Investigation of Trichloroethene Destruction for the Degreasing Industry

Eleanor Binner

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

Carried out at:

Industrial Research Institute of Swinburne University of Technology

Jointly funded by:

Industrial Research Institute of Swinburne University of Technology and Collaborative Research Centre for Intelligent Manufacturing Systems and Technology

September 2005
**Dedications and Acknowledgements**

I would like to dedicate this thesis to the late Bernie Penetrante and the late Leslie Binner. Bernie Penetrante was instrumental in reviving this field in 1992 by bringing the international community together at a NATO workshop held in Cambridge. His own contributions to the field are also respected by many researchers the world over. I was lucky enough to meet him shortly before his death. Leslie Binner was my grandfather, and instrumental in his own way (with help from my grandmother Betty) in improving the British education system. I will never forget his pride when I told him I had accepted the offer to do this PhD.

Many people have helped me in various ways throughout the PhD, and without that help I’m sure I wouldn’t have made it. I would like to thank Damian Frank, John Dods, Ron Fisher and Frank Bambino for help with the chemical analysis, and Fiona O’Donnell for library-related help. Thank you Alex Taube and Yuri Shramkov for building and maintaining the microwave plasma reactor. Special thanks go to John Schulze and Bob Western for their help with the chemical analysis and who really got their teeth stuck into the project. I’d like to thank my family, who have put up with me abandoning them to live on the other side of the world, and Engida Lemma and John Bishop, who have put up with me during lunchtimes throughout the last four years. Finally, I’d like to thank my supervisor Rowan Deam and my boyfriend Kim Nuyen. Rowan has really gone above and beyond the call of duty as a supervisor and without his help and friendship you would not be reading this thesis. Kim has supported me through it all and if he hadn’t scraped me off the walls on several occasions, well, I’d still be splattered all over them. Thanks guys!
Declarations

This is to certify that the work described in this thesis is my own except where otherwise indicated. The results of this research, which was conducted at the Industrial Research Institute of Swinburne University of Technology from 2001 – 2005, is not submitted for any other degree at any other institution.

Publications

It is expected that the main conclusions from this work will be published in a referred journal. This is currently work in progress.

Binner, E. and Deam, R., 2004 ‘Microwave plasma: Pollution reducer or producer?’ Proceedings of the 13th World clean air and environmental protection congress and exhibition, London, abstract no. 429

Binner E., 2002 ‘Design study for the destruction of trichloroethene’ poster presentation, 3rd World congress on microwave and radio frequency applications, Sydney
Abstract

The major objective of this project was to assess the application of atmospheric pressure microwave induced plasmas to the control of trichloroethene vapour emissions from industrial cleaning processes. Laboratory experiments, chemical modelling and chemical analysis were the three major elements of the project. A typical stream to be treated, as measured at the project test site, was 60 lmin\(^{-1}\) of air contaminated with 2 % trichloroethene vapour.

The practical experiments carried out were trichloroethene dissociation by microwave plasma, propane-assisted microwave plasma and conventional propane combustion. Flow rates of 4 – 12 lmin\(^{-1}\), trichloroethene concentrations of 0 – 6 % in air and plasma powers of up to 3 kW were investigated. The processes were simulated using both equilibrium and kinetic modelling in CHEMKIN. Chemical analysis was done using gas chromatography with an electron capture detector, with gas chromatography/mass spectrometry to identify eluted compounds.

The destruction and removal efficiencies, by-products, temperature and robustness of each process were investigated. A simple economic and environmental analysis was done, and the results were compared with currently available processes.
# Table of Contents

Dedications and Acknowledgements......................................................i
Declarations and Publications............................................................ii
Abstract............................................................................................iii
Table of Contents.................................................................................iv
List of Figures.......................................................................................vi
List of Tables.......................................................................................ix
Nomenclature.......................................................................................x
Index of chemicals..............................................................................xi

## Main Body

Chapter 1: Introduction.........................................................................1
Chapter 2: Objectives...........................................................................19
Chapter 3: Literature review...............................................................24
Chapter 4: Experimental methods.......................................................38
Chapter 5: Plasma temperature............................................................60
Chapter 6: Chemical modelling............................................................74
Chapter 7: Results qualification............................................................106
Chapter 8: Results quantification and verification...............................135
Chapter 9: Environmental and economic assessment..........................154
Chapter 10: Project summary ...............................................................167

## Appendices

1A: Properties of trichloroethene (TCE).............................................175
1B: World TCE usage..........................................................................179
1C: Environmental impact.................................................................183
1D: Health effects................................................................................185
1E: Guidelines and standards..............................................................189
2A: Health and safety: Possible by-products........................................195
4A: Saturated vapour pressure of trichloroethene and water..............196
4B: Gas chromatography details.........................................................197
6A: CHEMKIN chemistry input file for AURORA..............................202
6B: CHEMKIN AURORA input file......................................................211
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6C: Equilibrium Modelling</td>
<td>212</td>
</tr>
<tr>
<td>6D: Kinetic Modelling</td>
<td>220</td>
</tr>
<tr>
<td>7A: Error charts</td>
<td>222</td>
</tr>
<tr>
<td>7B: Correlation of ECD elution times with MS elution times</td>
<td>230</td>
</tr>
<tr>
<td>7C: Pyrex chimney: HCl and chlorine bleed peaks</td>
<td>232</td>
</tr>
<tr>
<td>7D: Estimation of inorganic content of chimney residue</td>
<td>233</td>
</tr>
<tr>
<td>8A: Further results</td>
<td>234</td>
</tr>
<tr>
<td>9A: Environmental impact of TCE treatment processes spreadsheet</td>
<td>237</td>
</tr>
<tr>
<td>9B: Economic analysis of TCE treatment processes spreadsheet</td>
<td>238</td>
</tr>
<tr>
<td><strong>Bibliography</strong></td>
<td>239</td>
</tr>
<tr>
<td><strong>References</strong></td>
<td>241</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1 Trichloroethene vapour degreasing machine, HPM, Sydney....................... 5
Figure 2.1 Desired overall reactions in the trichloroethene destruction methods ...... 21
Figure 4.1: Schematic of experimental rig ................................................................. 41
Figure 4.2: Propane burner rig .................................................................................. 42
Figure 4.3: Diagram of microwave-induced plasma rig .............................................. 43
Figure 4.4: Photo of Microwave-induced Plasma Rig ............................................... 44
Figure 4.5: Vapour Generator .................................................................................. 45
Figure 4.6: Schematic of Gas Chromatograph .......................................................... 54
Figure 4.7: Chromatogram from 1st column (EC-1, ref) ........................................... 56
Figure 4.8: Example of a chromatogram of the plasma effluent .............................. 57
Figure 4.9: Determination of linear dynamic range .................................................... 58
Figure 5.1: Energy flows in the plasma reactor .......................................................... 63
Figure 5.2: Predicted electron densities and temperatures in the microwave plasma. 65
Figure 5.3: Comparison of predicted plasma temperature with and without heat losses .............................................................................................................................. 66
Figure 5.4: Flow conditions for propane in air plasma with heat loss ....................... 66
Figure 5.5: Absorption length against electron density .............................................. 67
Figure 5.6: Plasma power absorption (enthalpy with no losses) for 2 % TCE in air . 68
Figure 5.7: Comparison of predicted (3 % TCE) and experimental (2 % TCE) enthalpies for 1.8 kW absorbed power (3 kW incident) ............................................. 70
Figure 5.8: Maximum enthalpy of plasma against TCE concentration ..................... 70
Figure 5.9: Power absorbed at 3 kW incident power and 2 % TCE inlet concentration .......................................................................................................................... 71
Figure 5.10: Effect of TCE inlet concentration on maximum stable flow rate range for 1.4 kW absorbed power (experimental) and 1.2 and 1.5 kW absorbed power (predicted) ............................................................................................................. 72
Figure 6.1: Equilibrium products of pure trichloroethene (TCE) ............................. 82
Figure 6.2a: Equilibrium products of TCE in humid air at 1,000 K (Mole fraction 1x10^{-3} to 1) ......................................................................................................................... 83
Figure 6.2b: Equilibrium products of TCE in humid air at 1,000 K (Mole fraction 1x10^{-9} to 1x10^{-3}) ......................................................................................................................... 83
Figure 7.4: Chart comparing peaks found in plasma (copper chimney, 6 % TCE, 8 l/min) with HCl injection products

Figure 7.5: Formation of 4.66 minutes peak at 10 l/min

Figure 7.6: Chart comparing peaks found in plasma with “bleach gas” injection products

Figure 7.8: Mass formed in plasma reactor against TCE inlet concentration

Figure 8.1: Destruction and removal efficiencies of various TCE destruction methods (conditions: 10 l/min, 3 % TCE in, plasma power 2 kW)

Figure 8.2: TCE Destruction and Removal Efficiency at 10 l/min

Figure 8.3: Final concentration of TCE in 2 kW dry plasma experiments, with temperatures estimated for 2 % in air plasma

Figure 8.4: Destruction and removal efficiency for varying plasma powers (for 10 l/min, 2 % TCE in dry air) with estimated plasma temperatures

Figure 8.5: Estimation of percent of NO formed during various TCE destruction methods (for 10 l/min containing 3 % TCE)

Figure 8.6: Formation of NO at 10 l/min

Figure 8.7: NO in 2 kW dry plasma experiments (copper chimney)

Figure 8.8: Effect of TCE concentration on phosgene formation at 10 l/min

Figure 8.9: Final concentration of phosgene for various plasma powers (for 10 l/min containing 2 % TCE)

Figure 8.10: Carbon tetrachloride formation for various TCE destruction methods (conditions: 10 l/min, 3 % TCE in, plasma power 2 kW)

Figure 8.11: Kinetic model prediction for CCl₄ production

Figure 8.12: Formation of carbon tetrachloride at 10 l/min

Figure 8.13: Formation of tetrachloroethene in various TCE destruction experiments

Figure 8.14: Tetrachloroethene in 2 kW dry plasma experiments (copper chimney)
Figure 7.4: Chart comparing peaks found in plasma (copper chimney, 6 % TCE, 8 l/min) with HCl injection products ................................................................. 123
Figure 7.5: Formation of 4.66 minutes peak at 10 l/min .............................. 124
Figure 7.6: Chart comparing peaks found in plasma with “bleach gas” injection products ................................................................. 125
Figure 7.8: Mass formed in plasma reactor against TCE inlet concentration .... 131
Figure 8.1: Destruction and removal efficiencies of various TCE destruction methods (conditions: 10 l/min, 3 % TCE in, plasma power 2 kW) ......................... 139
Figure 8.2: TCE Destruction and Removal Efficiency at 10 l/min ................. 139
Figure 8.3: Final concentration of TCE in 2 kW dry plasma experiments, with temperatures estimated for 2 % in air plasma ........................................... 141
Figure 8.4: Destruction and removal efficiency for varying plasma powers (for 10 l/min, 2 % TCE in dry air) with estimated plasma temperatures .......... 142
Figure 8.5: Estimation of percent of NO formed during various TCE destruction methods (for 10 l/min containing 3 % TCE) .............................................. 143
Figure 8.6: Formation of NO at 10 l/min ........................................................ 144
Figure 8.7: NO in 2 kW dry plasma experiments (copper chimney) ................. 145
Figure 8.8: Effect of TCE concentration on phosgene formation at 10 l/min ... 146
Figure 8.9: Final concentration of phosgene for various plasma powers (for 10 l/min containing 2 % TCE) ................................................................. 147
Figure 8.10: Carbon tetrachloride formation for various TCE destruction methods (conditions: 10 l/min, 3 % TCE in, plasma power 2 kW) ................. 148
Figure 8.11: Kinetic model prediction for CCl4 production .............................. 149
Figure 8.12: Formation of carbon tetrachloride at 10 l/min .......................... 150
Figure 8.13: Formation of tetrachloroethene in various TCE destruction experiments ................................................................. 151
Figure 8.14: Tetrachloroethene in 2 kW dry plasma experiments (copper chimney) 152
List of Tables

Table 1.1: Efficiencies of existing VOC control technologies........................................ 16
Table 3.1 Table summarising published dissociation efficiencies of TCE in non-thermal
and microwave plasmas (pps = pulses per second) .................................................... 33
Table 3.2: Technical Comparison of TCE and Alternatives (Gamble 1998) ............... 34
Table 4.1: Summary of experiments undertaken ......................................................... 47
Table 7.1: Area of 4.66 minutes peak from three injections of 4 % TCE plasma off-gas
into Gas Chromatograph (GC) .............................................................................. 112
Table 7.2: Overall standard deviation of normalised averages .................................. 114
Table 7.3: Response factors of standards when compared with TCE ......................... 118
Table 7.4: Results of analysis of dry sampling comparison ........................................ 121
Table 7.6: Overall peak identification ....................................................................... 126
Table 7.7: Metal ions found in solid residue ......................................................... 130
Table 7.8: Results of the XRD analysis ................................................................. 132
Table 9.1: Summary of environmental impact of TCE treatment processes ('potency
factors') assuming 2 % inlet TCE (*may not be applicable above 1 % TCE) .... 159
Table 9.2: List of chemicals produced in TCE destruction experiments .................... 160
Table 9.3: Scrubber flow rate requirements assuming water is absorbent ............... 162
Table 9.4: Economic and engineering comparison of TCE treatment processes (12.6
barrels/year) ........................................................................................................ 165
Nomenclature

<table>
<thead>
<tr>
<th>Value</th>
<th>Symbol</th>
<th>Units</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed dose</td>
<td></td>
<td>1 Gray = 1Jkg(^{-1})</td>
<td>Gy</td>
</tr>
<tr>
<td>Charge of 1 electron</td>
<td>e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration by volume(^{*})</td>
<td></td>
<td>Parts per million by volume</td>
<td>ppm</td>
</tr>
<tr>
<td>Concentration by volume(^{*})</td>
<td></td>
<td>Parts per billion by volume</td>
<td>ppb</td>
</tr>
<tr>
<td>Concentration by mass(^{*})</td>
<td></td>
<td>Parts per million by mass</td>
<td>ppm(m)</td>
</tr>
<tr>
<td>Concentration by mass(^{*})</td>
<td></td>
<td>Parts per billion by mass</td>
<td>ppb(m)</td>
</tr>
<tr>
<td>Destruction and removal efficiency (of trichloroethene)</td>
<td>DRE</td>
<td>Number of nines e.g. 90% = 1 nine</td>
<td>Nines</td>
</tr>
<tr>
<td>Electron Density</td>
<td>n(_e)</td>
<td>Electrons per cm(^3)</td>
<td>electrons.cm(^{-3})</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>h</td>
<td>Joules per litre</td>
<td>Jl(^{-1})</td>
</tr>
<tr>
<td>Frequency</td>
<td>f</td>
<td>Hertz</td>
<td>Hz, GHz</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>FR</td>
<td>Litres per minute</td>
<td>lmin(^{-1}), lpm</td>
</tr>
<tr>
<td>Length</td>
<td>l</td>
<td>Metres</td>
<td>mm, cm, m</td>
</tr>
<tr>
<td>Mass of 1 electron</td>
<td>m(_e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permitted daily exposure</td>
<td>PDE</td>
<td>Milligrams per day</td>
<td>mg.day(^{-1})</td>
</tr>
<tr>
<td>Plasma frequency</td>
<td>(\omega_p)</td>
<td>Hertz</td>
<td>GHz</td>
</tr>
<tr>
<td>Power</td>
<td>P</td>
<td>Watts</td>
<td>W, kW</td>
</tr>
<tr>
<td>Pulsed power frequency</td>
<td></td>
<td>Pulses per second</td>
<td>pps</td>
</tr>
<tr>
<td>Tolerable daily intake</td>
<td>TDI</td>
<td>Micrograms per kilogram body weight per day</td>
<td>(\mu g.kgbw^{-1}.day^{-1})</td>
</tr>
<tr>
<td>Temperature</td>
<td>T</td>
<td>Kelvin</td>
<td>K</td>
</tr>
<tr>
<td>Time</td>
<td>t</td>
<td>Seconds, Minutes</td>
<td>s, min</td>
</tr>
<tr>
<td>Voltage</td>
<td>V</td>
<td>Volts</td>
<td>V, kV</td>
</tr>
</tbody>
</table>

*See appendix A for conversion between mass and volumetric concentration.*
# Index of chemicals

<table>
<thead>
<tr>
<th>IUPAC Name (Common Name)</th>
<th>Abbreviation</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium chloride</td>
<td>A1_2Cl_6</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>Barium titanium oxide</td>
<td>BaTiO_3</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C_6H_6</td>
<td></td>
</tr>
<tr>
<td>Carbon monochloride</td>
<td>CCl</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td></td>
</tr>
<tr>
<td>Carbonic dichloride (phosgene)</td>
<td>COCl_2</td>
<td></td>
</tr>
<tr>
<td>Chloric (I) acid</td>
<td>HClO</td>
<td></td>
</tr>
<tr>
<td>Chloric (IV) acid</td>
<td>HClO_3</td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl_2</td>
<td></td>
</tr>
<tr>
<td>Chlorine radical/atomic chlorine</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>C_6H_5Cl</td>
<td></td>
</tr>
<tr>
<td>Chlorocuprous acid</td>
<td>H_2Cu_2Cl_4</td>
<td></td>
</tr>
<tr>
<td>Chloroethene (vinyl chloride)</td>
<td>C_2H_5Cl</td>
<td></td>
</tr>
<tr>
<td>Chloro-, 2-chloroethyl ester (chloroethyl chloroformate)</td>
<td>C_3H_4Cl_2O_2</td>
<td></td>
</tr>
<tr>
<td>Chloromethanal (formyl chloride)</td>
<td>CHClO</td>
<td></td>
</tr>
<tr>
<td>Chloromethane (methyl chloride)</td>
<td>CH_2Cl</td>
<td></td>
</tr>
<tr>
<td>Chloromethylene (chlorocarbene)</td>
<td>HCCl</td>
<td></td>
</tr>
<tr>
<td>1-chloronaphthalene</td>
<td>C_10H_7Cl</td>
<td></td>
</tr>
<tr>
<td>Chlorosyl chloride</td>
<td>OCl_2</td>
<td></td>
</tr>
<tr>
<td>Chlorosyl</td>
<td>ClO</td>
<td></td>
</tr>
<tr>
<td>Chloryl</td>
<td>ClO_2</td>
<td></td>
</tr>
<tr>
<td>Copper (I) chloride (cuprous chloride)</td>
<td>CuCl</td>
<td></td>
</tr>
<tr>
<td>Copper nitrate</td>
<td>Cu(NO_3)_2</td>
<td></td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>C_6H_4Cl_2</td>
<td></td>
</tr>
<tr>
<td>Dichloroethanoyl chloride (dichloroacetyl chloride)</td>
<td>C_2HCl_3O</td>
<td></td>
</tr>
<tr>
<td>Dichloroformurandione</td>
<td>C_4Cl_2O_3</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane (methylene chloride)</td>
<td>CH_2Cl_2</td>
<td></td>
</tr>
<tr>
<td>Dichloromethylene (dichlorocarbene)</td>
<td>CCl_2</td>
<td></td>
</tr>
<tr>
<td>Ethene</td>
<td>C_2H_4</td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene (perchlorobenzene)</td>
<td>C_6Cl_6</td>
<td></td>
</tr>
<tr>
<td>Hexachloroethene (perchloroethane)</td>
<td>C_2Cl_6</td>
<td></td>
</tr>
<tr>
<td>Hexafluoroethane (perfluoroethane)</td>
<td>C_2F_6</td>
<td></td>
</tr>
<tr>
<td>Hydrogen atom</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Hydrogen chloride gas</td>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl_(aq)</td>
<td></td>
</tr>
<tr>
<td>Hydrogen ion</td>
<td>H^+</td>
<td></td>
</tr>
<tr>
<td>Hydroperoxy radical</td>
<td>HO_2</td>
<td></td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td>Hypochlorite ion (monochlorine monoxide radical)</td>
<td>ClO^- (ClO)</td>
<td></td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HOCl</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td></td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Symbol/Formula</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td></td>
</tr>
<tr>
<td>Methyl benzene (toluene)</td>
<td>TOL CH₃C₆H₅</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td></td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>NOₓ</td>
<td></td>
</tr>
<tr>
<td>Nitrosyl ion</td>
<td>NO⁺</td>
<td></td>
</tr>
<tr>
<td>Nitrosyl chloride</td>
<td>NOCl</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td></td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>5CB C₆HCl₅</td>
<td></td>
</tr>
<tr>
<td>Perfluorocarbon (group of chemicals)</td>
<td>PFC</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅OH</td>
<td></td>
</tr>
<tr>
<td>Polychloroethene (polyvinylchloride)</td>
<td>PVC n(C₂H₃Cl)</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td></td>
</tr>
<tr>
<td>Tetrachlorobenzene</td>
<td>4CB C₆H₂Cl₄</td>
<td></td>
</tr>
<tr>
<td>1,1,2,2-tetrachloro-1,2-difluoroethane (Freon 112)</td>
<td>CFC-112 CCl₂FCCl₂F</td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethene (perchloroethene)</td>
<td>PCE, PERC C₂H₄</td>
<td></td>
</tr>
<tr>
<td>Tetrachloromethane (carbon tetrachloride)</td>
<td>CCl₄</td>
<td></td>
</tr>
<tr>
<td>1,1,1,2-tetrafluoroethane (Freon 134a)</td>
<td>CF₃CH₂F</td>
<td></td>
</tr>
<tr>
<td>Tetrafluoromethane</td>
<td>CF₄</td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td></td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>3CB C₆H₃Cl₃</td>
<td></td>
</tr>
<tr>
<td>1,1,1-trichloroethane (methyl chloroform)</td>
<td>TCA CCl₃CH₃</td>
<td></td>
</tr>
<tr>
<td>Trichloroethene (trichloroethylene)</td>
<td>TCE C₂HCl₃</td>
<td></td>
</tr>
<tr>
<td>Trichloromethane (chloroform)</td>
<td>CHCl₃</td>
<td></td>
</tr>
<tr>
<td>1,1,2-trichloro-2-oxo-ethyl radical</td>
<td>CCl₂CClO</td>
<td></td>
</tr>
<tr>
<td>1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)</td>
<td>CFC-113 CCl₂FCCl₂F</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td></td>
</tr>
</tbody>
</table>
1. INTRODUCTION

1.1 Abstract

1.2 Summary

1.3 The problem
   1.3.1 Vapour degreasing process
   1.3.2 Trichloroethene
   1.3.3 Environmental Impact
   1.3.4 Regulation and compliance
   1.3.5 Cleaning Industry’s Problem

1.4 VOC control/minimisation technologies
   1.4.1 Condensation Processes
   1.4.2 Adsorption techniques
   1.4.3 Absorption/scrubbing techniques
   1.4.4 Oxidation processes
      1.4.4.1 Overview
      1.4.4.2 Thermal incineration
      1.4.4.3 Catalytic Oxidation
   1.4.5 Summary

1.5 Plasmas
   1.5.1 General plasma concepts
   1.5.2 Microwave-Induced Plasmas (MIPs)
1. Introduction

1.1 Abstract

The potential for large fines and poor public image resulting from environmental non-compliance has lead to a trend of increasing expenditure on pollution abatement in developed countries. Volatile Organic Compounds (VOCs) are one of the groups of chemicals under scrutiny for their potential to adversely affect health and the environment. Many industrial cleaning processes require chlorinated hydrocarbon solvents (classed as VOCs) and so must comply with emission regulation. The aim of this research is to investigate the treatment of gas-phase emissions of one such solvent, trichloroethene (TCE), with a gas flame and a microwave-induced plasma.

1.2 Summary

Industrial processes are a major source of solid, liquid and gaseous environmental pollution. As environmental agencies and the general public become increasingly aware of these issues, governments must make legislation to control environmental contaminants. In the development of new products, manufacturing companies are also subject to pressure from consumers to deliver environmentally ‘safe’ products. These developments not only result in increasingly stringent emission limits, but also challenge conventional methods of industrial processing. Therefore, the need for the development of new technologies to minimise pollutant emissions has become an important issue for manufacturing companies, governments and the general public.

Several processes in industry cause pollution via the generation of Volatile Organic Compounds (VOCs). Potential deleterious effects of the release of these compounds include: acute (e.g. respiratory and nervous system) and chronic (carcinogenic and mutagenic) health effects, soil and ground-water contamination, global warming and ozone depletion (World Health Organisation 2000).

VOCs are a sub-group of a group of compounds referred to as ‘air toxics’ or ‘hazardous air pollutants’. Although there is no universally accepted definition of these terms, it is generally agreed that they are pollutants, they are present in low concentrations in the atmosphere and that they are known or, at least suspected, to be
hazardous to health and/or the environment. The World Health Organisation defines VOCs as “all organic compounds in the boiling range of 50 – 260°C, excluding pesticides” (Environment Australia 2001).

In manufacturing industries, metallic parts are normally cleaned following machining and prior to assembly. This process is known as ‘degreasing’ and a variety of degreasing methods and solvents are currently available. Vapour degreasing with halogenated solvents is an important part of many industries, in particular fabricated metal products, electric and electronic equipment, transportation equipment and miscellaneous manufacturing industries. However, it is used in many other manufacturing and non-manufacturing industries and is required when a high degree of cleanliness is specified. The most popular solvent used in vapour degreasing is trichloroethene (TCE).

Conventional methods used to control VOC pollution are condensation, carbon adsorption, catalytic oxidation and thermal incineration. These processes either destroy the VOC in question or recover it with an altered composition. They are energy intensive and produce further wastes for treatment. Other processes are now available, such as biofiltration and membrane separation, which may be more attractive options.

Continuing research effort is put into not only the development of novel processes to treat or avoid the production of these wastes, but also into improving existing ones. There is great emphasis on reducing the addition of chemicals to processes, reducing the energy requirements of these processes and, of course, increasing the efficiency, as commercial competition is vital to the survival of any process. One of these techniques is the implementation of plasma processes for pollution control.

1.3 The problem

1.3.1 Vapour degreasing process

The use of halogenated solvents to clean or otherwise condition the surface of metal parts, electronic components and other non-porous substrates was introduced in the 1930’s and has been widely used for the cleaning of metal parts ever since. The
solvent can be used in its liquid form (cold cleaning) or, more often, as a vapour (vapour degreasing).

Vapour degreasing is used when a high level of cleanliness is required or when the parts have an awkward shape. Solvent in a sump or reservoir is boiled to produce dense, rising solvent vapours. The vapour displaces the air in the bottom of the machine to form a solvent layer. The parts to be cleaned, known as the work, are usually small metal parts and electronic components of any shape. They are introduced into the vapour zone, where the vapour condenses onto the cold surface of the work. Once on the parts, the condensed vapour dissolves the soils. This liquid mixture of soils and solvent then runs off the parts, thereby cleaning them (Radian Corporation 1991). Any vapour that does not condense will eventually be released, in varying concentrations, into the ambient air. Vapour degreasing processes can be batch, usually Open Topped Vapour Cleaners (OTVCs), or continuous/semi-continuous, which are covered and usually known as in-line cleaners.

Solvent emissions from vapour degreasing machines vary significantly depending on the machine design, solvent used and the operating parameters. Figure 1.1 shows a schematic of a vapour degreasing machine at HPM in Sydney. The stream exiting the machine into the atmosphere above the factory was found to contain 2% TCE vapour at a total flow of about 60 lmin⁻¹. This equates to a maximum of 4 tonnes of emissions per year. Surface Technologies in Melbourne estimate that they lose 0.8 – 1.6 tonnes of TCE as air emissions every year (Downes 2005). At the current price (February 2005) of $2.20/kg, typical losses therefore cost an estimated AUD$1,000 - AUD$10,000 per year. Therefore, TCE is a slight economic as well as an environmental concern. A detailed investigation of degreasing emissions and related issues was conducted by the Radian Corporation (1991).
1.3.2 Trichloroethene

Trichloroethene (TCE, C₂HCl₃) is an unsaturated aliphatic halogenated hydrocarbon belonging to the group of chemicals known as volatile organic compounds (VOCs). It is a colourless liquid of moderate volatility and is a powerful solvent (World Health Organisation 1987). The IUPAC and CAS name of the chemical is trichloroethene, but it is more commonly referred to as trichloroethylene. Some common synonyms for TCE are: ethene trichloro-, ethylene trichloro-, ethylene trichloride, acetylene trichloride, ethinyl trichloride, 1,1,2-trichloroethylene, 1-chloro-2,2-dichloroethylene, 1,1-dichloro-2-chloroethlyene, TCE and TRI. (National Institute of Standards and Technology 2003; World Health Organisation 1985). See appendix 1A for physical and chemical properties of TCE.

There are no known natural sources of TCE (World Health Organisation 1987). Its origins date back to 1864, when it was prepared by Fischer by the reduction of hexachloroethane (C₂Cl₆) with hydrogen. Commercial production of TCE began in Europe in 1908 and within twenty years America had followed suit (National Industrial Chemicals Notification and Assessment Scheme 2000).
TCE has been used for many different purposes but today, as historically, its primary use is as a liquid or vapour solvent in the metal fabricating industry. Degreasing accounts for as much as 80 – 90 % of the TCE used worldwide (National Toxicology Program 2001). Overseas, another major use of TCE is as an intermediate in the production of chemicals such as fluorochemicals and polychloroethene (polyvinylchloride, PVC). Other uses of TCE include as a solvent in speciality paints, coatings, adhesives and aerosol formulations, as a low temperature heat transfer medium and to clean leather and textiles (Halogenated Solvents Industry Alliance 2001; Department of the environment 1976; Environment Canada 2001a). More information on TCE usage is given in appendix 1B.

Properties such as high solvency, low flammability, non-corrosiveness, high stability, low specific heat, low boiling point, low heat of vaporisation and low production cost make TCE an excellent solvent in a wide range of applications (Halogenated Solvents Industry Alliance 2001). TCE degreases more thoroughly and several times faster than alkaline cleaners and is compatible with smaller equipment that consumes less energy (Halogenated Solvents Industry Alliance 2001). In fact, according to the Dow Chemical Company (1999), “with the proper selection and choice of the options available, vapour degreasing with chlorinated solvents is the cleaning process that is most efficient, most cost effective and least detrimental to the environment”. TCE is the most widely used of the available halogenated solvents in vapour degreasing processes.

Total world-wide chlorinated solvent usage is nearly 1 million tonnes per annum (European Chlorinated Solvent Association 2002), at least 250,000 tonnes of which is TCE at AUD$2,200 per tonne (Dow Chemical Company 2005). The boom in information technology has led to a trend towards increasing levels of required cleanliness. This means that more processes will require the performance that only halogenated hydrocarbons can deliver.

1.3.3 Environmental Impact

The National Industrial Chemicals Notification and Assessment Scheme’s “Priority Existing Chemicals Report” on TCE (2000) and the European Chlorinated Solvents
Association (2002) are excellent sources of information about TCE’s environmental impact.

Practically all of the TCE used in Australia enters the air unchanged. TCE emission control is classed as poor. Emission factors (percentage used that is released to the air) of 91% for uncontrolled TCE sources and 87% for controlled ones are published (Environment Australia 1999). For example, 83 – 91% of the TCE used by Surface Technology Coatings is emitted to the atmosphere in the vapour phase (Downes. 2005). Ambient air concentrations of TCE typically range from less than 1 µg/m³ in rural areas to 10 µg/m³ in urban areas (World Health Organisation 2000).

Once released into the air, TCE may react photochemically with hydroxyl radicals (OH) and, to a lesser extent, ozone (O₃) to produce phosgene (carbonic dichloride, COCl₂), dichloroethanoyl chloride (dichloroacetyl chloride, C₂HCl₃O), chloromethanal (formyl chloride, CHClO) and other degradation products. Phosgene is a colourless gas with an unpleasant, irritating odour at high concentrations. It is poisonous above 50 ppm in air and inhalation causes severe and often fatal oedema of the lungs within a few hours. It is over three times heavier than air and so may accumulate in the workplace. Direct photolysis occurs as a minor transformation process. TCE does not readily undergo chemical oxidation or hydrolysis in the atmosphere (National Industrial Chemicals Notification and Assessment Scheme 2000). TCE is responsible for a small amount of ozone creation (European Chlorinated Solvent Association 2002).

The half-life of TCE in the air varies with latitude, climate and concentration of hydroxyl radicals. The World Health Organisation (1987) has estimated a half life of 70 hours in Europe, based on yearly average concentrations of 5 x 10⁻⁸ and 0.040 ppm of hydroxyl radicals and ozone respectively. Canadian calculations of the half-life of TCE illustrate the possible variation; in the north in winter, the half-life increases to several months, whereas in summer in the south of the country it falls to a single day. Since Australia’s climate is always much warmer than Canada’s winter extreme, the half-life is expected to vary over a smaller range at the lower end of the scale. TCE does travel short and medium distances under conducive conditions, such as high
winds, however the relatively short atmospheric half-life prevents long range transport of TCE to the stratosphere. Therefore, TCE is decomposed in the troposphere and is not considered to contribute significantly to global warming or stratospheric ozone depletion (National Industrial Chemicals Notification and Assessment Scheme 2000).

There is concern that TCE may be carcinogenic and it is generally considered as a probable weak carcinogen (see appendix 1D). It can also cause acute effects on organs and systems of the body, especially the central nervous system and liver. Irritation of the respiratory tract may occur at concentrations of 150 – 650 ppm. Brief exposure to TCE is mildly irritating to human skin. Prolonged contact could lead to burning and repeated exposure causes various types and degrees of dermatitis, depending on the person. An alcohol intolerance, known as “degreaser’s flush”, may occur.

The amount of TCE entering environmental media other than the air is small. TCE has a moderate potential to bioaccumulate. The degradation of TCE in the air and aquatic compartment is relatively fast but is expected to be much slower in ground water. Therefore, ground water contamination with TCE would be of concern. Fortunately, this would only arise from improper handling, disposal and storage, or spillages caused by these practices. In Australia, procedures are such that this is unlikely (National Industrial Chemicals Notification and Assessment Scheme 2000).

Therefore the main concern in the control of TCE emissions should be to reduce the exposure of people (and wildlife) in the vicinity of its use. Appendices 1C and 1D discuss the environmental impact and health effects of TCE in more detail.

1.3.4 Regulation and compliance

In the past, a wide variety of solvents were used to clean parts in industry. The five standard solvents were dichloromethane (methylene chloride, MC), trichloroethene (TCE), tetrachloroethene (perchloroethylene, PCE), trichlorotrifluoroethane (CFC-113) and 1,1,1-trichloroethane (methyl chloroform, TCA). The cleaning process usually simply involved dipping the parts to be cleaned into a solvent and waiting.
the 1980s the Montreal Protocol called for the phase-out of ozone depleting substances. This meant that many users of vapour degreasing processes were forced to change their cleaning process, and is what caused a technological cleaning revolution and the birth of the industry as it is today.

To help industry with this transition, the US EPA compiled a list of acceptable alternatives for the banned substances (Significant New Alternatives Policy, SNAP). TCE, PCE and MC were listed as acceptable alternatives for ozone depleting substances in metal cleaning. In 1990, in a Clean Air Act amendment, National Emission Standards for Hazardous Air Pollutants (NESHAP) were published. These standards are summarised in Hill (1995). These standards set limits on the emission (but not use or production) of volatile organic compounds, including TCE, MC and PCE. Please note that while these substances are regulated as volatile organic compounds, they are not considered as ozone depleters or greenhouse gases. Therefore, they will not be banned within the foreseeable future.

In 1995, “New regulation controlling air emissions from solvent cleaning machines (degreasers)” was published (United States Environmental Protection Agency). This regulation applies to owners of solvent cleaning machines of any size in a facility of any size. This regulation gives users of vapour degreasers three compliance options:

- Alternative standards – comply by keeping the emissions below a certain limit while operating the degreaser; i.e. 150, 153 and 99 kg m⁻² mo⁻¹ for batch vapour, existing in-line and new in-line machines respectively
- Idling emissions – comply by keeping the solvent emissions below certain limits while the degreaser is idling, i.e. 0.22 and 0.1 kg m⁻² hr⁻¹ for batch vapour and in-line machines respectively
- Control combinations – Add a pre-defined combination of control technologies to the degreaser (includes carbon adsorber, freeboard refrigeration device and super-heated vapour). All combinations involve at least two control measures. This is based on the idea of ‘Best Available Control Technology (EPA compliance)’.
Alternative cleaning processes may avoid emission control issues. However, wastewater disposal, energy requirements and safety are issues that must also adhere to regulation. In particular, tightening wastewater regulations are predicted by many people.

Similar regulation is in place in Australia. Environment Australia has implemented AS 2661-1984 (Standards Australia), which controls the design, installation and operation of vapour degreasing plants. However, it refers readers to state environment agencies’ emission limits, which are not generally known or enforced. The National Occupational Health and Safety Commission (1989) have published health and safety information and preventative measures regarding the use of chlorinated solvents in vapour degreasing processes. The National Industrial Chemicals Notification and Assessment Scheme is the best source of information on TCE in Australia.

The use of chlorinated solvents is not specifically regulated in Europe or Asia. However, under international standard ISO 14000, companies are encouraged to control emissions, avoid pollution and generally use ‘industrial good practice’ (European Chlorinated Solvents Association 1999).

There is significant indication that social factors are encouraging companies to take voluntary steps to reduce emissions. There have been cases in the US and Canada where companies have complied with emission limits that were more stringent than the government requirements.

The Halogenated Solvents Industry Alliance (2001) states in its White Paper on TCE that: “In addition to complying with these various regulatory requirements, many prudent operators of degreasing and other equipment have elected to adopt practices and standards for the use, management, and disposal of trichloroethylene and trichloroethylene-containing wastes that go beyond the strict legal requirements”.

More information about guidelines and standards can be found in appendix 1E.
1.3.5 Cleaning Industry’s Problem

Within the last few years, chlorinated solvent users have had two options: switch to a different solvent or process, or apply emission control measures to the existing machine. The first option usually involves investment in a larger and more expensive machine that may not meet cleaning requirements and costs several orders of magnitude more to run. It can also cause safety and wastewater disposal problems. There are several measures that can be taken to reduce emissions from an existing machine. However, these all require significant investment of energy, making them expensive and compromising their environmentally friendly status.

Until concern was raised over ozone depletion by industrial solvents in the 1980s, the industrial cleaning was not considered a distinct industry. The situation is still that many companies with different core businesses are facing similar problems but may not be aware of possible solutions. Good sources of information for the cleaning industry are CleanTech Magazine and The Halogenated Solvents Industry Alliance.

The main requirements for a suitable control technology are: low capital investment, robustness and the option to retrofit. Ideally, operating cost would also be low. The device emissions must remain within regulatory limits under all conditions. If this is not the case, a simple cut-off system must be possible so that highly skilled operators are not required.

Working emissions of TCE from an OTVC have been reported to be 0.3 kgm\(^{-2}\)hr\(^{-1}\) (Radian 1990). Idling emissions were not reported for TCE. However, comparison of idling and working data for other solvents suggests that idling emissions are in fact very similar to working emissions. There is no emission data for in-line machines; however, Radian (1990) state that they are expected to be less than from their open-topped counterparts. Therefore, it can be assumed that 0.3 kgm\(^{-2}\)hr\(^{-1}\) (~ 220 kgm\(^{-2}\)mo\(^{-1}\)) is the maximum possible emission rate of TCE from a vapour degreasing machine. Overall US emission limits are 99 – 150 kgm\(^{-2}\)mo\(^{-1}\) (section 1.3.4). Therefore, required destruction and removal efficiencies are estimated to be 30 – 55 %.
1.4 VOC control/minimisation technologies

1.4.1 Condensation Processes

Condensation systems are often used for the control of VOCs, especially in processes with low flow rates and high pollutant concentrations. In general, the process involves cooling the waste stream to a temperature below its dew point and collecting the mixture as a liquid. The VOC can then be separated and recovered, or treated for disposal (Jain et al. 1997). All vapour-degreasing machines are fitted with a primary condenser. Diffusional losses from the machine can be reduced by replacing the cooling water with a refrigerant or cooled water or, alternatively, adding a second condenser higher up in the system, known as a freeboard refrigeration device.

Different solvents (and varying initial temperatures) display different sensitivities to increased cooling, and so the effect on diffusional losses varies significantly. For a machine using Genesolve DFX (90.9 % CFC-113), the addition of an above-freezing freeboard refrigeration device decreased losses by only 8 %. However, the installation of a below-freezing freeboard refrigeration device into the same machine resulted in solvent savings of 69 %. Similar results (62 %) were found for tetrachloroethene (PCE) (Radian Corporation 1991).

1.4.2 Adsorption techniques

Amongst currently available technologies, adsorption is the most efficient process for the removal of chlorinated solvents (Jain et al. 1997). In the conventional adsorption process, the gaseous waste stream is passed over a granular bed (usually activated carbon), onto which the solvent is collected. Upon saturation, the solvent is desorbed from the granular bed by regeneration with steam, hot air or inert gas, or the bed is replaced. This mixture is then condensed and passed through a water separator, recovering the solvent for re-use. In continuous systems, a second granular bed is required to enable simultaneous adsorption and desorption.

Activated carbon adsorption can be used on flow rates of up to 300,000 lmin$^{-1}$ with concentrations less than 50 gm$^{-3}$, which corresponds to less than 1 % TCE. Although operating costs are high, initial capital investment is low, adsorption is flexible to flow variations and can process a variety of concentrations and contaminants.
However, activated carbon is subject to temperature constraints of 20 – 40°C, a humidity of less than 50 % and is a fire hazard. Regular replacement of the carbon bed is also expensive and inconvenient. The regeneration process is also slow and expensive. However, research into different adsorption surfaces and desorption techniques has improved the efficiency of this technique (see Chapter 3).

The Radian Corporation (1991) reported that carbon adsorbers could reduce emissions by 60 – 65 %. Urashima and Chang (2000) claim that adsorption systems can decrease low-concentration solvent losses by 90 %. More specifically, the Radian Corporation survey (1991) quoted a control efficiency of 61 % for a vapour-degreasing machine using TCE.

1.4.3 Absorption/scrubbing techniques

This is the transfer of pollutants from a gas stream into a liquid stream. This technique is more common in the removal of inorganic compounds, particularly odorous ones, where the absorption is accompanied by a chemical reaction. However, valuable organic products may be removed by scrubbing (Jain et al. 1997). Scrubbing can be applied to VOC concentrations above 200 ppm. Its advantages include that it is easy to use, excellent for odour removal, and calculation methods, based on experience, are available. However, scrubbing is not applicable to all VOCs and waste liquid solution must be treated. In addition, when oxidation accompanies the absorption process, the capital and operating costs are quite significant, and corrosion and toxicity must be considered.

1.4.4 Oxidation processes

1.4.4.1 Overview

In these processes a waste is oxidised, or incinerated, to provide a less bulky, toxic or noxious material. For oxidation to be a viable option, the waste material must be combustible to some extent. See the ‘Handbook of hazardous waste incineration’ (Calvin and Brunner 1989) for more information for further information.

