

Chlorine and Hydrogen Chloride Monitoring Utilizing Ion Mobility Spectroscopy (IMS)

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ABSTRACT

Increasing regulatory pressure has produced great interest in monitoring for hydrogen chloride (HCl) and chlorine (Cl₂) in stacks and from other sources. Measurement of these gases has important process control implications as well¹. Traditional spectroscopic methods have been used in these applications, but have not always been found to be satisfactory. This paper describes the use of IMS in performing these measurements. This technique is shown to have distinct advantages over competing techniques. Both compounds can be measured in a single instrument, limits of detection are in the area of 0.5 ppb, and no interference is found at high humidity levels. Theory of operation, hardware design, sensitivity and specificity will be discussed.

INTRODUCTION

HCl and Cl₂ are used or produced in a wide variety of chemical processes. They may also be produced by incineration of chlorine containing materials. Very often they are present at the same time, depending on temperature, humidity and other parameters. When produced as a byproduct of a process or incineration, they are typically disposed of by a wet scrubbing process and released up a stack. While HCl is very water soluble even under relatively low pH conditions, Cl₂ typically requires a caustic scrubbing solution. Because of this, scrubber optimization has economic as well as environmental implications.²

The environmental concerns related to these compounds are an important factor. Both are toxic and corrosive. However, Cl₂ is often considered a more dangerous compound. For this reason, specific monitoring for both compounds is becoming an important issue with local, state and federal agencies. These concerns have pushed desired detection limits to low ppm and in some cases ppb levels.

Traditional spectroscopic methods have been used to monitor for these compounds. HCl is usually monitored using infrared spectroscopy (IR), and Cl₂ with ultraviolet spectroscopy (UV). However, these methods have some drawbacks. Two separate analyzers are required, one for each compound. In some cases coexisting compounds (in some cases even water vapor) present an interference problem. Limits of detection for these techniques are often insufficient to meet compliance or other requirements.

IMS has been used to monitor for both of these compounds in a wide variety of stacks, ambient air and process streams at levels down to 0.5 ppb. Because it is equally sensitive to both compounds, mixtures of the two provide a “total chloride” reading, without interference from organic chlorine containing compounds. Because of the differences in solubility, it is possible to scrub HCl from a stream without removing Cl₂. This is easily accomplished by using a commonly used sample system component, the chiller. Chillers are very commonly used in extractive type sampling systems to remove water from the stream prior to introduction into analyzers. Chillers work by providing a chamber chilled to 4°C using thermoelectric or other devices. Water in the stack sample is condensed out providing a sample with a 4°C dewpoint. This process takes place very quickly, so that compounds of low water solubility pass through with little or no loss. However, compounds of high solubility are removed with the water.

This principle can be used to obtain independent measurements for Cl₂ and HCl using a single IMS analyzer. The sample is presented directly to the analyzer to obtain a “total chloride” reading. The sample is then switched to the chiller to provide a chlorine only reading. HCl is then determined by difference. In practice, the non-chilled sample is run through a PermaPure™ dryer which removes water but not HCl or Cl₂. This is done so that both the total chloride and chlorine measurements are obtained on a dry basis. Where a continuous output is required, the two streams (one through a chiller, the other through a PermaPure™ drier) can be directed to a single analyzer with two sensors.

In streams that contain only one of these compounds (or if a total chloride measurement is satisfactory), the measurement can be made directly without removal of the water. This eliminates the need for the chiller or other driers. In some cases, a dilution type probe may be used.

THEORY OF OPERATION

IMS is an ionization based time of flight technique, performed at atmospheric pressure. A description of the IMS cell is seen in figure 1. The sample is drawn over a semipermeable membrane by way of an internal eductor. The membrane serves several purposes. It serves to protect the interior of the cell from particles and high moisture levels, provides a degree of selectivity, and allows various levels of sensitivity based on permeation rate. The molecules of interest permeate through the membrane, and are picked up by the carrier flow, which sweeps the other side of the membrane. The carrier stream delivers the sample molecules to the reaction region of the cell, which contains a small Ni⁶³ radioactive source. There the sample is ionized as a result of a series of ion-molecule reactions. In most cases, compounds known as dopants are added to the carrier stream. These dopants enter into the ion-molecule chain of reactions to provide a degree of selectivity based on the charge affinity of the analyte. Once the sample has

