

# Developments in Abatement Tool Characterization: Continuous, In-Line RGA Analysis of Chlorinated Gases in Moisture Saturated Conditions

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## ABSTRACT

**T**he microelectronic revolution has advanced at the expense of using materials which are exceptionally toxic and damaging to the environment. The often reactive nature of these gas streams has posed considerable challenges not only to manufacturers of pollution control equipment, but to analysts attempting to characterize their composition. This paper describes an innovative analytical method to measure low concentrations of chlorine and hydrogen chloride in water vapour saturated conditions. The method was developed to characterize, in real time, acid gases at the exhaust of a point-of-use water scrubber. The technique involved the use of a residual gas analyser, an in-line Perma Pure sample gas dryer, and a novel sample collection set-up. The essential components of the set-up, analytical method, calibrations, and testing results are discussed, demonstrating the advantages of this method over existing analytical techniques.

## INTRODUCTION

The layering, patterning, and doping steps leading to the manufacture of integrated circuits require the use of reactive and toxic gases posing significant hazards to the integrity of the processes, to humans, and to the environment. During semiconductor processing, only a small portion of the reactant gases are deposited onto the wafers. Pollution control equipment is therefore needed to abate not only reaction by-products but a large portion of un-utilized materials. For instance, etching of aluminium and aluminium alloy films uses chlorine containing gases such as  $\text{BCl}_3$ ,  $\text{SiCl}_4$ , and  $\text{Cl}_2$  to allow plasma removal of aluminium. These reactive gases are either carcinogenic or highly toxic and require efficient point-of-use (POU) abatement technologies to avoid their release. In addition, hydrolysis of the chlorine or chlorine-containing residues generates HCl leading to corrosion problems down the exhaust line.

EcoSys is a world market leader in POU pollution abatement for the semiconductor industry providing wet

(Vector® Series), dry (Novapure® Series), and thermal (Guardian®, Phoenix®, ReCat® Series) solutions [1]. Liquid scrubbing utilizes gas absorption and/or gas reaction to separate the target toxic species from the process stream. The rate of absorption (mass transfer) is affected by the scrubber dimension, type of packing employed, gas and liquid flow rates, and the specific gas involved. In addition, the scrubber efficiency depends on the gas and liquid phase concentration gradient of the solute. This condition is dictated by the vapour-liquid equilibrium (VLE) and varies with the water pH, solute concentration, and the specific characteristics of the polluting gas. Gas absorption of HCl,  $\text{BCl}_3$ , and  $\text{NH}_3$  using a Vector® ES-100 scrubber has been published elsewhere [2]. Detailed investigation involving wet scrubbing of chlorine has since remained a challenge due to the added complexity of chlorine hydrolysis reactions and the difficulties involved in the development of suitable analytical methods.

## SCRUBBER PERFORMANCE ASSESSMENT: ANALYTICAL CHALLENGES

A major part of evaluating the performance of an abatement tool relies on the determination of pollutant removal efficiencies and by-product characterization. The vast majority of analytical methods utilized in this area involve grab samples or impingement techniques. Grab samples provide snapshot information of the gas stream being analysed. Impingement, the EPA approved analytical method to determine acid gas emissions (Method 26a), is adequate to determine average concentrations over an extended period of time. Neither technique can provide data about continuous changes in analyte concentration and are frequently developed to measure a single component in the gas stream. Continuous measurements of multiple components add a new dimension to the characterization of gaseous streams, and are essential to the study of time dependent reactions, such as fluctuations due to kinetic and equilibrium processes. This type of information is crucial in the development of improvements to our existing products and to the design of innovative abatement tools. In order to enhance the accuracy of the scrubber removal efficiency measurements, analysis of the inlet of the water scrubber was incorporated in addition to the outlet stream. These analytical advances are accomplished at the expense of using costly and sophisticated analytical instruments and complex sampling configurations.