Complete combustion is the most commonly used method for the destruction of concentrated waste streams as it provides very high removal efficiencies through
relatively simple means. Furthermore, the waste produced by this process is minimal, often eliminating the need for further control of the stream. Other major advantages of combustion are that it can be applied to any solvent, including non-soluble and non-adsorbable ones, and it can cope with varying VOC concentrations and compositions as well as variations in the volume of the stream. The process also provides the option of heat recovery (Jain et al. 1997). A scrubber control system is usually placed downstream of the incinerator to remove further unwanted compounds being released into the environment.

Combustion is the least favoured option for the treatment of dilute VOC streams however, as additional fuel must be added to the process, making it much more energy intensive. In addition, the combustion of compounds containing sulphur or halogens produces toxic compounds such as sulphur dioxide and hydrogen chloride (Jain et al. 1997).

Thermal and Catalytic Oxidation are both established combustion processes.

1.4.4.2 Thermal incineration

The waste air is burned in a flame at very high temperatures (800 – 1000°C). This process is very efficient, producing destruction and removal efficiencies (DREs) in excess of 99.99 %, but is extremely energy intensive. There are many different combustion techniques available to enhance the process, such as adding lime or additional oxygen to the combustion chamber, but most are designed for solids and sludges.

In terms of heat recovery, there are three types of thermal incinerator. The first, a simple direct flame incinerator, comprises a combustion chamber and a fuel reserve. An evolution of this is the addition of heat exchangers that transfer heat from the exit gases to the inlet gas (recuperative oxidation). In a regenerative oxidation system, the inlet gases are passed over a hot bed before being oxidised in another chamber. The treated stream is then redirected across the hot bed to maintain the temperature without the need for fuel. This third option is used for low levels of contamination.
Recuperative oxidation can remove 95 % of TCE, methyl benzene (toluene) and benzene at temperatures between 730 and 930°C (Urashima and Chang 2000). Pollutant concentrations exceeding 1000 ppm are usually used and the process is impractical for low concentrations. Depending on the operating temperature, nitrogen oxides (NOₓ), dioxins and furans may be formed.

1.4.4.3 Catalytic Oxidation

Catalytic Oxidation is a reasonably mature technology that has been in use since the 1940s. The flame is replaced with a catalyst bed. The gases are preheated in a mixing chamber and then oxidised on a granular catalyst bed. Platinum, copper or chromium oxides are used to enhance the rate of VOC oxidation. Considerably lower temperatures than for thermal incineration (200 - 500°C) are required. Catalytic incinerators commonly achieve DREs of 70 – 90 %, although 98 % removal is feasible for many sources. However, these efficiencies may require large volumes of catalyst and high operating temperatures, depending on the inlet concentration. Jennings et al. (1985) reported that VOC destruction efficiencies in catalytic processes ranged from 42.5 to 99 % for concentrations ranging from 15 – 2100 ppm. The highest destruction efficiency was achieved at the highest concentration and in general, high efficiencies were only achieved in highly concentrated streams. Urashima and Chang (2000) reported DREs for toluene in catalytic oxidation processes of 25 % at 150°C and 95 % at 260°C.

Although this process is much less energy intensive than thermal incineration, problems such as catalyst cracking, poisoning and deactivation are likely to occur, severely affecting the efficiency of the process. Catalysts have an average lifetime of 2 – 5 years (Jennings et al. 1985; Jain et al. 1997). Owing to the lower operating temperatures, furans and dioxins are not produced in this process and the amount of NOₓ produced is also less than in thermal processes. If a recuperative system is operated between 150 and 370°C, the VOCs are converted to carbon dioxide (CO₂) and water vapour or inorganic acid, which can be scrubbed.
1.4.5 Summary

Table 1.1 summarises the control efficiencies of these processes where specific information is available.

<table>
<thead>
<tr>
<th>Control method</th>
<th>Conditions</th>
<th>Solvent</th>
<th>DRE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeboard refrigeration</td>
<td>Above freezing</td>
<td>CFC-113</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Below freezing</td>
<td>CFC-113</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Below freezing</td>
<td>PCE</td>
<td>62</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Carbon</td>
<td>TCE</td>
<td>61</td>
</tr>
<tr>
<td>Biofiltration</td>
<td>Ambient</td>
<td>TCE</td>
<td>75</td>
</tr>
<tr>
<td>Membrane</td>
<td>Ambient</td>
<td>Not specified</td>
<td>90-99</td>
</tr>
<tr>
<td>Thermal oxidation</td>
<td>Recuperative</td>
<td>TCE</td>
<td>95</td>
</tr>
<tr>
<td>Catalytic oxidation</td>
<td>260°C</td>
<td>TOL</td>
<td>95</td>
</tr>
<tr>
<td>UV oxidation</td>
<td>&lt;1 lmin⁻¹</td>
<td>C₂H₄, CH₄</td>
<td>98</td>
</tr>
<tr>
<td>Thermal plasma</td>
<td>3.3 kW plasma jet</td>
<td>CFC-12</td>
<td>~100*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₆H₄ClOH</td>
<td>99.9999</td>
</tr>
</tbody>
</table>

Table 1.1: Efficiencies of existing VOC control technologies

(Radian Corporation 1991; Lee et al. 2000; Forest Products Laboratory; Urashima and Chang 2000)

DRE: Destruction and Removal Efficiency

*100 % removal is not possible. The source does not state the detection limits of the analytical technique used.

1.5 Plasmas

1.5.1 General plasma concepts

Plasma is ionised gas and has unique properties, and so is often referred to as the “fourth state of matter”. There are several different types of plasma with different properties. However, a common feature of all plasmas is that they are composed of equal amounts of positive and negative charge. The two main properties that are used to classify plasmas are the electron density and the plasma temperature (the electron temperature in particular). Braithwaite (2000) gives a good introduction to gas discharges.

There are various ways to supply the energy required to ionise gas, including thermal energy, adiabatic compression and addition of energetic beams. For technological
purposes, plasma is generated by applying an electric current or electromagnetic radiation to neutral gas. Any gas contains a small number of electrons and ions as a result of, for instance, cosmic rays. These charged particles are accelerated by the energy applied to the gas, and go on to ionise the neutral gas particles. Hence, plasma is formed.

Plasma generation is possible with several different sources of energy; direct current (DC), alternate current (AC) at high voltage, radio frequency (RF) and microwaves are some of the common energy sources used to generate plasma. Conrads and Schmidt (2000) give a good introduction to plasma generation, sources and applications.

In thermal plasma, electrons and heavy particle temperatures are within the same range (6,000K+), i.e. it is in ‘local thermodynamic equilibrium (LTE)’. A welding torch is an example of thermal plasma.

In non-thermal (non-LTE, cold) plasma, the electrons have higher temperatures, and therefore higher mean energies, than the heavy particles (i.e. atoms, molecules, free radicals). One definition of non-thermal plasma is that the heavy particles are at or near to ambient temperature (i.e. 300 K) (Graham 2001). In this case, non-thermal plasmas are not in LTE, unlike those in thermal plasmas. Other sources state that if the electrons have a higher mean energy (or temperature) than the heavy particles, the plasma is non-thermal (McAdams 2001). A fluorescent light is an example of non-thermal plasma. Non-thermal plasma is attractive for the treatment of dilute waste streams as energy is directed into the formation of electrons, which can break down the pollutant molecules, rather than bulk heating of the waste stream.

**1.5.2 Microwave-Induced Plasmas (MIPs)**

Gas discharges that are excited and sustained by microwaves are of interest for potential industrial application. The widespread commercial availability of magnetrons, the type of microwave generator used in microwave ovens, contributes to the development of this technique. The main advantages of microwaves as plasma generators are that magnetrons are very cheap and no electrodes are required in the
plasma chamber. The absence of electrodes greatly reduces the inevitable corrosion problem caused by the acidic gases produced during the treatment of halogenated organics, resulting in lower maintenance requirements; it also minimises contamination of the plasma.

Microwaves are directed through a waveguide into the plasma chamber. Different resonant modes can be achieved depending on the dimensions of the reactor.

Atmospheric pressure microwave plasmas are often referred to as non-thermal plasmas, e.g. McAdams (2001). However, their electron density and heavy particle temperatures are much higher than those in classic non-thermal plasmas such as silent discharge plasmas and low-pressure microwave plasmas. Timmermans et al. (1998) reported a heavy particle temperature range of 1,000 – 4,000 K, which is significantly lower than the electron temperature range, reported as 7,000 – 20,000 K. Therefore, microwave plasmas at atmospheric pressure can be referred to as either thermal or non-thermal, depending on the definition used; in reality, they are somewhere in between. In theory, adjusting the power absorbed can vary the mean temperature of the plasma. The comparatively high electron density means that atmospheric pressure microwave plasmas are good for treating moderately concentrated waste streams.

The plasma frequency is related to the electron density in the plasma and therefore to the plasma temperature. The plasma frequency must be equal to or greater than the microwave frequency for the microwaves to be successfully absorbed. Therefore, the larger the frequency of electromagnetic radiation supplied, the higher the minimum plasma temperature.
2. OBJECTIVES ........................................................................................................19

2.1 Abstract.................................................................................................................20

2.2 Summary...............................................................................................................20

2.3 System variables...................................................................................................21
  2.3.1 Reactor temperature.........................................................................................21
  2.3.2 Fuel provision ...............................................................................................22
  2.3.3 Quench rate ...................................................................................................22
  2.3.4 Residence time ..............................................................................................23
2. Objectives

2.1 Abstract
In order to find the best way of dissociating trichloroethene in contaminated air streams of various concentrations into benign products, the following phenomena will be studied and compared: dissociation in a propane gas flame, a microwave-induced plasma, and a “propane-assisted” microwave-induced plasma. The aims are to contribute to the understanding of microwave-induced plasmas and appropriate waste treatment.

2.2 Summary
The aim of this project is to assess the ability of an atmospheric pressure microwave-induced plasma to treat a stream of air contaminated with typically 2 % trichloroethene (TCE), by dissociating it into acceptable products. Its performance will be compared with other techniques in terms of destruction and removal efficiency (DRE), energy efficiency, production of by-products and capital cost. The DRE is given on a log scale, such that if 99.99 % of the target compound were destroyed and/or removed, the DRE would be given as ‘4 nines’. Equation 2.1 defines the DRE in number of nines, where \( x \) is the fraction of TCE destroyed or removed in the process.

\[
DRE = -\log(1 - x)
\]  

Equation 2.1

Microwave-induced plasma is of interest for engineering applications as it requires no fuel or electrodes and involves very low capital cost. However, a conventional gas flame was also investigated, as if its performance were acceptable, it would involve lower operating costs and complexity. It was suspected, however, that the richer gas flame would produce chlorinated organic products, including chlorinated benzenes, which may lead to the formation of dioxins and furans. These compounds are known to be highly carcinogenic (see appendix 2A), and so their formation must be avoided. The third option was the propane-assisted plasma, which required less propane addition than the flame (see figure 2.1). It was chosen in an attempt to exploit the advantages of both processes, i.e. cheap fuel provision by propane, hopefully reducing the electrical power required to operate the plasma, with plasma temperature and
leaner atmosphere, hopefully producing fewer hydrocarbons and less carbon monoxide.

\[
\begin{align*}
C_2HCl_3 + 2O_2 &= HCl + 2CO_2 + Cl_2 \quad \text{(air plasma)} \\
4C_2HCl_3 + 11O_2 + C_3H_8 &= 12HCl + 11CO_2. \quad \text{(propane plasma)} \\
13O_2 + 2C_2HCl_3 + 2C_3H_8 &= 6H_2O + 10CO_2 + 6HCl \quad \text{(propane flame)}
\end{align*}
\]

Figure 2.1 Desired overall reactions in the trichloroethene destruction methods

The emphasis on this assessment has been on the overall robustness of the process. Vapour degreasing is usually a low-tech, low-investment operation with one minimally-trained operator. The machine must be simple to operate and completely self-regulating. Therefore, the allowable range of trichloroethene concentrations, quench rates, reactor powers, etc. must be defined. The potential consequences of running off-specification must be known for a proper assessment of this process.

There are three elements of this project: experimentation, modelling and chemical analysis. Experiments involve dissociating a trichloroethene/air mixture in a gas flame and/or a microwave-induced plasma. The principal modelling element is chemical kinetic modelling with CHEMKIN (Reaction Design), a commercially available chemical kinetics package. Chemical analysis is required to verify the model with the experimental results. The chemical analysis is a very important element of this research, as without meaningful analysis the results of the experiments would be unknown and the model could not be verified. In fact, this aspect has been the most time-consuming, difficult and expensive part of the project.

2.3 System variables

2.3.1 Reactor temperature

Thermal combustion is a conventional method of treating concentrated waste streams, while non-thermal plasmas are recognised for their ability to treat dilute waste streams. There is some dispute whether microwave-induced plasmas at atmospheric pressure are thermal or non-thermal plasmas. That is, whether the application of microwave power to a gas can either cause heating of the entire gas (heavy and light species), or the light species (electrons) to become much hotter than the heavy species (e.g. oxygen and nitrogen molecules in air), respectively. Therefore, if the microwave
plasma temperature is in between the traditional thermal and non-thermal temperatures, it may be an energy efficient way of treating intermediate concentrations of volatile organic compounds.

It was hoped that by varying the flow rate or the power supplied to the reactor, the power absorbed by the plasma, and hence its temperature, could be varied. The minimum possible temperature depends on the microwave frequency, which is set at 2.45 GHz. Propane flames operate at 1,200 – 1,400 K.

Therefore, reactor temperature and its effect on the process will be investigated.

2.3.2 Fuel provision

The addition of an alkane to the system will make it richer in both carbon and hydrogen. Although methane would provide the highest hydrogen to carbon ratio and be cheaper in an industrial system, propane was used in the laboratory for convenience (there was no methane supply). For carbon, richness is a measure of its ratio to oxygen in the system. Richness of hydrogen is in terms of its ratio to chlorine in the system. Therefore, although TCE (chemical formula C₂HCl₃) provides both carbon and hydrogen to the system, its addition only increases carbon richness and not hydrogen richness.

Increasing carbon richness in the system increases the potential to form hydrocarbons, possibly dioxins and furans, and carbon monoxide. The rich atmosphere does have the advantage of reducing the formation of nitrogen oxides (NOₓ), however, which are expected to be a problem in the lean air plasma.

It is hoped that an increase in hydrogen richness (by propane or water addition) will improve conversion of the chlorine in the system to hydrochloric acid, rather than chlorine gas or chlorinated hydrocarbons.

2.3.3 Quench rate

The quench rate, or temperature quench, is the rate that the reactor effluent is cooled on leaving the reactor, in degrees (K or °C) per unit time (s). Quench rate is not
formally controlled in the laboratory experiments. Therefore, quench is affected by changes in reactor power and flow rate.

2.3.4 Residence time

Residence time has not been investigated as it was assumed that equilibrium was reached virtually instantaneously in the reactor at plasma temperatures. This assumption may not be valid in the Bunsen burner.
3. LITERATURE REVIEW ........................................................................................................24

3.1 Abstract..............................................................................................................................25

3.2 Introduction.......................................................................................................................25

3.3 Plasmas applied to VOC control .....................................................................................26
  3.3.1 Thermal Plasmas ..........................................................................................................26
  3.3.2 Non-thermal plasmas ..................................................................................................26
    3.3.2.1 Electron beam discharges ..................................................................................26
    3.3.2.2 Corona discharges ..............................................................................................28
    3.3.2.3 Dielectric barrier processes ..............................................................................29
  3.3.3 Microwave-induced plasmas .....................................................................................31
  3.3.4 Summary of plasma destruction efficiencies .............................................................32

3.4 Other novel VOC control processes .............................................................................33
  3.4.1 Alternative solvents ..................................................................................................33
  3.4.2 Innovative adsorption processes ..............................................................................34
  3.4.3 Biofiltration ...............................................................................................................35
  3.4.4 Membrane separation ...............................................................................................36
  3.4.5 UV oxidation and photocatalysis (indirect plasma process) .....................................36

3.5 Flame temperatures .........................................................................................................37

3.6 Chemical Modelling .........................................................................................................37
3. Literature Review

3.1 Abstract

There are many ways of treating volatile organic compounds (VOCs). Thermal plasmas can achieve very high destruction levels in heavily contaminated streams, whereas non-thermal plasmas are good for treating diluted waste streams. Other areas of VOC control research include alternative solvents, innovative adsorption processes, biofiltration, membrane separation and advanced oxidation processes.

Average temperatures of 1,200 K and 1,000 – 4,000 K have been measured in diffusion flames and atmospheric pressure microwave plasmas respectively.

There are several chemical modelling packages and reaction schemes available that can be used to simulate the chemical processes undergone in VOC dissociation.

3.2 Introduction

Chapter 1 showed that there is a large potential market for volatile organic compound (VOC) control processes, including in the degreasing industry. Increasing regulation means that demand for pollution control methods is always increasing. Therefore, a significant amount of research into VOC treatment methods, including plasma technology, is carried out. Other innovative techniques of interest to the vapour degreasing industry include improved adsorption and alternative cleaning processes. Trichloroethene (TCE) is the most commonly used halocarbon in vapour degreasing processes.

There is a lot of literature reviewing VOC control processes. Urashima and Chang (Urashima and Chang 2000) present a thorough review of established and non-thermal plasma control technologies. Investigation of the application of non-thermal plasmas to pollution control was begun as early as the 1970s. The late Bernie Penetrante was instrumental in reviving this field in 1992 by bringing the international community together at a NATO workshop held in Cambridge (Penetrante et al. 1992). His own contributions to the field are also respected by many researchers the world
over. Other good references to plasma waste treatment include Cooper et al. (1998) and Veldhuizen (1999).

The measure used to assess pollution control processes is destruction and removal efficiency (DRE). It is the percentage of the pollutant that is destroyed or removed in the process. It is either quoted as a percentage or a number of nines. The number of nines is the negative log to the base ten of the fraction of the pollutant remaining in the waste stream, so that a DRE of 99.99% equates to 4 nines.

3.3 Plasmas applied to VOC control

3.3.1 Thermal Plasmas

Thermal plasmas can achieve almost complete destruction of VOC streams. However, large electrical powers are required, making them only practical for application to highly concentrated streams. It has been reported that a 3.3 kW DC plasma jet is capable of removing almost 100% of the CFC from a CFC-12, H₂ and O₂ mixture. Apart from excessive power consumption, thermal NOₓ is produced if the VOCs are burned in an air environment (Urashima and Chang 2000).

PLASCON is a thermal plasma system that has been implemented at several sites around the world. It can achieve a DRE of 6 nines of polychlorinated benzenes with no detectable production of dioxins and furans. Reported costs were A$2,000 per tonne destroyed in 1992, which is equivalent to AUD$3,600 in 2005 (Federal Reserve Bank of Minneapolis 2005).

3.3.2 Non-thermal plasmas

3.3.2.1 Electron beam discharges

In electron beam plasma reactors the electrons are generated outside the reaction chamber in a vacuum environment and injected through thin titanium or boron nitride films. The initial mono-energetic electrons have energies in the order of 100 keV to MeV’s. The plasma is created by elastic collisions, which thermalise the electrons, and inelastic collisions with the contaminated gas. More recently, pulsed electron beam reactors have been developed with a frequency of up to 100 Hz. Two obvious
advantages of electron beam reactors are the flow rates, being potentially $10^5$ times greater than those of other plasma reactors, and the small pressure drop across the reactor (Urashima and Chang 2000).

Early work on the use of electron beam discharges for pollution control was focused on the removal of nitrogen and sulphur oxides (NO$_x$ and SO$_x$); references include Tokunaga et al. (1984), Kawamura et al. (1980) and Frank (1988). The destruction of chloroethene (vinyl chloride, C$_2$H$_3$Cl) was investigated in 1981 (Slater and Douglas-Hamilton 1981).

Hadidi et al. (1999) investigated the treatment of dilute concentrations (1 – 3000 ppm) of hazardous compounds with a tunable electron beam plasma reactor. They reported dissociation energy requirements of 1 MJ per mole TCE and 10 MJ per mole CCl$_4$ destroyed. At 2005 prices of 6 c(kWhr)$^{-1}$, this equates to approximately AUD$130 per tonne of TCE destroyed.

The effects of electron-beam plasmas on low levels of VOCs in dry air streams have been investigated (Anshumali et al. 1997). The objectives were to develop a preliminary reaction kinetics model for the process, and to determine experimentally the relationship between the applied dose and the resulting extent of VOC destruction as well as how the initial VOC concentration affected those results.

The experiments were carried out at a pilot plant facility at the University of Tennessee Space Institute (UTSI). The main components of the plant were an electron beam reactor, a caustic soda scrubber (to neutralise inorganic acids exiting the reactor) and an activated carbon bed adsorber (to capture organic compounds exiting the reactor). A total hydrocarbon analyser (Thermo-environmental instruments model 51) was used for on-line detection. Concentrations of 50 - 1000 ppm of various VOCs were tested by applying a constant beam voltage whilst allowing the beam current to increase slowly from its initial value near zero to its maximum. The average rate of current increase was 0.003 mAs$^{-1}$ and so the data acquired was considered to be in pseudo steady state. The compounds studied were vinyl chloride (C$_2$H$_3$Cl), 1,1,1-trichloroethane (C$_2$H$_3$Cl$_3$), CFC-113 (CCl$_2$FCClF$_2$), CFC-112 (CCl$_2$FCCl$_2$F), perchloroethene (C$_2$Cl$_4$), TCE (C$_2$HCl$_3$) and propane (C$_3$H$_8$).
The results indicated that destruction efficiency increased rapidly with dose in lower ranges and then tended to level off at higher dose levels. It was also found that a higher initial VOC concentration resulted in lower efficiencies.

Hakoda et al. (2000) studied the dissociation of TCE concentrations ranging from 50 – 1800 ppm in humid air and found that a dose of 3.6 kGy (1 Gray = 1Jkg⁻¹) was required to decompose 90 % of input TCE, regardless of the initial concentration. With a dose of 4.4 kGy, almost total destruction of TCE is reported. The presence of small amounts of water (400 and 1000 ppm) did not affect the removal efficiency; at 25,000 ppm of water, the efficiency was slightly higher.

3.3.2.2 Corona discharges

A corona discharge is a DC discharge. However, with continuous current, the corona will become a spark discharge after a short period of time (about 5 s for a needle to plate reactor), resulting in a thermal plasma. Therefore, several variations of a corona discharge exist in an attempt to prevent the discharge from becoming a thermal plasma.

Pulsed corona discharges are used to maintain non-thermal plasmas by pulsing an applied voltage of 30 – 200 kV below the ion frequency (100 – 500 Hz). The impedance of the electrode system is proportional to the size of the reactor, causing scale-up problems. However, Yamamoto and Futamura (1998) reported the potential for this technology to process large gas volumes and that energy requirements of a scaled-up system would be favourable. An advantage of pulsed corona discharges is the small pressure drop across them.

A flow-stabilised discharge is one in which a fast gas flow passes directly through the inside of the electrodes, cooling the electrodes and hence stabilising it. Corona torch, capillary tube, corona radical injection and corona radical shower systems are all examples of this type of plasma. Flow stabilised plasmas may be driven by DC or pulsed power.
Early work on corona discharge treatment of sulphur dioxide (SO₂) was carried out by Matteson et al. (1972). Later, pulsed corona discharges were investigated by Mizuno et al. (1986), Masuda (1988), Gallimberti (1988) and Dinelli et al. (1990).

Penetrante et al. (1995) reported that the energy density required to decompose 90% of CCl₄ by pulsed corona processing is 1270 Jl⁻¹. Their pulsed corona experiments conducted on dichloromethane (CH₂Cl₂) in dry air showed that an increase in gas temperature significantly increased the dissociation rate.

Yamamoto et al. (1992; 1998) used a pulsed corona reactor producing a short pulse width with an extremely fast rise time to study the dissociation of TCE. Concentrations of 50 – 1000 ppm of TCE in nitrogen or air (wet and dry) were used. Maximum (nearly complete) removal was observed for all mixtures at 22 kV. With an initial concentration of 50 ppm, the same voltage and 110 pulses per second resulted in complete dissociation of TCE. Both nitrogen mixtures provided higher dissociation than those of air, and in both cases the dry background gas was dissociated to a greater extent than its wet counterpart.

3.3.2.3 Dielectric barrier processes

A dielectric barrier discharge is driven by AC current (10 – 10⁵ Hz) with applied voltage in the order of 5 – 20 kV. The electrodes are covered with a dielectric material such as glass, which retards arc formation and so ideally enables, on average, a uniform discharge. Silent Discharge Plasmas (SDP), surface discharges, ferro-dielectric packed bed discharges and trench-type discharges are examples of dielectric barrier. A disadvantage of barrier discharges is the large pressure drop across them.

An example of early work using an SDP to treat pollution (phosphorous-containing organics in particular) is Clothiaux et al. (1984).

Yoo et al. (1994) investigated the dissociation of TCE using a dielectric barrier discharge. The effect of frequency variation on the conversion of 631 ppm of TCE in dry air discharges was investigated for two flow rates. Conversions of over 95% were observed for frequencies of up to 700 Hz, above which conversion decreased.
dramatically. Increasing the flow rate from 2.9 lmin\(^{-1}\) to 4.4 lmin\(^{-1}\) at the optimum frequency of 500 Hz decreased the dissociation rate by about 3\%. This discrepancy was larger at other frequencies. Yoo et al (1994) explained this effect thus: the amount of power per unit volume of gas and the residence time in the reactor decrease with increasing flow rate. In further experiments, greater than 96\% conversion of TCE in a 2.9 lmin\(^{-1}\) stream was measured consistently for very low concentrations up to 15,000 ppm. Increasing the TCE concentration up to 20,000 ppm, however, led to a lower dissociation rate of 85\%. Humidification of the gas flow resulted in a slightly higher conversion (about 1\%).

Yamamoto et al. (1998) studied the dissociation of various VOCs, including TCE, in a ferroelectric packed-bed reactor. The reactor employed AC power at 50 Hz and a layer of barium titanium oxide (BaTiO\(_3\)) pellets, which were 1 mm in diameter. The packed bed was of coaxial type, with a gap distance of 15.4 mm, and the reactor length was 127 mm. VOCs were fed in wet and dry mixtures with nitrogen or air at concentrations of approximately 1000 ppm. The residence time varied from 3.0 s to 8.9 s in the flow rate range of 0.5 to 1.5 lmin\(^{-1}\). At 1.0 lmin\(^{-1}\) of dry nitrogen (N\(_2\)) and a field strength of 4.5 kVcm\(^{-1}\), 99\% dissociation of TCE was measured. The other mixtures were dissociated to a lesser extent, wet nitrogen being the next most efficient, followed by dry then wet air.

Evans et al. (1993) investigated the effects of an SDP on TCE. The cell had planar geometry, with a mean discharge area of 1236 cm\(^2\) and an active discharge volume of 0.31 litres. The power supply was capable of providing 4 kW at pulse repetition frequencies of up to 4.5 kHz. The plasma source gas was controlled with flow regulators, and optional humidification was possible through a water chamber. It contained 500 ppm of TCE in either argon (Ar) and oxygen (O\(_2\)) (80:20 ratio) or Ar, O\(_2\) and water (H\(_2\)O) (78:20:2 ratio) mixtures, at atmospheric pressure and 300K.

An energy deposition of 25 Jl\(^{-1}\) resulted in 90\% dissociation of TCE; specific energy deposition of 5 mJcm\(^{-3}\)pulse\(^{-1}\) was determined. The dry mixture discharge resulted in higher TCE dissociation, and the process efficiency decreased with increasing energy deposition per pulse. A figure of merit, \(\eta\), was used to compare wet and dry results.
(equation 3.1), where $\eta$ is the number of parts per million of TCE dissociated divided by the energy deposition in mJcm$^3$.

$$\eta_{dry} = 18, \eta_{wet} < 5$$  \hspace{1cm} (3.1)

The experimental results show that, after an initial decline in remediation with the addition of water, the removal efficiency increased with increasing water fraction. However, the largest water fraction tested was 10 %, yielding an efficiency of 65 %, which was still well below the destruction observed in the dry mixture. Evans et al. (1993) commented that removal efficiency might increase with large fractions of water. With an estimate of 30 % efficiency of the SDP cell, the cost of destruction of TCE was estimated to be less than US$1 kg$^{-1}$ with a SDP cell efficiency of 30 %.

### 3.3.3 Microwave-induced plasmas

Microwave-induced plasmas (MIPs) were introduced in section 1.4.2. Their role in pollution abatement has been investigated since the 1970s by researchers such as Bailin et al. (1975).

At AEA Technology, UK, Microwave energy at 2.45 GHz has been applied to high concentrations of Freon 134a (CF$_3$CH$_2$F), with inlet concentration of 5 gm$^{-3}$ (1098 ppm) in an air flow of 20 lmin$^{-1}$ (McAdams 2001). Microwave powers from 100 W to 800 W were applied and, at the maximum level, Freon was dissociated by almost 100 %. Dissociation of fluorinated compounds (CF$_4$ and C$_2$F$_6$) at concentrations of 1000 ppm (3.9 gm$^{-3}$ and 6.2 gm$^{-3}$ respectively) and a flow rate of 16 lmin$^{-1}$ of air is given. Specific energy of 43 Wmin$^{-1}$ dissociated over 75 % of C$_2$F$_6$ and 47 Wmin$^{-1}$ were required to dissociate approximately 70% of CF$_4$.

This technology has been sold to BOC Edwards for commercial prototyping of a unit to treat perfluorocarbons (PFCs). Carbon tetrafluoride (CF$_4$) is treated in a wet nitrogen atmosphere and flow rates of up 30 lmin$^{-1}$ are reported for an input power of 1.9 kW. Maximum destruction of almost 95 % was achieved at 21 lmin$^{-1}$ containing 1 % CF$_4$ by volume (Radiou 2003).
Ko et al. (2001) used a 1.5 kW low ripple magnetron at 2.45 GHz to investigate the destruction of gas phase TCE. Argon, oxygen and steam were added to the TCE, and the total flow rate was held constant at 10 l/min\(^{-1}\). The DRE for 1700 ppm of TCE was first evaluated for varying microwave powers with a feed of 30 % steam, 0.5 l/min\(^{-1}\) of oxygen and 6.0 l/min\(^{-1}\) of argon. Powers of 400 W and upward provided DREs higher than 99.97 %, which represented the limits of detection for the apparatus. Experiments to determine the effect of the variation of steam content (up to 30 %) were carried out at a constant power of 600 W and TCE input concentration of 1700 ppm. A DRE of 99.78 % was found with dry vapours. However, with more than 10 % humidity the DRE consistently exceeded the maximum detectable removal of 99.97 %.

Similar results were found for toluene (C\(_6\)H\(_5\)CH\(_3\)). At 500 ppm, the maximum detectable DRE of above 99.99 % was observed for powers of and above 400 W. Increasing the concentration to 800 ppm, a minimum of 500 W was required to achieve the same results.

All of the work discussed up to this point has addressed the destruction of halocarbons in the presence of air and water, i.e. oxidising systems. However, the reduction of chlorinated solvents in an atmosphere of hydrogen, producing hydrogen chloride (HCl) and light hydrocarbons, has been achieved with high dissociation rates. The conversion of chlorocarbons with H\(_2\) and H\(_2\)O as the hydrogen source in a tubular flow low-pressure (0.67 kPa) MIP reactor (0.6 kW, 2.45 GHz) was studied (Barat and Bozzelli 1989). Dissociation of 91.2 % was measured in a H\(_2\)/TCE mixture (1:50.7 molar ratio) with a microwave power of 325 W at 0.26 kPa. In a wet mixture, 99.99 % conversion was measured for a H\(_2\)O/TCE feed ratio of 1:2.38, incident microwave power of 500 W and pressure of 0.19 kPa.

### 3.3.4 Summary of plasma destruction efficiencies

The efficiency of TCE dissociation in these experiments is summarised in Table 3.1.
<table>
<thead>
<tr>
<th>Plasma reactor</th>
<th>Atmosphere</th>
<th>Flow rate</th>
<th>Concentration (ppm)</th>
<th>Frequency</th>
<th>Applied energy</th>
<th>DRE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-beam</td>
<td>Dry air</td>
<td>-</td>
<td>221</td>
<td>-</td>
<td>20 – 25 kJ/kg</td>
<td>≥ 75</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>-</td>
<td>1 – 3000</td>
<td>-</td>
<td>10 eV/mol</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>-</td>
<td>50 – 1800</td>
<td>-</td>
<td>3.6 kJ/kg</td>
<td>90</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>-</td>
<td>50 – 1800</td>
<td>-</td>
<td>4.4 kJ/kg</td>
<td>~100*</td>
<td>3</td>
</tr>
<tr>
<td>Pulsed corona</td>
<td>Dry N₂</td>
<td>0.5 – 1.5 l/min</td>
<td>200 – 1000</td>
<td>&gt; 110 pps</td>
<td>22 kV</td>
<td>100*</td>
<td>4</td>
</tr>
<tr>
<td>Dielectric barrier</td>
<td>Ferroelectric packed-bed, dry N₂</td>
<td>1 l/min</td>
<td>1000</td>
<td>50 – 60 Hz</td>
<td>4.5 kV</td>
<td>99</td>
<td>5</td>
</tr>
<tr>
<td>Dry air</td>
<td>2910 ml/min</td>
<td>≤15,000</td>
<td>&lt;700 Hz</td>
<td>105 – 110 W</td>
<td>&gt; 95</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Ar/O₂ 80/20</td>
<td>-</td>
<td>500</td>
<td>0.1 – 4.5</td>
<td>25 J/l</td>
<td>90</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>MIP</td>
<td>Ar/O₂/steam</td>
<td>6.0 l/min /0.5 l/min / 30 %</td>
<td>1700</td>
<td>2.45 GHz</td>
<td>≥ 400 W</td>
<td>~100*</td>
<td>8</td>
</tr>
<tr>
<td>H₂ 26 kPa</td>
<td>Space time = 37.4 ms</td>
<td>50.7=H₂/TCE</td>
<td>2.45 GHz</td>
<td>325 W</td>
<td>91</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>H₂O 0.19 kPa</td>
<td>Space time = 101.9 ms</td>
<td>2.38=H₂O/TCE</td>
<td>2.45 GHz</td>
<td>500 W</td>
<td>~100*</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 Table summarising published dissociation efficiencies of TCE in non-thermal and microwave plasmas (pps = pulses per second)

*100% destruction actually means that the treated stream contained a concentration of TCE below the limits of the detector used.

Reference key:
1. Anshumali et al. (1997)
2. Hadidi et al. (1999)
3. Hakoda et al. (2000)
5. Futamura et al. (1997)
6. Yoo et al. (1994)
7. Evans et al. (1993)
8. Ko et al. (2001)

### 3.4 Other novel VOC control processes

#### 3.4.1 Alternative solvents
The solvent most commonly used in vapour degreasing operations is TCE. However, alternative agents have been developed, most of which can be classified as aqueous, semi-aqueous or hydrocarbon solvents. These alternative cleaning agents present disadvantages when compared with TCE: multiple stages are often required, capital costs and space requirements are increased; power requirements are often significantly higher; the cleaning process may take longer due to additional drying...
requirements; waste-water output may be increased; odour and toxicity problems may occur; the parts to be cleaned may be incompatible with the solvent, and flammability problems may arise. A summary of the capabilities of solvent replacements is shown in Table 3.2.

<table>
<thead>
<tr>
<th>TECHNICAL FEATURE</th>
<th>TCE</th>
<th>Semi-aqueous(^1) and aqueous(^2) systems</th>
<th>Hydro-carbon Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Function</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-polar removal</td>
<td>Excellent</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>Polar removal</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Compatibility with range of materials</td>
<td>Excellent</td>
<td>Moderate</td>
<td>Very good</td>
</tr>
<tr>
<td><strong>Operation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drying time</td>
<td>Short</td>
<td>Longer (may need dryer)</td>
<td>Moderate</td>
</tr>
<tr>
<td>Space limitations</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Energy requirements</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Compatibility with existing machinery</td>
<td>Very low</td>
<td>Moderate</td>
<td></td>
</tr>
<tr>
<td><strong>Safety/Other</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flammability</td>
<td>Very low</td>
<td>Low(^1), none(^2)</td>
<td>Very High</td>
</tr>
<tr>
<td>Waste water/sludge generation</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>In-plant recycling capability</td>
<td>High</td>
<td>Moderate</td>
<td>Very high</td>
</tr>
</tbody>
</table>

Table 3.2: Technical Comparison of TCE and Alternatives (Gamble 1998)

3.4.2 Innovative adsorption processes

The use of electromagnetic induction, in the form of microwave heating to regenerate adsorbents, has been studied since the 1980s and is already available to industry (American Purification). Microwave desorption has many advantages over conventional desorption. Lower energy and less cooling are required between cycles and the process is more efficient than conventional desorption. The regeneration time is shorter, minimising down-time and the amount of adsorbent required. The absence of water in the microwave process also means that no stripping of the stabilisers occurs, therefore microwave desorption can be applied to a much larger range of solvents (Opperman and Brown 1999).
Activated carbon is the most common adsorbent used in adsorption processes. However, there are other adsorbents available, or under development, that may offer superior properties. A natural alternative, zeolites have been used in adsorption processes since the 18th century (Jain et al. 1997). Polymeric adsorbents and conventional molecular sieves are also available. Price and Schmidt (1998) compared the effectiveness and costs of these adsorbents. They found that, based on several different criteria, polymeric adsorbents and zeolites exhibit more attractive properties than the more conventional alternatives of activated carbon and molecular sieves. The problems of humidity, range of applicable solvents and flammability are all eliminated with these two adsorbents.

### 3.4.3 Biofiltration

Biological processes have become established as an attractive process for the removal of odours and, more recently, have been used to treat VOCs. Material containing selected microbes is fixed onto an inert bed through which organic compounds flow (Jain et al. 1997). Additional energy is supplied to the microbes by a carbon-containing growth substrate, e.g. phenol (C₆H₅OH) (Lee et al. 2000). The inlet stream must be free of dust, saturated with water and of appropriate temperature. A constant feed to the reactor is required and an enclosed design has been found to be desirable. This process converts VOCs to harmless substances such as carbon dioxide (CO₂), H₂O and mineral salts.

Streams with low concentrations of contaminants are treated efficiently with a degradation efficiency of up to 95 % for some pollutants. The stream should contain no more than 1 mgm⁻³ of contaminants, have a flow rate up to 30,000 m³hr⁻¹ and be cooler than 40°C (Jain et al. 1997). In general, the degradation of halogenated hydrocarbons by microbes is very slow. Research is being conducted to find microbes, or combinations of microbes, that can degrade various pollutants more efficiently and quickly. Lee et al. (2000) conducted a 95-day trial on the degradation of TCE and concluded that the degradation efficiency had a strong dependence on time and conditions. The mode, however, was about 75 % from days 30 to 55. Removal efficiencies of 80 – 90 % were observed, but at the expense of reactor size.
Biological treatment of contaminated streams is the most economical option in terms of capital and operating costs. Other advantages are that the process is adaptable to flow variations, produces little residue and is capable of treating a wide range of compounds. Its major disadvantage is that it requires very long reaction times and hence very large units. In addition, the feed to the bed must be carefully controlled and the gas flow distribution may become irregular; the large pressure drop across the bed results in the need for periodic stirring to prevent caking (Jain et al. 1997).

3.4.4 Membrane separation

This process utilises a semi-permeable composite polymer membrane, which allows the passage of organic vapours, but is relatively impermeable to air. Membranes with a large surface area are incorporated into compact spiral-wound modules through which vapour transport is induced by differential vapour pressure. Having passed through the membrane, the organic vapour is condensed and removed as a liquid. Since the membrane is 10 – 100 times more permeable to organic vapour than to air, 90 – 99+% VOC removal is achieved. The purified air stream is usually diluted and vented to the atmosphere (Forest Products Laboratory).

The advantages of this process are that it: produces no secondary wastes, requires no additional chemicals, is capable of treating a wide range of compositions and flow rates and is compact and therefore mobile. Disadvantages associated with this process include: the pressure drop, high gas pressures, strong membrane dependence and cleaning requirements.

3.4.5 UV oxidation and photocatalysis (indirect plasma process)

This process is capable of providing near-complete VOC destruction. Ultraviolet (UV) light is generated with mercury (Hg) or excimer lamps and combined with an oxygen-based oxidant (e.g. ozone or peroxide) to convert the VOCs into CO₂ and water vapour or halogenated acid (e.g. hydrochloric acid). The main disadvantages of this process are the low efficiency of the lamps and the long residence times. The former problem has been overcome to some extent by the addition of a photocatalyst, e.g. titanium dioxide (TiO₂), to the process; UV can be provided from a natural
source, e.g. sunlight. However, the by-products coat the catalyst surface, and this problem must be overcome before UV oxidation becomes widespread.

Glass fibres coated with TiO₂ have shown a removal efficiency of 98 % for 10,000 ppm of ethene (C₂H₄) and methane (CH₄) with flow rates below 1 l/min⁻¹ (Urashima and Chang 2000).

3.5 Flame temperatures

Combustion and plasma flame temperatures have been reported on extensively by various researchers. Information pertinent to this project is listed in this section.

Peak values of 1150 – 1250°C have been measured in turbulent diffusion flames for natural gas (Babrauskas 1997).

Atmospheric pressure microwave plasmas have been reported to have heavy particle temperatures of 2,000 K (McAdams 2001) and 1,000 – 4,000 K (Timmermans et al. 1998), with electron temperatures of 13,000 K and 7,000 – 20,000 K respectively.

3.6 Chemical Modelling

CHEMKIN (Reaction Design) is probably the most widely used commercially available chemical modelling package. Therefore, many reaction schemes are provided in CHEMKIN-friendly formats, there is a comprehensive manual and a users’ forum, etc. Subscriptions are not cheap, however, and much trial and error is still required to make it run smoothly.

There are several other packages available that would perform a similar task. One example of a free software with a good users’ group is PLASMAKIN (Pinhao 2001).

