

In-Line Analysis of Acid Gases in Water Vapor Saturated Environments

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Biography

Josep Arnó is a research chemist at ATMI-EcoSys working on technology development and effluent characterization. He received a B.S. in chemistry and physics in 1990, and a Ph.D. in physical chemistry from Texas A&M university in 1995. His research experience includes development of innovative abatement technologies, molecular spectroscopy, and computational chemistry.

Abstract:

The exceptional advances in the field of microelectronic manufacturing have evolved at the expense of using materials that are potentially hazardous to humans and toxic to the environment. The reactive nature of many materials used in wafer processing has posed considerable challenges to manufacturers of pollution control equipment and analysts attempting to characterize effluent gas streams. Continuous, in-line measurement of acid gases in wet streams is especially difficult due to the loss of analyte brought about by condensation and other sample degradation mechanisms. This paper describes an innovative analytical and sampling method to measure low concentrations of corrosive gases in water vapor saturated conditions. The method was developed to perform real time characterization of acid gases at the exhaust of a point-of-use water scrubber. The technique involved the use of spectroscopic analytical methods, an in-line gas dryer based on permeation, and a novel sample collection setup. The essential components of the setup, analytical method, calibrations, and testing results are discussed demonstrating the advantages of this method over existing analytical techniques.

Data:

Gas phase characterization of acid gases is of special importance in the semiconductor industry. Processes such as silicon epitaxi, aluminum metal etch, and ion implant can generate toxic by-products such as hydrogen chloride and fluoride (HCl, HF), chlorine (Cl₂), boron trifluoride and trichloride (BF₃, BCl₃), and a number of chlorinated and fluorinated silicon compounds (1). Silicon tetrafluoride (SiF₄) and HF are also produced in a number of chamber clean procedures. These acid gases are not only hazardous to humans, but to the integrity of the exhaust system, and ultimately to the environment. Driven by reaction and/or absorption mechanisms, point-of-use (POU) water scrubbers can reduce the level of most acid emissions (2). In order to evaluate the performance of such POU abatement tools, specialized analytical methods are needed to measure small concentrations of unscrubbed corrosive species concealed in carrier gas saturated with water vapor.

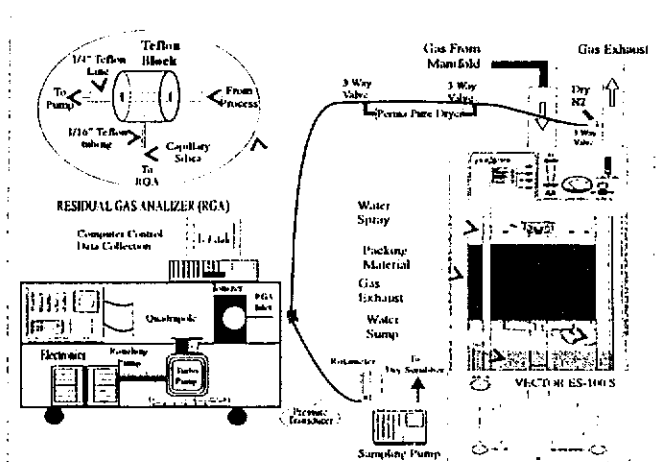
In general, real-time continuous monitoring is essential when trying to understand time dependent reactions, such as fluctuations caused by kinetic and equilibrium processes. Considering the changing nature of toxic emissions released during semiconductor manufacturing, continuous on-line analysis is especially important. Existing process analytical methods are inadequate in providing real time information about variations in concentration of acid gases in water vapor saturated conditions. Grab samples and chromatographic methods only confer snapshot data about species present at a given time. Impingement techniques are capable

of establishing average measurements over extended periods of time. Even the most sophisticated real-time analytical tools fail to provide reliable quantitative information about gas phase concentration of acid gases in the presence of high levels of moisture. Most of the difficulties are associated with degradation of the highly reactive species in the presence of water, condensation of analytes onto the walls of sampling lines and analytical instrument, and corrosion effects. Our earlier attempts to detect acid gases in wet streams using traditional residual gas analyzing (RGA) sampling methods confirmed the aforementioned difficulties. Infrared analytical techniques such as Fourier transform infrared (FTIR) spectroscopy are highly susceptible to spectral interferences from water vapor. This problem is accentuated by the long infrared beam pathlengths required to detect low concentrations of acid gases.

The analytical methods presented in this proceeding were developed to characterize the performance of a point-of use water scrubber. In particular, these investigations were designed to provide information about the kinetic steps leading to a steady state operation of the abatement tool. Discussions will focus primarily on chlorine gas analysis and abatement. Additional testing validating the use of this method to measure HCl and HF will be introduced briefly.