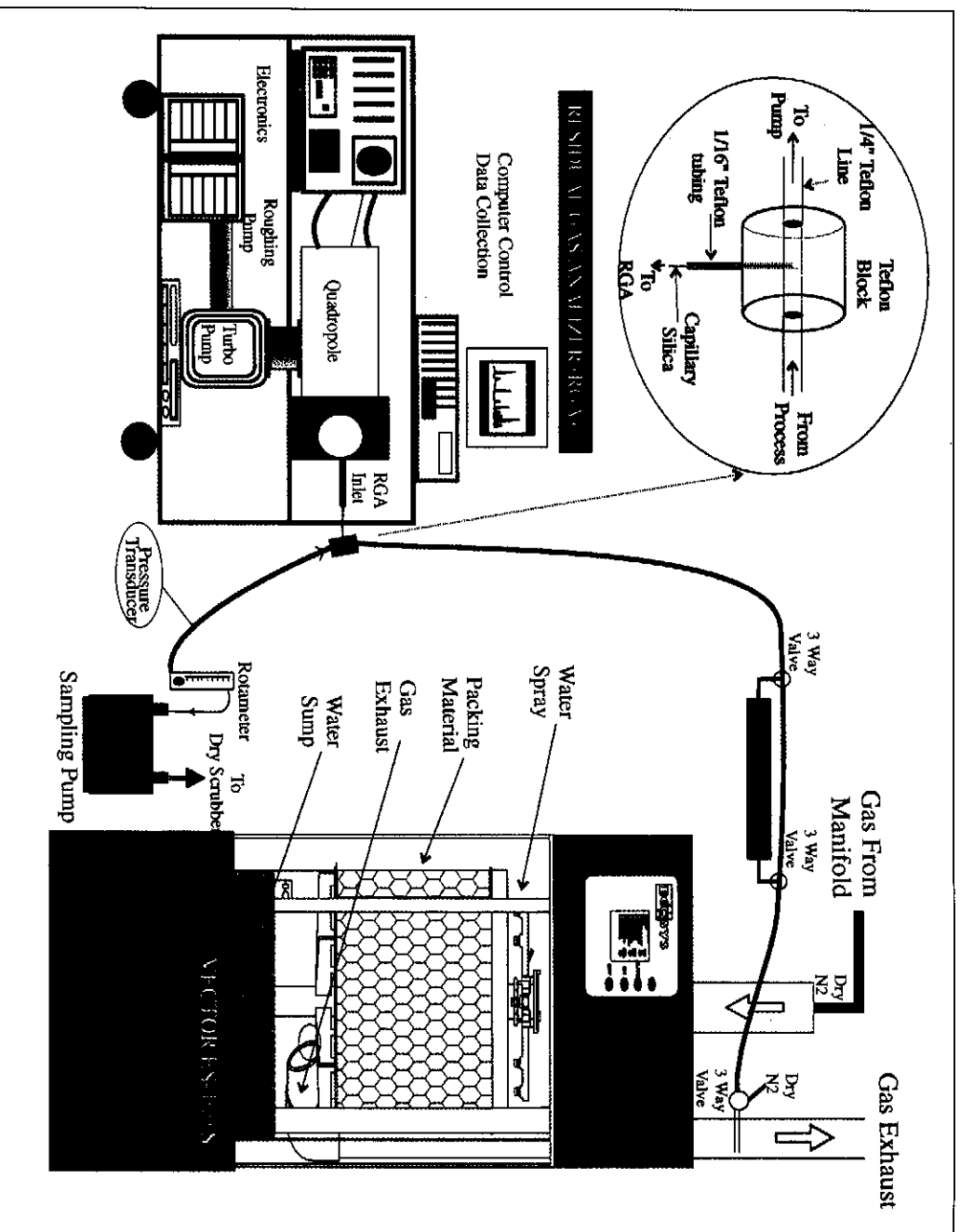


Fig. 1. Sketch of the water scrubber, mass spectrometer, and sampling set-up.