Many researchers have carried out chemical kinetic modelling of the dissociation of VOCs. Specifically, Evans et al. (1993) and Falkenstein (1996) have studied TCE dissociation in detail.
4. EXPERIMENTAL METHODS ................................................................. 38

4.1 Abstract .............................................................................................. 40

4.2 Experimental Rig .................................................................................. 40
  4.2.1 Introduction ....................................................................................... 40
  4.2.2 The Reactor ....................................................................................... 41
    4.1.2.1 Conventional Combustion with Propane ...................................... 41
    4.2.2.2 Microwave-induced plasma rig .................................................... 43
  4.2.3 Vapour Generator ............................................................................ 45
  4.2.4 Flow meters ..................................................................................... 46
  4.2.5 Exhaust ............................................................................................. 46
  4.2.6 Summary of experiments undertaken .............................................. 47

4.3 Health and Safety Issues ...................................................................... 48
  4.3.1 Radiation ......................................................................................... 48
  4.3.2 By-products of trichloroethene dissociation ...................................... 49
  4.3.3 Explosion risk .................................................................................. 50

4.4 Chemical Analysis Techniques ............................................................ 49
  4.4.1 Introduction ..................................................................................... 49
  4.4.2 Industrial Implications ..................................................................... 50
  4.4.3 Available Chemical Analysis Techniques ........................................ 50
    4.4.3.1 Gas Chromatography ................................................................. 50
    4.4.3.2 Spectroscopic Techniques .......................................................... 52
    4.4.3.3 External Analysis ....................................................................... 53
  4.4.4 Selected Chemical Analysis Techniques ........................................... 53
  4.4.5 Details of GC in IRIS laboratory ...................................................... 54
    4.4.5.1 Schematic of Gas Chromatograph .............................................. 54
    4.4.5.2 Sampling technique ................................................................. 54
    4.4.5.3 Column Selection ..................................................................... 55
    4.4.5.4 Gas Chromatography (GC) Method .......................................... 56
    4.4.5.4 Chromatograms ...................................................................... 57
    4.4.5.5 Linear Dynamic Range .............................................................. 57
4.4.5.6 Split Ratio ................................................................................................58
4.4.5.7 Calibration.............................................................................................58
4.4.6 Conclusions..............................................................................................58
4. Experimental Methods

4.1 Abstract

The two reactors used for this project were a modified Bunsen burner (for the conventional combustion experiments) and a microwave plasma reactor (for the air plasma and propane—assisted plasma experiments). Typical flow rates were 4 – 12 lmin\(^{-1}\), with TCE inlet concentrations from 0 – 6 %. Plasma power could be varied between about 2 and 5 kW. Microwave radiation, VOC exposure and explosion were the health and safety issues that had to be addressed in experimental design.

Good chemical analysis was vital to the success of the project. The main analytical technique used was gas chromatography with an electron capture detector.

4.2 Experimental Rig

4.2.1 Introduction

The aim of the experimental rig is not to simulate the eventual industrial unit but to gain information about its potential performance. The three main issues are to ascertain the destruction and removal efficiencies (DREs), by-products and energy requirements that could be expected in a real-life operating system. The experimental rig is not to scale and there is a slight pressure drop through the vapour generator and associated pipe-work (estimated to be up to 1 kPa). A realistic commercial design would need to minimise the pressure drop to prevent excessive pumping requirements.

It should be noted that even though microwaves are used to generate the plasma, microwave technology is reasonably established and not a key issue in this project. The nature of atmospheric-pressure microwave-induced plasmas is of interest, however, and is addressed in chapter 5.

All experiments carried out for this project can be described by the schematic in figure 4.1, where \(F_1\) is dry air, \(F_2\) is air saturated with trichloroethene (TCE) at 17°C (about 6 % TCE) and \(F_3\) is propane. The reactor in figure 4.1 represents a microwave plasma chamber or a modified Bunsen burner.
There are three distinct experiments in this project. These are treatment of TCE by:

- Conventional combustion (propane in Bunsen burner)
- Microwave-induced plasma (dry/humid air + TCE in plasma rig)
- Propane-enhanced plasma (dry air + TCE + propane in plasma rig)

4.2.2 The Reactor

4.1.2.1 Conventional Combustion with Propane

This is a Bunsen burner modified to take TCE and air (from F1 and F2), as shown in figure 4.2.
The propane rig was operated at a total TCE and air flow of 10 lmin\(^{-1}\) (\(F_1 + F_2 = 10\) lmin\(^{-1}\)). The flame was lit without the chimney. The chimney was then put into place after the flame was alight.

The overall reaction for normal air in the Bunsen burner is given in equation 4.1.

\[
\text{Oxygen} + \text{Propane} = \text{water} + \text{carbon dioxide}
\]

or

\[
5\text{O}_2 + C_3\text{H}_8 = 4\text{H}_2\text{O} + 3\text{CO}_2 \tag{4.1}
\]

Given that the oxygen flow is \(\sim 20\%\) of the total air flow, which is 10 lmin\(^{-1}\) when TCE flow is 0, and using the above stoichiometry, propane flow for a lean flame is:

\[
\text{Stoichiometric propane flow} = (0.2 \times 10)/5 = 0.4 \text{ lmin}^{-1}
\]

However, as TCE was introduced into the flame, it used up some oxygen, which reduced the necessary flow of propane. Lean flames were not possible at all at high TCE concentrations. Both lean and rich flames were investigated where possible.
4.2.2.2 Microwave-induced plasma rig

The microwave-induced plasma rig is a resonant cavity that operates in mode TE013. It can operate at variable power (from 2 – 5 kW) and flow rates (4 – 15 lmin⁻¹). See figures 4.3 and 4.4 for a diagram (Demyashev 2003) and photo of the microwave plasma rig, respectively. Incident and reflected power are measured and logged online with a data transfer card. The plasma was ignited by producing a spark in the reactor exit. The plasma chamber is made of aluminium.

Figure 4.3: Diagram of microwave-induced plasma rig

Magnetron power supply: frequency = 2.45 GHz, power = 2 – 5 kW

1. Inlet flow splitter 5. Circulator
2. Plasma 6. Chimney
3. Alumina sheet 7. Extraction to atmosphere
4. Waveguides
In the TCE in air only experiments, $F_1$ and $F_2$ are combined upstream of the reactor and flow into the reactor through the three inlets, which flow perpendicular to the reactor sides in a ‘whirlwind’ motion, to allow good mixing. Dry air is used for most experiments. However, some experiments with humid air were carried out to test the hypothesis that the propane served to provide necessary hydrogen, which could also be provided by water. In these experiments, $F_1$ was bubbled through water in a conical flask before being joined with $F_2$.

In the propane-assisted plasma experiments, $F_1$ and $F_2$ flow in through two inlets, and the third is used to introduce the propane flow.

In these experiments, the propane is required to provide hydrogen rather than fuel value. Therefore, required flows were calculated using the stoichiometry in equation 4.2.
TCE + oxygen + propane = hydrogen chloride + carbon dioxide

or \[ 4C_2HCl_3 + 11O_2 + C_3H_8 = 12HCl + 11CO_2 \] (4.2)

Plasma experiments were therefore carried out using no, lean, stoichiometric and rich propane flows.

4.2.3 Vapour Generator

A diagram of the TCE vapour generator is given in figure 4.5

Dry air from the compressor was bubbled through TCE. Since the compressed air supply is colder than room temperature and evaporation takes place during the process, the TCE becomes colder with time. However, the concentration of the TCE vapour generated depends on the vapour pressure of TCE in air, which varies with temperature. Therefore a heater was added to the design to hold the TCE at a constant temperature. The temperature chosen was 17°C (which corresponds to a vapour pressure of 6 kPa, as shown in Appendix 4A (National Institute of Standards and Technology 2003)). This temperature was chosen as it is slightly below normal room temperature and therefore prevents condensation of TCE in the lines and hence the need for heated lines.

The TCE concentration from the vapour generator was calibrated using known TCE standards in the gas chromatograph. For volumes of at least 400 ml TCE in the vapour generator, the efficiency was found to be close to 100 % for all flow rates.
Therefore, the concentration of TCE in F$_2$ is always 6% and TCE concentration in (F$_1$ + F$_2$) can be varied from 0 – 6%.

4.2.4 Flow meters

Accurate flow meters are required to enable reproducible experiments. The error in the flow meters is up to 2% (at the minimum flow rate of 4lmin$^{-1}$). The difference in density between TCE vapour and air means that at the maximum TCE concentration of 6%, the actual concentration was 10% lower (i.e. 5.4%). This is a systematic error, however, did not affect the reproducibility of the experiments, and was corrected for where necessary.

TCE attacks plastics. It was found that glass rotameters were required in the occasional event that pressure pulses in the system pushed TCE through the flow meters. Aalborg rotameters with 150 mm borosilicate glass flow tubes, aluminium fittings and valves, Buna N o-rings, Carboloy floats and aluminium, acrylic and polycarbonate frames were selected and found to withstand TCE. One-way valves were also installed to protect the flow meters.

4.2.5 Exhaust

Exhaust gases exited through a chimney and were then mixed with air and vented to atmosphere through a stainless steel pipe with an exhaust fan to prevent entry of the fumes into the laboratory.

Copper and Pyrex were considered as possible materials for the chimney. Copper’s high conductivity would allow rapid removal of the heat from the flame to environment, hence reducing the temperature reached by the chimney. The potential for copper to act as a catalyst in the after-flame was considered minimal as the surface area was low and little gas could contact it. Since copper is lower in the activity series than hydrogen (Mechalke 2000), hydrogen chloride should not react with the copper chimney. A Pyrex chimney would have allowed observation of the flame and been completely inert. However, there was concern that as it would be subject to rapid heating to high temperatures, thermal expansion may cause cracking of the Pyrex. Therefore, a copper chimney was chosen for safety reasons.
However, a Pyrex chimney was used for the final experiments for reasons that will be explained in the Chapter 7. The risk of the Pyrex cracking was minimised by starting each experiment with a low flow rate to allow gradual temperature increase of the Pyrex, and limiting experiments to only 1–2 minutes.

Any differences in results between the two chimneys are expected to be attributable to the slightly higher quench rate in the copper chimney.

4.2.6 Summary of experiments undertaken

Table 4.1 gives a summary of the experiments undertaken throughout the project. Each run was repeated at least three times.

<table>
<thead>
<tr>
<th>Type</th>
<th>Power (kW)</th>
<th>Flow Rate (lmin⁻¹)</th>
<th>TCE Concentration (%)</th>
<th>Propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane Burner</td>
<td>0</td>
<td>10</td>
<td>0 – 4</td>
<td>Lean if possible</td>
</tr>
<tr>
<td>Dry Plasma</td>
<td>2 kW</td>
<td>4 – 12</td>
<td>0 – 6</td>
<td>None</td>
</tr>
<tr>
<td>Dry Plasma</td>
<td>2.5 – 3 kW</td>
<td>4 - 12</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>Dry Plasma, Py*</td>
<td>2.3 kW</td>
<td>10</td>
<td>3</td>
<td>None</td>
</tr>
<tr>
<td>Humid Plasma</td>
<td>2 kW</td>
<td>6</td>
<td>1</td>
<td>None</td>
</tr>
<tr>
<td>Propane Plasma</td>
<td>3 kW</td>
<td>10</td>
<td>3</td>
<td>Lean - rich</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of experiments undertaken

*Experiments had a copper chimney unless marked Py (Pyrex chimney)

The maximum flow rate of 12 lmin⁻¹ in the plasma rig was the highest stable flow rate under most conditions. The maximum TCE concentration generated at 17°C is limited to 6% by its saturated vapour pressure.
Although 10 lmin$^{-1}$ is the standard flow rate for the experiments, the humid plasma experiments were carried out at 6 lmin$^{-1}$. This is because the humid air was supplied at water vapour pressure in F$_1$ (as measured by Cole-Parmer thermohygrometer A-37950-03), while the TCE was supplied at its vapour pressure in F$_2$. This limited the possible flow rates if the desired stoichiometry in equation 4.3 were to be satisfied.

\[ C_2HCl_3 + H_2O + 1.5O_2 = 2CO_2 + 3HCl \quad (4.3) \]

At 10 lmin$^{-1}$, a ratio of 1 mole of water vapour per mole of TCE would result in an inlet TCE concentration of 1.5 %. In order to compare with the dry experiments, which were carried out at 0, 0.1, 1, 2, 3, 4, 5 and 6 % TCE, 1 % TCE at 6 lmin$^{-1}$ was chosen instead.

**4.3 Health and Safety Issues**

**4.3.1 Radiation**

Up to 6 kW of microwave power is generated in the plasma rig. Emission of microwave radiation was found to be well below acceptable levels during normal operation. However, during ignition of the plasma (when the chimney was not in place) the radiation levels increased and operators were required to stay a safe distance from the rig. Microwave radiation was measured with a hand-held microwave leakage detector with digital read-out (MD-2000 EMC Directive from Safeea Incorp.). Since the amplitude of the waves is inversely proportional to the distance from the source of emission, 1m was found to be sufficient.

Yellow safety glasses were worn to protect operators from the ultra-violet emissions from the plasma flame.

**4.3.2 By-products of trichloroethene dissociation**

As explained in chapter 2, one of the major issues of this project was to identify the by-products of TCE dissociation by various methods, and assess whether they are more or less harmful than the original solvent, TCE. Since the formation of chlorinated aromatics was suspected, which are known precursors for dioxins and furans, health and safety information regarding these chemicals, as well as TCE, was
necessary (see appendix 2A). Protection from acidic gases such as hydrogen chloride (HCl) and chlorine (Cl₂) was also necessary.

Practical steps taken were that the treated gases were exhausted to atmosphere and operators wore activated carbon filter masks during the experiments.

4.3.3 Explosion risk

When the propane-assisted plasma experiments were planned, there was concern that mixing propane and air in a 2 l reactor may pose an explosion risk. Therefore, a method involving filling the propane line with propane (and no air), flowing air through the reactor to clear it of propane, lighting plasma and then starting the propane flow, was adopted. Explosive mixture compositions were also calculated using published explosion limit data (International Chemical Safety Cards), and the desired operating conditions were found to be well outside the explosive region (see figure 5.4).

4.4 Chemical Analysis Techniques

4.4.1 Introduction

Chemical analysis is required to verify the model with the experimental results. The chemical analysis is a very important element of this research, as without meaningful analysis the results of the experiments would be unknown and the model could not be verified. In fact, this aspect has been the most time-consuming, difficult and expensive part of the project.

There are many different chemical analysis techniques available. Requirements for meaningful analysis are: choice of appropriate technique, method and sampling technique, and understanding of results and factors affecting them.

The following section outlines the risks posed to industry by inadequate chemical analysis at the laboratory level, and cannot be emphasised enough. Section 4.4.3 describes the chemical analysis techniques available for analysis of the various products formed during this project. The choice of techniques used for this research
is then explained in section 4.3.4. Finally, a more detailed explanation of the gas chromatograph method is given.

4.4.2 Industrial Implications
Thorough chemical analysis is vital for proper design of VOC dissociation equipment. Insufficient analysis during the design of industrial equipment could lead to the emission of unexpected chemicals (very low levels of dioxins, for instance) as well as a failure to meet the original specifications (e.g. removal of TCE). The consequences of this could be dire: the safety of process operators and the general public may be compromised; both designers and users of equipment could be subject to damaged reputation and legal action including fines.

4.4.3 Available Chemical Analysis Techniques

4.4.3.1 Gas Chromatography
Chromatography is ‘the separation of components in a mixture by a series of equilibrium operations that results in separation of the entities as a result of their partitioning between two phases, one stationary with a large surface and the other a moving (mobile) phase in contact with the first’ (Grob 1995). Gas chromatography (GC) is a very versatile technique and can be used for the direct separation and analysis of gaseous samples, liquid solutions and volatile solids. In gas chromatography, the stationary phase can be liquid or solid, and the moving phase is a gas (e.g. nitrogen). The (vaporised) sample to be analysed is transported onto the column by the carrier gas (moving phase). The column can be an open tubular (capillary) or packed column. After separation in the column, the moving phase passes through a detector, which monitors the time of elution of various chemicals and the magnitude of the signal they produce. There are various types of detectors available, which use various methods of detection (e.g. electron capture detector (ECD), flame ionisation detector (FID) and thermal conductivity detector (TCD)). GC analysis typically takes five to twenty minutes.

The type of detector/s used depends on the types of compounds being analysed and the sensitivity required. Some of the properties that must be noted when selecting a detector are: minimum detectable level, sensitivity of detector response to a change in
concentration, selectivity of detector to certain compounds, and the linear range (i.e. the range of concentrations the detector can quantify).

FIDs are the most commonly used detectors in GC. Some reasons for this are that: they respond with high sensitivity to most organic compounds; they are robust enough to withstand variations in operating conditions; they have a wide linear range and can be adjusted easily. They measure the total hydrocarbons in a compound. Inorganic gases have little or no response in an FID.

Another popular detector in GC is the TCD. Relying on the thermal conductivity of the target compounds, it has notoriously low sensitivity. However, it enables detection of inorganic gases such as carbon monoxide and nitrogen oxides.

ECDs are characterised by very high sensitivity to selected compounds (down to picogram or even femtogram levels). They detect electronegative species and so are excellent for detecting chlorinated species. The linear response of ECDs is between two and five orders of magnitude above the minimum detectable level.

Gas Chromatography/Mass Spectrometry (GC/MS) provides high resolution separation of components with very selective and sensitive detection. It is a very powerful technique as it enables direct identification of the eluted compounds.

GC is a very good technique for VOC detection and quantification, and several researchers have used it in VOC destruction experiments. For instance, plasma VOC destruction work at Los Alamos National Laboratory was analysed by GC. Evans et al. (1993) investigated TCE destruction with silent discharge plasma; they detected and quantified a wide range of chlorinated hydrocarbons, hydrochloric acid, chlorine, carbon dioxide and carbon monoxide using GC/MS. Penetrante et al. (1997), at Lawrence Livermore National Laboratory, used FTIR and GC/MS in a detailed kinetic study of the destruction of various pollutants, including TCE.

For more information on gas chromatography techniques refer to (Grob 1995) or (McNair and Miller 1998).
4.4.3.2 Spectroscopic Techniques

4.4.3.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Another powerful analysis technique is Fourier Transform Infra Red (FTIR) spectroscopy. Its main advantage over GC is that results are instantaneous and so can be used for on-line monitoring. It detects species whose electric dipole change when they emit or absorb radiation. This includes a wide range of organic and inorganic compounds, including TCE and excluding oxygen and nitrogen. Subtraction of background compounds (such as water) from the species of interest can be difficult. This technique is used by some researchers for VOC analysis (e.g. McAdams (2001)).

4.4.3.2.2 Non-dispersive infrared (filter)

There are a wide range of species-specific detectors that can be useful for measuring gases such as nitrogen, oxygen and carbon monoxide. Cross-interference is possible, however. For instance, methane may register on a carbon monoxide detector.

4.4.3.2.4 Atomic Absorption Spectroscopy

According to quantum mechanics, atoms can only exist in certain energy states, and a set amount of energy must be absorbed or released by an atom to change between two specific states. Atomic absorption spectroscopy uses this fact to quantify the number of metal atoms that are present in a sample by using equation 4.4,

$$
\Delta E = \frac{hc}{\lambda}
$$

(4.4)

where $\Delta E =$ energy change in between states, $h =$ Planck’s constant, $c =$ the speed of light and $\lambda =$ wavelength of light absorbed/released.

Therefore, the sample of interest is aspirated in a flame. A light of specific wavelength is shone through the flame onto a detector. If the atom of interest is present, the light intensity registered by the detector will be decreased, as those atoms absorb some of the light (proportional to their concentration in the sample). Shining different wavelengths enables identification and quantification of different metal atoms. For more information on atomic absorption refer to Cantle (1982).
4.4.3.3 External Analysis

It is possible to send samples to independent laboratories for analysis. The advantage of this is access to expertise and equipment not available in-house. However, there are several reasons why this is not usually practical. Each sample analysed increases project expenditure and so experiments may be restricted. This may also mean that (inevitable) unplanned developments are not affordable. The approximately two week delay between carrying out experiments and receiving results prevents researchers from using feedback from one run to the next, and may mean problems go unnoticed. Sample collection is also an issue as gases may leak during collection or in transit. A chemically active sample may also have dissociated into other products by the time it reaches the analytical laboratory.

4.4.4 Selected Chemical Analysis Techniques

GC with an ECD was been chosen as the primary analytical technique, as it was important to be able to detect very low levels of chlorinated hydrocarbons for this project. A Varian GC 3600 is located in the IRIS laboratory and was used for immediate analysis of sample gases.

GC/MS was required to identify the compounds detected in GC. By using the same method and column, a direct comparison between the peaks observed was made. As GC/MS was not available in the IRIS laboratory, samples were analysed at other laboratories within Swinburne University (namely the Sensory Neuro Laboratory and Industrial Sciences) and Anexus, a commercial chemical analysis company.

Atomic absorption was used to analyse solid residues formed during the experiments. This enabled quantification of metal ions present in samples and hence estimation of the proportion of solid residue which was formed as a result of hydrogen chloride attack on metal components of the experimental rig.

Solid residues (formed mainly on the copper chimney) were sent to Anexus for further organic and inorganic analysis.
4.4.5 Details of GC in IRIS laboratory

4.4.5.1 Schematic of Gas Chromatograph

Figure 4.6 shows a schematic diagram of a typical gas chromatograph (GC).

![Schematic of Gas Chromatograph](image)

Figure 4.6: Schematic of Gas Chromatograph

4.4.5.2 Sampling technique

The off-gas from the experimental rig was sampled directly from the plasma and injected into the GC injector with a 100 µl gas-tight syringe. This risked damage to the column as significant formation of acidic gases such as hydrogen chloride (HCl) was expected in the experiments. The proposed industrial process would scrub the gases with water or an alkali before emission to atmosphere. However, this would remove some products from the gas stream (e.g. phosgene). Therefore, most samples were not scrubbed in these experiments to enable full analysis of the results in the gas phase. Liquid phase analysis (e.g. High Pressure Liquid Chromatography (HPLC)) was not available at IRIS.

Some experiments were carried out by sampling with a 50 ml gas-tight syringe and then taking the 100 µl sample from there. This was for two reasons. Firstly, the physical distance between the GC/MS machines used and the experiments meant the
minimum time between sample collection and injection was 30 minutes. The tap on the large gas-tight syringe made this delay possible. Secondly, some experiments were scrubbed with water in the large syringe to help with peak identification (i.e. to see which ones were soluble).

Some of the GC/MS experiments were scrubbed in the large syringe with saturated salt solution. The aim was to reduce the column bleed problem without dissolving all of the chlorinated species into the liquid phase. This is known as ‘silting out’.

4.4.5.3 Column Selection

Column selection is important to the success of chemical analysis. Capillary columns are more common as they are more efficient. An important factor in column choice is the stationary phase. There are no hard and fast rules governing column selection, however, “like dissolves like” is a good starting point; i.e. chlorinated hydrocarbons, the compounds of interest in this project, are polar, so a polar column should retain them more strongly. However, a non-polar column (100% dimethylpolysiloxane, EC-1, (Alltech 2003/4)) was used initially to minimise degradation of the column by acidic gases (also polar). Unfortunately, when moderate concentrations of TCE were treated a large peak was observed at 15 minutes (see figure 4.7). Initially, this peak was thought to be a dissociation product, such as a chlorinated benzene. However, the peak size was not consistent and it appeared in blank runs. The peak became very broad and irregular. It became clear that the ‘15 minute peak’ was not an eluted component but the result of column attack by the acidic gases being formed in the experiments. The compounds being eluted around the 15 minutes period were the products of acids in the sample (assumed to be mainly hydrogen chloride (HCl)) reacting with the stationary phase. Note that the baseline in figure 4.7 drifts upwards as the temperature of the column increases. This is ‘column bleed’.
Both graphs show the same data on different scale

The problems of column bleed and attack made interpreting the results around the 14 – 16 minute period impossible. Therefore, later experiments were done with an MS grade low-bleed column (BPX5, (SGE 2001)). This greatly improved the quality of the chromatograms.

4.4.5.4 Gas Chromatography (GC) Method

Significant time and effort were taken to find the best method for the gas chromatography (GC). There were several parameters that had to be experimented with before this was achieved. The column was temperature programmed to allow good resolution of the lighter components and elution of the heavier components within a reasonable time. The final method started at 35°C and ended at 270°C. Injector and detector temperatures, among other GC settings, had to be optimised. For the full GC method see appendix 4B. Other factors included: injection size and technique, appropriate split ratios, and contamination control.
4.4.5.4 Chromatograms

A gas or liquid sample is injected into the GC injector. The injector operates at a high temperature (e.g. 250°C) so that all samples are in gas phase as they enter the column. Some of the compounds are retained on the column, depending on the column type, the compound and its molar mass. See figure 4.8 for an example of a chromatogram. The unretained compounds pass through the detector first, as the ‘unretained peak’, at a characteristic time of $T_0$. Other compounds then all pass through the detector at characteristic ‘elution times’. If the size of the peak detected is within the ‘linear dynamic range’, the concentration of the compound eluted is proportional to the peak area. Therefore, known standards can be used to identify and quantify compounds.

![Figure 4.8: Example of a chromatogram of the plasma effluent](image)

4.4.5.5 Linear Dynamic Range

This is the range of concentrations over which a linear response is registered by the GC detector, hence the quantifiable range of concentrations. This range can be found experimentally by plotting the response of the detector (peak area divided by mass of a compound to the detector) against the peak area (see figure 4.9).
4.4.5.6 Split Ratio

The Varian 3600 was operated in split mode, i.e. the injected sample was split into two streams of known proportion, the smaller of which is then sent to the column. This enabled quantification of a much larger range of concentrations. Split ratios of 5 – 300 were used. Higher split ratios were possible, but since a bubble flow meter was used to measure the split flow, precise measurement at high flow rates becomes impossible. A split ratio of 20 was found to be appropriate for the 100µl plasma injections.

4.4.5.7 Calibration

Liquid standards were required to calibrate peaks. For this research, TCE was used as the standard compound and the detector’s response to TCE (in Area Counts/Mass to detector) was calculated. Other compound standards (identified as experimental products by GC/MS) were calibrated relative to TCE, so that their ‘relative response’ could be used to convert their peak areas into concentrations.

4.4.6 Conclusions

Validation of the chemical kinetic model with experimental results is very important for proper assessment of the performance of the process. Thorough chemical analysis is essential for this validation. This section has explained options available for the chemical analysis of volatile organic compounds and given a brief outline of the
techniques that have been selected for this project. See appendix 4B for more details of the GC.
5. PLASMA TEMPERATURE.......................................................................................... 60

5.1 Abstract.................................................................................................................. 61

5.2 Overview .................................................................................................................... 61

5.3 Temperature Modelling............................................................................................ 62
  5.3.1 Energy flows in the plasma reactor................................................................. 62
  5.3.2 Plasma temperature and electron density....................................................... 64
  5.3.3 Plasma power absorption................................................................................ 67

5.4 Experimental Results............................................................................................. 68

5.5 Conclusion ............................................................................................................... 72
5. Plasma Temperature

5.1 Abstract

Equilibrium modelling was used to predict the electron density assuming the plasma was thermal. This was used to predict the plasma frequency and hence minimum flow rate of the plasma. Experimental measurements of maximum flow rates for various measured absorbed powers were very close to those predicted by equilibrium modelling. Therefore, the atmospheric pressure microwave plasma can be treated as a thermal plasma even though the electron temperatures may be higher than the heavy particle temperatures. The only exception to this is at around 3 % TCE, where the electron density in the experiments was anomalously low.

The heavy particle temperature range for the IRIS reactor is 3,000 – 4,000 K. The minimum temperature is limited by the microwave frequency, and the maximum is limited by heat losses. The maximum power absorption was at 10 – 12 lmin⁻¹, corresponding with the optimum absorption length. Heat losses from the reactor walls could be neglected in a commercial unit as the fraction of heat lost by the walls decreases with increasing flow rate.

5.2 Overview

In thermal plasma, electrons and heavy particle temperatures are within the same range (6,000K+), i.e. it is in ‘local thermodynamic equilibrium (LTE)’.

In non-thermal (non-LTE, cold) plasma, the electrons have higher temperatures, and therefore higher mean energies, than the heavy particles (i.e. atoms, molecules, free radicals). One definition of non-thermal plasma is that the heavy particles are at or near to ambient temperature (i.e. 300 K) (Graham 2001). In this case, non-thermal plasmas are not in LTE and so the electrons have a non-Maxwellian energy distribution, unlike those in thermal plasmas. Other sources state that if the electrons have a higher mean energy than the heavy particles, the plasma is non-thermal (McAdams 2001). In this case, the electrons may have a Maxwellian energy distribution.
Atmospheric pressure microwave plasmas are often referred to as non-thermal plasmas. However, their electron density and heavy particle temperatures are much higher than those in classic non-thermal plasmas such as silent discharge plasmas and low-pressure microwave plasmas. Timmermans et al. (1998) reported a heavy particle temperature range of 1,000 – 4,000 K, which is significantly lower than the electron temperature range, reported as 7,000 – 20,000 K. Therefore, microwave plasmas at atmospheric pressure can be referred to as either thermal or non-thermal, depending on the definition used; in reality, they are somewhere in between. For the purposes of this project, the issue is whether it is possible to predict plasma behaviour (i.e. power absorption and chemical processes) by allocating a single average temperature to the plasma in the model.

There was no method of directly measuring the plasma temperature available. It is possible to measure plasma temperature spectroscopically (Kim et al. 2003). However, that was beyond the means of the IRIS laboratory. The power absorbed by the plasma was used to calculate the enthalpy of the plasma, which was used to estimate the average temperature of the plasma thermodynamically with CHEMKIN EQUIL. Since the electron mass is almost negligible when compared with the heavy particles, this is essentially the temperature of the bulk species. It was hoped that plasma temperature could be controlled by varying flow rate and incident power.

Equilibrium modelling with EQUIL was used to predict the minimum possible plasma temperature. For more about EQUIL see chapter 6.

This approach to the investigation of plasma stability analysis is complementary to others that have appeared in the literature, e.g. Rummel and Grotjohn (2002).

5.3 Temperature Modelling

5.3.1 Energy flows in the plasma reactor

Figure 5.1 shows a simple model of the energy flows in the plasma reactor, where FR is the flow rate through the reactor (lmin⁻¹), h is the enthalpy of the flow, \( P_{\text{abs}} \) is the power absorbed by the plasma (kW) and \( Q_{\text{loss}} \) is the rate of energy lost from the reactor (kJ). The energy flows are therefore related by equation 5.1.
The power absorbed in the experiments carried out for this project was 1.4 – 1.8 kW. The flows varied from 4 – 12 lmin\(^{-1}\).

Losses were estimated using a net emission coefficient proposed by Naghizadeh-Kashani et al. (2002) for air plasmas. Equation 5.2 shows the equation that fitted their calculations for temperatures up to about 4,000 K. These are radiative losses; convective losses are assumed to be negligible.

\[
Q_{\text{loss}} = 4\pi V_{\text{plas}} A e^{\alpha T}
\]  

(5.2)

In equation 5.2, \(V_{\text{plas}}\) is 0.001231504 m\(^3\) (the volume of the plasma assumed to be a cylinder of diameter 140 mm and height 60 mm), \(\alpha\) is 0.00363698 and \(A\) is 0.001825742 (best fit to Naghizadeh-Kashani et al. (2002)). Note that the presence of TCE or other contaminants is not accounted for in the loss estimation.

Therefore, the enthalpy (\(\Delta h\)) could be calculated for a range of flow rates using equation 5.1.
5.3.2 Plasma temperature and electron density

The plasma frequency ($\omega_p$) is given by equation 5.3, where $e$ is the charge of an electron, $m_e$ the mass of an electron, $n_e$ is the electron density and $\varepsilon_0$ the dielectric constant in free space.

$$\omega_p^2 = \frac{e^2 n_e}{m_e \varepsilon_0}$$  \hspace{1cm} (5.3)

For a microwave plasma frequency of 2.45 GHz, this corresponds to an electron density ($n_e$) of about $7.5 \times 10^{10}$ electrons.cm$^{-3}$. The plasma frequency must be higher than the microwave frequency for microwave power to be absorbed. Therefore, the microwave frequency determines the minimum electron density of the plasma.

Figure 5.2 is an EQUIL plot of air containing TCE flowing through a reactor absorbing 1.5 kW, assuming equilibrium conditions, i.e. for thermal plasma, and heat losses as in equation 5.2. As the flow varies, the enthalpy of the plasma varies (as estimated in section 5.2.1) and therefore different equilibrium temperatures ($T_{av}$) and electron densities result. The plot shows the electron density required for a plasma frequency of 2.45 GHz. Below this electron density, the plasma could not be sustained. The plot can therefore be used to predict the maximum flow rate (minimum $h$, $n_e$ and $T_{av}$) sustainable by the reactor. If the flow rate is too high, the plasma frequency falls below the microwave frequency and so the microwaves are not absorbed.
Figure 5.2: Predicted electron densities and temperatures in the microwave plasma

For this reactor, the maximum flow rate is predicted to be about 18 lmin⁻¹ and the exit temperature to be 3,000 – 3,500 K. This model predicts that the maximum possible flow rate will decrease with increasing TCE concentration. The temperature is predicted to decrease slightly with increasing TCE concentration for the same flow rate.

Figure 5.3 compares the predicted plasma temperatures for an ideal reactor with no losses with one with heat losses as calculated by equation 5.2. It shows that at high flow rates the two lines will virtually converge and therefore heat losses could be neglected in an industrial unit. These temperatures correspond with a minimum energy expenditure of about 7,000 Jl⁻¹.
Figure 5.3: Comparison of predicted plasma temperature with and without heat losses.

Figure 5.4 shows the maximum theoretical flow for a plasma with an initial composition of air and propane. It shows that the maximum flow increases slightly with propane concentration. The desired concentration of 0.5% propane does not approach the composition of an explosive mixture.

Figure 5.4: Flow conditions for propane in air plasma with heat loss.
5.3.3 Plasma power absorption

The plasma can only respond to electric fields at frequencies lower than the plasma frequency. At frequencies higher than the plasma frequency, the plasma is transparent to microwaves (no absorption). At frequencies lower than the plasma frequency, the electromagnetic waves are absorbed with a skin depth given by equation 5.4, where $c$ is the velocity of light in a vacuum.

$$\delta = \frac{c}{\sqrt{\omega_p^2 - \omega^2}} \tag{5.4}$$

Figure 5.5 is a plot of the absorption length for microwaves at 2.45 GHz against electron density.

Figure 5.5 shows that below the minimum electron density of $7.5 \times 10^{10}$ the absorption length becomes effectively infinite. This corresponds to high flow rates through the reactor and under these conditions the microwave power passes straight through the gas. Therefore the power is reflected by the reactor walls, resulting in no plasma. As the electron density increases (flow rate decreases), the resistance of the plasma decreases, its conductivity increases, and power can be absorbed. Eventually, the electron density becomes so high and the absorption length so small that the power
cannot penetrate the plasma significantly. The plasma then behaves like a metal, reflecting the microwave power excessively and becoming inefficient. Therefore, there is a range of ideal absorption lengths and hence flow rates, where the power absorption in maximised. The impedance matching of the microwave source to the plasma requires the optimal absorption length.

5.4 Experimental Results

It was possible to measure plasma incident and reflected powers, and therefore the power absorbed by the plasma. This enabled calculation of the mean enthalpy of the plasma (h in Jl⁻¹) under standard temperature and conditions (STP) without heat losses (enthalpy without losses = absorbed power/flow rate). Since the heat losses are a function of temperature, the temperature was not directly calculable.

Figure 5.6 shows the enthalpy with no losses for air plasma containing 2 % TCE. It shows that the enthalpy can be decreased slightly by decreasing the inlet power. At some flow rates, a 3,000 Jl⁻¹ enthalpy range can be achieved. This may not indicate a temperature difference as heat losses are higher at higher temperatures. The plasma extinguishes below a certain minimum electron density, as explained in section 5.2, resulting in a minimum plasma temperature at about 8,000 Jl⁻¹.
There was no practical method of measuring the plasma temperature available. The power absorption measurements could only be used to calculate the enthalpy of the plasma with no heat losses, since the losses depend on the temperature, which was not known. Therefore, the enthalpy of the plasma with losses was estimated by comparing the modelling results with the experimental measurements of absorbed power. Figure 5.7 shows the enthalpy of the plasma for 1.8 kW absorbed power. Figure 5.8 shows that, although the modelling predictions are for 3 % TCE and the experiments were carried out at 2 % TCE, this makes hardly any difference to the enthalpy of the plasma. Therefore the comparison in figure 5.7 is valid, and estimation of the actual enthalpy with heat losses is possible, using the results of Naghizadeh-Kashani et al. (2002), as represented by the blue line. Figure 5.7 shows that, as predicted in figure 5.3, the heat losses account for a significant fraction of the absorbed power at low flow rates, but could be neglected at high flow rates.

Figure 5.8 shows the effect of TCE concentration on plasma enthalpy (without losses). It suggests that the absorbed power, and therefore enthalpy and plasma temperature, are slightly increased with increasing TCE concentration up to 2 % TCE, after which concentration it levels out.
Figure 5.7: Comparison of predicted (3 % TCE) and experimental (2 % TCE) enthalpies for 1.8 kW absorbed power (3 kW incident)

Figure 5.8: Maximum enthalpy of plasma against TCE concentration

Figure 5.9 shows the power absorbed by the plasma with increasing flow rate. It shows that the optimum absorption is between 10 and 12 l/min. This corresponds to a power absorption efficiency of about 70 %. At higher flow rates, the plasma
became transparent to microwaves as the absorption length approached the reactor size; this lead to instability and eventually extinction. Below 10 lmin⁻¹, the plasma becomes hotter, leading to more radiative losses, but also increasing the conductivity of the plasma and thus increasing the reflected power slightly, the formation of the plasma is thus a slightly less efficient process at these lower flows.

Retuning the cavity may have enabled the plasma absorption to be optimised at flow rates for which the absorption was not maximised (e.g. 5 lmin⁻¹). This was beyond the scope of the project but is discussed in more detail by Rummel and Grotjohn (2002).

Figure 5.9: Power absorbed at 3 kW incident power and 2% TCE inlet concentration

Figure 5.10 shows the maximum flow rate (corresponding to the minimum possible plasma temperature) for various TCE inlet concentrations for 1.4 kW absorbed power (blank lines). CHEMKIN predictions for 1.2 and 1.5 kW absorbed power are shown in red. The range between the maximum stable and minimum unstable experimental flow rates represents the range of for which the plasma may become unstable and extinguish; i.e. the plasma is stable at flow rates below this range, and it is not possible to light the plasma at all at flow rates above this range. Even allowing for this range, this was not a very precise or accurate experiment as the minimum unstable flow rate was very difficult to ascertain and may have been even higher than
reported here in some cases. The error bars represent experimental variation, which was mainly caused by uncontrollable fluctuations in the absorbed power inherent in the plasma.

Figure 5.10: Effect of TCE inlet concentration on maximum stable flow rate range for 1.4 kW absorbed power (experimental) and 1.2 and 1.5 kW absorbed power (predicted)

Figure 5.10 shows that the actual extinction flow rates are very close to the predicted ones (i.e. between the two red lines) for most concentrations of TCE. There is an anomaly at around 3%. The most likely explanation for this is that an oxidising species peaks in concentration at 3% TCE, hence taking electrons from the plasma. It could be due to experimental error; however, it seems too persistent for this to be a satisfactory explanation. The fact that equilibrium modelling can be used to predict the extinction flow rate suggests that it is a reasonable approximation to assume that the electrons are in equilibrium with the heavy particles.

5.5 Conclusion

Plasma behaviour has been successfully predicted with equilibrium modelling. Therefore, for engineering and chemistry purposes, atmospheric-pressure microwave plasmas can be considered thermal plasmas. The electron temperature may be a few
thousand degrees hotter than the bulk temperatures predicted here; however, if they were much hotter, the extinction flow rates should be higher than those predicted by equilibrium modelling. The temperature estimates made in this chapter agree with bulk temperature measurements reported by Timmermans et al. (1998).

Plasma temperature can be varied in a limited way by adjustment of flow rate. Increases in incident power increase the power absorbed by the plasma but also increase losses and so probably do not affect the plasma temperature significantly. The microwave frequency limits the minimum temperature to about 3,000 K. Reactor losses limit the maximum temperature to about 4,000 K. Maximum power efficiency was predicted to be 7,000 Jl⁻¹ and found to be about 8,000 Jl⁻¹. For 3 kW incident power, the optimal absorption for treating 2 % TCE in this reactor was achieved between 10 and 12 lmin⁻¹. The electron density at about 3 % inlet TCE is anomalously low, possibly due to a peak in an oxidising species at this concentration. Scale-up would effectively reduce radiative heat losses to nothing, so that they may be neglected in engineering calculations.
6. CHEMICAL MODELLING .........................................................................................74

6.1 Abstract .................................................................................................................76

6.2 Introduction ..........................................................................................................77

6.3 Input files ..............................................................................................................78

6.3.1 Overview .........................................................................................................78

6.3.2 Chemistry input file ........................................................................................78

6.3.3 Equil run file ...................................................................................................79

6.3.4 Aurora run file ................................................................................................80

6.3.5 Thermodynamic data ......................................................................................80

6.4 Equilibrium Modelling ........................................................................................80

6.4.1 Composition of system ...................................................................................80

6.4.2 Overall results .................................................................................................81

6.4.3 Potential formation of chlorinated hydrocarbons ...........................................81

6.4.4 Effect of trichloroethene concentration on equilibrium products ...............82

6.4.5 Effects of equilibrium temperature .................................................................84

6.4.6 Effect of air humidity ......................................................................................86

6.4.7 Effects of propane concentration ....................................................................87

6.4.8 Conclusions .....................................................................................................90

6.5 Kinetic Modelling .................................................................................................90

6.5.1 Introduction .....................................................................................................90

6.5.2 Predicted destruction and removal efficiencies ..............................................91

6.5.3 Conversion of trichloroethene to hydrogen chloride and chlorine ...............93

6.5.4 Conversion of carbon in the system to carbon dioxide ...................................95

6.5.5 Formation of organic by-products ...................................................................96

6.5.5.1 Overall ......................................................................................................96

6.5.5.2 Chlorinated aliphatics ..............................................................................96

6.5.5.3 Chlorinated aromatics ..............................................................................97

6.5.6 Formation of inorganic by-products ...............................................................99

6.5.6.1 Overall ......................................................................................................99

6.5.5.2 Nitrogen oxide (NO₃) formation ..................................................................99
6. Chemical Modelling

6.1 Abstract

Equilibrium and kinetic modelling were carried out in order to predict the products formed in the experiments. There was good agreement between both models for all species except chlorinated aromatics, where kinetic modelling was required.

The major products were expected to be nitrogen, chlorine, hydrogen chloride, carbon dioxide and oxygen. Very high destruction and removal efficiencies (DREs) were predicted in both plasmas. The Bunsen burner was not expected to be able to treat streams containing much more than 1 % TCE.

Several percent of nitrogen oxides are expected in the plasma runs, while carbon monoxide will be produced in the Bunsen.

The only organic products predicted to be present in significant amounts are oxygenated chlorinated aliphatics. Very low levels (mole fractions of \( \sim 10^{-11} \)) of chlorinated aromatics are predicted in both plasmas (slightly more in the propane plasma).

The products formed are expected to be essentially independent of all reactor temperatures that can be achieved in the IRIS laboratory.

The quench rate is the rate at which the reactor effluent is cooled on exiting the reactor. It is expected to affect the products, especially in the propane plasma. Decreasing the quench rate from 10,000 Ksec\(^{-1}\) to below 1,000 Ksec\(^{-1}\) is predicted to reduce the formation of chlorinated aliphatics and aromatics and hopefully halve nitrogen oxide production in the plasma.