Analytical Setup- A schematic of the setup used to study chlorine abatement is included in Figure 1. A Questor™ IV (Extrel Corporation) residual gas analyzer (RGA) was positioned 2 feet from a Vector® ES-100 water scrubber (ATMI-EcoSys). A 10 foot long, 1/4 inch outer diameter (O.D.) 1/8 inch inner diameter (I.D.) Teflon tubing was used to transport the sample from the outlet port of the scrubber to a two stage Gast® pump (Gast Manufacturing Company). The sample gas flow rate was controlled using a rotameter, keeping the pressure constant at 650 Torr. The RGA capillary silica inlet was positioned perpendicular to the gas flow and at the center of a custom made heated Teflon tee. A three way valve

located at the scrubber outlet port enabled selection of either purging dry nitrogen or sample gas to be drawn towards the RGA. A Perma Pure gas dryer (Perma Pure Inc.) was installed in a bypass arrangement. In a continuous drying process, moisture is selectively removed by passing the sample gas stream through an array of Nafion tubes (DuPont Corporation); this allows water molecules to permeate out of the sample gas stream into a counter-current purging flow of dry nitrogen. The caustic injection system, manifold used to deliver the contaminated gases to the scrubber, and batch neutralization system used to treat the water before releasing it to the drain are not shown in Figure 1. Additional analyses involving HF and HCl were accomplished using a MIDAC I-2000 (MIDAC Corporation) FTIR spectrophotometer equipped



with a ZnSe 10 cm and 10 meter pathlength gas cells, and a nitrogen cooled MCT detector.

Figure 1. Schematic of chlorine abatement experimental setup.

Testing of Analytical Setup- The RGA response was calibrated against representative concentrations of Cl₂ prepared from certified gas standards. In order to minimize uncertainties from sampling configuration, these calibrations were performed *in-situ* keeping the experimental setup identical to the testing conditions. Similar methods were used to generate chlorine/moisture saturated gas mixtures. These wet streams were analyzed with and without the in-line Perma Pure dryer to ascertain the effects of sample

conditioning to the concentration of species of interest. Figure 2 depicts a representative example of the concentrations of Cl_2 and water measured with and without the dryer. The Perma Pure device was successful in removing 90 % of moisture from the gas stream without affecting the concentration of chlorine. Figures 3 and 4

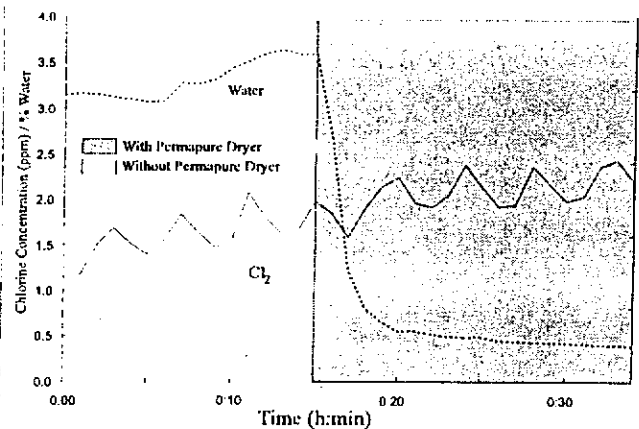


Figure 2. Effect of moisture reducing process on Chlorine and water concentration.

