# Chlorine atom concentration determination via gas phase titration with butane

**Sreerupa Basu**
**Ohio University, Athens Ohio, USA**

## Introduction

The aim of this research is to have a better understanding of the chlorine dissociation reaction to form chlorine plasma. This understanding will help to analyze the mechanism for the reaction between the elemental mercury and chlorine. This research delves into analyzing the residence times of chlorine atoms, which oxidizes the elemental mercury present in the flue gas before the stack gas leaves the Electrostatic Precipitator. Burning of coal releases mercury into the environment. There are broadly three forms in which Mercury is present in the atmosphere; inorganic mercury, generally as a compound with Chlorine, such as $HgCl_2$; organic mercury, generally as a compound with Methane, such as methyl mercury with properties of bio-accumulating and which had created a havoc a few years back when a significantly lethal amount of this compound was detected in the fishes, or dimethyl mercury which is supposed to be the most poisonous, a few microlitres of this compound spilled on even a latex glove can be toxic enough to cause death; and the third form with the greatest potential for public concern (Senior et.al.) is the elemental mercury which exists as a vapor form, as the elemental form can be transported within the food chain and then form the dangerous organic compounds within the living organisms (ATSDR, toxicological profile of mercury). Mercuric compounds can cause respiratory, gastrointestinal, cardiovascular effects and even gene mutation and death. The 1990 Clean Air Act categorized mercury as one of the 189 Hazardous Air Pollutants required to be controlled. USEPA report tells that 90% of the anthropogenic source of mercury in the environment is the coal-fired power plants in the US.

## Mercury speciation in coal combustion formed flue gas

Mercury is present in the coal in three forms: Elemental mercury, particle bound mercury and oxidized mercury. There are various models aimed at explaining the different Hg speciation pathways possible in the post-combustion stream from coal burning. One of the most accepted speciation pathway is heating mercury within the temperature range of 400 to $500^0$C forming its oxide, which at a temperature above $500^0$C decomposes (Dajak and Lockwood, 2001; Niksa and Heble, 2001). The oxide is changed to the chloride form via homogeneous gas phase reaction with hydrogen chloride or chlorine present in the flue gas. A heterogeneous gas-solid reaction is also possible forming the particulate bound mercury species (Senior et.al). Another speciation pathway leads to direct gas-phase oxidation of elemental mercury by active chlorine atoms (Horne 1968, Ariya 2002). The oxidized form ($Hg^{2+}$) is totally soluble in water and hence can be easily removed in the scrubbers.

The problem arises where most of the mercury is not oxidized and released in the stack gas as elemental mercury. Elemental form of mercury is very stable at high temperatures of coal-fired boilers. Formation of the oxides of mercury is controlled by the amount of the oxidizing agents present and quench rate of the flue gas. A report from EPRI 1996 indicates that on an average 0.02 to 0.25 ppm of mercury is present in coal. Several areas of research and technology are being worked on today, with collaboration of stalwart agencies that have taken up the pioneering responsibilities to protect the environment; to minimize the amount of the elemental Mercury released with the exhaust gases from the coal combustion. Efforts are being put in the direction of optimized yield of mercuric chloride from the elemental form via reaction with chlorine atoms derived from different chlorine species like chlorine and hydrogen chloride gases present in the flue stream. In order to optimize the product, a better understanding of the reaction between $Hg^0$ and Cl has to be made.

## Using Electrostatic Precipitator as a mercury emission control technology

For removal of gaseous pollutants like mercury and $NO_x$, plasma enhanced electrostatic precipitation technique works more efficiently. A plasma enhanced electrostatic precipitator uses the physics of plasma with the basic working principles of a wet ESP. An oxidizing gas or the reagent gas is passed through the discharge electrodes, and a plasma of the oxidizing particles is formed, which can more effectively oxidize the elemental mercury present in the background gas in the precipitator. There are wet membranes near the collecting electrodes that dissolve the oxidized form of mercury and the slurry is removed. The voltage is such applied to the precipitator that the potential very near to the discharge electrode is high and it ionizes the air near it to form a plasma (a stage before it can become conductive) around this region. The current, which is generated by the ions in this plasma region, forms the visible corona around the tips of the discharge electrodes. The ions near the discharge electrodes will eventually pass the charge to nearby areas of lower potential and recombine to form neutral particles. Thus, the environment in the precipitator, besides the region near the discharge electrodes is kept neutral. The Ohio University has a wet membrane Plasma Enhanced Electrostatic Precipitator in the Stocker lab 045. Experiments have been performed with injecting steam and hydrochloric acid as the reagent gas to study the increased efficiency of mercury removal using an electrostatic precipitator.

## Uniqueness of this research

The idea of using hydrogen chloride gas as the reagent gas for a previous experiment (Jayaram, 2005) was based on the fact that the amount of chlorine containing species in the coal has been reported to have a positive affect on the amount of mercury oxidized in the flue gas (EPRI, year). The reaction due to the attack of the Cl atom on the elemental mercury is believed to be the primary path for forming the mercuric chloride (Helble et.al 2000, 2001; Niksa et.al 2000; Sliger et.al. 2000). The chlorine atoms are created in the chlorine plasma formed when the chlorine gas or hydrogen chloride gas is injected through the discharge electrodes. To have a better understanding of this reaction pathway, a fundamental study of the chlorine dissociation in plasma is required. Various studies have been made to understand the chlorine plasma chemistry in different test scenarios as inductively coupled chlorine plasma, or photoluminescence induced chlorine dissociation. This research aims to quantify the trend of chlorine atom formation with time in the chlorine plasma formed near the discharge electrodes in a simulated ESP condition, minus the presence of other radical groups as in flue gas. The experiment is carried out in a pyrex glass chamber where atmospheric temperature and pressure conditions are maintained and chlorine gas is injected through a discharge electrode which charges up the chlorine molecules to form the charged chlorine atoms and ions resulting in the chlorine plasma. In a later experiment, elemental mercury can be put in the generated chlorine plasma and the amount of mercuric chloride formed in the process can then be measured. If the trend of mercuric chloride formed in the later process can be related to the chlorine atom formation trend arrived at earlier, at the summation of this research project, then we can have a better say in the postulated reaction pathway of the yield of mercuric chloride in the flue gas. However, to optimize the amount of chlorine required to determine a desired efficiency of the working of the ESP requires numerous other factors like the presence of other compounds like NO, $O_2$, steam, constituents of the fly ash particles, temperature of the stream, need to be considered. The objective of this research is:

1. To set up a reaction chamber in which chlorine plasma can be generated at standard temperature and pressure conditions, and the chlorine atoms generated in the plasma are collected in the sample bulbs containing Butane for analysis using the FTIR spectrometer.
2. To quantify the chlorine atoms collected at a particular time by reacting it with the Butane.
3. To study the trend of chlorine atom formation with variation in the residence time of the chlorine gas in the plasma chamber.

## Oxidation of elemental mercury with chlorine and chlorine containing species

Understanding the reaction pathway for the reaction between mercury and chlorine has been the objective of various research works for many years until date. This reaction has atmospheric implications because the atmospheric reactive halogen (chlorine) atoms react with abundantly available elemental mercury in the surrounding air, to form mercuric compounds which have a fatal characteristic of bioaccumulation (Ariya, et.al. 2002). Also, the reaction pathway is important for optimizing the mercury removal efficiency of a PEESP using chlorine as the reagent gas. Thus the kinetics of this reaction is important from a coal fired boilers' researcher's viewpoint, trying to minimize the pollutants from a boiler stack gas into the atmosphere. The data is available from literature that the most popularly postulated reaction pathway is the dissociation of chlorine molecules to form chlorine atoms that oxidizes the elemental mercury. The dissociation of chlorine molecules into chlorine atoms is thus an important and desired step from an environmental viewpoint because the oxidized form of mercury is readily soluble in water and hence can be easily scrubbed away with the residues collected from the electrostatic precipitator (Wilcox, et.al, 2004). The study of the combination of mercury and chlorine atoms dates back to the year 1968, when Horne, et.al. had done photolysis dissociation of $CF_3Cl$ molecules to form Cl atoms and then reacted them with elemental mercury vapor to study the formation of $HgCl_2$ and also $Hg_2Cl_2$ from the HgCl radicals . Using the absorption spectrum data of HgCl radicals, the kinetics of the reaction in 720 torr pressure and temperature of 110° to 170°C reaction conditions, was followed. It was concluded that the dimerization of HgCl to form $Hg_2Cl_2$ is second order in [HgCl]. Again in 2002, Ariya, et.al. further studied the same reaction products and kinetics at standard atmospheric pressure and temperature conditions , but now along with chlorine and also different halogen atoms and molecule and other natural oxidants as HO. The rate constant for the reaction $Hg^0 + Cl \rightarrow products$ is determined as $(1.0\pm0.4)*10^{-11}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$. The values of the rate constants of the reaction of vapor mercury with the molecular halogens infer that these reactions are not very important for mercury oxidations at atmospheric conditions. Li, et.al, 2003 had theoretically determined the rate constant of the reaction yielding mercuric chlorides from elemental mercury by reacting with chlorine species, using the Ab Initio MP2 method based on transition state theory for the following reaction system,

$$\begin{aligned}
&Hg + HOCl \rightarrow HgCl + OH \\
&Hg + HCl \rightarrow HgCl + H \\
&HgCl + Cl_2 \rightarrow HgCl_2 + Cl \\
&HgCl + HCl \rightarrow HgCl_2 + H \\
&HgO + HCl \rightarrow HgCl + OH \\
&HgO + HOCl \rightarrow HgCl + HO_2 \\
&Hg + HgCl_2 \rightarrow Hg_2Cl_2
\end{aligned} \tag{1}$$

The oxychloride is formed from the oxidation of chlorine species like HCl in presence of oxygen or ozone formed in the flue gas stream. The reaction rate constants determined for these reactions according to this mechanism agrees with their experimental conclusions, and also do not vary more than 0.4% from the rate constant value determined earlier. Then again in 2004, Wilcox, et.al, came up with the kinetic studies for the oxidation reaction of elemental mercury with chlorine atoms using computational methods. Using the already available data for the reaction set 1 from literature, and the

$$HgCl + M \frac{k_1}{k_{-1}} Hg + Cl + M \tag{2}$$

In the above equation, the M represents a parameter which does not take part in the reaction directly but helps in carrying out the reaction. It can be the catalytic wall effect for instance. Scrodinger wave equation solutions for molecular systems, they arrived at a value of $1.95 \times 10^{10}$ $M^{-1}$ $s^{-1}$ for the above reverse reaction or the reaction of the present study. Varying the concentration of M the rate constant for the reaction agrees well with data available from literature. This value had also taken into factual consideration the recombination rate of chlorine atoms with a collisional efficiency in the range of 0.1 to 0.2, and so in the equation (2) the M represents the wall effect on the reaction. In the plasma enhanced electrostatic precipitator, the chlorine atoms are formed due to the charged electron impact on the chlorine molecules near the cathode region. Since the number density of the chlorine atoms within the plasma region is an important factor affecting the rate of oxidization of the elemental mercury, steps should be taken to minimize the recombination of the chlorine atoms.

