### CONTROLLING A FIELD TEST ELECTRON BEAM-GENERATED PLASMA SYSTEM FOR THE DECOMPOSITION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN AIR STREAMS

by

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#### Abstract

Present methods of treating hazardous chlorinated volatile organic compounds ("VOCs") in dilute concentrations in air are generally inefficient or very expensive. A new, low cost, energy selective treatment method under development uses a 150-175 keV electron beam to generate an atmospheric-pressure plasma through which the contaminated air stream flows. The plasma, and therefore the level of contaminant destruction, is highly controllable through the adjustment of electron beam voltage and current. This paper discusses the control aspects of an electron beam generated plasma reactor and its role in a complete field-test remediation system. Accomplishments include the automation of a 150-175 keV electron beam for computerized control, the incorporation of a Fourier Transform Infrared Analyzer as a setpoint generator for closed-loop control of the plasma reactor, and the implementation of a personal computer-based data acquisition and control system for the coordinated operation of the entire plasma reactor field test system. Initial field tests of the plasma remediation system will occur at the U.S. Department of Energy ("US DOE") Hanford facility through the US DOE VOC-Arid Integrated Demonstration.

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#### 1. Introduction

Twenty years ago, government and industry disposed of their toxic waste solvents by burying them in the ground. Chlorinated volatile organic compounds ("VOCs"), such as carbon tetrachloride and trichloroethylene, comprise the largest amounts of industrial solvents dumped. These hydrocarbons are routinely used in large quantities for metal degreasing, dry cleaning, and paint stripping. Many of these compounds, classified as hazardous, have induced cancerous tumors in lab rats, are suspected to be human carcinogens, and, in the presence of nitrogen oxides, form ground-level ozone, itself a hazardous compound[1].

The improper disposal and subsequent dispersion of these compounds into the groundwater creates a public health risk. Although the U.S. Environmental Protection Agency ("US EPA") heavily regulates the present production, distribution, and use of most hazardous materials in the U.S., much of the dumping occurred several decades ago, well before such regulations were enacted. Remediation, which consists of extracting toxic

solvents from soil and groundwater and treating them in preparation for final disposal, is quite expensive. Current extraction techniques are fairly successful in recovering VOCs. However, present treatment methods are ineffective. They can be expensive, can create hazardous byproducts, do not offer final disposal, or must be performed off-site.

Using low-temperature plasmas, researchers at the Massachusetts Institute of Technology Plasma Fusion Center ("PFC") and supported by the U.S. Department of Energy ("US DOE") through the Volatile Organic Compound-Arid Integrated Demonstration Program ("VOC-Arid ID") have developed a new, low cost technology for complete on-site treatment. Focusing on the chemical and physical nature of solvent decomposition by plasma processing, researchers at the PFC have studied the feasibility of using electron beam-generated plasmas to break up chlorinated VOCs in laboratory experiments. Initial investigations indicate that substantial savings in cost and energy expenditure may be possible by using plasmas instead of conventional technology for low concentration waste streams. However, the development of a complete field-operable demonstration system will act as a better indicator of the viability and cost-effectiveness of this process. Moreover, demonstrating automatic and remote control of the complete system would optimize the efficiency of the process and eliminate the need for around-theclock staffing during continuous-duty operation.

The author of this thesis has designed and implemented the automatic control infrastructure necessary for adaptive operation of a demonstration plasma reactor-based remediation system. The three major accomplishments in this work include the modification of a 150-175 keV electron beam for automatic control, the incorporation of a Fourier Transform Infrared ("FTIR") gas composition analyzer into a follow-up, limitcycle control loop, and the design and implementation of a personal computer-based control system for the coordinated operation of the entire system. As the author completed this work in context of a team engineering project, the author discusses, where necessary, background information and general aspects of the project.

This thesis is organized in the following way. Chapter Two focuses on the status of the new VOC remediation technology and the plans for field testing of the plasma treatment system. Chapter Three describes the author's work in designing and implementing automatic controls and indicators for the 150-175 keV electron beam. In Chapter Four, the author discusses the operation and use of an FTIR gas composition analyzer and its role in various closed-loop control algorithms. Chapter Five outlines the author's work in selecting and assembling instrumentation for a personal computer-based control system to oversee operation of the entire field unit. Chapter Six describes the projected layout of the trailer-based plasma remediation system, operation of the scrubber and dryer subsystems, and aspects of integrated control of the full system. Chapter Seven gives conclusions and suggestions for future work.

#### 2. Research Motivation, Accomplishments, and Goals

#### **2.1 Current Remediation Technologies**

Remediation of sites polluted by the improper disposal of these hazardous compounds requires two steps. First, the contaminants must be extracted from the soil or groundwater. Two present technologies -- soil vapor extraction and air stripping -- work to recover organic solvents from contaminated soil and groundwater. Both recovery techniques make use of the volatility, or high vapor pressure, typical of most VOCs. In soil vapor extraction, vacuum pumps suck air from wells cut into the contaminated ground. While soils exist as inhomogeneous solids, small air pockets reside between soil particles. The vacuum extraction process pulls the air from these pockets, and along with the air comes the evaporated chlorinated solvent. In air stripping, clean air is sparged or bubbled through the contaminated water. Hydrocarbons generally have low solubility in water. Thus, when presented with a medium for escape like clean air, the concentration gradient kicks the solvent molecules from the water into the air. The hazardous waste emerges from both soil vapor extraction and air stripping as an air stream near atmospheric pressure.

The second step of the remediation process involves the treatment of the air stream carrying dilute concentrations of gas-phase solvent. The four most common treatment alternatives presently used for gaseous VOC destruction are incineration, catalytic oxidation, gas-phase concentration followed by incineration or catalytic oxidation, and liquification followed by incineration or catalytic oxidation. As indicated below, none of these alternatives adequately treats low concentration gas streams.

The first of these alternatives, incineration, involves the burning of organic contaminants in flames. Incineration does not effectively treat low concentration (1-1000 ppm) streams because energy use is non-selective and therefore highly inefficient. Although many solvents will undergo combustion in a hot flame, a large fraction of the added energy goes towards raising the temperature of the background gas while only a small fraction actually destroys the contaminant molecules. In addition, maintaining a hot flame requires an auxiliary fuel stream, which upon its own combustion adds considerably to the overall mass of the waste stream. Finally, incineration of chlorinated VOCs produces phosgene, a highly toxic gas. Without scrubbing mechanisms to dissolve and break up this gas, release of phosgene after combustion may be more hazardous than the original VOCs. Although wet scrubbing technology is presently used on some incinerators, the cost of refitting existing incinerators with add-on scrubbers is apparently very expensive.

The second treatment method, catalytic oxidation, differs from incineration only by using catalysts to induce the same chemical reactions at lower temperatures. Although catalytic oxidation successfully reduces the high operating temperature necessary for solvent combustion, energy addition is still non-selective. Moreover, replacement of precious metal catalysts is generally quite expensive. As with incineration, this process also generates phosgene as a reaction product.

Gas-phase concentrators, the third current treatment alternative, work by adsorbing VOCs on porous media, such as granular activated charcoal ("GAC"). Adsorption in GAC canisters provides for excellent capture and recovery of low concentration solvents and, upon canister regeneration, results in higher concentration solvent streams more suitable for combustion. However, GAC is quite expensive. Moreover, using GAC requires an added stage in the waste handling process and does not provide for final disposal of the hazardous material. Unless an incinerator is available onsite, the waste canisters must still be transported to an incinerator or other suitable treatment facility.

Finally, liquification, the fourth treatment method, involves the use of membranes to liquefy the solvent waste stream. Membranes are not effective for treating low concentration streams because they require the VOCs to be near their saturation limit. Saturation implies a high concentration stream. As indicated earlier, soil vapor extraction and air stripping systems generally result in low concentration streams. Another problem with liquification is that, as with GAC, it does not offer final disposal: incineration or some other suitable final treatment, either on- or off-site, is still required.

# 2.2 Cold Plasma Processing: A New and Improved Remediation Technology

The inefficiencies of the current treatment methods demonstrate the need for an on-site, single-stage process for treating the dilute waste stream in a contaminant-selective and energy-efficient manner. A cold plasma process has been developed and tested in laboratory experiments at the PFC which satisfies these initial requirements. In addition, it creates primarily non-hazardous inorganic gases and salts as final waste products.

The cold plasma process consists of three parts. In the first stage, a desiccant dryer removes water vapor from the contaminated waste stream. In the second stage, an electron beam irradiates the dried gas stream, generating a highly-reactive lowtemperature plasma which decomposes the chlorinated VOCs into mostly carbon oxides, chlorine, and hydrochloric acid. In the third stage, a caustic scrubber stabilizes the still highly-toxic chloride compounds into sodium salts via acid-base chemistry, while the carbon oxides are vented to the atmosphere.

