

# Analysis in Vinyl Chloride (VCM) Production Process

Applied Analytics Application Note No. AN-030



## Application Summary

Analytes:	in direct chlorination effluent	$\text{FeCl}_3$ , $\text{Cl}_2$
	in EDC / VCM	$\text{H}_2\text{O}$
	in vent gas	$\text{O}_2$ , $\text{C}_2\text{H}_4$ , $\text{CO}$ , $\text{CO}_2$
Detectors:	<ul style="list-style-type: none"><li>• OMA-300 Process Analyzer (UV-Vis spectrophotometer)</li><li>• MicroSpec Series Modules</li></ul>	

## Introduction

PVC is a ubiquitous plastic favored in construction, piping, and many other industries due to the properties of the polymer, including light weight, chemical resistance, and versatility. PVC is produced by polymerizing vinyl chloride (VCM), a highly toxic/explosive chemical intermediate which is manufactured strictly for this purpose.

The process of producing VCM from raw materials is sensitive and requires careful monitoring to avoid contaminated products and equipment failure. Typically, VCM is made by thermal cracking of ethylene dichloride (EDC, formally 1,2-dichloroethane), which is produced on site from feed stocks of ethylene and chlorine.

The modern VCM production process sacrifices some efficiency in order to recycle byproducts and operate at less expense. Maintaining yield purity and conversion efficiency throughout the various stages therefore requires continuous online monitoring of the production stream composition.

Applied Analytics provides a complete, field-proven set of solutions for EDC/VCM production process analysis. Our online chemical concentration monitors provide the real-time readings needed for optimization of the process at various critical analysis points. The OMA-300 Process Analyzer (UV-Vis spectrophotometer) monitors chlorine compounds, with integrated MicroSpec modules for additional measurements, providing a totally solid state, automated solution set.

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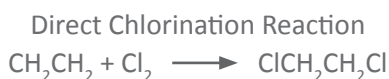
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## The VCM Production Process Overview

Producing sales quality PVC from raw materials involves several steps. Initially, ethylene dichloride (EDC) must be produced from the feed stocks of ethylene and chlorine. The EDC is then thermally cracked to produce vinyl chloride (VCM), which is the chemical precursor to the PVC polymer. The VCM must be purified and dosed with a polymerization inhibitor to prevent spontaneous polymerization. Below, we will examine each stage of the process and the analysis requirements.

### » Direct Chlorination Process for Producing EDC

The direct chlorination process involves a liquid phase reaction of ethylene and chlorine using an  $\text{FeCl}_3$  catalyst. This exothermic reaction is controlled by mass transfer and can be operated either at low temperature (for low byproduct generation) or high temperature (in order to recycle heat).



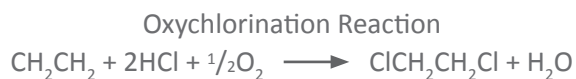
A properly optimized direct chlorination reactor produces an effluent stream of 99% EDC purity with trace amounts of trichloroethane, HCl, ethylene, and chlorine. Some operations inject oxygen into the reactor to subdue free radicals and increase selectivity to EDC product. Inhibiting the formation of trichloroethane is especially important because it is very difficult to remove through distillation.

Downstream from the reactor, a caustic scrubber using NaOH removes  $\text{FeCl}_3$  contamination from the catalyst. The EDC then goes through a water wash and 2 distillation columns to achieve >99.5% purity. This EDC is sent to a storage tank for later processing.

Direct chlorination produces waste gas saturated with HCl which is repurposed in the oxychlorination process, which also produces raw EDC.

### » Oxychlorination Process for Producing EDC Using Recycled HCl

The oxychlorination process is used to obtain additional EDC using the HCl-rich waste gas from the direct chlorination reaction. The ethylene feed stock is reacted with HCl and oxygen to produce EDC and water in an exothermic reaction (using a  $\text{CuCl}_2$  catalyst):



Oxychlorination is a less efficient process than direct chlorination due to the significant formation of water and carbon oxides; the typical reactor effluent stream contains 47 mol% EDC, 47 mol% water, 5 mol%  $\text{CO}_2$ , and trace amounts of oxygen, HCl, ethylene, and various chlorinated hydrocarbons.