Kirillov et.al, 2002 used relaxation techniques to study the rate coefficient for recombination reaction of chlorine atoms to produce back chlorine molecules. The method is based on the principle of tracking the rate of the chemical system in plasma by measuring the change in concentration of the chlorine in the plasma region at different times corresponding to the intervals between current pulses supplied to the discharge producing the chlorine plasma. The rate coefficient for the wall catalyzed recombination reaction was determined = $389 \pm 58$ $s^{-1}$. Neuilly et.al, 2002 had determined the chlorine dissociation fraction in 'inductively coupled' chlorine plasma measured by UV spectroscopy. They arrived at a global model to explain the chlorine dissociation rate as a function of the source power and the gas pressure. The possible chlorine reactions in chlorine plasma stated in Neuilly et.al, 2002 are:

$$Cl_2 + e^- \to 2Cl + e^- \cdots Dissociation(k_{diss})$$
$$Cl_2 + e^- \to Cl^- + Cl \cdots Dissociative\,attachment(k_{dat})$$
$$Cl_2 + e^- \to Cl_2^+ + 2e^- \cdots Ionization(k_{ion})$$
$$2Cl + wall \to Cl_2 \cdots surface\ recombination(\gamma_{rec})$$

According to the kinetics of the above set of equations, the rate of conversion of chlorine molecules into atoms is given as:

$$k_{tot}[Cl_2] = (k_{diss} + k_{ion} + k_{dat})[Cl_2]$$

This model however may not be directly relevant to the present research interest mainly due to the differences in the plasma conditions. The inductively coupled chlorine plasma they had used is formed at very low pressures of the order of mili torrs and so these data and model can be more adequately fitted for low pressure plasmas. Effremov, et.al, 2003 were inquisitive about the 'active species' or the chlorine atoms in chlorine plasma and its chemistry. Again, an inductive chlorine plasma was generated in a quartz discharge cell with chlorine molecules excited with DC and RF discharges. A set of 19 reactions consisting of electron impact reactions, charged volume reactions, neutral volume reactions and heterogeneous reactions were stated by Effremov, et.al. It was concluded that electron impact dissociation and ionization are the two main steps to yield the chlorine atoms and radicals which are the 'active species' in chlorine plasma. The main difference between these works and this present research is the mode and condition of yielding the chlorine plasma. Because the present interest is in the chlorine plasma formed in a PEESP, the plasma is formed by electric discharge around the electrode through which the chlorine gas is injected and hence charged to form the cluster of charged and neutral chlorine species. The temperature and pressure conditions are maintained at atmospheric conditions. A research team in collaboration of MSE Technology, CRCAT and EPRI, Battleson et.al, 2003 performed a set of experiments to study the mercury removal efficiency of a plasma enhanced electrostatic precipitator using chlorine as the reagent gas under different set of simulated flue gas of varying constituents. The PEESP has demonstrated higher mercury removal efficiency when different chlorine species were added to the plasma region inside the precipitator. This further validates the importance of the oxidation of elemental mercury by the chlorine species.

There are actually numerous ways which helps to detect plasma properties. But in order to cope with the facilities and space available in the Stocker 045 lab, Ohio University, a novel method for tracking the chlorine atom formation from dissociation of chlorine molecules in the plasma region, has been devised. A sample is being collected from the plasma region and reacted immediately with a reducing gas which will yield products which can be analyzed for the chlorine atom concentration in the sample. Hydrogen as the reducing gas was explored at initial stages, but the hydrogen and chlorine reaction was found to be an exploding chain reaction which tends to go out of control. Besides analyzing for the low ppm values for the HCl or Hydrogen Chloride, we will be working with; using a gas chromatograph in the laboratory is not feasible. NOCl or Nitrosyl Chloride seemed to be a very good option for the reducing gas, at a certain point of time, but it was abandoned later for NOCl being a poisonous green gas and its hard to obtain nature for calibrating equipment purposes. Now, Butane (alkane) will be reacted with the sample to yield butyl chlorides and hydrochloric acid. The amount of the products formed, for a particular sample will then be analyzed with FTIR (Fourier Transform

Infrared Spectrometer). An elementary molecular balance for the said reaction can relate the amount of HCl formed can be directly to the actual amount of chlorine atoms present in the original sample collected from the plasma region, which reacted with butane. This particular reaction between the alkane and chlorine atoms is also being widely delved with in the literature. The absolute rate of the reaction is 1.94*$10^{-10}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$

**The reaction of chlorine atoms with Butane**

Nesbitt, et.al, 1982 have studied the $Cl_2$ and hydrocarbon reactions. They have chalked out a chain pathway for the reaction as:

$$\begin{aligned} &initiation: && Cl_2 \rightarrow 2Cl^{\cdot} \\ &propagation: && Cl^{\cdot} + RH \xrightarrow{k_1} R^{\cdot} + HCl^{*} \\ & && R^{\cdot} + Cl_2 \xrightarrow{k_2} RCl^{*} + Cl^{\cdot} \\ &deactivation: && HCl^{*} + M \rightarrow HCl + M \\ & && RCl^{*} + M \rightarrow RCl + M \end{aligned} \qquad (3)$$

