ANALYSIS AND CONTROL OF HARMFUL EMISSIONS FROM COMBUSTION PROCESSES

A Thesis Submitted for the Degree of doctor of Philosophy

by

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IN THE NAME OF GOD, MOST GRACIOUS, MOST MERCIFUL

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Abstract

The harmful effects of air pollutants on human beings and environment have been the major reason for efforts in sampling, analysis and control of their sources. The major pollutants emitted to atmosphere from stationary combustion processes are nitrogen oxides, inorganic acids, carbon dioxide, carbon monoxide, hydrocarbon and soot.

In the current work two methods are developed for sampling and analysis of volatile chlorinated aromatic hydrocarbons and semi-volatile chlorinated aromatic hydrocarbons for example 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) by using solid sorbent, thermal desorption and high resolution GC-MS. The capacity of several solid sorbents is compared by breakthrough value and percentage recovery of the analyte from the sorbent.

The thermal stability of polyvinyl chloride (PVC) and PVC in the presence of metals is studied because PVC is a polymer commonly found in solid waste derived from medical waste, car recycling and electrical cable.

Harmful pollutant emissions from combustion and pyrolysis of PVC are measured using the novel method developed in this work. The main inorganic volatile is HCl while benzene is the major volatile organic formed under pyrolysis and combustion conditions. The thermal degradation of PVC produces a large number of chlorinated aromatic hydrocarbon, aromatic hydrocarbon and short chain linear gases.

A study is designed for control of harmful pollutants from combustion of PVC including HCl, aromatic hydrocarbon, chlorinated aromatic hydrocarbons and soot. It is reported that the presence of metal oxides have the ability to control the level of harmful emissions by facilitating the producing of more short chain linear gases.

Two methods are developed for the control of soot from liquid and gas combustion process by using applied fields, Magnetic and electric fields. In this study, it is shown that an increase in applied field strength leads to an increase in flame temperature but a decrease in the length of flame. The level of soot emission was decreased in presence of an applied field. A discussion of the effect of applied fields on the combustion process is given.

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1.1. A REVIEW OF GENERAL AIR POLLUTION

1.1.1. Defining air pollution

Most people have thought about air pollution problems since the Industrial Revolution; indeed, air pollution problems have annoyed Man for centuries. It can be supposed that smoke and fumes from forest fires, volcanoes, domestic heating, cooking, sand and dust from windstorms and fog existed even before the Industrial Revolution.

The Engineers'Joint Council on "Air pollution and its control" gave the following definition:[1]

"Air pollution means the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas, mist, odour, smoke or vapour in quantities of characteristics and of duration such as to be injurious to human, plant or animal life or to property, or which unreasonably interferes with the comfortable enjoyment of life and property" .

The nature of some pollutants can be further defined as:[2, 3, 4, 5]

Aerosol: a dispersion of solid or liquid particles of microscopic size in gaseous media, such as smoke, fog or mist.

Dust: a term loosely applied to solid particles predominantly larger than colloidal, and usually with a diameter between 0.25 and 500 μm and capable of temporary suspension in air or other gases. Dusts do not tend to flocculate unless conditions change, e.g., under electrostatic force, adding water to air etc.

Fog: a loose term applied to visible aerosols in which the dispersed phase is liquid usually formed by condensation.

Fume: suspended solids in air less than 1.0μm in diameter, normally released from chemical or metallurgical processes.

Mist: a term loosely applied to low-concentration dispersion of liquid particles of larger size (with a diameter of less than 2.0μm).

Smoke: gas-borne solids with a diameter of less than 2 μm.

1.1.2. Historical perspective:

1.1.2.1. Before the Industrial Revolution:

One of the reasons the tribes of early history were nomadic was to move away periodically from the stench of the animal, vegetable, and human wastes they generated. When the tribesmen learned to use fire, they used it for millennia in a way that filled the air inside their living quarters with the products of incomplete combustion. Examples of this can still be seen today in some of the more primitive parts of the world. After its invention, the chimney removed the combustion products and cooking smells from the living quarters, but for centuries the open fire in the fireplace caused smoky emissions. In AD 61 the Roman philosopher Seneca reported thus on conditions in Rome: [6]

"As soon as I had got out of the heavy air of Rome and from the stink of the smoky chimney thereof, which, being stirred, poured forth whatever pestilential vapours and soot they had enclosed in them, I felt an alteration of my disposition."

Air pollution, associated with burning wood in Tutbury Castle in Nottingham, was considered "unendurable" by Eleanor of Aquitaine, the wife of King Henry II of England,.

When the smoke from isolated wood-burning fires of early cave dwellers became the smoke from isolated wood-burning furnaces in heavily populated cities, the effects of air pollution become severe enough to alarm some of the inhabitants of those cities. In 1273 Edward I was sufficiently troubled by the smoke and fog over London to forbid the burning of coal.[7] Richard III (1377-1399) and later Henry V (1413 -1422) took steps to regulate and restrict the use of coal, because of the smoke and odours produced by its combustion.[8, 9]

The principal industries associated with the production of air pollution in the centuries preceding the Industrial Revolution were metallurgy, ceramics, and preservation of animal products. In the bronze and iron ages, villages were exposed to dust and fumes from many sources and clay was baked and glazed to form pottery and bricks before 4000 BC. Iron was in common use and leather has been tanned for millenia. Coal was mined and used for fuel before AD 1000, although it was not made into coke until about 1600 and coke did not enter metallurgical practices significantly until about 1700. [10]

1.1.2.2.The Industrial Revolution:

The Industrial Revolution was the consequence of the harnessing of steam to provide power to pump water and move machinery. This began in the early years of the eighteenth century, when Savery, Papin, and Newcomen designed their pumping engines and culminated in 1784 in Watt's reciprocating engine. The reciprocating steam engine reigned supreme until it was displaced by the steam turbine in the twentieth century. Steam engines and steam turbines require steam boilers, which, until the advent of nuclear power, were fired by vegetable or fossil fuels. During most of the nineteenth century, coal was the principal fuel, although some oil was used for steam generation late in the century.

The predominant air pollution problem of the nineteenth century was smoke and ash from the burning of coal or oil in the boiler furnaces of stationary power plants, locomotives and marine vessels, and in home-heating fireplaces and furnaces. Britain took the lead in addressing this problem, and in the words of Sir Hugh Beaver: [11]

"By 1819, there was sufficient pressure for parliament to appoint the first of a whole dynasty of committees "to consider how far persons using steam engines and furnaces could work them in a manner less prejudicial to public health and comfort". Nothing, however, was done as a result of their committee's deliberations.

In 1843, there was another parliamentary select committee, and in 1845, a third. In that same year, during the great railway boom, an Act of Parliament disposed of trouble from locomotives "once and for all" by laying down the dictum that they must consume their own smoke. The Town improvement Clauses Act two years later applied the same panacea to factory furnaces. The year 1853 and 1856 witnessed two Acts of Parliament dealing specifically with London and empowering the police to enforce provisions against smoke from furnaces, public baths, washhouses and furnaces used in the working of steam vessels on the Thames."

Smoke and ash abatement in Great Britain was considered to be a health agency responsibility and this was confirmed by the first Public Health Act of 1848 and later ones of 1866 and 1875. Air pollution from the emerging chemical industry was considered a separate matter and was made the responsibility of the Alkali Inspectorate created by the Alkali Act of 1863.

In the USA, smoke abatement was considered a municipal responsibility. There were no federal or state smoke abatement laws or regulations. The first municipal ordinances and regulations limiting the emission of black smoke and ash appeared in the 1880s and were directed toward industrial, locomotive, and marine rather than domestic sources.

The principal technological developments in the control of air pollution by engineering during the nineteenth century were the stoker for mechanical firing of coal, the scrubber for removing acid gases from effluent gas streams, cyclones and bag house dust collectors, and the introduction of physical and chemical principles into process design.

1.1.2.3.The twentieth century:

During the period 1900-1925 there were great changes in technology resulting in the production of air pollution and the engineering control of pollution, but there were no significant changes in legislation, regulations, understanding of the problems involved, or in public attitudes towards the problems. As cities and factories grew in size, the severity of the pollution problem increased.

When the electric engine replaced the steam engine the change transferred the smoke and ash emission from the boiler house of the factory to the boiler house of electricity generating station. At the start of this period, coal was hand fired in the boiler house; by the middle of this period, it was mechanically fired by stokers and by the end of the period, pulverised coal, oil and gas firing had begun to take over. The most significant change, however, was the rapid increase in the number of automobiles from almost none at the turn of the century to millions by 1925. The principal technological changes in the engineering control of air pollution were: (1)-the perfection of the motor driver fan, which allowed large scale gas–treating systems to be built. (2)-the invention of the electrostatic precipitator, which made particulate control in many processes feasible, and (3)-the development of a chemical engineering capability for the design of process equipment, which made the control of gas and vapour effluents feasible. Smog due to pollution first appeared in Los Angles in the 1940s and the first state air pollution law in the United States was adopted by California in 1947.

A major technological change resulted from the exploitation of natural gas and, where this occurred, there was rapid displacement of coal and oil as home heating fuels with dramatic improvements in air quality.

In general the necessary action to control air pollutants has only been taken after the damages and danger in terms of mortality and irritant properties have been realised on a large scale. For example, when in December 1952, 4000 deaths were attributed to air pollution, the Clean Air Act was passed in England.

Air pollution control in the EU is now subject to specific directions that have to be implemented by the community countries. Stricter legislation to control air pollution is now in place in many countries and for example: The south coast Air Quality Management District (in Los Angeles) in 1990 introduced 160 rules for the future clean up of the air in Los Angeles Basin.

International conventions such as the Montreal protocol have resulted in the setting of targets. The industrialised nations agreed to halt the production of most ozone–destroying chlorofluorocarbons by the year 2000 although this deadline was later changed to 1996. Table 1-1 lists some of the most reported pollution incidents from 1873-1986. [12-13]

Table 1-1: Air pollution problems from 1873 -1986

Date	Location	Reported deaths from air pollution	Reported illness
1873, Dec. 9-11	London		
1880. Jan. 26-29	London		
1892, Dec. 28-30	London		
1930, Dec.	Meuse valley, Belgium	63	600
1948, Oct.	Donora, Pennsylvania	17	6000
1948, Nov. 26-Dec. 1	London	700-800	
1952, Dec. 5-9	London	4000	
1953, Nov.	New York		
1956, Dec. 5-9	London	1000	
1967, Dec. 2-5	London	700-800	
1958	New York		
1959, Jan. 26-31	London	200-250	
1962, Dec. 5-10	London	700	
1963, Jan. 7-22	London	700	
1963, Jan. 9, Feb. 12	New York	200-400	
1966, Nov. 23-25	New York		
1986*	Tehran		

1.1.3. Sources of air pollution

The sources of air pollution are nearly as numerous as grains of sand. In fact, the grains of sand themselves form natural air pollution when the wind entrains them and they become airborne. Many of the pollutants of concern are formed and emitted through natural processes. For example, naturally occurring particulates include pollen grains,

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* In 1986, industrial oil waste was burned south of Tehran resulting in "black" rain.

fungus spores, salt spray, smoke particles from forest fires and dust from volcanic eruptions. [14]

Manmade sources of pollutants can be conveniently classified as stationary combustion, transportation, industrial processes and solid waste disposal sources. The principal pollutant emissions from stationary combustion processes are particulate pollutants, such as fly ash and smoke, sulphur and nitrogen oxides, hydrocarbon and sometimes inorganic acids. Transportation sources, particularly automobiles using the internal combustion engine, constitute a major source of air pollution. Particulate emission from the automobile includes smoke and lead particles; gaseous pollutants include carbon monoxide, nitrogen oxides and hydrocarbons. Pollution emissions from industrial processes reflect the ingenuity of modern industrial technology. Thus, nearly every imaginable form of pollutant is emitted in some quantity by some industrial operation.

1.1.4. Clean air and air quality standards:

Table 1-2 shows the concentration of atmosphere gases in clean and dry air at ground level of the troposphere. [8] The troposphere is the layer in which most living things exist and it is of the greatest interest in pollution control.

Primary pollutants are those emitted by an identifiable source. The more significant of these are CO_2, NO_x, SO_x, particulates, hydrocarbons and metals.

Secondary pollutants are those formed in the atmosphere by chemical reactions and include O_3, other photochemical oxidants and oxidised hydrocarbons.

Primary ambient air quality standards define the level of air quality judged to be necessary, with an adequate margin of safety, to protect the public health. Table 1-3 shows the ambient air quality standards for USA, California, the EU, WHO, and Germany.[16]

Table 1-2: Concentration of atmosphere gases in clean and dry air at ground level

Gas	Concentration, ppm by volume	Concentration, % by volume
Nitrogen (N_2)	280,000	78.09
Oxygen(O_2)	209,500	20.95
Argon (Ar.)	9,300	0.93
Carbon dioxide (CO_2)	320	0.032
Neon (Ne)	18	0.0018
Helium (He)	5.2	0.00052
Methane (CH_4)	1.5	0.00015
Krypton (Kr.)	1.0	0.0001
Hydrogen (H_2)	0.5	0.00005
Nitrous oxide (N_2O)	0.2	0.00002
Carbon monoxide (CO)	0.1	0.00001
Xenon (Xe)	0.08	0.000008
Ozone (O_3)	0.02	0.000002
Ammonia (NH_3)	0.006	0.0000006
Nitrogen dioxide (NO_2)	0.001	0.0000001
Nitric oxide (NO)	0.0006	0.00000006
Sulphur dioxide (SO_2)	0.0002	0.00000002
Hydrogen sulphide (H_2S)	0.0002	0.00000002

Secondary ambient air quality standards define levels of air quality judged necessary to protect the public welfare (structures, crops, animals, fabrics) and are designed to protect even the most sensitive individuals, including the elderly and those with respiratory ailments.

Table 1-3: International ambient air quality standard for criteria pollutants *

pollutant	average time	USA federal USEPA µg/ m_3	California µg /m_3	EC directive µg /m_3	WHO air quality guideline µg/ m_3	TA luft Germany µg/ m_3
CO	13 min				100000	
	30 min				60000	
	1 h	40000	23000		30000	30000
	8 h	10000	10000		10000	10000
NO_2	1 h		470	200	400	200
	24h				150	80
	Annual	100				
O_3	1 h	235	180		200	
	8 h					
	24 h				65	
	100 day				60	
SO_2	10 min				500	
	1 h		655		350	
	3 h	1300				400
	24h	365	105	250-350	125	140
	Annual	80		80-120	40-60	60
Particulates (PM10)	24 h	150	50	250	125	150-300
	Annual	50	30	80	50	
SO_2+ PM10	24 h			100-150		
	Annual			40-60	60-90	
Pb (Lead)	1 month		1.5			
	3 month	1.5		2	0.5-1	2
Total suspended particulates	24 h	260				
	annual	75				
HC	3 h	160 (non-CH_4)				

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[*] Where no standard in the EU exists for a particulate pollutant it is common for countries to adopt the TA luft

1.1.5. Criteria pollutants:

1.1.5.1.Carbon monoxide

Carbon monoxide (CO) is a colourless, tasteless and odourless gas. Carbon monoxide sources are both natural and anthropogenic. The Argon National Laboratory has concluded that 312 billion tonnes of CO are produced annually in nature by oxidation of methane gas from decaying vegetation. The hydroxyl radical (OH°) serves as the initial oxidising agent and reacts with CH_4 to an alkyl radical [17]

$$CH_4 + OH^\circ \longrightarrow CH_3^\circ + H_2O$$

$$CH_3^\circ + O_2 + 2(hv) \longrightarrow CO + H_2 + OH^\circ$$

Another source of CO is the human metabolism because we exhale approximately one ppm CO. About 70 percent of all CO comes from mobile sources.

Carbon monoxide is a serious pollutant because it reacts with the haemoglobin (Hb) in blood to give carboxy haemoglobin (COHb) [18] and since the affinity of haemoglobin for carbon monoxide is more than 200 times as great as its affinity for oxygen, CO can seriously impair the transport of O_2 even when present at low concentrations.

1.1.5.2.Nitrogen oxides:

Although seven oxides of nitrogen are known to occur the only two that are important in the study of air pollution are NO and NO_2, along with the acids, nitrous acid (HNO_2) and nitric acid (HNO_3) that can be formed when they are dissolved in moisture.

NO_x is produced during the combustion of fossil fuels, by two processes usually in the form of NO which rapidly oxidises to NO_2 in the presence of O_2 or O_3. The NO_2 may in turn dissociate to NO or be further oxidised to the acids HNO_3 or HNO_2. NO_2 can also react with organic compounds to produce peroxyacetyl nitrates (PAN) or with hydrocarbons in the presence of sunlight to produce smog:

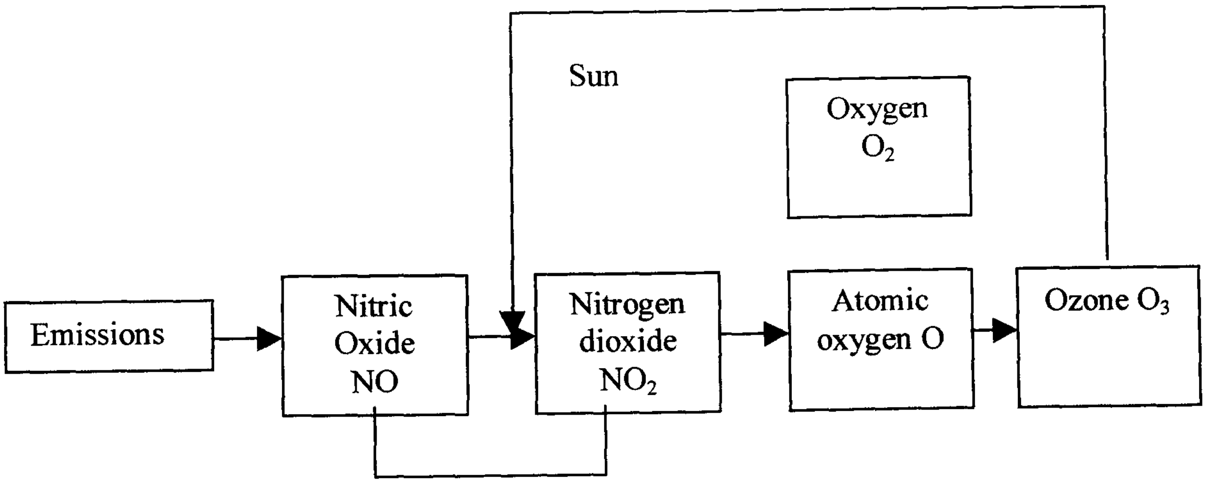
$$HC + NO_2 \xrightarrow[\text{sun light}]{} \text{Photochemical smog}$$

Figure 1-1 shows a simplified atmospheric nitrogen photolytic cycle (excluding the effects of hydrocarbons) [19] and Table 1-4 lists emission of NO_x by country. [20]

Table1- 4: The quantities of NO_x emissions by country (Gg)

Country	1985	1990	1994
Austria	245	222	177
Belgium	325	352	345
Denmark	301	279	272
Finland	275	300	282
France	1615	1585	1682
Germany	3276	2640	2210
Greece	306	392	357
Ireland	91	115	117
Italy	1589	2047	2157
Luxembourg	22	23	23
Netherlands	576	575	542
Portugal	96	221	1223
Spain	839	1178	372
Sweden	426	411	2422
United Kingdom	2454	2897	1235

Figure 1-1: A simplified atmospheric nitrogen photolytic cycle



Nitrogen oxides can cause respiratory problems and contribute to smog, which can cause pulmonary and bronchial diseases.

1.1.5.3.Oxides of sulphur:

Oxides of sulphur (SO_x) include six different gaseous compounds but sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are the two of particular concern in air pollution. Over 80 % of anthropogenic sulphur oxide emissions are the result of fossil fuel combustion in stationary sources. Almost 85 % is released from electricity generating plants with only 2 % arising from highway vehicles.

SO_2 is a colourless, non-flammable and non-explosive gas with a suffocating odour. It has a taste threshold of 0.3 ppm and an odour threshold (0.5 ppm). SO_2 is highly soluble in water to give sulphurous and sulphuric acids (H_2SO_3 and H_2SO_4) which are components of acid rain. It is estimated that SO_2 remains air borne on average 2 to 4 days, during which time it may be transported as far as 1000 km. Thus the problem of SO_2 pollution can become an international one.

In a dusty atmosphere, SO_2 is particularly harmful because the particulates carry with them concentrated amounts of SO_2, thus bringing the irritant chemical into direct prolonged contact with delicate lung tissue. The SO_2- particulate combination has been cited as the cause of death in several air pollution tragedies; e.g. Meuse valley in Pennsylvania in 1948, London in 1952 and New York in 1953.

Much work has been done on the responses of plants to SO_2. The relationship between SO_2 concentration in ambient air, exposure time and injury to vegetation can be either acute or chronic. Sulphuric acid aerosols will readily attack building material, especially those containing carbonate, such as marble, limestone, roofing slate.

1.1.5.4. Lead

Lead (Pb) is a heavy metal and is significant in air pollution. Before 1986 between 80 to 90 % of lead in ambient air came from the combustion of leaded petrol containing tetraethyl lead $(C_2H_5)_4Pb$ The smelting of lead in mining is another source of air pollution.

Air borne lead may affect humans by direct inhalation. People living nearest to highways are at greatest risk. Of course, lead can be ingested by eating food stuffs. It has been estimated that about one-third of the lead particles inhaled are deposited in the respiratory system and that about half of those are absorbed by the bloodstream. Lead can cause aggressive, hostile and destructive behavioural changes as well as learning disabilities, seizures, severe and permanent brain damage and even death.

1.1.5.5. Particulate matter

Air borne particulate matter can consist of organic and/or inorganic substances, such as those indicated in Table 1-5.[16]

Table 1-5: Particulate matter size

Group description	Composition	Particle size	
		WHO	USEPA (PM10)
Coarse	Dust ,earth crust matter	>2.5μm	>10μm
Fine	Aerosols, combustion particles, recondensed organic and metal vapours	<2.5μm	< 10μm

A number of terms are used to categorise particulates, depending on their size and phase, for example, aerosol, dust, fume, mist, fog, smoke etc, but the most general term is aerosol, which applies to any tiny particles, liquid or solid, dispersed in the atmosphere. Although particles may have very irregular shapes, their size can be described by an equivalent aerodynamic diameter determined by comparing them with perfect spheres having the same setting velocity.[20]

Particulate matter is emitted in urban areas from power plants, industrial processes, vehicular traffic, domestic coal burning and industrial incinerators. The ability of the human respiratory system to defend itself against particulate matter is determined by the size of the particles. Sedimentation in human lung is most effective for particles between 2 and 4 μm.

1.1.5.6.Ozone

Ozone (O_3) is a secondary pollutant whose background atmospheric concentration in surface air at sea level is about 0.01-0.03ppm. Ozone is a dominant constituent of photochemical smog and is capable of oxidising substance not oxidizable by oxygen.

The clinically recognised immediate effects from inhaling O_3 range from dislike of the odour, dryness of the mucous membranes of the mouth, nose and throat, changes in visual acuity and headache, pulmonary congestion and oedema.

1.1.5.7.Hydrocarbons:

Hydrocarbons are organic compounds containing only carbon and hydrogen and include most of the major chemicals in gasoline and other petroleum products. Hydrocarbons present in the atmosphere are from both natural and anthropogenic sources. Natural background levels of methane in the atmosphere range from 1.2 to 1.5 ppm on a worldwide basis. Most natural hydrocarbons are from biological sources and small amounts of these hydrocarbons come from geothermal areas, coal fields, natural gas from petroleum fields and natural fires.

The anthropogenic sources and estimated quantities of hydrocarbons emitted into the atmosphere are given in Table 1-6. [23] Table 1-7 shows the emission data for non-methane volatile organic compounds by country. [20]

Table 1-6: Sources and quantities of hydrocarbon emissions (million tonnes per year)

Source	1968	1970	1975	1977	1980
Transportation	16.6	16.8	10.4	11.5	7.8
Fuel combustion in stationary sources	0.7	0.5	1.3	1.5	0.2
Industrial processes	4.6	4.8	2.7	10.1	10.8
Solid -waste disposal and miscellaneous	10.1	7.6	12.6	5.2	3.0
Total	32.0	30.0	27.0	28.3	21.8

Table 1- 7: Non-methane volatile organic compounds emissions by country (Gg)

Country	**1985**	**1990**	**1994**
Austria	400	418	358
Belgium	407	332	320
Denmark	198	175	156
Finland	210	209	190
France	2393	2393	2308
Germany	3290	3155	2153
Greece	155	293	362
Ireland	102	102	93
Italy	1850	2080	2239
Luxembourg	20	19	17
Netherlands	493	420	375
Portugal	199	202	227
Spain	1265	1051	1120
Sweden	553	526	459
United Kingdom	2439	2623	2354

1.2. THE NATURE OF COMBUSTION:

Combustion is a commonly observed phenomenon. From a scientific viewpoint, combustion stems from chemical oxidation reaction kinetics and mechanisms. The term combustion is generally used for those reactions which take place very rapidly with large conversion of chemical energy to heat energy.

1.2.1. Fuels:

Fuels are those substances which, when heated, undergo a chemical reaction with an oxidising agent (typically oxygen in air) to liberate heat. Commercially important fuels contain carbon and hydrogen, which provides the calorific value. Fuels may be gaseous, liquid, or solid. Some fuels such as fossil fuels are non-renewable, while other such as biomass fuels are renewable. Fossil fuels consist primarily of natural gas, petroleum-derived fuels and coal. Biomass fuels consist primarily of wood, agricultural residues and refuse.

1.2.2. Gaseous fuels:

The main gaseous fuels are natural gas and liquefied petroleum gas. Gaseous fuels are also produced from coal, wood, petroleum and natural gas.

Natural gas is found compressed in porous rock and shale formations sealed in rock strata below the ground. Natural gas frequently exists near or above oil deposits. It is a mixture of hydrocarbons with small quantities of other components. Raw natural gas contains methane as the major component with smaller amounts of ethane, propane, butane and pentane. Sulphur and organic nitrogen levels are negligible in natural gas. Carbon dioxide and nitrogen are sometimes present, although generally the levels of noncombustibles present are very low.

1.2.3. Liquid fuels:

Liquid fuels are derived primarily from crude oil although, in the future, they may increasingly be derived from oil shale, tar sand, coal, and biomass. Crude oil is a mixture of naturally occurring liquid hydrocarbons which contain small amounts of sulphur, nitrogen, oxygen, trace metals and minerals. The ultimate analysis of crude oil does not vary greatly around the world, with roughly 84% carbon, up to 3% sulphur, and up to 0.5 % nitrogen and 0.5% oxygen. Crude oil is sometimes burned directly but, because of the wide range of densities, viscosities and impurities, it is generally refined before use as a fuel.

Chemically, crude oil consists primarily of alkanes (C_nH_{2+n}), cycloalkanes (C_nH_{2n}) and aromatics (containing substituted C_6H_6 rings) Petroleum fuels also contain alkenes, which are formed during the cracking part of the refining processes.

1.2.4. Solid fuels:

Naturally occurring solid fuels include wood and other forms of biomass, peat, lignite and coal. Municipal and certain industrial refuse can also be used as a fuel.

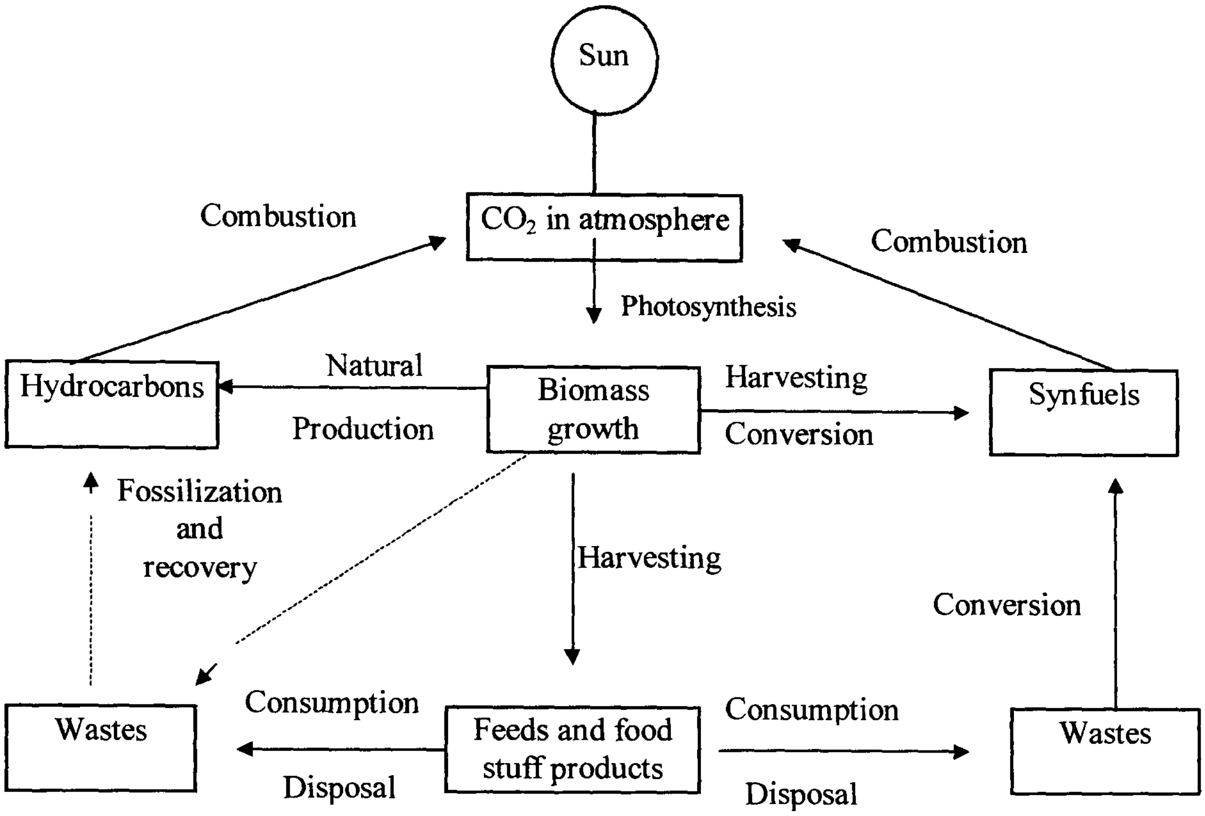
In addition to carbon and hydrogen, solid fuels contain significant amounts of oxygen, water and ash, as well as nitrogen and sulphur. The oxygen is chemically bound in the fuel and varies from 45% by weight in wood to 2 % in anthracite coal (on a dry, ash free basis). Moisture can exist in two forms in solid fuels as free water and as bound water. Free water is unbound and exists between the cell walls in wood or in the larger pores of low grade coal and is drawn into these pores by capillary attraction. Ash is the inorganic residue remaining after the fuel is completely burned. Wood usually has only a few tenths of a percent ash, while coal typically has 10% or more. Typically, the ash begins to soften at 1200 °C and becomes fluid at 1300 °C.

1.2.4.1.Biomass:

Biomass is cellulosic material, which can be broadly classified as woody and nonwoody biomass. Woody biomass may be further split into softwoods and hardwoods. Nonwoody biomass that can be used as a fuel includes agricultural residue such as bagasse, straw, stalks, husks, pits and manure. Tall grasses also have been grown as an energy crop. [24, 25]

Charcoal is made by heating wood in the absence of air to produce a char that is a relatively clean burning fuel. Charcoal can be pulverised easily and made into briquettes by the addition of a binder such as starch. Figure 1-2 shows the cycle of biomass to energy.[26]

Figure 1-2: Biomass -to-energy technology



1.2.4.2.Peat:

Peat is formed from decaying woody plant, reeds, sedges, and mosses in watery bogs, usually in northern climates. Peat forms in wet environments in which air is largely excluded. In the presence of bacterial action, chemical decomposition proceeds by a humification process: [24, 25]

$$2\ C_6H_{10}O_5 \xrightarrow{\text{Bacterial action}} C_8H_{10}O_5 + CH_4 + 2CO_2$$

Since the rate of formation of a peat bed is about 3 cm per 100 years, peat is not a renewable resource. Some of the hemicellulose and cellulose present is decomposed into humic acid bitumens and other compounds. Since freshly harvested peat typically contains 80 to 90 % water, it must be dried before being used as a fuel. Peat also contains 1 to 10 % mineral matter.

1.2.4.3.Solid fuel from waste:

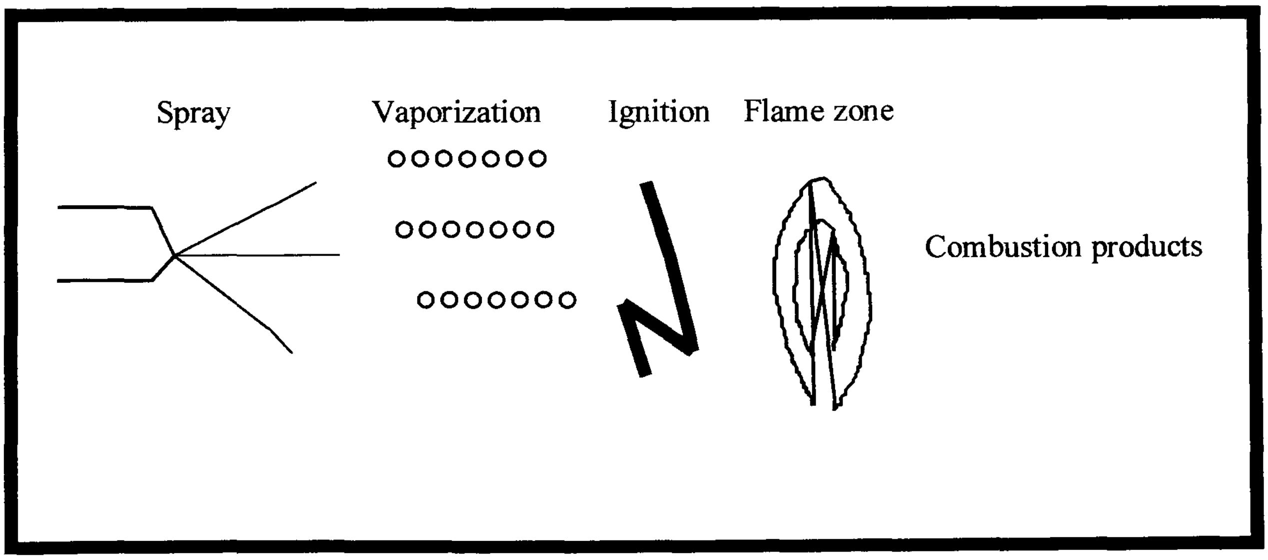
Refuse that can be used to make solid fuel includes municipal, solid waste and commercial, institutional, industrial and agricultural wastes. Usually these waste materials are disposed of by landfill and incineration without energy recovery, but refuse can be burned directly in specially designed boilers or processed to give, what is called refuse-derived fuel (RDF).

