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Decomposition of Chlorinated Organic Compounds in Gaseous Hazardous Waste using a Tunable Plasma Reactor

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by
Mathias Koch*

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Abstract

An experimental investigation was performed of the Cold Plasma Decomposition of the chlorinated methanes CCl₄ (Tetrachloro Methane) and CHCl₃ (Trichloro Methane) and the chlorinated ethene C₂HCl₃ (Trichloro Ethene) in gaseous hazardous waste using a Tunable Plasma Reactor.

The cold plasma in this reactor was generated by an electron beam. The electron and radical concentration of the cold plasma was controlled through the electron beam current. the average electron energy of the cold plasma was controlled through the sub-breakdown electric field voltage superimposed to the electron beam.

In addition to the "tunability" provided by the electron beam current and the electric field voltage, the mass flow rate of the gaseous hazardous waste through the cold plasma could be varied and chemical compounds that form reactive chemical species, such as radicals, upon electron irradiation could be added to the gaseous hazardous waste in order to enhance the "tunability".

The chemical analysis of the reactor intake and exhaust was performed via Gas Chromatography with Electron Capture Detector, Thermal Conductivity Detector and Mass Selective Detector and via Stand-Alone, On-Line, Real-Time Mass Spectrometry developed in the present work on the basis of the Mass Selective Detector.

The electron beam dosimetry was performed via a combination of Facsimile Paper Radiography, Aluminum Plate Calorimetry, one-dimensional Monté-Carlo Simulation of the electron beam power deposition and N₂O Chemical Dosimetry.

The cold plasma decomposition of CCl₄ in air was found to be selective in the sense that a decreased intake concentration required a decreased electron beam dose to achieve a constant exhaust concentration.

The decomposition of CHCl₃ in dry air was found to require a higher electron beam dose than the decomposition of CCl₄ in dry air. Also, the decomposition of CCl₄ and CHCl₃ in dry air was found to require a ten to hundred times higher electron beam dose than the decomposition of C₂HCl₃ in dry air.
Moreover, the decomposition of CCl₄ and CHCl₃ in wet air was found to require a higher electron beam dose than the decomposition in dry air. For a comparable intake and exhaust concentration, the electron beam dose was found to be up to five times higher in wet air than in dry air. No such effect of the relative humidity of air was observed for the decomposition of C₂HCl₃.

The superposition of an electric field to the electron beam was found to result in a lower exhaust concentration for CHCl₃ and C₂HCl₃ and a higher exhaust concentration for CCl₄ for a given electron beam dose and intake concentration in dry air. Also, the effect of the electric field on the exhaust concentration of CCl₄ and CHCl₃ was found to be larger in wet air than in dry air.

These experimental results were found to be consistent with bimolecular dissociative electron attachment as the chemical reaction primarily responsible for the decomposition. The selectivity of the decomposition of CCl₄ in dry air was modeled through a semi-quantitative heuristic equation on the basis of the G-Value for production of electrons.

In addition, a chlorine radical chain reaction with C₂HCl₃, initiated through bimolecular dissociative electron attachment to C₂HCl₃, was found to be very likely responsible for the low electron beam dose required for the decomposition of C₂HCl₃.

The decomposition of CCl₄ in dry air and wet air was found to result in the formation of CO, CO₂, HCl and Cl₂ as stable decomposition products and COCl₂ (Carbonyl Chloride) as an intermediate decomposition product. The decomposition of COCl₂ to sub ppm levels required a comparable electron beam dose as the decomposition of CCl₄ to sub ppm levels.

The decomposition of C₂HCl₃ in dry air and wet air was found to result in the formation of HCl and Cl₂ as stable decomposition products and COCl₂ and C₂HCl₃O (Dichloro Acetyl Chloride) as intermediate decomposition products. No chemical analysis was performed for the formation of CO and CO₂. The decomposition of C₂HCl₃O and COCl₂ to sub ppm levels required a ten to hundred times higher electron beam dose than the decomposition of C₂HCl₃ to sub ppm levels.

At a destruction and removal efficiency of higher than 99%, the energy expense for CCl₄ Cold Plasma Decomposition in dry air was found to be less than 150 eV per CCl₄ molecule decomposed or 25 kWh/kg of CCl₄ decomposed. These values were found to apply independently of the CCl₄ intake concentration.

Therefore, the Cold Plasma Decomposition of CCl₄ in a Tunable Plasma Reactor may be achieved at substantially lower operational cost than the customary Flame Decomposition, which, at a CCl₄ intake concentration of lower than 500 ppm, requires more than approximately 600 eV or 100 kWh/kg, respectively.

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__________________________________________

Well, the race is almost over now, soon I'll be cooling the engine. It's been running reliably, although the RPMs have been in the red almost permanently. It's been fun at times, but not even a Mercedes-Benz can do it for ever. Gotta learn how to drive in the green now or I will be worn out to pieces by the time I hit the thirties.
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Chapter 1

Introduction

1.1 Introduction

The compliance with a large number of regulatory acts concerning environmental pollution requires improved pollution remediation and pollution control through treatment of hazardous waste [1].

A major fraction of this waste is solid and liquid hazardous waste, while only a minor fraction is gaseous hazardous waste. However, a major fraction of the solid and liquid hazardous waste is converted into gaseous hazardous waste through treatment. In particular, much of this gaseous hazardous waste contains low concentrations of hazardous chemical compounds and high concentrations of air.

The objective of the treatment of such gaseous hazardous waste is the decomposition of hazardous chemical compounds into less hazardous or non-hazardous decomposition products. The decomposition is to be achieved with a minimum of energy, decomposition by-products and secondary waste per amount of hazardous chemical compound decomposed.

A number of approaches to treatment of gaseous hazardous waste exist [2]. The conventional approach is the decomposition of hazardous chemical compounds in a flame at atmospheric pressure [3]. One of the unconventional approaches is the decomposition of hazardous chemical compounds in a cold plasma at atmospheric pressure.

A flame is unselective in that the amount of energy required for the treatment of gaseous hazardous waste is independent of the concentrations of the hazardous chemical compounds. A cold plasma is selective in that the amount of energy required for the treatment of the gaseous hazardous waste is dependent on the concentrations
of the hazardous chemical compounds.

Therefore, while the decomposition in a flame may be efficient at high concentrations, the decomposition in a cold plasma may be efficient at low concentrations. This difference may be likened to the difference between a shotgun and a rifle. The shotgun takes out many targets unselectively while the rifle takes out few targets selectively.

In a very simplistic perspective, a cold plasma is distinguished from a flame through a higher concentration of electrons and a higher concentration of radicals. Therefore, a cold plasma may be especially suitable for decomposition of hazardous chemical compounds for which dissociative electron attachment or radical attack initiate the decomposition.

The present work focuses on the investigation of cold plasma decomposition of hazardous chemical compounds by dissociative electron attachment and radical attack. The halogenated methanes and ethenes, a subset of aliphatic organic hazardous chemical compounds, are selected for the investigation.

On the basis of the high electron affinity of halogenated chemical compounds in general and the absence of a fragile carbon double bond, dissociative electron attachment may be expected to initiate the decomposition of halogenated methanes. On the basis of the presence of a fragile carbon double bond, radical attack may be expected to initiate the decomposition of halogenated ethenes.

A number of approaches to the generation of a cold plasma exist. However, because of the inherently high rate of generation of electrons and the inherently high rate of generation of radicals, generation of a cold plasma by an energetic electron beam is of particular interest.

Moreover, dissociative electron attachment is expected to be dependent on the average electron energy. Therefore, an electric field may be superimposed to the electron beam so that the electron concentration and the radical concentration are controlled by the electron beam current and the average electron energy is controlled by the electric field voltage.

Individually, dissociative electron attachment, radical attack, generation of a cold plasma by an energetic electron beam and electric fields are well known. However, their integration into a plasma chemical reactor for decomposition of hazardous chemical compounds has received relatively little attention [4] and therefore represents a major contribution of the present work. The superposition of the electron beam and the electric field gives rise to the name Tunable Plasma Reactor (TPR) for such a plasma chemical reactor.

The development of a qualitative and semi-quantitative understanding of the par-
ticularities of decomposition of halogenated methanes and ethenes and the demonstration of the potential usefulness of the Tunable Plasma Reactor for decomposition of halogenated methanes and ethenes represent a significant outcome of the present work.

An important part of the qualitative and semi-quantitative understanding is the difference between initiation of decomposition via dissociative electron attachment and initiation of decomposition via radical attack.

Moreover, as a classical example of the applied sciences, the investigation of the decomposition of above hazardous chemical compounds in the Tunable Plasma Reactor on a laboratory scale allows for the implementation of this reactor on a field scale.

1.2 Background

1.2.1 Environmental Pollution and Hazardous Waste

Over the past few decades, concerns over Environmental Pollution have precipitated in a large number of regulatory acts devised to restore the environment through Pollution Remediation and to protect the environment through Pollution Control and Pollution Prevention. The more prominent of these regulatory acts are the Clean Air Act (CAA), the Comprehensive Environmental Responsibility and Compliance Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA) [5].

In general terms, environmental pollution may be defined as the contamination of the lithosphere, hydrosphere or atmosphere through hazardous chemical compounds resulting for example in contaminated soil, water and air. The hazardous chemical compounds are contained in solid, liquid or gaseous hazardous waste entering the three spheres.

The hazard associated with hazardous waste is a function of the concentrations of hazardous chemical compounds in such waste and of the hazard associated with these chemical compounds. According to the Environmental Protection Agency (EPA) Chapter 40 Code of Federal Regulations Part 261 (EPA 40 CFR 261), solid, liquid or gaseous hazardous waste may be classified on the basis of hazard codes [6].

The hazardous chemical compounds in hazardous waste may represent virtually the entire spectrum of chemical compounds known to mankind. In particular, the molecules of these chemical compounds may contain virtually the entire spectrum of elements known to mankind.
The contamination of the lithosphere, hydrosphere or atmosphere is tolerable below and intolerable above, certain concentrations of hazardous chemical compounds in the three spheres. Such concentration may be referred to as the Contamination Tolerance Threshold.

The intent of pollution remediation is to reduce the concentrations of hazardous chemical compounds in the lithosphere, hydrosphere or atmosphere to or below the contamination tolerance threshold through treatment of contaminated soil, water or air.

The purpose of pollution control is to maintain the concentrations of hazardous chemical compounds in the lithosphere, hydrosphere and atmosphere at or below the contamination tolerance threshold through treatment of solid, liquid or gaseous hazardous waste entering the three spheres.

The objective of pollution prevention is to reduce the solid, liquid or gaseous hazardous waste entering the lithosphere, hydrosphere or atmosphere altogether.

Frequently, pollution control requires the decomposition of hazardous chemical compounds in hazardous waste into less hazardous or non-hazardous chemical compounds.

In addition to the generation of such less hazardous or non-hazardous decomposition products, generation of hazardous or non-hazardous decomposition by-products as well as secondary hazardous waste may take place during treatment of primary hazardous waste. Such generation depends on the technical particularities of pollution control technology.

Therefore, the decomposition is to be achieved with a minimum of energy, decomposition by-products and secondary waste per amount of hazardous chemical compound decomposed.

1.2.2 Context of Present Work

The present work is concerned with pollution control through treatment of gaseous hazardous waste entering the atmosphere. Of the hazard codes listed in EPA 40 CFR 261, only Hazard Code T is of interest to the present work. This hazard code represents (gaseous) hazardous waste for which the hazard is associated with, the carcinogenic, mutagenic and/or teratogenic toxicity of the hazardous chemical compounds.

Moreover, for the present work, the hazardous chemical compounds in such gaseous
hazardous waste represent halogenated aliphatic organic chemical compounds. The molecules of these chemical compounds only contain the elements Hydrogen (H), Carbon (C), Fluorine (F), Bromine (Br) and/or Chlorine (Cl).

The desired decomposition products are Water (H₂O), Carbon Monoxide (CO), Carbon Dioxide (CO₂), Fluorine (F₂), Chlorine (Cl₂), Bromine (Br₂), Hydrogen Fluoride (HF), Hydrogen Chloride (HCl) and Hydrogen Bromide (HBr). The latter six chemical compounds may be converted into non-hazardous salts through chemical reaction with Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) or other chemical compounds of the Alkali Metals.

The gaseous hazardous waste considered here is generated as secondary waste in pollution remediation such as Vapor Extraction, Air Stripping and Activated Charcoal Adsorption/Desorption. Such gaseous hazardous waste is also generated as off gas in industrial processes such as Semiconductor Manufacturing, Chemical Compound Manufacturing, Dry Cleaning and Spray and Brush Painting.

1.3 Motivation

At the US Department of Energy’s (USDoE) Hanford Site in Washington state, large quantities of the industrial solvent Carbon Tetrachloride (CCl₄) were used and subsequently disposed of in the soil below the site via Leaching Fields [7], [8].

The CCl₄ now threatens to migrate from the soil into the groundwater below the site. Such migration and the subsequent migration of the CCl₄ into the nearby Columbia River is to be prevented since CCl₄ is a suspected human teratogen and carcinogen [9], [10], [11].

Efforts under USDoE’s Volatile Organic Compound - Arid Integrated Demonstration Program (VOC-Arid-ID) are directed at Vapor Extraction of the CCl₄ from the soil [8], [12], [13].

At the very least, the air stream resulting from this process is expected to contain high concentrations of Water (H₂O) and low concentrations of CCl₄. Owing to the hazard associated with the latter chemical compound, this air stream represents gaseous hazardous waste. In response to an ever eroding acceptance level for Flame Decomposition of hazardous waste [14], [15], the decomposition of CCl₄ in above gaseous hazardous waste is to be accomplished without such flame decomposition.

1 In aliphatic organic chemical compounds, the elements are arranged in “lines”, while in aromatic organic chemical compounds, the elements are arranged in “circles”.
Funding has been made available to the MIT-Plasma Fusion Center (PFC) in order to develop a plasma chemical reactor for Cold Plasma Decomposition that can perform this decomposition with a minimum of energy, decomposition by-products and secondary waste per amount of CCl4 decomposed.

The CCl4 is to be decomposed into chemical compounds that do not require further treatment, such as Carbon Monoxide (CO) and Carbon Dioxide (CO₂), or that require very little further treatment, such as conversion of Hydrogen Chloride (HCl) and Chlorine (Cl₂) into Sodium Chloride (NaCl) via reaction with Sodium Hydroxide (NaOH).

Moreover, the development of the plasma chemical reactor is to be performed with the intent of application not only to the decomposition of CCl₄, but also to the decomposition of other hazardous chemical compounds, such as Trichloro Ethylene (C₂HCl₃), which are commonly found at USDoE, US Department of Defense (USDoD) and non-government sites.

1.4 Objective

1.4.1 Tunable Plasma Reactor

The objective of the present work is the experimental investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste through Cold Plasma Decomposition at atmospheric pressure.

This objective requires several tasks, including the design, construction and operation of a Gas Mixing System for simulation of the gaseous hazardous waste, a Tunable Plasma Reactor (TPR) for decomposition of the hazardous chemical compounds and a Gas Analysis System for chemical analysis of the concentrations of the hazardous chemical compounds as well as the decomposition products and decomposition by-products.

In the Tunable Plasma Reactor, the cold plasma at atmospheric pressure is generated by an energetic electron beam, while an electric field may be applied across the plasma. An atmospheric pressure cold plasma allows for higher gaseous hazardous waste mass flow rates than a sub-atmospheric pressure cold plasma.

The electron concentration and the average electron energy in such a plasma may be controlled independently via the electron beam current and the electric field voltage, respectively. Moreover, the electron and/or radical concentration may be controlled through the addition of "promoters" to the gaseous hazardous waste. Such "promot-
ers” are chemical compounds that easily ionize or easily dissociate into radicals. The combination of electron beam current, electric field and “promoters” represents the “tunability” of the Tunable Plasma Reactor.

The advantages of Cold Plasma Decomposition in the Tunable Plasma Reactor over Flame Decomposition are expected to be a reduced energy consumption and less hazardous or non-hazardous decomposition products as well as a reduced amount of decomposition by-products and less secondary waste per amount of hazardous chemical compound decomposed. Moreover, better controllability of the decomposition through “tunability” and easier scalability to smaller units through use of electricity are expected.

In order to meet the objective and to prove or disprove some of these expected advantages, determination — to the extent possible — of the energy, the decomposition products, the decomposition by-products and the secondary waste per amount of hazardous chemical compound decomposed is required.

Moreover, the chemical reactions that effect the decomposition of hazardous chemical compounds in gaseous hazardous waste are to be identified and/or ascertained — to the extent possible. The present work then provides a basis for evaluation of the feasibility of the decomposition of hazardous chemical compounds in gaseous hazardous waste through Cold Plasma Decomposition in a Tunable Plasma Reactor.

1.4.2 Hazardous Chemical Compounds

As indicated earlier, the hazardous chemical compounds of interest in the present work are halogenated methanes and ethenes, which are derived from non-halogenated methane (CH₄) and ethene (C₂H₄) via halogenation, i.e. substitution of Hydrogen (H) by Fluorine (F), Chlorine (Cl), Bromine (Br) and/or Iodine (I).

The investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste through Cold Plasma Decomposition in a Tunable Plasma Reactor focuses on Tetrachloro Methane (Carbon Tetrachloride), a chlorinated methane with the chemical formula CCl₄, Trichloro Methane (Chloroform), a chlorinated methane with the chemical formula CHCl₃, and Trichloro Ethene (Trichloroethylene), a chlorinated ethene with the chemical formula C₂HCl₃.

The chemical structure of these hazardous chemical compounds is shown in Figure 1.1. Moreover, as a supplement, the naming convention for chlorinated methanes and ethenes is discussed in Appendix A.1.

These three hazardous chemical compounds are experimental carcinogens and ter-
Figure 1.1: Chemical Structure of Hazardous Chemical Compounds
atogens [9], [10], [11] and are found frequently in gaseous hazardous waste. However, on the basis of the motivation of the present work, the main emphasis of the investigation is placed on CCl₄.

1.5 Overview

1.5.1 Organization of Present Work

The First Chapter provides, besides this Overview of the present work, the Introduction, the Background, the Motivation and the Objective of the present work, i.e. the decomposition of hazardous chemical compounds in gaseous hazardous waste through Cold Plasma Decomposition in a Tunable Plasma Reactor.

The Second Chapter describes the scientific background of the present work. The description includes the comparison of Flame, Cold Plasma and Hot Plasma, the projection of the Energy Expense per amount of hazardous chemical compound decomposed for Flame Decomposition and Cold Plasma Decomposition, the discussion of the Chemical Species and Chemical Reactions of importance to radiation and plasma chemistry as well as the definition of the G-Value as a classical quantity in radiation and plasma chemistry.

The Third Chapter provides a description of the Gas Mixing System developed for generation of particular concentrations of hazardous chemical compounds in simulated gaseous hazardous waste. The description includes a discussion of Dynamic Gas Mixing via Static or Dynamic sources of hazardous chemical compounds, such as Compressed Gas Cylinders or Vapor Generators, respectively, and a discussion of the calibration of the Rotameter volume flow meters used in the present work.

The Fourth Chapter provides a description of the Tunable Plasma Reactor developed for decomposition of hazardous chemical compounds in simulated gaseous hazardous waste. The description includes the Reaction Chamber, the Electron Beam and the Electric Field. The Electron Beam is generated by an Electron Beam Gun, whose principal components are the Vacuum System, the Electron Generation, the Electron Acceleration and the Vacuum-to-Atmosphere Interface.

The Fifth Chapter provides a description of the Gas Analysis System developed for the chemical analysis of hazardous chemical compounds in simulated gaseous hazardous waste and the chemical analysis of decomposition products as well as decomposition by-products. The description includes the Gas Chromatograph, the Gas Chromatograph/Mass Spectrometer and the Mass Spectrometer.
The Sixth Chapter provides a description of the Electron Beam Dosimetry developed for determination of the electron beam power deposition in simulated gaseous hazardous waste and therefore the energy per amount of hazardous chemical compound decomposed. The description includes the Facsimile Paper Radiography, the Aluminum Plate Calorimetry, the Monte-Carlo Simulation of the electron beam power deposition and the N\textsubscript{2}O Chemical Dosimetry, i.e. the decomposition of Nitrous Oxide (N\textsubscript{2}O) into N\textsubscript{2} and O\textsubscript{2}.

The Seventh Chapter provides a description of the Experimental Procedure along with a presentation of the Experimental Results of the investigation of the decomposition of the hazardous chemical compounds Tetrachloro Methane (CCl\textsubscript{4}), Trichloro Methane (CHCl\textsubscript{3}), and Trichloro Ethene (C\textsubscript{2}HCl\textsubscript{3}) in gaseous hazardous waste through Cold Plasma Decomposition in a Tunable Plasma Reactor.

The Eighth Chapter provides an Interpretation of the experimental results on the basis of the scientific background of the present work and on the basis of current literature pertinent to the present work. Particular emphasis is placed on electron chemistry and radical chemistry.

The Ninth Chapter provides the Summary and Conclusion of the present work and the Recommendations for future work.

Note that scientific and engineering constants used in the present work are listed in Appendix A.2 and solutions to differential equations used in the present work are listed in Appendix A.3 and Appendix A.4.

1.5.2 New Aspects of Present Work

The major new contributions of the present work to the decomposition of hazardous chemical compounds in gaseous hazardous waste through Cold Plasma Decomposition are as follows:

1. A comprehensive and contrasting investigation of the decomposition of CCl\textsubscript{4}, CHCl\textsubscript{3} and C\textsubscript{2}HCl\textsubscript{3} through Cold Plasma Decomposition in a Tunable Plasma Reactor via chemical analysis of the reactor intake and reactor exhaust through Gas Chromatography, Gas Chromatography/Mass Spectrometry and Mass Spectrometry has not been performed prior to the present work. A number of investigations of cold plasma decomposition of halogenated methanes and ethenes are performed in parallel to the present work at other institutions [16], [17], [18], [19], [20], [21], [22], [23], [24], [25].
However, these investigations show relatively little attention to the decomposition of halogenated methanes and ethenes in a cold plasma generated by an energetic electron beam and only the first one and the last two of the referenced investigations employ such a cold plasma at all.

2. The superposition of an electron beam and an electric field to establish independent control of the electron concentration and the average electron energy of the cold plasma represents a technology transfer from the field of laser machining to the field of air pollution control [26].

3. The combination of Facsimile Paper Radiography, Aluminum Plate Calorimetry, Monte-Carlo Simulation of electron beam power deposition and N₂O Chemical Dosimetry represents an innovative approach to electron beam dosimetry in gas.


Moreover, Hewlett-Packard Company, Palo Alto, California is currently investigating a similar conversion of their Mass Selective Detector in cooperation with Tufts University, Cambridge, Massachusetts [27].

5. The interpretation of the experimental results of the decomposition of CCl₄, CHCl₃ and C₂HCl₃ through Cold Plasma Decomposition in a Tunable Plasma Reactor in terms of the integration of dissociative electron attachment and radical attack as well as the contrasting of the initiation of the decomposition via dissociative electron attachment and radical attack has not been performed prior to the present work. Moreover, the application of a modified G-Value to the semi-quantitative description of the decomposition of CCl₄ in dry air represents an innovative approach.
Chapter 2

Background

2.1 Introduction to Cold Plasma Decomposition

2.1.1 General Remarks

A description of the scientific background of the present work is provided in the following. This very basic background comprises a qualitative discussion of Flame Decomposition, Hot Plasma Decomposition and Cold Plasma Decomposition, a quantitative discussion of Chemical Species and their Chemical Reactions of importance to the radiation and plasma chemistry encountered in Cold Plasma Decomposition of hazardous chemical compounds through Electron Beam Generated Plasmas and a quantitative discussion of the G-Value as a fundamental quantity in radiation and plasma chemistry.

2.1.2 The Difference Between A Flame and A Plasma

The decomposition of hazardous chemical compounds is usually effected through chemical reactions with Reactive Chemical Species. Frequently, these reactive chemical species are electrons e− and radicals, such as the excited oxygen atoms O(^3P) and O(^1D), the hydroxyl molecule OH or the chlorine atom Cl.

Owing to their fast reaction rate constants, the concentration of these chemical species need not be very high in order to result in significant decomposition of the hazardous chemical compounds they react with.

In order to generate these chemical species in gaseous hazardous waste, such waste
has to contain other chemical species that can produce these reactive chemical species upon addition of the appropriate amount and form of energy to the gaseous hazardous waste. While $e^-$ may be produced from virtually any chemical species, $O(^3P)$ and $O(^1D)$ may be produced from $O_2$, $OH$ may be produced from $H_2O$ or $H_2O_2$ and $Cl$ may be produced from chlorinated organic compounds.

In a *Flame*, the energy is provided in the form of thermal energy resulting in fast molecules which upon collision with appropriate other molecules generate above reactive chemical species. Such chemical reactions may be referred to as *Thermally Activated Chemical Reactions*, since a high flame temperature is required.

In a *Plasma*, the energy is provided in the form of electric energy resulting in fast electrons which upon collision with appropriate other molecules generate above reactive chemical species. Such chemical reactions may be referred to as *Non-Thermally Activated Chemical Reactions*, since a high plasma temperature is not required.

Since the reactive chemical species are typically generated by dissociative or non-dissociative electronic excitation or ionization, addition of energy in a form that favors such electronic excitation or ionization rather than translational, vibrational or rotational excitation should result in a more selective production of the reactive chemical species and therefore in a more selective decomposition of hazardous chemical compounds.

While such selectivity cannot be achieved in a flame due to unavoidable translational, vibrational or rotational excitation, it can be achieved in a plasma. This may be explained heuristically by the fact that in a flame atoms or molecules must cause electronic excitation or ionization, while in a plasma electrons can cause such excitation or ionization. Since electrons interact more efficiently with atomic or molecular electrons than atoms or molecules, they are more efficient in generating electronic excitation and ionization.

### 2.1.3 The Difference Between A Hot Plasma and A Cold Plasma

The electric energy is commonly provided to the plasma by an electric field applied across the plasma. The electric field may be applied as an *Electric Field with Electrodes* or an *Electric Field without Electrodes*. The minimum electric field required to generate a plasma corresponds to the *Breakdown Voltage*.

In a *Low Pressure Plasma*, the ohmic heating associated with the electric field does usually not cause a significant increase in the plasma temperature, i.e. the atom or molecule or atomic or molecular ion temperature, and a *Cold Plasma* is obtained. In
particular, the average electron energy is higher than the average atomic or molecular ion energy.

In a High Pressure Plasma, such as at atmospheric pressure, such ohmic heating does usually cause a significant increase in the plasma temperature and a Hot Plasma is obtained. In particular, the average electron energy is comparable to the average atomic or molecular ion energy.

Therefore, while the low pressure plasma allows for a low plasma temperature, i.e. low energy expense, the mass flow rate through such a plasma is limited by the low plasma pressure. And while the high pressure plasma allows for a high mass flow rate, the energy expense for such a plasma is unnecessarily high due to the high plasma temperature.

2.1.4 The Generation of A Cold Plasma

Obviously, the generation of a Cold Plasma at high, i.e. atmospheric pressure is essential to a high mass flow rate through and a low energy expense for such a plasma. This type of plasma is at the center of the the present work and may be generated in two fundamentally different ways.

First, rather than a Continuous Electric Field, a Pulsed Electric Field is applied across the plasma. Through a pulsed electric field, the average electron energy is “decoupled” from the average atomic or molecular ion energy. The latter energy remains approximately constant, while the former energy increases.

The pulse height, pulse frequency and pulse width are chosen such that in each pulse a much higher concentration of reactive chemical species is generated than in a continuous electric field and that the time between pulses is roughly on the order of the lifetime of the respective reactive chemical species.

The pulse height is typically on the order of the Breakdown Voltage, the pulse frequency typically represents microseconds to milliseconds, the pulse width typically represents nanoseconds or microseconds. This results in an extremely low Duty Cycle, because the pulse width represents only a small fraction of the pulse frequency [28], [29].

Therefore, the concentration of reactive chemical species in a pulsed electric field may on the average be as high as or lower than in a continuous electric field, while the ohmic heating in a pulsed electric field may be much lower than in a continuous electric field due to the extremely low duty cycle. Therefore, at atmospheric pressure, a similar chemical reactivity is achieved in a pulsed electric field at a much lower
plasma temperature than in a continuous electric field.

Second, rather than applying a Continuous or Pulsed Electric Field across the plasma, an energetic Electron Beam is introduced to the plasma. The electron beam generated cold plasma at atmospheric pressure forms the basis for the present work and represents an Externally Maintained Plasma in contrast to above Internally Maintained Plasma.

The ratio of inelastic collisions to elastic collisions of electrons with molecules increases with electron energy. Moreover, for inelastic collisions, the ratio of electronic excitation and ionization to vibrational, rotational or translational excitation increases with electron energy as well. At a high electron energy, typically, 50 % of the electron energy are channeled into electronic excitation, 50 % of the electron energy are channeled into ionization [30], [31], [32], [33], [34], [35].

Therefore it is essential to use an energetic electron beam with a rather high electron beam energy so that virtually only electronic excitation and ionization is obtained. Moreover, on these grounds, an electron beam generated plasma potentially results in a lower energy expense than a pulsed electric field generated plasma.

Although in an internally as well as in an externally maintained plasma electrons are generated through ionization, an important distinction has to be made regarding these electrons in an internally maintained plasma and an externally maintained plasma.

In an internally maintained plasma, electrons are generated entirely from within the plasma through ionization of atoms and molecules by Fast Electrons of the electron energy distribution. Moreover, through the presence of the electric field, the average electron energy of the electron energy distribution is higher than the average atomic or molecular ion energy.

In an externally maintained plasma, electrons are generated entirely from without the plasma through ionization of atoms and molecules by Fast Electrons of the electron beam. Moreover, through the absence of an electric field, the average electron energy of the electron energy distribution may be comparable to the average atomic or molecular ion energy. Nevertheless, the superposition of a sub-breakdown electric field may increase the average electron energy above such value.

Therefore, while the minimum average electron energy in an internally maintained plasma is approximately determined by the breakdown voltage, the minimum average electron energy in an externally maintained plasma may be as low as the plasma temperature. As will be discussed shortly, this may represent quite an important difference with respect to the decomposition of hazardous chemical compounds.
While a cold plasma generated via a pulsed electric field is frequently *Spatially Non-Uniform* and obviously *Temporally Non-Uniform*, a cold plasma generated via an energetic electron beam is usually *Spatially Uniform* and *Temporally Uniform*.

A cold plasma with spatial and temporal uniformity appears to be more suitable for the decomposition of hazardous chemical compounds since it ensures greater spatial and temporal uniformity of the chemical reactions that effect the decomposition of hazardous chemical compounds.

### 2.1.5 The Shotgun and The Rifle

On the basis of above selectivity, the decomposition of hazardous chemical compounds in a *Flame* or a *Hot Plasma* may be referred to as the *Shotgun* approach and the decomposition of hazardous chemical compounds in a *Cold Plasma* at atmospheric pressure may be referred to as the *Rifle* approach to such decomposition.

As will be discussed shortly, for the shotgun approach, the energy per amount of hazardous chemical compound decomposed is roughly inversely proportional with the concentrations of hazardous chemical compounds in gaseous hazardous waste. For the rifle approach, the energy per amount of hazardous chemical compound decomposed is roughly constant with the concentrations of hazardous chemical compounds in gaseous hazardous waste.

As a function of these concentrations, the rifle approach may therefore require more or less energy per amount of hazardous chemical compound decomposed than the shotgun approach. Consequently, the rifle approach may therefore be less or more economic than the shotgun approach with respect to energy cost. In particular, the shotgun approach appears to be attractive for high concentrations, the rifle approach appears to be attractive for low concentrations.

Obviously, *Cold Plasma Decomposition* may be applicable to the treatment of gaseous hazardous waste containing low concentrations of very special hazardous chemical compounds. On the other hand, *Flame Decomposition* and *Hot Plasma Decomposition* may be applicable to the treatment of solid, liquid and gaseous hazardous waste containing low or high concentrations of very general hazardous chemical compounds. Therefore, speciality and a low energy expense may be traded for generality and a high energy expense and vice versa.
2.1.6 Review of Current Research in Cold Plasma Decomposition

Types of Cold Plasmas, referred to as Discharge, currently under investigation at various national and international research institutions for decomposition of hazardous chemical compounds in gaseous hazardous waste are Dielectric Barrier Discharge, Packed Bed Discharge, Pulsed Corona Discharge, Corona Discharge, Gliding Arc Discharge, Glow Discharge, Microwave Glow Discharge and Electron Beam Discharge.

The following list represents a fraction of up-to-date research on cold plasma decomposition of hazardous chemical compounds in gaseous hazardous waste. The list contains the institutions at which the research is conducted, the type of plasma that is used for the research, the hazardous chemical compounds investigated in the research and the references that pertain to the research.

Note that the range of hazardous chemical compounds investigated extends beyond the range of hazardous chemical compounds of interest to the present work. Therefore, those hazardous chemical compounds that are not of interest to the present work are placed in parenthesis.

- **Dielectric Barrier Discharge:**
  - Auburn University, Auburn, Illinois; University of Illinois, Chicago, Illinois; Los Alamos National Laboratory, Los Alamos, New Mexico; University of California, Los Angeles, California: Trichloro Methane, Tetrachloro Methane. Trichloro Ethane, Trifluoro Trichloro Ethane, Trichloro Ethene, (Benzene). (Octane), (Formaldehyde), (Phosphonofluoridic Acid Methyl 112 Trimethyl Ester), (Dimethyl Sulfide) [19], [20], [21], [22], [23].
  - University of Tokyo, Tokyo, Japan; Fukui Institute of Technology, Tokyo, Japan: Difluoro Monochloro Methane, Trifluoro Trichloro Ethane, (Nitrogen Oxides) [36], [37].

- **Packed Bed Discharge:**
  - Toyohashi University of Technology, Toyohashi, Japan: (Ammonia), (Nitrogen Oxides) [38].
  - Air and Energy Research Laboratory, Research Triangle Park, North Carolina: Methane, Dichloro Methane, Trichloro Trifluoro Ethane, (Ethanol), (Hexane), (Cyclohexane), (Hexene), (Benzene), (Toluene), (Styrene), (Methy Ethyl Ketone) [39], [40], [41], [42].

- **Pulsed Corona Discharge:**
2.2 Energy Expense

The energy per molecule of a hazardous chemical compound decomposed represents the Energy Expense for the decomposition and is a function of the Destruction and Removal Efficiency. This latter efficiency for hazardous chemical compound $j$ may be defined as:

$$\eta_j = \frac{\dot{m}_{j0} - \dot{m}_j}{m_{j0}} = \frac{\dot{n}_{j0} - \dot{n}_j}{n_{j0}} = \frac{\Delta \dot{m}_j}{\dot{m}_{j0}} = \frac{\Delta \dot{n}_j}{\dot{n}_{j0}} = \frac{\Delta \hat{\dot{n}}_j}{\hat{\dot{n}}_{j0}}$$

2.2 Energy Expense

The energy per molecule of a hazardous chemical compound decomposed represents the Energy Expense for the decomposition and is a function of the Destruction and Removal Efficiency. This latter efficiency for hazardous chemical compound $j$ may be defined as:

$$\eta_j = \frac{\dot{m}_{j0} - \dot{m}_j}{m_{j0}} = \frac{\dot{n}_{j0} - \dot{n}_j}{n_{j0}} = \frac{\Delta \dot{m}_j}{\dot{m}_{j0}} = \frac{\Delta \dot{n}_j}{\dot{n}_{j0}} = \frac{\Delta \hat{\dot{n}}_j}{\hat{\dot{n}}_{j0}}$$
Here, \( \dot{m} \), \( \dot{n} \) and \( \dot{N} \) are mass, mole and number flow rates and \( \eta_j \) is the destruction and removal efficiency of hazardous chemical compound \( j \) and the subscript 0 represents pre-decomposition conditions. Apparently, for complete decomposition \( \eta_j = 1 \) and for incomplete decomposition \( \eta_j < 1 \).

The energy expense for Flame Decomposition of hazardous chemical compound \( j \) may be readily derived. In order to obtain a destruction and removal efficiency \( \eta_j \), the temperature of the gaseous hazardous waste must be increased by \( \Delta T_W \). The gaseous hazardous waste has a mass flow rate \( \dot{m}_W \) and a mass specific heat capacity \( c_W \). The thermal power \( \dot{Q}_W \) to effect this temperature increase is therefore given by:

\[
\dot{Q}_W = c_W \dot{m}_W \Delta T_W
\]

The energy expense \( \epsilon_j \) for hazardous chemical compound \( j \) may then be defined as:

\[
\epsilon_j = \frac{\dot{Q}_W}{\Delta \dot{N}_j}
\]

Obviously, a low energy expense is more desirable than a high energy expense. The ratio of the number flow rate of hazardous chemical compound \( j \) to the mass flow rate of the gaseous hazardous waste results as:

\[
\frac{\Delta \dot{N}_j}{\dot{m}_W} = \eta_j \frac{\dot{N}_{j0}}{\dot{m}_W} = \eta_j \varphi_{j0} \frac{N_A}{M_W}
\]

Here, \( \varphi_{j0} \) is the concentration of hazardous chemical compound \( j \) in gaseous hazardous waste and \( M_W \) is the mole mass of the gaseous hazardous waste. The energy expense \( \epsilon_j \) therefore results as:

\[
\epsilon_j = \frac{c_W M_W \Delta T_W}{\eta_j \varphi_{j0} N_A}
\]

Apparently, the energy expense for flame decomposition is inversely proportional to the concentration and the destruction and removal efficiency, where the latter is a function of the temperature increase \( \Delta T_W \). Moreover, in order to obtain a particular energy expense, the concentration must be higher than:
The energy expense for **Cold Plasma Decomposition** of hazardous chemical compound \( j \) is found in the present work as on the order of 10 eV or 2 kWh/kg for **Trichloro Ethene** \( (C_2HCl_3) \) and on the order of 150 eV or 25 kWh/kg for **Tetrachloro Methane** \( (CCl_4) \) at a destruction and removal efficiency of \( \eta_j > 0.99 \) in dry air. In contrast to flame decomposition, these values are approximately independent of the concentration.

With \( M_W = 28.85 \, \text{g/mol}, \ c_W = 1000 \, \text{J/kg K}, \ \Delta T_W = 1000 \, \text{K}, \ \eta_j = 0.99 \) and \( \epsilon_j = 150 \, \text{eV}, \ \phi_j \) results as \( \phi_j \geq 2000 \, \text{ppm} \). With \( \epsilon_j = 10 \, \text{eV}, \ \phi_j \) results as \( \phi_j \geq 30000 \, \text{ppm} \). For flame decomposition, a \( \Delta T_W \) of 1000 K is referenced in [3] and [61] as sufficient for a \( \eta_j \) of \( > 0.99 \).

In order to illustrate the advantage of cold plasma decomposition over flame decomposition with respect to the energy expense more clearly, the variable \( \epsilon_j \) as a function of \( \phi_j \) for flame decomposition and the constant \( \epsilon_j \) of 10 eV and 150 eV for cold plasma decomposition are contrasted in Figure 2.1 for above \( M_W, c_W, \Delta T_W \) and \( \eta_j \).

As evident from this figure, only at high concentrations does flame decomposition become preferable over cold plasma decomposition with respect to the energy expense. Since for flame decomposition, the temperature increase for a particular destruction and removal efficiency is approximately independent of the concentration of the hazardous chemical compound, this lack of selectivity results in a high \( \epsilon_j \) for a low \( \phi_j \) and vice versa, demonstrating the difference between the shotgun and the rifle approach to decomposition.

Therefore, for flame decomposition, typically a high concentration of hazardous chemical compound \( j \) in gaseous hazardous waste is desired in order to arrive at a low \( \epsilon_j \). Such concentration is commonly achieved using adsorption onto and desorption from activated charcoal at high and low flow rates and low and high temperatures, respectively [62].

However, such **Charcoal Adsorption/Desorption** with subsequent **Flame Decomposition** represents an increased technical complexity and requires at least two more process mass flows, i.e. charcoal for adsorption and air or steam for desorption, which turn into hazardous waste themselves. Moreover, the “destruction and removal efficiency” achievable through this process appears to be limited by the relatively slow adsorption and desorption equilibrium. Therefore, although widely used **Charcoal Adsorption/Desorption** in combination with **Flame Decomposition** may not represent the Best Available Control Technology [62], [63].
Figure 2.1: Energy Expense for Flame Decomposition and Cold Plasma Decomposition
2.3 Chemical Species and Chemical Reactions

2.3.1 Chemical Species

The following considerations provide an overview over the chemical species and chemical reactions important to radiation and plasma chemistry. A comprehensive review of radiation and plasma chemistry is beyond the scope of the present work and can be found for example in [31], [55], [64], [65], [66], [67] and [68].

A Chemical Species may be defined as neutral atoms or molecules, positive or negative atomic or molecular ions or electrons. The atoms and molecules and atomic or molecular ions may furthermore be categorized as Non-Excited or Excited. The excitation may be Translational or Electronic for atoms or atomic ions and Translational, Vibrational, Rotational or Electronic for molecules or molecular ions. Moreover, the excitation may be Unstable or Metastable.

All chemical species have an energy distribution with an average energy. It may suffice here for atoms and molecules, atomic and molecular ions and electrons to consider one energy group represented by the average atom or molecule, atomic or molecular ion or electron energy.

In a simplistic perspective, chemical species that react strongly with other chemical species at low or high average chemical species energies, i.e. temperatures, may be referred to as Radicals, chemical species that react strongly with other chemical species only at high average chemical species energies, i.e. temperatures, may be referred to as Non-Radicals.

Although arguable, for the present work, the following classification may be made. Whether a chemical species represents a radical or a non-radical depends strongly on its electronic configuration. In general, the more electrons a chemical species may give to or take from another chemical species, and the more readily the chemical species may give or take these electrons, the closer the chemical species represents a radical.

This is an expression of the heuristic fact that all chemical reactions involve bound or free electrons and is corroborated by the rather high chemical reactivity of electrons, negative ions, positive ions and excited atoms or molecules [55].

2.3.2 Chemical Reactions

Any chemical reaction among chemical species generally may be Dissociative, Non-Dissociative or Associative in that it results in the dissociation, non-dissociation or
association of the participating chemical species.

Furthermore, it may be simplifyingly stated that all chemical reactions involve electrons. However, the electrons may be Free or Bound, i.e. have an association with an atom or molecule or atomic or molecular ion or may have no such association. The following are chemical reactions relevant to the Cold Plasma Decomposition of hazardous chemical compounds.

- Chemical Reactions Involving Bound-Bound Electrons
  - Excitation
  - De-Excitation
  - Excitation Transfer
  - Negative and Positive Charge Transfer
  - Negative Ion to Positive Ion Recombination
  - Radical Attack
- Chemical Reactions Involving Free-Bound Electrons
  - Ionization
  - Electron Detachment
  - Electron Attachment
  - Electron to Positive Ion Recombination
- Chemical Reactions Involving Free-Free Electrons
  - Bremsstrahlung
  - Inverse Bremsstrahlung
  - Pair Production

The decomposition of hazardous chemical compounds in gaseous hazardous waste requires associative or dissociative chemical reactions of molecules of the hazardous chemical compounds with reactive chemical species. The two chemical reactions of particular interest to the present work are the dissociative electron attachment and the dissociative radical attack, although the latter may be subordinate to the former.

The reaction rate constant for electron attachment is generally a function of the average electron energy. Through superposition of an electric field at Sub-Breakdown Voltage to the externally maintained plasma, the average electron energy of the cold plasma may be increased and the reaction rate constant for electron attachment may thus be varied.
For an internally maintained plasma, the minimum average electron energy is approximately determined by the breakdown voltage, while for an externally maintained plasma, the minimum average electron energy is approximately determined by the plasma temperature.

Therefore, internally maintained plasmas may utilize electron attachment most efficiently for chemical compounds for which the dissociative electron attachment reaction rate constant is higher at higher average electron energies, while externally maintained plasmas with superimposed electric field may additionally utilize dissociative electron attachment for chemical compounds for which the dissociative electron attachment reaction rate constant is higher at lower average electron energies.

The concept of unimolecular, bimolecular and termolecular chemical reactions as well as the concept of reaction rate constants is introduced only subsequently. However, in order to illustrate the dependence of the reaction rate constant for electron attachment on the average electron energy, Figure 2.2 shows the bimolecular dissociative electron attachment reaction rate constant for the three chlorinated organic compounds CCl₄, CHCl₃ and C₂HCl₃ [32], [69] of interest to the present work.

Since the electric field superimposed to the externally maintained plasma is much lower than the electric field in an internally maintained plasma, ohmic heating is minimized and the properties of a cold plasma essentially pertain.

The combination of the variation of the average electron energy and the introduction to the cold plasma of chemical species, so-called "promoters", that produce reactive chemical species very efficiently in non-thermally activated chemical reactions represents the "tunability" of the Tunable Plasma Reactor.

The chemical reaction of electrons and radicals with molecules of hazardous chemical compounds as well as with molecules of non-hazardous chemical compounds present in the gaseous hazardous waste may result in the generation of negative and positive ions and other radicals.

This may result in enhanced decomposition of molecules of hazardous chemical compounds via dissociative or associative positive or negative charge transfer or dissociative or associative radical reaction. A typical example for such enhancement are chain reactions, in which a radical decomposes a molecule of a hazardous chemical compound and is then re-generated in the process.
Figure 2.2: Bimolecular Dissociative Electron Attachment Reaction Rate Constant for CCl₄, CHCl₃ and C₂HCl₃, adapted from [32] and [69]
2.4 Chemical Kinetics

2.4.1 General Considerations

The following considerations provide an overview over the mathematical modelling of radiation and plasma chemistry in the framework of chemical kinetics.

A comprehensive theoretical investigation of the cold plasma decomposition of CCl₄, CHCl₃ and C₂HCl₃ in air and oxygen through mathematical modelling of radiation and plasma chemistry was pursued in parallel to the experimental investigation. However, such mathematical modelling failed.

This failure was very likely due to an incomplete or inconsistent set of chemical reactions and reaction rate constants and due to an inappropriate numerical algorithm for the solution of the "stiff" system of non-linear ordinary differential equations for the concentrations of the chemical species.

Nevertheless, the definitions developed in the following are important to the interpretation of the experimental results.

2.4.2 Reactants and Products

A mathematical formulation of chemical reactions may be obtained via concentrations of chemical species and reaction rate constants of chemical reactions. Generally, between one and three chemical species participate in a chemical reaction. These chemical reactions are therefore referred to as Unimolecular, Bimolecular and Termolecular. In these terms, "Molecular" is to include "Atomic". The chemical reactions may be represented through:

\[
\sum_{i=1}^{n_R} \nu_i^R R_i \rightarrow \sum_{i=1}^{n_P} \nu_i^P P_i
\]

Here, \( n_R \) is the number of reactants in a chemical reaction and \( n_P \) is the number of products in a chemical reaction. Apparently, when \( n_R \) is equal to one, two or three, a unimolecular, bimolecular or termolecular chemical reaction obtains.

Moreover, \( R_i \) represent the chemical species as Reactants and \( P_i \) represent the chemical species as Products of a chemical reaction. Also, \( \nu_i^R \) represent the stoichiometric coefficients for the reactants and \( \nu_i^P \) represent the stoichiometric coefficients for the
products. The chemical species that do not participate in a chemical reaction have stoichiometric coefficients of zero for the chemical reaction.

Moreover, a chemical species \( j \) may be a reactant in one reaction and a product in another reaction. Also, for termolecular chemical reactions, a chemical species \( j \) may be a reactant and a product in the same reaction. This is the case when this chemical species serves as a "Third Body", whose presence is generally required for energy conservation through inelastic collisions. The reaction rate \( \omega \) in \( 1/s \) for a chemical reaction may be defined as:

\[
\omega = k \prod_{i=1}^{n_R} N(R_i)^{\nu_i^R}
\]

Here, \( k \) is the reaction rate constant and \( N(R_i) \) in \( 1/cm^3 \) is the concentration of chemical species \( R_i \). The dimension of \( k \) is \( 1/s, \ cm^3/s \) or \( cm^6/s \), depending on whether it applies to a unimolecular, bimolecular or termolecular chemical reaction.

This expression is nonlinear, since the stoichiometric coefficients \( \nu_i^R \) for the reactants may be different from unity and since, with \( n_R \geq 2 \), the concentrations \( N(R_i) \) of the reactants vary for virtually all chemical species \( R_i \). The time rate of change of the concentrations \( N(R_i) \) and \( N(P_i) \) of chemical species \( R_i \) and \( P_i \) is connected to \( \omega \) via [70]:

\[
\omega = \frac{1}{\nu_i^R} \frac{dN(R_i)}{dt} + \frac{1}{\nu_i^P} \frac{dN(P_i)}{dt}
\]

Apparently, in order to achieve a desired \( \omega \), either \( k \) or \( N(R_i) \) may be modified. In a flame \( k \) is modified via the temperature, in a cold plasma, \( k \) is modified via the superimposed electric field or via the electron beam dose rate through the G-Value as defined subsequently.

### 2.4.3 Reaction Rate Constants

In *Thermally Activated Chemical Reactions*, the reaction rate constant \( k \) is typically assumed to follow the Arrhenius temperature dependence:

\[
k(T) = k_0 \left( \frac{T}{T_0} \right)^n e^{-\frac{E_0}{k_B T}}
\]
Here, $k_0$ and $n$ are constants, and $E_0$ is an equivalent Activation Energy. The atoms and molecules as well as atomic and molecular ions are assumed at thermodynamic equilibrium, so that the average energies of the corresponding energy distributions are equivalent to the temperature $T$.

For chemical reactions whose reaction rate constants increase with temperature, the equivalent activation energy $E_0 > 0$, for chemical reactions whose reaction rate constants decrease with temperature, the equivalent activation energy $E_0 < 0$.

Moreover, there are chemical reactions whose reaction rate constants $k$ do not follow the Arrhenius temperature dependence. However, their description is beyond the scope of the present work. The reaction rate constants with Arrhenius and Non-Arrhenius temperature dependence may be found for example in [55], [71] and [72].

In Non-Thermally Activated Chemical Reactions for internally maintained plasmas and for externally maintained plasmas with a superimposed electric field, the reaction rate constant $k$ is typically assumed to be a function of the average electron energy $\bar{z}$. This energy is determined by the Reduced Electric Field, i.e. the ratio of the electric field to the total concentration.

Moreover, there are chemical reactions whose reaction rate constants $k$ are a function of the electron beam dose rate as well. This is described through the G-Value as defined subsequently and applies especially to externally maintained plasmas.

The reaction rate constants may be found in [31], [32], [33], [55], [64], [66], [68], [73] and [74].

Moreover, information about reaction rate constants in Thermally Activated Chemical Reactions and Non-Thermally Activated Chemical Reactions abounds in numberless articles on the subjects of Physical Chemistry and Chemical Physics, some of which will be referenced in the context of the interpretation of the experimental results of the present work.

### 2.4.4 Concentration of Chemical Species

The non-steady state, three-dimensional, non-linear partial differential equation for the concentration $N_j$ of chemical species $j$ as a function of convection, diffusion and chemical reactions is given by:

$$\frac{\partial N_j}{\partial t} + \mathbf{v} \cdot \nabla N_j = -\nabla \cdot q_j - \sum_{r=1}^{R} \nu_j^R(r) \omega_j^R(r) + \sum_{r=1}^{R} \nu_j^P(r) \omega_j^P(r)$$
Here, $q_j = -D_j \nabla N_j$ and $N_j$ is the concentration of chemical species $j$, $D_j$ is the diffusion coefficient of chemical species $j$ and $v$ is the convection velocity of the cold plasma.

Moreover, $R$ is the number of chemical reactions, $\nu_j^R(r)$ is the stoichiometric coefficient of chemical species $j$ as a reactant in chemical reaction $r$ and $\nu_j^P(r)$ is the stoichiometric coefficient of chemical species $j$ as a product in chemical reaction $r$. Also, $\omega_j^R(r)$ is the reaction rate of chemical reaction $r$ with chemical species $j$ as a reactant and $\omega_j^P(r)$ is the reaction rate of chemical reaction $r$ with chemical species $j$ as a product.

Since $n_S$ chemical species are present, a system of $n_S$ non-steady state, three-dimensional, non-linear partial differential equations for the concentrations $N_j$ of $n_S$ chemical species $j$ as a function of convection, diffusion and chemical reactions must be solved simultaneously.

Furthermore, in order to obtain the proper convection velocity $v$ of the plasma, the proper diffusion coefficient $D_j$ of chemical species $j$ and the proper reaction rate constants for chemical reactions involving chemical species $j$, the temperature $T$ and the average electron energy $\bar{\epsilon}$ are required.

Therefore, the non-steady state, three-dimensional, non-linear partial differential equations for the momentum and the energy as well as the Maxwell-Boltzmann differential equation for the electron energy distribution in addition to the system of $n_S$ non-steady state, three-dimensional, non-linear partial differential equation for the concentrations $N_j$ of $n_S$ chemical species $j$ must be solved as a function of convection, diffusion and chemical reactions.

The solution of such a system of non-steady, three-dimensional, non-linear partial differential equations is analytically definitely and numerically close to impossible and certainly beyond the scope of the present work. However, the subject of Chemical Kinetics is concerned with this type of numerical solution. A more detailed background of chemical kinetics and a computer code for the numerical solution may be found in [75].

Nevertheless, mathematical simplifications may be obtained on the basis of particular assumptions. The above non-steady state, three-dimensional, non-linear partial differential equation for the concentration $N_j$ of chemical species $j$ may be reduced to a steady state, one-dimensional, non-linear ordinary differential equation neglecting diffusion under assumption of $\frac{\partial N_j}{\partial t} = 0$, $\gamma \cdot \nabla N_j = -v \frac{dN_j}{dz}$ and $D_j = 0$. Here, $\gamma$ is the direction perpendicular to the energetic electron beam and the energetic electron beam is assumed to irradiate the gaseous hazardous waste over a distance $L$ along this direction.
Moreover, under assumption of approximately constant convection velocity \( v \) along the direction of \( z \) and constant temperature \( T \) of the gaseous hazardous waste and an approximate electron energy distribution determined by a Maxwell or a Druyvesteyn energy distribution [74], the ordinary partial differential equation for the concentration \( N_j \) of chemical species \( j \) allows for simple qualitative and semi-quantitative considerations.

Furthermore, a Reactor Time \( \tau = \frac{z}{v} \) may be defined such that the Reactor Residence Time is \( T = \frac{L}{v} \), and the steady state, one-dimensional, non-linear ordinary differential equation for the concentration \( N_j \) of chemical species \( j \) results as:

\[
\frac{dN_j}{d\tau} = -\sum_{r=1}^{R} \nu_j^R(r) \omega_j^R(r) + \sum_{r=1}^{R} \nu_j^P(r) \omega_j^P(r)
\]

In particular, the electron beam dose rate may be assumed variable along the direction of \( z \) and thus variable with reactor time \( \tau \).

### 2.4.5 Example for Chemical Kinetics

In order to develop an appreciation for the difficulty of the solution of even the system of steady state, one-dimensional, non-linear ordinary differential equations for the concentrations \( N_j \) of \( n_s \) chemical species \( j \), the following simple example may be considered.

Only four chemical species and bimolecular chemical reactions shall be accounted for. The chemical species are the electrons \( N_e \), the negative atomic or molecular ions \( N^- \), the positive atomic or molecular ions \( N^+ \) and the neutral atoms or molecules \( N \).

These chemical species are connected via ionization \( k_i \), electron attachment \( k_a \), electron detachment \( k_d \), electron to positive ion recombination \( k_e^+ \) and negative ion to positive ion recombination \( k_e^- \). Moreover, ionization occurs through the electron beam via the G-Value \( G_e \) for production of an electron-ion pair as defined subsequently.

\[
\begin{align*}
\frac{dN_e}{dt} &= \frac{M}{N_A} G_e N \dot{D} + k_i N_e N + k_d N^- N - k_a N_e N - k_e^+ N_e N^+ \\
\frac{dN^+}{dt} &= \frac{M}{N_A} G_e N \dot{D} + k_i N_e N - k_e^- N_e N^+ - k_e^+ N^- N^+ \\
\frac{dN^-}{dt} &= k_a N_e N - k_d N^- N - k_e^- N^- N^+
\end{align*}
\]
\[
\frac{dN}{dt} = k_dN^-N + k_eN^-N^+ + k_iN^-N^+ - k_iN_eN - k_aN_eN - \frac{M}{N_A} GeN \dot{D}
\]

Note that \(N^+ = N^- + N_e\). The resulting system of differential equations is difficult to solve even in steady state, because of its non-linear nature and because the different reaction rate constants represent different time scales, so that the system of differential equations is generally "stiff" [76], [77].

2.5 G-Value

2.5.1 Definition of G-Value

The chemistry in an electron beam generated cold plasma represents a combination of radiation and plasma chemistry. The G-Value is a classical quantity in radiation and plasma chemistry. The equations derived here are generally applicable to gas, liquid and solid material, although only the application to gas is of interest in the present work.

The absorption of energy by a chemical species \(k\) results in its destruction and the production of one or more chemical species \(j\). This process may be seen as a regular chemical reaction which is quantified by the G-Value.

Under the assumption that \(dN_j\) molecules of chemical species \(j\) are produced per energy \(dQ_k\) absorbed by \(N_k\) molecules of chemical species \(k\), the G-Value \(G_{kj}\) may be defined as:

\[
G_{kj} = \frac{dN_j}{dQ_k}
\]

It is generally assumed that \(G_{kj} \approx \text{const.}\) and that \(G_{kj}\) is a function of chemical species \(k\) and \(j\) only. Also, traditionally, the dimension of \(G_{kj}\) is \(1/100\text{eV}\).

For the present work, the absorbed energy originates from fast electrons provided by an energetic electron beam. The energy absorption proceeds via interaction of these fast electrons with atomic and molecular electrons, mainly through dissociative and non-dissociative excitation and ionization of atoms and molecules.

Therefore, the absorbed energy is distributed among all chemical species not according to their atom or molecule fractions, but according to their atomic or molecular
electron fractions. This distribution of absorbed energy is referred to as *Energy Partitioning* [78], [79].

Under the assumption that \( N_k \) molecules of chemical species \( k \) are present among \( R \) molecules, that a molecule of chemical species \( k \) has \( Z_k \) electrons while a molecule has \( Z \) electrons on the average and that \( N_k \) molecules of chemical species \( k \) absorb energy \( dQ_k \) while \( R \) molecules absorb energy \( dQ \), energy partitioning mandates:

\[
\frac{dQ_k}{dQ} = \frac{Z_k}{Z} \frac{N_k}{N}
\]

Therefore:

\[
dN_j = G_{kj} \frac{Z_k}{Z} \frac{N_k}{N} dQ
\]

Under the assumption that \( R \) molecules represent mole number \( n \), mass \( m \) and mole mass \( M \), the electron beam dose \( D \) may be defined as:

\[
D = \frac{Q}{m} = \frac{1}{M} \frac{Q}{n} = \frac{N_A}{M} \frac{Q}{R}
\]

\[
Q = \frac{M}{N_A} R D
\]

Under the assumption that \( R \approx \text{const.} \) and \( M \approx \text{const.} \), the differential equation for \( R_j \) results as:

\[
dR_j = \frac{M}{N_A} G_{kj} \frac{Z_k}{Z} R_k dD
\]

With \( n_S \) the number of chemical species, \( R, M \) and \( Z \) are defined through definition of the concentration \( \varphi_i = \frac{R_i}{R} \):

\[
R = \sum_{i=1}^{n_S} N_i
\]
\[ M = \frac{\sum_{i=1}^{n_S} N_i M_i}{\sum_{i=1}^{n_S} N_i} = \sum_{i=1}^{n_S} \varphi_i M_i \]
\[ Z = \frac{\sum_{i=1}^{n_S} N_i Z_i}{\sum_{i=1}^{n_S} N_i} = \sum_{i=1}^{n_S} \varphi_i Z_i \]

Also, since typically \( M_i \approx 2Z_i u N_A \), the ratio of \( M \) to \( Z \) may be approximated through the atomic mass unit \( u \) as:

\[ \frac{M}{Z} = 2u N_A \approx \text{const.} \]

Therefore also:

\[ dN_j = 2uG_{kj}Z_k R_k dD \]

Although the derivation of these equations is performed using the static quantities \( N, n, m \) and \( Q \), alternatively this derivation could be performed using the dynamic quantities \( \dot{N}, \dot{n}, \dot{m} \) and \( \dot{Q} \) as well.

As a sidebar, closely related to the G-Value is the W-Value, i.e. the absorption of energy required for production of a positive ion-electron pair via ionization. Since the dimension of \( W \) is eV, \( G_e \) for the production of a positive ion-electron pair via ionization and \( W \) are linked via:

\[ G_e = \frac{100}{W} \]

### 2.5.2 G-Value in Chemical Dosimetry

For chemical dosimetry applications, typically \( N \approx N_k \approx \text{const.} \) and \( N_j \ll N_k \). Therefore \( M \approx M_k \) and \( Z \approx Z_k \). The differential equation for \( \varphi_j \) may then be obtained from the differential equation for \( N_j \):
\[ \frac{d\mathcal{N}_j}{dt} = \frac{M}{N_A} G_{kj} \mathcal{N}_j \frac{dD}{dt} \]

\[ \frac{d\varphi_j}{dt} = \frac{M}{N_A} G_{kj} dD \]

This equation is used for chemical dosimetry since it exhibits a direct linkage between \( \varphi_j \) and \( D \), i.e. it allows for estimation of \( D \) from the measured \( \varphi_j \).

However, the implied linear relation between \( \varphi_j \) and \( D \) only holds in the absence of additional chemical reactions that may affect \( \varphi_j \). Such additional chemical reactions may be the destruction of chemical species \( j \) and the production of one or more chemical species \( l \) by a corresponding G-Value \( G_{jl} \). The absence of such chemical reactions typically only obtains for low \( D \).

Sometimes, the presence of such additional chemical reactions is emulated by assuming \( G_{kj} \) as a function of \( D \), rather than a constant. This practice is somewhat questionable, because it is a mathematical manipulation, rather than a physical or chemical interpretation. Therefore, no attempt is made to use above equation for chemical dosimetry at high \( \varphi_j \) or high \( D \).

2.5.3 G-Value in Chemical Kinetics

For chemical kinetics applications, definition of the electron beam dose rate \( \dot{D} \) results in a modification to the differential equation for \( \mathcal{N}_j \):

\[ \dot{D} = \frac{dD}{dt} \]

And:

\[ \frac{d\mathcal{N}_j}{dt} = \frac{M}{N_A} G_{kj} \frac{Z_k}{Z} \mathcal{N}_k \dot{D} \]

In most all cases, use of the concentration \( N_j \) rather than the number of molecules \( \mathcal{N}_j \) is preferred:
\[ N_j = \frac{N_j}{V} \]
\[ \frac{dN_j}{dt} = \frac{M}{N_A} G_{kj} \frac{Z_k}{Z} N_k \dot{D} \]

Here, \( V \) is the volume corresponding to mass \( m \) and mole number \( n \) and the division by \( V \) may only be performed when \( V \approx \text{const.} \) obtains, such as with approximately constant pressure and temperature.

This equation is used for chemical kinetics since it allows for an expression of the time rate of change of \( N_j \). In particular, with \( G_{kj} \approx \text{const.} \) and \( \frac{M}{Z} \approx \text{const.} \), a unimolecular chemical reaction rate constant may be defined as:

\[ k = \frac{M}{N_A} G_{kj} \frac{Z_k}{Z} \dot{D} \]
\[ \frac{dN_j}{dt} = kN_k \]

Here, \( \dot{D} \) may be a function of time \( t \).

### 2.5.4 G-Value in Destruction and Removal Efficiency

The equations derived for the production of chemical species \( j \) from destruction of chemical species \( k \) also apply to the destruction of chemical species \( k \) directly, when the subscript \( j \) is changed to \( k \) and the destruction is accounted for through a minus sign in combination with the corresponding G-Value \( G_{kk} \). Also, dynamic rather than static quantities are used:

\[ d\dot{N}_k = -\frac{M}{N_A} G_{kk} \frac{Z_k}{Z} \dot{N}_k dD \]

Under the assumption that \( G_{kk} \approx \text{const.} \) and \( \frac{M}{Z} \approx \text{const.} \), the solution to this differential equation results as:

\[ \dot{N}_k = \dot{N}_{k0} e^{-\frac{M}{N_A} G_{kk} \frac{Z_k}{Z} D} \]

59
The Destruction and Removal Efficiency $\eta_k$ may then be defined as:

$$\eta_k = \frac{\dot{N}_{k0} - \dot{N}_k}{\dot{N}_{k0}} = \frac{\dot{n}_{k0} - \dot{n}_k}{\dot{n}_{k0}} = \frac{\dot{m}_{k0} - \dot{m}_k}{\dot{m}_{k0}} = 1 - e^{-\frac{Z}{\eta_k} G_{kk} \frac{Z}{Z_k} D}$$

### 2.5.5 G-Value in Energy Expense

The equation for the destruction and removal efficiency $\eta_k$ as a function of the electron beam dose allows for the expression of $D$ through $\eta_k$ with $\frac{M}{Z} \approx \text{const.}$:

$$D = \frac{N_A}{M} \frac{1}{G_{kk}} \frac{Z}{Z_k} \ln \frac{1}{1 - \eta_k}$$

The energy $\epsilon_k$ per molecule of chemical species $k$ decomposed, i.e. the Energy Expense, may then be defined with $M \approx \text{const.}$ such that:

$$\epsilon_k = \frac{\dot{Q}}{\dot{N}_{k0} - \dot{N}_k} = \frac{\dot{Q}}{\eta_k \dot{N}_{k0}} = \frac{\dot{Q}}{\eta_k \varphi_{k0} \dot{N}} = \frac{1}{\eta_k \varphi_{k0}} \frac{M}{N_A} D$$

$$\epsilon_k = \frac{1}{G_{kk} \varphi_{k0}} \frac{Z}{Z_k} \frac{1}{\eta_k} \ln \frac{1}{1 - \eta_k}$$

Although the G-Value $G_{kk}$ is assumed to be constant with time $t$ or electron beam dose $D$, it may still be a function of the concentration $\varphi_{k0}$ of chemical species $k$. The limiting cases of $\epsilon_k$ are:

$$\lim_{\eta_k \to 0} \frac{1}{\eta_k} \ln \frac{1}{1 - \eta_k} = \lim_{\eta_k \to 0} \frac{1 - \eta_k}{(1 - \eta_k)^2} (-1) = \lim_{\eta_k \to 0} \frac{1}{1 - \eta_k} = 1$$

And:

$$\lim_{\eta_k \to 0} \epsilon_k = \frac{1}{G_{kk} \varphi_{k0}} \frac{Z}{Z_k}$$
A plot of $\varepsilon_k$ vs. $\eta_k$ starts at this limit of $\varepsilon_k$ for $\eta_k = 0$ and approaches positive infinity for $\eta_k = 1$. However, this approach is very slow. For example, at $\eta_k = 0.9999$, $\eta_k = 0.999999$ and $\eta_k = 0.99999999$, respectively, the $\frac{1}{\eta_k} \ln \frac{1}{1-\eta_k}$ are $9.21$, $13.82$ and $18.42$, respectively.