Although the first and third stages are established chemical engineering practices, the second stage represents an innovative use of plasma for chemical processing. In the second stage, an electron beam with electron acceleration voltages in the 150 to 175 kV range is used to create a highly-controllable atmospheric-pressure air plasma. At room temperature, air is composed of a mix of gases, dominated mostly by nitrogen and oxygen. Even though an extremely small fraction of this gas continually undergoes ionization by cosmic rays and natural background radioactivity, most gas atoms exist as bound, neutrally-charged molecules. The electron beam provides a source of electrons sufficiently energetic to ionize air molecules. The ionization products, including free electrons, excited atoms, radicals, and ions, are charged or excited.

Such a collection of charged, excited, and neutral particles is specifically called a non-thermally equilibrated plasma since each species (electrons, ions, neutrals) may independently exhibit a spread of energies not at all resembling a Maxwellian distribution. The electrons can heat up while the ions and background gas remain relatively cold. The useful property of such a reactive collection of particles is their ability to induce chemical reactions that may otherwise only occur at high temperatures. In particular, a type of chemical reaction known as dissociative electron attachment appears to drive the decomposition process for the chlorinated VOCs of interest through the ionization cascade.

Efforts at testing the viability of plasma-induced decomposition of chlorinated organic compounds started with the construction of a laboratory scale beam and reaction cell. At first, simple flow systems made from Tygon tubing, a rudimentary electron beam built from scavenged parts and equipment, and an elementary caustic bubbler were hastily assembled to test the principle. Various hardware upgrades, such as the switch to polished stainless steel flow tubing, a second generation reaction cell, and inclusion of a highquality gas chromatograph and thereafter a mass spectrometer, allowed for improved data accuracy. Benchmarks were established for destruction and removal efficiency, byproduct identification and quantification, and irradiation dose requirements for various contaminant inlet concentrations and air flow rates. Early work is documented in papers published in Physics Letters A in 1993 [2],[3].

The three compounds scrutinized so far include carbon tetrachloride, chloroform, and trichloroethylene. The experimental setup used in determining benchmark destruction and removal data for carbon tetrachloride (CCl<sub>4</sub>), trichloroethylene ( $C_2HCl_3$ ), and chloroform (CHCl<sub>3</sub>) is outlined in Figure 2.1.

Destruction efficiencies were measured as functions of the following parameters:

- electron beam voltage
- electron beam current
- air volume flow rate
- initial inlet concentration
- superposed sub-breakdown DC electric field voltage
- carrier gas composition, i.e. varied oxygen, nitrogen, and argon concentrations
- air stream water vapor content, i.e. relative humidity

The results of this data, generated by Mathias Koch and discussed in detail in his doctoral thesis, show the anticipated strong dependence of decomposition on increased beam current, decreased air mass flow rates, and decreased initial inlet contaminant concentrations. Observed destruction requirements for CCl<sub>4</sub> range nearly exponentially up

from approximately 40 eV per molecule at 60% destruction efficiency to about 100 eV per molecule at 95% destruction efficiency.  $C_2HCl_3$  destruction requirements were observed to be one order of magnitude lower than those for CCl<sub>4</sub> with a similar approximately-exponential dependence on destruction efficiency [4].



Figure 2.1: Diagram of experimental setup for initial tests of CCl<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub>, and CHCl<sub>3</sub> destruction [2].

Figure 2.2 shows representative destruction efficiencies for dry carbon tetrachloride decomposition achieved with the lab beam, displaying exhaust concentration as a function of absorbed dose and initial inlet concentration. Absorbed dose is calculated from beam power, air mass flow rate, and power deposition efficiency.



Electron Beam Power Deposition [kW/(kg/s)]



Measured byproducts from carbon tetrachloride and trichloroethylene decomposition include primarily chlorine gas, hydrochloric acid, carbon monoxide, and carbon dioxide. Measured intermediate byproducts include phosgene for carbon tetrachloride and both phosgene and dichloroacetyl chloride for trichloroethylene. Use of conventional scrubbing with a basic solution effectively stabilizes each of the above chloride compounds. For this reason, a packed-tower scrubber was included downstream from the plasma reactor in the demonstration system design.

For carbon tetrachloride and chloroform decomposition, reductions by factors of two to four in dose requirement were observed for streams dried to under 150 ppm water vapor compared with humid streams of greater than five percent relative humidity. For this reason, the desiccant dryer was added upstream of the plasma reactor in the field system design. This relative humidity effect was not observed in trichloroethylene decomposition.

#### 2.3 Controlling a Cold Plasma Processor

Notwithstanding the impressive results of the laboratory experiments, the viability of the cold plasma treatment system can be proven only through on-site field testing. To date, the effort has focused primarily on the study of the chemical and physical mechanisms involved in VOC decomposition via the cold plasma process. To truly gauge the cost-effectiveness of the process, however, a mobile field-test demonstration system, consisting of an operational trailer-housed plasma reactor with gas drying and scrubbing subsystems, is being developed at the PFC. A major factor in the cost-effectiveness of the plasma process is the capacity for remote, unmanned operation. Consequently, the author has designed and implemented an adaptive, computerized control system as an integral part of the demonstration unit.

Including a control system in the demonstration unit provides many benefits. A major motivation for automatic control of the plasma reactor in a remediation system is to eliminate the around-the-clock manpower requirement and significant associated cost that comes with continuous-duty operation. Second, significant gains in efficiency can be made by employing an adaptive control algorithm which can automatically tune process parameters according to changes in inlet stream conditions. Finally, once fully

computerized control is enacted, the jump to remote control is simply a matter of computer-to-computer communication, a common capability with modern computer technology.

As the above empirical destruction data indicate, there exists a strong correlation between contaminant destruction efficiency and absorbed dose. Thus the goal of an automatic control system is to dial in the proper absorbed dose to destroy the inlet VOCs to a sufficient level for any given inlet concentration. A minimum of three out of four system variables must be prescribed to determine the dose and destruction state of the plasma reactor system for any given inlet concentration. Those are the beam acceleration voltage, the beam current, the air mass flow rate, and the desired final exhaust concentration. The work performed for this thesis involved establishing the ability to control the state of the plasma reactor via this set of variables.

The control system is comprised of various electrical and mechanical hardware components, two computers, and a half-dozen computer programs. These are configured to offer measurement and control of all the important plasma reactor parameters from the computer terminal. Three major steps were performed by the author towards the automation of the plasma reactor system.

The first step was the design and implementation of personal computer-based data acquisition and control instrumentation. This included selection and installation of proper analog and digital input/output electronics, signal conditioning and isolation hardware, and a graphically-oriented software system for the measurement, control, and display of all important system functions and variables. Execution of this step required integration of both hardware and software components.

The second step was the conversion of an Energy Sciences Inc. CB 150 Electrocurtain System electron beam to a computer-controlled plasma reactor. This was accomplished via the design and installation of several large electrical circuits, including beam voltage and current transmitters and an array of motor-driven variable transformers. This step was strictly hardware oriented.

The third step was the incorporation of a KVB/Analect Diamond 20 Fourier Transform Infrared Gas Analyzer as a setpoint generator in a closed-loop adaptive control scheme. This included writing several software-implemented routines enabling serial communication with the analyzer system and employing various models for generation of setpoint information from gas composition data. Execution of this step was primarily software oriented, as the Diamond 20 was installed preconfigured by KVB/Analect for the present measurement needs. However, understanding and adjusting the preconfigured software, as well as development of original programs, were prime accomplishments.

Although many additional engineering tasks were performed along the way, these three form the basis for rudimentary control of the complete system. Due to shipping and construction delays, the full plasma reactor system was not available for a complete demonstration of the control system at the time of this writing. However, tests of the individual hardware components, such as the automated beam circuit, and implementation of closed-loop software algorithms closely resembling those to be used in operation of the final system each proved successful in benchtop demonstrations. A full demonstration will be performed shortly, as the remaining construction work reaches completion and final preparations for field testing are made.

#### 2.4 Field Test of Cold Plasma Processor at Hanford, WA

The first field test of the cold plasma processor will be at the Hanford Reservation, a former weapons production facility operated by the US DOE located near Richland, WA. In the past, many pits, cribs, and trenches where dug for use as dumping grounds for organic solvents at Hanford. One of the largest environmental cleanup operations presently underway at Hanford involves a large quantity of carbon tetrachloride that had been directly discharged into the soil. Although carbon tetrachloride had long been available as a household cleanser, its commercial ban by the US EPA in the 1970s prompted the end of its wholesale manufacture and subsequently reduced the threats of continuing carbon tetrachloride pollution. However, the ban came too late to prevent the Hanford problem: several hundred thousand gallons of carbon tetrachloride were discharged to cribs in the soil between the 1950s and 1970s. As of June 1993, an estimated 95% of the initial amount still presently pervades the soil vadose zone, the layer of soil between the surface and the water table. The arid soil structure at Hanford prevents rapid transport of suspended contaminants, yet groundwater samplings revealing concentrations as high as 8000 ppb, 1600 times the US EPA drinking water standard,

indicate that carbon tetrachloride is definitely leaching from the vadose zone to the water table.[5]

The US DOE Office of Technology, Development, Environmental Restoration and Waste Management launched the VOC-Arid ID in order to spur development of new VOC monitoring, recovery, and destruction technologies necessary to better handle the enormous soil remediation tasks ahead. As a participant technology in the Integrated Demonstration, the electron beam-generated plasma system will be used in field testing of chlorinated VOC destruction on the Hanford site. The trailer-housed plasma reactor will process a partial stream from a presently-operating soil vapor extraction unit in both shakedown and endurance trials.