The gas phase characterization of chlorine and hydrogen chloride mixed with water vapour entails a number of additional challenges. Sample degradation of the highly reactive species is difficult to avoid as chlorine is readily converted into HCl in the presence of water. In turn, hydrogen chloride is highly soluble in water and condenses onto the walls of sampling lines and analytical instruments. To complicate matters still further, the acidic nature of these compounds can lead to corrosion, intensifying sample degradation and deterioration of the entire analytical set-up. Non-intrusive infrared techniques, such as FTIR, are not suitable options as chlorine is not infrared active. Heat tracing the lines to avoid moisture condensation was shown to favour undesired sample loss due to gas phase reactions involving chlorine and water encouraged by temperature dependent equilibrium constants.

Mass spectrometry (MS) is recognized as a powerful tool for gas phase process and environmental monitoring [5]. It is capable of measuring multiple species in a continuous mode, and practically in real time. With proper calibrations, mass spectrometry can be a quantitative analytical tool with high sensitivity, and wide linear dynamic range of detection. Moreover, mass spectrometers can be built to withstand reactive and corrosive environments. Together with infrared methods, MS has been established

as the most powerful technique for in-line process analysis. Industrial applications of MS (including residual gas analysers, RGAs) are diverse (2) and include among others, materials, food, and chemical manufacturing, ultrapure gas analysis, and semiconductor process analysis [4, 5].

The analytical method presented in this article was developed to provide continuous measurement of gas phase chlorine and hydrogen chloride in water vapour saturated conditions at the exhaust of our water scrubbers. The technique involved a residual gas analyser, an in-line drying device, and a novel sample collection set-up. The analytical method was validated after comprehensive testing and put to use in the analysis of real process gas streams.

## TEST DESCRIPTION

### Analytical instrument

The process effluent stream was analysed using a Questor™ IV (Extrel Corporation) residual gas analyser. The Questor™ IV MS-250 RGA is a quadrupole mass spectrometer designed for general purpose analytical applications of gases and vapours with molecular weights between 2 and 250 amu. The analyser is capable of detecting concentrations ranging from 10 ppb (parts per billion) using an electron multiplier detector to 100% using a Faraday cup detector. In this study, chlorine and

hydrogen chloride were detected using the electron multiplier detector operating at 1800 V, while the high concentrations of water expected at the outlet were measured using a Faraday cup detector. The instrument operated in continuous ion monitoring mode to represent the changes in concentration of selected ions with respect to time.

Additional analysis was accomplished using a MIDAC I-2000 (Midec Corporation) Fourier transform infrared spectrometer (FTIR) equipped with a ZnSe 10 cm and 10 m pathlength gas cells, and a nitrogen cooled mercury cadmium telluride (MCT) detector.

#### Process abatement tool

The Vector® ES-100 (ATMI-EcoSys) is a point-of-use water scrubber designed for the abatement of water soluble gases (Fig. 1). Detailed description of the tool is beyond the scope of this article which will be limited to features relevant to the analytical method and results. The scrubber operates using a co-current flow of water and contaminated gas stream. Mass transfer of the water reactive gases occurs mainly within the packed bed, as gas and liquid interact over the large surface area provided by the packing. As the water droplets egress through the bed they drop to a water reservoir or sump. The abated, moisture saturated gas stream exits the scrubber through a vertical 6 inch pipe connected to a blower. Water dynamics within the abatement tool includes fresh water flowing into the system, waste water draining out, and continuous recirculation of water stored in the sump. The necessary balance between incoming and exiting water was controlled in these tests 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. The scrubber was also equipped with a chemical injection system capable of delivering metered doses of a 50% NaOH solution to improve chlorine abatement.