For comparison, the derivative of $\dot{N}_k$ with respect to $\dot{Q}$ and the inverse of this derivative result as:

\[
\frac{d\dot{N}_k}{d\dot{Q}} = -G_{kk} \frac{Z_k}{Z} \frac{\dot{N}_k}{\dot{R}} d\dot{Q} = -G_{kk} \frac{Z_k}{Z} \frac{\dot{N}_k}{\dot{R}} e^{-\frac{M}{\lambda_k} G_{kk} \frac{Z_k}{Z} d\dot{Q}}
\]

\[
\frac{d\dot{Q}}{d\dot{N}_k} = -\frac{Z}{Z_k G_{kk} \phi_{ko}} \frac{1}{1-\eta_k}
\]

Moreover, the derivative of $\dot{N}_k$ with respect to $\dot{Q}_k$ and the inverse of this derivative result as:

\[
\frac{d\dot{N}_k}{d\dot{Q}_k} = -G_{kk} d\dot{Q}_k
\]

\[
\frac{d\dot{Q}_k}{d\dot{N}_k} = -\frac{1}{G_{kk}}
\]

Apparently, $\varepsilon_k$, $\frac{d\dot{Q}}{d\dot{N}_k}$ and $\frac{d\dot{Q}_k}{d\dot{N}_k}$ have very different values.
2.6 Typical Parameters of Electron Beam Generated Cold Plasma

2.6.1 General Considerations

Of the large number of reactive chemical species present in a cold plasma, three reactive chemical species may be considered as examples in the following. These chemical species are the electrons $e^-$, the atomic oxygen radicals $O(1D)$ and $O(3P)$ and the negative molecular oxygen ions $O^−$. In particular, the electrons and the radicals are of interest to the decomposition of halogenated methanes and ethenes.

In the following, the steady state concentrations of these chemical species are estimated for an electron beam generated cold plasma in air and oxygen at atmospheric pressure and temperature. The concentrations are calculated in the absence of halogenated methanes and ethenes and, depending on the corresponding reaction rate constant, may be as high or lower in the presence of halogenated methanes and ethenes. Also, only the chemical reactions with the fastest reaction rate constants are considered for each of these chemical species.

A cold plasma in nitrogen is recombination controlled. A cold plasma in air or oxygen is attachment controlled. As will be shown, the electron concentration in the attachment controlled cold plasma is significantly lower than the electron concentration in the recombination controlled cold plasma. Moreover, in the absence of significant electron detachment, the negative ion concentration in the attachment controlled plasma is significantly higher than the electron concentration.

On the basis of the electron, the negative ion and the positive ion concentration, an estimate of the importance of diffusion with respect to chemical reactions may be obtained via comparison of the electron, the negative ion and the positive ion loss time.

2.6.2 G-Value for Production of Electrons and Atomic Oxygen Radicals

The cold plasma in the Tunable Plasma Reactor is approximately at atmospheric temperature and atmospheric pressure. The total concentration in such a cold plasma is given via the ideal gas law. For $T = 298.15K$ and $p = 1.01325 \cdot 10^5$ Pa, this results in approximately $N \approx 2.5 \cdot 10^{19} 1/cm^3$. Moreover, for air the $O_2$ concentration is 20 % of the total concentration, i.e. $N_{O_2} = 5.0 \cdot 10^{18} 1/cm^3$, for oxygen, the $O_2$ concentration is 100 % of the total concentration, i.e. $N_{O_2} = 2.5 \cdot 10^{19} 1/cm^3$. 
The mole mass is \( M = 28.01 \text{ g/mol} \) for nitrogen, \( M = 28.85 \text{ g/mol} \) for air and \( M = 32 \text{ g/mol} \) for oxygen. In a cold plasma, electrons and atomic oxygen radicals are produced via their respective G-Values. The overall G-Value for production of electrons is approximately \( G_e = 3 /100 \text{eV} \), the overall G-Value for production of O(\(^{1}\text{D}) \) and O(\(^{3}\text{P}) \) atomic oxygen radicals from molecular oxygen is approximately \( G_{O(1D)} = G_{O(3P)} = G_{O} = 2 /100 \text{eV} \) [55].

For the Tunable Plasma Reactor, a typical electron beam power deposition is 1W/cm\(^2\), corresponding to an electron beam dose rate of approximately \( \dot{D} = 100 \text{Mrad/s} \).

Therefore, the volumetric production rate \( \frac{M}{N_A} G_e \dot{N} \dot{D} \) of electrons is \( 2.2 \cdot 10^{17} \text{ 1/cm}^3 \text{ s} \) in nitrogen, \( 2.25 \cdot 10^{17} \text{ 1/cm}^3 \text{ s} \) in air and \( 2.5 \cdot 10^{17} \text{ 1/cm}^3 \text{ s} \) in oxygen. Also, the volumetric production rate \( \frac{M}{N_A} G_{O} \dot{N}_{O_2} \dot{D} \) of atomic oxygen radicals is \( 3 \cdot 10^{16} \text{ 1/cm}^3 \text{ s} \) in air and \( 1.65 \cdot 10^{17} \text{ 1/cm}^3 \text{ s} \) in oxygen.

### 2.6.3 Electrons in Recombination Controlled Cold Plasma

In order to estimate the electron and the positive ion loss time in a recombination controlled plasma, such as a cold plasma in nitrogen, the concentration of electrons and positive ions must be determined. For a cold plasma controlled by bimolecular electron to positive ion recombination, the electron concentration may be determined from:

\[
\frac{dN_e}{d\tau} = \frac{M}{N_A} G_e N \dot{D} - k_e^r N^+ N_e
\]

Typically, the electron to positive ion recombination reaction rate constant is \( k_e^r \approx 1.5 \cdot 10^{-7} \text{ cm}^3 /\text{s} \) at \( T = 298.15 \text{ K} \) [55]. Under the assumption that \( N^+ \approx N_e \) and \( \frac{dN_e}{d\tau} \approx 0 \), the electron concentration results as:

\[
N_e = \sqrt{\frac{M}{N_A} \frac{G_e N \dot{D}}{k_e^r}}
\]

Therefore, \( N_e \approx 1.2 \cdot 10^{12} \text{ 1/cm}^3 \). Moreover, the electron loss time via electron to positive ion recombination results as \( \tau_e^r = \frac{1}{k_e^r N^+} \), i.e. approximately \( 6 \mu\text{s} \). Also, the positive ion loss time is equal to the electron loss time.
2.6.4 Electrons in Attachment Controlled Cold Plasma

In order to estimate the electron, the negative ion and the positive ion loss time in an attachment controlled plasma, such as a cold plasma in air or oxygen, the concentration of electrons, negative ions and positive ions must be determined. For a cold plasma controlled by termolecular non-dissociative electron attachment to O$_2$ with O$_2$ and N$_2$ as the "third body", the electron concentration may be determined from:

\[
\frac{dN_e}{d\tau} = \frac{M}{N_A} G_e N \dot{D} - k_a(O_2)N_{O_2}^2N_e - k_a(N_2)N_{N_2}N_{O_2}N_e
\]

Typically, the electron attachment reaction rate constant is \(k_a(O_2) \approx 2.0 \cdot 10^{-30}\) cm$^6$/s and \(k_a(N_2) \approx 1.5 \cdot 10^{-31}\) cm$^6$/s at \(T = 298.15\) K [80]. Under the assumption that \(\frac{dN_e}{d\tau} \approx 0\), the electron concentration results as:

\[
N_e = \frac{M}{N_A} \frac{G_e N \dot{D}}{[k_a(O_2)N_{O_2} + k_a(N_2)N_{N_2}]N_{O_2}}
\]

Therefore, \(N_e \approx 3.5 \cdot 10^9\) 1/cm$^3$ in air and \(N_e \approx 2 \cdot 10^8\) 1/cm$^3$ in oxygen. Moreover, the electron loss time via electron attachment results as \(\tau_a = \frac{1}{[k_a(O_2)N_{O_2} + k_a(N_2)N_{N_2}]N_{O_2}}\), i.e. approximately 15 ns in air and 800 ps in oxygen.

2.6.5 Negative Ions in Attachment Controlled Cold Plasma

For a cold plasma controlled by termolecular non-dissociative electron attachment to O$_2$ and bimolecular negative ion to positive ion recombination, such as a cold plasma in air or oxygen, the negative ion concentration may be determined from:

\[
\frac{dN^-}{d\tau} = k_a(O_2)N_{O_2}^2N_e + k_a(N_2)N_{N_2}N_{O_2}N_e - k_r^iN^+N^-
\]

Typically, the negative ion to positive ion recombination reaction rate constant is \(k_r^i \approx 7.5 \cdot 10^{-6}\) cm$^3$/s at \(T = 298.15\) K [55]. Under the assumption that \(N^+ \approx N^-\) and \(\frac{dN^-}{d\tau} \approx 0\), the negative ion concentration in combination with the above electron concentration results as:
Therefore, $N^- \approx 1.7 \cdot 10^{11} 1/cm^3$ in air and $N^- \approx 1.8 \cdot 10^{11} 1/cm^3$ in oxygen, which justifies the assumption $N^+ \approx N^-$ for air and oxygen. Moreover, the negative ion loss time via negative ion to positive ion recombination results as $\tau_r^i = \frac{1}{k_f N_T}$, i.e. approximately 770 ns in air and 730 ns in oxygen. Also, the positive ion loss time is equal to the negative ion loss time.

For a cold plasma controlled by termolecular non-dissociative electron attachment to O$_2$ and termolecular associative negative charge transfer from O$_2^-$ to O$_2$, such as a plasma in air or oxygen, the O$_2^-$ concentration may be determined from:

\[
\frac{dN_{O_2^-}}{d\tau} = k_a(O_2)N_{O_2}N_e + k_a(N_2)N_N_2N_{O_2}N_e - k_x NN_{O_2}N_{O_2^-}
\]

Typically, the negative charge transfer reaction rate constant is $k_x \approx 3.5 \cdot 10^{-3} cm^6/s$ at $T = 298.15 K$ [55]. Under the assumption that $\frac{dN_{O_2^-}}{d\tau} \approx 0$, the O$_2^-$ concentration in combination with the above electron concentration results as:

\[
N_{O_2^-} = \frac{M G_e N \dot{D}}{N_A k_x NN_{O_2}}
\]

Therefore, $N_{O_2^-} \approx 5.2 \cdot 10^9 1/cm^3$ for air and $N_{O_2^-} \approx 1.2 \cdot 10^9 1/cm^3$ for oxygen. Moreover, the O$_2^-$ loss time via negative charge transfer results as $\tau_x = \frac{1}{k_x NN_{O_2}}$, i.e. approximately 23 ns for air and 6 ns for oxygen. Therefore, the O$_2^-$ negative ions convert to O$_4^-$ negative ions immediately, so that the major negative ion in air or oxygen is O$_4^-$ rather than O$_7^-$. This was also observed by [81].

2.6.6 Atomic Oxygen Radicals in Cold Plasma

For a cold plasma controlled by bimolecular non-dissociative de-excitation of O(1D) through O$_2$ and N$_2$, such as a cold plasma in air or oxygen, the O(1D) concentration may be determined from:
\[
\frac{dN_{O(1D)}}{d\tau} = \frac{M}{N_A} G_O N_{O_2} \dot{D} - k_1 N_{O_2} N_{O(1D)} - k_2 N_{N_2} N_{O(1D)}
\]

Typically, the de-excitation reaction rate constant is \(k_1(O_2) \approx 3.4 \cdot 10^{-11} \text{ cm}^3/\text{s}\) and \(k_2(N_2) \approx 2.6 \cdot 10^{-11} \text{ cm}^3/\text{s}\) at \(T = 298.15 \text{ K}\) [23], [55]. Under the assumption that \(\frac{dN_{O(1D)}}{d\tau} \approx 0\), the \(O(1D)\) concentration results as:

\[
N_{O(1D)} = \frac{M}{N_A} \frac{G_O N_{O_2} \dot{D}}{k_1 N_{O_2} + k_2 N_{N_2}}
\]

Therefore, \(N_{O(1D)} \approx 4.4 \cdot 10^7 \text{ 1/cm}^3\) in air and \(N_{O(1D)} \approx 1.9 \cdot 10^8 \text{ 1/cm}^3\) in oxygen. Moreover, the \(O(1D)\) loss time via de-excitation results as \(\tau_c = \frac{1}{k_1 N_{O_2} + k_2 N_{N_2}}\), i.e. approximately 1 ns in air and oxygen.

For a cold plasma controlled by termolecular associative de-excitation of \(O(3P)\) through \(O_2\) and bimolecular non-dissociative re-excitation through \(O(1D)\) and \(O_2\), such as a cold plasma in air or oxygen, the \(O(3P)\) concentration may be determined from:

\[
\frac{dN_{O(3P)}}{d\tau} = \frac{M}{N_A} G_O N_{O_2} \dot{D} + k_1 N_{O_2} N_{O(1D)} - k_3 N_{O_2} N_{O(1D)}
\]

Typically, the de-excitation reaction rate constant is \(k_3 \approx 6.9 \cdot 10^{-34} \text{ cm}^3/\text{s}\) at \(T = 298.15 \text{ K}\) [23]. Under the assumption that \(\frac{dN_{O(3P)}}{d\tau} \approx 0\), the \(O(3P)\) concentration in combination with the above \(O(1D)\) concentration results as:

\[
N_{O(3P)} = \frac{M}{N_A} \frac{G_O \dot{D}}{k_3 N} \left[ 1 + \frac{k_1 N_{O_2}}{k_1 N_{O_2} + k_2 N_{N_2}} \right]
\]

Therefore, \(N_{O(3P)} \approx 4.3 \cdot 10^{11} \text{ 1/cm}^3\) in air and \(N_{O(3P)} \approx 7.7 \cdot 10^{11} \text{ 1/cm}^3\) in oxygen. Moreover, the \(O(3P)\) loss time via de-excitation results as \(\tau_c = \frac{1}{k_3 N_{O_2} N}\), i.e. approximately 12 µs in air and 2 µs in oxygen.

Therefore, for a cold plasma in air or oxygen, the \(O(1D)\) concentration may be comparable to or lower than the electron concentration, while the \(O(3P)\) concentration may be a hundred to a thousand times higher than the electron concentration.
2.6.7 Importance of Diffusion to Chemical Reactions

In order to estimate the importance of electron, negative ion and positive ion diffusion in comparison to chemical reactions such as electron to positive ion recombination, negative ion to positive ion recombination, electron attachment and negative charge transfer, the electron, negative ion and positive ion loss time via diffusion $\tau_e = \frac{1}{D_e}$, $\tau^- = \frac{1}{D^-}$ and $\tau^+ = \frac{1}{D^+}$, respectively, may be compared to the loss time for recombination, attachment and charge transfer.

Table 2.1 [74] shows the product of the total concentration and the electron diffusion coefficient for two values of the reduced electric field. With $N \approx 2.5 \cdot 10^{19} \text{ cm}^{-3}$ and $ND_e \approx 10 \cdot 10^{21} \text{ cm}^{-1} \text{ s}$, the electron diffusion coefficient results as $D_e \approx 400 \text{ cm}^2 \text{ s}^{-1}$. With $\lambda \approx 1 \text{ cm}$, the electron loss time via diffusion results as $\tau_e \approx 2.5 \text{ ms}$.

<table>
<thead>
<tr>
<th>$\nu_N$</th>
<th>$ND_e$(Air)</th>
<th>$ND_e$(O$_2$)</th>
<th>$ND_e$(N$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Td = $10^{-17} \text{ V cm}^2$</td>
<td>$10^{21} \text{ cm}^{-1} \text{ s}$</td>
<td>$10^{21} \text{ cm}^{-1} \text{ s}$</td>
<td>$10^{21} \text{ cm}^{-1} \text{ s}$</td>
</tr>
<tr>
<td>1.2</td>
<td>11.04</td>
<td>21.1</td>
<td>12.78</td>
</tr>
<tr>
<td>12.0</td>
<td>18.45</td>
<td>38.1</td>
<td>17.09</td>
</tr>
</tbody>
</table>

Table 2.1: Product of Number Densities and Electron Diffusion Coefficients [74]

Table 2.2 [74] shows the negative ion diffusion coefficient and the positive ion diffusion coefficient for dry and wet air and for dry and wet O$_2$. With $D^- \approx 0.04 \text{ cm}^2 \text{ s}^{-1}$, $D^+ \approx 0.03 \text{ cm}^2 \text{ s}^{-1}$ and $\lambda \approx 1 \text{ cm}$, the negative ion and positive ion loss time via diffusion result as $\tau^- \approx 25 \text{ s}$ and $\tau^+ \approx 33 \text{ s}$, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Air dry</th>
<th>Air wet</th>
<th>O$_2$ dry</th>
<th>O$_2$ wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^-$</td>
<td>0.043</td>
<td>0.035</td>
<td>0.0396</td>
<td>0.0358</td>
</tr>
<tr>
<td>$D^+$</td>
<td>0.028</td>
<td>0.032</td>
<td>0.0250</td>
<td>0.0288</td>
</tr>
</tbody>
</table>

Table 2.2: Positive Ion and Negative Ion Diffusion Coefficients [74]

The recombination, attachment and charge transfer loss time $\tau_e^r$, $\tau_a^+$, $\tau_d^a$ and $\tau_e$ is shorter than $\mu$s and typically on the order of ns. The diffusion loss time $\tau_e$, $\tau^-$ and $\tau^+$ is on the order of ms or s.

Therefore, diffusion may be neglected in comparison to recombination, attachment and charge transfer. Moreover, since almost all chemical reactions of interest to the present work occur on a similar time scale as recombination, attachment or charge transfer, diffusion may be neglected altogether.
2.6.8 Importance of Residence Time to Chemical Reactions

The cold plasma volume in the reaction chamber of the Tunable Plasma Reactor is approximately 10 cm$^3$. The gas volume flow rates through the cold plasma are typically 2,500 cm$^3$/min, 5,000 cm$^3$/min and 10,000 cm$^3$/min. Therefore, the residence times of the gas in the cold plasma are on the order of 240 ms, 120 ms and 60 ms, respectively.

As demonstrated above, the chemical reactions involving electrons, positive ions, negative ions and radicals may be expected to reach equilibrium within $\mu$s or ns. Therefore, with respect to such chemical reactions, steady state prevails in the cold plasma.

The reaction chamber of the Tunable Plasma Reactor is connected to the gas analysis system via tubing of approximately 2 m length, $\frac{1}{4}$ inch outside diameter and 0.035 inch wall thickness. With above gas volume flow rates, the residence times of the gas in the tubing are on the order of 0.8 s, 0.4 s and 0.2 s, respectively.

In view of the speed of above chemical reactions in general, this time appears to be sufficiently long for all chemical reactions that may take place in the exhaust of the Tunable Plasma Reactor to reach equilibrium. Therefore, it may be expected that the effective exhaust composition is analyzed by the gas analysis system.
Chapter 3

Gas Mixing System

3.1 Introduction to Gas Mixing System

For the present work, simulated rather than actual gaseous hazardous waste is employed because the scientifically satisfactory investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste is based on complete knowledge of the composition of the gaseous hazardous waste.

The simulated gaseous hazardous waste is generated through a dynamic gas mixing system. In the context of this system, a hazardous chemical compound is referred to as a Standard and gaseous hazardous waste is referred to as Standard Gas. A standard is contained in Standard Carrier Gas at a certified concentration. The standard gas is obtained by mixing Carrier Gas with one or more Standard Carrier Gases.

The gas mixing is accomplished via Rotameter volume flow meters. With the appropriate volume flow meters, carrier gas and standard carrier gases, it is possible to generate standard gases containing a wide range of standards and concentrations of standards. However, for the present work, the standard gas contains at most two standards, one of them being H$_2$O.

The standard carrier gases containing the standards at certified concentrations may be generated either statically or dynamically. Statically generated standard carrier gases require Compressed Gas Cylinders, dynamically generated standard carrier gases require Vapor Generators.

Also, Statically Generated standard carrier gases are more expensive than Dynamically Generated standard carrier gases since they provide certified concentrations of the standards with higher accuracy, precision and reproducibility. For this reason, a compromise with respect to the use of these standard carrier gases is made.
The standard gas required for calibration of the gas analysis system is produced via static generation of standard carrier gases, while the standard gas required for investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste is produced via dynamic generation of standard carrier gases.

3.2 Description of Gas Mixing System

3.2.1 Volume Flow Meter Combinations

The calibration of the gas analysis system and the investigation of the decomposition of the hazardous chemical compounds in gaseous hazardous waste are performed on very similar gas mixing systems. In particular, the standard gas is passed through the reaction chamber for both purposes. This is done in order to account in the calibration for any loss of standards inherent to the gas mixing system and the reaction chamber.

However, four variations with respect to the connections among the volume flow meters and with respect to the incorporation of the vapor generators are used. The first two variations use statically generated standard carrier gases and the standard gas and the standard carrier gas may be different. The last two variations use dynamically generated standard carrier gases and the standard gas and the standard carrier gas are identical. The variations of the gas mixing system are shown in Figure 3.1. The different volume flow meters are numbered “VFMi” and their specifications are listed in Section 3.6.

In the first variation, the carrier gas is passed through volume flow meter number 6. The statically generated standard carrier gas is passed through volume flow meter number 5. This variation is used to perform dynamic gas mixing for calibration of the gas analysis system with dry carrier gas. The variation uses the singly dashed and the upper triply dashed lines in above figure.

In the second variation, the carrier gas is passed through volume flow meter number 6, then split into a stream passing through volume flow meter number 4 and a stream passing through volume flow meter number 8 into the vapor generator containing pure water. These streams then are recombined so that the carrier gas has a particular relative humidity. The statically generated standard carrier gas is passed through volume flow meter number 5. This variation is used to perform dynamic gas mixing for calibration of the gas analysis system with wet carrier gas. The variation uses the doubly dashed and the lower triply dashed lines in above figure.

In the third variation, the carrier gas is passed through volume flow meter number 4. The standard carrier gas is passed through volume flow meter number 1 into the vapor
generator containing the pure liquid of the standard in order to produce dynamically generated standard carrier gas. This variation is used to perform dynamic gas mixing for investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste in dry carrier gas. The variation uses neither the singly nor the doubly dashed but the middle and lower triply dashed lines in above figure.

In the fourth variation, the carrier gas is split into a stream passing through volume flow meter number 4 and a stream passing through volume flow meter number 8 into the vapor generator containing pure water. These streams then are recombined so that the carrier gas has a particular relative humidity. The standard carrier gas is passed through volume flow meter number 1 into the vapor generator containing the pure liquid of the standard in order to produce dynamically generated standard carrier gas. This variation is used to perform dynamic gas mixing for investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste in wet carrier gas. The variation uses neither the singly nor the doubly dashed but the middle and lower triply dashed lines in above figure.

3.2.2 Vapor Generators

The Vapor Generators are based on a 100 ml pyrex glass graduate cylinder for CCl₄, CHCl₃ and C₃HCl₃ and a 250 ml pyrex glass graduate cylinder for H₂O. The open
cylinder is closed with a rubber stopper, through which two pieces of electropolished stainless steel tubing provide access to the vapor. The temperature of the pure liquid of the standard contained in the vapor generator is adjusted by heat tape wrapped around the cylinder.

A pyrex glass graduate cylinder is filled with the pure liquid of the standard, typically to $\frac{1}{4}$ to $\frac{1}{2}$ capacity. The piece of tubing that ends right above the level of the pure liquid of the standard then represents the inlet, the piece of tubing that ends right below the level of the rubber stopper represents the outlet of the vapor generator.

Condensation of standards on the tubing wall is observed at the outlet of the vapor generators. Such condensation is eliminated by extending the region wrapped with heat tape from the pure liquid of the standard to the outlet of the vapor generator, up to the point where mixing of the standard carrier gas with the carrier gas prevents further condensation.

### 3.2.3 Tubing

All connections among the volume flow meters within the gas mixing system as well as the connections from the gas mixing system to the reaction chamber of the Tunable Plasma Reactor and from this reaction chamber to the gas analysis system are made from 316L SMLS EPSS Electropolished Stainless Steel tubing obtained from High Purity Technology Inc., Poughkeepsie, New York through Banner Industries of New England, Beverly, Massachusetts.

The special stainless steel tubing has an outer diameter of $\frac{1}{4}$ inch, a wall thickness of $\frac{35}{1000}$ inch and an inner surface roughness of $R_a \leq 10 \mu m$. Such surface roughness represents a mirror-like surface quality and is thought to be essential in the prevention of loss of standard to the tubing wall.

Such loss of standard to the tubing wall can be of either chemical or physical nature. Loss of chemical nature is represented by Thermally Activated Surface Chemical Reactions of standards with the tubing wall. Loss of physical nature is represented by condensation of standards on the tubing wall.

A mirror-like surface quality reduces the area for thermally activated surface chemical reactions and also reduces the number of Active Sites, which are known to enhance thermally activated surface chemical reactions. Moreover, such a surface quality reduces the number of Condensation Cores.

While loss of chemical nature is important for reactive standards but is rather negligible for non-reactive standards, loss of physical nature is equally important for
both reactive standards and non-reactive standards. The most important reactive standards used in the present work are HCl and Cl₂.

Also, for reactive standards, the tubing wall may have to be passivated by exposing it to high concentrations of the standard, such that all remaining active sites for this standard become pacified. However, *Passivation* with too high a concentration will result in later release of the reactive standard into the standard gas, while passivation with too low a concentration will result in continued loss of the standard to the tubing wall.

A number of tubing materials were tested in the present work in order to identify the material with the least loss of standard to the tubing wall. Among the materials tested were tygon, teflon, copper, unpolished stainless steel and electropolished stainless steel. Only the latter tubing material was found to be acceptable.

### 3.2.4 Stainless Steel to Pyrex Glass Interface

All connections of the \( \frac{1}{4} \) inch stainless steel tubing are made with \( \frac{1}{4} \) inch stainless steel *Swagelok* fittings. This also holds for the connection to the *Old Reaction Chamber*. However, for the connection to the *New Reaction Chamber*, an interface between pyrex glass and stainless steel tubing needs to be devised. This is accomplished by glass-welding to the pyrex glass of the new reaction chamber short pieces of pyrex glass tubing with ball-and-socket fittings at their free ends.

These ball-and-socket fittings are connected to additional short pieces of pyrex glass tubing with \( \frac{1}{4} \) inch outside diameter and ball-and-socket fittings at one end and straight pyrex glass tubing at the other end. This free end of the pyrex glass tubing and a free end of the stainless steel tubing then are connected via stainless steel *Swagelok* fittings, with a teflon ferrule on the pyrex glass side and a stainless steel ferrule on the stainless steel side. The use of ball-and-socket fittings introduces the mechanical flexibility required with the use of pyrex glass tubing.

### 3.3 Theory of Dynamic Gas Mixing

The standard gas is generated by dynamic mixing of a carrier gas with \( n \) standard carrier gases, each of which contains one standard at a particular concentration. An equation for the concentrations of these standards \( j \) in the standard gas is given by:
\[ \varphi_j = \frac{n_j}{n_j^{SC}} \]
\[ \dot{n}^S = \dot{n}^C + \sum_{k=1}^{n} \dot{n}_k^{SC} \]
\[ \varphi_j^S = \frac{n_j}{\dot{n}^S} \]
\[ \varphi_j^SC = \frac{\varphi_j}{1 + \frac{\dot{n}^C}{\dot{n}_j^{SC}} + \sum_{k=1}^{j-1} \frac{n_k^{SC}}{n_j^{SC}} + \sum_{k=j+1}^{n} \frac{n_k^{SC}}{n_j^{SC}}} \]

The superscripts are \( S \) for the standard gas, \( C \) for the carrier gas, \( SC \) for the standard carrier gas. The subscript is \( j \) for the standard. The symbol \( \varphi \) represents concentrations and the symbol \( \dot{n} \) represents mole flow rates.

This equation allows for the determination of \( \varphi_j^S \) as a function of given \( \varphi_j, \dot{n}^C, \dot{n}_j^{SC} \) and \( n_k^{SC} \). Therefore, \( \dot{n}^S \) is determined as a function of these parameters as well.

In contrast, the determination of \( \dot{n}_j^{SC} \) as a function of given \( \varphi_j^S, \varphi_j, \) and \( \dot{n}^S \) is accomplished through:

\[ \dot{n}_j^{SC} = \frac{\varphi_j^S}{\varphi_j} \dot{n}^S \]

A restriction that must be placed on this equation is given by:

\[ 1 = \frac{\dot{n}^C}{\dot{n}^S} + \sum_{k=1}^{n} \frac{\varphi_k^S}{\varphi_k} \]

Under the assumption that both the carrier gas and all standard carrier gases are at the same temperature and pressure, ratios of mole flow rates \( \dot{n} \) are equivalent to ratios of volume flow rates \( \dot{V} \) via the ideal gas law. Volume flow rates are then easily measured by volume flow meters.

In order to obtain useful standard gases, it is important to maintain the characteristics of the carrier gas. This means that the concentrations of the standards in the standard carrier gases have to be rather high, so that the standard carrier gas volume flow rates may be rather low and the dominating volume flow rate is that of the carrier gas. This is important in view of the fact that the standard carrier gases may be different from the carrier gas.
3.4 Static Generation of Standard Carrier Gases

All statically generated standard carrier gases are produced by Matheson Gas Products, Gloucester, Massachusetts and by Matheson Gas Products, Rutherford, New Jersey. In contrast, all carrier gases are obtained from Northeast Airgas, Manchester, New Hampshire.

In principle, a pre-cleaned and surface treated compressed gas cylinder is filled with the standard carrier gas to a particular pressure. A particular mass or volume of the pure liquid or the pure gas of the standard is added. Then, equilibrium is allowed to establish between the gas phase of the standard carrier gas and the liquid or gas phase of the standard so as to obtain the required concentration of the standard in the standard carrier gas.

It is important to prevent condensation of the standard in the compressed gas cylinder. Without condensation, the required concentration of the standard in the standard carrier gas always obtains in the compressed gas cylinder. However, with condensation, the standard is always at its vapor pressure and the concentration of the standard in the standard carrier gas depends on the pressure of the standard carrier gas in the compressed gas cylinder. In particular, the concentration increases with decreasing pressure of the standard carrier gas. This situation prevails until no condensation remains.

In order to prevent condensation of the standard, the pressure of the standard carrier gas before adding a particular mass of the pure liquid of the standard must be limited. This limit is a function of the required concentration of the standard in the standard carrier gas and may be readily derived by consideration of the gas-liquid-phase equilibrium of a binary mixture:

\[
\begin{align*}
    p_j^{SC} V &= n_j^{SC} R_m T \\
    p_j^{SC} V &= n_j^{SC} R_m T \\
    p_j V &= n_j R_m T
\end{align*}
\]

Here, \( V \) is the volume of the compressed gas cylinder and \( T \) is the temperature of the compressed gas cylinder. Also, \( p_j^{SC} \) and \( n_j^{SC} \) are the pressure and mole number of the standard carrier gas before, and \( p_j^{SC} \) and \( n_j^{SC} \) are the pressure and mole number of the standard carrier gas after adding mass \( m_j \) of the pure liquid of the standard. Also, \( p_j \) and \( n_j \) are the pressure and mole number of the standard. The equations may be combined to yield:
\[ n_j = \frac{m_j}{M_j} \]
\[ n_j^{SC} = n_j^{SC} + n_j \]
\[ p_j^{SC} = p_j^{SC} + p_j \]
\[ \varphi_j = \frac{n_j}{n_j^{SC}} = \frac{p_j}{p_j^{SC}} \]
\[ p_j^{SC} = \frac{1}{1 - \varphi_j} p_j^{SC} \]

Here, \( M_j \) is the mole mass of the standard and \( \varphi_j \) is the concentration of the standard in the standard carrier gas. These equations may then be combined to result in:

\[ \varphi_j = \frac{1}{1 + \frac{p_j^{SC}}{R_{mT}} \frac{M_j}{m_j} \frac{\varphi_j}{1 - \varphi_j}} \]
\[ m_j = \frac{p_j^{SC}}{R_{mT}} \frac{M_j}{1 - \varphi_j} \]

Also:

\[ \phi_j = \frac{p_j}{p_j^*(T)} = \frac{\varphi_j}{1 - \varphi_j} \frac{p_j^{SC}}{p_j^*(T)} \]
\[ \phi_j = \frac{m_j}{M_j} \frac{R_{mT}}{p_j^*(T)V} \]

Here, \( \phi_j \) is the “relative humidity” of the standard in the standard carrier gas, and \( p_j^*(T) \) is the vapor pressure of the standard at temperature \( T \). The equations may be combined to yield:

\[ p_j^{SC} = \phi_j \frac{1 - \varphi_j}{\varphi_j} p_j^*(T) \]
\[ m_j = \phi_j \frac{M_j V}{R_{mT}} p_j^*(T) \]
These last two equations are to be evaluated under the condition that $\phi_j \leq 1$.

The standards and standard carrier gases and the respective concentrations of the standards in these statically generated standard carrier gases are listed in Table 3.1. For standards with more than one concentration listed, only one concentration is in use at any time, so the listed concentrations represent successively used standards in standard carrier gases. The mole masses of the standards and standard carrier gases are listed in Table 3.2.

Depending on the chemical reactivity of the standard, it may react with the wall of the compressed gas cylinder via thermally activated surface chemical reactions and thus the concentration of the standard in the standard carrier gas obtained in equilibrium will decrease over time.

In order to determine how the concentrations of different standards in their standard carrier gases would be affected by thermally activated surface chemical reactions in compressed gas cylinders, the four most frequently used standards in their standard carrier gases were returned to Matheson Gas Products, Gloucester, Massachusetts and to Matheson Gas Products, Rutherford, New Jersey for re-analysis.

As a result of the original analysis and the re-analysis, the HCl standard with a concentration of 2315 ppm had dropped to 2030 ppm over a period of several months, and the Cl$_2$ standard with a concentration of 1960 ppm had dropped to 1210 ppm over the same period.

Also, the CCl$_4$ standard with a concentration of 1033 ppm had only dropped to 1020 ppm over this period of several months, and the CHCl$_3$ standard with a concentration of 975 ppm had only dropped to 972 ppm over the same period.

### 3.5 Dynamic Generation of Standard Carrier Gases

Dynamically generated standard carrier gases are produced via vapor generators in the gas mixing system. In principle, the standard carrier gas is passed over the pure liquid of the standard. With a sufficiently low volume flow rate of the standard carrier gas, vapor pressure equilibrium is allowed to establish between the gas phase of the standard carrier gas and the liquid phase of the standard.

Since the pure liquid of the standard is used in the vapor generator rather than a solution of the standard in a liquid solvent, vapor pressure equilibrium applies rather than a more complicated equilibrium described by Henry's equation.

The concentration of a chemical compound in the gas phase above its liquid phase is
<table>
<thead>
<tr>
<th>Standard</th>
<th>Standard Carrier Gas</th>
<th>Concentration $\varphi_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ppm</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>N$_2$</td>
<td>881</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Air</td>
<td>844</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Air</td>
<td>1053</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>re-analyzed</td>
<td>1020</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>Air</td>
<td>1950</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>N$_2$</td>
<td>975</td>
</tr>
<tr>
<td></td>
<td>re-analyzed</td>
<td>972</td>
</tr>
<tr>
<td>C$_2$HCl$_3$</td>
<td>N$_2$</td>
<td>890</td>
</tr>
<tr>
<td>C$_2$HCl$_3$</td>
<td>N$_2$</td>
<td>870</td>
</tr>
<tr>
<td>C$_2$H$_4$Cl$_2$</td>
<td>N$_2$</td>
<td>1005</td>
</tr>
<tr>
<td>CO</td>
<td>N$_2$</td>
<td>975</td>
</tr>
<tr>
<td>CO</td>
<td>N$_2$</td>
<td>1000</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>N$_2$</td>
<td>1004</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>N$_2$</td>
<td>1000</td>
</tr>
<tr>
<td>HCl</td>
<td>N$_2$</td>
<td>106</td>
</tr>
<tr>
<td>HCl</td>
<td>N$_2$</td>
<td>1950</td>
</tr>
<tr>
<td>HCl</td>
<td>N$_2$</td>
<td>2315</td>
</tr>
<tr>
<td></td>
<td>re-analyzed</td>
<td>2030</td>
</tr>
<tr>
<td>HCl</td>
<td>N$_2$</td>
<td>2265</td>
</tr>
<tr>
<td>HCl</td>
<td>N$_2$</td>
<td>2080</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>N$_2$</td>
<td>2150</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>N$_2$</td>
<td>1960</td>
</tr>
<tr>
<td></td>
<td>re-analyzed</td>
<td>1210</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>N$_2$</td>
<td>2120</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>N$_2$</td>
<td>1920</td>
</tr>
<tr>
<td>N$_2$</td>
<td>He</td>
<td>5367</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Ar</td>
<td>5710</td>
</tr>
<tr>
<td>O$_2$</td>
<td>He</td>
<td>5154</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Ar</td>
<td>5020</td>
</tr>
<tr>
<td>NO</td>
<td>He</td>
<td>5011</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>Air</td>
<td>1002</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>Ar</td>
<td>1970</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>Ar</td>
<td>100000</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>N$_2$O</td>
<td>$&gt;$990000</td>
</tr>
</tbody>
</table>

Table 3.1: Standards and Standard Carrier Gases
<table>
<thead>
<tr>
<th>Standard</th>
<th>Mole Mass $M_j$ g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>153.82300</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>119.37790</td>
</tr>
<tr>
<td>C$_2$HCl$_3$</td>
<td>131.38890</td>
</tr>
<tr>
<td>C$_2$H$_4$Cl$_2$</td>
<td>98.95960</td>
</tr>
<tr>
<td>CO</td>
<td>28.01040</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>44.00980</td>
</tr>
<tr>
<td>HCl</td>
<td>36.46090</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>70.90600</td>
</tr>
<tr>
<td>N$_2$</td>
<td>28.01340</td>
</tr>
<tr>
<td>O$_2$</td>
<td>31.99880</td>
</tr>
<tr>
<td>Air</td>
<td>28.85033</td>
</tr>
<tr>
<td>NO</td>
<td>30.00610</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>44.01280</td>
</tr>
<tr>
<td>He</td>
<td>4.00260</td>
</tr>
<tr>
<td>Ar</td>
<td>39.94800</td>
</tr>
</tbody>
</table>

Table 3.2: Mole Masses of Standards and Standard Carrier Gases, adapted from [83]

described by its vapor pressure. An equation for the vapor pressure may be obtained from fundamental thermodynamic equations under the assumption of a thermodynamic system at equilibrium. The derivation of the vapor pressure of a pure liquid is provided in Appendix B.1. In general terms for chemical compound $j$, the vapor pressure is given by:

$$p_j^e(T) = p_j^e e^{-\frac{T^*}{T_j}}$$

$$T_j^* = \frac{M \Delta h_v}{R_m}$$

Table 3.3 shows among other quantities the fitting parameters $T_j^*$ and $p_j^e$ as well as the heat of vaporization $\Delta h_v$ obtained from these fits for the three hazardous chemical compounds investigated in the present work, i.e. for CCl$_4$, CHCl$_3$, CHCl$_3$, and for H$_2$O. The fitting parameters are obtained by fitting tabulated data from [84] to above equation for the vapor pressure.

Table 3.4 shows the ratio of the fitted vapor pressure $p_j^e(T)$ to 760 torr at various temperatures of the liquid phase for the three hazardous chemical compounds and water. This pressure ratio is equal to the concentration $\varphi_j$ of the hazardous chem-
### Table 3.3: Mole Mass $M_j$, Melting Temperature $T_{m,j}$, Boiling Temperature $T_{b,j}$, Liquid Mass Density $\rho_j$, Fitting Parameters $T_j^*$ and $p_j^*$ and Heat of Vaporization $\Delta h_{v,j}$ for Hazardous Chemical Compounds and Water, adapted from [84]

<table>
<thead>
<tr>
<th></th>
<th>CHCl₃</th>
<th>CCl₄</th>
<th>C₂HCl₃</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_j$ g/mol</td>
<td>119.38</td>
<td>153.82</td>
<td>131.39</td>
<td>18.02</td>
</tr>
<tr>
<td>$T_{m,j}$ °C</td>
<td>-63.5</td>
<td>-23.0</td>
<td>-73.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$T_{b,j}$ °C</td>
<td>61.7</td>
<td>76.5</td>
<td>87.0</td>
<td>100.0</td>
</tr>
<tr>
<td>$\rho_j$ kg/m³</td>
<td>1.4832²⁰/₄</td>
<td>1.5940²⁰/₄</td>
<td>1.4642²⁰/₄</td>
<td>1.0</td>
</tr>
<tr>
<td>$p_j^*$ 10⁶ mmHg</td>
<td>49</td>
<td>57</td>
<td>52</td>
<td>585</td>
</tr>
<tr>
<td>$T_j^*$ K</td>
<td>3703</td>
<td>3927</td>
<td>4007</td>
<td>5057</td>
</tr>
<tr>
<td>$\Delta h_{v,j}$ kJ/kg</td>
<td>260</td>
<td>212</td>
<td>253</td>
<td>2336</td>
</tr>
</tbody>
</table>

On the basis of these rather high concentrations, the standard carrier gas volume flow rate need not be very high in order to generate a required concentration of a particular standard in the standard gas. Therefore, the establishment of vapor pressure equilibrium is supported.

In particular, a concentration shown in Table 3.4 is expected to be equal to the concentration in the standard carrier gas. Also, the standard carrier gas volume flow rate is low enough to ensure that the standard gas maintains the characteristics of the carrier gas.

Since the sensitivity of the vapor pressure to the temperature of the pure liquid of the standard is rather high, this temperature needs to be controlled narrowly. However, the simple heat tape used to maintain the temperature of the pure liquid of the standard in the vapor generator is not equipped with temperature control.

Therefore, the dynamic generation of standard carrier gases via vapor pressure equilibrium may be acceptable only when it is sufficient to know the concentration of a standard in the standard gas within an order of magnitude.

### 3.6 Calibration of Rotameter

All volume flow meters used for the present work are rotameters with glass floats. The respective manufacturers provide representative calibrations for batches of a particular volume flow meter model but no individual calibrations for a particular volume flow meter. Therefore, all volume flow meters require re-calibration with respect to a
<table>
<thead>
<tr>
<th>$T$</th>
<th>CHCl$_3$</th>
<th>CCl$_4$</th>
<th>C$_2$HCl$_3$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>5</td>
<td>10.67</td>
<td>5.54</td>
<td>3.80</td>
<td>0.98</td>
</tr>
<tr>
<td>10</td>
<td>13.49</td>
<td>7.10</td>
<td>4.89</td>
<td>1.35</td>
</tr>
<tr>
<td>15</td>
<td>16.93</td>
<td>9.04</td>
<td>6.26</td>
<td>1.84</td>
</tr>
<tr>
<td>20</td>
<td>21.08</td>
<td>11.40</td>
<td>7.93</td>
<td>2.48</td>
</tr>
<tr>
<td>25</td>
<td>26.05</td>
<td>14.28</td>
<td>9.97</td>
<td>3.31</td>
</tr>
<tr>
<td>30</td>
<td>31.97</td>
<td>17.74</td>
<td>12.45</td>
<td>4.38</td>
</tr>
<tr>
<td>35</td>
<td>38.98</td>
<td>21.89</td>
<td>15.43</td>
<td>5.74</td>
</tr>
<tr>
<td>40</td>
<td>47.23</td>
<td>26.83</td>
<td>18.99</td>
<td>7.46</td>
</tr>
<tr>
<td>45</td>
<td>56.87</td>
<td>32.67</td>
<td>23.22</td>
<td>9.62</td>
</tr>
<tr>
<td>50</td>
<td>68.10</td>
<td>39.55</td>
<td>28.21</td>
<td>12.30</td>
</tr>
<tr>
<td>55</td>
<td>81.09</td>
<td>47.59</td>
<td>34.08</td>
<td>15.61</td>
</tr>
<tr>
<td>60</td>
<td>96.05</td>
<td>56.95</td>
<td>40.93</td>
<td>19.67</td>
</tr>
<tr>
<td>65</td>
<td>67.80</td>
<td>48.90</td>
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<td>70</td>
<td>80.30</td>
<td>58.12</td>
<td>58.12</td>
<td>30.61</td>
</tr>
<tr>
<td>75</td>
<td>94.64</td>
<td>68.73</td>
<td>68.73</td>
<td>37.83</td>
</tr>
<tr>
<td>80</td>
<td>80.89</td>
<td>46.47</td>
<td>46.47</td>
<td>56.75</td>
</tr>
<tr>
<td>85</td>
<td>94.78</td>
<td>68.93</td>
<td>68.93</td>
<td>83.28</td>
</tr>
</tbody>
</table>

Table 3.4: Ratio of Vapor Pressure $p_j^*(T)$ to 760 torr at Various Temperatures $T$ for Hazardous Chemical Compounds and Water, adapted from [84]
normal that is maintained at the National Bureau of Standards (NBS). The representative calibrations are typically generated for air at a temperature of 70°F = 21.1 °C and a pressure of 0 psig = 1 atm = 1.01325 \cdot 10^5 Pa.

The re-calibration is accomplished by measuring volume flow rates with a DryCal DC-1H Flow Calibrator from BIOS International Corporation, Pompton Plains, New Jersey. The flow calibrator is traceable to a normal that is maintained at the NBS. However, it is not possible to measure volume flow rates below 20 cm³/min with this flow calibrator.

Therefore, a Soap Film Flow Meter 100 ml from Hewlett-Packard Company, Wilmington, Delaware and a stop watch are used to measure these volume flow rates. However, the suitability of the soap film flow meter for the calibration of the volume flow meters has to be demonstrated.

This is accomplished by measuring volume flow rates of 20, 30, 40 cm³/min and comparing the measurements from the soap film flow meter to those from the flow calibrator. These measurements are found to be in agreement within a few percent. Since the accuracy and precision of soap film flow meters increases with decreasing volume flow rate, it is assumed that the soap film flow meter can be used for the calibration of the volume flow meters at volume flow rates below 20 cm³/min.

The needle valve at the inlet of each volume flow meter to be calibrated is connected to a compressed air cylinder with regulator, while the outlet of the volume flow meter is connected to the inlet of either the flow calibrator or the soap film flow meter. The outlet of the flow calibrator or soap film flow meter is open to atmospheric pressure.

The pressure at the inlet of the needle valve of each volume flow meter and the pressure at the outlet of each volume flow meter are measured. Between three and ten volume flow rate measurements are taken for each setting on a volume flow meter and then arithmetically averaged. Between ten and sixteen settings on each flow meter are calibrated.

The assumption is made and supported by corresponding pressure gauge measurements that the flow calibrator and soap film flow meter operate at near atmospheric pressure, so that each volume flow meter is at near atmospheric pressure as well. The needle valve of each flow meter then reduces the compressed air cylinder regulator pressure of 10 psig to near atmospheric pressure.

The difference between the actual atmospheric pressure and 1.01325 \cdot 10^5 Pa is assumed small. The room in which the calibration is performed is kept nearly at 21.1 °C and the air streaming from the compressed air cylinder is assumed to be near this temperature, despite cooling due to expansion. The difference between the actual temperature and 21.1 °C again is assumed small.
Under these assumptions, Table 3.5 shows the volume flow meters that are calibrated and their assigned numbers and Table 3.6 shows these volume flow meters, their setting ranges, their nominal volume flow rate ranges as determined by the respective manufacturer and their actual volume flow rate ranges as determined by the above flow calibrator or soap film flow meter.

<table>
<thead>
<tr>
<th>VFM</th>
<th>Volume Flow Meter</th>
<th>Nominal Volume Flow Range</th>
<th>Actual Volume Flow Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Omega FL-220 (No. 1)</td>
<td>0.2 - 90.0 cm³/min</td>
<td>0.7 - 103.4 cm³/min</td>
</tr>
<tr>
<td>2</td>
<td>Omega FL-220 (No. 2)</td>
<td>0.2 - 90.0 cm³/min</td>
<td>0.7 - 101.8 cm³/min</td>
</tr>
<tr>
<td>3</td>
<td>Omega FL-221</td>
<td>1.0 - 280.0 cm³/min</td>
<td>2.0 - 320.4 cm³/min</td>
</tr>
<tr>
<td>4</td>
<td>Omega FL-224</td>
<td>1000.0 - 36000.0 cm³/min</td>
<td>906.1 - 41140.0 cm³/min</td>
</tr>
<tr>
<td>5</td>
<td>Matheson E603</td>
<td>5 - 150 mm</td>
<td>44.3 - 2410.9 cm³/min</td>
</tr>
<tr>
<td>6</td>
<td>Matheson E605</td>
<td>10 - 150 mm</td>
<td>963.5 - 24921.7 cm³/min</td>
</tr>
<tr>
<td>7</td>
<td>Dwyer (No. 1)</td>
<td>1 - 10 ft³/h</td>
<td>471.9 - 4719.5 cm³/min</td>
</tr>
<tr>
<td>8</td>
<td>Dwyer (No. 2)</td>
<td>1 - 10 ft³/h</td>
<td>471.9 - 4719.5 cm³/min</td>
</tr>
</tbody>
</table>

Table 3.5: Volume Flow Meters

The experimental setup for the volume flow meter calibration is shown in Figure 3.2. The nominal and actual volume flow rates for each volume flow meter are provided in Appendix B.2.

In order to correct the volume flow rate measured on a rotameter for fluids different from that for which the rotameter is calibrated, it is instrumental to review the theory of operation of the rotameter as presented in Appendix B.3.

As a result, the volume flow rate of air is measured and then converted to the volume
flow rate of the fluid by multiplying the volume flow rate of air by the square root of the ratio of the mole mass of air to the mole mass of the fluid. For the remainder of the present work, such procedure is implicitly assumed when mentioning is made of gases and their volume flow rates.
Chapter 4

Tunable Plasma Reactor

4.1 Components of Tunable Plasma Reactor

The components of the Tunable Plasma Reactor comprise the Reaction Chamber, the Electron Beam and the Electric Field. The Electron Beam is generated by an Electron Beam Gun, whose principal components are the Vacuum System, the Electron Generation, the Electron Acceleration and the Vacuum to Atmosphere Interface or Electron Beam Window.

4.2 Reaction Chamber

4.2.1 Old vs. New Reaction Chamber

The reaction chamber provides the flow channel for passage of the gaseous hazardous waste through the cold plasma. The flow channel generates a known flow profile for such passage. The structure material of the flow channel is chosen such that Thermally Activated Surface Chemical Reactions with the gaseous hazardous waste are minimized. Also, the reaction chamber provides the electrodes for the electric field superimposed to the electron beam.

For the present work, two different reaction chambers are used. These are referred to as the Old Reaction Chamber and the New Reaction Chamber. The three major differences of these reaction chambers relate to the flow channel, the structure material and the electrodes. While the old reaction chamber was designed with no particular attention to these areas, the new reaction chamber was designed with more attention to these areas.
As evident from the following description of the reaction chambers, the old reaction chamber appears to be less suited for the present work than the new reaction chamber. As evident from the experimental results, however, no significant difference between the two reaction chambers is observed with respect to the decomposition of hazardous chemical compounds in gaseous hazardous waste. Nevertheless, the old reaction chamber was replaced by the new reaction chamber after a few initial experiments for "good measure".

The reaction chambers incorporate a large number of details so that their comprehensive description is beyond the scope of the present work. Therefore, only a description of the most important features of each reaction chamber is presented in the following. Note that the old reaction chamber was designed on the basis of a reaction chamber described in [16].

4.2.2 Old Reaction Chamber

The most important features of the Old Reaction Chamber are shown in Figure 4.1. The flow channel is formed through four Pyrex Glass Plates, an Aluminum Block, an Aluminum Back Plate and an Aluminum Front Plate.

The flow channel is "U"-shaped with a square flow channel cross section area of 1 x 1 inch$^2$ outside and a rectangular flow channel cross section area of 1 x $\frac{5}{8}$ inch$^2$ inside the region of the cold plasma. The dimension of $\frac{5}{8}$ inch$^2$ is measured along the direction of the electron beam.

The flow profile was not determined experimentally. Moreover, although the straight portion of the "U" may ensure a near-laminar or near-turbulent flow profile, such near-laminar or near-turbulent flow profile is expected to be perturbed as soon as the flow enters the curved portion of the "U".

The Pyrex Glass Cylinder is supported via groves in the Aluminum Front Plate and the Aluminum Back Plate, while the aluminum block is bolted to the aluminum back plate. The aluminum front plate and the aluminum back plate are bolted together via threaded plastic rods not shown in the figure. The structure thus formed is rigid and serves as structural support for the four pyrex glass plates, which are only loosely supported via groves in the aluminum front plate and the aluminum back plate.

While the pyrex glass cylinder is sealed against the aluminum front plate and the aluminum back plate, the four pyrex glass plates are not sealed against these plates. Also, the four pyrex glass plates are not sealed against the aluminum block or against each other. Therefore, a fraction of the reactor intake and reactor exhaust may exchange with each other as well as with the dead volume formed between the four
Figure 4.1: Old Reaction Chamber
pyrex glass plates and the pyrex glass cylinder.

Moreover, aluminum is a poor choice for the structure material since it is known to react with reactive chemical compounds containing chlorine. In particular, an experimental chlorine balance involving HCl and Cl₂ may be severely impacted by thermally activated surface chemical reactions.

The electric field is applied between the aluminum block and the aluminum front plate, including the electron beam window. Since sharp edges are present at the end of the aluminum block in the region of the cold plasma, high voltage arcing is more likely to occur due to the “Tip Effect”.

Although the inferiority of the old reaction chamber is not necessarily reflected in the experimental results, the less sensible design of this reaction chamber makes it the less preferred choice for the present work.

4.2.3 New Reaction Chamber

The most important features of the New Reaction Chamber are shown in Figure 4.2. The flow channel is formed through a Pyrex Glass Frame, a Titanium Back Plate and a Titanium Front Plate.

The flow channel is “I”-shaped with a rectangular flow channel cross section area of $< 1 \times \frac{1}{2}$ inch$^2$ outside and a rectangular flow channel cross section area of $1 \times \frac{5}{8}$ inch$^2$ inside the region of the cold plasma. The dimension of $\frac{5}{8}$ inch$^2$ is measured along the direction of the electron beam.

The flow profile was determined experimentally via Hot Wire Anemometry [85]. The flow profile was found to be near-turbulent, i.e. the flow velocity is approximately constant over the flow channel cross section area.

The Pyrex Glass Frame is supported via friction against the Titanium Front Plate and the Titanium Back Plate. The titanium front plate and the titanium back plate are bolted together via threaded plastic bolts not shown in the figure. The structure thus formed is rigid.

The pyrex glass frame is sealed against the titanium front plate and the titanium back plate. No exchange of the reactor intake and reactor exhaust with each other can take place and no dead volume is formed.

Moreover, titanium is a good choice for the structure material since it is known to react very little with reactive chemical compounds containing chlorine. In particular, an experimental chlorine balance involving HCl and Cl₂ may not be severely impacted
Figure 4.2: New Reaction Chamber
by thermally activated surface chemical reactions.

The electric field is applied between the titanium back plate and the titanium front plate, including the electron beam window. Since no sharp edges are present in the region of the cold plasma, high voltage arcing is less likely to occur due to the “Tip Effect”.

Although the superiority of the new reaction chamber is not necessarily reflected in the experimental results, the more sensible design of this reaction chamber makes it the more preferred choice for the present work.

4.3 Electron Beam

4.3.1 Fundamental Considerations

The present work requires irradiation of a volume, rather than irradiation of an area. Also, the cross section of the volume perpendicular to the electron beam represents a large area rather than a small area.

Two options exist for irradiation of this volume. A small area electron beam may be used to cover the required large area dynamically, i.e. by scanning, or a large area beam may be used to cover the required large area statically.

Moreover, the electron beam has to be generated and accelerated in vacuum but the electron beam power deposition has to take place in atmosphere. Therefore a vacuum to atmosphere interface for the electron beam is required. Electrons are typically generated at the cathode and then accelerated towards the anode represented by this vacuum to atmosphere interface.

Small area electron beam guns are commercially available and inexpensive from the laboratory perspective\(^1\). However, these electron beam guns are generally designed for use in vacuum, thus lacking the required vacuum to atmosphere interface. Also, the effort for implementation of a scanning system on such electron beam guns is found to be not justifiable for the present work.

Large area electron beam guns are likewise commercially available but expensive from the laboratory perspective\(^2\). However, these electron beam guns are generally designed for use in atmosphere, thus providing the required vacuum to atmosphere interface. Nevertheless, the expense for such electron beam guns is found to be not

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\(^1\) Kimball Physics, Inc., Wilton, New Hampshire

\(^2\) Energy Sciences, Inc., Wilmington, Massachusetts
justifiable for the present work.

Therefore, a custom-made electron beam gun is deployed, featuring a custom-made vacuum system, a custom-made electron generation and acceleration as well as a custom-made vacuum to atmosphere interface. All components of the electron beam gun were scavenged from existing laboratory stock and mostly represent outdated second hand equipment.

4.3.2 Electron Beam Generation

Two options exist for generation of the electron beam. The electron emitting cathode may be heated directly or indirectly. A directly heated cathode consists of a resistively heated, electron emitting filament. An indirectly heated cathode consists of a radiatively heated, electron emitting plate [86]. A filament typically serves as the radiative heat source. In either case, the filament is suspended on springs so as to prevent sagging of the filament upon heating.

Typical materials are Tungsten (W) for the filament and Lanthanum Hexaboride (LaB₆) for the plate. Also, directly heated cathodes require higher operating temperatures than indirectly heated cathodes for comparable electron emission.

In order to generate the required large area electron beam, the filament must be strung across the large area accordingly to emulate large area emission, while the plate generates large area emission naturally.

The directly heated filament generates a cloud of electrons around the filament. If this cloud is localized at the filament, the electron beam very likely does not have the desired large area cross section, but rather the cross section of the filament strung across the large area. This is referred to as Filament Mapping. If, however, this cloud is not localized at the filament, the electron beam does have the desired large area cross section.

The tungsten filament oxidizes and ruptures upon loss of vacuum to air during operation. The lanthanum hexaboride plate oxidizes upon loss of vacuum to air during operation. Thus, the filament has to be replaced, while the plate can be reconditioned and then reused.

In order to obtain as uniform as possible an electron beam energy deposition in atmosphere over time, the filament — both the directly heated cathode and the radiative heat source for the indirectly heated cathode — is heated by DC low voltage. This also avoids temperature cycling of the filament due to AC low voltage induced heating and cooling and associated mechanic fatigue failure.
In view of the lack of experience with indirectly heated cathodes, the greater expense for a lanthanum hexaboride plate than for a tungsten filament and a cathode design that allows the filament to be readily replaced, the indirectly heated cathode cannot be justified and the directly heated cathode is implemented.

The filament voltage and filament current of this directly heated cathode are on the order of 25 V and 5 mA, respectively, with a filament diameter of approximately 250 μm and a filament length of approximately 50 cm. Therefore, the filament power is on the order of 125 W.

### 4.3.3 Electron Beam Acceleration

Two options exist for generation of the electron beam acceleration voltage. The low frequency AC low voltage from the laboratory power supply line may be transformed to the required high voltage via a large transformer. Alternatively, the low frequency AC low voltage from the laboratory power supply line may be transformed to high frequency first and then to the required high voltage via a small transformer.

In order to obtain as uniform as possible an electron beam energy deposition in atmosphere over time, rectification of the AC high voltage to DC high voltage is required for both options. However, the high frequency rectification results in a smoother DC high voltage than the low frequency rectification.

The former option requires several times as much space as the latter option and is certainly not preferable when a compact electron beam gun is needed. However, in view of the more sophisticated electronic circuitry required for the low to high frequency transformation, the lack of a need for a compact electron beam gun, and the lack of experience with low to high frequency transformation, the latter option cannot be justified and the former option is implemented.

The electron beam voltage and electron beam current are on the order of 100 kV and 1 mA to 4 mA, respectively. Therefore, the electron beam power is on the order of 100 W to 400 W. Although the electron beam power is on the same order as the filament power, the electron beam power absorbed in the standard gas is only on the order of 6 W per 1 mA of electron beam current. This number will be derived in the discussion of electron beam dosimetry in Section 6.5.

Hence, for 1 mA electron beam current, 125 W of filament power and 100 W of electron beam power are required, while only 6 W out of these 225 W are utilized for generation of the cold plasma in the standard gas. This low energy efficiency of approximately 3 % applies to the electron beam gun of the present work only. Commercially available electron beam guns operate at energy efficiencies of 70 % and
4.3.4 Electron Beam Shaping and Electron Beam Current Control

The classical Pierce electron beam gun design featuring a large area electron emitting cathode and electron beam focusing or defocusing electrodes is not realized [87]. The electron beam current for such an electron beam gun may be controlled by the temperature of the large area cathode.

Instead, a triode electron beam gun design featuring constant large area cathode temperature and electron beam current control via modified triode electronics is realized. This design does not feature focusing or defocusing electrodes. Also, maintaining the cathode temperature constant prevents mechanical fatigue failure due to temperature cycling.

The distances among the electrodes of the triode are small compared to the areas of the electrodes. Therefore, to first approximation, electric fields are parallel to the electron beam gun axis and any deviation from this approximation is due to the action of space charge or electron beam lenses [87], [88].

The three familiar components of a triode may be distinguished along the axis of the electron beam gun as shown in Figure 4.3. The cathode is at the negative electron acceleration voltage $V_A$, which is nominally 110 kV. The control grid is at the same voltage $V_A$, however its voltage can be increased or decreased by an electron extraction or retardation voltage $V_{ER}$, which may be up to 100 V.

The control grid encloses the cathode and represents in fact an impermeable barrier to electrons, except for a small grid opening in front of the cathode. This grid opening determines the cross section of the electron beam at the axis of the electron beam gun. The anode is electrically grounded.

With $V_{ER}=0$, the electric field between cathode and control grid is non-zero on the basis of imperfect electric shielding action of the grid opening of the control grid, i.e. leakage of the electric field between control grid and anode through the grid opening of the control grid occurs.

Therefore, electrons are not only propelled isotropically towards the control grid by space charge at the cathode, but also extracted anisotropically from the space between cathode and control grid through the control grid opening.

Hence, a large fraction of the electrons emitted by the cathode penetrate through
Figure 4.3: Triode Electron Beam Gun Design
the grid opening of the control grid, while only a minority is intercepted by the impermeable barrier of the control grid. Those many electrons that penetrate through the grid opening then experience acceleration towards the anode due to $V_A$ and represent the electron beam current.

The effective voltage distribution between the cathode and the control grid and the effective voltage distribution between the control grid and the anode which result from the superposition of the electric field leakage from $V_A$ and the electric fields from three different $V_{ER}$ are shown schematically in Figure 4.4.

![Figure 4.4: Effective Triode Voltage Distribution](image)

When $V_{ER}$ is increased from zero, the control grid becomes more positive with respect to the cathode and the fraction of electrons emitted by the cathode that is intercepted by the impermeable barrier of the control grid would increase. However, the electric field due to leakage of the electric field between control grid and anode through the grid opening of the control grid increases as well and the fraction of electrons emitted by the cathode that is extracted from the space between cathode and control grid increases and the electron beam current increases as well. In this case, $V_{ER}$ represents an extraction voltage.
When, however, $V_{ER}$ is decreased from zero, then the control grid becomes more negative with respect to the cathode and the fraction of electrons emitted by the cathode that is intercepted by the impermeable barrier of the control grid would decrease. However, the electric field due to leakage of the electric field between control grid and anode through the grid opening of the control grid decreases as well and the fraction of electrons emitted by the cathode that is extracted from the space between cathode and control grid decreases and the electron beam current decreases as well. In this case, $V_{ER}$ represents a retardation voltage.

For the present work, the voltage $V_{ER}$ of the control grid is always negative, so that $V_{ER}$ may only be decreased from zero to minimum. A maximum electron beam current is obtained for zero $V_{ER}$ through electric field leakage. A zero electron beam current is obtained for minimum $V_{ER}$ through compensation of the electric field leakage. The reason for keeping $V_{ER}$ negative is the minimization of interception of electrons by the impermeable barrier of the control grid, i.e. the "electron waste" is minimized. On the basis of this scheme, the electron beam current $I_0$ can be varied from 0 mA to 4 mA for the present work.

Although the notion of *Thermionic Emission Limitation* and *Space Charge Limitation* is only introduced subsequently, it may be noted here that at zero $V_{ER}$, the electron beam gun operates near *Thermionic Emission Limitation*, while at minimum $V_{ER}$, the electron beam gun operates near *Space Charge Limitation*. Therefore, generally, the "cloud" of electrons accumulated at the filament prevents *Filament Mapping*.

A mathematical description of the one-dimensional electric field leakage through a control grid opening may be found in [89] and [90]. The cathode and the control grid are at high voltage and require precautions against high voltage arcing toward the encasing vacuum chamber, which, together with the anode, is electrically grounded. Therefore, round edges and smooth surfaces are implemented wherever possible in order to prevent high voltage arcing due to the "Tip Effect".

The electric field between cathode and control grid due to leakage of the electric field between control grid and anode and due to variation of $V_{ER}$ may be expected to be approximately parallel to the electron beam gun axis.

However, the voltage across the filament of the directly heated cathode required to drive the resistive heating current generates an electric field approximately perpendicular to the electron beam gun axis. The latter is a small fraction of the former electric field so that the resulting electric field between the cathode and the control grid may not be exactly parallel to the electron beam gun axis.

To compensate for this fact, the control grid, i.e. the grid opening, is tilted accordingly with respect to the cathode. The proper amount of "tilting" is found by trial
and error until the electron beam centers on the electron beam gun axis as determined from the "blackening" of facsimile paper. The use of facsimile paper is described in the discussion of electron beam dosimetry in Section 6.2.

The filament of the cathode consists of tungsten, the control grid consists of stainless steel and the anode, which is identical with the vacuum to atmosphere interface or the electron beam window, consists of a water-cooled copper support grid and an aluminum or aluminum/titanium foil.

This triode electron beam gun design may have undesired effects on the cross section of the electron beam. Since no focusing or defocusing electrodes are implemented, the electron beam may increase or decrease in cross section between the control grid opening and the anode. Such concern is based on space charge action and, more importantly, on lens action of any opening under voltage through which an electron beam passes in vacuum [87], [88]. In particular, electron beam spreading in between the control grid and the anode is observed as described in the discussion of electron beam dosimetry in Section 6.2.

4.3.5 Richardson’s Equation and Child’s Equation

4.3.5.1 General Remarks

A comprehensive modeling of the electron current density between the directly heated cathode and the control grid and the control grid and the anode is beyond the scope of the present work. It involves the numerical simulation of electric fields and electron concentrations in vacuum under space charge conditions in three-dimensional geometry.

Although their application to the electron beam gun used in the present work is limited due to the rather complicated geometry, Richardson's equation and Child's equation, together with the Paraxial Ray equation, are the two most classic equations used in electron beam gun design [87], [88]. They may therefore be discussed here.

Richardson's equation governs Thermionic Emission Limitation, i.e. the maximum current density of electrons emitted from a heated surface as a function of the temperature of the surface. Child's equation governs Space Charge Limitation, i.e. the maximum current density of electrons between two electrodes under space charge conditions in vacuum as a function of the distance and the voltage difference between the two electrodes.

Therefore, Richardson’s equation may be applied to estimate the electron current density emitted from the directly heated cathode, while Child’s equation may be
applied to estimate the current density between the heated cathode and the control grid, the space charge consisting of the cloud of electrons around the directly heated filament.

In general, when the electron current density generated by thermionic emission is much lower than that between the two electrodes, no space charge is built up and the electron beam current is determined by the temperature of the cathode. When, however, the current density generated by thermionic emission is much higher than that between the two electrodes, then space charge is built up, and the electron beam current is determined by the voltage difference between the two electrodes.