Following the oxychlorination reactor, the produced EDC is sent through a caustic scrubber (removing HCl) and a flash (removing impurities) before entering the purification stage.

### » EDC Cracking

The purified EDC is sent to a thermal cracker (pyrolyzer) which outputs VCM and HCl. The EDC cracker runs an endothermic

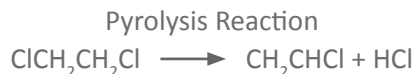
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reaction at 500 °C and 15-30 atm with VCM selectivity of >90%, yet only has a conversion rate of ~50%.

The pyrolysis of EDC involves a complex set of reactions that can be summarized as below:



The effluent must be immediately quenched to avoid forming coke or tar. The VCM product is then sent through a flash drum to prepare it for purification. There are many undesirable products from EDC cracking that can foul the reactor and reduce the end product quality, while other impurities (e.g. chloromethanes) may actually be desirable for their promotion of VCM selectivity and are sometimes added intentionally.

## » VCM Purification

The VCM purification unit comprises two distillation columns which are tasked with producing 99.9 %wt VCM. The first column removes HCl as the overhead product, sending the HCl gas back to the oxychlorination unit as raw material. The second column removes EDC and other impurities as the bottoms, sending this stream back to the EDC purification unit. VCM is produced as the overhead of the second column.

Following the distillation columns, catalytic oxidation and hydrogenation steps are usually performed on the distillation byproducts to recover some of the unwanted chlorinated hydrocarbons formed, converting them to CO<sub>2</sub>, HCl, and water.

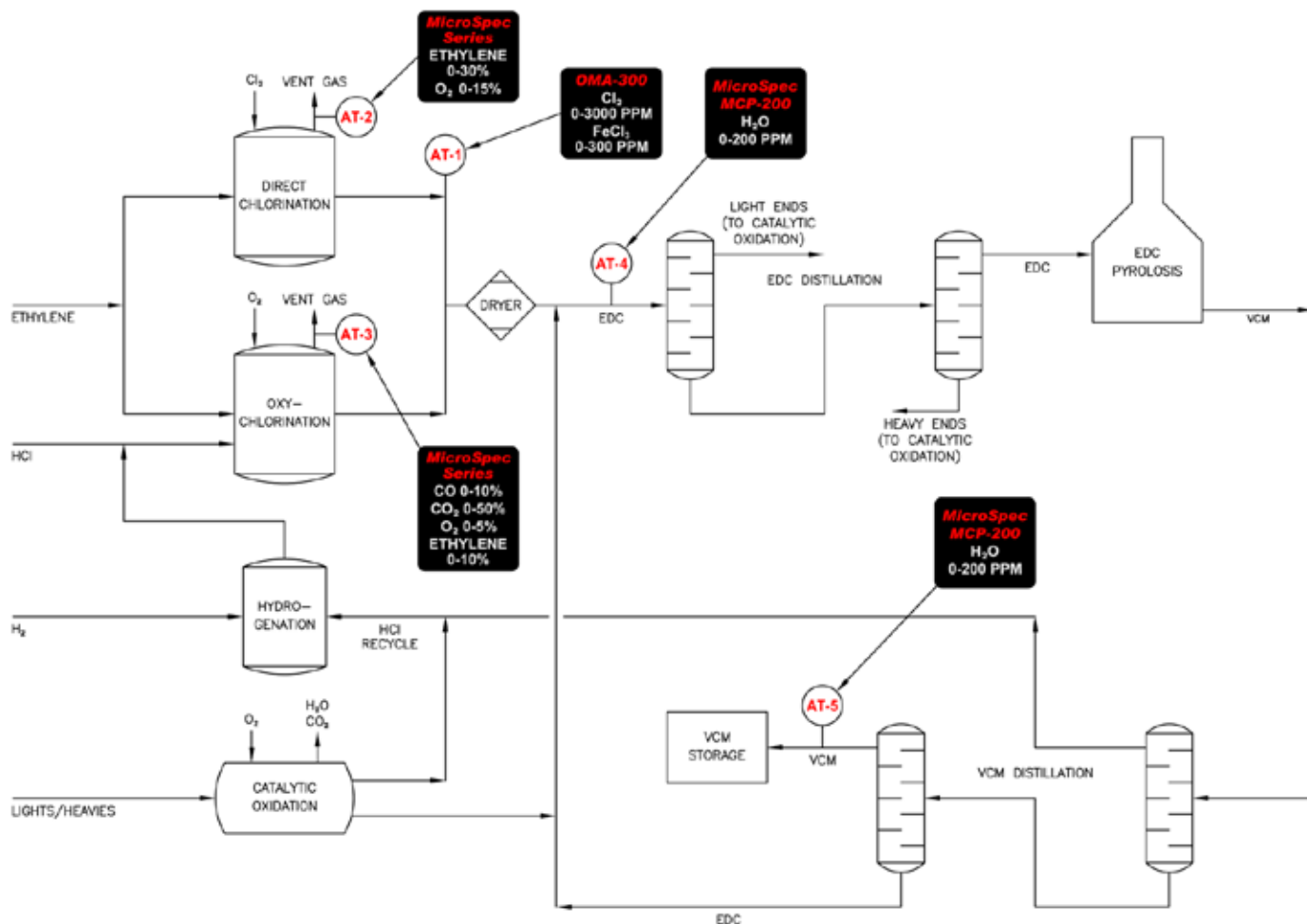
The purified VCM is dosed with a polymerization inhibitor (e.g. benzoquinone diimide) at under 500 ppm to prevent spontaneous polymerization of the monomer in pipes and vessels.