#### Set-up

A schematic of the set-up is included in Fig. 1. The RGA was positioned 2 feet from the Vector® ES-100 water scrubber. A 10 foot long, 1/4 inch outer diameter (O.D.) 1/8 inch inner diameter (I.D.) Teflon tube was used to transport the sample from the outlet port of the scrubber to a two stage Cast® pump (Cast Manufacturing Company). The sample gas flow rate was controlled, using a rotameter, and the pressure kept constant at 650 Torr. The RGA capillary silica inlet was positioned perpendicular to the gas flow and at the centre 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. In order to study the performance of a Perma Pure gas dryer (Perma Pure Inc.) the in-line sample conditioning device was installed in a bypass arrangement as shown in Fig. 1. In this continuous drying process, moisture is selectively removed by passing the sample stream through a bundle of Nafion® tubes (DuPont Corporation); this allows water to permeate out of the sample gas stream into a counter-current purging flow of dry nitrogen [6]. The caustic injection system, the manifold used to deliver the contaminated gases to the scrubber, and the batch neutralization system used to treat the water before releasing it to the drain, are not shown in Fig. 1.

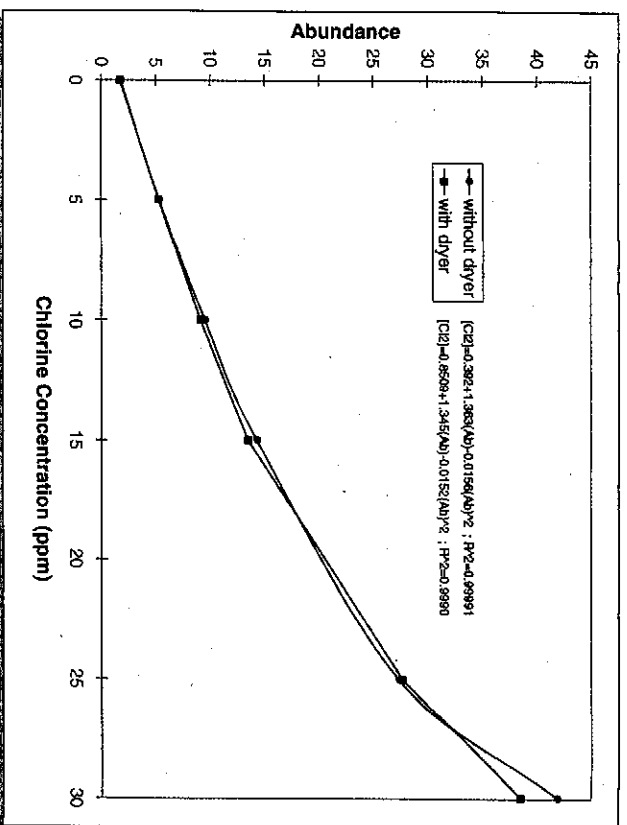


Fig. 2. Calibration curves of dry chlorine.

#### CALIBRATIONS

In this study, calibrations served two equally important purposes. First, we wanted to determine the response of the analytical instrument to different concentrations of HCl and Cl<sub>2</sub> prepared from 1000 ppm certified standards. Secondly, we needed to ensure that the in-line moisture reducing process did not in turn remove or affect the concentrations of the species of interest.

#### Dry

In order to minimize uncertainties from the sampling configuration, calibrations at the outlet of the scrubber were performed in situ, keeping the experimental set-up identical to the testing conditions. Excess volumes of calibrating dry Cl<sub>2</sub> (0 to 30 ppm range) and HCl (0 to 50 ppm range) were delivered into the exhaust of the water scrubber. The same procedure utilized during testing was used to draw a portion of the calibrating gas into the RGA. For each species, we generated two independent calibration curves: one with the drying device in-line, and another unconditioned. The generated experimental data indicated that, in dry gaseous streams, neither HCl or Cl<sub>2</sub> were removed by the Nafion tubing in the Perma Pure device. Fig. 2 illustrates both calibration curves for chlorine.