Increasing TCE and propane concentrations in the system make the system richer in carbon and hydrogen and so the formation of carbon monoxide and organics is increased (and therefore the DRE is decreased), and nitrogen oxide formation is
decreased. However, it appears that it will be more effective to control nitrogen oxide formation with quench rate than by adding fuel to the system.

6.2 Introduction

Chemical modelling helps to plan experiments and minimise the number of runs required. It helps to ensure the robustness of the system, as all conditions and worst case scenarios can be tested. Modelling verifies the experimental data (or not) and helps to explain it. It is also useful in optimising the scale-up of laboratory processes.

CHEMKIN (Reaction Design) was chosen as the chemical modelling package for this project because its widespread use means that data is usually supplied in CHEMKIN format. Also, there is a users’ forum. Two of the CHEMKIN packages were used: EQUIL (equilibrium modelling) and AURORA (kinetic modelling).

Equilibrium modelling is a good initial approach to the problem. EQUIL uses the thermodynamic properties of all defined possible products to determine what products would be in equilibrium for user-defined chemical compositions and conditions. The equilibrium model is vital to the understanding of the system in terms of planning sensible experiments and detecting nonsensical kinetics results.

Kinetic modelling enables a temperature-programmed reactor simulation, and therefore also requires reaction rate data as well as the thermodynamic properties of all defined species. Surface reactions can also be modelled.

It is important to know all possible species and have thermodynamic and reaction rate data for them. Missing a single vital species or reaction could render the model meaningless. For instance, in this project, the formation of chlorinated aromatics is a key issue. Therefore, mechanisms for their formation must be complete and correct for the model to aid in their prediction.
6.3 Input files

6.3.1 Overview

The input files required to run CHEMKIN are the chemistry and surface chemistry files, the run file and thermodynamic data. Surface reactions were assumed to be insignificant due to the low contact surface area and are therefore not modelled.

6.3.2 Chemistry input file

The chemistry input file defines the elements and species present. The AURORA chemistry input file (given in appendix 6A) also requires a list of reaction rate constants.

The Arrhenius Equation in the form given in equation 6.1 is used to generate the reaction rate constant (k), where A and n are constants, T is the temperature and R is the ideal gas constant (Frost and Pearson 1961).

\[ k = AT^n e^{-E/RT} \]  

(6.1)

An example of the AURORA input format for the production/dissociation of phosgene (COCl₂) is given below, where CO is carbon monoxide (CO) and Cl₂ is chlorine (Cl₂):

\[ \text{CO} + \text{Cl}_2 = \text{Cl}_2\text{CO} \quad 6.32\text{E12} \quad 0 \quad 110 \quad !1924\text{BOD/PLA399} \quad 2 \quad 621-725 \]

First the reaction is defined and the following three numbers define A, n and –E respectively. Units used were moles, kJ, bar and cm³. Comments after the exclamation mark are not part of the input and are the reaction data reference, reaction order and temperature range.

Most of the reaction data was sourced from NIST (National Institute of Standards and Technology 2000), although other sources, including extracts from existing reaction schemes (Evans et al. 1993 and Leylegian et al. 1998), were used. Where several reaction rate constants were available, priority was given to data that provided all three values (A, n and –E). Where there were still several reaction rate constants available, they were ranked by appropriateness of the temperature range (1,000 –
6,000 K was ideal) and then the date that the data was published (more recent was considered more reliable).

A complete model could not be built due to omissions in reaction rate data. Omitted reactions are for rare species, however, and are not expected to be important.

Reactions of electrons and ions were not included in the chemistry file (and are not generally available). The justification for this is that they react very rapidly, such that equilibrium is reached almost instantaneously. Therefore, even a very fast quench could not prevent equilibrium being attained until the temperature dropped below electron and ion temperatures (i.e. until the plasma reverts to gas).

### 6.3.3 Equil run file

The EQUIL run file defines the composition and conditions of the system. One example input condition is given below. The run file consists of a list of these non-equilibrium conditions, usually changing one system parameter across a range of values (e.g. TCE inlet concentration from 0 – 10 % at a set temperature). An example of one item in the list is given below, where H2O is water (H₂O), O₂ is oxygen (O₂), CL₂CCHCL is trichloroethene (C₂HCl₃, TCE), and N₂ is nitrogen (N₂).

```
REAC  H2O    1
REAC  O2     19.4
REAC  CL2CCHCL 2
REAC  N2     77.6
TP
TEMP    300
PRES    1
CNTN
END
```

The output file lists the compounds and their mole fractions that would exist if the system were allowed to come to equilibrium under these conditions for this composition of elements.
6.3.4 Aurora run file

The AURORA run file defines the input composition of the system and then sets a temperature profile for the theoretical reactor to follow. An example of an AURORA input file is given in appendix 6B. The parameters time-step (STPT or DELT and DTSV), absolute tolerance (ATOL) and relative tolerance (RTOL) can be varied in a trial and error fashion in order to compromise between accuracy and computability.

6.3.5 Thermodynamic data

The data consists of a list of coefficients that are used to calculate the thermodynamic properties of each species. Two sources were used: Reaction Design (1997) and Burcat (2001). The file used is available on request.

6.4 Equilibrium Modelling

6.4.1 Composition of system

The possible constituents of any experiments carried out for this project are:

1. Air  
   20 % oxygen (O₂), 80 % nitrogen (N₂)

2. Trichloroethene, TCE  
   Maximum: saturated vapour ~ 8 %
   Usual: 2 %

3. Water  
   Average of 1 % in air
   None in experimental compressed air

4. Propane (C₃H₈)  
   To provide fuel in the Bunsen flame (4 %)
   To provide hydrogen in the plasma (0 – 1 %)

The components of the system are carbon, chlorine, hydrogen, nitrogen and oxygen.
6.4.2 Overall results

EQUIL predicts the eventual products of a system of user-defined composition, temperature and pressure.

Initially, the system was broken down to see how isolated parts of the system would behave. These results can be seen in detail in appendix 6C.

In general, molecules are stable at 300 K and gradually break down into atoms and radicals at higher temperatures. For chlorine, this dissociation becomes significant at 1,000 K, and by 2,000 K the mole fraction of Cl (chlorine radical/atomic chlorine) exceeds that of Cl₂. Other species follow similar patterns. At even higher temperatures, electron and ions are formed. Between 4,000 and 6,000 K, the electron density can increase by a factor of 100.

Therefore, the Bunsen burner at about 1,000 K may produce different products than the plasma at temperatures exceeding 4,000 K.

6.4.3 Potential formation of chlorinated hydrocarbons

The equilibrium products of pure TCE are useful in determining what temperatures may result in worst-case scenario product formation. There is concern that chlorinated aromatics may be formed, possibly leading to the formation of dioxins and furans, which are the most toxic pollutants. Figure 6.1 shows the equilibrium products of pure TCE.

It is clear from figure 6.1 that at plasma temperatures (above 4,000 K), all of the chlorine is in the form of Cl and hydrogen chloride (HCl). Note that between about 2,000 and 3,000 K, precursors to chlorinated aromatics such as dichloromethylene (CCl₂) may be formed. Therefore, if the plasma equilibrium products were quenched quickly enough, the formation of any chlorinated hydrocarbons could be avoided.
At Bunsen burner temperatures of about 1,000 K, significant amounts of hexachlorobenzene ($C_6Cl_6$, HCB), pentachlorobenzene ($C_6HCl_5$), tetrachloroethene ($C_2Cl_6$) and carbon tetrachloride ($CCl_4$) are formed. Therefore, the potential to form chlorinated aromatics and other harmful products is higher in the Bunsen burner experiments. The formation of Cl$_2$ gas may indicate the potential conditions for these unwanted products to form.

### 6.4.4 Effect of trichloroethene concentration on equilibrium products

At 300 K, and below an initial concentration of 8 % TCE, the major equilibrium products are N$_2$, O$_2$, carbon dioxide (CO$_2$), Cl$_2$ and H$_2$O, with a small amount of HCl. When the TCE concentration exceeds about 8 %, the O$_2$ runs out. After this point, HCl formation is significantly higher, and Cl$_2$ concentration drops off rapidly; the equilibrium concentrations of the unwanted products discussed in the previous section (6.2.3) are significant and phosgene appears at just below parts per thousand levels.

At 1,000 K, approximately the temperature expected in the Bunsen burner flame, a similar transition happens as the TCE concentration exceeds 9 % (see figures 6.2a and b).
Figure 6.2a: Equilibrium products of TCE in humid air at 1,000 K (Mole fraction 1x10^{-3} to 1)

Figure 6.2b: Equilibrium products of TCE in humid air at 1,000 K (Mole fraction 1x10^{-9} to 1x10^{-3})
Theoretically, the maximum possible concentration of TCE to be treated from the vapour degreasing process, based on its vapour pressure (appendix 4A), is about 8%. However, the concentration measured at the HPM machine was about 2%. This was caused by the negative pressure operation of the machine (for the workers’ safety) resulting in room draughts diluting the vapour stream before emission to the atmosphere. Since the TCE concentration will not exceed 8%, the formation of unwanted by-products such as CCl₄ and phosgene is not possible under equilibrium conditions at room or Bunsen temperatures.

At plasma temperatures (5,000 K), this transition does not occur at high TCE concentrations. The major equilibrium products of TCE in humid air are: N₂, atomic oxygen (O), Cl, CO, atomic hydrogen (H), atomic nitrogen (N) and nitric oxide (NO). Therefore, it is theoretically possible to treat TCE concentrations above 8% with the plasma, while the Bunsen burner is limited to concentrations below 8%. As discussed already, from the equilibrium point of view, both are feasible for all actual concentrations of TCE vapour.

6.4.5 Effects of equilibrium temperature

Figures 6.3a and b show the equilibrium products of 6% TCE in air.

![Equilibrium products of 6% TCE in humid air (mole fraction 1x10⁻³ to 1)](image)

Figure 6.3a: Equilibrium products of 6% TCE in humid air (mole fraction 1x10⁻³ to 1)
Figure 6.3a shows that \( N_2, CO_2, Cl_2, O_2 \) and \( H_2O \) would be in equilibrium at room temperature. Quenching from 1,000 K would lead to the formation of these products. However, quenching from plasma temperatures (above 4,000 K), may lead to the formation of \( NO \) and \( CO \). Below 1,000 K, \( Cl_2 \) dominates \( HCl \), whereas above about 1,000 K, more \( HCl \) than \( Cl_2 \) is formed.

Figure 6.3b shows that chlorosyl radical (\( ClO \)), hypochlorous acid (\( HOCl \)) and nitrosyl chloride (\( NOCl \)) may play a role. Electron and ions density increases with temperature. Between 4,000 and 6,000 K electron density increases a thousand fold to just under parts per thousand levels. Therefore, if fast enough quenches can be achieved, the chemistry in the plasma may be different at different temperatures.

Under these oxidising conditions, the potential for aromatic formation is very low. The only precursors to these compounds present are carbon monochloride (\( CCl \)), carbon ion (\( C^+ \)) and chloride ion (\( Cl^- \)), which are present at very low concentrations above 4,000 K. Given that these calculations were performed using the worst-case scenario of 6 % TCE, it seems that a plasma could be used to safely treat TCE.

Figure 6.3b: Equilibrium products of 6 % TCE in dry air: Chlorinated species (except \( Cl, Cl_2 \) and \( HCl \)) and ions

Note that these results are almost identical for dry and humid air.
6.4.6 Effect of air humidity

The provision of hydrogen is a key issue in this project. The compressed air used for the experiments is dry, whereas normal air contains an average of 1 % water vapour, which varies depending on the weather (figures from the Australian Bureau of Meteorology (2005)). EQUIL was used to investigate whether this would have a significant effect on the results. The humidity was varied from 0 – 1.5 % of the inlet stream. Unsurprisingly, increasing water vapour concentration increased the concentration of all hydrogen-containing species. Since there is already excess oxygen in the system, the oxygen provision had a negligible effect.

At 1,000 K, the major products are N₂, CO₂, Cl₂ and HCl. The only significant variation is that the Cl₂ concentration reduces with increasing H₂O concentration, while the HCl concentration increases. HCl concentration exceeds Cl₂ concentration above 0.5 % water vapour (see figure 6.4).

Therefore the dry plasma experiments are likely to yield more Cl₂ than those done using humid air. This may also mean that chlorinated hydrocarbon formation is more likely in the lab experiments than it would be if the actual process stream were treated in the same way.

At 5,000 K, the major products are N₂, O, Cl, CO, H, N and NO. The only one of these that varies over the humidity range is H, which increases from about 4 – 7 %. HCl increases from 0.2 – 0.3 %.
6.4.7 Effects of propane concentration

In the Bunsen burner experiments, enough propane for a lean flame (i.e. 4 %) is supplied and the TCE concentration varied. At 300 K and below an initial concentration of about 6 % TCE, the major equilibrium products are N₂, HCl, CO₂, H₂O and methane (CH₄). TCE seems to take oxygen preferentially. Therefore, when the oxygen begins to run out at 6 %, non-chlorinated aromatic hydrocarbons are formed. Eventually (above 8 % TCE input), TCE runs out of oxygen too and chlorinated aromatics are formed. Therefore, the addition of propane to the TCE stream lowers the ideal maximum amount of TCE that could be treated from 8 to 6 %. However, as 6 % TCE is approaching the theoretical maximum concentration to be treated from vapour degreasing processes (and in practice 2 % is a realistic figure), Bunsen burner treatment is theoretically feasible from the point of view of by-product formation. Unwanted by-products at high TCE concentrations may be controllable by quench rate (see kinetic modelling, section 6.3).

The aim of adding propane to the plasma is to provide hydrogen to maximise the formation of HCl and suppress the formation of chlorinated hydrocarbons and NOₓ.
Figures 6.5a, b and c show the equilibrium products of the plasma (at 5,000 K) with varying propane flow for a TCE inlet concentration of 6 %.

The actual propane concentrations used in the plasma runs were 0.3 – 1 %. Over this range of interest, H, CO, hydroxyl radical (OH), H$_2$O, hydrogen ion (H$^+$), hydroperoxy radical (HO$_2$) and HOCl (in order of decreasing concentration) all increase with increasing propane concentration. All other oxygenated species decrease with increasing propane concentration. Therefore, the addition of a small amount of propane to the plasma should decrease nitrogen oxide (NO$_x$) formation and encourage the formation of HCl.

![Equilibrium products of 6 % TCE in air at 5,000 K](image)

Figure 6.5a: Equilibrium products of 6 % TCE in air at 5,000 K (mole fraction 1x10$^{-3}$ to 1)
Figure 6.5b: Equilibrium products of 6 % TCE in air at 5,000 K (mole fraction $1\times10^{-6}$ to $1\times10^{-3}$)

Figure 6.5c: Equilibrium products of 6 % TCE in air at 5,000 K (mole fraction $1\times10^{-9}$ to $1\times10^{-6}$)
6.4.8 Conclusions

The major equilibrium products of the system are N₂, Cl₂, CO₂, O₂ and hydrochloric acid. The species ClO, HOCl and NOCl may also play a role in the chemistry. TCE concentrations up 8 % in the plasma and 6 % in the Bunsen burner could be treated without excessive chlorinated hydrocarbon formation. The electron density in the plasma varies by a factor of 10² – 10³ over the predicted plasma temperature range (see Chapter 5 for plasma temperature predictions).

The main disadvantage of the plasma is that the combination of a highly oxidising atmosphere and very high temperature is ideal for the formation of nitrogen oxides (NOₓ). This effect can be reduced by the addition of hydrogen (in the form of propane in this case). However, hydrogen addition at plasma temperatures may encourage the formation of CO instead of CO₂.

Unwanted organics such as chlorinated benzenes are more likely to be formed in the Bunsen burner. However, the plasma must be quenched rapidly below about 3,000 K to avoid formation of these organics and their precursors. High temperature and hydrogen addition aid the formation of HCl (desired) rather than Cl₂.

6.5 Kinetic Modelling

6.5.1 Introduction

Inlet composition and temperature profile can be varied with the AURORA program. The effects of varying TCE and propane concentration, reactor temperature and quench rate were investigated. Some of the predicted products are unlikely (see section 5.3.6). However, the model seems close enough to reality for the purposes of this project.

Modelling the breakdown of propane in AURORA increased the complexity of the problem to unmanageable levels. Therefore, propane was modelled by assuming that it is all converted to CO₂ and H₂O on entry into the reactor.

In order to interpret the complicated results, many compounds have been grouped into categories. This is relevant because members of these groups would have similar
environmental consequences. Also, since the model does not provide every possible reaction pathway, quoting exact concentrations of minor species may not be meaningful at this stage. Predictions for individual compounds are compared with experimental results in Chapter 7 where possible. See appendix 6D for a list if all compounds predicted to appear above 1 ppb in any run, with the range of predicted concentrations for each TCE destruction method.

6.5.2 Predicted destruction and removal efficiencies

Figure 6.6 shows the destruction and removal efficiencies under all three experimental conditions. All three lines represent simulations of the treatment of 3 % TCE in dry air. The propane plasma and Bunsen runs have sufficient propane added to provide stoichiometric hydrogen (0.5 %) and carbon (4 %) respectively. Therefore, the actual mole fraction of TCE is reduced proportionally to the amount of propane added. All simulations were quenched to 300 K at 10,000 Ksec⁻¹.

![Figure 6.6: Effect of reactor temperature on destruction and removal efficiency of 3 % TCE](image)

Figure 6.6 shows that 6 - 7 nines’ destruction is predicted in the propane plasma, while 9.5 – 10.5 nines’ destruction is predicted in the air plasma. Since the minimum microwave plasma reactor temperature is predicted to be about 3,000 K (see Chapter
maximum destruction is predicted in the air plasma at just above 5,000 K. However, the difference of 1 nine at this high level of destruction is academic and in engineering terms, the microwave plasma reactor temperature is likely to make little difference to the destruction efficiency. The temperature range in the Bunsen flame is reported to be 1,200 – 1,400 K (Babrauskas 1997). Therefore, figure 6.6 predicts that less than 3 nines’ destruction would be achieved in the Bunsen burner. This is low when compared with plasma destruction efficiencies, but is comparable with currently available technologies (see Chapter 1). A non-thermal plasma reactor operating at or below 2,000 K would provide the highest TCE DRE.

Plotting the DRE can be misleading for two reasons. The absolute tolerance, i.e. the smallest meaningful mass fraction in the model, is set to 1x10^{-20}. Therefore, higher destructions cannot be calculated. However, such small mass fractions are not physically meaningful and destruction efficiencies above 10 nines’ can be considered to be ‘total destruction’. Also, since the same output concentration of TCE would register a higher DRE for a high input concentration than a low one, it is not necessarily the clearest indication of what is going on in the model.

It was found that up to 10 % TCE could theoretically be treated in the air plasma before the outlet concentration of TCE reached parts per million levels. Figure 6.7 shows the effect of varying TCE inlet concentration from 1 to 6 % on the DRE. Plasma temperatures of 5,300 K and Bunsen temperatures of 1,300 K were quenched to 300 K at 10,000 Ksec^{-1}. The dashed line, ‘TCE in’ shows the Bunsen burner inlet TCE concentration. Other series are outlet concentrations.

Figure 6.7 shows that both the air and propane-enhanced plasmas should provide high levels of destruction across the applicable range of TCE concentration. Small peaks in TCE outlet concentration are seen in the air plasma just above 1 and 2 %, and in the propane plasma just below 3 % inlet TCE. These may correspond with the anomaly around 3 % in experiments (see chapter 5) or may be numerical error in the model.
Figure 6.7: Effect of TCE inlet concentration on TCE outlet concentration

Assuming that 1 ppm is the largest acceptable output concentration (roughly 4 nines’ destruction), the Bunsen could treat TCE levels of up to about 1.5 %. At higher levels, the model predicts unacceptable TCE destruction in the Bunsen.

The effect of quench rate on DRE was also investigated. TCE concentrations of 5 % were treated in the plasma runs. However, since the maximum concentration of TCE in the Bunsen without flame extinction is 4 %, that was the input concentration used in the Bunsen simulations. The quench rate was varied from 200 – 10,000 Ksec\(^{-1}\) and found to have little effect on the output concentration of TCE in the Bunsen and air plasma runs. The propane plasma was predicted to be most efficient at 200 Ksec\(^{-1}\) (15 nines), decreasing to 8 nines at 2,000 Ksec\(^{-1}\) then gradually improving with a further increase in quench rate. However, at these high levels of destruction, quench rate is not expected to be crucial in terms of TCE DRE.

### 6.5.3 Conversion of trichloroethene to hydrogen chloride and chlorine

The desired reaction involves conversion of TCE into HCl (preferred) and Cl\(_2\). In general, both plasmas are predicted to provide high conversion rates of TCE to these desired products. However, the air plasma is predicted to produce about twice as much Cl\(_2\) as HCl, while the propane plasma will produce twice as much HCl as Cl\(_2\),
the latter being preferable. The Bunsen burner is not expected to produce any Cl\textsubscript{2} and the highest conversion to HCl is predicted in the Bunsen at low TCE concentrations.

The effect of reactor temperature on the conversion of the chlorine from TCE to HCl and Cl\textsubscript{2} was investigated for 3 % inlet TCE concentration. Reactor temperature was found to have no affect on the plasma results. Virtually no Cl\textsubscript{2} was formed in the Bunsen simulation, and less than 50 % of the inlet TCE was converted to HCl. If a plasma temperature Bunsen flame could be achieved, however, an almost 90 % conversion of TCE to HCl would be possible.

Figure 6.8 shows the effect of inlet TCE concentration on conversion to major chlorinated products.

![Figure 6.8: Effect of TCE inlet concentration on conversion of TCE to HCl and chlorine](image)

The best result of almost complete conversion to HCl is predicted at low concentrations in the Bunsen burner. However, the propane plasma is almost as effective at 1 % inlet TCE and better at higher concentrations. While conversion to HCl decreases with increasing TCE concentration in the propane plasma and flame, it is constant in the air plasma, presumably owing to the highly lean atmosphere.
Across this TCE concentration range, 99.4 – 99.8 % of the chlorine is predicted to be converted to either Cl\textsubscript{2} or HCl by the air plasma, 99.7 – 99.8 % by the propane plasma, and 11.7 – 99.1 % by the Bunsen flame.

Quench rate was found to have little effect on these results. The conversion to HCl increased slightly and the conversion to Cl\textsubscript{2} decreased slightly in the propane plasma runs as the quench rate was increased. The Bunsen is predicted to perform slightly better at low quench rates. The air plasma results are virtually the same across the whole quench range tested.

Please note that if the fraction of the products as a function of the amount of TCE destroyed instead of the inlet TCE concentration is plotted, the plasma results are almost the same, and the conversion to HCl in the Bunsen is only slightly increased.

The overall conclusion is that the propane plasma is predicted to be the most effective method of converting TCE into HCl under all conditions (although the Bunsen is slightly better at and below 1 % TCE inlet concentration). Both plasmas convert over 95 % of the chlorine in the system into HCl and Cl\textsubscript{2} gas, both acceptable products.

### 6.5.4 Conversion of carbon in the system to carbon dioxide

Carbon dioxide is the desired end point for the carbon in the system. Figure 6.9 shows the conversion of carbon to CO\textsubscript{2}. Almost total conversion is predicted in both plasmas. Quench rate and reactor temperature have no effect on CO\textsubscript{2} production under experimental conditions for this project. However, conversion of carbon to CO\textsubscript{2} would drop off rapidly in non-thermal plasma below 2,000 K. For an initial TCE concentration of 2 %, the concentration of CO\textsubscript{2} in the outlet streams are predicted to be 4, 5, and 10 % for the air and propane plasmas and the Bunsen, respectively.
6.5.5 Formation of organic by-products

6.5.5.1 Overall

Formation of non-chlorinated aromatics is predicted to be negligible under all conditions. Non-chlorinated aliphatics at parts per million levels are predicted in both plasmas at the maximum quench rate (10,000 K), although none are predicted in the Bunsen.

The chlorinated organics have been grouped into aliphatics and aromatics. The chlorinated aliphatics include all chlorinated organic straight-chained compounds, except those that contain oxygen, which are classes as ‘oxychlorinated aliphatics’.

6.5.5.2 Chlorinated aliphatics

Figure 6.10 shows the fraction of the chlorine from the treated TCE that is predicted to be output as chlorinated aliphatics. Assuming that the Bunsen method would only be used for treating TCE concentrations of less than 1.4 %, all three methods would produce 10 – 100 times more oxygenated than non-oxygenated chlorinated aliphatics at most TCE concentrations. Production of ‘oxychlorinated aliphatics’ was highest in
the Bunsen (accounting for about 1 % of the total chlorine), and lowest in the air plasma (0.01 % of chlorine at moderate TCE concentrations). The irregular peaks and troughs displayed by the non-oxygenated chlorinated aliphatics may correspond with the anomaly around 3 % TCE in the experiments (see chapter 5) or may be caused by numerical error in the model.

Reactor temperature had no significant effect on aliphatic product formation. Decreasing the quench rate decreased the formation of both groups of chlorinated aliphatics in the plasmas. This effect was most marked in the propane plasma and at very low quench rates.

6.5.5.3 Chlorinated aromatics

CHEMKIN predicts that it is not possible to form the precursors to chlorinated aromatics at Bunsen temperatures. Therefore, although the Bunsen flame is operated at ideal chlorinated aromatic formation temperatures, none will be formed. Very low levels are predicted in the plasma runs. Figure 6.11 shows the conversion of chlorine from TCE into chlorinated aromatics against reactor temperature. Its shows that the
propane plasma has the highest propensity to form chlorinated aromatics, even though this is still at very low levels. Chlorinated aromatic formation is predicted to increase with reactor temperature. Simulations also show that the formation of chlorinated aromatics increases with increasing quench rate and TCE inlet concentration.

![Figure 6.11: Effect of reactor temperature on the formation of chlorinated aromatics](image)

Figure 6.11: Effect of reactor temperature on the formation of chlorinated aromatics

Figure 6.12 shows the progress of the formation of chlorinated benzenes with reactor temperature in the quench. It shows that they are formed in order of decreasing chlorination (i.e. HCB first and chlorobenzene (C₆H₅Cl) last) between 2,400 K and 600 K.

It was found that increasing the quench rate increased the range of temperatures at which chlorinated aromatics were formed but decreased the rate of formation. For aromatics to form, precursors such as CCl must be present and the formation temperature range (below about 2,500 K) must be held for sufficient time. Since 300 K is within this range, the presence of precursors is the vital condition. Fast quenching increases the likelihood that these precursors will be present (e.g. CCl is in equilibrium above 4,000 K only) but allows less time for aromatic formation (hence the shallower gradient). It is assumed that formation ceases below 600 K because the precursors are depleted, and therefore the gradient is irrelevant. Further increases in
quench rate may reveal a levelling out of formation. This is because above a certain quench rate, there would be no time for the precursors to react between 4,000 K and 300 K and so their concentration would become constant on arrival at 300 K and maximum chlorinated aromatic formation would occur.

![Figure 6.12: Formation of chlorinated aromatics in the propane plasma against temperature in the quench for 6 % inlet TCE and 10,000 Ksec⁻¹ quench](image)

**6.5.6 Formation of inorganic by-products**

6.5.6.1 Overall

About 10 % of the Bunsen output is predicted to be H₂O, with up to a percent in the propane plasma and hardly any in the air plasma. Other inorganics formed at percent levels are NO and CO. Other inorganics are expected at very low concentrations only.

6.5.5.2 Nitrogen oxide (NOₓ) formation

No NOₓ formation is predicted at Bunsen temperatures. About 2 % of both plasma outputs are predicted to be NOₓ, with slightly more in the air plasma. NO predominates with nitrogen dioxide at around parts per million levels and N₂O around parts per billion levels.
NO\textsubscript{x} formation is constant in both plasmas for reactor temperatures above about 2,500 K (i.e. all achievable plasma temperatures). Below that, NO\textsubscript{x} formation would drop off rapidly (e.g. to parts per 10,000 by 2,000 K).

NO\textsubscript{x} formation is inversely proportional to inlet TCE concentration, as shown in figure 6.13.

![Figure 6.13: Effect of TCE inlet concentration on NO\textsubscript{x} formation](image)

Note that Bunsen values are 0

NO\textsubscript{x} formation increases with quench rate. Figure 6.14 shows predicted NO\textsubscript{x} formation in the treatment of a 5 % TCE in air stream (air plasma omitted). Reducing the quench from 10,000 Ksec\textsuperscript{-1} to 200 Ksec\textsuperscript{-1} would approximately halve NO\textsubscript{x} production in the propane plasma. There is no NO\textsubscript{x} formed in the Bunsen flame.
In conclusion, NO\textsubscript{x} formation is highest in hot (above 2,500 K), lean environments. The addition of propane to the plasma is not expected to eliminate the NO\textsubscript{x} problem (only a 5 – 10 % reduction). However, very slow quench rates could reduce NO\textsubscript{x} production by 50 %.

6.5.6.3 Carbon monoxide (CO) formation

The only significant formation of CO is predicted in the Bunsen. For a 3 % TCE input, predicted CO concentrations are 2 %, 10 – 20ppm. and 5 – 50ppb in the Bunsen, propane plasma and air plasma respectively.

Figure 6.15 shows the effect of inlet TCE concentration on CO formation. It shows that CO formation increases rapidly from an insignificant amount to percentage levels between 0 and 1 % inlet TCE. At higher TCE inlet concentrations, CO formation is roughly constant in the Bunsen. Although CO formation in the plasmas is not very high, the irregular variations predicted in other species’ formation between 1 and 3 % TCE are seen. Again, these variations may correspond with the anomaly around 3 % TCE in the experiments (see chapter 5) or may be caused by numerical error in the model.
Figure 6.15: Effect of TCE inlet concentration on the formation of carbon monoxide

The formation of CO in the Bunsen burner is predicted to be unaffected by the quench rate.

6.5.6.4 Other

The only compounds not already addressed that appear above part per billion levels are: hypochlorite (ClO⁻), chlorosyl chloride (OCl₂), chloryl radical (ClO₂) and HOCl (classed as chlorine oxides and oxyacids) and NOCl.

NOCl formation is not expected in the Bunsen burner. The amount of chlorine in the system that is converted to NOCl in the air plasma is predicted to be 0.6 % at 1 % TCE, decreasing with increasing TCE concentration to 0.2 % at 6 % TCE. Less NOCl is formed in the propane plasma (0.19 – 0.14 % between 1 and 6 % inlet TCE). Quench rate and reactor temperature are not significant in NOCl formation.

2 – 0.2 ppm of chlorine are converted to chlorine oxides and oxyacids from 1 – 6 % TCE in propane plasma. Air plasma slightly less at 1 % but decreases more slowly than in propane plasma and therefore exceeds concentration in propane plasma above 2 % TCE. Formation decreases much more rapidly with TCE concentration in the
Bunsen; it is about the same as in the plasmas at 1 % TCE, but above that its formation is insignificant. Reactor temperature and quench rate have little effect on the formation of chlorine oxides and oxyacids, except that their formation drops off, especially in the air plasma, at a quench of 200 Ksec⁻¹.

6.5.7 Accuracy of model

All of the elements balanced in mass by at least 99.99999 % (5 decimal places). Figure 6.16 shows the results of the mass balance by element at 3 % TCE inlet concentration. These results do no vary significantly with initial TCE concentration. All of the elements except nitrogen balance to within the relative tolerance defined within the model.

![Figure 6.16: Elemental mass balance for 3 % TCE inlet concentration](image)

Some by-products predicted in the plasma are unlikely to be stable at atmospheric temperature and pressure because they have unpaired electrons. The most significant, 1,1,2-trichloro-2-oxo-ethyl radical (CCl₂CClO), appears to be present throughout the entire temperature range, which is clearly impossible according to the equilibrium results. However, the total mole fraction of these unstable species (see table 1, appendix 6D) is a maximum of parts per thousand (in the burner).
6.5.8 Overall

Very high destruction and removal efficiencies have been predicted in both plasmas, especially in the air plasma (8 nines). The Bunsen burner is not expected to be able to treat streams containing much more than 1 % TCE.

Highest conversion to HCl is predicted in the propane plasma (and the Bunsen below about 1 % TCE), about double that in the air plasma. However, overall conversion to HCl and Cl₂, as well as CO₂, is slightly higher in the air plasma.

The only organic products predicted to be present in significant amounts are oxygenated chlorinated aliphatics. Their formation is expected to be 10 – 100 times higher in the Bunsen (accounting for a few percent of the chlorine in the system) than the plasmas. Very low levels (10⁻¹¹) of chlorinated aromatics are predicted in both plasmas (slightly more in the propane plasma).

Several percent of NOₓ are expected in the plasma runs, while CO will be produced in the Bunsen.

The products formed are expected to be essentially independent of all reactor temperatures that can be achieved in the IRIS laboratory. The formation of chlorinated aromatics does increase with reactor temperature but is expected to be barely detectable at all levels.

The quench rate is expected to affect the products, especially in the propane plasma. Decreasing the quench rate from 10,000 Ksec⁻¹ to below 1,000 Ksec⁻¹ is predicted to reduce the formation of chlorinated aliphatics and aromatics and hopefully halve NOₓ production in the plasma.

Increasing TCE and propane concentrations in the system make the system richer in carbon and hydrogen and so the formation of CO and organics is increased (and therefore the DRE is decreased), and NOₓ formation is decreased. However, it appears that it will be more effective to control NOₓ formation with quench rate than by adding fuel to the system.
6.6 Conclusions

The main difference between the equilibrium and kinetic predictions are regarding the formation of chlorinated aromatics. Although the equilibrium model predicted a higher propensity for their formation in the Bunsen, the kinetic modelling has revealed that Bunsen temperatures do not enable it. Also, the kinetic simulations indicate that increasing the quench through their formation temperature range would in fact increase it.

The plasma reactor temperature is not vital in terms of the final outcome of the chemistry; an increase in plasma temperature from 3,000 K to 4,000 K does not change the chemistry of the quenched system significantly.

Fluctuations in the model may reflect the anomaly observed around 3 % TCE inlet concentration in the experiments (see chapters 5 and 8).
7. RESULTS QUALIFICATION .................................................................................................................. 106

7.1 Abstract ........................................................................................................................................... 108

7.2 Introduction ..................................................................................................................................... 108

7.2 General observations ..................................................................................................................... 109
  7.2.1 Bunsen burner ......................................................................................................................... 109
  7.2.2 Preliminary plasma rig (TCE in dry air only) ........................................................................ 110
  7.2.3 Final plasma rig ........................................................................................................................ 110

7.3 Accuracy of results .......................................................................................................................... 111

7.4 Gas phase by-product identification ............................................................................................... 115
  7.4.1 Introduction ............................................................................................................................ 115
  7.4.2 Initial peak identification by Gas Chromatography/Mass Spectrometry (GC/MS) .................. 115
  7.4.3 Quantification by Gas Chromatography with Electron Capture Detector (GC/ECD) .............. 117
  7.4.4 Further GC/MS analysis ......................................................................................................... 118
  7.4.5 Injection of scrubbed samples ................................................................................................. 120
    7.4.5.1 Introduction ...................................................................................................................... 120
    7.4.5.2 Sampling technique .......................................................................................................... 120
    7.4.5.3 Results of peak solubility experiments ............................................................................ 121
  7.4.6 Effect of acidic/oxidative attack on column ............................................................................. 122
    7.4.6.1 Introduction ...................................................................................................................... 122
    7.4.6.2 Hydrogen chloride (HCl) ................................................................................................ 122
    7.4.6.3 Chlorine (Cl₂) .................................................................................................................. 124
  7.4.7 Overall Results and Conclusions ............................................................................................. 126

7.5 Solid residue formation .................................................................................................................. 128
  7.5.1 Introduction/Importance ........................................................................................................... 128
  7.5.2 Description .............................................................................................................................. 128
  7.5.3 Atomic Absorption Spectroscopy ............................................................................................ 130
  7.5.4 Mass formation (solid) ............................................................................................................. 130
7.5.5 External Analysis

7.5.6 Chemistry

7.5.6 Pyrex Chimney
7. Results qualification

7.1 Abstract

The experiments were found to be quite robust once initial engineering challenges were overcome. The plasma was stable at all possible TCE vapour concentrations and the Bunsen burner remained lit up to about 4 % TCE inlet concentration. Flow rates exceeding 15 lmin⁻¹ were possible in the plasma under some conditions.

The production of large amounts of hydrogen chloride and chlorine gas in the experiments caused the formation of metal chlorides in the reactor and chimney. It also made chemical analysis difficult as the acids degraded the gas chromatography column, causing extra peaks that were easily confused with experimental products. Various techniques were used to try to distinguish product peaks from column degradation peaks: gas chromatography with mass spectrometry was carried out; the areas of the peaks were normalised and their distribution assessed; chlorine and hydrogen chloride were injected in an attempt to reproduce column bleed and the samples were scrubbed in an attempt to minimise column degradation.

Most of the peaks were found to be attributable to column attack. The organic compounds identified with reasonable confidence were: phosgene, carbon tetrachloride, tetrachloroethene and hexachlorobenzene. All were present in very low concentrations (see chapter 8). It was also concluded that nitric oxide was one of the major peaks.

7.2 Introduction

Engineering challenges and occupational health and safety issues (OH&S) in experimental rig design and commissioning meant that it took several iterations (and about a year) to develop reliable and efficient experimental methods. These challenges included: prevention of condensation of TCE throughout the rig, safe ignition of the plasma/flame, control of back-pressure, and protection of the rotameters in the event of a back-pressure surge. Safe and reliable operation also required development of start-up, operating and shut-down protocols. However, once in full operation, the experiments were easy and quick to run. The reactor was also
found to be quite robust, occasionally requiring retuning. However, the unexpected formation of large amounts of residues in the copper chimney and some in the reactor itself made the experiments quite messy.

The majority of time and effort during this project was dedicated to chemical analysis techniques. Selection, set-up and operation required a substantial degree of expertise, and even then the interpretation of results was difficult. The nature of the sampling techniques (i.e. small batch sampling) and column degradation problems meant that the experiments were not very reproducible. Interpretation of the results was also difficult because when one input was changed, several of the system properties were changed simultaneously. For example, when the flow rate is increased, plasma temperature decreases. However, the residence time in the reactor and the quench rate are also decreased. The concentration of TCE flowing into the plasma also affects the plasma properties.

This chapter will begin by giving general observations of the experiments. The interpretation of the gas chromatography will then be explained. Quantification of the results is attempted in Chapter 8.

7.2 General observations

7.2.1 Bunsen burner

Propane flames were blue when lean and orange when rich. The addition of TCE to the lean flame resulted in a turquoise flame. It also contributed to the fuel value of the propane, meaning that as the TCE concentration increased, the required propane flow decreased. Since TCE is not flammable on its own, a flame cannot be achieved above a certain TCE concentration. The highest concentration of TCE combustible in the propane flame was found to be 4% in these experiments; this was an unstable, mainly orange, flame.

Some green solid was formed in the chimney. The flame colour changed to green when the copper chimney exceeded approximately 200°C.
7.2.2 Preliminary plasma rig (TCE in dry air only)

Preliminary TCE in dry air plasma experiments were carried out in a 1 kW plasma rig with a cooled lid. It was found that the plasma was stable throughout the whole range of TCE concentrations (up to saturated vapour pressure of 6 %). White/cream-coloured fumes were observed on opening the rig after a run, which are thought to have been hydrogen chloride (HCl) and chlorine (Cl₂). HCl has a steamy appearance and Cl₂ is green. Therefore, the fumes could have been a mixture of these two gases. The quantity of these fumes formed increased with TCE concentration treated.

Significant amounts of green, white and black oily residues were formed on the rig, especially inside the lid. Increasing the flow rate through the reactor decreased the rate of formation of these residues, presumably because the solids were being carried out of the reactor by the gas stream.

7.2.3 Final plasma rig

The plasma was stable at all concentrations of TCE and could exceed flow rates of 15 l/min under some conditions. It was also robust, being able to run at low powers for in excess of 30 minutes without any problems. At higher powers, however, the Teflon disk in the bottom of the reactor chamber burned, resulting in black wispy plastic. This was probably caused by residue falling onto the Teflon and forming a plasma arc, rather than the plasma volume actually touching the Teflon under normal operation.

The pitch of the plasma could be heard to change with flow rate, supporting the theory that the plasma temperature (which is related to plasma frequency) would change with flow rate (or residence time).

Various smells were detected in the reaction chamber and chimney throughout the plasma experiments. In the dry air, humid air and propane-enhanced experiments, sweetish smells reminiscent of aldehydes, ketones and esters were detected. Smells similar to those of commercial product “TCP” (trichlorinated phenol) and chlorosyl ion (ClO⁻) (swimming pool) and sharp, acidic smells were present at times.
Since the condensation of solids in the reactor lid was a problem with the primary rig, lid cooling was not used in the final rig. This decreased solid formation somewhat. There were still some white, yellow and sooty deposits found inside the reactor however, and the formation of a waxy residue in the chimney became a problem as it ran into the reactor when the chimney reached about 170°C and affected the plasma operating conditions. See section 5.7 for a more detailed discussion of the residues formed.

7.3 Accuracy of results

Each of the experimental runs was repeated at least three times. Since this is a viability study, larger numbers of repeats were sacrificed for experimentation over a wide range of conditions. With only three points, however, statistical analysis is difficult. The nature of these experiments also means that the peaks sizes are not very reproducible between one run and the next. For instance, some of the inlet stream may by-pass the flame. The quench rate varies depending on the flow rate, which chimney is used, and its starting temperature; although the first two are constant for any given experiment, the latter varies. Also, the compounds being detected are at very low levels (down to 1 part per million), so a small variation may well lead to a 100% fluctuation in the Electron Capture Detector (ECD) signal.

Spread of the results was assessed by calculation of the standard deviation of the normalised area for each peak. The normalised area is the peak area divided by the average of that peak for all runs of the same condition. The peak eluted at 4.66, which is one of the predominant peaks in the plasma runs, will be used to illustrate this method.

Table 7.1 shows the peak areas of the peak in the dry plasma, for an inlet of 8 l/min of air containing 4% TCE and microwave power of 2 kW. The same injection size and split ratio were used for all three injections, making direct comparison of the areas possible.
<table>
<thead>
<tr>
<th>Area 1</th>
<th>205,321</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area 2</td>
<td>1,509,007</td>
</tr>
<tr>
<td>Area 3</td>
<td>629,812</td>
</tr>
<tr>
<td>Average</td>
<td>781,380</td>
</tr>
</tbody>
</table>

Table 7.1: Area of 4.66 minutes peak from three injections of 4 % TCE plasma off-gas into Gas Chromatograph (GC)

From table 7.1:

Normalised Area 1 = Area 1/Average = 0.26

Therefore, an area normalised to 1 can be calculated for each peak in each run. The distribution can be plotted on a histogram. However, since the middle of the distribution is at one, and the number of points below 1 (0 – 1) should equal the number above 1 (1 – infinity), the distribution is not symmetrical. Therefore the log of these numbers must be plotted to view the distribution. Figure 7.1 shows the distribution of the normalised averages of the 4.66 minutes peak for all runs. It is based on a population of 179 points. The x-axis shows the log to the base 10 of the highest normalised average in the range (-1 corresponds to points within range 0 - 0.1, 0.7 represents all points above 5).