These two cases are referred to as **Temperature Limited Operation** and **Space Charge Limited Operation**. As will be seen shortly, Richardson’s current is very sensitive to the temperature. Therefore, depending on the temperature of the directly heated filament, Richardson’s current may be less or greater than Child’s current. In the former case, this translates into temperature limited operation and in the latter case, this translates into space charge limited operation.

### 4.3.5.2 Richardson’s Equation

**Richardson’s** equation describes the electron current density $j$ of electrons emitted from the surface of a material with surface temperature $T$ [91], [82]. Two mathematically different expressions for $j$ as a function of $T$ may be used, giving similar results for surface temperatures $T$ from 1,000 K to 3,000 K:

\[
\begin{align*}
    j_1 &= j_0 e^{-\frac{T}{T_1}} \\
    j_2 &= \alpha T^2 e^{-\frac{T}{T}}
\end{align*}
\]

Here, $\Phi$ is the surface work function of the material in eV. Also, $\alpha$ may be expressed in $A/m^2 K^2$ through physical constants as follows:

\[
\alpha = \frac{2\pi mk^2e}{h^3}
\]

This expression for $\alpha$ evaluates to $\alpha = 6 \cdot 10^8 A/m^2 K^2$. Table 4.1 presents commonly used parameter sets $j_0$ and $\Phi$ or $\alpha$ and $\beta$, respectively, for tungsten [91].
Table 4.1: Commonly Used Parameter Sets for Richardson's Law [91]

<table>
<thead>
<tr>
<th>Set</th>
<th>$j_0$</th>
<th>$\Phi$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-]</td>
<td>A/m²</td>
<td>eV</td>
<td>A/m² K²</td>
<td>K</td>
</tr>
<tr>
<td>1</td>
<td>$2.0 \cdot 10^{13}$</td>
<td>4.85</td>
<td>$7.2 \cdot 10^6$</td>
<td>52,430</td>
</tr>
<tr>
<td>2</td>
<td>$1.2 \cdot 10^{13}$</td>
<td>4.79</td>
<td>$6.0 \cdot 10^5$</td>
<td>52,320</td>
</tr>
</tbody>
</table>

Table 4.2: Electron Current Densities for Commonly Used Parameter Sets for Richardson's Equation

<table>
<thead>
<tr>
<th>Set</th>
<th>$T = 2,000$ K</th>
<th>$T = 2,250$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[-]</td>
<td>$j_1$</td>
<td>$j_2$</td>
</tr>
<tr>
<td>1</td>
<td>12.01</td>
<td>11.87</td>
</tr>
<tr>
<td>2</td>
<td>10.21</td>
<td>10.45</td>
</tr>
</tbody>
</table>

Table 4.2 presents electron current densities at $T = 2,000$ K and $T = 2,250$ K for the commonly used parameter sets $j_0$ and $\Phi$ or $\alpha$ and $\beta$, respectively, for tungsten.

The average of these electron current densities is $j = 11.1$ A/m² at $T = 2,000$ K and $j = 254.1$ A/m² at $T = 2,250$ K. Note that 1 A/m² = $10^{-1}$ mA/cm². A filament of diameter $D = 250 \mu$m and length $L = 50$ cm thus emits an electron current of:

$$I = \pi DLj$$

This results in a current of $I = 4.4$ mA at $T = 2,000$ K and $I = 99.9$ mA at $T = 2,250$ K. This demonstrates the enormous sensitivity of the electron current density $j$ towards the surface temperature $T$.

4.3.5.3 Child’s Equation

Child’s equation describes the voltage distribution between an electron emitting cathode and an anode in vacuum under space charge conditions. The electrodes are assumed to have infinite area and be parallel in orientation. The emission of electrons from the cathode results in an electron current density between the two electrodes.

The derivation of Child’s equation is given in Appendix C.1. With $s$ the distance between the two electrodes, the electron current density may be expressed as a function of the voltage difference $V_s - V_0$ between the two electrodes:
\[ j = 4 \frac{\sqrt{2}}{9} \frac{\epsilon_0 (V_s - V_0)^2}{s^2} \left( \frac{q}{m} \right)^{\frac{1}{2}} \]

With a distance and voltage between the two electrodes of \( s = 1.0 \text{ cm} \) and \( V_s - V_0 = 100 \text{ V} \), respectively, the electron current density is \( j = 23.3 \text{ A/m}^2 \). Over an area of approximately \( 10 \text{ cm}^3 \), this results in a current of \( I = 2.3 \text{ mA} \).

4.3.6 Electron Beam Generation and Acceleration Circuit

The electron beam generation voltage is floating on the electron beam acceleration voltage, which is accomplished by providing the latter by an isolation transformer. This allows to install the entire electron beam generation electronics on a so-called High Voltage Deck.

The electron beam generation voltage is provided by a ITO-1-1-2-175 Isolation Transformer from Universal Voltronics, Kisco, New York which provides a maximum voltage of 115 V AC at a maximum current of 17.4 A.

The electron beam acceleration voltage is generated by a BAL-130-5.5 High Voltage Transformer from Universal Voltronics, White Plains, New York which provides a maximum voltage of 130 kV DC at a maximum current of 5.5 mA.

A VD120-3.1-B-K-A High Voltage Probe from Ross Engineering Corporation, Campbell, California is used to check the quality of the electron beam acceleration voltage. In particular, the high voltage from the high voltage transformer is only half-wave rectified. However, the capacitance to ground of the cable carrying the high voltage to the high voltage deck is sufficiently high to provide additional smoothing of this initially rather poor rectification.

For reasons of completeness, the electron beam generation circuit is shown in Figure 4.5. The electron beam acceleration circuit is shown in Figure 4.6.

4.3.7 Electron Beam Gun Vacuum System

The pressure of the vacuum system of the electron beam gun is maintained by a R-1402 Duo-Seal Rotary Vane Vacuum Pump from The Welch Scientific Company, Skokie, Illinois and a TurboVac 1000 Turbomolecular Ultra High Vacuum Pump from Leybold-Heraeus GmbH, c/o Leybold-Inficon Inc., East Syracuse, New York. The latter pump is controlled by a Turbotronik NT 1000/1500 Turbomolecular Ultra High
Isolation Transformer

Figure 4.5: Electron Beam Generation Circuit
Figure 4.6: Electron Beam Acceleration Circuit

The pressure of the vacuum system of the electron beam gun is monitored by a #2/B-275 Convectron Gauge from Granville-Phillips, Boulder, Colorado and a 274005 Ion Gauge from Granville-Phillips, Boulder, Colorado. Both gauges are controlled by a 303 Vacuum Process Controller from Granville-Phillips, Boulder, Colorado.

The pump-down procedure is such that the turbomolecular high vacuum pump is only operated after the rotary vane vacuum pump has pumped the vacuum system down to an initial pressure of approximately $3 \cdot 10^{-3}$ torr. The turbomolecular pump then pumps the vacuum system down to a final pressure of in between $10^{-7}$ torr to $10^{-6}$ torr, depending on the condition of the vacuum to atmosphere interface and the contamination of the inside surfaces of the vacuum system. Heating of these inside surfaces results in outgassing of the contamination and a faster pump-down. Upon operation of the filament, the associated outgassing of the filament results in an operating pressure of approximately $5 \cdot 10^{-6}$ torr to $5 \cdot 10^{-5}$ torr.

Upon loss of vacuum to air during operation, the rotary vane vacuum pump continues pumping air, while the turbomolecular ultra high vacuum pump trips into safe shutdown and can be re-started without problems after the cause of the loss of vacuum has been eliminated. This is a remarkable feat, considering the fact that the rotors of the turbomolecular ultra high vacuum pump are spinning at on the order of hundred thousand revolutions per minute and the loss of vacuum increases the load on their filigrae blades temporarily by several orders of magnitude.

After loss of vacuum to air and replacement of the directly heated filament, the final and/or operating pressure is reached within a few hours after initiation of pump-down.

4.4 Electron Beam Window

4.4.1 Fundamental Considerations

Although the electron beam is generated and accelerated in vacuum, the electron beam energy deposition takes place in gas at atmospheric pressure. Thus a vacuum to atmosphere interface is required which separates the vacuum from the gas at atmospheric pressure. This interface must be transparent to the electron beam, i.e. it must absorb the electron beam energy and current as little as possible.

Such a vacuum to atmosphere interface is commonly referred to as an Electron
**Beam Window.** Two fundamentally different design approaches to such a window exist.

The first design allows for a continuous transition of pressure from vacuum to atmosphere. This is accomplished by placing a pipe, pumped in stages, in the electron beam such that the electron beam axis and the pipe axis are colinear and vacuum obtains at one end of the pipe and atmospheric pressure at the other end. Although such a window is rather thick, it is almost fully transparent to the electron beam, even though electron scattering takes place towards the atmospheric pressure end of the pipe. Staged pumping is only feasible for pipes with small cross section. Thus this window limits the electron beam to small cross sections.

The second design allows for non-continuous transition of pressure from vacuum to atmosphere. This is accomplished by placing a foil, supported by a support grid, in the electron beam such that vacuum obtains on one side of the foil and atmospheric pressure on the other side. Although such a window is rather thin, it is not fully transparent to the electron beam. The electron beam is not necessarily limited to small cross sections.

Since an electron beam with a large cross section is required for the present work, the second design approach is chosen. This approach is not necessarily easier to realize, because the complexity of a design for staged pumping is traded for the complexity of a design for a support grid and a foil.

The foil is subjected to both mechanical and thermal load. The former originates from the pressure difference between vacuum and atmospheric pressure, the latter from the absorption of electron beam power. Both loads can combine to cause mechanical failure of the foil when the actual foil stress exceeds the maximum allowable foil stress at foil temperature. Generally, the maximum allowable foil stress decreases with increasing foil temperature.

Because of the required large electron beam cross section and the combined mechanical and thermal load, the foil requires support by a support grid. The support grid should have as large a transmission to the electron beam as possible, while at the same time providing support and cooling for the foil. Apparently, the foil is too thin to be able to support bending stress, so all mechanical stress is due to tension stress and shear stress.

The following is a list of technical criteria in order of decreasing importance for selection of the foil material.

- Minimum electron beam power absorption.
- Maximum thermal conductivity.
- Maximum high temperature mechanical strength.
- Maximum chemical inertness.
- Maximum melting temperature.
- Minimum x-ray generation.
- Minimum vacuum outgassing.

Materials that may therefore be considered as foil material are Be, C, Al, Si, Ti and V. However, only Al and Ti are technically practical.

While aluminum is inexpensive and has very good thermal conductivity, it has low mechanical strength. While titanium is expensive and has very poor thermal conductivity, it has high mechanical strength. Additionally, aluminum displays a very non-inert behavior when exposed to reactive chemical compounds, in particular in the presence of H₂O, while titanium displays a very inert behavior.

In principle, it is possible to use aluminum as the foil material. However, in a chemically reactive atmosphere, aluminum will be subject to corrosion. This leads to formation of pinholes in the foil, around which the mechanical stress is enhanced. This in turn leads to a growth of the pinholes. Such growth continues to the point of catastrophic failure of the foil. This pathway to failure is not unlike that encountered in Stress-Assisted Corrosion Cracking (SACC).

The loss of vacuum associated with catastrophic failure of the foil generally destroys the electron generation part of the electron beam gun reversibly or irreversibly and places the ultra high vacuum pump of the electron beam gun vacuum system under a tremendous momentary mechanical load. Therefore, catastrophic failures of the foil are to be avoided.

The corrosion may be slowed down to a certain extent by maintaining the foil at low temperatures, so that temperature enhanced surface reactions leading to corrosion and formation of pinholes are slowed down. If such procedure fails to be effective, a different material for the foil has to be chosen.

Although titanium will not be subject to corrosion in a chemically reactive atmosphere, it lacks the thermal conductivity to maintain the foil at low temperatures. Thus the foil may fail due to the combined mechanical and thermal load.

A composite of aluminum and titanium appears to be an excellent compromise. Here the foil thickness is composed of approximately 90% aluminum and 10% titanium. The aluminum provides the thermal conductivity, while the titanium provides the chemical inertness to prevent corrosion and formation of pinholes.
However, for the present work, it is found that the required foil life-times are short enough to prefer the inexpensive aluminum over the expensive titanium or aluminum-titanium composite as the foil material.

The following is a list of technical criteria in order of decreasing importance for selection of the support grid material.

- Maximum thermal conductivity.
- Minimum x-ray generation.
- Minimum vacuum outgassing.

Materials that may therefore be considered as support grid material are Al and Cu. However, to avoid any compromise on the thermal conductivity, copper is chosen as the support grid material.

The x-ray generation is generally proportional to $Z^2E_0$, where $Z$ is the atomic number of the foil material or the support grid material, and $E_0$ is the electron beam energy. In terms of x-ray generation, low $Z$ materials such as aluminum or titanium are preferable over high $Z$ materials such as copper. Due to the rather low electron beam energy, overall generation of x-rays is low to begin with. Therefore, the increased generation of x-rays from copper as opposed to that from aluminum as the support grid material is traded for the better thermal conductivity.

4.4.2 Support Grid Geometry

4.4.2.1 Slot and Rib Areas

The support grid is machined out of a solid disk of copper. An array of openings and the associated array of ribs provide for the required transmission to the electron beam and the mechanical and thermal support for the foil, respectively.

For ease of machining, the openings are chosen to be slots rather than holes. Also, slots aid in the analysis of the temperature of the support grid and the foil and the analysis of the mechanical stress of the foil, since they provide for reasonably good one-dimensional approximations. The geometry of the support grid is shown in Figure 4.7.

The array of slots and the associated array of ribs have width $w$ and height $h$. Each of the $n$ slots is of length $h$ and width $a$, the ends of a slot being semi-circular in
Figure 4.7: Support Grid Geometry

\[ a = \frac{1}{8} \text{ inch} \]
\[ b = \frac{1}{24} \text{ inch} \]
\[ g = \frac{1}{24} \text{ inch} \]
\[ h = \frac{11}{12} \text{ inch} \]
\[ v = 1.0 \text{ inch} \]
\[ w = 1.0 \text{ inch} \]
shape. Each of the $n$ ribs is of length $h$ and width $b$. The accurate and approximate areas of slots and ribs are $A_S$ and $A_R$, respectively:

$$
A = (a+b)h
$$

$$
A_S = (h-a)a + \frac{\pi}{4}a^2 = ah\left[1 - \left(1 - \frac{\pi}{4}\right)\frac{a}{h}\right] \approx ah
$$

$$
A_R = A - A_S = bh + \left(1 - \frac{\pi}{4}\right)a^2 = ah\left[\frac{b}{a} + \left(1 - \frac{\pi}{4}\right)\frac{a}{h}\right] \approx bh
$$

The support grid seals against the vacuum system of the electron beam gun via a simple Viton O-ring. Likewise, the foil seals against the support grid via a simple Viton O-ring.

### 4.4.2.2 Transmission to Electron Beam

The transmission $\tau_0$ of an array of openings is defined as the ratio of the transmitting area to the sum of transmitting and non-transmitting area. For the present work, slots represent the transmitting area, ribs approximately represent the non-transmitting area. The transmission may be calculated using the parameters shown in Figure 4.7.

$$
w = n(a+b)
$$

$$
A_0 = hw
$$

$$
A = nA_S
$$

$$
A_0 = nah\left(1 + \frac{b}{a}\right)
$$

$$
A = nah\left[1 - \left(1 - \frac{\pi}{4}\right)\frac{a}{h}\right]
$$

$$
\tau_0 = \frac{A}{A_0} = \frac{1}{1 + \frac{b}{a}} \left[1 - \left(1 - \frac{\pi}{4}\right)\frac{a}{h}\right] \approx \frac{1}{1 + \frac{b}{a}}
$$

The assumption is made that the electron beam has a cross section of $A_0$. However, an electron beam with a larger cross section $A^*$ will result in an overall transmission $\tau$ of:
The support grid parameters are \( n = 6, w = 1, h = \frac{11}{12} \) inch, \( a = \frac{1}{8} \) inch and \( b = \frac{1}{24} \) inch. Substitution of these parameters into above equation for \( \tau_0 \) results in \( \tau_0 = 0.73 \).

### 4.4.3 Thermal Load on Support Grid and Foil

#### 4.4.3.1 Definition of Thermal Load

With respect to the coordinate system shown in Figure 4.7, the electron beam is directed along the z-axis, the window is located in the x/y-plane. The electron beam energy right before passage through the window is \( E_0 \). The electron beam current density upon passage through the electron beam window is \( j \).

The window consists of a support grid and a foil. Upon passage of the electron beam through the window, one fraction of the electron beam is blocked by the support grid, another fraction of the electron beam passes through the support grid to the foil. The foil causes an electron beam energy loss.

The electron beam energy loss in the support grid is \( E_0 \), based on complete blockage. The electron beam energy loss in the foil is \( \Delta E_f \). These electron beam energy losses result in heating of the support grid and the foil. The heat has to be removed by active cooling. Thus, the support grid contains cooling channels that run parallel to the x-axis right at the respective ends of the slots and ribs. The coolant is water. The coolant temperature \( T_c \) may be assumed to remain constant.

It may be assumed that heat transport occurs in two stages. In the first stage, the heat generated in the foil is transported to the ribs, in the second stage, this heat and the heat generated in the support grid is transported along the ribs to the cooling channels. This assumption is fair for a support grid where \( h \gg a \).

Therefore, the maximum support grid and foil temperatures may be estimated by simple one-dimensional, symmetric, steady state analysis. In particular, the support grid temperature varies along the y-axis and the foil temperature varies along the x-axis. The two stages may be described by the partial differential equation for heat
conduction in a solid body. The solution to this partial differential equation is derived in Appendix C.2:

\[ \hat{T} = T|_{\psi=0} = T_\psi + \frac{q''\Psi^2}{8\lambda} \]

\[ \Delta \hat{T} = \frac{q''\Psi^2}{8\lambda} \]

Here, \( \lambda \) is the thermal conductivity and \( q'' \) is the volumetric heat generation rate of the solid body, \( \psi \) with \(-\frac{\Psi}{2} \leq \psi \leq \frac{\Psi}{2} \) is the one-dimensional coordinate, \( \Psi \) is the maximum extension along this coordinate and \( T_{\psi} = T|_{\psi=\pm\frac{\Psi}{2}} \) is the temperature at the boundaries of this coordinate.

This solution may be applied to the support grid and the foil in order to obtain estimates for the maximum support grid and foil temperatures. However, appropriate forms for \( T_g, T_f, \lambda_g, \lambda_f, \psi_g, \psi_f, \Psi_g, \Psi_f, q_g'', q_f'' \) and \( q_h'' \) as defined in Appendix C.2 need to be selected. Here, subscript \( g \) represents the support grid, subscript \( f \) represents the foil.

### 4.4.3.2 Maximum Support Grid Temperature

The one-dimensional coordinate \( \psi_g \) is given by \( y \) and \( \Psi_g \) is given by \( h \). Moreover, \( \lambda_g \) is equal to \( \lambda_{Cu} \) and \( T_g, \psi \) may be assumed to be equal to \( T_c \). Also, \( q_g'' \) evaluates to:

\[ A_g = A_R \approx hb \]
\[ A_f = A_S \approx ha \]
\[ V_g = A_g t_g \]

\[ \dot{Q}_g = j(A_g E_0 + A_f \Delta E_f) \]
\[ q_g'' = \frac{\dot{Q}_g}{V_g} \]
\[ q_g'''' = \frac{\dot{Q}_g}{t_g} \left( 1 + \frac{a}{b} \frac{\Delta E_f}{E_0} \right) \]

Here, \( t_g \) is the support grid thickness, \( A_g \) is the support grid area, \( V_g \) is the support grid volume and \( A_f \) is the foil area. The maximum support grid temperature \( \hat{T}_g \) and the maximum support grid temperature difference \( \Delta \hat{T}_g \) may then be calculated as:
$$\hat{T}_g = T_c + \frac{jE_0 h^2}{8\lambda_g t_g} \left[1 + \frac{a}{b} \frac{\Delta E_f}{E_0}\right]$$

$$\Delta \hat{T}_g = \frac{jE_0 h^2}{8\lambda_g t_g} \left[1 + \frac{a}{b} \frac{\Delta E_f}{E_0}\right]$$

### 4.4.3.3 Maximum Foil Temperature

The one-dimensional coordinate $\psi_f$ is given by $x$ and $\Psi_f$ is given by $a$. Moreover, $\lambda_f$ is equal to $\lambda_{Al}$ and $T_{f\psi}$ may be assumed to be equal to $\hat{T}_g$. Also, $q''_f$ evaluates to:

$$A_f = A_S \approx ha$$

$$V_f = A_f t_f$$

$$\dot{Q}_f = j(A_f \Delta E_f)$$

$$q''_f = \frac{\dot{Q}_f}{V_f}$$

$$q'''_f = \frac{j\Delta E_f}{t_f}$$

Here, $t_f$ is the foil thickness, $A_f$ is the foil area, $V_f$ is the foil volume. The maximum foil temperature $\hat{T}_f$ and the maximum foil temperature difference $\Delta \hat{T}_f$ may then be calculated as:

$$\hat{T}_f = \hat{T}_g + \frac{j\Delta E_f a^2}{8\lambda_f t_f}$$

$$\hat{T}_f = T_c + \frac{j\Delta E_f a^2}{8\lambda_f t_f} \left[1 + \frac{\lambda_f}{\lambda_g} \frac{t_f}{t_g} \left(\frac{h}{a}\right)^2 \left(\frac{a}{b} + \frac{E_0}{\Delta E_f}\right)\right]$$

$$\Delta \hat{T}_f = \frac{j\Delta E_f a^2}{8\lambda_f t_f}$$
4.4.3.4 Maximum Support Grid and Foil Temperature

The electron beam energy loss $\Delta E_f$ in the foil depends on the electron beam energy $E_0$. Estimates for the electron beam energy loss are obtained by one-dimensional Monte-Carlo Simulations using the TIGER code of the Integrated Tiger Series code package. The details of these Monte-Carlo Simulations are described in the discussion of the electron beam dosimetry in Section 6.5.

For these Monte-Carlo Simulations, it is assumed that the foil is made of 1 mill (1/1000 inch) aluminum, and that the electron beam is travelling in vacuum before the foil and in either cold or hot air or $N_2O$ after the foil. It is determined that the electron beam energy loss in the foil decreases with the electron beam energy.

At the nominal electron beam energy of $E_0 = 110$ keV, the electron beam energy loss in the foil is generally on the order of $\Delta E_f = 50$ keV.

With $\lambda_f = \lambda_{Al} = 222$ W/m K [92], $\lambda_g = \lambda_{Cu} = 394$ W/m K [92], $j = 0.65$ mA/cm$^2$ and $T_c = 15$ °C, the maximum temperature and maximum temperature difference of the support grid and foil become $\hat{T}_g = 112$ °C, $\Delta \hat{T}_g = 97$ °C, $\hat{T}_f = 192$ °C and $\Delta \hat{T}_f = 80$ °C.

The value for the current density $j$ represents the maximum current density at which the electron beam is ever operated for an extended period of time.

4.4.4 Mechanical Load on Foil

4.4.4.1 Definition of Mechanical Load

The foil of thickness $t$ is suspended over a slot of length $h$ and width $a$, the ends of the slot being semi-circular in shape. The pressure $p$ acts perpendicular to the foil, such that it pushes the foil into the slot, thereby generating tension stress $\sigma_t$ and shear stress $\sigma_s$.

4.4.4.2 Foil Tension Stress

The equation for the approximate foil tension stress $\tilde{\sigma}_t$ is derived in Appendix C.3 and results as:
Here, $E$ is the elasticity modulus of the foil material, $p$ is the pressure of the atmosphere against which the foil is sustaining the vacuum, $a$ is the width of a slot of the support grid and $t$ is the foil thickness.

With $p = 1.01325 \cdot 10^5$ Pa, $E = E_{Al} = 69.0 \cdot 10^9$ Pa \cite{92}, $a = \frac{1}{8}$ inch and $t = \frac{1}{1000}$ inch, the approximate foil tension stress $\sigma_t$ becomes $\sigma_t = 77 \text{ N/mm}^2$.

Note that the maximum allowable foil stress at the maximum foil temperature is on the same order as the approximate foil tension stress. This leaves a safety factor of order unity. In fact, foil failure is frequently observed when the electron beam current density is increased by less than 20\% over that at which the electron beam is ever operated for an extended period of time.

### 4.4.4.3 Foil Shear Stress

The equation for the approximate foil shear stress $\sigma_s$ is derived in Appendix C.4 and results as:

$$\sigma_s \approx \frac{1}{2} \frac{a}{t} p$$

Here, $p$ is the pressure of the atmosphere against which the foil is sustaining the vacuum, $a$ is the width of a slot of the support grid and $t$ is the foil thickness.

With $p = 1.01325 \cdot 10^5$ Pa, $a = \frac{1}{8}$ inch and $t = \frac{1}{1000}$ inch, the approximate foil shear stress $\sigma_s$ becomes $\sigma_s = 6 \text{ N/mm}^2$.

Note that the approximate foil shear stress is less than a tenth of the approximate foil tension stress. Therefore, the combined stress, i.e. the design stress, is virtually equal to the foil tension stress.
4.4.5 Aluminum-Titanium Composite Foil

4.4.5.1 Advantage of Composite Foil

In the following, it will be demonstrated that neither the elasticity modulus nor the thermal conductivity of an aluminum foil and of an aluminum/titanium composite foil are significantly different. Therefore, the only important difference between an aluminum foil and an aluminum/titanium composite foil is the reduction of thermally activated surface chemical reactions obtained for the titanium side of the composite foil.

4.4.5.2 Modulus of Elasticity

For a composite foil of two materials \(i = 1, 2\) (e.g. aluminum and titanium), the composite modulus of elasticity may be calculated based on equal strain \(\epsilon\) in both materials:

\[
\epsilon_1 = \epsilon_2 = \epsilon
\]

\[
F_i = \sigma_i A_i = E_i \epsilon A_i
\]

\[
F = F_1 + F_2 = (E_1 A_1 + E_2 A_2)\epsilon = E(A_1 + A_2)\epsilon
\]

\[
E = \frac{E_1 A_1 + E_2 A_2}{A_1 + A_2}
\]

\[
A_i = t_i w
\]

\[
E = \frac{E_1 t_1 + E_2 t_2}{t_1 + t_2}
\]

\[
E = \frac{t_1}{t_1 + t_2} E_1 + \frac{t_2}{t_1 + t_2} E_2
\]
Here, $\sigma_1$ and $\sigma_2$ are the stresses induced by forces $F_1$ and $F_2$ acting on areas $A_1$ and $A_2$ of the two materials. In particular $t_1$ and $t_2$ are the foil thicknesses of the two materials and $E_1$ and $E_2$ are the elasticity moduli of the two materials. Apparently, the composite elasticity modulus applies to the foil tension stress and has no effect on the foil shear stress.

With $E_1 = E_{AI} = 69$ N/mm$^2$ [92] and $E_2 = E_{Ti} = 116$ N/mm$^2$ [92], and with $t_1 = t_{AI} = \frac{9}{10000}$ inch and $t_2 = t_{Ti} = \frac{1}{10000}$ inch, the elasticity modulus of the composite foil becomes $E = 74$ N/mm$^2$. Thus, the properties of an aluminum foil are essentially conserved.

### 4.4.5.3 Thermal Conductivity

For a composite foil of two materials $i = 1, 2$ (e.g., aluminum and titanium), the composite thermal conductivity may be calculated based on equal temperature difference $\Delta T$ in both materials:

\[
Q_i = \alpha_i A_i \Delta T
\]

\[
Q = Q_1 + Q_2 = (\alpha_1 A_1 + \alpha_2 A_2) \Delta T = \alpha (A_1 + A_2) \Delta T
\]

\[
\alpha = \frac{\alpha_1 A_1 + \alpha_2 A_2}{A_1 + A_2}
\]

\[
A_i = t_i w
\]

\[
\alpha = \frac{\alpha_1 t_1 + \alpha_2 t_2}{t_1 + t_2}
\]

\[
\alpha = \frac{t_1}{t_1 + t_2} \alpha_1 + \frac{t_2}{t_1 + t_2} \alpha_2
\]

\[
\alpha = \frac{\lambda}{h}
\]

\[
\alpha_i = \frac{\lambda_i}{h}
\]
\[ \lambda = \frac{t_1}{t_1 + t_2} \lambda_1 + \frac{t_2}{t_1 + t_2} \lambda_2 \]

Here, \( Q_1 \) and \( Q_2 \) are the powers induced by thermal conductivities \( \alpha_1 \) and \( \alpha_2 \) effective on areas \( A_1 \) and \( A_2 \) of the two materials. In particular \( t_1 \) and \( t_2 \) are the foil thicknesses of the two materials and \( \lambda_1 \) and \( \lambda_2 \) are the thermal conductivities of the two materials.

With \( \lambda_1 = \lambda_{Al} = 222 \text{ W/m K} [92] \) and \( \lambda_2 = \lambda_{Ti} = 172 \text{ W/m K} [92] \), and with \( t_1 = t_{Al} = \frac{9}{10000} \) inch and \( t_2 = t_{Ti} = \frac{1}{10000} \) inch, the thermal conductivity of the composite foil becomes \( \lambda = 217 \text{ W/m K} \). Thus, the properties of an aluminum foil are essentially conserved.

### 4.5 Electric Field

The electric field superimposed to the electron beam of the *Tunable Plasma Reactor* is applied across the cold plasma via parallel plate electrodes. The cathode is represented through the electron beam window, the anode is represented through an aluminum or titanium surface opposite to the electron beam window. The electrode spacing is approximately \( \frac{5}{8} \) inch.

The anode is at positive high voltage, the cathode is electrically grounded. The electric field voltage is generated by a *PS022-200-2 High Voltage Transformer* from *DEL Electronics Corporation, Mount Vernon, New York* that provides a maximum positive high voltage of 20 kV DC at a maximum current of 200 mA.

However, with the electron beam operating, positive high voltage arcing across the cold plasma typically occurs at an electric field voltage of on the order of 3000 V and an electric field current of on the order of 30 mA. These parameters depend on the standard gas in which the cold plasma is generated.

A detailed investigation of the electric field and the average electron energy in the cold plasma as a function of the electron beam current, the electric field voltage and the standard gas is far beyond the scope of the present work. Therefore, the electric field voltage is taken as a "black box" parameter. However, rough estimates of the reduced electric field, i.e. the ratio of the electric field divided by the total concentration, and of the average electron energy may be obtained using the following simplifications.

An estimate of the electric field in the cold plasma may be taken simply as the ratio of the electric field voltage applied across the cold plasma to the electrode spacing.
Therefore, at a total concentration of $2.5 \cdot 10^{19}$ 1/cm³, an electric field voltage of 300 V and 3000 V and an electrode spacing of approximately 1.5 cm, the reduced electric field results as $8 \cdot 10^{-18}$ V cm² or 0.8 Td and $8 \cdot 10^{-17}$ V cm² or 8 Td, respectively.

An estimate of the average electron energy in the cold plasma may be obtained under the assumption that the presence of the electron beam and the presence of electron attachment do not affect the average electron energy significantly when compared to standard measurements of the average electron energy as referenced in the literature. For example, the average electron energy as a function of the reduced electric field is presented in [32] for nitrogen and argon, in [74] for oxygen, nitrogen and air and in [93] for oxygen. The corresponding experimental results are shown in Figure 4.8.

Therefore, at above 0.8 Td and 8 Td, the average electron energy would be approximately 0.2 eV and 1 eV, respectively. The error in this rough estimate is expected to be larger for the estimate of the reduced electric field than for the estimate of the average electron energy on the basis of this reduced electric field.

Nevertheless, the average electron energy may range from 0.525 eV for no electric field voltage to 1 eV for the maximum electric field voltage achievable without high voltage arcing. Therefore, it appears to be possible to cover the range of average electron energies over which the variation of the bimolecular dissociative electron attachment reaction rate constant for CCl₄, CHCl₃ and C₂HCl₃ varies with the average electron energy as presented in Section 2.3.2.

Obviously, on closer inspection, the average electron energy with or without electric field is expected to be higher for an electron beam generated plasma than for a non-electron beam generated plasma. Moreover, the average electron energy with or without electric field is expected to be higher for a cold plasma with electron attaching chemical species than for a cold plasma without electron attaching chemical species.

This expectation is based on the gain of fast electrons at high energies through ionization by fast electrons of the electron beam and on the loss of slow electrons at low energies provided by electron attachment.

For example, the increase in average electron energy due to the presence of electron attachment is found in [33] to be on the order of 20 % for 100 ppm Sulfur Hexafluoride (SF₆) in nitrogen at a reduced electric field of 1 Td. The increase in average electron energy due to the presence of the electron beam may be assumed to be less than 20 % [34], [35]. Note that SF₆ is the only known chemical compound that attaches electrons even faster than CCl₄ [32].

Moreover, the average electron energy is expected to be lower for wet standard gas than for dry standard gas. This expectation is based on the electron to molecule
Figure 4.8: Average Electron Energy as Function of Reduced Electric Field, adapted from [32], [74] and [93]
momentum transfer cross section, which may be on the order of 100 times higher for H\textsubscript{2}O than for O\textsubscript{2} and N\textsubscript{2} [74]. In combination with a H\textsubscript{2}O concentration of on the order of 1 \%, this difference in the momentum transfer cross section could cause a variation of the overall momentum transfer cross section by a factor of two.
Chapter 5

Gas Analysis System

5.1 Introduction to Gas Analysis System

The following is a description of the Gas Analysis System developed for the chemical analysis of hazardous chemical compounds in gaseous hazardous waste and the chemical analysis of decomposition products as well as decomposition by-products of these hazardous chemical compounds. The description includes the Gas Chromatograph, the Gas Chromatograph/Mass Spectrometer and the Mass Spectrometer.

The gaseous hazardous waste before entering and after exiting the Tunable Plasma Reactor is referred to as the intake and exhaust of the reactor, respectively. The chemical analysis of the intake and the exhaust of the reactor is of prime importance to the performance characterization of the Tunable Plasma Reactor. The goal of the chemical analysis is the identification and quantitation of the chemical compounds contained in the intake or the exhaust as a function of the reactor operation parameters.

Generally, a chemical analysis determines the identity and the quantity of the chemical compounds in Samples from the intake or the exhaust of the reactor. The results of such chemical analysis are then extrapolated from these samples to the intake or exhaust of the reactor as a whole. Of interest are generally the identity and the quantity of chemical compounds, not the identity and the quantity of the elements of which these chemical compounds are composed.

In a simplistic view, there are two fundamentally different forms of chemical analysis. The first may be referred to as Wet Chemistry Analysis, the second as Dry Chemistry Analysis. The latter form of chemical analysis is more commonly referred to as Instrumental Chemical Analysis, and the device used for such chemical analysis is referred to as an Analytical Chemistry Instrumentation Device.
The quality of a chemical analysis is characterized by its Accuracy, Precision and Reproducibility. The term accuracy refers to the similarity of the measured and the actual identity and quantity. The term precision refers to the statistical spread in a series of measurements of the same actual identity and quantity. Narrow spreads represent high precision, wide spreads represent low precision. In particular, a chemical analysis may be accurate but not precise and it may be precise but not accurate [94].

The term reproducibility refers to the statistical spread in several series of such measurements over an extended period of time. Narrow spreads represent good reproducibility, wide spreads represents poor reproducibility.

For the present work, statistical spreads are approximately given by the ratio of the minimum to the average or the ratio of the average to the maximum.

Moreover, the Detection Limit refers to the smallest quantity of a chemical compound that can be measured with reasonable accuracy, precision and reproducibility. Therefore, a high detection limit is less desirable than a low detection limit. In contrast, the Sensitivity sometimes refers to the equivalent of the inverse detection limit. Therefore, a high sensitivity is more desirable than a low sensitivity.

For reasons of greater convenience and superior accuracy, precision and reproducibility of dry chemistry analysis compared to wet chemistry analysis, the chemical analysis for the present work is performed using analytical chemistry instrumentation devices.

A chemical analysis may be performed separatively or non-separatively. Separative Analysis is based on the spatial and/or temporal separation of the chemical compounds contained in the sample and subsequent identification and quantitation of each chemical compound separately. Non-Separative Analysis is based on the presumption that a signal from the sample is a convolution of signals from all chemical compounds contained in the sample. Thus identification and quantitation of each chemical compound is performed via Deconvolution of the signal from the sample.

Several analytical chemistry instrumentation devices are available, most all of which operate on principles of spectrometry. Some examples for such devices are the Gas Chromatograph, the Mass Spectrometer, the Gas Chromatograph/Mass Spectrometer, the Fourier-Transform Absorption or Emission Infrared Spectrometer, the Plasma Induced Emission Spectrometer, the Laser Induced Absorption and Emission Spectrometer and the x-ray Induced Absorption and Emission Spectrometer.

The gas chromatograph represents a device for separative analysis, all other listed analytical chemistry instrumentation devices, in particular the mass spectrometer, represent devices for non-separative analysis.
The most commonly used devices for environmental chemical analysis are the *Gas Chromatograph* (GC), the *Gas Chromatograph/Mass Spectrometer* (GC-MS) and the *Mass Spectrometer* (MS).

All three devices are quasi-recommended by the *Environmental Protection Agency* (EPA) as preferable analytical chemistry instrumentation devices [95], [96]. Owing to their common use, these devices also tend to be among the less expensive of those listed. Moreover, the established use of GC, GC-MS and MS provides support in the solution of unexpected problems. Therefore, GC, GC-MS and MS are selected as the analytical chemistry instrumentation devices for the present work.

In the following, the GC, the GC-MS and the MS are described. Information pertaining to the GC, GC-MS as well as the MS and information pertaining to the MS only is covered in different sections. These different sections correspond approximately to the description of separative analysis via GC and GC-MS and the description of non-separative analysis via MS.

In addition to the GC, the GC-MS and the MS, *Relative Humidity Meters* are available for the present work. However, these devices shall not be discussed further, with the exception of mentioning their models, manufacturers and measurement ranges.

One relative humidity meter is a *KM-8104* from *Kane-May Measuring Instruments Ltd.*, *Welwyn Garden City/Hertfordshire, Great Britain* with a range from 0 %RH to 100 %RH. Another relative humidity meter is a *340 Trace Moisture Analyzer* from *Rosemount Analytical Instruments Inc.*, *LaHabra, California* with a range from 1 ppm to 1000 ppm. However, only the former relative humidity meter was used in the present work.

### 5.2 Gas Chromatograph and Gas Chromatograph/Mass Spectrometer

#### 5.2.1 Separative Analysis

The gas chromatograph used in the present work is a *Hewlett-Packard 5890 Series II Gas Chromatograph* from *Hewlett-Packard, Wilmington, Delaware* [97], [98], [99], [100], [101]. In any gas chromatograph, the chemical compounds contained in the sample are temporally and spatially separated and thus a "fingerprint" characteristic of the sample is produced. This fingerprint is referred to as a *Gas Chromatogram*.

This gas chromatographic separation is accomplished via a gas chromatographic *Column*. The sample is injected onto such a column via a sample introduction sys-
tem at the entrance of the column. While a Carrier Gas flushes the sample through the column, temporal and spatial separation of the chemical compounds is accomplished. The temporally and spatially separated chemical compounds are identified and quantified by a gas chromatographic Detector at the exit of the column.

The detectors used in the present work are the Thermal Conductivity Detector (TCD), the Electron Capture Detector (ECD) and the Mass Selective Detector (MSD).

The TCD and the ECD are Non-Confirmative detectors, which can perform only quantitation of chemical compounds. Nevertheless, the identification of chemical compounds may in principle be performed on the basis of their temporal and spatial separation. More often than not, however, such identification is ambiguous or even impossible. Moreover, these detectors have different detection limits for different chemical compounds.

The MSD used in the present work is a Hewlett-Packard 5971A Mass Selective Detector from Hewlett-Packard, Palo Alto, California [102], [103]. Despite the understatement conveyed by the notion of a mass selective detector, this MSD is a virtually complete mass spectrometer.

In any mass spectrometer, ions of different mass to charge (M/Z) ratios produced upon irradiation by ionizing radiation of a chemical compound are temporally and spatially separated and thus a "fingerprint" characteristic of the chemical compound is produced. This fingerprint is referred to as a Mass Spectrum.

Therefore, a Mass Selective Detector (MSD) as a detector for a gas chromatograph is a Confirmative detector, which can perform both identification and quantitation of chemical compounds. The combination of a gas chromatograph and a mass spectrometer in the form of a MSD represents the gas chromatograph/mass spectrometer.

With proper temporal and spatial separation of the chemical compounds contained in the sample, the gas chromatograph/mass spectrometer represents a powerful analytical chemistry instrumentation device.

In the following, the sample introduction system, the gas chromatographic columns and the gas chromatographic detectors are described. Moreover, very good introductions to gas chromatography may be found in [104], [105] and [106] and in the catalogs of all major suppliers of gas chromatograph accessories, such as Hewlett-Packard, ChromPack, Supelco, Alltech, Restek and J & W.
5.2.2 Sample Introduction System

5.2.2.1 Principle of Operation

The sample introduction may be performed either manually or automatically. Automatic sample introduction is generally preferable over manual sample introduction for reasons of accuracy, precision and reproducibility.

For manual sample introduction, the gas chromatograph is equipped with an Injector. The injector is temperature controlled and contains a tube which is inserted in the carrier gas flow. Access to this tube by the needle of a Syringe is provided via a Septum. A septum is a disc of approximately $\frac{1}{2}$ inch diameter and $\frac{1}{8}$ inch thickness made from special rubber. Upon injection of the sample from the syringe into the tube, the sample is flushed onto and through the column by the carrier gas. The sample volume is equal to the injected syringe volume.

This manual sample introduction allows for the sample to be in the gas phase or in the liquid phase. When the temperature of the tube is sufficiently high, a sample in the liquid phase is vaporized upon injection from the syringe. Assuming that the temperatures of the remaining components of the gas chromatograph are sufficiently high as well, such a sample in the vaporized liquid phase effectively behaves like a sample in the gas phase.

For automatic sample introduction, the gas chromatograph is equipped with a Sampling Valve. The sampling valve is temperature controlled and contains a Sample Loop. In the sampling position of the sampling valve, the sample loop is inserted in the sample gas flow and thus filled with the sample. In the flushing position of the sampling valve, the sample loop is inserted in the carrier gas flow and the sample is flushed onto and through the column by the carrier gas. The sample volume is equal to the flushed sample loop volume. Note that the sample gas flow is a fraction of the gaseous hazardous waste flow.

For the present work, only automatic sample introduction is used, with the exception of occasional manual sample introduction for control purposes. The sampling valve is a C6WP Six-Port Valve from Valco Instruments Company Inc., Houston, Texas. The sample loops are SL2C6W, SL250C6W and SL2KC6W Sample Loops from Valco Instruments Company Inc., Houston, Texas. Note that a Sample Pump is used in order to maintain flow through the sample loop.

Moreover, the default configuration of the automatic sample introduction system provides for flushing of the sample onto one column only, so that typically only one column is installed in the gas chromatograph. However, the present work requires the use of two columns. The change of a column is labor and time intensive.
It is desirable to modify the sample introduction system such that it provides for flushing of the sample onto either one of two columns. Thereby, both columns can be installed in the gas chromatograph. This is accomplished through a Column Switching Valve, i.e. another C6WP Six-Port Valve from Valco Instruments Company Inc., Houston, Texas.

The automatic sample introduction system with the sampling valve and the column switching valve is shown in Figure 5.1.

![Figure 5.1: Automatic Sample Introduction System](image)

The sample loop volumes are 2 µl and 250 µl. The 2 µl sample loop, for example, is used for chemical analysis of CCl₄, CHCl₃, C₂HCl₃, COCl₂ and C₂HCl₃O, the 250 µl sample loop, for example, is used for chemical analysis of CO, CO₂ and N₂O.

In general, the 250µl sample loop is used for chemical compounds that are detected on the TCD, the 2 µl sample loop is used for chemical compounds that are detected on the ECD, reflecting the different detection limits of these detectors.

### 5.2.2.2 Theory of Operation

A sample of volume \( V_s \) in the gas phase contains mass \( m_{js} \) of chemical compound \( j \) with mole mass \( M_j \). The relation between mass \( m_{js} \) and concentration \( \varphi_{js} \) of chemical compound \( j \) in volume \( V_s \) is given via the ideal gas law:
\[ p_s V_s = n_s R_m T_s \]
\[ n_{js} = \varphi_{js} n_s \]
\[ m_{js} = n_{js} M_j = \varphi_{js} \frac{p_s V_s}{R_m T_s} M_j \]
\[ \varphi_{js} = \frac{m_{js}}{M_j} \frac{R_m T_s}{p_s V_s} \]

Here, subscripts \( s \) and \( j \) represent the sample and the chemical compound \( j \). Also, \( m, n \) and \( M \) represent mass, mole number and mole mass, and \( p, T \) and \( V \) represent pressure, temperature and volume.

Therefore, if sample pressure \( p_s \), sample temperature \( T_s \) and sample volume \( V_s \) are constant, mass \( m_{js} \) directly corresponds to concentration \( \varphi_{js} \). In particular, this correspondence holds independently of the mole mass of the sample.

This observation is as trivial as it is important, since the detector signal for chemical compound \( j \) always represents mass \( m_{js} \), never concentration \( \varphi_{js} \). Through the above relation, the mass and thereby the detector signal can be related directly to the concentration. Naturally, an appropriate sample pressure, sample temperature and sample volume have to be used.

For example, in order for samples of different volume \( V_s \) to produce the same detector signal, \( \varphi_{js} \) has to be varied such that \( m_{js} \) is maintained constant. However, generally \( \varphi_{js} \) is maintained constant while \( V_s \) is increased, thereby increasing \( m_{js} \) and thus the detector signal. This effectively decreases the detection limit. However, care must be taken not to increase \( m_{js} \) too much since otherwise Column Overload occurs.

Also, with respect to manual sampling, a sample of volume \( V_s \) in the gas phase and a sample of volume \( V_s \) in the liquid phase with identical concentrations of chemical compound \( j \) contain vastly different masses of chemical compound \( j \):

\[ m_s^l = \rho_s^l V_s = n_s^l M_s^l \]
\[ p_s^l V_s = n_s^l R_m T_s^l \]
\[ n_{js}^l = \varphi_{js} n_s^l \]
\[ n_{js}^g = \varphi_{js} n_s^g \]
\[ \frac{n_{js}^l}{n_{js}^g} = \frac{m_{js}^l}{m_{js}^g} = \frac{\varphi_{js}^l \rho_s^l R_m T_s^g}{\varphi_{js}^g M_s^l p_s^g} \]
Here, superscripts $^l$ and $^g$ represent the liquid phase and the gas phase and subscripts $s$, and $j$ represent the sample and the chemical compound $j$. Also, $m$, $n$ and $M$ represent mass, mole number and mole mass, and $p$, $T$ and $V$ represent pressure, temperature and volume.

With $\varphi_{js}^l = \varphi_{js}^g$, $\rho_s \approx 1\, \text{g/cm}^3$ (water), $M_s^l \approx 18\, \text{g/mol}$ (water), $p_s^g = 1.01325 \cdot 10^5$ Pa (atmosphere) and $T_s^g = 298.15\, \text{K}$ (atmosphere) it follows $\frac{n_l^j}{n_s^j} \approx 1400$. In other words, under assumption of an identical sample introduction system, the analysis of ppm concentrations of chemical compounds in air produces a similar detector signal as the analysis of ppb concentrations in water.

5.2.2.3 Technical Considerations

The problem with manual and automatic sample introduction systems is the loss of chemical compounds to the syringe wall, tube wall or sample loop wall. Moreover, sufficient filling time for the syringe or the sample loop has to be provided, such that the syringe or the sample loop contains a representative sample.

For automatic sample introduction, the problem of loss of chemical compounds to the sample loop wall is solved by using a sample loop made from $\frac{1}{16}$ inch outside diameter electroformed nickel tubing. This tubing has a mirror-like inside surface, which reduces the surface area for Thermally Activated Surface Chemical Reactions of chemical compounds with the sample loop wall. Such a surface also reduces the number of Active Sites, which are known to enhance thermally activated surface chemical reactions.

Such thermally activated surface chemical reactions occur in particular for reactive chemical compounds, but are rather negligible for non-reactive chemical compounds. In addition to such chemical reactions, loss of chemical compounds to the sample loop wall may occur through condensation. However, such condensation may be prevented by appropriate choice of the sample loop temperature.

On the one hand, in order to minimize thermally activated surface chemical reactions, the sample loop temperature should be as low as possible. On the other hand, in order to minimize condensation, the sample loop temperature should be as high as possible. Apparently, a trade-off is required in order to arrive at the most appropriate sample loop temperature. However, for the present work, the concentrations of chemical compounds in the sample are sufficiently low to prevent condensation even at a low sample loop temperature.

Also, for reactive chemical compounds, the sample loop wall may have to be subjected to Passivation by exposing it to high concentrations of these (or other) reactive
chemical compounds. Thereby, all active sites for these chemical compounds are pacified. However, passivation with too high a concentration will result in later release of chemical compounds into the sample, passivation with too low a concentration will result in continued loss of chemical compounds to the sample loop wall. For the present work, such passivation was approximately obtained on the basis of the almost permanent exposure of the sample loop to the sample gas flow.

For automatic sample introduction, the problem of providing sufficient filling time for the sample loop is solved by sampling for a period of time equal to several times the sample loop residence time $\tau$. The sample loop of volume $V_s$ is filled through insertion in the sample gas flow of volume flow rate $\dot{V}_s$, so that the sample loop residence time $\tau$ is given as:

$$\tau = \frac{V_s}{\dot{V}_s}$$

In more general terms, one priority with analytical chemistry instrumentation devices is the avoidance of unnecessary volume as this increases the residence time of chemical compounds in the device and thus the effect of thermally activated surface chemical reactions and condensation.

### 5.2.3 Gas Chromatographic Columns

#### 5.2.3.1 Principle of Operation

The gas chromatographic separation of chemical compounds contained in the sample at different concentrations in the gas phase is accomplished via gas chromatographic columns. These columns typically consist of long tubing whose volume, besides a Gas Phase, contains a Solid Phase onto which a Liquid Phase is coated$^1$. The separation is based on the different equilibria that different chemical compounds assume with respect to their distribution between the gas phase and the liquid phase when the sample is injected onto and flushed through the column.

$^1$More general, the gas phase is referred to as the Mobile Phase, while the liquid phase is referred to as the Stationary Phase. This allows for a liquid phase or a solid phase to be coated onto the solid phase.
5.2.3.2 Theory of Operation

Two different theories, i.e. the Plate theory discussed in Appendix D.1 and the Gauss theory discussed in Appendix D.2, describe the gas chromatographic separation by two equivalent equations.

In these equations, \( m_j \) is the mass of chemical compound \( j \) in the sample, \( K_d \) is the equilibrium constant (or distribution coefficient) of chemical compound \( j \) between the gas phase and the liquid phase, \( \rho_l \) is the mass density of the liquid phase and \( \epsilon \) is an equivalent porosity of the column. The equation for the Plate theory results as:

\[
m_{ji}^{\text{Plate}}(k) = m_{ja} \frac{(k - 1)!}{(i - 1)!(k - i)!} x^{k-i} y^i
\]

\[
x = \frac{1}{1 + \frac{1}{K_d \rho_l} \frac{\epsilon}{1-\epsilon}} \quad \text{and} \quad y = \frac{1}{1 + K_d \rho_l \frac{1-\epsilon}{\epsilon}}
\]

Here, \( m_{ji}^{\text{Plate}}(k) \) is the mass of chemical compound \( j \) in the gas phase on plate \( i \) at the \( k^{th} \) plate residence time, \( x \) and \( y \) are parameters describing the equilibrium between the gas phase and the liquid phase. The equation for the Gauss theory results as:

\[
m_j(z,t) = \frac{m_{ja}}{A \sqrt{4\pi D_j^R t}} e^{-\frac{(z-v_g^R)R_j}{4D_j^R t}}
\]

\[
v_g^R = \frac{v_g}{R_j} \quad \text{and} \quad D_j^R = \frac{D_j}{R_j}
\]

\[
R_j = 1 + K_d \rho_l \frac{1-\epsilon}{\epsilon}
\]

Here, \( m_j(z,t) \) is the mass of chemical compound \( j \) in the gas phase at location \( z \) along the column at time \( t \), \( R_j \) is the retardation factor, \( v_g^R \) is the retarded linear flow velocity \( v_g \) of the carrier gas and \( D_j^R \) is the retarded diffusion coefficient \( D_j \) for chemical compound \( j \). Also, \( A \) is the area of the cross section of the column.

The separation of chemical compounds is a result of different values for \( x \) and \( y \) and different values for \( v_g^R \) and \( D_j^R \), respectively. \( K_d \) and \( \rho_l \) are functions of the liquid phase, while \( \epsilon \) is a function of the phase ratio, i.e. the ratio of the volume of the liquid phase to that of the gas phase.
Therefore, a wide range of liquid phases and phase ratios are available for gas chromatography in order to accomplish optimum separation of the chemical compounds contained in a particular sample. Since $K_d$, is also a function of the temperature, gas chromatographs are typically equipped with temperature control to optimize the separation even further.

As pointed out in Appendix D.1 and in Appendix D.2, the separated chemical compounds elute from the column as **Gas Chromatographic Peaks** in the shape of *Gaussian curves*.

The time at which each peak elutes from the column is referred to as **Retention Time**. The temporal separation with which two consecutive peaks elute from the column is referred to as **Resolution**. The maximum resolution obtains for maximum temporal separation of these peaks.

However, the optimum resolution is obtained for minimum temporal separation of these peaks while still providing a clear distinction between these peaks. This implies that narrow peak widths are fundamental to optimum resolution.

The *Plate* theory and the *Gauss* theory assume instant equilibrium between the gas phase and the liquid phase. As long as the mass of a chemical compound contained in the sample is small, this assumption is justified. However, this assumption becomes increasingly unsustainable with increasing mass. In particular, the gas chromatographic peaks do not elute from the column in the shape of *Gaussian curves* any more. This condition is referred to as **Column Overload**.

### 5.2.3.3 Technical Considerations

For reasons of mechanical flexibility, short retention times and superior resolution of peaks, *Capillary Columns* have almost completely replaced *Packed Columns*. The latter are more and more relegated to the area of special applications [106].

In capillary columns, the liquid phase is supported as a film by the wall of the column, while in packed columns, the liquid phase is supported as a film by support grains. These grains are sieved on a certain mesh size. This fundamentally different design of the liquid phase support gives rise to different diffusion coefficients of chemical compounds in these columns.

Although turbulent diffusion does not contribute significantly to the overall diffusion coefficient in a capillary column, it contributes significantly to the overall diffusion coefficient in a packed column. Therefore, the peaks tend to be wider and the resolution tends to be poorer in packed columns than in capillary columns.
For capillary columns, the phase ratio is commonly expressed through the film thickness of the liquid phase on the wall. For packed columns, the phase ratio is commonly expressed through the mesh size of the support grains and the mass loading of the liquid phase on those support grains.

Packed columns have a larger diameter than capillary columns. The contact area between the gas phase and the liquid phase at any location along a packed column may therefore be larger than at any location along a capillary column. This translates into a faster separation of chemical compounds, which in turn is reflected in the shorter length of packed columns compared to that of capillary columns.

Moreover, for this reason the mass of a chemical compound that can be separated without column overload is larger on a packed column compared to that on a capillary column.

However, packed columns typically also feature larger carrier gas volume flow rates than capillary columns in order to achieve comparable retention times. Larger carrier gas volume flow rates dilute chemical compounds more than smaller carrier gas volume flow rates. The higher dilution with packed columns compared to that with capillary columns results in higher detection limits, since most detectors are concentration dependent rather than mass dependent detectors.

Similar considerations for the resolution, the column length, the mass of chemical compound that can be separated without column overload and the detection limit apply when Megabore capillary columns are compared to Microbore capillary columns. The former have an inside diameter of 530 µm, the latter have an inside diameter of 320 µm.

The present work exclusively uses Megabore capillary columns as a compromise between potential column overload with Microbore capillary columns and potential increase in detection limit with packed columns. The capillary columns used in the present work and the chemical compounds that are separated on them in the present work are listed in Table 5.1. Here, HP stands for High Performance and PLOT stands for Porous Layer Open Tubular.

A trade-off has to be made between the minimization of the retention times and the maximization of the resolution. The shorter the retention times, the narrower the peaks, but the closer together, i.e. the less resolved, these peaks.

With constant temperature during the entire separation, early eluting peaks are generally narrow and late eluting peaks are generally wide. With variable temperature during the entire separation, this can be counteracted by varying the temperature such that late eluting peaks experience less retardation and thus elute narrow rather than wide.
<table>
<thead>
<tr>
<th>Name</th>
<th>Hewlett-Packard HP-5</th>
<th>ChromPack PLOT ForaPLOT U</th>
<th>ChromPack PLOT MolSieve 5A</th>
</tr>
</thead>
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<tr>
<td>Catalog Number</td>
<td>19095J-123</td>
<td>7584</td>
<td>7538</td>
</tr>
<tr>
<td>Serial Number</td>
<td>741-33-05, 757-38-06</td>
<td>453218</td>
<td>458206</td>
</tr>
<tr>
<td>Inner Diameter</td>
<td>530 μm</td>
<td>530 μm</td>
<td>530 μm</td>
</tr>
<tr>
<td>Outer Diameter</td>
<td>700 μm</td>
<td>700 μm</td>
<td>700 μm</td>
</tr>
<tr>
<td>Length</td>
<td>30 m</td>
<td>25 m</td>
<td>25 m</td>
</tr>
<tr>
<td>Particle Trap</td>
<td>N.A.</td>
<td>2.5 m</td>
<td>N.A.</td>
</tr>
<tr>
<td>Film Thickness</td>
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<td>20 μm</td>
<td>50 μm</td>
</tr>
<tr>
<td>Support</td>
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<td>Fused Silica</td>
<td>Fused Silica</td>
</tr>
<tr>
<td>Stationary Phase</td>
<td>5 % Diphenyl-Diphenyl</td>
<td>Porous Polymer</td>
<td>Molsieve 5A</td>
</tr>
<tr>
<td></td>
<td>95 % Dimethyl-Polymer</td>
<td>(x-linked)</td>
<td></td>
</tr>
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<td>Polarity</td>
<td>Non-Polar</td>
<td>Polar</td>
<td>Non-Polar</td>
</tr>
<tr>
<td>Maximum Operating</td>
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<td>190 °C</td>
<td>300 °C</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation</td>
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<td>CO₂</td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td>CHCl₃</td>
<td>N₂O</td>
<td>O₂/Ar</td>
</tr>
<tr>
<td></td>
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<td>H₂O</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>COCl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂HCl₃O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: Capillary Columns
The linear flow velocity of the carrier gas may be measured by injecting a chemical compound that is not separated, or retarded, on a particular column. The (non-retarded) "retention" time of this chemical compound combined with the length of the column yields an estimate of the linear flow velocity of the carrier gas.

In the early stages of the present work, when the TCD and the MSD were not available yet and the ECD was the only available detector, the carrier gas was nitrogen, argon or argon/methane. With addition of the TCD and the MSD the carrier gas was changed to helium. Typical carrier gas volume flow rates for capillary columns are on the order of $10 \text{ cm}^3/\text{min}$.

5.2.4 Gas Chromatographic Detectors

5.2.4.1 Types of Detectors

A wide variety of gas chromatographic detectors for identification and quantitation of chemical compounds is available. Some examples for such detectors are the Flame Ionization Detector (FID), the Thermal Conductivity Detector (TCD), the Electron Capture Detector (ECD) and the Mass Selective Detector (MSD). These detectors exhibit different detection limits for different chemical compounds. Therefore, a single detector is typically not sufficient for a comprehensive chemical analysis.

In the following, the operation of the Thermal Conductivity Detector (TCD), the Electron Capture Detector (ECD) and the Mass Selective Detector (MSD) is explained in very limited terms. Moreover, some considerations common to some or all of these detectors are presented.

5.2.4.2 Sample Dilution

The capillary columns used in the present work are operated at rather low carrier gas volume flow rates. However, the detectors used in the present work by design have rather large volumes. In order to decrease the response time of the detector, i.e. the residence time of the separated chemical compounds in the detector, Make-Up Gas is added to the carrier gas at the entrance of the detector.

More importantly, the make-up gas provides the desired operation characteristics of the detector. This implies that the carrier gas volume flow rate is typically much lower than the make-up gas volume flow rate. The mixture of the carrier gas and the make-up gas is referred to as the detector gas.

The mixing of the make-up gas with the carrier gas, which contains the separated
chemical compounds. results in the dilution of the chemical compounds and, in the case of concentration dependent detectors, in a corresponding increase in the detection limit of the detector.

The TCD and the ECD are connected in series, the TCD being the first, the ECD being the second detector. Thus, the volume flow rate entering the TCD is that of the carrier gas, the one exiting the TCD and entering the ECD is that of the carrier gas and the TCD make-up gas, and the one exiting the ECD is that of the carrier gas, the TCD make-up gas and the ECD make-up gas.

Therefore, the dilution increases from the TCD to the ECD. Nevertheless, this detector arrangement is chosen for its complementary nature. Also, by design of the detectors, use of make-up is sensible only for the TCD and the ECD, not for the MSD.

5.2.4.3 Concentration Dependent Detectors

The chemical compounds are contained in the sample at their respective concentrations. Upon injection onto and flushing through the column, the chemical compounds are separated and diluted by the carrier gas, resulting in a concentration change. Upon entering a detector, the chemical compounds are further diluted by the make-up gas, resulting in an additional concentration change. The TCD, ECD and MSD are Concentration Dependent Detectors, but care must be taken in the interpretation of this statement.

Reference is made to the actual concentrations of the chemical compounds in the detector. As long as the concentrations of the chemical compounds in the detector is constant, the detector signal for the chemical compounds is constant. A change of the detector volume by a factor of $n$ and a change of the mass of the chemical compounds in the detector by a factor of $n$ result in the same concentrations in the detector, i.e. the same detector signal.

Reference is not made to the actual concentrations of the chemical compounds in the sample. A change of the sample volume by a factor of $n$ and a change of the masses of the chemical compounds in the sample by a factor of $n$ result in the same concentrations in the sample, but due to the different masses of the chemical compounds and the different dilution via carrier gas and make-up gas, these changes result in different concentrations in the detector, i.e. a different detector signal. In particular, the detector signal increases with sample volume, since the concentrations in the detector increase with increasing masses of the chemical compounds in the sample.
Thus, the detector signal of a concentration dependent detector is a function of the sample volume, the concentrations of the chemical compounds in the sample, the carrier gas volume flow rate and the make-up gas volume flow rate.

5.2.4.4 Quantitation

Quantitation of chemical compounds is accomplished by comparison of peak areas or heights of unknown concentrations to peak areas or heights of known concentrations. The peak areas or heights of unknown concentrations are obtained in Chemical Analysis, the peak areas or heights of known concentrations are obtained in Calibration. Typically, Internal Calibration and External Calibration are distinguished.

For Internal Calibration, a "tracer" chemical compound of known concentration, besides the chemical compounds of unknown concentrations, is contained in the sample for a chemical analysis. The assumption is made that detector signals for comparable concentrations of different chemical compounds are comparable. The unknown concentrations may be interpolated from the corresponding peak areas or heights and from the peak area or height of the known concentration of the "tracer".

For External Calibration, peak areas or heights of known concentrations are obtained for each chemical compound prior to chemical analysis. These peak areas or heights and known concentrations represent Calibration Curves for each chemical compound. The unknown concentrations may then be interpolated from the corresponding peak areas or heights and from the calibration curves.

Although internal calibration provides a convenient means of quantitation, the practicality of internal calibration is rather restricted due to the different sensitivities of the detectors to different chemical compounds. Therefore, external calibration is generally preferred. However, external calibration is very labor and time intensive, because due to detector "drift", calibration curves have to be generated prior to every major chemical analysis.

In order to acquire and analyze peaks, the gas chromatograph hardware is supported through extensive gas chromatograph software, i.e. the HP-GC-ChemStation Software from Hewlett-Packard, Wilmington, Delaware [107], [108], [109], [110], [111], [112].

In addition, the mass spectrometer hardware is supported through extensive mass spectrometer software, i.e. the HP-MS-ChemStation Software from Hewlett-Packard, Palo Alto, California [113], [114], [115]. In particular, this software accounts for the fact that the MSD in contrast to the TCD and ECD, which are non-confirmative detectors, is a confirmative detector.
An extensive review of both the gas chromatometer software is enormously interesting but not the present work.

5.2.5 Thermal Conductivity Detector

5.2.5.1 Principle of Operation

The Thermal Conductivity Detector (TCD) was designed for the detection of chemical compounds that have significantly different thermal conductivities from the detector gas. The difference in the thermal conductivity between the absence and the presence of chemical compounds is used to measure their concentration [105].

In principle, the design of the TCD comprises a ratio of tube to wire and a wire with small diameter wire along the cylinder axis. For mathematical purposes, the three-dimensional geometry can therefore be simplified to a one-dimensional geometry along the one-dimensional coordinate.

The wire is heated by constant electric current, and the temperature of the wire determines the balance of the Wheatstone bridge. The temperature difference is in accordance with the thermal conductivity of the gas.

The wire is heated by a current, and the temperature of the wire determines the balance of the Wheatstone bridge. The temperature difference is in accordance with the thermal conductivity of the gas.

The make-up gas and the carrier gas containing the chemical compound enter at the detector entrance and the detector gas flows along the cylinder axis.

A second hollow cylinder with a wire mounted along the cylinder axis is added as another part of the Wheatstone bridge. A separate Reference Channel is added along the cylinder axis.

The resulting tandem arrangement allows for the detection of the detector signal other than those originating in an increase in the detector gas through the presence of chemical compounds.

Naturally, the carrier gas, the make-up gas and the reference gas are of the same type. In the present work, all three gases are He. The flow rate of the make-up gas is on the order of 5 cm$^3$/min, and the carrier gas flow rates are on the order of 25 cm$^3$/min.
Chemical compounds with thermal conductivities higher than that of the detector gas result in a decrease of the wire temperature and resistance, chemical compounds with thermal conductivities lower than that of the detector gas result in an increase of the wire temperature and resistance. The theory of operation of the TCD is described in Appendix D.3.

5.2.5.2 Technical Considerations

Apparently, the balance of the Wheatstone bridge may be perturbed in opposite directions, representing either negative or positive polarity of the detector signal, i.e. downward or upward pointing peaks. In order to have all upward or all downward pointing peaks, the detector gas is selected such that it has either the lowest or the highest thermal conductivity of all chemical compounds.

It appears to be desirable to have low thermal conductivity for the detector gas in the absence of chemical compounds as well as high thermal conductivity for the chemical compounds. Thus small concentrations of the chemical compounds result in large changes of the thermal conductivity of the detector gas in the presence of chemical compounds.

However, it also appears to be easier to identify detector gases that have a higher thermal conductivity than all expected chemical compounds than to identify those that have a lower thermal conductivity than all expected chemical compounds. The thermal conductivities for several chemical compounds are given in Table 5.2 [84].

As can be seen from Table 5.2, the largest difference in thermal conductivities exists between either hydrogen or helium and the remaining chemical compounds. Therefore, the preferred carrier gas, make-up gas and reference gas for TCD operation is either helium or hydrogen. An alternative choice for these gases is nitrogen.