#### Wet

In order to determine the effects of the water removal process, we compared the measured concentrations of wet chlorine and hydrogen chloride with and without the use of the in-line sample dryer. Different concentrations of moisture saturated gas mixtures were generated in situ during the water scrubbing process: chlorine not only dissolves in water but reacts with it generating aqueous HCl and HOCl. By changing the concentration of the chlorine/nitrogen mixture delivered into the water scrubber, the concentrations of chlorine and HCl at the exhaust varied accordingly. The large volume of recir-

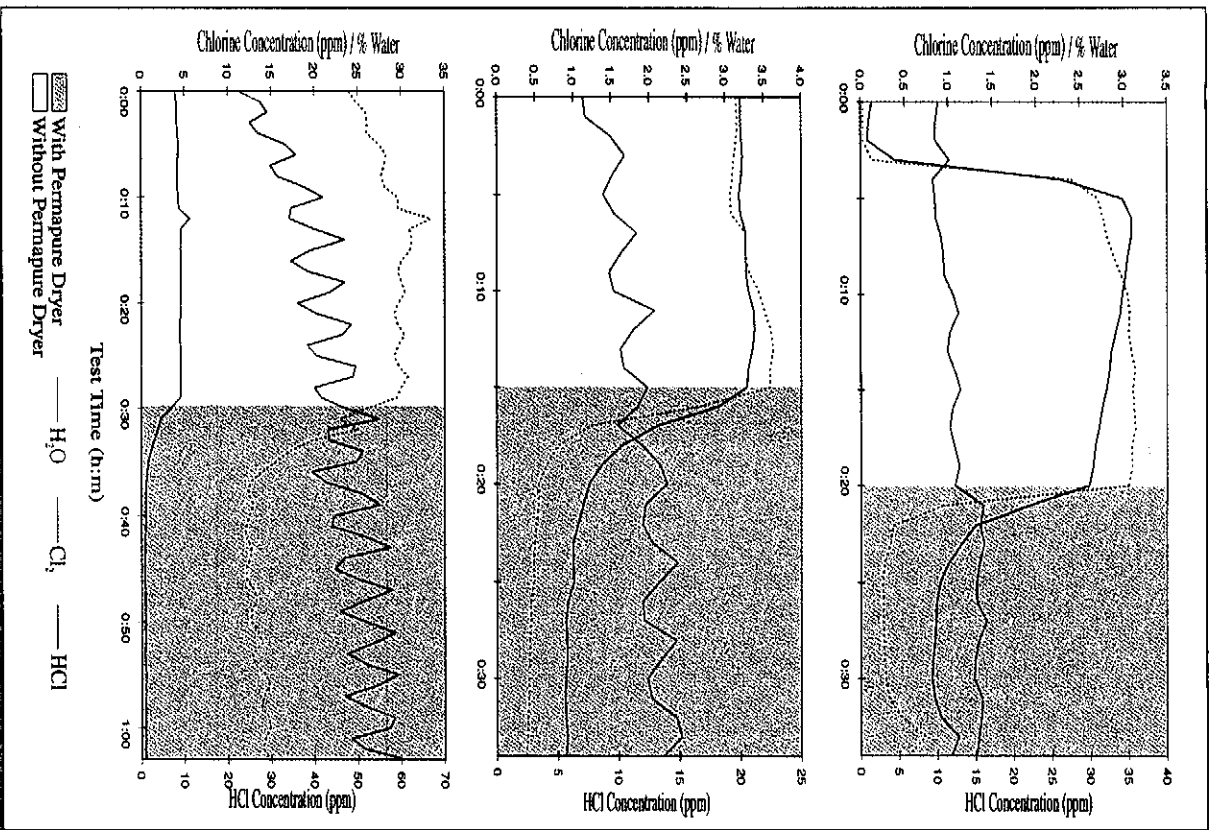


Fig. 3. Effect of sample gas moisture reducing process on chlorine, water, and hydrogen chloride.

culating water guaranteed the moisture saturated conditions of the effluent gas stream. Fig. 3 illustrates the different concentrations of Cl<sub>2</sub>, HCl, and H<sub>2</sub>O measured at the exhaust of the scrubber using and bypassing the Perma Pure device. All three graphs illustrate a significant drop in water and HCl concentrations in the dried gas stream. However, chlorine concentration with and without the dryer remained virtually unchanged, providing successful removal of water without affecting the concentration of chlorine. It is worth pointing out that extended operation of the spectrometer without the dryer resulted in recurrent clogging of the RGA. Microscopic analysis of the obstructed capillary silica indicated that water condensation was the cause, emphasizing the importance of removing moisture from the gas stream.