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## Critical Analysis Points in the VCM Balanced Process

Required analytes, measurement ranges, and suitable Applied Analytics detectors indicated.



## The Need for Monitoring FeCl<sub>3</sub> and Cl<sub>2</sub> in Direct Chlorination Effluent (EDC)

Location: AT-1

The direct chlorination catalyst is known to contaminate the effluent EDC with FeCl<sub>3</sub> — a highly corrosive compound which fouls machinery. Reasons for controlling FeCl<sub>3</sub> and Cl<sub>2</sub> levels using analysis at this point include:

- **Coke formation.** FeCl<sub>3</sub> has been found to be a major contributor to coke formation in EDC crackers; a cracker can be shut down within 3 weeks of startup for cleaning due to FeCl<sub>3</sub> contamination as low as 30 ppm.
- **Loss of VCM product quality.** VCM containing appreciable FeCl<sub>3</sub> is often deemed unacceptable for commercial use.
- **Degradation of Oxychlorination Catalyst.** FeCl<sub>3</sub> levels as low as 0.1% can have deleterious effects on the oxychlorination reactor, including deactivating or shortening the life of the cupric chloride catalyst as well as coke formation. Controlling the level using AT-1 analysis serves to prevent FeCl<sub>3</sub> from entering the oxychlorination process as a contaminant in the HCl recycle gas.

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- **Corrosion of stainless steel piping.** This corrosion not only requires maintenance but also serves to generate more  $\text{FeCl}_3$  in the stream by freeing the iron content from the stainless steel, thus compounding related issues.
- **Unwanted reactions.**  $\text{FeCl}_3$  can react with water to form HCl contamination in the EDC product.
- **Reaction inefficiency.** Monitoring free chlorine concentration at AT-1 provides a real-time measure of direct chlorination conversion rate: excess  $\text{Cl}_2$  indicates incomplete reaction with ethylene and/or waste of  $\text{Cl}_2$  feedstock. This allows for fast response to problems and upsets at the first stage of the VCM balanced process.
- **Downstream  $\text{FeCl}_3$  formation due to free chlorine.** Even if  $\text{FeCl}_3$  levels at AT-1 are below the threshold of concern, free chlorine reacts with ferrous material from the piping to generate  $\text{FeCl}_3$  downstream from this analysis point. This is a major source of  $\text{FeCl}_3$  in the EDC cracker feed stream and is extremely important to control.  $\text{Cl}_2$  levels as low as 20 ppm at AT-1 are considered problematic for the EDC cracker. Excess ethylene is often used to minimize free chlorine output, but this safeguard can still allow 200-3000 ppm  $\text{Cl}_2$  in the direct chlorination effluent. Analysis at AT-1 allows control of  $\text{Cl}_2$  as well as optimized use of ethylene feedstock.