If the demonstration field test goes as planned, then the commercialization of electron beam plasma technology may be shortly realized. Use of electron beams with higher voltages and larger current capacities, larger scrubbing and drying towers, and reaction cells designed for high power deposition efficiency could increase process throughput dramatically. Pilot scale unit operations would facilitate the cleanup of both the Hanford plume and other government and non-government sites contaminated with chlorinated VOCs. Further laboratory research into the decomposition of other types of solvents or hazardous compounds and identification of their reaction byproducts will complement field operations.

#### 3. Automation of an Electron Beam for use as a Plasma Reactor

The plasma used to decompose chlorinated solvents in air streams is generated by a moderate-voltage electron beam. Modification of the commercially-manufactured beam was necessary to prepare it for computerized operation. This chapter describes the plasma generation mechanism, the author's work in upgrading the electron beam to motorized, computer-interfaced control, and the performance aspects of the plasma reactor cell as presently configured.

#### 3.1 The Plasma Reactor

The ionization-driven plasma is generated by a 150-175 keV electron beam. Electron beam technology has matured for the past century. Early experiments in electrostatics resulted in rudimentary devices producing controlled streams of electrons. Vacuum-tube electronics and television picture tubes of today consist of basically the same elements. Specifically, within an evacuated enclosure a heated filament -- or thermionic cathode -- acts as a source of electrons. A high voltage acceleration grid speeds the electrons up to high energy. Voltages applied to various shaping electrodes control the beam direction and beam current or intensity. See Figure 3.1 for a simplified discussion.

In the case of a TV tube, the electrons in the beam are only accelerated to an energy (~18 keV) sufficient to excite the phosphor coating on the inside of the screen, and voltages applied to the up-down and left-right pairs of shaping electrodes raster the beam back and forth across the screen to produce picture images. In the case of the electron beam used as a plasma generator, a linear filament produces a sheet of electrons which spans the length of the vacuum enclosure, eliminating the need for rastering. Also, the beam acceleration voltage is sufficiently high that the electrons pierce through the equivalent "picture screen", a thin titanium foil window, and continue on into the atmospheric-pressure air. For our beam and similar commercially-available hardware, acceleration voltages are sufficiently low (below 300 kV) that radiation shielding requirements are moderate, and a labyrinthine lead liner, along with safety interlocks and radiation leakage detectors, acts as a built-in part of the safeguarded, self-shielded beam housing.

Although many electrons are slowed down in the foil and a few are stopped entirely, many succeed in passing entirely through the foil barrier while retaining sufficient energy to ionize the air. In keeping with the TV tube analogy, the ionized air glows somewhat like a picture tube, in both cases stemming from deexcitation of raised atomic



Figure 3.1 Simplified representation of plasma decomposition process.

and molecular energy states. The glow is typical of many plasmas, and the beam configuration is called an air discharge. The primary (i.e. fast, high energy) electrons in the discharge collide with air molecules to produce many secondary (i.e. slow) electrons along with the corresponding ion fragments. As a rough estimate of the number of secondary electrons generated, approximately 35 eV of energy is required in general to generate an electron/ion pair. Therefore an electron accelerated to 150 keV produces about 150 keV / 35 eV or ~ 4500 secondary electrons. Free electron-induced chemical reactions, known as dissociative attachment reactions, describe to a great extent the decomposition process of the chlorinated organic molecules we have examined. The dissociative attachment chemistry resembles high temperature flame oxidation in which oxygen rather than a free electron-dependence and in their reaction product distribution.

#### **3.2 Electron Beam Modification**

The 150-175 keV electron beam is the model CB 150 Electrocurtain System manufactured by Energy Sciences Inc. ("ESI"), Wilmington, MA. The physical beam variables available to the operator for changing the properties of the plasma include the beam acceleration voltage and the beam current. The voltage setting influences how fast the primary electrons can go, while the current setting influences how many primary electrons participate. Proper manual adjustment of these settings and of the air flow through the reactor enables sufficient destruction for the given inlet VOC concentration. Motorized adjustment additionally provides the ability for computerized or remote control and for optimized beam utilization for time-varying inlet conditions.

From off the factory floor, the ESI CB 150 beam required two major alterations. The first involved converting it to a gas processor, the second involved adding automated controls. Normally, this model of beam, a small version of ESI's production units, sees use in irradiating trays of plastic or thin-film coated parts and webs of polymer sheet and plastic-coated paper. Beam energy initiates crosslinking of the polymer chains in the plastics, induces bond scissions and grafting in certain molecular structures, rapidly heats and cures plastic coatings, inks, and dyes, and sterilizes medical instruments or tools. ESI performed the first modification, namely replacing the conveyor system used for moving



Figure 3.2: Diagram of plasma reactor.[6]

parts trays with a titanium reaction chamber, titanium ductwork, and new lead shielding to cover the duct (see Figure 3.2 and Figure 3.3). The author performed the second modification, discussed below.



Figure 3.3: Electron beam schematic diagram.[7]

ESI designed the CB 150 primarily for use in laboratory prototype testing, for quality control of larger processes, and for small pilot plant operations. The operator is given only manually-operated dials and switches to control the available beam parameters, including the acceleration voltage, the beam current, and the cathode filament power. In order to ready this beam for automatic control, computer-interfaced replicas of all the available user controls and indicators were installed in parallel with the existing ones. For control of the voltage, current, and cathode power, this meant installing motor-actuated variable transformers in parallel with the existing manually-actuated transformers. For measurement of the beam voltage and current, this meant installing viewing resistors with 4-20 mA transmitters in series with the existing panel meters. This second alteration was conceived and performed by the author with consultation from Paul Thomas, Technical Supervisor at the PFC.

Figure 3.4 shows the part of the original transformer circuit and part of the new circuit, using the beam high voltage (VAT3 on the CB 150 circuit diagram) as an example of the changes made. Output from the variable transformer, adjustable approximately from zero to 120 VAC, is fed to a step-up transformer in the high voltage power supply assembly. The step-up transformer produces the useful 150 to 175 kV acceleration voltage that drives the beam. Addition of a motor-actuated variable



Figure 3.4: Sample of original and modified variable transformer circuits.

transformer in parallel with the original transformer, along with a switch to select which transformer is used, allows for motorized control of the acceleration voltage. In reality, the selector switch is a heavy-duty electromechanical relay, since the circuit must carry a maximum current of nearly 20 A at 120 VAC. The drive motor requires 120 VAC input and a pair of switches or relays to produce either clockwise or counterclockwise rotation of the variable transformer. The discrete, binary action of opening and closing switches is an easy task for just about any computer.

Two of the front panels were removed from the CB 150 and replaced with two new panels, one to accommodate the three additional variable transformers and another to accommodate a switch network. As a safety precaution, a lock-out circuit was employed to ensure that a change in the selection of transformers -- manual to motorized or vice versa -- could not be made while the beam is turned on. Also, although motor switching was made available for control computer, additional selector switches wired in parallel retain adjustability at the front-panel. Indicator lights and motor shaft position pointers annunciate the status of manual-versus-motorized control and variable transformer angular position.

Computerized adjustment of beam parameters is quite important, but equally important is the computerized measurement of parameter values. To accomplish this, the author installed viewing resistors in series with the existing beam voltage and beam current panel meters. The panel meters have needles which deflect due to D'Arsonval movement. Current flowing through the meters produces this movement. The same currents that flow

through the meters flow through the added viewing resistors, and the resulting voltage drop (on the order of one volt) gives a proportional representation of the beam voltage and current. The viewing resistor voltages are sensed by two 4-20 mA current loop transmitters, which then transmit a noise-resistant current signal to the computer.

As a measure of redundancy, angular position potentiometers were mounted by the author on the motor-driven variable transformers. Each motor shaft drives a gear train which simultaneously turns the variable transformer shaft and a potentiometer shaft. Potentiometer voltage outputs ranging from around two to four volts give a representation of transformer angular position. When the beam functions properly, a one-to-one mapping exists between the beam parameter values and their corresponding position values. If the corresponding values deviate from their mapping beyond an acceptable range, then there is a strong indication that the beam is running improperly. If the deviation is slight, the computer annunciates an error on the monitor; if the deviation is huge, the computer shuts the system down until the offending error is diagnosed and righted.