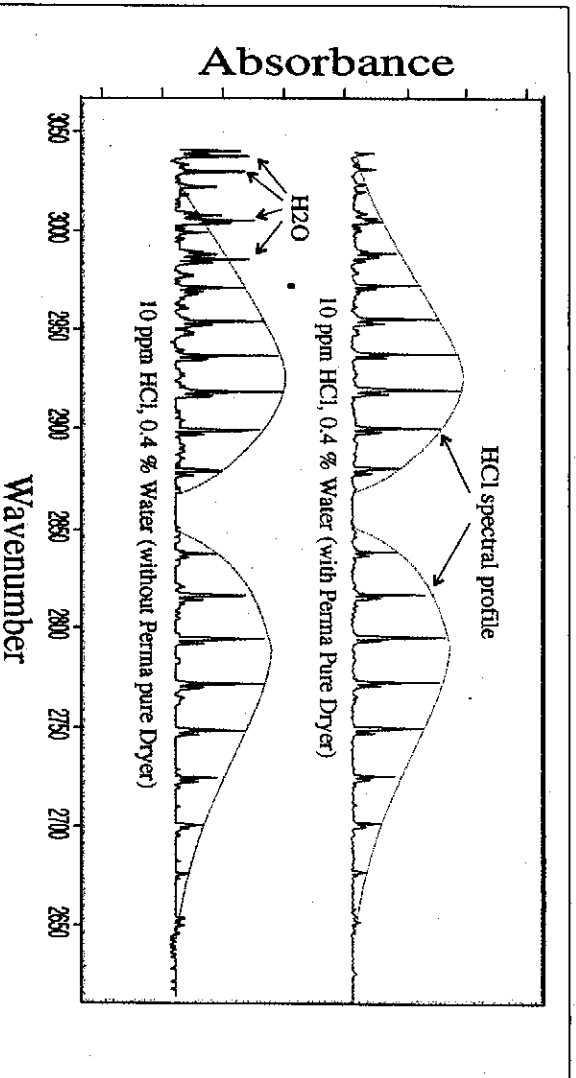
The effect of sample conditioning on hydrogen chloride remained inconclusive and warranted additional study. Small concentrations of hydrogen chloride diluted in nitrogen and water vapour were generated in a calibration manifold and delivered into the 10 meter pathlength cell FTIR spectrometer previously described. As for the RGA calibrations, the same sample gas mixtures were delivered unconditioned, and with the dryer in line. Fig. 4 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 indicates practically identical HCl concentrations. At the limit of water vapour saturation and low HCl concentrations (Fig. 5), the most intense HCl peaks are still discernible in the dried sample (top) but vanish in the wet stream (bottom) due to either spectral interference of water or condensation effects. These results verify that water removal from the gas stream is accomplished without the removal of hydrogen chloride.