Figure 7.1 shows a reasonable normal distribution for the 4.66 minutes peak. Similar graphs were plotted for all of the major peaks (see appendix 7A). These graphs were used to divide the peaks between three categories: those that followed a reasonable normal distribution, those that clearly didn’t and borderline cases. The standard deviation of each major peak series is shown in figure 7.2. The standard deviation of the normalised averages for all peaks is 0.95, or roughly 100 %. The peaks are coloured according to how the normalised average distribution was categorised.
In general, the better the normal distribution of values, the lower the standard deviation. The red peaks should be held in extreme doubt, as their peak sizes are seemingly random. The air peak (2.1 minutes) and the 2.32 minutes peak, which is suspected to be nitric oxide (NO), showed the smallest spread. This is not surprising considering that percentages were being detected for these compounds, rather than parts per million as for other compounds. The 4.4 and 4.66 minutes peaks also appear to be reasonably consistent. It is unclear from this information whether the other black peaks and the blue peaks are actual products or not. Table 7.2 shows the improvement in the overall standard deviation if the peaks with doubtful reproducibility are excluded.

It should be noted that some of the suspected products are chlorinated aromatics, some of which have low vapour pressures. This means that any concentration detected in the gas phase would only provide an indication of the minimum amount formed, the rest having been deposited elsewhere as a solid (no liquids were formed). This means that if chlorinated aromatics are detected, they may not result in reproducible chromatogram peaks. Section 7.5 discusses investigation into the composition of the solid residues formed.
Figure 7.2: Standard deviation of normalised averages by peak

**Peak Categories:**

*Black: Normal distribution*

*Red: No normal distribution*

*Blue: Borderline*

<table>
<thead>
<tr>
<th>Peaks excluded</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.95</td>
</tr>
<tr>
<td>Red peaks</td>
<td>0.79</td>
</tr>
<tr>
<td>Red and blue peak</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 7.2: Overall standard deviation of normalised averages

This analysis has shown that the experimental values may display an error of 100 % or more. However, since environmental issues are usually discussed on a logarithmic scale (e.g. destruction and removal efficiency (DRE) is given in terms of number of nines, on a log scale as in equation 7.1), the accuracy of these results should suffice for environmental assessment purposes.

\[
DRE = -\log_{10}(R) \tag{7.1}
\]

In equation 7.1, R is the fraction of the target compound (i.e. TCE) remaining in the pollutant stream after treatment.
7.4 Gas phase by-product identification

7.4.1 Introduction

Identification of the products formed in the plasma has been the single most difficult and time-consuming element of this project. Product identification by Gas Chromatography/Mass Spectrometry (GC/MS) and then calibration on the Gas Chromatograph (GC) with standards was expected to be sufficient. However, as the following sections reveal, further GC/MS, sample scrubbing and column bleed tests were carried out in an attempt to clarify the products formed in the plasma. Sections 7.4.1 – 7.4.6 describe the steps in this peak identification process. The distribution of the peak areas presented in section 7.3 also provided useful information. The overall results of these experiments are presented in table 7.6, section 7.4.7, along with justification of the identities assigned to the peaks.

7.4.2 Initial peak identification by Gas Chromatography/Mass Spectrometry (GC/MS)

Early on in the experiments, some samples were scrubbed with saturated salt solution in a 50 ml gas-tight syringe and taken to the Sensory Neuro Laboratory at Swinburne University for GC/MS analysis. These were sampled using Solid Phase Microextraction (SPME). In SPME, a fibre is coated with a liquid (polymer) and/or a solid (sorbent), which absorbs/adsorbs compounds from the sample. The fibre is then placed into the GC injector for sample desorption. SPME requires no use of solvent, concentrates samples, gives linear results over a wide range of concentrations and is compatible with any GC or GC/MS (Supelco).

Several of the major peaks were identified. However, many of the peaks observed were not possible TCE dissociation products. Two of the major peaks in the GC traces were not observed/identified in the GC/MS. This may have been due to the sampling technique. That is, the compounds dissolved in the salt solution, they may not have been adsorbed onto the SPME, or they reacted to form other products in the solution or on the SPME.
The major peaks observed (largest peak area first) were: TCE, benzene (C₆H₆), tetrachloroethene (C₂Cl₄), carbon tetrachloride (CCl₄), chloroform (CHCl₃), chloroformyl chloroformate (C₃H₄Cl₂O₂), chlorobenzene (C₆H₅Cl), toluene (CH₃C₆H₅) and 1,2-dichloroethene (C₂H₂Cl₂). Of the other peaks, some were credible compounds such as di-, tri-, tetra- and hexachlorobenzene, and naphthalene (C₁₀H₈) and chloronaphthalene (C₁₀H₇Cl); others were obviously column bleed and others were not realistically identified. Figure 7.3 shows one of these GC/MS chromatograms. Since silicon is ionised more easily than the compounds of interest, the ion trap detector registers larger peaks for column bleed, making the chromatograms rather difficult to interpret.

Figure 7.3: GC/MS chromatogram showing products of dissociation of TCE in a propane gas flame.

Although these results were not ideal, they provided a useful starting point for peak identification on the GC.
7.4.3 Quantification by Gas Chromatography with Electron Capture Detector (GC/ECD)

Standards were obtained for as many of the suspected products as possible. These standards were used to find the characteristic elution time for each compound in the GC. The amplitude of the response of the Electron Capture Detector (ECD) to the compound when compared with its response to TCE was measured. Therefore, the GC could now be used to identify and quantify several of the products of TCE dissociation. Table 7.3 shows the absolute response of the ECD to TCE and the relative response of the other compounds calibrated.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Formula</th>
<th>Relative Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Chloride</td>
<td>MC</td>
<td>CH₃Cl</td>
<td>2.0E-04</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CCHCl</td>
<td>CHCl₃</td>
<td>3.7E-01</td>
</tr>
<tr>
<td>Dichloroethene</td>
<td>DCE</td>
<td>C₂H₂Cl₂</td>
<td>1.4E-03</td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>TCA</td>
<td>C₂H₃Cl₃</td>
<td>5.2E-01</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>CTet</td>
<td>CCl₄</td>
<td>4.0E+00</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>DCA</td>
<td>C₂H₄Cl₂</td>
<td>1.3E-01</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>PCE</td>
<td>C₂Cl₄</td>
<td>2.8E+00</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>CB</td>
<td>C₆H₅Cl</td>
<td>8.4E-05</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>2CB</td>
<td>C₆H₄Cl₂</td>
<td>9.7E-03</td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>3CB</td>
<td>C₆H₃Cl₃</td>
<td>6.0E-02</td>
</tr>
<tr>
<td>Tetrachlorobenzene</td>
<td>4CB</td>
<td>C₆H₂Cl₄</td>
<td>1.2E-01</td>
</tr>
<tr>
<td>Chloronaphthalene</td>
<td>Cnap</td>
<td>C₁₀H₇Cl</td>
<td>3.4E-03</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>HCB</td>
<td>C₆Cl₆</td>
<td>2.8E+00</td>
</tr>
</tbody>
</table>

Table 7.3: Response factors of standards when compared with TCE

Notes:

*Absolute Response of Detector to TCE = 175 Mcounts µg⁻¹ (Area per mass to detector)*

Peak area resulting from 1 µg of compound X to ECD = Absolute Response (TCE) x Relative Response (X/TCE)

7.4.4 Further GC/MS analysis

There were still some peaks that needed identification. GC/MS was performed at Industrial Sciences, Swinburne University using the GC/MS grade low-bleed column BPX5 (SGE 2001) and the same method as in the GC/ECD runs (see appendix 4B for details). The use of this column ensured minimal column bleed and the same elution order as in the GC/ECD with the same column. However, peak elution times were different as different carrier gas and flow rate were used (helium rather than nitrogen as in GC/ECD).

To determine which peaks corresponded with ones seen on the GC/ECD chromatograms, standards were injected.

Examples of typical plasma runs were carried out and injected into both the GC/ECD and the GC/MS and results were compared. Initially, the plasma off-gas was sampled
using a 50 ml gas-tight syringe; 100 µl samples were then taken from this syringe for both injections. This method was chosen to ensure that the two samples had the same (or as similar as possible) composition. However, it was found that this method appeared to dilute the sample, resulting in smaller peaks than desired in the GC/MS chromatograms. Therefore, the 100 µl syringe was used to take the sample directly from the rig; this improved peak sizes as well as reducing the possible sources of contamination. The disadvantage of this sampling method is that the two samples were taken about 30 seconds apart, rather than at the same time.

The results of this second attempt at GC/MS were much clearer. The largest peaks were column bleed, but were clearly identified as such. Several new chlorinated compounds were detected. The relationship between the MS and ECD peak times was determined with the help of standards. Plotting MS elution time against ECD elution time revealed that the relationship could be described by two linear equations: the first applicable up to 5.6 minutes on the ECD axis, and the second applicable after this time. This enabled the prediction of expected MS peak times for given ECD peak times. Using these predictions as a guide, and trial and error, various attempts at matching up the peak times were made. These correlations were assessed by plotting them as two linear series until a good match was found. See appendix 7B for these correlations; agreement is good in the final iteration.

Most of the peaks in the GC/ECD were identified/confirmed by these experiments. Ideally, more standards should have been injected to cross check these conclusions. However, the GC/MS with the BPX5 column only became available during the write-up phase, and further investigation wasn’t possible.

Not all of the products identified in the first phase of GC/MS were confirmed in these experiments. This means that they were either misidentified initially, or the products of the plasma were slightly different in the two sets of experiments. Either explanation is plausible, but given the variable nature of the experiments and the fact that different plasma rigs were used, it is likely that most of the products identified in both GC/MS attempts were formed in the plasma under some conditions. In fact this
highlights the unpredictable nature of combustion, a factor that must be considered in its assessment as a waste treater.

The results of these experiments can be found in table 7.6, Section 7.4.7.

7.4.5 Injection of scrubbed samples

7.4.5.1 Introduction

Some of the experiments were sampled with a 50 ml gas-tight syringe containing 15 ml of distilled water, scrubbing the gas of water-soluble products before being injected into the GC. The comparison of these chromatograms with those from un-scrubbed plasma off-gas injections provided useful information when confirming the identity of peaks. Reduction or elimination of peak area by scrubbing may indicate that the eluted compound is soluble in water to some extent, or may indicate that the peak was eluted as a result of column attack by an acidic gas that is soluble in water.

7.4.5.2 Sampling technique

An extra step was added to the sampling process in order to scrub the plasma off-gas. This may have diluted the sample. Also, if any compounds were condensed on the sides of the syringe, this effect would be decreased in the large syringe. Therefore, the effect of using the large syringe as an intermediate with no water, rather than sampling directly from the plasma, was tested. This was done by comparing peak areas attained from identical plasma runs (6 % TCE, 6 l/min) by the normal sampling method with those attained by sampling the plasma with a dry 50 ml syringe, from which the 100 µl sample was then taken. The statistical analysis described in section 7.3 was carried out on the results of these experiments. The ratios of the peak areas detected in the normal sample to those of the headspace sample were also calculated. These results are shown in table 7.4. If the two sets of data are assumed to be one series, the standard deviation of the normalised averages is 0.8, while considered separately each data set had a standard deviation of half that value. This suggests that the two sets of data are in fact two distinct series. However, since the standard deviation of the normalised averages of all of the experiments carried out during the project is 1, this is not conclusive. The peak areas resulting from the normal sampling technique are on average 1.5 times larger than those from the indirect sampling
technique. However, the standard deviation of these area ratios is roughly the same, and so this is probably not statistically significant.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio (Normal/Headspace)</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Ratio (Normal/Headspace)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Both methods</td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>Normal sampling (from flame)</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Indirect sampling (from 50ml syringe)</td>
<td></td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 7.4: Results of analysis of dry sampling comparison

Therefore, it is concluded that the sampling method may dilute the sample slightly, but any peak reduction of more than 3 times cannot be accounted for by the different sampling technique.

The time between sampling and injection was varied between a few seconds and three hours, and found to have no effect on the peak areas attained.

7.4.5.3 Results of peak solubility experiments

The results were not clear-cut in many cases. Some of the peaks were completely removed by scrubbing the sample before injection. Most of them were reduced to some extent. Graphs of the scrubbed and dry sample peak sizes were plotted and used to estimate the peak reduction caused by scrubbing. Since this was very variable, peaks were put into generalised categories of no reduction (0 %), moderate reduction (66 – 80 %), large reduction (81 – 99 %) and total reduction (100 %) of peak area by scrubbing. Of the peaks that were reduced, all were reduced by at least three times. Therefore, any peak reduction was due to scrubbing and not the different sampling technique. The results were added to the other information that has been gathered in table 7.6. Table 7.6 and a discussion of the reasoning behind the final identities assigned to the peaks are presented in section 7.3.6.

As stated at the beginning of this section, peak reduction by scrubbing may indicate that the eluted compound is soluble or partially soluble in water; it may also indicate that the peak was eluted as a result of column attack by an acidic gas that is soluble or partially soluble in water. In general, the peaks suspected to be reduced or completely removed were nitrogen oxides, oxygenated organics (such as phosgene COCl₂) and
column attack products. Most of the results were consistent with the suspected identities of the eluted compounds. Some were very useful in confirming or eliminating suspected identities.

For instance, the peaks eluted at 5.9 and 20.1 minutes were not affected by scrubbing. This puts the GC/MS identification of the 5.9 minutes peak as chloroacetic acid in extreme doubt as it is completely soluble in water. HCB would elute at 20.1 minutes and was detected in the first phase of GC/MS analysis. A small peak has eluted at that time throughout the experiments. However, it was suspected to be column bleed as no HCB was found in the solid samples (see section 5.7) or the second gas phase GC/MS. This new information may suggest that some HCB was in fact eluted. Conversely, the peak suspected to be C₆H₂Cl₄ was completely removed by scrubbing, which means that it is more consistent with column bleed.

7.4.6 Effect of acidic/oxidative attack on column

7.4.6.1 Introduction

Some experiments were done to determine which peaks were column or septum breakdown products. The gases that are suspected of being responsible for column attack are HCl and Cl₂. The chemical modelling predicts the formation of these two gases in the plasma to the order of several percent. The model predicts that the only other oxidative species present above 10⁻⁹ levels are the radical ClCO (which is unlikely) and COCl₂. However, these were only expected to be present at around parts per million levels and so are not likely to contribute towards oxidative breakdown of the column.

7.4.6.2 Hydrogen chloride (HCl)

The propane-assisted plasma and bunsen burner experiments are expected to yield the most HCl. Equation 7.2 below shows the desired stoichiometry for these experiments.

\[ 4C₂HCl₃ + 11O₂ + C₃H₈ = 12HCl + 11CO₂ \]  \hspace{1cm} (7.2)

Therefore, since the maximum TCE input is 6 %, 18 % is the maximum output of HCl.
Headspace was taken from a small vial of concentrated hydrochloric acid (37 %). The same sample size and split ratio as in the experiments were used for the GC injection. The vapour pressure of concentrated HCl is 100 kPa (Stull 1947). This injection was therefore equivalent to at least five times more than the amount that could be injected in the TCE destruction experiments.

Figure 7.4 compares the GC peaks resulting from this HCl headspace injection with those from a 6 % TCE plasma destruction run using the copper chimney. Results were similar for the Pyrex chimney experiments (see appendix 7C). The copper chimney did react with some of the gases, however, and so peaks were generally larger in the Pyrex chimney experiments. These may not all have been column attack peaks, as products like chloromethane (CH₃Cl) may have reacted with the copper chimney (see section 7.5).

Figure 7.4: Chart comparing peaks found in plasma (copper chimney, 6 % TCE, 8 l/min) with HCl injection products

Figure 7.4 shows that although the chromatograms do have some peaks in common, the peaks in the plasma are much larger and therefore could not be the result of HCl column attack alone. The peaks that they do share (4.66 and 6.4 minutes peaks) were also smaller in the experiments with added propane, further supporting the argument
that those peaks are not primarily caused by HCl attack. For an example of this see figure 7.5.

![Graph](image)

Figure 7.5: Formation of 4.66 minutes peak at 10 lmin⁻¹

The largest peak found in the HCl headspace chromatogram was at 2.15 minutes and not present in the plasma chromatograms. It is suspected that this is actually the HCl peak and that the lower concentration of HCl in the plasma injections was not sufficient to register a response on the ECD detector.

7.4.6.3 Chlorine (Cl₂)

Maximum Cl₂ production was expected when no hydrogen was added to the plasma. In this case the overall reaction could be as in equation 7.3.

\[
C_2HCl_3 + 2O_2 = HCl + Cl_2 + 2CO_2 \]  \hspace{1cm} (7.3)

This means that the maximum amount of Cl₂ formed in the experiments is 1 mole for every mole of TCE destroyed, i.e. 6 %.

Cl₂ was produced by adding a few drops of concentrated HCl to bleach (containing 42 gl⁻¹ sodium hypochlorite, NaOCl) in a small container. The reaction vigorously produced a greenish gas and it was assumed that the headspace in the container
contained approximately 100 % Cl₂. Therefore, injections of approximately 1 % and
10 % Cl₂ were made, again using the same sample volume and split ratio as in the
TCE destruction experiments. Figure 7.6 compares the peaks in these chromatograms
with those from the destruction of 6 % TCE at 8 lmin⁻¹. Results were similar in the
Pyrex chimney experiments (see appendix 7C).

Figure 7.6: Chart comparing peaks found in plasma with “bleach gas” injection
products

Peak 4.66, the largest peak found in the plasma experiments, is identical to the 4.66
minutes peak resulting from the injection of 10 % Cl₂. However, there were very
large peaks formed at 10.1 and 13.2 minutes in the Cl₂ injections. Although these
peaks did feature in the TCE destruction chromatograms, they were an order of
magnitude smaller than those shown in figure 7.6. It is suspected that these peaks
were caused by other oxidative species present in the “bleach gas”. Ozone (O₃), for
instance is highly oxidising and would be expected to attack the column more
vigorously than Cl₂. Unfortunately, the formation of these unwanted species means
that the quantity of Cl₂ injected cannot be derived from these experiments. However,
it is assumed that the “bleach gas” contains at least 50 % Cl₂ and so the 10 % “bleach
gas” injection was equivalent to an injection of 5 – 10 % Cl₂. This peak was about the
same size as the 6 % TCE plasma peak at the same time. Since the plasma runs are
expected to contain about 6% Cl₂, these experiments are consistent with Cl₂ being the main contributor to column and septum breakdown products.

### 7.4.7 Overall Results and Conclusions

Table 7.6 shows the results of the peak identification process.

<table>
<thead>
<tr>
<th>Elution time (mins)</th>
<th>Suspected Compound</th>
<th>Confidence in identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.26</td>
<td>Phosgene (COCl₂)</td>
<td>Reasonable</td>
</tr>
<tr>
<td>2.32</td>
<td>Nitric oxide (NO)</td>
<td>Good</td>
</tr>
<tr>
<td>2.4</td>
<td>Methyl chloride (MC)</td>
<td>Present but not sure when eluted</td>
</tr>
<tr>
<td>3.95</td>
<td>Chloroform (CHCl₃)/Acid attack</td>
<td>Low</td>
</tr>
<tr>
<td>4</td>
<td>Chlorinated hydrocarbon</td>
<td>MS only</td>
</tr>
<tr>
<td>4.4</td>
<td>Carbon tetrachloride (CCl₄)/Acid attack</td>
<td>Reasonable</td>
</tr>
<tr>
<td>5.2</td>
<td>Chloromethylbutene (C₅H₉Cl)</td>
<td>MS only</td>
</tr>
<tr>
<td>5.8</td>
<td>TCE (C₂HCl₃)</td>
<td>Good</td>
</tr>
<tr>
<td>8.6</td>
<td>Tetrachloroethene (C₂Cl₄)</td>
<td>Reasonable</td>
</tr>
<tr>
<td>10.5</td>
<td>Chlorinated, oxygenated hydrocarbon</td>
<td>MS only</td>
</tr>
<tr>
<td>12.8</td>
<td>Furan</td>
<td>MS only</td>
</tr>
<tr>
<td>20.1</td>
<td>Hexachlorobenzene (C₆Cl₆)</td>
<td>Reasonable</td>
</tr>
</tbody>
</table>

Table 7.6: Overall peak identification

The main products are concluded to be: HCl, Cl₂, COCl₂, NO, CCl₄ and C₂Cl₄.

Phosgene was difficult to locate on the ECD chromatograms as there was no standard for phosgene available. It is also difficult to get good chromatography for peaks that elute so early in the temperature program. However, as phosgene is a major product of atmospheric TCE and it also featured in the kinetic modelling, it is very likely that it was present in the plasma products. The peak was located by correlation of the MS times with the ECD times as explained in section 7.4.4. The peak displayed a normal distribution and high solubility in water, which are both arguments for its identification as phosgene.

Some peaks, eluting at 2.29, 2.32 and 2.5 minutes were present in experiments with no added TCE. These peaks were identified as nitrogen oxides. The only major and persistent peak of these three was 2.32. This is likely to be NO, as indicated by the
kinetic modelling (see section 6.3.6). Nitrosyl chloride (NOCl) may be present in low concentrations.

Methyl chloride was clearly identified by GC/MS. However, the low response of the ECD to methyl chloride meant that standard injection resulted in small broad peaks with ill-defined elution times. The ECD standard injection resulted in an elution time of 2.4 minutes, while the MS correlation suggested it may be eluted slightly later. There are several peaks around that time that are possible candidates.

C₂Cl₄ is another likely product. Although there is some column bleed confusing identification, the 8.6 minutes peak was not removed by scrubbing and so is probably C₂Cl₄.

The formation of chlorinated aromatics and cyclics is crucial to this project but difficult to detect as the later sections of the chromatograms were seriously affected by column attack. Standards were used to find expected elution times after finding C₆H₅Cl and HCB in the first phase phase of GC/MS. C₆H₂Cl₄ and dichlorofuranione (C₄Cl₂O₃) were detected in the second phase of GC/MS. All of these compounds appeared to be present in the ECD chromatograms. However, their formation did not seem regular and appeared more likely to be the product of column attack than plasma products. As stated in section 5.4.5, scrubbing the samples shed new light onto this subject. The suspected C₆H₅Cl and C₆H₂Cl₄ peaks really do appear to be column attack products. However, the 20.1 peak was not removed by scrubbing and so may be HCB. It is possible that the irregularities were caused by HCB’s low vapour pressure, which contaminated the syringe and rig for several runs after its formation. The possible dichlorofuranone peak is soluble in water, which is consistent with its structure. However, since no other dioxins and furans were detected in any of the experimental runs, and the chemical modelling does not predict significant formation of their precursors, the presence of this furan seems unlikely. Although the MS identification may not be precise, it does indicate with reasonable certainty that the eluted compound is a chlorinated, oxygenated, cyclic hydrocarbon. It is concluded from this information that some chlorinated aromatics, including HCB, are formed during this process. However, the concentrations of these compounds formed are
very low and variable. Their low vapour pressure makes quantification in the gas phase impossible.

7.5 Solid residue formation

7.5.1 Introduction/Importance

As explained in section 7.2, various residues were formed in the rig and chimney throughout the experiments. There were more formed during the plasma experiments than the burner runs. Identification of these solids is vital as many of the potential aromatic by-products, such as HCB, have low vapour pressures. Therefore, if they were formed in the plasma, a significant proportion may be deposited in the solid phase.

It was suspected that most of the solids formed were products of acidic gases attacking the metal surfaces present (i.e. aluminium and copper). However, since even small concentrations of chlorinated aromatics are relevant to the results, a thorough investigation of these solids was undertaken.

7.5.2 Description

Green, yellow, brown, red, black, white and grey residues were found in various parts of the rig. The grey residues were usually a thin layer of fluffy crystals in the sides of the reactor; the others ranged from dry powder to oily liquid depending on the temperature, humidity and time after formation. See figure 7.7 for some photos of the residues found inside the reactor lid (a and b) and in the reactor sides and Teflon base (c). The mass of residue formed decreased with increasing flow rate.
All residues formed were found to be partially soluble in water and insoluble in TCE, suggesting that they were predominantly inorganic. The residue in the copper chimney appeared to melt when the chimney reached about 170°C.

Figure 7.7a

Figure 7.7b

Figure 7.7c

Figure 7.7: Residues formed in the aluminium plasma reactor

a. Red (dry) and grey (wet and blistered) deposits and some pitting in aluminium surface
b. Red/brown deposits and pitting
c. Green and white solid/ green liquid (runs down from chimney) and grey crystals formed on sides (see jet marks from gas inlets)
7.5.3 Atomic Absorption Spectroscopy

The residues formed in the preliminary plasma reactor were analysed using atomic absorption spectroscopy at Industrial Sciences, Swinburne University. This reactor was made from brass with a stainless steel lid and the chimney was copper, and so the major ions expected were copper (Cu), zinc (Zn) and iron (Fe). The minimum and maximum amounts of various metal ions are shown in table 7.7.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Minimum % Metal Chloride</th>
<th>Maximum % Metal Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>58</td>
<td>79</td>
</tr>
<tr>
<td>Copper</td>
<td>18</td>
<td>53</td>
</tr>
<tr>
<td>Nickel</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Iron</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>79</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

Table 7.7: Metal ions found in solid residue

Therefore, the maximum metal chloride concentration in residue was 100 % and the minimum was 79 %. Therefore, it is possible that up to 21 % of the solid being formed was organic.

7.5.4 Mass formation (solid)

The mass formed in the experiments was reasonably unpredictable and impossible to measure exactly. However, some experiments were done to estimate the mass formation rates in the preliminary plasma reactor. This was done by running each TCE inlet concentration for 10 minutes and then wiping off the residue with tissue paper and measuring the change in mass of the paper before and after wiping. The results of these experiments are shown in figure 7.8.
Figure 7.8 is not conclusive. However, most of the points suggest that a linear relationship between the mass formation rate and inlet TCE concentration. If this is the case, the anomalies are at 0.1 and 2 % TCE. These are both higher than expected.

Experiments also revealed that the mass of residue formed was up to 50 % of the mass of TCE treated in the reactor.

7.5.5 External Analysis

Some of the solid formed during the aluminium plasma rig experiments was analysed by Anexus, a chemical analysis laboratory. Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) was used to determine the quantities of specific metallic elements. X-ray diffraction (XRD) was then used to identify the organic components in the sample. Nuclear Magnetic Resonance (NMR) was used to identify organic components (above 1 % w/w). The solid was also heated on a hot plate to verify physical properties.

The ICP-AES showed that 56.0 % of the sample was copper and 3.05 % was zinc. Aluminium and iron were also detected, but below 0.1 % levels. The reason these ratios differ from the original atomic absorption results, is that the reactor materials
were different (the final rig is aluminium rather than brass and steel). The XRD results are shown in table 7.8.

<table>
<thead>
<tr>
<th>Compound detected</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl (copper I chloride)</td>
<td>Major</td>
</tr>
<tr>
<td>Cu(OH)Cl (Belloite)</td>
<td>~ 2 – 3 %</td>
</tr>
<tr>
<td>Unidentified crystalline</td>
<td>&lt;2 %</td>
</tr>
<tr>
<td>Amorphous</td>
<td>Minor</td>
</tr>
</tbody>
</table>

Table 7.8: Results of the XRD analysis

Very small amounts of organic material were detected by NMR. These were consistent with highly branched hydrocarbons. Trace levels of aromatic compounds were also detected.

Using these results, the composition can be estimated. Using the results from the ICP and XRD analyses, and assuming that CuCl and Cu(OH)Cl are the only copper compounds present, the inorganic composition was estimated (appendix 7D). CuCl makes up for about 85% of the residue and zinc chloride (ZnCl₂) accounts for just over 6%. With 2 –3% Cu(OH)Cl, the total inorganic content is about 94%. This means that up to 6% of the residue formed may be organic. However, small amounts of water and hydrochloric acid were also suspected to be present in the sample.

7.5.6 Chemistry

Copper (I) chloride (CuCl, cuprous chloride) is a white/grey solid that turns green in moist air, brown in sunlight, and melts between 415°C and 422°C (Mallinckrodt Baker 2004; Parkes and Mellor 1939).

The solid formed in the chimney had become molten well below 200°C. The hot plate test revealed that although the green and white solid dried out and became dark brown/purple on heating, no melting occurred below 300°C. Hydrochloric acid (HCl) can react with CuCl to give chloro-cuprous acid (H₂Cu₂Cl₄) as in equation 7.4 (Parkes and Mellor 1939).

\[
2\text{CuCl} + 2\text{HCl} = \text{H}_2\text{Cu}_2\text{Cl}_4
\] (7.4)
The apparent phase change in the chimney was probably caused by this reaction after the initial formation of CuCl. Presumably, the transition on the hot plate was caused by the reaction being reversed on heating, to release HCl. The presence of small amounts of hydrocarbons may have enabled the apparent waxiness above certain temperatures.

In general, acids do not react with copper, as hydrogen is below copper in the electrochemical series. However, a reaction is possible if the acid is an oxidising agent or forms complex ions with copper (Parkes and Mellor 1939). Cl₂, chloric (I) and (IV) acids (HClO and HClO₃), and COCl₂ are oxidising agents, and so were probably responsible for the attack on copper to produce CuCl. The absence of copper nitrate (Cu(NO₃)₂) in the solid analysis rules out the presence of nitric acid in the off-gas.

Two plausible mechanisms for copper reacting to form copper (I) chloride (National Institute of Standards and Technology 2000) are reaction with chlorine gas and reaction with chloromethane.

\[
\text{Cu}(s) + \text{Cl}_2(g) \rightarrow \text{CuCl}(s) + \text{Cl}^- \tag{7.5}
\]

\[
\text{CH}_3\text{Cl}(g) + \text{Cu}(s) \rightarrow \cdot\text{CH}_3^+ + \text{CuCl} \tag{7.6}
\]

The reaction of HCl with copper to give “products” is also listed in the NIST Chemical Kinetic Database, so HCl may also play a role in the initial attack.

**7.5.6 Pyrex Chimney**

The Pyrex chimney was introduced to minimise the formation of inorganic residue so that the organic residue formation could be investigated. The amount of residue formed was greatly reduced, but not eliminated. A thin layer of white/yellow solid gradually appeared on the inside of the chimney over the duration of several runs (about a hour of operation). It did not appear to melt or change in any way throughout the run cycle.
Acetone was swirled around the inside of the chimney to dissolve some of the solid into solution for GC/MS injection. A straw coloured solution resulted. No chlorinated aromatics were found in the GC/MS chromatogram. The only compound that was detected in the sample that was not found in the blank was a small amount of chlorobutanol (peak area 3.5 kCounts). The solid dissolved more readily in concentrated hydrochloric acid (HCl\(_{\text{aq}}\)) to give a yellow solution.

These results suggest that this residue is mainly inorganic, probably aluminium chloride (Al\(_2\)Cl\(_6\)). The absence of chlorinated aromatics in the solid phase suggests that they are also absent in the gas phase.
8. RESULTS QUANTIFICATION AND VERIFICATION .............................................. 135

8.1 Abstract ........................................................................................................... 136

8.2 Introduction ...................................................................................................... 136

8.3 Destruction and Removal Efficiencies (DREs) .............................................. 137

8.4 By-product formation (gas phase) ................................................................. 142
   8.4.1 Nitric oxide (NO) formation .................................................................... 142
   8.4.2 Phosgene (COCl₂) Formation ................................................................. 145
   8.4.3 Carbon tetrachloride (CCl₄) formation .................................................. 147
   8.4.4 Tetrachloroethene (C₂Cl₄) formation ...................................................... 150

8.5 Conclusions ...................................................................................................... 152
8. Results quantification and verification

8.1 Abstract

An attempt to quantify the experimental results and compare them with the chemical modelling is made in this chapter.

TCE destruction of 4 – 5 nines’ DRE was measured for all three TCE destruction methods. The Bunsen burner could treat concentrations up to 3 % TCE, while the plasmas could treat TCE up to its saturated vapour pressure. The model predicted the maximum TCE concentration treatable by the Bunsen would be about 1.5 %. Reactor temperature and quench were not found to have much effect on the DRE, except for anomalies at 1 % initial TCE for 8 and 10 lmin⁻¹.

As expected, a few percent of nitric oxide were formed in the air plasma. Phosgene appears to have been present at ppb(m) levels, which concurs with the model. Carbon tetrachloride was detected at ppb(m) levels, and was highest in propane plasma. The amounts of nitric oxide, phosgene and carbon tetrachloride formed were all anomalously low for an inlet TCE concentration of 3 %.

Parts per billion levels of tetrachloroethene were measured but results are not very consistent and do not agree with the model. This, and the presence of column bleed peaks in the vicinity, suggests that this peak may not in fact be tetrachloroethene.

Chlorinated aromatic formation is barely detectable in the experimental results and the model predicts mole fractions in the order of 10⁻¹¹. Therefore, chlorinated aromatic formation is not an issue.

8.2 Introduction

In this chapter, an attempt to compare the quantified experimental results with the kinetic modelling predictions is made.

It was established in chapter 7 that the column bleed was not quantifiable. Therefore, an overall chlorine balance on the experimental results is not possible. Several of the
peaks, especially early eluting ones, are not clearly identified. This makes comparison of the overall results (e.g. chlorinated aliphatic formation) with the modelling predictions difficult. However, the model predicted very low levels of chlorinated aliphatics (mainly oxygenated) and chlorinated aromatics; the experimental results are consistent with this. Unfortunately, the chlorinated aromatic formation, which was of particular interest, was too low to make comments on patterns and amounts. Carbon monoxide (CO) and carbon dioxide (CO$_2$) cannot be monitored with the electron capture detector. However, the modelling indicates a few percent of CO should be formed in the Bunsen flame, with hardly any in the plasmas.

In addition, some of the variants in the experimental system (flow rate and applied power) cannot be directly converted into modelling parameters (quench rate and plasma temperature). Increasing the flow rate may affect the quench rate (by an unknown amount) and decreases the plasma temperature (by a maximum of 1,000 K). Increasing the applied power may increase the plasma temperature slightly. Unfortunately, there was no quench control in the laboratory system. Therefore, the equipment, including the exhaust pipe, got hotter in the higher power experiments, while the reactor temperature also increased. This means that the quench rate may have varied with increasing power. It should also be noted that the residence times in the microwave reactor are different from those in the Bunsen burner, and may contribute to any variation in results.

Compounds that have been quantified are nitric oxide (NO), phosgene (COCl$_2$), carbon tetrachloride (CCl$_4$) and tetrachloroethene (C$_2$Cl$_4$).

8.3 Destruction and Removal Efficiencies (DREs)

The Destruction and Removal Efficiency (DRE) is the standard measure of how effective a process is at reducing pollution and is the percentage of the compound in question that has been destroyed or removed from the atmosphere. It is usually presented on the logarithmic scale, such that rather than percentage, the “number of nines” removal is quoted. For example, “1 nine” is 90 % and “4 nines” are 99.99 % destruction and removal. Equation 8.1 shows the DRE in relation to R, the fraction of the target compound that remains in the treated stream.
The minimum chromatogram peak area accepted in the GC/ECD analysis was 5,000 area counts. This corresponds with 1 ppb by mass (1 µg/l) of trichloroethene (TCE) under the usual GC injection conditions (split ratio of 20 and injection size of 100 µl). The limit of detection of TCE under normal injection conditions is therefore 1 ppb(m), and the maximum measurable DRE varies from 4.8 nines (99.9983 % for 1 % TCE in) to 5.5 nines (99.9997 % for 6 % TCE in). Some experiments were carried out at lower split ratios, enabling lower limits of detection and more precise DRE measurement. However, all results below the threshold peak area of 5,000 are reported as having achieved 5 nines destruction. It is likely that even higher destruction was achieved under some conditions.

Figure 8.1 shows the TCE DRE achieved using various destruction methods (see legend) in order of decreasing hydrogen input. It shows that all methods are efficient at TCE destruction, with just under four nines being the lowest DRE. There is no clear relationship between hydrogen provision and DRE.

Figure 8.1 does not agree with the kinetic modelling predictions. Virtually no destruction was expected in the Bunsen burner with virtually complete destruction in the air plasma. Although the TCE concentration in the air plasma is approaching the limit of detection, the Bunsen results strongly disagree with the predictions.

The kinetic modelling was done on a PC and so the complexity of the problem had to be limited to enable successful computation. One assumption that was made was that the propane added to the model was immediately oxidised to CO₂ and water (H₂O). This assumption was valid in the plasma since the very fast kinetics brought the system to equilibrium virtually instantaneously, and the starting products were therefore irrelevant; only the starting composition was relevant. However, the kinetics in the Bunsen flame were slower and the formation of radicals such as OH from the reaction of propane and oxygen may have been relevant. Also, the modelling suggested that chlorinated hydrocarbons may react preferentially to non-
chlorinated ones (appendix 6D, section 3.1). Therefore, complete combustion of propane may have been suppressed in favour of TCE dissociation.

![Figure 8.1: Destruction and removal efficiencies of various TCE destruction methods](image)

Figure 8.1: Destruction and removal efficiencies of various TCE destruction methods (conditions: 10 lmin⁻¹, 3 % TCE in, plasma power 2 kW)

<table>
<thead>
<tr>
<th>No.</th>
<th>Run</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Propane Burner</td>
<td>Rich</td>
</tr>
<tr>
<td>2</td>
<td>Propane Plasma</td>
<td>Rich</td>
</tr>
<tr>
<td>3</td>
<td>Propane Plasma</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>4</td>
<td>Propane Plasma</td>
<td>Lean</td>
</tr>
<tr>
<td>5</td>
<td>Dry Air Plasma, copper chimney</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>Dry Air Plasma, Pyrex chimney</td>
<td>None</td>
</tr>
</tbody>
</table>

Legend for figure 8.1

Figure 8.2 shows the DRE with increasing effluent TCE concentration for the dry air plasma and the Bunsen burner. Again, the Bunsen burner seems to perform better than expected, while the plasma performance is slightly disappointing. Above 3 % TCE, the performance of the burner drops off. This was expected to happen above 1.4 %. As predicted, the plasma can treat all experimental TCE concentrations.
Figure 8.2: TCE Destruction and Removal Efficiency at 10 lmin\(^{-1}\)

Figure 8.3 suggests that the final concentration of TCE in the air plasma is independent of flow rate and, largely, treated TCE concentration. An exception to this was seen in the treatment of 8 – 10 lmin\(^{-1}\) of 1 % TCE, where higher than expected levels were observed. The kinetic modelling predicted peaks in the outlet TCE concentration at 1 and 2 % TCE in, and these two concentrations do dominate figure 8.3, contrary to intuition. Varying the flow rate affects the quench rate (increases with flow rate) and the plasma temperature (decreases with flow rate). The modelling predicts a slight peak in the DRE at around 5,200 K. The peak seen in figure 8.3 is below 4,400 K and possibly unrelated to plasma temperature. The quench modelling does not explain this peak either. Modelling TCE concentrations between 1 and 2 % may throw some light on this subject.

Also note from figure 8.3 that the TCE concentration in the outlet stream varies from 1 – 500 ppb(m), and the modelling predicted an absolute maximum of 1 ppm(m).
Figure 8.3: Final concentration of TCE in 2 kW dry plasma experiments, with temperatures estimated for 2% in air plasma.

Figure 8.4 shows the effect of power on DRE. This slight improvement in DRE with increasing temperature agrees with the modelling. However, since this trend was not seen across a larger temperature range in figure 8.3, this apparent increase in destruction with power is probably not due to reactor temperature changes, and may even be caused by experimental error.
8.4 By-product formation (gas phase)

8.4.1 Nitric oxide (NO) formation

The response of the NO peak can only be estimated by comparing the maximum concentration predicted by the modelling with the largest peaks eluted in the experiments.

The maximum NO concentration predicted in the kinetic modelling is 2.5 %. The largest corrected NO peak (peak area x split ratio/injection size) was about 250,000. Therefore, the factor of 100,000 corrected area counts per percent of NO was used to estimate the amount of NO produced.

Figure 8.5 compares the amount of NO formed during the different TCE destruction experiments. It shows that adding propane to the plasma does eliminate NO production, and that the amount predicted (sufficient for total conversion of chlorine from TCE to hydrogen chloride (HCl), rather than chlorine (Cl₂)). The reason for the difference in results between the copper and Pyrex chimneys is unknown. Possibly the NO reacted with the large amounts of copper chloride formed in the chimney, or
the copper/copper chloride inhibited NO formation in some way. Using humid rather that dry air in the plasma halved NO production. Therefore, providing hydrogen through propane rather than air humidity is more effective in terms of nitrogen oxide (NOx) formation control.

Figure 8.5: Estimation of percent of NO formed during various TCE destruction methods (for 10 lmin⁻¹ containing 3 % TCE)

<table>
<thead>
<tr>
<th>No.</th>
<th>Run</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Propane Burner</td>
<td>Rich</td>
</tr>
<tr>
<td>2</td>
<td>Propane Plasma</td>
<td>Rich</td>
</tr>
<tr>
<td>3</td>
<td>Propane Plasma</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>4</td>
<td>Propane Plasma</td>
<td>Lean</td>
</tr>
<tr>
<td>5</td>
<td>Dry Air Plasma, copper chimney</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>Dry Air Plasma, Pyrex chimney</td>
<td>None</td>
</tr>
</tbody>
</table>

Legend for figure 8.5

Figure 8.6 shows the formation of NO against inlet TCE concentration. No NO is formed in the Bunsen burner at all. NO formation in the air plasma increases with inlet TCE concentration, with a dramatic dip at 3 % TCE. Modelling predicted that increasing the TCE concentration would decrease NO production. This difference may be explained by the fact that reactor temperature increases with TCE concentration, and NO formation increases with temperature.
Figure 8.6: Formation of NO at 10 lmin⁻¹

Figure 8.7 shows a general increase in NO formation with flow rate. The modelling suggested that reducing the quench would reduce NO formation, and this may explain the trend in figure 8.7. A more satisfactory explanation is that EQUIL predicts a fall in NO production above 4,000 K, which may be achieved at the minimum flow rate. The 3 % initial TCE stream points are abnormally low (as in figure 8.6), except for at 4 lmin⁻¹, which is higher than the other points and probably anomalous.

The relationship between power and NOₓ formation is unclear as NO formation was highest at the highest power, but lowest at the intermediate power. Therefore, NO production is assumed to be independent of incident power.
8.4.2 Phosgene (COCl₂) Formation

The concentration of COCl₂ in the experiments is estimated by assuming that the response factor of COCl₂ is half that of TCE. This is based purely on comparison with known response factors.