#### **3.3** Plasma Reactor Dimensions/Air Stream Parameters

Physically, the plasma reactor is an approximately one inch length cross section of a six inch by one inch titanium duct. A 25  $\mu$ m-thick titanium foil window separates the irradiated atmospheric air stream from the evacuated space where the electrons are generated and accelerated. A hole in the top reactor wall cut to the same area as the foil window provides the entrance for accelerated electrons into the air stream. The mean

slowing-down distance, called the range, of a 175 keV electron in air is about 30 cm, whereas the range of a 175 keV electron in titanium is about 75  $\mu$ m.[8] Accurate modeling of the electron slowing-down cascade requires a more sophisticated analysis, but these rough numbers indicate where most of the beam power is deposited: in the first millimeter-thick skin of the back reactor wall.

Thus the small depth of the reactor, one linear inch, ensures a stiff, uniform radiation profile across the reactor. The spatial shape of the absorbed dose profile, however, depends on the shapes of both the radiation profile and the flow velocity profile. To keep scaling of reactor capacity independent of reactor volume, these profiles must be kept as flat as possible. Plots of radiation profile (see Figure 3.5), measured by ESI, and flow velocity profile (see Figure 3.6), measured by the author using a heated-thermistor anemometer, verify flat profile shapes for this particular beam and duct combination. Power deposition efficiency was sacrificed to ensure dose uniformity, but the flat shapes of these plots indicate that first-order approximated scalings to larger units can be done independent of reactor shape or volume. Extensive modeling of the dose penetration profile with a Monte Carlo-type analysis was beyond the scope of this work, but such an analysis will be performed to improve reactor shape and depth and thus ensure high power deposition efficiency in a commercial unit.



Figure 3.5: Electron beam irradiation uniformity profile.[9]



Figure 3.6: Air velocity uniformity profile.

Although the operating air volumetric flow rate will depend on the inlet concentration, the design flow rate covers a range from two to ten cubic feet per minute. The wetted perimeter of the reactor is fourteen inches, and therefore the Reynolds numbers which describe air flow through the reactor range from 80 to 800. Flow is in the transition regime, which, although not fast enough to go fully turbulent, does exhibit a nearly flat velocity profile across the width of the duct. For the given design flow rate range, reactor residence times range from 20 to 100 milliseconds. Residence time for the entire system ranges from approximately 200 milliseconds to two seconds. For similar destruction efficiencies, remediation technologies with short residence times are desirable to expedite site cleanup.

At a stable operating point, volume flow rate remains fairly constant. However, air mass flow rate can be adjusted by throttling the flow with a pair of restrictor valves, specifically motor-actuated butterfly valves. In the system, there are two blowers in series, one at the dryer inlet and one at the scrubber outlet, and the design flow rate is well below the nominal flow rates of both of these blowers. Even though this configuration provides the over-capacity to process high flow rates of very low concentration VOCs, at higher concentrations where low flow rates are a necessity, the blowers fight the flow restrictions and each other. Although the throttled configuration results in greater stress on the blowers and lower pumping efficiency, the net power loss is negligible in comparison with the rate of beam power consumption. The throttled configuration also allows for adjustment of the pressure in the flow channel and scrubber, which should as a safety

measure be kept slightly below atmospheric pressure to prohibit gas leaking out from seals, seams and pipe fittings.

#### 4. On-line Gas Composition Analysis and Feedback Control

The ability to measure the constituent compounds in the initial inlet and final exhaust air streams is critical for characterizing process performance. In addition, confident measurements of species concentrations can be used to establish adaptive control of the plasma decomposition system. This chapter covers the operation and use of an infrared gas composition analyzer and work done by the author towards employing this analyzer in closed-loop algorithms for controlling the plasma reactor system.

#### 4.1 Experience with Gas Analysis

In our lab experiments, a gas chromatograph and a mass spectrometer, specifically the Hewlett Packard 5890 Series II Gas Chromatograph, Hewlett-Packard, Wilmington, DE, and the Hewlett Packard 5971A Mass Selective Detector, Hewlett-Packard, Palo Alto, CA, have been used to perform chemical analyses of the daughter products from the destruction of carbon tetrachloride, chloroform, and trichloroethylene. For carbon tetrachloride decomposition, these analyses yield evidence of phosgene as an intermediate by-product, and chlorine gas, hydrochloric acid, carbon dioxide, and carbon monoxide as the only stable byproducts. For trichloroethylene decomposition, dichloroacetyl chloride is an intermediate by-product in addition to the same set of by-products as for carbon tetrachloride decomposition.

Incorporation of a high-quality analytical chemistry instrument into the field-scale electron beam reactor system is necessary not only for adequate waste stream characterization and byproduct identification, but more importantly for this work to provide a means for feedback control of important physical and chemical variables. The compositional monitor selected for use in the field system is the Diamond 20 Fourier Transform Infrared ("FTIR") Analyzer manufactured by KVB/Analect, Irvine, CA. In addition to the Diamond 20 analyzer, a Bruel & Kjaer 1302 Multi-gas Monitor infrared absorption analyzer will be used as a backup, redundant measurement of final exhaust. Performance aspects common to the FTIR and other established analysis technologies are briefly reviewed in the following section.

#### 4.2 Compositional Monitor Performance Criteria

Many types of compositional monitors are readily available on the market, and improvements to those instruments are continually sought by both the device vendors and end-users. Although many measurement applications have special requirements, for the measurement of the various components of a gaseous air stream, a handful of technologies dominate the market. The few most prevalent technologies include gas chromatography, mass spectrometry, infrared spectrometry, ultra-violet/visible spectrometry, and x-ray activation spectrometry. There are also many subordinate branches within each of these categories, each a specialization of the parent technology geared towards particular physical and chemical conditions.

For applicable measurement conditions, every compositional analyzer must be able to identify and quantify chemical components in the sample under investigation. Design criteria for which any such analyzer is constructed include:

- calibration accuracy: agreement between accepted standards and model values (i.e. from interpolation, curve fitting, etc.) which then predict measured values
- measurement accuracy: agreement between accepted standards and measured values
- measurement precision: measure of repeatability of measurement values for identical sample composition and conditions
- resolution: measure of minimum detectable difference between measured compositions
- dynamic range: range of measured variable over which measurement accuracy remains acceptable
- detection limit: lowest measurable quantity with sufficient measurement accuracy; bottom end of dynamic range
- saturation limit: highest measurable quantity with sufficient measurement accuracy; upper end of dynamic range
- robustness: ability to tolerate all types of compounds without substantial deterioration
- reliability: weighted sum of accuracy, precision, availability, robustness, and periodicity of maintenance; usually only a qualitative criterion
- repeat rate: measure of minimum time necessary between successive measurements
- calibration stability: measure of maximum time allowed between calibrations without unacceptable degradation of calibration accuracy
- cost: capital cost of system, service charges, maintenance costs, training and configuration time

In our experience, the GC/MS arrangement provided excellent calibration and measurement accuracy, precision, and resolution, yet proved disappointing in issues of cost, robustness, reliability, configuration time and effort, and, especially for the MS, calibration stability and robustness. Although the GC/MS configuration is the official US EPA standard for quantitative analysis of chlorinated hydrocarbons, the KVB/Analect FTIR was selected in place of a GC/MS system in hopes of gaining improved simplicity of operation, faster repeat rates, lower capital and operating costs, and a recalibration period on the order of six to twelve months instead of six to twelve days.

# 4.3 Gas Analysis by Fourier Transform Infrared Spectrometry

The three components of the KVB/Analect FTIR system include the infrared spectrometer with gas analysis cell, a gas sampling manifold and a data analysis computer.

An infrared spectrometer is an analytical instrument that passes IR radiation through a substance and measures its absorbance. Because each substance has a characteristic absorbance pattern -- absorbing some wavelengths but not others -- the substance can be qualitated or identified. And because the amount of the substance is proportional to the amount of absorbance, the substance can also be quantitated.

The spectrometer components include an interferometer, a gas analysis cell, and an IR detector. The historical Michelson interferometer is comprised of an IR source, a fixed beam splitter, an IR detector, and two mirrors, one fixed and one moving. KVB/Analect's Transept interferometer includes the IR source and detector, but substitutes two fixed corner cube mirrors and a sliding-wedge beam splitter for the other three components. This fixed-mirror arrangement provides for great stability against misalignment of the IR beam and consequently allows for recalibration periods on the order of six to twelve months.



# A Simple Michelson Interferometer

The Transept Interferometer

# Figure 4.1: A simple Michelson interferometer and the KVB/Analect Transept interferometer.[10]

Although a detailed description of the operation of the interferometer is beyond the scope of this work, a brief description is necessary to understand how the instrument functions. The basic unit of information produced by the interferometer by a single traverse of the beam-splitter is called the scan. A scan produces a temporal interference pattern detected by the IR detector as changing transmittance (or absorbance) levels. Since the IR source is broad-band, information from all transmitted wavelengths contributes simultaneously to the detector signal -- or interferogram -- in the time domain. Information concerning each individual wavelength is extracted by Fourier transforming the interferogram into the frequency domain. The transformed interferogram is called the spectrum, and the IR spectrum for any given substance is a "finger-print" for that substance. A single scan takes less than one second, yet accuracy and resolution improve through averaging many scans and therefore result in slower repeat rates. For two wavenumber IR absorbance resolution (equivalent to about 1 ppm concentration resolution), repeat rate is about sixty seconds.