In the above set of reactions, the dot superscript indicates an excited state substrate, which is also inherently very unstable. Assuming the reaction medium obtains a steady state, the Chlorine atom concentration is given in terms of the rate constant coefficients as:

$$[Cl^{\cdot}]_{ss} = [Cl_0]\frac{k_2[Cl_2]}{k_1[RH] + k_2[Cl_2]} \qquad (4)$$

Correspondingly, the chain rate constant for excess Butane condition is given by

$$k_{chain} = \frac{k_1[RH]k_2[Cl_2][Cl]_0}{k_1[RH] + k_2[Cl_2]} \qquad (5)$$

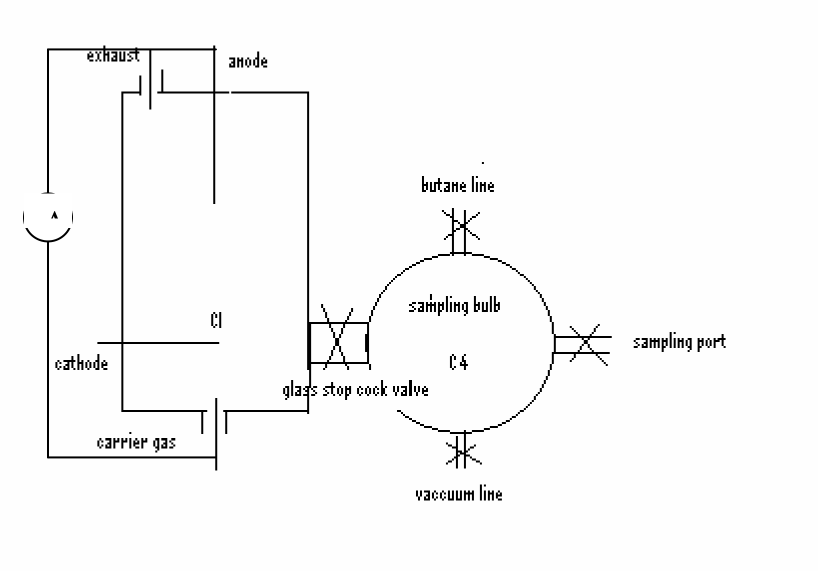
So when all the data is available of the quantities of butane and undissociated chlorine in a particular sample, and the $k_{chain}$ is known, the initial chlorine atom concentration can be back calculated. The research paper also points out that the deactivation kinetics for a reaction medium with excess butane is described as:

$$[Cl_2(t)] = [Cl_2]_0 e^{-k_2[Cl]_0 t} \qquad (6)$$

A closer analysis of the above expression will show that this expression can be very conveniently used for obtaining the chlorine atom concentration, ($[Cl]_0$) results for the present work. Hooshiyar, et.al, 1995 have studied the gas phase reactions of Cl atoms with different alkanes at a temperature of 296±2 K. The experimentation measured the rate constants for the reaction of chlorine atoms with different alkanes with reference to the rate constant for the reaction between the chlorine atoms and n-butane. The results indicate that the rate of the reaction increases with increase in the carbon number. So butane has been chosen as the reducing gas for the experiment, because higher gases become heavier and denser. Sarzynski, et.al, 2002 had explicitly studied the reaction of chlorine atoms with n-butane and iso-butane. With n-butane two reaction paths are possible, one yielding 1-chlorobuatne and the other yield 2-chlorobutane. The reaction yielding 1-chlorobuatne has a rate constant given by $(9.9 \pm 2.2) * 10^{-11} * e^{[-\frac{106\pm75}{T}]}$, and the reaction yielding the 2-chlorobuatne has the rate constant expression as $(13.0 \pm 1.8) * 10^{-11} * e^{[-\frac{104\pm50}{T}]}$. The composite reaction rate constant is determined to be equivalent to $1.94*10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Tyndall, et.al, 1996 further studied the relative formation of the two chlorides, and concluded that the reaction produces 21±2% 1-butyl chloride and the rest 79±2% 2-butyl chloride, and with an increasing total pressure, the branching ratio almost equals to 1 as the yield of 2-butyl chloride increases. The yield of chloro butyls and HCl is tracked with FTIR and GC and then the results were compared to conclude their parity.

**Set-up layout**

A schematic of the initial set-up is shown below. It has a main circular tube, termed as the plasma chamber, of dimensions 3cmX10cm, which houses the cathode and the anode.



It is a 3cm*10cm circular tube made of pyrex glass. It houses mainly an anode and a cathode. The anode is a stainless steel (100 mesh) plate. The cathode is a 2.5 cm long tube of internal diameter 1.5mm. It has 2 holes and a few projected thorns along the sides.

The chlorine gas is injected in through the cathode and it ejects into the plasma chamber through the holes along its longitudinal axis. The chlorine line, made of teflon tubing is used to prevent corrosion related problems due to carrying acid, and is connected to the cathode, from the $Cl_2$ cylinder to transport the chlorine gas into the cathode. The flow rate of the chlorine gas through the cathode is altered for different runs of the experiment to change the bulk velocity of the gas flowing through the plasma chamber. A rotameter on the line of the flow detects the flow rate of the chlorine gas at the inlet. DC voltage is applied to the electrodes using….. This charges the chlorine gas and the projections on the cathode concentrate the charge in their vicinity to form the plasma. The plasma region consists of dissociated chlorine atoms and undissociated chlorine molecules. The plasma chamber is also connected to the sampling sphere, aligned at a perpendicular axis, which is termed as the 'reaction chamber'. A solenoid valve opens and closes the path in between the two chambers. The reaction chamber itself is also connected to the vacuum line, the helium line, and the butane line. There is a vacuum pump at the end of the vacuum line. To start with, the reaction chamber is brought to a vacuum condition. The butane line and the helium lines are simple plastic tubing connected to the 99% research grade butane and helium cylinders respectively on one end and the valve openings to the reaction chamber on the other end. A pressure-monitoring meter is required on the reaction vessel. This will monitor the next step of filling the reaction chamber with Butane gas till a considerable pressure, $P_{\text{reaction chamber}}$ (of around 600 torr) is achieved. Now, by setting a certain pressure difference, ($P_{\text{reaction chamber}} - P_{\text{plasma chamber}}$) between the reaction chamber and the plasma chamber, a known volume of sample consisting of chlorine atoms and undissociated chlorine molecules is pulled from the plasma region into the reaction vessel. This reacts with the butane to yield butyl chlorides and hydrogen chloride gas. This whole piece of glassware is coated with halocarbon wax from the inside. This special coating is required to ward off the wall-effects on the chlorine dissociation reaction and so the experimental results.