## ANALYTICAL SOLUTION: OMA-300 PROCESS ANALYZER

The OMA-300 simultaneously monitors  $\text{FeCl}_3$  and  $\text{Cl}_2$  in the direct chlorination effluent stream. Using a high resolution dispersive UV-Vis spectrophotometer, this system provides unrivaled dynamic range in measuring chlorine compounds from trace to high concentration. Since the device uses an ultra-safe fiber optic cable design, the corrosive sample fluid is confined to a specialized flow cell and never enters the analyzer electronics enclosure.

## The Need for Monitoring **Moisture** in EDC and VCM

Location: AT-4, AT-5

Moisture is known to form a highly corrosive mixture with HCl and  $\text{Cl}_2$ . Above 100 ppm,  $\text{H}_2\text{O}$  will aggravate the corrosive effects of the produced EDC and VCM streams. The moisture also carries other undesirable impurities which reduce the quality of these products. Since removal of moisture is more economically viable than removing other components of the corrosive mixture, this is the main target of corrosion control.

VCM process operators typically measure 0-200 ppm moisture at these analysis points for process control.

## ANALYTICAL SOLUTION: MICROSPEC MCP-200 MODULAR IR ANALYZER

The MCP-200 is a rugged NDIR concentration monitor designed for simple reliability in continuous moisture measurement. This solid state device has a zero offset feature which removes the need to obtain totally dry (zero  $\text{H}_2\text{O}$ ) zeroing fluid, thus making the Auto Zero functionality practical and inexpensive without sacrificing accuracy. This system provides the fast response 0-200 ppm moisture reading required for tight VCM process control.

## The Need for Monitoring **CO**, **CO<sub>2</sub>**, **Ethylene**, and **Oxygen** in Vent Gas

Location: AT-2, AT-3

This measurement set provides a range of benefits to the process operator:

- **Safety.** Oxygen in the vent gas should be controlled below the flammable limit, thus obligating a 0-15%  $\text{O}_2$  measurement at AT-2 and a 0-5%  $\text{O}_2$  measurement at AT-3.
- **Ethylene waste prevention.** Ethylene measurement in the vent gas provides feedback control for the flow rate of

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the ethylene feedstock into the direct chlorination and oxychlorination reactors. While the tendency to use excess ethylene is justified by the effect of reducing  $\text{Cl}_2$  and  $\text{HCl}$  in the EDC and preventing corrosion, overshooting the optimal flow rate leads to waste of an expensive raw material. Measuring ethylene at AT-2 and AT-3 allows for real-time optimization of the ethylene feedstock flow rate into the initial stage of VCM production.

- **Oxychlorination efficiency validation and optimization.**  $\text{CO}/\text{CO}_2$  ratio measurement in the oxychlorination reactor vent gas is an excellent indicator of reaction efficiency (an increasing ratio signifies decreasing efficiency). The concentration readings also provide a control parameter for the reactor temperature, as higher temperature promotes  $\text{CO}$  and  $\text{CO}_2$  formation instead of the desired products.

## SOLUTION: MICROSPEC SERIES MODULAR ANALYZERS

The MicroSpec series of rugged, ultra-modular concentration monitors offers a dedicated solution for each of these measurements. An integrated interface reads the concentration outputs from all of the connected MicroSpec units. This design leverages the modular design of the MicroSpec series by performing Auto Zero on all detectors synchronously (maximizing system uptime) and minimizing the system's physical footprint.