The spectrometer operates in conjunction with the sampling manifold and the data analysis computer. The sampling manifold controls which gas streams are sampled in what order. The data analysis computer runs a suite of software programs that perform different mathematical and graphical display operations on the raw scan data to produce useful composition information. The first operation is the Fourier transform of the interferogram to produce the raw spectrum. To improve accuracy, the computer averages several scans of the same sample into a mean spectrum. The mean spectrum is ratioed against a background spectrum to subtract the baseline signal due to air. Absorbance peaks in the baseline-subtracted spectrum are compared with peaks collected in a matrix of calibration spectra generated from standards of known composition and concentration. If the peaks from an unknown composition occur at the same wavelengths as for a calibration standard, then (barring interferences from other substances) the computer identifies the unknown substance. The computer then calculates the concentration value for the identified substance from the ratio of peak areas.

#### 4.4 Adaptive Control

Often compositional monitors are used strictly as monitors. Scientists or engineers use the output from such detectors either to gather scientific data or to ensure process quality. Changes made to the system under observation are performed after a human observer recognizes a need for system change, makes a decision to change the system, and finally intervenes to alter available system parameters. Although this essentially provides for system feedback, human intervention is required for the loop to complete. This control action is called an open feedback loop. If the operator fails to respond to system disturbances, then the system may not operate in its intended manner. For continuous-duty systems, such as a field-operated remediation system, a closed feedback loop is preferable. In a closed feedback loop, either electrical circuitry or computer intervention provides the path whereby on-line information can be used to automatically manipulate the system parameters. The faster the feedback loop executes, the faster a system can respond to and correct for disturbances or setpoint changes.

Simple feedback systems employ limit cycle operation to control the plant, a realworld physical quantity and usually represented by a single mathematical variable. The quintessential control example is a thermostat. In this case, the plant consists of a spaceheated or air conditioned room, and the physical variable of interest is the temperature. In generic limit cycle systems, a setpoint, usually with upper and lower alarm limits, determines the desired operating point, and a measurement transducer determines the actual value of the physical variable. If due to external disturbances the physical variable drifts beyond either alarm point due to some disturbance, an actuator provides a means to correct the drift until the alarm point is again satisfied.



Figure 4.2: Diagram of a simple, generic feedback loop.

In the thermostat example, if a thermostat is set to  $70^{\circ}$  degrees, the alarm points are probably  $68^{\circ}$  and  $72^{\circ}$  degrees. If the measured temperature falls below  $68^{\circ}$ , then the heater turns on until the temperature rises to  $70^{\circ}$ . If the temperature rises above  $72^{\circ}$ , then the air conditioner turns on until the temperature falls to  $70^{\circ}$ . Systems which act to maintain a constant setpoint in spite of external disturbances are called regulator systems. Those which respond to a continuously-varying setpoint are known as follow-up systems. Since the inlet concentration of the plasma reactor changes over time, the adaptive control sequence for the plasma remediation system is categorized as a follow-up, limit-cycle control algorithm.

Although limit cycle or "bang-bang" control is fairly easy and usually quite inexpensive to implement, control errors may sometimes occur. If the heater turns on at 68° but the temperature overshoots beyond 70°, the temperature may oscillate between 68° and say 71° and never actually settle right at 70°. This is known as chattering. If the heater turns on at 68° and overshoots beyond 72°, then the air conditioner will turn on to force the temperature back down, and the temperature will violently oscillate back and forth beyond the comfortable range. This is known as hunting. Chattering and hunting may be unacceptable for sensitive control processes where either the required alarm limit window is very small, wide oscillations are strictly forbidden, or setpoints may change very rapidly. If any of these conditions are necessary, then a more sophisticated control mode must be employed. Common control laws for different plants employ both linear and non-linear models. For systems with many variables, combinations of these modes may be used as in feedforward or cascaded control, and complex systems require advanced control schemes, such as neural networks, artificial intelligence, state-space models, or other expert system configurations.

Incorporating a compositional monitor such as the FTIR into a feedback control scheme provides for real-time, operator-independent operation of the plasma reactor,

provided the feedback loop executes substantially faster than disturbances in the system may occur. The inlet concentration of the soil vapor-extraction waste stream is expected to fluctuate due to:

- barometric pressure changes
- diurnal and seasonal temperature changes
- long-term depression of local concentration as more contaminant is removed from the soil, and
- possibly high concentration puffs as air pockets open up.

These changes occur on time spans of minutes to months. Although the speed of control loop execution depends on the how fast the control computer microprocessor can run, the speed at which setpoints are updated is limited by the repeat rate of the FTIR. As with any instrument that averages input data, there is a tradeoff between measurement accuracy and measurement repeat rate, since high accuracy usually requires many scans to ensure adequate averaging statistics. Accordingly, the control loop executes several times per second, but the setpoints generated by the FTIR concentration measurements are updated only about every two minutes. Due to the sluggish nature of the concentration changes listed above, the two-minute update time is not anticipated to cause a loss in performance efficiency.

The Diamond 20 FTIR is an industrial-grade process monitor. The package we purchased includes all the interferometer hardware and software items discussed earlier and an additional software package written by KVB/Analect specifically for continuous process measurement. The process monitoring software controls the sampling manifold, reads raw data from the interferometer, and calculates concentration information using the calibration matrix, all with about a two minute repetition period. Concentration information for each compound of interest is output from the data analysis computer serial port in the form of ASCII text files. These files must be read by the supervisory computer and the concentration data must be converted into meaningful setpoint information. Control sequences relying on the strong correlation between concentration information, contaminant destruction, and absorbed dose are covered in the following section.

#### 4.5 Dose Mapping Control Sequence

The fundamental quantity used in describing the effects of ionizing radiation is the absorbed dose. Ionizing radiation exists in many forms, including X-rays, gamma rays, and accelerated particles, such as electrons, protons, neutrons, and heavy ions. The absorbed dose related to each of these forms of radiation quantifies the energy absorbed per unit mass of matter contained in the exposed target. For moderate energy radiation (below 1 MeV), the incident particles or electromagnetic photons knock bound electrons from stable molecular or atomic orbits. Often these freed electrons are energetic enough to knock yet additional electrons free from other molecules or atoms. Deexcitation of atoms with recently-removed or freshly-recaptured electrons results in reradiation of X-ray,

ultraviolet, and optical wavelength electromagnetic energy. Thus the end result for all the different sources of radiation is an electron/photon cascade.

Although the dose required to generate one electron-ion pair in air is on the order of 35 eV, several systems of units are commonly used for describing the doses absorbed by targets of larger mass. The Systeme Internationale/MKS derived unit of absorbed dose is the Gray ("Gy"). It is equivalent to the absorbed dose when the energy per unit mass imparted to matter by ionizing radiation is one joule per kilogram. Equivalent labels for the same quantity but used by different radiological fields include the specific energy imparted, the kerma, and the absorbed dose index. Another unit is the rad, for which one Gray equals one hundred rads. Equivalently, ten kGy (or kilojoules per kilogram) equals one Mrad. The absorbed dose rate is the energy per unit mass imparted to matter per unit time, or equivalently the specific power imparted. Therefore, the time integral of the absorbed dose rate equals the absorbed dose.

In the case the electron beam-based plasma reactor, the variables that contribute to the absorbed dose include the beam acceleration voltage, the beam current, and the mass flow rate of the air stream under irradiation. For a specified inlet contaminant concentration, destruction improves with increasing absorbed dose. However, destruction also improves with decreasing initial inlet concentration for a specified dose. These trends were shown for dry carbon tetrachloride decomposition in Figure 2.2

An approximate functional form for carbon tetrachloride destruction determined from the empirical data shown earlier is given as follows, where  $C_0$  is the initial contaminant concentration, C the final concentration, D the absorbed dose, and a a positive coefficient with units ppm/kGy:

$$C \cong C_0 \exp(-\frac{aD}{C_0})$$
 Equation 4.1

Absorbed dose is the power deposited,  $P_d$ , per unit mass flow rate, Q. The power deposition is the product of the acceleration voltage, V, the beam current, I, and the power deposition efficiency,  $\xi$ :

$$D = \frac{P_d}{Q} = \xi \cdot \frac{V \cdot I}{Q}$$
 Equation 4.2

Curve fitting the data shows with fair agreement that for each given inlet concentration, exhaust concentration falls off nearly exponentially with increasing energy deposition. See Figure 4.3: Curve

An exponential-approximation destruction model is drawn from such curves. Fitting each string of data points to an exponential function with C,  $C_0$ , and  $D_a$  known, we may determine the values for a as a function of inlet concentration. Once a is known for



#### **Concentration Dependence for CCI4 Decomposition**

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Figure 4.3: Curve fit of the dose and concentration dependencies of CCl<sub>4</sub> decomposition.

all inlet concentrations of interest, then for any given inlet concentration and required outlet concentration, the system operating point is uniquely determined, as shown in the following plot, Figure 4.3. Thus, in order to achieve a desired outlet concentration, for any measured inlet contaminant concentration one must irradiate the gas stream with a certain dose according approximately to either Figure 4.3 or to Equation 4.1.