**Optimizing the reaction environment parameters**

An optimization needs to be done to characterize the actual conditions in the experimental set up. The distance between the electrodes is hold at 2cm, and the voltage supplied to these electrodes is varied gradually and the corresponding current readings are noted. The minimum voltage to form the corona near the cathode and the maximum voltage when the corona breaks to form the arc-discharge between the electrodes are noted. The V-I characteristics of this particular set-up will help determine the optimum power-density to scale up the plasma chamber when required. (Battleson et.al). It also helps to determine the optimum voltage required to form the chlorine plasma inside the plasma chamber.

**The experimentation procedure:**

The valve on the chlorine cylinder is opened to let out the chlorine gas. By adjusting the escape pressure on the cylinder, the chlorine gas flow rate is set at 1.2 $\text{cm}^3$/sec. This flow rate is change to change the residence time of the gas inside the plasma chamber.

The minimum optimum voltage is applied to the electrodes to form the corona. This creates chlorine plasma in the vicinity of the sharp edges of the cathode.

The valve on the vacuum line from the reaction chamber is opened to create a very low pressure or vacuum in the reaction chamber.

Then the valve on the butane line is opened to the reaction chamber and the butane flows into the chamber till the pressure inside it is 600 torr.
After a certain time when the plasma region is assumed to have obtained a steady state, the valve on the connection to the reaction chamber is opened and the chlorine atoms and chlorine gas is swept into the later due to the pressure difference. The valve is left open till the pressure meter of the reaction chamber reads a 700 torrs.

The butane and the chlorine atoms are allowed to react for some time, when a steady state in the reaction chamber can be assumed.

The valve on the helium line to reaction chamber is now opened to allow the inert gas in, till the pressure is increased to a few torrs above the atmospheric pressure.

The valve on the sampling line is now opened and the reaction products are transported into the FTIR analysis cell.

The same 8 steps described above are then repeated for different set values for the bulk gas velocity in the plasma chamber.

The products of the reaction between butane and chlorine atoms in the reaction chamber constitute the sample to be sent to the FTIR cell for analysis. Teflon tubing, chosen for its non reactive and flexible properties, connects the sampling port on the reaction sphere and the inlet port on the FTIR gas-analysis cell. This Teflon lining is also required to be heated to prevent the hydrochloric acid from being condensed in the line. There are three ports on a typical gas cell, the inlet, the vent and the vacuum connections. For very low concentration analysis, a low pressure environment is necessary, which is created with a diaphragm vacuum pump connected through the vacuum connection on the gas cell. Then the sample is sucked into the cell through the inlet port till a pressure of about 600 torr is generated. A 750 ml gas cell has been chosen with a path length of 6.8 m, which can detect HCl concentrations as low as 100 ppm. After the analysis is done, the sample is purged out through the vent connection. Proper cleaning is done and the gas cell is then prepared for the next sample again.

**Calculating the chlorine atom concentration**

The FTIR analyses the reaction products for butane, butyl chloride and hydrogen chloride concentrations. Then from a simple molecular correlation on the reaction

$$RH + 2\,Cl = RCl + HCl \qquad (7)$$

the amount of chlorine atom reacted can be arrived at. In the reaction (7), the R represents the methyl or the $CH_3$ group in RH or the alkane. For every one mole of HCl generated a mole of Cl atoms have reacted and for every mole of RCl generated another mole of chlorine atoms have reacted. Hence [Cl] can be summarized as:

$$N_{Cl} = N_{HCl} + N_{RCl} \qquad (8)$$

In the equation (8), the N represents the number of moles of a species which is indicated by the subscripts. Knowing the moles of the chlorine atoms can be very conveniently converted to its concentration value, considering that volume of the reacting sample is known.

Using the volume of the gas inside the FTIR gas analysis cell as V, the number of moles of that particular species can be related as,

$$N_i = (Volume\ of\ the\ FTIR\ gas\ cell, V) * \frac{(concentration\ of\ the\ i^{th}\ species)}{(molar\ weight\ of\ the\ i^{th}\ species)} \qquad (9)$$

Besides, in the present experimenting conditions, the partial pressure of the butane in the reaction chamber is much higher compared to the partial pressure of the chlorine atoms. In this case, the number of moles of the Cl atoms reacted can be directly related to the moles of HCl. Referring to Nesbitt et.al a pseudo-unimolecular mechanism has been assumed for the above reaction 3.5.1. From the stoichiometry of the equation set (ref: reaction 2.4.1-5), when the [RH]>>50*[Cl], the Cl is the limiting reactant and is assumed to be totally consumed. In this case, the final exhaustion of the chain reaction has been described as

$$[Cl_2(t)] = [Cl_2]_0 e^{-k_2[Cl]_0 t}$$

So, if we can have the values of the concentration of the unreacted chlorine molecules after a time t, the initial concentration of the chlorine gas in the reaction chamber and the value for the $K_2$ from the literature, the initial concentration of the chlorine atoms that reacted can be arrived at.