1.2.5. Combustion of sprays of liquid fuel

The combustion of sprays of liquid fuel is of considerable technological importance in a diversity of applications ranging from steam raising, furnaces, space heating, diesel engines and space rockets.

Spray combustion was first used in the 1880s as a powerful method of burning relatively involatile liquid fuels. The basic process involved is the atomisation of the liquid fuel to produce small droplets to increase the surface area so that the rates of heat and mass transfer during combustion are greatly enhanced. The fuel is thus used in the from of discrete liquid droplets that may have a range of sizes and may move in different directions with different velocities to that of the main stream of gas. [27] Figure 1-3 shows a model of idealised spray combustion.

Figure 1-3: A model of idealised spray combustion



The process in spray combustion is very complicated because the mixing of the fuel and oxidant takes place inside a chamber and thus the mechanism of the mixing process plays an important role. This mixing process is controlled to a large extent by the geometry of the combustion chamber, the spatial distribution and momentum of the injected spray, the direction and momentum of the air flow and the influence of any flame stabilisation devices. Consequently, the atomiser and combustion chamber must be designed as an integrated unit rather than as independent items. Figure 1-4 shows the major combustion processes in a combustion chamber. [28]

1.2.5.1.The sources of liquid fuels used in spray combustion:

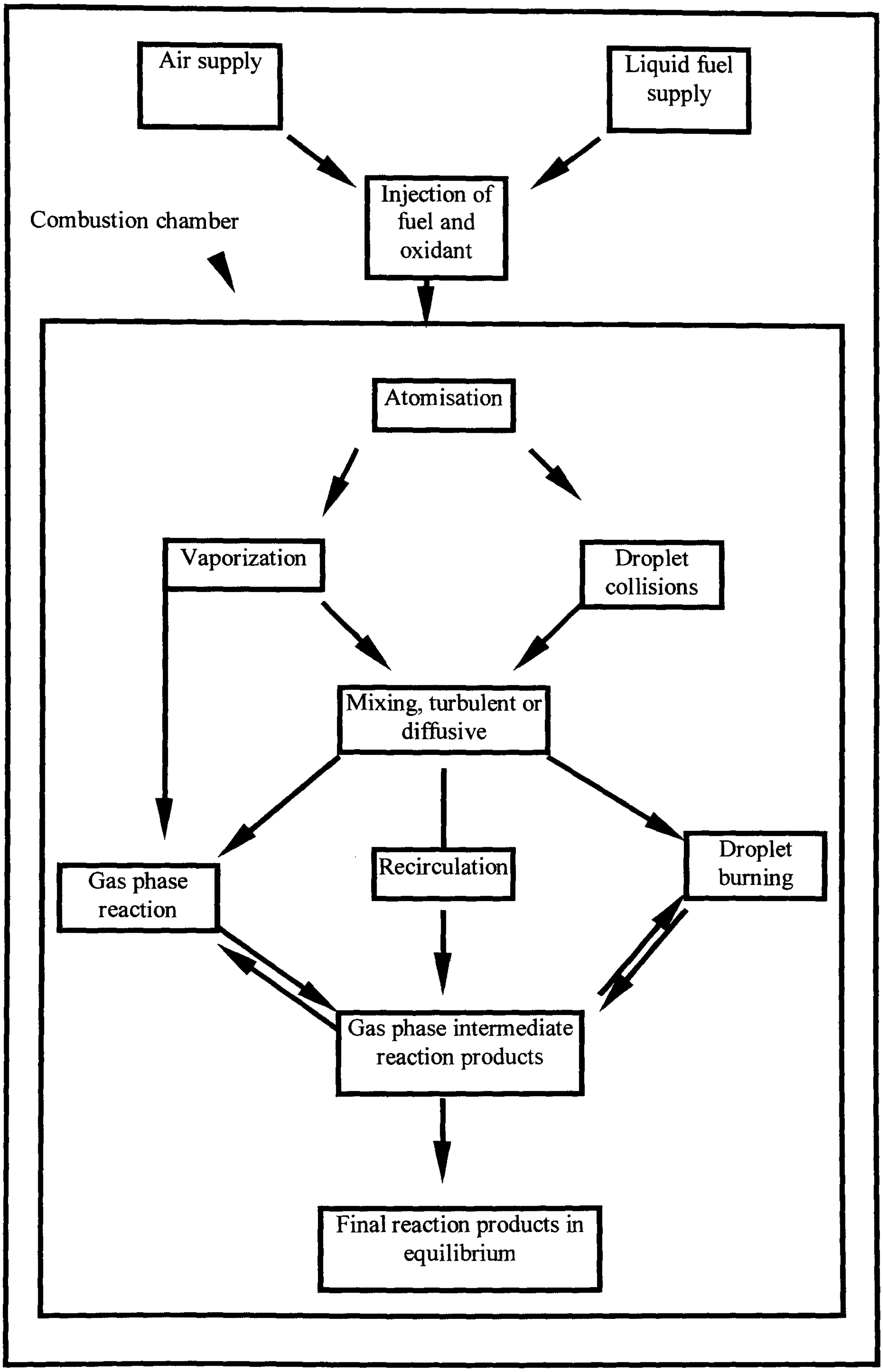
The liquid fuels used at the present time are almost exclusively the fuel oils. The term fuel oil means different things in different countries but essentially it covers the range of products from gas oil to extremely viscous products of high molecular weight. This group encompasses both diesel fuel and industrial fuels used in boilers and furnaces. Their major source is crude oil, but liquid fuels can also be produced from coal, shale oil and tar sands.

1.2.5.1.1. Fuel oils from crude oil

The main source of liquid fuels at the present time is crude petroleum. Crude oil consists essentially of hydrocarbons together with smaller quantities of sulphur, oxygen and nitrogen containing hydrocarbons and some organo-metallic compounds, particularly of vanadium. Gaseous, liquid and solid (or semi-solid) compounds may be present in crude oil and these are separated at the well-head and during the refining processes to give a range of liquid products, some of which are used as fuels for spray combustion.

The hydrocarbons in crude oils have differing boiling points and are separated by the process of distillation into a range of primary products. A number of additives may be incorporated into the final product. In the case of fuels used for spray combustion the additives normally present are anti-oxidants, anti-wear additives and anti-rust additives may be present.

Figure 1-4: The major combustion processes in a combustion chamber



1.2.5.1.2.Oil from shale and tar sands:

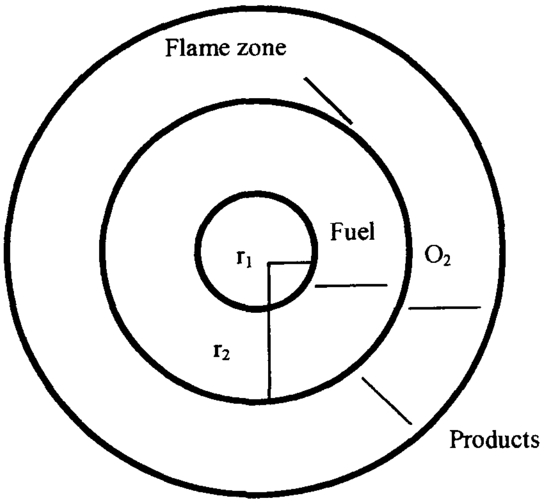
Extensive deposits of oil shales and tar sands (oil sands) exist throughout the world. Tar sands consist of deposits containing heavy hydrocarbons that are the same as those in conventional oil but have higher viscosities, i.e. they are tar-like. Oil shales are significantly different, since they contain no free oil, but consist of a solid mixture of organic compounds, called "kerogen", which decompose on heating, yielding a light shale oil.

1.2.5.2.The combustion of droplets of liquid fuels

The initial basic approach to liquid droplet combustion is a spherico-symmetric model based on a vaporizing droplet in which the rate-controlling process is molecular diffusion rather than chemical kinetic factors. The following assumptions are generally made in the basic model: [29]

1-The combustion system has spherical symmetry as shown in Figure 1-5. The spherical droplet of radius r_1 is surrounded by a concentric flame zone then another outer boundary that is taken to be at infinite distance from the droplet.

Figure 1-5 -Idealised model of droplet burning



2-The flame is assumed to be supported by the exothermic reaction of fuel and oxygen in the flame zone, the oxidant diffusing in from the outer boundary to the flame zone while the fuel vapour diffuses from the droplet surface. Heat is transferred from the flame zone to the droplet to provide the latent heat of vaporization of the liquid fuel. This is not necessary in the special case of combustion in critical conditions. As the critical temperature and pressure are approached the latent heat of vaporization decreases to zero.

3- Thermal diffusion effects are neglected.

4-The effect of radiant heat transfer from the gas phase or adjacent particles is negligible

1.2.5.2.1.Ignition of droplets:

There are essentially two types of processes by which the ignition of a droplet may be accomplished. The first is thermal ignition, which occurs when a cold droplet is exposed to hot air or other oxidising atmosphere, as in a diesel engine. The second is the network mechanism, which occurs when cold droplets are in contact with a burning spray and ignition results from the combined influence of the transfer of heat and of free radicals from the burning droplets to the approaching cold droplets. This mechanism is important in stationary combustion systems such as furnaces.

1.2.5.2.1.1.Thermal ignition

This type of ignition proceeds via a series of steps as follows:

1-The surface temperature of the droplet increases primarily by conduction processes and the vapour pressure of the fuel increases.

2-The fuel vapour mixes with the oxygen in the air and the temperature of the fuel vapour-air mixture increases.

3-The composition of the mixture comes within the inflammability limits for the particular fuel-air mixture and the temperature increases so that it exceeds the ignition temperature. At this point the rate of the hydrocarbon - oxygen chain reaction exceeds the critical limit and ignition occurs.

1.2.5.2.1.2.Network ignition

This form of ignition is applicable to spray situations. As the cool droplets approach a flame front they are heated by convection and radiation, and furthermore, free radicals also diffuse to them thus initiating the chemical reaction between the hydrocarbon vapour and the oxygen. Thus this form of ignition is not very dependent upon the chemical composition of the fuel.

1.2.6. Combustion of solid material

Commonly, solid materials used as a source of energy are coal and wood. The advantages of solids as fuel are their relatively high density, flame temperature and heat of combustion.

The rate of burning of any fuel is strongly influenced by the heat flux incident upon the fuel surface. In the case of a simple solid, reaction takes place at its surface whereas in the case of liquid or a pyrolysing solid, it takes place in the gas phase. The problem of combustion of pyrolysing solids requires a detailed understanding of both the internal (solid phase) and external (gas phase) heat and species conservation. The combustion of a carbon particle is accompanied by high surface temperatures. Oxygen diffuses from the free stream to the surface where it reacts directly with the solid to release a great quantity of heat, much of which is lost to the surroundings by radiation.

Any heterogeneous oxidation reaction involves the following five steps in series:

1- Oxygen has to diffuse to the fuel surface

2- Diffused oxygen has to be absorbed by the surface

3- Absorbed oxygen has to react with the solid to form absorbed products

4- Absorbed products have to be desorbed from the surface

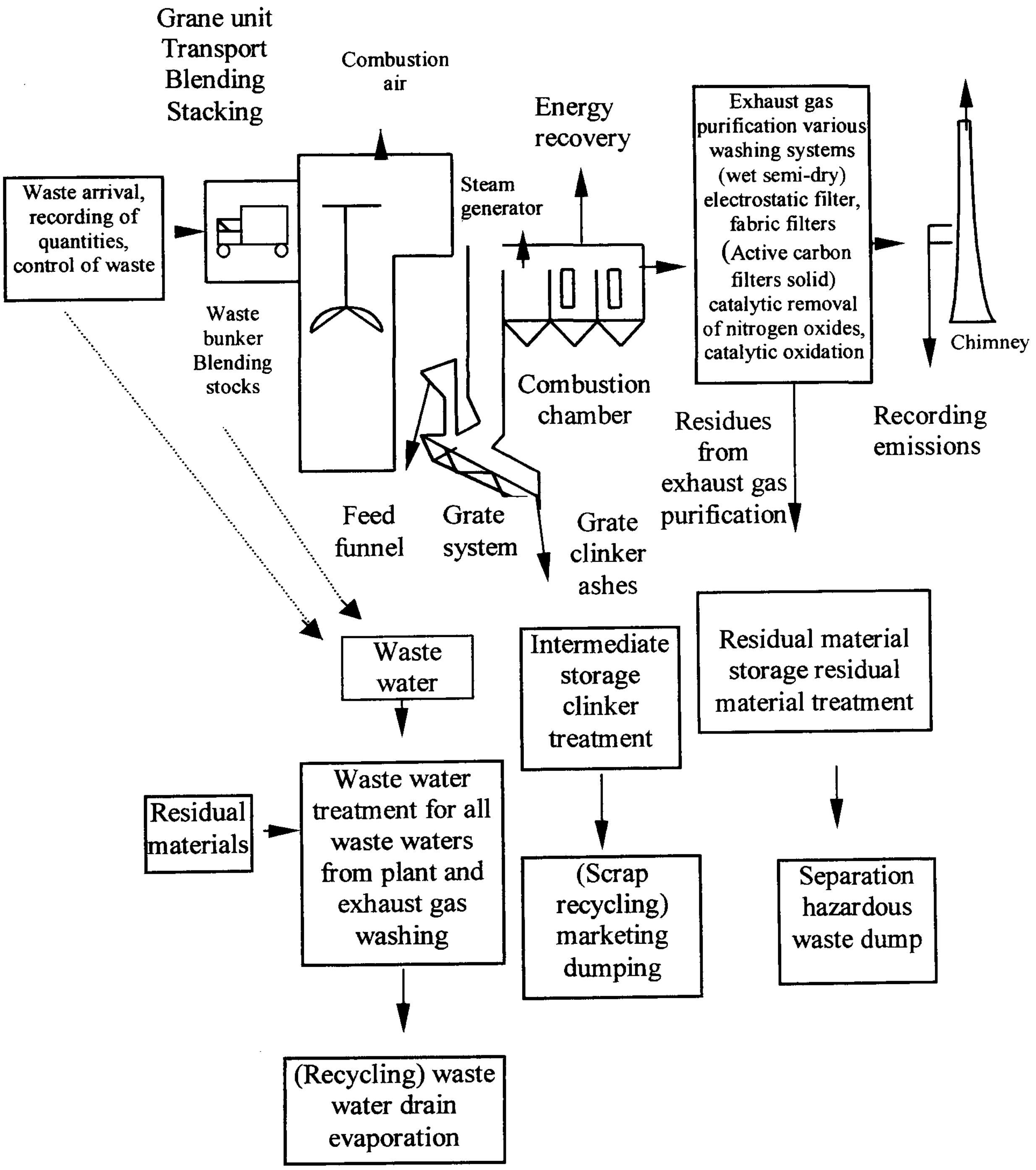
5 -Desorbed products have to diffuse away from the surface

When the particle temperature is low, the particle is small and flow around it is weak. Step 3 is known to be much slower than steps 1 or 5.

1.2.6.1.Waste incineration:

Waste incineration has been employed since 1895 for its " historical purpose", that of reducing the volume of waste while transforming it into hygienically safe residues. But modern waste incineration technology has even more to offer. The main process units of a waste incineration plant are shown in Figure 1-6.

Figure 1- 6: Main process units of a waste incineration plant



1.2.6.1.1.The combustion process in a waste incinerator:

Waste incineration is, in principle, similar to combustion of other solid fuels. The combustion process can be divided into three phases:

1-Drying

2- Gas pyrolysis and gas combustion

3-Combustion of carbon residue

The drying takes place in the first part of the grate. When the waste is dried and heated, gasification takes place in the second part in an oxygen deficient atmosphere. Here easily evaporated hydrocarbons are released and some with low combustion temperatures are burned just above the waste. Others escape to the secondary combustion chamber where combustion takes place at a higher temperature, 950 °C to 1050°C in an oxygen rich atmosphere. The solid residue, mainly consisting of ash and carbon, is burned in a fourth grate.

The combustion of solid waste is very similar to the combustion of coal.

1.2.6.2.Coal

Most of the coal presently being consumed is by direct combustion of finely pulverised coal in large-scale utility furnaces for the generation of electric power etc. Diffusional combustion of a carbon sphere depends upon the extra variable of stoichiometry. Three possibilities arise:[30, 31] at moderately high temperature, oxygen diffuses to the carbon surface and reaction occurs to form CO_2. The fuel/ oxygen ratio, f, for this mechanism is 12/32 and the product CO_2 diffuses away from the surface. If there is a shortage of oxygen CO may be formed instead of CO_2. The stoichiometric fuel-oxygen ratio for this mechanism is naturally higher, f= 12/16. The third mechanism, which occurs when the temperature is high. There is negligible amount of both CO_2 and O_2 present in the gas phase near the carbon surface.

Most of the energy released in a combustion reaction is thermal although a fraction is released in the form of light due to incandescent solid particles such as carbon in the flames.

1.2.6.2.1.Ignition :

Forced ignition occurs as a result of local energy addition from an external source such as an electrically heated wire, an electric spark, a pilot flame, etc. A flame is initiated locally near the ignition source and it propagates into the rest of the mixture. Under certain conditions of heating are brought about by an external source of energy such as a spark, hot vessel wall, compression, etc. There is always some temperature of the reacting mixture at which the rate of heat generation exceeds the loss rate. This excess heat increases the mixture temperature which in turn leads to higher reaction rate. An uncontrollably fast reaction is known as an explosion. Closed vessel explosions are very common in practice

1.2.6.2.2.Gasification:

The origin of the manufacture of gas from coal date from the end of the 18th century. The incentive for the early work was the production of tar from coal.

Many chemical reactions may occur in a gasifier, the three main types being [30, 31]

- Pyrolysis reactions
- Gasification reactions
- Acceptor reactions

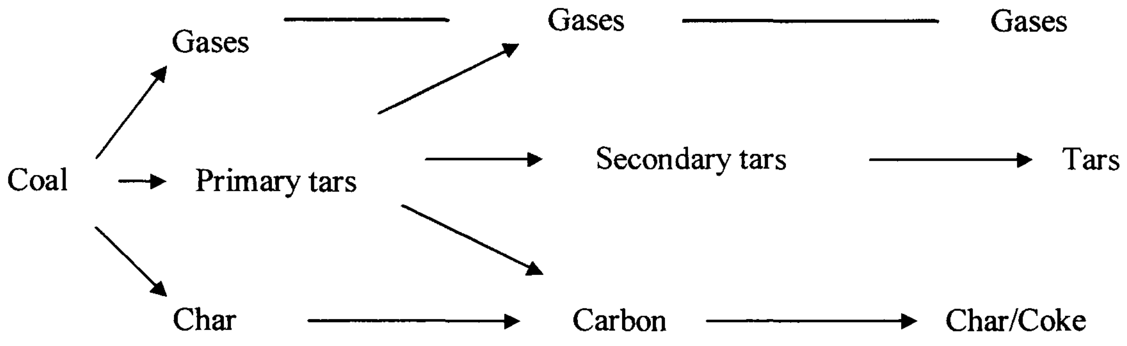
The importance of each type of reaction and the extent of the interactions between them depends on the gasifier design.

Pyrolysis is defined as the thermal decomposition of coal in a substantially oxygen -free environment. The chemical reactions that take place may be represented in simple terms as the following two processes occurring sequentially.

1-The release of gases and primary tars arising from the thermal decomposition of the coal structure.

2-Thermal cracking (and polymerisation) of the primary tars to produce gases, lighter (lower molecular weight) secondary tars and carbonaceous residue. The reaction scheme is illustrated in Figure 1-7.

Figure 1-7: Stages in pyrolysis



As coal is heated, the first stage of decomposition is associated with the breaking of the links between aromatic cluster units. In coking coal, this results in the coal particles softening and eventually forming a coherent plastic mass. At high temperature, hydrogen gas is the predominant product and its evolution may be attributed mainly to the loss of aromatic hydrogen. The final product is carbon.

Combustible gases can be produced by the reaction of coal, char or volatile matter with oxygen, carbon dioxide, hydrogen or steam. The main reactions are listed below (for simplicity, only reactions with carbon are shown).

Partial - combustion reaction

$$C + \frac{1}{2} O_2 \longrightarrow CO$$

Boudouard reaction

$$C + CO_2 \longrightarrow 2CO$$

Hydrogasification reaction

$$C + 2H_2 \longrightarrow CH_4$$

Water - gas reaction

$$C + H_2O \longrightarrow CO + H_2$$

Combustion reaction

$$C + O_2 \longrightarrow CO_2$$

Most of the methane formed appears to result from hydrocracking of the primary tar rather than from hydrogasification of the coal or char in gasifiers that are designed to take advantage of the hydrogasification reaction.

The following gas - phase reactions may also occur

Shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Methanation reaction

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

The sulphur in the coal is released mainly as hydrogen sulphide and the nitrogen mainly as elemental nitrogen and ammonia. Traces of other compounds (for example hydrogen cyanide) are also formed.

Acceptor reactions:

In some gasifiers, lime stone or dolomite may be used to retain the sulphur. If the acceptor is calcined before feeding to the gasifier, carbon dioxide may also be retained. The reactions for calcined lime stone are given below.

Sulphur retention

$$CaO + H_2S \longrightarrow CaS + H_2O$$

Carbon dioxide acceptor

$$CaO + CO_2 \longrightarrow CaCO_3$$

A summary of gasification reactions is shown in Table 1-8

Table 1-8: Summery of gasification reaction

Reaction	Equation	Effect of increase in temperature	Effect of increase in pressure	Kinetic	Heat of reaction
Pyrolysis	Coal+H_2,CH_4, H_2O,CO_2,tar, etc	→	←	Fast	Exothermic (mildly)
Partial combustion	$C+\frac{1}{2}O_2=CO$		←	Fast	Exothermic
Boudouard	$C+CO_2=2CO$	→	←	Rather slow	Exothermic
Hydrogasi - fication	$C+2H_2=CH_4$	←	→	Slow	Exothermic (mildly)
Water-gas	$C+H_2O=CO+H_2$	→	←	Moderate	Exothermic
Combustion	$C+O_2=CO_2$			Fast	Exothermic (strongly)
Shift	$CO+H_2O=CO_2+H_2$	←		Moderate	Exothermic (mildly)
Methanation	$CO+3H_2=CH_4+H_2O$	←	→	Slow	Exothermic (strongly)
Sulphur retention	$CaO+H_2S=Ca+S+H_2O$	←		Fairly slow	Exothermic (slightly)
carbon dioxide acceptor	$CaO+CO_2=Ca+CO_3$	←	→	Fairly slow	Exothermic

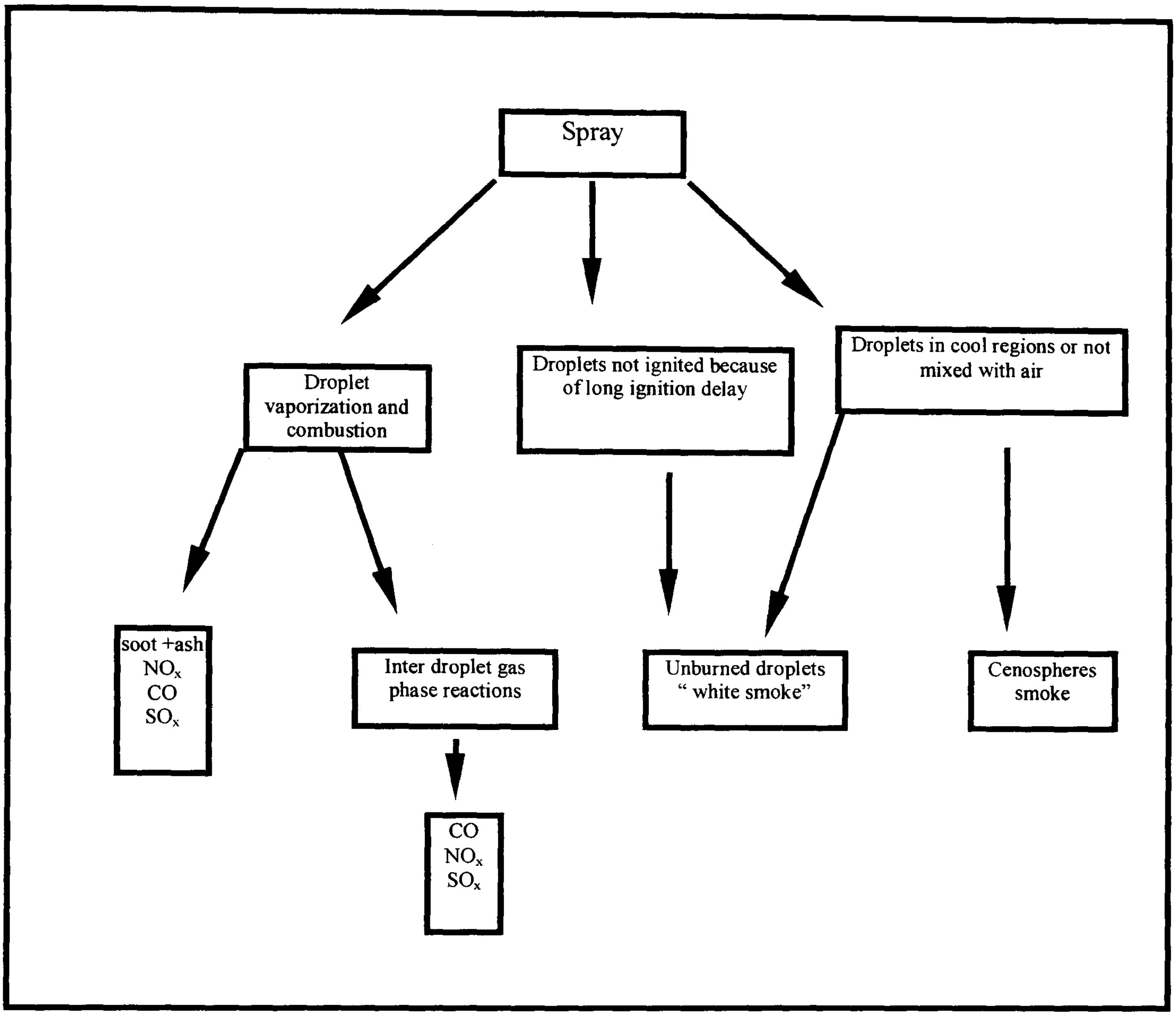
1.2.7. Formation of pollutants

The nature of the pollutants formed in combustion are dependent on several factors, e.g.:

A) Type of fuel, B) Size of fuel or droplet, C) Type of process (e.g., combustion, gasification), E) Type of technology, and combustor, F) Temperature, G) Pressure, H) Ratio of fuel and air

Figure 1-8 shows the formation of pollutants during spray combustion.

Figure 1-8: Diagrammatic representation of the formation of pollutants during spray combustion



The following is a description of some pollutants:

1.2.7.1.Particulate matter:

The particulate material found in the combustion products from liquid or solid fuel may be termed carbon, smoke, soot or stack solids depending upon the particular application.

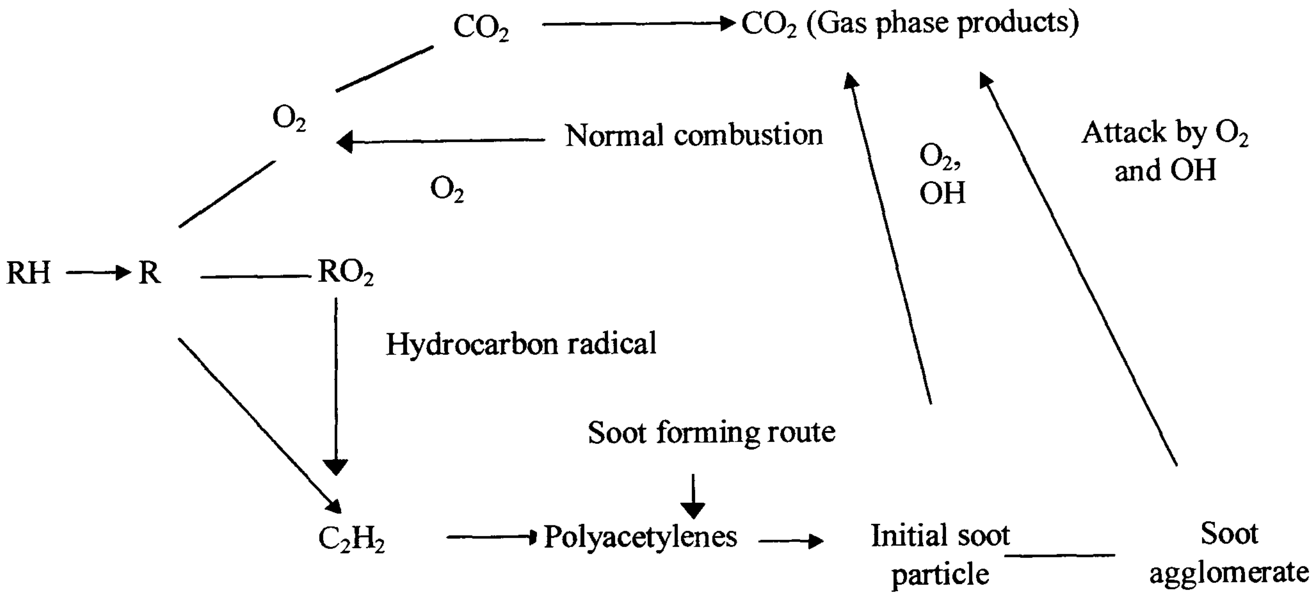
1-This comprises particles of carbon (that is soot) and droplets of condensed tar (tar fog) and results from the incomplete combustion of the tar components of some solid fuel such as coal or liquid fuel.

2-Dust and grit are both essentially ash; "dust" refers to the smaller particle size (less than about 75 microns in diameter) and "grit" refers to coarser particles. The ash originates from the mineral matter in the fuel which is changed chemically by being subjected to high temperatures during the combustion process.

3-It may contain any unburned droplets although this is only rarely a problem, being mainly encountered in incorrectly adjusted diesel engines, where it is termed "white smoke", or sometimes in aviation gas turbines particularly under take-off conditions.

During the combustion of paraffinic hydrocarbons it is generally accepted that the hydrocarbon radicals that play an important role during the combustion of hydrocarbons are decomposed (degraded) forming ethylene and acetylene. The acetylene thus produced then polymerises to form polyacetylenes; these polyacetylenes then form soot particles that coagulate to give the final products. The nature of the final product is dependent upon the composition of the fuel oil, particularly with respect to the concentrations of aromatics and asphaltenes. Figure 1-9 shows a schematic of a combustion process.

Figure 1-9: A schematic of combustion process



The properties of soot produced are very much dependent upon the residence times and temperatures. Typically the product contains 90-98 % (wt) carbon and only small amounts of oxygen. The particle sizes vary widely but are usually in the range of 10-1000nm. If aromatics are present the properties may markedly change as well as their yield, which is enhanced.

For soot to be produced, fuel-rich conditions must be attained, otherwise the "normal combustion" route above is followed and little or no soot results. In droplet or spray combustion this condition is always achieved in part since the region between the droplet surface and the surrounding flame is always fuel-rich. Inevitably, soot is always produced in this region during the combustion of hydrocarbons and the flame zone always exhibits a yellow luminosity. The soot yield may be correlated to the injection velocity and the droplet size. It should be noted that small droplets are less prone to smoke formation.

1.2.7.2.The formation of carbon monoxide

Carbon monoxide is found in the combustion products of all carbonaceous fuels and generally in concentrations somewhat above that expected from equilibrium considerations. For any system that is in equilibrium the carbon monoxide concentration is given by the overall reaction.

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2 \qquad \text{I}$$

and thus

$$[CO] = \frac{K[CO_2]}{[O_2]^{\frac{1}{2}}}$$

It is clear that the equilibrium level of carbon monoxide is dependent on the temperature and the level of excess air. Low levels of excess air result in higher concentrations of carbon monoxide if a constant temperature is maintained.

Carbon monoxide is formed in flames by the rapid oxidation of hydrocarbons by oxygen in the reaction zone. The carbon monoxide is subsequently slowly oxidised to carbon dioxide by the reactions II and III that combined from the water-gas equilibrium reaction:

$$CO + OH^\circ \rightleftarrows CO_2 + H^\circ \qquad \text{II}$$

$$H^\circ + H_2O \rightleftarrows H_2 + OH^\circ \qquad \text{III}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \text{IV}$$

Since the carbon monoxide is formed rapidly in the reaction zone but only slowly consumed, the concentrations of carbon monoxide present in the reaction zone are above the equilibrium values. The slow conversion of carbon monoxide to carbon dioxide in the post-flame gases is termed after-burning.

1.2.7.3.The mechanism for the formation sulphur oxides

Various sulphur oxides, designated SO_x, are a major pollutant species emitted from stationary combustion sources using fossil fuel. The origin of these sulphur oxides is the fuel, which contains sulphur in amounts ranging from a trace to more than 7% by weight. All petroleum products contain organo-sulphur compounds, which are present as sulphides, disulphides, or cyclic compounds. Coals contain high levels of sulphur. The sulphur in coal exists principally in two forms: inorganic, mainly FeS, and organic, incorporated into the various organic structures present in coal. Trace amounts of various sulphate species also are present in coal. Many of the sulphur-containing compounds in fuel oil have been identified, including thiols, organic sulphides and disulphides, and thiophenes. The sulphur-containing compounds in gaseous fuels, include H_2S and lesser amounts of CS_2 and COS. Desulphurization is one of the principal techniques for control of SO_x emission from combustion sources.