#### Dose Mapping: Dependence of Destruction and Removal Efficiency for CCI4 Decomposition on Initial Concentration

Figure 4.3: Dose mapping for specified DRE or specified final concentration.

Equation 4.1 may be reexpressed in terms of the destruction and removal efficiency, DRE:

$$DRE = \frac{C_o - C}{C_0} \cdot 100 = [1 - \exp(-\frac{aD}{C_0})] \cdot 100$$
 Equation 4.3

Three system parameters, namely the voltage, current, and mass flow rate, may be manipulated in order to achieve the proper dose.

In developing an adaptive control scheme, three input variables must be specified by the user. The primary input is the required destruction, and the two secondary inputs are any two of the three parameters that contribute to the dose, namely voltage, current, and mass flow rate. For any inlet concentration, required destruction is specified either as a final exhaust concentration limit or as a destruction and removal efficiency. A "destruction dial" is then fashioned around the destruction correlation outlined above.

Solving the above equations for the required absorbed dose,  $D_r$ , in terms of the required outlet concentration,  $C_r$ , or the required destruction efficiency,  $DRE_r$ , yields the following expressions:

$$D_r = -\frac{C_0}{a} \ln(\frac{C_r}{C_0})$$
 Equation 4.4  
$$D_r = -\frac{C_0}{a} \ln(1 - \frac{DRE_r}{100})$$
 Equation 4.5

In order to achieve adequate destruction, the actual dose,  $D_a$ , must be manipulated until it is equal to or greater than the required dose  $D_r$ :

$$D_a = \xi \cdot \frac{V \cdot I}{Q} \ge D_r$$
 Equation 4.6

Normally, the voltage is maintained constant at its maximum permissible setting, then the current and flow rate are adjusted such that the actual dose exceeds required dose.

As an example, for a carbon tetrachloride inlet concentration of 500 ppm, a destruction efficiency requirement of 99%, and an empirically determined value of *a* of 11 ppm/kGy, then the required dose equals:

$$D_r \approx -\frac{500}{11} \cdot \ln(1 - \frac{99}{100}) \approx 200 \text{ kGy}$$
 Equation 4.7

The electron beam retrofitted for use as a plasma generator is rated for 175 kV and 10 mA, or 1.75 kW maximum power, and the power deposition efficiency is around ten percent. Thus, with voltage and current settings fixed, to keep  $D_a$  greater than or equal to 200 kGy ( $D_r$ ), we must set the flow rate to .0015 kg/sec or correspondingly to an air volume flow rate of 2 cfm. The reactor channel was designed to keep the stiffness of the beam high, such that scaling to larger beams would be independent of reactor volume. The high stiffness results in a low power throughput efficiency, and consequently a low air volume flow rate. For the given example, the three setpoints, namely V=175kV, I=10mA and Q=2cfm, are fed to the control program and the physical parameters are tuned accordingly.

Although this example works out nicely to produce reasonable setpoint values for dry carbon tetrachloride decomposition, in the real world gas streams are composed of mixes of different compounds with different destruction requirements. Thus trying to curve-fit the destruction efficiencies for all the various permutations of gas mixtures found at all the different waste sites would be an enormous and probably futile task. A more realistic control model would use a "table look-up" to determine setpoints. Dose requirement experience gained with actual site conditions would be stored in a readily accessible database, and proper setpoints would be "looked-up" according to the given set of input conditions.

A third possible control scheme could use incremental stepping of system parameters to adapt to changing inlet conditions. An operator would adjust initial parameters appropriately for the starting concentration conditions for the flow stream. The control code would then calculate its destruction efficiency as inlet concentration diminishes over time and slowly relax the dose step by step. To maximize beam utilization, voltage and current would be left high, and flow rate would slowly be stepped up. Next the beam current would be stepped down. The voltage really wouldn't need to be stepped down, because if the current had stepped down to zero, there must not have been anything left in the stream to destroy.

Looking to the future, the limited voltages, currents, and flow rates achievable with the lab-scale beam we're using could be improved by upgrading to production-scale beams with optimized reactor cell designs. These commercially-available units reach 300 keV acceleration voltage and 500 mA current with the same modest shielding requirements. If the "stiffness" requirement is relaxed, then a detailed analysis of the power deposition profile with a 3D Monte Carlo-type computer code would aid in designing reaction channels with high power deposition efficiencies -- upwards to perhaps 70% or 80% beam utilization -- thereby raising the flow rate limit to perhaps several hundred cubic feet per minute.

#### 5. Construction of a PC-Based Data Acquisition and Control System

The author's main contribution to the plasma reactor project has been the design and implementation of a personal computer ("PC")-based data acquisition and control system. The controlled system variables include beam acceleration voltage, beam current, thermionic cathode power, air volume flow rate, scrubber sodium hydroxide addition rate, and scrubber makeup water volume flow rate. Additional measured variables which influence the controlled variable setpoints include inlet contaminant concentration, outlet contaminant concentration, and scrubber pH. Limit cycle control, as outlined earlier, is the premise on which most control functions are performed.

Each controlled variable has at least one measurement transducer, an actuator, a setpoint, and high and low alarm limits. The operation of each feedback loop is to:

- 1. measure the variable of interest with the appropriate sensors
- 2. compare this value with the setpoint (i.e. the alarm limits)
- 3. if the measured value falls between the upper and lower alarm limits, then the actuator sits idle

- 4. if the measured value falls above the upper alarm limit, then the actuator should operate to bring the value back down
- 5. if the measured value falls below the lower alarm limit, then the actuator should operate to bring the value back up
- 6. repeat the sequence

In limit cycle mode, signals to the actuators are discrete, signaling either to turn them on or to turn them off. Such is the case of the thermostat example discussed previously. In the proportional or "P" linear control mode, signals sent to the actuators are proportional to the difference or "error" between the measured value and the setpoint value of the controlled variable. Adding a term to the actuator signal proportional to the time integral of the error smoothes out high frequency disturbances and eliminates the steady state error introduced by a setpoint change in proportional control. Adding a term proportional to the time derivative of the error reduces overshoot and ringing introduced with setpoint changes. The different permutations of linear control schemes utilizing the proportional, integral, and derivative terms include the P, PI, PD, and PID modes and each enhances the time response and accuracy of the adaptive control loop. In our case, actuators with the capability to respond proportionally well exceed our performance specifications, plus their costs exceed our resources. Since we desire only minute-level responses, bang-bang control suits our needs accordingly.

The need for rugged electronics hardware capable of performing switching and other Boolean logic functions in a hostile, industrial environment is not new. A common solution to actuator switching is the use of relay logic -- specifically hardwiring electromechanical relays such that a few user-operated switches appropriately control a myriad of machine functions. Unfortunately, only a single set of control functions may be performed once the relays are wired. To reprogram such a system, one must rip out the wires and start over essentially from scratch. Although relay logic has proven quite rugged and highly reliable, redesigning relay panels for every machine upgrade is quite costly. Thus the programmable logic controller, a microprocessor-based, reprogrammable alternative to hardwired relays, has seen dramatically increased use in manufacturing and robotics applications during the past fifteen years.

Although a programmable logic controller ("PLC") would be quite adequate for a commercial plasma reactor system, we opted for a PC-based controller system due to the adolescent nature the prototype unit. Using multi-function data acquisition cards, we have the capability to read and write analog and discrete digital signals, and subsequently monitor all measurable variables and control all actuator functions. Although these inputs and outputs are also available with PLCs, the data acquisition cards ("DAQs") coupled with a high-level software package, gives us the opportunity to use the computational speed, expansive data storage and memory capacities, and well-developed communications capabilities of modern PCs. Plus, once all the useful inputs and outputs are wired, we can interactively reprogram appropriate logic functions, or we can download and run improved control algorithms as they are developed off-line at our convenience. Although PLC programming languages have seen continued improvement in user-friendliness, they still lag behind other conventional high-level languages presently available for personal computers. Thus in using a PC-based control system over a PLC we

obtain equivalently high levels of operability while retaining the flexibility and room for growth necessary in developing a fledgling technology.

#### **5.1** Control Variables

As mentioned earlier, for any given contaminant compound, the fundamental quantities which describe and govern the operation of the plasma reactor are the contaminant inlet concentration, the absorbed dose, and the contaminant outlet concentration. The contaminant type and inlet concentration are uncontrolled parameters determined only by the nature of the air stream under treatment. The desired contaminant outlet concentration is determined from regulatory concerns, either in the form of a maximum permissible exhaust emissions rate or in the form of a minimum allowable destruction and removal efficiency. We can measure inlet and outlet concentrations with the FTIR. We must therefore dial in the constrained variable, namely the absorbed dose, such that the outlet concentration regulation is satisfied for the given inlet concentration.