Since the volume, pressure and temperature in the FTIR gas cell is known, the total number of moles in this cell is known. The components present in the FTIR cell are HCl, RCl , chlorine gas and the background Helium gas.

$$N_{Cl_2} + N_{He} = N_{total} - (N_{RCl} + N_{HCl} + N_{RH}) \qquad (10)$$

Thus, when the total and the individual number of moles of the HCl and the RCl can be analyzed by the FTIR, the number of moles of the chlorine gas in the cell can be calculated easily. Then this $[Cl_2(t)]$ can be fit into equation (2.4.3) to calculate the $[Cl]_0$.

$$[Cl]_0 = \frac{N_{Cl}}{V} \qquad (11)$$

The $[Cl]_0$ calculated in these two ways, first from the table 3.5.1 and then the result from the equation 3.5.5 can be compared. At this point, any discrepancies in the two values can be attributed to the error allowed due to the assumption of the gas mixture as an ideal gas mixture.

## Test Plan

The objective of this research work is to devise and set up an apparatus in which we create chlorine plasma at an atmospheric pressure and temperature conditions. For a particular value of the residence time of the chlorine gas injected in through the cathode, the reactive chlorine atoms are pulled out from the plasma region and reacted with butane to analyze for the amount of the chlorine atoms created. It is required to obtain the data set of chlorine atom concentrations for residence time of the chlorine gas inside the plasma chamber varying from 40 ms to 200 ms. A detailed approximated idea for the flow rate of the required chlorine gas and the carrier gas supply, to obtain a residence time of the chlorine gas inside the chamber in the range between the 40 ms to 200 ms is attached in the appendix A2. The flow rate of the chlorine gas is changed from 1.19 $cm^3/sec$ to 5.99 $cm^3/sec$ and the carrier gas flow rate is maintained at a value which is 98% more of the value of the flow rate of the chlorine gas. The various parameters while experimentation has been noted in the previous section. Initially, the voltage to be supplied, current flow inside the chamber, temperature and pressure conditions (which is to be maintained at standard conditions) and the inlet flow conditions of the various components are to be decided, and then the following steps to obtain the desired chlorine concentration values are to be designed.

1. The voltage is kept constant at an optimum value

Referring to the appendix A1, the minimum value of the voltage to create a corona in between the electrodes spaced at 2 cm from each other has been calculated to be equivalent to 20 KV. The optimization test for the current-voltage characterization of the plasma chamber helps to determine the working voltage for the later set of experiments. In consideration of the $V_{min}$ = 20KV as calculated before, a minimum voltage of 15 KV is selected to start the optimization experiments, and then gradually increased till a corona is observed and then to 25KV or till a higher value when an arc discharge is observed.

Also, to study the effect of the chlorine gas concentration inside the plasma chamber, if any, on the corona forming voltage, the chlorine gas is injected in through the cathode with a flow rate varying from 0cm$^3$/sec to 300 cm$^3$/sec for each instance of the voltage applied. It is expected that the chlorine gas velocity factor has a very negligible effect on the current flow measured as compared to the effect of the change in the voltage supplied. The case when an arc discharge is observed between the electrodes, the corresponding voltage is noted as the maximum voltage. The later experiments are to be operated at an optimum voltage, $V_{optimum}$ at which the apparatus is stable and a corona is formed between the electrodes.

2. The distance between the two electrodes is kept constant at 2cm. This value has been decided by me, for simplicity of designing the table top plasma chamber.

After setting the values of the voltage supplied, current and the distance between the electrodes, the next important objective is to find out the time after which the quasi-steady state condition in the plasma chamber may be assumed. Design gas velocity inside the plasma chamber is changed from 10cm/sec, 25cm/sec, 40cm/sec and 50cm/sec (reference Appendix A2). The number of data points is chosen as four or five to minimize the confidence interval for the results, as well as keep within the time constraints for finishing the experimentation(s). The time, $T_i$ for collecting the samples of the reaction products of the butane and the chlorine atom reactions is changed from 30 sec, 60 sec, 90 sec, 120 sec and 150 sec.

The gas velocity inside the chamber is the cumulative of the individual gas velocities of the chlorine and the carrier gases, considering the conservation of momentum principle, and is measured with a pitot tube. The residence time of the gas is obtained by dividing the distance traveled by the gas with the velocity with which the gas is flowing. (Refer Appendix A2). The chlorine atom concentration is obtained from the analysis done by the FTIR. When the chlorine atom concentration, corresponding to each gas velocity, is constant over the five T's, it can be assumed that after time $T_i$ (i=1,2,3,4,5), a quasi steady state can be assumed inside the plasma chamber. For the next set of runs of the experimentation, the sampling of the chlorine atoms from the plasma chamber into the reaction chamber will commence after the time $T_i$.

Experimentation is done to quantize the chlorine atom concentration for different residence time of the chlorine gas in the plasma chamber. The voltage applied to the system is kept constant at $V_{optimum}$. The temperature and pressure conditions are maintained at the standard conditions. The inlet velocities of the chlorine and the carrier gas is maintained such as to obtain the residence time of the gas inside the plasma chamber varying between 40 milliseconds and 200 milliseconds. The detailed calculations are referred from Appendix A2. The velocity of the chlorine gas is changed from 1.2cm$^3$/sec to 6cm$^3$/sec and correspondingly the velocity of the carrier gas is changed from 64cm$^3$/sec to 347 cm$^3$/sec .

The chlorine atom concentration for a particular residence time of the injected gas inside the plasma chamber is calculated from the HCl concentration (refer Appendix: ) It is expected that the obtained curve between the chlorine atom concentration and the residence time of the gas inside the chamber ,will resemble an increasing curve which can be accounted by the fact that the more time the gas is present in the chamber, the more it is dissociated and then it will attain a constant value after a certain value of the residence time which indicates the optimum residence time value for the chlorine gas or the reagent gas injection, and then it will gradually decrease , if we consider that the gas has actually resided for a very long time in the plasma region, when more chlorine atoms is recombining back into chlorine molecules. However, due to experimental constraints, it may happen so that the range of the residence time of the gas inside the plasma chamber when the chlorine atom concentration is gradually increasing may be missed out, and we obtain only a decreasing curve.