Note that the detection limit decreases with decreasing detector temperature [105]. For the present work, the detector temperature is set to 150 °C.

5.2.6 Electron Capture Detector

5.2.6.1 Principle of Operation

The Electron Capture Detector (ECD) was developed specifically for the analysis of chemical compounds that dissociatively or non-dissociatively attach electrons. The difference in the electron density in the ECD detector gas in the absence and the
The presence of electron attachment by these chemical compounds is the basis for the detector signal [116].

The electrons are generated as secondary electrons in the ECD detector gas by ionization of detector gas molecules via β radiation. This radiation originates from the radioactive nickel isotope $^{63}\text{Ni}$, with maximum β particle energies of 67 keV [116]. Apparently, due to the radioactive decay of $^{63}\text{Ni}$ with a half-life of approximately one hundred years, the detector has a finite lifetime.

In principle, the design of the ECD comprises a hollow cylinder with small diameter to length ratio and a wire with small diameter which is mounted along the cylinder axis. For mathematical purposes, the three-dimensional cylindrical geometry may therefore be simplified to a one-dimensional geometry with the cylindrical radius as the one-dimensional coordinate.

The hollow cylinder is coated with $^{63}\text{Ni}$ and serves as a cathode, the wire serves as an anode. The voltage applied between the wire and the hollow cylinder results in electron current [116]. Chemical compounds that do attach electrons cause a decrease of the electron density and thus of the electron current, while chemical compounds that do not attach electrons cause no change of the electron density and the electron current.

---

Table 5.2: Thermal Conductivities of Chemical Compounds, adapted from [84]

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>Molecular Formula</th>
<th>Thermal Conductivity $10^{-3}$ W/m K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>79% N$_2$, 21% O$_2$</td>
<td>26.9</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>25.8</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>18.5</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO$_2$</td>
<td>17.5</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>26.0</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl$_2$</td>
<td>9.2</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>154.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H$_2$</td>
<td>192.1</td>
</tr>
<tr>
<td>Hydrogen Chloride</td>
<td>HCl</td>
<td>14.7</td>
</tr>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>35.8</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>26.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N$_2$</td>
<td>26.8</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>N$_2$O</td>
<td>18.3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>27.6</td>
</tr>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>18.7</td>
</tr>
</tbody>
</table>
The make-up gas and the carrier gas containing the chemical compounds are mixed at the detector entrance and the detector gas then flows freely through the cylinder along the cylinder axis. Separate anode-purge gas is used to purge the volume around the anode from potentially present negative ions. The anode-purge gas becomes part of the detector gas as well.

Naturally, the carrier gas, the make-up gas and the anode-purge gas should be of the same type. In the present work, however, the carrier gas is helium, while the make-up gas and the anode-purge gas is argon/methane. Typical ECD make-up gas volume flow rates are on the order of $50 \text{ cm}^3/\text{min}$, typical ECD anode-purge gas volume flow rates are on the order of $10 \text{ cm}^3/\text{min}$.

In the early stages of the present work, when the TCD and the MSD were not available yet and the ECD was the only available detector, all three gases were nitrogen, argon or argon/methane.

### 5.2.6.2 Modes of Operation

Three operation modes for the ECD may be distinguished. The first mode operates with constant voltage and the variation of the electron current is used as the detector signal [117], [118]. The second mode operates with pulsed voltage and the variation of the electron current is used as the detector signal [118]. The third mode operates with pulsed voltage and the pulse frequency is adjusted so that the electron current remains constant. The variation of the pulse frequency is used as the detector signal [119].

The voltage amplitude experiences no variation in all three modes of operation. The most important differences between the constant voltage mode of operation and the pulsed voltage modes of operation are described in the following [116].

The average electron energy with constant voltage is generally higher than that with pulsed voltage. However, many chemical compounds have the largest reaction rate constants for electron attachment at low average electron energies rather than at high average electron energies. This results in a higher detection limit with constant voltage than with pulsed voltage. In fact, with pulsed voltage, the detection limit may be adjusted by adjusting the pulse frequency [119].

With constant voltage, not only electrons but also negative ions are likely to contribute to the current. Therefore, in detector gases for which the recombination of electrons with positive ions is comparable to, or stronger than, the recombination of negative ions with positive ions, a decrease of the electron density due to electron attachment does not necessarily result in a significant decrease of the current, i.e. a
weak detector signal is generated.

This can only be prevented, if the recombination of electrons with positive ions is weaker than the recombination of negative ions with positive ions. Under these conditions, the current is approximately equal to the electron current and a decrease of the electron density due to electron attachment does result in a significant decrease of the electron current, i.e. a strong detector signal is generated.

With pulsed voltage, negative ions possess too large a mass inertia as that they could be accelerated during the pulse width and thus do not contribute to the current to begin with.

Also, due to the small dimensions of the ECD and depending on the detector gas, with constant voltage, breakdown is likely to occur at rather low voltages while with pulsed voltage, breakdown is not likely to occur if pulse width and pulse frequency are selected properly.

With pulsed voltage, the preference for selection of current variation or pulse frequency variation as the detector signal is chiefly a matter of obtaining as wide a linear range of the detector signal as possible. This appears to be easier with the latter rather than the former operation mode. For the reasons listed, generally the pulsed voltage operation mode is preferable over the constant voltage operation mode. The theory of operation of the ECD is described in Appendix D.4.

5.2.7 Mass Selective Detector

5.2.7.1 Difference Between TCD or ECD and MSD

In contrast to the TCD and the ECD, which are offered by Hewlett-Packard as accessories to their gas chromatograph, the Mass Selective Detector (MSD) is offered by Hewlett-Packard as an independent device, which nevertheless needs to be operated in combination with a Hewlett-Packard or non-Hewlett-Packard gas chromatograph. Note that every MSD is essentially a mass spectrometer, but not every mass spectrometer is a MSD.

5.2.7.2 Gas Chromatograph-Mass Spectrometer Interface

The MSD operates under vacuum conditions, while the gas chromatograph, including TCD and ECD, operates under atmospheric conditions. Therefore, the coupling of the column to the MSD is more complex than the coupling of the column to the TCD or the ECD.
The MSD vacuum is maintained by a vacuum system comprised of an *E2M2 Rotary Vane High Vacuum Pump* from Edwards, Crawley/Sussex, Great Britain and a *EO-50/60 Diffusion Ultra High Vacuum Pump* from Edwards, Crawley/Sussex, Great Britain. The pumping speed of the latter is approximately 60 l/s.

The entrance to the MSD consists of a fused silica capillary tubing of 115 μm inside diameter and 50 cm length. This capillary tubing serves as a flow rate restrictor such that the vacuum system may maintain the MSD vacuum against the restricted flow rate. In particular, the MSD end of the capillary tubing is at vacuum pressure while the free end of the capillary tubing is at lower than atmospheric, atmospheric or higher than atmospheric pressure.

For atmospheric or lower than atmospheric pressure on the free end of the capillary tubing, the MSD pressure may be maintained below the safe shutdown pressure and the MSD does not trip into safe shutdown. However, for higher than atmospheric pressure on the free end of the capillary tubing, the MSD pressure may not be maintained below the safe shutdown pressure and the MSD does trip into safe shutdown. Such safe shutdown is performed in order to protect the diffusion ultra high vacuum pump.

Several devices exist for maintaining the free end of the capillary tubing at atmospheric or lower than atmospheric pressure when connected to the gas chromatographic column. These devices represent a particular form of *Gas Chromatograph/Mass Spectrometer Interface*. Only the two devices considered for the present work are described here [120].

In a *Capillary Direct Interface*, the free end of the capillary tubing is connected directly to the capillary column. In order to prevent higher than atmospheric pressure on this end, the carrier gas flow rate has to be lower than the restricted flow rate. Such an interface can typically accommodate only capillary columns of 320 μm or narrower inside diameter, since only these columns provide a low enough carrier gas flow rate for the flow rate restrictor.

In a *Capillary Split Interface*, the free end of the capillary tubing is connected indirectly to the capillary column. In order to prevent higher than atmospheric pressure on this end, a major fraction of the carrier gas flow rate is split to lower than atmospheric or atmospheric pressure while only a minor fraction of the carrier gas flow rate is split into the MSD. Such an interface can typically only accommodate capillary columns of 530 μm or wider inside diameter since only these columns provide a high enough carrier gas flow rate for the split.

The split is accomplished via a simple tee, where the carrier gas flow rate enters the tee through one straight end and the minor fraction of the carrier gas flow rate split into the MSD exits the tee through the other straight end. The major fraction
of the carrier gas flow rate split to lower than atmospheric or atmospheric pressure exits the tee through the angled end of the tee.

The fraction of the carrier gas flow rate split into the MSD is then on the order of 1 cm$^3$/min, while the fraction of the carrier gas flow rate split to lower than atmospheric or atmospheric pressure is on the order of 10 cm$^3$/min.

A capillary split interface results in a significant increase in detection limit for the MSD since a major fraction of the separated chemical compounds contained in the carrier gas is split to atmospheric pressure as well. However, this fraction may be passed on to both the TCD and the ECD. In fact, this is implemented in the present work and allows for use of the MSD in parallel to the TCD and the ECD. The detection limits for both the TCD and the ECD are not increased significantly.

For both the capillary direct interface and the capillary split interface, the MSD pressure adjusts itself according to the pumping speed of the vacuum system and the restricted flow rate through the capillary tubing. No control of the MSD pressure is possible.

Also, since the carrier gas flow rate for packed columns is higher than that for capillary columns, even those of 530 μm inside diameter, and since the detection limit for packed columns is higher than that for capillary columns in the first place, the use of a MSD is virtually limited to capillary columns.

5.2.7.3 Principle of Operation

On the inside of the MSD, the fused silica capillary tubing passes the carrier gas into the Ion Source. Here, irradiation of the carrier gas and the chemical compounds contained in the carrier gas by ionizing radiation ionizes the chemical compounds to produce ions of several mass to charge (M/Z) ratios.

The ionizing radiation is represented by an electron beam of approximately 70 eV electron beam energy, which is generated by thermionic emission from a filament and accelerated by an electric field.

The ions are extracted from the ion source and accelerated into the Mass Filter by additional electric fields. The mass filter pressure has to be maintained low enough to warrant virtually collision-free passage of the ions through the mass filter. After passage through the mass filter, the ions impinge on the electron multiplying surface coating of the Electron Multiplier Detector.

The Electron Multiplier Voltage (EMV) determines the number of electrons generated per ion impinging on the electron multiplying surface coating. The resulting
electron current represents the MSD detector signal. The detector signal increases approximately exponentially when the EMV increases linearly. This translates into a decrease in detection limit with an increase in EMV.

Also, over the duration of the present work, the EMV had to be increased from approximately 1700 V to 2700 V in order to maintain a constant detector signal. This reflects the wear-out of the electron multiplying surface coating.

The production of ions in the ion source and therefore the detection limit depends on the extent of pollution of the ion source. A clean ion source produces more ions and thus a stronger MSD detector signal than a dirty ion source. Such pollution cannot be avoided and therefore, the ion source has to be cleaned when the detector signal cannot be maintained constant anymore.

At any particular moment in time, the mass filter allows for passage of only one M/Z ratio, thereby accomplishing mass filtering. The M/Z ratios allowed to pass through the mass filter are scanned from a minimum to a maximum M/Z ratio within several tenths of a second. Any M/Z ratio that produces an Abundance during this scan contributes to the mass spectrum acquired during the scan. Since a gas chromatographic peak typically has a width of several tenths of a minute, a single peak contains several hundred scans, i.e. mass spectra.

Therefore, in contrast to the TCD and the ECD, the detector signal of the MSD shows not only one peak for each separated chemical compound, but as many peaks as different M/Z ratios are produced for this chemical compound.

The number of ions and the M/Z ratios of these ions produced in the ion source are a function of the carrier gas, the chemical compounds, the ion source pressure, the electron beam energy and the electron beam current.

Apparently, in order to reduce the background abundances, the carrier gas should be such that no ions are produced from it with M/Z ratios in the above scan range for the M/Z ratios. Such carrier gas may either be hydrogen or helium.

5.2.7.4 Theory of Operation

Although the ion source and the electron multiplier detector are important as well, the most important component of the MSD and a mass spectrometer in general is the mass filter. The theory of operation therefore may be limited to the mass filter.

The classical mass filter is a quadrupole, which consists of four metal rods of identical diameter and length. The rods are arranged in parallel such that their axes run through the four corner points of a square. The axis of the mass filter runs through
the center point of the square.

The mass filter of the HP-5971A MSD consists of a tube with four ceramic walls that are coated with metal on the inside of the tube. The walls are identical and have the cross section of a segment of a hyperbola. The walls are arranged such that their curvatures point toward the axis of the tube. The axis of the mass filter runs along the axis of the tube.

The difference between the classical and Hewlett-Packard's approach lies in the fidelity of generation of a truly hyperbolic voltage within the mass filter by application of voltage to either the rods or the walls. While the classical mass filter accomplishes this goal only approximately, the Hewlett-Packard mass filter generates a perfectly hyperbolic voltage.

As can be seen in Appendix D.5, the theory of mass filtering in a quadrupole mass filter is based on the presence of this kind of voltage in the mass filter. Notwithstanding this requirement, the mathematical description of the classical and Hewlett-Packard's mass filter is identical and involves the derivation of an equation for the voltage within the mass filter and of equations of motion for the ions within the mass filter.

The derivations of the equation for the voltage and of the equations of motion along the ξ-axis and the η-axis perpendicular to the mass filter axis, i.e. the z-axis, are given in Appendix D.5 and are based on [121]. These equations have the form of Mathieu equations:

\[
\frac{\partial^2 \xi}{\partial \varphi^2} = -Q\left(\frac{A}{Q} + 2\cos 2\varphi\right)\xi \\
\frac{\partial^2 \eta}{\partial \varphi^2} = +Q\left(\frac{A}{Q} + 2\cos 2\varphi\right)\eta
\]

Here, \(\varphi = \frac{1}{2}\omega t\), where \(\omega\) is the frequency of the AC component of the voltage applied to the rods or the walls, \(Q\) is proportional to the AC component of this voltage and \(\frac{A}{Q}\) represents the ratio of the DC component to the AC component of this voltage.

An analytical solution to these equations is possible, but beyond the scope of the present work. Qualitative remarks on how these equations bring about mass filtering may suffice here. These remarks are based on a numerical solution to the above equations.

The solution to the equations is desired during the period \(\tau\) required for the ions to traverse the mass filter along the z-axis. This time in turn is determined by the length
of the mass filter and the initial velocity $v_{io}$ of the ions along the $z$-axis. Generally, $	au$ is on the order of millionth of a second. As a function of $\omega$, $Q$ and $\frac{A}{Q}$, several cases may be distinguished.

If $\omega \ll \frac{1}{\tau}$, then $2 \cos 2\varphi$ is virtually constant during period $\tau$, and the solutions are classically oscillatory for $\xi$ or $\eta$ and exponential for $\eta$ or $\xi$, respectively. This holds independently of the value of $\frac{A}{Q}$. The exponential solution grows extremely rapidly, the more the larger $Q$ and/or $\frac{A}{Q}$. Thus for all ions, either $\xi$ or $\eta$ assumes a value much larger than that of the mass filter before period $\tau$ has passed. Hence, all ions are lost to the rods or the walls.

If $\omega \geq \frac{1}{\tau}$ and $\frac{A}{Q} \ll 2$, then the oscillatory nature of $2 \cos 2\varphi$ becomes apparent and the solutions result in the passage of all ions without their being lost to the rods or walls. This holds independently of the value of $Q$.

If $\omega \geq \frac{1}{\tau}$ and $\frac{A}{Q} < 2$, then the oscillatory nature of $2 \cos 2\varphi$ competes with constant $\frac{A}{Q}$, and the solutions are essentially exponentially oscillatory. However, the exponential increases much slower than for $\omega \ll \frac{1}{\tau}$. This increase is a function of $Q$. Therefore, depending on $Q$, ions can be passed selectively.

If $\omega \geq \frac{1}{\tau}$ and $\frac{A}{Q} \gg 2$, then the constant $\frac{A}{Q}$ determines the solution, giving rise again to rapidly growing exponential and oscillatory solutions and resulting in the loss of all ions to the rods or the walls.

### 5.3 Mass Spectrometer

#### 5.3.1 Non-Separative Analysis

In *Gas Chromatography/Mass Spectrometry* (GC-MS), the *Hewlett-Packard 5971A Mass Selective Detector* from Hewlett-Packard, Palo Alto, California is used as a confirmative detector for the *Gas Chromatograph* (GC). This gas chromatographic separation of chemical compounds and their subsequent mass spectrometric identification and quantitation very likely represents the most reliable instrumental chemical analysis.

The gas chromatographic separation, however, is frequently impractical for reactive chemical compounds. Although these chemical compounds may be reacted with non-reactive chemical compounds and their reaction products then may be separated, identified and quantified by means of *Derivatization Gas Chromatography* [104], [122], [123], [124], [125], [126], [127], [128], this approach requires experience and skills frequently not available to the average GC operator.
Also, gas chromatographic separation is inappropriate where implementation and enforcement of pollution control regulation requires analytical chemistry instrumentation devices capable of stand-alone, on-line and real-time pollution monitoring, i.e. chemical analysis. In particular, the duration of separation of chemical compounds prevents real-time chemical analysis.

A stand-alone, on-line and real-time approach to chemical analysis also results in benefits unrelated to environmental pollution control. The rapid feedback on process control made possible by this approach may be used to stabilize a process against perturbations. Additionally, such approach facilitates process development, because a large process parameter space may be explored in relatively short time.

Moreover, it is desirable to perform a chemical analysis for as many chemical compounds as possible by using a single analytical chemistry instrumentation device. A mass spectrometer, rather than a gas chromatograph or gas chromatograph/mass spectrometer, may then be well suited for such a stand-alone, on-line and real-time analytical chemistry instrumentation device, since each chemical compound has a mass spectrum with one or more characteristic M/Z ratios and the mass spectra of different chemical compounds are generally different.

Therefore, it is attempted in the present work to convert the MSD from a GC-MS detector to a Stand-Alone, On-Line, Real-Time Mass Spectrometer (SOR-MS) detector. Such conversion involves the modification of the MSD sample introduction system and the MSD data analysis software. These modifications then allow for evaluation and demonstration of the feasibility of this conversion.

A limited number of experiments were conducted for such evaluation and demonstration. These experiments indicate that with sufficient care and awareness of the potential and limitations, it appears to be possible to convert the MSD from a GC-MS detector to a SOR-MS detector, although the accuracy, precision and reproducibility of such a SOR-MS detector may not be quite as high as those of a GC-MS detector.

The conversion is attempted in the context of chemical analysis of gaseous hazardous waste. In particular, the conversion focuses on the chemical analysis of gaseous hazardous waste containing chlorinated organic compounds, such as CCl₄, CHCl₃ and C₂HCl₃, and their chlorinated decomposition products, such as HCl, Cl₂ and COCl₂ and C₂HCl₃O. This focus is a natural outcome of the present work.
5.3.2 SOR-MS Sample Introduction System

5.3.2.1 Principle of Operation

For GC-MS, the flow rate into the MSD is that of a fraction of the carrier gas and the separated chemical compounds contained therein, while for SOR-MS, the flow rate into the MSD is that of a fraction of the gaseous hazardous waste and the unseparated chemical compounds contained therein.

Also, while for GC-MS the sample is a volume taken from the gaseous hazardous waste and introduced discontinuously into the MSD, for SOR-MS the sample is obviously a volume flow taken from the gaseous hazardous waste and introduced continuously into the MSD.

For GC-MS and SOR-MS, the entrance to the MSD consists of a fused silica capillary tubing of approximately 115 μm inside diameter and 50 cm length. For GC-MS, the capillary tubing is connected to the gas chromatographic column via a capillary direct interface or a capillary split interface. For SOR-MS, the capillary tubing is connected to the intake or exhaust tubing of the Tunable Plasma Reactor.

With such a sample introduction system, as with the capillary direct interface or the capillary split interface, the MSD pressure adjusts itself according to the pumping speed of the MSD vacuum system and the restricted flow rate through the capillary tubing. Therefore, no control of the MSD pressure is available.

However, MSD pressure control may be desirable for modification of the detection limit of chemical compounds and the prevention of the MSD trip into safe shutdown. Two modifications to the sample introduction system may be considered for this purpose.

First, the small capacity diffusion ultra high vacuum pump of the MSD vacuum system could be exchanged against a large capacity diffusion or turbomolecular ultra high vacuum pump equipped with a throttle valve. In combination with this throttle valve, a metering valve inserted in the capillary tubing then could control the restricted flow rate into the MSD and thus the MSD pressure. The implementation of this solution requires a large financial and technical effort.

Second, a fraction of the restricted flow rate through the capillary tubing could be pumped away via a metering valve and a high vacuum pump, which could control the restricted flow rate into the MSD and thus the MSD pressure. The implementation of this solution required a small financial and technical effort because a spare EDM2 Rotary Vane High Vacuum Pump from Edwards, Crawley/Sussez, Great Britain was available in the laboratory. This modification was therefore chosen. The details of
the implementation are shown in Figure 5.2.

![SOR-MS Sample Introduction System](image)

Figure 5.2: SOR-MS Sample Introduction System

A straight end of a ZTJC Zero Dead Volume Tee from Valco Instruments Inc., Houston, Texas is connected to the free end of the capillary tubing that represents the entrance to the MSD. An identical second capillary tubing is connected to the other straight end of the tee. The free end of this second capillary tubing is connected to the intake or exhaust tubing of the Tunable Plasma Reactor.

The angled end of the tee between the two capillary tubings is connected to the spare rotary vane high vacuum pump. This connection is throttled by a SS-4MGD Double-Stem Metering Valve from Nupro Company, Willoughby, Ohio.

The use of two instead of one capillary tubings results in a decreased restricted flow rate through the capillary tubing in the first place, which in connection with the metering valve and the high vacuum pump is decreased even further.

Moreover, the use of two capillary tubings increases the flexibility of the sample introduction system in that it allows for a stationary location of the metering valve and the high vacuum pump and a mobile location of the connection to the intake or the exhaust tubing of the Tunable Plasma Reactor.

With this sample introduction system, the detection limit of chemical compounds increases with decreasing MSD pressure on the basis of the decreasing amount of chemical compounds entering the MSD ion source. On the other hand, the detection
limit of chemical compounds increases with increasing MSD pressure on the basis of increasing adverse effects on the generation of ions in the MSD ion source and the passage of ions through the MSD mass filter. The minimum in the detection limit as a function of MSD pressure is rather broad and located at higher rather than lower MSD pressures.

5.3.2.2 Theory of Operation

The following pertains to the restricted flow through the capillary tubing. In particular, it pertains to either a sample introduction system without MSD pressure control via a metering valve and a high vacuum pump or a sample introduction system with MSD pressure control via such metering valve and high vacuum pump but with a fully closed metering valve.

With a constant flow rate of the restricted sample flow entering the MSD, the MSD pressure is approximately given by:

\[
\dot{n}_s = \frac{p_s \dot{V}_s}{R_m T_s}
\]
\[
\dot{n}_v = \frac{p_v \dot{V}_v}{R_m T_v}
\]
\[
\dot{n}_v = \dot{n}_s
\]
\[
p_v = \frac{p_s}{V_v} R_m T_v
\]

Moreover:

\[
p_s \dot{V}_s = \dot{n}_s R_m T_s
\]
\[
p_v = \frac{\dot{n}_s}{V_v} R_m T_v
\]

Here, \( p_s, T_s, \dot{n}_s \) and \( \dot{V}_s \) are the pressure, temperature, mole flow rate and volume flow rate of the restricted sample flow. Also, \( p_v \) and \( T_v \) are the MSD pressure and temperature, and \( \dot{n}_v \) or \( \dot{V}_v \) is the pumping speed of the MSD vacuum system.

However, since the restricted sample flow enters the MSD through a capillary tubing, its mole flow rate is determined by the following equations, depending on whether molecular or viscous flow obtains over most of the capillary tubing [120]:

149
\[ \dot{n}_s^m = \frac{\pi d^3}{3L} \frac{p_s - p_v}{\sqrt{2\pi M_s R_m T_s}} \]
\[ \dot{n}_s^v = \frac{\pi d^4}{256 L \eta_s R_m T_s} \left( \frac{p_s^2 - p_v^2}{2} \right) \]

Hence, \( \dot{n}_s = \dot{n}_s^m \) or \( \dot{n}_s = \dot{n}_s^v \). Here \( d \) and \( L \) are the inside diameter and the length of the capillary tubing, \( M_s \) and \( \eta_s \) are the mole mass and the kinematic viscosity of the sample flow. Also, generally \( p_v \ll p_s \), i.e. \( p_v \) may be negligible compared to \( p_s \). The superscript \( ^m \) stands for "molecular" flow and the superscript \( ^v \) stands for "viscous" flow. The mole masses and kinematic viscosities of various gases are given in Table 5.3.

<table>
<thead>
<tr>
<th>( M_s ) (g/mol)</th>
<th>( \eta_s ) (10^{-6} kg/s m)</th>
<th>0 °C</th>
<th>20 °C</th>
<th>100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>2.02</td>
<td>8.35</td>
<td>8.74</td>
<td>10.30</td>
</tr>
<tr>
<td>He</td>
<td>4.00</td>
<td>18.60</td>
<td>19.41</td>
<td>22.81</td>
</tr>
<tr>
<td>N(_2)</td>
<td>28.01</td>
<td>16.59</td>
<td>17.48</td>
<td>20.79</td>
</tr>
<tr>
<td>O(_2)</td>
<td>32.00</td>
<td>18.90</td>
<td>20.24</td>
<td>24.28</td>
</tr>
<tr>
<td>Air</td>
<td>28.85</td>
<td>17.08</td>
<td>18.34</td>
<td>21.92</td>
</tr>
<tr>
<td>Ar</td>
<td>39.95</td>
<td>20.96</td>
<td>22.17</td>
<td>26.95</td>
</tr>
</tbody>
</table>

Table 5.3: Mole Masses \( M_s \) and Kinematic Viscosities \( \eta_s \) of Various Gases, adapted from [84]

For air at \( p_s = 1.01325 \cdot 10^5 \) Pa and \( T_s = 298.15 \) K and with \( M_s = 28.85 \) g/mol, \( \eta_s \approx 2 \cdot 10^{-5} \) kg/s m, \( d = 115 \) \( \mu \)m, \( L = 1.0 \) m and \( \dot{V}_s = 60 \) l/s, the flow rate of the restricted sample flow and the resulting MSD pressure for molecular and viscous flow become:

\[ \dot{n}_s^m = 7.6 \cdot 10^{-9} \text{ mol/s} \]
\[ \dot{n}_s^v = 4.4 \cdot 10^{-7} \text{ mol/s} \]
\[ \dot{V}_s^m = 0.01 \text{ cm}^3/\text{min} \]
\[ \dot{V}_s^v = 0.65 \text{ cm}^3/\text{min} \]
\[ p_v^m = 3.2 \cdot 10^{-4} \text{ Pa} \approx 2.4 \cdot 10^{-6} \text{ torr} \]
\[ p_v^v = 1.8 \cdot 10^{-2} \text{ Pa} \approx 1.4 \cdot 10^{-4} \text{ torr} \]

The distinction between molecular flow and viscous flow is made via the Knudsen number \( Kn \). Typically, viscous flow obtains for \( Kn \leq \frac{1}{100} \) and molecular flow obtains...
for $Kn \geq 1$. Also, transition flow obtains for $\frac{1}{100} \leq Kn \leq 1$. The Knudsen number may be defined as:

$$Kn = \frac{\lambda_s}{d}$$

$$N_s = \frac{n_s N_a}{V} = \frac{p_s N_A}{R_m T_s}$$

$$\lambda_s = \frac{1}{\Sigma_s} = \frac{1}{N_s \sigma_s} = \frac{R_m T_s}{p_s N_A \sigma_s}$$

Here, $\sigma_s \approx \frac{\pi}{4} d_s^2$ and $d_s \approx 5a_0$, where $\sigma_s$ is the average cross section of the average sample molecule for collision with another average sample molecule, $d_s$ is the diameter of such molecule for such collision and $a_0$ is the Bohr radius. Moreover, $\lambda_s$ is the average mean free path of the average sample molecule for collision with another average sample molecule.

Typically, the experimentally observed MSD pressure is on the order of $p_v = 10^{-5}$ torr to $p_v = 10^{-4}$ torr. Therefore, viscous flow rather than molecular flow appears to prevail over most of the capillary tubing. Also, based on the equation for the Knudsen number, the pressure required to obtain viscous flow is approximately $p_s \geq 490$ torr, while the pressure required to obtain molecular flow is approximately $p_s \leq 5$ torr.

Note that at a pressure of $p_v = 10^{-4}$ torr instead of $p_s$, the average mean free path $\lambda_v$ becomes $\lambda_v = 6$ cm. Since the MSD inside dimensions are on the order of cm, such pressure $p_v$ may be considered the maximum reasonable operation pressure from the viewpoint of avoidance of inter-molecule collisions inside the MSD.

5.3.2.3 MSD Pressure Monitoring

The MSD pressure is monitored by a #2/B-275 Convectron Gauge and a 274005 Ion Gauge from Granville-Phillips, Boulder, Colorado. The convectron gauge is mounted close to the intake of the diffusion ultra high vacuum pump at the exit of the mass filter, while the ion gauge is mounted close to the ion source at the entrance of the mass filter. Therefore, the MSD pressure indicated by the ion gauge is very close to the MSD ion source pressure.

The convectron gauge is controlled by a 486/33 Personal Computer from Insight, Tempe, Arizona via the HP-MS-ChemStation Software from Hewlett-Packard, Palo
Alto, California. The ion gauge is controlled by a 303 Ion Gauge Controller from Granville-Phillips, Boulder, Colorado.

The convectron gauge utilizes the thermal conductivity of a gas to measure the pressure. The ion gauge utilizes the ionization potential of a gas to measure the pressure. Therefore, even though the actual pressure may be identical for different gases, the indicated pressure varies with these gases and a pressure correction factor has to be applied [129].

The ion gauge is calibrated for $N_2$. Therefore, if $N_2$ is the dominant gas in the MSD, indicated pressure and actual pressure are identical. For other dominant gases in the MSD, the ion gauge pressure correction factors are given in Table 5.4:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.18</td>
</tr>
<tr>
<td>Ne</td>
<td>0.30</td>
</tr>
<tr>
<td>$D_2$</td>
<td>0.35</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.46</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>Air</td>
<td>1.00</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.01</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.12</td>
</tr>
<tr>
<td>NO</td>
<td>1.16</td>
</tr>
<tr>
<td>Ar</td>
<td>1.29</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.42</td>
</tr>
<tr>
<td>Kr</td>
<td>1.94</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>2.50</td>
</tr>
<tr>
<td>Xe</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Table 5.4: Ion Gauge Pressure Correction Factors [129]

The convectron gauge pressure triggers the MSD trip into safe shutdown. The safe shutdown pressure is based on indicated and not actual convectron gauge pressure because the convectron gauge has no way of knowing which gas is the dominant gas in the MSD.

A particular volume or mole flow rate of either He or air passing through the capillary tubing into the MSD results in an identical actual MSD pressure for these two gases. However, by virtue of the pressure correction factor, such volume or mole flow rate also results in a lower indicated MSD pressure for He than for air. Therefore, it is possible for the MSD to trip into safe shutdown for air but not for He.

Since for GC-MS the carrier gas consists of He while for SOR-MS the gaseous
hazardous waste consists mainly of a; this different behavior of the MSD with respect to a trip into safe shutdown is of concern. In fact, this concern is the most important reason for implementation of the outlined sample introduction system with MSD pressure control.

The convectron gauge pressure and the ion gauge pressure are not well correlated since they indicate in different pressure ranges. However, the safe shutdown pressure does correspond to a particular ion gauge pressure. Also, the convectron gauge pressure is displayed on demand only while the ion gauge pressure is displayed continuously. Therefore, the MSD pressure and the proximity to safe shutdown is monitored exclusively via the ion gauge.

Finally, any MSD pressure mentioned in the present work is indicated and not actual ion gauge pressure and is accurate to within one digit after the decimal point.

5.3.3 SOR-MS Data Analysis

5.3.3.1 Principle of Operation

For GC-MS and SOR-MS, quantitation of a particular chemical compound is based on the abundance of a characteristic M/Z ratio in the mass spectrum of this compound. This M/Z ratio is referred to as the Quant Ion. Such quant ion may be chosen as the M/Z ratio with the largest abundance or a special uniqueness in the mass spectrum of the particular chemical compound. For detection limit reasons, the former option is usually preferred over the latter option.

For GC-MS, quantitation is accomplished via the gas chromatographic peak height or area for the quant ion. However, for SOR-MS no gas chromatographic separation is available, and quantitation must be accomplished via the mass spectrometric step height for the quant ion.

Moreover, the chemical compounds of a mixture generally have mass spectra in which some of the M/Z ratios are different and some of the M/Z ratios are similar. Without gas chromatographic separation, several chemical compounds of a mixture may therefore contribute to the abundance of the quant ion of a chemical compound. Hence, the abundance of the quant ion of this chemical compound cannot simply be measured but must be calculated. This is accomplished by Deconvolution of the mass spectrum.

However, such a deconvolution may only be performed, if a Calibration Curve for the abundance as a function of the concentration can be obtained for all chemical compounds contributing to the abundance of the quant ion. Since such a calibration
curve is generally non-linear, the deconvolution must be non-linear as well. As far as possible, in the present work, calibration curves for the abundance as a function of the concentration are generally obtained for all chemical compounds and for all quant ions.

Hence, a calibration curve for a chemical compound is actually a collection of calibration curves for the abundance as a function of the concentration for the quant ions of all chemical compounds of interest to the present work. Thus, although the abundance of the quant ion of some chemical compounds may have no contribution from other chemical compounds, a full deconvolution is always possible.

The chemical compounds and their quant ions of interest to the present work are shown in Table 5.5.

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>M/Z Ratio</th>
<th>Quant Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>36</td>
<td>HCl</td>
</tr>
<tr>
<td>Cl₂</td>
<td>70</td>
<td>Cl₂</td>
</tr>
<tr>
<td>COCl₂</td>
<td>63</td>
<td>COCl</td>
</tr>
<tr>
<td>CCl₄</td>
<td>117</td>
<td>CCl₃</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>83</td>
<td>CHCl₂</td>
</tr>
<tr>
<td>C₂HCl₃</td>
<td>130</td>
<td>C₂HCl₃</td>
</tr>
<tr>
<td>C₂HCl₃O</td>
<td>83</td>
<td>CHCl₂</td>
</tr>
</tbody>
</table>

Table 5.5: Chemical Compounds and Quant Ions

5.3.3.2 Technical Considerations

The MSD is delivered with the standard HP-MS-ChemStation Software from Hewlett-Packard Company, Palo Alto, California. This software operates in MS-Windows 3.1 from MicroSoft Corporation, Redmond, Washington.

The HP-MS-ChemStation Software accommodates five major tasks, i.e. Instrument Control, Instrument Diagnostics, Instrument Tuning, Data Acquisition and Data Analysis. This software also utilizes a Command Language Processor (CLP) to interpret commands contained in macros. Each one of the above five tasks is implemented via a series of such macros.

For the modification of the data analysis software performed in the present work, the series of macros for the data analysis task is enhanced by additional macros. Moreover, two programs in MS-FORTRAN 5.1 from MicroSoft Corporation, Redmond, Washington are developed that are called from these macros. The additional
macros allow for custom-made extraction of the abundances of selected M/Z ratios from the mass spectrum, while the two programs allow for processing of the thus extracted abundances.

The first of the two programs is referred to as HPMSONE. It fits the abundances of selected M/Z ratios for various concentrations of a chemical compound to a quadratic function for each of these M/Z ratios and thus creates calibration curves. The second of these programs is referred to as HPMSTWO. It deconvolves the abundances of selected M/Z ratios using the calibration curves obtained through HPMSONE.

The two programs may be called independently. In particular, the information generated by HPMSONE may be used by HPMSTWO an unlimited number of times, since this information merely represents the calibration curves for the chemical compounds.

By design of the HP-MS-ChemStation Software for analysis of gas chromatographic peaks, data acquisition and data analysis are sequential tasks. Therefore, while the data acquisition task is truly SOR, the data analysis task is not truly SOR.

This problem could be solved by gaining access to the CLP section of the HP MS-ChemStation Software source code. The data acquisition task and the data analysis task, as far as extraction of abundances and calling of HPMSTWO are concerned, could then be made parallel. The data acquisition task and the data analysis task, as far as extraction of abundances and calling of HPMSONE are concerned, must still be sequential. However, such a modification is beyond the scope of the present work.

5.3.3.3 Theory of Operation

The theory behind the two MS-FORTRAN77 5.1 programs is described in the following. The abundance of any M/Z ratio is assumed to be a linear superposition of non-linear functions of the concentrations of the chemical compounds which contribute to this particular M/Z ratio.

This assumption is an extension of the linear superposition of linear functions as outlined for example in [121]. Although such linear superposition may be arguable on the grounds of chemical reactions among chemical compounds in the ion source, the applicability of this linear superposition is nevertheless assumed for the present work.

For the purpose of the present work, the non-linear functions of the concentrations are assumed to be quadratic functions. However, in principle any other form for these functions may be assumed. The equations describing the linear superposition are:
\[ A_{ij} = \alpha_{ij} + \beta_{ij} \varphi_j + \gamma_{ij} \varphi_j^2 \]
\[ \alpha_{ij} \approx A_{i0} \]
\[ f_{ij} = A_{ij} - \alpha_{ij} = \beta_{ij} \varphi_j + \gamma_{ij} \varphi_j^2 \]
\[ A_i = A_{i0} + \sum_{j=1}^{n} f_{ij} \]

Here, \( A_{ij} \) is the abundance of M/Z ratio \( i \) due to concentration \( \varphi_j \) of chemical compound \( j \). \( A_{ij} \) is fitted as a non-linear function of the concentration of chemical compound \( j \).

With a quadratic form of this non-linear function, the parameters of the function are \( \alpha_{ij} \), \( \beta_{ij} \) and \( \gamma_{ij} \). These parameters are obtained by non-linear curve-fitting to the calibration curve of chemical compound \( j \). The task of non-linear curve-fitting is performed by HPMSONE.

Also, \( A_i \) is the total abundance of M/Z ratio \( i \) due to the contributions of the respective \( n \) chemical compounds. \( A_{i0} \) is the constant background of M/Z ratio \( i \), assumed to be approximately equal for both calibration and chemical analysis.

Each chemical compound \( j \) is represented by a quant ion \( i \), so that there are as many chemical compounds as quant ions. Thus, the above equations represent a quadratic system of non-linear equations, which can be solved by the Newton-Raphson method as outlined in [77]. Each of the above equations for \( A_i \) may be rewritten such that:

\[ f_i = A_i - A_{i0} - \sum_{j=1}^{n} f_{ij} = 0 \]

This function of vector \( \varphi = \varphi_1, ..., \varphi_i, ..., \varphi_n \) can be expanded into a Taylor series which terminates after the linear terms:

\[ f_i(\varphi + \Delta \varphi) \approx f_i(\varphi) + \sum_{j=1}^{n} \frac{\partial f_i}{\partial \varphi_j}(\varphi) \Delta \varphi_j \]

The partial derivatives of \( f_i \) with respect to \( \varphi_k \) are given by:

\[ \frac{\partial f_i}{\partial \varphi_k} = \frac{\partial}{\partial \varphi_k}(A_i - A_{i0} - \sum_{j=1}^{n} f_{ij}) = -\frac{\partial}{\partial \varphi_k}(\sum_{j=1}^{n} f_{ij}) \]
Where:

\[ f_{ik} = \beta_{ik}\varphi_k + \gamma_{ik}\varphi_k^3 \]
\[ \frac{\partial f_{ik}}{\partial \varphi_k} = \beta_{ik} + 2\gamma_{ik}\varphi_k \]

Now, by assuming that the \( f_i \) evaluated at \( \varphi + \Delta\varphi \) are closer to the desired value of zero than those evaluated at \( \varphi \), and thereby are in fact set to zero, the following system of linear equations in \( \Delta\varphi \) may be written:

\[
\begin{align*}
    f_i(\varphi + \Delta\varphi) & \approx 0 \\
    -f_i(\varphi) & \approx \sum_{j=1}^{n} -\frac{\partial f_{ij}(\varphi_j)}{\partial \varphi_j}(\varphi_j)\Delta\varphi_j
\end{align*}
\]

A simplification may be obtained by defining:

\[ b_i = -f_i(\varphi) \quad \text{and} \quad a_{ij} = -\frac{\partial f_{ij}}{\partial \varphi_j}(\varphi_j) \]

Thus, the system of linear equations in \( \Delta\varphi \) is given by:

\[ b_i \approx \sum_{j=1}^{n} a_{ij}\Delta\varphi_j \]

By iteratively solving this system using \( \varphi_j^{\text{new}} = \varphi_j^{\text{old}} + \Delta\varphi_j \) ever better approximations of \( \varphi_j \) are obtained. The iteration may be terminated when \( \frac{\Delta\varphi_j}{\varphi_j^{\text{old}}} \leq \epsilon \) for all chemical compounds \( j \).

Unfortunately, fairly good estimates for \( \varphi \) must be available to begin this iteration process. Fortunately, however, the matrices in \( \alpha_{ij}, \beta_{ij} \) and \( \gamma_{ij} \) describing above
quadratic system of non-linear equations are very close to diagonal in many cases of interest, that is \( \alpha_{ij} \approx 0, \beta_{ij} \approx 0 \) and \( \gamma_{ij} \approx 0 \) for \( i \neq j \). This fact may be exploited to obtain the required good estimates:

\[
    f_i \approx A_i - A_{i0} - f_{ii} \approx 0
\]

\[
    \varphi_i \approx -\frac{\beta_{ii}}{2\gamma_{ii}} \pm \sqrt{\left(\frac{\beta_{ii}}{2\gamma_{ii}}\right)^2 + \frac{A_i - A_{i0}}{\gamma_{ii}}}
\]

The task of obtaining these estimates and the task of solving the quadratic system of non-linear equations is performed by HPMSTWO and is referred to as non-linear deconvolution.

In order for this non-linear deconvolution to be successful, it is necessary to calibrate the MSD for all chemical compounds in the gaseous hazardous waste that contribute to a particular M/Z ratio. Therefore, before the MSD may be used as a SOR-MS, it is advisable to determine qualitatively these chemical compounds to the extent possible via other means, such as GC-MS. Naturally, this determination needs to be done only once, and may be viewed as preparatory work for setting up the MSD as a SOR-MS.

Failure to calibrate for any chemical compound contributing to a particular M/Z ratio will lead to an overestimation of the concentration of the particular chemical compound for which this M/Z ratio is the quant ion. This overestimation becomes more severe, the larger the contributions of the lacking chemical compounds to the particular M/Z ratio.

5.3.4 Potential and Limitations

5.3.4.1 Feasibility of Conversion

In order to evaluate and demonstrate the feasibility of the conversion of the MSD from a GC-MS detector to a SOR-MS detector, a number of experiments preliminary to the actual investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste were conducted. As a result of these experiments, the following potential and limitations are to be considered when using the MSD as a SOR-MS detector.

For this discussion, it is occasionally helpful to recall the definition of standard, standard carrier gas, carrier gas and standard gas introduced in the context of the
discussion of the gas mixing system in Section 3.1. In the following, reference will be made to the MSD as a SOR-MS detector. Therefore, the carrier gas of the gas mixing system may not be confounded with the gas chromatographic carrier gas.

5.3.4.2 Tuning

For GC-MS as well as for SOR-MS, the MSD has to undergo Instrument Tuning before it can be used. The instrument tuning involves the adjustment of several MSD parameters such that for certain M/Z ratios, these M/Z ratios are located accurately on the M/Z ratio axis of the mass spectrum, two adjacent M/Z ratios are resolved accurately on the M/Z ratio axis of the mass spectrum, and particular abundances are achieved.

Therefore, instrument tuning requires the presence of ions at these certain M/Z ratios in the MSD. In particular, these ions should have approximately equal abundance at the low, medium and high end of the M/Z ratio range to be scanned for the chemical analysis. Through experience, it was found that among other chemical compounds, Perfluorotributylamine ([C₄F₉]₃N, PFTBA) [84] fulfills these requirements [102].

The adjustment of MSD parameters requires experience and skills frequently not available to the average MS operator. Therefore, the HP-MS-ChemStation Software optionally provides for automatic instrument tuning via its instrument tuning task.

A very characteristic feature of automatic instrument tuning is the automatic increase of the EMV for compensation of the wear-out of the electron multiplying surface coating and the pollution of the ion source. Such compensation is necessary mainly in order to achieve the above-mentioned particular abundances for certain M/Z ratios which in turn is necessary to ensure the calibration stability of the MSD. Therefore, frequent calibration of the MSD for the chemical compounds is not required.

However, for the MSD used in the present work, the EMV is limited to 3000 V. Towards the end of the lifetime of the electron multiplier, the EMV cannot be increased any further. From this point on, the automatic instrument tuning does not compensate any longer for the wear-out of the electron multiplying surface coating and the pollution of the ion source.

Moreover, the particular abundances for certain M/Z ratios are no longer achieved and the calibration stability can no longer be ensured. Therefore, continued use of the MSD for chemical analysis becomes dependent on frequent calibration of the MSD for the chemical compounds. It is observed that for SOR-MS, the EMV limit of 3000 V is reached much faster than for GC-MS.
Also, for GC-MS, PFTBA is introduced when the dominant gas in the MSD is the gas chromatographic carrier gas, which to a major fraction is helium. However, for SOR-MS, PFTBA is introduced when the dominant gas in the MSD is the gaseous hazardous waste, which to a major fraction is air. It is observed that although automatic instrument tuning functions properly for helium, it fails to function properly for air.

Therefore, for the present work, automatic instrument tuning is performed to the extent possible, the MSD is calibrated for the chemical compounds and the chemical analysis of the intake or the exhaust of the reactor is performed for the chemical compounds within as short a time period as possible after calibration.

Through such procedure, the wear-out of the electron multiplying surface coating and the pollution of the ion source may not have a significant effect on the chemical analysis. However, again frequent calibration for the chemical compounds is required. This frequency typically translates to calibration on a daily to weekly basis.

5.3.4.3 Electron Multiplier Voltage

In the present work, the only modification made to the tuning parameters obtained through automatic tuning via the tuning task of the HP-MS-ChemStation Software is the reduction of the Electron Multiplier Voltage (EMV) to 1965 V. Again, the maximum available EMV for the MSD is 3000 V.

The higher the EMV, the faster the wear-out of the electron multiplying surface coating [102]. Thus, a decrease of the EMV from that obtained through automatic tuning is thought to significantly enhance the life-time of the electron multiplier. Also, the wear-out is observed to be rather slow for GC-MS but rather fast for SOR-MS. This is very likely a result of the difference between helium and air as the dominant gas in the MSD for GC-MS and SOR-MS, respectively.

Although the decrease of the EMV is effected at the expense of an increase in detection limit, it is more important to maintain the electron multiplying surface coating in as steady a condition as possible by ensuring slow wear-out.

Nevertheless, no good measure for adjusting the EMV exists. In the present work, the EMV is set to 1965 V simply as a reflection of the author’s year of birth.
5.3.4.4 Pressure

The abundance of the M/Z ratios for the chemical compounds exhibits a profound dependence on the MSD pressure. In air, such abundance is non-existent in the region below $10^{-5}$ torr. The abundance increases with increasing MSD pressure in the region between $10^{-5}$ torr and $7.5 \cdot 10^{-6}$ torr, displaying a very strong sensitivity to the MSD pressure. The abundance then saturates in the region above $7.5 \cdot 10^{-6}$ torr.

Moreover, in the region between $10^{-5}$ torr and $7.5 \cdot 10^{-5}$ torr the sensitivity of the abundance to the MSD pressure increases with increasing concentration of chemical compounds.

The safe shutdown pressure of the MSD is on the order of $2.0 \times 10^{-4}$ torr. Therefore it is most reasonable and preferable to operate the MSD in the saturation region of the abundance in order to avoid interference of MSD pressure perturbations with the abundance.

However, for much of the present work, the MSD pressure is nominally kept at $5.0 \cdot 10^{-5}$ torr for a safety factor of four towards the safe shutdown pressure. Unfortunately this means operation of the MSD in the region of relatively high sensitivity of the abundance to the MSD pressure.

In fact, the operation of the MSD in this region may explain some of the rather large spreading of the concentrations obtained for the chemical compounds on the basis of the corresponding abundances. This is supported by the fact that such spreading tends to be larger at higher concentrations, which in turn is commensurate with the increased sensitivity of the abundance to the MSD pressure at higher concentrations.

Finally, the MSD pressure is observed to vary as a function of the flow rate of the gaseous hazardous waste, from which the sample flow rate into the MSD is taken. However, such MSD pressure variation is rather weak. With respect to this MSD pressure variation, there are two different modes of operation of the MSD, only the first of which was implemented for the investigation of the decomposition of hazardous chemical compounds in gaseous hazardous waste.

First, for any particular gaseous hazardous waste and flow rate thereof, the metering valve opening may be adjusted so that the MSD pressure is maintained constant. Second, for any particular gaseous hazardous waste and flow rate thereof, the metering valve opening may be maintained constant so that the MSD pressure is allowed to vary.

For the present work, the following practice may be assumed with respect to these two different modes of operation of the MSD. When the MSD pressure is maintained constant, it is set to $5 \cdot 10^{-5}$ torr. When the metering valve opening is maintained
constant, the MSD pressure is initially set to $5 \cdot 10^{-5}$ torr at the maximum flow rate of the gaseous hazardous waste.

The effect of maintaining either the MSD pressure or the metering valve opening constant appears to be rather weak for air and $N_2$ as the carrier gas, but rather strong for $O_2$ as the carrier gas. Notwithstanding the particular position of $O_2$, the latter mode of operation of the MSD represents less perturbance of the MSD than the former. This mode of operation is thus preferable as long as the MSD pressure is in the saturation region, i.e. at approximately $7.5 \cdot 10^{-5}$ torr.

Finally, since a decrease in EMV voltage and an increase in MSD pressure represent an increase and a decrease in detection limit, respectively, a high MSD pressure, up to the saturation region of the abundance, may be combined with a low EMV while maintaining a reasonable detection limit. Thus, the life-time of the electron multiplying surface coating could be extended even further through this measure. However, a remote possibility exists for a decrease in this life-time with an increase in MSD pressure.

5.3.4.5 Relative Humidity

It is expected that $H_2O$ at a given relative humidity in the standard gas reacts with $HCl$ and $Cl_2$ and significantly decreases the abundance of the $M/Z$ ratios of these chemical compounds. However, in spite of the high chemical reactivity of $HCl$ and $Cl_2$, this is not the case. Also, the effect of relative humidity in the standard gas on the abundance of the $M/Z$ ratios of $CCl_4$, $CHCl_3$ and $C_2HCl_3$ appears to be as small as expected on the basis of their low chemical reactivity.

5.3.4.6 Passivation

For $HCl$ and $Cl_2$ as very reactive chemical compounds, clear evidence of passivation of the tubing wall of the gas mixing system can be observed. When the gas mixing system had not been in contact with $HCl$ or $Cl_2$ for a period of days and standard gas containing $HCl$ or $Cl_2$ at a particular concentration is generated, the abundance for the corresponding $M/Z$ ratios remains at background level for several minutes.

Eventually, a slow and steady increase of the abundance to a steady state level is observed, which again takes several minutes to reach. After this passivation, any changes of the $HCl$ or $Cl_2$ concentration in the standard gas result in almost instantaneous changes in the abundance at apparent steady state levels.

The remote possibility exists that what is perceived by the author as a steady state
level of the abundance for the corresponding M/Z ratios is in fact a very slow non-steady state or quasi-steady state passivation, so that any changes in the abundance will occur over an extended period of time and thus go unnoticed by the author. Such times are typically on the order of hours.

5.3.4.7 Selected Ion Monitoring vs. Full Scan Monitoring

In contrast to Full Scan Monitoring (FSM), where the M/Z ratios are scanned in increments of unity from their lowest to their highest values, in Selected Ion Monitoring (SIM) the M/Z ratios are scanned only to selected quant ions. Therefore, for a given Scan Time, the Dwell Time for each M/Z ratio may be longer for SIM than for FSM.

The dwell time determines for how long during any scan the mass filter allows for the passage of ions of a particular M/Z ratio. Also, the probability for the extraction of such an ion from the ion source and the passage of this ion through the mass filter and the subsequent impact of this ion on the electron multiplying surface coating increases with increasing dwell time. Therefore, the detection limits for SIM are typically lower than for FSM by a factor on the order of ten.

In the present work, the SIM dwell time for any M/Z ratio is set to 10 ms. Even when monitoring as many as 20 ions, the SIM scan time is less than \( \frac{1}{5} \) of a second. This allows sufficient time resolution for many real-time chemical analysis problems. Note that the modification to the MSD data analysis software is designed to work for both SIM and FSM.

5.3.4.8 Accuracy, Precision, Reproducibility and Detection Limit

A statement about the accuracy of both GC-MS detection and GC-SOR detection is difficult to make, because the concentration measurement is performed on the basis of a relative and not an absolute calibration. In particular, it may be assumed that GC-MS detection and SOR-MS detection are as accurate as the concentrations of the standards in their respective standard carrier gases used for calibration.

A comparison of the concentration measurement via GC-TCD and GC-ECD to that via SOR-MS can only provide a relative measure of accuracy under the assumption that GC-TCD and GC-ECD are accurate owing to their well established use. However, such a comparison is not performed.

A general inspection of concentration measurements for chemical compounds reveals an estimated typical precision of approximately 90%. This precision can potentially be increased when concentration measurements are made in the MSD pressure satu-
ration region for the abundance.

The reproducibility at the high EMV used for SOR-MS detection is severely impacted by the wear-out of the electron multiplier surface coating and the pollution of the ion source. However, at the low EMV used for GC-MS, a general inspection of concentration measurements for chemical compounds reveals an estimated typical reproducibility of approximately 90%.

Moreover, for the present work, SIM is required to achieve a detection limit of typically 1 ppm for any chemical compound.

5.3.4.9 Deconvolution

Three types of Ion Interference in the deconvolution of a mass spectrum may be distinguished. The first relates standards to their standard carrier gases or the carrier gas. The second relates a standard with a very high concentration to a standard with a very low concentration. The third relates standards with approximately equal concentrations.

For the first type, standards producing M/Z ratios equal to those produced by the standard carrier gases or the carrier gas cannot be detected since the concentration of the standard in the standard gas is too low as that their abundances could represent little more than perturbations to the abundances of the standard gas. An example for this type is the interference of Carbon Monoxide (CO, M/Z=28) and Carbon Dioxide (CO₂, M/Z = 28, 44) with Nitrogen (N₂, M/Z=28) or with CO₂ (M/Z=28, 44) contained in the carrier gas.

For the second type, standards with very low concentrations producing M/Z ratios equal to those produced by standards with very high concentrations cannot be detected for similar reasons as given for the first type. An example for this type is the interference of Hydroxyl (OH, M/Z=17) and Water (H₂O, M/Z=17, 18).

For the third type, standards producing M/Z ratios equal to those produced by a multitude of other standards cannot be detected since the number of calibrations required for deconvolution becomes too large. This is particularly true for reactive standards. An example for this type is the interference of Nitric Oxide (NO, M/Z=30), Nitrogen Dioxide (NO₂, M/Z = 30, 46) and Nitrous Oxide (N₂O, M/Z=30, 44).
5.3.5 Feasibility of GC-MS to SOR-MS Conversion of MSD

With sufficient care and awareness of the outlined potential and limitations, it appears to be possible to convert the MSD from a GC-MS detector to a SOR-MS detector.

Although floor-space mass spectrometers with full mass spectral deconvolution via spectral mathematics may well be able to serve as SOR-MS detectors, the capital expense for these mass spectrometers is prohibitive for small laboratories and for process control applications.

The conversion of a MSD from a GC-MS detector to a SOR-MS detector is therefore attractive, and particularly so where the capabilities of the MSD of an existing GC-MS system need to be enhanced, or gas chromatographic separation of chemical compounds cannot be accomplished.

In particular, it appears to be possible to perform the chemical analysis of the rather reactive chemical compounds HCl, Cl₂ by SOR-MS detection. Thus SOR-MS detection could be an attractive dry chemical analysis alternative to the more common wet chemical analysis of reactive chemical compounds.
Chapter 6

Electron Beam Dosimetry

6.1 Introduction to Electron Beam Dosimetry

The Electron Beam Dosimetry developed for determination of the electron beam power deposition in gaseous hazardous waste and therefore the energy per amount of hazardous chemical compound decomposed or the energy expense is described in the following. The description includes the Facsimile Paper Radiography, the Aluminum Plate Calorimetry, the Monte-Carlo Simulation of the electron beam power deposition and the \( \text{N}_2\text{O} \) Chemical Dosimetry, i.e. the decomposition of Nitrous Oxide (\( \text{N}_2\text{O} \)) into \( \text{N}_2 \) and \( \text{O}_2 \).

The electron beam uniformity over the electron beam cross section area, the electron beam spreading inside the electron beam gun vacuum chamber, the electron beam power transmission through the electron beam window and the electron beam power deposition in the gas are of prime importance to the performance characterization of the electron beam and therefore the Tunable Plasma Reactor.

The electron beam uniformity over the electron beam cross section area and the electron beam spreading inside the electron beam gun vacuum chamber are measured by means of Radiography, i.e. the interception of the electron beam by a piece of facsimile paper and the associated colorization of this piece of facsimile paper.

The electron beam power transmission through the electron beam window and the electron beam power deposition in the gas are calculated by a one-dimensional Monte-Carlo Simulation of the electron beam energy deposition.

The electron beam power transmission through the electron beam window is also measured by means of Calorimetry, i.e. the interception of the electron beam by an aluminum plate and the associated increase in temperature of this aluminum plate.
The electron beam power deposition in the gas is also measured by means of Chemical Dosimetry, i.e. the decomposition of Nitrous Oxide (N\textsubscript{2}O) into N\textsubscript{2} and O\textsubscript{2} and the associated energies for the production of a N\textsubscript{2} or O\textsubscript{2} molecule from the destruction of a N\textsubscript{2}O molecule.

The measurement of the increase in temperature of the gas flowing through the reaction chamber is found to be inappropriate for determination of the electron beam power deposition in the gas. This is attributed to the non-adiabatic design of the reaction chamber and the inability to account properly for related non-adiabatic effects.

Since the electron beam cross section area and the depth along the direction of the electron beam is approximately identical for the old reaction chamber and the new reaction chamber, the electron beam power deposition is expected to be comparable for these reaction chambers.

6.2 Facsimile Paper Radiography

6.2.1 Principle of Operation

Upon electron beam irradiation, facsimile paper colorizes in different shades from white to black to brown to gray. The colorization depends on the electron beam energy, the electron beam current and the duration of irradiation. The utilization of this effect to measure the electron beam energy, the electron beam current or the duration of irradiation may be referred to as radiography.

Nevertheless, for the present work, it is not possible to obtain a calibration of the different shades of the facsimile paper as a function of the electron beam energy, the electron beam current or the duration of irradiation. Moreover, these functions appear to be strongly non-linear.

Also, the product of electron beam current and duration of irradiation may not exceed a particular value in order to prevent incineration of the facsimile paper. In particular, for the electron beam currents typically used in the present work, the duration of irradiation has to be on the order of tenths of seconds.

Since the electric circuitry of the electron beam gun has a finite characteristic time, the times required to turn on and to turn off the electron beam at a pre-selected electron beam energy and electron beam current are on the order of tenths of seconds as well. Therefore, for the duration of irradiation of the facsimile paper, the electron beam energy and electron beam current may not be considered constant.
and sometimes do not even reach their pre-selected values.

However, in view of lack of a calibration for the colorization of the facsimile paper, this deficiency is considered not important, particularly since mainly qualitative statements are sought.

6.2.2 Electron Beam Uniformity Over Electron Beam Cross Section Area

In order to obtain an estimate of the electron beam uniformity over the electron beam cross section area, radiographic measurements are performed.

The standard water-cooled copper support grid and the standard aluminum foil are used for these measurements. The facsimile paper is taped to the atmospheric pressure side of the foil, with the heat sensitive side of the facsimile paper facing the foil. The electron beam is then turned on and off within several tenths of seconds.

It is determined that colorization of the facsimile paper occurs over the entire electron beam area on the atmospheric pressure side of the foil. However, while the edges of this area show black colorization, the center of this area shows brown to gray colorization, indicating the existence of a Hot Spot in the center of the electron beam. An example for such a measurement of the electron beam uniformity, or lack thereof, over the electron beam cross section area is shown in Figure 6.1.

![Figure 6.1: Electron Beam Uniformity Over Electron Beam Cross Section Area, $E_0 \approx 110$ keV, $I_0 \approx 1.0$ mA, $t \approx 100$ ms](image)

Although, no quantitative statements can be made about electron beam uniformity over the electron beam cross section area, the most important qualitative statement
is that the electron beam is non-uniform over this area.

Moreover, in view of the hot spot in the center of the electron beam, and under assumption of uniformity of the electron beam energy over the electron beam cross section area, the distribution of the electron beam current over the electron beam cross section area may to first approximation be represented by a Gaussian curve.

6.2.3 Electron Beam Spreading Inside Electron Beam Gun Vacuum Chamber

In order to obtain an estimate of the electron beam spreading inside the electron beam gun vacuum chamber, radiographic measurements are performed as well.

A custom non-cooled aluminum support grid and the standard aluminum foil are used for these measurements. The facsimile paper is taped to the atmospheric pressure side of the foil, with the heat sensitive side of the facsimile paper facing the foil. The electron beam is then turned on and off within several tenths of seconds.

The custom support grid features an array of holes, while the standard support grid features an array of slots. Also, the array of holes in the custom support grid extends over an area of approximately 4 inch$^2$, while the array of slots in the standard support grid extends over an area of approximately 1 inch$^2$.

The grid opening of the control grid of the electron beam gun extends over an area of 1 inch$^2$. Therefore, an increase in the electron beam cross section area between the control grid and the foil from 1 inch$^2$ up to 4 inch$^2$ may be measured by measuring the colorized area of the facsimile paper.

It is determined that the colorization of the facsimile paper occurs over an area approximately twice as large as that of the grid opening. This indicates a significant increase in the electron beam cross section area, referred to as electron beam spreading. This electron beam spreading may be assumed to be approximately independent of the electron beam current. An example for such a measurement of the electron beam spreading inside the electron beam gun vacuum chamber is shown in Figure 6.2.

Under assumption of approximate uniformity of the electron beam energy over the electron beam cross section area and under consideration of the electron beam spreading, an equation for the electron beam current transmission through the electron beam window may readily be obtained:

$$ I_0 = j_0 A_0 $$
The relations among these various areas and electron beam currents for analysis of the electron beam spreading inside the electron beam gun vacuum chamber are shown in Figure 6.3.

The electron beam current and the electron beam current density are connected via:

\[ \begin{align*}
I^* &= j^* A^* \\
I &= j A
\end{align*} \]

Therefore:

\[ \begin{align*}
I^* &= I_0 \\
j &= j^*
\end{align*} \]

Moreover:

\[ \begin{align*}
j^* &= \frac{A_0}{A^*} j_0 \\
I &= \frac{A}{A^*} I^*
\end{align*} \]

Figure 6.2: Electron Beam Spreading Inside Electron Beam Gun Vacuum Chamber, \( E_0 \approx 110 \text{ keV}, I_0 \approx 1.0 \text{ mA}, t \approx 100 \text{ ms} \)
Figure 6.3: Relations Among Areas and Electron Beam Currents for Analysis of Electron Beam Spreading Inside Electron Beam Gun Vacuum Chamber
\[
\tau_0 = \frac{A}{A_0} \\
\tau^* = \frac{A_0}{A^*} \\
\tau = \tau^* \tau_0
\]

Therefore:

\[
I = \frac{A}{A^*} I_0 \\
I = \frac{A_0}{A^*} \frac{A}{A_0} I_0 \\
I = \tau^* \tau_0 I_0
\]

Here, subscript \( \tau_0 \) refers to quantities at the grid opening, superscript \( \tau^* \) refers to quantities at the electron beam window on the vacuum side and no sub- or superscript refers to quantities at the electron beam window on the atmospheric pressure side. Also, \( A \) is the electron beam cross section area, \( \tau \) is the transmission, \( I \) is the electron beam current and \( j \) is the electron beam current density.

A transmission \( \tau^* \approx 0.5 \) is determined on the basis of the electron beam spreading. A transmission \( \tau_0 = 0.73 \) is determined in Section 4.4.2.2 on the basis of the support grid transmission to the electron beam.

In view of the lack of uniformity of the electron beam current over the electron beam cross section area, an estimate of the decrease in electron beam current density should not simply be based on the above electron beam cross section area ratio \( \tau^* \). However, in lack of a calibration for the colorization of the facsimile paper, such an estimate is assumed nevertheless as the best one available.

### 6.3 Aluminum Plate Calorimetry

#### 6.3.1 Principle of Operation

In order to obtain an estimate for the electron beam power transmission through the electron beam window, calorimetric measurements are performed.
An aluminum plate of equal or larger area than the electron beam or electron beam window cross section area is used to intercept the electron beam on the atmospheric pressure side of the electron beam window.

The aluminum plate is suspended in parallel and as close as possible to the foil. Therefore, the electron beam power loss in the thin layer of air between the foil and the aluminum plate is minimized.

The electron beam is operated for several seconds at a pre-selected electron beam energy and electron beam current. The time required to turn on and to turn off the electron beam is on the order of tenths of seconds, since the electric circuitry of the electron beam gun has a finite characteristic time.

Therefore, perfect step functions in terms of turning on and turning off the electron beam may not be obtained. However, the time of operation of the electron beam is much longer than the time of turning on and turning off the electron beam. Therefore, the latter time may be neglected when compared to the former time.

The increase in the aluminum plate temperature due to the interception of the electron beam power is measured. From the known mass of the aluminum plate and the known mass specific heat capacity of aluminum, the increase in the aluminum plate temperature can be converted to the electron beam energy deposition in the aluminum plate.

In combination with the time of operation of the electron beam, this energy yields an estimate for the electron beam power deposition in the aluminum plate. This power may be assumed approximately equal to the electron beam power transmission through the electron beam window.