In the combustion of sulphur - containing fuels, virtually all of the sulphur appears as various sulphur oxides in the combustion products. Some of these oxides are gaseous species, such as SO_2 and SO_3, while others are aerosols, comprising various primary sulphates such as H_2SO_4. In the combustion of fuels with significant inorganic content, such as coal and heavy oils, some of the sulphur oxides, mainly inorganic sulphates, will be incorporated in the fly ash. For temperatures in excess of 1000°K, equilibrium considerations show that the principal sulphur oxide is SO_2, with lesser amounts of SO_3, primary sulphates and H_2S. Experimental data from laboratory flames indicate that, at flame temperatures, SO_2 is the principal sulphur oxide, but that SO_3 levels are larger than local equilibrium values. Stack sampling data show that SO_x emissions from stationary power plants are mainly SO_2, with only small amounts of SO_3 and trace amounts of primary sulphates.

Although the mechanism for the oxidation of simple sulphur compounds is not completely understood, there is a consensus that, at flame temperatures, the reaction proceeds by a sequence of steps,

$$\begin{tikzcd}
 & R^{\circ}S \arrow[dr] & & & \\
\text{Fuels-s} \arrow[ur] \arrow[rr] & & SO \arrow[r] & SO_2 \arrow[r] & SO_3
\end{tikzcd}$$

where $R^{\circ}S$ is a sulphur-containing radical such as HS, CS, CH_3S or S. Available data indicate that SO_2 formation in the flame is rapid, occurring on a timescale comparable to that of the fuel oxidations. The rapid progress of the SO_2 formation process is due principally to rapid bimolecular reactions between sulphur species and OH° radicals. Measurements in the post flame zone of premixed hydrogen - air flames doped with small amounts of H_2S show that several of these bimolecular reactions, as well as the bimolecular reactions involving OH° species, are partially equilibrated, including

$$SO + OH^{\circ} \rightleftharpoons SO_2 + H^{\circ}$$

$$H_2O + H^{\circ} \rightleftharpoons OH^{\circ} + H_2$$

$$SO + H_2O \rightleftharpoons SO_2 + H_2$$

Hence, the relative SO_2 and SO concentrations can be calculated from thermodynamic considerations at the local gas temperature.

The principal reaction responsible for SO_3 formation in flames is

$$SO_2 \quad + \quad O^{\circ} \ + \!\!\longrightarrow \quad SO_3$$

This reaction proceeds rapidly near the flame zone, where the O-atom concentrations significantly exceed final equilibrium values. Some of the SO_3 formed in this reaction is subsequently reconverted to SO_2 by:

$$SO_3 \quad + \quad O^{\circ} \quad \longrightarrow \quad SO_2 \ + \ O_2$$

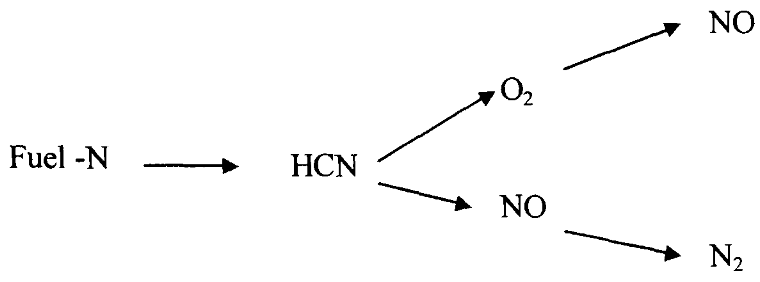
$$SO_3 \quad + \quad H^{\circ} \quad \longrightarrow \quad SO_2 \ + \ OH^{\circ}$$

1.2.7.4.The mechanism of formation of nitrogen oxides

During the combustion of fuels with air, a small part of the nitrogen present in the air or in the fuel itself reacts with oxygen to form nitric oxide in the flame gases. This nitric oxide reacts further in the flame or when the combustion products leave the combustion unit to form NO_2 and to a limited extent N_2O_4. The mixture of these oxides of nitrogen so formed is called NO_x.

NO can be formed by 3 separate reaction processes: thermal NO, prompt NO, and fuel NO.

Thermal NO is formed by oxidation of atmospheric molecular nitrogen at temperatures below 1600-1800°K. Prompt NO, which has a weak temperature dependence, is formed by hydrocarbon fragments attacking molecular nitrogen near the reaction zone of the flame. Fuel NO is formed in the gas phase resulting from the oxidation of devolatilized nitrogen constituents at low temperature and usually accounts for 60- 80 % of total NO formed.[32,33] The proposed reactions apply specifically to NO formation following the formation of HCN [34]



The total NO_x content of combustion gases is usually in the range 400 - 1000 ppm (by volume) for coal combustion.

It is important to note that fossil fuel combustion accounts for only about 20 per cent of the total NO_x emissions to the atmosphere.

1.2.7.5.Trace elements

Trace elements are present, both organic and inorganic forms, in coal. The residues arising from combustion may leave the system in two ways: as solids for disposal or as emissions to atmosphere. Some of them are antimony, arsenic, beryllium, boron, cadmium, chlorine, chromium, cobalt, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, thallium, titanium, thorium, tungsten, zinc, vanadium, uranium.

1.2.7.6.Trace gases.

On combustion, other organic and inorganic compounds may be present in trace quantities for example: methane, ethylene, higher hydrocarbons, carbon monoxide, nitrous oxide, hydrogen cyanide, hydrogen sulphide, carbonyl sulphide, carbon disulphide.

1.2.7.7.Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are a class of organic compounds that are contained in the volatile matter evolved from coal above about 450°C. They are important because some of them have known carcinogenic properties.

Other classes of complex, coal-derived, organic compounds such as aromatic amines, benzene, substituted benzenes and methyl sulphates are known to be carcinogenic.

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CHAPTER TWO - NOVEL METHOD FOR SAMPLING AND ANALYSIS OF DIOXIN AND CHLORINATED AROMATIC HYDROCARBONS

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2.1. INTRODUCTION

The chlorinated aromatic hydrocarbon gases include a wide range of compounds. They can occur in particles or in the vapour and gas phase and are often emitted into the atmosphere by way of the combustion process or from pesticides.

In the sampling of volatile aromatic hydrocarbons the most commonly used adsorbents are Tenax, XAD-2 and activated carbon. [1,2,3,4,5,6,7,8,9]

Nineteen chlorine-containing species, including vinyl chloride and substituted benzenes, have been detected in ambient air samples collected in Houston and Los Angeles by adsorption on Tenax. [10] Collection on Tenax is normally used at ambient temperature for the less volatile chlorinated organic materials using a sampling rate determined by the "safe sampling volume" for the particular organic to be collected.[3,4,11]

Chlorinated hydrocarbons are generally desorbed from Tenax TA using an organic solvent such as toluene. Desorption from activated carbon is often achieved with carbon disulphide and from XAD-2 using carbon tetrachloride. [12,13,14,15,16,17]

Chlorinated pesticides and polychlorinated biphenyls (PCBs) have been efficiently adsorbed from large volumes of air onto plugs of polyurethane foam, at levels down to pg m^{-3} [18,19]. Recoveries of hexachlorobenzene are, however, poor using this procedure. A comparison of the collection efficiencies of Tenax-GC, XAD-2 and polyurethane foam has been undertaken for high-volume sampling of PCB [20] in air and the results confirmed that the foam was unable to retain the more volatile compounds (e.g. hexachlorobenzene and some PCBs) quantitatively, and that the resins were superior.

Nader Vahdat et al. have shown that no single adsorbent is capable of trapping all four of the compounds toluene, n-hexane, methylene chloride, methyl ethyl ketone.[21]

Rothweiler et al have shown in a comparison of Tenax TA and Carbotrap for sampling volatile organic compounds in air that both adsorbents can adsorb a wide range of volatile organic compounds (VOCs). [22]

A number of different sampling systems have been used for the determination of polyaromatic hydrocarbons (PAHs) and polychlorinateddibenzo-dioxin (PCDD). The majority methods for sampling and analysis of PCDD are, however, based on the US Environmental Protection Agency (EPA) Method 5 for particulates which has been adapted to trap gaseous organic micro pollutants and is the proposed EPA Method 23. In this method isokinetic sampling is used to trap the coarse and fine particulates on a glass fibre filter held in an oven maintained at 180 °C before the gases are cooled in a condenser and the organic components remaining in the gas phase are removed using an adsorption resin such as XAD-2. [9,23,24,25,26]

2.1.1. Instrumentation:

In this study, the following equipments were used to examine the sampling and analysis of aromatic and chlorinated aromatic hydrocarbons.

1-Sampling pump, 2-Flow meter, 3-Glass fibre filter, 4-Carbotraps 150, 300 and 370, 5-Glass tube 6 mm OD x 4 mm ID x 11.5 cm, 6- Empty glass flask 1 litre, 7-Thermal desorber unit, 8-Gas chromatograph and GC-Mass Spectrometer, 9-Tenax TA, activated carbon, Carbotrap B, Carbotrap C and Carbosieve S-III

2.1.1.1. Rotameter:

A rotameter is required to measure the amount of gas drawn through the sampling device. Rotameters consist of a ball or float in a glass tube. The tube, mounted vertically, has a slightly tapered bore with the diameter decreasing downward.

In this study, a rotameter with a range 0-160 ml min $^{-1}$ was used. The rotameter was calibrated with a soap bubble flow meter at room temperature.

2.1.1.2. Vacuum Pump:

To operate a collection device it is necessary to draw a measured quantity of air through the system. A SKC personal pump model 224-PC x R8 was used for the collection of gas and aerosol. The pump has two connection tubes, one for sampling and other containing a flow adjustment valve.

2.1.1.3. Glass Fibre Filter:

A 37mm diameter SKC microfibre filter was used to obtain samples of particulates in air and to trap aerosol.

2.1.1.4. Gas Chromatograph-Mass spectrometer:

A Fison's MD 800 gas chromatograph- mass spectrometer (GC-MS) was used with:

a) A 30m x 0.25mm, 0.25 μm film capillary column for the identification of chlorinated aromatic and aromatic hydrocarbons. This column is coated with poly (5% diphenyl, 95% dimethyl siloxane) and has an upper useable temperature of 320 °C.

b) A 60m x 0.32 mm, 0.2 μm film capillary column for the identification of 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD). This column is coated with cyanosilicone resin and has an operating temperature range from subambient to 275 °C.

The separation of the chlorinated aromatic hydrocarbon and 2,3,7,8-TCDD was achieved by GC and each component was detected by MS.

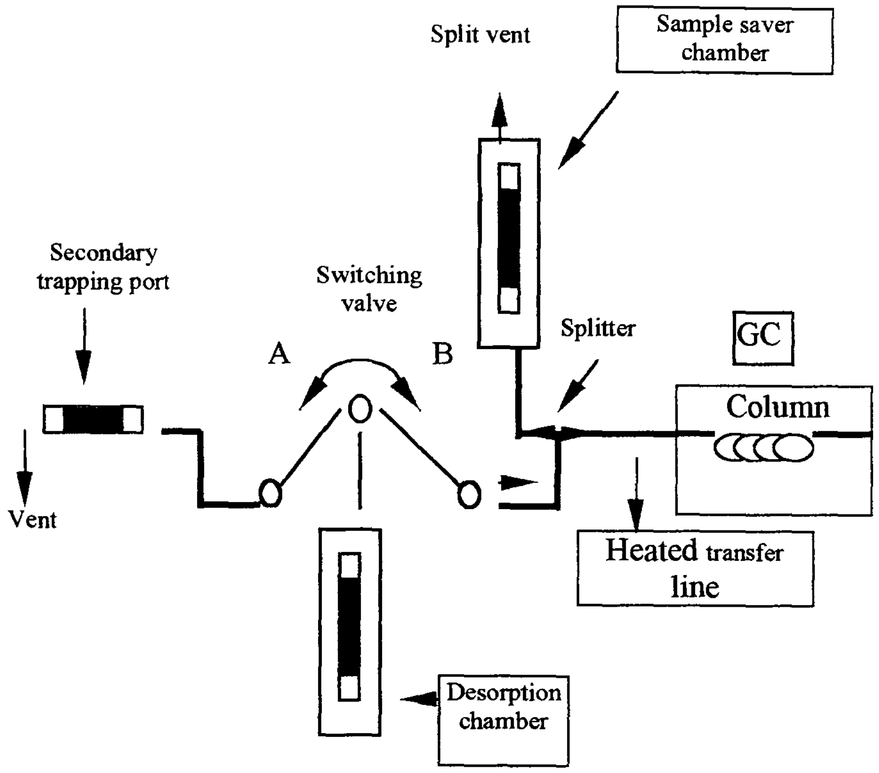
Lab-base software was used to obtain the chromatogram from the total ion current. Each peak in the chromatogram was identified by comparing the MS scan with those in the LBS data base and a library prepared from single standard injections.

2.1.1.5. Thermal desorption unit:

Thermal desorption, a technique in which heat and a flow of inert gas are used to extract some compounds from solid or liquid matrices, is now widely used in environmental monitoring. A major advantage of thermal desorption in this field is that by doing away with the inevitable dilution step of conventional solvent extraction procedures, up to 100 % of the pollutants retained on the porous polymer or charcoal sorbents may be transferred to the GC. Thermal desorption techniques also save sample preparation time and, because the adsorbent tubes usually can be reused many times, adsorbent tube costs are lower in the long run.

In this study, a Supelco Thermal Desorption Unit Model 890 was used. Figure 2-1 shows the schematic of this unit.

Figure 2-1: The schematic of thermal desorption unit



The system has:

Dual flow Pathways: The left path way, A, in Figure 2-1, is used to desorb a sample from an wide ID adsorbent tube to a narrow ID tube in the trapping port, for more efficient subsequent delivery to the GC column. This flow pathway also can be used to thermally extract components of a solid sample and deliver them to an adsorbent tube in the trapping port. The right pathway, B, delivers samples that are ready for analysis to the chromatography column.

Accurate heating: The sample is heated rapidly (e.g. 30°C to 400°C in 26 seconds) and reproducibly delivered to the analytical column, for sharp symmetrical peaks. Highly accurate temperature control allows reliable thermal fractionation analyses of polymers, etc.

Trapping port: A narrow bore adsorbent tube is installed here to trap components that have been thermally extracted from a sample focus compound in a wide bore adsorbent tube. This allows for better chromatography without cryogenic focussing.

Sample saving chamber: This can be used to save part of sample for a second analysis.

Inert flow pathways: A heated nickel transfer line or fused silica transfer line prevents sample adsorption or condensation during transfer to the analytical column.

2.1.2. Selective sampling methods:

In selective sample collection methods only a part of the total sample is collected, but that part must include all of the components that have to be determined. The first advantage of the selective sampling technique is that the permanent gases of the atmosphere are not collected, The second is that a concentration stage is introduced which simplifies the measurement stage that follows. These techniques, however, introduce a number of sources of possible errors. These can arise from unforeseen chemical reactions with (1) the trapping systems, (2) the difficulty of handling the small quantities involved, and (3) incomplete retention of the required substances in the traps. Selective sampling methods include: solvent scrubbing, trapping by specific chemical reagent, condensation methods, collection on a filter and collection of sample on solid adsorbents.

2.1.2.1. Solvent scrubbing:

In this technique the atmospheric gases are bubbled through a solvent that will dissolve and retain the components to be measured. A device called an impinger, in which the solvent is contained, is often used in this technique. An impinger consists of a cylindrical vessel of capacity 3-30 ml containing a central tube that is sealed into the stopper of the vessel. The solvent is contained in the vessel and sample enters through the central tube that terminates in a fine nozzle near the base of the vessel.

The efficiency of operation of a scrubbing system is affected by the vapour pressures of the solvent and of the substance being collected. Evaporation of the solvent can lead to significant losses in collected substances, especially if these are volatile.

2.1.2.2. Trapping by specific chemical reagent:

The solvent in an impinger or scrubbing train can be replaced by a solution of chemicals that will react with the analytes of interest. The rate of reaction with a reagent is usually more rapid than the rate of solution in a solvent and so shorter contact times may be used. Further, the product of the reaction is often less volatile than the substance being trapped. However, if the reaction between the sample and the reagent causes a precipitate to be formed, a bubbler that terminates in a sintered glass disc should not be used because the sinter may become blocked by the precipitate.

2.1.2.3. Condensation methods:

Sample collection by condensation involves passing the atmospheric gases through a trap, which is maintained at a low temperature, and in which organic substances will condense and be retained. The collection efficiency of a simple trap is, however, generally poor and depends on the chemical and physical properties of substances being trapped. Volatile substances can be collected only if the trap is very cold, and the low temperature must be maintained until the sample is removed from the trap for analysis.

The greatest problem with this method arises from the presence of water vapour in the atmospheric sample, which appears as ice in the trap. Many pollutants also dissolve in the water after the sample is warmed to ambient temperature.

2.1.2.4. Collection on a filter:

If collection on a filter is used, the filter should never be allowed to become blocked with the sample material. A possible source of error arises from evaporation of the mist particles after trapping, if they contain volatile components and the air is unsaturated with their vapour.

2.1.2.5. Collection of sample on solid adsorbents:

The adsorption of gases on solids is a phenomenon that has long been recognised. Scheele in 1773 and Fontana in 1777 described the removal of gases from the atmosphere by adsorption on charcoal. The process was highly developed during World War I when traps using highly adsorbent charcoal were used for respiratory protection against war gases. [13]

There are two main processes by which a gas is retained on a solid. The first is physical adsorption in which the gas is held by Van der Waals' forces, and the second is chemical adsorption in which there is a greater binding energy. Physical adsorption is a non-specific process and arises between any solid and any gas provided the temperature is sufficiently low. A third process may occasionally be involved when gases are trapped on solids. In certain cases the vapour may enter into solid solution. This process, however, is very slow and the solubility of vapours and gases in most solids is very low.

2.1.2.5.1. Type of carbon sorbents:

Various kinds of carbon sorbent are available which may be utilised for the enrichment of analytes: (1) activated carbon, (2) molecular sieves, (3) graphitised carbon black, (4) porous carbon

They differ in their physico-chemical, thermodynamic and kinetic characteristics. The important physico-chemical properties are pore size and shape, surface area, functionality of the surface and chemical inertness. The important kinetic and thermodynamic properties (breakthrough volumes, adsorption isotherms and intermolecular interaction mechanisms occurring at the adsorbate/carbon sorbent interface) strongly influence the pre-concentration and/or pre-separation step. The characteristics of the carbon sorbents based on their properties will depend upon : the type of starting material, the procedure chosen for preparation of the product and the conditions under which it is used.

2.1.2.5.2. Activated carbon:

Activated carbons have been used since the time of the ancient Egyptians, when charcoals were employed for medicinal purposes. Industrial applications originated in the late 18th century, when it was discovered that activated carbons could adsorb gases and remove colour species from solution. A stimulus to industrial production was the development of protective gas masks after the introduction of chemical weapons. Activated carbons are now used extensively in diverse applications:[27,28] potable and waste water treatment, respirators, solvent recovery from a process stream, air and gas purification and prevention of gasoline vapour emission from automobiles. More specialised applications, sometimes involving the addition of impregnants, can be found in catalysis, medicine, military gas masks and gold recovery.

Commercial sources for activated carbons include biomass materials e.g. wood, coconut shell, fruit pits, and fossilised plant matter (peats, lignites and all ranks of coal) and synthetic polymers. [29] Adsorbent carbons are usually produced by a two-step process of carbonisation and then activation by partial gasification. The highly porous structure produced during activation provides the large surface area of an activated carbon on which its usefulness as an adsorbent depends.

Problems in using carbon for analytical work are related to the large variations in the physical and chemical properties of the different sources of carbon. Also there are difficulties in obtaining low background contamination levels compared to other sorbents. The fact that many organic compounds are adsorbed so strongly on carbon means that desorption can only be accomplished in very low yields.

Activated carbon has a very complex surface structure containing a wide range of functional groups including phenolic, carboxylic, aldehydic, etheric, peroxidic, quinone and lactone [30,31]. The principal binding mechanisms include hydrophobic interactions, charge-transfer complexation, hydrogen bonding, cation exchange and other specific interactions. The surfaces of such carbons possess a high sorption capacity, but are very heterogeneous. Low recovery of many organic solutes is often associated with the strength of multiple binding interactions, which provide an efficient adsorption mechanism accompanied by inefficient solvent elution, leading to a low overall recovery.

2.1.2.5.3. Molecular sieves:

Carbon molecular sieves are formed by the controlled pyrolysis of suitable polymeric material (e.g. polyvinyl chloride) or petroleum pitch materials at temperatures usually above 400°C. They have a highly porous structure with almost uniform micropores. [22, 32, 33] They are comprised of very small crystallites crosslinked to yield a disordered cavity-aperture structure. Carbon molecular sieves are microporous and have a high surface area, with a very pronounced retention of organic compounds, but they can be very easily contaminated by impurities from air [34]. The structure, the purity of the starting polymer material and the technology used for carbonisation dictate the particle size and the distribution and size of pores of the final product. The presence of polymer impurities substantially decreases the homogeneity of the porous structure.

2.1.2.5.4. Graphitised carbon black:

Graphitised carbon blacks (GCBs) as adsorbent for GC were studied in the sixities by Kiseler and his co-workers [35], as well as Horvath [36] and Guichon and co-workers [37]. GCBs are materials with a homogeneous surface and without micropores. They adsorb compounds on their external surfaces based on the molecular size and shape of the adsorbed molecule. GCBs are prepared by heating ordinary carbon blacks to about 3000°C in an inert gas atmosphere [38, 39]. This eliminates volatile, tarry residues and induces the growth of graphite crystallites, particles in which graphite crystals are arranged in the form of polyhedrons. At the same time various functional groups originally present on the carbon black surface are destroyed. The surface of graphitised carbon blacks is almost completely free of unsaturated bonds, lone electron pairs, free radicals and ions.

The trapping of compounds on GCBs can be explained on the basis of the availability of two types of adsorption sites [40,41]. The vast majority of the surface sites are nonpolar and correspond to a graphite-like array of carbon atoms. These sites show no tendency to interact preferentially with molecules carrying functional groups and dispersive interactions dominate the retention behaviour. Polar adsorption sites are few in number but they can establish specific, strong interactions with polar compounds.

Preliminary treatment of the adsorbent may be used to reduce their number. For example, heating to 1000°C in a stream of hydrogen has been used to minimise those active sites associated with the presence of surface oxygen complexes. [41, 42] Washing with perchloric or phosphoric acid eliminates basic carbonium-oxygen complexes and sulphur present as sulphide. [43]

2.1.2.5.5. Porous carbon:

Porous carbon adsorbents are materials with a homogeneous hydrophobic surface. [44, 45, 46, 47, 48, 49] They attracted attention because of their stability over a wide pH range and their mechanical stability. They are produced by impregnating a suitable silica gel or another porous template with a phenol-formaldehyde resin mixture, phenol-hexamine mixture, saccharose or another material. [47, 50] After polymerization within the pores of the template material, the polymer is converted to glassy carbon by heating in an inert atmosphere to about 1000°C. The silica template is then removed by alkali to give porous graphitic carbon (PGC). Finally, the material is fired in an inert atmosphere at a high temperature in the range 2000-2800 °C to anneal the surface, remove micropores and, depending upon the temperature, produce some degree of graphitization. The particle size, shape, porosity and pore size are determined by the choice of template material. The surface chemistry is determined by the choice of template material and by the final heat treatment and any subsequent chemical treatment. It is thus possible in principle to produce PGCs with a range of pore and surface properties tailored to specific requirements.

2.1.2.5.6. Porous polymeric sorbents:

Resins of various compositions that are suitable for use as adsorbents are available commercially. This group includes Tenax, Porapak, Chromosorb, and XAD tubes. Most porous polymers are co-polymers in which one entity is styrene, ethylvinyl benzene or divinyl-benzene and the other monomer is a polar vinyl compound. These substances offer a wide range of physical properties with different polarities, and different characteristics of adsorption. Limitations of this group are displacement of less volatile compounds (especially by carbon dioxide), irreversible adsorption of some compounds (such as amines and glycols), oxidation, hydrolysis and polymerization reactions of the sample, chemical changes of the contaminant in the presence of reactive gases and vapours (such as nitrogen oxides, sulphur dioxide, and inorganic acids) artifacts arising from reaction and thermal desorption, limited retention capacity, thermal instability and limitations of sampling volume, flow and time. [44]

The Porapaks have a wide range of polarity. The least polar member, Porapak P, is used in gas chromatography columns, and the most polar, Porapak T, can separate water and formaldehyde. Porapak P is used to collect acetone, cyanohydrin, and dimethyl sulphate. Porapak T is recommended for sampling hexachloro-1, 3-cyclopentadiene.

The Chromosorbs are similar to the Porapaks. Chromosorb 101 is the least polar and Chromosorb 104 the most polar.

XAD resins are a brand name referring to a number of different porous polymer types. XAD-2, the most commonly used, is equivalent to Chromosorb 102 and is used to collect anisidine and tetraethyl lead. Amberlite XAD-2 is a styrene - divinyl benzene polymer.

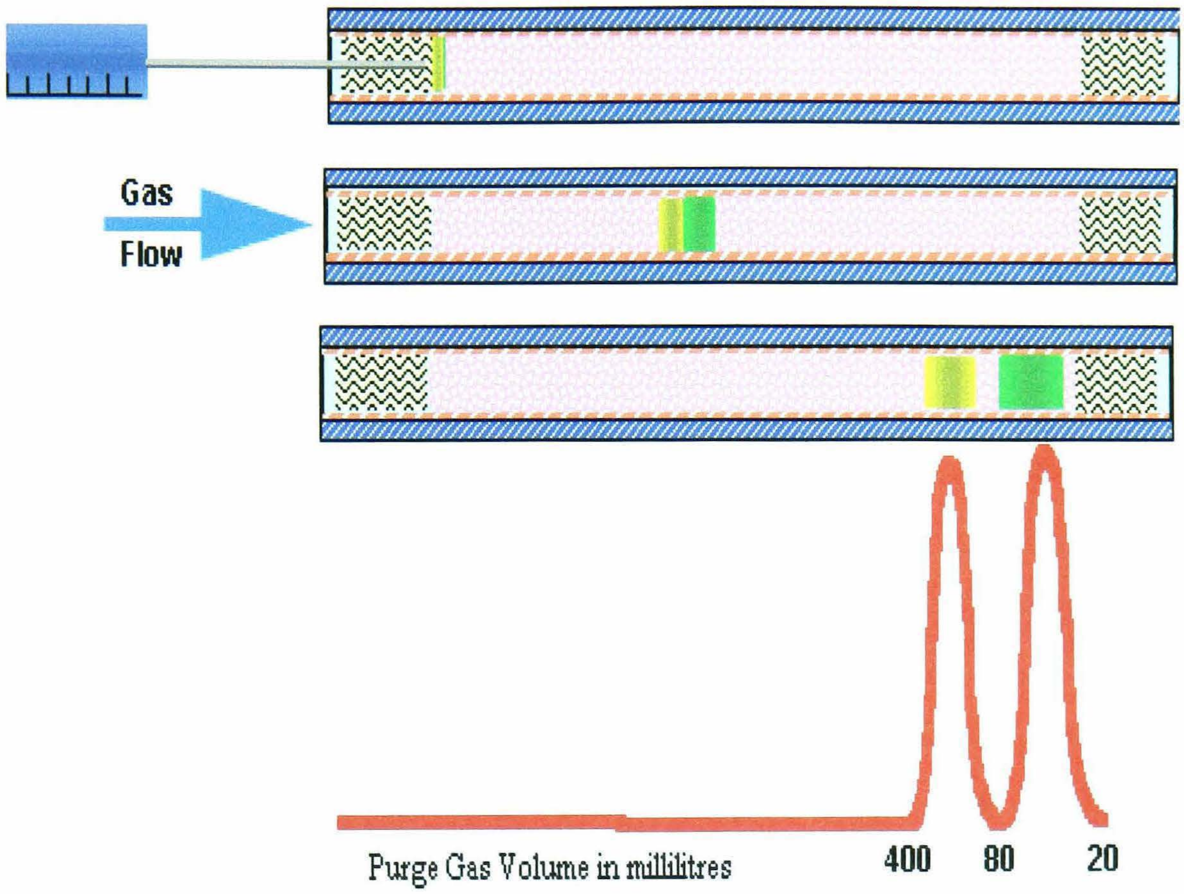
Tenax is a polymer of 2,6-diphenyl-p-phenylene oxide and can be used to collect organic compounds. Tenax is used mostly for sampling low concentration of volatile compounds. Tenax reacts with strong oxidising agents, such as chlorine, ozone, nitrogen oxides, and sulphur oxides, to form benzaldehyde, acetophenone, and phenol. [1]

2.2. DEFINITION OF BREAKTHROUGH VOLUME:

The term "breakthrough volume" has been referred to as retention volume and also the specific retention volume. The units of breakthrough volume are usually expressed as the volume of gas per weight of adsorbent as litres per gram, or millilitres per gram. [52]

The term breakthrough volume is defined as the calculated volume of carrier gas per gram of adsorbent that causes the analyte molecules to migrate from the front of the adsorbent bed to the back of the adsorbent bed. Figure 2-2 shows the elution of analytes from an adsorbent.

Figure 2-2: Elution of analytes from adsorbent



In this diagram a desorption tube is packed with a known weight of adsorbent with glass wool plugs at both ends to hold the adsorbent in place. This adsorbent bed now can be visualised much like a GC column in which an analyte is injected onto the front of the adsorbent bed and then, purged with carrier gas, is eluted at the opposite end of the bed. If carrier gas is purged through the adsorbent bed at a constant flow rate and the analyte detected on elution at the end of the adsorbent bed, a GC chromatogram type peak will be detected. The top of this peak corresponds to the retention time for the analyte to migrate from the front of the adsorbent bed and out the opposite end. Multiplying this retention time by the flow rate through the packed adsorbent bed produces the gas volume that caused the analyte to migrate through the absorbent bed. Dividing this gas volume by the weight of the adsorbent packed in the tube produces the breakthrough volume (BV) data. This model assumes that a small narrow plug of analyte migrates through the adsorbent bed. [21, 53, 54, 55, 56, 57]

The data that are really important is the gas volume at which the analyte is first eluted off the adsorbent bed (Bs). This value is called the safe sample volume or initial elution volume. When collecting a sample onto the adsorbent bed, this safe sample volume (l/g) should not be exceeded to ensure that all the analyte is trapped on the adsorbent bed.

A second factor that is important is the complete sample elution volume (Bf). This is the gas volume at a particular temperature at which the sample will be completely eluted off the adsorbent bed.

2.2.1. Indirect calculation of breakthrough volume:

In this method a gas generator is used to provide standard gas concentration of the analytes continuously, over a period of time, to an adsorbent, by pumping at specific flow and temperature. The tube is then separated and analysed by GC or GC-MS. The disadvantage of this method is that, if the sample is collected over a long enough period, it is possible to purge the analytes off one end of adsorbent bed while they are still being collected at the front end of the adsorbent bed [55,57].

Also, this may be possible when injecting internal standards or liquid samples onto the absorbent bed. This is not the case when collecting air samples or purging gas samples from liquid or solid samples.

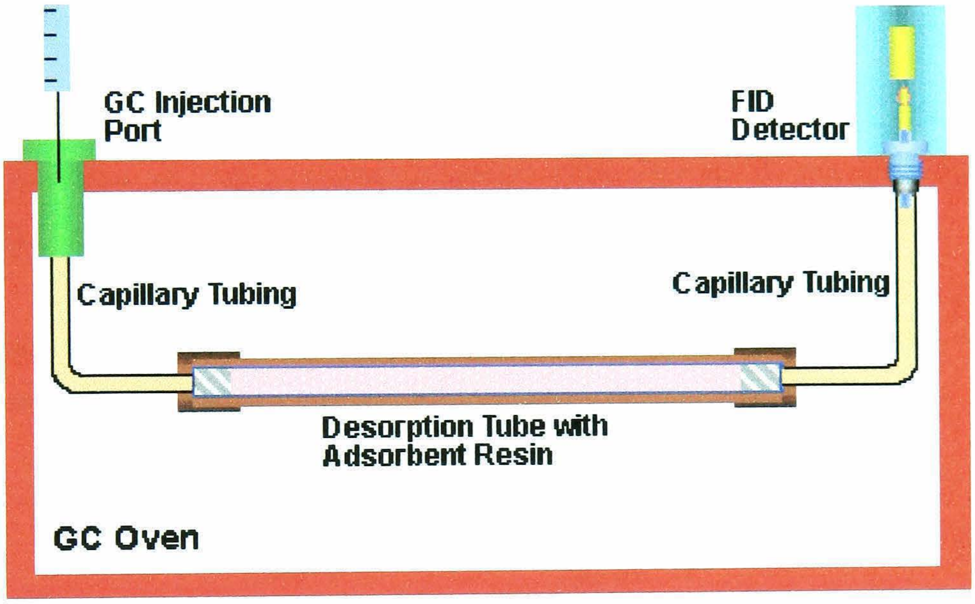
2.2.2. Experimental determination of breakthrough volume:

Figure 2-3 shows the system for the determination of the breakthrough volume as a function of temperature. To construct the adsorbent bed a desorption tube (6mm OD x 4mm ID x 115mm long) was packed with an accurately weighed quantity of adsorbent (20mg-1g) and sealed at both ends with glass wool plugs. Stainless steel connecting lines and a small piece of capillary column, or only stainless steel connecting lines, were connected to both ends of the adsorbent bed. One of these lines was connected to the injection port of a GC and the other end to the MS or the flame ionisation detector.

The breakthrough volume was determined for each analyte of interest in separate experiments using the desorption tube as a packed column.

Helium was used as the carrier gas with the flow accurately adjusted between 2-3.5 ml min $^{-1}$ for the GC-MS and 5-500 ml min $^{-1}$ for the GC and flame ionziation detector. Accurate measurement of adsorbent bed weight, carrier gas flow and oven temperature are necessary for the accurate determination of breakthrough volumes. The GC oven temperature was between 80°C and 260°C for the determination of the breakthrough volumes as a function of this temperature.

Figure 2-3: System for the determination of breakthrough volumes of adsorbent as a function of temperature



Approximately 1-20ng of each of the analytes studied were injected into the GC injection port.