been ionized, the ions begin to drift towards the opposite end of the cell due to the influence of an electrostatic field. A shutter grid is located in the tube which can be biased electrically to either block the ions, or allow them to pass through. This shutter grid is pulsed periodically to allow the ions into the drift region. There, they begin to separate out based on their size and shape while flowing counter to a drift gas flow which is introduced at the end of the drift tube. A collector plate located at the end of the tube detects the arrival of the ions by producing a current. This current is amplified to produce a time of flight spectrum. Ions are identified by their characteristic drift time position in the spectrum. Spectra reflect the charge sharing phenomenon characteristic of IMS. The Ni^{63} source provides a finite amount of charge. The sample gas is ionized by accepting charge from the dopant ion. Thus, as the concentration of the sample gas increases the sample ion peak height increases, while the dopant ion peak height decreases.

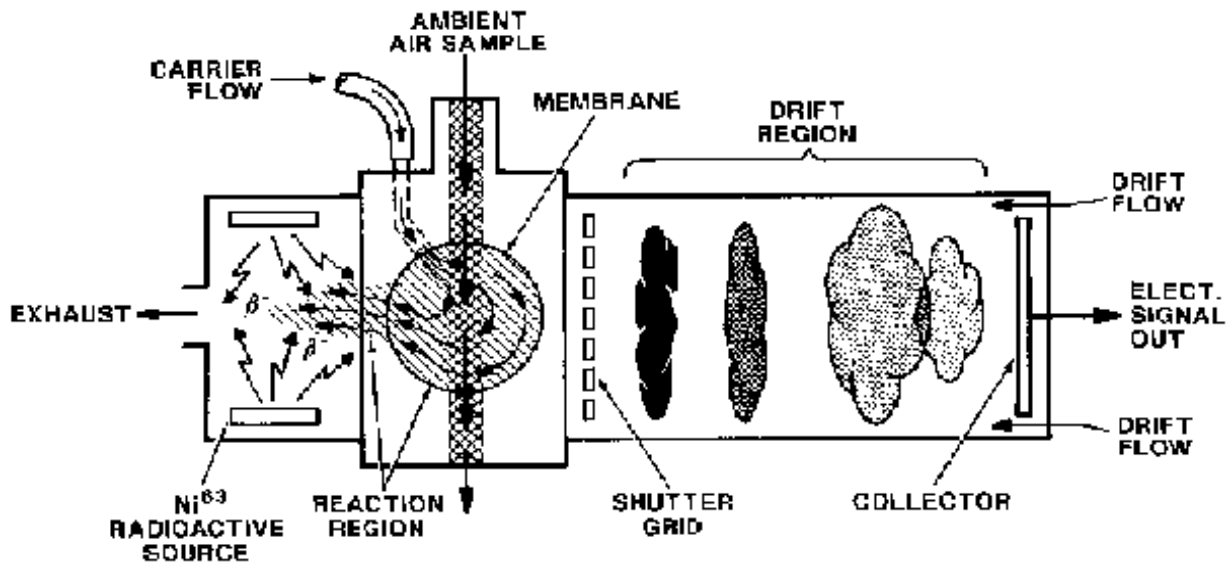


Figure 1-IMS Cell

ANALYZER AND SAMPLE SYSTEM DESCRIPTION

The analyzer is seen in figure 2 below. Housed in a stainless or painted steel enclosure, the controlling electronics are located on the left hand side and the temperature controlled pneumatics are located in an inner enclosure on the right hand side. The front panel contains the user interface via a flat touch panel and back-lit LCD display. From the front panel the operator can perform calibrations, set alarm levels, set password protection, acknowledge alarms and all related tasks. The front panel also displays the concentration, diagnostics information, as well as analyzer and alarm status. Remote indication of concentration is provided by RS-232 and/or 4-20 mA loop, and contact closures provide alarm status. The analyzer can be supplied with on-board calibration, allowing the operator to periodically check for accuracy. However, stack monitoring requirements typically require calibration through the sample probe, using certified gas cylinders.

Utility requirements are 110-240 VAC and clean dry instrument air. A block diagram of a typical system is seen in figure 3. The analyzer has the capability of controlling the automatic switching valve as well as performing the calculations to determine HCl and Cl₂ concentrations.