### 6.3.2 Theory of Operation

The theory of the calorimetric measurement of the electron beam power transmission through the electron beam window may be based on a model where the only power gain of the aluminum plate is from the electron beam and the only power loss of the aluminum plate is from thermal convection to the surrounding air. The partial differential equation describing this problem is:

\[
\rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot q'' + q'''
\]

\[
q'' = -\lambda \nabla T
\]
Here, $\rho$, $c_p$ and $\lambda$ are the mass density, the mass specific heat capacity and the thermal conductivity of aluminum. Also, $q''$ is the heat flux density in the aluminum plate and $q'''$ is the volumetric heat generation rate in the aluminum plate. Under conditions where $\nabla \cdot q'' < q'''$, the partial differential equation reduces to an ordinary differential equation:

$$\rho c_p \frac{dT}{dt} = q''$$

where:

$$q''' = \frac{P}{V} - \frac{2\alpha A(T - T_{Air})}{V}$$

Here, $V$ is the volume and $A$ is the area of one side of the aluminum plate, $T_{Air}$ is the temperature of the surrounding air, $\alpha$ is the heat convection coefficient to the surrounding air and $P$ is the intercepted electron beam power. With $m = \rho V$ the mass of the aluminum plate, the ordinary differential equation becomes:

$$\frac{dT}{dt} = \frac{P}{mc_p} - \frac{2\alpha A}{mc_p} (T - T_{Air})$$

A simplification may be obtained by defining:

$$A = wh$$

$$m = \rho Ad$$

$$\frac{A}{m} = \frac{1}{\rho d}$$

$$\tau = \frac{mc_p}{2\alpha A} = \frac{\rho c_p d}{2\alpha}$$

Here, $w$ is the width, $h$ is the height and $d$ is the thickness of the aluminum plate, and $\tau$ is the characteristic time of the increase in temperature of the aluminum plate. Then the solution to the ordinary differential equation under the boundary condition $T|_{t=0} = T_0$ as derived in Appendix A.3 becomes:

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\[ T = T_{\text{Air}} + \frac{P}{2\alpha A} \left[ 1 - e^{-\frac{t}{\tau}} \right] + (T_0 - T_{\text{Air}}) e^{-\frac{t}{\tau}} \]

Under conditions where thermal convection is negligible, \( t \ll \tau \), i.e. \( e^{-\frac{t}{\tau}} \approx 1 - \frac{t}{\tau} \). Also, under such conditions \( T_0 \approx T_{\text{Air}} \). Therefore, the solution may be approximated via:

\[ T \approx T_0 + \frac{P}{2\alpha A} \frac{t}{\tau} \]

\[ T \approx T_0 + \frac{P}{mc_p} t \]

This is the desired linear relation between the increase in the aluminum plate temperature \( T - T_0 \), the intercepted electron beam power \( P \), i.e. approximately the electron beam power transmission through the electron beam window, and the time of operation of the electron beam \( t \).

The characteristic time \( \tau \) of the increase in aluminum plate temperature may be estimated readily from \( w = 1 \frac{9}{16} \text{ inch} \), \( h = w \), \( d = \frac{1}{16} \text{ inch} \), \( \rho = \rho_{Al} = 2700 \text{ kg/m}^3 \), \( c_p = c_p\text{Al} = 900 \text{ J/kg K} \) and \( \alpha = 10 \text{ W/m}^2 \text{ K} \). Therefore, the characteristic time becomes \( \tau = 128.6 \text{ sec} \).

The approximation \( e^{-\frac{t}{\tau}} \approx 1 - \frac{t}{\tau} \) is good for approximately \( \frac{t}{\tau} \leq \frac{1}{10} \). Therefore, for times \( t \geq 12.86 \text{ sec} \), the linear relation between the increase in the aluminum plate temperature \( T - T_0 \), the intercepted electron beam power \( P \) and the time of operation of the electron beam \( t \) no longer holds.

### 6.3.3 Technical Considerations

The electron beam is intercepted by the front of the aluminum plate, the K-Type\(^1\) thermocouple used to measure the aluminum plate temperature is attached to the center of the back of the aluminum plate. The thickness of the aluminum plate has to be small enough so as to provide for instantaneous thermal equilibration from the front to the back of the aluminum plate. However, the thickness of the aluminum plate also has to be large enough to intercept the entire electron beam energy.

Further thermal equilibration is provided for by measuring the aluminum plate temperature only a short time after operation of the electron beam. The temperature

\(^1\)Chromel-Alumel, i.e. Chromium-Nickel and Aluminum-Nickel
is in fact measured right before it begins to decrease. It is assumed that thermal equilibration has progressed to the greatest extent at that time, i.e. that the aluminum plate temperature is as uniform as it would be.

Geometry constraints mandate that the aluminum plate be mounted from $\frac{1}{8}$ inch to $\frac{1}{4}$ inch away from the foil. Owing to the electron beam power loss in this thin layer of air, the measured electron beam power transmission is lower than the actual electron beam power transmission through the electron beam window. As will be shown shortly, the electron beam power loss in the thin layer of air is negligible.

It is important to ensure adiabatic conditions for the aluminum plate. Therefore, it is suspended on thin Nylon wire, so that the only path for thermal conduction is the K-Type thermocouple itself. Also, at all times, the aluminum plate temperature is well below the point where thermal radiation becomes important.

Finally, as has been shown already, thermal convection to the surrounding air is negligible for reasonably short times of operation of the electron beam. Therefore, virtually adiabatic conditions prevail, and the increase in aluminum plate temperature is expected to be linear in the intercepted electron beam power and the time of operation of the electron beam.

The mounting holes for the Nylon wire and any deviations from a perfectly rectangular shape of the aluminum plate are assumed to be negligible.

Finally, since the aluminum plate is otherwise electrically insulated via the Nylon wire, but the electron beam deposits charge on the aluminum plate, a thin wire cut out of foil is attached to the plate and connected to electric ground to prevent charge build up.

In between measurements, the aluminum plate is cooled from its final temperature to its initial temperature with air from a compressed air cylinder. This ensures approximately equal initial conditions for each measurement.

### 6.3.4 One-Dimensional Monte-Carlo Simulation of Electron Beam Power Transmission Through Electron Beam Window

For an aluminum foil of thickness $\frac{1}{100}$ inch, a thin layer of air$^2$ of thickness $\frac{1}{4}$ inch or $\frac{1}{4}$ inch and an aluminum plate of thickness $\frac{1}{16}$ inch, a one-dimensional Monte-Carlo Simulation of the electron beam energy loss is performed.

$^{2}$21% O$_2$, 79% N$_2$, $p = 1.01325 \cdot 10^5$ Pa, $T = 298.15$ K, $M = 28.85$ g/mol
The electron beam energy loss in the thin layer of air is approximately 4 keV or 8 keV and the electron beam energy loss in the aluminum plate is approximately 47 keV or 43 keV.

In comparison, the electron beam energy loss in a thin layer of air of thickness \( \frac{1}{1000} \) inch is 0 keV and the electron beam energy loss in the aluminum plate for such thin layer of air is approximately 50 keV.

Therefore, a support grid transmission to the electron beam of \( \tau_0 = 0.73 \), an electron beam spreading of \( \tau^* \approx 0.5 \), an average electron beam energy loss in the aluminum plate of \( \Delta E = 45 \) keV and electron beam currents of \( I_0 = 0.5 \) mA and \( I_0 = 1 \) mA result in an electron beam power deposition in the aluminum plate of \( P = 8.2 \) W and \( P = 16.4 \) W, respectively.

The theory of one-dimensional Monte-Carlo Simulation of electron transport in gas, liquid or solid material is described in Section 6.5.

### 6.3.5 Electron Beam Power Transmission Through Electron Beam Window

For several electron beam currents \( I_0 \), measurements of the increase in aluminum plate temperature \( T - T_0 \) are performed. Also, for each electron beam current, the increase in aluminum temperature is measured for two different times of operation of the electron beam \( t \).

Therefore, the linear relation between the increase in the aluminum plate temperature \( T - T_0 \), the intercepted electron beam power \( P \) and the time of operation of the electron beam \( t \) may be checked. The results of the measurements are shown in Table 6.1.

It can be seen that for electron beam currents of 0.5 mA and 1 mA, the electron beam power deposition is approximately independent of the time of operation of the electron beam. Also, the electron beam power is approximately linear in electron beam current.

For these electron beam currents, the electron beam power deposition in the aluminum plate obtained by measurement of the increase in aluminum plate temperature agrees quite well with the electron beam power deposition in the aluminum plate obtained by one-dimensional Monte-Carlo Simulation of the electron beam energy loss.

However, for electron beam currents of 2 mA and presumably higher, such agreement is not found, i.e. the measured electron beam power deposition in the aluminum plate...
Table 6.1: Results of Aluminum Plate Calorimetry

<table>
<thead>
<tr>
<th>$I_0$</th>
<th>$T_0$</th>
<th>$T$</th>
<th>$T - T_0$</th>
<th>$t$</th>
<th>$\frac{T - T_0}{t}$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA</td>
<td>°C</td>
<td>°C</td>
<td>K</td>
<td>s</td>
<td>K/s</td>
<td>W</td>
</tr>
<tr>
<td>0.5</td>
<td>19.6</td>
<td>26.4</td>
<td>6.7</td>
<td>5.8</td>
<td>1.2</td>
<td>7.1</td>
</tr>
<tr>
<td>0.5</td>
<td>19.6</td>
<td>33.0</td>
<td>13.4</td>
<td>10.9</td>
<td>1.2</td>
<td>7.5</td>
</tr>
<tr>
<td>0.5</td>
<td>17.1</td>
<td>28.6</td>
<td>11.5</td>
<td>10.6</td>
<td>1.1</td>
<td>6.6</td>
</tr>
<tr>
<td>0.5</td>
<td>16.9</td>
<td>23.5</td>
<td>6.6</td>
<td>5.5</td>
<td>1.2</td>
<td>7.2</td>
</tr>
<tr>
<td>1.0</td>
<td>23.2</td>
<td>50.7</td>
<td>27.4</td>
<td>10.5</td>
<td>2.6</td>
<td>15.9</td>
</tr>
<tr>
<td>1.0</td>
<td>23.1</td>
<td>38.4</td>
<td>15.3</td>
<td>7.6</td>
<td>2.8</td>
<td>16.8</td>
</tr>
<tr>
<td>2.0</td>
<td>22.6</td>
<td>77.2</td>
<td>54.6</td>
<td>12.4</td>
<td>4.4</td>
<td>26.7</td>
</tr>
<tr>
<td>2.0</td>
<td>23.0</td>
<td>46.2</td>
<td>23.3</td>
<td>6.0</td>
<td>3.9</td>
<td>23.6</td>
</tr>
</tbody>
</table>

appears to be lower than that predicted on the basis of the one-dimensional Monte-Carlo Simulation of the electron beam energy loss. This may be explained by a different heat convection coefficient than the $\alpha = 10 \text{ W/m}^2\text{K}$ assumed earlier.

This is likely since the electron beam energy deposition in the thin layer of air will lead to an increase in the air temperature at higher electron beam currents. The natural convection in the thin layer of air is thus increased as well, which results in an increase for $\alpha$ and thus a decrease for $\tau$ and an earlier deviation from linearity.

### 6.4 Definition of Electron Beam Dose

The measurement or calculation of the electron beam power and energy deposition in the gas is referred to as electron beam dosimetry. The electron beam power deposition in the gas may be expressed as the electron beam power $\dot{Q}$ in dimensions of $\text{W}$ or the electron beam dose rate $D$ in dimensions of $\text{rad/s}$ or $\text{J/kg\,s}$. The electron beam energy deposition in the gas may be expressed as the electron beam energy $Q$ in dimensions of $\text{J}$ or the electron beam dose $D$ in dimensions of $\text{rad}$ or $\text{J/kg}$.

In the context of the gas mixing system, the standard gas is generated by mixing a carrier gas with several standard carrier gases. A standard carrier gas contains a standard at a certified concentration. Since these concentrations are rather high, the flow rates of the standard carrier gases required to generate a particular concentration of a standard in the standard gas are rather low.

Therefore, the standard gas in many respects virtually retains the properties of the carrier gas. In particular, the electron beam power deposition in the standard gas and the carrier gas are expected to be identical. Therefore, the electron beam dosimetry is performed for carrier gas only.
Under the assumption of ideal gas conditions, an equation for the residence time of the gas in the electron beam irradiation volume may be derived. Note that the electron beam irradiation volume is generally smaller than the reaction chamber volume:

\[
\begin{align*}
  pV &= m \frac{R_m}{M} T \\
  \rho &= \frac{m}{V} = \frac{pM}{R_m T} \\
  \rho_0 &= \frac{\dot{m}_0}{V_0} = \frac{p_0 M_0}{R_m T_0} \\
  \overline{\rho} &= \frac{\bar{m}}{\bar{V}} = \frac{\bar{p} M}{R_m \bar{T}} \\
  \tau &= \frac{\bar{m}}{\dot{m}_0} = \frac{\overline{\rho} \bar{V}}{\rho_0 V_0} = \frac{\bar{p} M}{p_0 M_0} \frac{T_0 \bar{V}}{V_0}
\end{align*}
\]

Here, \( \dot{m}_0 \) and \( V_0 \) are the mass and volume flow rate of the gas in the reaction chamber intake. Also, \( p_0, T_0 \) and \( M_0 \) are the pressure, temperature and mole mass of the gas in the reaction chamber intake. Under the assumption of standard conditions in the reaction chamber intake, \( p_0 = 1.01325 \cdot 10^5 \) Pa and \( T_0 = 298.15 \) K.

Moreover, \( \bar{m} \) and \( \bar{V} \) are the average mass and volume of the gas in the electron beam irradiation volume. Also, \( \overline{\rho}, \bar{T} \) and \( \bar{M} \) are the average pressure, temperature and mole mass of the gas in the electron beam irradiation volume. The calculation of these average quantities is rather complex. However, the details of this calculation are irrelevant at this point.

Finally, \( \tau \) is the residence time of the gas in the electron beam irradiation volume. Notwithstanding the problem of estimating \( \bar{T} \), typically \( p_0 \approx \overline{\rho} \) and \( M_0 \approx \bar{M} \), so that an approximation to the residence time results as:

\[
\tau = \frac{T_0 \bar{V}}{\bar{T} V_0}
\]

Under incorporation of the thus defined residence time, simple equations for the interconversion of electron beam power deposition and electron beam energy deposition in their respective dimensions may be derived:
\[ Q = Q_t \quad \text{or} \quad D = D_t \]
\[ D = \frac{Q}{m} \quad \text{or} \quad D = \frac{Q}{m_0} \]
\[ \dot{D} = \frac{\dot{Q}}{m} \quad \text{or} \quad \dot{D} = \frac{Q}{m_0 \tau^2} \]

Here, \( Q \) and \( Q_t \) are the electron beam power and energy to the gas, expressed in dimensions of \( W \) and \( J \), respectively. Also, \( D \) and \( D_t \) are the electron beam dose rate and dose to the gas, expressed in dimensions of \( \text{rad/s} \) or \( J/\text{kg s} \) and \( \text{rad} \) or \( J/\text{kg} \), respectively.

6.5 One-Dimensional Monte-Carlo Dosimetry

6.5.1 Principle of Monte-Carlo Dosimetry

The TIGER code of the Integrated Tiger Series (ITS) Monte-Carlo code package from Sandia National Laboratory, Albuquerque, New Mexico for simulation of electron transport in gas, liquid and solid material is used to perform simulations of the electron beam energy loss in the various components of the reactor [130].

The electron transport in gas, liquid or solid material comprises elastic and inelastic collisions of electron beam electrons with atoms and molecules. The collisions result in energy loss and deflection of those electrons. The combination of energy loss and deflection determines the electron beam energy loss in the various components of the reactor.

In general, Monte-Carlo Simulation of particle transport in gas, liquid or solid material involves tracking one by one a large number of particles in this material on the basis of probability distributions for the energy loss and the deflection. A tracked particle is referred to as a History. The statistical uncertainty of the simulation of particle transport decreases with increasing number of histories, even though such decrease is typically asymptotic.

Two methods of Monte-Carlo Simulation of particle transport in gas, liquid or solid material may be distinguished. The first may be referred to as the Detailed History method and derives its probability distributions from single-scattering theory. The second may be referred to as the Condensed History method and derives its probability distributions from multiple-scattering theory [131].
The difference in these two methods becomes apparent when comparing the Monte-Carlo Simulation of light particle transport, such as for electrons, to that of heavy particle transport, such as for neutrons. In particular, for elastic collisions the energy loss is a function of the ratio of the particle mass to the atom or molecule mass and the deflection is a function of the particle energy.

In general, light particles experience less energy loss and more deflection than heavy particles. Therefore, in order for light particles to lose the same energy as heavy particles, a larger number of collisions and thus a larger number of histories is required. This larger number of histories can be reduced, if probability distributions are not applied to single collisions as in single-scattering theory, but to multiple collisions as in multiple-scattering theory [131].

In order to limit the number of histories, the ITS Monte-Carlo code package employs the condensed history method of Monte-Carlo Simulation of electron transport in gas, liquid or solid material [130].

A further reaching introduction to Monte-Carlo Simulation of electron transport in gas, liquid or solid material is beyond the scope of the present work, but can be found in [130] and [131].

### 6.5.2 Principle of TIGER Code

Besides the one-dimensional TIGER code, the two-dimensional CYLTRAN code and the three-dimensional ACCEPT code are available as part of the ITS Monte-Carlo code package. The probability distributions for the energy loss and the deflection are identical in all three codes, but the accounting for the electron transport is different in that one-dimensional, two-dimensional and three-dimensional geometries, respectively, are used.

However, the one-dimensional code offers advantages over the two-dimensional and three-dimensional codes with respect to greater simplicity of input and output and shorter CPU time required. Simpler input is less error prone and easier to generate, simpler output is easier to process and display. Shorter CPU time allows for a larger number of cases with large numbers of histories to be simulated more efficiently. These advantages make it acceptable to sacrifice the depth of information obtainable with the two-dimensional and three-dimensional codes to the breadth of information obtainable with the one-dimensional code.

For the one-dimensional TIGER code, a three-dimensional geometry is modeled as a one-dimensional geometry of several parallel layers of different materials. Each layer

---

3 The name TIGER for the one-dimensional Monte-Carlo Simulation code derives from several
is further divided into several parallel sublayers in order to provide a one-dimensional resolution of the electron beam energy deposition in each layer.

A rectangular coordinate system may be chosen such that the x-axis and the y-axis are parallel to the layers and the z-axis is perpendicular to the layers. The electron beam is modeled by a plane perpendicular to the z-axis, which uniformly emits monoenergetic electrons at the desired electron beam energy and the desired direction with respect to the z-axis.

For each sublayer, the one-dimensional TIGER code calculates the electron beam energy loss of electron beam electrons, of electrons produced by ionization through electron beam electrons and of electrons produced by ionization through photons generated by electron beam electrons. Moreover, for each layer, reflectivities and transmissivities are calculated for both electron beam energy and electron beam current.

Electrons with energies below 1 keV are not tracked by the ITS Monte-Carlo code package and on-the-spot loss of this energy is assumed.

On the basis of the low electron beam energies and the low Z materials, it is found that the electron beam energy loss of electrons produced by ionization through electron beam electrons and of electrons produced by ionization through photons generated by electron beam electrons is negligible compared to the electron beam energy loss of electron beam electrons.

6.5.3 Electron Beam Energy Loss of TIGER Code

For the one-dimensional TIGER code, each layer $j = 1, \ldots, n$ is divided into $i_j = 1, \ldots, n_j$ sublayers. The code calculates for each sublayer $i_j$ the lower and upper dimension along the z-axis in cm$^2$/g and the stopping power along the z-axis in MeV cm$^2$/g. In order to obtain useful information, for each sublayer the lower and upper dimension need to be converted into cm and the stopping power needs to be converted into MeV, then representing the electron beam energy loss:

\[
egin{align*}
  z^l(i_j) &= z^u(n_{j-1}) + \frac{\zeta^l(i_j) - \zeta^u(n_{j-1})}{\rho(i_j)} \\
  z^u(i_j) &= z^u(n_{j-1}) + \frac{\zeta^u(i_j) - \zeta^u(n_{j-1})}{\rho(i_j)}
\end{align*}
\]

parallel layers of different materials resembling the stripes of a tiger.
\[ \Delta E(i_j) = \frac{1}{\rho} \frac{dE}{dz}(i_j) \left[ z^u(i_j) - z^l(i_j) \right] \rho(i_j) \]

Here, \( z^l(i_j) \) and \( z^u(i_j) \) are the lower and upper dimension of a sublayer in \( \text{cm}^2/\text{g} \), \( \rho(i_j) \) is the mass density of a sublayer, \( \frac{dE}{dz}(i_j) \) is the stopping power of a sublayer in MeV \( \text{cm}^2/\text{g} \) and \( \Delta E(i_j) \) is the electron beam energy loss in a sublayer in MeV.

The electron beam energy loss \( \Delta E(j) \) in layer \( j \) of \( n \) layers may be calculated as the sum of the electron beam energy loss \( \Delta E(i_j) \) in all \( n \) sublayers:

\[ \Delta E(j) = \sum_{i_j=1}^{n_j} \Delta E(i_j) \]

The electron beam energy loss is normalized to a single electron entering the one-dimensional geometry. Therefore, the electron beam power deposition in layer \( j \) is readily obtained by multiplying the electron beam energy loss in layer \( j \) by the electron beam current entering the one-dimensional geometry:

\[ P(j) = \Delta E(j) I \]

Here, \( P(j) \) is the electron beam power deposition.

### 6.5.4 Reflectivity and Transmissivity of TIGER Code

The electron beam energy loss \( \Delta E(j) \) and the electron beam current loss \( \Delta I(j) \) in layer \( j \) of \( n \) layers may be calculated from the electron beam energy and electron beam current reflectivities and transmissivities of layer \( j \):

\[ \Delta E(j) = \left[ \tau_{j-1}^E + \rho_{j+1}^E - (\tau_j^E + \rho_j^E) \right] E_0 \]

\[ \Delta I(j) = \left[ \tau_{j-1}^I + \rho_{j+1}^I - (\tau_j^I + \rho_j^I) \right] I \]

Here, \( \rho_j^E \) and \( \rho_j^I \) and \( \tau_j^E \) and \( \tau_j^I \) are the electron beam energy and electron beam current reflectivities and transmissivities of layer \( j \), respectively. Also, \( E_0 \) and \( I \) are
the electron beam energy and the electron beam current entering the one-dimensional geometry.

In particular, for the first layer with \( j = 1 \), \( \tau_{j-1} = 1 \) and for the last layer with \( j = n \), \( \rho_{j+1} = 0 \), so that the electron beam energy loss and electron beam current loss in all \( n \) layers result as:

\[
\Delta E = \sum_{j} \Delta E(j) = \left[ 1 - \rho_{1}^{E} - \tau_{n}^{E} \right] E_{0}
\]

\[
\Delta I = \sum_{j} \Delta I(j) = \left[ 1 - \rho_{1}^{I} - \tau_{n}^{I} \right] I
\]

Apparently, the electron beam energy reflectivity and transmissivity are normalized to the electron beam energy entering the one-dimensional geometry. Also, the electron beam current reflectivity and transmissivity are normalized to a single electron entering the one-dimensional geometry.

The above relations are specific to the one-dimensional TIGER code. Owing to the particular method of normalization, these relations are also counter-intuitive. Therefore the relations are mentioned in order to enhance the understanding of the one-dimensional TIGER code.

6.5.5 Geometries of Simulated Cases

For the present work, the one-dimensional geometry consists of three or four layers, depending on whether aluminum or aluminum/titanium composite is chosen as the foil material. In the former case, these layers are referred to as foil, gas and dump layer. In the latter case, these layers are referred to as thick foil, thin foil, gas and dump layer. The electron beam enters the one-dimensional geometry at the foil side and exits at the dump side.

Note that the support grid cannot be modeled in the one-dimensional geometry, as it is a truly three-dimensional object. Therefore, the effect of the support grid has to be accounted for by its transmission to the electron beam \( \tau_{0} \).

In particular, the electron beam current \( I_{0} \) has to be multiplied by the support grid transmission as well as by the electron beam spreading \( \tau^{*} \) in order to calculate the electron beam current entering the one-dimensional geometry:
Several cases, i.e. combinations of layers and combinations of electron beam energies, are calculated to obtain insight into the electron beam energy deposition. Tables 6.2, 6.3, 6.4 and 6.5 list the details for these cases. The values in these tables represent the actual geometry in one-dimensional approximation.

| Electron Beam Energy: 70 keV, 90 keV, 110 keV, 130 keV, 150 keV |
| Foil Thickness: $\frac{1}{1000}$ inch = 0.00254 cm |
| Foil Material: Al |
| Gas Thickness: $\frac{5}{8}$ inch = 1.5875 cm |
| Gas Material: Air, N\textsubscript{2}O |
| Gas Temperature: 298.15 K, 598.15 K |
| Dump Material: Ti |
| Dump Thickness: $\frac{1}{2}$ inch = 1.27 cm |

Table 6.2: 1-D Monte-Carlo Simulation, First Case

The first case is calculated in order to compare the electron beam energy loss in air and N\textsubscript{2}O at low and high gas temperature and various electron beam energies. In particular, this is of use in the interpretation of the results of N\textsubscript{2}O dosimetry discussed in Section 6.6.

| Electron Beam Energy: 70 keV, 90 keV, 110 keV, 130 keV, 150 keV |
| Foil Thickness: $\frac{1}{1000}$ inch = 0.00254 cm |
| Foil Material: Al |
| Gas Thickness: $\frac{5}{8}$ inch = 1.5875 cm |
| Gas Material: O\textsubscript{2}, N\textsubscript{2}, Ar |
| Gas Temperature: 298.15 K, 598.15 K |
| Dump Material: Ti |
| Dump Thickness: $\frac{1}{2}$ inch = 1.27 cm |

Table 6.3: 1-D Monte-Carlo Simulation, Second Case

The second case is calculated in order to compare the electron beam energy loss in O\textsubscript{2}, N\textsubscript{2} and Ar at low gas temperature and various electron beam energies. This is an extension of the first case and of interest because some experiments are conducted with O\textsubscript{2}, N\textsubscript{2} or Ar rather than air as the carrier gas.

The third case is calculated in order to compare the electron beam energy loss in air and N\textsubscript{2}O at different gas temperatures and a single electron beam energy, with aluminum as the foil material. Again, this is of use in the interpretation of the results of N\textsubscript{2}O dosimetry discussed in Section 6.6.
Electron Beam Energy: 110 keV
Foil Thickness: \( \frac{1}{1000} \) inch = 0.00254 cm
Foil Material: Al
Gas Thickness: \( \frac{5}{8} \) inch = 1.5875 cm
Gas Material: Air, N\(_2\)O
Gas Temperature: 273.15 K, 298.15 K, 398.15 K,
498.15 K, 598.15 K, 698.15 K, 798.15 K
Dump Material: Ti
Dump Thickness: \( \frac{1}{8} \) inch = 0.3175 cm

Table 6.4: 1-D Monte-Carlo Simulation, Third Case

Electron Beam Energy: 110 keV
Thick Foil Thickness: \( \frac{9}{10000} \) inch = 0.00229 cm
Thick Foil Material: Al
Thin Foil Thickness: \( \frac{1}{10000} \) inch = 0.000254 cm
Thin Foil Material: Ti
Gas Thickness: \( \frac{5}{8} \) inch = 1.5875 cm
Gas Material: Air, N\(_2\)O
Gas Temperatures: 273.15 K, 298.15 K, 398.15 K,
498.15 K, 598.15 K, 698.15 K, 798.15 K
Dump Material: Ti
Dump Thickness: \( \frac{1}{8} \) inch = 0.3175 cm

Table 6.5: 1-D Monte-Carlo Simulation, Fourth Case
The fourth case is calculated in order to compare the electron beam energy loss in air and N₂O at different gas temperatures and a single electron beam energy, with aluminum/titanium composite as the foil material. Although such a foil material is actually never used in the present work, this case demonstrates that essentially the same electron beam energy loss is obtained as with aluminum as the foil material.

Moreover, the number of sublayers in the foil, or thin foil and thick foil, layer is on the order of 10, the number of sublayers in the gas layer is on the order of 100 and the number of sublayers in the dump layer is on the order of 10. Also, the number of histories is on the order of 10,000.

6.5.6 Results of Simulated Cases

The electron beam energy loss in the foil, or thick foil and thin foil, gas and dump layers as well as the electron beam energy and electron beam current reflectivities and transmissivities for these layers are calculated. The reflectivities and transmissivities are calculated for control purposes only. Therefore, only the electron beam energy loss for the above layers is presented here. The nominal electron beam energy for the present work is $E_0 = 110$ keV.

For the first and second case, the results are shown in Figures 6.4 and 6.5, respectively. The following statements may be obtained from these figures.

The electron beam energy loss in the foil at the low and high gas temperature and for electron beam energies from 70 keV to 150 keV varies from approximately 62 keV to 42 keV for air, N₂O, O₂, N₂ and Ar. Therefore, the foil is virtually opaque to the electron beam at electron beam energies below 70 keV.

The electron beam energy loss in the gas at the low and high gas temperature and for electron beam energies from 70 keV to 150 keV exhibits saturation beyond approximately 110 keV.

Moreover, the electron beam energy loss in the gas at the low gas temperature and for the nominal electron beam energy of 110 keV is approximately 19 keV for air, N₂, O₂ and Ar, and 27 keV for N₂O. At the high gas temperature, values of approximately 10 keV for air and 15 keV for N₂O are obtained.

For the third case, the results are shown in Figures 6.6, and 6.7. The following statements may be obtained from these figures.

The electron beam energy loss in the foil at the nominal electron beam energy of 110 keV and for gas temperatures from 273.15K to 798.15K varies from approximately 52 keV to 55 keV for air and from approximately 50 keV to 53 keV for N₂O.
Figure 6.4: Electron Beam Energy Loss in Air and N₂O at Various Electron Beam Energies, First Case
Figure 6.5: Electron Beam Energy Loss in O$_2$, N$_2$ and Ar at Various Electron Beam Energies, Second Case
Figure 6.6: Electron Beam Energy Loss in Air at Various Gas Temperatures, Foil Material Aluminum, Third Case
Figure 6.7: Electron Beam Energy Loss in N₂O at Various Gas Temperatures, Foil Material Aluminum, Third Case
Also, the electron beam energy loss in the gas at the nominal electron beam energy of 110 keV and for gas temperatures from 273.15 K to 798.15 K varies from approximately 21 keV to 8 keV for air and from approximately to 29 keV to 12 keV for N₂O. The electron beam energy loss in the gas exhibits a \( T^{\frac{1}{2}} \) dependence, where \( T \) is the gas temperature.

In particular, the ratio of the electron beam energy loss in the gas for N₂O to air for gas temperatures from 273.15 K to 798.15 K varies from 1.39 to 1.48. This ratio may therefore be assumed constant at the simple arithmetic average of 1.44.

For the fourth case, the results are shown in Figures 6.8 and 6.9. The following statements may be obtained from these figures.

The electron beam energy loss in the thick foil at the nominal electron beam energy of 110 keV and for gas temperatures from 273.15 K to 798.15 K varies from approximately 47 keV to 49 keV for air and from approximately 47 keV to 48 keV for N₂O. For the thin foil, values from 9 keV to 10 keV for both air and N₂O are obtained.

Also, the electron beam energy loss in the gas at the nominal electron beam energy of 110 keV and for gas temperatures from 273.15 K to 798.15 K varies from approximately 20 keV to 8 keV for air and from approximately to 27 keV to 12 keV for N₂O. The electron beam energy loss in the gas exhibits a \( T^{\frac{1}{2}} \) dependence, where \( T \) is the gas temperature.

In particular, the ratio of electron beam energy loss in the gas for N₂O to air for gas temperatures from 273.15 K to 798.15 K varies from 1.35 to 1.47. This ratio may therefore be assumed constant at the simple arithmetic average of 1.41.

### 6.5.7 Interpretation of Simulated Cases

The gas temperature of the gas flowing through the reaction chamber increases from the intake to the exhaust through the electron beam power deposition in the gas. The electron beam power deposition is proportional to the electron beam energy loss which in turn is inversely proportional to the gas temperature. Therefore, the electron beam power deposition in the gas decreases from the intake to the exhaust. Moreover, the electron beam power deposition is proportional to the electron beam current.

Under the assumption that the gas temperature does not increase from 298.15 K by more than 100 K or 200 K, the electron beam energy loss in the gas does decrease approximately from 19 keV to 15 keV or 12 keV, respectively, for air. As a compromise, the arithmetic average of \( \Delta E_{gas} = 17 \) keV is taken to be the representative electron beam energy loss in the gas for air at the nominal electron beam energy of 110 keV.
Figure 6.8: Electron Beam Energy Loss in Air at Various Gas Temperatures, Foil Material Aluminum/Titanium Composite, Fourth Case
Figure 6.9: Electron Beam Energy Loss in N₂O at Various Gas Temperatures, Foil Material Aluminum/Titanium Composite, Fourth Case
and under the assumption of an average increase in the gas temperature by 100 K.

Independently of the gas temperature, the electron beam energy loss in the gas is similar for air, O$_2$, N$_2$ and Ar, but higher by a factor of approximately 1.4 for N$_2$O. Therefore, the electron beam power deposition in N$_2$O obtained from N$_2$O dosimetry may be converted to the electron beam power deposition in air, O$_2$, N$_2$ or Ar by division by this factor of approximately 1.4.

When aluminum and a 90% aluminum/10% titanium composite are compared as the foil material, very little difference is observed in the electron beam energy loss in the gas.

### 6.5.8 Electron Beam Power Deposition and Electron Beam Dose of Simulated Cases

With a support grid transmission to the electron beam of $\tau_0 = 0.73$, an electron beam spreading of $r^* = 0.5$ and an electron beam energy loss in the gas of $\Delta E_{\text{Gas}} = 17\text{ keV}$, the electron beam power deposition in the gas and the electron beam dose in the gas may be calculated for various gas volume or mass flow rates for air.

The volume flow rates chosen for the present work are shown in Table 6.6. Here, the conversion from volume flow rates to mass flow rates is performed under the assumption of standard conditions, i.e. $p = 1.01325 \cdot 10^5 \text{ Pa}$, $T = 298.15 \text{ K}$ and $M = 28.85 \text{ g/mol}$, which results in $\rho = 1.18 \text{ kg/m}^3$.

<table>
<thead>
<tr>
<th>$V_0$ (cm$^3$/min)</th>
<th>$\dot{m}_0$ (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>$4.91 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>5000</td>
<td>$9.83 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>10000</td>
<td>$1.97 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>15000</td>
<td>$2.95 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>20000</td>
<td>$3.93 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 6.6: Air Volume and Mass Flow Rates

For these gas volume and mass flow rates the electron beam power deposition and the electron beam dose are shown in Table 6.7.

Note that most gases have a mass specific heat capacity of $c_p \approx 1000 \text{ J/kg K}$. Therefore, an electron beam dose of 10 Mrad or $10^5 \text{ J/kg}$ represents an adiabatic increase in the gas temperature by 100 K.

As can be seen from the table, with the exception of very high electron beam...
Table 6.7: Electron Beam Power Deposition and Electron Beam Dose in Air

<table>
<thead>
<tr>
<th>$I_0$ mA</th>
<th>$I$ mA</th>
<th>$Q$ W</th>
<th>$D_{2500}$ Mrad</th>
<th>$D_{5000}$ Mrad</th>
<th>$D_{10000}$ Mrad</th>
<th>$D_{15000}$ Mrad</th>
<th>$D_{20000}$ Mrad</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.09</td>
<td>1.55</td>
<td>3.16</td>
<td>1.58</td>
<td>0.79</td>
<td>0.53</td>
<td>0.40</td>
</tr>
<tr>
<td>0.50</td>
<td>0.18</td>
<td>3.10</td>
<td>6.31</td>
<td>3.16</td>
<td>1.58</td>
<td>1.05</td>
<td>0.79</td>
</tr>
<tr>
<td>0.75</td>
<td>0.27</td>
<td>4.65</td>
<td>9.47</td>
<td>4.74</td>
<td>2.37</td>
<td>1.58</td>
<td>1.18</td>
</tr>
<tr>
<td>1.00</td>
<td>0.37</td>
<td>6.21</td>
<td>12.63</td>
<td>6.31</td>
<td>3.16</td>
<td>2.10</td>
<td>1.58</td>
</tr>
<tr>
<td>1.50</td>
<td>0.55</td>
<td>9.31</td>
<td>18.94</td>
<td>9.47</td>
<td>4.74</td>
<td>3.16</td>
<td>2.37</td>
</tr>
<tr>
<td>2.00</td>
<td>0.73</td>
<td>12.41</td>
<td>25.26</td>
<td>12.63</td>
<td>6.31</td>
<td>4.21</td>
<td>3.16</td>
</tr>
<tr>
<td>3.00</td>
<td>1.10</td>
<td>18.62</td>
<td>37.89</td>
<td>18.94</td>
<td>9.47</td>
<td>6.31</td>
<td>4.74</td>
</tr>
<tr>
<td>4.00</td>
<td>1.46</td>
<td>24.82</td>
<td>50.52</td>
<td>25.26</td>
<td>12.63</td>
<td>8.42</td>
<td>6.31</td>
</tr>
</tbody>
</table>

currents in combination with very low gas volume or mass flow rates, the electron beam dose is on the order of, or less than, 10 Mrad.

Also, the reaction chamber is non-adiabatic and an increase in the gas temperature by 100 K becomes less likely. Therefore, above average electron beam energy loss of $\Delta E_{\text{Gas}} = 17$ keV represents a valid assumption.

### 6.5.9 Electron Beam Stopping Power

The most simple estimate of the electron beam power deposition is based on the assumption that electrons of the electron beam lose their energy to electrons of the medium they traverse. Thus, an equation may be derived for the energy loss of an electron beam electron along its path of travel through the medium. This energy loss is referred to as stopping power.

An excellent review of the equation for the stopping power presented here is given in [132]. This equation includes relativistic effects. Therefore, the relativistic parameters of the electron beam may be determined first:

$$\beta = \frac{v}{c}$$

$$\frac{1}{\gamma} = \sqrt{1 - \beta^2}$$

$$m = \gamma m_e = \frac{m_e}{\sqrt{1 - \beta^2}}$$

$$T = E + m_e c^2 = mc^2$$
\[ T = \frac{m_e}{\sqrt{1 - \beta^2}} c^2 \]
\[ \beta = \sqrt{1 - \left( \frac{m_e c^2}{E + m_e c^2} \right)^2} \]

Here, \( \frac{1}{\gamma} \) is the Lorentz factor, \( v \) is the kinetic velocity, \( E \) is the kinetic energy and \( T \) is the total (relativistic) energy of an electron of the electron beam. Assuming an electron beam energy of \( E_0 = 110 \text{ keV} \), the relativistic parameters of the electron beam are:

\[
\begin{align*}
    m_e c^2 &= 0.511 \text{ MeV} = 511 \text{ keV} \\
    E_0 &= 110 \text{ keV} = 0.11 \text{ MeV} \\
    \beta &= 0.57 \\
    \gamma &= 1.22
\end{align*}
\]

The stopping power is then given as follows[132]. Note that the dimension of the stopping power is traditionally given as \( \text{MeV cm}^2/\text{g} \):

\[
\frac{dE}{dz} = -\frac{2\pi N_A q_e^4 \rho Z}{m_e v^2 M} \left[ \log \frac{m_e v^2 E}{2I^2(1 - \beta^2)} - f(\beta) \right]
\]
\[
f(\beta) = (2\sqrt{1 - \beta^2} - 1 + \beta^2) \log 2 - (1 - \beta^2) - \left( \frac{1}{8} (1 - \sqrt{1 - \beta^2})^2 \right)
\]
\[
I = R_y Z \\
R_y = \frac{m_e q_e^4}{8\hbar^2 c_0^2} = 13.61 \text{ eV}
\]

To estimate the importance of electron energy loss via radiative processes rather than the presented collisional processes, an equation is provided in [132] for the ratio of the electron energy loss in radiative to that in collisional processes:

\[
\frac{\frac{dE_{\text{rad}}}{dz}}{\frac{dE_{\text{col}}}{dz}} = \frac{EZ}{800}
\]
Again, assuming an electron beam energy of $E_0 = 110$ keV and $N_2$ for the gas the electron beam energy loss occurs in, this ratio becomes:

$$Z = 14(N_2)$$

$$\frac{dE_{rad}}{dz}/\frac{dE_{coll}}{dz} = 0.19\%$$

From above equation for the stopping power, an equation for the dose rate in $J/kg\cdot s$ may be derived, where $j$ is the electron beam current density. Recalling the dependence of the stopping power on $\rho$, it can be seen then, that $\dot{D}$ is independent of $\rho$.

$$\dot{D} = \frac{dE}{dz} \frac{j}{\rho}$$

The discussion of the one-dimensional Monte-Carlo Simulation of the electron transport in gas, liquid and solid material refers to the condensed history method which derives its probability distributions for energy loss and deflection of electron beam electrons from multiple-scattering theory. The above equation for the stopping power represents such a theory for the energy loss.

However, the electron beam energy loss obtained from one-dimensional Monte-Carlo Simulation is approximately two to three times higher than the electron beam energy loss obtained from above equation for the stopping power. This discrepancy is thought to be due to the following effects.

The above equation for the stopping power is derived assuming only elastic collisions [132] of electron beam electrons with electrons of the medium they traverse. However, inelastic collisions account for a significant fraction of the energy loss and should be properly included in the derivation.

Also, the above equation describes the stopping power for a direction along the path of travel of the electron. However, due to scattering of the electron, this direction is not the same as that along the $z$-axis in the sense of the one-dimensional Monte-Carlo Simulation.

Thus, when projecting the direction of the path of travel to the direction of this $z$-axis, the same electron beam energy loss occurs over a shorter distance and the stopping power along this $z$-axis increases correspondingly.
Finally, the above equation for the stopping power does not account for the scattering of electrons, i.e. the multiple traverse of a single position along the z-axis in the sense of the one-dimensional *Monte-Carlo Simulation.*

### 6.6 Nitrous Oxide Dosimetry

#### 6.6.1 Principle of Nitrous Oxide Dosimetry

When *Nitrous Oxide* (N\textsubscript{2}O) is passed through the reaction chamber under electron beam irradiation, N\textsubscript{2}O is destroyed and N\textsubscript{2} and O\textsubscript{2} are produced. The concentrations of N\textsubscript{2} and O\textsubscript{2} in N\textsubscript{2}O are related linearly to the electron beam dose via their respective G-Values of production from destruction of N\textsubscript{2}O. Therefore, measurement of the concentrations of N\textsubscript{2} and/or O\textsubscript{2} allows for estimation of the dose to N\textsubscript{2}O.

The direct measurement of the destruction of N\textsubscript{2}O is impractical, because the N\textsubscript{2}O concentration is so large (100\%) that the small decrease in this concentration due to decomposition of N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{2} would fall well within the measurement error of the N\textsubscript{2}O concentration. In fact, the N\textsubscript{2}O concentration may be assumed constant for the purpose of the present work.

#### 6.6.2 History of Nitrous Oxide Dosimetry

The N\textsubscript{2}O dosimeter was suggested in [133] for \(\gamma\)-, \(\beta\)- and neutron-radiation at high dose rates and doses characteristic of nuclear power plants. The uranium isotope \(^{235}\text{U}\) was used to generate neutron-radiation at doses\(^4\) of \(10^6\) R to \(10^{10}\) R, nuclear fission products were used to generate \(\beta\)-radiation at comparable doses and the cobalt isotope \(^{60}\text{Co}\) was used to generate \(\gamma\)-radiation at doses of \(5 \cdot 10^4\) R to \(3 \cdot 10^7\) R. The production of N\textsubscript{2} and O\textsubscript{2} was found to be linear in dose up to \(10^7\) R, and “practically” linear up to \(10^8\) R.

Lower dose rates and doses were investigated in [134]. The hydrogen isotope \(^{3}\text{H}\) was used to generate \(\beta\)-radiation with an average energy of 5.5 keV, the cobalt isotope \(^{60}\text{Co}\) was used to generate \(\gamma\)-radiation with an average energy of 93 keV and a 4 MeV electron beam was used to generate x-radiation. The dose rates were on the order of \(10^{-6}\) Mrad/s to \(10^{-5}\) Mrad/s and the doses were on the order of 1 Mrad to 10 Mrad.

Comparable dose rates and doses were investigated in [135]. The cobalt isotope \(^{60}\text{Co}\)

\(^4\)1 R \(\approx 2.59 \cdot 10^{-4}\) C/kg \(\approx 8.63 \cdot 10^{-3}\) Gy \(\approx 1\) rad in air at \(p = 1.01325 \cdot 10^5\) Pa, \(T = 273.15\) K, \(M = 28.85\) g/mol and \(W = 33.3\) eV. The conversion from R to rad is shown in Appendix E.1.
was used to generate γ-radiation. The dose rates were on the order of $10^{-5}$ Mrad/s to $5 \cdot 10^{-5}$ Mrad/s and the doses were on the order of 1 Mrad to 25 Mrad.

Much higher dose rates and doses were investigated in [136]. A 600 keV electron beam was used to generate electron-radiation. The dose rates were on the order of $3 \cdot 10^8$ Mrad/s and the doses were on the order of 1 Mrad.

Overviews over other N₂O dosimetry studies are provided in [65] and [137], the latter remarking that doses of $4 \cdot 10^{-2}$ Mrad to 1 Mrad are reliably measured with a linear relation between N₂ concentration and dose, but that doses as high as $8 \cdot 10^3$ Mrad were measured as well using a non-linear relation between N₂ concentration and dose.

The results of these studies may be summarized as follows. The production of N₂ and O₂ from the destruction of N₂O is a linear function of the dose up to least 3 Mrad. Moreover, the production of N₂ and O₂ from destruction of N₂O appears to be a function of the dose only and not a function of the dose rate.

In the range of atmospheric pressure and temperature, no pressure or temperature dependence is found for the G-Values of production of N₂ and O₂ from destruction of N₂O. The lack of temperature dependence is very likely due to the small thermal decay rate constant [133] for N₂O, which is given as:

$$k = 4.2 \cdot 10^9 e^{-\frac{53,000}{R_mT}} \text{ 1/s}$$

At 298.15 K, the thermal decay rate constant is 2.18 1/s, while at 598.15 K, the thermal decay rate constant is $9.89 \cdot 10^4$ 1/s.

Also, the measurement of the concentration of N₂ is preferred over the measurement of the concentration of O₂, because the latter is readily affected by impurities contained in N₂O.

Under the investigated conditions, the G-Value for production of N₂ from destruction of N₂O varies from 9/100eV to 13/100eV. The average of 11/100eV is chosen for the purpose of the present work.

Finally, when the concentration of N₂O significantly deviates from 100 %, Sensitization is observed, i.e. the G-Value for production of N₂ from destruction of N₂O increases sharply over above mentioned 11/100eV. This is particularly true for small concentrations of N₂O in noble gases as demonstrated in [137] and [138].
6.6.3 Theory of Nitrous Oxide Dosimetry

The theory of N\textsubscript{2}O dosimetry is based on the theory of the G-Value discussed in Section 2.5:

\[ d\varphi_{N_2} = \frac{M_{N_2O}}{N_A} G_{N_2O}^{N_2} dD_{N_2O} \]
\[ d\varphi_{O_2} = \frac{M_{N_2O}}{N_A} G_{N_2O}^{O_2} dD_{N_2O} \]

Here, \( \varphi_{N_2} \) and \( \varphi_{O_2} \) are the concentrations of N\textsubscript{2} and O\textsubscript{2}, \( G_{N_2O}^{N_2} \) and \( G_{N_2O}^{O_2} \) are the G-Values for production of N\textsubscript{2} and O\textsubscript{2} from destruction of N\textsubscript{2}O, respectively. \( M_{N_2O} \) is the mole mass of N\textsubscript{2}O. Therefore:

\[ D_{N_2O} = \frac{\varphi_{N_2} - \varphi_{N_2}^0}{G_{N_2O}^{N_2}} \frac{N_A}{M_{N_2O}} \]
\[ D_{N_2O} = \frac{\varphi_{O_2} - \varphi_{O_2}^0}{G_{N_2O}^{O_2}} \frac{N_A}{M_{N_2O}} \]

The dose \( D_{N_2O} \) may be converted to the power deposition \( \dot{Q}_{N_2O} \) in N\textsubscript{2}O via the N\textsubscript{2}O mass flow rate \( \dot{m}_{N_2O}^0 \):

\[ D_{N_2O} = \frac{\dot{Q}_{N_2O}}{\dot{m}_{N_2O}^0} \]

\[ \dot{Q}_{N_2O} = \frac{\varphi_{N_2} - \varphi_{N_2}^0}{G_{N_2O}^{N_2}} \frac{N_A}{M_{N_2O}} \dot{m}_{N_2O}^0 \]
\[ \dot{Q}_{N_2O} = \frac{\varphi_{O_2} - \varphi_{O_2}^0}{G_{N_2O}^{O_2}} \frac{N_A}{M_{N_2O}} \dot{m}_{N_2O}^0 \]

Here, the N\textsubscript{2}O mass flow rate \( \dot{m}_{N_2O}^0 \) is determined from the N\textsubscript{2}O volume flow rate \( \dot{V}_{N_2O} \), which is readily measured by volume flow meters, as well as from \( p_{N_2O} = 1.01325 \cdot 10^5 \) Pa, \( T_{N_2O} = 298.15 \) K and \( M_{N_2O} = 44.01 \) g/mol:
On the basis of the one-dimensional Monte-Carlo Simulation of the electron beam energy loss $\Delta E_{N_2O}$ in the gas, the power deposition $\dot{Q}_{N_2O}$ is expected to be linear in the electron beam current $I$, where:

$$\dot{Q}_{N_2O} = \Delta E_{N_2O} I$$

$$I = \tau^* \tau_0 I_0$$

In particular, if $\varphi_{N_2}$ and or $\varphi_{O_2}$ are plotted vs. $\frac{I_0}{m_{N_2O}}$ with $\tau^* = \text{const.}$ and $\tau_0 = \text{const.}$, no dependence of the $N_2$ and/or $O_2$ concentration on the $N_2O$ mass or volume flow rate should be observed up to the dose for which the production of $N_2$ and $O_2$ from the destruction of $N_2O$ becomes a non-linear function of the dose.

### 6.6.4 Results of Nitrous Oxide Dosimetry

In the $N_2O$ dosimetry performed for the present work, $N_2O$ is passed through the reaction chamber at three different $N_2O$ mass or volume flow rates and the $N_2$ and $O_2$ concentration in the reactor exhaust are measured as a function of the electron beam current. The volume and mass flow rates are shown in Table 6.8.

<table>
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<th>$V_{N_2O}^0$</th>
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</thead>
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<td>kg/s</td>
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<tr>
<td>5429.37</td>
<td>1.63 $\cdot$ 10$^{-4}$</td>
</tr>
<tr>
<td>2845.84</td>
<td>0.85 $\cdot$ 10$^{-4}$</td>
</tr>
</tbody>
</table>

Table 6.8: $N_2O$ Volume and Mass Flow Rates for $N_2O$ Dosimetry

The measurements are performed using the gas analysis system described in Section 5.2. It is found that in fact only the $N_2$ concentration is of value to $N_2O$ dosimetry, since the $O_2$ concentration is in fact affected by impurities in the $N_2O$. 

\[ \dot{m}_{N_2O}^0 = \rho_{N_2O} \dot{V}_{N_2O}^0 \]

\[ \rho_{N_2O} = \frac{\rho_{N_2O} M_{N_2O}}{R_m T_{N_2O}} \]
Figure 6.10 shows the $N_2$ concentration as a function of the ratio of electron beam current to $N_2O$ mass flow rate. It can be seen from this figure that, as expected, for low ratios of electron beam current to $N_2O$ mass flow rate, no dependence of the $N_2$ concentration on the $N_2O$ mass flow rate is observed. However, for high ratios of electron beam current to $N_2O$ mass flow rate, such dependence is observed.

Therefore, $N_2O$ dosimetry appears to be only applicable to electron beam currents $I_0$ up to $0.25$ mA, $0.5$ mA and $1.0$ mA at volume flow rates of $N_2O$ of $2,500$ cm$^3$/min, $5,000$ cm$^3$/min and $10,000$ cm$^3$/min, respectively.

This is consistent with the remarks made in the discussion of the history of $N_2O$ dosimetry in Section 6.6.2. Moreover, it suffices to determine the electron beam energy loss $\Delta E_{N_2O}$ from the $N_2$ concentrations and the combinations of electron beam current $I_0$ and $N_2O$ mass or volume flow rate. Then the proportionality between $\dot{Q}_{N_2O}$ and $I_0$ may be used for further calculations. Note again that actually $I$ and not $I_0$ is of interest here and that these are connected via the constants $r^*$ and $\tau_0$.

Tables 6.9, 6.10, 6.11 and 6.12 show the $N_2$ concentration in $N_2O$, the electron beam dose in $N_2O$, the electron beam power deposition in $N_2O$ and the electron beam power deposition in air as a function of the electron beam current and the $N_2O$ volume flow rate. Note that for each volume flow rate, two series of measurements were taken in order to ascertain reproducibility.

<table>
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<tr>
<th>$I_0$ (mA)</th>
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<th>$8593.40$ cm$^3$/min</th>
<th>$8593.40$ cm$^3$/min</th>
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<th>$5429.37$ cm$^3$/min</th>
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Table 6.9: $N_2$ Concentration $\varphi_{N_2}$ in $N_2O$ in ppm for $N_2O$ Dosimetry

The electron beam power deposition $\dot{Q}_{N_2O}$ in $N_2O$ is converted to the electron beam power deposition $\dot{Q}_{Air}$ in air by means of the results of the one-dimensional Monte-Carlo Simulation of the electron beam energy deposition in the gas.

It may be recalled that the ratio of the electron beam energy deposition in $N_2O$ to the electron beam energy deposition in air is approximately 1.4. Under the assumption of a linear relation between the electron beam power deposition and the electron beam current, the conversion from $\dot{Q}_{N_2O}$ to $\dot{Q}_{Air}$ simply results as:
Figure 6.10: \(N_2\) Concentration vs. Ratio of Electron Beam Current to Mass Flow Rate of \(N_2O\) for \(N_2O\) Dosimetry
Table 6.10: Electron Beam Dose $D_{N_2O}$ in N$_2$O in Mrad for N$_2$O Dosimetry

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Table 6.11: Electron Beam Power Deposition $\dot{Q}_{N_2O}$ in N$_2$O in W for N$_2$O Dosimetry

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Table 6.12: Electron Beam Power Deposition $\dot{Q}_{Air}$ in Air in W for N$_2$O Dosimetry

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\[
\dot{Q}_{\text{Air}} = \frac{1}{1.4} \dot{Q}_{N_2O}
\]

It can be seen from Tables 6.7 and 6.12 that for electron beam currents of 0.25 mA, 0.5 mA and 1 mA, the electron beam power deposition obtained from Monte-Carlo dosimetry and the electron beam power deposition obtained from N\textsubscript{2}O dosimetry agree reasonably well.

However, for higher electron beam currents, the deficiencies of the N\textsubscript{2}O dosimetry in terms of lack of linearity between N\textsubscript{2}O concentration and electron beam dose or electron beam current become apparent. In particular, the measurements performed for the present work confirm the inception of such lack of linearity at electron beam doses on the order of 3 Mrad.
Chapter 7

Experimental Procedures and Results

7.1 General Considerations

In the interest of contextual coherence, the experimental procedure and the experimental results are presented in a single chapter rather than devoting separate chapters to the procedure and the results, respectively. A number of experiments were performed, and the corresponding procedure and results are presented for each experiment as applicable. Moreover, the experiments are presented in chronological order.

All calibrations of the Gas Chromatograph with Thermal Conductivity Detector (GC-TCD), with Electron Capture Detector (GC-ECD) and with Mass Selective Detector (GC-MS) and all calibrations of the Stand-Alone, On-Line, Real-Time Mass Spectrometer (SOR-MS) for the various chemical compounds were performed using standards from compressed gas cylinders.

The GC-ECD, GC-TCD, GC-MS and SOR-MS were typically calibrated shortly before the experiments and as a check of calibration stability shortly after the experiments as well. The calibration stability was found to be satisfactory in all cases. Provided the certified concentrations of the standards used for calibration were accurate, the concentration measurements for the experiments were expected to be accurate as well, except where noted otherwise.

All investigations of the decomposition of CCl₄, CHCl₃ and C₂HCl₃ were performed using standards from vapor generators. In particular, intake concentrations were not adjusted with a particularly high precision. In fact, intake concentrations "in the right ballpark" were accepted in order to avoid extended periods of adjustment of
intake concentrations to actually desired values. This procedure typically resulted in intake concentrations within 25% of such actually desired values.

The effect of the CCl₄ intake concentration and the electron beam dose, the effect of the relative humidity and the effect of air or oxygen on the decomposition of CCl₄ was investigated using the old reaction chamber and the electron beam without superimposed electric field.

The transition from the old to the new reaction chamber was then performed. The effect of air or oxygen on the decomposition of CCl₄ was investigated one more time using the new reaction chamber and the electron beam without superimposed electric field in order to document this transition.

In order to evaluate the importance of the electric field, the effect of such electric field on the decomposition of CCl₄ and CHCl₃ was investigated using the new reaction chamber and the electron beam with superimposed electric field.

Subsequently, experiments were performed to investigate the products of the CCl₄ decomposition using the new reaction chamber and the electron beam without superimposed electric field.

Moreover, the effect of the relative humidity and the effect of the electric field on the decomposition of C₂HCl₃ was investigated. Also, experiments were performed to investigate the products of the C₂HCl₃ decomposition. These investigations also used the new reaction chamber and the electron beam without superimposed electric field.

Given the motivation and focus of the present work, the investigation of the decomposition of chlorinated organic compounds through Cold Plasma Decomposition in a Tunable Plasma Reactor was most comprehensive for CCl₄ and less comprehensive for CHCl₃ and C₂HCl₃.

In the following, the combination of the electron beam dose, the intake concentration and the resulting destruction and removal efficiency is referred to as the decomposition efficiency. In particular, for a given intake concentration and destruction and removal efficiency, a low electron beam dose represents a high decomposition efficiency and vice versa.

As a reminder, the electron beam dose is the electron beam power absorbed in the standard gas per mass flow rate of the standard gas. The electron beam dose is given in dimensions Mrad, where 100 rad is equal to 1 J/kg, or 1 Mrad is equal to 10⁴ J/kg. Moreover, with a typical mass specific heat capacity of 1000 J/kg K for the standard gas, such electron beam dose corresponds to an adiabatic increase in the temperature of the standard gas by 10 K.

The correlation among electron beam current, electron beam power, standard gas
volume flow rate and electron beam dose is presented in tabulated form in Section 6.5.8 for air as the carrier gas.

A different standard gas volume flow rate requires a different electron beam current, or electron beam dose rate, in order to obtain a constant electron beam dose. It was determined in preliminary experiments that for a given intake concentration and a given electron beam dose, the variation of the standard gas volume flow rate and thereby the variation of the electron beam dose rate, had no significant effect on the destruction and removal efficiency. This indicates that the decomposition is in fact an explicit function of the electron beam dose rather than the electron beam dose rate.

This is particularly important in view of the limitation of the electron beam current. For a low intake concentration, the electron beam dose for a high destruction and removal efficiency may be obtained at low or high volume flow rates without operation at maximum electron beam current. For a high intake concentration, the electron beam dose for a high destruction and removal efficiency may be obtained only at low volume flow rates with operation at maximum electron beam current.

The electron beam window foil showed severe corrosion and deposition after extended operation of the electron beam for the decomposition of chlorinated organic compounds. This corrosion and deposition may have adversely affected the transparency of the foil to the electron beam and therefore may have resulted in a lower than expected electron beam dose to the standard gas.

A few smaller inconsistencies in the experimental observations described here, such as variations in the decomposition efficiency of up to estimated 25%, may be explained through such corrosion and deposition.

Moreover, the electron beam current and voltage were troubled by poor control due to the fact that the electron beam gun was built from less than state of the art second hand equipment. Moreover, marginal high voltage shielding resulted in frequent high voltage arcing over the entire duration of the present work.

A few larger inconsistencies in the experimental observations described here, such as variations in the decomposition efficiency of up to estimated 50% and in isolated cases up to estimated 100%, may be explained through such poor control and high voltage arcing.

Unfortunately, at the time these problems did not receive the proper attention so that for example no records were kept on the frequency of the change and the condition of the electron beam window foil, i.e. correlations with the experiments could not be made.
Note that a paper on the effect of the CCl₄ intake concentration and the electron beam dose on the CCl₄ decomposition was published as [139], and a paper on the effect of the electric field on the decomposition of CCl₄ and CHCl₃ was published as [140]. In the former paper, the electron beam dose was quoted approximately a factor of two too high in lack of proper electron beam dosimetry at the time.

### 7.2 Effect of Intake Concentration and Electron Beam Dose on CCl₄ Decomposition

The CCl₄ exhaust concentration was measured for different CCl₄ intake concentrations as a function of the electron beam dose, which results from the combination of electron beam current and volume flow rate. The intake concentration was taken as the exhaust concentration with zero electron beam dose.

For this experiment, dry air was used as the carrier gas of the gas mixing system. The 2 μl sample of the Hewlett-Packard HP-5 capillary column and the GC-ECD were employed for the chemical analysis.

In order to establish the precision and reproducibility of the concentration measurements for this experiment, the following experimental procedure was adapted. For each intake concentration and electron beam dose, the exhaust concentration was measured from one to four times and then averaged. Moreover, for each intake concentration, the series of exhaust concentration measurements, with a stepwise increase of the electron beam dose from zero to maximum value, was performed twice.

The intake concentration was measured before and after such series of exhaust concentration measurements to ensure that this concentration was approximately constant. Moreover, in between the two series of exhaust concentration measurements, blank exhaust concentration measurements, i.e. measurements with pure dry air without CCl₄, were performed to ensure that the background concentration was negligible.

The results are presented in Figure 7.1. In this figure, for each intake concentration, the first series of exhaust concentration measurements is shown with symbols, the second series is shown without symbols. The resulting two curves for each intake concentration give an indication of precision and reproducibility.

The precision and reproducibility of an intake concentration measurement, i.e. exhaust concentration measurement with zero electron beam dose, was found to be on the order of 95 %, while the precision and reproducibility of an exhaust concentration measurement with non-zero electron beam dose was found to be on the order of 90
Figure 7.1: Effect of Intake Concentration and Electron Beam Dose on CCl₄ Decomposition in Dry Air
Variations of the reproducibility may be expected from a transient upset of the vapor pressure equilibrium in the vapor generator, although generally the vapor generator was allowed to assume vapor pressure equilibrium for up to 15 minutes prior to each series of exhaust concentration measurements.

Several weeks after this original experiment, a repeat of the experiment was performed with only one instead of two series of exhaust concentration measurements for each intake concentration. In general, the decomposition efficiencies in the original experiment and the repeat experiment were comparable, although the reproducibility represented by these two experiments is less than the 90% indicated above. Moreover, for some intake concentrations, the CCl₄ exhaust concentration as a function of the electron beam dose exhibited a less striking "tail" at low exhaust concentrations for the original experiment than for the repeat experiment.

Nevertheless, both experiments show that for a given exhaust concentration, the electron beam dose decreases with decreasing intake concentration. This indicates the selectivity of the CCl₄ decomposition. Moreover, the exhaust concentration appears to be an approximately exponential function of the electron beam dose.

### 7.3 Effect of Relative Humidity on CCl₄ Decomposition

In order to estimate the effect of relative humidity on the decomposition of CCl₄, the previously described experiment was repeated using wet air instead of dry air as the carrier gas for the gas mixing system. The remainder of the equipment and procedure was equivalent to the equipment and procedure described for the previous experiment.

The relative humidity of the wet air was approximately 20%RH at 100°F as indicated by the relative humidity meter. The results are presented in Figure 7.2 as an approximate equivalent to Figure 7.1.

As can be seen from comparison of these two figures, the electron beam dose for a given intake concentration and a given exhaust concentration is significantly higher for wet air than for dry air.

An example of a comparison of this experiment for wet air to the experiment for dry air is as follows. In dry air it takes approximately 4.5 Mrad to reduce an intake concentration of 161 ppm to an exhaust concentration of 1 ppm, while in wet air it
Figure 7.2: Effect of Relative Humidity on CCl₄ Decomposition in 20 %RH Wet Air
takes approximately 23 Mrad to reduce a comparable intake concentration of 179 ppm to 1 ppm.

Several weeks after this original experiment, a repeat of the experiment was performed with only one instead of two series of concentration measurements for each intake concentration. Moreover, the relative humidity of the air was approximately 5 %RH at 100 °F and 40 %RH at 100 °F, respectively, as indicated by the relative humidity meter.

In general, the decomposition efficiencies in the original experiment and the repeat experiment were comparable, although the different relative humidity in the repeat experiment compared to the original experiment resulted in a different decomposition efficiency. Moreover, for some intake concentrations, the CCl₄ exhaust concentration as a function of the electron beam dose again exhibited a less striking “tail” at low exhaust concentrations for the original experiment than for the repeat experiment.

Examples of a comparison of the repeat experiment for dry air to that for wet air are as follows. In dry air it takes approximately 9 Mrad to reduce an intake concentration of 256 ppm to an exhaust concentration of 1 ppm, while in wet air of 5 %RH, it takes approximately 16.5 Mrad to reduce a comparable intake concentration of 269 ppm to 1 ppm and in wet air of 40 %RH, it would take approximately 25 Mrad to reduce a comparable intake concentration of 268 ppm to 1 ppm.

Also, in dry air it takes approximately 5 Mrad to reduce an intake concentration of 125 ppm to an exhaust concentration of 1 ppm, while in wet air of 5 %RH, it takes approximately 11 Mrad to reduce a comparable intake concentration of 136 ppm to 1 ppm and in wet air of 40 %RH, it takes approximately 15 Mrad to reduce a comparable intake concentration of 116 ppm to 1 ppm.

Therefore, the electron beam dose for a given intake concentration and a given exhaust concentration is from two to five times higher in wet air than in dry air. Also, such decomposition efficiency is not a strong function of the relative humidity as long as the relative humidity is higher than a few percent. A lower relative humidity was not accessible to the experiment due to the limitations of the relative humidity meter.

### 7.4 Effect of Air and Oxygen on CCl₄ Decomposition

At this point it was suspected that nitrogen oxides formed upon electron beam irradiation of air combined with water in wet air to form Nitric Acid (HNO₃). Such
nitric acid is characterized by a high bimolecular dissociative electron attachment reaction rate constant and thus might have interfered with the suspected bimolecular dissociative electron attachment to CCl₄.

Therefore, a comparative experiment with air and oxygen as the carrier gas of the gas mixing system was performed. In this experiment, dry as well as wet carrier gas was investigated. Since no nitrogen oxides are formed in oxygen upon electron beam irradiation, a higher decomposition efficiency in wet oxygen than in wet air resulting from the lack of formation of HNO₃ was expected.

The same experimental equipment and procedure as in the previous experiments was used, however, only one intake concentration was investigated and only one series of exhaust concentration measurements was performed. Also, while the procedure of one to four exhaust concentration measurements for each electron beam dose was maintained as well, these measurements were not averaged in order to indicate precision and reproducibility. The relative humidity of wet air and wet oxygen was 12.5 %RH at 100 °F. The results are presented in Figure 7.3.

As can be seen from this figure, for dry standard gas, a lower decomposition efficiency is achieved for air than for oxygen. Moreover, for wet standard gas, the decomposition efficiency is comparable for air and for oxygen. Moreover, the CCl₄ exhaust concentration as a function of the electron beam dose again exhibits a "tail".

Unless the oxygen used in this experiment contained a nitrogen impurity of several hundred ppm, which is extremely unlikely for Ultra High Purity Grade, or other unrecognized sources of nitrogen existed, these results indicate that HNO₃ was not responsible for the lower decomposition efficiency in wet air compared to dry air.

The higher decomposition efficiency in dry oxygen compared to dry air was not expected, since oxygen is characterized by a relatively high termolecular non-dissociative electron attachment reaction rate constant, i.e. the interference with the bimolecular dissociative electron attachment to CCl₄ was expected to increase with increasing oxygen concentration.