The retention time in minutes was multiplied by the carrier gas flow in ml min $^{-1}$ and this was divided by the weight of the adsorbent. A correction was made for the dead volume of the packed adsorbent and connecting lines. This dead volume was determined by injecting a non-retained analyte into the GC injection port and calculating its retention volume.

Carbotrap C, Carbotrap B, Carbosieve S-III and Tenax TA were used as adsorbent.

The analyte first begins to elute from the adsorbent at a carrier gas volume of Bs (safe sample volume) and is totally eluted from the absorbent bed at a carrier gas volume of Bf (complete sample elution volume). If the breakthrough volume data are being used for the adsorption of an analyte onto the absorbent bed, then the value Bs must be used so as not to purge off any of the analyte during the sampling step.

From experience, the values of Bs and Bf were selected where the peak height is 5% of the maximum peak height and calculated as:

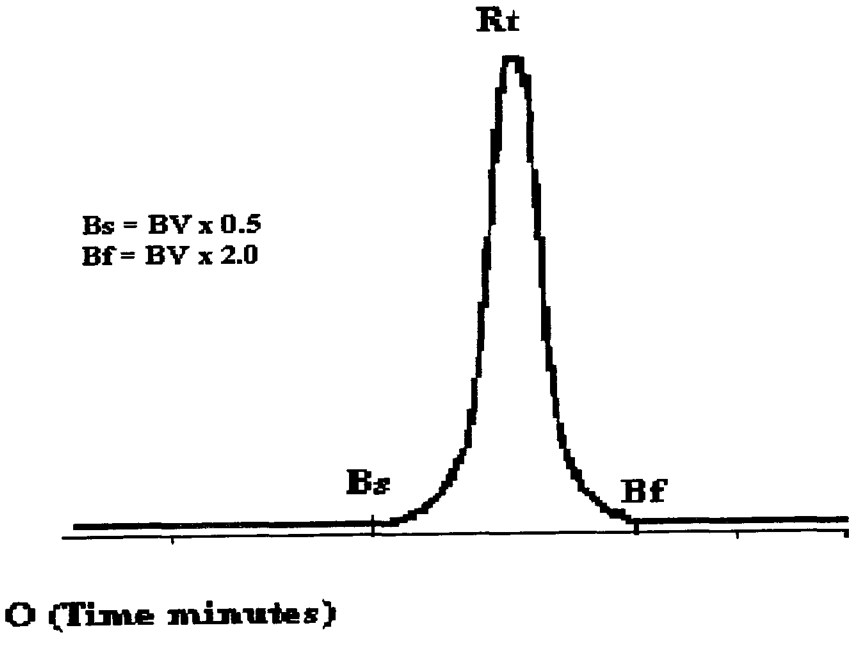
$$Bs = BV \times 0.5$$

Complete sample elution volume (thermal desorption) can be calculated as:

$$Bf = BV \times 2.0$$

Figure 2-4 shows a chromatogram with the positions of retention time, safe sample volume and the complete sample elution volume.

Figure 2-4: A chromatogram with the position of retention time, safe sample volume and complete sample elution volume



2.2.3. Results:

The results of the breakthrough volume tests in this work are shown in Table 2-1. The results show that Carbotrap C has a good capacity for heavy molecular weight compounds and Carbosieve S-III has a good capacity for volatile compounds, as has Tenax TA. The problem with Tenax is its unsuitability for use at high temperature for the desorption of the majority of non-volatile compounds. It is therefore not suitable for 2,3,7,8-TCCD.

Table 2-1: Breakthrough volume for Tenax, Carbotrap B, Carbotrap C, and Carbosieve S-III (l/g)

Sample	Temperature °C	Tenax TA	Carbotrap B	Carbotrap C	Carbosieve S-III
Benzene	60	8.10	1.35	0.174	373
Toluene	80	2.70	4.5	0.56	15.6
Chlorobenzene	80	4	15	1	31
Dichlorbenzene	100	4.5	184	7.3	2.6
Tetrachloro benzene	120	2.3	188	66.37	5.82
Pentachloro benzene	140	3.7	80.6	864	0.071
Hexachloro benzene	160	5.6	19	2419	0.003
Tetrachloro ethylene	80	2.2	5.4	0.67	73
2,3,7,8-TCDD	260	0.024	1.1	>700	$4.6\text{x}10^{-7}$

2.3. RECOVERY:

Several solid sorbents for air sampling were evaluated in this study for their analytical application in thermal desorption in a GC-MS system. Some of the more common groups of materials that have found general usage with air sampling and purge-and-trap methods include: porous polymer, carbon and silica gel. Initially, five sorbent materials were screened for their retentive capacities and thermal desorption potential for various compounds then, evaluative testing was conducted on three commercially available types of tubes containing multisorbent combinations. The tubes used in the study were made of Pyrex glass 11.5 cm long x 6 mm OD x 4 mm ID. In the initial part of the work, these tubes were packed with 150 mg of individual sorbents to be tested. Later, the Carbotrap 150, Carbotrap 300 and Carbotrap 370 were evaluated. The amount of each sorbent in the Carbotrap tube is shown in Table 2-2. All of these Carbotraps were supplied by Supelco.

Table 2-2: The amount of each sorbent in the tube

Tube	Carbotrap 150 (mg)	Carbotrap 300 (mg)	Carbotrap370 (mg)
Carbotrap B	_	48	20
Carbotrap C	200	72	50
Carbotrap F	-	-	40
Carbosieve S-III	-	30	-
Glass beads	200	-	-

All of the packed tubes were preconditioned before each use at 350 °C, except Tenax which was heated at 260 °C, for 30 minutes with a carrier gas flow of helium through the tube of 5 ml min $^{-1}$. The conditioned tubes were stored in screw-cap glass containers.

The total helium carrier gas flow through the tube desorber in the thermal desorption unit was 2.5 ml min $^{-1}$.

A sorbent tube to be evaluated was spiked with a known amount of a standard solution of each compound. To achieve this the sorbent tube was placed in the side port of the desorber unit and the required amount of standard was injected into an empty tube in the desorption chamber. This chamber was then heated to allow the standard to pass to the sorbent tube in the carrier gas stream. The tube was then returned to its capped storage container and held for analysis.

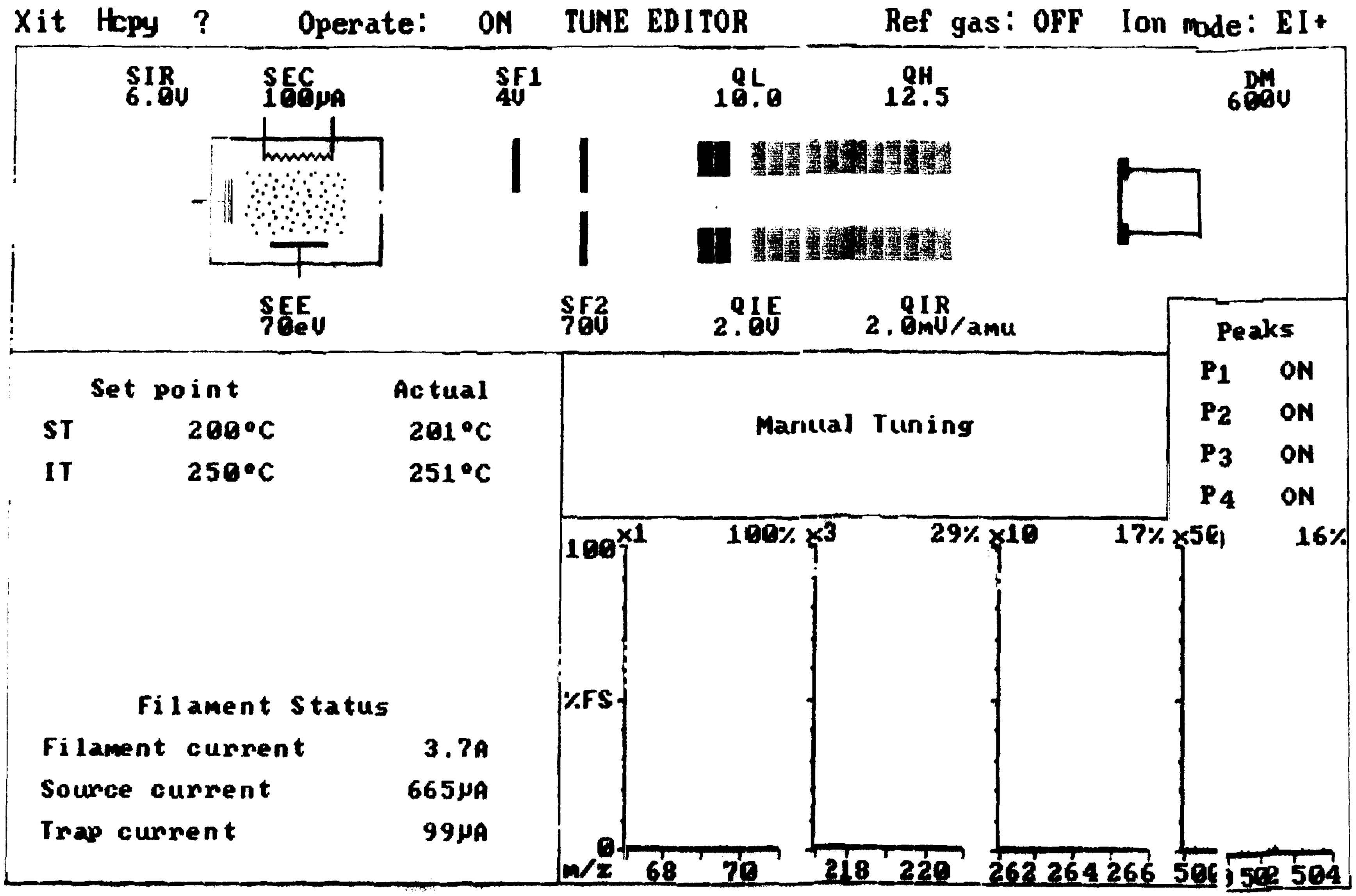
The initial testing on single sorbent tubes was conducted using spikes of 1 μg of each solvent. The main study on the combination Carbotrap tubes used spikes of 0.1,1.0 and 2.0 μg of each analyte.

One set of tubes was stored at room temperature for one month after spiking in order to check the effects of holding time on the tubes.

Analysis was conducted by placing a sample tube into the desorbing chamber of the tube desorber and heating it to desorb its contents onto the column. Table 2-3 shows the temperature programming of the gas chromatograph. Conditions for the MSD are shown in Figure 2-5 for 2,3,7,8-TCDD and Figure 2-6 for group I compounds which include toluene, chlorobenzene, dichlorobenzene, tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene and tetrachloroethylene. The MSD was operated in the SCAN mode, scanning between 30 - 350.

Table 2-3: The temperature programming of gas chromatograph:

Sample	**Initial temperature**	**First stop**	**Ramp C°/min**	**Final temperature**	**Second stop**
Group I	30	5	5	200	10
2,3,7,8- TCDD	200	1	8	260	20



Operate: ON TUNE EDITOR Ref gas: OFF Ion mode: EI+

SIR 6.0V
SEC 100µA
SF1 4V
QL 10.0
QH 12.5
DM 600V
SEE 70eV
SF2 70V
QIE 2.0V
QIR 2.0mV/amu

	Set point	Actual
ST	200°C	201°C
IT	250°C	251°C

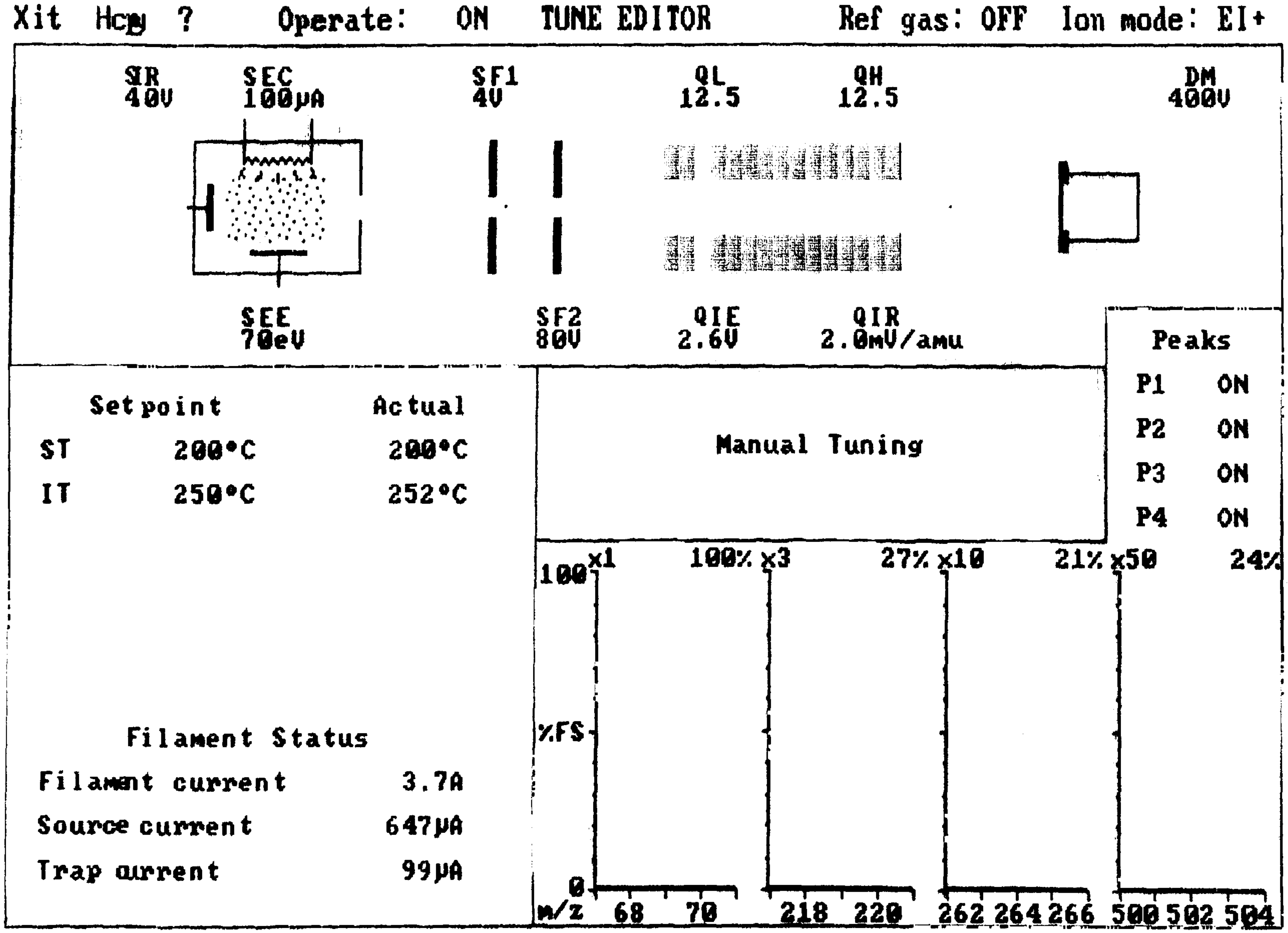
Manual Tuning

Peaks	
P1	ON
P2	ON
P3	ON
P4	ON

Filament Status

Filament current	3.7A
Source current	665µA
Trap current	99µA

Figure 2-5: MSD conditions for 2,3,7,8-TCDD



Xit Hcpy ? Operate: ON TUNE EDITOR Ref gas: OFF Ion mode: EI+

SIR 40V
SEC 100µA
SF1 4V
QL 12.5
QH 12.5
DM 400V
SEE 70eV
SF2 80V
QIE 2.6V
QIR 2.0mV/amu

	Setpoint	Actual
ST	200°C	200°C
IT	250°C	252°C

Manual Tuning

Peaks
P1 ON
P2 ON
P3 ON
P4 ON

Filament Status
Filament current 3.7A
Source current 647µA
Trap current 99µA

Figure 2-6: MSD conditions for group I compounds

2.3.1. Results and discussion:

The results for the preliminary tests on tubes packed with individual sorbents are presented in Table 2-4. It is apparent from these results that no single sorbent material is capable of collecting all solvent types used. In some instances this is because the sorbents are not retentive of light materials (Carbotrap C). In other cases it is because they are too retentive for easy desoption of the heavier solvents (activated charcoal).

The best approach to the problem is clearly to construct tubes containing several different materials to attain the desired collection and desorption characteristics. The use of tubes packed with two or three combinations of sorbents with different characteristics was investigated. The first sorbent should have the capability of retaining heavy volatile compounds followed by adequate desorption. The second should be intermediate in nature (adsorbing a wide range of compounds), and the third should be able to handle low molecular weight compounds. The materials would ideally have the ability to stand up to repeated use and heating without changing their characteristics and should additionally give a low background on a chromatogram. It is also desirable that they would have a low affinity for water.

All types of tubes tested in this study gave relatively clean chromatographic peaks.

Table 2-5 shows the recoveries for the analyte compounds spiked at three different concentration levels.

The storage stability was tested by spiking one set of tubes at the same time as the others at a level of 0.1μg of each compound. This set was stored in a dark box at room temperature for one month before analysis. The results are compared in Table 2-6 with those for the tubes analysed within one day of sampling. The loss over the course of a month is represented in Table 2-6 by the column labelled "% loss". This was derived by subtracting the recovery values of stored tubes from the values for non-stored tubes.

Table 2-4: Per cent recoveries of standard solution from selected sorbents via thermal desorption

Solvent	**Carbotrap B**	**Carbotrap C**	**Activated charcoal**	**Carbosieve III**	**Tenax**
Toluene	101	0	65	28	98
Chlorobenzene	104	0	67	24	100
p-Dichlorobenzene	103	0	66	22	98
o-Dichlorobenzene	103	0	67	22	98
1,2,4,5-Tetrachlorobenzene	105	0	69	19	88
Pentachlorobenzene	108	5	72	13	45
Hexachlorobenzene	108	3	70	14	52
Tetrachloroethylene	38	0	33	65	88
2,3,7,8 -TCDD	91	104	71	10	_

Table 2-5: Per cent recoveries of analyte compounds at different concentration from combination sorbent tubes

Solvent	Tube	0.1µg	1.0µg	2.0µg
Toluene	Carbotrap 370	100±3	98±2	96±5
	Carbotrap 300	102±2	101±2	95±3
	Carbotrap 150	0	0	0
Chlorobenzene	Carbotrap 370	99±8	97±6	95±6
	Carbotrap 300	101±12	100±4	94±5
	Carbotrap 150	0	0	0
p-Dichloro- benzene	Carbotrap 370	98±4	98±5	95±6
	Carbotrap 300	102±7	101±6	98±4
	Carbotrap 150	0	0	0
o-Dichloro- benzene	Carbotrap 370	98±6	96±4	94±5
	Carbotrap 300	102±5	100±5	98±2
	Carbotrap 150	0	0	0
1,2,4,5- Tetrachloro-benzene	Carbotrap 370	99±4	97±3	96±6
	Carbotrap 300	100±3	98±3	197±4
	Carbotrap 150	0	0	0
Pentachloro- benzene	Carbotrap 370	98±7	96±7	93±5
	Carbotrap 300	102±4	99±5	97±2
	Carbotrap 150	5±2	3±3	1
Hexachloro- benzene	Carbotrap 370	100±6	97±7	95±3
	Carbotrap 300	100±2	98±4	95±2
	Carbotrap 150	8±3	6±4	2±1
Tetrachloro- ethylene	Carbotrap 370	94±3	92±5	89±4
	Carbotrap 300	102±5	98±2	96±3
	Carbotrap 150	0	0	0
2,3,7,8- TCDD	Carbotrap 370	98±6	98±4	97±5
	Carbotrap 300	100±3	100±4	99±2
	Carbotrap 150	102±4	102±3	102±1

Table 2-6: Per cent recoveries from combination sorbent tubes, and losses after one month's storage

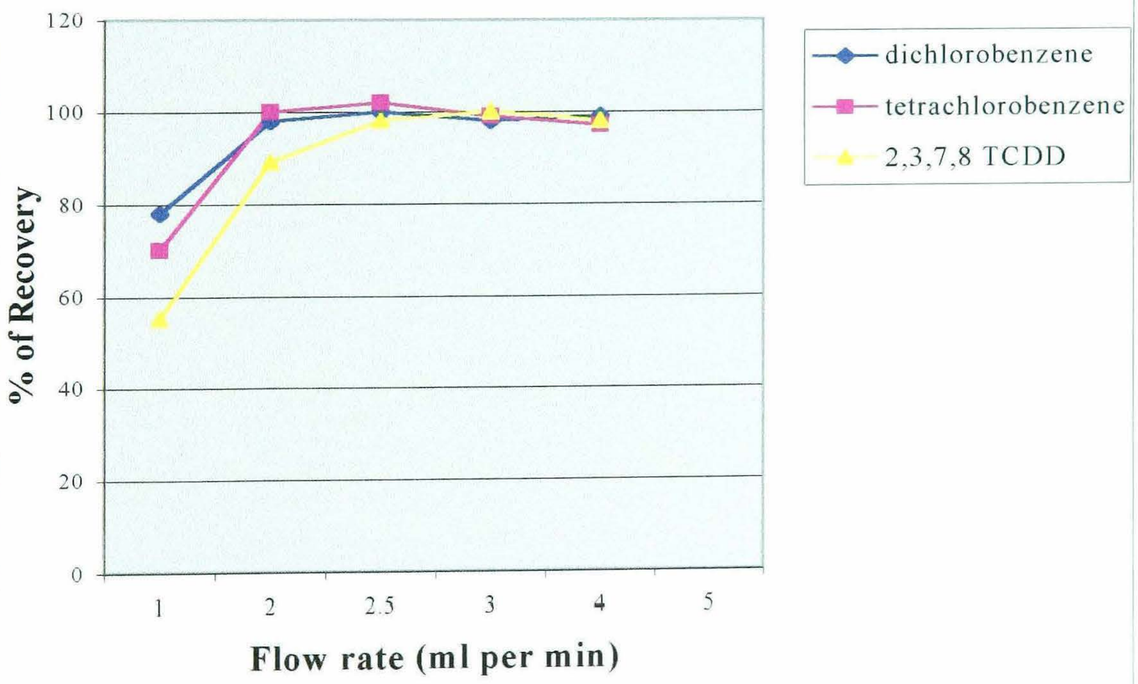
Solvent	Tube	One day	One month	% loss
Toluene	Carbotrap 370	100±3	96±4	4±7
	Carbotrap 300	102±2	97±3	
	Carbotrap 150	0	0	5±5
Chlorobenzene	Carbotrap 370	99±8	98±7	1±15
	Carbotrap 300	101±12	100±4	1±16
	Carbotrap 150	0	0	
p-Dichloro-benzene	Carbotrap 370	98±4	98±5	0±9
	Carbotrap 300	102±7	101±7	1±14
	Carbotrap 150	0	0	
o-Dichloro-benzene	Carbotrap 370	98±6	97±3	1±9
	Carbotrap 300	102±5	101±6	1±11
	Carbotrap 150	0	0	
1,2,4,5-Tetrachloro-benzene	Carbotrap 370	99±4	98±4	1±8
	Carbotrap 300	100±3	101±5	0±8
	Carbotrap 150	0	0	
Pentachloro-benzene	Carbotrap 370	98±7	97±2	1±9
	Carbotrap 300	102±4	102±3	0±7
	Carbotrap 150	5±2	0	5±2
Hexachloro-benzene	Carbotrap 370	100±6	99±7	1±13
	Carbotrap 300	100±2	99±8	1±10
	Carbotrap 150	8±3	2±1	6±4
Tetrachloro-ethylene	Carbotrap 370	94±3	84±6	10±9
	Carbotrap 300	102±5	89±4	13±9
	Carbotrap 150	0	0	
2,3,7,8- TCDD	Carbotrap 370	98±6	98±3	0±9
	Carbotrap 300	100±3	99±4	1±7
	Carbotrap 150	102±4	102±2	0±6

2.4. OPTIMISATION OF CONDITIONS FOR THERMAL DESORPTION:

2.4.1. Optimum flow rate:

The optimum flow rate was determined by the injection of 1 μl dichlorobenzene and tetrachlorobenzene or 2,3,7,8-TCDD into a one litre glass flask with a septum port. The flask was warmed and shaken to facilitate the evaporation of the chloro-organic compounds. A small vacuum pump was used to transfer these standard gases to a Carbotrap 300 for dichloro- and tetrachlorobenzene and a Carbotrap 150 for 2,3,7,8-TCDD. The flow rate of the vacuum pump was 25 ml min^{-1} Figure 2-7 shows the recovery of dichlorobenzene, tetrachlorobenzene and dioxin at different flow rates. The optimum flow rate is between 2 and 2.5 ml min^{-1} for dichlorobenzene and tetrachlorobenzene, and 2.5-3 ml/minute for 2,3,7,8-TCDD.

Figure 2-7: Recovery of dichlorobenzene, tetrachlorobenzene and 2,3,7,8-TCDD at different desorbing flow rate



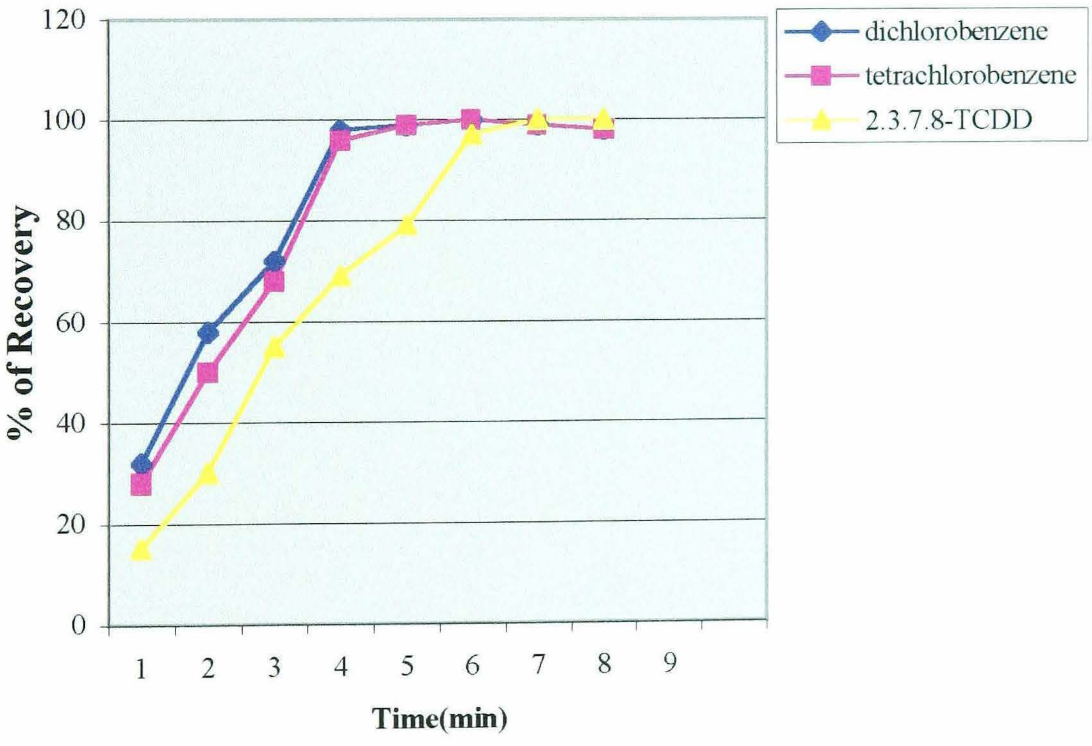
2.4.2. Length of time for desorption:

To determine the optimum time for desorption of a sample from a Carbotrap, a Carbotrap 300 or 150 was exposed to standard gas as described in section 2.4.1.

The desorption was performed at different times with a flow of 2.0-2.5ml min $^{-1}$ for dichloro- and tetrachlorobenzene and 2.5-3ml min $^{-1}$ for dioxin and the results compared with direct injection data in Figure 2-8.

An optimum desorption time of 4-6 minutes for the desorption of dichlorobenzene and tetrachlorobenzene and 5-7 minutes for the desorption of dioxin was observed.

Figure 2-8: Recovery of dichlorobenzene, tetrachlorobenzzene and 2,3,7,8-TCDD with different desorbing time



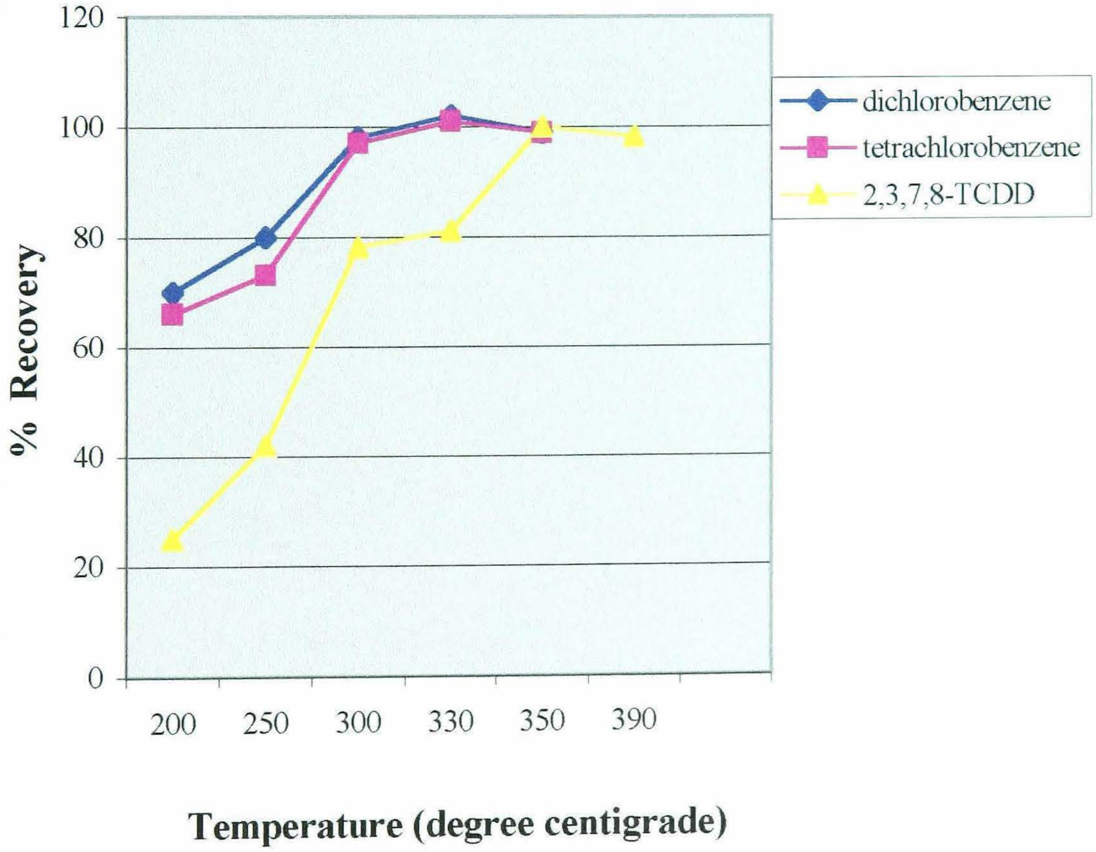
2.4.3. Determination of optimum temperature for desorption

To determine the optimum temperature for desorption a Carbotrap 300 and a Carbotrap 150 were exposed to standard gas as described in section 2.4.1.

The desorptions were performed at different temperatures with a flow rate of 2-2.5 ml min $^{-1}$ and a desorption time of 4-6 minutes for dichloro-and tetrachlorobenzene and with a flow rate 2.5-3 ml min $^{-1}$ and desorption time of 5-7 minutes for dioxin. The results are compared with direct injection data in Figure 2-9.

The optimum desorption temperatures were found to be 330 °C for dichloro and tetrachlorobenzene and 350°C for dioxin.

Figure 2-9: Recovery of dichlorobenzene, tetrachlorobenzene and 2,3,7,8-TCDD at different temperatures



2.4.4. Determination of optimum flow rate for preparation:

The optimum flow rates were determined by injection of 1μl of dichlorobenzene and tetrachlorobenzene or 5μl of dioxin solution into a glass tube 6 mm OD x 4mm ID x 11.5 cm packed with fibre glass filter at different flow rates. A Carbotrap 300, or 150, with 2 mm ID was placed into the preparation port of the thermal desorption unit. Figure 2-10 shows the percentage recovery compared with direct injection data. The optimum flow rates for dichloro and tetrachlorobenzene were found to be 13-15 ml min $^{-1}$ and for 2,3,7,8- TCDD 25 ml min $^{-1}$.