## Applied Analytics Technology vs. Gas Chromatography

The solid state absorbance spectrometers deployed by Applied Analytics have concrete benefits over the GC systems used historically in these measurement applications:

- **Capital cost.** GC systems have notoriously expensive price tags. Applied Analytics analyzers have a comparatively attractive price point, with value maximized when multiple detectors are integrated into a single interface.
- **Response time.** While a GC system provides discrete measurements at a slow 3-10 minute cycle, the OMA and MicroSpec devices provide real-time readings within seconds — variation depending on sampling system design. In the VCM balanced process, there are several points of feedback control (e.g. ethylene feedstock flow rate) which require fast response in order to maximize savings.
- **Maintenance costs.** We manufacture solid state instruments that use no consumables other than zero fluid. This distinction translates to a much lower cost of ownership than GC instruments with moving parts and consumables.

## Economic Insight

The sensitivity of the VCM balanced process is easily expressed in economic terms. Without effective process analytics, a plant that produces 300,000 tons/yr of VCM at a conservative price of \$900/ton will lose about \$225,000 of VCM product per month to the quality control problems described above.

By implementing trusted Applied Analytics solutions into the process, the majority of that loss can be recouped through reducing waste of ethylene feedstock, maximizing conversion rates, protecting catalysts and piping from damage, reducing maintenance downtime, and reducing VCM waste disposal costs.

As always, safety of personnel comes before economics. Corrosion prevention and real-time analytics protect workers from the dangers of VCM leaks and other industrial hazards.

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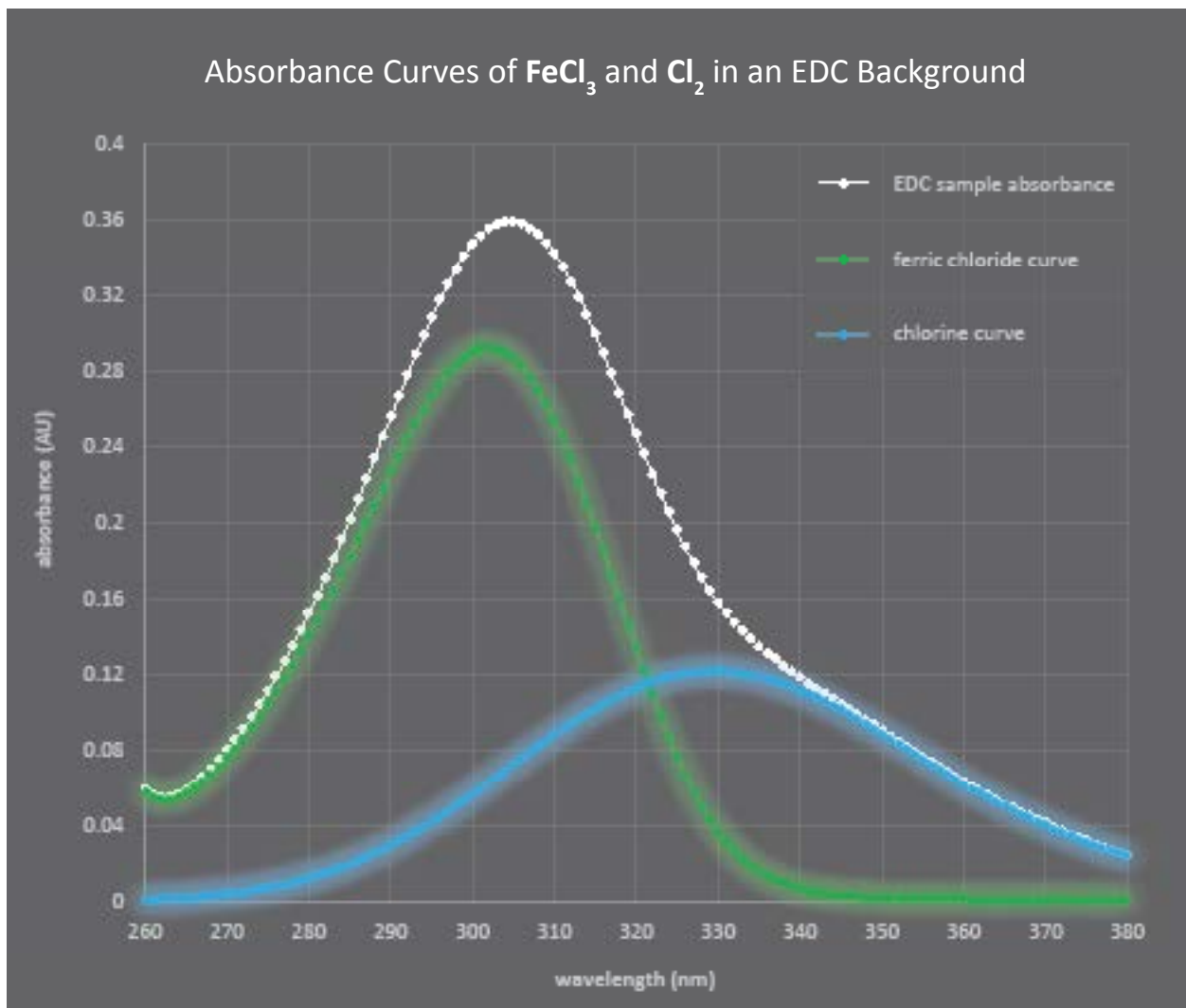
## Multi-Component Chlorine Compound Analysis by OMA