Appendix:

**A1: estimating the reaction parameters:**

The parameters for this experiment are as listed below:

The independent variables are :

1. Pressure and temperature, which is maintained at STP conditions.
2. The velocity of the gas in the plasma chamber, which is altered between 0.01cm/sec to 0.05cm/sec for different runs of the experimentation.
3. The voltage applied to the electrodes, which is maintained at an optimum value for creating a corona for a particular electrode placement.
4. The distance between the two electrodes: this is kept constant as 2cm, for this particular experiment.

The dependent variables are:

1. The chlorine atom concentration at the sampling point near the cathode region.
2. The residence time of the chlorine gas in the plasma chamber.

An estimation of the reaction parameters are computed using certain established mathematical relationships. However, once the test rig is actually set up, it needs to be optimized for these parameters.

1. *estimating the voltage required in the set up:*

There are two types of voltages associated with a corona. The voltage in which a corona is visible is termed as the *visible voltage*. The corona remains visible till the voltage reaches the *disruptive critical voltage*.

Basis of these calculations (as referred from Peek et. al.):

The cathode and the anode are arranged parallel to each other.

S is the distance between the two electrodes = 2 cm

r is the radius of the electrode wires = 1.5 mm

(For two wires in a parallel orientation, a corona does not form when $\frac{S}{r} < 5.85$ )

The visual critical voltage or the minimum voltage required to be supplied to the electrodes in this set up to form a visual corona is calculated as,

$V(\min) = mg\delta r(1 + 0.301/\sqrt{r})\ln(S/r)$

m implies the roughness of the wire = 0.98 for roughened wires

g is the disruptive critical voltage gradient, for two parallel wires has been experimentally determined as = 29.8 KV/cm

δ is the air density factor = 1 ( at atmospheric temperature and pressure)

Putting the values for each factors,

V(min) = 20 KV

The voltage supplied can be increased from 20 KV to change the strength of the electric field, till the disruptive critical voltage is reached. This is the computed value of the voltage to be supplied for the corona discharge. However, optimization of the current-voltage characteristics can be done only after the set-up has been built.

Capacitance in the wire is calculated as

$$Cw = \frac{5.55X10\wedge(-13)}{\cosh\wedge(-1)[\frac{S}{r}]} = 0.17 \text{ picofarads/cm}$$

Length of the electrode wire = 1.5 cm

Total capacitance stored in the wire = 0.17 * 10^(-12) farads

So, the energy in the wire = $0.5CwV\wedge(2)$ = 3.38*10^(-5) Joules

Energy required to dissociate 1 molecule of chlorine ≈ 10^(-18) Joules

An estimate of the number of chlorine molecules that can be dissociated in these voltage conditions = 3.38*10^(13)

Volume of the spherical tip of the electrode = $\frac{4}{3}\Pi r(tip)\wedge(3)$ = 5.2*10^(-4) $cm^3$

Concentration of chlorine which can be injected through the cathode that can be dissociated = $\frac{3.38*10\wedge(13)}{5.2*10\wedge(-4)*2.4*10\wedge(13)} \approx 2700ppm$

*2. estimating the velocity of the gas required in the plasma chamber:*

The typical velocity of the flue gas in a precipitator is between 0.91 m/sec to 4.4 m/sec (White et.al referred from Jayaram). A separate reference from Parker, et. al. referred from Lakshmi states that the gas velocity inside most cold-side ESP's have a velocity of 1 m/sec at atmospheric temperature and pressure conditions. The gas velocity is changed to obtain different residence times of the chlorine gas in the plasma chamber.

A sample calculation for the residence time factor for a gas velocity of 1m/sec in the plasma chamber:

When the distance between the two electrodes is 2 cm, the characteristic residence time can be calculated as:

$$t(characteristic) = \frac{0.02mt}{1mt/\sec} = 0.02\sec onds = 20mili\sec onds$$

## A2. Balancing the flow rates of the chlorine gas and the carrier gas to maintain certain velocity of the composite gas inside the chamber to obtain the desired range of its residence time

The basis of the estimations of the parameters to be used:

Assuming a minimum of 100 ppm of HCl can be detected in a FTIR gas cell of volume 750 ml having a pathlength of 6.8 m.

Volume of the FTIR cell = 750 ml

Moles of gas in the FTIR cell = $\frac{(1atm)*(0.75l)}{(8.314*1000l\,atm\,K^{-1}\,mol^{-1})*(298K)}$ = 0.0242126

A minimum of 100 ppm of HCl is present in the FTIR cell,

Moles of HCl in the FTIR cell = $(100ppm)*(0.024216moles)*10^{(-6)}$ =2.421*10^(-6)