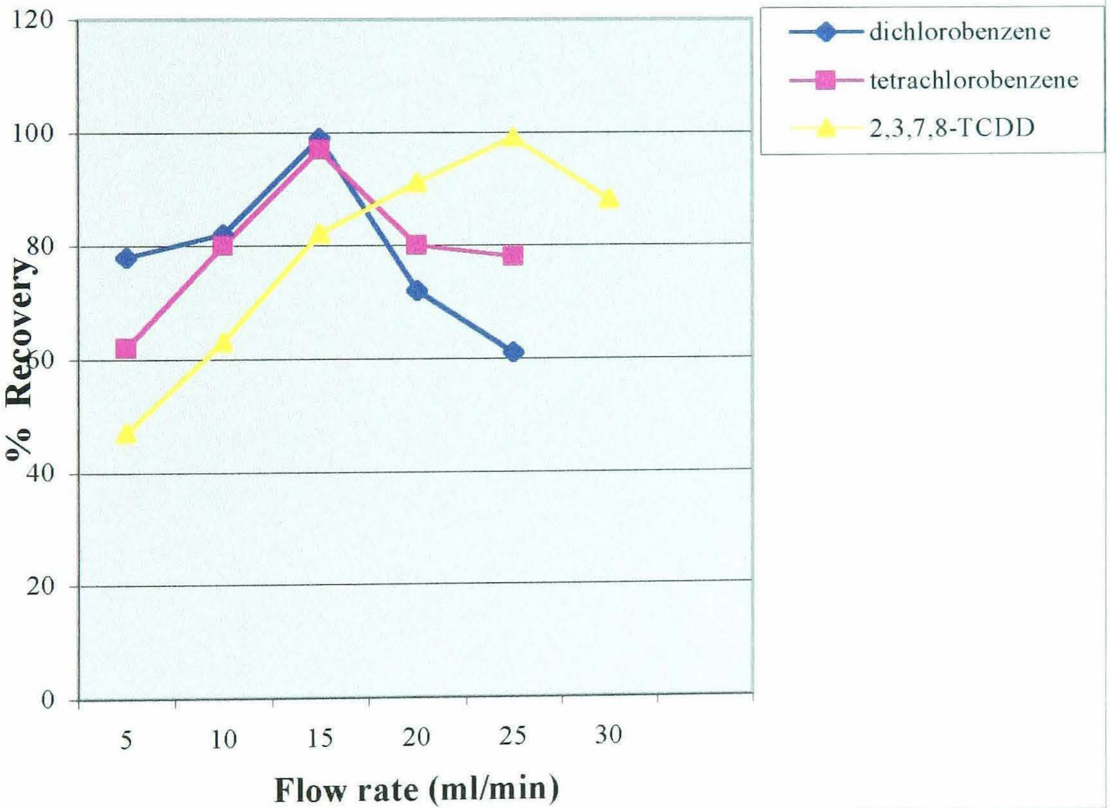


Figure 2-10: Recovery of dichlorobenzene, tetrachlorobenzene and 2,3,7,8-TCDD with different flow rates for preparation

2.4.5. Length of time for preparation:

The optimum length of time for preparation was determined by the injection of 1μl of dichlorobenzene and tetrachlorobenzene or 5 μl of dioxin solution into a glass tube with a flow rate 12-15 ml min $^{-1}$ for dichloro-and tetrachlorobenzene and a flow rate 20-

25 ml min^{-1} for 2,3,7,8-TCDD. The same procedures were used as described in section 2.4.4. Figure 2-11 shows the percentage recovery compared with direct injection data. The length of time for preparation of dichloro- and tetrachlorobenzene was found to be 14 minutes and for 2,3,7,8-TCDD to be 17 minutes.

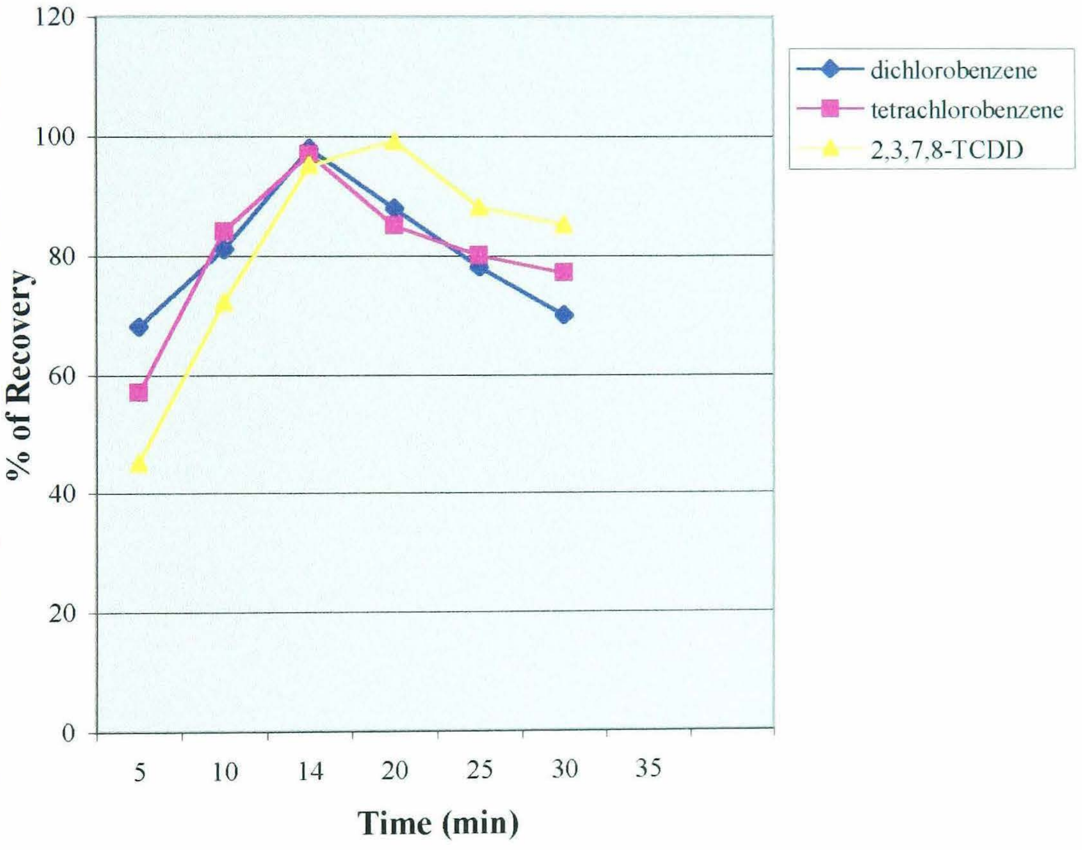


Figure2-11: Recovery of dichlorobenzene, tetrachlorobenzene and 2,3,7,8-TCDD at different time for preparation

2.4.6. Summary of optimum conditions for thermal desorption:

A summary of optimum conditions is shown in Table 2-7.

Table 2-7:The optimum conditions for thermal desorption

Sample	Group I	2,3,7,8 TCDD
Flow rate for desorption	2-2.5	2.5-3
Temperature for desorption	330	350
Length of time for desorption	4	6
Flow rate for preparation	13-15	25
Length of time for preparation	14	17
Valve temperature	220	220
Transfer line temperature	220	250

2.5. SUMMARY:

A novel method has been developed for the sampling and analysis of chlorinated aromatic hydrocarbons and 2,3,7,8-TCDD with solid sorbent and thermal desorption GC-MS. The capacity of the sorbent used, the breakthrough value and percentage recovery of the analyte from the sorbent are reported. A high resolution GC-MS was used for the analysis of 2,3,7,8-TCDD and the thermal desorption unit was also used to transfer compounds from the Carbotrap to GC-MS. A 30 metre capillary column, coated with poly (5% diphenyl, 95% dimethyl siloxane), was used to separate the chlorinated hydrocarbons. A 60 metre capillary column, coated with cyanosilicone resin, was used to separate the 2,3,7,8 TCDD. The results are presented for mixed sorbent tubes because single bed sorbent tubes are not capable of sampling for a wide range of compounds.

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CHAPTER THREE - THE RESIDUE OF COMBUSTION OF PVC AND THE EFFECT OF COPPER COMPOUNDS ON THE CONCENTRATION OF POLLUTANT IN THE COMBUSTION

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3.1 INTRODUCTION

The aim of the work described in this chapter is to determine the effects of the presence of copper, cupric oxide and copper (II) chloride on the products of combustion and pyrolysis of PVC. This has important environmental implications because, although neither PVC nor copper is listed as hazardous in the Basel Convention Annexes [1], concern has been expressed on the use of incineration to recover copper from PVC-coated cable.

The incineration of municipal refuse has become an alternative to the practice of dumping refuse in landfill sites.[2] There is a wide variety of wastes which have the potential to be used for energy production including domestic and municipal solid waste (MSW), general industrial waste from commerce and light industry and a variety of specialised industrial wastes such as clinical waste, tyres, fragmentised residues, animal litter and waste wood. The energy potential of this waste material is considerable, equivalent to some 26 million tonnes of coal per year in the UK. [3]

Incinerating refuse in plants close to urban areas offers the advantages of low transportation costs, reduction in the volume of solid wastes and the possibility of energy recovery. [4] However, the uncontrolled incineration of refuse, and combustion processes in general, emit potentially hazardous substances into the environment, especially into the atmosphere. [2, 5, 6, 7, 8, 9] Incineration units can emit dioxins, furans, acid gases and heavy metals all of which can cause damage to the environment and health. In a review of organic compounds found in incinerator effluent, Junk and Ford listed over 330 substances, including aliphatic hydrocarbons, polynuclear aromatic hydrocarbons, substituted benzene, carbonyl compounds and sulphur-and nitrogen-containing compounds [10]. Jay et. al. have also identified 250 individual organic compounds at concentrations above 50 ng/m^3 in the emission from waste incineration plants. [11]

Since 1977, when Olie et al [12] discovered chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans in the effluent of a municipal incinerator in The Netherlands, attention has been focused on these toxic compounds. Chlorinated dioxins have since been found in fly ash from incinerators located in Canada, Japan, Switzerland, France, Norway and the USA. These compounds are toxic and the toxicology of dioxin is discussed in appendix A.

It is well known that during incineration of chlorinated plastic, hydrochloric acid (HCl) is a major toxic emission, accounting for more than one third of HCl production by incineration [13, 14, 15]. Plastic waste can originate from a multitude of sources including the distribution industries representing 21.79 % of all plastic waste and municipal solid waste which accounts for 60.4%. [16]

Polyvinyl chloride (PVC) has played a key role in the development of the plastics industry over the past 40 years and continues to be a polymer of major importance. PVC overwhelmingly dominates the production of chlorinated plastics. Common uses for PVC are in the construction and plumbing industries and in some food, shampoo, and household product containers.

Plastic has become an increasing environmental problem in many industrialised countries. Concern over the volume being created has led to a number of governments introducing new legislation for its recovery as a resource. In western Europe 6-10 % of municipal waste is composed of plastics 9.3 million tons in 1992, of which PVC is 195300 tons. [17]

3.1.1 Behaviour of HCl in the atmosphere:

The behaviour of HCl in the atmosphere is different from that of sulphur and nitrogen oxides because of its high solubility and reactivity which affect the deposition pattern of the gas, and make it a locally significant pollutant even though the total amount emitted may be small. HCl is a highly reactive gas, and after release and dispersal into the atmosphere, it is quickly removed by adsorption onto surfaces such as soil, water or vegetation as soon as it comes into contact with them. This process is known as dry deposition and is an extremely effective method of removal of HCl from the atmosphere. HCl is also a very soluble gas, and if cloud or rain is present at the time of emission, it will dissolve in these. It will then be removed by the process of wet deposition. For example, HCl dissolved in cloud water reaches the ground when precipitation occurs, or when mists or low cloud come into contact with the land (rainout). Alternatively, HCl may dissolve in rain as it falls to ground (washout) and this also is a very effective removal process for HCl. Measurements around a large coal fired power station in the USA suggest that all of the chloride emitted is deposited within a radius of 15 km during rain.

3.1.2 Polymer degradation:

Polymer degradation has been known since the earliest times [18, 19] and there are several everyday examples such as the degradation of cellulose in wood, rubber in car tyres and the cracking and yellowing of paint films. The degradation and oxidation processes of natural polymers are however complicated. With the advent of modern synthetic thermoplastics many new problems have arisen, each varying in type and complexity. Thus, at high temperatures whilst polymethylmethacrylate will depolymerise to give almost 100 % monomer, PVC will degrade rapidly by an unzipping mechanism to give coloured unsaturated polymer materials together with hydrochloric acid.

The types of degradation processes found in polymers are:

1) Thermal degradation: this occurs during processing or use at elevated temperatures and may involve either oxidation or non-oxidative degradation.

2) Mechanical degradation: this occurs on the application of force or physical breakage. Chain scission may also occur by a mechanical route.

3) Ultrasonic degradation: the application of sound at certain frequencies may induce the polymer chains to vibrate and split.

4) Hydrolytic degradation: this occurs in polymers containing functional groups which are sensitive to the effects of water. Here de-esterification and the formation of products such as acids and glycols are important.

5) Chemical degradation: in this case corrosive chemicals or gases, e.g. ozone, may attack the basic structural functionalities in the polymers causing chain scission and oxidation.

6) Biological degradation: this is specific to only a few polymers which contain functional groups that are attacked by microorganisms.

7) Radiation degradation: on exposure to sunlight or high energy radiation, either the polymer itself, or impurities in the polymer, will absorb the radiation and induce reactions resulting in a loss of properties. In the case of high energy radiation the polymer chains will split directly.

3.1.3 Thermal degradation of PVC:

It is well known that thermal degradation of polyvinyl chloride evolves HCl and that the dehyrochlorination proceeds along the polymer chain resulting in the formation of a conjugated polyene which is responsible for the dark colour of the degraded polymer. The initial reaction is believed to be the elimination of a chlorine atom adjacent to a carbon-carbon double bond or at a tertiary C-Cl bond which is weaker than a secondary C-Cl site [18, 19, 20, 21, 22, 23].

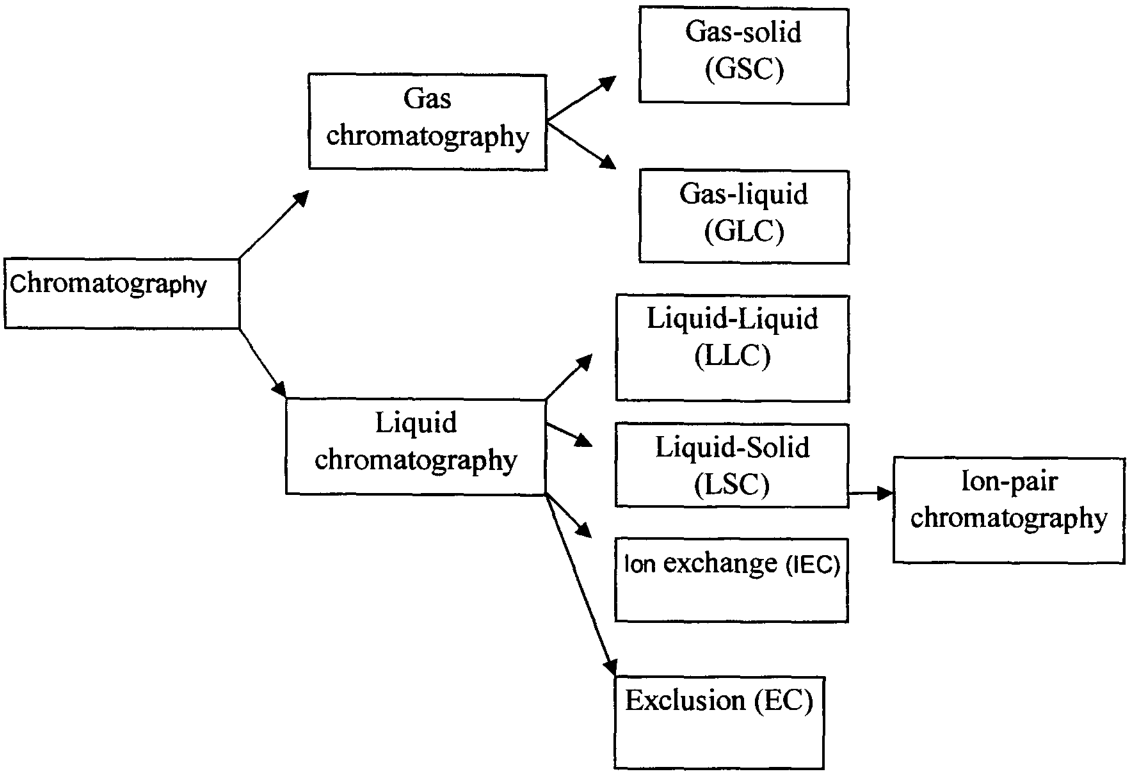
3.1.4 Chromatography:

Chromatographic techniques have been used extensively in this work to identify the decomposition products of PVC.

The term "chromatography" is the general name for a wide range of physico-chemical separation processes in which the components to be separated are distributed between a stationary and a mobile phase. Figure 3-1 shows a classification of the various types of chromatography where the stationary phase can be liquid or solid. [24, 25, 26, 27]

A sample introduced into a mobile phase is carried along through a column containing a distributed stationary phase. Species in the sample undergo repeated interactions with the mobile phase and the stationary phase. When both phases are properly chosen, the sample components are gradually separated into bands in the mobile phase.

Figure 3-1: A classification of various types of chromatography

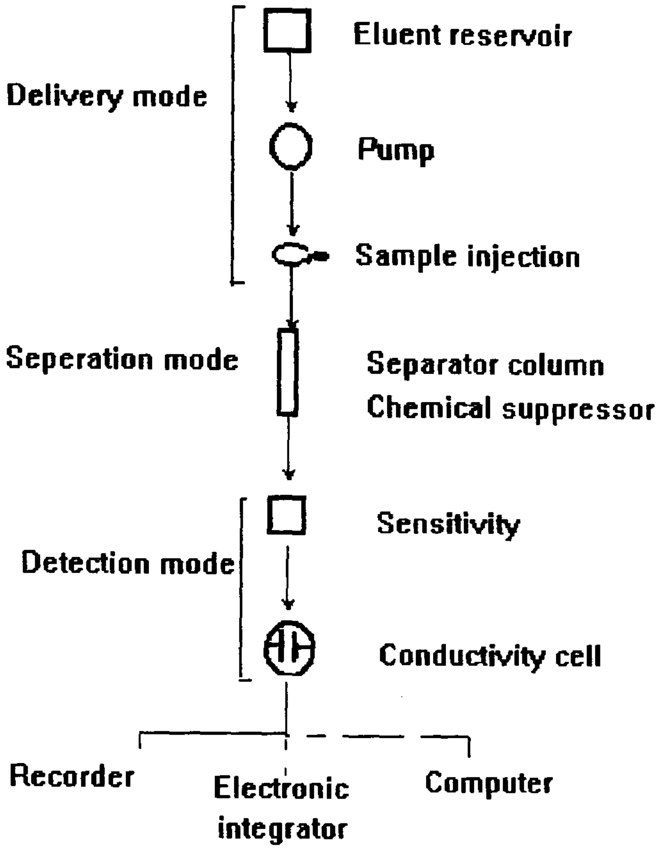


The separation column is the heart of the chromatograph. It provides versatility in the types of analyses that can be performed. This versatility, due to the wide choice of material for the stationary phase, means that molecules that differ only slightly in their physical and chemical properties can be separated.

3.1.4.1 Ion-chromatography:

After the introduction of high pressure or high performance liquid chromatography (HPLC) in 1965, ion-chromatography was introduced in 1975 and within a short space of time has developed into an independent analytical technique which today is used to determine inorganic or organic ions. The combination of ion exchange columns and conductivity detection continues to represent the most important type of ion chromatography. A typical flow scheme for the two-column chromatography method is shown in Figure 3-2.

Figure 3-2: A typical ion chromatography flow scheme for anion analysis



3.1.4.2 Ion exchange as a separation mechanism:

The vast majority of ion chromatographic separations occur by ion exchange on stationary phases with charged functional groups. The corresponding counter ions are located in the vicinity of the functional groups and can be exchanged with other ions of the same charge in the mobile phase. For every ion, the exchange process is characterised by a corresponding ion exchange equilibrium, which determines the distribution between the mobile and stationary phase; for example, in the case of an anion A^- and an eluent anion E^-.

$$E^{-}_{stat} + A^{-}_{mob} \longleftrightarrow A^{-}_{stat} + E^{-}_{mob}$$

$$K_A = \frac{[A^{-}]_{stat} \times [E^{-}]_{mob}}{[A^{-}]_{mob} \times [E^{-}]_{stat}}$$

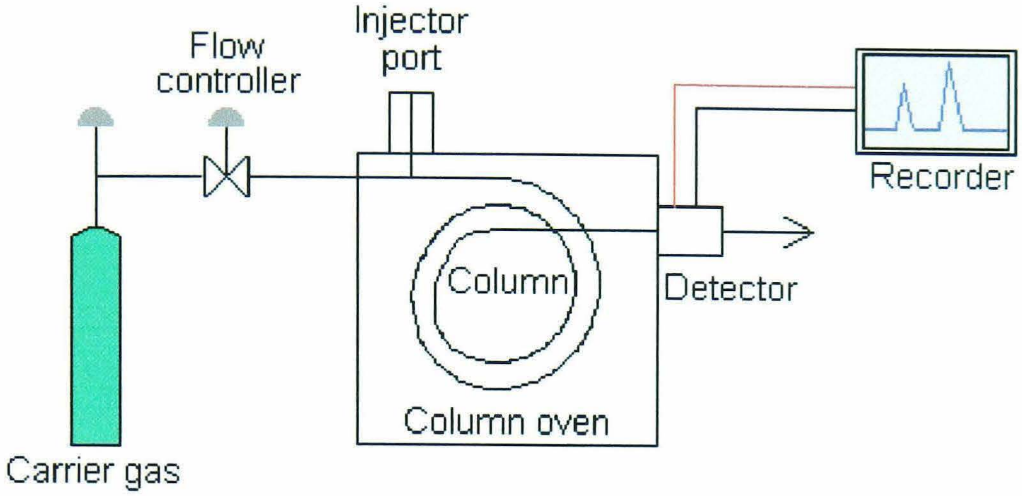
The ionic components of a sample can thus be separated on the basis of their different affinities for the stationary phase of the ion exchanger (different equilibrium constants K). The most important group of ion exchangers used consists of organic materials based on synthetic resins.

3.1.4.3 Gas chromatography:

Gas chromatography is the technique of choice for the separation of thermally stable and volatile organic and inorganic compounds. Gas liquid chromatography (GLC) accomplishes the separation by partitioning the components of a chemical mixture between a moving (mobile) gas phase and a stationary liquid phase held on a solid support. Gas-solid chromatography (GSC) uses a solid adsorbent as the stationary phase. The availability of versatile and specific detectors and the possibility of coupling the gas chromatograph to a mass spectrometer or an infrared spectrophotometer further enhance the usefulness of gas chromatography.

A gas chromatograph consists of several basic modules joined together to: (1)- provide a constant flow of carrier (mobile phase) gas, (2)- permit the introduction of sample vapours into the flowing gas steam, (3)- contain the appropriate length of stationary phase, (4)- maintain the column at the appropriate temperature (or temperature-program sequence), (5)- detect the sample components as they elute from the column, and (6)- provide a readable signal proportional in magnitude to the amount of each component. Figure 3-3 shows schematically the modules of gas chromatography.

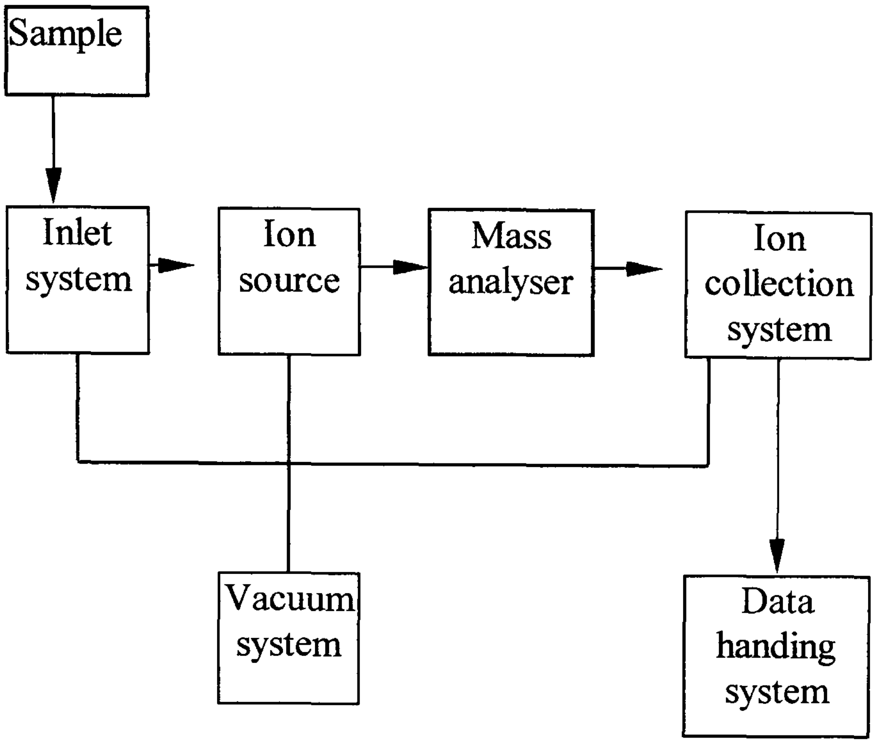
Figure 3-3: A schematic of the modules of gas chromatography



3.1.4.4 GC-MS instruments:

Two types of mass spectrometer can be used as detectors for GC-MS work: magnetic sector mass spectrometers and quadrupole mass filters. Three characteristics affect the compatibility of GC-MS units: scan speed, sensitivity, and useful dynamic range. [26, 27, 28,29,30, 31] Fast peak switching is important for qualitative and quantitative multi-ion selection analyses. In magnetic sector instruments, electromagnets exhibit a kind of inertia, called reluctance that limits the rate at which a magnet can be forced to change field strength. This phenomenon limits scan rates to 0.1 sec /decade (a decade is 50- 500 mass units). About 0.2 sec is required to rest the magnet between scans. Hence, the scan repetition rate for magnetic sector instruments is 3-4 Hz. Using quadrupole mass filters, a maximum scan rate of about 780 mass units per second can be reached. Somewhat faster scan rates can be achieved by increasing the ion energy concurrently with the mass scan ramp in order to maintain a time for heavier ions. The useful upper scan repetition rate is 4-8Hz. Figure 3-4 shows the components of a mass spectrometer.

Figure 3-4: Components of a mass spectrometer



3.1.5 Thermal analysis:

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of temperature. Thermal analysis techniques include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermal analysis (DTA) [24, 25, 26]. In these techniques the sample is heated at a programmed rate in the controlled environment of a furnace. Changes in selected properties of a sample are monitored by specific transducers, which generate voltage signals. The signal is then amplified and recorded. Figure 3-5 shows, schematically, a thermal analysis system.

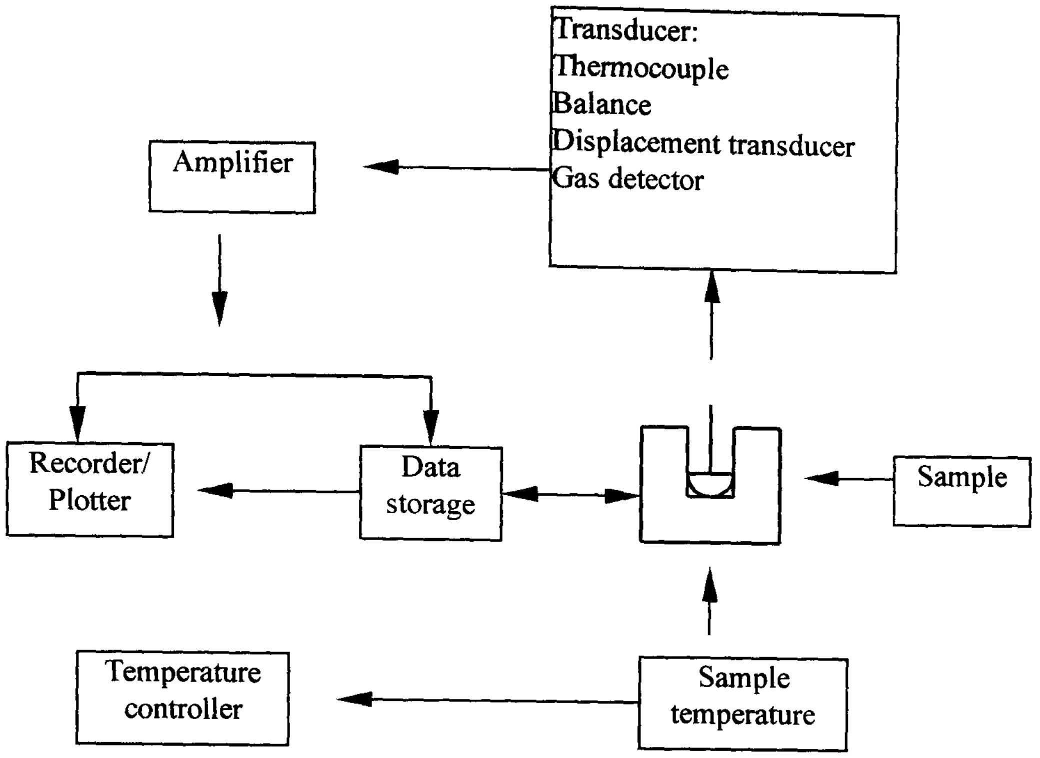


Figure 3-5: A schematic of a thermal analysis system

3.1.5.1 Thermogravimetry:

Thermogravimetry (TG) or thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. For example, TG can record directly loss in weight as a function of temperature or time (when operating under isothermal conditions) for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The rates of these thermally induced processes are often a function of the molecular structure changes resulting in changes in physical structure. Changes in weight result from physical and chemical bonds forming and breaking at elevated temperatures. These processes may result in the evolution of volatile products or the formation of reaction products that result in a change in weight of the sample. TG data are useful in characterising materials as well as in investigating the thermodynamics and kinetics of reaction and transitions that result from the application of heat to materials. In TG the weight of sample is continuously recorded as the temperature is increased.

3.1.6 Infrared spectroscopy:

Infrared spectroscopy is one of the most important analytical techniques. Infrared spectrometers have been commercially available since the 1940s. The most significant advances in infrared spectroscopy have come about with the introduction of Fourier–transform spectrometers. This type of instrument employs an interferometer and exploits the well established mathematical process of Fourier transformation. FT-IR spectroscopy has dramatically improved the quality of infrared spectra and minimised the time required to obtain data. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state can be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined by a judicious choice of sampling technique. Polymers, drugs, organic compounds, inorganic samples, biological samples, paints, oils, lubricants, fibres, catalysts, minerals, organometallics, coal, forensic samples, clays, atmospheric samples and food additives have all been studied using infrared spectroscopy.

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is obtained by passing radiation through a sample and determining what fraction of the incident radiation is adsorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of vibrations of the sample molecule [31,34, 35,36].

3.1.6.1 Representation of spectra:

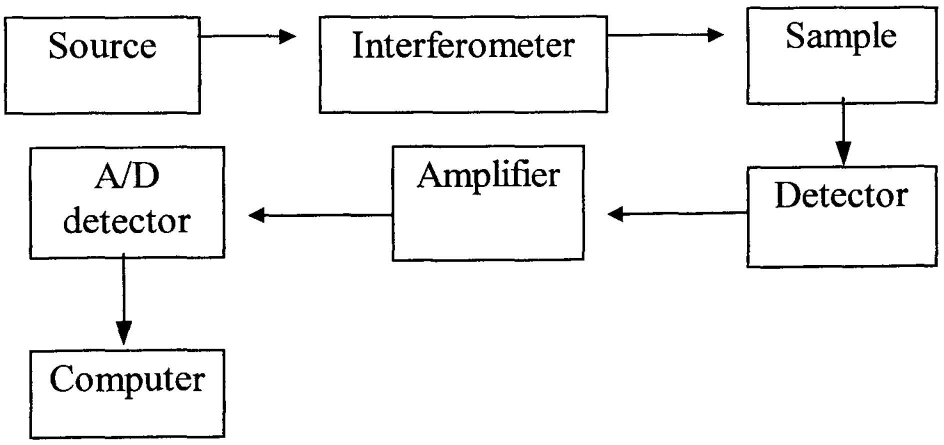
Early infrared instruments recorded percentage trasmittance over a linear wavelength range. It is now unusual to use wavelength for routine samples and inverse wavelength units are used. This is wave number scale and the units used are cm^{-1}.

The infrared spectrum can be divided into three regions: A) The far infrared below 400cm^{-1}, B) The mid infrared 400-4000 cm^{-1}, C) The near infrared 4000-14285 cm^{-1}. Most infrared applications employ the mid-infrared region but the near and far infrared regions can also provide information about certain materials including; for example, lattice vibrations.

3.1.6.2 Fourier-transform infrared spectrometers:

The basic components of a FT-IR spectrometer are shown schematically in Figure 3-6. The radiation emerging from the source is passed to the sample through an interferometer before reaching a detector. Upon amplification of the signal, in which height–frequency contributions have been eliminated by an analog-to-digital converter and then transferred to the computer for Fourier transformation to perform.

Figure 3-6: A schematic of the basic components of a FT-IR spectrometer



The most common interferometer used is a Michelson interferometer which consists of two perpendicular plane mirrors, one of which can travel in a direction perpendicular to the plane. A semi-reflecting film, the beam splitter, bisects the planes of these two mirrors. The beam splitter material has to be chosen according to the region to be examined. Materials such as germanium or iron oxide are coated on to an infrared-transparent substrate such as potassium bromide or caesium iodide to produce beam splitters for mid, or near infrared regions. Thin organic films such as polyethylene terephthalate, are used in the far infrared region

3.2 MATERIAL

The chemicals used in this study were: (A) PVC supplied by Aldrich with the following as received specification: d =1.400, inherent viscosity 0.68. (B) cupric oxide (CuO), A.R. supplied by Fisons, (C) copper chloride ($CuCl_2$) supplied by BDH limited , (D) copper powder with particle size less than 120 µm, (E) sodium carbonate anhydrous supplied by BDH limited, (F) sodium hydrogen carbonate supplied by Fisons, (G) potassium bromide (KBr) supplied by BDH limited

3.3 PVC COMBUSTION AND PYROLYSIS IN THE PRESENCE OF COPPER, COPPER (II) CHLORIDE AND CUPRIC OXIDE:

The effects of the presence of copper, copper chloride (II) and cupric oxide in the combustion and pyrolysis of PVC have been studied using the following technique:

- Thermogravimetry
- FT-IR spectroscopy
- Gas chromatography
- Thermal desorption gas chromatography mass spectroscopy

3.3.1 Thermogravimetry:

Thermal stability was determined by thermogravimetric analysis using a Stanton Redcroft STA 780 Simultaneous Thermal analyser. The sample is heated in an aluminium crucible in microfurnace. The temperature programming was from 20 to 590°C at a heating rate of 10C° per minute in air or nitrogen flowing at 35 ml per minute. The weight of sample used was about 2mg. When the polymer contained copper or a copper compound the amount of the additive in the sample was 10% of the PVC weight. To convert the results for mixture to the corresponding for pure PVC results the following formula was used:

$$C = \frac{W_1 \times \% L}{W_2}$$

C = % converted loss of weight, W_1 = PVC weight by itself (mg), W_2 = PVC weight in mixture, %L = %loss of weight in graph

3.3.1.1 Results:

Figure 3-7 shows the thermal analysis data corresponding to PVC and PVC in the presence of CuO, $CuCl_2$ and copper in an air atmosphere. It is clear that degradation occurs in 2 steps, except for PVC in the presence of $CuCl_2$ which has 3 steps. This figure shows 59 % loss of weight for PVC, 50 % loss of weight for PVC in the presence of copper, 35 % loss of weight for PVC in the presence of CuO and 7 % loss of weight for PVC in the presence of $CuCl_2$ in the first step. In the second step, loss of weight is 96 % for PVC, 74 % for PVC in presence of copper, 84 % for PVC in the presence of CuO, and 57 % for PVC in the presence of $CuCl_2$. In the third step, in the curve related PVC in the presence of $CuCl_2$, an 87 % loss of weight is shown. The results of these measurements converted to PVC decomposition are in Table 3-1.