A multi-component analyzer is trusted to accurately measure multiple chemicals simultaneously. Chemicals whose absorbance curves overlap can be de-convoluted by AAI's multi components algorithm\*. Unlike traditional multi-wavelength photometers, the OMA uses a high resolution dispersive UV-Vis spectrophotometer which produces a complete 200-800 nm absorbance spectrum. The light intensity at each integer wavelength in that range is measured by a dedicated photodiode on a 1,024-element array.

This has significant implications for the  $\text{Cl}_2 + \text{FeCl}_3$  measurement at AT-1. The OMA is de-convoluting the overlapping UV absorbance curves of the two analytes using many data points (where a simpler photometer might use 2 measurement wavelengths and a reference).

The major advantages here include noise reduction through averaging the modeled concentration from all data points simultaneously as well as expanded dynamic range by access to non-peak absorbance wavelengths in high-concentration scenarios — a critical capability for maintaining accuracy during process upsets.

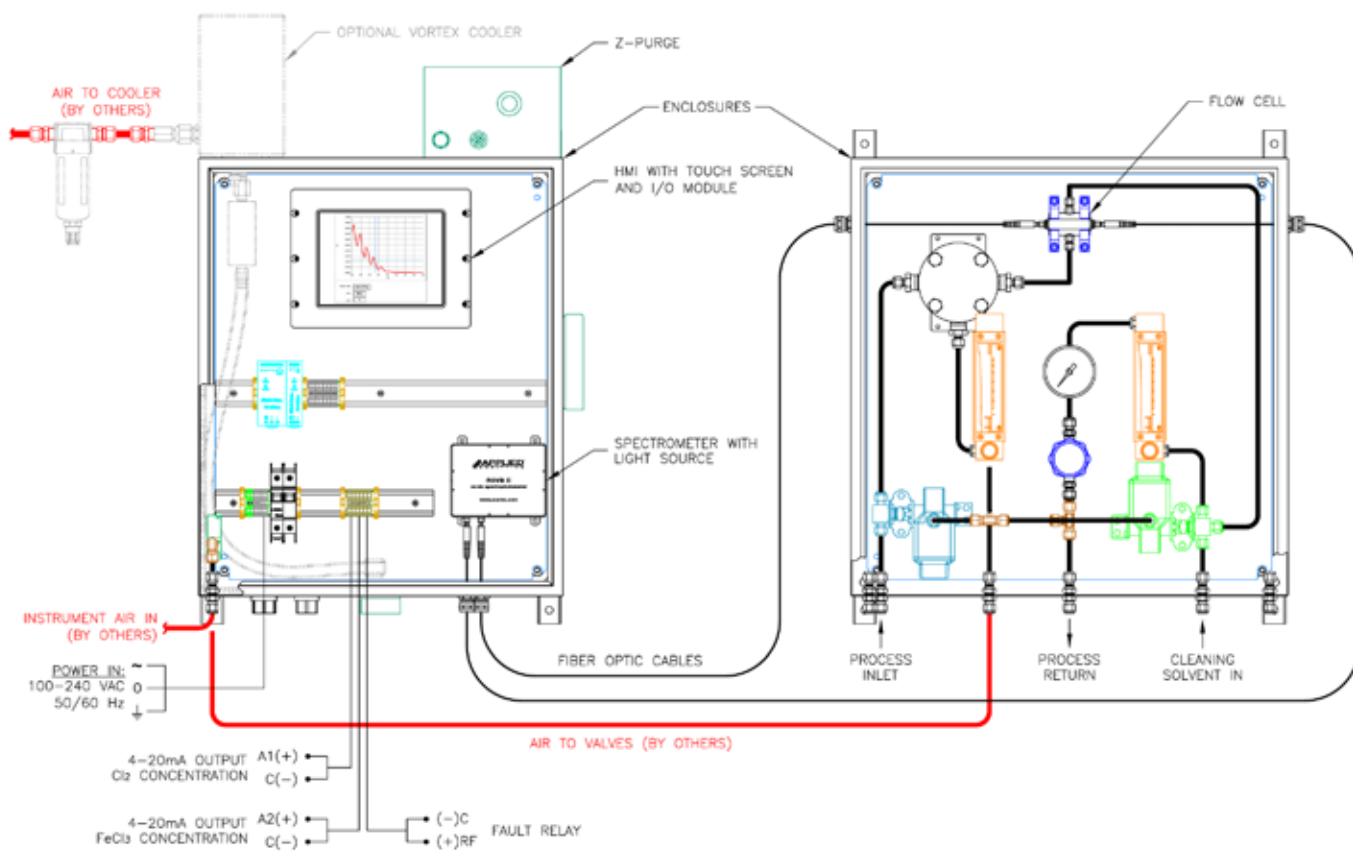
\*Provide sample matrix to AAI for verification.