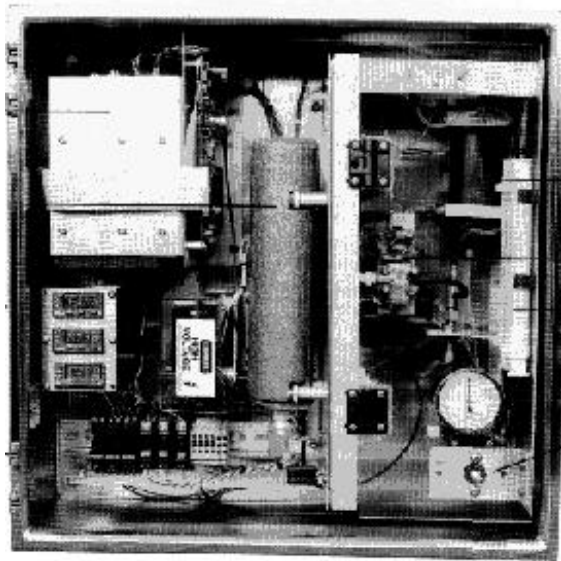


Figure 2-IMS Analyzer

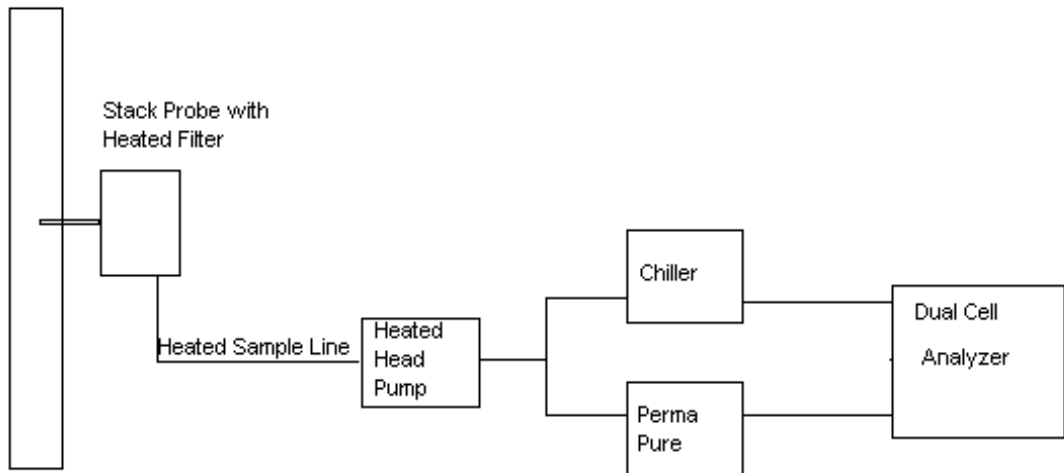


Figure 3-Block Diagram of HCl/Cl₂ Stack Monitoring System

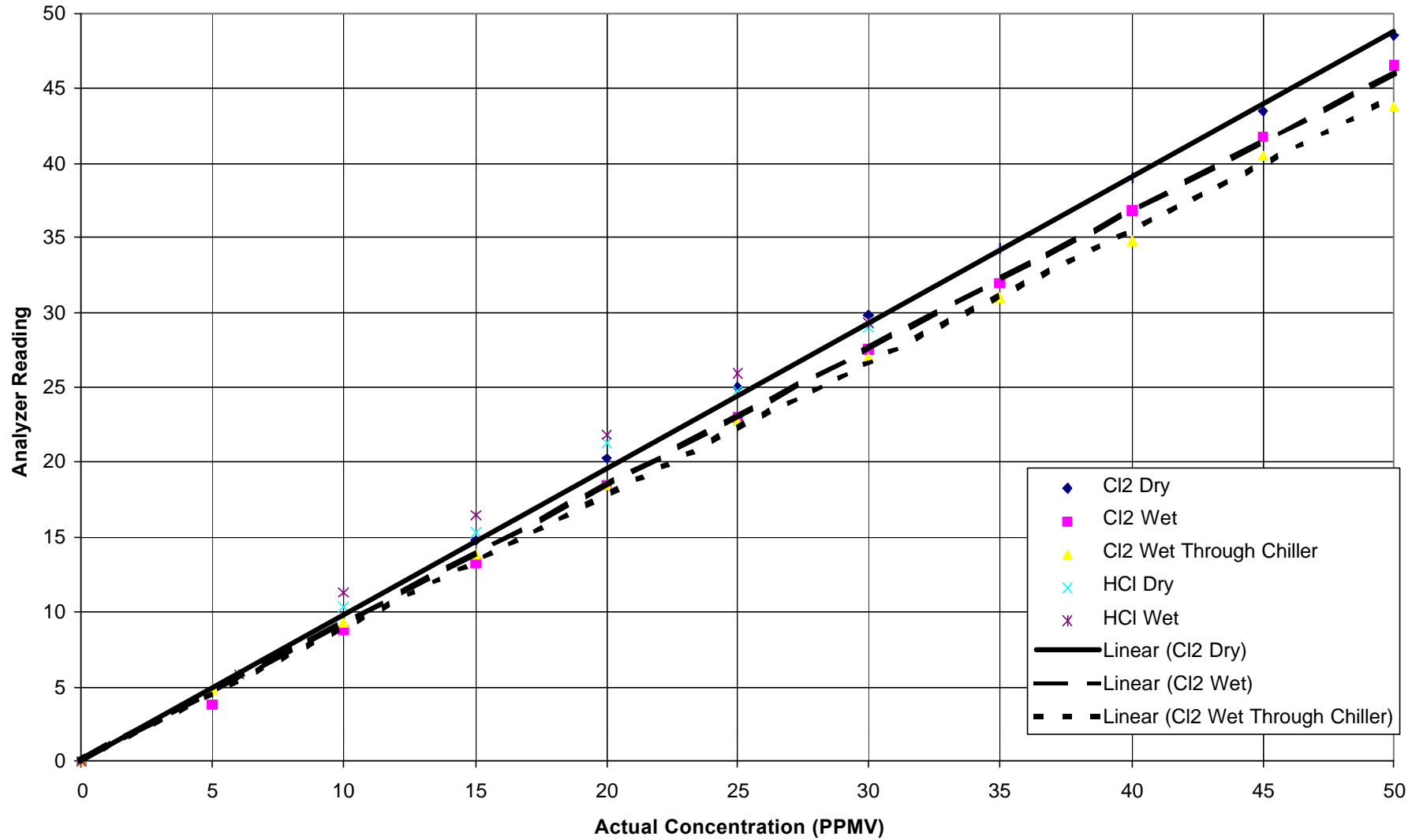
EXPERIMENTAL

To test the response of the analyzer to known concentrations of PPM levels of HCl and Cl₂, various concentrations of the gases were generated by diluting a certified cylinder using air at different humidities. Concentrations of Cl₂ from 0-50 ppm were generated using zero air (0% RH). These same concentrations were generated in a humidified air stream by bubbling the dilution air through DI water to obtain >85% RH. Various concentrations of HCl were generated in the same manner. These concentrations were also run through a chiller and PermaPure drier to simulate a typical stack monitoring system. A standard chlorine analyzer, calibrated in the range of 0-50 ppm (with Cl₂) was used to determine response to the gases. The analyzer response was noted, as indicated below:

Actual Gas Conc. (PPM)	Analyzer Reading (PPM)					
	Cl ₂ Dry	Cl ₂ Wet	Cl ₂ Wet Through Chiller	HCl Dry	HCl Wet	HCl Wet (Through Chiller)
0.0	0.0	0.0	0.0	0.0	0.0	0.0
5.0	4.8	3.8	4.8			0.0
6.0					5.8	0.0
10.0	9.5	8.8	9.3	10.3	11.3	0.0
15.0	14.8	13.3	13.8	15.3	16.5	0.0
20.0	20.3	18.5	18.5	21.3	21.8	0.0
25.0	25	23	22.8	24.8	26.0	0.0
30.0	29.8	27.5	27.0	29.0	29.3	0.0
35.0	34.3	32.0	31.0	33.0	33.3	0.0
40.0	39	36.8	34.8	36.5	36.8	0.0
45.0	43.5	41.8	40.5	40.5	40.1	0.0
50.0	48.5	46.5	43.8	44.8	44.5	0.0
550.0						0.0

A plot of this data is seen on the following page.