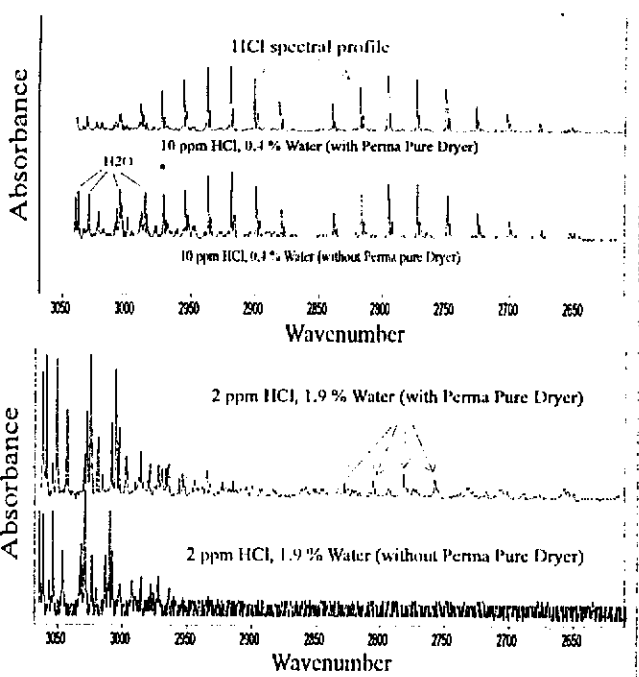
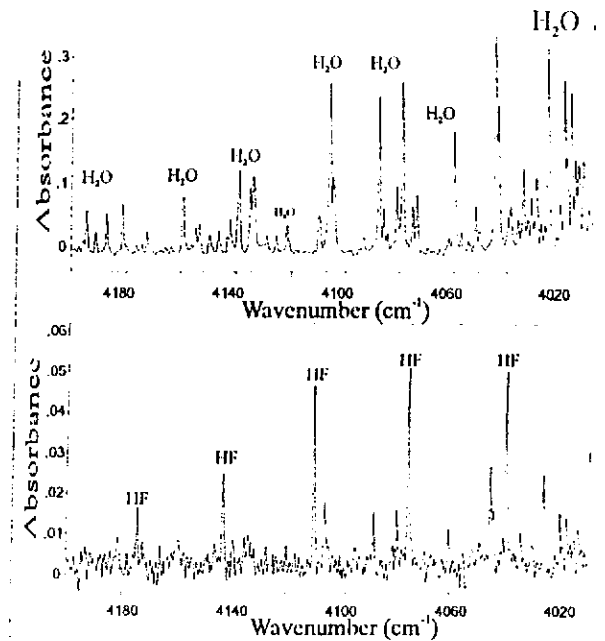


Figure 3. FTIR spectra of conditioned and unconditioned gas samples: 10ppm HCl, 0.4 % water (top), and 2 ppm HCl, 1.9 % (water bottom).



illustrate similar tests for HCl and HF respectively using FTIR spectroscopic methods. Figure 3 (top) illustrates conditioned and unconditioned absorbance spectra of 10 ppm of hydrogen chloride in 0.4 % water. Comparison of the absorbance spectra of the wet and dried sample gas streams indicate practically identical HCl concentrations. At the limit of water vapor saturation and low HCl concentrations (bottom of Figure 3), the most intense HCl peaks are still discernible in the dried sample but vanish in the wet stream due to either spectral interference of water or condensation effects. Due to the proximity between HF and water infrared absorption regions, the advantage of removing moisture from the gas sample is further demonstrated in Figure 4. Hydrogen fluoride peaks could not be discerned in the absorbance spectrum of a gas mixture containing near 3% water and 3 ppm of HF balanced with nitrogen (top of Figure 4). The same gas mixture conditioned with a Perma Pure dryer results in an attenuation of water spectral interference, allowing the high energy side of the HF profile to emerge (bottom of Figure 4).

Figure 4. FTIR spectra of conditioned (bottom) and unconditioned (top) gas samples containing 3% water vapor and 3 ppm of HF in nitrogen.

Chlorine Abatement Results- Mechanisms leading to the abatement of chlorine using water are complicated by two factors: (a) it reacts

chemically with water forming HCl and HOCl; and (b) the extent of this reaction is pH dependent. In addition, the rate of chlorine gas absorption into the liquid phase is dependent on this reversible hydrolysis reaction (3). Using the RGA analytical method described above, we investigated the removal efficiency of chlorine using a Vector[®] ES-100 water scrubber exposed to inlet chlorine concentrations ranging from 160 to 3700 ppm and overall flow rates of 100 and 200 standard liters per minute (slpm). Water temperature was kept constant throughout this study at 30 °C. Caustic solution was injected when outlet chlorine concentrations surpassed its Immediate Danger to Life and Health level (IDLH = 30 ppm). The NaOH caustic solution was dosed into the water scrubber using a metering pump maintaining the water sump pH at an average value of 10.2. Chlorine concentrations were measured at both inlet and outlet streams of the scrubber. Measured concentrations of chlorine delivered into the water scrubber were 30 % lower than the expected values calculated from the mass flow controller readouts used to generate the gas mixtures. The unexpected disparity between measured and theoretical concentrations stressed the importance of analyzing both inlet and outlet streams during characterization of the performance of a scrubber.