These data shows that CuO is a good retardant for thermal degradation of PVC and that copper and $CuCl_2$ have a lesser effect.

Figure 3-8 shows thermal degradation of PVC and PVC in the presence of CuO, $CuCl_2$ and copper in a nitrogen atmosphere. This figure shows 58 % loss of weight for PVC, 53 % loss of weight for PVC in presence of copper, 52.5 % loss of weight for PVC in the presence of CuO and 7 % loss of weight for PVC in the presence of $CuCl_2$ in the first step. In the second step loss of weight is 85 % for PVC, 67 % for PVC in presence of copper, 67 % for PVC in the presence of CuO, and 53 % for PVC in the presence of $CuCl_2$. In the third step, the curve related to PVC in the presence of $CuCl_2$, a 67 % loss of weight is shown. The results of these measurements converted to PVC decomposition are in Table 3-2.

It has been reported that in the first step of thermal degradation of PVC, loss of weight is due to HCl and Cl^- formation [2o, 23]. The second step is due to the formation of polyene.

Figure 3-9 shows the degradation of CuO, $CuCl_2$. The curve for $CuCl_2$ shows a loss of weight that is related to loss of water.

Figure 3-7: TG of PVC and PVC in presence of copper, CuO, $CuCl_2$ in air

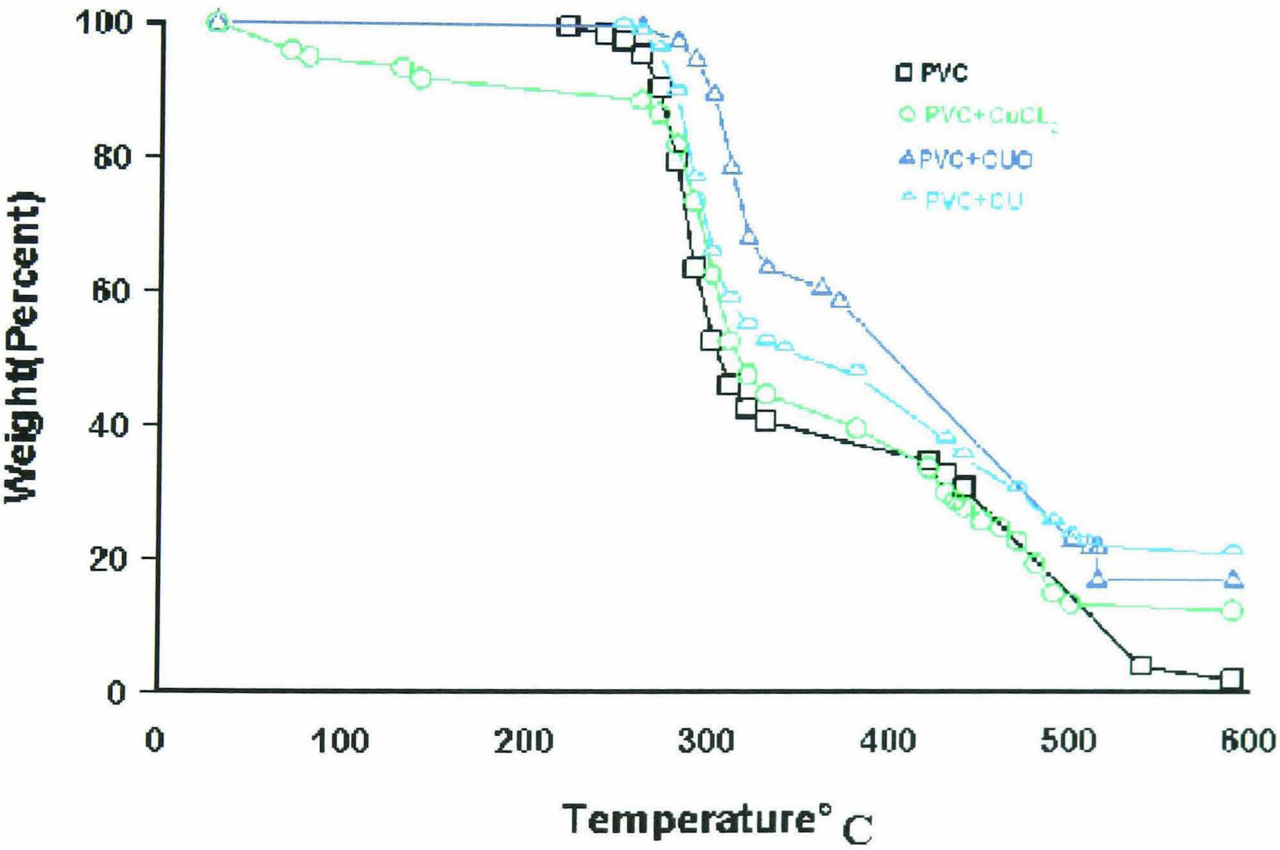


Figure 3-8: TG of PVC and PVC in presence of copper, CuO, $CuCl_2$ in nitrogen

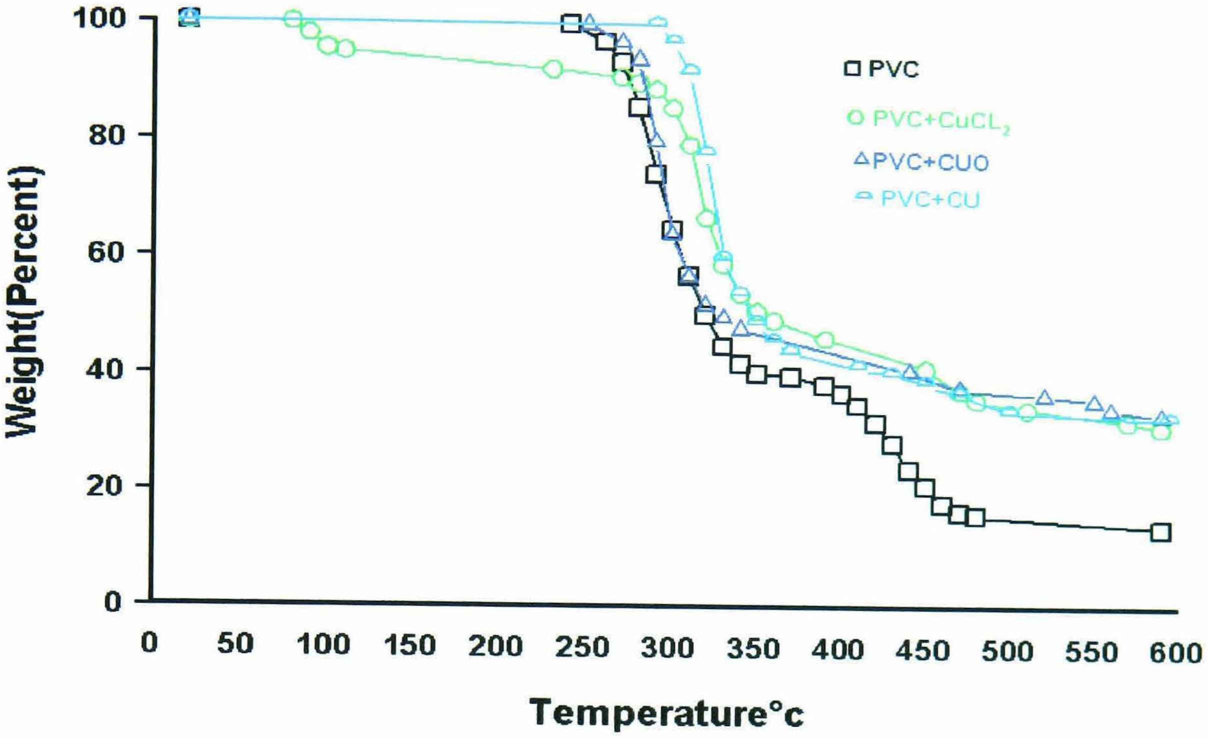


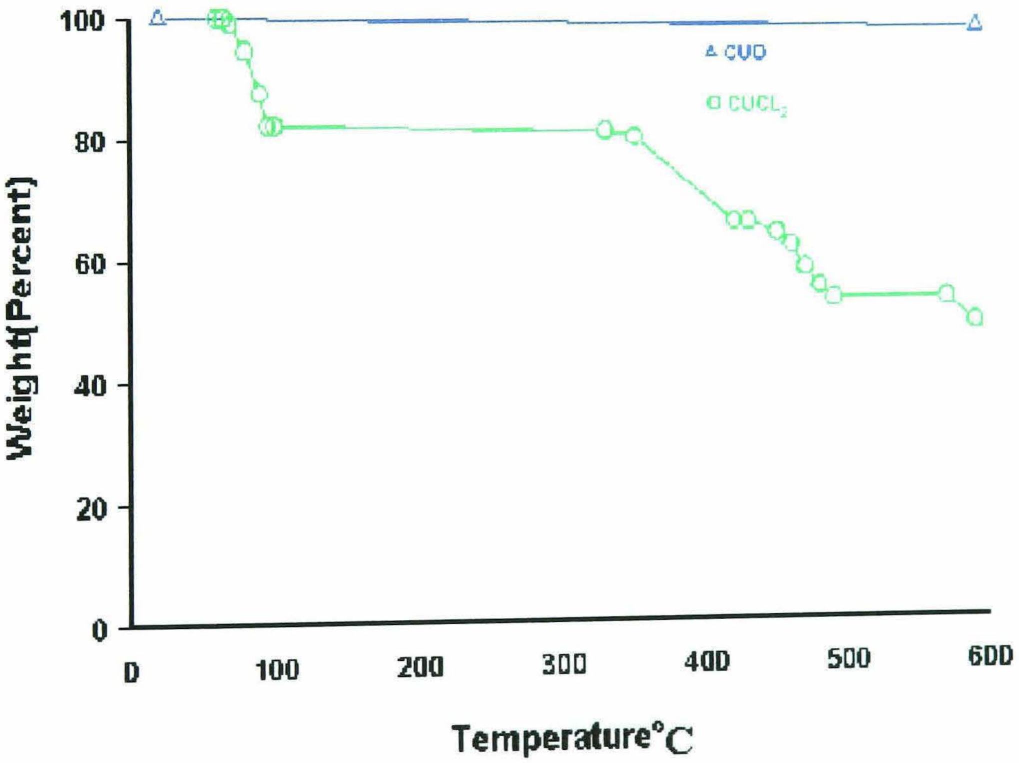
Table 3-1: The converted results for Figure 3-7:

Sample	Step 1 (%)	Step 2 (%)	Step 3 (%)
PVC 2mg	59	37	-
PVC (1.8mg)+ Copper (0.2mg)	55	27	-
PVC (1.8mg) + CuO (0.2mg)	39	55	-
PVC (2mg) + $CuCl_2$ (0.2mg)	-	56	33

Table 3-2: The converted results for Figure 3-8

Sample	Step 1 (%)	Step 2 (%)	Step 3 (%)
PVC 2mg	58	27	-
PVC (1.8mg)+ Copper (0.2mg)	59	16	-
PVC (1.8mg) + CuO (0.2mg)	58	16	-
PVC (2mg) + $CuCl_2$ (0.2mg)	-	56	24

Figure 3-9: TG of CuO and $CuCl_2$ in air



3.3.2 FT-IR spectroscopy of residual compound:

A Nicolet 550 Spectrometer was used to obtain IR spectra of the combustion and pyrolysis residues with 20 scans and resolution 8. All spectra were scanned from 500 to 4000 cm^{-1}. Copper compounds were removed from the sample by nitric acid dissolution. The residue was collected by filtration and washed with distilled water and dried. About 5% of these residues and 95% KBr were used for making discs for the FT-IR studies. After removing copper, the residue of PVC in presence of copper at 270 °C was dissolved in chloroform and a film prepared from this

3.3.2.1 PVC combustion in a furnace:

The pyrolysis or combustion of PVC and PVC in the presence of copper and copper compounds was performed in an electric furnace. The sample was mixed and put into the furnace via a gate valve as a thin layer in silica combustion boat. The reactor was a silica tube of 5cm diameter and approximately 100 cm in total length. The sample was heated from room temperature up to the temperature of first or second or third step of TG curve in a stream of 35 ml per minute air or nitrogen at heating rate 10C° per minute. The residue was collected after 0 min, 15 min, 30 min at the final temperature.

3.3.2.2 Results:

Figures 3-10, 3-11, 3-12 and 3-13 show a series of spectra corresponding to PVC at increasing temperatures and pyrolysis time under air and nitrogen atmospheres.

The bands in the region 600 -700 cm^{-1}, are assigned to C-Cl, and the bands at 3000-3100 cm^{-1} to the C-H stretching groups of PVC. The spectra clearly show that the nature of the residues depends upon both the temperature and the combustion or pyrolysis programs time. The pyrolysis time, even at 250°C, can change the shape of the peaks. At 370°C very significant modifications in the spectra are occur, in both the positions and shapes of absorption bands.

$$\mathrm{CnHmCly} \xrightarrow{\Delta} \mathrm{yHCl}$$

Figure 3-10: IR spectra of PVC after 250°C heating under nitrogen A) after 0 min. B) after 15 min, C) after 30 min

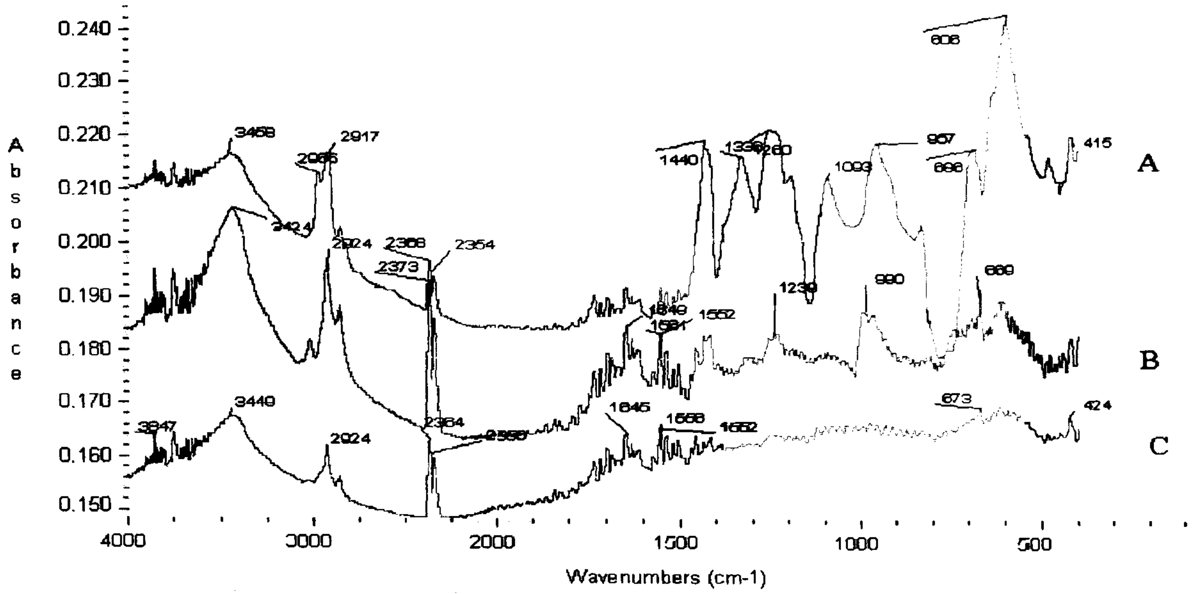


Figure 3-11: IR-spectra of PVC after 250°C heating under air A) after 0 min. B) after 15 min. C) after 30 min

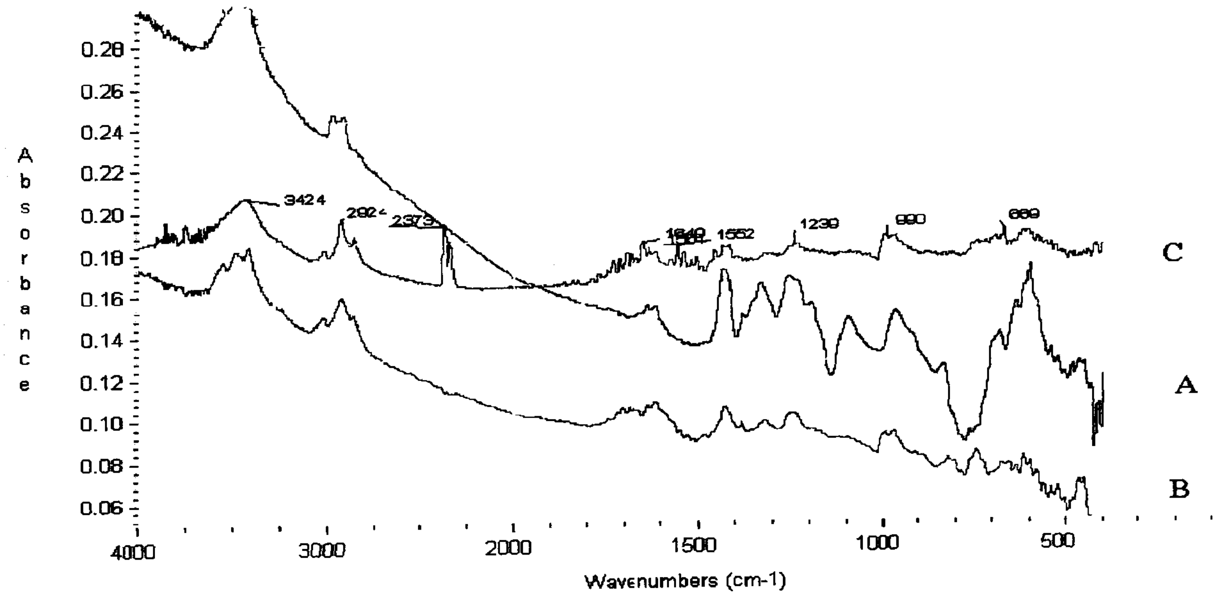


Figure 3-12: IR-spectra of PVC after 340°C heating under nitrogen A) after 0 min. B) after 15 min. C) after 30 min

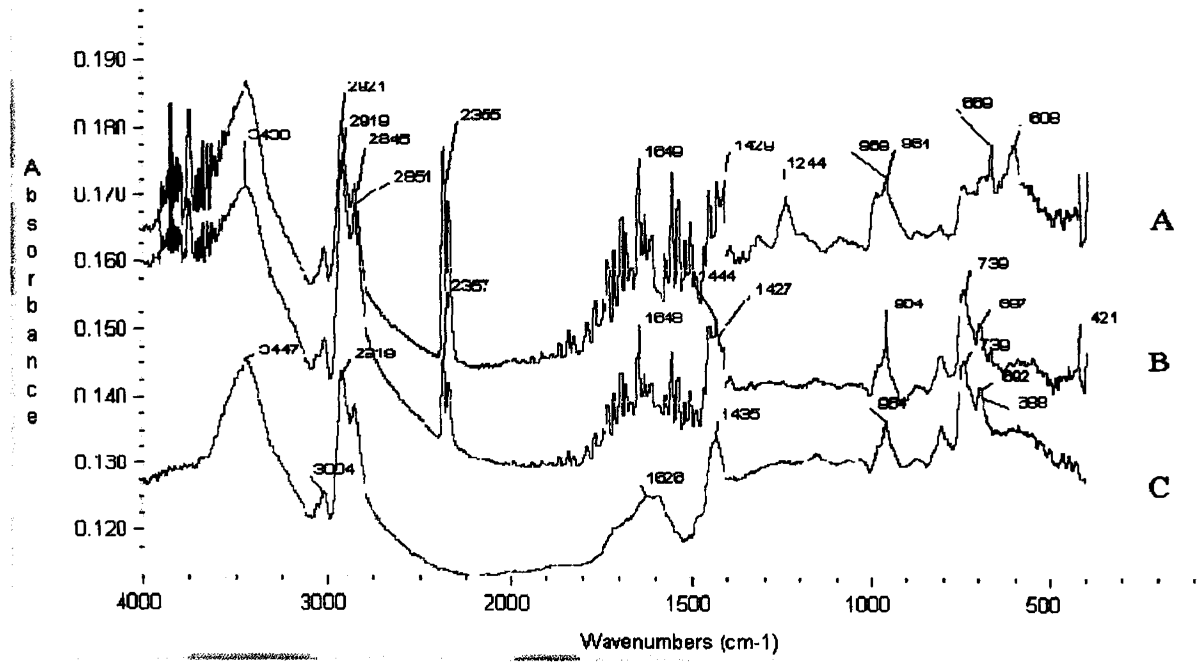
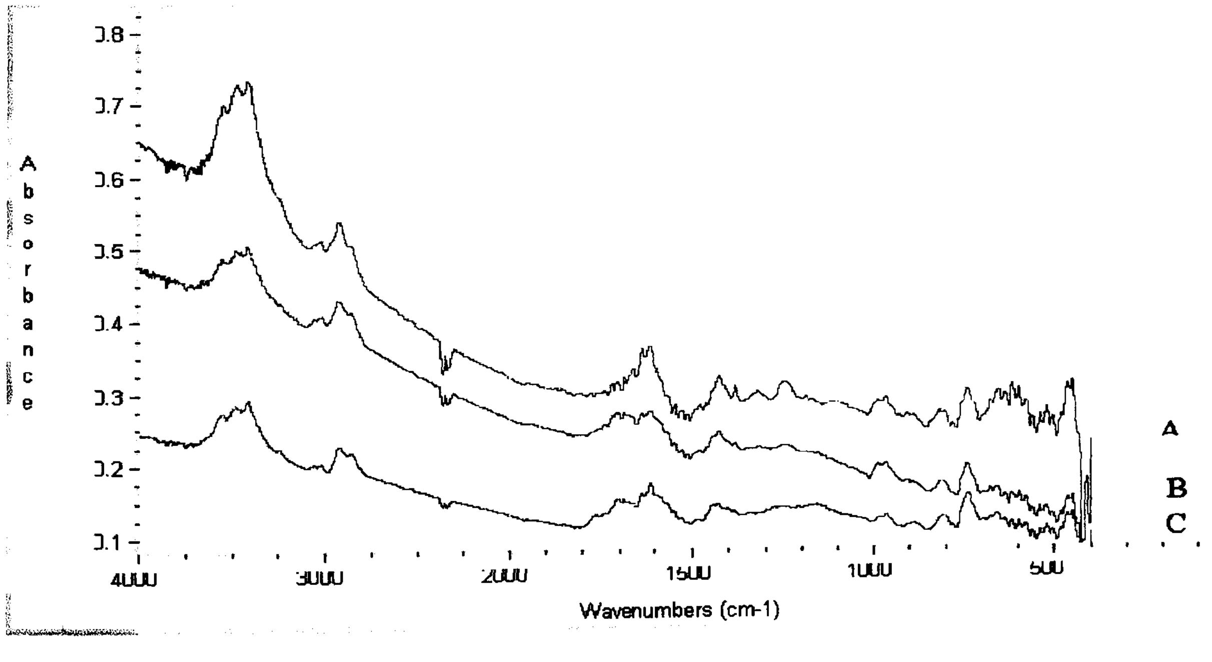


Figure 3-13: IR-spectra of PVC after 340 °C heating under air -A) after 0 min. B) after 15 min. C) after 30 min



Figures 3-14, 3-15 and 3-16 show the series of spectra for PVC heated in the presence of $CuCl_2$ at different temperatures and pyrolysis times. Figure 3-14 shows that at 100°C there is no difference in the spectra with pyrolysis time and are the same as those obtained at room temperature. Figure 3-15 and Figure 3-16 show major differences in the shape of peaks for samples heated to 340°C and 380°C.

Several workers have reported that strong electrophilic metal chlorides, such as $ZnCl_2$, $FeCl_3$ and $AlCl_3$, can considerably accelerate the dehyrochlorination of PVC [37, 38, 39, 40, 41].

Figures 3-17, 3-18, 3-19 and 3-20 show the series of spectra corresponding to PVC in the presence of CuO at increasing temperatures and pyrolysis time under air and nitrogen atmosphere.

Figure 3-14: IR-spectra of PVC in the presence of $CuCl_2$ after 100°C heating A) after 0 min. B) after 15 min. C) after 30 min.

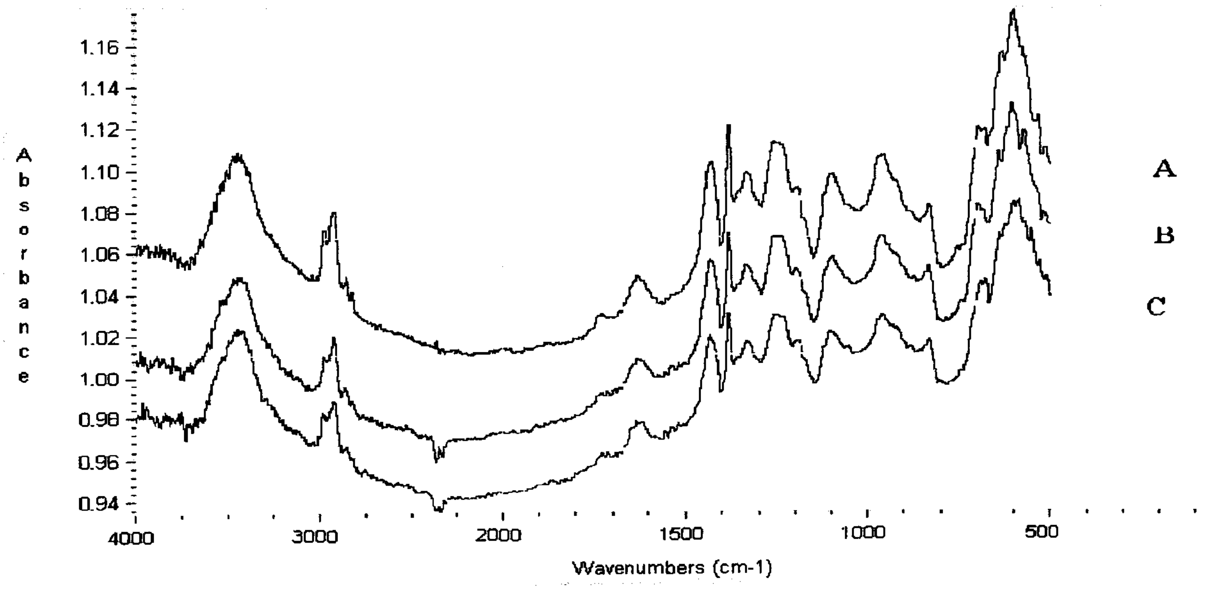


Figure 3-15: IR-spectra of PVC in the presence of $CuCl_2$ after 380°C heating under nitrogen -A) after 0 min. B) after 15 min. C) after 30 min.

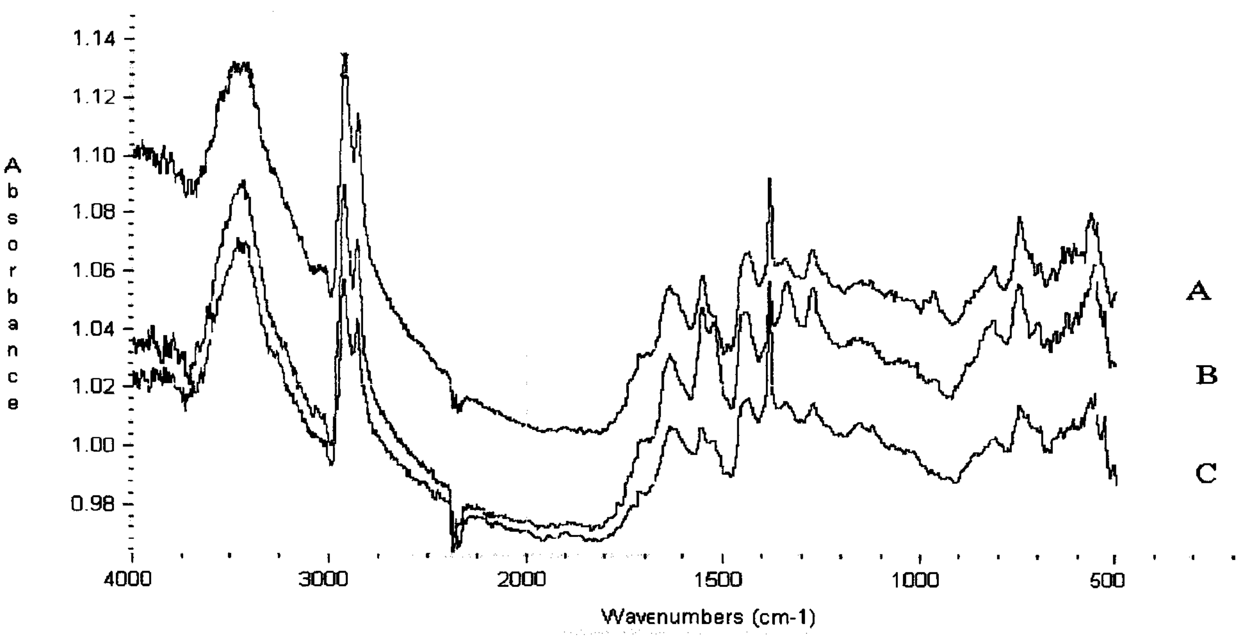
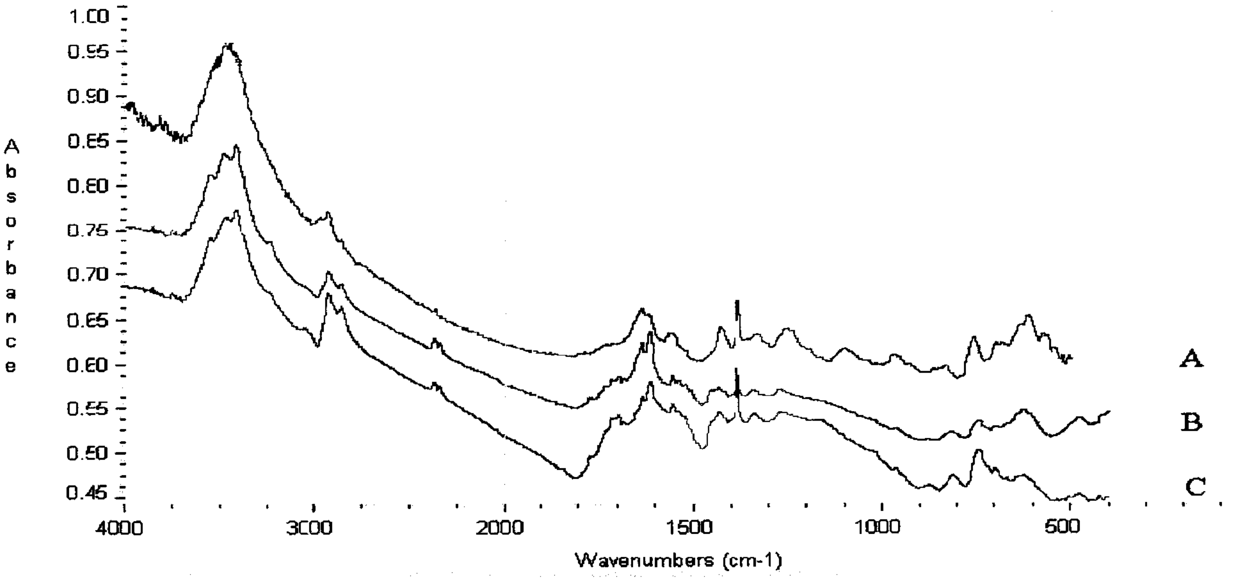


Figure 3-16: IR-spectra of PVC in the presence of $CuCl_2$ after 340 °C heating in air - A) after 0 min. B) after 15 min. C) after 30 min.



The degradation can be followed by the change in the position and shapes of the absorption bands and the disappearance of some peaks with pyrolysis time.

Figures 3-21, 3-22, 3-23 and 3-24 show the series of spectra of PVC in the presence of copper at different times and temperatures under nitrogen and air atmospheres. The spectra show the changes in the positions and shapes of absorption bands and particularly those associated C-Cl and C-H vibrations.

Figure 3-25 shows a series spectra corresponding PVC at room temperature and PVC in presence of copper, CuO, $CuCl_2$ after heating the mixtures to 600 °C. The data show that all bands related to PVC have disappeared at 600°C.

Figure 3-17: IR-spectra of PVC in the presence of CuO after 280°C heating in nitrogen - A) after 0 min. B) after 15 min. C) after 30 min.

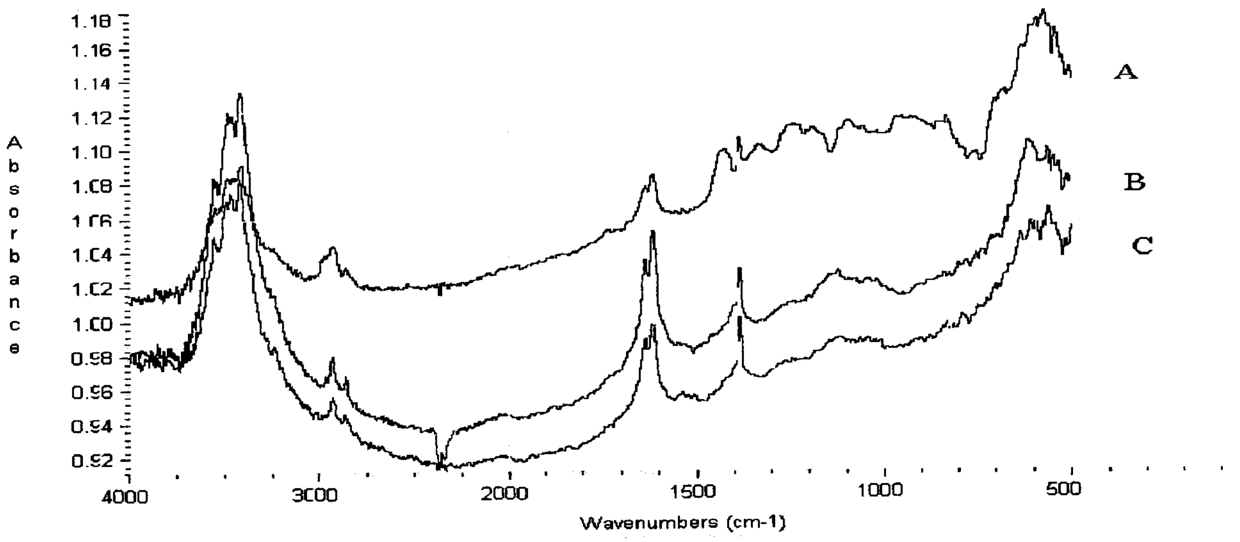


Figure 3-18: IR-spectra of PVC in the presence of CuO after 290°C heating under air -A) after 0 min. B) after 15 min. C) after 30 min.