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Example Arrangement: **OMA** for  $\text{Cl}_2$  and  $\text{FeCl}_3$  in EDC

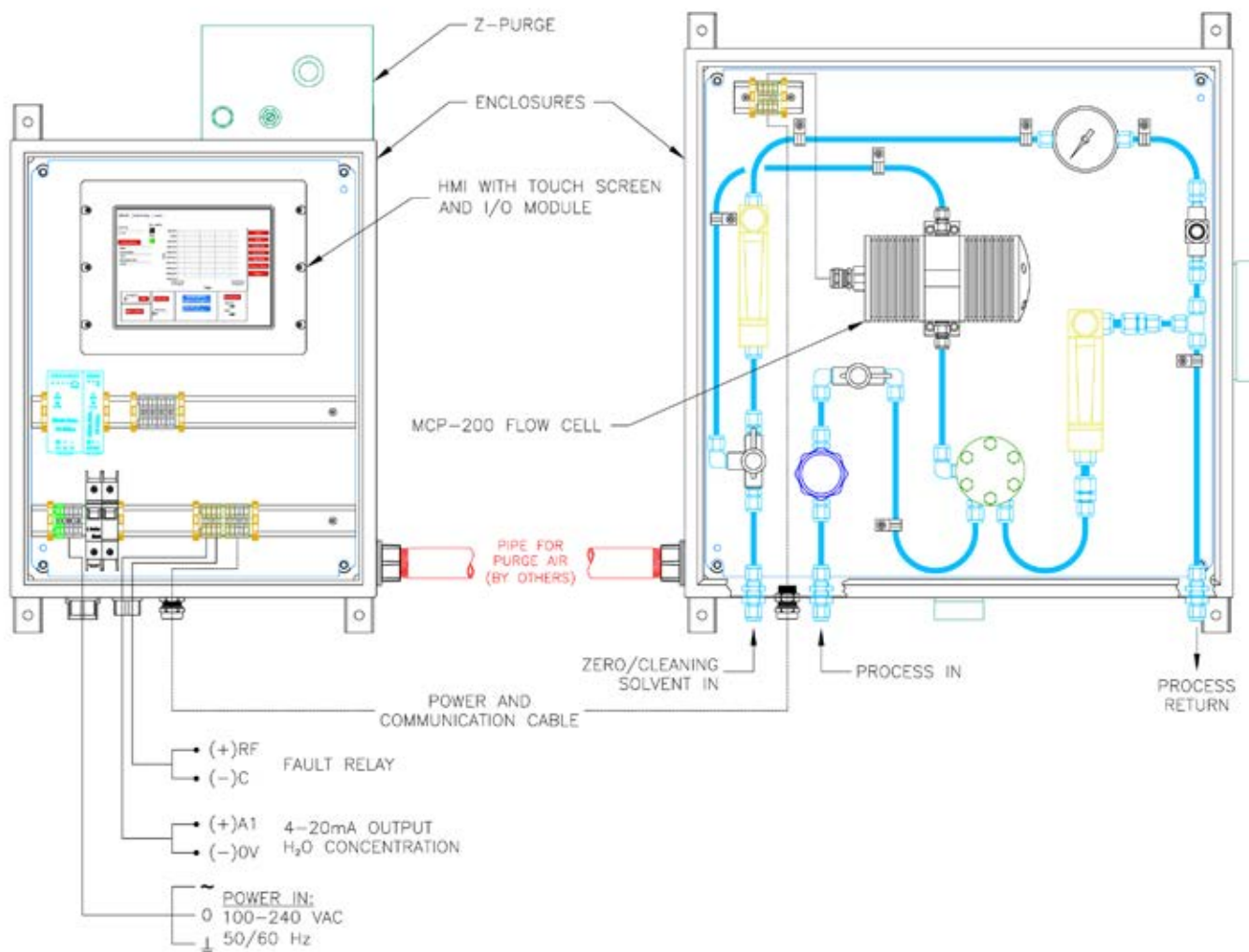




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Example Arrangement: **MCP-200 for Moisture in EDC / VCM**



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The specifications below represent performance of Applied Analytics analyzers in typical EDC/VCM plant applications.

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		
Location	Analytes	Measurement Range
<i>Custom measurement ranges available; example ranges below.</i>		
<b>AT-1</b> (direct chlorination effluent)	<b>FeCl<sub>3</sub></b>	0-300 ppm
	<b>Cl<sub>2</sub></b>	0-3000 ppm
<b>AT-2</b> (direct chlorination vent gas)	<b>O<sub>2</sub></b>	0-15%
	<b>C<sub>2</sub>H<sub>4</sub></b>	0-30%
<b>AT-3</b> (oxychlorination vent gas)	<b>CO</b>	0-10%
	<b>CO<sub>2</sub></b>	0-50%
	<b>O<sub>2</sub></b>	0-5%
	<b>C<sub>2</sub>H<sub>4</sub></b>	0-10%
<b>AT-4</b> (EDC yield)	<b>H<sub>2</sub>O</b>	0-200 ppm