Figure 5 depicts over 4 hours of continuous monitoring of Cl₂ at the exhaust of the water scrubber using fixed overall flow rates of 100 slpm. The effluent concentration of chlorine escalated as the inlet concentration of chlorine increased. Real time, continuous analysis provided valuable kinetic information about the steps leading to steady state operation of the scrubber. The 30 ppm limit was reached using Cl₂ inlet concentration of 330 ppm. The observed periodic oscillations in the concentration of chlorine are related to water level fluctuations in the sump of the scrubber. In this specific scrubber, the necessary balance between incoming and exiting water was controlled using high and low water level float switches located at the sump. These switches automatically opened

and closed the water delivery valve resulting in periodic oscillations of the water level in the sump. As a consequence, when the sump level decreased (water being discharged with no fresh water coming in) chlorine emissions increased. Once the water level in the sump reached its lowest point and fresh water entered the scrubber, the concentration of chlorine at the exhaust decreased. These large water level fluctuations were shown to have an important effect in the abatement efficiency of the scrubber. It is important to note that Vector[®] water scrubbers that use gravity to drain their sump are not affected by this drawback. In addition to fluctuations in gaseous emissions, the sump pH also oscillated with the cyclic changes in the water level. The addition of caustic solution (pH ≈ 10) converted incoming chlorine into aqueous sodium hypochlorite drastically reducing Cl₂ emissions. Table 1 summarizes the percent removal efficiencies illustrated in Figure 5 at different inlet concentrations.

In order to investigate the effects of overall inlet flow rate on chlorine removal efficiency, we repeated the test described above by increasing the inlet flow rates from 100 to 200 slpm. The overall flow rates were doubled keeping chlorine flow rates identical. These changes resulted in reduced residence times through the scrubber, and lower inlet chlorine concentrations. The results were remarkably similar to Figure 5, and are reported in Table 1. The 100 and 200 slpm results show that chlorine scrubbing efficiency depends on absolute chlorine mass flow rate rather than concentration. Regardless of the total gas flow rate, the delivery of 200 mg/min of Cl₂ marked a significant increase in chlorine exhaust concentration. This information suggests that chlorine gas absorption is primarily limited by vapor-liquid equilibrium and hydrolysis reaction effects and to a lesser extent to mass transfer rates. Additional studies involving changing the make-up water flow rate and water temperature will further substantiate this theory.

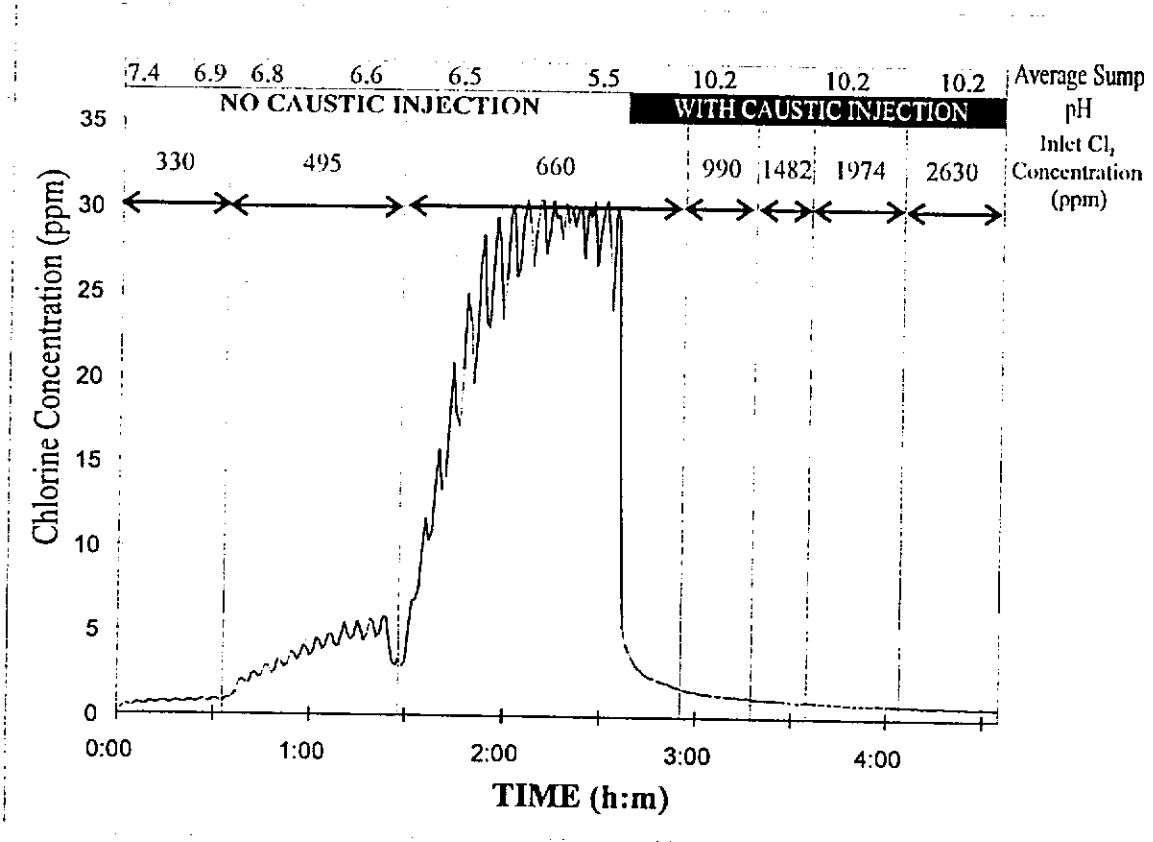
Recent characterization studies performed at the outlet of an Applied Materials 8330 metal etcher