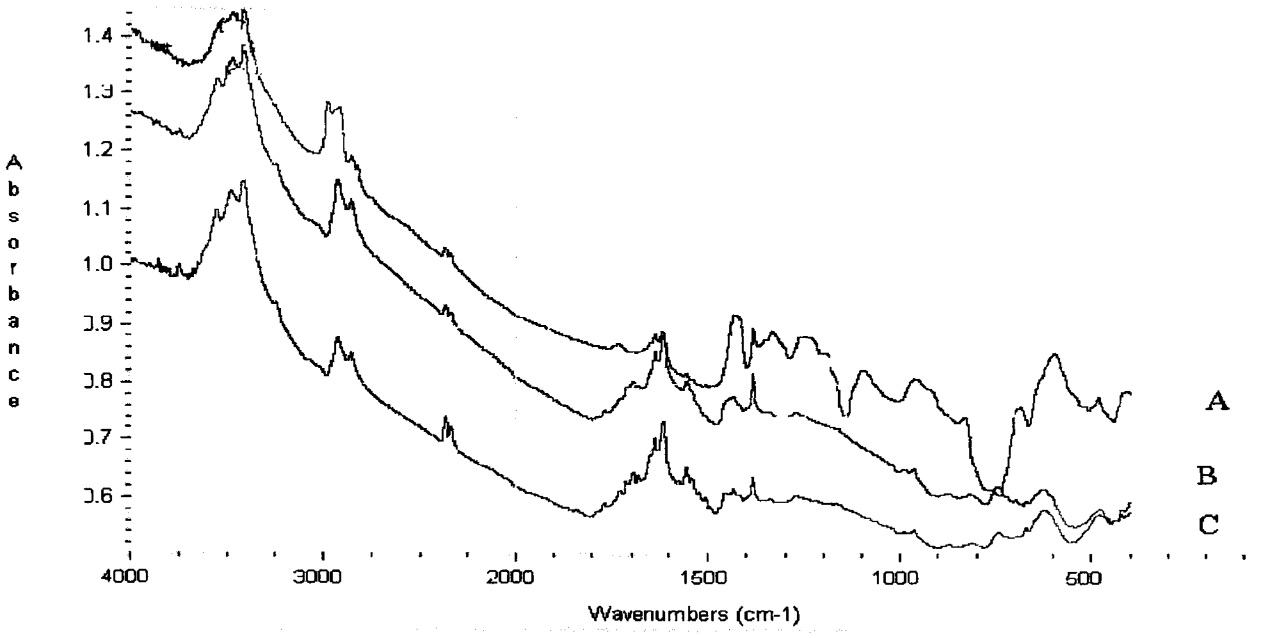


Figure 3-19: IR spectra of PVC in the presence of CuO after 370 °C heating under nitrogen -A) after 0 min. B) after 15 min. C) after 30 min.

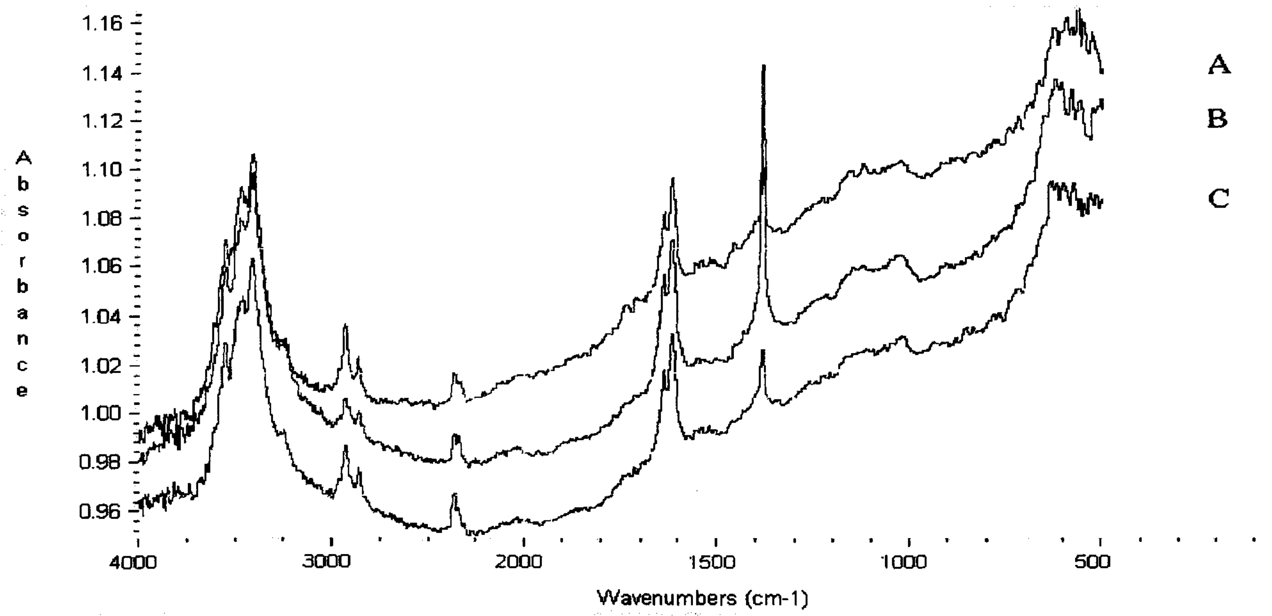


Figure 3-20: IR-spectra of Pvc in the presence of CuO after 370°C heating under air - A) ater 0 min. B) after 15 min. C) after 30 min.

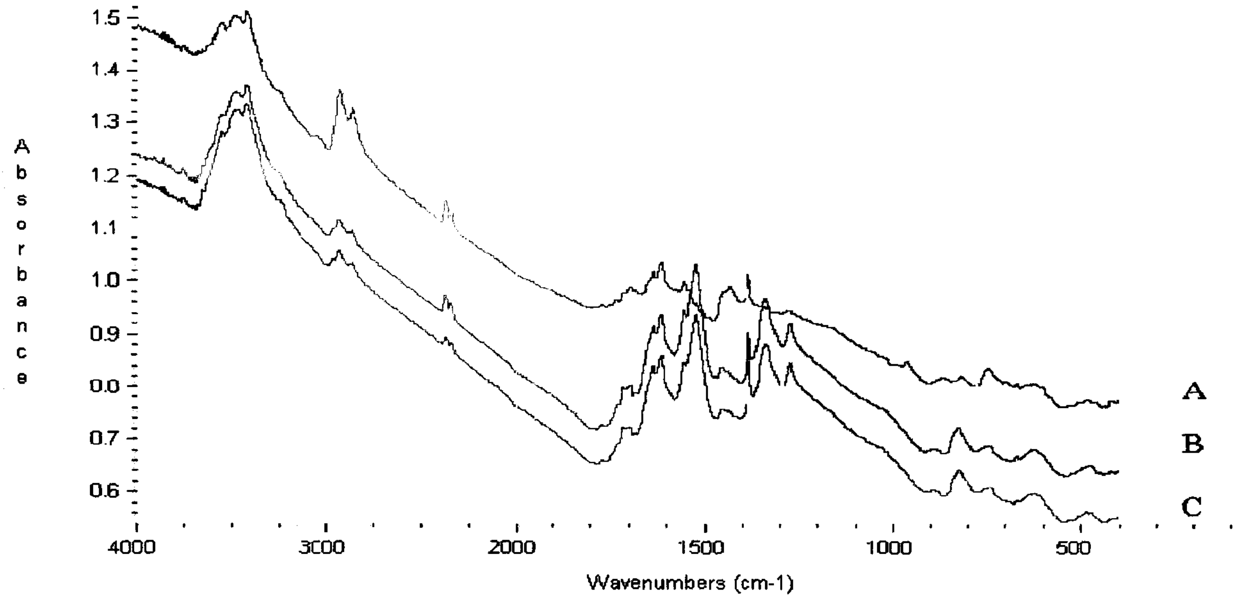


Figure 3-21: IR spectra PVC in the presence of copper after 270°C heating under nitrogen - A) after 0 min. B) after 15 min. C) after 30 min.

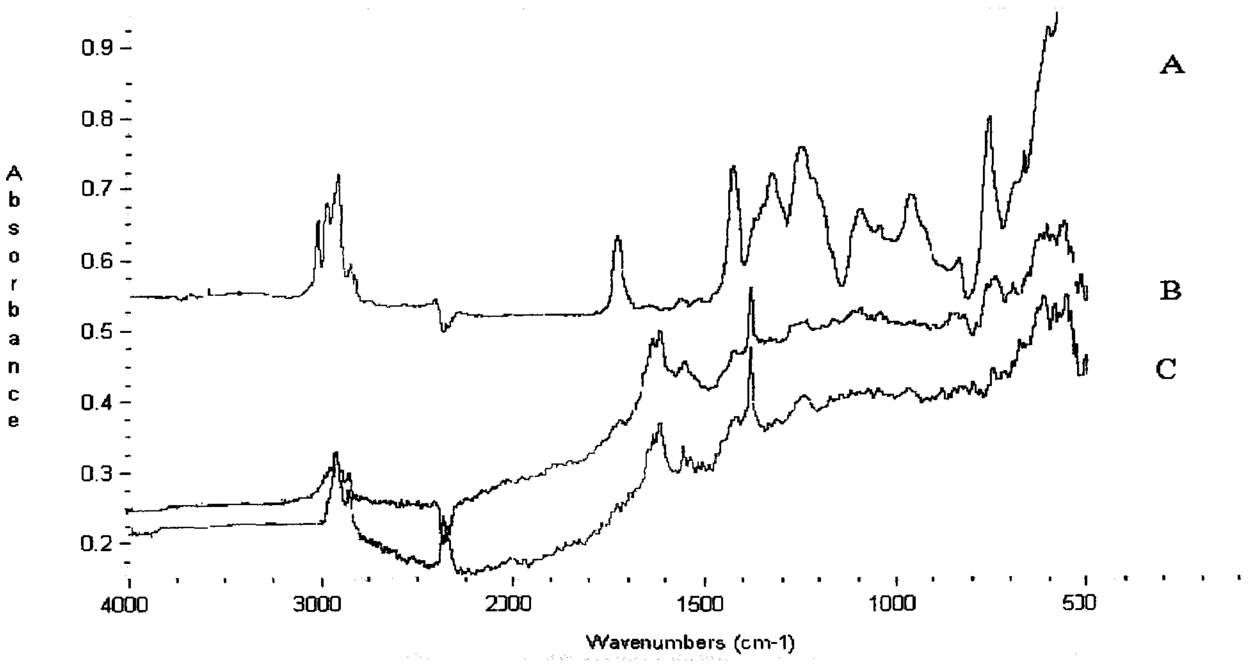


Figure 3-22: IR spectra of PVC in the presence of copper after 270 °C heating under air -A) after 0 min. B) after 15 min. C) after 30 min.

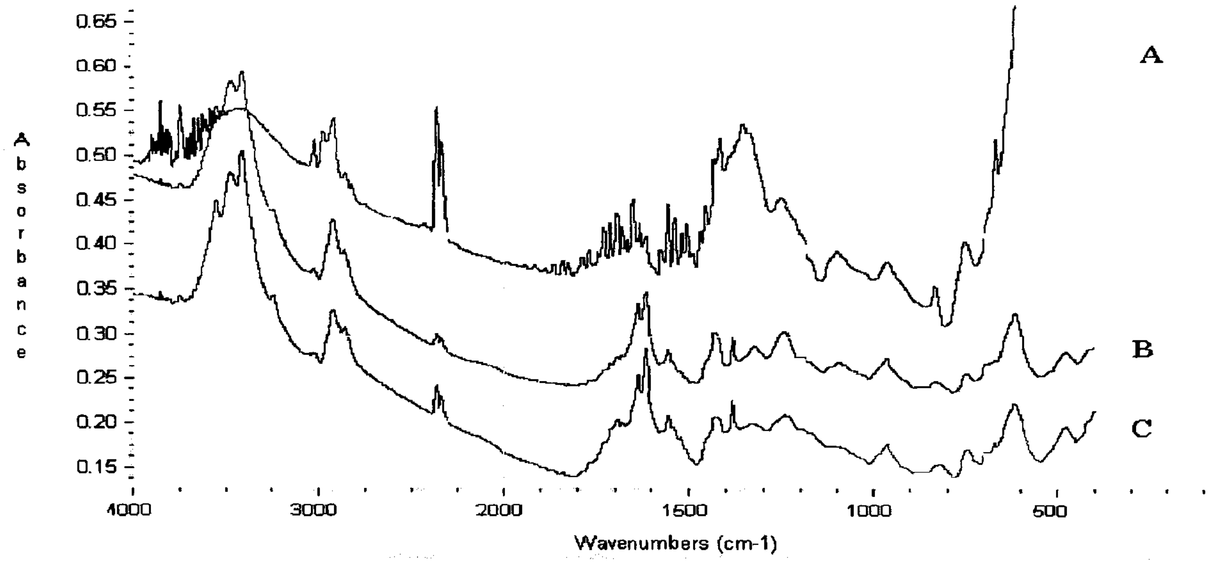


Figure 3-23: IR spectra of PVC in the presence of copper after 380 °C heating under nitrogen - A) after 0 min. B) after 15 min. C) after 30 min.

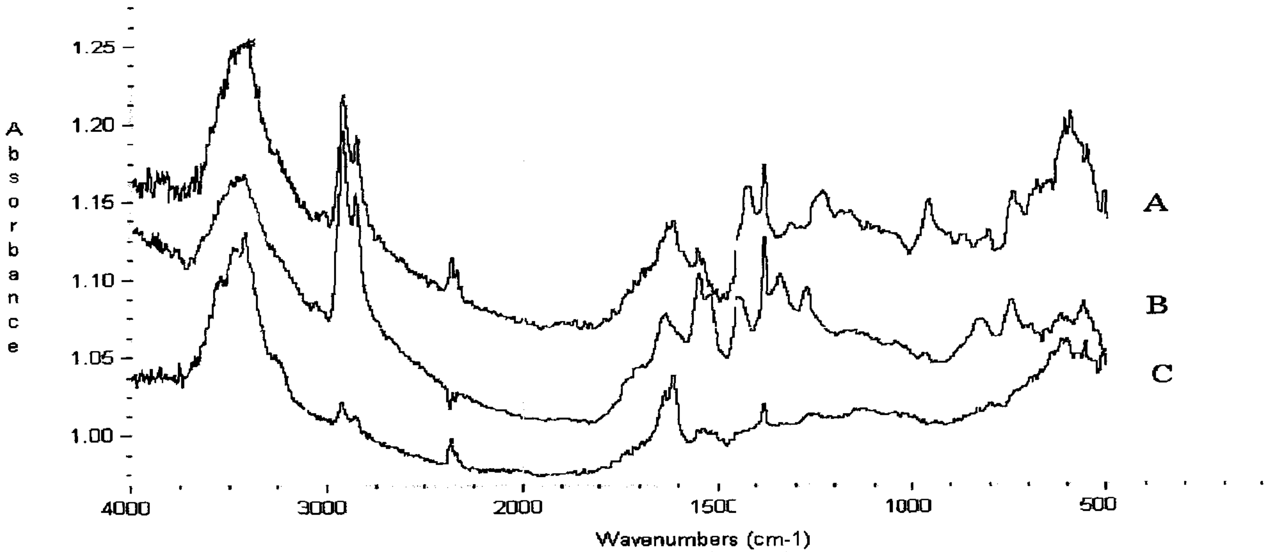


Figure 3-24: IR spectra of PVC in the presence of copper after 340 °C heating under air - A) after 0 min. B) after 15 min. C) after 30 min.

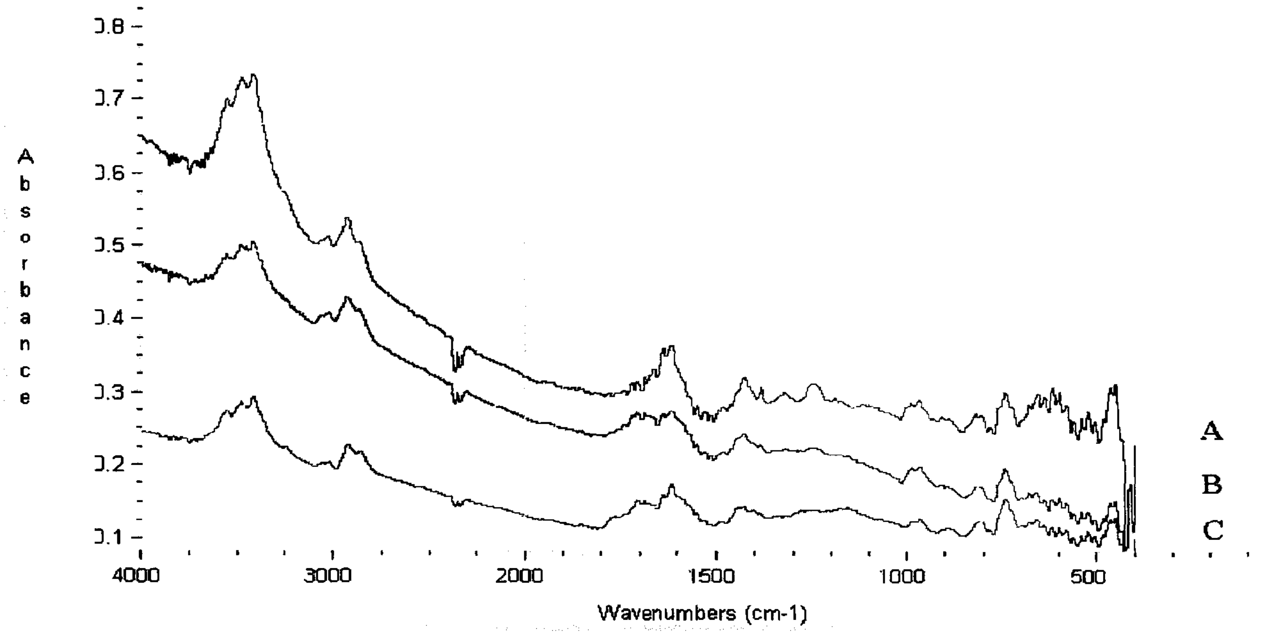
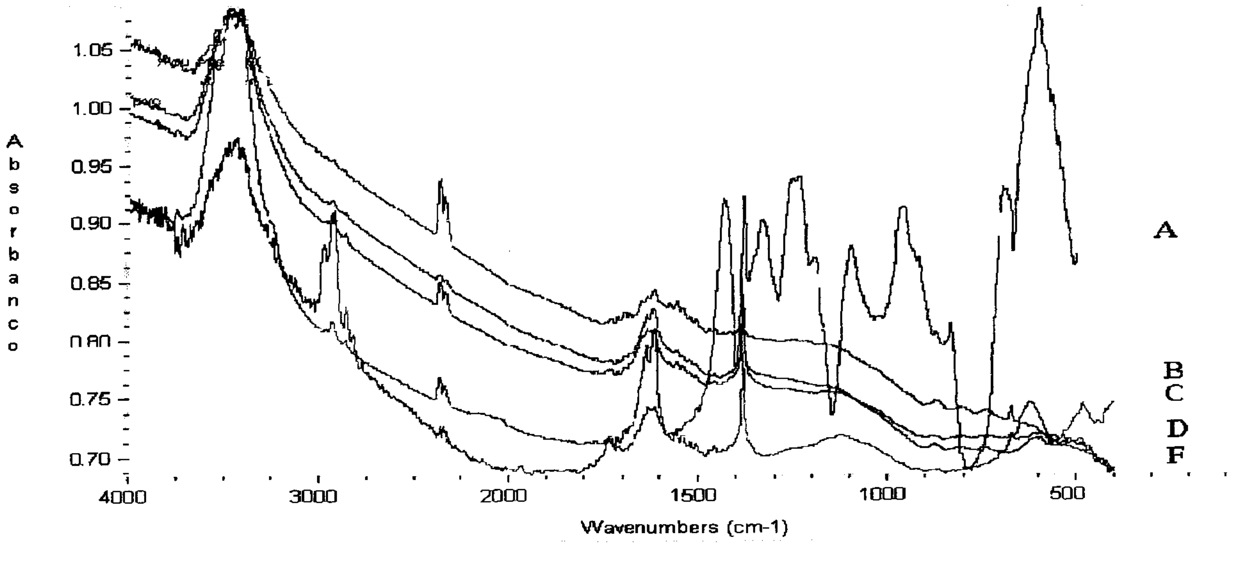


Figure 3-25: IR-spectra of A) PVC ,B) PVC in the presence of CuO, C)PVC in the presence of copper , D) PVC in the presence of $CuCl_2$



3.3.3 Sampling and analysis of hydrogen chloride:

In this study, 2mg samples of pure PVC, or a mixture of PVC with copper, cupric oxide or copper (II) chloride were heated in an electric furnace. The samples were placed as a thin layer in a silica combustion boat and fed to the furnace via a gate. Temperature programming started from room temperature and increased to the final temperature at a rate of 10 C° per minute under air or nitrogen. The weight of the copper compounds used was 10% of the PVC weight. For the determination of HCl and Cl$^-$ the sampling time was either the same as the temperature programming time or up to a further 15 and 30 minutes extra. Figure 3-26 shows sampling method used for HCl and Cl$^-$.

HCl is very water soluble and usually water was used as absorbent in the sampling bubbler or impinger. The efficiency of the collection of chloride in water is, however, very low and for this reason the adsorption solution used in this study for Cl$^-$ and HCl collection had the same composition as the chromatographic eluent used subsequently in the analyse that is 0.00075M $NaHCO_3$ + 0.0022M Na_2CO_3.

HCl and chloride in the gas were trapped by drawing the gases through a bubbler containing 30 ml of the absorption solution and then through a fritted bubbler containing 30 ml of absorption solution. The flow rate was 0.75 litre per minute for the duration of sampling.. The solutions were the analysed for chlorine and HCl by ion chromatography.

A Dionex Ion Chromatograph Model 2010I was used for the analysis of HCl and chloride. The configuration used is as follows:

Eluent: 0.00075M $NaHCO_3$ + 0.0022M Na_2CO_3

Reagent for suppresor: 0.025N H_2SO_4

Column: HPIC-AS4A and guard AG4A

Pressure in main regulator: 100psi

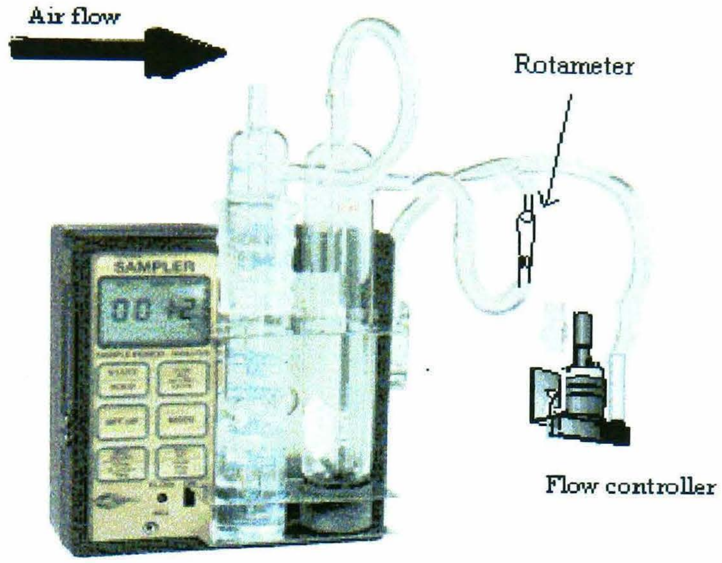
Pressure in suppressor regulator: 5psi

Suppressor flow: ~2.5 ml/min

Pressure: 620 psi

Detector: Conductivity

Figure 3-26: Sampling line for determination of HCl and Cl⁻



All samples were filtered with an acid-free filter paper to separate particulates and oily compounds. Care was taken to ensure that the analyte samples did not contain interfering anions.

The concentration of Cl^- or HCl in some samples was very high, therefore 0.5 or 1ml of sample was diluted to 50 or 100 ml with distilled water.

3.3.3.1 Results:

Table 3-3 shows the concentration of Cl^- plus HCl in gas emissions from samples heated in air at different temperatures and sampling times. The results show the concentration of Cl^- increases with increasing temperature and sampling time. The concentration of Cl^- in gas emissions from a mixture of PVC and CuO was less than other mixtures with PVC while the emissions from PVC with $CuCl_2$ were the highest. Table 3-4 shows the concentrations of Cl^- plus HCl in gas emissions from samples heated in nitrogen at different temperatures with different sampling times. The results show that the concentration of Cl^- in the gas emissions of PVC and a mixture of PVC and $CuCl_2$ in air is more than that in nitrogen. For mixtures of PVC and CuO and PVC and copper in air the concentrations of HCl plus Cl^- are less than that in nitrogen.

Table 3-3: Concentration of Cl^- plus HCl in gas emission from the combustion of sample in air.

Sample	Temperature °C	Conc. on reaching final temp. ppm	Conc. after 15 min at final temp. ppm	Conc. after 30 min at final temp. ppm
PVC	250	190	2250	5560
PVC	340	4500	9900	10000
PVC	600	-	10950	-
PVC +$CuCl_2$	100	45	96	112
PVC + $CuCl_2$	340	7825	9700	10750
PVC + $CuCl_2$	600	-	11825	-
PVC + CuO	290	1175	5000	6000
PVC + CuO	370	3850	5700	5800
PVC + CuO	600	-	6500	-
PVC + Cu	270	900	4550	7500
PVC + Cu	380	5100	6925	7700
PVC + Cu	600	-	8250	-

Table 3-4: Concentration of Cl^- plus HCl in gas emission from the combustion of sample in nitrogen

Sample	Temperature °C	Conc. on reaching final temp. ppm	Conc. after 15 min at final temp. ppm	Conc. after 30 min at final temp. ppm
PVC	250	180	2050	5075
PVC	340	4400	9700	9750
PVC	600	-	10600	-
PVC + $CuCl_2$	100	43	92	105
PVC + $CuCl_2$	380	7950	9275	9000
PVC + $CuCl_2$	600	-	9900	-
PVC + CuO	280	1225	6500	8125
PVC + CuO	370	5475	8100	8250
PVC + CuO	600	-	8500	-
PVC + Cu	270	1000	5275	8425
PVC + Cu	380	5825	7900	8500
PVC + Cu	600	-	9045	-

3.3.4 Sampling and analysis of short chain hydrocarbons:

For sampling short chain hydrocarbons, the flue gas stream was passed through a cooling trap and then drawn through a 37mm fibre glass filter and collected in a Tedlar sampling bag using a small personal pump. The sampling flow was controlled to a constant 30 ml/min. The short chain linear gases were determined by gas chromatography using a Pye Unicam PU4500. The GC temperature programme was 4 minutes at 50°C then rising at 16 C° per minute to 200 °C, where the temperature was held for 10 minutes. A one metre packed column of 60 -80 mesh Chromosorb 102 and flame ionisation detector at 200°C were used. The carrier gas was nitrogen with a head pressure of 0.55kg/cm^2.

3.3.4.1 Quantitative analysis of samples:

Qualitative analysis of the components in the samples was performed by ion chromatography and GC after the compound has been separated and identified with the response being measured by peak area. The standard gases were injected into the GC in a similar way and under the same conditions as the sample. The following equations were used to relate peak area to the weight of compound in the sample.

$$\frac{W_1}{W_2} = \frac{A_1}{A_2}$$

$$W_2 = \frac{W_1 \times A_2}{A_1}$$

Where: W_1 = Weight of compound in standard gas, W_2 = Weight of compound in sample, A_1 = Area of compound in standard sample, A_2 = Area of compound in sample

The concentration of each gas in the sample was calculated using the following equation:

$$\frac{W_2}{C} = \frac{V_s}{1}$$

Where: W_2 = Weight of compound in sample, V_s = Volume of samples at standard condition (STP), C = Concentration of compound in a litre air

The volume of each gas sample was calculated to the volume under the standard conditions 25°C and 760mm Hg by the following equation:

$$V_s = V_m \times \frac{P}{760} \times \frac{298}{273 + t}$$

Where V_s = Volume at standard condition (litre), V_m = Volume of sample (litre), P = Barometric pressure, mm Hg, t = Ambient temperature, °C

3.3.4.2 Results:

Figure 3-27 and Table 3-5 show the concentrations of methane, ethylene, ethane, propylene, propane and n-butylene in the gaseous products from pyrolysis of PVC alone and PVC in the presence of copper, cupric oxide, and copper (II) chloride under nitrogen. It is clear that the largest concentration of methane and ethylene is observed in the presence of cupric oxide. The data in this figure also show that the concentrations of short chain gases produced in the presence of CuO, $CuCl_2$ and copper are higher than that from the pyrolysis of PVC alone.

Figure 3-28 and Table 3-6 contains data on short chain linear gases produced by the combustion of PVC alone and in the presence of copper, copper (II) chloride and cupric oxide. It is clear that the combustion of PVC in presence of CuO, $CuCl_2$ and copper generates more short chain gases than does PVC alone.

Figure 3-27 :Concentration of short chain gasses produced of pyrolysis of PVC alone and in the presence of copper and some copper compounds under nitrogen

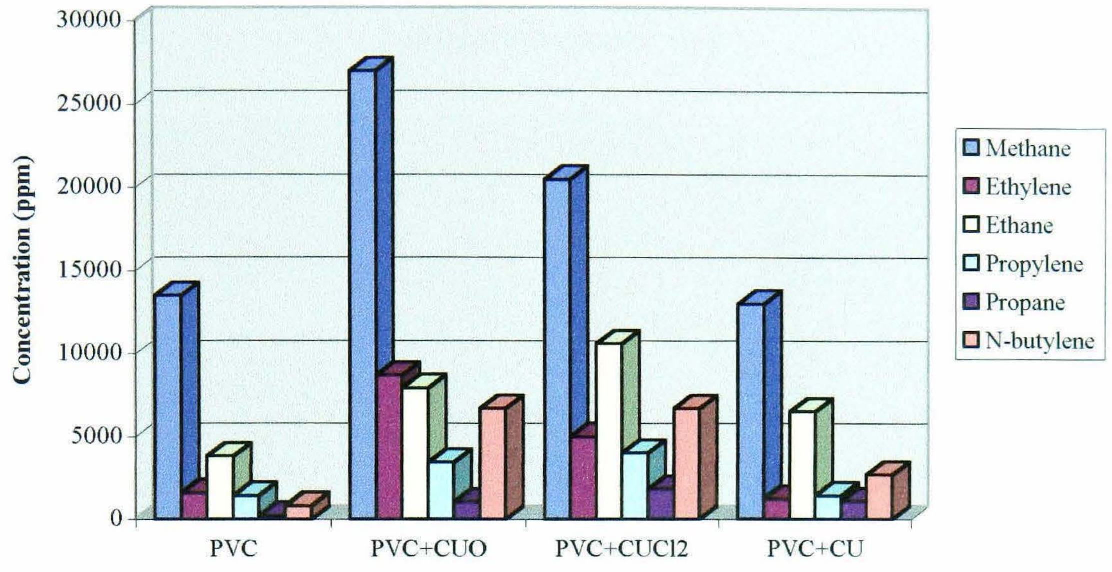


Table 3-5: Concentration of short chain gases produced by the pyrolysis of PVC alone and in the presence of some copper compounds under nitrogen (ppm)

Sample	Methane	Ethylene	Ethane	Propylene	Propane	N-butylene
PVC	13500	1600	3800	1400	200	800
PVC+CuO	27000	8700	7925	3425	1000	6700
PVC+$CuCl_2$	20500	5000	10600	4000	1800	6700
PVC+Cu	13000	1200	6500	1400	1050	2700

Figure 3-28: Concentration of short chain liner gasses producted of combustion of PVC alone and in the present of copper and some copper compound in air

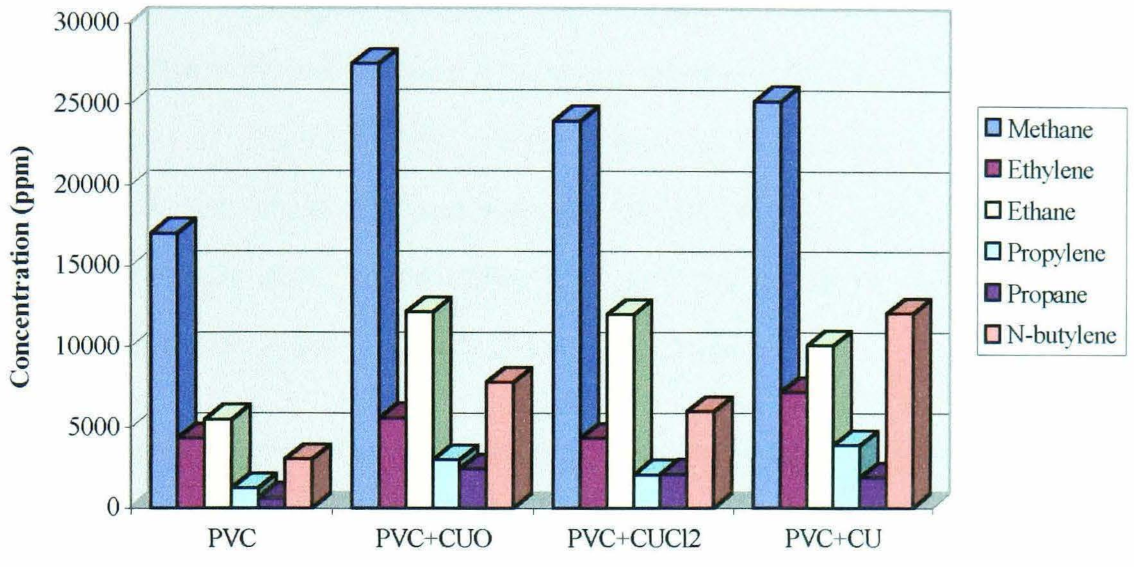


Table 3-6: Concentration of short chain linear gases produced by the combustion of PVC alone and in the presence of some copper compounds under air (ppm)

sample	Methane	Ethylene	Ethane	Propylene	Propane	N-butylene
PVC	17000	4300	5520	1250	600	3050
PVC+CuO	27500	5600	12200	3000	2400	7800
PVC+$CuCl_2$	18300	4300	12000	2050	2100	6000
PVC+Cu	25200	7200	10100	3900	1900	12100

3.3.5 The monitoring of Aromatic and Chlorinated Aromatic Hydrocarbons in Gas Emissions :

In this study, about 2mg sample of pure PVC and of mixtures of PVC and copper, or copper (II) chloride or cupric oxide were heated in an electric furnace at 300°C and 600°C at a heating rate of 10C° per minute from room temperature in a flow gas of air or nitrogen with a flow rate 35 ml per minute. The weights of copper, cupric oxide and copper (II) chloride used were about 10% of the PVC weight. For the determination of dioxin, about 100 mg samples of pure PVC and the same ratio of PVC with copper compounds were burnt under the same temperature conditions. The air or nitrogen flow in this case, however, was 50 ml per minute.