We have at our disposal three "dials" corresponding to the three factors which contribute to the absorbed dose. We can dial in the beam acceleration voltage, the beam current, and the air mass flow rate such that the appropriate dose is achieved. Thus three independent control loops, one each for voltage, current, and mass flow rate, are constructed with the appropriate transducers and actuators. Due to the strong correlation between destruction efficiency and absorbed dose for any given inlet concentration, we

consequently have a "dial" corresponding to destruction. The three parameter setpoints are thus interrelated and predetermined by concentration information. Values for the three setpoints cannot be chosen purely at random. Each of the three controlled variables has a limited dynamic range. Acceleration voltage cannot be set higher than 175 kV, beam current cannot be set higher than 10 mA, and air mass flow rate cannot be set lower than zero kg/min. In actual operation, two variables would be held fixed while the third is actively modulated such that the proper dose level is maintained.

In preparation for fully adaptive control, semi-automatic computer control of the available system parameters needed to be achieved. The following monitors and controls have been implemented by the author:

- Concentration information gathered with the FTIR and its dedicated spectral analysis computer is sent to the supervisory computer over an RS232C serial communication cable in the form of spreadsheet files, each record in the file indicating either an FTIR status code or a numerical concentration value for each compound found in a scan.
- Series viewing resistors with voltage transmitters send the acceleration voltage and beam current values to analog DAQ inputs.
- The CB 150 electron beam comes with manually-driven variable transformers for acceleration voltage, beam current, and cathode power adjustment. Three additional motor-driven transformers were installed in parallel with the manual transformers to allow computerized adjustment. Discrete DAQ outputs switch the

drive motors on and off in the appropriate direction to raise or lower the transformer output voltages.

- A heated-thermistor anemometer sends air velocity, or correspondingly air volume flow rate, information to another analog DAQ input. Air flow rate is adjusted using two motor-actuated damper valves, which slow the air flow by throttling the input and outlet blowers' pumping power.
- The remaining analog DAQ inputs monitor analog transducer signals from the input relative humidity meter, the scrubber pH meter, the thermionic cathode power meter, three position feedback potentiometer voltages corresponding to each motorized variable transformer, and a compressor pressure gauge.
- The remaining discrete DAQ inputs monitor tank and scrubber overflow and dryout float switches, various pump status indicators, a recirculation flow rate deviation switch, and dryer malfunction indicators.
- The remaining discrete DAQ outputs switch on and off the caustic feed pump, the water makeup pump, the waste saline pump, the scrubber recirculation pump, and the process inlet blower.

A diagram showing sample feedback loops in relation to the control computers and data acquisition hardware is given in

In comparison with a full scale chemical plant, the number of inputs and outputs we must deal with is still relatively low. Yet the number of monitored variables is high enough that a less than clear man-machine interface could lead a confused operator



Figure 5.1: Control system schematic diagram showing typical feedback loop configurations.

towards operational errors and reduced efficiency during semi-automatic, interactive operation. Even when fully automated computer control governs the system operation, an occasional glance at the computer screen by a human supervisor (or preferably a remote human supervisor) is critical to ensure proper continuous operation. Therefore, the manmachine interface must give clear, immediately recognizable interpretations of each of the important system variables with a reasonable update rate.

For these reasons, the author has written the control codes and sequences using the LabVIEW for Windows programming language, purchased from National Instruments, Austin, TX. Like C, BASIC, FORTRAN, and other programming languages, LabVIEW provides extensive libraries of structures and functions to perform conditional comparisons, looping, mathematical analysis, and text manipulation. LabVIEW's two major advantages to conventional languages are the extensive use and availability of userconfigurable graphics tools and a primary focus on high-level instrument drivers facilitating communication with laboratory test and measurement equipment. The broad palette of graphics tools helps in creating a fully understandable, easily-operable front end to the control program setpoints and measurement values. The instrument drivers provide a seamless back end to the incoming data to be acquired and the outgoing actuator instructions. Fragments of the master control code written in LabVIEW, along with critical subroutines, are included and further discussed in the Appendix.

#### **5.2** Computer/Data Acquisition Resources

The field test plasma reactor requires two dedicated computers for both automatic and semi-automatic operation. The supervisory computer communicates with all the system sensors and actuators via the two data acquisition boards, and it runs the master control program. The spectral analysis computer receives raw absorbance data from the FTIR analyzer, computes gas compositions using a spectral deconvolution algorithm, and relays concentration data to the supervisory computer via a serial link. Both machines are 486-based PC-compatibles manufactured by Dell Corporation, Austin, TX. The two data acquisition boards, models AT-MIO-16D and PC-DIO-24, and their associated signal conditioning and isolation boards, models 5B and SSR Series backplanes, were purchased

from National Instruments. The AT-MIO-16D has sixteen analog read data channels, two analog write channels, and thirty-two read/write digital channels, while the PC-DIO-24 has twenty-four read/write digital channels. Excluding the supervisory computer cost, the cost per isolated analog channel is around \$200, the cost per isolated digital channel is around \$50, and both figures are commensurate with PLC channel costs.

The first decision to make in designing any data acquisition system is the choice of which software package to use, for the system is useless if the software cannot speak to the hardware. The decision to go with LabVIEW was initially governed purely by economics: the lab next door gave us their copy of LabVIEW V.2 free of charge. Normally the second decision in designing a data acquisition system is selecting hardware which allows the software to interface with the real world phenomena to be measured and controlled. The DAQ boards were ordered before acquiring the free software, but the two together proved happily compatible. After discovering the ease of programming and simplicity of interfacing to hardware with LabVIEW, economics went out the window, and a bona-fide copy of LabVIEW V.3 was purchased. In addition, the isolation cards were included as a "precaution" only after the author destroyed the supervisory computer's motherboard with a bad DAQ connection. Although a few wrong turns were made at the outset, the various pieces of the control system finally came together and presently operate at a sufficiently reliable level.

#### **5.3 Remote Operation**

We plan to eventually demonstrate aspects of remote monitoring and control, thereby eliminating the need for around-the-clock maintenance personnel. We plan to use twin modems, one on the supervisory computer and one on a remote laptop or desktop computer, and a remote control software package to communicate with the field system. Although remote control has not yet been implemented on the field-test system, remote control of personal computers is an established practice for the telecommuters of today, and once the supervisory computer has bullet-proof control over all the necessary system parameters, the technological leap to remote computing should not be too taxing.

#### 6. Final Projected Layout of Field Test System

The trailer-mounted demonstration system being assembled for field operation was designed with incorporation of standard, commercially-available, modular hardware as a high priority. Building any prototype system requires some retrofitting of existing hardware or even development of new hardware. Nevertheless, we tried to keep custombuilt components out and vendor-replaceable or stock-item parts in, because it is generally easier to order new parts than it is to make them.

Fortunately, all five of the major hardware components, namely the electron beam, the caustic scrubbing tower, the desiccant dryer, the FTIR analyzer system, and the computer control components, have required only slight modification before being incorporated into the system. Although the electron beam required a fair amount of modification in replacing a parts conveyor system with a ductwork channel, the amount of new engineering work was a minuscule fraction of the amount that went into the original design. Plus, the alterations were made on the factory floor by experienced technicians. The control system hardware components were selected with expandability and flexibility in mind. In reality, their assembly has been more of an agglomeration of pieces than a catalog line-item purchase.

For field testing, all the components of the trailer based system must be controlled. Therefore, in addition to control of the electron beam plasma reactor, computer control of the desiccant dryer and the caustic scrubber must be implemented. Descriptions of the operation of the dryer and scrubber follow in the next section. A conceptual block diagram of the orientation of the system components and the information flow between them is given below in Figure 6.1.



Figure 6.1: Block diagram of projected field test system.

#### **6.1** Dryer Operation

The relative humidity effect specifically for carbon tetrachloride destruction described earlier warrants the inclusion of a dryer at the inlet of the flow stream. The type we have included is the 123PE HyDryer regenerating tower system manufactured by PSB Industries Inc., Erie, PA. In the HyDryer, two packed towers loaded with molecular sieve desiccant are switched between on-stream drying and off-line reactivation, thus achieving continuous-duty drying of the VOC air stream. The molecular sieve desiccant removes water from the air through adsorption of water molecules onto the porous surfaces of the desiccant particles. The zeolite 3A desiccant has pore openings three angstroms (or 3 10<sup>-10</sup> meters) across and pore cavities of around twelve angstroms in diameter. Therefore only molecules with dimension smaller than three angstroms may enter into the pore cavities. Carbon tetrachloride and other big solvent molecules are too large to enter the pore openings, thus they pass through the drying tower. Water molecules manage to fit into the pore openings and, due to their built-in dipolar charge arrangement, adhere strongly to the inner pore walls.