and a Novapure™ (EcoSys) dry scrubber (4) determined that during etching processes, the reactor released on average 10 mg/min of Cl₂, 17 mg/min of BCl₃, and 45 mg/min HCl. The volumes of chlorine detected are over an order of magnitude below the breakthrough levels delivered to the water scrubber. This data suggests that a water scrubber could be used in this application without requiring chemical injection (NaOH). It is important to note however, that in this hypothetical application the scrubbing efficiency would be hindered due to the lower water pH (~ 3.5) brought about the dissociation of HCl and BCl₃.

Conclusion:

We demonstrated that spectroscopic analyzers combined with a Perma Pure dryer can be used for multi-component, in-line process analysis of acid gases in wet streams. The RGA method generated accurate continuous measurement of the species of interest for over 40 hours of trouble free operation. Removal of moisture from the gas

Figure 5. Chlorine concentration measured at the outlet of a Vector® ES-100 as a function of inlet challenge and water pH.



stream combined with large sample throughput reduced the degradation of the analytes. The analytical method was instrumental in characterizing chlorine abatement using a Vector® ES-100 water scrubber. In addition to valuable scrubber efficiency data, the method provided important time dependent operation parameters.

References:

1. Holst, M., and Woods, K. *Semiconductor Fabtech*, 5 th Edition, 23 (1997).
2. Dietz, J., Lane, S., Roessler, L. Proceedings of the 18th Annual International Hygiene & Environmental Conference. San Diego, Ca. 1996
3. Brian, P.L.T, Vivian, J.E., and Piazza C. *Chem. Eng. Sci.* 21, 551 (1965).
4. Arnó, J. *The Journal of The Electrochemical Society*. Submitted August, 10 (1997)

Overall Flow Rate (slpm)	Measured Inlet Cl ₂ Conc. (ppm)	Inlet Cl ₂ Delivery Rate (g/min)	Sump pH ¹	Measured Outlet Cl ₂ Conc. ¹ (ppm)	Cl ₂ Removal (%)
100	330	0.11	6.9	1.2	99.6
	495	0.16	6.6	4.7	99.0
	659	0.21	6.1	27.2	95.9
	989	0.31	10.2	1.4	99.86 ²
	1482	0.47	10.2	1.2	99.92 ²
	1974	0.62	10.2	1.0	99.95 ²
	2629	0.83	10.2	0.9	99.97 ²
200	165	0.11	7.0	3.6	97.8
	330	0.21	6.1	22.6	93.2
	495	0.31	10.6	1.6	99.7 ²
	740	0.47	10.6	1.3	99.8 ²
	990	0.62	10.2	1.2	99.9 ²

¹ Values averaged between low and high sump level measurements.

² With caustic injection

Table 1. Summary of Vector[®] ES-100 water scrubber efficiencies determined from experimental data.

In-Line Analysis of Acid Gases in Water Vapor Saturated Environments

Prepared for SEMICON
Southwest[®]97

October 14, Austin TX



J. Arnó - SEMI Show - Slide 1

Outline

- ☐ Introduction
- ☐ Analytical section
 - ☐ Instrumentation
 - ☐ Setup
 - ☐ Calibration
- ☐ Results and Discussion
- ☐ Conclusion



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Analytical Objectives

- ☐ Tool Effluent Characterization
 - ☐ Regulatory
 - ☐ Tool performance
 - ☐ Environmental / Safety
- ☐ Abatement Tool Characterization
 - ☐ Validation of Performance



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Analytical Challenges

- ☐ Changing Composition/Concentration
- ☐ Toxic, Reactive Nature of Species
 - ☐ Hydrides, Acids, PFC's, Organics
- ☐ Wide Concentration Ranges
- ☐ Special Issues
 - ☐ Moisture, Condensation, Particulates



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Analytical Requirements

- ☐ Continuous
- ☐ In-Line
- ☐ Real Time
- ☐ Multi Component
- ☐ Low & High Detection Limits
- ☐ Custom Designed Sampling Methods