Nevertheless, this observation is in agreement with preliminary experiments where a very high electron beam dose was required for a particular CCl₄ intake concentration and destruction and removal efficiency in argon and nitrogen. Therefore it may be stated that the electron beam dose required for a particular destruction and removal efficiency for CCl₄ decreases with increasing O₂ intake concentration.
Figure 7.3: Effect of Air and Oxygen on CCL₄ Decomposition in Dry Air and Oxygen and 12.5 %RH Wet Air and Oxygen, Old Reaction Chamber
7.5 Transition from Old Reaction Chamber to New Reaction Chamber

As mentioned in Section 4.2, a number of problems were associated with the old reaction chamber, such as dead volume and dead flow regions, which could be virtually eliminated through transition to the new reaction chamber.

In order to evaluate the effect of this transition on the CCl₄ decomposition efficiency, the previous experiment performed with the old reaction chamber regarding the decomposition efficiency of CCl₄ in dry and wet air and oxygen was repeated with the new reaction chamber.

Figure 7.4 presents the results of this experiment for the new reaction chamber. Note that the exhaust concentration as a function of the electron beam dose exhibits no "tail".

Also, Figure 7.5 presents a comparison of the results of this experiment for the old and new reaction chamber for dry air and oxygen.

As can be seen from Figure 7.5, the new reaction chamber appears to result in a higher CCl₄ decomposition efficiency than the old reaction chamber. This difference can currently not be explained, since in other experiments, the old reaction chamber resulted in a comparable decomposition efficiency as the new reaction chamber.

It is conceivable that residual relative humidity in the dead volume at the time of the corresponding experiment with the old reaction chamber could have caused this discrepancy. However, since the old reaction chamber was not going to be used again in the present work, it was deemed not useful to check the results for the old reaction chamber by a repeat of the corresponding experiment.

7.6 Effect of Electric Field on CCl₄ and CHCl₃ Decomposition

The concept of the Tunable Plasma Reactor is based on the superposition of an electron beam and an electric field. While the previous experiments investigated the decomposition efficiency as a function of the electron beam dose, i.e. electron beam current and volume flow rate, this experiment investigated the decomposition efficiency as a function of the electric field voltage, i.e. electric field.

The CCl₄ and CHCl₃ exhaust concentration was measured at a constant volume
Figure 7.4: Effect of Air and Oxygen on CCL₄ Decomposition in Dry Air and Oxygen and 12.5%RH Wet Air and Oxygen, New Reaction Chamber
Figure 7.5: Effect of Air and Oxygen on CCl₄ Decomposition in Dry Air and Oxygen, Old vs. New Reaction Chamber
flow rate as a function of the electric field voltage, i.e. electric field, with the electron beam current, i.e. electron beam dose, and the relative humidity of the standard gas as parameters.

The decomposition of CCl₄ and CHCl₃ was suspected to be initiated by bimolecular dissociative electron attachment. However, the bimolecular dissociative electron attachment reaction rate constant for CHCl₃ is lower than that for CCl₄. Also, the dependence of the reaction rate constant on the average electron energy is essentially opposite, i.e. the rate constant for CHCl₃ exhibits a maximum and the rate constant for CCl₄ exhibits a minimum with increasing average electron energy [32]. This is also discussed in Section 2.3.2.

Those differences were expected to become apparent in this experiment in the form of a maximum for CCl₄ and a minimum for CHCl₃ in the exhaust concentration with increasing electric field voltage, assuming that the appropriate average electron energies could be covered through the available electric field.

For the experiment, wet and dry air was used as the carrier gas for the gas mixing system. Also, at this point the conversion of the MSD from a GC-MS detector to a SOR-MS detector was completed, so that the SOR-MS rather than the GC-ECD was employed for the chemical analysis.

The exhaust ion abundance for the M/Z ratio 83 (CHCl₂) for CHCl₃ and the M/Z ratio 117 (CCl₃) for CCl₄ was measured and converted into the exhaust concentration via the FORTRAN77 programs HPMSONE and HPMSTWO as discussed in Section 5.3.3.

In order to establish the precision and reproducibility of the measurements for these experiments, the following experimental procedure was adapted. For each electric field voltage, the exhaust ion abundances were averaged over approximately one minute. With two exceptions, two series of exhaust concentration measurements, with the electric field voltage increasing stepwise from zero to maximum value, were performed for one CCl₄ and one CHCl₃ intake concentration. At the beginning and the end of each series, the electron beam dose and the electric field were set to zero in order to check the CCl₄ and CHCl₃ intake concentration.

The relative humidity for the case of CCl₄ in wet air was 12 %RH at 100°F, the relative humidity for the case of CHCl₃ in wet air was 11 %RH at 100°F. The results for CCl₄ and CHCl₃ are presented in Figures 7.6 and 7.7 for dry air and in Figures 7.8 and 7.9 for wet air, respectively.

In these figures, the first series of exhaust concentration measurements is shown with symbols, the second such series is shown without symbols to indicate the precision and reproducibility. As evident from these figures, the precision and reproducibility
Figure 7.6: Effect of Electric Field on CCl₄ Decomposition in Dry Air
Figure 7.7: Effect of Electric Field on CHCl₃ Decomposition in Dry Air
Figure 7.8: Effect of Electric Field on CCl₄ Decomposition in 12% RH Wet Air
Figure 7.9: Effect of Electric Field on CHCl₃ Decomposition in 11 %RH Wet Air
are rather high and comparable to those obtained through the GC-ECD.

Also, at an air volume flow rate of approximately 5000 cm$^3$/min, an electron beam current of 0.25 mA, 0.5 mA, 1.0 mA and 2.0 mA corresponds to an electron beam dose of approximately 1.58 Mrad, 3.16 Mrad, 6.31 Mrad and 12.63 Mrad, respectively.

As can be seen from Figures 7.6 and 7.7 and from Figures 7.8 and 7.9, the effect of the electric field on the decomposition of CCl$_4$ and CHCl$_3$ in dry and wet air appears to be not as large as expected. However, the expected maximum for CCl$_4$ and the expected minimum for CHCl$_3$ are approximately observed, with the minimum for CHCl$_3$ more pronounced than the maximum for CCl$_4$. Also, the effect of the electric field on the decomposition is larger in wet air than in dry air.

Although it may be stated that the observed maximum and minimum in the CCl$_4$ and CHCl$_3$ exhaust concentration correspond to the minimum and maximum in the CCl$_4$ and CHCl$_3$ bimolecular dissociative electron attachment reaction rate constant, such statement is not entirely defendable since the average electron energy is not really known for the Tunable Plasma Reactor.

For example, the maximum and the minimum seem to appear at a lower electric field in dry air and at a higher electric field in wet air. This indicates a lower average electron energy in wet air than in dry air. Moreover, the minima and maxima are not always fully developed and may therefore not actually represent minima and maxima.

As an additional result of these experiments, the CCl$_4$ and CHCl$_3$ exhaust concentration as a function of the electron beam dose was obtained through the measurements at zero electric field, with zero electron beam dose for the intake concentration and non-zero electron beam dose for the exhaust concentration. These additional results are presented for CCl$_4$ and CHCl$_3$ in dry and wet air in Figure 7.10.

With respect to the decomposition of CCl$_4$, a doubling of the intake concentration in dry air results approximately in a doubling of the electron beam dose for a given (low) exhaust concentration.

The CHCl$_3$ intake concentration in dry air was less than twice as high as the CCl$_4$ intake concentration in dry air. Therefore, if the decomposition of CHCl$_3$ was as efficient as the decomposition of CCl$_4$, the electron beam dose for a given (low) exhaust concentration should be less than twice as high for CHCl$_3$ as for CCl$_4$.

However, as can be seen from this figure, for a given exhaust concentration, the electron beam dose appears to be more like four to five times as high for CHCl$_3$ as for CCl$_4$. Therefore it may be stated that the decomposition efficiency is higher for CCl$_4$ than for CHCl$_3$.

This observations is consistent with the higher bimolecular dissociative electron
Figure 7.10: Effect of Electron Beam Dose on CCl₄ and CHCl₃ Decomposition in Dry Air and in 11 %RH and 12 %RH Wet Air
attachment reaction rate constant for CCl₄ than for CHCl₃. Moreover, the same effect of relative humidity on the decomposition efficiency is observed for CHCl₃ as for CCl₄.

Moreover, the electron beam dose required to reduce a CCl₄ intake concentration of 254 ppm in dry air to 1 ppm is approximately 6.5 Mrad. A comparable electron beam dose from Figure 7.5 is 9.5 Mrad to reduce a CCl₄ intake concentration of 310 ppm in dry air to 1 ppm. Such agreement is certainly not excellent but still approximately consistent.

### 7.7 Products and By-Products of CCl₄ Decomposition

#### 7.7.1 General Considerations

The desirable decomposition products of CCl₄ are CO *Carbon Monoxide* and CO₂ *Carbon Dioxide* as well as HCl *Hydrogen Chloride* and Cl₂ *Chlorine*.

Moreover, it was found in preliminary experiments using the 2 µl sample loop, the *Hewlett-Packard HP-5* capillary column and the GC-MS that COCl₂ *Carbonyl Chloride* (Phosgene) was formed as a transient decomposition product.

It was also found in preliminary experiments using the 250 µl sample loop, the *ChromPack PoraPLOT U* capillary column and the GC-MS that N₂O *Nitrous Oxide*, a representative of the nitrogen oxides, was formed as a decomposition by-product.

Although the production of *Ozone* (O₃) as a decomposition by-product was not specifically measured, its presence was confirmed by the typical "ozone smell" that developed when the electron beam was operated in the atmosphere.

Other decomposition products or decomposition by-products, if present at all, were either not separated on the column or their concentration was below the detection limit of the GC-MS.

Therefore, in this experiment, the CO, CO₂ and N₂O exhaust concentration as well as the CCl₄, COCl₂, Cl₂ and HCl exhaust concentration or ion abundance was measured as a function of the electron beam dose with the CCl₄ intake concentration and the relative humidity of air as parameters. In this experiment, dry air and wet air was used as the carrier gas for the gas mixing system.

The experiment was performed for a CCl₄ intake concentration of 278 ppm in dry
air, a CCl₄ intake concentration of 105 ppm in wet air of 9 %RH at 100 °F and a CCl₄ intake concentration of 224 ppm in wet air of 11 %RH at 100 °F. Two series of exhaust concentration measurements with a stepwise increase of the electron beam dose from zero to maximum value were performed for each intake concentration.

The 250 μl sample loop, the ChromPack MolSieve 5A capillary column and the GC-TCD were used for chemical analysis of CO. The 250 μl sample loop, the ChromPack PoraPLOT U capillary column and the GC-TCD were used for chemical analysis of CO₂ and N₂O.

Since CO and CO₂ or N₂O separate on different capillary columns and only one column may be in operation at any time, the first series of exhaust concentration measurements analyzed for CO, while the second series of exhaust concentration measurements analyzed for CO₂ and N₂O. Moreover, up to three exhaust concentration measurements were performed for each electron beam dose. These measurements were not averaged in order to indicate precision and reproducibility.

The SOR-MS was used for chemical analysis of CCl₄, COCl₂, Cl₂ and HCl. However, no standard of COCl₂ in a compressed gas cylinder could be obtained due to prohibitive safety requirements for the use of COCl₂ in the laboratory. In lack of a calibration of the SOR-MS for COCl₂, the exhaust ion abundance rather than the exhaust concentration was measured. An ion abundance measurement may still be as useful as a concentration measurement.

As a reminder, the ion abundance in a mass spectrum is roughly proportional to the number of ions of a particular mass to charge or M/Z ratio produced by a particular chemical compound in the ion source and passed through the mass filter of the mass spectrometer.

The N₂O exhaust concentration was measured as an indicator for the total NOₓ exhaust concentration. The exhaust concentration of the remaining NOₓ, i.e. NO, NO₂, NO₃, N₂O₄ and N₂O₅, may be assumed on the same order as the N₂O exhaust concentration.

This statement is based on the observation that the ion abundance of M/Z ratio 46 (NO₂) for NO₂ was determined in preliminary experiments to be on the same order as the ion abundance of M/Z ratio 44 (N₂O) for N₂O.
7.7.2 Measurement of CCl₄ Decomposition Products CO and CO₂ and CCl₄ Decomposition By-Product N₂O

The results of these measurements are shown in Figures 7.11, 7.12 and 7.13. The results for CO as well as the results for CO₂ and N₂O may be fitted to a \( \varphi = \varphi_\infty(1 - e^{-\alpha D}) \) function.

As may be seen from these figures, the sum of the CO and CO₂ exhaust concentration represents approximately 80 % of the 278 ppm CCl₄ intake concentration for dry air and approximately 100 % of the 105 ppm and 224 ppm CCl₄ intake concentration for wet air of 9 % and 11 % relative humidity, respectively. The electron beam dose required for such almost complete conversion of CCl₄ to CO and CO₂ in dry air is approximately half the electron beam dose required for this conversion in wet air.

Moreover, the N₂O represents approximately 100 ppm in dry air while it represents approximately 150 ppm in wet air at a comparable electron beam dose of approximately 15 Mrad. Therefore, the N₂O concentration appears to be higher in wet air than in dry air.

As a complement to these concentration measurements, Figures 7.14 and 7.15 represent additional CO and CO₂ exhaust concentration measurements obtained on other occasions.

These measurements indicate as well a nearly 100% conversion of CCl₄ to CO and CO₂. Also, it appears as though in every case the CO exhaust concentration is higher than the CO₂ exhaust concentration.

Since CO, CO₂ and N₂O are very non-reactive chemical compounds, standards of CO, CO₂ and N₂O in compressed gas cylinders are available at reliable concentrations. Therefore, the measurement of the CO, CO₂ and N₂O exhaust concentration may be considered reliable as well.

7.7.3 Measurement of CCl₄ and CCl₄ Decomposition Products COCl₂, Cl₂ and HCl

The exhaust ion abundance of the M/Z ratios 36 (HCl) for HCl, 70 (Cl₂) for Cl₂, 63 (COCl) for COCl₂ and 117 (CCl₃) for CCl₄ was measured and the exhaust ion abundance was deconvolved for the M/Z ratios 36, 70, and 117 via HPMSONE and HPMSTWO as discussed in Section 5.3.3 to yield the exhaust concentration.

The results of these measurements are shown in Figures 7.16, 7.17 and 7.18. In these figures, the exhaust concentration is shown on the left hand side y-axis, while
Figure 7.11: CCl₄ Decomposition Products and By-Products CO, CO₂ and N₂O in Dry Air for 278 ppm CCl₄ Intake Concentration
Figure 7.12: CCl₄ Decomposition Products and By-Products CO, CO₂, and N₂O in 9% RH Wet Air for 105 ppm CCl₄ Intake Concentration
Figure 7.13: CCl₄ Decomposition Products and By-Products CO, CO₂ and N₂O in 11 %RH Wet Air for 224 ppm CCl₄ Intake Concentration
Figure 7.14: CCl₄ Decomposition Products CO and CO₂ in Dry Air for 125ppm CCl₄ Intake Concentration
Figure 7.15: CCl₄ Decomposition Products CO and CO₂ in 10 %RH Wet Air for 142 ppm CCl₄ Intake Concentration
one tenth of the exhaust ion abundance is shown on the right hand side y-axis. The results for CCl₄ may be fitted to a \( \varphi = \varphi_0 e^{-\alpha D} \) function, the results for Cl₂ may be fitted to a \( \varphi = \varphi_\infty (1 - e^{-\alpha D}) \) function.

As an analogy to the area of radioactivity, the disappearance of CCl₄ and the appearance of COCl₂ and Cl₂ resemble very much a radioactive decay chain, where CCl₄ is the "radioactive" mother, COCl₂ is a shortlived "radioactive" daughter and Cl₂ is a stable daughter of the "radioactive" daughter. However, while in the area of radioactivity only unimolecular reactions take place, in the area of the present work unimolecular, bimolecular and termolecular reactions may take place.

Since CCl₄ is a very non-reactive chemical compound, standards of CCl₄ in compressed gas cylinders are available at very reliable concentrations. Therefore, the measurement of the CCl₄ exhaust concentration may be considered reliable as well.

Since HCl and Cl₂ are very reactive chemical compounds, standards of HCl and Cl₂ in compressed gas cylinders are not available at very reliable concentrations. Therefore, the measurement of the HCl and Cl₂ exhaust concentration may be considered rather unreliable as well.

As mentioned in Section 3.4, through original analysis and re-analysis of the concentrations of the HCl and the Cl₂ standard in their respective compressed gas cylinders by Matheson Gas Products, Gloucester, Massachusetts, it was established that these concentrations had decayed significantly over a period of several months. It is interesting to note that such decay was unheard of by Matheson Gas Products up to this point [141] and may be due to their use of compressed gas cylinders made from aluminum.

The experiment was performed in between the two dates of analysis, although the date of the experiment was closer to the date of the re-analysis than to the date of the original analysis.

The concentrations of HCl and Cl₂ in above figures were based on calibration of the SOR-MS shortly prior to the experiment, with concentrations of the HCl and Cl₂ standard as determined from the re-analysis. As can be seen from above figures, a chlorine underbalance was obtained. In a comparative test with concentrations of the HCl and Cl₂ standard as determined from the original analysis, a chlorine overbalance was obtained as expected.

Although an exponential decay of the concentrations of the HCl and the Cl₂ standard in their respective compressed gas cylinders due to unimolecular chemical reaction with the compressed gas cylinder wall or due to bimolecular reaction with impurities of the standard carrier gas may be assumed, the true time dependence of the decay in concentrations of the HCl and the Cl₂ standard is not known.
Figure 7.16: CCl₄ Decomposition Products HCl, Cl₂ and COCl₂ in Dry Air for 278 ppm CCl₄ Intake Concentration
Figure 7.17: CCl₄ Decomposition Products HCl, Cl₂ and COCl₂ in 9 %RH Wet Air for 105 ppm CCl₄ Intake Concentration
Figure 7.18: CCl₄ Decomposition Products HCl, Cl₂ and COCl₂ in 11 %RH Wet Air for 224 ppm CCl₄ Intake Concentration
The long lead time for ordering HCl and Cl₂ standards from Matheson Gas Products, Gloucester, Massachusetts and the considerable uncertainty as to the accurate concentration of the standards in their compressed gas cylinders made a second attempt at a better chlorine balance little promising.

However, despite the lack of an accurate knowledge of the concentrations of the HCl and the Cl₂ standard in their respective compressed gas cylinders, and thereby the lack of an accurate knowledge of the concentrations in this experiment, the qualitative dependence of the HCl and Cl₂ on the electron beam dose was expected to be correct. In particular, the achievement of a fairly complete carbon balance and the leveling out of the Cl₂ concentration with electron beam dose indicate the achievement of a fairly complete chlorine balance despite the uncertainties.

The assumption of a virtually complete carbon balance through CO and CO₂ at a high electron beam dose results in a very low COCl₂ exhaust concentration at such electron beam dose. The assumption of a virtually complete chlorine balance through HCl and Cl₂ at this electron beam dose may then be used to estimate the maximum COCl₂ exhaust concentration observed at a lower electron beam dose on the basis of Figures 7.11 and 7.16 as follows.

The complete conversion of CCL₄ to Cl₂ at a CCL₄ intake concentration of 278 ppm in dry air results in a Cl₂ exhaust concentration of 556 ppm. The ratio of this expected Cl₂ exhaust concentration to the Cl₂ exhaust concentration of 375 ppm measured on the basis of above rather uncertain Cl₂ calibration may then be used as a multiplier to obtain a more realistic Cl₂ exhaust concentration.

At an electron beam current of 0.5 mA, or an electron beam dose of approximately 1.58 Mrad, the Cl₂ exhaust concentration is therefore 334 ppm rather than the measured 225 ppm. In combination with a CCL₄ exhaust concentration of 75 ppm at this electron beam current or dose, the COCl₂ exhaust concentration results as 72 ppm.

Also, on the basis of a CO exhaust concentration of 60 ppm and a CO₂ exhaust concentration of 45 ppm at this electron beam dose, a CCL₄ intake concentration of 278 ppm and a CCL₄ exhaust concentration of 75 ppm result in a COCl₂ exhaust concentration of 98 ppm, which is very roughly consistent with above 72 ppm.

A similar calculation may be performed for Figures 7.13 and 7.18. With above multiplier, the Cl₂ exhaust concentration at a high electron beam current, or electron beam dose, results as 356 ppm rather than the measured 240 ppm. In combination with a negligible CCL₄ and COCl₂ exhaust concentration at this electron beam current or dose, the HCl exhaust concentration may be calculated as follows.

The complete conversion of CCL₄ to HCl and Cl₂ at a CCL₄ intake concentration of 224 ppm in wet air results in an effective Cl exhaust concentration of 896 ppm.
Since 712 ppm are already accounted for by the Cl₂, the remaining 184 ppm must correspond to the HCl exhaust concentration. The ratio of this expected HCl exhaust concentration to the HCl exhaust concentration of 120 ppm measured on the basis of above rather uncertain HCl calibration may be used as a multiplier to obtain a more realistic HCl exhaust concentration.

At an electron beam current of 1 mA, or an electron beam dose of 6 Mrad, the Cl₂ exhaust concentration is therefore 326 ppm rather than the measured 220 ppm. Also, the HCl exhaust concentration is therefore 92 ppm rather than the measured 60 ppm. In combination with a CCl₄ exhaust concentration of 30 ppm at this electron beam current or dose, the COCl₂ exhaust concentration results as 16 ppm.

Also, on the basis of a CO exhaust concentration of 85 ppm and a CO₂ exhaust concentration of 55 ppm at this electron beam dose, a CCl₄ intake concentration of 224 ppm and a CCl₄ exhaust concentration of 30 ppm result in a COCl₂ exhaust concentration of 54 ppm.

Finally, a similar calculation may be performed for Figures 7.12 and 7.17. With above multiplier, the Cl₂ exhaust concentration at a very high electron beam dose is 163 ppm rather than the measured 110 ppm. Also, with above multiplier, the HCl exhaust concentration at such electron beam dose is 69 ppm rather than the measured 45 ppm. The effective Cl exhaust concentration is therefore 395 ppm, which is very roughly consistent with the conversion of a CCl₄ intake concentration of 105 ppm in wet air to an effective Cl exhaust concentration of 420 ppm.

At an electron beam current of 0.25 mA, or an electron beam dose of 1.58 Mrad, the Cl₂ exhaust concentration is 111 ppm rather than the measured 75 ppm. Also, the HCl exhaust concentration at this electron beam current is 46 ppm rather than the measured 30 ppm. In combination with a CCl₄ exhaust concentration of 30 ppm at this electron beam current or dose, the COCl₂ exhaust concentration results as 16 ppm.

Also, on the basis of a CO exhaust concentration of 40 ppm and a CO₂ exhaust concentration of 20 ppm at this electron beam dose, a CCl₄ intake concentration of 105 ppm and a CCl₄ exhaust concentration of 30 ppm result in a COCl₂ exhaust concentration of 15 ppm, which is fairly consistent with above 16 ppm.

The exhaust concentration of COCl₂ appears to be higher in dry air than in wet air, indicating that the presence of water in fact reduces the COCl₂ concentration, potentially by conversion to HCl or Cl₂.

Also, since a carbon balance was definitely achieved and a chlorine balance was effectively achieved, the concentration of COCl₂ at a high electron beam dose may not be higher than several ppm. Moreover, at an electron beam dose where CCl₄ has
virtually disappeared, COCl₂ has virtually disappeared as well.

These considerations are also roughly consistent with an average ion abundance of approximately 100 and 500 for a concentration on the order of 10 ppm and 50 ppm, respectively, for many chemical compounds used for calibration of the SOR-MS.

Moreover, from Figure 7.17 it may be concluded that a fraction of Cl₂ is beginning to be converted to HCl at a sufficiently high electron beam dose in wet air.

7.8 Effect of Relative Humidity on C₂HCl₃ Decomposition

In order to determine the effect of the relative humidity of air on the decomposition of C₂HCl₃, an experiment was performed with dry air and wet air as the carrier gas for the gas mixing system. The C₂HCl₃ exhaust concentration was measured as a function of the electron beam dose. The SOR-MS was used for chemical analysis via measurement of the exhaust ion abundance for M/Z ratio 130 and conversion to the exhaust concentration.

The experiment was performed for a C₂HCl₃ intake concentration of 517 ppm in dry air and a C₂HCl₃ intake concentration of 490 ppm in wet air of 11%RH at 100°F. Two series of exhaust concentration measurements were performed for each intake concentration. In each series, the electron beam dose was increased stepwise from zero to the maximum value.

The results are presented in Figure 7.19. Here, the first series of exhaust concentration measurements is shown with symbols, the second series is shown without symbols in order to indicate precision and reproducibility.

A pronounced difference in the exhaust concentration of CCl₄ and CHCl₃ as a function of the electron beam dose was observed for wet and dry air, while no such pronounced difference was observed in the exhaust concentration of C₂HCl₃.

Moreover, based on Figure 7.1, an electron beam dose of 25 Mrad would have been required to reduce a CCl₄ intake concentration of 677 ppm in dry air to 1 ppm. Based on Figure 7.19, an electron beam dose of only 1.5 Mrad was sufficient to reduce a C₂HCl₃ intake concentration of 517 ppm in dry (and wet) air to 1 ppm.

Therefore, the decomposition efficiency for C₂HCl₃ may be an order of magnitude higher than the decomposition efficiency for CCl₄. As a contrast to CCl₄ and CHCl₃, this is a strong indication for initiation or continuation of the decomposition of C₂HCl₃ through a chemical reaction other than bimolecular dissociative electron attachment.
Figure 7.19: Effect of Relative Humidity on C₂HCl₃ Decomposition in Dry Air for 517 ppm C₂HCl₃ Intake Concentration and in 11 %RH Wet Air for 490 ppm C₂HCl₃ Intake Concentration
7.9 Measurement of C$_2$HCl$_3$ and C$_2$HCl$_3$ Decomposition Products C$_2$HCl$_3$O, COCl$_2$, Cl$_2$ and HCl

As for CCl$_4$, CO Carbon Monoxide and CO$_2$ Carbon Dioxide as well as HCl Hydrogen Chloride and Cl$_2$ Chlorine are desired decomposition products for C$_2$HCl$_3$ as well.

Moreover, it was found in preliminary experiments using the 2 µl sample loop, the Hewlett-Packard HP-5 capillary column and the GC-MS that COCl$_2$ Carbonyl Chloride (Phosgene) and C$_2$HCl$_3$O Dichloro Acetyl Chloride were formed as transient decomposition products.

Other decomposition products or decomposition by-products, if present at all, were either not separated on the column or their concentration was below the detection limit of the GC-MS.

In the limited framework of this experiment, the CO, CO$_2$ and N$_2$O exhaust concentration was not measured. However, the C$_2$HCl$_3$, C$_2$HCl$_3$O, COCl$_2$, Cl$_2$ and HCl exhaust concentration or exhaust ion abundance was measured as a function of the electron beam dose. These measurements were obtained in combination with the previous experiment performed to investigate the effect of relative humidity on the decomposition.

The SOR-MS was used for chemical analysis of C$_2$HCl$_3$, C$_2$HCl$_3$O, COCl$_2$, Cl$_2$ and HCl. The exhaust ion abundance for the M/Z ratios 36 (HCl) for HCl, 70 (Cl$_2$) for Cl$_2$, 63 (COCl) for COCl$_2$, 83 (CHCl$_2$) for C$_2$HCl$_3$O and 130 (C$_2$HCl$_3$) for C$_2$HCl$_3$ was measured. The exhaust ion abundance was deconvolved for the M/Z ratios 36, 70 and 130 via HPMSONE and HPMSTWO as discussed in Section 5.3.3 to yield the exhaust concentration.

However, no standard of COCl$_2$ or C$_2$HCl$_3$O in a compressed gas cylinder could be obtained due to prohibitive safety requirements for the use COCl$_2$ or C$_2$HCl$_3$O in the laboratory. Moreover, a vendor for a C$_2$HCl$_3$O standard in a compressed gas cylinder could not be identified. In lack of a calibration of the SOR-MS for COCl$_2$ and C$_2$HCl$_3$O, the exhaust ion abundance rather than the exhaust concentration was measured.

The results are presented in Figures 7.20 and 7.21. Here, only the first of the two series of exhaust concentration measurements is shown in order to avoid information overload in these figures. The precision and reproducibility were comparable to those observed for the experiment investigating the CCl$_4$ decomposition products. The results for C$_2$HCl$_3$ may be fitted to a $\varphi = \varphi_0 e^{-\alpha D}$ function, the results for Cl$_2$ may
be fitted to a \( \varphi = \varphi_\infty (1 - e^{-\alpha D}) \) function.

It is important to note that the M/Z ratio 83 (CHCl₂) is produced only by C₂HCl₃O, even though an unlikely contribution to this M/Z ratio through potentially formed CHCl₂ may be possible. The M/Z ratio 63 (COCl₂) is produced to a large fraction by COCl₂ and to a small fraction by C₂HCl₃O. Without standards for calibration of the SOR-MS for COCl₂ and C₂HCl₃O, it was impossible to deconvolve the concentrations. Moreover, above figures show the exhaust ion abundance of the M/Z ratio 63 and ascribe this abundance to COCl₂, even though it originates from COCl₂ and C₂HCl₃. A qualitative argument with respect to these exhaust ion abundances may be made along the following lines.

When the exhaust ion abundance as a function of electron beam dose runs parallel for the M/Z ratios 63 and 83, the actual COCl₂ exhaust concentration must be constant. When the exhaust ion abundances as a function of electron beam dose converge for these M/Z ratios, the actual COCl₂ exhaust concentration must increase and the actual C₂HCl₃O concentration must decrease.

For dry and wet air, these exhaust ion abundances converge. As will be seen in the framework of the interpretation of the experimental results, this indeed should correspond to a conversion of C₂HCl₃O to COCl₂. Moreover, such convergence is stronger in dry air than in wet air. Also, the COCl₂ and C₂HCl₃O exhaust ion abundance are comparable for dry and wet air.

The exhaust ion abundance for the M/Z ratio 83, i.e. C₂HCl₃O, is highest at the electron beam dose where the exhaust concentration of C₂HCl₃ has just reached virtually zero. Above this electron beam dose, the experiment could be viewed as the Cold Plasma Decomposition of C₂HCl₃O, rather than that of C₂HCl₃.

Again, as in the case of CCl₄ decomposition, an analogy to the area of radioactivity may be invoked, where COCl₂ is a longlived “radioactive” daughter of the very longlived “radioactive” daughter C₂HCl₃O of the mother C₂HCl₃. Also, HCl and Cl₂ are the stable daughters of the longlived “radioactive” daughter.

Since C₂HCl₃ is a very non-reactive chemical compound, standards of C₂HCl₃ in compressed gas cylinders are available at very reliable concentrations. Therefore, the measurement of the C₂HCl₃ exhaust concentration may be considered rather reliable as well. However, for HCl and Cl₂ the remarks made in the context of the investigation of the CCl₄ decomposition products hold.

For dry air, the HCl concentration appears to be comparable to the Cl₂ concentration, while for wet air, the HCl concentration appears to be larger than the Cl₂ concentration. The calibration of the SOR-MS for HCl and Cl₂ was performed several weeks later than the experiment, because the HCl and Cl₂ standards in compressed
Figure 7.20: C₂HCl₃ Decomposition Products HCl, Cl₂, COCl₂ and C₂HCl₃O in Dry Air for 517 ppm C₂HCl₃ Intake Concentration
Figure 7.21: C₂HCl₃ Decomposition Products HCl, Cl₂, COCl₂ and C₂HCl₃O in 11% RH Wet Air for 490 ppm C₂HCl₃ Intake Concentration
gas cylinders were not available at the time of the experiment.

A comparison of a calibration of the SOR-MS for C₂HCl₃ from the date of the experiment and from the date when the HCl and Cl₂ calibration was performed indicates that the calibration for C₂HCl₃ had not changed significantly. Therefore it was assumed that the calibration for HCl and Cl₂ had not changed significantly either.

However, when such HCl and Cl₂ calibration was used for above investigation of the C₂HCl₃ decomposition products, a chlorine overbalance was obtained. This indicates that at the time of calibration of the SOR-MS for HCl and Cl₂, a decrease in the certified concentration of the HCl and Cl₂ standards in their respective compressed gas cylinders had already occurred, potentially during transport of these cylinders.

Therefore, a similar problem was encountered for the exhaust concentration measurement of HCl and Cl₂ in the investigation of the decomposition products of C₂HCl₃ as was in the investigation of the decomposition products of CCl₄. Nevertheless, a re-analysis as in the case of the HCl and Cl₂ standards used for calibration of the SOR-MS for investigation of the CCl₄ decomposition products was not performed.

An upper estimate for the combined COCl₂ and C₂HCl₅O exhaust concentration may be obtained under the assumption that the certified concentration of HCl and Cl₂ in the compressed gas cylinders had decreased to 60 % of that obtained in the original analysis through Matheson Gas Products.

In Figure 7.20, at a high electron beam dose, the HCl and Cl₂ exhaust concentration then is approximately 480 ppm and 450 ppm rather than the measured 800 ppm and 750 ppm, respectively. With a C₂HCl₃ intake concentration of 517 ppm the expected effective Cl exhaust concentration is 1551 ppm. Since 960 ppm and 375 ppm are accounted for, the resulting effective Cl exhaust concentration of 216 ppm would correspond to an exclusive COCl₂ exhaust concentration of 108 ppm or an exclusive C₂HCl₅O exhaust concentration of 72 ppm.

This is very roughly consistent with an average ion abundance of approximately 1000 corresponding to a concentration on the order of 100 ppm for many chemical compounds used for calibration of the SOR-MS. Moreover, a similar argument may be considered in Figure 7.21 to result in comparable concentrations.

The assumed decrease in the concentration of the HCl and Cl₂ standard to 60 % of the certified concentration is rather high and a more realistic decrease may be by 30 % rather than 40 %. In this case, however, the C₂HCl₃ or COCl₂ exhaust concentration would be expected to be almost negligible.

Apparently, for future experiments, strong emphasis has to be placed on the timely
calibration of the SOR-MS for HCl and Cl₂. This calibration must be performed immediately upon receipt of the compressed gas cylinders and as close as possible to the date of the experiment. This represents simply a scheduling difficulty.

7.10 Effect of Electric Field on C₂HCl₃ Decomposition

At this point it was apparent that, when compared to the decomposition of CCl₄, dissociative electron attachment alone could not be expected to be responsible for the decomposition of C₂HCl₃ on the basis of the much lower electron beam dose required for a particular destruction and removal efficiency. Therefore, an effect of the electric field on C₂HCl₃ decomposition was not expected.

This experiment was performed nevertheless, because it was found that C₂HCl₃ has a similar bimolecular dissociative electron attachment reaction rate constant as CHCl₃ [69]. This is also discussed in Section 2.3.2. Moreover, the decomposition of CHCl₃ was investigated in an earlier experiment and is expected to be roughly consistent with bimolecular dissociative electron attachment.

Two series of measurements of the C₂HCl₃ exhaust concentration as a function of the electric field were performed. In each series, the electric field was increased stepwise from zero to the maximum value. Dry air was used as the carrier gas for the gas mixing system. The SOR-MS was used to measure the exhaust concentration of C₂HCl₃ via the exhaust ion abundance of M/Z ratio 130 and conversion to the exhaust concentration.

The results of these measurements are presented in Figure 7.22. The first series of exhaust concentration measurements is shown with symbols, the second series is shown without symbols in order to indicate precision and reproducibility.

Although the precision and reproducibility are not excellent, an effect of the electric field on the decomposition of C₂HCl₃ is reproducibly observed. This indicates that bimolecular dissociative electron attachment to C₂HCl₃ may after all be involved in the decomposition of C₂HCl₃.
Figure 7.22: Effect of Electric Field on C₂HCl₃ Decomposition in Dry Air
Chapter 8

Interpretation of Experimental Results

8.1 Scope of Interpretation

A comprehensive and consistent interpretation of all experimental observations is extremely difficult in view of missing and inconsistent information on chemical reactions and reaction rate constants. In fact, on the basis of the multivariate nature of a physical-chemical process such as the cold plasma decomposition of chlorinated organic compounds, it is the firm opinion of the author that such an interpretation is virtually impossible.

Nevertheless, it appears to be possible to explain selected aspects of the experimental observations through selected qualitative and semi-quantitative physical-chemical models, although it is not easily possible to integrate these models into a thorough understanding of the cold plasma decomposition of chlorinated organic compounds.

Such an explanation of selected aspects of the experimental observations in the investigation of the decomposition of Tetrachloro Methane CCl₄, Trichloro Methane CHCl₃ and Trichloro Ethene C₂HCl₃ through Cold Plasma Decomposition in a Tunable Plasma Reactor will be presented in the following.

In particular, many experimental observations are consistent with the decomposition of CCl₄, CHCl₃ and C₂HCl₃ through bimolecular dissociative electron attachment. Therefore, such electron attachment is the focus of the discussion.

However, in addition to electron attachment, additional chemical reactions very likely have to be invoked for a comprehensive explanation of all experimental observations. Unfortunately, these additional chemical reactions are still largely unknown.
On this basis, the decomposition in dry air is understood best and therefore another focus of the discussion.

In the framework of a qualitative discussion of the decomposition, chemical reactions that explain some experimental observations are presented for CCl₄, CHCl₃ and C₂HCl₃. In the framework of a semi-quantitative discussion, a proof for the decomposition of CCl₄ through bimolecular dissociative electron attachment in dry air as well as a heuristic equation for prediction of the CCl₄ exhaust concentration as a function of the intake concentration and the electron beam dose in dry air are presented.

The formulation of such a heuristic equation was mainly possible because of the more comprehensive experimental investigation of the decomposition of CCl₄ compared to the less comprehensive experimental investigation of the decomposition of CHCl₃ and C₂HCl₃.

8.2 Qualitative Discussion of CCl₄ and CHCl₃ Decomposition

8.2.1 CCl₄ and CHCl₃ Decomposition

The bimolecular dissociative electron attachment reaction rate constants for CCl₄ and CHCl₃ are among the highest experimentally observed for chemical compounds [32], [69]. In fact, only Sulfur Hexafluoride (SF₆) has a higher bimolecular dissociative electron attachment reaction rate constant than CCl₄. Therefore, it appears to be reasonable to explain the decomposition of CCl₄ and CHCl₃ in terms of such electron attachment.

However, decomposition of CCl₄ and CHCl₃ could be accomplished via attack through O(^1D) oxygen, OH hydroxyl and Cl chlorine radicals as well. Therefore, it is helpful to compare the reaction rate constants for bimolecular dissociative electron attachment to those for bimolecular dissociative radical attack through O(^1D), OH and Cl. These reaction rate constants are given in the literature as:

\[
\begin{align*}
e^- + CCl_4 & \rightarrow CCl_3 + Cl^- \quad k = 2.5 \times 10^{-7} \text{ cm}^3/\text{s} \quad [32],[69],[142] \\
e^- + CHCl_3 & \rightarrow CHCl_2 + Cl^- \quad k = 5.0 \times 10^{-9} \text{ cm}^3/\text{s} \quad [32],[69],[142] \\
o(D) + CCl_4 & \rightarrow \text{Products} \quad k = 3.3 \times 10^{-10} \text{ cm}^3/\text{s} \quad [72],[143] \\
OH + CCl_4 & \rightarrow \text{Products} \quad k < 4.0 \times 10^{-15} \text{ cm}^3/\text{s} \quad [72] \\
OH + CHCl_3 & \rightarrow \text{Products} \quad k = 1.0 \times 10^{-13} \text{ cm}^3/\text{s} \quad [72] \\
Cl + CHCl_3 & \rightarrow \text{Products} \quad k = 1.5 \times 10^{-13} \text{ cm}^3/\text{s} \quad [144]
\end{align*}
\]
For CCl₄, this indicates that the O(¹D) concentration must be 760 times higher and the OH concentration must be 62,500,000 higher than the electron concentration in order to result in a comparable decomposition reaction rate. With respect to OH, this appears to be very unlikely.

Also, as calculated in Section 2.6.6, the O(¹D) concentration in dry air was up to two orders of magnitude lower than the electron concentration in dry air. Therefore, the O(¹D) concentration appears likely not to be significantly higher than the electron concentration even in the presence of CCl₄ in dry air.

For CHCl₃, this indicates that the OH concentration must be 50,000 times higher and the Cl concentration must be 33,333 higher than the electron concentration in order to result in a comparable decomposition reaction rate. Again, for OH and Cl, this appears to be very unlikely.

Moreover, as will be seen in the qualitative discussion of the C₂HCl₃ decomposition, the reaction rate constant for chemical reaction of C₂HCl₃ with Cl is two orders of magnitude higher than that for chemical reaction of CHCl₃ with Cl. Also, the chemical reaction of C₂HCl₃ with Cl is a chain reaction in which the Cl radical is not consumed. No such chain reaction was found in the literature for the chemical reaction of CHCl₃ with Cl.

Therefore, in dry air, the attack on CCl₄ through O(¹D) or OH as well as the attack on CHCl₃ through OH or Cl are very likely insignificant in comparison to bimolecular dissociative electron attachment to CCl₄.

### 8.2.2 Reaction Mechanism of CCl₄ and CHCl₃ Decomposition

On the basis of the foregoing argument, the decomposition of CCl₄ and CHCl₃ is assumed to be effected through bimolecular dissociative electron attachment. The chemical reactions subsequent to the decomposition involve radicals and result in the formation of the experimentally observed stable chemical species CO, CO₂, HCl and Cl₂ via the transient chemical species COCl₂ [145], [146], [147], [148].

While this reflects a fairly complete understanding of the decomposition of CCl₄ and CHCl₃ in dry air and dry oxygen, the understanding of such decomposition in wet air and wet oxygen is much less complete and is not discussed here.

The decomposition of CCl₄ results in the formation of the Trichloro Methyl radical (CCl₃) through electron attachment to CCl₄. The oxidation of CCl₃ to Carbonyl Chloride (COCl₂) and the bimolecular dissociative electron attachment to and chlo-
rine attack on COCl\textsubscript{2} result in the formation of COCl. These chemical reactions may be summarized as:

\[
\begin{align*}
\text{CCl}_4 + e^- & \rightarrow \text{CCl}_3 + Cl^- \\
\text{CCl}_3 + O & \rightarrow \text{COCl}_2 + Cl \\
\text{CCl}_3 + O_2 & \rightarrow \text{COCl}_2 + ClO \\
\text{CCl}_3 + Cl_2 & \rightarrow \text{CCl}_4 + Cl \\
\text{COCl}_2 + e^- & \rightarrow \text{COCl} + Cl^- \\
& \quad \rightarrow CO + Cl_2^- \\
\text{COCl}_2 + Cl & \rightarrow \text{COCl} + Cl_2 \\
\end{align*}
\]

Also, the decomposition of CHCl\textsubscript{3} results in the formation of the *Dichloro Methyl* radical (CHCl\textsubscript{2}) through electron attachment to CHCl\textsubscript{3}. The oxidation of CHCl\textsubscript{2} to *Formyl Chloride* (COHCl) and the chlorine attack on COHCl again result in the formation of COCl. These chemical reactions may be summarized as:

\[
\begin{align*}
\text{CHCl}_3 + e^- & \rightarrow \text{CHCl}_2 + Cl^- \\
\text{CHCl}_2 + O & \rightarrow \text{COHCl} + Cl \\
\text{CHCl}_2 + O_2 & \rightarrow \text{COHCl} + ClO \\
\text{COHCl} + Cl & \rightarrow \text{COCl} + HCl \\
\end{align*}
\]

Obviously, the O\textsubscript{2} is not only used directly in the oxidation of CCl\textsubscript{3} and CHCl\textsubscript{3}, but is also used indirectly via appropriate G-Values to provide O radicals, such as O(\textsuperscript{3}P) and O(\textsuperscript{1}D), for the oxidation of these and other intermediate chemical species of the decomposition.

In particular, the decomposition of COCl through oxidation results in the formation of CO, CO\textsubscript{2}, Cl, Cl\textsubscript{2}. The chemical reactions for COCl may be summarized as:

\[
\begin{align*}
\text{COCl} + O & \rightarrow \text{CO}_2 + Cl \\
& \quad \rightarrow CO + ClO \\
\text{COCl} + O_2 & \rightarrow \text{CO}_2 + ClO \\
\text{COCl} + Cl & \rightarrow \text{CO} + Cl_2 \\
\end{align*}
\]

The Cl and the *Chlorine Oxide* (ClO) formed in above chemical reactions may become part of the chlorine-oxygen cycle, which is well known from atmospheric
chemistry [149], [150] and which is described for example in [151]. This cycle is responsible for the Ozone \((O_3)\) depletion in the earth's upper atmosphere. In the present work, \(O_3\) is produced as a decomposition by-product in air and in oxygen. The most prominent chemical reactions of the chlorine-oxygen cycle as described in [151] may be summarized as:

\[
\begin{align*}
2Cl & \rightarrow Cl_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + O & \rightarrow Cl + O_2 
\end{align*}
\]

For \(CCl_4\), above chemical reaction mechanism is consistent with the experimentally observed formation of \(COCl_2\) as a transient chemical species and the experimentally observed formation of \(CO\) and \(Cl_2\) as stable chemical species. A fraction of the \(CO\) may be converted to \(CO_2\). Moreover, in wet rather than dry air, a fraction of the \(Cl_2\) may be converted to \(HCl\).

The "back reaction" for re-formation of \(CCl_4\) from \(CCl_3\) deserves attention. In argon, nitrogen, air and oxygen, electrons are generated via comparable G-Values. Also, if the electron concentration in these gases is controlled by bimolecular dissociative electron attachment to \(CCl_4\), a comparable decomposition efficiency for \(CCl_4\) is expected in these gases.

However, the experimentally observed lack of significant decomposition of \(CCl_4\) in nitrogen and argon appears to indicate that the initial decomposition of \(CCl_4\) through electron attachment is eventually reversed through re-formation of \(CCl_4\) via the "back reaction".

If the "back reaction" was sufficiently fast, it could explain the difference in decomposition efficiency between dry air and dry oxygen along similar lines. With increasing \(O_2\) concentration, the \(CCl_3\) reacts to form \(CCl_3O_2\) rather than re-form \(CCl_4\).

It must be pointed out, however, that according to [146] and [147], the reaction rate constant for the "back reaction" may be comparable to or lower than the reaction rate constant for oxidation. Therefore, such "back reaction" may not be able to compete against oxidation of \(CCl_3\) at \(O_2\) concentrations comparable to or higher than the maximum expected \(Cl_2\) concentration.

Hence, while the difference in the \(CCl_4\) decomposition efficiency between argon or nitrogen and air or oxygen may be explained conclusively by such a "back reaction", the difference in the \(CCl_4\) decomposition efficiency between air and oxygen may not be explained conclusively by this "back reaction".
8.3 Electron Attachment Frequencies

8.3.1 General Considerations

In contrast to CCl₄, CHCl₃ and C₂HCl₃, which react with electrons via bimolecular dissociative electron attachment, the O₂ present in air or oxygen reacts with electrons via termolecular non-dissociative electron attachment [80], [152], [153].

The electron attachment reaction rate constant is much lower for O₂ than for CCl₄, CHCl₃, or C₂HCl₃, while the concentration is much higher for O₂ than for CCl₄, CHCl₃ or C₂HCl₃.

Moreover, the reaction rate constant for termolecular non-dissociative electron attachment to O₂ depends on the "third body". For the present work, only O₂, N₂ and H₂O have sufficiently high concentrations to be of interest as a "third body".

Therefore, the combination of reaction rate constant and concentration may result in competition for electrons between O₂ and CCl₄, CHCl₃ or C₂HCl₃. The competition may be characterized via the electron attachment frequency.

The electron attachment frequency is the product of the electron attachment reaction rate constant, the concentration of the electron attaching chemical species and, for termolecular electron attachment, the concentration of the "third body".

The electron attachment frequency is an estimate of the disappearance rate of electrons due to electron attachment. Moreover, attachment frequencies may be calculated not only for O₂ and above chlorinated organic compounds, but also for decomposition products and decomposition by-products.

When the electron attachment frequencies for two different chemical species are comparable to within one order of magnitude, these chemical species may be competitors for electron attachment.

For the calculation of the electron attachment frequencies, ideal gas conditions at atmospheric pressure (1.01325 · 10⁵ Pa) and temperature (298.15 K) are assumed. Therefore, the total concentration is approximately 2.5 · 10¹⁹ 1/cm³.

8.3.2 O₂, CCl₄, CHCl₃ and C₂HCl₃

In order to calculate the electron attachment frequencies for O₂, CCl₄, CHCl₃ and C₂HCl₃, the electron attachment reaction rate constants are required. These reaction
rate constants are found in the literature and may be reliable to within a factor of two:

\[
\begin{align*}
e^- + 2O_2 & \rightarrow O^- + O_2 \quad k_a = 2.0 \times 10^{-30} \text{ cm}^6/\text{s} \quad [80],[153],[154] \\
e^- + O_2 + N_2 & \rightarrow O^- + N_2 \quad k_a = 1.5 \times 10^{-31} \text{ cm}^6/\text{s} \quad [80],[153] \\
e^- + CCl_4 & \rightarrow CCl_3 + Cl^- \quad k_a = 2.5 \times 10^{-7} \text{ cm}^3/\text{s} \quad [32],[69],[142] \\
e^- + CHCl_3 & \rightarrow CHCl_2 + Cl^- \quad k_a = 5.0 \times 10^{-9} \text{ cm}^3/\text{s} \quad [32],[69],[142] \\
e^- + C_2HCl_3 & \rightarrow C_2HCl_2 + Cl^- \quad k_a = 2.0 \times 10^{-9} \text{ cm}^3/\text{s} \quad [69]
\end{align*}
\]

The attachment frequencies for typical concentrations of O2, CCl4, CHCl3 and C2HCl3 result as:

\[
\begin{align*}
20\%, \ 80\% \ O_2, N_2 (\text{Air}) & \quad \nu_a = 6.50 \times 10^7 \text{ 1/s} \\
100\% \ O_2 & \quad \nu_a = 1.25 \times 10^8 \text{ 1/s} \\
100 \text{ ppm} \ CCl_4 & \quad \nu_a = 6.25 \times 10^6 \text{ 1/s} \\
10 \text{ ppm} \ CCl_4 & \quad \nu_a = 6.25 \times 10^7 \text{ 1/s} \\
100 \text{ ppm} \ CHCl_3 & \quad \nu_a = 1.25 \times 10^7 \text{ 1/s} \\
10 \text{ ppm} \ CHCl_3 & \quad \nu_a = 1.25 \times 10^6 \text{ 1/s} \\
100 \text{ ppm} \ C_2HCl_3 & \quad \nu_a = 5.00 \times 10^6 \text{ 1/s} \\
10 \text{ ppm} \ C_2HCl_3 & \quad \nu_a = 5.00 \times 10^5 \text{ 1/s}
\end{align*}
\]

Therefore, with the exception of CCl4 in dry air, the O2 in dry air and dry oxygen appears to control the electron concentration of the cold plasma via termolecular non-dissociative electron attachment. In particular, the CCl4 decomposition efficiency should be higher in dry air than in dry oxygen. However, the opposite is experimentally observed. This apparent contradiction is currently not understood, even when the previously mentioned "back reaction" is invoked.

Also, since for CCl4 in dry air, the CCl4 appears to control the electron concentration and for CHCl3 or C2HCl3 in dry air, the O2 appears to control the electron concentration, the effect of the electric field may be expected stronger for CHCl3 and C2HCl3 than for CCl4. This is because an increase in the electron attachment reaction rate constant for CHCl3 and C2HCl3 shifts the electron loss from O2 to CHCl3 and C2HCl3, while such an increase does not cause such a shift for CCl4. This stronger effect of the electric field on the CHCl3 and C2HCl3 decomposition compared to the CCl4 decomposition is in fact experimentally observed.

The exceptional position of CCl4 with respect to O2 justifies a distinction between the case of a low CCl4 intake concentration and the case of a high CCl4 intake concentration with respect to the O2 concentration for the subsequent semi-quantitative
discussion of the CCl₄ decomposition in dry air. Moreover, this exceptional position made possible the derivation of a heuristic equation for the CCl₄ decomposition in dry air in this semi-quantitative discussion.

It may be noted that the bimolecular dissociative electron attachment reaction rate constant to halogenated methanes and ethenes typically increases with temperature. However, for CCl₄, CHCl₃ and very likely C₂HCl₃, such reaction rate constant is expected not to increase significantly in the temperature range of interest to the present work [155], [156].

8.3.3 HCl, Cl₂ and COCl₂

As will be seen in the subsequent semi-quantitative discussion of the CCl₄ decomposition in dry air, the experimentally observed CCl₄ exhaust concentration as a function of the electron beam dose is in agreement with bimolecular dissociative electron attachment up to a destruction and removal efficiency of approximately 70%. This holds for a sufficiently high CCl₄ intake concentration and then also holds independently of the CCl₄ intake concentration.

At a higher destruction and removal efficiency, the experimentally observed CCl₄ exhaust concentration is higher than that which would be in agreement with bimolecular dissociative electron attachment. This indicates competition with CCl₄ for electron attachment in dry air through decomposition products or through decomposition by-products.

The approximate invariance of above 70% with CCl₄ intake concentration for a sufficiently high CCl₄ intake concentration suggests the competition through decomposition products rather than through decomposition by-products at a destruction and removal efficiency higher than 70%.

In order to assess such competition through the electron attachment frequencies for HCl, Cl₂ and COCl₂ as the most important decomposition products, the electron attachment reaction rate constants are required. These reaction rate constants are again found in the literature and may be reliable to within a factor of ten:

\[
\begin{align*}
\text{e}^- + \text{COCl}_2 & \rightarrow \text{COCl} + \text{Cl}^- \quad k_a = 5.0 \cdot 10^{-8} \text{ cm}^3/\text{s} \quad [142] \\
& \rightarrow \text{CO} + \text{Cl}_2^- \\
\text{e}^- + \text{Cl}_2 & \rightarrow \text{Cl} + \text{Cl}^- \quad k_a = 1.0 \cdot 10^{-9} \text{ cm}^3/\text{s} \quad [142],[157],[158] \\
\text{e}^- + \text{HCl} & \rightarrow \text{H} + \text{Cl}^- \quad k_a = 1.0 \cdot 10^{-10} \text{ cm}^3/\text{s} \quad [158]
\end{align*}
\]

The attachment frequencies for typical concentrations of HCl, Cl₂ and COCl₂ result
as:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Species</th>
<th>( \nu_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm</td>
<td>HCl</td>
<td>( 2.50 \cdot 10^5 ) 1/s</td>
</tr>
<tr>
<td>500 ppm</td>
<td>HCl</td>
<td>( 1.25 \cdot 10^6 ) 1/s</td>
</tr>
<tr>
<td>100 ppm</td>
<td>Cl(_2)</td>
<td>( 5.00 \cdot 10^6 ) 1/s</td>
</tr>
<tr>
<td>500 ppm</td>
<td>Cl(_2)</td>
<td>( 2.50 \cdot 10^7 ) 1/s</td>
</tr>
<tr>
<td>50 ppm</td>
<td>COCl(_2)</td>
<td>( 6.25 \cdot 10^7 ) 1/s</td>
</tr>
</tbody>
</table>

Therefore, COCl\(_2\) and Cl\(_2\) represent a potential competition for electron attachment to CCl\(_4\), CHCl\(_3\) or C\(_2\)HCl\(_3\), although such competition is expected to be less pronounced for CCl\(_4\) than for CHCl\(_3\) or C\(_2\)HCl\(_3\).

Moreover, upon closer examination, it is striking that the experimentally observed COCl\(_2\) exhaust concentration in dry air seems to assume its maximum at an electron beam dose where the destruction and removal efficiency for CCl\(_4\) in dry air is on the order of 70\%.

The CCl\(_4\) is decomposed into the decomposition products COCl\(_2\) and Cl\(_2\). At a low electron beam dose, the CCl\(_4\) exhaust concentration is rather high and the COCl\(_2\) exhaust concentration is higher than the Cl\(_2\) exhaust concentration. At a high electron beam dose, the CCl\(_4\) exhaust concentration is rather low and the COCl\(_2\) exhaust concentration is lower than the Cl\(_2\) exhaust concentration. Therefore, COCl\(_2\) at a low electron beam dose and Cl\(_2\) at a high electron beam dose may be dominantly competing with CCl\(_4\) for electron attachment, respectively.

Hence, if CCl\(_4\) is considered the reactant \( R \) and the sum of COCl\(_2\) and Cl\(_2\) is considered the product \( P \), the following consideration provides an estimate for the average electron attachment reaction rate constant required for the product to be in competition for electron attachment with the reactant at a destruction and removal efficiency of greater than 70\%.

The exhaust concentration \( N_P \) and \( N_R \) of the product and the reactant are given as a function of the destruction and removal efficiency \( \eta_R \) and the intake concentration \( N_R^0 \) of the reactant under the assumption of production of two product molecules per destruction of one reactant molecule:

\[
N_P = 2(N_R^0 - N_R) = 2\eta_R N_R^0
\]

\[
N_R = N_R^0 - (N_R^0 - N_R) = (1 - \eta_R)N_R^0
\]

Under the assumption that the attachment frequency for the product must be at
least one tenth of the attachment frequency for the reactant in order to represent a competition for electron attachment, the following ratio of the electron attachment reaction rate constant for the product $k_a(P)$ and the reactant $k_a(R)$ may be derived:

$$
k_a(P)N_P > \frac{1}{10}k_a(R)N_R
$$

$$
2k_a(P)\eta_R > \frac{1}{10}k_a(R)(1 - \eta_R)
$$

$$
k_a(P) \frac{1}{k_a(R)} > \frac{1}{20} \left[ \frac{1}{\eta_R} - 1 \right]
$$

With $\eta_R = 0.7$, this ratio becomes approximately $k_a(P) \approx 2 \cdot 10^{-2}$, i.e. with $k_a(R) = 2.5 \cdot 10^{-7}$ cm$^3$/s it follows $k_a(P) = 5 \cdot 10^{-9}$ cm$^3$/s. This is roughly on the order of the electron attachment reaction rate constant for COCl$_2$ or Cl$_2$.

### 8.3.4 O$_3$, NO$_2$ and N$_2$O

Since the exhaust concentration of decomposition by-products is a function of the electron beam dose and relatively independent of the CCl$_4$ intake concentration, the competition of decomposition by-products with CCl$_4$ for electron attachment would very likely not exhibit a relatively constant destruction and removal efficiency at which above deviation takes place.

In order to calculate the electron attachment frequencies for O$_3$, NO$_2$ and N$_2$O as the most important decomposition by-products, the electron attachment reaction rate constants are required. These reaction rate constants are again found in the literature and may be reliable to within a factor of ten to one hundred:

$$
e^- + O_3 \rightarrow O^- + O_2 \quad k_a < 1.0 \cdot 10^{-11} \text{ cm}^3/\text{s} \quad [159]
e^+ + NO_2 \rightarrow NO_2^- \quad k_a < 2.0 \cdot 10^{-10} \text{ cm}^3/\text{s} \quad [159],[160]
e^- + N_2O \rightarrow O^- + N_2 \quad k_a < 4.0 \cdot 10^{-15} \text{ cm}^3/\text{s} \quad [161],[162]
e^- + 2N_2O \rightarrow N_2O^- + N_2O \quad k_a < 6.0 \cdot 10^{-33} \text{ cm}^6/\text{s} \quad [159],[163]
$$

The attachment frequencies for typical concentrations of O$_3$, NO$_2$ and N$_2$O result as:
Although a reaction rate constant of \( k_a < 1.0 \cdot 10^{-7} \text{ cm}^3/\text{s} \) is presented in [159] for the bimolecular dissociative electron attachment to \( \text{N}_2\text{O} \), such a high rate is very unlikely. Therefore, neither \( \text{O}_3 \), \( \text{NO}_2 \) nor \( \text{N}_2\text{O} \) are likely to represent a competition for electron attachment to \( \text{CCl}_4 \), \( \text{CHCl}_3 \) or \( \text{C}_2\text{HCl}_3 \).

### 8.3.5 \( \text{H}_2\text{O} \) and \( \text{HNO}_3 \)

In wet air or wet oxygen, the decomposition efficiency for \( \text{CCl}_4 \) and \( \text{CHCl}_3 \) is dramatically reduced compared to the decomposition efficiency in dry air or dry oxygen. Although it is currently not understood what causes this reduction in decomposition efficiency, several potential explanations may be evaluated on the basis of the electron attachment frequency.

In wet air or wet oxygen, a third chemical reaction for termolecular non-dissociative electron attachment to \( \text{O}_2 \) is available with \( \text{H}_2\text{O} \) besides \( \text{O}_2 \) and \( \text{N}_2 \) as the "third body". The reaction rate constant for the chemical reaction \( e^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2^- + \text{H}_2\text{O} \) is \( k_a = 1.5 \cdot 10^{-29} \text{ cm}^6/\text{s} \) [152].

With a typical \( \text{H}_2\text{O} \) concentration of 1 %, corresponding to a relative humidity of approximately 33 %RH [84], the attachment frequency results as \( \nu_a = 8.0 \cdot 10^7 \text{ 1/s} \) for wet air and as \( \nu_a = 1.3 \cdot 10^9 \text{ 1/s} \) for wet oxygen. Here, the \( \text{O}_2 \) and \( \text{N}_2 \) concentrations were taken to be 19.5 % and 79.5 % for air and 99 % and 0 % for oxygen.

Therefore, the electron attachment frequency in wet air or wet oxygen is only weakly enhanced through the presence of \( \text{H}_2\text{O} \) as the third body, so that such termolecular non-dissociative electron attachment to \( \text{O}_2 \) with \( \text{H}_2\text{O} \) as a "third body" does not represent a significantly increased competition for the electron attachment to \( \text{CCl}_4 \), \( \text{CHCl}_3 \) or \( \text{C}_2\text{HCl}_3 \).

The bimolecular or termolecular dissociative or non-dissociative electron attachment to \( \text{H}_2\text{O} \) could provide another explanation for the dramatic reduction of the decomposition efficiency for \( \text{CCl}_4 \) and \( \text{CHCl}_4 \) in wet air and wet oxygen. However, corresponding chemical reactions and consistent values for the corresponding reaction rate constants could not be found in the literature.

Nevertheless, a reaction rate constant for bimolecular electron attachment to \( \text{H}_2\text{O} \) of on the order of \( k_a = 10^{-11} \text{ cm}^3/\text{s} \) and \( k_a < 10^{-13} \text{ cm}^3/\text{s} \) is presented in [164] and
respectively. These reaction rate constants result in an attachment frequency of \( \nu_a = 2.5 \cdot 10^6 \text{ 1/s} \) and \( \nu_a < 2.5 \cdot 10^4 \text{ 1/s} \), respectively, at above \( H_2O \) concentration of 1%. This indicates that direct electron attachment to \( H_2O \) may not be competitive with electron attachment to \( CCl_4, CHCl_3 \) or \( C_2HCl_3 \).

As mentioned in Section 7.4, the dramatic reduction of the decomposition efficiency for \( CCl_4 \) and \( CHCl_3 \) in wet air may also be caused by the formation of \textit{Nitric Acid} \( HNO_3 \). As pointed out in [166], the \( H_2O \) in air is converted rapidly to \( HNO_3 \) at a high electron beam dose.

This conversion is confirmed by the reaction mechanism suggested in [54] and [59] for the decomposition of \textit{Nitrogen Oxides} (NO\(_x\)) in fossil fuel power plant exhaust through irradiation of this exhaust with an electron beam. In this reaction mechanism, the NO\(_x\) is converted to \textit{Nitric Acid} (HNO\(_3\)) via O\(_3\), OH and HO\(_2\) produced from O\(_2\) and H\(_2O\) in the exhaust. The HNO\(_3\) is then converted to \textit{Ammonium Nitrate} (NH\(_4\)NO\(_3\)) through reaction with \textit{Ammonia} (NH\(_3\)). The NH\(_4\)NO\(_3\) precipitates from the exhaust as as solid salt. Since electron attachment is not involved in this reaction mechanism, the importance of HNO\(_3\) as a competitor for electron attachment was not investigated in [54] and [59].

The reaction rate constant for the bimolecular dissociative electron attachment to HNO\(_3\) via \( e^- + HNO_3 \rightarrow NO_2^- + OH \) is presented in [167] as \( k_a = 5 \cdot 10^{-8} \text{ cm}^3/\text{s} \). This results in an attachment frequency of \( \nu_a = 2.5 \cdot 10^{10} \text{ 1/s} \) under the assumption that all H\(_2O\) is converted to HNO\(_3\) at a ratio of two HNO\(_3\) molecules per H\(_2O\) molecule and a H\(_2O\) concentration of 1%. In order to compete with 100 ppm C\(_2H_4\) for electron attachment, however, a HNO\(_3\) concentration of 500 ppm is sufficient.

This remarkable electron attachment frequency was the reason behind the investigation of the C\(_2H_4\) decomposition in wet oxygen rather than wet air. The elimination of NO\(_x\) formation in O\(_2\) was expected to prevent the formation of HNO\(_3\) and thus the competition for electrons with C\(_2H_4\). However, the expected effect was not observed experimentally.

The oxygen used in the corresponding experiment was of \textit{Ultra High Purity Grade} and according to \textit{Northeast Airgas, Manchester, New Hampshire} had a N\(_2\) concentration in the single digit ppm range. Also, the H\(_2O\) vapor generator used in the corresponding experiment was purged with oxygen for several minutes before performing the experiment. With a liquid volume of a few cm\(^3\), this purge period was thought adequate to remove all N\(_2\) dissolved in the liquid H\(_2O\). It is possible, however, that this was not the case and therefore H\(_2O\) as well as N\(_2\) was picked up by the oxygen. A N\(_2\) concentration of 250 ppm is sufficient to generate a HNO\(_3\) concentration of 500 ppm.

Therefore, neither the enhancement of termolecular non-dissociative electron at-
attachment to O₂ through H₂O as a "third body" nor the direct electron attachment to H₂O are likely to provide an explanation for the dramatic reduction in the decomposition efficiency for CCl₄ or CHCl₃ in wet air and wet oxygen. However, with the caveat that the N₂ concentration in oxygen was unknown, the bimolecular dissociative electron attachment to HNO₃ could provide such explanation.

Moreover, indications exist in the literature that electron attachment to so-called cluster molecules of H₂O is much stronger than electron attachment to the H₂O molecule itself [168], [169], [170], [171], [172]. However, no reaction rate constants could be found in the literature. The formation of cluster ions with H₂O was observed, for example, in [81] and [173].

8.4 Semi-Quantitative Discussion of CCl₄ Decomposition

8.4.1 General Considerations

When the electron attachment frequency is higher for O₂ than for CCl₄, the electron concentration of the cold plasma may be controlled by termolecular non-dissociative electron attachment to O₂. This is the case for a low CCl₄ intake concentration, i.e. less than approximately 10 ppm in dry air.

However, when the electron attachment frequency is higher for CCl₄ than for O₂, the electron concentration of the cold plasma may be controlled by bimolecular dissociative electron attachment to CCl₄. This is typically the case for a high CCl₄ intake concentration, i.e. more than approximately 10 ppm in dry air.

The two cases are discussed in the following for dry air as the standard carrier gas. Equations are presented that describe the CCl₄ exhaust concentration as a function of the CCl₄ intake concentration and the electron beam dose. Application of these equations to wet air or to dry oxygen or wet oxygen as the standard carrier gas was not attempted.