Reactivation is necessary in order to recycle the desiccant after all the available pores fill with water. Hot, dry air is forced through the tower, pulling out a large fraction of the trapped water molecules. The hot, humid air is passed though a heat exchanger, and water in the cooled air condenses and is removed as a liquid. The air is reheated and sent back into the tower until as much of the water as possible is removed. Although this captive air mass contains trace carbon tetrachloride, upon completion of bed regeneration, the towers are again switched and this air is sent through the plasma reactor for treatment

as a normal part of the cycle. Use of twin towers provides for continuous duty drying by allowing the towers to switch roles when one tower saturates with water. When the online tower requires reactivation, the regenerated tower goes on-line to take its place, and vice versa. The regeneration cycle time may be fixed or adaptive, and a 16-hour fixed NEMA cycle is the standard control sequence included in the HyDryer we purchased.

Desiccant Dryer Schematic Diagram



Figure 6.2: Desiccant dryer schematic diagram.[11]

Unfortunately, use of a desiccant drying system introduces a new waste stream into the overall system, i.e. spent desiccant. Although the molecular sieve desiccant may be reactivated a great number of times, its water collection effectiveness degrades over an extended period. Eventually, it must be replaced with fresh desiccant, and the spent desiccant must be disposed of properly. It is hoped that desiccant changeovers will be quite infrequent, on the order of yearly, due to the arid nature of the vadose layer and the subsequent low initial humidity of the waste air stream. Although refrigerator/condensertype dehumidifiers were explored, these apparently have the tendency to drop out condensed VOCs as liquids along with the condensed water vapor and are incapable of reaching the low relative humidities that the molecular sieve desiccants can achieve.

Due to the fixed regeneration cycle configuration, no active controls are necessary for the dryer. Instead, read-only malfunction indicators will be installed. If the dryer malfunctions, the entire system will shut down until the error can be rectified. Eventually, the fixed cycle will be replaced with an adaptive cycle. This is an add-on upgrade available through PSB Industries. No extensive hardware changes, other than the inclusion of humidity meters, would be required to execute this upgrade.

## 6.2 Scrubber Operation

As stated earlier, the main byproducts from carbon tetrachloride decomposition are carbon dioxide, carbon monoxide, hydrogen chloride, and chlorine with trace amounts of phosgene, a water soluble chloride. The carbon oxides may be released to the atmosphere, but the chlorides are highly toxic and require stabilization. Passing the gas stream through a water scrubber would produce a solution of mostly hydrochloric acid. However, retention of chlorine gas and phosgene is improved greatly by scrubbing with a basic solution. Thus sodium hydroxide is added to the scrubbing solution and a solution predominantly of sodium chloride -- salt water -- is the final waste form. Although salt water still is quite corrosive and is not particularly friendly to plants and microorganisms,

it is at least a non-carcinogenic, naturally-abundant (especially as sea water), inorganic substance and may be returned to the natural mineralogical cycle as a non-hazardous waste.

We are using a single packed tower, the Aqua Trim AT5-711S manufactured by Delta Cooling Towers Inc., Fairfield, NJ, as a caustic scrubber. Water is recirculated over a stack of perforated stainless steel trays countercurrent to the waste acid gas stream. The chlorine and hydrogen chloride dissolve into the basic solution. The pH level in the sump is monitored and maintained at a sufficiently basic (between pH 9 and pH 13) level to maintain high mass transfer rates from the gas phase to the aqueous phase, with caustic solution and water reservoirs continuously making up for neutralized base and evaporation. Sump bottoms are pumped out for final neutralization and disposal. Waste air





Scrubbing Tower: Aqua-Trim Compact Air Stripper, Delta Cooling Towers, Fairfield, NJ pH Probe: PX 380, Omega Engineering, Stamford, CT Solution Reservoirs: Star System Chlorinators, Blue White Inds, Claremont, CA

Figure 6.3: Caustic scrubber schematic diagram.[12]

is sampled for fugitive chlorides, then released to the atmosphere. During the Integrated Demonstration, waste air will pass finally through a granular activated charcoal ("GAC") canister, allowing for final destruction efficiency assessment and quality assurance. Future commercial units would not require GAC.

The control aspects of scrubber operation include monitoring and control of pH, sump level, and recirculating flow. If the measured pH lies outside the proper range (i.e. too low) then the computer instructs a metering pump to add more sodium hydroxide. If the measured sump level is too low, the computer instructs a second metering pump to add clean water. Float switches in the scrubber, sodium hydroxide reservoir and clean water reservoir indicate when liquid levels are too low. Float switches in the scrubber and waste salt water barrel indicate when liquid levels are too high. A rotameter with an adjustable deviation switch indicates a loss of flow in the recirculating loop. The computer reads each of these discrete actions and reacts with either warning signals or system shutdown accordingly.

#### 7. Conclusions

#### 7.1 Summary

Control systems will play an important role in the development of electron beam plasmas for treatment of chlorinated VOC-contaminated air streams. In furthering the development of a field-test plasma reactor system, author made three major accomplishments. First, the conversion of a manually-operable Energy Sciences CB 150 electron beam into a motorized control, computer-interfaced plasma reactor. Second, the incorporation of a KVB/Analect Diamond 20 Fourier Transform Infrared spectrometer as an on-line gas composition analyzer and adaptive control setpoint generator. Third, the implementation of a personal computer-based data acquisition system for the monitoring and control of the CB 150 electron beam, a caustic scrubbing tower, a desiccant dryer, and various additional devices, including pressure and flow transducers, pumps, valves, and status indicators. These components will eventually be used in field tests of the completed trailerbased plasma remediation system at the US DOE Hanford facility.

#### 7.2 Suggestions for Future Work

In the short term, several improvements to the field test plasma reactor system and the associated computer controls should be considered. First, existing plasma reactor cell should be redesigned to raise the power deposition efficiency. The dose mapping control algorithm would also need to be updated accordingly. Second, controlled addition of chemical "promoters" might further reduce destruction energy requirements for the compounds of present interest or for compounds yet to be examined. Third, small improvements to the FTIR sampling system, such as adding new compounds to the calibration matrix or adding a pressure transducer on the gas cell and wiring it to directly provide a first-order concentration correction to pressure changes, may enhance the generality of the present system for field tests at additional sites. Finally, although using PC-based data acquisition hardware is appropriate for developmental operation, switching over to PLC-based data acquisition and control may provide a more compact, robust, and industrial quality system more suited to continuous operation.

In the long term, control of large throughput (500-1000 cfm) systems requires somewhat more sophisticated hardware. Large, industrial grade PLCs with PCs as userterminals could control the operation of 300 kV/500 mA electron beams, high capacity dryers, and large scrubbing towers. To further expedite cleanup of extremely large waste sites, several large plasma reactor systems could be used in parallel. Output from several soil vapor extractors or air strippers might be manifolded to the inputs of several large plasma systems. Peak destruction efficiency may be attained through either concentration control or throughput control. For arrays of plasma reactor systems, networks of PCs or PLCs could coordinate the operation of the parallel systems. If sampling lines could be kept sufficiently short and repeat rates sufficiently high, then multiplexing or timesharing gas composition analyzers like the FTIR between the parallel streams would help keep hardware overhead costs down.

## 7.3 Closing

In general, beams with 150 to 300 keV acceleration voltages can provide a flexible, low cost, highly selective, and self-shielded alternative to thermal or adsorptive treatments of low concentration chlorinated VOCs. Ionization-induced plasmas offer a highly reactive, highly controllable means for destruction of a wide variety of compounds. Moderate capacity systems can be constructed simply enough to allow automatic control using modest computer resources. Systems can largely be built with existing commercial technology, emphasizing low cost and ease of maintenance. Although the problems of buried and ongoing production of hazardous waste in the U.S. are far from solved, plasma processing of hazardous wastes offers a new, efficient, low cost option for tackling a piece of the problem.

## **ENDNOTES**

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## APPENDIX

Below is a sample fragment of LabVIEW code. Instead of lines of text found in other programming languages, LabVIEW is entirely graphical in nature. Functions, subroutines, and mathematical operators are literally "wired" together in the proper order as shown in the figures below. The graphical nature allows for faster code writing, debugging, and inherent commenting of code structure. In addition, the absence of lines of code carries over into the order of execution as well. Execution is data dependent instead of line-by-line dependent, thus each element of the code executes when all its inputs have arrived. This provides for interesting parallel and asynchronous algorithms.

In LabVIEW, every program -- called a virtual instrument or "VI" -- is a subroutine. Therefore, after writing a short program that performs a specific operation, the user can quickly incorporate it into a larger program. This top-down style is known as the hieracrchy, also shown below.

There are three components to every VI: the front panel, the block diagram, and the connnector. The front panel contains indicators and controls that the user may operate during program execution. The block diagram contains all the operational elements or "nodes" of the program, including functions, subroutines, constants, arithmetic operators, and the "wires" which carry variable values from node to node. The connector acts as a parameter list in a FORTRAN or C subroutine; variable values are passed into and out of subroutines through the connector.

In the example below, the upper loop reads and parses concentration data files sent via serial port from the FTIR data analysis computer. The lower loop transforms Ccl4 concentration values into a variac position setpoint. This value is compared against the present variac position, and adjustment of position is made by turning on the proper position drive motors.

Virtual Instrument Hierarchy with Connector Pane (blank in this case)





## Front Panel



## Block Diagram