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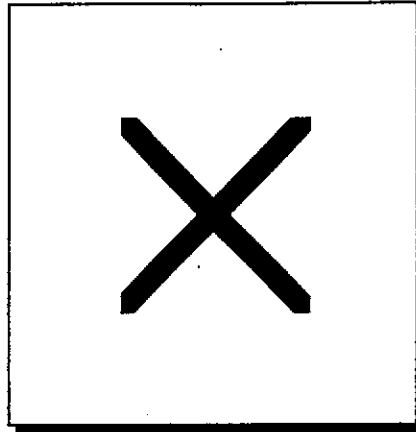
Acid Gas Analyses in Wet Streams

- ☐ Goal: To measure low concentrations of gas phase/water reactive species in moisture saturated conditions
- ☐ Why? Acid Cleans, **Water Scrubbers**



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Vector® ES-100 Water Scrubber



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Acid Gas Analyses in Wet Streams (How?)

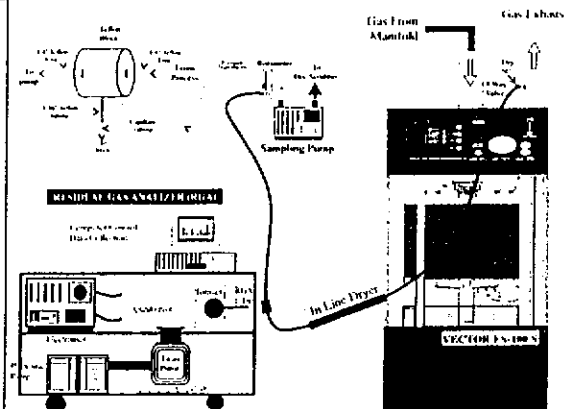
- ☐ RGA (Mass Spectrometer): **Quester™ IV Extrel**
- ☐ FTIR Spectrometer: **MIDAC I2000**
 - ☐ 10 m Temp. & Pres. Controlled ZnSe gas cell
- ☐ In-Line Gas Dryer: **Perma Pure**



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RGA Setup (Cl₂)

High Flow
Rate, RGA
Sampling
Setup



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Analytical Section (background)

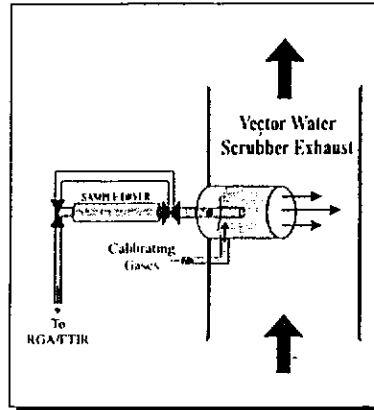
- ☐ Reduced Condensation:
 - ☐ 90 % water removed
 - ☐ high sample flow rates (5 slpm)
 - ☐ low pressures (650 torr)
- ☐ Collection of sample closer to RGA (Quick response Time)
- ☐ Capillary Clog -free operation



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In-Situ Calibrations

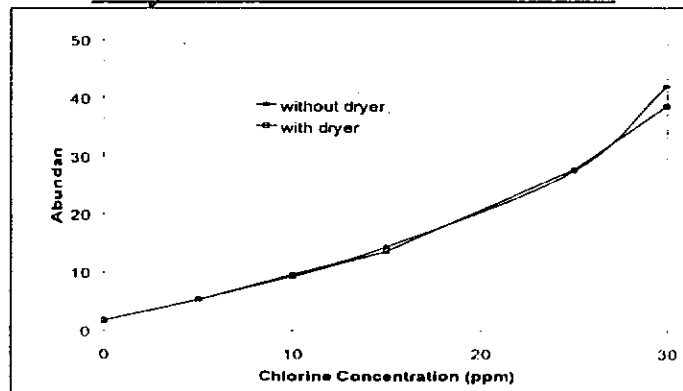
- ☐ Determine analyzer response to low conc. of Cl_2 (RGA), and HCl, HF (FTIR)
- ☐ Validate use of in-line dryer (no analyte loss)



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In-Situ Calibration (Cl_2)

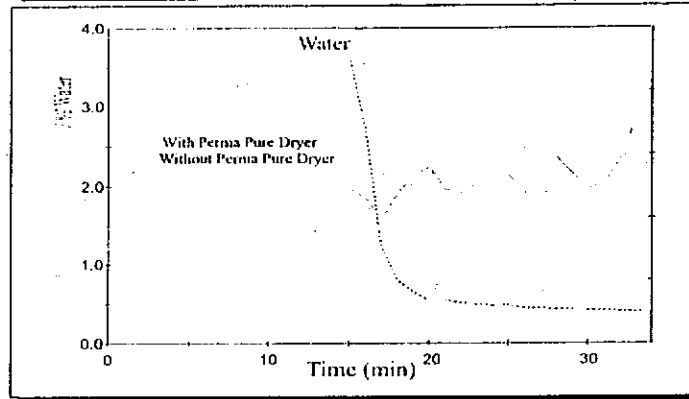
Dry Chlorine Calibration



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In-Situ Calibration (Cl_2)