8.4.2 Low CCl₄ Intake Concentration

In the following, CCl₄ is represented through chemical species a. The electron concentration Nₑ and the exhaust concentration Nₑ of chemical species a for a low intake concentration may then be determined from:
\[
\frac{dN_e}{d\tau} = \frac{M}{N_A} G_e N \dot{D} - k_a(O_2) N_{O_2}^2 N_e - k_a(N_2) N_{N_2} N_{O_2} N_e
\]

\[
\frac{dN_a}{d\tau} = -k_a(a) N_a N_e
\]

Here, \( M \) is the mole mass of the standard gas, \( \dot{D} \) is the electron beam dose rate to the standard gas, \( G_e \) is the G-Value for production of electrons, \( N \) is the total concentration, \( N_{O_2} \) and \( N_{N_2} \) is the \( O_2 \) and \( N_2 \) concentration, respectively, \( k_a(O_2) \) and \( k_a(N_2) \) is the termolecular non-dissociative electron attachment reaction rate constant for attachment to \( O_2 \) with \( O_2 \) and \( N_2 \) as the "third body", respectively, and \( k_a(a) \) is the bimolecular dissociative electron attachment reaction rate constant for attachment to chemical species \( a \).

These equations hold under the assumption that dissociative or non-dissociative electron attachment and recombination of electrons to other chemical species as well as diffusion of electrons is negligible during reactor time \( \tau \). The former assumption may be valid at a low electron beam dose, the validity of the latter assumption has been demonstrated in Section 2.6.7.

Therefore, with \( \dot{D} \approx \text{const.} \) and \( N \approx \text{const.} \), as well as with \( \frac{dN_e}{d\tau} \approx 0 \), the electron concentration is approximately constant, and the electron concentration and the concentration of chemical species \( a \) result as:

\[
N_e = \frac{M}{N_A} \frac{G_e}{\varphi_{O_2} k_a(O_2) + \varphi_{N_2} k_a(N_2)} \frac{1}{\varphi_{O_2} N} \dot{D}
\]

\[
N_a = N_{a0} e^{-\frac{D}{D_0}}
\]

\[
\varphi_a = \varphi_{a0} e^{-\frac{D}{D_0}}
\]

Here, defining the electron beam dose as \( D = \dot{D} t \), the constant \( D_0 \) evaluates to:

\[
D_0 = \frac{N_A}{M} \frac{\varphi_{O_2} k_a(O_2) + \varphi_{N_2} k_a(N_2)}{k_a(a)} \frac{\varphi_{O_2} N}{G_e}
\]

Moreover, \( \varphi_{O_2} = \frac{N_{O_2}}{N} \), \( \varphi_{N_2} = \frac{N_{N_2}}{N} \) and \( \varphi_a = \frac{N_a}{N} \) are the concentrations of \( O_2 \), \( N_2 \) and chemical compound \( a \).
Consequently, at a low intake concentration of chemical species $a$, the decomposition is independent of such intake concentration. With $M = 28.85 \text{ g/mol}$, $k_a(O_2)$, $k_a(N_2)$ and $k_a(a)$ for $\text{CCl}_4$, $G_e = 3 / 100 \text{ eV}$, $\varphi_{O_2} = 0.2$ and $\varphi_{N_2} = 0.8$, $D_0$ results as $D_0 \approx 116 \text{ krad}$.

However, the investigated intake concentrations were not sufficiently low to render above equation valid, because even at a $\text{CCl}_4$ intake concentration of 10 ppm, electron attachment to $\text{CCl}_4$ rather than to $O_2$ seems to control the electron concentration in air.

The equation, however, should be valid for $\text{CHCl}_3$ and for $\text{C}_2\text{HCl}_3$, because for these hazardous chemical compounds, electron attachment to $O_2$ rather than to $\text{CHCl}_3$ or $\text{C}_2\text{HCl}_3$ controls the electron concentration in air. Due to the limited investigation of the decomposition of these hazardous chemical compounds, however, no further statements regarding this matter can be made.

Moreover, since in above equation a dependence on $k_a(a)$ is present, the effect of the electric field on the decomposition is expected to be rather large at least at a low electron beam dose. This is consistent with the experimentally observed larger effect of the electric field on the decomposition of $\text{CHCl}_3$ and $\text{C}_2\text{HCl}_3$ than on that of $\text{CCl}_4$.

### 8.4.3 High $\text{CCl}_4$ Intake Concentration

In the following, $\text{CCl}_4$ is represented through chemical species $a$. The electron concentration $N_e$ and the exhaust concentration $N_a$ of chemical species $a$ for a high intake concentration may then be determined from:

\[
\frac{dN_e}{d\tau} = \frac{M}{N_A} G_e N \dot{D} - k_a(a) N_a N_e
\]

\[
\frac{dN_a}{d\tau} = -k_a(a) N_a N_e
\]

These equations hold under the assumptions already mentioned for a low $\text{CCl}_4$ intake concentration. Moreover, the equations only hold as long as the concentration of chemical species $a$ is high enough to control the electron concentration.

Therefore, with $\dot{D} \approx \text{const.}$ and $N \approx \text{const.}$, as well as with $\frac{dN_e}{d\tau} \approx 0$, the electron concentration is a function of $N_a$, and the electron concentration and the concentration of chemical species $a$ result as:
\[ N_e = \frac{M}{N_A} \frac{G_e}{k_a(a)} \frac{N}{N_a} \dot{D} \]

\[ N_a = N_{a0} - \frac{M}{N_A} G_e N D \]

\[ \varphi_a = \varphi_{a0} - \frac{M}{N_A} G_e D \]

Here, again \( D = \dot{D} \tau \). With \( M = 28.85 \text{ g/mol} \) and \( G_e = 3 \text{ /100eV} \), \( \frac{M}{N_A} G_e \) results as \( \frac{M}{N_A} G_e \approx 90 \text{ ppm/Mrad} \). Moreover, the destruction and removal efficiency \( \eta_a \) and the energy expense \( \epsilon_a \) result as:

\[ \eta_a = \frac{\varphi_{a0} - \varphi_a}{\varphi_{a0}} = \frac{M}{N_A} \frac{G_e}{\varphi_{a0}} D \]

\[ \epsilon_a = \frac{1}{\eta_a \varphi_{a0}} \frac{M}{N_A} D = \frac{1}{G_e} \]

In application of the equation to the cold plasma decomposition of CCl₄, it is observed that the experimental observations are matched reasonably well for a high CCl₄ intake concentration and a low electron beam dose. At a low CCl₄ intake concentration, above equations are not valid any longer since electron attachment to \( O_2 \) in air begins to be important.

Moreover, at a high electron beam dose, a lower than experimentally observed CCl₄ exhaust concentration is obtained. This discrepancy occurs at a much higher exhaust concentration than the minimum expected intake concentration for which above equations are expected to be valid.

This indicates that at a high electron beam dose, chemical species, either as decomposition products or decomposition by-products, are generated which interfere or compete with bimolecular dissociative electron attachment to CCl₄.

Figure 8.1 represents the results of measurements of the exhaust concentration as function of the intake concentration and the electron beam dose. For all intake concentrations, above equation was added to the figure to demonstrate that for a high intake concentration and a low electron beam dose, this semi-quantitative discussion and the experimental observation agree reasonably well.

Moreover, since in above equation no dependence on \( k_a(a) \) is present, the effect of the electric field on the decomposition is expected to be rather small, as was experimentally observed for CCl₄.
Figure 8.1: High CCl₄ Intake Concentration Approximation
8.4.4 Heuristic Equation for CCl₄ Decomposition

As demonstrated in the discussion of the G-Value in Section 2.5, the concentration \( N_a \) may be described through the G-Value \( G_{aa} \):

\[
\varphi_a = \varphi_{a0} e^{-\frac{M}{N_A} G_{aa} \frac{Z_a}{Z} D}
\]

At a low electron beam dose, i.e. a low reactor time or electron beam dose rate, the classical approximation \( e^\gamma \approx 1 - \gamma \) for the exponential function results in:

\[
\varphi_a \approx \varphi_{a0} - \varphi_{a0} \frac{M}{N_A} G_{aa} \frac{Z_a}{Z} D
\]

Under such conditions, this equation and the equation for a high CCl₄ intake concentration are equivalent and the equation for \( G_{aa} \) as a function of \( G_e \), \( \varphi_{a0} \), \( Z \) and \( Z_a \) results as:

\[
G_{aa} = G_e \frac{Z}{Z_a} \frac{1}{\varphi_{a0}}
\]

Note that this "hand-shake" of an equation derived on the basis of bimolecular dissociative electron attachment and an equation derived on the basis of the G-Value represents a "trick" to obtain \( G_{aa} \) as a function of \( G_e \) and \( \varphi_{a0} \).

Here, \( \varphi_{a0} = \frac{N_{a0}}{N} \). Since \( G_e \) is independent of the intake concentration of chemical species \( a \), the G-Value for the destruction of chemical species \( a \) is inversely proportional to the intake concentration of chemical species \( a \). Moreover, although this equation for \( G_{aa} \) is derived for a short reactor time and a low electron beam dose rate, the G-Value \( G_{aa} \) is expected to be approximately constant and may hold for longer \( \tau \) as well as for higher \( \dot{D} \).

\[
\varphi_a = \varphi_{a0} e^{-\frac{M}{N_A} G_e \frac{D}{\varphi_{a0}}}
\]

In application of these equations to the cold plasma decomposition of CCl₄, these equations appear to match the CCl₄ exhaust concentration as a function of the electron beam dose with a \( G_e \) which is within a factor of two of the above assumed
$G_e = 3 /100$eV. In particular, the dependence of the CCl₄ exhaust concentration as a function of the electron beam dose on the CCl₄ intake concentration is in good agreement.

Figure 8.2 represents the results of measurements of the exhaust concentration as function of the intake concentration and the electron beam dose. For all intake concentrations, above equation was added to the figure to demonstrate that for a high intake concentration and a low or high electron beam dose, this semi-quantitative discussion and the experimental observation agree reasonably well when $G_e = 6 /100$eV rather than $G_e = 3 /100$eV is chosen.

While at a low electron beam dose a $G_e$ of $3 /100$eV and the $G_{aa}$ derived on the basis of such $G_e$ have a physical-chemical meaning, such meaning is lost at a high electron beam dose and through modification of $G_e$ from $3 /100$eV to $6 /100$eV, i.e. $G_e$ has simply become a fitting parameter.

Note that a high CCl₄ intake concentration in the sense of the present discussion corresponds to a CCl₄ intake concentration of higher than at least 10 ppm.

### 8.4.5 Heuristic Energy Expense for CCl₄ Decomposition

On the basis of above heuristic equation for the CCl₄ decomposition, the destruction and removal efficiency of chemical species $a$ at a high CCl₄ intake concentration is given with $N \approx \text{const.}$ as:

$$\eta_a = \frac{\varphi_{a0} - \varphi_a}{\varphi_{a0}} = 1 - e^{-\frac{M}{N_A} G_e \frac{D}{\varphi_{a0}}}$$

This equation may be rearranged to yield an equation for the electron beam dose as a function of the destruction and removal efficiency:

$$D = \frac{N_A}{M} \frac{1}{G_e} \varphi_{a0} \ln \frac{1}{1 - \eta_a}$$

Therefore, the energy expense $\epsilon_a$, defined in the discussion of the G-Value in Section 2.5, for decomposition of chemical species $a$ results as:

$$\epsilon_a = \frac{1}{\eta_a \varphi_{a0}} \frac{M}{N_A} D = \frac{1}{G_e} \frac{1}{\eta_a} \ln \frac{1}{1 - \eta_a}$$

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Figure 8.2: Heuristic CCl₄ Exhaust Concentration Approximation
Therefore, the energy expense is on the order of the inverse of the G-Value for production of electrons, which is intuitively consistent with electron attachment to CCl₄ controlling the electron density.

Figure 8.3 represents the results of measurements of the exhaust concentration as a function of the intake concentration and the electron beam dose. However, the results were converted to reflect the energy expense and the destruction and removal efficiency.

The above equation for \( \varepsilon_a \) was added to the figure to demonstrate that for a high intake concentration and a high destruction and removal efficiency, this semi-quantitative discussion and the experimental observation agree reasonably well when \( G_e = 6/100\text{eV} \) rather than \( G_e = 3/100\text{eV} \) is chosen. Again, note that \( G_e \) has become a fitting parameter now rather than being a physical-chemical quantity.

As an example, for a destruction and removal efficiency of \( \eta_a = 0.99 \), which corresponds to a reduction of a CCl₄ intake concentration of 100 ppm to 1 ppm, the energy expense results as \( \varepsilon_a = 77 \text{eV} \) or 13 kWh/kg. For \( \eta_a = 0.999 \), this energy expense results as \( \varepsilon_a = 115 \text{eV} \) or 20 kWh/kg. Hereby, the conversion from eV to kWh/kg is obtained through multiplication by the constants \( q_e \) and \( N_A \) and division by \( M_a \) and the constant \( 3.6 \cdot 10^6 \).

8.4.6 Heuristic Scaling Law for CCl₄ Decomposition

Consequently, for a constant destruction and removal efficiency \( \eta_a \), the ratio of the electron beam dose \( D \) to the intake concentration \( \varphi_{a0} \) results as:

\[
\frac{D}{\varphi_{a0}} = \frac{N_A}{M} \frac{1}{G_e} \ln \frac{1}{1 - \eta_a} = \text{const.}
\]

Since \( D = \frac{Q}{\dot{m}} \), the following relation among two sets of \( \dot{Q}, \dot{m} \) and \( \varphi_{a0} \) holds for constant \( \eta_a \):

\[
\frac{\dot{Q}_1}{\varphi_{a01}\dot{m}_1} = \frac{\dot{Q}_2}{\varphi_{a02}\dot{m}_2}
\]

This equation may serve as a "scaling law" for calculation of the power, mass flow rate or intake concentration for an unknown condition from the power, mass flow rate and intake concentration of a known condition.

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Figure 8.3: Heuristic CCl₄ Energy Expense Approximation
8.5 Qualitative Discussion of $\text{C}_2\text{HCl}_3$ Decomposition

8.5.1 $\text{C}_2\text{HCl}_3$ Decomposition

As shown in Section 2.3.2, the bimolecular dissociative electron attachment reaction rate constant for $\text{C}_2\text{HCl}_3$ is comparable in magnitude and dependence on average electron energy to the bimolecular dissociative electron attachment reaction rate constant for $\text{CHCl}_3$ [69], [174], [175]. Therefore, if the decomposition of $\text{C}_2\text{HCl}_3$ was effected via bimolecular dissociative electron attachment, a comparable intake concentration and electron beam dose would result in a comparable destruction and removal efficiency for $\text{C}_2\text{HCl}_3$ and $\text{CHCl}_3$.

However, the experimentally observed electron beam dose for a particular intake concentration and a particular destruction and removal efficiency is lower by two orders of magnitude for the decomposition of $\text{C}_2\text{HCl}_3$ than for the decomposition of $\text{CHCl}_3$.

A similar consideration applies to the decomposition of $\text{C}_2\text{HCl}_3$ in comparison to the decomposition of $\text{CCl}_4$. However, the bimolecular dissociative electron attachment reaction rate constant for $\text{CCl}_4$ is almost two orders of magnitude higher than the bimolecular dissociative electron attachment reaction rate constant for $\text{C}_2\text{HCl}_3$. Still, the electron beam dose for a particular intake concentration and destruction and removal efficiency is an order of magnitude lower for the decomposition of $\text{C}_2\text{HCl}_3$ than for the decomposition of $\text{CCl}_4$.

Hence, for the decomposition of $\text{C}_2\text{HCl}_3$, other chemical reactions sequential and/or parallel to bimolecular dissociative electron attachment must be important.

In contrast to $\text{CCl}_4$ or $\text{CHCl}_3$, $\text{C}_2\text{HCl}_3$ features a carbon to carbon double bond, which is much more readily attacked by $\text{O}(^{3}\text{P})$ oxygen, $\text{OH}$ hydroxyl or $\text{Cl}$ chlorine radicals than the carbon to hydrogen or carbon to chlorine single bond of $\text{CCl}_4$ or $\text{CHCl}_3$. Therefore, a sequential and/or parallel chemical reaction for the decomposition of $\text{C}_2\text{HCl}_3$ may be such radical attack on the carbon double bond in contrast to bimolecular dissociative electron attachment.

Hence, it is helpful to compare the reaction rate constant for bimolecular dissociative electron attachment to that for bimolecular dissociative radical attack on the carbon double bond. These reaction rate constants are given in the literature as:
\[ e^- + C_2HCl_3 \rightarrow Products \quad k = 2.0 \cdot 10^{-9} \text{ cm}^3/s \]  
\[ O(3P) + C_2HCl_3 \rightarrow Products \quad k = 1.0 \cdot 10^{-13} \text{ cm}^3/s \]  
\[ OH + C_2HCl_3 \rightarrow Products \quad k = 2.5 \cdot 10^{-12} \text{ cm}^3/s \]  
\[ Cl + C_2HCl_3 \rightarrow Products \quad k = 8.0 \cdot 10^{-11} \text{ cm}^3/s \]  

This indicates that the \( O(3P) \) concentration must be at least 20,000 times higher, the \( OH \) concentration must be at least 800 times higher and the \( Cl \) concentration must be at least 25 times higher than the electron concentration in order to result in a comparable \( C_2HCl_3 \) decomposition reaction rate.

As calculated in Section 2.6.6, the \( O(3P) \) concentration in dry air or dry oxygen was only a hundred to a thousand times higher than the electron concentration. This ratio may be expected not to change significantly in the presence of \( C_2HCl_3 \).

Moreover, the G-Value for production of electrons is comparable to the G-Value for production of \( O(3P) \) radicals. Since the reaction rate of \( C_2HCl_3 \) with electrons appears to be faster than the reaction rate with \( O(3P) \) radicals, a comparable or lower electron beam dose would be expected for the decompositon of \( C_2HCl_3 \) through electrons than through \( O(3P) \) radicals. Therefore, even if radical attack of the carbon double bond through \( O(3P) \) was significant, it alone could not explain the experimentally observed low electron beam dose.

Therefore, the radical attack on the carbon double bond through \( O(3P) \) may be insignificant in comparison to bimolecular dissociative electron attachment.

Although the \( OH \) concentration in wet air could not be calculated easily, this concentration may be assumed to be in between the \( O(1D) \) and \( O(3P) \) concentration. The radical attack on the carbon double bond through \( OH \) may therefore be as well insignificant in comparison to bimolecular dissociative electron attachment.

On the basis of the high \( C_2HCl_3 \) intake concentration, the \( Cl \) concentration is expected to be rather high as well once a small amount of \( C_2HCl_3 \) is decomposed. Therefore, in combination with the above rather high reaction rate constant, radical attack on the carbon double bond through \( Cl \) is likely to represent a chemical reaction for decomposition of \( C_2HCl_3 \) in sequence with bimolecular dissociative electron attachment.

Therefore, bimolecular dissociative electron attachment in air may be necessary in order to produce a sufficiently high \( Cl \) concentration so that the radical attack on the carbon double bond through \( Cl \) may become significant.

On the one hand, this is supported by the experimentally observed comparable \( C_2HCl_3 \) decomposition efficiency and the comparable \( COCl_2 \) and \( C_2HCl_3O \) exhaust...
concentration in dry air and wet air. Since the reaction mechanism for \( \text{C}_2\text{HCl}_3 \) decomposition and thus the \( \text{C}_2\text{HCl}_3 \) decomposition products would be expected to be different for radical attack on the carbon double bond through \( \text{O}^3\text{P} \) and through \( \text{OH} \), this indicates that \( \text{O}^3\text{P} \) and \( \text{OH} \) may not be significant in the decomposition of \( \text{C}_2\text{HCl}_3 \).

On the other hand, this is supported by the experimentally observed effect of the electric field on the decomposition efficiency. The average electron energy and the bimolecular dissociative electron attachment rate constant increase [69] and the \( \text{C}_2\text{HCl}_3 \) exhaust concentration decreases with increasing electric field.

### 8.5.2 Reaction Mechanism of \( \text{C}_2\text{HCl}_3 \) Decomposition

The decomposition of \( \text{C}_2\text{HCl}_3 \) via radical attack on the carbon double bond through the oxygen, hydroxyl and chlorine radicals is discussed in [145], [148], [178], [176] and [179].

Since radical attack on the carbon double bond through \( \text{O}^3\text{P} \) or \( \text{OH} \) may be insignificant compared to radical attack on the carbon double bond through \( \text{Cl} \) and compared to bimolecular dissociative electron attachment, the following discussion is limited to the \( \text{Cl} \) radical attack reaction mechanism. It may be assumed that the \( \text{Cl}^- \) very likely produced as a result of bimolecular dissociative electron attachment to \( \text{C}_2\text{HCl}_3 \) neutralizes through negative ion to positive ion recombination.

According to the above literature, the intermediate chemical species \( \text{Dichloro Acetyl Chloride} \), \( \text{Trichloro Acetyl Chloride} \) and \( \text{Trichloro Acetic Acid} \) as well as the intermediate chemical species \( \text{Formyl Chloride} \) and \( \text{Carbonyl Chloride} \) are of interest in the decomposition of \( \text{C}_2\text{HCl}_3 \). The chemical structure of these chemical species is shown in Figure 8.4.

In order to indicate the location of a carbon single or double bond, \( \text{Trichloro Ethene} \) is represented as \( \text{Cl}_2\text{C} = \text{CHCl} \), \( \text{Dichloro Acetyl Chloride} \) is represented as \( \text{Cl}_2\text{HC} - \text{COCl} \) and \( \text{Trichloro Acetyl Chloride} \) is represented as \( \text{Cl}_3\text{C} - \text{COCl} \) and \( \text{Trichloro Acetic Acid} \) is represented as \( \text{Cl}_3\text{C} - \text{COH} \) in the following.

The decomposition of \( \text{C}_2\text{HCl}_3 \) via radical attack on the carbon double bond through the \( \text{Cl} \) chlorine radical is described in [148] and [178]. The \( \text{Cl} \) may attack the carbon double bond either at the less heavily chlorinated carbon atom or at the more heavily chlorinated carbon atom of the carbon double bond. In the following, both modes of radical attack are discussed, although generally the carbon double bond is attacked at the less heavily chlorinated carbon atom [148].
Figure 8.4: Chemical Structure of Chemical Species in \( \text{C}_2\text{HCl}_3 \) Decomposition
As will be seen shortly, the radical attack on the carbon double bond through Cl represents a chain reaction in which the decomposition of \( \text{C}_2\text{HCl}_3 \) through Cl results in the re-generation of the Cl. Therefore, the Cl is not consumed in the decomposition of \( \text{C}_2\text{HCl}_3 \), which may explain the experimentally observed low electron beam dose.

In particular, the bimolecular dissociative electron attachment only has to provide for losses of Cl unrelated to the decomposition of \( \text{C}_2\text{HCl}_3 \). Moreover, since the \( \text{Cl}^- \) very likely produced in such bimolecular dissociative electron attachment is very likely subject to losses in parallel to negative ion to positive ion recombination to Cl, the electron attachment has to provide for losses of \( \text{Cl}^- \) as well.

As mentioned earlier, would the decomposition be initiated and continued via \( \text{O}^3\text{P} \) or OH, such low electron beam dose would not be expected on the basis of the rather low G-Values for the generation of \( \text{O}^3\text{P} \) or OH and a very likely lack of a chain reaction for these radicals.

The radical attack on the more heavily chlorinated carbon atom through Cl involves the following chemical reactions [148]:

\[
\begin{align*}
\text{Cl}_2\text{C} &= \text{CHCl} + \text{Cl} \rightarrow \text{Cl}_2\text{C} - \text{CHCl} \\
\text{Cl}_3\text{C} - \text{CHCl} + \text{O}_2 &\rightarrow \text{Cl}_3\text{C} - \text{CHClO}_2 \\
2\text{Cl}_3\text{C} - \text{CHClO}_2 &\rightarrow 2\text{Cl}_3\text{C} - \text{CHClO} + \text{O}_2 \\
\text{Cl}_3\text{C} - \text{CHClO} &\rightarrow \text{Cl}_3\text{C} - \text{COH} + \text{Cl} \\
&\rightarrow \text{CCl}_3 + \text{COHCl} \\
&\rightarrow \text{Cl}_3\text{C} - \text{COCl} + \text{H} \\
\end{align*}
\]

Note that the decomposition of \( \text{Cl}_3\text{C}-\text{CHClO} \) to Trichloro Acetyl Chloride is energetically less favorable and therefore not very likely to take place [148]. The radical attack on the less heavily chlorinated carbon atom through Cl involves the following chemical reactions [148]:

\[
\begin{align*}
\text{Cl}_2\text{C} &= \text{CHCl} + \text{Cl} \rightarrow \text{Cl}_2\text{C} - \text{CHCl}_2 \\
\text{Cl}_2\text{C} - \text{CHCl}_2 + \text{O}_2 &\rightarrow \text{O}_2\text{Cl}_2\text{C} - \text{CHCl}_2 \\
2\text{O}_2\text{Cl}_2\text{C} - \text{CHCl}_2 &\rightarrow 2\text{OCl}_2\text{C} - \text{CHCl}_2 + \text{O}_2 \\
\text{OCl}_2\text{C} - \text{CHCl}_2 &\rightarrow \text{ClOCl} - \text{CHCl}_2 + \text{Cl} \\
&\rightarrow \text{COCl}_2 + \text{CHCl}_2 \\
\end{align*}
\]

The radical attack on the carbon double bond at the more heavily chlorinated carbon atom results in the formation of \( \text{Cl}_3\text{C} - \text{COH} \), while the radical attack on the carbon double bond at the less heavily chlorinated carbon atom results in the
formation of \(\text{Cl}_2\text{HC} - \text{COCl}\). The fact that \(\text{Cl}_2\text{HC} - \text{COCl}\) rather than \(\text{Cl}_3\text{C} - \text{COH}\) is experimentally observed is consistent with radical attack on the carbon double bond at the less heavily chlorinated carbon atom.

As a supplement to the decomposition of \(\text{C}_2\text{HCl}_3\) via radical attack on the carbon double bond through Cl, such radical attack can also take place through \(\text{Cl}\) rather than \(\text{Cl}\). The chlorine oxide may be expected to be formed as part of the chlorine-oxygen cycle well known from atmospheric chemistry [149], [150]. Such reaction mechanism is presented in [145] as:

\[
\begin{align*}
\text{Cl}_2\text{C} + \text{CHCl} + \text{ClO} &\rightarrow \text{ClOCl}_2\text{C} - \text{CHCl} \\
\text{ClOCl}_2\text{C} + \text{CHCl} &\rightarrow \text{ClOClC} = \text{CHCl} + \text{Cl} \\
\text{ClOClC} = \text{CHCl} &\rightarrow \text{ClOC} - \text{CHCl}_2 \\
\text{ClOC} - \text{CHCl}_2 &\rightarrow \text{COCl} + \text{CHCl}_2 \\
\text{ClOC} - \text{CHCl}_2 &\rightarrow \text{CO} + \text{CHCl}_3
\end{align*}
\]

### 8.5.3 Reaction Mechanism of ClOC-CHCl₂ Decomposition

Although the \(\text{O}(^{3}\text{P})\) and \(\text{OH}\) radicals may be insignificant with respect to the decomposition of \(\text{C}_2\text{HCl}_3\), they nevertheless may play an important role in the decomposition of \(\text{ClOC-CHCl}_2\). According to [178], the reaction mechanism for the decomposition of \(\text{ClOC-CHCl}_2\) through \(\text{OH}\) involves the abstraction of a hydrogen atom:

\[
\begin{align*}
\text{ClOC} - \text{CHCl}_2 + \text{OH} &\rightarrow \text{ClOC} - \text{CCl}_2 + \text{H}_2\text{O} \\
\text{ClOC} - \text{CCl}_2 + \text{O}_2 &\rightarrow \text{ClOC} - \text{CCl}_2\text{O}_2 \\
2\text{ClOC} - \text{CCl}_2\text{O}_2 &\rightarrow 2\text{ClOC} - \text{CCl}_2\text{O} + \text{O}_2 \\
\text{ClOC} - \text{CCl}_2\text{O} &\rightarrow \text{COCl} + \text{COCl}_2
\end{align*}
\]

A similar reaction mechanism may be invoked to explain the decomposition of \(\text{ClOC-CHCl}_2\) through \(\text{O}(^{3}\text{P})\) via hydrogen abstraction.

The importance of \(\text{OH}\) and \(\text{O}(^{3}\text{P})\) in the decomposition of \(\text{ClOC-CHCl}_2\) is supported by the rather high electron beam dose for a significant destruction and removal efficiency of \(\text{ClOC-CHCl}_2\), i.e. a Cl chain reaction may not be involved in the decomposition of \(\text{ClOC-CHCl}_2\).

With respect to the decomposition products of the \(\text{C}_2\text{HCl}_3\) decomposition, the photocatalytic oxidation of \(\text{C}_2\text{HCl}_3\) in air was investigated in [178]. The \(\text{C}_2\text{HCl}_3\) intake concentration was approximately 110 ppm and the \(\text{Cl}_2\text{HC-COCl}\) and \(\text{COCl}_2\)
exhaust concentrations were between 1 ppm and 4 ppm and between 32 ppm and 73 ppm, respectively.

However, long residence times, equivalent to high electron beam doses, were required to reduce the Cl$_2$HC-COCl exhaust concentration to these levels. A carbon balance was obtained via consideration of C$_2$HCl$_3$, Cl$_2$HC-COCl, COCl$_2$, CO and CO$_2$. A chlorine balance was obtained via additional consideration of Cl$_2$.

In the present work, the Cl$_2$HC-COCl exhaust concentration was rather high and the COCl$_2$ exhaust concentration was rather low compared to above photocatalytic oxidation.

Such discrepancy could be explained by the fact that Cl$_2$HC-COCl has a significant cross section for interaction with photons [180], while it apparently does not react very efficiently with electrons. Therefore, the conversion of Cl$_2$HC-COCl to COCl$_2$ is less efficient through electrons than through photons.

**8.5.4 Reaction Mechanism of CCl$_3$ and CHCl$_2$ Decomposition**

In the decomposition of Cl$_2$C=CHCl via radical attack on the carbon double bond through Cl, the Trichloro Methyl radical (CCl$_3$) and the Dichloro Methyl radical (CHCl$_2$) are formed. In the presence of O$_2$, these radicals decompose to Formyl Chloride (COHCl) and Carbonyl Chloride, (Phosgene, COCl$_2$) via the following chemical reactions [148]:

\[
\begin{align*}
CHCl_2 + O_2 & \rightarrow COHCl + OH \\
CCl_3 + O_2 & \rightarrow COCl_2 + ClO \\
& \rightarrow CCl_3O_2 \\
2CCl_3O_2 & \rightarrow 2CCl_3O + O_2 \\
CCl_3O & \rightarrow COCl_2 + Cl
\end{align*}
\]

The chain reaction that is initiated through the decomposition of C$_2$HCl$_3$ via radical attack on the carbon double bond through Cl terminates through chemical bonding of Cl in the case of CHCl$_2$ and continues through regeneration of Cl in the case of CCl$_3$.

The decomposition of COHCl and COCl$_2$ was explained in the qualitative discussion of the decomposition of CCl$_4$ and CHCl$_3$. Moreover, both COHCl and COCl$_2$ are expected to dissociate upon solvation in (liquid) water.
8.5.5 Reaction Mechanism of CCl₂ and CHCl Decomposition

In the decomposition of C₂HCl₃ via radical attack on the carbon double bond through Cl, the Dichloro Methylene radical (CCl₂) and the Monochloro Methylene radical (CHCl) are formed. In the presence of O₂, these radicals decompose to CO and Cl via the following chemical reactions [148]:

\[
\begin{align*}
CHCl + O₂ & \rightarrow OH + COCl \\
CCl₂ + O₂ & \rightarrow ClO + COCl \\
COCl & \rightarrow CO + Cl
\end{align*}
\]

Such decomposition only applies to electronically excited "Triplet" states, not to electronically excited "Singlet" states. The chain reaction that is initiated through the decomposition of C₂HCl₃ via radical attack on the carbon double bond through Cl continues through regeneration of Cl.

8.6 Comparison of Cold Plasma Energy Expense

In order to compare the decomposition efficiency of CCl₄ and C₂HCl₃ in a Tunable Plasma Reactor to the decomposition efficiency of CCl₄ and C₂HCl₃ in other cold plasma reactors, the exemplary Energy Expense for decomposition of CCl₄ and C₂HCl₃ is calculated for the present work and three parallel experimental investigations.

These experimental investigations employed 1) a Corona Discharge [18], 2) a Dielectric Barrier Discharge [21], 3) a High Energy Electron Beam Discharge [24] and 4) a Low Energy Electron Beam Discharge as described in the present work. Note that experimental investigations 1), 3) and 4) were performed in 80 % N₂ and 20 % O₂ while experimental investigation 2) was performed in 80 % Ar and 20 % O₂. Moreover, no relative humidity was considered for this comparison of the decomposition efficiency.

Tables 8.1 and 8.2 provide for the decomposition of CCl₄ and C₂HCl₃, respectively, a summary of the volume flow rate, the cold plasma power, the intake concentration, the (electron beam) dose and the energy expense for exemplary cold plasma conditions of these experimental investigations, referred to as cases.

On the basis of this table, it appears that cold plasmas generated by electron beams
Table 8.1: Comparison of Cold Plasma Energy Expense for CCl₄ Decomposition at 99 % Destruction and Removal Efficiency

<table>
<thead>
<tr>
<th>Case</th>
<th>Volume Flow Rate</th>
<th>Cold Plasma Power</th>
<th>Intake Concentration</th>
<th>(Electron Beam) Dose</th>
<th>Energy Expense</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm³/min</td>
<td>W</td>
<td>ppm</td>
<td>Mrad</td>
<td>eV</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10,000</td>
<td>1000.0</td>
<td>750</td>
<td>400.0</td>
<td>2141 [23]</td>
</tr>
<tr>
<td>4</td>
<td>2,500</td>
<td>8.6</td>
<td>675</td>
<td>16.5</td>
<td>74</td>
</tr>
</tbody>
</table>

Table 8.2: Comparison of Cold Plasma Energy Expense for C₂HCl₃ Decomposition at 99 % Destruction and Removal Efficiency

<table>
<thead>
<tr>
<th>Case</th>
<th>Volume Flow Rate</th>
<th>Cold Plasma Power</th>
<th>Intake Concentration</th>
<th>(Electron Beam) Dose</th>
<th>Energy Expense</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm³/min</td>
<td>W</td>
<td>ppm</td>
<td>Mrad</td>
<td>eV</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30,000</td>
<td>100.0</td>
<td>500</td>
<td>16.00</td>
<td>97 [18]</td>
</tr>
<tr>
<td>2</td>
<td>10,000</td>
<td>175.0</td>
<td>650</td>
<td>70.00</td>
<td>432 [23]</td>
</tr>
<tr>
<td>3</td>
<td>7,500,000</td>
<td>250.0</td>
<td>35</td>
<td>0.16</td>
<td>14 [25]</td>
</tr>
<tr>
<td>4</td>
<td>10,000</td>
<td>2.3</td>
<td>500</td>
<td>1.10</td>
<td>7</td>
</tr>
</tbody>
</table>

are most efficient for the decomposition of CCl₄ and C₂HCl₃, and low energy electron beams may be slightly more efficient than high energy electron beams.

The higher energy expense for cold plasmas other than cold plasmas generated by electron beams may indicate that the production of electrons in these cold plasmas is less efficient and therefore the less efficient chemical reactions of O(¹D) and O(³P) radical attack on CCl₄ and C₂HCl₃ rather than bimolecular dissociative electron attachment to CCl₄ and C₂HCl₃ may become more important to the decomposition.
Chapter 9

Summary and Conclusion

9.1 Summary

The Cold Plasma Decomposition of Tetrachloro Methane (Carbon Tetrachloride, CCl₄), Trichloro Methane (Chloroform, CHCl₃) and Trichloro Ethene (Trichloro Ethylene, C₂HCl₃) at concentrations of several ten to hundred ppm in air was investigated experimentally. The emphasis was placed on the experimental investigation of the cold plasma decomposition of CCl₄. All three chemical compounds represent hazardous chemical compounds frequently encountered in gaseous hazardous waste.

The experimental investigations were performed using a Tunable Plasma Reactor. The cold plasma in such a reactor is generated by an electron beam in air at atmospheric pressure. A sub-breakdown electric field is superimposed to the electron beam. Therefore, the electron concentration is controlled by the electron beam current and the average electron energy is controlled by the electric field voltage.

The electron beam was generated and accelerated by a Triode electron beam gun. The DC electric field was generated through parallel plate electrodes. The gas mixing system for simulation of the gaseous hazardous waste containing the hazardous chemical compounds CCl₄, CHCl₃ and C₂HCl₃ was based on vapor generators and compressed gas cylinders.

The gas analysis system was based on a commercially available Gas Chromatograph and a commercially available Mass Spectrometer. However, the mass spectrometer, referred to as a Mass Selective Detector and originally designed as a detector for the gas chromatograph, was converted to a Stand-Alone, On-Line, Real Time Mass Spectrometer through modification of the hardware and software. In particular, this enabled chemical analysis of the reactive chemical compounds HCl and Cl₂.
The electron beam dose to the cold plasma was determined via a combination of Facsimile Paper Radiography, Aluminum Plate Calorimetry, Monte Carlo Simulation of electron beam power deposition and N₂O Chemical Dosimetry.

The destruction and removal efficiency of CCl₄, CHCl₃ and C₂HCl₃ was found to be a function of the electron beam dose rather than the electron beam dose rate. The electron beam dose is the ratio of the electron beam power absorbed in the air to the irradiated air mass flow, while the electron beam dose rate is the ratio of the electron beam power absorbed in the air to the irradiated air mass.

The bimolecular dissociative electron attachment to rather than the bimolecular dissociative O, OH or Cl radical attack on CCl₄, CHCl₃ and C₂HCl₃ was found to be the chemical reaction likely responsible for the decomposition in such a cold plasma. However, in contrast to the decomposition of CCl₄ and CHCl₃, the decomposition of C₂HCl₃ was found to be likely continued through Cl radical attack once the decomposition of C₂HCl₃ is initiated through electron attachment.

The experimentally observed electron beam dose for a comparable destruction and removal efficiency of CCl₄, CHCl₃ and C₂HCl₃ at a comparable intake concentration was approximately an order of magnitude lower for C₂HCl₃ than for CCl₄ and CHCl₃. This difference was found to be likely caused by a chain reaction that is represented by the Cl radical attack on C₂HCl₃ and in which the Cl radical is re-generated in the decomposition of C₂HCl₃.

Moreover, the experimentally observed electron beam dose for a comparable destruction and removal efficiency and a comparable intake concentration of CCl₄ and CHCl₃ was up to five times higher in wet air than in dry air. No such difference was observed for the decomposition of C₂HCl₃ in wet air and dry air. An explanation for the detrimental effect of H₂O on the decomposition of CCl₄ and CHCl₃ is currently not available.

The electron beam dose for a particular destruction and removal efficiency was found to increase with increasing CCl₄ intake concentration. This is consistent with a selectivity of the decomposition of CCl₄ in the cold plasma. Also, the destruction and removal efficiency of CCl₄ in dry oxygen was found to be higher than that in dry air for a given electron beam dose and intake concentration. An explanation for the enhanced decomposition of CCl₄ in dry oxygen compared to dry air is currently not available.

The bimolecular dissociative electron attachment reaction rate constants of CCl₄, CHCl₃ and C₂HCl₃ are functions of the average electron energy of the cold plasma. The variation of the average electron energy through variation of the voltage of the electric field superimposed to the electron beam was found to result in a variation of the destruction and removal efficiency at a given electron beam dose and a given
Moreover, this variation was found to be stronger for CHCl₃ and C₂HCl₃ than for CCl₄ and also was found to be stronger in wet air than in dry air for CCl₄ and CHCl₃. These observations are in qualitative agreement with bimolecular dissociative electron attachment as the chemical reaction responsible for the decomposition.

The decomposition products of CCl₄ were found to be the stable chemical species CO, CO₂ and Cl₂ and the intermediate chemical species COCl₂ (Carbonyl Chloride, Phosgene) in dry air and additionally the stable chemical species HCl in wet air. Within the accuracy and precision characteristic of the gas analysis system employed in the present work, a carbon and chlorine balance could be obtained. Also, the COCl₂ and CCl₄ exhaust concentration were reduced to sub ppm levels at a comparable electron beam dose.

The decomposition products of CHCl₃ were not analyzed for, but on the basis of the similarity of the reaction mechanism for decomposition of CCl₄ and of CHCl₃ are expected to be similar to those of CCl₄.

The decomposition products of C₂HCl₃ were found to be the stable chemical species HCl and Cl₂ and the intermediate chemical species COCl₂ and C₂HCl₃O (Dichloro Acetyl Chloride) in dry air and wet air. The C₂HCl₃O was found to convert into COCl₂. The decomposition products CO and CO₂ were not analyzed for but are expected on the basis of investigations referenced in the literature. Moreover, the C₂HCl₃O exhaust concentration was reduced to sub ppm levels at an electron beam dose between one and two orders of magnitude higher than the electron beam dose necessary to reduce the C₂HCl₃ exhaust concentration to sub ppm levels.

Moreover, a decomposition by-product of CCl₄ and very likely of CHCl₃ and C₂HCl₃ was found to be N₂O (Nitrous Oxide) in dry air and wet air. The decomposition by-products O₃ (Ozone), NO (Nitric Oxide), NO₂ (Nitrogen Dioxide) in dry air and additionally HNO₃ (Nitric Acid) in wet air were not analyzed for but are expected on the basis experimental observations and investigations referenced in the literature.

9.2 Conclusion

The Tunable Plasma Reactor provides "tunability" with respect to the decomposition of hazardous chemical compounds in gaseous hazardous waste through four "tuning knobs". These are represented through the electron beam current, the flow rate, the electric field voltage and chemical compounds, so-called "promoters", that may be introduced to the cold plasma together with the gaseous hazardous waste in order to generate particular reactive chemical species.
As discussed subsequently, although the full range of such “tunability” may not be required for a practical system implementing the cold plasma decomposition of CCl₄ or CHCl₃, it may well prove valuable for a practical system implementing the cold plasma decomposition of C₂HCl₃.

The Cold Plasma Decomposition of CCl₄ in dry air is characterized by a significantly lower energy expense than the Flame Decomposition of CCl₄ in dry air. Although the energy expense in wet air appears to be from two to five times higher than the energy expense in dry air, this advantage is still apparent. Moreover, the CCl₄ decomposition products may be easily removed from the exhaust and converted to non-hazardous chemical compounds.

A practical system may therefore feature a Dryer in the intake and a Scrubber in the exhaust of the Tunable Plasma Reactor. The dryer removes the H₂O to ensure the low energy expense for dry air and the scrubber removes the stable decomposition products HCl, Cl₂ and the intermediate decomposition product COCl₂ from the exhaust and converts these decomposition products into Sodium Chloride (NaCl) by reaction with aqueous Sodium Hydroxide (NaOH). Therefore, the exhaust of this practical system contains only CO and CO₂.

In fact, such a practical system for Cold Plasma Decomposition of CCl₄ is currently under assembly at MIT’s Plasma Fusion Center. This practical system employs a commercial electron beam gun and is scheduled to operate in field tests at the US Department of Energy’s (USDoE) Hanford Site in Washington state. In following through on the motivation, the present work provided the experimental data that formed the basis for the technical specifications of the practical system.

On the basis of an energy expense of less than approximately 150 eV or approximately 25 kWh/kg for the decomposition of CCl₄, and on the basis of an energy efficiency of a commercial Tunable Plasma Reactor of greater than 70 % and electricity cost of $0.1/kWh, the decomposition of CCl₄ may be achieved for less than $5/kg, as compared to currently typical $30/kg.

The practicality of the cold plasma decomposition of CHCl₃ may be expected comparable to the practicality of the cold plasma decomposition of CCl₄, despite the somewhat higher energy expense for CHCl₃ than for CCl₄. However, the practicality of the cold plasma decomposition of C₂HCl₃ requires slightly different considerations.

Although the energy expense for the cold plasma decomposition of C₂HCl₃ is significantly lower than the energy expense for the cold plasma decomposition of CCl₄ in dry air as well as in wet air, the potentially high exhaust concentration of the intermediate decomposition product C₂HCl₃O Dichloro Acetyl Chloride and therefore COCl₂ Carbonyl Chloride, even at a high electron beam dose, could present a problem for the practicality of the cold plasma decomposition of C₂HCl₃.
Further investigation of the cold plasma decomposition of $C_2HCl_3O$, rather than of the chlorinated ethene $C_2HCl_3$, is required to solve this problem. The “tunability” of the Tunable Plasma Reactor reactor may prove valuable in this endeavor. In particular, the electric field may enhance a potential dissociative electron attachment reaction rate constant for $C_2HCl_3O$ or the introduction of $H_2O_2$ to the cold plasma may result in the very efficient production of OH radicals which then effect the decomposition of $C_2HCl_3O$.

In fact, although “tunability” via “promoters” was not fully investigated in the present work, preliminary experiments indicate that the Dichloro Acetyl Chloride ($C_2HCl_3O$) produced as an intermediate decomposition product of $C_2HCl_3$ may be decomposed to sub ppm levels at a lower electron beam dose in the presence of Hydrogen Peroxide ($H_2O_2$) than in the absence of $H_2O_2$. This may in fact be attributed to the efficient production of OH radicals from $H_2O_2$, which then attack $C_2HCl_3O$ through Hydrogen Abstraction.

Moreover, it may prove feasible to simply increase the electron beam dose beyond the range investigated in the present work. This does not necessarily render marginal the advantage of Cold Plasma Decomposition over Flame Decomposition.

Also, it may be conceivable to implement a practical system as a hybrid system. In such a (speculative) hybrid system, the decomposition of $C_2HCl_3$ could be effected through the Tunable Plasma Reactor, while the decomposition of $C_2HCl_3$ in the exhaust could be effected through a Photo Oxidation Reactor as outlined in [178] and [180].

This represents an interesting approach, since the decomposition of $C_2HCl_3$ may be more efficiently accomplished through electrons, while the decomposition of $C_2HCl_3O$ may be more efficiently accomplished through photons.

The superposition of the electric field to the electron beam was found to decrease the exhaust concentration for a given intake concentration and electron beam dose by up to a factor of two for $CHCl_3$ and $C_2HCl_3$. Therefore, less expensive electric field power may be substituted for more expensive electron beam power at a comparable exhaust concentration. The electron beam power and the substituting electric field power were found to be approximately comparable.

However, the superposition of an electric field to the electron beam was found particularly useful as a diagnostics tool. This is based on the dependence of the dissociative electron attachment reaction rate constant on the average electron energy, which in turn is a function of the electric field. The variation of the exhaust concentration of a (hazardous) chemical compound which dissociatively attaches electrons with variation of the electric field may be used as an indication for the importance of dissociative electron attachment in the decomposition of this (hazardous) chemical
compound.

The Cold Plasma Decomposition and the Flame Decomposition of hazardous chemical compounds in air may be expected to produce decomposition by-products, i.e. mainly Ozone (O₃) and Nitrogen Oxides (NOₓ), at concentrations comparable to those of the hazardous chemical compounds. Hence, no significant advantage or disadvantage with respect to these decomposition by-products may be expected for the Tunable Plasma Reactor compared to Flame Decomposition.

However, the NOₓ may be removed from the exhaust through the Electron Beam Dry Scrubbing process outlined in [54] and [59]. The NOₓ could be converted to Ammonium Nitrate (NH₄NO₃) and/or potentially Ammonium Chloride (NH₄Cl) through introduction of the exhaust together with H₂O and NH₃ into a second Tunable Plasma Reactor. The ammonium nitrate and the ammonium chloride represent salable fertilizer base material.

In addition to these conclusions regarding the implementation of a practical system for cold plasma decomposition of CCl₄, CHCl₃ and C₂HCl₃, additional conclusions were reached in the present work regarding the conversion of a Mass Selective Detector for chemical analysis and regarding the Electron Beam Dosimetry.

With respect to the Mass Selective Detector, it was shown that the conversion of such a Mass Selective Detector (MSD) from a Gas Chromatography/Mass Spectrometry (GC-MS) detector to a Stand-Alone, On-Line, Real-Time Mass Spectrometry (SOR-MS) detector may be feasible and may result in reasonable accuracy and precision of chemical analysis.

Such conversion may be of interest because it can enhance the chemical analytical capabilities of a laboratory equipped with a Hewlett-Packard GC-MS gas analysis system without the need for adding a dedicated expensive floor space mass spectrometer to the bench top mass spectrometer represented by the MSD.

Moreover, the chemical analysis of reactive chemical compounds becomes possible because the surface area for Thermally Activated Surface Chemical Reactions is significantly reduced and the surface material is significantly less reactive compared to a GC-MS.

With respect to Electron Beam Dosimetry, it was demonstrated that the combination of Facsimile Paper Radiography, Aluminum Plate Calorimetry, One-Dimensional Monte-Carlo Simulation of electron beam power deposition and N₂O Chemical Dosimetry may be used to obtain the electron beam dose to air or air-like gases.

Moreover, the close match of the exhaust concentration of CCl₄ as a function of the electron beam dose and the CCl₄ intake concentration in dry air to a heuristic
equation derived on the basis of the G-Value is remarkable. This match not only allows for prediction of the CCl₄ exhaust concentration in dry air. It also indicates the potential usefulness of the decomposition of CCl₄ in dry air as a Chemical Dosimeter for electron beam irradiation of air or air-like gases.

The experimentally observed G-Value for the decomposition of CCl₄ is constant with electron beam dose and inversely proportional to the CCl₄ intake concentration. The proportionality constant is closely related to the G-Value for production of electrons via ionization.

Therefore, a variation of the CCl₄ intake concentration results in a variation of the G-Value, so that the CCl₄ Chemical Dosimeter may be adjusted to the electron beam dose to be measured by adjustment of the G-Value. In the literature, such adjustment is referred to as Sensitization [138].

This is particularly important because the N₂O Chemical Dosimeter only functions properly for an electron beam dose below approximately 3 Mrad, while the CCl₄ Chemical Dosimeter may be made to function properly up to an electron beam dose in the 10 Mrad to 100 Mrad range.

9.3 Recommendations for Future Work

9.3.1 General Remarks

The cold plasma decomposition of hazardous chemical compounds is currently of great interest in the treatment of gaseous hazardous waste. Moreover, the present work has demonstrated that electron beam generated cold plasmas may be particularly efficient where bimolecular (or termolecular) dissociative electron attachment to hazardous chemical compounds represents the major chemical reaction responsible for the decomposition.

Therefore, the Tunable Plasma Reactor project at MIT’s Plasma Fusion Center will certainly continue for a while in order to further explore the cold plasma decomposition of hazardous chemical compounds. Hence, it is appropriate to present a few suggestions for future work. These suggestions concern experiments as well as the experimental equipment.
9.3.2 Experiments

The complementation of the experimental investigation of the decomposition of CHCl₃ and C₂HCl₃ along the same lines as the experimental investigation of the decomposition of CCl₄ as well as the expansion of the experimental investigation of CCl₄, CHCl₃ and C₂HCl₃ are very likely to further increase the understanding of the decomposition of these chlorinated organic compounds.

The identification of the chemical reactions that cause a decrease in the decomposition efficiency for CCl₄ and CHCl₃ in wet air or oxygen compared to dry air or oxygen is of importance to a more comprehensive understanding of the reaction mechanism of the decomposition. In this context, a repeat of the investigation of the decomposition of CCl₄ in wet oxygen and wet air should be performed with emphasis on the complete elimination of all possible nitrogen sources in experiments with oxygen, in particular the residual nitrogen in the water vapor generator.

Moreover, the identification of the chemical reactions that cause an increase in the decomposition efficiency for CCl₄ in dry oxygen compared to dry air is of importance to a more comprehensive understanding of the reaction mechanism of the decomposition as well.

Since termolecular non-dissociative electron attachment in air represents less of a competition to bimolecular dissociative electron attachment to CCl₄, CHCl₃ and C₂HCl₃ than termolecular non-dissociative electron attachment in oxygen, the effect of the electric field on the destruction and removal efficiency of CCl₄, CHCl₃ and C₂HCl₃ at a given electron beam dose and intake concentration should be stronger in oxygen than in air. A corresponding experiment could therefore corroborate the notion of bimolecular dissociative electron attachment as the chemical reaction responsible for the decomposition.

The effect of "promoters" on the decomposition of CCl₄, CHCl₃ and C₂HCl₃ and in particular on the decomposition of COCl₂ and C₂HCl₃O has not been studied in the present work and requires a separate detailed investigation. For example, although the decomposition of C₂HCl₃ is much more efficient than the decomposition of CCl₄, the C₂HCl₃ decomposition product C₂HCl₃O requires an electron beam dose comparable to or higher than that for decomposition of CCl₄. Therefore, the energy expense advantage of C₂HCl₃ over CCl₄ may not be fully utilized. Preliminary experiments with H₂O₂ and the resulting OH as a "promoter" indicate that this unsatisfying situation could be improved significantly via this kind of "tunability".

With the exception of HCl and Cl₂, the chemical analysis of the decomposition products and decomposition by-products had to be limited to chemical compounds that could be separated gas chromatographically and that displayed a significant
signal on the GC-ECD, GC-TCD or GC-MS. In the case of CCl₄, such procedure was sufficient to arrive at a carbon and chlorine balance on the ppm level.

For C₂H₁₃Cl₃, such procedure was sufficient to arrive at an approximate chlorine balance involving the stable chemical species HCl and Cl₂ and the intermediate chemical species C₂HCl₃O and COCl₂. A carbon and chlorine balance for CHCl₃ and a carbon balance for C₂HCl₃ should be attempted in order to complete the analysis of the decomposition products.

Moreover, a refinement of the chemical analysis with greater attention to chemical compounds that displayed an insignificant signal on the GC-ECD, GC-TCD or GC-MS could improve the carbon and chlorine balance on the ppb level. However, exhaust concentrations on the ppb level are rarely of practical interest.

The investigation of Cold Plasma Decomposition of hazardous chemical compounds in gaseous hazardous waste may be expanded to other hazardous chemical compounds than those considered in the present work. Moreover, rather than investigating the decomposition of separate chemical compounds, it would be interesting to investigate the decomposition of mixed chemical compounds.

Since gaseous hazardous waste rarely contains only one hazardous chemical compound, such investigation would represent a major contribution to the demonstration of the practicality of the Tunable Plasma Reactor beyond the decomposition of CCl₄, CHCl₃ and C₂HCl₃.

In order to improve the understanding of the reaction mechanisms important to the cold plasma decomposition of hazardous chemical compounds, the failed mathematical modelling of the chemical kinetics of cold plasma decomposition should be re-visited.

Since the preparation and conduction of experiments is time and labor intensive, it is worthwhile to roughly estimate the value of a proposed experiment through mathematical modelling. Furthermore, an understanding of the reaction mechanisms important to the cold plasma decomposition of hazardous chemical compounds could be used for optimization of such cold plasma decomposition.

Moreover, the capability of a combined experimental and theoretical investigation of the cold plasma decomposition of hazardous chemical compounds would strengthen the position of MIT's Plasma Fusion Center and its Tunable Plasma Reactor project in the cold plasma decomposition community.
9.3.3 Experimental Equipment

The electron beam gun that generates the electron beam for the Tunable Plasma Reactor was constructed "on the fly" from outdated second hand equipment. A significant amount of maintenance was required to keep this electron beam gun in operating condition over the entire course of the present work.

Moreover, many problems regarding the control and monitoring of the electron beam voltage and the electron beam current of the electron beam gun were encountered. Of particular concern in this context was the prevention of high-voltage arcing, which would frequently result in damage to the voltage and current gauges and which would also temporarily affect the electron beam voltage and electron beam current.

A significant re-design of the electron beam gun with attention to these problems would make its operation for future experiments more reliable and less frustrating. A re-design was not attempted in the present work for fear of time limitation and fear of loss of reproducibility. However, on the basis of the fairly reliable CC4 Chemical Dosimetry developed and suggested in the present work, the latter fear may be allayed.

In addition, the expansion of the Monte-Carlo Simulation of the electron beam power deposition in air from one dimensions to two or three dimensions could prove the assumed spatial uniformity of such electron beam power deposition.

The electric field voltage was used in a "black box" manner. In particular, a detailed investigation of the voltage distribution and the electron energy distribution in the cold plasma as a function of the electric field voltage applied across the electron beam generated cold plasma was not attempted.

In view of the complexity of not only the chemistry but also the physics of electron beam generated cold plasmas, this investigation would represent a project separate from the present work altogether. Nevertheless, such investigation would also represent a significant contribution to the area of cold plasma physics.

The significance of this investigation could be enhanced by studying the effect of nitrogen, air and oxygen and of electron attaching chemical species on the voltage distribution and the electron energy distribution in such an electron beam generated cold plasma.

The conversion of the Mass Selective Detector (MSD) from a GC-MS detector to a SOR-MS detector was developed to the point where the SOR-MS software and hardware could be used rather reliably. However, a detailed analysis of the effect of the standard gas flow rate, the relative humidity of the standard gas, the standard gas, the MSD pressure and the MSD temperature on the ion abundance would be required for quality assurance and quality control purposes. Moreover, improvements
to the SOR-MS software and hardware would make operation of the SOR-MS more user friendly.

Also, a more comprehensive comparison of concentration measurements obtained through GC-ECD, GC-TCD or GC-MS to concentration measurements obtained through SOR-MS would firmly establish the feasibility of the conversion of the MSD from a GC-MS detector to a SOR-MS detector.

In order to improve the accuracy, precision and reproducibility of the gas analysis for HCl and Cl₂, it may be interesting to investigate the loss of these reactive chemical compounds to the walls of the compressed gas cylinders that contain the corresponding standards and the passivation of the walls of the tubing used in the gas mixing system.

9.4 Overall Perspective for Tunable Plasma Reactor

The Cold Plasma Decomposition of CCl₄ and CHCl₃ in (dry) air using a Tunable Plasma Reactor appears to be very practical, because the energy expense is substantially lower than the energy expense for the customary Flame Decomposition and all chlorinated decomposition products are convertible to non-hazardous salt.

Moreover, if found necessary, the superposition of an electric field to the electron beam may allow for substitution of less expensive electric field power for more expensive electron beam power. This may be particularly applicable to the decomposition of CHCl₃ in wet air.

The development of the field reactor on the basis of the laboratory reactor for decomposition of CCl₄ is not only a rewarding result of the present work but also demonstrates the ongoing interest in Cold Plasma Decomposition, such as provided through a Tunable Plasma Reactor.

The Cold Plasma Decomposition of C₂HCl₃ in (dry) air using a Tunable Plasma Reactor appears to be even more practical, although a major issue has to be resolved on the road to practicality. The practicality depends to a large extent on the demonstration of the reduction of the exhaust concentration of the C₂HCl₃ decomposition product Dichloro Acetyl Chloride (C₂HCl₃O) to sub ppm levels through broader application of “tunability”.

This broader application of “tunability” may be represented through a higher electron beam dose, a superimposed electric field or a “promoter”. Although preliminary experiments using “tunability” through a superimposed electric field have shown some potential, preliminary experiments using “tunability” through H₂O₂ as a “promoter”
have shown an even larger potential for the reduction of the $\text{C}_2\text{HCl}_3\text{O}$ exhaust concentration.
Bibliography


[37] T. Oda, T. Takahashi, H. Nakano and S. Masuda, "Decomposition of Fluorocarbon Gaseous Contaminants by Surface Discharge Induced Plasma Chemical Processing", University of Tokyo — Faculty of Engineering, Tokyo, Japan.


Appendix A

Appendix to Chapter 1

A.1 Naming Convention for Chlorinated Methanes and Ethenes

The halogenated methanes, ethanes and ethenes are derived from non-halogenated methane (CH₄), ethane (C₂H₆) and ethene (C₂H₄) via halogenation, i.e. substitution of Hydrogen (H) by Fluorine (F), Chlorine (Cl), Bromine (Br) and/or Iodine (I). The chemical formulae for these hazardous chemical compounds are shown in Table A.1.

<table>
<thead>
<tr>
<th>Halogenated Methanes</th>
<th>CH₄FₐCl₏BrcId</th>
<th>h+a+b+c+d=4</th>
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<tr>
<td>Halogenated Ethanes</td>
<td>C₂H₆FₐCl₏BrcId</td>
<td>h+a+b+c+d=6</td>
</tr>
<tr>
<td>Halogenated Ethenes</td>
<td>C₂H₄FₐCl₏BrₖcId</td>
<td>h+a+b+c+d=4</td>
</tr>
</tbody>
</table>

Table A.1: Chemical Formulas for Halogenated Methanes, Ethanes and Ethenes

The trade names established for these hazardous chemical compounds by convention are Chloro-Fluoro-Carbon CFC-xyz. For fluorinated and/or chlorinated methanes, ethanes and ethenes, c = 0 and d = 0 and the suffix xyz is generated according to xyz = 100 + 10 · h + a − 90 for methanes, according to xyz = 200 + 10 · h + a − 90 for ethanes and according to xyz = 1200 + 10 · h + a − 90 for ethenes [181]. Naturally, methanes and ethanes only have single bonds, while ethenes have a carbon-carbon double bond.

For brominated and/or iodated or for fluorinated, chlorinated, brominated and/or iodated methanes, methanes, ethanes and ethenes, the suffix xyz is generated according to the rules for fluorinated and/or chlorinated methanes, ethanes and ethenes and the number of bromine or iodine atoms is indicated by the addition of the suffix Brc and/or Id to the suffix xyz.
As an example, *Tetrachloro Methane* (Carbon Tetrachloride), a chlorinated methane with the chemical formula $\text{CCl}_4$, is named CFC-10, *Trichloro Methane* (Chloroform), a chlorinated methane with the chemical formula $\text{CHCl}_3$, is named CFC-20, and *Trichloro Ethene* (Trichloroethylene), a chlorinated ethene with the chemical formula $\text{C}_2\text{HCl}_3$, is named CFC-1120.

### A.2 Scientific and Engineering Constants

<table>
<thead>
<tr>
<th>Name</th>
<th>Mantissa</th>
<th>Exponent</th>
<th>Dimension</th>
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<td></td>
</tr>
<tr>
<td>$g$</td>
<td>9.80665</td>
<td></td>
<td>m/s²</td>
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<tr>
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<td>m</td>
</tr>
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<td>10⁻¹²</td>
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<td>As</td>
</tr>
<tr>
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<td>kg</td>
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<td>kg</td>
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<td>$u$</td>
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<td>$N_A$</td>
<td>6.0221367(36)</td>
<td>10²³</td>
<td>1/mol</td>
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Table A.2: Scientific and Engineering Constants [83]

### A.3 General Solution to Differential Equation, Part One

The general solution is sought to the following ordinary differential equation:

$$\frac{df}{dx} = a - b(f - f^*)$$

Here, $a$, $b$ and $f^*$ are constants. By substitution of $g = f - f^*$, the ordinary differential equation may be rewritten as:
\[
\frac{dg}{dx} = a - bg
\]

Under initial conditions where \( f|_x=0 = f_0 \), i.e. \( g|_x=0 = f_0 - f^* \), the solution to the ordinary differential equation results as:

\[
\int_{g_0}^{g} \frac{dg}{a - bg} = \int_{0}^{x} dx
\]

\[-\frac{1}{b} \ln(a - bg)|_{g_0}^{g} = x|_{0}^{x}
\]

\[-\frac{1}{b} [\ln(a - bg) - \ln(a - bg_0)] = -\frac{1}{b} \ln \frac{a - bg}{a - bg_0} = x
\]

\[
\ln \frac{a - bg}{a - bg_0} = -bx
\]

\[
a - bg = [a - bg_0] e^{-bx}
\]

\[
\frac{a}{b} - g = \left[\frac{a}{b} - g_0\right] e^{-bx}
\]

\[
g = \frac{a}{b} - \left[\frac{a}{b} - g_0\right] e^{-bx}
\]

\[
g = \frac{a}{b} \left[1 - e^{-bx}\right] + g_0 e^{-bx}
\]

By back-substitution, the solution to the ordinary differential equation results as:

\[
f = f^* + \frac{a}{b} \left[1 - e^{-bx}\right] + (f_0 - f^*)e^{-bx}
\]

Apparently, when \( b \ll x \) and \( f_0 \approx f^* \), the solution to the ordinary differential equation may be approximated as:

\[
e^{-bx} \approx 1 - bx
\]

\[
f \approx f^* + \frac{a}{b} bx = f^* + ax
\]
A.4 General Solution to Differential Equation, Part Two

The general solution is sought to the following ordinary differential equation:

$$\frac{d^2 f}{dx^2} = \frac{a}{\sqrt{b f}}$$

Here, $a$ and $b$ are constants. By substitution of $g = \frac{df}{dx}$, the ordinary differential equation may be rewritten as:

$$\frac{d^2 f}{dx^2} = \frac{dg}{dx} = \frac{dg}{df} \frac{df}{dx} = \frac{dg}{df} g = \frac{1}{2} \frac{dg^2}{df}$$

$$dg^2 = \frac{2a}{\sqrt{b f}} df$$

The solution to this ordinary differential equation results as:

$$g^2 = 4 \frac{a}{b} \sqrt{b f} + c$$

Under boundary conditions where $g|_{f=0} = 0$, the solution to the ordinary differential equation results as:

$$g = 2 \sqrt[4]{\frac{a}{b} \sqrt[3]{b f}}$$

Therefore:

$$\frac{df}{dx} = 2 \sqrt[4]{\frac{a}{b} \sqrt{b f}}$$

$$\frac{df}{\sqrt{f}} = 2 \sqrt[4]{\frac{a}{b} \sqrt{b}} dx$$

$$\frac{4}{3} f^3 = 2 \sqrt[4]{\frac{a}{b} \sqrt{b}} x + c$$
Under boundary conditions where \( f|_{x=0} = 0 \), the solution to the ordinary differential equation results as:

\[
\frac{4}{3} f^3 = 2 \sqrt{\frac{a}{b}} \sqrt{b} x
\]

\[
f = \left[ \frac{3}{2} a^\frac{1}{2} b^{-\frac{1}{4}} x \right]^\frac{4}{3}
\]

\[
f = \left( \frac{3}{2} \right)^\frac{4}{3} a^\frac{2}{3} b^{-\frac{1}{3}} x^\frac{4}{3}
\]
Appendix B

Appendix to Chapter 3

B.1 Vapor Pressure of Pure Liquid

The enthalpy $h$, the free energy $g$, the entropy $s$, the temperature $T$, the pressure $p$ and the mass specific volume $v$ of a thermodynamic system are connected via the following fundamental thermodynamic equations:

\[
 g = h - Ts \quad \text{and} \quad dh = Tds + vdp
\]

These equations may be combined to result in:

\[
 dg = dh - sdT - Tds \quad \text{and} \quad dg = -sdT + vdp
\]

It is important to note that the temperature and the pressure in the gas-liquid-phase region of a chemical compound are constant:

\[
 T = \text{const.} \quad p = \text{const.} \quad dT = 0 \quad dp = 0
\]
Therefore, in this gas-liquid-phase region, the following relations hold:

\[
\begin{align*}
\frac{dh}{T} &= \frac{ds}{s'' - s'} \\
h'' - h' &= T(s'' - s') \\
s'' - s' &= \frac{1}{T}(h'' - h')
\end{align*}
\]

Here, the superscript ' represents values at the liquid-phase/gas-liquid-phase line and the superscript '' represents values at the gas-liquid-phase/gas-phase line of the gas-liquid-phase region. Along the liquid-phase/gas-liquid-phase line and the gas-liquid-phase/gas-phase line, the following relations hold:

\[
\begin{align*}
dg' &= -s'dT + v'dp \\
dg'' &= -s''dT + v''dp
\end{align*}
\]

For simultaneous equilibrium between the liquid-phase and the gas-liquid-phase regions and the gas-liquid-phase and the gas-phase regions, the difference in free energy between these two lines must be minimized, i.e. \(d(g'' - g') = 0\):

\[
d(g'' - g') = -(s'' - s')dT + (v'' - v')dp
\]

This is the familiar Clausius-Clapeyron equation. Assuming the ideal gas law along the gas-liquid-phase/gas-phase line, this equation may be simplified:

\[
pV = m\frac{R_m T}{M}
\]

\[
\rho = \frac{m}{V} = \frac{M}{R_m} \frac{p}{T}
\]
Here, \( \rho \) is the gas-phase mass density determined through the ideal gas law. Moreover, the heat of vaporization \( \Delta h_v \) is defined via:

\[
\begin{align*}
    h'' - h' &= \Delta h_v \\
    v'' - v' &\approx v'' = \frac{1}{\rho}
\end{align*}
\]

Therefore:

\[
\begin{align*}
    \frac{dp}{dT} &= \frac{\Delta h_v}{T} \frac{M_p}{R_m T} \\
    \frac{dp}{p} &= \frac{M \Delta h_v}{R_m T^2} dT
\end{align*}
\]

This differential equation may readily be solved:

\[
\begin{align*}
    \ln \frac{p}{p_0} &= \frac{M \Delta h_v}{R_m} \left( \frac{1}{T_0} - \frac{1}{T} \right) \\
    p &= p_0 e^{\left( \frac{M \Delta h_v}{R_m T_0} \right) e^{\left( -\frac{M \Delta h_v}{R_m T} \right)}} \\
    p &= p^*(T) = p^* e^{\left( -\frac{T}{T^*} \right)}
\end{align*}
\]

Where, for the purpose of simplicity \( T^* \) and \( p^* \) are defined as:

\[
\begin{align*}
    T^* &= \frac{M \Delta h_v}{R_m} \\
    p^* &= p_0 e^{\left( \frac{T^*}{T_0} \right)}
\end{align*}
\]

Thus, the vapor pressure \( p^*(T) \) of a chemical compound in the gas phase above its liquid-phase at temperature \( T \) is a function of the temperature \( T \) alone.
B.2 Rotameter Calibration

Tables B.1 through B.8 provide a comparison of the nominal volume flow rates as provided by the respective manufacturers of the rotameters to the actual volume flow rates as obtained from re-calibration measurements with a flow calibrator and a soap film flow meter.