Moles of chlorine atoms required to form the above number of moles of HCl = 2*2.421*10^(-6) = 4.843E-06
Assuming the chlorine is only 20% dissociated to form the chlorine atoms,
The number of moles of chlorine molecules required in the plasma chamber = 4.843E-07
Volume of the plasma chamber, $V = 3.14 * (1.5)^2 * (10) = 70.65 cm^3$
Total number of moles of gas in the plasma chamber = 2.852E-05
ppm of chlorine in the plasma chamber = $\frac{4.843\mathrm{E}-07}{2.852\mathrm{E}-05} * 10^6 = 16982 ppm = 1.7\%$ of Chlorine in He gas.
The matrix below tabulates the flow rates of the chlorine gas stream and the carrier gas stream to obtain the desired residence time of the gas in the plasma chamber.
Velocity of the gas in the plasma chamber, V(g) = $\frac{dis\tan ce\, between\, the\, electrodes}{resdience\, time}$
Area of cross section of the plasma chamber, $A = 3.14 * (1.5)^2 = 7.065 cm^2$
Volumetric flow rate of the gas, $Q(g) = V(g) * A$
Molar flow rate of the gas, $M(g) = Q(g) * \frac{P * V}{R * T}$
Molar flow rate of the chlorine gas stream (assuming the stream contains 1.7% chlorine in inert gas like Helium), $M(Cl_2) = (ppm\, of\, Cl_2) * (M(g)) * 10^{-6}$
Then the Q( $Cl_2$ ) is calculated as = $\frac{M(Cl_2) * R * T}{V}$
From these values, the volumetric flow arte of the chlorine gas stream and the carrier gas stream can also be calculated. $Q(He) = Q(g) - Q(Cl_2)$

| **resdience time (msec)** | **dist (cm)** | **V(g) (cm/sec)** | **A (cm2)** | **Q(g) (cm3/sec)** | **M(g) (mol/sec)** | **M(Cl2) (mol/sec)** | **Q(Cl2) (cm3/sec)** | **Q(He) (cm3/sec)** | **% Q** |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 2 | 50.0 | 7.065 | 353.2 | 0.014 | 24.549E-05 | 6.0 | 347.2 | 0.982725 |
| 50 | 2 | 40.0 | 7.065 | 282.6 | 0.011 | 19.639E-0.5 | 4.8 | 277.8 | 0.982725 |
| 75 | 2 | 26. 7 | 7.065 | 188.4 | 0.008 | 13.093E-0.5 | 3.2 | 185.2 | 0.982725 |
| 100 | 2 | 20.0 | 7.065 | 141.3 | 0.006 | 9.819E-05 | 2.4 | 138.9 | 0.982725 |
| 125 | 2 | 16.0 | 7.065 | 113.1 | 0.005 | 7.855E-05 | 1.2 | 111.1 | 0.982725 |
| 150 | 2 | 13.4 | 7.065 | 94.2 | 0.004 | 6.546E-05 | 1.6 | 92.6 | 0.982725 |
| 175 | 2 | 11.4 | 7.065 | 80.7 | 0.003 | 5.611E-05 | 1.4 | 79.3 | 0.982725 |
| 200 | 2 | 10.0 | 7.065 | 70.6 | 0.002 | 4.909E-05 | 1.2 | 69.4 | 0.982725 |

The flow rate of the carrier gas stream is changed from 69 $cm^3$/sec to a maximum value of 347 $cm^3$/sec. the flow rate of the carrier gas is maintained at a value which is 98% more than the flow rate of the chlorine stream through the cathode. This arrangement is to obtain the residence time of the gas in the plasma chamber varying from a minimum of 40 milliseconds to a maximum of 200 milliseconds.

## REFERENCES:

A.M. Effremov, et.al, “Volume and heterogeneous chemistry of active species in chlorine plasma”, Thin Solid Films, 435, (2003), pp. 83-88

Francois Neuilly, et.al, “Chlorine dissociation fraction in an ….by ultraviolet absorption spectroscopy” , J.Vac. Sci. Technol. A, 20(1), (2001), pp.225-229

Parisa A. Ariya, et.al, “Reactions of gaseous mercury with atomic and molecular halogens”, J. Phys. Chem. A 106, (2002), pp. 7310-7320

D.G.Horne, et.al, “Reactions of Metal atoms:….dimerization of HgCl”, The J. Chem. Phys. 48(10), (1968), pp. 4758-4764

Lai-Cai Li, et.al, “ A study on the reaction mechanism and kinetic of mercury oxidation by chlorine species”, J. Mol. Structure 625, (2003), pp. 277-281

Yu. V. Kirillov, et.al, “ Detemination of the rate coefficient for the ….by the relaxation technique”, High Energy Chemistry 38, (2004), pp. 203-206

Ralph Altman, et.al, “ Pilot scale test results on plasma enhanced electrostatic precipitation technology for mercury removal”.

Parisa Ariya Hooshiyar, et.al, “ Rate constants for the gas phase reactions of Cl-atoms with $C_2$-$C_8$ alkanes at T=296±2K”, Int. J. Chem. Kinetics 27, (1995), pp. 1197-1206

M. V. Malyshev, et.al, “diagnostics of inductively coupled plasmas”, J. App. Phys. 88(11), (2000), pp.6207-6215

David J. Nesbitt, et.al, “ laser initiated Cl2/hydrocarbon chain reactions”, J. Phys. Chem. 86, (1982), pp.4962-4973

G.S Tyndall, et.al, " Kinetics and mechanisms of the reactions of chlorine atoms with….and n-Butane”

Dariusz Sarzynski, et.al, “gas phase reactions of Cl atoms with propane, n-butane and iso-butane”, 2002 Wiley Periodicals, Inc.

Peek, F.W., Dielectric Phenomena in Hifh Voltage Engineering, McGraw-Hill, p.p 48-108

Montgomery John L, Battleson Daniel M, Whitworth Clarence G, Ray Isaac, Buckley Wayne, Reynolds James, Altman Ralph F, *Latest Developments of the Plasma- Enhanced Electrostatic Precipitator for Mercury Removal in Coal Fired Boiler Flue Gas*

Varalakshmi Jayaram, " capture of mercury in wet membrane PEESP using hydrochloric acid as the reagent gas" , November 2005

David J. Nesbitt and Stephen R. Leone, J. Phys. Chem. 1982,86,p.p 4962-4973