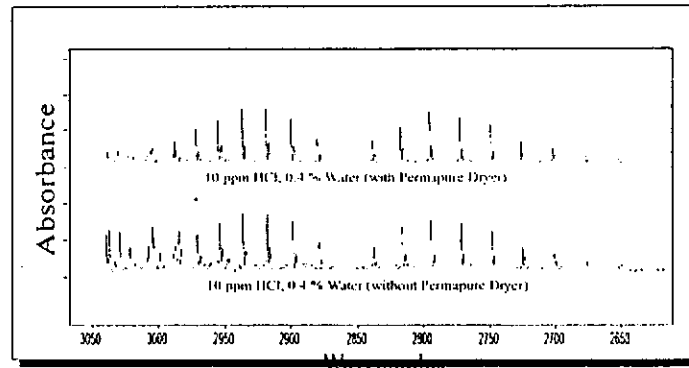
Wet Chlorine Calibration (RGA)



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In-Situ Calibration (HCl)

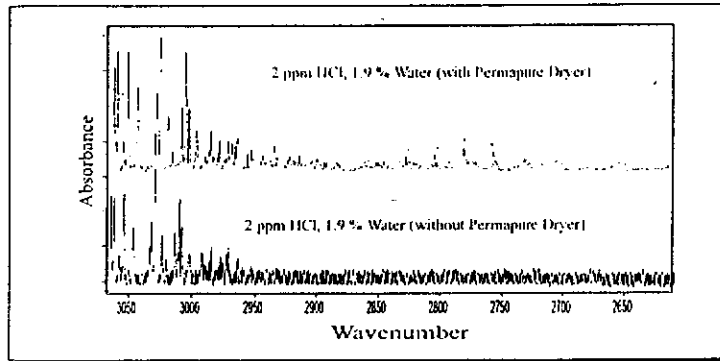
FTIR Calibration of HCl in Water Vapor



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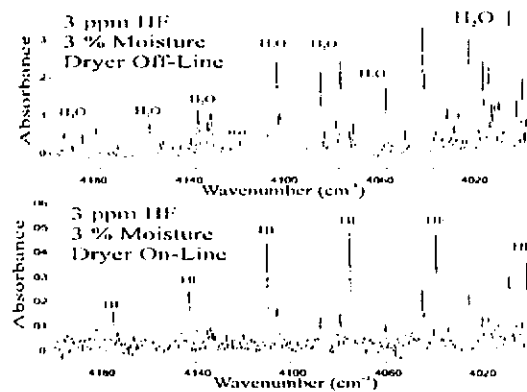
In-Situ Calibration (HCl)

FTIR Spectra of HCl in Water Vapor



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In-Situ Calibration (HF)



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Chlorine Abatement Study

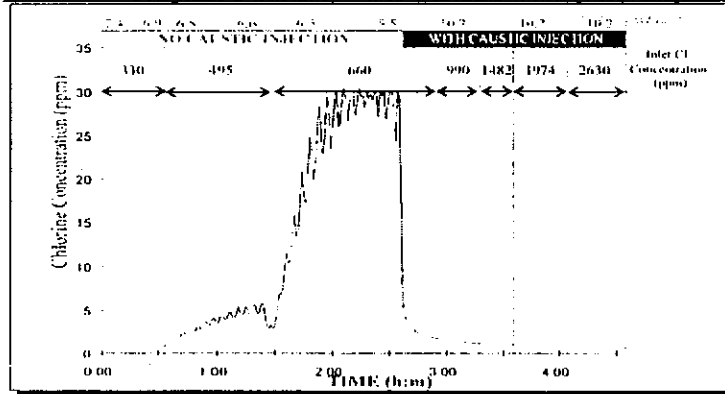
- ☐ Water Scrubber: Vector® ES-100 (EcoSys)
- ☐ Chlorine inlet concentration Range: 250-4000 ppm
- ☐ N₂ flow rates: 100 and 200 slpm
- ☐ Average Make up water: 1 gpm
- ☐ Water temperature: 30 °C