PPM Levels of HCl and Cl₂: Dry, Wet and Through Chiller



Analysis of Mixtures

A limited amount of testing was performed to validate the ability of the analyzer to quantitate mixtures of HCl and Cl₂. These tests were performed on humidified samples. The Cl₂/HCl samples were run first through a PermaPure drier to determine total Chloride, and then through the chiller to determine Cl₂. The analyzer was calibrated with wet chlorine to eliminate response artifacts (see discussion below). The HCl was determined by difference. The following results were obtained:

Actual Conc.	Analyzer Reading Through Chiller (Cl₂ Only Reading)	Analyzer Reading Through PermaPure (Total Chloride)	HCl Reading (by Difference)
30 ppm HCl+30 ppm Cl ₂	29.5	60.5	31.0
10 ppm HCl+10 ppm Cl ₂	10.5	19.5	9.0
30 ppm HCl+10 ppm Cl ₂	10.5	39.0	28.5

DISCUSSION

The chlorine results obtained in this test are very similar to those previously reported for 0-100 ppb. In both sets of tests, the response to wet chlorine through the chiller is approximately 10% lower than the response to dry chlorine. This may not be an actual loss of chlorine due to solubility. It is known that chlorine reacts with water to form species such as HCl and HOCl. These compounds are water soluble and would be removed by the chiller. The ppb data leads some credence to this argument. If the loss of chlorine is due to water solubility, the ppb data should show a significantly higher loss than the ppm data, which it does not. If the reaction of chlorine with water takes place to form fixed ratios of these compounds, the loss through the chiller should be a fixed percentage at all concentrations. This is what is observed. However, no confirmation of this hypothesis was attempted.

The data shows quantitative removal of HCl by the chiller. The response to 550 ppm HCl through the chiller was below the minimum detectable limit of the analyzer, indicating >99.9% removal efficiency. Response to Cl₂ and HCl are seen to be nearly identical. Minor deviation from linearity are easily correctable in the analyzer software when determining HCl by difference. No loss of HCl or Cl₂ was noted when passing the HCl through the PermaPure drier.

The data shows good linearity over the full range of the analyzer, and demonstrates the feasibility of using this method for determining both chlorine and hydrogen chloride in a mixed stream.

FIELD EXPERIENCE AND APPLICATIONS

The chiller technique been successfully used to monitor ambient air levels of chlorine near a town located within 25 miles of a major chlorine producer. The analyzer has a range of 0-500 ppb, and is located in a remote monitoring station where it runs unattended except for weekly inspections. The system has run for nearly 2 years without problems. Typical levels measured were less than 20 ppb, and no interference has been noted from HCl or other gases.

IMS has also been successfully used in monitoring for HCl and Cl₂ emissions from the combustion of rocket fuel at the low ppb level, with good agreement with standard wet methods.³ PPB and low ppm level analyzers have been used in applications as diverse as ambient air monitoring in chemical and plastic manufacturing plants, for testing wet scrubber efficiency and for monitoring Cl₂ levels in corrosion test chambers. In many cases, IMS was the only technique with sufficient sensitivity, accuracy and specificity to make the required real time measurements.

A number of stack applications have been addressed with IMS analyzers as well. PPM levels of HCl have been monitored in hazardous waste incinerators and in stacks associated with pigment production. Cl₂ has been monitored at the ppm level in stacks associated with TiO₂ manufacturing, precious metal recovery, crematoriums, vinyl chloride production, and a wide variety of other industries. The IMS systems have performed well in these demanding applications, where other techniques have either failed or were not usable. At a number of locations, the analyzers are required by state or local regulations. As such, they are subject to the same quality control specifications as other Continuous Emission Monitors for accuracy, stability and reliability. Very good performance has been noted in zero and span drift tests, as well as quarterly calibration gas audits.

Use of IMS is by no means limited to stack and ambient air applications. Process monitoring applications include monitoring for HCl in vinyl chloride, chlorofluorocarbons and hydrogen. Stack and process analyzers are also in use for hydrogen fluoride (HF), Ammonia (NH₃), Chlorine dioxide (ClO₂), n-methyl pyrrolidone (NMP), bromine (Br₂), sulfur dioxide (SO₂) and other compounds.

REFERENCES

1. Charles C. Allgood and Jeremy Blanks, "Examining Purification and Certification Strategies for High Purity C₂F₆ Process Gas", Micro, April 1998, pp 35-45
2. R. Gravely, M. Boedigheimer, B. Moore, S. Bischke, J. Obert "Process Exhaust Monitoring: Motivations, Techniques, and Case Studies", Semiconductor Fabtech, 7th Edition, 1998, Section 2, pp 55-63
3. Mitch Lindsay, Michael Graziano and Regan McMorris, "Field Performance of an Ion Mobility Monitor for Chlorine in Ambient Air", paper 96-TA30.03, AWMA 89th Annual meeting in Nashville Tenn., 1996