Up to 300 ppb(m) of COCl₂ were measured in the experimental effluents, while the model predicted well below ppb(m) levels for all experiments and conditions. Therefore, the estimated response factor could be out by a factor of several hundred, this product could be misidentified, or there is more COCl₂ formed that predicted.

There was no clear relationship between propane flow and COCl₂ production, with the most formed in the ‘stoichiometric’ propane plasma, and none in the Bunsen. The humidity of the air also had no effect on COCl₂ production.

Figure 8.8 shows COCl₂ production against initial TCE concentration. COCl₂ concentration initially increases with initial TCE concentration, and then seems to level out above 4 %. The 3 % anomaly is seen again in figure 8.8.
The modelling suggested that the COCl₂ concentration produced in both plasmas would increase with increasing quench rate. The flow rate experiments were not consistent enough to confirm this. Figure 8.9 shows that the amount of COCl₂ produced in the air plasma decreased with increasing power. Since plasma temperature was predicted to have no effect on COCl₂ production, this must be caused by the reduction of quench rate with increasing power.

Figure 8.8: Effect of TCE concentration on phosgene formation at 10 lmin⁻¹
8.4.3 Carbon tetrachloride (CCl₄) formation

Figure 8.10 shows that CCl₄ was detected at ppb(m) levels in all runs. There is no definite trend, although it may increase with decreasing addition of propane. The air humidity also had no clear effect.
Figure 8.10: Carbon tetrachloride formation for various TCE destruction methods
(conditions: 10 lmin⁻¹, 3 % TCE in, plasma power 2 kW)

<table>
<thead>
<tr>
<th>No.</th>
<th>Run</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Propane Burner</td>
<td>Rich</td>
</tr>
<tr>
<td>2</td>
<td>Propane Plasma</td>
<td>Rich</td>
</tr>
<tr>
<td>3</td>
<td>Propane Plasma</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>4</td>
<td>Propane Plasma</td>
<td>Lean</td>
</tr>
<tr>
<td>5</td>
<td>Dry Air Plasma, copper chimney</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>Dry Air Plasma, Pyrex chimney</td>
<td>None</td>
</tr>
</tbody>
</table>

Legend for figure 8.10

Figure 8.11 shows the kinetic modelling predictions for CCl₄ production. It agrees with the Bunsen burner measurement in figure 8.10. The air plasma and Bunsen measurements are lower than predicted. However, the general trend (of more formation in the plasmas than the Bunsen burner) is the same in both experiments and model. Please note that the electron capture detector has a very high response to CCl₄. The first calibration suggested that it was 25 times more responsive to CCl₄ than TCE. However, later on a response of 4 was measured, and used in the calculations. Therefore these figures may be 6 times too large and disagreement between experiments and model may be larger than calculated.
Figure 8.12 shows the measured CCl₄ production against initial TCE concentration. Whereas there is a dip in the model air plasma at 2 %, the experiments record a dip at 3 %. This may be the same dip, although the chemistry is unknown and may be related to the anomalous behaviour of the plasma around this concentration of TCE.

There is no clear relationship between CCl₄ production and flow rate, although there is an anomalous peak (higher than other runs) at 8 lmin⁻¹ for 3 % initial TCE.
8.4.4 Tetrachloroethene (C₂Cl₄) formation

Parts per thousand levels of C₂Cl₄ were expected in the Bunsen burner above 1 % initial TCE concentration. Virtually no C₂Cl₄ was predicted in either plasma. Figure 8.13 shows that the experimental results disagree with this. It is possible that the elution of several peaks around the same time has made the identification of this peak too difficult. In the 1 % TCE, 6 lmin⁻¹ plasma, the humid run had virtually no C₂Cl₄ (less than 1 ppb(m)), while the dry run contained about 50 ppb(m).
Figure 8.13: Formation of tetrachloroethene in various TCE destruction experiments

<table>
<thead>
<tr>
<th>No.</th>
<th>Run</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Propane Burner</td>
<td>Rich</td>
</tr>
<tr>
<td>2</td>
<td>Propane Plasma</td>
<td>Rich</td>
</tr>
<tr>
<td>3</td>
<td>Propane Plasma</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>4</td>
<td>Propane Plasma</td>
<td>Lean</td>
</tr>
<tr>
<td>5</td>
<td>Dry Air Plasma, copper chimney</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>Dry Air Plasma, Pyrex chimney</td>
<td>None</td>
</tr>
</tbody>
</table>

Legend for figure 8.13

Hardly any (up to 2 ppb(m)) C₂Cl₄ was detected in the Bunsen burner runs, even at high TCE concentrations. The dry air plasma produced similar levels until the initial TCE concentration reached 5 %, when it increased to 20 – 50 ppb/m. This is consistent with this peak being column bleed, a possibility that should be considered.

Figure 8.14 shows the C₂Cl₄ formation in the air plasma with varying flow rate.
It appears C$_2$Cl$_4$ may be minimised at 6 lmin$^{-1}$. If this is actually happening, it is probably caused by the change in quench rate caused by changing the flow rate. However, the modelling does not predict formation above a mole fraction of $10^{-20}$ in the air plasma, i.e. below the absolute tolerance of the model.

### 8.5 Conclusions

TCE destruction of 4 – 5 nines DRE was measured for all three TCE destruction methods. The Bunsen burner produces higher DREs than the plasma methods up to 3 % TCE (subject to experimental error). The plasmas provide higher DREs above 3 % (up to its saturated vapour pressure). The model predicted the maximum TCE concentration treatable by the Bunsen would be about 1.5 %. Reactor temperature and quench were not found to have much effect on the DRE, except for anomalies at 1 % initial TCE for 8 and 10 lmin$^{-1}$.

As expected, a few percent of NO were formed in the air plasma. However, its mole fraction increased with TCE, contrary to expectations. This may be due to the fact that the plasma temperature increases with increasing TCE inlet concentration. Reducing the quench rate reduced NO formation.
COCl₂ is estimated to have been present at ppb levels, which was slightly lower than predicted by the model. As predicted, it increased with increasing quench and TCE concentration.

CCl₄ was detected at ppb levels, and was highest in propane plasma.

The amounts of nitric oxide, COCl₂ and CCl₄ formed are all anomalously low for 3 % initial TCE.

Parts per billion levels of C₂Cl₄ were measured but results are not very consistent and do not agree with the model. This, and the presence of column bleed peaks in the vicinity, suggests that this peak may not in fact be C₂Cl₄.

Chlorinated aromatic formation is barely detectable in the experimental results and the model predicts mole fractions in the order of 10⁻¹¹. Therefore, chlorinated aromatic formation is not an issue.

Further results can be found in appendix 8A.
9. Environmental and economic assessment

9.1 Abstract

Effective treatment of all possible trichloroethene (TCE) concentrations (up to about 8 % TCE) was achieved in both the air and propane plasmas (at least 4 nines’ destruction). The propane flame was only effective below a TCE concentration of 1.4 % (according to the model) and 3 % (according to the experiments). Adsorption processes are also limited to solvent concentrations of about 1 %. Therefore, contaminated streams would have to be diluted with excess air to enable treatment by gas burner or adsorption.

A scrubber would be required to remove acidic gases (mainly chlorine and hydrogen chloride) from all three dissociation processes. The scrubber off-gas would contain very low levels (up to parts per million) of chlorinated organics (possibly including aromatics). Nitric oxide (a few percent) would be produced in both plasma systems, and carbon monoxide (a few percent) would be produced in the conventional combustion chamber.

The destruction processes (especially the plasma processes) reduce the ozone creation potential of the effluents by 1,000 to 10,000 times. They do produce a small amount of ozone depleting chemicals, however. There is no significant impact on global warming potential of the effluent. The destruction processes significantly reduce the chronic health effects of the effluent. Acute health effects are harder to assess, but are estimated to be similar for the destruction processes and release of untreated solvent, but reduced by the techniques that involve solvent recovery.

In terms of cost, direct emission to the environment is the cheapest option, closely followed by condensation and the methane burner (methane would be used rather than propane for economic reasons). Therefore, it is concluded that if the current regulatory situation persists, no control beyond room temperature cooling is indicated. If TCE prices increase by 100 % or more, condensation will become the cheapest option. If regulation becomes significantly more stringent, a methane burner will be the cheapest way of complying. However, if TCE price increases and regulation
becomes more stringent, a below-freezing condenser followed by a methane burner will be indicated. Plasma treatment is not indicated, as better performance can be attained with a methane burner for 50% of the cost.

9.2 Introduction

This project has investigated three potential trichloroethene (TCE) destruction processes: microwave plasma, gas-assisted microwave plasma and gas burner. This chapter assesses these processes in terms of environmental and economic cost. It also compares them with currently available control processes and emission of uncontrolled TCE to the atmosphere. Although there are many different techniques available, adsorption and condensation are the only ones that are currently used to control emissions from vapour degreasing processes. Alternative solvents are available and were discussed in section 3.4.1. However, they are not suitable for all applications, cannot be retrofitted and are typically very energy intensive. Environmental and economic assessment of alternative solvents would have to be made on a case-by-case basis.

The emphasis of this assessment has been on the overall robustness of the process. Vapour degreasing is usually a low-tech, low-investment operation with one minimally-trained operator. The machine must be simple to operate and completely self-regulating. Therefore, the allowable range of trichloroethene concentrations, quench rates, reactor powers, etc. must be defined. The potential consequences of running off-specification must be known for a proper assessment of this process.

9.4 Assessment of process

9.4.1 Overall process description

An 8 kW plasma reactor would be required to treat the 60 lmin⁻¹ effluent stream that was measured at HPM in Sydney. Both the air and propane plasmas were found capable of treating all feasible TCE concentrations (up to saturated vapour pressure of 6 – 8 %, depending on the air temperature). The flow rate is limited only by the power supplied and the size of the reactor. An automated, robust system could be engineered reasonably easily.
The gas (propane) flame was limited to concentrations up to about 1.4 % (lower than the typical 2 % TCE to be treated), and so the contaminated stream would have to diluted before treatment. The results of a fluctuation in TCE concentration above 1.4 % could lead to the production of significant concentrations of unwanted chlorinated organics. The conventional flame is therefore not as robust as the proposed plasma systems. The higher concentration of gas required may raise safety issues in terms of explosions, but would otherwise be a simple engineering challenge.

A scrubber would be required to remove acidic gases from the reactors’ effluent streams. Almost all of the TCE is converted into hydrogen chloride (HCl) and chlorine (Cl₂) in all three processes studied. The addition of gas (e.g. propane) provides hydrogen to suppress Cl₂ formation in favour of HCl formation. Since HCl is much more soluble in water than Cl₂, scrubber size would be largest in the case of the air plasma and smallest for the conventional gas flame (see table 9.3).

The scrubber effluent, in all three cases, would contain very low levels of chlorinated aliphatics, chlorinated oxygenated aliphatics (although phosgene would be scrubbed out) and possibly chlorinated aromatics. A few percent of nitric oxide (NO) would be produced in both plasmas (to a lesser extent in the gas-assisted plasma) and a few percent of carbon monoxide (CO) would be produced in the gas flame. The environmental impact of these products is assessed in section 9.4.3.

9.4.2 Destruction and Removal Efficiencies (DREs)

At least 4 nines’ destruction were achieved in the air and propane-assisted plasmas at all concentrations (up to 6 % TCE concentration). The air plasma achieved the best destruction of the three techniques between 1.5 and 3.5 % TCE concentration. The propane-assisted plasma provided the highest destruction below 1.5 and above 4 % TCE. The propane flame also achieved 4 nines’ destruction below 1.4 % TCE according to the model and 3 % according to the experiments.

The DREs achieved in the processes investigated for this project are comparable with other destruction techniques (i.e. incineration and thermal plasma destruction) and
higher than available reclamation techniques (i.e. adsorption and condensation). Classic non-thermal plasma techniques cannot treat the required VOC concentrations of a few percent due to insufficient electron densities.

9.4.3 Environmental Impact

Conversion rates to the desirable products HCl and Cl₂ were 99.4 – 99.8 % in the air plasma, 99.7 – 99.8 % in the propane-assisted plasma and 99.1 % (at 1 % TCE) in the propane flame. It follows that fewer undesirable (chlorinated organic) products were formed in the propane-assisted plasma than the other processes, but only marginally.

The overall impact of the process on the environment was assessed by estimating the amount of each unscrubbed by-product produced per 200 l barrel of TCE treated. The products were put into categories: ozone depleters, global warmers, ozone creators, acute health hazards and carcinogens. The potency index (e.g. Ozone Depletion Potential) was then multiplied (or divided in the case of permitted daily exposure) by the mass produced per 200 l of TCE to attain a ‘potency factor’ for each environmental or health aspect. These figures were normalised to 1, such that the process with the most detrimental effect in each category scored 1. Note that these figures are relative only: the larger the number, the more serious the adverse effect. This figure was then compared for the various processes investigated in this project, release of untreated TCE and existing treatment processes. Sources for the potency indices include Kojima (1997), Resource Futures International (2003), the European Chlorinated Solvent Association (2002) and The Centre for International Earth Science Information Network (2002). These results can be seen in table 9.1 and the original spreadsheet is provided in appendix 9A. Table 9.2 summarises the products formed during the TCE dissociation experiments in terms of their detrimental effects to health and the environment.

By-products formed in producing the power required by TCE treatment processes are not included in the environmental impact analysis, as a coal-fired power station would have completely different products than a hydroelectric dam.
Table 9.1: Summary of environmental impact of TCE treatment processes ('potency factors') assuming 2 % inlet TCE (*may not be applicable above 1 % TCE)

Assumptions:

- TCE Global Warming Potential is quoted as ‘much less than 9’. Therefore, an arbitrary figure of 1 was chosen. This may be misleading.

- Destruction and removal efficiencies for alternative technologies are taken from table 1.1. Novel adsorption is assumed to achieve 90 % removal of TCE.

In terms of direct emission to the atmosphere, the reclamation processes of adsorption and condensation reduce detrimental environmental effects across the board since the amount of TCE emitted is decreased and no new chemicals are produced. Very low levels (probably less than 1 ppm) of ozone depleting chemicals are formed in the dissociation processes (i.e. the plasmas and flame). The global warming potential of the effluent is similar for all dissociation processes and emission of untreated TCE to atmosphere. The plasma and propane combustion processes have a significant positive environmental impact on emissions in terms of photochemical smog formation potential, which is at least a 1,000 times lower than in any other scenario, including the solvent reclamation processes. Although the main fear regarding the dissociation of TCE was the formation of more potent carcinogens, table 9.1 shows that the dissociation processes are at least 1,000 times less harmful to health than direct release to the environment and currently available treatment techniques. Another surprising finding is that the propane burner (at 1 % TCE) is better than the plasma processes in all categories except global warming, where it is about the same (remembering that the volume treated would be doubled, doubling the factor quoted in table 9.1).
### Table 9.2: List of chemicals produced in TCE destruction experiments

<table>
<thead>
<tr>
<th>Effect</th>
<th>Chemicals (decreasing potency where known)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone Depleters</td>
<td>Carbon tetrachloride (CCl₄), methyl chloride (CH₃Cl)</td>
</tr>
<tr>
<td>Global warmers</td>
<td>CCl₄, Methylene chloride (CH₂Cl₂), tetrachloroethene (C₂Cl₄), TCE, carbon dioxide (CO₂)</td>
</tr>
<tr>
<td>Smog producers</td>
<td>TCE, C₂Cl₄, CH₂Cl₂</td>
</tr>
<tr>
<td>Acute health hazards</td>
<td>Chlorinated aliphatics (CxHyClz), NO, CO, NOCl</td>
</tr>
<tr>
<td>Carcinogens</td>
<td>Hexachlorobenzene (C₆Cl₆), CCl₄, chloroform (CHCl₃), C₂Cl₄, TCE, CH₂Cl₂</td>
</tr>
</tbody>
</table>

Acute health effects are not comparable in the same way as the other effects. It is assumed, however, that all destruction methods would be similar in terms of acute health effects. The justification for this is that a few percent of TCE could be exchanged for a few percent of NO or a few percent of CO, depending on the process used. The relative harm done by these chemicals is not easily assessed. Carbon adsorption and condensation would reduce overall acute health effects as they reduce the total mass of chemicals released into the vapour phase.

#### 9.4.4 Operating cost

Energy requirements for the plasma processes rely only on the total flow rate to be treated, assumed to be 60 lmin⁻¹, 24 hrs.day⁻¹, 365 days.yr⁻¹. There are always some emissions, even during downtime and idling, so theoretically, a control process must be running all of the time. It is assumed that the same negative pressure is maintained in the machine at all times, therefore resulting in the same flow rate to be treated. If the extractor fan flow rate were varied depending on emissions, the energy requirements would be reduced. Since the plasma processes could treat saturated TCE vapour, energy costs could be reduced by a third if the extractor fan power was reduced by one third. For a gas burner or adsorption system, the extractor fans would have to be turned up in order to double the flow rate of air into the exhaust system, so that the TCE stream could be diluted to 1 %, to enable effective treatment. This would double the amount of methane required to sustain the flame in the burner.

Solvent emissions are estimated assuming and emission rate of 60 lmin⁻¹ of 2 % TCE in air, 24 hours per day (i.e. 12.6 barrels per year). Solvent savings due to recycling
in adsorption and condensation systems are accounted for in the annualised cost estimates.

Using the figure of 8,000 J l⁻¹ from chapter 5, and assuming 90 % of the TCE that is used is emitted to the air (Environment Australia 1999) at a concentration of 2 %, and that 60 % of power supplied is converted to microwave power (Lucas 2001), the microwave energy cost per 200 l barrel of TCE used is AUD$550. For 60 l min⁻¹, 8,000 J l⁻¹ translates to a 13 kW power supply.

It was shown in figure 5.4 that the introduction of propane to the plasma increases the maximum flow rate achievable very slightly. This difference would be less than a litre even at 60 l min⁻¹, however, and is not acknowledged in this economic analysis.

The cost of the fuel required is factored into the analysis. Natural gas (mainly methane (CH₄)) would be used rather than propane in an industrial unit, as it is cheaper and more readily available. It would also be a more effective hydrogen provider. The stoichiometries used to calculate the methane required in the gas burner and the propane plasma are given in equations 9.1 and 9.2, respectively.

\[
\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(9.1)}
\]

\[
0.5\text{CH}_4 + \text{C}_2\text{H}_2\text{Cl}_3 + 2.5\text{O}_2 = 2.5\text{CO}_2 + 3\text{HCl} \quad \text{(9.2)}
\]

The approximate natural gas price of US$5 ft⁻³ (Dailyfutures 2005) is used in the cost analysis.

Assuming the Cl₂ and HCl produced in the process were scrubbed with water, and using the solubilities of 7.1 g l⁻¹ and 360 g l⁻¹ respectively (Weast R.C.), scrubber requirements would be as given in table 9.3. Therefore, the addition of alkane gas to the plasma could reduce the scrubber size by 4 times. Also note that the burner scrubber would yield hydrochloric acid to a reasonable purity and may be saleable. These facts are not factored into the economic analysis.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Flow rate (l/min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air plasma</td>
<td>0.4</td>
</tr>
<tr>
<td>Propane plasma</td>
<td>0.1</td>
</tr>
<tr>
<td>Propane burner</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 9.3: Scrubber flow rate requirements assuming water is absorbent

It was not possible to get exact energy requirements for alternative processes. A conservative estimate of AUD$5,000 per year is used in this analysis. For adsorption processes, the main energy cost would be in regeneration of the adsorbent bed. For condensation, the refrigeration costs are the only energy requirement.

See table 9.4 for the estimated annualised costs of each process.

### 9.4.5 Capital costs

The cost of a microwave power supply with two 6 kW power supplies is quoted as AUD$48,000 (Tran 2005); this would allow for a 50 % increase in typical treated flow rates. A 15 % discount could be attained if ten or more reactors were purchased. The reaction chamber and scrubber are estimated to be AUD$5,000 and AUD$10,000 respectively. The cost of adding a gas supply source to the reactor is assumed to be negligible.

Costs of alternative technologies are taken from the Radian Corporation report (1991). These figures are not current, and were converted to 2005 values using a consumer price index calculator (Federal Reserve Bank of Minneapolis 2005). The capital cost of a novel adsorption process is estimated to be twice that of conventional adsorption based on the fact that novel regeneration processes are involved and the lower volume of sales would demand higher pricing.

See table 9.4 for capital cost estimates.

### 9.4.6 Maintenance requirements

Maintenance requirements of the plasma/combustion unit would be minimal if it was engineered with corrosion in mind. It is likely that the corrosive environment would mean regular replacement (e.g. yearly) of some parts, but this would be easy and
cheap. Labour costs would be negligible. Annual maintenance and labour costs are assumed to be 5% of the capital cost of the reactor.

Carbon adsorption requires regular regeneration or replacement of the carbon bed. If regeneration is done on site, additional facilities and expertise are required and the process is energy intensive. The solvent recovered is not the same grade as the original solvent since additives and stabilisers may be lost. The bed itself gradually deteriorates and is replaced as required. If the bed is replaced rather than regenerated, it is hazardous waste and therefore disposal is costly. This must be done every 3–4 months. Maintenance costs are assumed to be 10% of the capital cost of the reactor.

The adsorbents used in novel adsorption processes are more expensive than activated carbon, but are regenerated more effectively and so require less frequent replacement. For instance, costs are US$20 kg\(^{-1}\) for polymeric adsorbents compared with $2 kg\(^{-1}\) for activated carbon (Cohen 1998). Maintenance costs of 10% of the capital cost of the reactor are used for novel processes. This results in double the maintenance costs of conventional adsorption, which seems reasonable, given the longer lifetime of the adsorbents, their significantly higher cost and that they are typically easier to regenerate than carbon beds.

9.4.7 Robustness

The plasma destruction process is very robust, being able to treat any possible TCE concentration under any conditions. The only situation in which the process would go off-specification would be in the case of liquid TCE being put through the plasma unit; it would not be possible for this to happen by accident. If the plasma went out the emission of untreated TCE would not be a disaster. Control systems could be built in to alarm operators to this event. If stricter regulations were in place, the TCE vapour could be automatically trapped until the plasma unit came back online and then recycled through it. The maximum treatable flow rate is merely a function of the power of the system, and therefore any flow rate could be treated by increasing the number of microwave power sources.
The gas burner would be less robust as unexpected increases in solvent concentration could lead to the emission of very harmful chemicals. Also, undetected extinction of the flame or leaks in the system could lead to explosion hazards. A detector warning if the solvent concentration exceeded treatable concentrations would be vital for health and safety reasons. This would be activated, for instance, if the exhaust fans cut out, failing to dilute the solvent stream sufficiently.

Activated carbon adsorption can be used on flow rates up to 20,000 m\(^3\)hr\(^{-1}\) with concentrations less than 50 gm\(^{-3}\) (this corresponds to 1 % TCE vapour). Although operating costs are high, capital investment is low, adsorption is flexible to flow variations and can process a variety of concentrations and contaminants. However, activated carbon is subject to temperature constraints of 20 – 40\(^{\circ}\)C, a humidity of less than 50 %, and is a fire hazard.

Condensation processes are robust as they can treat any concentration of solvent to the same emission level, and no off-spec incident (including total shutdown of the condenser) would result in an occupational health and safety disaster.

**9.4.8 Overall**

The information detailed in the previous sections was used to estimate the annualised costs of the various TCE treatment processes (see table 9.4). See appendix 9B for the full spreadsheet. The formula used to estimate these costs is given in equation 9.3, where the Return on Average Investment is assumed to be 15 %.

\[
\text{Annualised Cost} = (\text{Return on Average Investment} \times \text{Capital Cost}) + \text{Energy Costs} + \text{Solvent Costs} + (\text{Maintenance} + \text{Labour})
\]

\[ (9.3) \]
Table 9.4: Economic and engineering comparison of TCE treatment processes (12.6 barrels/year)

<table>
<thead>
<tr>
<th>Process</th>
<th>Capital Cost (AUD$)</th>
<th>Annualised Cost (AUD$/yr)</th>
<th>Robustness</th>
<th>Solid/liquid Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Plasma</td>
<td>$63,000</td>
<td>$27,714</td>
<td>High</td>
<td>Acidic liquid</td>
</tr>
<tr>
<td>Methane Plasma</td>
<td>$63,000</td>
<td>$27,774</td>
<td>High</td>
<td>Acidic liquid</td>
</tr>
<tr>
<td>Methane Flame (1% TCE)</td>
<td>$15,000</td>
<td>$12,284</td>
<td>Medium</td>
<td>HCl</td>
</tr>
<tr>
<td>Conventional adsorption*</td>
<td>$171,600</td>
<td>$51,146</td>
<td>Medium</td>
<td>Spent carbon</td>
</tr>
<tr>
<td>Novel adsorption*</td>
<td>$343,200</td>
<td>$91,611</td>
<td>Varies</td>
<td>Spent bed</td>
</tr>
<tr>
<td>Condensation*</td>
<td>$39,683</td>
<td>$15,371</td>
<td>High</td>
<td>None</td>
</tr>
<tr>
<td>Release to atmosphere</td>
<td>$0</td>
<td>$8,114</td>
<td>Maximum</td>
<td>None</td>
</tr>
</tbody>
</table>

*Annual energy costs of $5,000 are estimated*

The cheapest options are direct release of TCE to the atmosphere, methane burner and condensation, in order of increasing cost. If solvent prices increased significantly, condensation would become more economic. Adsorption processes are very expensive, at an annual cost of 5 to 10 times the annual cost of the TCE. The methane burner may be cheaper still if the HCl from the scrubber could be sold.

9.5 Conclusions

Both plasma processes and gas burner (with air dilution) provide much higher DREs than currently available techniques. All three processes also significantly reduce the detrimental effects of TCE use in terms of chronic health effects and photochemical smog formation. There is no appreciable difference between any of the processes in terms of global warming. The processes investigated for this project do produce very low levels of ozone depleting chemicals, which are not produced in any of the other scenarios.

In terms of cost, direct emission to the environment is the cheapest option, closely followed by condensation and the methane burner. Therefore, it is concluded that if the current regulatory situation persists, no control beyond room temperature cooling is indicated. If TCE prices increase by 100 % or more, condensation will become the cheapest option. If regulation becomes significantly more stringent, a methane burner will be the cheapest way of complying. However, if TCE price increases and regulation becomes more stringent, a below-freezing condenser followed by a
methane burner will be indicated. Plasma treatment is not indicated as better performance can be attained with a methane burner for 50% of the cost. However, the plasma processes are the most robust, and so may be attractive to users who are prepared to pay more for fewer off-spec scenarios, hence ensuring lower maintenance requirements and continuous compliance.
10. SUMMARY ........................................................................................................168
10.1 Abstract.............................................................................................................168
10.2 Introduction......................................................................................................168
10.3 General Comments ..........................................................................................169
10.4 Reactor Performance.......................................................................................170
10.5 Scientific findings.............................................................................................171
10.6 Consequences to industry...............................................................................172
10.7 Further Work...................................................................................................173
10.8 Conclusions.......................................................................................................174
10. Summary

10.1 Abstract

The objectives of the project have been met and the outcomes are discussed in this chapter. A multi-disciplinary approach was taken, with chemical analysis proving the most difficult discipline. The air plasma and propane plasma both achieved very high levels of destruction (at least 4 nines) for all TCE inlet concentrations. The propane burner performed well below 1 – 3 %. The major products were hydrogen chloride and chlorine gas. Nitrogen oxide (NO\textsubscript{x}) formation was a problem in the plasmas, and carbon monoxide formation was a problem in the Bunsen burner. Very low levels of chlorinated organics were formed, possibly including hexachlorobenzene, but it is unlikely that dioxins or furans were formed.

The plasma was found to have a heavy particle temperature of 3,000 – 4,000 K, and its properties could be predicted with equilibrium modelling. Therefore, for practical purposes, microwave plasmas are thermal plasmas. Anomalies at 3 % inlet TCE were unexplained, but probably caused by a peak in an unidentified oxidising species around that concentration.

Environmental analysis showed that the three processes investigated would have a positive effect on health and the environment when compared with other available options. However, economically, direct release of TCE to the environment is the best option, followed by a gas burner then condensation. Increases in solvent prices would make condensation more attractive, and tightening regulation would make a natural gas burner the best option. Plasma destruction will never be the cheapest option unless electricity becomes much cheaper (unlikely).

Environmental agencies must catch up with technology before any control is advisable to industry on anything other than a moral level.

10.2 Introduction

In order to find the best way of dissociating trichloroethene in contaminated air streams of various concentrations into benign products, the following phenomena
were studied and compared: dissociation in a propane gas flame, a microwave-induced plasma, and a “propane-assisted” microwave-induced plasma. The aims were to contribute to the understanding of microwave-induced plasmas and appropriate waste treatment.

Thorough assessment of these processes required a multi-disciplinary approach. Identification of all possible by-products of this process was vital for its assessment in terms of its environmental impact and occupational health and safety. This required considerable expertise in chemical analysis techniques and was, in fact, the most time-consuming, difficult and expensive part of the project. Economics, scale-up and simplification of the problem in engineering terms were necessary for the study to be industrially applicable. Also, a skilled microwave plasma technician was required to tune the microwave plasma effectively.

The emphasis of this assessment has been on the overall robustness of the process. Vapour degreasing is usually a low-tech, low-investment operation with one minimally-trained operator. The device must be simple to operate and completely self-regulating. Therefore, the allowable range of trichloroethene concentrations, quench rates, reactor powers, etc. were defined. The potential consequences of running off-specification were vital to a proper assessment of this process.

Plasma temperature, chemical composition of products, environmental impact, engineering issues and economics have been investigated.

10.3 General Comments

Once the plasma reactor and Bunsen burner were fully commissioned and experimental protocols were developed, the experiments were robust, safe, and easy to run and maintain. The comparison between plasma and conventional combustion would have been more accurate if the reactors were the same size, as equilibrium may not have been reached in the Bunsen burner. The acidic reaction products (mainly chlorine and hydrochloric acid) caused corrosion problems that would have to be addressed in a commercial unit.
The chemical analysis was complicated but essential for a proper health and environmental assessment of the processes investigated. The decision to analyse the samples un-scrubbed caused severe confusion in terms of column degradation, but ensured holistic analysis. Gas chromatography with electron capture made identification and quantification difficult. However, it enabled the detection of chlorinated products down to parts per billion levels, which was necessary for the environmental assessment given that some compounds (e.g. dioxins and furans) are many orders of magnitude more toxic than trichloroethene, the chemical to be treated.

Chemical modelling was reasonably successful in predicting the products of the dissociation reactions, and turned out to be the easiest part of the project. The accuracy of the model could have been improved with a more powerful computer and more complete input data (thermodynamic and reaction constants for exotic compounds and reactions).

10.4 Reactor Performance

Effective treatment of all possible trichloroethene (TCE) concentrations (up to about 8% TCE) was achieved in both the air and propane plasmas (at least 4 nines’ destruction). The propane flame was only effective below a TCE concentration of 1.4% (according to the model) and 3% (according to the experiments). Therefore, the contaminated stream would have to be diluted to enable successful treatment by conventional gas burning. The processes were reasonably insensitive to variations in flow rate and inlet TCE concentration. Plasma power requirements were independent of TCE concentration, at 7,000 – 8,000 Jl⁻¹.

The TCE was converted almost entirely to hydrogen chloride (HCl) and chlorine (Cl₂), which could be scrubbed in an industrial process. The addition of propane increased HCl formation and decreased Cl₂ formation. The scrubber off-gas would contain very low levels (up to parts per million) of chlorinated organics, e.g. carbon tetrachloride. Nitric oxide (a few percent) would be produced in both plasma systems, and carbon monoxide (a few percent) would be produced in the conventional combustion chamber. Some chlorinated aromatics may be formed at barely detectable
levels (parts per billion) but it is almost certain that no dioxins or furans would be produced.

10.5 Scientific findings

The atmospheric pressure microwave plasma temperature range was found to be 3,000 – 4,000 K, which agrees with the literature (Timmermans et al. 1998). Heat losses prevented higher temperatures in the IRIS laboratory reactor, whereas the microwave frequency precluded lower temperatures. Varying the plasma temperature within this range had no significant effect on the chemistry of TCE destruction, due to the almost instantaneous breakdown of the gas into its constituent components at these temperatures. The electron temperature may be higher that the heavy particle temperature; however, since the extinction flow rates agree with the EQUIL model, they are not significantly higher. For the intermediate TCE concentrations studied for this project, the microwave plasma temperature is ideal. A classic non-thermal plasma would not be able to treat such high concentrations and a classic thermal plasma would use excessive energy.

The plasma process has been modelled surprisingly accurately using equilibrium modelling. The only limitation of EQUIL was in the prediction of chlorinated aromatic formation, where kinetic modelling in AURORA was necessary. Kinetic modelling is required to predict aromatic formation because their precursors are formed at very high temperatures and then need to be quenched rapidly so that their recombination doesn’t take place until the low temperatures that favour aromatic formation (below 2,500 K). The lower temperatures present in the propane flame meant that equilibrium was not reached almost instantaneously as in the plasma. Therefore, predictions were not as accurate for the propane flame. A larger reactor (hence higher residence times) would probably solve this problem. Also, a more powerful computer would be able to model the kinetics processes of combustion fully, and there are schemes available, e.g. Leylegian et al. (1998).

Various anomalies in the results were observed at and around 3 % TCE concentration. Investigation of the extinction flow rate and absorbed powers revealed that for the same applied power, electron densities were lower around 3 % than for other
concentrations. The most likely explanation for this is that an unidentified oxidising species peaks in concentration at 3 % TCE, hence taking electrons from the plasma. It could be due to experimental error; however, it seems too persistent for this to be a satisfactory explanation. It is possible that inclusion of electrons and ions in the model would have helped to identify any possible rogue species.

10.6 Consequences to industry

An environmental and economic analysis of techniques investigated for this project and currently available control methods was carried out.

The environmental impact analysis revealed that all three TCE destruction processes investigated were far superior to all other options (i.e. release of untreated TCE, condensation and adsorption) in terms of improvements in health effects and photochemical smog formation potential of the degreaser effluents. Global warming potential of all effluents were roughly the same (slightly better with novel adsorption techniques). The destruction processes investigated would produce very low levels of ozone depleting chemicals, none of which are produced by the other options (including direct release of TCE).

The economic analysis ruled out adsorption processes immediately, as annualised costs were several orders of magnitude higher than what companies currently spend on degreasing. In terms of financial cost, direct emission to the environment is the cheapest option, closely followed by condensation and the methane burner. Therefore, it was concluded that if the current regulatory situation persists, no control beyond room temperature cooling is indicated. If TCE prices increase by 100 % or more, condensation will become the cheapest option. If regulation becomes significantly more stringent, a methane burner will be the cheapest way of complying. However, if TCE price increases and regulation becomes more stringent, a below-freezing condenser followed by a methane burner will be indicated. Plasma treatment is not indicated as better performance can be attained with a methane burner for 50 % of the cost. Plasma treatment is the most robust option, and so may become more attractive if regulators start to monitor emissions more stringently and impose
significant penalties for any non-compliance. However, good failsafe engineering management of a methane burner could make it almost as robust.

10.7 Further Work

This was a viability study, and as such has left many details to be refined. Time and money were also limiting factors.

Firstly, identification of other industrial applications for the microwave plasma may increase interest in developing the technology. Vapour degreasing is not capital intensive enough to be appropriate. The next step would be to design and commission a scaled up version of the reactor with a scrubber. These two steps would not be difficult.

The chemical analysis could be done more accurately by a qualified chemical analyst in a fully equipped laboratory. There is still uncertainty regarding identification and quantification of peaks. For instance, a phosgene standard should be injected to confirm its identification as a product.

The chemical modelling could be refined with a more powerful computer. Research is also required into reaction rate constants for uncommon reactions. This would help to eliminate the prediction of unlikely products in AURORA. Thermodynamic data for exotic products is also required to enable the generation of constants in FITDAT, part of the CHEMKIN package. Further modelling runs should be carried out around the 3 % TCE mark, to help to uncover the mystery of the anomalies found there. The inclusion of electrons and ions in the kinetic model, and electron energy distribution function calculations, may help in this regard. A sensitivity analysis to determine the key reactions in the process would be interesting. NOx formation must also be addressed.

Experimental measurement of the plasma temperature (electrons in particular) would clarify the conclusions on the nature of the atmospheric microwave plasma. This could be done by spectroscopic means (Kim et al. 2003). The resonant sound
frequency could be measured experimentally with a microphone, as further confirmation of the plasma temperature.

10.8 Conclusions

This study has shown that microwave plasmas and conventional gas burners can be used to successfully treat TCE, resulting in an overall positive effect on health and the environment. However, it is cheaper to release TCE to the environment untreated and so is not indicated in engineering terms. Therefore, the overall conclusion in terms of degreasing is that environmental agencies must catch up with technology before change is seen.

There are many potential applications for plasma technology, and this project has shown that atmospheric-pressure microwave plasmas are effective, robust and relatively cheap waste treaters of moderately contaminated streams. They are often used very effectively in conjunction with a catalyst or scrubber.
Appendix 1A: Properties of trichloroethene (TCE)

1. Physical properties

Trichloroethene is an unsaturated aliphatic halogenated hydrocarbon. It is a clear, colourless or blue mobile liquid with an ethereal, chloroform-like odour. (National Industrial Chemicals Notification and Assessment Scheme 2000). Properties such as high solvency, low flammability, non-corrosiveness, high stability, low specific heat, low boiling point, low heat of vaporisation and low production cost make it an excellent solvent in a wide range of applications (Halogenated Solvents Industry Alliance 2001). It is slightly soluble in water and miscible with most organic solvents. Trichloroethene vapour is heavier than air.

See table 1A.1 for physical properties of trichloroethene. Conversions between concentrations given by volume (parts per million) and by mass (micrograms per cubic metre) are given in table 1A.2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>$\text{C}_2\text{HCl}_3$</td>
<td>1</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>131.4</td>
<td>1</td>
</tr>
<tr>
<td>CAS number</td>
<td>79-01-6</td>
<td>1</td>
</tr>
<tr>
<td>Odour threshold</td>
<td>100 ppm</td>
<td>2</td>
</tr>
<tr>
<td>Boiling point</td>
<td>86.7°C</td>
<td>2</td>
</tr>
<tr>
<td>Freezing point</td>
<td>- 86.5 °C</td>
<td>2</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.465 gml$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>Relative vapour density**</td>
<td>4.54</td>
<td>3</td>
</tr>
<tr>
<td>Density (20°C)</td>
<td>1.465 gml$^{-1}$</td>
<td>2</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.58 cP</td>
<td>3</td>
</tr>
<tr>
<td>Vapour pressure (20°C)</td>
<td>7.87 kPa</td>
<td>3</td>
</tr>
<tr>
<td>Surface Tension at 20°C</td>
<td>29.5 dynescm$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>0.0293 Nm$^{-1}$</td>
<td>2</td>
</tr>
<tr>
<td>Lower flammability limit at 25°C *</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>Upper flammability limit at 25°C</td>
<td>9.2 (vapour saturation point)</td>
<td>1</td>
</tr>
<tr>
<td>Lower flammability limit at 100°C</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>Upper flammability limit at 100°C</td>
<td>44.8</td>
<td>1</td>
</tr>
<tr>
<td>Flash point</td>
<td>None</td>
<td>3</td>
</tr>
<tr>
<td>Autoignition temperature</td>
<td>410 °C</td>
<td>3</td>
</tr>
<tr>
<td>Decomposition point</td>
<td>&gt; 125°C</td>
<td>3</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>271°C</td>
<td>3</td>
</tr>
<tr>
<td>Sublimation point</td>
<td>Not applicable</td>
<td>3</td>
</tr>
<tr>
<td>% volatile by volume</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>Solubility – solvent in water</td>
<td>1.07 g/l or 0.10 g/100g</td>
<td>3</td>
</tr>
<tr>
<td>Solubility – water in solvent</td>
<td>0.04 g/100g</td>
<td>3</td>
</tr>
</tbody>
</table>
### Table 1A.1: Physical properties of trichloroethene

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_v$</td>
<td>31.4 kJmol$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>$C_p$ at 400 K</td>
<td>91.2 Jmol$^{-1}$K$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>$C_p$ at 600 K</td>
<td>104.9 Jmol$^{-1}$K$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>$C_p$ at 800 K</td>
<td>112.7 Jmol$^{-1}$K$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>$C_p$ at 1000 K</td>
<td>117.8 Jmol$^{-1}$K$^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>pH</td>
<td>Not appl.</td>
<td>3</td>
</tr>
<tr>
<td>Evaporation rate</td>
<td>Not av.</td>
<td>3</td>
</tr>
<tr>
<td>Partition Coefficient – Log $K_{ow}$</td>
<td>2.42</td>
<td>2</td>
</tr>
<tr>
<td>Partition Coefficient – Log $K_{oc}$</td>
<td>2.03 – 2.66</td>
<td>2</td>
</tr>
</tbody>
</table>

* % Solvent in air by volume, ** Relative vapour density of air = 1

Table 1A.1 reference key:

1. Halogentaed Solvents Industry Alliance (2001)
3. Orica Chemicals (MSDS)
4. Lange’s Handbook (Dean 1999)

### Table 1A.2: Conversion factors (National Industrial Chemicals Notification and Assessment Scheme 2000)

<table>
<thead>
<tr>
<th>Environment</th>
<th>Conversion Factor</th>
<th>Reference</th>
<th>Conversion Factor (w/v)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air at 20°C</td>
<td>1 mgm$^{-3}$</td>
<td>1 ppm</td>
<td>0.18 ppm</td>
<td>5.46 mg.m$^{-3}$</td>
</tr>
<tr>
<td>Water</td>
<td>1 ppm (w/v)</td>
<td>1 mg.l$^{-1}$</td>
<td>1.465 mg.l$^{-1}$</td>
<td>1 ml.m$^{-3}$</td>
</tr>
<tr>
<td>HPM flue gas</td>
<td>16,000 ppm</td>
<td>87.36 g.m$^{-2}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Chemical Structure

The chemical structure of trichloroethene is given below:

$$\text{Cl} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{Cl}$$

Molecular weight = 131.40 kg.kmol$^{-1}$ (World Health Organisation 1985)

3. Nomenclature

The IUPAC and CAS name of the chemical is trichloroethene, but it is more commonly referred to as trichloroethylene. Some common synonyms for trichloroethene are: ethene trichloro-, ethylene trichloro-, ethylene trichloride,
acetylene trichloride, ethinyl trichloride, 1,1,2-trichloroethylene, 1-chloro-2,2-
dichloroethylene, 1,1-dichloro-2-chloroethlyene, TCE and TR I. (National Institute of
Standards and Technology 2003; World Health Organisation 1985).