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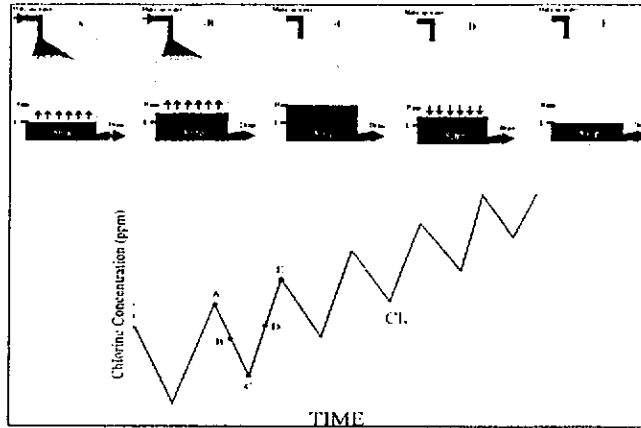
Cl₂ Abatement Results

RGA Analysis of Scrubber Exhaust(100 slpm)



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Cl₂ Abatement Results



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Cl₂ Abatement Results

Vector Water Scrubber Chlorine Removal Efficiencies (100 slpm Nitrogen)

Sump level	Measured Cl ₂ Delivery Rate		Water Sump pH	Outlet Cl ₂ Concentration (ppm)	% Removal
	ppm	g/min		Measured	
Low	330	0.11	6.9	1.3	99.6
High			7.0	1.0	99.7
Low	495	0.16	6.6	6.3	98.7
High			6.6	3.1	99.4
Low	659	0.21	6.3	10.2	95.4
High			6.0	24.3	96.3
Low	989	0.31	10.6	1.4	99.86
High			10.0		
Low	1482	0.47	10.2	1.2	99.92
High			10.0		
Low	1974	0.62	10.9	1.0	99.95
High			10.3		
Low	2629	0.83	10.1	0.9	99.97
High					



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Cl₂ Abatement Results

Vector Water Scrubber Chlorine Removal Efficiencies (100 slpm Nitrogen)

Sump level	Measured Cl ₂ Delivery Rate		Water Sump pH	Outlet Cl ₂ Concentration (ppm)	% Removal
	ppm	g/min		Measured	
Low	165	0.11	7.1	3.9	97.6
High			7.0	3.3	98.0
Low	330	0.21	6.3	26.5	92.0
High			5.9	18.6	94.3
Low	495	0.31	10.9	1.6	99.7
High			10.3		
Low	740	0.47	10.4	1.3	99.8
High			10.8		
Low	990	0.62	10.5	1.2	99.9
High			10.0		



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Cl₂ Abatement Results

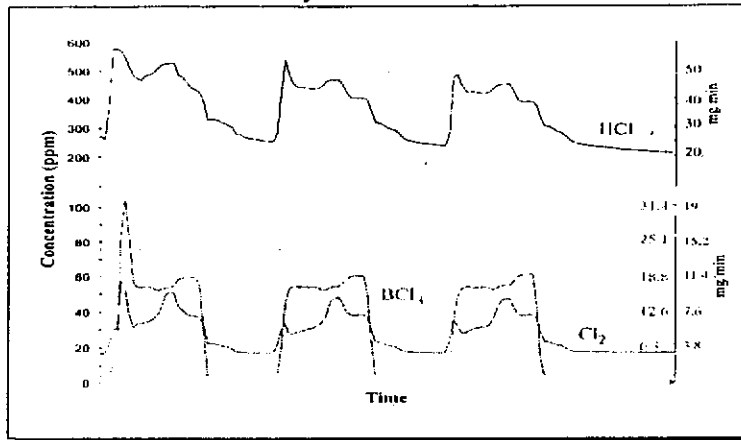
- ☐ Chlorine abatement is limited by Vapor Liquid Equilibrium (VLE) and hydrolysis reaction effects.
- ☐ Vector ES-100 can remove up to 0.2 g/min. Cl₂ without caustic injection.
- ☐ High Cl₂ concentrations are efficiently scrubbed using caustic injection.



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Metal Etch Tool Exhaust

In-line RGA Analysis of AMAT 8330 Effluents



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Conclusions

- ☐ The spectroscopic / In-line dryer analytical method was proven effective in real-time, continuous characterization of acid gases in wet streams
- ☐ The method provided valuable dynamic information regarding scrubbing efficiencies, and steady state performance of the abatement tool



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Conclusions

- ☐ Vector® ES-100 chlorine abatement study using this method concluded:
 - ☐ Cl₂ removal is limited by VLE/Reaction effects
 - ☐ Cl₂ can be scrubbed below TLV when challenged with < 200 mg/min Cl₂
 - ☐ Higher Cl₂ levels can be abated using caustic injection (pH ~10)



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