<b>AT-5</b> (VCM yield)	<b>H<sub>2</sub>O</b>	0-200 ppm

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## Further Reading

Subject	Location
OMA-300 Process Analyzer Data sheet	<a href="http://www.a-a-inc.com/documents/AA_DS001A_OMA300.pdf">http://www.a-a-inc.com/documents/AA_DS001A_OMA300.pdf</a>
MicroSpec MCP-200 Analyzer Data sheet	<a href="http://www.a-a-inc.com/documents/AA_DS003A_MCP200.pdf">http://www.a-a-inc.com/documents/AA_DS003A_MCP200.pdf</a>
Advantage of Collateral Data Technical Note	<a href="http://www.a-a-inc.com/documents/AA_TN-202_CollateralData.pdf">http://www.a-a-inc.com/documents/AA_TN-202_CollateralData.pdf</a>
Dynamic Range Technical Note	<a href="http://www.a-a-inc.com/documents/AA_TN-204_DynamicRange.pdf">http://www.a-a-inc.com/documents/AA_TN-204_DynamicRange.pdf</a>
Multi-Component Analysis Technical Note	<a href="http://www.a-a-inc.com/documents/AA_TN-203_MultiComponentAnalysis.pdf">http://www.a-a-inc.com/documents/AA_TN-203_MultiComponentAnalysis.pdf</a>



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