4. Chemical reactivity

- TCE undergoes auto-oxidation, with the formation of products such as hydrogen
chloride and phosgene. The reaction rate is increased in the presence of oxygen
and ultraviolet light; insufficient hydrogen chloride is formed to give warning
before overexposure to phosgene occurs.
- Dichloroethyne (dichloroacetylene), which is spontaneously combustible, highly
neurotoxic and carcinogenic for animals and probably for man, is formed in the
presence of strong alkalis, such as sodium hydroxide, by the dehydrochlorination
of TCE.
- Under pressure, at 150°C, TCE reacts with alkalis to produce hydroxyethanoic
acid (hydroxyacetic acid, glycolic acid);
- It reacts with sulphuric acid to form chloroethanoic acid (monochloroacetic acid);
- and TCE attacks some plastics (Dow Chemical Company 1999; National
Industrial Chemicals Notification and Assessment Scheme 2000; World Health
Organisation 1985).

5. Chemical degradation

- The chemical degradation of TCE in water is very slow;
- in contact with finely divided or hot metals (300 - 600°C), such as aluminium and
magnesium, it decomposes to form phosgene and hydrogen chloride (Dow

6. Photochemical degradation

- When exposed to ultraviolet light and humidity, TCE degrades to give acids that
have mean half-lives ranging from 6 to 12 weeks. Taking the yearly mean OH
concentration to be 5 x 10^-8 ppm and that of ozone to be 0.040 ppm, TCE’s half
life can be estimated to be about 70 hours (World Health Organisation 1987;
World Health Organisation 1985);
• dichloroethanoic acid (dichloroacetic acid) and hydrochloric acid are formed, which are both highly corrosive and reactive with metals;
• other decomposition products formed are carbon monoxide, trichloroethene ozonides and trichloroethene epoxide (Dow Chemical Company 1999; National Industrial Chemicals Notification and Assessment Scheme 2000; World Health Organisation 1985).

7. Additives in commercial grades

Commercial trichloroethene formulations include a stabiliser system to help prevent solvent breakdown caused by contaminants such as acids, metal chips and fines, exposure to light, heat and oxygen (Halogenated Solvents Industry Alliance 2001). Mixed amines and butylene oxide act as acid acceptors when solvent degradation leads to the formation of hydrogen chloride. Commercial grades contain up to 99% TCE with additives including: butanone, 1,2-butylene oxide, diisopropylamine, ethyle acetate, epoxybutane, glycidyl ether, isopropyl acetate, 1-methlyepyrrole, 2-methyl-3-butin-2-ol, thymol, triethylamine, trimethyl oxirane, 2,2,4-trimethyle pentene and 2,4-di-tertbutylphenol (National Industrial Chemicals Notification and Assessment Scheme 2000).
Appendix 1B: World TCE Usage

TCE is the solvent most commonly used in vapour degreasing operations. However, in general there has been a decline in its demand over the last thirty years. This decline was caused by concerns over the safety of the solvent regarding human health and the environment. More recently, concerns over some of the alternatives for TCE and the introduction of the use of TCE as a precursor in the manufacture of chlorofluorocarbon alternatives have lead to renewed growth in the demand for TCE. Conversely, increasing trends in the recovery and recycling of trichloroethene, and more efficient use in general, may reduce production. The penetration of alternative solvents and non-solvent based technologies into the market has also led to a general decline in the use of TCE (Gamble 1998).

A brief description of the worldwide trends in TCE production and importation follows.

1. North America

Several factors led to a decline in demand for TCE the USA for about thirty years. In 1968 Los Angeles adopted rule 66, which limited emissions of the substance. Other states enacted similar legislation during the next few years and the Clean Air Act of 1970 led to the replacement of TCE with alternative solvents by many users. By 1975, industry agreed that TCE was photoreactive and federal and local governments severely restricted the use and emission of TCE in degreasing operations in many areas. The same year saw a “memorandum of alert” on TCE issued by the U.S. National Cancer Institute when preliminary bioassays of the solvent indicated that it caused carcinogenic effects in mice. This resulted in another push for replacement by reputedly safer solvents, such as tetrachloroethene and 1,1,1-trichloroethane (TCA). These trends led to a decline in TCE production in America. For instance, the demand for TCE dropped from 245,000 tonnes in 1971 to 68,000 tonnes in 1990 (National Industrial Chemicals Notification and Assessment Scheme 2000).

Ironically, 1996 saw this trend reversed with the phase out of TCA under the Montreal Protocol. TCA had been a major degreasing agent since the 1980s and
several processes reverted to TCE following this regulation (Environment Canada 2001a).

In 1998, the American demand for trichloroethene was about 77,700 tonnes. Of this, 54% was used as a chemical intermediate, 42% was used for metal cleaning/degreasing and the remainder was used for miscellaneous purposes. Approximately 109,000 tonnes of trichloroethylene were produced in the U.S.A. in 1998 (Halogenated Solvents Industry Alliance 2001).

Canada imports all of its TCE requirements from the U.S.A. and Europe. Over 90% of the 3,000 tonnes of trichloroethene imported in 1994 were used for degreasing (Environment Canada 2001a), whereas it is estimated that only 73% of the 2,200 tonnes imported in 1993 were used for degreasing (Gamble 1998). A survey of 300 companies, conducted by Dow Chemicals Advanced Cleaning Systems in 1994, indicated that 1/3 of the companies that had already replaced TCA were using TCE instead (Environment Canada 2001b).

2. European Union

Usage of TCE in Europe declined in much the same way as in America; it was reduced by 50% between the mid-seventies and 1996 (National Industrial Chemicals Notification and Assessment Scheme 2000). The total production in Western Europe in 1981 is estimated to be 270,000 tonnes (World Health Organisation 1987). In the early 1970’s, TCE production exceeded 10,000 tonnes per year in Sweden, but by 1992 it had fallen to about 3000 tonnes (National Industrial Chemicals Notification and Assessment Scheme 2000).

3. China

In China, demand for trichloroethene has increased very rapidly in recent years. For example, in one year, from 1994 to 1995, the demand rose from nearly 2000 tonnes to 22,000 tonnes. In 1999, China’s TCE usage was approximately 31,000 tonnes per year and output was 9000 tonnes (Chen and Yang 1999).
Production of TCE in China did not begin until the early 1970s. China’s rapid economic development in the 1980s meant that domestic production could not match the demand, and imports were necessary. The amount of TCE imported increased steadily from less than 600 tonnes in 1990 to over 12,000 tonnes in 1998. To increase the production capacity, the production processes were improved and several new units were constructed from 1987-9 and again in the 1990s. By 1998, some of the units were capable of producing a product purity of 99.99 %, reaching the standard of similar international products. China also exports a small amount of TCE (Chen and Yang 1999).

The main use of TCE in China is as a cleaning agent for metal and electronic components. Despite the boom in TCE usage in recent years, its market share of petroleum series solvents is only 2 % compared with 90 % in advanced countries. The growth of the machine building and electronics industries in China is likely to improve this share significantly, however. TCE is also used as a solvent and extraction agent in mainly caprolactam, pesticides and pharmaceuticals. About 5000 tonnes are used in caprolactam production every year. The demand for TCE as an extraction agent of pharmaceutical intermediates is increasing. Another area of significant growth is the use of TCE as a chemical intermediate. Much research effort is being put into the production of freon alternatives and several chemicals are already being produced, such as HFC134a (Chen and Yang 1999).

The trends observed in more advanced countries are not seen in China. The use and production of TCE is a growing industry and there are no signs of its curtailment.

4. Australia

TCE was manufactured in Australia for about thirty years, until the early 1980s. The national demand for the chemical, approximately 3000 tonnes per year, is now met by imports from France, the U.K. and the U.S.A. The main use of TCE in Australia is as a degreasing agent in both small and large industrial operations.

TCE usage has seen the same trends in Australia as throughout other developed countries. That is a decline coinciding with the announcement of TCE’s potentially
carcinogenic nature and its replacement with TCA. Import data obtained from the ABS indicate an increase in TCE imports from 1994 to 1996. This coincides with Australia’s adoption of the Montreal Protocol leading to the phase out of TCA. Conversely, increasing trends to recycle the chemical may counteract this effect. At present, more than 185 tonnes of TCE are recycled every year, either by distillation at the work-site or off-site recycling companies.

The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) conducted a survey to identify TCE’s uses in Australia. Questionnaires were sent to a range of companies and organisations formulating, selling, using or recycling TCE and TCE-containing products, with the aim of representing TCE users across the board. The final response represented about 25 % of the total number of organisations that buy TCE directly from importers. Therefore, the data may be considered representative but not complete.

The survey found that the major use of TCE in Australia is metal cleaning. Vapour degreasing was the most common use of TCE, accounting for 75 % of end-users. Twenty nine percent of end-users also used TCE for cold cleaning, a higher proportion than that reported in overseas studies. TCE is not used as a feedstock for other chemicals in Australia. The survey also identified some uses of TCE that appear to have ceased in Australia: as an anaesthetic agent, in dry cleaning, in correction fluid and as a solvent in pesticide formulations. Finally, TCE is being considered for use in scouring wool.

Solvent degreasing involves the use of a solvent to remove water insoluble soils from surfaces prior to processes such as painting, plating, repair, inspection, assembly, heat treatment or assembly. It does not constitute a complete industrial sector, but a process used by many industries, and as such it is difficult to catalogue and regulate its use. Vapour degreasing has been shown to be the most common use of TCE in several studies (National Industrial Chemicals Notification and Assessment Scheme 2000).
Appendix 1C: Environmental Impact

According to the World Health Organisation, about 99% of TCE that is used ends up being emitted to the atmosphere. Therefore, annual emissions are almost identical to usage figures. For instance, 219,000 tonnes of the 270,000 tonnes of TCE used in Europe in 1981 were emitted to the atmosphere. An estimate of global emissions in 1997 (allowing for 50% error) is 435,000 tonnes (World Health Organisation 1987). U.S. Toxics Releases Inventory (TRI) data claims that over 90% of all solvents used in degreasing are released to the environment as air emissions. Recycling activities are not reflected in the data (Environment Canada 2001a). The European Chlorinated Solvent Association estimates that 60% of TCE consumed is emitted to the air as a result of end use. It is assumed that the remainder is incinerated, recycled or released into other environmental media. The National Industrial Chemicals Notification and Assessment Scheme assumed that the releases of TCE into the Australian environment almost equalled the net consumption (National Industrial Chemicals Notification and Assessment Scheme 2000).

In estimating the daily emission of TCE into the Australian environment, NICNAS selected three categories of release: those incurred during the handling of imported TCE, vapour degreasing and other operations. The NICNAS survey indicated that the proportion of trichloroethylene emitted from Australian degreasing machines ranged from <1% to 100%. NICNAS referred to the United Kingdom’s “SIDS Initial Assessment Report on Trichloroethylene” of 1996 for estimates of emissions from degreasing operations; it is assumed that 70% of the TCE used in vapour degreasing operations is released into the environment, 90% of which is expected to partition to the air. The results of the NICNAS assessment are shown in table 1C. It is clear that vapour degreasing is the major source of TCE emission in Australia.
Table 1C: Estimates of daily release of trichloroethylene (TCE) Australia wide
(National Industrial Chemicals Notification and Assessment Scheme 2000)

According to the level 1 Fugacity Model by ASTER (U.S. EPA 1994), at equilibrium, 99.64% of the TCE released will partition into the atmosphere with 0.35% partitioning to water and only 0.01% entering the soil. Therefore, practically all of the TCE used in Australia enters the air unchanged. Ambient air concentrations of TCE typically range from less than 1 μg·m⁻³ in rural areas to 10 μg·m⁻³ in urban areas (World Health Organisation 2000).

<table>
<thead>
<tr>
<th>Situation</th>
<th>Daily Quantity (kg.day⁻¹)</th>
<th>Estimate of TCE release (%)</th>
<th>Release to Air (kg.day⁻¹)</th>
<th>Release to Water (kg.day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Handling of imported TCE</td>
<td>10,000</td>
<td>0.4</td>
<td>40</td>
<td>0.025</td>
</tr>
<tr>
<td>Vapour degreasing</td>
<td>8,000</td>
<td>70</td>
<td>5,040</td>
<td>560</td>
</tr>
<tr>
<td>Other uses</td>
<td>2,000</td>
<td>100</td>
<td>1,800</td>
<td>200</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td><strong>6,880</strong></td>
<td><strong>760</strong></td>
</tr>
</tbody>
</table>
Appendix 1D: Health effects

Many studies have been conducted in an attempt to determine and quantify the risk that TCE exposure poses to human health. These studies have been reviewed by various sources. This section draws from several of these, in particular, The World Health Organisation’s “Environmental Health Criteria 50: Trichloroethylene” and subsequent publications of “Air Quality Guidelines for Europe” (2000; World Health Organisation 1987). Publications by The Halogenated Solvents Industry Alliance (HSIA), Inc., The (American) Occupational Safety and Health Association (1999) and The European Centre for Ecotoxicology and Toxicology of Chemicals are also useful references (1994).

There is concern that TCE may be carcinogenic and have deleterious effects on organs and systems of the body, especially the central nervous system and liver.

In terms of acute effects, studies have shown that narcosis usually dominates other symptoms. Acute effects on the central nervous system are usually reversible and take place in two stages: excitation and depression. At first, inebriation and euphoria are present (World Health Organisation 1985). Depression symptoms would start as drowsiness, poor concentration and mood swings. Further exposure would cause dizziness, slurred speech and poor co-ordination. Extreme overexposure could lead to loss of consciousness, coma and death (Occupational Safety and Health Association 1999). Concentrations over 5000 ppm have been used for analgesia and anaesthesia in the past, although safer and more effective drugs are now used. Other clinical effects may be acute hepatic and renal toxicity (World Health Organisation 1985). At very high exposure levels, TCE can sensitise the heart to the effects of adrenaline and similar agents, which may lead to sudden cardiac arrest (Halogenated Solvents Industry Alliance 2001). Irritation of the respiratory tract may occur at concentrations of 150 – 650 ppm. Chronic and acute exposure can lead to urinary tract effects, although it is likely that this is caused by impurities in industrial TCE (World Health Organisation 1985). Brief exposure to TCE is mildly irritating to human skin. Prolonged contact could lead to burning and repeated exposure causes various types and degrees of dermatitis, depending on the person. An alcohol intolerance, known as “degreaser’s flush”, may occur. Exposure of the eye to liquid, or high concentration
TCE vapour, causes irritation and superficial damage to the cornea with complete recovery within a few days (World Health Organisation 1985).

Laboratory and workplace studies have been carried out to determine the extent of these effects and the exposure levels involved. Several studies have shown that the primary effects of TCE are on the central nervous system and the liver; furthermore some of these studies indicated that chronic exposure to concentrations less than 100 ppm was associated with nervous disturbances. One study reported nervous system effects in workers exposed to 1 – 335 ppm for a period of at least five years. This, and another concurring workplace study, observed an increase in the frequency of these complaints above 40 ppm. These results could not be duplicated in controlled laboratory experiments; human subjects were exposed to 50 – 1000 ppm for much shorter periods (about 2 hours) and effects were rarely observed below about 250 ppm (Occupational Safety and Health Association 1999). A correlation between observed toxic effects and the urinary excretion of trichloroacetic acid has been shown in several studies. The reports, of adverse health effects at 50 mg/l of trichloroacetic acid corresponding with 25 ppm TWA (Time weighted average over an 8 hour working day), are fairly consistent. The American Conference of Governmental Industrial Hygienists, Inc. recognised that the symptoms reported by workers were subjective and often found amongst members of the unexposed population; it ruled, however, that the weight of the evidence “suggests the possibility of some subjective complaints as concentrations exceed about 50 ppm” (Occupational Safety and Health Association 1999).

Extensive studies have been conducted to assess the mutagenic and carcinogenic potential of TCE. Analysis of the results is challenging, however, due to limitations in the design of the studies. The main flaw is that some of the additives present in TCE are carcinogens; in vivo studies are further complicated by the fact that workers are often exposed to a cocktail of chemicals. In addition, few studies had a large cohort.

Mice, rat and hamster studies have given both positive and negative results. An increase in lung and liver tumours was found in some mice; in some studies, male rats suffered from a slight increase in kidney tumours (Halogenated Solvents Industry Alliance 2001). The (American) Science Advisory Board noted, however, that “while
[the incidence of these tumours] is clearly in excess, [it does]… not approach the incidence of 100 % that occurred from chloroform, for example.” For example, the (American) National Toxicology Program reported that the kidney tumour response of 3 out of 49 rats was only statistically significant after correction for high mortality were made (Occupational Safety and Health Association 1999).

There have been many epidemiological studies conducted on the carcinogenicity of TCE. Unfortunately, many are studies of workers exposed to a mixture of chemicals that contain known carcinogens. The World Health Organisation’s “Environmental Health Criteria 50: Trichloroethylene” summarises these studies up to 1985. Details of tests carried out by the (American) National Toxicology Program can be found on their internet site. Only two of the epidemiological studies that have been conducted to date are considered to be of good design and conduct. Between them they studied nearly 9000 workers over a period of 30 to 37 years and found no connection between TCE exposure and any type of cancer (European Centre for Ecotoxicology and toxicology of chemicals 1994). Although more recent studies have connected TCE exposure with kidney cancer, reviewers have heavily criticised these studies and confounding seems likely (Halogenated Solvents Industry Alliance 2001).

The implications of these results are unclear. Response to TCE exposure not only differs between humans and rodents but different types of rodents, and even different strains of the same species. This is probably due to species differences in the TCE metabolism and reaction to the metabolites (Halogenated Solvents Industry Alliance 2001).

It is clear that much research into the fate of TCE in the human body must be done before there can be any certainty of TCE’s carcinogenic nature. Regulating bodies recognise that there is no evidence that it is a carcinogen to humans. However, most err on the side of caution and proclaim it is potentially a weak human carcinogen (see table 1D).

These classifications are from the sources already quoted in this section. In addition, The NOHSC’s exposure standards have been referred to.
<table>
<thead>
<tr>
<th>Body</th>
<th>Carcinogenicity Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Conference of Governmental Industrial Hygienists, Inc (ACGIH).</td>
<td>A5: Not suspected as a human carcinogen</td>
</tr>
<tr>
<td>Canadian Environmental Protection Act (CEPA)</td>
<td>2: Probable carcinogen</td>
</tr>
<tr>
<td>[German] Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area</td>
<td>IIIA1: Capable of producing malignant tumours as shown by experience with humans</td>
</tr>
<tr>
<td>European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC)</td>
<td>Does not present a carcinogenic hazard to man</td>
</tr>
<tr>
<td>International Agency for Research on Cancer (IARC)</td>
<td>2A: probably carcinogenic to humans</td>
</tr>
<tr>
<td>[American] National Toxicology Program (NTP)</td>
<td>Reasonably anticipated to be a human carcinogen</td>
</tr>
<tr>
<td>UK Health and Safety Executive (HSE)</td>
<td>3: possible carcinogen</td>
</tr>
</tbody>
</table>

Table 1D: International Cancer Risk Classification of TCE
Appendix 1E: Guidelines and standards

1. Guidelines from The World Health Organisation

The World Health Organisation (WHO) provides information on air pollution to aid governments in setting standards and developing control measures. They have been assessing the risk that pollutant chemicals pose to human health since the 1950. The first ever guideline values were released in 1958. “Air quality guidelines for Europe” were published in 1987 and updated from 1993 onwards. A WHO Expert Task Force meeting was held in 1997, when the guidelines were extended to provide international applicability. Air quality control and assessment issues were also discussed in more detail (Environment Australia 2001).

In the most recent assessment of TCE by WHO, it was concluded that the chemical is mutagenic and carcinogenic and as such a safe level cannot be recommended. From the data available, it was considered that animal studies provide the best quantitative information on cancer risk. Linear extrapolation from the animal tumour data was used and the most sensitive endpoint was taken. The most conservative figure, derived from studies of Leydig cell tumours in rats’ testes, was a unit risk of $4.3 \times 10^{-7}$ per $\mu$g$m^{-3}$ (World Health Organisation 2000).

In converting these guidelines into workable standards and pollution control programs, governments have to consider how the information can be applied to their locality. The legal system is a major factor affecting the new legislation. The level of adverse health effects that a population tolerates may vary because of factors such as different cultural backgrounds and different background levels of health status. The susceptibility of the exposed population varies between countries; that is the age distribution, number of people suffering from disease and exposure patterns effect the risk posed to the population and hence the decisions made about protective measures. The exposure-response relationships given in the guidelines may have to be modified for variations in climate, geography and population structure (World Health Organisation 2000). This is illustrated by the fact that in Canada the half-life of TCE varies from days to months depending on climate and geography (Environment Canada 2001a). The evaluation of costs and benefits of potential schemes may vary...
between countries. The level of awareness and participation of all parties affected by the legislation is likely to affect cooperation at all stages of implementation (World Health Organisation 2000).

2. Classification of TCE

2.1 Terminology

TCE belongs to a group of pollutants known as ‘air toxics’ or ‘hazardous air pollutants’ (HAPs). These terms can be used interchangeably and have no universally accepted definition; however, most recognised definitions include:

- that air toxics are pollutants,
- that they are present in low concentrations in the atmosphere and
- that they are known or suspected to be hazardous to health and/or the environment.

Regulatory and environmental bodies have designated various sub-groups of air toxics. TCE is usually grouped as a ‘halogenated organic compound’ or a ‘volatile organic compound’ (VOC) (Environment Australia 2001).

The World Health Organisation defines VOCs as “all organic compounds in the boiling range of 50-260°C, excluding pesticides” (Environment Australia 2001).

2.2 International Air Quality Indicators

In recognition of the fact that atmospheric monitoring and reporting vary considerably among member countries, The Organisation for Economic Co-operation and Development (OECD) undertook the ‘Advanced Air Quality Indicators and Reporting’ project. According to Environment Australia, “The proposed methodology is expected to improve comparative air quality analyses, assessment and communication at international level.”

The project focused on the six major air pollutants (carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter and sulphur dioxide). Fifteen indicators for hazardous air pollutants were also identified, of which TCE was one.
2.3 US regulation

Congress passed the first Clean Air Act in 1970. This was the first time the government had the power to set national standards in an attempt to protect health and the environment. However, twenty years later, nearly half of the population still lived in non-attainment areas. The Clean Air Act of 1990 was a major revision of the original act (Environmental Protection Agency 1991).

The US “National Air Toxics Program – The Integrated Urban Strategy” was finalised in 1999. It identified a list of 33 urban air toxics and the 29 industry source categories mainly responsible for their emission. TCE was one of the air toxics, and halogenated solvent cleaners were listed as a source category.

US standards are based on “maximum available control technology” for the industry in question (Environment Australia 2001). Areas of non-attainment are classified by their severity; attainment deadlines and the stringency of the control measure are set accordingly. Long term planning is also a legal requirement and failure to meet deadlines is addressed (Environmental Protection Agency 1991).

2.4 European regulation

Countries in Europe are governed by national regulations and those imposed by the EU. As yet, the European Community has not exercised its right to propose measures to regulate the amount of trichloroethene in the air (Kemikalieinspektionen v Toolex Alpha AB 2000). There are rules limiting the discharge of trichloroethene to water courses, however (Eur-Lex 1990).

Individual countries are at liberty to impose their own regulations on the usage of TCE (Kemikalieinspektionen v Toolex Alpha AB 2000). Germany has introduced rules governing the use of chlorinated solvents, designed to achieve substantial reductions in emissions. There also regulations, in Austria and Switzerland, banning certain solvent applications.
In 1991, Sweden banned the sale, transfer and use of chemical products containing TCE, dichloroemethane and tetrachloroethene. The ban came into effect with respect to industry in 1996 (National Industrial Chemicals Notification and Assessment Scheme 2000). It is interesting to note that the Kemikalieinspektionen (Chemicals Inspectorate) had to defend this prohibition in court on the grounds that it was not consistent with European Community law. The court ruled, in 2000, that:

‘National legislation which lays down a general prohibition on the use of trichloroethylene for industrial purposes and establishes a system of individual exemptions, granted subject to conditions, is justified…on grounds of the protection of health of humans’.

In 1991, an Expert Panel on Air Quality Standards (EPAQS) was jointly established by the Department of the Environment, Transport and the Regions (DETR), the Scottish Executive, The National Assembly for Wales and the Department of the Environment for Northern Ireland. The recommendations were adopted as the benchmark standards in the UK DETR National Air Quality Strategy (Environment Australia 2001). As yet, there is no report available for TCE. The current status of the EPAQS reports can be checked at the Department for the Environment, Foods and Rural Affairs internet site.

2.5 New Zealand regulation

The 1994 Ambient Air Quality Guidelines, released by the New Zealand Ministry of the Environment, contained a list of 140 air toxics and ‘advocated a cautionary approach to minimise their emissions’ (Environment Australia 2001).

In 1998, a review of these guidelines began but has not yet been implemented. While the NZ Ministry didn’t identify TCE as an indicator compound, it did identify volatile hydrocarbon as a group of priority compounds.

In New Zealand, regional councils and unitary authorities are responsible for maintaining clean air. Therefore, they can develop regional plans under the Resource Management Act of 1991. There are no values for TCE at present (Environment Australia 2001).
2.6 Canadian regulation

Canada developed a unique approach to pollution. In response to a challenge from the federal government to reduce and eliminate emissions of toxic substances, The Accelerated Reduction/Elimination of Toxics (ARET) Program ran from 1991 – 2000. A collaboration of industry, health and professional organisations and governments across Canada worked together to reduce pollution, on average, by about 80%. In most cases, the goal for 2000 was comfortably exceeded by the actual reduction achieved.

2.7 Australian regulation

Until 1998, Australia had no national air quality standards; it was the responsibility of individual states. In 1998 the National Environmental Protection Council (NEPC) created the National Environmental Protection Measure (NEPM) for Ambient Air Quality, which set standards for the six ‘criteria’ pollutants, namely carbon monoxide, nitrogen dioxide, photochemical oxidants, sulphur dioxide, lead and particulates.

Air toxics are still under state regulation. However, in June 2001, the NEPC decided to develop an Ambient Air Toxics NEPM. Five chemicals, excluding TCE, were identified for consideration in the initial stage of the NEPM. Completion of a draft Ambient Air Toxics NEPM is expected by December 2002.
2.8 Permissible exposure limits

Table 1E shows examples of permissible exposure limits to TCE worldwide.

<table>
<thead>
<tr>
<th>Body</th>
<th>Limit</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Australian] National Health and Safety Commission</td>
<td>TWA</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>15 minute STEL</td>
<td>200</td>
</tr>
<tr>
<td>[American] Occupational Safety and Health Association (OSHA)</td>
<td>TWA</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>15 minutes STEL</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Peak</td>
<td>300</td>
</tr>
<tr>
<td>Sweden (1987)</td>
<td>TWA</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>15 minute STV</td>
<td>50</td>
</tr>
<tr>
<td>U.K. Health and Safety Executive (1989)</td>
<td>TWA</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>10 minute STEL</td>
<td>150</td>
</tr>
<tr>
<td>West Germany (1988)</td>
<td>TWA</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Type II, 2</td>
<td>250</td>
</tr>
<tr>
<td>Japan</td>
<td>Annual average</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Table 1E: Permissible exposure limits

From 1989 to 1993, the OHSA’s TWA for TCE was 50 ppm and several states maintain this lower limit (Halogenated Solvents Industry Alliance 2001).
Appendix 2A: Health and Safety - Possible by-products

There was concern that the experiments may produce compounds that are more far more harmful than trichloroethene (TCE) under some conditions. The main concern was that chlorinated benzenes may be formed that could be precursors for dioxins and furans, the most carcinogenic compounds known. Table 2A shows the tolerable daily intakes (TDIs) of these compounds compared with TCE, in order to highlight this concern. References are Resource Futures International (2003), World Health Organisation (1998) and Health Canada (2003).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>TDI ug/kgbw/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichloroethene (TCE)</td>
<td>1.5E+00</td>
</tr>
<tr>
<td>Total polychlorinated benzenes</td>
<td>1.0E+00</td>
</tr>
<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>2.7E-01</td>
</tr>
<tr>
<td>Total dioxins and furans</td>
<td>1.0E-05</td>
</tr>
<tr>
<td>2,3,7,8-tetrachlorodibenzo-p-dioxin (the most toxic dioxin)</td>
<td>1.0E-06 - 4.0E-06</td>
</tr>
</tbody>
</table>

Table 2A: Tolerable daily intakes of TCE and worst-case scenario products

Table 2A shows that the formation of very low levels of chlorinated benzenes would not be disastrous, but the formation of dioxins and furans must be avoided.

See Calvin and Brunner (1989) for more information on dioxins and furans.
Appendix 4A: Vapour Pressure of trichloroethene and water

Appendix 4A: Saturated vapour pressure trichloroethene (TCE) and water. Antoine Equation Source: NIST chemistry web book
Appendix 4B: Gas chromatography details

1. Specifications

- Gas Chromatograph: Varian 3600
- Software: Varian Star 5.5
- Channel 16: ADCB GC to PC
- Channel 17: PC to GC (Varian 3600)

Split/splitless flow

*The splitter enables varying proportions of the sample to reach the detector. This increases the quantifiable range by up to a thousand times.*

- Column length: 30 m
- Column ID: 0.25 mm
- Film Thickness: 0.25 µm

*The smaller the thickness, the higher the resolution.*

- Column Volume = \( \pi \cdot 0.0125^2 \cdot 3000 \text{ cm}^3 = 1.47 \text{ cm}^3 \)
- Elution time of unretained peak = \( t_0 \)

*Varies with column temperature and split flow (i.e. velocity through column)*

- Column flow = Column volume/\( t_0 \) = read-out from column status

- Noise ~ 0.4 mV after new septum installed (was 1 mV initially)
- Therefore, limit of detection is about 0.8 mV (2 mV max)

- Injector 1077, required length = 5.7 cm

*Original injector was changed for SPME work to improve peak resolution*

- ECD: Varian Serial A6805, Model 02-1972-01, required length from detector to ferrule = 11.5 cm
2. Nomenclature

<table>
<thead>
<tr>
<th></th>
<th>( \rho_{\text{TCE}} )</th>
<th>1.456 g ml(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency vapour generator</td>
<td>( \eta_{\text{VG}} )</td>
<td>fraction</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>( V_{\text{Inj}} )</td>
<td>( \mu l )</td>
</tr>
<tr>
<td>Split Ratio</td>
<td>( \text{SR} )</td>
<td>ml min(^{-1} )</td>
</tr>
<tr>
<td>Vapour pressure of x in air</td>
<td>( P_{\text{TCE}} )</td>
<td>fraction</td>
</tr>
<tr>
<td>Air flow</td>
<td>( F_1 )</td>
<td>l min(^{-1} )</td>
</tr>
<tr>
<td>TCE/Air flow</td>
<td>( F_2 )</td>
<td>l min(^{-1} )</td>
</tr>
<tr>
<td>Liquid standard concentration</td>
<td>( C_{\text{std}} )</td>
<td>( \mu g \text{ml} )</td>
</tr>
<tr>
<td>Mass to detector</td>
<td>( M_{\text{det}} )</td>
<td>( \mu g )</td>
</tr>
</tbody>
</table>

3. Method

Range = 10  
Attenuation = 8  
Recommended velocity for nitrogen carrier gas = 15 – 30 cms\(^{-1} \)  
Pressure ~ 10  
Velocity ~ 24 cms\(^{-1} \)  
Column flow ~ 1 cms\(^{-1} \)  
Flow out of ECD = 32 ml min\(^{-1} \)  
Temperature = 35°C for 5.5 mins, ramp at 15°C per minute to 270°C for 5 mins.  
Replace septum every 100 injections/once per week  
Bake out method run once per week or after any upset (e.g. Nitrogen runs out).

4. General Relationships

Total flow (green knob) = Column flow (column display) + Split flow (bubble flow meter)

Split ratio = Total flow/Column flow

Volume of TCE to ECD = Volume of TCE injected/Split ratio

Density of TCE (\( \rho_{\text{TCE}} \)) = 1.456 g ml\(^{-1} \) (25°C)


5. Calibration

Industrial trichloroethene (TCE) is being used to simulate the vapour degreasing process as closely as possible. This contains additives and stabilisers such as butylene oxide. Hexane is used as the solvent in the liquid samples.

Trichloroethene liquid standards were prepared for calibration. Since the flow was split, constant volume injections of 1 µl were used to ensure that the same proportion of the injection reached the detector during each run.

Careful injection technique ensured uniformity:

- Syringes were rinsed in hexane, baked in the GC oven and cooled to minimise cross-contamination of samples. The syringe was then rinsed with the sample about 20 times (discarding the first 2-3).
- Excess liquid was drawn and air bubbles removed.
- Liquid was expelled until the exact amount required was read at parallax.
- The needle was wiped with a tissue to remove excess liquid.
- Some air was drawn into the syringe to be injected with the sample.
- The sample was injected quickly and the needle held in the injector for a few seconds (to allow complete vaporisation of the liquid).

In order to calibrate within the desired range, the expected amounts of TCE were estimated for each planned experiment. Basic relationships between concentrations and absolute values were formulised to enable easy calculation.

6. Absolute amounts: Gas samples

Volume of TCE to ECD = Volume of TCE injected/ Split Ratio

Absolute Amount to ECD = \( \rho_{tce} V_{\text{Inj}(tce)}/SR \)

= \( \rho_{tce} P_{tce} \eta_{VG}\left[F_2/(F_1 + F_2)\right] V_{\text{Inj}}/SR \)

For \( \rho \text{ (g.ml}^{-1}) \) and \( V_{\text{Inj}} \text{ (µl)} \), units are mg.

7. Absolute amounts: Liquid standards

Absolute Amount to ECD = \( C_{\text{std}}(V_{\text{Inj}}/SR).10^{-6} \)
For $C_{std}$ (µg.ml$^{-1}$) and $V_{inj}$ (µl), units are mg

To convert $C_{std}$ from µl.l$^{-1}$ (ppm/v) to µg.ml$^{-1}$ (ppm/m):
Density units are g.ml$^{-1}$.
To get top half to µg, mass (µg) = density ($10^3$.g/ml) x volume (µl)
To get bottom half, convert from litres to millilitres
$C_{std/m} = C_{std/v} \cdot \rho$

$[\mu g/ml = (\mu l/l).10^3.\rho.10^{-3}]$

8. Results of calibration

Limit of Detection = 2 x noise

Response factor plotted: Can determine Linear Dynamic Range (expect $10^2 – 10^5$ for an ECD depending on set-up)

Calibration curve

9. Processing Gas Chromatography Results from Interactive Graphics

Results from Start System Control are written to Interactive Graphics. Here the chromatogram can be viewed and integrated. Integration parameters can be specified in the method. The computer-generated report (listing elution times and areas, etc.) and chromatogram can be printed.
As gas chromatography, indeed chemical analysis in general, has been a new skill to be learnt for this project, the results processing method has evolved throughout the work. It was not always obvious which data could be translated into useful information and which was merely spurious. For example, the minimum peak area considered relevant must be decided upon. However, using a systematic approach was difficult as some runs had many seemingly meaningless peaks if the same parameters were used as when integrating “cleaner” runs. Concern that relevant raw data may be discarded was also a concern.

In the end, the raw data was used together with the chromatograms. The chromatogram was used to identify relevant peaks and then the raw data was referred to for peak areas.
Appendix 6A: CHEMKIN chemistry input file for AURORA

!===============================================================================================!
! APPENDIX 6A: CHEMISTRY INPUT FILE FOR AURORA
!===============================================================================================!

Plasma trichloroethene destruction reaction scheme for carbon, chlorine, hydrogen, nitrogen and oxygen without charged species.

Although propane is included in the model, there are insufficient reactions for its combustion.

Therefore, propane is assumed to be converted to CO2 and water on entry into reactor. This is a fair assumption in the plasma since products reach equilibrium "instantaneously".

References for each reaction are listed. See bottom for references from Lylegian, Wang and Law.

Numbered reactions can be found in Evans et al.(1993).

!===============================================================================================!

\[ R = 8.31442 \times 10^{-3} \text{ kJ/mol.K} \]
\[ \text{N}(\text{A}) = 6.02214199 \times 10^{23} \]
\[ \text{UNITS are in moles, kJ/mol, cm}^3 \]

SPECIES

N-C_{3}H_{7} \text{ n-Propyl radical CH}_{3}CH_{2}CH_{2}
1-C_{3}H_{7} \text{ iso-Propyl radical CH}_{3}CH\text{CH}_{3}
C_{6}H_{5} \text{ Phenyl radical C}_{6}\text{H}_{5}.
C_{6}H_{7} \text{ 2,4-Cyclohexadien-1-yl}
A-C_{3}H_{5} \text{ allyl radical CH}_{2}CHCH_{2}
C_{4}H_{6} \text{ butadiene CH}_{2}CHCHCH_{2}
C_{5}H_{9} \text{ 3-Methyl-1-buten-3-yl radical \((CH_{3})_{2}CHCHCH\)
S_{C5H9} \text{ (CH}_{3} \text{ )_{2}CHCHCH \text{ radical}}
S_{C6H6} \text{ SINGLET}
S_{C6H6} \text{ 1,2,4,5 hexatetraene CH}_{2}CHCHCHCCH_{2}

 ELEMENTS C H Cl O N E AR END

SPECIES

AR
C
CCL CCl_{2} CCl_{2}H O CCL_{3} CCl_{3}O E CCL_{4}
CH CHCl CHCl_{2} CHCl_{3} CH Cl(S) CHCl_{2} CH_{2}O CH Cl Cl C Cl Cl Cl Cl
C_{2}
CCL_{2}CH CCL_{2}OH CH CCL_{2}OH CCL CCL_{3} CCL_{2}CLO CCL_{2}CH CCL_{2}CLO C Cl(S)H CCl_{2}CLO
CCL_{3}CLO CCL CCl Cl CCl Cl CCl Cl CCl
C_{2}H CHCl CCL_{2}CLO CCL_{2}CLO CCL_{2}CLO C CCl CCl CCl CCl CCl CCl
C_{2}H_{2} CH_{2}CCH CCL_{2}CLO CCL_{2}CLO C CCl CCl CCl CCl CCl CCl
C_{2}H_{3} CH_{2}CCH CCL_{2}CLO CCL_{2}CLO C CCl CCl CCl CCl CCl CCl
C_{3}
C_{3}H_{2} C_{3}H_{3} C_{3}H_{2}CCH CCH CCl CCl CCl CCl CCl CCl CCl CCl CCl
C_{4}
C_{4}H_{2} C_{4}H_{2} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3} C_{4}H_{3}
<table>
<thead>
<tr>
<th>REACTIONS</th>
<th>MOLES</th>
<th>KIJOULES/MOLE</th>
<th>SQUIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2+M=H+H+M</td>
<td>8.47E+17</td>
<td>-0.70</td>
<td>437</td>
</tr>
<tr>
<td>C+C+C2-M=C2+M</td>
<td>1.98E+17</td>
<td>-1.6</td>
<td>0</td>
</tr>
<tr>
<td>H2+HO2=H2O2+H</td>
<td>3.01E+13</td>
<td>0</td>
<td>109</td>
</tr>
<tr>
<td>H2+O=OH+H</td>
<td>3.86E+4</td>
<td>2.70</td>
<td>26.19</td>
</tr>
<tr>
<td>H2+O2=HO2+H</td>
<td>1.45E+11</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+M=O+O+M</td>
<td>1.6E+18</td>
<td>1.30</td>
<td>15.30</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>3.13E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>OH+H+H2O=M</td>
<td>4.46E+20</td>
<td>-1.18</td>
<td>2.58</td>
</tr>
<tr>
<td>OH+H2O=OH+H2O</td>
<td>2.43E+12</td>
<td>2.45</td>
<td>0.42</td>
</tr>
<tr>
<td>O2+H=OH+H</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>O2+M+O=O+O2</td>
<td>6.71E+15</td>
<td>0.55</td>
<td>49.64</td>
</tr>
<tr>
<td>O2+H=OH+O</td>
<td>2.23E+13</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>O2+O2=O2+O2+O</td>
<td>1.15E+12</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Activation Energy</td>
<td>References</td>
</tr>
<tr>
<td>----------</td>
<td>---------------</td>
<td>--------------------</td>
<td>------------</td>
</tr>
<tr>
<td>( \text{CO}_2 + \text{CO} \rightarrow \text{CO} + \text{O} )</td>
<td>1.09E+14</td>
<td>0</td>
<td>1997ERE/ZIB-7</td>
</tr>
<tr>
<td>( \text{CO} + \text{O} \rightarrow \text{C} + \text{O} )</td>
<td>9.18E+19</td>
<td>-3.1</td>
<td>1073</td>
</tr>
<tr>
<td>( \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} )</td>
<td>5.37E+15</td>
<td>-1</td>
<td>307</td>
</tr>
<tr>
<td>( \text{C}_2 + \text{O} \rightarrow \text{CO} + \text{C} )</td>
<td>5.06E+13</td>
<td>0</td>
<td>264</td>
</tr>
<tr>
<td>( \text{O}_2 \rightarrow \text{O} + \text{O} )</td>
<td>3.61E+14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} )</td>
<td>2.41E+01</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>1.99E+12</td>
<td>0</td>
<td>21.0</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{O} \rightarrow \text{C}_2 \text{H}_2 \text{O} + \text{H} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{OH} \rightarrow \text{C}_2 \text{H}_2 \text{O} + \text{H} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>1.05E+11</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{OH} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{OH} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{OH} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{OH} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{C}_2 \text{H}_2 + \text{OH} \rightarrow \text{C}_2 \text{H}_2 \text{Cl} + \text{H} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
</tbody>
</table>

### Reactions with TCE

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>1.99E+12</td>
<td>0</td>
<td>21.0</td>
</tr>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>1.00E+13</td>
<td>0</td>
<td>8.40</td>
</tr>
<tr>
<td>( \text{Cl}_2 + \text{C}_2 \text{H}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{C}_2 \text{H}_2 \text{Cl} )</td>
<td>3.15E+10</td>
<td>0</td>
<td>-3.78</td>
</tr>
</tbody>
</table>

### Reactions with H, Cl and O

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl} + \text{O} + \text{H} \rightarrow \text{O}_2 + \text{Cl} )</td>
<td>1.81E+13</td>
<td>0</td>
<td>-0.58</td>
</tr>
<tr>
<td>( \text{O}_3 + \text{Cl} \rightarrow \text{O}_2 + \text{ClO} )</td>
<td>6.02E+11</td>
<td>0</td>
<td>33.26</td>
</tr>
<tr>
<td>( \text{OH} + \text{Cl} \rightarrow \text{HCl} + \text{O}_2 )</td>
<td>1.93E+11</td>
<td>0</td>
<td>-2.70</td>
</tr>
<tr>
<td>( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{OH} )</td>
<td>3.01E+8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{HO}_2 + \text{Cl} \rightarrow \text{OH} + \text{ClO} )</td>
<td>2.89E+11</td>
<td>0</td>
<td>-5.82</td>
</tr>
<tr>
<td>( \text{Cl} + \text{O} + \text{HCl} \rightarrow \text{HCl} + \text{Cl} + \text{O} )</td>
<td>1.81E+13</td>
<td>0</td>
<td>-0.58</td>
</tr>
<tr>
<td>( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{OH} )</td>
<td>1.63E+13</td>
<td>0</td>
<td>4.41</td>
</tr>
<tr>
<td>( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{OH} )</td>
<td>1.81E+13</td>
<td>0</td>
<td>4.41</td>
</tr>
<tr>
<td>( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{OH} )</td>
<td>1.81E+13</td>
<td>0</td>
<td>4.41</td>
</tr>
</tbody>
</table>
CLOO + O₂ + CLO  1.45E12  0  7.98  !1997 ATK/BAU521-1011  2  240 - 400  fast
HCL + OH + CL  4.5E2  3.13  12.89  !1990 MAH/KIM2994  2  350 - 1480
forward to eqm (lower at high T)

OH + HCL + H₂O + CL  1.11E7  1.66 -2.78  !1997STE/THU3926-3933  2  138 -
1060 normal, backwards
HCL-H₂ + CL  3.97E8  1.44 10.31  !1997 STE/THU3926-3933  2  138 -
1060 forward to eqm (lower at high T)

OH + HCL = H₂O + CL  1.11E7  1.66 -2.78  !1997STE/THU3926-3933  2  138 -
1060 normal, backwards
HCL + H = H₂ + CL  3.97E8  1.44 10.31  !1994 ADU/FON801-808  2  200 - 1200
duplicate?
HOCL + H = H₂ + CL  1.00E13  0  4.20  !1997 ATK/BAU521-1011  2  200 - 300
duplicate
H₂ + CL = HCL + H  2.74E8  1.59 13.97  !1994 KUM/LIM9487-9498  2  200 - 1200
duplicate?

