of process analysis, the problem with opaque liquids is that they don't allow light to pass through at all. UV spectroscopy is severly impaired in any liquid process that has high opacity, contains particulates which scatter light, or contains chemicals that absorb heavily in the UV range and thus interfere with the signal.

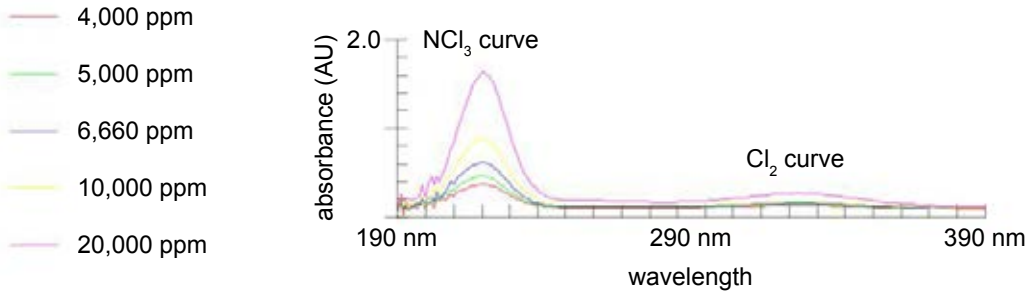
Henry's Law states that the amount of a certain gas dissolved in a solution at a given temperature is directly proportional

to the partial pressure of that gas above the solution. The takeaway message here is: given certain constant conditions (temperature, pressure, carrier gas flow rate, and liquid sample flow rate), the chemical composition of the headspace gas can be correlated to the composition of the opaque liquid sample.

The OMA runs real-time analysis on a continuously drawn sample from the headspace gas above the solvent. NCl_3 has strong absorbance curve features in the UV range and can easily be monitored from low to high concentrations. The concentration of NCl_3 in the headspace gas is correlated directly to the concentration of NCl_3 in the liquid.

NCl_3 Absorbance Spectra at Different Concentrations

The spectra below demonstrate how the OMA experiences different levels of NCl_3 in the presence of chlorine. The spectra were taken on headspace gas (50 psig chlorine above solution of NCl_3 in CCl_4). The system calibration needs to include chlorine as a second analyte in order to correct for the overlapping absorbance and not mis-attribute the absorbance to NCl_3.