<table>
<thead>
<tr>
<th>Nominal Volume Flow Rate [cm³/min]</th>
<th>Actual Volume Flow Rate [cm³/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>1.0</td>
<td>2.3</td>
</tr>
<tr>
<td>2.0</td>
<td>3.6</td>
</tr>
<tr>
<td>4.0</td>
<td>7.4</td>
</tr>
<tr>
<td>6.0</td>
<td>10.2</td>
</tr>
<tr>
<td>10.0</td>
<td>11.8</td>
</tr>
<tr>
<td>20.0</td>
<td>18.9</td>
</tr>
<tr>
<td>30.0</td>
<td>25.4</td>
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<tr>
<td>40.0</td>
<td>34.9</td>
</tr>
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<td>50.0</td>
<td>48.4</td>
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</tr>
<tr>
<td>80.0</td>
<td>89.0</td>
</tr>
<tr>
<td>90.0</td>
<td>103.4</td>
</tr>
</tbody>
</table>

Table B.1: Volume Flow Meter 1: Omega FL-220 (No.1) (Glass Float)

B.3 Theory of Rotameter Operation

The standard rotameter features a vertically mounted tapered tube, with the narrow end pointing downwards and the wide end pointing upwards. A float, typically of spherical shape, moves freely along the tapered tube. The location of the float along the tapered tube is representative of the volume flow rate of the fluid through the rotameter.

A simple equation for the volume flow rate of the fluid through the rotameter as a function of the location of the float along the tapered tube may be obtained from the vertical force equilibrium, comprising the dynamic pressure force \( F_p \) of the fluid on
### Table B.2: Volume Flow Meter 2: Omega FL-220 (No.2) (Glass Float)

<table>
<thead>
<tr>
<th>Nominal Volume Flow Rate [cm$^3$/min]</th>
<th>Actual Volume Flow Rate [cm$^3$/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
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<td>0.5</td>
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<tr>
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<tr>
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<td>80.0</td>
<td>86.7</td>
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<tr>
<td>90.0</td>
<td>101.8</td>
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Table B.2: Volume Flow Meter 2: Omega FL-220 (No.2) (Glass Float)

### Table B.3: Volume Flow Meter 3: Omega FL-221 (Glass Float)

<table>
<thead>
<tr>
<th>Nominal Volume Flow Rate [cm$^3$/min]</th>
<th>Actual Volume Flow Rate [cm$^3$/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
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<td>2</td>
<td>3.1</td>
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<td>6</td>
<td>5.0</td>
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<td>10</td>
<td>6.7</td>
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<tr>
<td>20</td>
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<tr>
<td>50</td>
<td>44.8</td>
</tr>
<tr>
<td>100</td>
<td>106.4</td>
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<td>150</td>
<td>149.5</td>
</tr>
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<td>200</td>
<td>200.9</td>
</tr>
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<td>250</td>
<td>265.1</td>
</tr>
<tr>
<td>290</td>
<td>320.4</td>
</tr>
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</table>

Table B.3: Volume Flow Meter 3: Omega FL-221 (Glass Float)
Table B.4: Volume Flow Meter 4: Omega FL-224 (Glass Float)

<table>
<thead>
<tr>
<th>Nominal Volume Flow Rate [cm³/min]</th>
<th>Actual Volume Flow Rate [cm³/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>906.1</td>
</tr>
<tr>
<td>2000</td>
<td>1762.0</td>
</tr>
<tr>
<td>4000</td>
<td>3996.0</td>
</tr>
<tr>
<td>5000</td>
<td>5046.0</td>
</tr>
<tr>
<td>7000</td>
<td>6874.0</td>
</tr>
<tr>
<td>9000</td>
<td>8799.0</td>
</tr>
<tr>
<td>10000</td>
<td>9769.0</td>
</tr>
<tr>
<td>15000</td>
<td>14320.0</td>
</tr>
<tr>
<td>20000</td>
<td>19120.0</td>
</tr>
<tr>
<td>25000</td>
<td>24220.0</td>
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<tr>
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<tr>
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<tr>
<td>39000</td>
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</table>

Table B.5: Volume Flow Meter 5: Matheson E603 (Glass Float)

<table>
<thead>
<tr>
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<th>Nominal Volume Flow Rate [cm³/min]</th>
<th>Actual Volume Flow Rate [cm³/min]</th>
</tr>
</thead>
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<tr>
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<tr>
<td>10</td>
<td>166.9</td>
<td>109.1</td>
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<td>394.2</td>
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<td>601.8</td>
<td>576.7</td>
</tr>
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<td>794.0</td>
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<td>70</td>
<td>1310.4</td>
<td>1380.0</td>
</tr>
<tr>
<td>80</td>
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</tr>
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</tr>
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</tr>
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<td>150</td>
<td>2410.9</td>
<td>2517.0</td>
</tr>
<tr>
<td>Setting</td>
<td>Nominal Volume Flow Rate [cm³/min]</td>
<td>Actual Volume Flow Rate [cm³/min]</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
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<td>6706.0</td>
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<td>80</td>
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<td>13160.0</td>
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</tr>
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</tr>
<tr>
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<td>18730.0</td>
</tr>
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</tr>
<tr>
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<td>22650.0</td>
</tr>
<tr>
<td>150</td>
<td>24921.7</td>
<td>24810.0</td>
</tr>
</tbody>
</table>

Table B.6: Volume Flow Meter 6: Matheson E605 (Glass Float)

<table>
<thead>
<tr>
<th>Setting</th>
<th>Nominal Volume Flow Rate [ft³/h]</th>
<th>Actual Volume Flow Rate [cm³/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>471.9</td>
<td>463.4</td>
</tr>
<tr>
<td>2</td>
<td>943.9</td>
<td>908.2</td>
</tr>
<tr>
<td>3</td>
<td>1415.8</td>
<td>1372.0</td>
</tr>
<tr>
<td>4</td>
<td>1887.8</td>
<td>1797.0</td>
</tr>
<tr>
<td>5</td>
<td>2359.7</td>
<td>2270.0</td>
</tr>
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<td>6</td>
<td>2831.7</td>
<td>2735.0</td>
</tr>
<tr>
<td>7</td>
<td>3303.6</td>
<td>3127.0</td>
</tr>
<tr>
<td>8</td>
<td>3775.6</td>
<td>3627.0</td>
</tr>
<tr>
<td>9</td>
<td>4247.5</td>
<td>4124.0</td>
</tr>
<tr>
<td>10</td>
<td>4719.5</td>
<td>4563.0</td>
</tr>
</tbody>
</table>

Table B.7: Volume Flow Meter 7: Dwyer (No.1) (Glass Float)
the float, the buoyancy force $F_b$ of the fluid on the float and the mass force $F_m$ of the float. For simplicity, an incompressible fluid is assumed and dynamic or kinematic viscosity effects of the fluid are neglected:

$$F_p = F_m - F_b$$

$$\frac{1}{2} \rho_{\text{fluid}} v_{\text{fluid}}^2 A_{\text{fluid}} = \rho_{\text{float}} V_{\text{float}} g - \rho_{\text{fluid}} V_{\text{float}} g$$

$$v_{\text{fluid}}^2 = 2 \frac{\rho_{\text{float}} - \rho_{\text{fluid}}}{\rho_{\text{fluid}}} \frac{V_{\text{float}}}{A_{\text{fluid}}} g$$

$$v_{\text{fluid}} = \sqrt{2 \frac{\rho_{\text{float}} - \rho_{\text{fluid}}}{\rho_{\text{fluid}}} \frac{V_{\text{float}}}{A_{\text{fluid}}} g} = \sqrt{2 \left( \frac{\rho_{\text{float}}}{\rho_{\text{fluid}}} - 1 \right)} \frac{V_{\text{float}}}{A_{\text{fluid}}} g$$

Here, $\rho_{\text{float}}$ and $\rho_{\text{fluid}}$ are the mass density of the float and the fluid, respectively. Also, $V_{\text{float}}$ is the volume of the float, $A_{\text{fluid}}$ is the area over which the dynamic pressure of the fluid acts on the float and $v_{\text{fluid}}$ is the flow velocity of the fluid creating the dynamic pressure of the fluid.

Under the assumption of $\frac{\rho_{\text{float}}}{\rho_{\text{fluid}}} \gg 1$, the volume flow rate of the fluid through the rotameter results as:

$$\dot{V}_{\text{fluid}} = v_{\text{fluid}} A$$
\[ \dot{V}_{\text{Fluid}} \approx A \sqrt{\frac{2 \rho_{\text{Float}} V_{\text{Float}}}{\rho_{\text{Fluid}} A_{\text{Fluid}}}} \]

Here, \( A \) is the area of the cross section of the tapered tube at the location of the float along the tapered tube and \( \dot{V}_{\text{Fluid}} \) is the volume flow rate of the fluid through the rotameter. The area \( A \) is related to the location of the float along the tapered tube via:

\[
\begin{align*}
    r &= a + bz \\
    A &= \pi r^2 \\
    A &= \pi (a + bz)^2
\end{align*}
\]

Here, \( r \) is the radius of area \( A \), assuming a circular cross section of the tapered tube, \( z \) is the location of the float along the tapered tube and \( a \) and \( b \) are constants characteristic of the tapered tube. Therefore, the volume flow rate of the fluid through the rotameter is given by:

\[
\dot{V}_{\text{Fluid}} = \pi (a + bz)^2 \sqrt{\frac{2 \rho_{\text{Float}} V_{\text{Float}}}{\rho_{\text{Fluid}} A_{\text{Fluid}}}}
\]

Also, the volume flow rates of two different fluids 1 and 2 are given by:

\[
\begin{align*}
    \dot{V}_1 &= \pi (a + bz_1)^2 \sqrt{\frac{2 \rho_{\text{Float}} V_{\text{Float}}}{\rho_1 A_1}} \\
    \dot{V}_2 &= \pi (a + bz_2)^2 \sqrt{\frac{2 \rho_{\text{Float}} V_{\text{Float}}}{\rho_2 A_2}}
\end{align*}
\]

\[
\frac{\dot{V}_1}{\dot{V}_2} = \frac{(a + bz_1)^2}{(a + bz_2)^2} \sqrt{\frac{\rho_2 A_2}{\rho_1 A_1}}
\]

With the same location \( z_1 = z_2 \) of the float along the tapered tube for both fluids and under the assumption of \( A_1 \approx A_2 \) as well as and under the assumption of the ideal gas law, this equation for the ratio of the volume flow rates of two different fluids may be rewritten as:
\[ pV = m \frac{R_m T}{M} \]
\[ \rho = \frac{m}{V} = \frac{p M}{R_m T} \]
\[ \rho_1 = \frac{p_1 M_1}{R_m T_1} \]
\[ \rho_2 = \frac{p_2 M_2}{R_m T_2} \]
\[ \frac{\rho_1}{\rho_2} = \frac{M_1}{M_2} \]

\[ \frac{\dot{V}_1}{\dot{V}_2} = \sqrt{\frac{M_2}{M_1}} \]

Therefore, if the rotameter is calibrated for air as fluid 2, the Volume flow rate of fluid 1 is related to the volume flow rate of air at the same location of the float along the tapered tube by:

\[ \dot{V}_1 = \sqrt{\frac{M_{Air}}{M_1}} \dot{V}_{Air} \]

Thus, the volume flow rate of air is measured via the location of the float along the tapered tube and then converted to the volume flow rate of the fluid by multiplying the volume flow rate of air by the square root of the ratio of the mole mass of air to the mole mass of the fluid.
Appendix C

Appendix to Chapter 4

C.1 Child’s Equation

Child’s equation describes the voltage distribution between an electron emitting cathode and an anode in vacuum under space charge conditions. The electrodes are assumed to have infinite area and be parallel in orientation. The emission of electrons from the cathode results in an electron current density between the two electrodes.

The voltage distribution between the electrodes can then be found in one-dimensional geometry, with the electron current density exclusively sustained by the electron emitting cathode.

Several mathematical steps are involved in arriving at the voltage distribution between the electrodes. First, the electron velocity is expressed as a function of the voltage. Second, the electron density is expressed as a function of the voltage. Third, the voltage is expressed as a function of the distance from the cathode. The electron current density serves as a parameter for the second and the third step.

The significance of Child’s equation lies in the fact that given the voltage and distance between the two electrodes, the electron current density between the two electrodes can be calculated [82].

The relations among the electric field $E$, the voltage $V$, the electron mass $m$, the electron charge $q$ and the electron velocity $v$ in vacuum are:

$$E = -\nabla V$$
\[
\frac{m}{\text{d}t} \frac{\text{d}v}{\text{d}t} = qE \\
\frac{m}{\text{d}t} \frac{\text{d}v}{\text{d}t} = -q\nabla V
\]

In one-dimensional geometry, a mathematical simplification may be obtained, resulting in an ordinary differential equation for the electron velocity as a function of the voltage. It amounts to a ballistic description of the electron motion:

\[
\frac{m}{\text{d}t} \frac{\text{d}v}{\text{d}t} = -q \frac{\text{d}V}{\text{d}z} \\
\frac{m}{\text{d}t} \frac{\text{d}z}{\text{d}t} \frac{\text{d}v}{\text{d}t} = -q dV \\
\frac{m}{\text{d}t} v \frac{\text{d}v}{\text{d}t} = -q dV \\
\frac{1}{2} m v^2 = -q dV
\]

Here, \( z \) is the distance from the cathode, and:

\[
v = \frac{dz}{dt}
\]

Under boundary conditions where \( V(z=0) = V_0 \) and \( v(z=0) = 0 \), the solution to this ordinary differential equation is obtained:

\[
v = \sqrt{-\frac{2q}{m} (V - V_0)}
\]

The relations among the electron mass \( m \), the electron charge \( q \), the electron velocity \( v \), the electron density \( n \) and the electron current density \( j \) in vacuum are:

\[
j = n q v \\
n = \frac{1}{q v^2} j \cdot v
\]
In one-dimensional geometry, a mathematical simplification may be obtained, resulting in an equation for the electron density as a function of the voltage:

\[ n = \frac{j}{qv} \]
\[ n = \frac{j}{q\sqrt{-\frac{2q}{m}(V - V_0)}} \]

The relations among the particle density electric field \( E \), the voltage \( V \), the electron charge \( q \), the electron density \( n \) and the charge density \( \rho \) in vacuum are:

\[ \nabla E = \frac{\rho}{\epsilon} \]
\[ \nabla^2 V = -\frac{\rho}{\epsilon} \]

In one-dimensional geometry, a mathematical simplification may be obtained, resulting in an ordinary differential equation for the voltage as a function of the distance from the cathode:

\[ \rho = nq \]
\[ \frac{d^2V}{dz^2} = -\frac{\rho}{\epsilon} = -\frac{nq}{\epsilon} \]
\[ \frac{d^2V}{dz^2} = -\frac{j}{\epsilon\sqrt{-\frac{2q}{m}(V - V_0)}} \]
\[ \frac{d^2V}{dz^2} = \frac{d^2(V - V_0)}{dz^2} \]

Under boundary conditions where \( \frac{dV}{dz}|_{z=0} = 0 \), the solution to this ordinary differential equation as derived in Appendix A.4 results as:

\[ V = V_0 + \left[ \frac{3}{2} \right]^{\frac{1}{3}} \left[ \frac{j}{\epsilon_0} \right]^{\frac{3}{2}} \left[ -\frac{2q}{m} \right]^{-\frac{1}{3}} z^{\frac{3}{2}} \]
With $s$ the distance between the two electrodes, the electron current density may be expressed as a function of the voltage $V_s$ between the two electrodes:

$$ j = 4 \frac{\sqrt{2}}{9} \frac{\varepsilon(V_s - V_0)^{3/2}}{s^2} \left[ - \frac{q}{m} \right]^{1/2} $$

### C.2 One-Dimensional Temperature Distribution

The partial differential equation describing the heat conduction within a solid body is given as:

$$ \rho c_p \frac{\partial T}{\partial t} = -\nabla \cdot q'' + q''' $$

$$ q'' = -\lambda \nabla T $$

$$ \rho c_p \frac{\partial T}{\partial t} = \nabla \cdot \nabla \lambda T + q''' $$

Here, $T$ is the temperature of the solid body, $\rho$, $c_p$ and $\lambda$ are the mass density, mass heat capacity and thermal conductivity, respectively, of the solid body. The heat flux density and the volumetric heat generation rate within the solid body are represented by $q''$ and $q'''$, respectively.

Under conditions where $\lambda = \text{const.}$, $q''' = \text{const.}$, steady state conditions prevail, i.e. $\frac{\partial T}{\partial t} = 0$ and one-dimensional linear geometry obtains, i.e. $\nabla^2 T = \frac{\partial^2 T}{\partial \psi^2}$, the partial differential equation reverts to an ordinary differential equation, whose general solution results as:

$$ \lambda \frac{\partial^2 T}{\partial \psi^2} = -q''' $$

$$ T = C_1 + C_2 \psi - \frac{q'''}{2\lambda} \psi^2 $$

Here, $\psi$ is the one-dimensional coordinate. The problem is symmetric about $\psi = 0$. The coordinate $\psi$ is bounded by:
\[-\frac{\psi}{2} \leq \psi \leq \frac{\psi}{2}\]

Under boundary conditions where \(\frac{\partial T}{\partial \psi}|_{\psi=0} = 0\) and \(T|_{\psi=\pm \frac{\psi}{2}} = T_{\psi}\), the integration constants \(C_1\) and \(C_2\) evaluate to:

\[
\begin{align*}
C_2 &= 0 \\
C_1 &= T_{\psi} + \frac{q''}{8\lambda} \Psi^2
\end{align*}
\]

Thus, the maximum temperature \(\hat{T}\) and maximum temperature difference within \(\Psi\), i.e. \(\Delta \hat{T} = \hat{T} - T_{\psi}\), result as:

\[
\begin{align*}
T &= T_{\psi} + \frac{q''\Psi^2}{8\lambda} \left[ 1 - 4 \left( \frac{\psi}{\Psi} \right)^2 \right] \\
\hat{T} &= T|_{\psi=0} = T_{\psi} + \frac{q''\Psi^2}{8\lambda} \\
\Delta \hat{T} &= \frac{q''\Psi^2}{8\lambda}
\end{align*}
\]

**C.3 Foil Tension Stress**

An equation for the approximate foil tension stress may be derived from a force balance along the x-axis and the z-axis, i.e. via \(F_x\) and \(F_z\) as shown in Figure C.1. This figure details the force balance on a section through the foil in the x/z-plane.

If the extension of the foil along the y-axis is assumed to be infinite, the foil may be viewed as a one-dimensional object in the x/z-plane. This is a fair assumption for slots with \(h \gg a\).

The foil areas \(A_p\) and \(A_t\), upon which the pressure \(p\) and the tension stress \(\sigma_t\) are acting may be readily calculated. Approximations are based on \(h \gg a\):

\[
\begin{align*}
A_p &= A_S \approx ha \\
A_t &\approx ht
\end{align*}
\]
Figure C.1: Foil Tension Stress Force Balance
The pressure \( p \) acting along the x/y-plane may be converted into a linear force \( f \) acting along the x-axis:

\[
fa = pAp \\
f \approx hp
\]

Since \( p = \text{const.} \), it follows that \( f = \text{const.} \). The force balance along the x-axis and the z-axis then results in an equation for the tension force \( F_t \). This force is a function of the linear force \( f \) and the constant force \( F_t^0 \):

\[
F_x = F_t^0 \\
F_z = fx \\
F_t = \sqrt{F_x^2 + F_z^2} = F_t^0 \sqrt{1 + \left[ \frac{fx}{F_t^0} \right]^2}
\]

The constant force \( F_t^0 \) may be obtained by considering the coupling of the maximum stress \( \sigma_t \) and the maximum strain \( \varepsilon_t \) via the modulus of elasticity \( E \). For a one-dimensional object, \( \sigma_t \) occurs at the location of \( \varepsilon_t \):

\[
\sigma_t = E\varepsilon_t
\]

Thus, by expressing both the maximum stress \( \sigma_t \) and the maximum strain \( \varepsilon_t \) as functions of the force \( F_t^0 \), a heuristic equation for this force may be obtained. The maximum strain \( \varepsilon_t \) is simply:

\[
\varepsilon_t = \frac{L - a}{a} = \frac{L}{a} - 1
\]

Thus it is necessary to determine next the length of the strained foil \( L \), across the slot, as opposed to \( a \), the length of the unstrained foil across the slot:

\[
L = \int_{-\frac{b}{2}}^{\frac{b}{2}} dl \\
\int dl = \sqrt{(dx)^2 + (dz)^2} = \sqrt{1 + \left[ \frac{dz}{dx} \right]^2} dx
\]

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An equation for \( \frac{dz}{dx} \) can be derived by using the force balance along the x-axis and the z-axis:

\[
\tan \theta = \frac{F_z}{F_x} = \frac{dz}{dx}
\]

\[
\frac{dz}{dx} = \frac{f_x}{F_t^0}
\]

A mathematical simplification may be obtained by defining \( \beta \) and re-expressing \( F_t^0 \) and \( \frac{f_x}{F_t^0} \) in terms of \( \beta \):

\[
\beta = \frac{fa}{2F_t^0}
\]

\[
F_t^0 = \frac{fa}{2\beta}
\]

\[
\frac{f_x}{F_t^0} = 2\beta \frac{x}{a}
\]

Also note that:

\[-\frac{L}{2} \leq l \leq \frac{L}{2}, -\frac{a}{2} \leq x \leq \frac{a}{2}, -\frac{1}{2} \leq \frac{x}{a} \leq \frac{1}{2}\]

Thus \( \frac{dz}{dx} \) is given by:

\[
\frac{dz}{dx} = 2\beta \frac{x}{a}
\]

This allows for calculation of \( L \):

\[
dl = a\sqrt{1 + \left[2\beta \frac{x}{a}\right]^2} \frac{dx}{a}
\]

\[
L = a\int_{-\frac{1}{2}}^{\frac{1}{2}} \sqrt{1 + \left[2\beta \frac{x}{a}\right]^2} \frac{dx}{a}
\]

\[
L = \frac{a}{2} \left[ \sqrt{1 + \beta^2 + \frac{1}{\beta \ar sinh \beta}} \right]
\]
Since typically $\beta \ll 1$, further mathematical simplifications may be obtained. Both the $\sqrt{1 + \beta^2}$ function and the $\text{arsinh}\beta$ function are expanded into series which are terminated after the first non-linear term containing $\beta$:

\[
\sqrt{1 + \beta^2} \approx 1 + \frac{1}{2} \beta^2
\]

\[
\text{arsinh}\beta = \beta - \frac{1}{6} \beta^3 + \frac{3}{40} \beta^5 - \ldots
\]

Based on these mathematical simplifications, the strained foil length $L$ and the maximum strain $\varepsilon_t$ result as:

\[
L \approx a \left[1 + \frac{1}{6} \beta^2\right]
\]

\[
\varepsilon_t \approx \frac{1}{6} \beta^2
\]

While this equation couples $F_t^0$ to $\varepsilon_t$ via $\beta$, an equation is now needed that couples $F_t^0$ to $\varepsilon_t$ via $\beta$. The maximum stress $\sigma_t$ is simply:

\[
\sigma_t = \frac{\hat{F}_t}{A_t}
\]

The maximum force $\hat{F}_t$ can be determined as:

\[
F_t = F_t^0 \sqrt{1 + \left[2\beta \frac{x_1}{a}\right]^2}
\]

\[
\hat{F}_t = F_t|_{x=\frac{a}{2}}
\]

\[
\hat{F}_t = F_t^0 \sqrt{1 + \beta^2} \approx F_t^0
\]

The maximum stress $\sigma_t$ results as:
\[
\dot{\sigma}_t \approx \frac{F_t^0}{A_t} = \sigma_t^0 = \frac{fa}{2\beta A_t}
\]

Combination of the maximum strain \(\dot{\varepsilon}_t\) and the maximum stress \(\dot{\sigma}_t\) via the modulus of elasticity \(E\) results in a cubic equation for \(\beta\), i.e. \(F_t^0\):

\[
\beta^3 \approx 3 \frac{fa}{EA_t}
\]

With the previously derived equations for \(A_t\) and \(f\), the solutions for \(\beta\), \(F_t^0\) and \(\sigma_t^0\) are:

\[
\beta = \sqrt[3]{3} \frac{fa}{EA_t} = \sqrt[3]{3} \frac{P}{E} \frac{a}{t}
\]

\[
F_t^0 = \sqrt[3]{\frac{1}{24} EA_t (fa)^2}
\]

\[
\sigma_t^0 = \sqrt[3]{\frac{1}{24} Ep^2 \left[\frac{a}{t}\right]^2}
\]

The approximate foil tension stress \(\dot{\sigma}_t\) is now given by the maximum foil stress \(\dot{\sigma}_t\), which in turn is approximated by the equation for \(\sigma_t^0\):

\[
\dot{\sigma}_t \approx \dot{\sigma}_t \approx \sigma_t^0 = \sqrt[3]{\frac{1}{24} Ep^2 \left[\frac{a}{t}\right]^2}
\]

With \(p = 1.01325 \cdot 10^5\) Pa, \(E = E_{Al} = 69.0 \cdot 10^9\) Pa [92], \(a = \frac{1}{8}\) inch and \(t = \frac{1}{1000}\) inch, the approximate foil tension stress becomes \(\dot{\sigma}_t \approx \dot{\sigma}_t \approx \sigma_t^0 \approx 77\) N/mm\(^2\). Also, \(\beta\) evaluates to \(\beta = 8.2 \cdot 10^{-2} \ll 1\).

### C.4 Foil Shear Stress

An equation for the approximate foil shear stress may be derived from a force balance along the z-axis, i.e. via \(F_p\) and \(F_s\) as shown in Figure C.2.
Figure C.2: Foil Shear Stress Force Balance
The foil areas $A_p$ and $A_s$, upon which the pressure $p$ and the shear stress $\sigma_s$ are acting are given by:

\[
\begin{align*}
A_p &= A_s \\
A_s &= [2(h - a) + \pi a] t
\end{align*}
\]

The force balance then results in an equation for the shear stress $\sigma_s$:

\[
F_p = F_s
\]

\[
pA_p = \sigma_s A_s
\]

\[
\sigma_s = \frac{\frac{h}{a} - \left(1 - \frac{a}{\pi}\right) \frac{a}{2} \pi}{2h - (2 - \pi) t} p
\]

The limit of very long slots, i.e. $h \gg a$, then results in the approximate shear stress $\tilde{\sigma}_s$.

\[
\tilde{\sigma}_s \approx \frac{1}{2} \frac{a}{t} p
\]

With $p = 1.01325 \cdot 10^5$ Pa, $a = \frac{1}{8}$ inch and $t = \frac{1}{1000}$ inch, the approximate foil shear stress $\tilde{\sigma}_s$ becomes $\tilde{\sigma}_s = 6$ N/mm$^2$. 
Appendix D

Appendix to Chapter 5

D.1 Plate Theory of Gas Chromatographic Separation

The gas chromatographic column is assumed to be a serial assembly of "plates". The total number of plates in the column being $n$. Each plate may have mass $m_i$ of the liquid phase and volume $V_g$ of the gas phase, so that the total mass of the liquid phase is $nm_i$ and the total volume of the gas phase is $nV_g$.

The equilibrium of chemical compound $j$ between the liquid phase and the gas phase on each plate $i$ at time $t$ then is described mathematically via its distribution coefficient $K_{d_j}$:

$$\frac{m_j^{li}(t)}{m_i} = K_{d_j} \frac{m_j^{gi}(t)}{V_g}$$

$$m_j^i(t) = m_j^{li}(t) + m_j^{gi}(t)$$

Here, $m_j^{li}(t)$ and $m_j^{gi}(t)$ represent the mass of chemical compound $j$ on plate $i$ in the liquid phase and the gas phase, respectively, at time $t$. Consequently, $m_j^i(t)$ represents the total mass of chemical compound $j$ on plate $i$ at time $t$. These equations may readily be manipulated to yield:

$$m_j^{li}(t) = x m_j^i(t)$$
$$m_j^{gi}(t) = y m_j^i(t)$$
Where \( x \) and \( y \) are defined as:

\[
x = \frac{K_d m_l}{V_g + K_d m_l}
\]

\[
y = \frac{V_g}{V_g + K_d m_l}
\]

Here, \( x \) and \( y \) represent the fraction of mass \( m_j^i(t) \) that is in the liquid phase and gas phase, respectively, at equilibrium on the plate. Note that \( x \) and \( y \) are constant both with respect to plate \( i \) and time \( t \). Definition of the liquid density \( \rho_l \) and the porosity \( \epsilon \) via the volume \( V_l \) of the liquid phase leads to modified equations for \( x \) and \( y \):

\[
\rho_l = \frac{m_l}{V_l}
\]

\[
\epsilon = \frac{V_g}{V_g + V_l}
\]

\[
x = \frac{1}{1 + \frac{1}{K_d \rho_l} \frac{\epsilon}{1-\epsilon}}
\]

\[
y = \frac{1}{1 + \frac{1}{K_d \rho_l} \frac{1-\epsilon}{\epsilon}}
\]

The underlying assumption of Plate theory is the establishment of equilibrium on the plate during one plate residence time:

\[
\tau = \frac{V_g}{V_g}
\]

Here, \( \tau \) represents the plate residence time and \( \dot{V}_g \) represents the volume flow rate of carrier gas through the gas chromatographic column. The plate residence time may be regarded as a synchronization time for the gas chromatographic separation, as will become apparent shortly.
It is appropriate then to consider only times \( t \) at which equilibrium is established, i.e. to express time \( t \) as an integer multiple of the plate residence time:

\[
   t = k \tau \\
   k = \frac{tV}{V_g}
\]

Then, index \( k \) is an integer such that it represents the \( k^{th} \) plate residence time. The gas chromatographic separation then proceeds as follows, where time \( t \) now is replaced by index \( k \).

A mass \( m_{js} \) of chemical compound \( j \) is injected onto plate 1. This mass equilibrates to yield \( m_{j1}^{11}(1) \) and \( m_{j1}^{31}(1) \). Mass \( m_{j1}^{31}(1) \) is passed on to plate 2 and equilibrates to yield \( m_{j2}^{12}(2) \) and \( m_{j2}^{32}(2) \), while mass \( m_{j1}^{11}(1) \) equilibrates on plate 1 to yield \( m_{j1}^{11}(2) \) and \( m_{j1}^{31}(2) \). Mass \( m_{j2}^{22}(2) \) is passed on to plate 2, while mass \( m_{j1}^{11}(2) \) equilibrates on plate 1 to yield \( m_{j1}^{11}(3) \) and \( m_{j1}^{31}(3) \). Mass \( m_{j2}^{12}(2) \) is passed on to plate 3 and equilibrates to yield \( m_{j2}^{12}(3) \) and \( m_{j2}^{32}(3) \), while mass \( m_{j2}^{12}(2) \) and mass \( m_{j2}^{32}(2) \) equilibrate on plate 2 to yield \( m_{j2}^{12}(3) \) and \( m_{j2}^{32}(3) \), and so on.

In general terms, for each plate \( i \) and index \( k \), mass \( m_{j2}^{(i-1)}(k-1) \) and \( m_{j1}^{(i)}(k-1) \) combine to equilibrate to mass \( m_{j2}^{(i)}(k) \) and mass \( m_{j1}^{(i)}(k) \), where the equilibration is described mathematically by the fractions \( x \) and \( y \). Apparently, for \( j = 1 \) and \( k = 1 \) it follows \( m_{j}^{0}(0) = m_{js} \) and \( m_{j}^{1}(0) = m_{j}^{1}(1)(0) = 0 \) as the initial conditions.

Since the total volume of the gas phase is \( nV_g \), \( n \) plate residence times pass before equilibrium is established for the first time on plate \( n \).

A summary of above process for the first five plates and the first five plate residence times is shown in Table D.1, where the columns represent different plates \( i \) and the rows represent different plate residence times \( k \). Note that \( i \) and \( f \) stand for initial and final, representing the start and stop of the \( k^{th} \) plate residence time. Note that for a given index \( k \), \( i \) can only be \( i = 1, 2, \ldots, k \), representing the fact that the progress of the initially injected mass \( m_{js} \) along plates \( i \) can only occur in synchronization with index \( k \).

The pattern emerging from this table can be collapsed into a simple equation using the binomial expansion theorem:

\[
   \binom{u}{v} = \frac{u!}{v!(u-v)!}
\]
The result is an equation for mass \( m_j^{gi}(k) \) and mass \( m_j^{li}(k) \) present on plate \( i \) at the \( k^{th} \) plate residence time.

\[
m_j^{gi}(k) = m_{js} \frac{(k-1)!}{(i-1)!(k-i)!} x^{k-i} y^i
\]

\[
m_j^{li}(k) = m_{js} \frac{(k-1)!}{(i-1)!(k-i)!} x^{k-i+1} y^{i-1}
\]

When \( m_j^{gi}(k) \) is plotted on the y-axis and \( k \) on the x-axis for a constant \( i \), a temporal shape is obtained which resembles that of a Gaussian curve. Plate \( n \) approximately corresponds to the location of the detector, and so \( m_j^{gn}(k) \) represents approximately the temporal shape of the detector signal, assuming the detector response is approximately linear in the mass or concentration of chemical compound \( j \).

### D.2 Gauss Theory of Gas Chromatographic Separation

This theory is based on the mass balance of chemical compound \( j \) over a differential volume in a gas chromatographic column of arbitrary cross section. The geometry of the column is assumed to be one-dimensional, with the length of the column much
greater than the cross section. Within the differential volume, equilibrium between the gas phase and the liquid phase is established instantaneously.

Only the mass in the gas phase is allowed to move via convection and diffusion, the mass in the liquid phase is not allowed to move. The partial differential equation describing the movement of the mass of chemical compound $j$ in the gas phase is given as:

$$\frac{\partial m_j(z,t)}{\partial t} + v_g \frac{\partial m^g_j(z,t)}{\partial z} = D_j \frac{\partial^2 m^g_j(z,t)}{\partial z^2}$$

Here, $z$ and $t$ are the space and time coordinates, respectively, $m_j(z,t)$ is the mass of chemical compound $j$ at distance $z$ and time $t$, $m^g_j(z,t)$ is the mass of chemical compound $j$ at distance $z$ and time $t$ in the gas phase, $D_j$ is the diffusion coefficient of chemical compound $j$ in the gas phase and $v_g$ is the linear velocity of the gas phase. With a carrier gas volume flow rate $\dot{V}_g$ through the column and a column cross section $A$, the linear velocity is given as:

$$v_g = \frac{\dot{V}_g}{A}$$

A solution to the partial differential equation may be found, if a (preferentially linear) relation between $m^g_j$ and $m_j$ can be identified. This relation is given through the equilibrium of chemical compound $j$ between the gas phase and the liquid phase at distance $z$ and time $t$:

$$\frac{m^l_j(z,t)}{m_l} = K_{d_j} \frac{m^g_j(z,t)}{V_g}$$

Here, $m^g_j(z,t)$ and $m^l_j(z,t)$ are the mass of chemical compound $j$ in the gas phase and liquid phase, respectively, $V_g$ is the volume of the gas phase in the differential volume, $m_l$ is the mass of the liquid phase in the differential volume and $K_{d_j}$ is the distribution coefficient of chemical compound $j$.

Definition of the density $\rho_l$ of the liquid phase and the porosity $\epsilon$ of the differential volume via the volume of the liquid phase $V_l$ results in the modified equilibrium:

$$\rho_l = \frac{m_l}{V_l}$$
\[ \epsilon = \frac{V_g}{V_g + V_i} \]

\[ \frac{m_j^l(z,t)}{V_g} = K_d \rho_l \frac{1 - \epsilon}{\epsilon} \frac{m_j^g(z,t)}{V_g} \]

Definition of the retardation factor \( R_j \) of chemical compound \( j \) results in the desired relation between \( m_j^g(z,t) \) and \( m_j(z,t) \):

\[ m_j(z,t) = m_j^g(z,t) + m_j^l(z,t) \]

\[ R_j = \frac{m_j(z,t)}{m_j^g(z,t)} = 1 + K_d \rho_l \frac{1 - \epsilon}{\epsilon} \]

\[ m_j(z,t) = R_j m_j^g(z,t) \]

Substitution of this result into above partial differential equation results in a modified partial differential equation, which can be solved for \( m_j^g(z,t) \):

\[ R_j \frac{\partial m_j^g(z,t)}{\partial t} + v_g \frac{\partial m_j^g(z,t)}{\partial z} = D_j \frac{\partial^2 m_j^g(z,t)}{\partial z^2} \]

\[ \frac{\partial m_j^g(z,t)}{\partial t} + v_g^R \frac{\partial m_j^g(z,t)}{\partial z} = D_j^R \frac{\partial^2 m_j^g(z,t)}{\partial z^2} \]

Here, \( v_g^R = \frac{v_g}{R_j} \) and \( D_j^R = \frac{D_j}{R_j} \) are the retarded linear velocity and the retarded diffusion coefficient.

Under the assumption that a mass \( m_{js} \) of chemical compound \( j \) is injected onto the gas chromatographic column as a Dirac impulse \( \delta(z) \) centered at distance \( z = 0 \) at time \( t = 0 \), the initial condition and the boundary condition become:

\[ m_j^g(z,t)_{t=0} = m_j^g(z,0) = \delta(z) \frac{m_{js}}{A} \]

\[ m_j^g(z,t)|_{z=\pm\infty} = m_j^g(\pm\infty, t) = 0 \]

The solution to above partial differential equation with this initial condition and this boundary condition can be found via Fourier-Transformation. In general, a function
\( f(z) \) is Fourier-Forward (FTF) transformed and a function \( F(s) \) is Fourier-Backward (FTB) transformed via the following equations:

\[
FTF[f(z)] = F(s) = \int_{-\infty}^{+\infty} f(z)e^{-isz} dz \\
FTB[F(s)] = f(z) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(s)e^{isz} ds
\]

The Fourier-Forward transforms of the first and second derivate of \( f(z) \) are:

\[
FTF[f'(z)] = isF(s) \\
FTF[f''(z)] = -s^2 F(s)
\]

The Fourier-Forward transform of a Dirac Impulse \( \delta(z) \) is:

\[
FTF[\delta(z)] = 1
\]

These Fourier-Forward transforms can be applied to above partial differential equation to result in:

\[
\frac{\partial M_j^g(s, t)}{\partial t} + isv^R_j M_j^g(s, t) = -s^2 D^R_j M_j^g(s, t) \\
\frac{\partial M_j^g(s, t)}{\partial t} = -(s^2 D^R_j + isv^R_j)M_j^g(s, t)
\]

The solution to this forward-transformed partial differential equation is:

\[
M_j^g(s, t) = M_j^g(s, 0)e^{-(s^2 D^R_j + isv^R_j)t} \\
M_j^g(s, 0) = FTF[m_j^g(z, 0)]
\]

Here, \( FTF[m_j^g(z, 0)] \) is as follows:
$$\text{FTF}[m_j^g(z, 0)] = \text{FTF}[\delta(z) \frac{m_{js}}{A}] = \frac{m_{js}}{A} \text{FTF}[\delta(z)] = \frac{m_{js}}{A}$$

$M_j^g(s, t)$ may now be backward-transformed by making use of the above Fourier-Backward transform:

$$F(s) = \frac{m_{js}}{A} e^{-(s^2D^R_j + is\nu^R_g)t}$$

$$F(s)e^{isz} = \frac{m_{js}}{A} e^{-(s^2D^R_j + is\nu^R_g)t} e^{isz}$$

$$= \frac{m_{js}}{A} e^{-s^2D^R_j t - is\nu^R_g t + isz}$$

$$= \frac{m_{js}}{A} e^{-s^2D^R_j t - i(v^R_g t - z)s}$$

$$= \frac{m_{js}}{A} e^{-[s^2D^R_j t + i(v^R_g t - z)s]}$$

The integral of this equation is given by:

$$\int_{-\infty}^{+\infty} e^{-(as^2 + bs + c)} ds = \sqrt{\frac{\pi}{a}} e^{\frac{(b^2 - 4ac)}{4a}}$$

Therefore:

$$a = D^R_j t$$
$$b = i(v^R_g t - z)$$
$$c = 0$$

And the solution to the partial differential equation becomes:

$$m_j^g(z, t) = \frac{m_{js}}{A \sqrt{4\pi D^R_j t}} e^{\frac{[s - v^R_g t]^2}{4D^R_j t}}$$

This equation describes the retarded movement of chemical compound $j$ through the gas chromatographic column.
When \( m_j(z,t) \) is plotted on the y-axis and \( t \) on the x-axis for a constant \( z \), a temporal shape is obtained that is exactly that of a Gaussian curve. If \( z = L \) is the location of the detector, then \( m_j(L,t) \) represents approximately the temporal shape of the detector signal, assuming the detector response is approximately linear in the mass or concentration of chemical compound \( j \).

### D.3 Theory of Thermal Conductivity Detector Operation

The partial differential equation describing the heat conduction within an incompressible gas body may be written most generally as:

\[
\rho c_p \left[ \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{u} T \right] = -\nabla \cdot \mathbf{q}'' + q'''
\]

\[
q'' = -\lambda \nabla T
\]

\[
\rho c_p \left[ \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{u} T \right] = \nabla \cdot \lambda \nabla T + q'''
\]

Here, \( \rho, c_p \) and \( \lambda \) are the mass density, mass heat capacity and coefficient of heat conduction, respectively, of the gas body. The convective velocity of the gas body is represented by \( \mathbf{u} \). The heat flux density and the volumetric heat generation rate within the gas body are represented by \( \mathbf{q}'' \) and \( q''' \), respectively.

Under conditions where \( \mathbf{u} = 0, \lambda = \text{const.}, q''' = 0 \), steady state conditions prevail, i.e. \( \frac{\partial T}{\partial t} = 0 \) and one-dimensional cylindrical geometry obtains, i.e. \( \nabla^2 T = \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial T}{\partial r} \right] \), the partial differential equation reverts to an ordinary differential equation, whose general solution is given by:

\[
T = A + B \ln r
\]

Under boundary conditions where \( T|_{r=r_1} = T_1 \) and \( T|_{r=r_2} = T_2 \), the solution becomes:

\[
T = T_1 - (T_1 - T_2) \frac{\ln \frac{r}{r_1}}{\ln \frac{r_2}{r_1}}
\]

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Since in the TCD, a wire of resistance $R$ is resistively heated by current $I$, the heat flux at the wire surface is given by:

\[ q'' = \frac{RI^2}{2\pi r_1 L} \]
\[ q'' = -\lambda \frac{\partial T}{\partial r} \bigg|_{r=r_1} = \lambda \frac{T_1 - T_2}{\ln \frac{r_2}{r_1}} \frac{1}{r_1} \]

Therefore:

\[ R = \frac{2\pi \lambda L}{I^2} \frac{T_1 - T_2}{\ln \frac{r_2}{r_1}} \]
\[ \lambda = \lambda_0(1 + \alpha \overline{T}_g) \]
\[ R = R_0(1 + \beta \overline{T}_w) \]

Note that $T_1$ is the temperature of the wire and $T_2$ is the temperature of the hollow cylinder, i.e. the detector temperature. Also, $\overline{T}_g$ is a suitable average temperature of the detector gas and $\overline{T}_w$ is a suitable average temperature of the wire. The temperature relations for $\lambda$ and $R$ are given for illustration and do not necessarily represent physical evidence.

D.4 Theory of Electron Capture Detector Operation

D.4.1 Non-Sensitized Electron Capture Detector

The mixtures of argon or nitrogen appear to be ideal detector gases, because the recombination of negative ions and positive ions appears to be stronger than the recombination of electrons and positive ions [116].

In the absence of chemical compounds that attach electrons, the negative charge rests entirely with electrons. In the presence of chemical compounds that attach electrons, the negative charge rests with both electrons and negative ions. In particular, negative charge subject to weak recombination (electrons) is transformed into negative charge subject to strong recombination (negative ions).
Therefore, not only do chemical compounds that attach electrons result in a decrease of the electron density and thus the electron current, but also in a decrease of the negative charge density, i.e. the negative charge is not merely transformed from electrons into negative ions.

The average electron energy in argon as the detector gas is rather high. However, as mentioned before, many chemical compounds have the largest reaction rate constants for electron attachment at low average electron energies rather than at high average electron energies.

Therefore, methane is added to argon as the detector gas, since methane very effectively decreases the average electron energy. Moreover, methane cools excited argon, which can react with chemical compounds via excitation transfer and subsequent ionization of the chemical compounds. This would result in an increase rather than a decrease of the electron density in the presence of the chemical compound. Typical concentrations of methane in argon are 5% or 10% for P5 or P10 ECD detector gas, respectively. In the present work, only P5 detector gas was used.

For inelastic collisional electron energy loss, neither rotational nor vibrational excitation energies are available to further reduce the electron energy as soon as the electron energy falls below the ionization and excitation energies of argon.

For elastic collisional electron energy loss, the elastic collision cross section of argon exhibits the so-called Ramsauer effect, i.e. this cross section has a sharp negative resonance which means the cross section is too low to further reduce the electron energy significantly below the electron energy of this negative resonance [74].

The addition of methane adds rotational and vibrational excitation energies which may be used via inelastic collisional electron energy loss to further reduce the electron energy.

The reason why nitrogen is an ideal detector gas as well, is that excited nitrogen, just as excited methane, does not appear to react with chemical compounds via excitation transfer and subsequent ionization of the chemical compounds. Moreover, nitrogen also possesses rotational and vibrational excitation energies and it does not exhibit the Ramsauer effect [74].

This combination may be used via inelastic and elastic collisional electron energy loss to result in a lower average electron energy for nitrogen than for argon. The simplified chemical reactions thought to be of importance in the ECD for Ar, Ar/CH₄ and N₂ in the absence of chemical compounds are [116]:

\[ \text{Ar} + \beta \rightarrow \text{Ar}^+ + e^- \]
The additional simplified chemical reactions thought to be of importance in the ECD in the presence of chemical compounds are [116]:

\[
\begin{align*}
\text{Ar} + e^-_f & \rightarrow \text{Ar}^+ + e^-_s \\
\text{Ar} + \text{Ar}^+ & \rightarrow 2\text{Ar} \\
\text{Ar}^+ + e^-_s & \rightarrow \text{Ar} \\
\text{CH}_4 & \rightarrow \text{CH}_4^+ + e^-_f \\
\text{CH}_4 + e^-_f & \rightarrow \text{CH}_4^* + e^-_s \\
\text{CH}_4 + \text{CH}_4^* & \rightarrow 2\text{CH}_4 \\
\text{CH}_4^+ + e^-_s & \rightarrow \text{CH}_4 \\
\text{CH}_4 + \text{Ar}^* & \rightarrow \text{CH}_4 + \text{Ar} \\
\text{Ar} + \text{CH}_4^* & \rightarrow \text{Ar} + \text{CH}_4 \\
\text{N}_2 + \beta & \rightarrow \text{N}_2^+ + e^-_f \\
\text{N}_2 + e^-_f & \rightarrow \text{N}_2^* + e^-_s \\
\text{N}_2 + \text{N}_2^* & \rightarrow 2\text{N}_2 \\
\text{N}_2^+ + e^-_s & \rightarrow \text{N}_2 \\
\end{align*}
\]

Here, the chemical compound AB may attach electrons non-dissociatively to form AB\(^-\), or it may attach electrons dissociatively to form A\(^-\) and B or A and B\(^-\).

The reaction rate constant for electron attachment generally increases with the number of halogen atoms contained in a molecule of a particular chemical compound.
The relative sensitivities of the ECD for chemical compounds of different degrees of halogenation are given in Table D.2 [97].

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-Cl-, Mono-F-Hydrocarbons</td>
<td>10^2</td>
</tr>
<tr>
<td>Mono-Br-, Di-Cl-, Di-F-Hydrocarbons</td>
<td>10^3</td>
</tr>
<tr>
<td>Tri-Cl-Hydrocarbons</td>
<td>10^4</td>
</tr>
<tr>
<td>Mono-I-, Di-Br-, Nitro-Hydrocarbons</td>
<td>10^5</td>
</tr>
<tr>
<td>Di-I-, Tri-Br-, Poly-Cl-, Poly-F-Hydrocarbons</td>
<td>10^6</td>
</tr>
</tbody>
</table>

Table D.2: Relative Sensitivities of Electron Capture Detector [97]

In addition, electron attachment to some chemical compounds is dependent on the detector gas temperature, which is equivalent to a higher average electron energy. The detector gas temperature is controlled by the detector temperature, i.e. the temperature of the hollow cylinder. For these chemical compounds, the reaction rate constant for electron attachment generally increases with detector gas temperature. This is a function of whether the electron attachment is endothermic or exothermic and whether the electron attachment is dissociative or non-dissociative [182]. For the present work, the detector temperature is set to 150 °C.

Excellent mathematical descriptions of the difference in electron density in the absence and the presence of electron attaching chemical compounds in the detector gas are given in [116], [118] and [119]. In particular, these descriptions account for the afore-mentioned chemical reactions in the constant voltage and the pulsed voltage operation modes.

D.4.2 Sensitized Electron Capture Detector

Under conditions where the carrier gas or the make-up gas is He, N_2, Ar or Ar/CH_4, chemical compounds that do not attach electrons generally result in weak detector signals. However, under conditions where either N_2O or O_2 is added to N_2 as the carrier gas or as the make-up gas, chemical compounds that do not attach electrons generally result in strong detector signals. This is a remarkable realization, because for a long time any impurities in the detector gas, including N_2O or O_2, were considered detrimental to the performance of the ECD.

This observation is explained by so-called N_2O sensitization and O_2 sensitization. The former has been explored in [183], [184] and [185], the latter has been explored in [186], [187] [188], [189], [190] and [191]. Both sensitization methods are based on the
interaction of chemical compounds with negative ions, rather than with electrons.

**D.4.2.0.1 N₂O Sensitization** When N₂O is added to N₂ as the carrier gas or as the make-up gas, the chemical reactions occurring in addition to those in N₂ are:

\[
\begin{align*}
N₂O + e^- & \rightarrow O^- + N₂ \\
N₂O + O^- & \rightarrow NO^- + NO \\
NO^- + N₂ & \rightarrow e^- + NO + N₂
\end{align*}
\]

Apparently, an electron is lost by dissociative attachment to N₂O and an electron is re-gained by non-dissociative detachment from NO⁻. The NO⁻ is produced by dissociative negative charge transfer from O⁻ to N₂O. This represents a closed attachment/detachment cycle.

In comparison to N₂ without N₂O as the detector gas, the electron density decreases insignificantly. However, in the presence of chemical compounds, the electron density decreases further due to additional associative, dissociative or non-dissociative negative charge transfer from O⁻ to chemical compounds. The production of NO⁻ and thus the non-dissociative electron detachment from NO⁻ is intercepted.

This apparent decrease in electron density results in a similar response of the ECD as that caused by direct electron attachment to chemical compounds.

Examples for chemical compounds that are susceptible to associative, dissociative or non-dissociative negative charge transfer from O⁻ as referenced in [183], [184] and [185] are CO, CO₂, O₂, H₂, H₂O, CH₄, C₂H₆, CCl₂F₂, CH₂Cl₂, CCl₃F, CHCl₃, CCl₄, C₂Cl₂F₄, C₂Cl₃F₃, C₂H₃Cl₃ and C₂Cl₄.

**D.4.2.0.2 O₂ Sensitization** When O₂, with H₂O as a potential impurity, is added to N₂ as the carrier gas or as the make-up gas, the chemical reactions occurring in addition to those in N₂ are:

\[
\begin{align*}
O₂ + O₂ + e^- & \rightarrow O^- + O_2 \\
O₂ + N₂ + e^- & \rightarrow O^- + N₂ \\
O₂ + H₂O + e^- & \rightarrow O^- + H₂O \\
O^- + O₂ & \rightarrow O₂ + O₂ + e^- \\
O^- + O₂ & \rightarrow O^- \\
O^- + H₂O & \rightarrow O^- (H₂O)
\end{align*}
\]
Apparently, an electron is lost by non-dissociative attachment to O₂ and an electron is re-gained by non-dissociative detachment from O₂⁻. The associative negative charge transfer from O₂⁻ to O₂ and H₂O represents the important difference between N₂O sensitization and O₂ sensitization. Therefore, this represents an open attachment/detachment cycle.

In comparison to N₂ without O₂ as the detector gas, the electron density decreases significantly due to associative negative charge transfer from O₂⁻ to O₂ and H₂O. However, in the presence of chemical compounds, the electron density decreases further due to additional associative, dissociative or non-dissociative negative charge transfer from O₂⁻ to chemical compounds. The non-dissociative detachment from O₂⁻ is intercepted.

This apparent decrease in electron density results in a similar response of the ECD as that caused by direct electron attachment to chemical compounds.

Examples for chemical compounds that are susceptible to associative, dissociative or non-dissociative negative charge transfer from O₂⁻ as referenced in [186], [187], [188], [189], [190] and [191] are CO₂, H₂O, N₂O, CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, C₂H₃Cl, C₂H₂Cl₂, C₂HCl₃, C₂Cl₄, C₂H₅Cl, C₂H₄Cl₂, C₂H₂Cl₄, CH₃Br, CF₃Cl, CHF₂Cl, CF₂Cl₂ and CFCl₃.

D.5 Mathieu Theory of Mass Filtering

The vacuum in the mass filter of a mass spectrometer is typically at 10⁻⁶ torr. This is necessary so that the ions in the mass filter cannot make collisions other than with rods or walls. Although ions are present in the mass filter, their number density is so low that they do not perturb the voltage within the mass filter. Therefore, this voltage may be described by Poisson's equation in vacuum:

\[
E = -\nabla V \\
\nabla \cdot E = 0 \\
\n\nabla \cdot (-\nabla V) = -\nabla^2 V = 0
\]

Here, \( E \) is the electric field and \( V \) is the voltage. The origin of the rectangular coordinate system is located on the axis of the mass filter. The coordinate along the axis of the mass filter is \( z \), the coordinates perpendicular to \( z \) are \( x \) and \( y \), such that they point in between two adjacent rods or to the cusp that forms where two walls meet.
Since the quadrupole cross section is symmetric, x and y are interchangeable. Since the dimension of the mass filter along the z-axis is much larger than the dimension along the x- or y-axis, no variation of voltage with z is assumed. Thus a two-dimensional approach in rectangular coordinates is justified for deriving an equation describing the mass filter. Exceptions are the end regions of the mass filter where a three-dimensional approach would be required. However, the end regions will be neglected for simplicity. Poisson's equation then reads:

\[
\frac{\partial^2 V(x, y)}{\partial x^2} + \frac{\partial^2 V(x, y)}{\partial y^2} = 0
\]

A separation of variables can be performed such that:

\[ V(x, y) = V_\alpha(x)V_\beta(y) \]

Two separate differential equations for \(V_\alpha(x)\) and \(V_\beta(y)\) emerge, where \(\alpha\) is the separation constant that connects these equations:

\[
\frac{\partial^2 V_\alpha(x)}{\partial x^2} = \alpha V_\alpha(x) \\
\frac{\partial^2 V_\beta(y)}{\partial y^2} = \alpha V_\beta(y)
\]

If \(\alpha\) is non-zero, the solution to \(V_\alpha(x)\) and \(V_\beta(y)\) will be oscillatory in \(x\) or \(y\) and exponential in \(y\) or \(x\), respectively. However, in order to meet the boundary conditions that follow, solutions that are perfectly symmetric about the mass filter axis are required. This means only non-oscillatory, non-exponential solutions are acceptable, which are obtained by setting \(\alpha\) to zero. Therefore, the general non-oscillatory, non-exponential separated solutions to Poisson's equation are:

\[
\frac{\partial^2 V_\alpha(x)}{\partial x^2} = 0 \\
V_\alpha(x) = A_\alpha + B_\alpha x
\]

\[
\frac{\partial^2 V_\beta(y)}{\partial y^2} = 0 \\
V_\beta(y) = A_\beta + B_\beta y
\]
The general non-oscillatory, non-exponential solution to Poisson's equation then is the product of these separated solutions:

\[V(x, y) = A + Bx + Cy + Dxy\]

\[A = A_x A_y\]
\[B = B_x A_y\]
\[C = A_x B_y\]
\[D = B_x B_y\]

Under boundary conditions where \(V(x, y)|_{y=0} = V(x, y)|_{x=0}\), i.e. where for symmetry reasons the voltage along the x-axis has to vary in the same manner as the voltage along the y-axis, the restriction \(y = x\) results in:

\[V(x, 0) = A + Bx\]
\[V(0, y) = A + Cx\]

Consequently, this means \(C = B\) and:

\[V(x, y) = A + B(x + y) + Dxy\]

Under boundary conditions where the voltage along a wall has to be equal to \(V_0\), an equation for the geometrical shape of the cross section of a wall has to be derived first.

This geometrical shape can be described mathematically with respect to the x- and y-axis in terms of a single characteristic dimension \(R_0\). This is defined as the closest distance between the mass filter axis and a wall. Therefore, \(R_0\) is directed 45° between the x- and y-axis. It can easily be shown then that the cross section of a wall follows the curve:

\[y = \frac{1}{2} \frac{R_0^2}{x}\]

Thus for \(y = \frac{1}{2} \frac{R_0^2}{x}\):
\[ V(x,y) = V_0 \]
\[ V(x,y) = A + B(x + \frac{1}{2}R_0^2) + D \frac{1}{2}R_0^2 \]

Consequently, this means \( B = 0 \) and:

\[ V(x,y) = A + Dxy \]

Under boundary conditions where for simplicity \( V(x,y)|_{x=y=0} = 0 \), \( A \) results as \( A = 0 \). Thus, under boundary conditions where \( V(x,y) = V_0 \) for \( xy = \frac{1}{2}R_0^2 \), \( D \) results as:

\[ D = 2 \frac{V_0}{R_0^2} \]

Thus, the final form of the voltage within the mass filter results as:

\[ V(x,y) = 2 \frac{V_0}{R_0^2} xy \]

Although it was convenient for the derivation of the voltage within the mass filter to chose a \( x-y-z \)-coordinate system, it is more convenient for the derivation of the equations of motion of ions within the mass filter to perform a rotation of this coordinate system by \( 45^\circ \) into a \( \xi-\eta-z \) coordinate system:

\[ x = \xi \cos 45^\circ - \eta \sin 45^\circ \]
\[ y = \xi \sin 45^\circ + \eta \cos 45^\circ \]
\[ xy = \frac{1}{2} (\xi^2 - \eta^2) \]

The voltage within the mass filter in terms of the coordinates of the rotated coordinate system then is:

\[ V(\xi, \eta) = \frac{V_0}{R_0^2} (\xi^2 - \eta^2) \]
The electric field in this coordinate system then is simply given by:

\[
E = -\nabla V(\xi, \eta)
\]

\[
E_{\xi} = -\frac{2V_0}{R_0}\xi
\]

\[
E_{\eta} = +\frac{2V_0}{R_0}\eta
\]

The voltage \( V_0 \) along a wall consists of a DC and an AC component. It can be expressed as:

\[
V_0 = V_0(t) = V_{DC} + V_{AC}\cos\omega t
\]

The equations of motion then can be derived via a force balance as follows:

\[
m\ddot{\xi} = qE_\xi
\]

\[
m\ddot{\eta} = qE_\eta
\]

\[
m\ddot{z} = 0
\]

\[
\ddot{\xi} = -2q \frac{V_{DC} + V_{AC}\cos\omega t}{mR_0^2}\xi
\]

\[
\ddot{\eta} = +2q \frac{V_{DC} + V_{AC}\cos\omega t}{mR_0^2}\eta
\]

\[
\ddot{z} = 0
\]

The equation for \( z \) can immediately be solved to yield:

\[
z = v_{z_0}t
\]

Here, \( v_{z_0} \) is the initial velocity of the ion along the \( z \)-axis. Definition of the dimensionless variable \( \varphi \):
\[ \varphi = \frac{1}{2} \omega t \]

and the dimensionless parameters \( A \) and \( Q \):

\[
A = \frac{8V_{DC} e}{R_0 \omega^2 m} \\
Q = \frac{4V_{AC} e}{R_0 \omega^2 m}
\]

results in:

\[
\frac{A}{Q} = \frac{2V_{DC}}{V_{AC}}
\]

and:

\[
\ddot{\xi} = \frac{\omega^2}{4} \frac{\partial^2 \xi}{\partial \varphi^2} \\
\ddot{\eta} = \frac{\omega^2}{4} \frac{\partial^2 \eta}{\partial \varphi^2}
\]

The equations of motion of ions then take the mathematical form of Mathieu equations:

\[
\frac{\partial^2 \xi}{\partial \varphi^2} = -(A + 2Q \cos 2\varphi) \xi \\
\frac{\partial^2 \eta}{\partial \varphi^2} = +(A + 2Q \cos 2\varphi) \eta
\]

The initial conditions for these equations are usually given as:

\[
\frac{\partial \xi}{\partial t} \bigg|_{t=0} = v_{\xi_0} \\
\frac{\partial \eta}{\partial t} \bigg|_{t=0} = v_{\eta_0}
\]
or:

\[
\begin{align*}
\frac{\partial \xi}{\partial \varphi} \bigg|_{\varphi=0} &= \frac{2}{3} \nu \xi_0 \\
\frac{\partial \eta}{\partial \varphi} \bigg|_{\varphi=0} &= \frac{2}{3} \nu \eta_0
\end{align*}
\]

For interpretation purposes, it is instrumental to rewrite these equations as:

\[
\begin{align*}
\frac{\partial^2 \xi}{\partial \varphi^2} &= -Q \left( \frac{A}{Q} + 2 \cos 2\varphi \right) \xi \\
\frac{\partial^2 \eta}{\partial \varphi^2} &= +Q \left( \frac{A}{Q} + 2 \cos 2\varphi \right) \eta
\end{align*}
\]
Appendix E

Appendix to Chapter 6

E.1 Conversion of R to rad as the Dimension of the Dose

The old definition of radiation dose to the gas phase is charge production per volume. The dimension *Röntgen* (R) for this radiation dose is unfortunately defined in the cgs-system:

\[
[D] = 1 \text{ R} = 1 \text{ esu/cm}^3
\]

In order to convert the dimension R in the cgs-system to the dimension C/m\(^3\) in the mks-system, the dimension esu in the cgs-system has to be converted to the dimension C in the mks-system. The charge \(q_{cgs}\) in the cgs-system is related to the charge \(q_{mks}\) in the mks-system via the electric permittivity \(\varepsilon_0\):

\[
q_{cgs}^2 = q_{mks}^2 \frac{q_{mks}}{4\pi\varepsilon_0} \\
q_{cgs} = q_{mks} \frac{q_{mks}}{\sqrt{4\pi\varepsilon_0}} \\
[q_{cgs}] = 1 \text{ esu} \\
[q_{mks}] = 1 \text{ C}
\]

The dimension of \(\varepsilon_0\) in the cgs-system may be converted to the dimension of \(\varepsilon_0\) in the mks-system via:
\[
[e_0] = 1 \text{ A/s/V m} = 1 \text{ C}^2/\text{J m} = 10^{-9} \text{ C}^2/\text{erg cm} = 10^{-9} \text{ C}^2/\text{esu}^2
\]

\[
1 \text{ J} = 10^7 \text{ erg}
\]

\[
1 \text{ m} = 10^2 \text{ cm}
\]

\[
1 \text{ esu} = 1 \sqrt{\text{erg cm}}
\]

\[
\epsilon_0 = 8.854187817 \times 10^{-12} \text{ A/s/V m} = 8.854187817 \times 10^{-21} \text{ C}^2/\text{esu}^2
\]

Therefore:

\[
q_{\text{cgs}} = 2.997924580 \times 10^9 q_{\text{mks}} \text{ esu/C}
\]

\[
q_{\text{mks}} = 3.335640952 \times 10^{-10} q_{\text{cgs}} \text{ C/esu}
\]

This conversion of the dimension esu to the dimension C allows for conversion of the dimension R to the dimension C/m³:

\[
1 \text{ R} \approx 333.56 \mu\text{C/m}^3
\]

Assuming the ideal gas law, the dimension R may be converted to the the dimension C/kg:

\[
pV = m\frac{R_m T}{M}
\]

\[
\rho = m\frac{pM}{V} = \frac{pM}{R_m T}
\]

Where:

\[
p = 1.01325 \cdot 10^5 \text{ Pa}
\]

\[
T = 273.15 \text{ K}
\]

\[
M = 28.85 \text{ g/mol}
\]

\[
\rho = 1.287 \text{ kg/m}^3
\]

Therefore:

360
1 R \approx 259.15 \mu C/kg

Assuming 33.3 eV per charge production the dimension R may be converted to the dimensions J/kg or rad:

\[
\begin{align*}
100 \text{ rad} &= 1 \text{ J/kg} \\
1R &= 8.63 \text{ mJ/kg} = 863 \text{ mrad} = 0.863 \text{ rad}
\end{align*}
\]

Therefore, the dimension R may be assumed approximately equivalent to the dimension rad in gas at \( p = 1.01325 \cdot 10^5 \text{ Pa} \), \( T = 273.15 \text{ K} \), \( M = 28.85 \text{ g/mol (air)} \) and 33.3 eV per charge production (air).