#### WATER SCRUBBER TESTING RESULTS

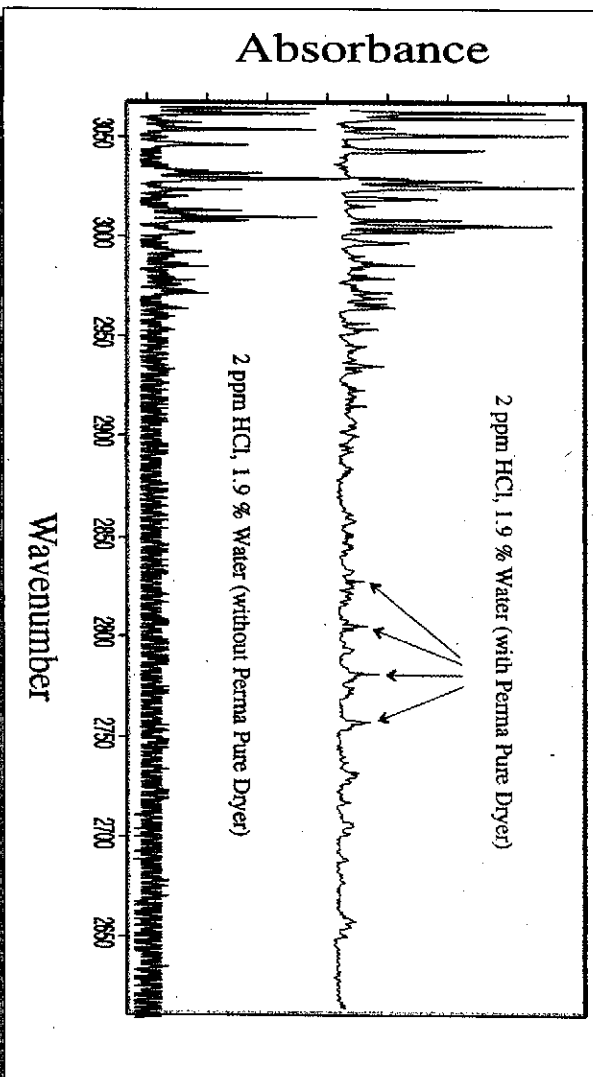
We have investigated the chlorine removal efficiency of a Vector® ES-100 water scrubber using measured inlet

**TABLE 1. VECTOR® ES-100 WATER SCRUBBER RESULTS FOR CHLORINE REMOVAL USING 200 SLPM INLET FLOW RATE.**

Water Inlet Level	Cl <sub>2</sub> Inlet ppm (actual)	Measured Inlet Cl <sub>2</sub> conc. ppm	Water Inlet ppm	Measured Inlet Cl <sub>2</sub> conc. ppm	% Cl <sub>2</sub> Removal
Low	50	165	7.06	3.90	97.6
High			7.04	3.31	98.0
Low	100	330	6.33	26.49	92.0
High			5.87	18.64	94.3
Low	150	495	10.92	1.58	99.7
High			10.26		
Low	225	740	10.37	1.29	99.8
High			10.85		
Low	300	990	10.54	1.16	99.9
High			9.87		



Above Top - Fig. 4. FTIR absorbance spectra of conditioned and unconditioned calibration gas samples (10 ppm HCl, 0.4% water), Above Bottom - Fig. 5. FTIR absorbance spectra of conditioned and unconditioned calibration gas (2 ppm HCl, 1.9% water).



chlorine concentrations ranging from 160 to 3700 ppm in nitrogen and overall flow rates of 100 and 200 standard litres per minute (slpm). Water temperature was kept at a constant 30 °C throughout this study. Caustic solution was injected when the outlet chlorine concentration surpassed the immediate danger to life and health level (IDLH = 30 ppm for chlorine). 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. Measured concentrations of chlorine delivered into the water scrubber were 30% lower than the readouts values calculated from the mass flow controller outputs used to generate the gas mixtures. The unexpected disagreement between measured and theoretical concentrations stressed the importance of analysing both inlet and outlet streams during characterization of the performance of a scrubber.

Fig. 6 depicts over 5 hours of continuous monitoring of Cl<sub>2</sub>, HCl, and H<sub>2</sub>O at the exhaust of the water scrubber using different inlet chlorine concentrations and fixed overall flow rates of 200 slpm. The abundances of these species were converted into concentrations using the calibration curves described above. The initial high concentration of chlorine shown in Fig. 6 corresponds to residual chlorine remaining in the sample lines from the immediately preceding inlet analysis (not included). As expected, effluent concentrations of chlorinated species escalated as the inlet concentration of chlorine increased. The 30 ppm mark was reached using an inlet Cl<sub>2</sub> flow rate of 100 scfm (330 ppm). The observed periodic oscillations in the concentration of chlorine corresponded to the high and low water levels in the sump of the scrubber: when the sump level decreased (water being discharged, with no fresh water coming in)