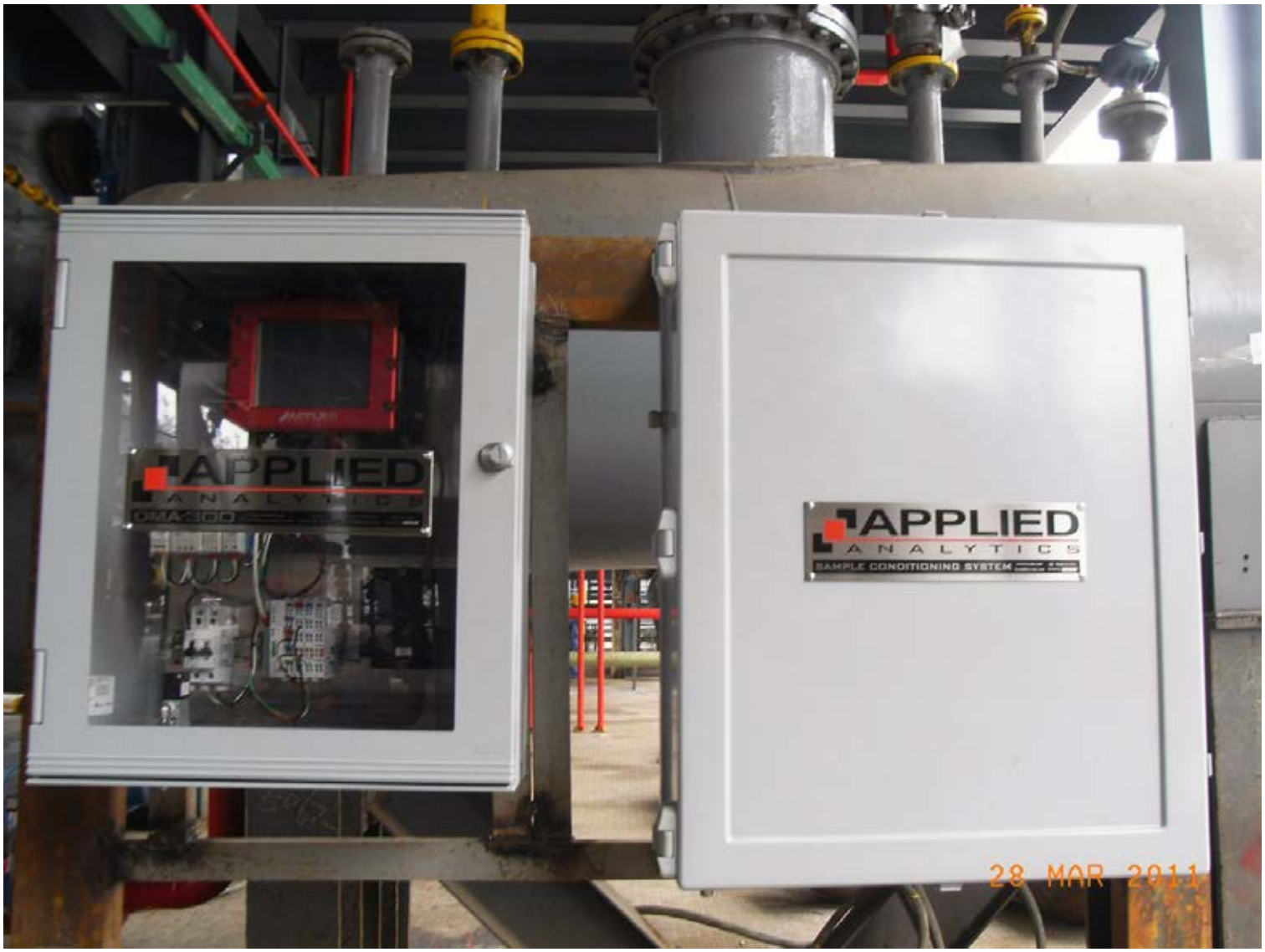


Sample Conditioner

In order to withstand the long-term corrosive effects of chlorine gas samples, the SCS used by the OMA for NCl_3 analysis is typically built with Teflon wetted parts. The example system below is used to measure 0-30% NCl_3.

Example Installation

The OMA pictured below measures NCl_3 and Cl_2 concentrations at a chlorine manufacturing facility in China. The headspace gas from above the solvent is sampled and brought into the SCS on the right side. Fiber optic cables transmit the signal from the analyzer unit (left side) to the SCS, so that the dangerous sample fluid does not need to be brought into the analyzer.



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The specifications below represent performance of the OMA-300 Process Analyzer in a typical NCl_3 control application.

For technical details about the OMA-300 Process Analyzer, see the data sheet:
http://www.a-a-inc.com/documents/AA_DS001A_OMA300.pdf

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.

Subject to modifications. Specified product characteristics and technical data do not serve as guarantee declarations.

Application Data		
Performance Specifications		
Accuracy	*Higher accuracies can be specified if sample pressure can be increased. Custom measurement ranges available; example ranges below.*	
	NCl_3	0-100 ppm: ±5 ppm 0-10,000 ppm: ±1% full scale 0-5%: ±1% full scale
	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 Process Analyzer Data sheet	http://www.a-a-inc.com/documents/AA_DS001A_OMA300.pdf
Advantage of Collateral Data Technical Note	http://www.a-a-inc.com/documents/AA_TN-202_CollateralData.pdf
Multi-Component Analysis Technical Note	http://www.a-a-inc.com/documents/AA_TN-203_MultiComponentAnalysis.pdf

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