OH + CL = HCL + O  5.9E12  0  23.78  !1981 BAU/DUX Suppl  2  290 -
720 hardly any reaction
300 duplicate
300 HCL + H₂ + CL = CLCO + CO  6.32E12  0  110  !1924 BOD/PLA399  2  621 - 725
300 CLOO + CO = CLCO + CO  6.02E9  0  0  !1988 HER967  2  292
300 CLOO + Cl₂ + CO = CLCO + CO  6.02E13  0  0  !1988 HER967  2  292
300 CLOO + Cl₂CO + O = CLCO + CO  1.00E14  0  0  !1988 HER967  2  292
300 CLOO + Cl₂CO = Cl₂CO + Cl  1.00E14  0  0  !1988 HER967  2  292
300

CLOO + Cl₂ = Cl₂CO  6.02E12  0  110  !1924 BOD/PLA399  2  621 - 725
Cl₂CO + O₂ + Cl₂CO  6.02E9  0  0  !1988 HER967  2  292
300 CLOO + Cl₂CO + Cl₂CO  6.02E13  0  0  !1988 HER967  2  292
300 CLOO + Cl₂CO = Cl₂CO + Cl  1.00E14  0  0  !1988 HER967  2  292
300

CLOO + Cl₂ = Cl₂CO  6.02E12  0  110  !1924 BOD/PLA399  2  621 - 725
Cl₂CO + O₂ + Cl₂CO  6.02E9  0  0  !1988 HER967  2  292
300 CLOO + Cl₂CO + Cl₂CO  6.02E13  0  0  !1988 HER967  2  292
300 CLOO + Cl₂CO = Cl₂CO + Cl  1.00E14  0  0  !1988 HER967  2  292
300
CCL4+O=CCL3+CLO 3.0E11 0 18.29 !1988HER967 2 300 - 1000 fast
5CCL4+O=CCL3+CLO 2.13E14 0 0 !23 species O(1D) try O duplicate
5O2+C2CL3=C2CL2O+CLO 3.16E11 0 21.0 !19 species C2CL2O
CCL3CHCL+O2=CHCL2CCLO+CLO 1.00E13 fast 0 21.0 !19E
CLCO+O=CCL3+CLO 6.02E10 0 0 !19E fast
CLCO+O+CLO 1.0E14 0 0 !19E fast

Reactions with and producing COCl 149 - 161

CLCO+O2=CO2+CL 6.02E10 0 0 !19E fast
CLCO+O2=CO+CL2O 6.02E10 0 21.0 !19E fast

Reactions with CnCLx 162 - 180

CCL4+OH=HOCL+CCL3 6.02E11 0 19.3 !22 SLIGHTLY forward over range
CCL3+CL=CCL4 3.52E13 0 0 !1996KUM/SU7541-7549 2 1050 - 2200 normal, backwards at high T
CCL3+CL2=CCL4+CL 2.51E12 0 25.11 !1980WEI/BEN403 2 300 - 670 normal, backwards at high T
CCL3+O2+M=CCL3O2+M 2.29E32 -6.00 0 !1997ATK/BAU521-1011 2 300 - 1000 normal, backwards, quite fast
CCL3+O2+M=CCL3OO+M 2.29E32 -6.00 1.45 !1997ATK/BAU521-1011 3 200 - 300 normal, backwards, quite fast
\[
\begin{align*}
\text{CCL}_3&+\text{CLCCCL} = \text{CCL}_5 + 31.6 \times 10^{11} \text{ TE} \quad \text{normal, backwards slow} \\
\text{CCL}_2&+\text{CLCL}_3 = \text{CL}_3\text{CO} + \text{CL}_3\text{CO} + \text{CCL}_3 + \text{CL} = 6.03 \times 10^{11} \text{ TE} \\
\text{CHCL}_3&+\text{CL} = \text{CCL}_3 + \text{HCL} + 2.95 \times 10^{12} \text{ TE} \quad \text{normal, slow}
\end{align*}
\]

\[\text{Miscellaneous reactions} 181 - 185\]

\[
\begin{align*}
\text{CHCL}_3&+\text{O} = \text{OH} + \text{CCL}_3 + 1.14 \times 10^{13} \text{ TE} \\
\text{CHCL}_3&+\text{OH} = \text{H}_2\text{O} + \text{CCL}_3 + 2.83 \times 10^{7} \text{ TE}
\end{align*}
\]

\[\text{C1 AND C2} 14 - 25\]

\[
\begin{align*}
\text{H}+\text{CH}_2&=\text{H}+\text{CH}_2 + 5.00 \times 10^{13} \text{ TE} \\
\text{H}+\text{CH}_3&=\text{H}+\text{CH}_2 + 5.00 \times 10^{13} \text{ TE} \\
\text{C}+\text{CH}_2&=\text{H}+\text{CH}_3 + 4.00 \times 10^{13} \text{ TE} \\
\text{C}+\text{CH}_3&=\text{H}+\text{CH}_4 + 6.00 \times 10^{13} \text{ TE} \\
\text{CH}_2&+\text{H} = \text{H} + \text{CH}_3 + 3.00 \times 10^{13} \text{ TE} \\
\text{CH}_2&+\text{H} = \text{CH}_2 + \text{H} + 3.00 \times 10^{13} \text{ TE} \\
\text{CH}_2&+\text{H} = \text{H} + \text{CH}_4 + 8.00 \times 10^{12} \text{ TE} \\
\text{CH}_2&+\text{H} = \text{CH}_3 + \text{H}_2 + 1.20 \times 10^{13} \text{ TE} \\
\text{C}+\text{CH}_4&=\text{H} + \text{CH}_2 + 2.27 \times 10^{13} \text{ TE} \\
\text{C}+\text{CH}_3&=\text{H} + \text{CH}_3 + 3.92 \times 10^{11} \text{ TE} \\
\text{CH}_2&+\text{CH}_2=\text{H} + \text{CH}_4 + 9.64 \times 10^{12} \text{ TE} \\
\text{CH}_2&+\text{H} + \text{CH}_3 = \text{CH}_3 + \text{CH}_2 + 6.64 \times 10^{48} \text{ TE} \\
\text{H}+\text{C}_2\text{H}_6&=\text{CH}_3 + \text{CH}_2 + 1.15 \times 10^{12} \text{ TE} \\
\text{C}+\text{CH}_2&+\text{H}_2 = \text{H} + \text{CH}_3 + 1.00 \times 10^{17} \text{ TE} \\
\text{H}+\text{C}_2\text{H}_2&+\text{H}_2 = 5.07 \times 10^{7} \text{ TE} \\
\text{H}+\text{C}_2\text{H}_2&+\text{H}_2 = \text{H} + \text{C}_2\text{H}_2 + 1.32 \times 10^{17} \text{ TE}
\end{align*}
\]
\[
C_2H5 + CH_3 + M = C_3H_8 + M \quad 2.91 \times 10^7 \quad -16.10 \quad 15.80 \quad 4 \quad 1983LAU/GAR560 \quad 3 \quad 100 - 2500
\]
\[
H + C_2H6 + CH_3CH_2H_2 = C_2H5 + CH_3 + M \quad 3.93 \times 10^5 \quad 2.50 \quad 24.36 \quad 5 \quad 1992TSA3-8 \quad 2 \quad 950 - 2500
\]
\[
C_3H_2 + CH_3 - H \quad 2.20 \times 10^{12} \quad 0.0 \quad 0.0 \quad 0 \quad 0 \quad 2 \quad 100 - 2500
\]

![Up to C4](100 - 2300)

\[
C_4H + H + M = C_4H_2 + M \quad 1.0 \times 10^{17} \quad -1.00 \quad 0.0 \quad 0 \quad 0 \quad 1 \quad 2100 - 2300
\]

![Up to C5](67 - 75)

\[
CH_3CHCH_3 + C_2H_2 = CH_3 + CH_2CHCH_2 \quad 2.77 \times 10^{10} \quad 0 \quad 27.19 \quad 0 \quad 0 \quad 1988TSA887 \quad 2 \quad 300 - 2500
\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}<em>6 \rightarrow \text{C}</em>{12}\text{H}_9\text{Cl} + \text{H} )</td>
<td>3.980E+11</td>
<td>0.00</td>
<td>14.22</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}<em>5\text{Cl} \rightarrow \text{C}</em>{12}\text{H}_8\text{Cl}_2 + \text{H} )</td>
<td>3.980E+11</td>
<td>0.00</td>
<td>14.22</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}_4\text{Cl}<em>2 \rightarrow \text{C}</em>{12}\text{H}_7\text{Cl}_3 + \text{H} )</td>
<td>3.980E+11</td>
<td>0.00</td>
<td>14.22</td>
</tr>
<tr>
<td>( \text{HCl} + \text{M} \rightarrow \text{Cl} + \text{H} + \text{M} )</td>
<td>4.4E13</td>
<td>0</td>
<td>342</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5 + \text{C}<em>6\text{H}<em>5 \rightarrow \text{C}</em>{12}\text{H}</em>{10} )</td>
<td>5.7E12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5 + \text{C}_6\text{H}<em>4\text{Cl} \rightarrow \text{C}</em>{12}\text{H}_9\text{Cl} )</td>
<td>1.000E+14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}_4\text{Cl}<em>2 \rightarrow \text{C}</em>{12}\text{H}_8\text{Cl}_2 )</td>
<td>1.000E+14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{H} + \text{C}_6\text{H}_3\text{Cl}_3 \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{Cl} )</td>
<td>1.900E+13</td>
<td>0</td>
<td>24.56</td>
</tr>
<tr>
<td>( \text{H} + \text{C}_6\text{H}_2\text{Cl}_4 \rightarrow \text{C}_6\text{H}_3\text{Cl}_3 + \text{Cl} )</td>
<td>1.900E+13</td>
<td>0</td>
<td>24.56</td>
</tr>
<tr>
<td>( \text{H} + \text{C}_6\text{H}_Cl_5 \rightarrow \text{C}_6\text{H}_2\text{Cl}_4 + \text{Cl} )</td>
<td>1.900E+13</td>
<td>0</td>
<td>24.56</td>
</tr>
<tr>
<td>( \text{H} + \text{C}_6\text{Cl}_6 \rightarrow \text{C}_6\text{H}_Cl_5 + \text{Cl} )</td>
<td>1.900E+13</td>
<td>0</td>
<td>24.56</td>
</tr>
<tr>
<td>( \text{Cl} + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HCO} )</td>
<td>4.940E+13</td>
<td>0</td>
<td>0.28</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{C}_6\text{H}_4\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCO} )</td>
<td>5.430E+03</td>
<td>2.81</td>
<td>25.52</td>
</tr>
<tr>
<td>( \text{H} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{HCl} + \text{H}_2\text{O} )</td>
<td>2.43E9</td>
<td>1.09</td>
<td>6.41</td>
</tr>
<tr>
<td>( \text{CHCl}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_3 + \text{Cl} )</td>
<td>5.18E11</td>
<td>0</td>
<td>10.31</td>
</tr>
<tr>
<td>( \text{CHCl}_2 + \text{O}_2 \rightarrow \text{Cl}_2\text{HOO} )</td>
<td>3.71E10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{CHCl}_2 + \text{CHCl}_2 \rightarrow \text{CHCl}_2\text{CHCl}_2 )</td>
<td>3.79E14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{CHCl}_2 + \text{C}_3\text{Cl}_3 \rightarrow \text{HCl} )</td>
<td>1.81E9</td>
<td>0</td>
<td>26.77</td>
</tr>
<tr>
<td>( \text{CHCl}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_2 + \text{Cl}_2 )</td>
<td>1.69E13</td>
<td>0</td>
<td>10.81</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CHCl}_2 + \text{Cl}_2 )</td>
<td>2.37E6</td>
<td>2.26</td>
<td>27.44</td>
</tr>
<tr>
<td>( \text{CHCl}_2 + \text{Cl} \rightarrow \text{CHCl}_2 + \text{Cl}_2 )</td>
<td>2.43E9</td>
<td>1.09</td>
<td>6.41</td>
</tr>
<tr>
<td>( \text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CHCl}_2 + \text{Cl}_2 )</td>
<td>6.3E8</td>
<td>0</td>
<td>155</td>
</tr>
<tr>
<td>( \text{N}_2 + \text{N} \rightarrow \text{N}_2 )</td>
<td>5.01E14</td>
<td>0</td>
<td>4.18</td>
</tr>
<tr>
<td>( \text{N}_2 + \text{N}_3 \rightarrow \text{N}_2 + \text{N}_2 )</td>
<td>8.43E13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{N} + \text{O} \rightarrow \text{NO} )</td>
<td>5.01E14</td>
<td>0</td>
<td>4.18</td>
</tr>
<tr>
<td>( \text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N} )</td>
<td>1.81E10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{H} + \text{ClO} \rightarrow \text{HCl} + \text{O} )</td>
<td>2.83E3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2 )</td>
<td>2.17E10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2 )</td>
<td>1.78E9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{N}_2 + \text{Cl} \rightarrow \text{N}_2 + \text{Cl} )</td>
<td>1.55E13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{N}_2 + \text{Cl} \rightarrow \text{N}_2 + \text{Cl} )</td>
<td>4.25E12</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
NOCL+CL=CL2+NO       3.97E13  0 -1.06   !1989ABB/TOO1022    2    220 - 450
NOCL+O=NO+CL          5.0E12   0 12.64   !1989ABB/TOO1022    2    220 - 450
NOCL+NOCL=CL2+NO+NO    3.16E12  0 98.11   !1962DEK/PAL139-150   2    880 - 1350
NOCL=NO+CL            1.3E15   0 134     !1981BAU/DUXSuppl     2    800 - 1500
CL2O+NO=NOCL+O2       1.37E11  0 4.99    !Reference reaction below
M+NO+CL=M+NOCL         1.85E16     0 0 !2001OLK/LI4522-4528    298   3

! Nitrogen reactions: H N O

NOCL+H=HCL+NO         4.6E13   0 3.80   !1976WAG/WEL1023     2  240 - 460
NOCL+OH=HOCL+NO       5.42E12  0 9.40    !1989ABB/TOO1022    2  220 - 450

! Nitrogen reactions: C CL N O

CLCO+NOCL=CL2CO+NO    4.79E13  0 4.76   !1952BUR/DAI52-62     2  298 - 328

END

! REFERENCES:

References (Leylegian, Law, etc.)


Appendix 6B: CHEMKIN AURORA input file

! This is a transient, closed-system pyrolysis simulation
! that involves gas-phase kinetics only.
! In this case the pressure is held constant by default
! and the temperature profile given. The system is assumed to
! be closed since no flow rate is specified.
!
! transient simulation
TRAN
! commented out solve sensitivity equations
SENS
! solve the kinetics with a given temperature/time profile
TGIV
! Temperature profile:
TPRO 0.0E-3 300
TPRO 1E-3 5300
TPRO 500.0E-3 5300
TPRO 1000.0E-3 300 !1000K per 0.1 secs quench
TPRO 1500E-3 300
! initial pressure in atmospheres (assumed constant)
PRES 1.0
! initial temperature in system
!TEMP 300.0
! initial gas moles in system
! note: input will be normalized to mole fractions
REAC N2 73.39896
REAC O2 19.690744
REAC Ar 0.87796
REAC CO2 0.032336
REAC C2CCCHCL 6
REAC H2O 0
! end time for the simulation
TIME 1500E-3
! STPT
STPT 1.5E-2
! DELT = time-step for printing to diagnostic output file
! Default = STPT value (was -3)
!DELT 1.0E-3
! DTSV = time-step for writing to binary solution file
! Default = STPT (was -4)
!DTSV 1.0E-4
! End of input keywords
! ATOL = absolute tolerance = indicator of accuracy in physical solution
! ATOL < smallest meaningful mass fraction
! Default = 1.E-20 (changed from -16)
ATOL 1.0E-20
! RTOL = relative tolerance
! Default = 1.E-8 (changed from -6)
RTOL 1.0E-8
END
Appendix 6C: Equilibrium Modelling

1. Components of the system

1.1 Equilibrium Products of Chlorine (Cl₂)

At 300 K, molecular chlorine (Cl₂) is stable. At higher equilibrium temperatures the Cl₂ begins to dissociate into radicals (Cl). Just above 1,000 K the radicals reach parts per thousand levels; shortly after 2,000 K the mole fraction of Cl approaches 1. The concentration of Cl₂ remains above ppm levels for the entire temperature range.

Formation of chlorine ions (Cl⁻, Cl²⁺ and Cl⁺) and electrons is relatively low at low temperatures and increases with equilibrium temperature. Cl⁻ and Cl²⁺ are dominant up to 3,000 K (10⁻¹⁰ at 2,000 K). Above 5,000 K, the mole fraction of Cl⁺ and electrons exceeds the other chlorine ions and eventually approaches 10⁻¹ levels.

1.2 Equilibrium Products of hydrogen gas (H₂)

H₂ is stable at 300 K and gradually the equilibrium shifts towards hydrogen radicals (H); H approaches 10⁻⁶ levels at about 1,400 K. At higher temperatures hydrogen ions and electrons are formed; H⁺ and electrons reach ppm levels just below 5,000 K and exceed H₂ concentration above 7,000 K. H⁻ ions are formed at much lower levels than H⁺ and electrons.

1.3 Equilibrium products of water (H₂O)

Water is in equilibrium with low levels of O₂, H₂ and OH at 300 K. O₂, H₂ and OH, along with much lower concentrations of HO₂, H₂O₂ and O₃, peak between 3,000 K and 4,000 K. By these temperatures, H and then O are the main components of the system. At much higher temperatures the components at concentrations above parts per million are (in order of decreasing concentration at 10,000 K): H, O, electrons, H⁺, O⁺, H₂, O₂, O⁻ and H⁻.

1.4 Equilibrium products of carbon

Carbon chains up to C₅ were included in the chemistry file and therefore C₅ represents soot. Soot is stable at 300 K and begins to break down into shorter carbon chains,
eventually dominated by C at 5,000 K. Ionisation is at ppm levels by 4,000 K, $C^+$ and $C^{2-}$ having the highest concentration of the ions. While $C^+$ continues to dominate the ions, $C^{2-}$ drops off at higher temperatures and is surpassed by $C^-$ by 7,000 K. The electrons follow a similar trend to the $C^+$.

1.5 Equilibrium products of trichloroethene (TCE)

Below 600 K, the main equilibrium products of pure TCE are: hydrochloric acid (HCl), hexachlorobenzene ($C_6Cl_6$), pentachlorobenzene ($C_6HCl_5$), carbon tetrachloride (CCl$_4$) and hexachloroethane (C2Cl6). As the equilibrium temperature increases the carbon rings break down into mainly chlorinated alkenes then chlorinated alkynes. For example, between 1,000 K and 2,500 K, C$_2$Cl$_4$ and then C$_2$Cl$_2$ and C$_2$HCl, etc. become significant, as well as chlorine gas (Cl$_2$). Above 2,500 K, virtually all of the chlorine is free as ions and the remaining alkynes are non-chlorinated ($C_2H_2$). At higher still temperatures, the compounds dissociate to the constituent parts: chloride ions (Cl), hydrogen ions (H) and soot (C2, C3 and C4).

It is interesting to note that while chlorinated alkynes (C$_2$Cl$_2$ and C$_2$HCl) peak around 2,000 K, their non-chlorinated relative C$_2$H$_2$ peaks around 3,200 K. Also note that temperatures below 2,500K may cause the formation of chlorinated benzenes.

1.6 Equilibrium products of dry air

Oxygen (O$_2$) and nitrogen (N$_2$) are stable at room temperature. Above 700 K, nitrogen oxides begin to exceed ppm levels and by 2,000 K, the mole fraction of nitrogen monoxide (NO) is about 1 %. Above 1,500 K, oxygen radicals (O) are formed and nitrogen radical (N) formation starts above 2,500 K. Eventually at 5,000 K, electrons and positive oxygen ions (O$^+$) are formed at ppm levels. Nitrosyl ions (NO$^+$) more or less follow the electron density between 3,000 and 4,000 K. Therefore, these ions are the most important for air plasmas at these temperatures.

$NO_x$ formation will be an issue above 700 K; above 2,000 K it will be a problem.
1.7 Equilibrium products of humid air

Up to 700 K, humid air is nitrogen (N₂), oxygen (O₂) and water (H₂O). NOₓ formation follows the same trends as for dry air. Radicals are formed in the order OH, O, H, N, etc. as the temperature increases. Eventually at 5,000 K, electrons, NO⁺ and negative oxygen ions (O⁻) are formed at ppm levels.

Since OH is an extremely reactive radical, the humidity of the air will be important. The equilibrium concentration of OH reaches ppm levels above 1,200 K and increases to a maximum of about 1 % around 3,000 K.

Also note that at 5,000 K, an equilibrium product of dry air is O⁺, while O⁻ is formed in the humid air system.

2. Experimental Conditions: Microwave plasma rig

2.1 Humid air plus TCE

2.1.1 2 % TCE, 3,00 K – 5,000 K

Carbon dioxide (CO₂), chlorine (Cl₂) and a small amount of hydrogen chloride (HCl) are present at room temperature in addition to N₂, O₂ and H₂O. Chlorine radicals (Cl) and ClO exceed ppm levels at around 700 K and just above 1,500 K Cl levels exceed 1 %, following a similar trend to NO. Between 1,000 K and 3,000 K, HOCl, the chlorine analogue of water, is stable at just above ppm levels. At 5,000 K, small amounts of C and CN are formed along with electrons and O⁻.

2.1.2. 300 K, 0 – 18 % TCE

These are the eventual products of a TCE-contaminated stream if left untreated. Below a TCE concentration of 9 %, the products are N₂, O₂, CO₂, Cl₂, H₂O and HCl. Above 9 %, higher levels of HCl are formed, as well as CCl₄, COCl₂, C₂Cl₆ and C₆HCl₅.

It should be noted that the saturated vapour pressure of TCE at room temperature is 6 – 8 %. Contaminated streams are very unlikely to contain more TCE than that.
Therefore, release of the contaminated stream to the atmosphere must be considered a viable option.

2.1.3 1,500 K, 0 – 18 % TCE

As discussed, with no TCE present, NO, OH and NO₂ are the only equilibrium products of interest.

With the addition of a small amount of carbon and chlorine, HCl, CO₂, Cl, Cl₂, ClO and HOCl appear as equilibrium products. Virtually all of the carbon in the system is oxidised to CO₂ until O₂ is depleted (C₂ (from TCE) + 2O₂ → CO₂). This occurs when the initial mole fraction of TCE is just below 10 %. An increase in input TCE would result in formation of carbon monoxide (CO) and, to a lesser extent, phosgene (COCl₂).

2.1.4 5,000 K, 0 – 6 % TCE

Figures 6C.1 and 6C.2 show the equilibrium products of varying concentrations of TCE in humid are at 5,000 K.
2.2 Dry air plus TCE

The equilibrium products are the same as in the humid air system. As expected, levels of hydrogen-containing species (OH, HCl, H, HOC1, HO2, etc.) are higher in the humid system.
2.3 Charged Species

The electron density depends on the concentrations of NO$^+$ and Cl$^-$. In air, the electron density at atmospheric pressure microwave plasma temperatures equals the NO$^+$ concentration. As TCE is added air at plasma temperatures, NO$^+$ and Cl$^-$ increase at approximately the same rate, with Cl$^-$ lagging slightly (see figure 6C.3). The electron concentration is the same as the difference between the NO$^+$ and Cl$^-$ concentrations. In humid air, the concentration of both of these ions is decreased slightly, resulting in the same electron concentration as in dry air.

![Figure 6C.3: Equilibrium concentrations of major charged species at 3,300 K](image)

3. Experimental Conditions: Thermal destruction rig

3.1 Stoichiometric mixture of propane and air (1:5 fuel: oxygen), 0 – 13 % TCE, 300 K

Nitrogen is stable throughout the range of TCE input concentration.

Up to 5 % TCE, while there is sufficient oxygen in the system, the other components are water, HCl, CO$_2$, CH$_4$ and some H$_2$. 

217
The three main equilibria at these concentrations are given in equations (1), (2) and (3), where H in equation 1 is supplied by propane and water vapour.

\[
\begin{align*}
C_2HCl_3 + 2O_2 + 2H &= 2CO_2 + 3HCl \\
C_2H_8 + 5O_2 &= 3CO_2 + 4H_2O \\
C_3H_8 + O_2 &= 2CH_4 + CO_2
\end{align*}
\]

Throughout the entire range of TCE concentration, equation (1) seems to dominate; that is, TCE oxidation takes preference over propane oxidation. At 6 % TCE there is not enough oxygen to sustain these equilibria, and aromatic formation begins. Between 6 and 8 % TCE these are mainly non-chlorinated and in the $10^{-3} – 10^{-2}$ concentration range. Above 8 % equation (1) is also deprived of oxygen, leading to the formation of chlorinated aromatics, eventually reaching about $10^{-2}$ levels.

### 3.2 Equilibrium products of humid air and propane at 2,000 K, 0 – 30 % propane

With no propane, the products are the same as for humid air, as previously discussed. The initial effect of the addition of propane is equation (1) above; that is oxygen is used to make CO$_2$ and water. Above about 5 % propane, equation (4) takes over:

\[
2C_3H_8 + 3O_2 = 6CO + 8H_2
\]

When the propane to oxygen ratio exceeds 2 to 3 (above about 12% propane), (4) continues to be the main equilibrium. However, there is also significant hydrocarbon formation, predominantly C$_2$H$_2$.

### 3.3 Equilibrium products of dry air and propane at 2,000K, 0 – 30% propane

These results are similar to the humid air results. The only difference is that the water provides some oxygen to the humid system. Therefore, the reducing environment that causes first the shift to CO and then hydrocarbon production occurs at lower propane concentrations in the dry air.
3.4 Equilibrium Products of air containing 2 % trichloroethene and 4 % propane, 200 – 2,500 K

The results for humid air and dry air were both examined and found to be almost identical. This is because the propane provides hydrogen to the system as well as the water. At standard conditions, the major equilibrium products are N₂, CO₂, H₂O, HCl and CH₄. H₂ and CO are also present and increase to significant concentrations with increasing equilibrium temperature. As these increase, the methane decreases to below ppm levels by 1,000 K (equation 5).

\[ \text{CO}_2 + \text{CH}_4 = 4\text{H}_2 + 2\text{CO} \quad (5) \]

Radicals are formed above 1,500 K. Cl, H, OH, NO, O₂ and O are the most concentrated radicals (in decreasing order). Above 2,000 K, OH concentration exceeds H concentration.
Appendix 6D: Kinetic modelling

The complete list of kinetic modelling products is supplied in this section.

Table 6D shows all of the products predicted to occur during the experiments at a concentration of 1 ppb or higher. The number given is $x \cdot \log_{10}[\text{mole fraction}]$, where the maximum mole fraction of the product in the effluent stream is $1 \times 10^x$ (such that ppm are represented by $-6$). * indicates improbable products. Since the propane burner cannot destroy TCE at high concentrations, the product concentrations at 1 % TCE are also given, as these are the relevant products in terms of environmental analysis.
<table>
<thead>
<tr>
<th></th>
<th>Air plasma</th>
<th>Propane plasma</th>
<th>Propane burner</th>
<th>Propane burner @ 1%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NON-CHLORINATED ALIPHATICS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-6</td>
<td>-6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C2H2</td>
<td>-6</td>
<td>-6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C2</td>
<td>-8</td>
<td>-9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C3</td>
<td>-6</td>
<td>-8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C3H2*</td>
<td>-6</td>
<td>-6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C3H3*</td>
<td>-9</td>
<td>-8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH3CH2CH2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C4</td>
<td>-8</td>
<td>-9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C4H*</td>
<td>-8</td>
<td>-9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C4H2*</td>
<td>-6</td>
<td>-5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>NON-CHLORINATED AROMATICS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6H6</td>
<td>0</td>
<td>-9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>CHLORINATED ALIPHATICS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC12</td>
<td>0</td>
<td>0</td>
<td>-6</td>
<td>0</td>
</tr>
<tr>
<td>CC13*</td>
<td>0</td>
<td>0</td>
<td>-9</td>
<td>0</td>
</tr>
<tr>
<td>CC14</td>
<td>-7</td>
<td>-7</td>
<td>-9</td>
<td>-9</td>
</tr>
<tr>
<td>CHC12*</td>
<td>0</td>
<td>0</td>
<td>-9</td>
<td>0</td>
</tr>
<tr>
<td>CHC13</td>
<td>-8</td>
<td>-9</td>
<td>-5</td>
<td>0</td>
</tr>
<tr>
<td>CH2C12</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>TCE</td>
<td>-8</td>
<td>-7</td>
<td>-2</td>
<td>-9</td>
</tr>
<tr>
<td>CHCICCl*</td>
<td>0</td>
<td>-7</td>
<td>-3</td>
<td>0</td>
</tr>
<tr>
<td>C2HC15</td>
<td>0</td>
<td>0</td>
<td>-7</td>
<td>0</td>
</tr>
<tr>
<td>CHC12CHCl2</td>
<td>0</td>
<td>0</td>
<td>-4</td>
<td>0</td>
</tr>
<tr>
<td>C2C14</td>
<td>0</td>
<td>-9</td>
<td>-4</td>
<td>0</td>
</tr>
<tr>
<td><strong>CHLORINATED ALIPHATICS (OXYGENATED)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC12CC1O*</td>
<td>-6</td>
<td>-5</td>
<td>-4</td>
<td>-4</td>
</tr>
<tr>
<td>CC13CC1O</td>
<td>0</td>
<td>0</td>
<td>-8</td>
<td>-7</td>
</tr>
<tr>
<td>CHC12CC1O</td>
<td>-8</td>
<td>-7</td>
<td>-3</td>
<td>-5</td>
</tr>
<tr>
<td>ClHCO</td>
<td>0</td>
<td>0</td>
<td>-4</td>
<td>0</td>
</tr>
<tr>
<td>Cl2CO</td>
<td>-8</td>
<td>-7</td>
<td>-7</td>
<td>-7</td>
</tr>
<tr>
<td><strong>INORGANICS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>Cl2</td>
<td>-2</td>
<td>-2</td>
<td>-5</td>
<td>-5</td>
</tr>
<tr>
<td>CO</td>
<td>-5</td>
<td>-4</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>CO2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>ClOCl</td>
<td>-8</td>
<td>-9</td>
<td>-8</td>
<td>-8</td>
</tr>
<tr>
<td>HOC1</td>
<td>-8</td>
<td>-8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H2</td>
<td>0</td>
<td>0</td>
<td>-3</td>
<td>-7</td>
</tr>
<tr>
<td>H2O</td>
<td>-4</td>
<td>-2</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>N2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>NO</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N2O</td>
<td>-8</td>
<td>-7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO2</td>
<td>-5</td>
<td>-5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NOCl</td>
<td>-4</td>
<td>-4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH</td>
<td>0</td>
<td>-4</td>
<td>-8</td>
<td>0</td>
</tr>
<tr>
<td>O2</td>
<td>-1</td>
<td>-3</td>
<td>-3</td>
<td>-5</td>
</tr>
</tbody>
</table>

Table 6D: List of all products above 1 ppb predicted in model
Appendix 7A: Error Charts

Chart showing distribution of average normalised points for Air Peak

Chart showing distribution of average normalised points for Phosgene Peak
Chart showing distribution of average normalised points for NOx Peak

Chart showing distribution of average normalised points for 3.95 Peak

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1
Chart showing distribution of average normalised points for 4 Peak

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1

Chart showing distribution of average normalised points for 4.4 Peak

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1
Chart showing distribution of average normalised points for 5.8 Peak

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1

Chart showing distribution of average normalised points for 5.8 + 5.9 Peaks

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1
Chart showing distribution of average normalised points for 6.4 Peaks

-0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1

Chart showing distribution of average normalised points for 8.6 peak

-0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1
Chart showing distribution of average normalised points for 8.7-8.8 peak

-0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1

Chart showing distribution of average normalised points for 8.9 peak

-0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1
Chart showing distribution of average normalised points for 9.5 peak

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1

Chart showing distribution of average normalised points for 12.8 peak

0.71 = all points above 5
-1 corresponds to points within range 0 - 0.1
Chart showing distribution of average normalised points for 16.4 peak

- 0.71 = all points above 5
- -1 corresponds to points within range 0 - 0.1

Chart showing distribution of average normalised points for 20.1 peak

- 0.71 = all points above 5
- -1 corresponds to points within range 0 - 0.1
Appendix 7B: Correlation of ECD elution times with MS elution times

Figure 7B.1 and 7B.2 show the correlation between the MS and ECD elution times. The standards are plotted in black, and the coloured lines are the experimental values. The different colours/sheets represent various iterations, with the final attempt being deemed a satisfactory correlation.

![Correlation of T(MS) with T(ECD), 0 - 5.5 minutes](image)

Figure 7B.1: Correlation of elution times up to 5.5 mins
Correlation of T(MS) with T(ECD) from 5.5 minutes onwards

Standards correlation:
y = 1.0691x - 3.3299
R² = 0.9984
1st attempt:
y = 1.0962x - 3.6835
R² = 0.9978
2nd attempt:
y = 1.1064x - 3.8143
R² = 0.9972
3rd attempt:
y = 1.0619x - 3.2682
R² = 0.9991

Figure 7B.2: Correlation of elution times after 5.5 mins
Appendix 7C: Pyrex chimney: HCl and chlorine bleed peaks

Figures 7C.1 and 7C.2 show the results of the column bleed experiments compared with the Pyrex chimney plasma peaks.

Figure 7C.1: HCl Bleed

Figure 7C.2: Cl₂ Bleed
Appendix 7D: Estimation of inorganic content of chimney residue

The 2-3 % of CU(OH)Cl translates into 1.1 – 1.65 % copper (assume 1.4 %). Therefore, the remaining copper (54.6 %) is in the form of CuCl.

\[
\text{No Moles per 100 g} = \frac{\text{Percent copper}}{\text{Molar mass}} = \frac{54.6}{63.5} = 0.86
\]

\[
\text{Mass per 100 g} = \text{Number moles} \times \text{molar mass} = 0.86 \times (63.5 + 35.5) = 85 \%
\]

Using the total zinc content in the same way, zinc chloride (ZnCl₂) content was estimated to be 6.35 %.

Therefore, total inorganic content was estimated to be about 94 % (85 + 2.5 + 6.35 = 93.85). However, small amounts of water and hydrochloric acid were also suspected to be present in the sample.
Appendix 8A: Further results

This section shows the results of the plasma products quantification experiments that are not included in the main body of the thesis.

Figure 8A.1: Formation of phosgene in various TCE destruction experiments
Figure 8.A.2: Phosgene in 2 kW dry plasma experiments (copper chimney)

Figure 8A.3: Carbon tetrachloride in 2kW dry plasma experiments (copper chimney)
Figure 8A.4: Final concentration of carbon tetrachloride for various plasma powers
(for 10 l/min containing 2 % TCE)

Figure 8A.5: Formation of tetrachloroethene in at 10 l/min
Appendix 9A: Environmental impact of TCE treatment

processes spreadsheet

APPENDIX 9A: Environmental Impact

<table>
<thead>
<tr>
<th>Process</th>
<th>Reference</th>
<th>Molar mass</th>
<th>Overall factor</th>
<th>g/200 l Mole fraction TCE in g/kg TCE g/200 l</th>
<th>Mole fraction TCE in g/kg TCE g/200 l</th>
<th>Mole fraction TCE in g/kg TCE g/200 l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global Warming</td>
<td></td>
<td></td>
<td>Overall factor</td>
<td>2.93E+15</td>
<td>Overall factor</td>
<td>2.93E+15</td>
</tr>
<tr>
<td>Chlorinated aliphatics</td>
<td></td>
<td></td>
<td>Overall factor</td>
<td>1.90E+21</td>
<td>Overall factor</td>
<td>1.90E+21</td>
</tr>
<tr>
<td>Acute Health Effects</td>
<td></td>
<td></td>
<td>Overall factor</td>
<td>1.78E+21</td>
<td>Overall factor</td>
<td>1.78E+21</td>
</tr>
<tr>
<td>Chemical effects</td>
<td></td>
<td></td>
<td>Overall factor</td>
<td>1.78E+21</td>
<td>Overall factor</td>
<td>1.78E+21</td>
</tr>
<tr>
<td>Photochemical smog</td>
<td></td>
<td></td>
<td>Overall factor</td>
<td>6.90E-01</td>
<td>Overall factor</td>
<td>6.90E-01</td>
</tr>
<tr>
<td>Photochemical smog</td>
<td></td>
<td></td>
<td>Overall factor</td>
<td>2.00E-02</td>
<td>Overall factor</td>
<td>2.00E-02</td>
</tr>
</tbody>
</table>

**Notes**:
- **Up to 1.4% TCE only**
- **Based on modelling figures**
- **ECSA**
- **http://www.ciesin.org/docs/011-551/tab4.gif, 3yr lag**
- **Based on modelling figures PCE should be 0, -9, -4 according to model. None was found in bunsen though.**

---

237
Appendix 9B: Economic analysis of TCE treatment processes spreadsheet

### Capital Costs

<table>
<thead>
<tr>
<th>Process</th>
<th>Gas Price/year</th>
<th>Return on Average Investment</th>
<th>Capital Cost</th>
<th>Energy Cost</th>
<th>Solvent Maintenance Cost</th>
<th>Labour and Maintenance Cost</th>
<th>Annualised Cost 15.00%</th>
<th>Robustness</th>
<th>Solid/liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Plasma</td>
<td>$63,000</td>
<td>High</td>
<td>$63,000</td>
<td>$7,000</td>
<td>$8,114</td>
<td>$3,150.00</td>
<td>$27,714.40</td>
<td>Acidic</td>
<td>Liquid</td>
</tr>
<tr>
<td>Methane Plasma</td>
<td>$63,000</td>
<td>High</td>
<td>$63,000</td>
<td>$7,060</td>
<td>$8,114</td>
<td>$3,150.00</td>
<td>$27,774.40</td>
<td>Acidic</td>
<td>Liquid</td>
</tr>
<tr>
<td>Methane Flame (1% TCE)</td>
<td>$15,000</td>
<td>High</td>
<td>$15,000</td>
<td>$1,170</td>
<td>$8,114</td>
<td>$750.00</td>
<td>$12,284.40</td>
<td>Medium</td>
<td>HCl</td>
</tr>
<tr>
<td>Conventional adsorption*</td>
<td>$171,600</td>
<td>Medium</td>
<td>$171,600</td>
<td>$5,000</td>
<td>$3,246</td>
<td>$17,160.00</td>
<td>$51,145.76</td>
<td>Spent carbon</td>
<td>Spent bed</td>
</tr>
<tr>
<td>Novel adsorption*</td>
<td>$343,200</td>
<td>Medium</td>
<td>$343,200</td>
<td>$5,000</td>
<td>$811</td>
<td>$34,320.00</td>
<td>$91,611.44</td>
<td>Varies</td>
<td>Spent bed</td>
</tr>
<tr>
<td>Condensation*</td>
<td>$39,683</td>
<td>High</td>
<td>$39,683</td>
<td>$5,000</td>
<td>$2,434</td>
<td>$1,984.13</td>
<td>$15,370.82</td>
<td>High</td>
<td>None</td>
</tr>
<tr>
<td>Release to atmosphere</td>
<td>$0</td>
<td>Maximum</td>
<td>$0</td>
<td>$0</td>
<td>$8,114</td>
<td>$0.00</td>
<td>$8,114.40</td>
<td>Maximum</td>
<td>None</td>
</tr>
</tbody>
</table>

### Assumptions

- Solvent recoveries:
  - Condenser: 70%
  - Adsorber: 60%
  - Novel adsorber: 90%

- Size of cleaner for alternative technologies = 38 ft²
Bibliography


References


Dow Chemical Company 1999, *Economical and efficient vapour degreasing with chlorinated solvents from Dow, U.S.A.*

Dow Chemical Company 2005, in *telephone sales enquiry Sydney.*

Downes, I 2005, in *personal communication, Surface Technology Coatings, Melbourne.*


Hill, E A 1995 'A summary of the national emission standards for halogenated solvent cleaning', Precision Cleaning '95 Proceedings, 16 - 17 May, pp. 69 - 81


sintering machine by electron beam irradiation,' *Environ. Sci. Technol.*, vol. 14, pp. 287 - 293

Kemikalieinspektionen v Toolex Alpha AB 2000, Vol. 2001 Proceedings of the Court of Justice and the Court of First Instance of the European Communities, no. 22/00.


Orica Chemicals *Materials Safety Data Sheet: Trineu, Substance key: 000031022902.*


Radiou, M T 2003, 'Non-equilibrium microwave plasmas for the abatement of PFCs' 9th International Conference on Microwave and RF Heating, Binner, J, Loughborough University, Loughborough University, U.K. Abstract no. 008mwo, pp. 413 - 416.

Reaction Design *CHEMKIN (Chemical Kinetics Package) version 3.7*,

Reaction Design 1997 *CHEMKIN III therm.dat version 3*


Standards Australia *AS 2661 - 1984: Vapour degreasing plant - design, installation and operation - Safety requirements*, Sydney.


Tran, N 2005, in *Sairon sales enquiry* Melbourne.


United States Environmental Protection Agency 1995, in *453/F-94-083*. 

249