**TABLE 2. VECTOR® ES-100 WATER SCRUBBER RESULTS  
FOR CHLORINE REMOVAL USING  
100 SLPM INLET FLOW RATE.**

INLET CHLORINE CONCENTRATION (PPM)	INLET FLOW RATE (SLPM)	INLET CHLORINE CONCENTRATION (PPM)	INLET FLOW RATE (SLPM)	OUTLET CHLORINE CONCENTRATION (PPM)	OUTLET FLOW RATE (SLPM)
Low	50	500	50	6.9	50
High	50	500	50	10.96	50
Low	75	495	75	6.64	75
High	75	495	75	9.5	75
Low	100	490	100	6.36	100
High	100	490	100	9.26	100
Low	150	399	150	6.05	150
High	150	399	150	21.9	150
Low	225	148.2	225	9.94	225
High	225	148.2	225	10.21	225
Low	300	197.4	300	10.02	300
High	300	197.4	300	10.33	300
Low	400	262.9	400	10.45	400
High	400	262.9	400	10.21	400

**ACKNOWLEDGEMENTS**

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from Texas A&M university in 1995. His research experiences include molecular spectroscopy, development of rf plasma abatement technology, and computational quantum chemistry. He is currently responsible for the development of spectroscopic (RGA and FTIR) in-line continuous analytical methods to characterize the performance of EcoSys abatement tools.

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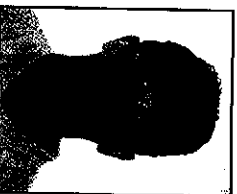
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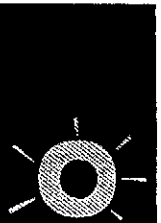
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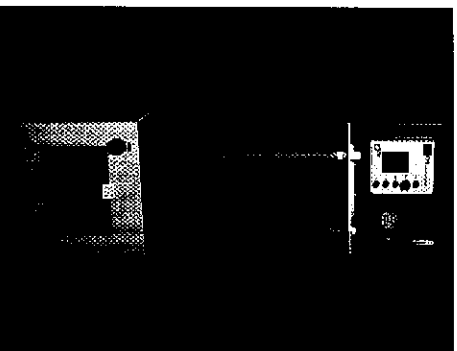
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### **Wet**

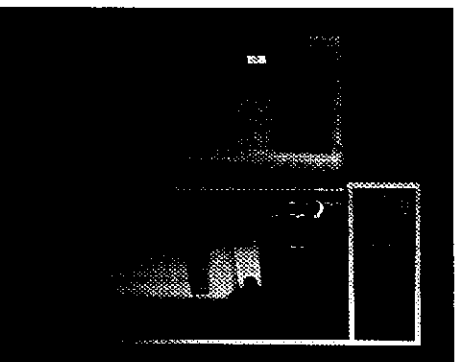
The EcoSys wet abatement product line, Vector® water scrubbers, are highly effective for treating water soluble gases and chemicals. Water use is minimized by recirculation. The Vector® entry device prevents particle formation and provides increased efficiency in the handling of high particulate effluents.



### **Dry**

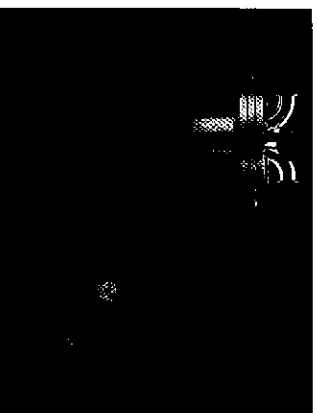
EcoSys has expertise in successfully developing and using dry resin materials. Packed beds of proprietary resins capture toxic gases and chemically convert them to non-hazardous material. The Novapure® dry scrubber and the emergency release scrubber(ERS) product lines use these resins to concentrate and convert toxic gases. The ERS is

designed to handle concentrated or emergency release abatement.



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solutions while working with tool vendors to develop abatement technologies for existing and future fab tools. The EcoSys Applications Lab provides a test site to develop abatement solutions for future chemicals, gases, and semiconductor tools.

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