In the present work a novel method was used to sample and analyse dioxin and chlorinated aromatic hydrocarbons. The details of methods are given in chapter 2.

The gas collection methods used in studies of the decomposition of PVC by other workers include: (1) McNeill and Memtea[23] used a cold liquid nitrogen trap for sampling all products except non-condensable gases produced in the pyrolysis of PVC. (2) Jay and Stieglitz [11] used a condensation vessel in series with a water cooler and 2 types of solid sorbents. The first was a multi-bed sorbent of XAD-16 and Tenax GR and the second was a multi-bed sorbent of XAD-1180, XAD-16 and XAD-4 for sampling volatile organic components in the emission flue gases from waste incineration. They used a soxhlet extractor for extracting dioxin compounds. (3) Gertler et. al.[42] used high volume polyurethane foam for sampling dioxin and furan emission from heavy duty diesel vehicles.

3.3.5.1 Chlorinated Aromatic Hydrocarbons:

For sampling chlorinated aromatic hydrocarbons, aromatic hydrocarbons and some volatile hydrocarbons a Supelco Carbotrap 300 with a gas flow rate of 35 ml per minute for 12 minutes was used. This Carbotrap is a multi-bed trap and contains the absorbent Carbotrap C, Carbotrap B and Carbosieve S-III. The sampling line is shown in Figure 3-29.

3.3.5.2 Sampling aerosol of aromatic and, chlorinated aromatic hydrocarbons:

To sample aromatic and chlorinated aromatic hydrocarbons aerosols in this work a 37mm diameter fibre glass SKC filter paper was used. After sampling, the filter paper was cut and placed in a glass tube 4mm ID for thermal desorption for analysis. Figure 3-30 shows this sampling line.

Figure 3-29: Sampling line for sampling of chlorinated aromatic, aromatic and volatile hydrocarbons.

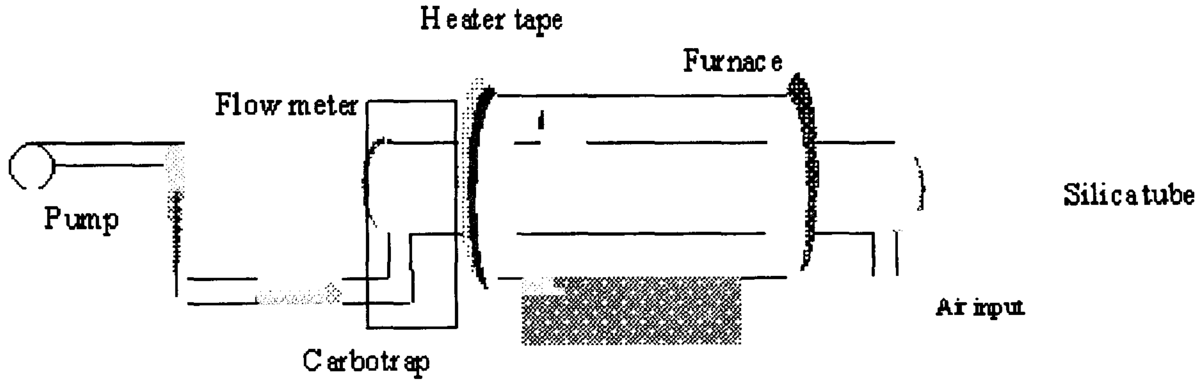
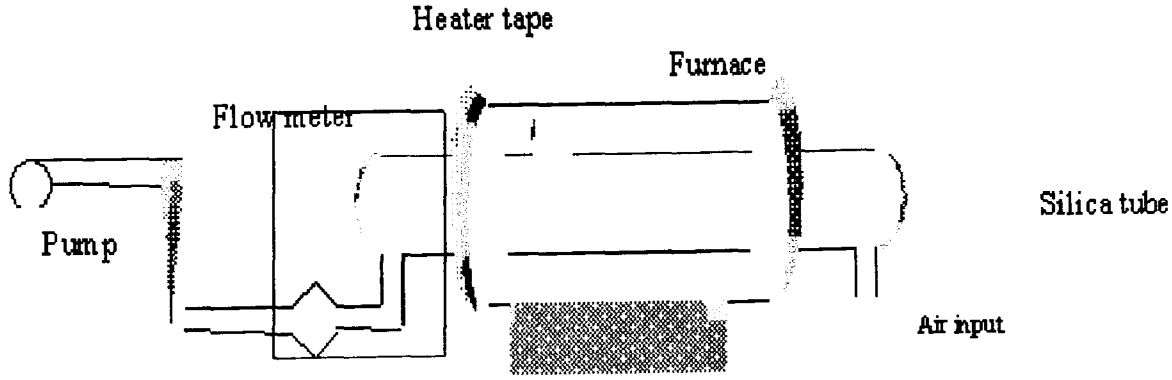


Figure 3-30: Sampling line for sampling of aerosol of aromatic and, chlorinated aromatic hydrocarbons



3.3.5.3 Sampling of dioxin:

2,3,7,8 TCDD is a semi-volatile organic compound. For sampling dioxin gas a Supelco Carbotrap 150 with a sampling flow rate of 50 ml and a time of 15 minutes was used. For aerosol 2,3,7,8 TCDD a 37mm diameter fiber glass filter paper was used. The filter holder and silica tube were held at 170 °C.

3.3.5.4 Analysis of samples:

In this study, total analysis was achieved using a Supelco thermal desorption model 890 linked to a high resolution GC and a mass spectrometer. The thermal desorption method is used as a direct extraction method to introduce analytes to GC for analysis in an on-line method. The conditions of preparation of samples and thermal desorption are in Table 3-7. Each Carbotrap was conditioned at 350 °C with a flow rate of 3 ml per minute helium for 30 minutes before use for sampling.

Table 3-7: Preparation and desorption conditions for thermal desorption of sample

Preparation condition					Desorption condition				
Sample	Flow of He ml	Tube temp.°c	Valve temp.°c	Time min	Flow of He ml	Tube temp.°c	Valve temp.°c	Transfer line temp.°c	time min
Aromatic and chlorinated hydrocarbon gas					2-2.5	330	220	220	4
Aromatic and chlorinated hydrocarbon aerosol	14	350	220	14	2-2.5	330	220	220	4
Dioxin gas					2.5-3	350	220	250	6
Dioxin aerosol	25	370	220	17	2.5-3	350	220	250	6

A gas chromatograph Fisons 8000 linked to a Fisons MD 800 mass spectrometer was used for analysis of the samples.

A Supelco fused silica capillary column 30m x 2.5mm x 2.5µm was used for the analysis of aromatic and chlorinated aromatic compounds and a Supelco fused silica capillary column 60 m x 0.25mm x 0.2µm was used for the analysis of dioxin.

GC temperature programming for the analysis of aromatic and chlorinated aromatic hydrocarbons and some volatile compounds was started at 30°C for 5 minutes and the temperature raised to 200 °C at rate of 5C° per minute and held at that temperature for 10 minutes. For 2,3,7,8-tetra chloro dibenzo-p-dioxin the temperature programme started at 200°C for 1 minute and then increased to 260°C at a rate of 8 °C per minute and held at 260°C for 20 minutes. The mass spectrometer used as detector is operated in the ion selective mode for the analysis of 2,3,7,8 TCDD. At a minimum, ions 320 and 322 are used. It is important to maintain the same set of ions for both calibration and sample analysis.

3.3.5.5 Results :

Table 3-8 lists the organic products identified from the combustion of pure PVC and mixtures of PVC in the presence of copper, copper (II) chloride and cupric oxide at 300°C in air. The results show that benzene is the major aromatic product.

The concentration of benzene, toluene and some chlorinated aromatic hydrocarbon decrease for the combustion of PVC in the presence of CuO. The concentration of 2,3,7,8-tetrachloro dibenzo-p dioxin, however, increase when PVC was burned in the presence of copper and copper compound.

Table 3-9 lists the products of combustion of pure PVC and of mixtures of PVC with copper, copper (II) chloride and cupric oxide at 600°C. Results show a decrease in the formation of aromatic hydrocarbons when combustion is carried out in the presence of the copper compounds.

Table 3-10 lists the pyrolysis products from PVC and PVC in the presence of copper, copper (II) chloride and cupric oxide under nitrogen at 300°C. While Table 3-11 lists the products of the same pyrolysis at 600°C. The results show that the concentration of aromatic and chlorinated aromatic hydrocarbons in nitrogen are higher than those obtained in air except for the concentration of 2,3,7,8 TCDD. The concentrations of aromatic and chlorinated aromatic hydrocarbons increased with increasing temperature.

Figure 3-31 and 3-32 shows a gas chromatogram of the combustion products of PVC and Figures 3-33, 3-34, 3-35, 3-36, 3-37, 3-38, 3-39, 3-40, 3-41, 3-42, 3-43 and 3-44, show spectra of some of the peaks.

It is concluded that cupric oxide promotes the formation of linear chain products rather than aromatic hydrocarbons and that more 2,3,7,8-TCDD is generated when the combustion temperature is low (about 300°C) and in the presence of copper compounds.

Table 3-8: The amount organic gases products from the combustion of pure PVC and mixtures of PVC in the presence of copper, copper (II) chloride and cupric oxide at 300°C under air. (μg)

Product	PVC	PVC+Cu	PVC+$CuCl_2$	PVC+CuO
Benzene	440	410	40	37
Toluene	11	4.1	3.2	2.1
o-xylene	-	-	-	-
Naphthalene	-	-	-	-
Chlorobenzene	2	2.1	0.008	0.003
Ethyl benzene	1	-	-	-
p-dichlorobenzene	-	0.008	0.003	0.001
o-dichlorobenzene	0.07	0.012	0.0007	0.0002
1,2,5-trichlorobenzene	-	-	-	-
1,2,4-trichlorobenzene	0.09	-	-	-
1,2,4,5-tetrachloro benzene	0.03	0.045	0.0009	0.0005
pentachlorobenzene	0.01	0.023	-	-
Hexachlorobenzene	0.03	0.08	-	-
2,3,7,8-TCDD	15ng	46ng	40ng	32ng
Tetrachloroethylene	1.01	1.03	1.2	2

Table 3-9: The amount organic gases products from the combustion of pure PVC and mixtures of PVC with of copper, copper (II) chloride and cupric oxide at 600°C under air. (μg)

Product	PVC	PVC+Cu	PVC+$CuCl_2$	PVC+CuO
Benzene	500	410	80	45
Toluene	68	54	33	2.0
o-xylene	0.9	0.8	0.32	0.2
Naphthalene	3.65	2.9	0.42	0.255
Chlorobenzene	1.22	1.27	0.9	0.7
Ethyl benzene	4.05	4	3.1	2.8
p-dichlorobenzene	0.35	0.5	0.12	0.08
o-dichlorobenzene	8.56	9.1	2.3	1.8
1,2,5-trichlorobenzene	1.2	1.1	9.1	0.62
1,2,4- trichlorobenzene	5	6.1	2.5	2
1,2,4,5-tetrachlorobenzene	6.2	7.8	3.1	2.2
pentachlorobenzene	3.8	4.7	1.6	1.1
Hexachlorobenzene	4	5.3	1.9	1.4
2,3,7,8-TCDD	8ng	29ng	23ng	16ng
Tetrachloroethylene	1.8	2.0	2.2	3.8

Table 3-10: The amount organic gases products from the combustion of pure PVC and mixtures of PVC with copper, copper (II) chloride and cupric oxide at 300°C under nitrogen. (μg)

Product	PVC	PVC+Cu	PVC+$CuCl_2$	PVC+CuO
Benzene	480	445	44	40
Toluene	30	11	8.2	6
o-xylene	-	-	-	-
Naphthalene	-	-	-	-
Chlorobenzene	3	3.3	0.01	0.007
Ethyl benzene	1.2	-	-	-
p-dichlorobenzene	-	0.012	0.005	0.001
o-dichlorobenzene	0.09	0.015	0.0008	0.0003
1,2,5-trichlorobenzene	-	-	-	-
1,2,4-trichlorobenzene	0.1	-	-	-
1,2,4,5-tetrachloro benzene	0.045	0.06	0.001	0.0008
pentachlorobenzene	0.02	0.028	-	-
Hexachlorobenzene	0.04	0.1	-	-
2,3,7,8-TCDD	-	-	-	
tetra chloroethylene	1	0.95	0.97	1.5

Table 3-11: The amount organic gases products from the combustion of pure PVC and mixtures of PVC with copper, copper (II) chloride and cupric oxide at 600°C under nitrogen. (μg)

Product	PVC	PVC+Cu	PVC+CuCl$_2$	PVC+CuO
Benzene	670	530	101	52
Toluene	158	121	75	3
o-xylene	1.17	1.05	0.40	0.22
Naphthalene	4.7	3.75	0.53	0.3
Chlorobenzene	1.65	1.6	1.134	0.79
Ethyl benzene	5.3	5	3.9	3.1
p-dichlorobenzene	0.45	0.5	0.15	0.085
o-dichlorobenzene	11	11.7	2.8	1.95
1,2,5-trichlorobenzene	1.6	1.4	11.5	0.7
1,2,4-trichlorobenzene	6.5	7.6	3.1	2.15
1,2,4,5-tetrachlorobenzene	8.2	7.5	3.15	2.35
pentachlorobenzene	5	6.1	1.95	1.2
Hexachlorobenzene	5.25	6.6	2.39	1.57
2,3,7,8-TCDD	-	-	-	5ng
Tetrachloroethylene	1.3	1.75	1.7	3.4

Figure 3-31: A gas chromatogram of dioxin.

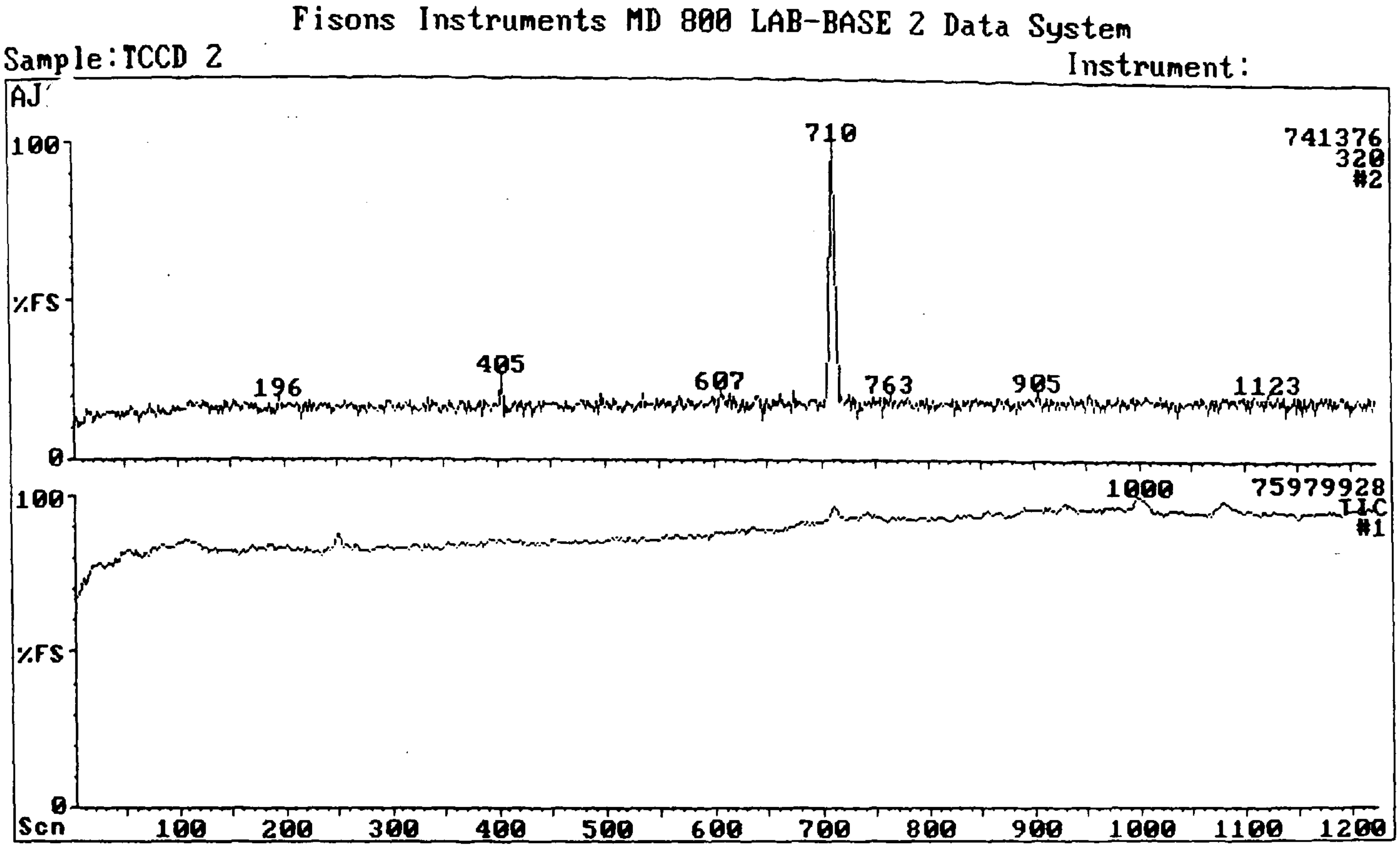


Figure 3-32: A gas chromatogram of products from combustion of PVC at 600°C

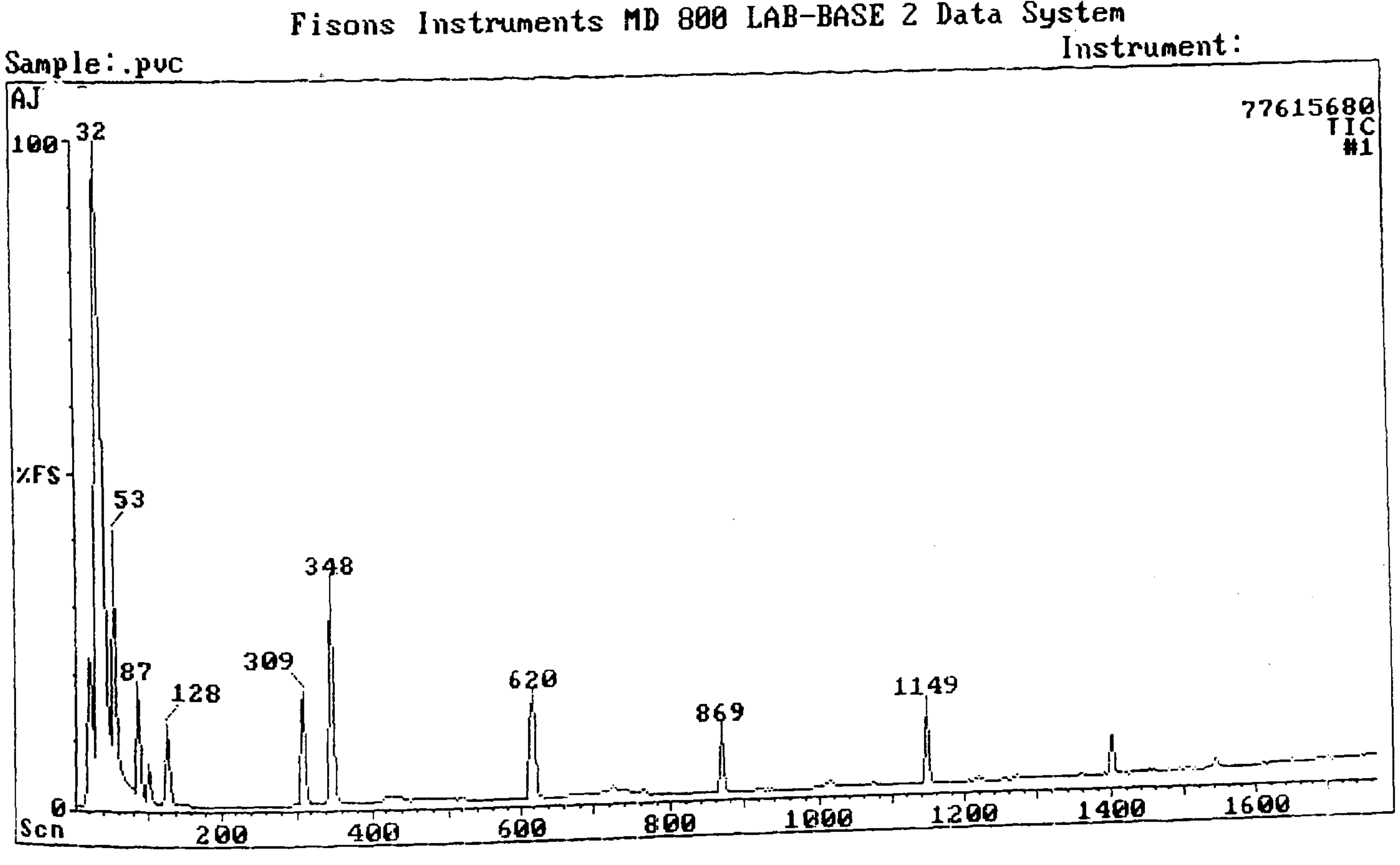


Figure 3-33: Mass spectrum of scan 775 (2,3,7,8-TCDD

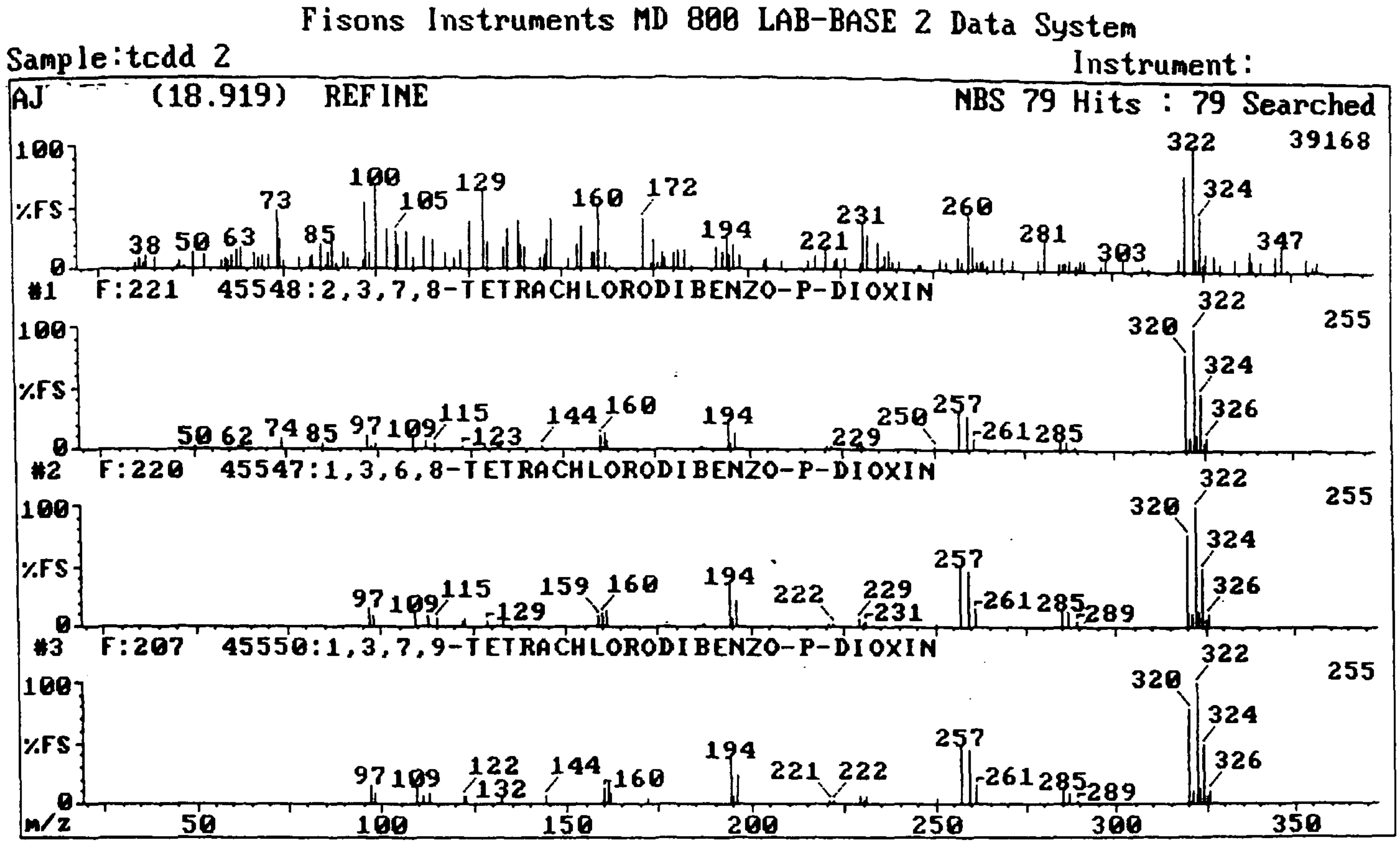


Figure 3-34 Mass spectrum of scan 44 (benzene)

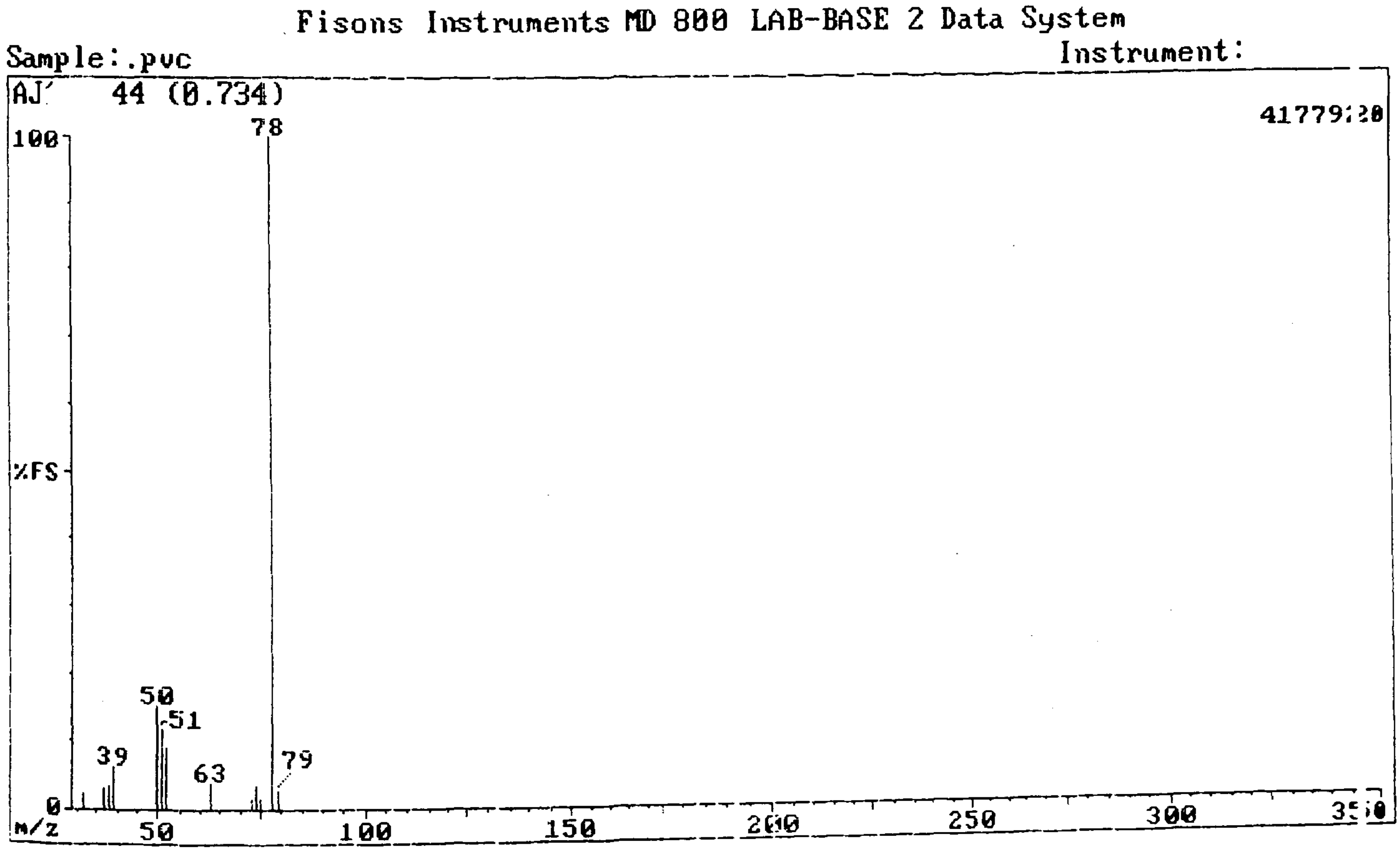


Figure 3-36: Mass spectrum of scan 56 (toluene)

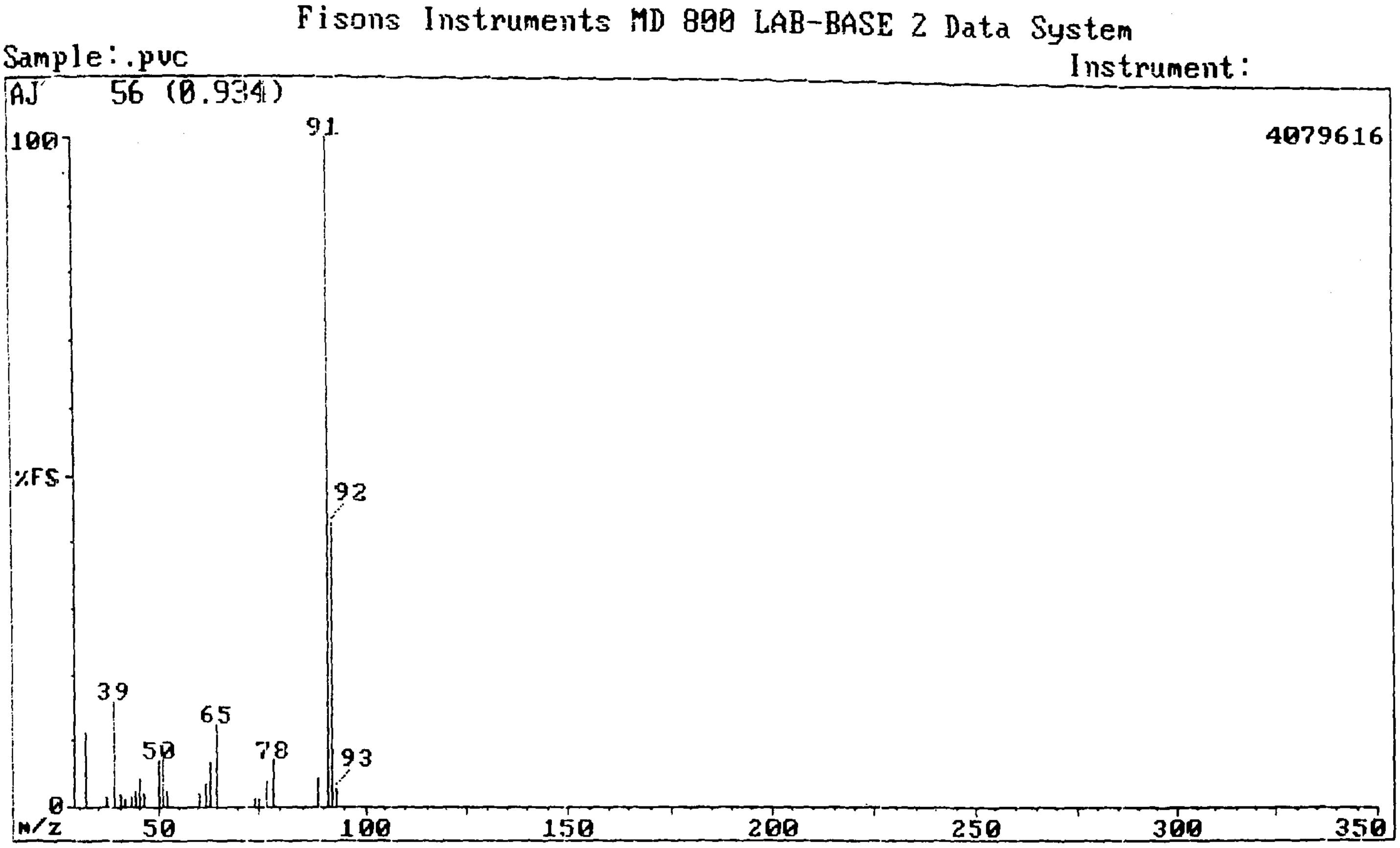


Figure 3-37: Mass spectrum of scan 98 (chlorobenzene)

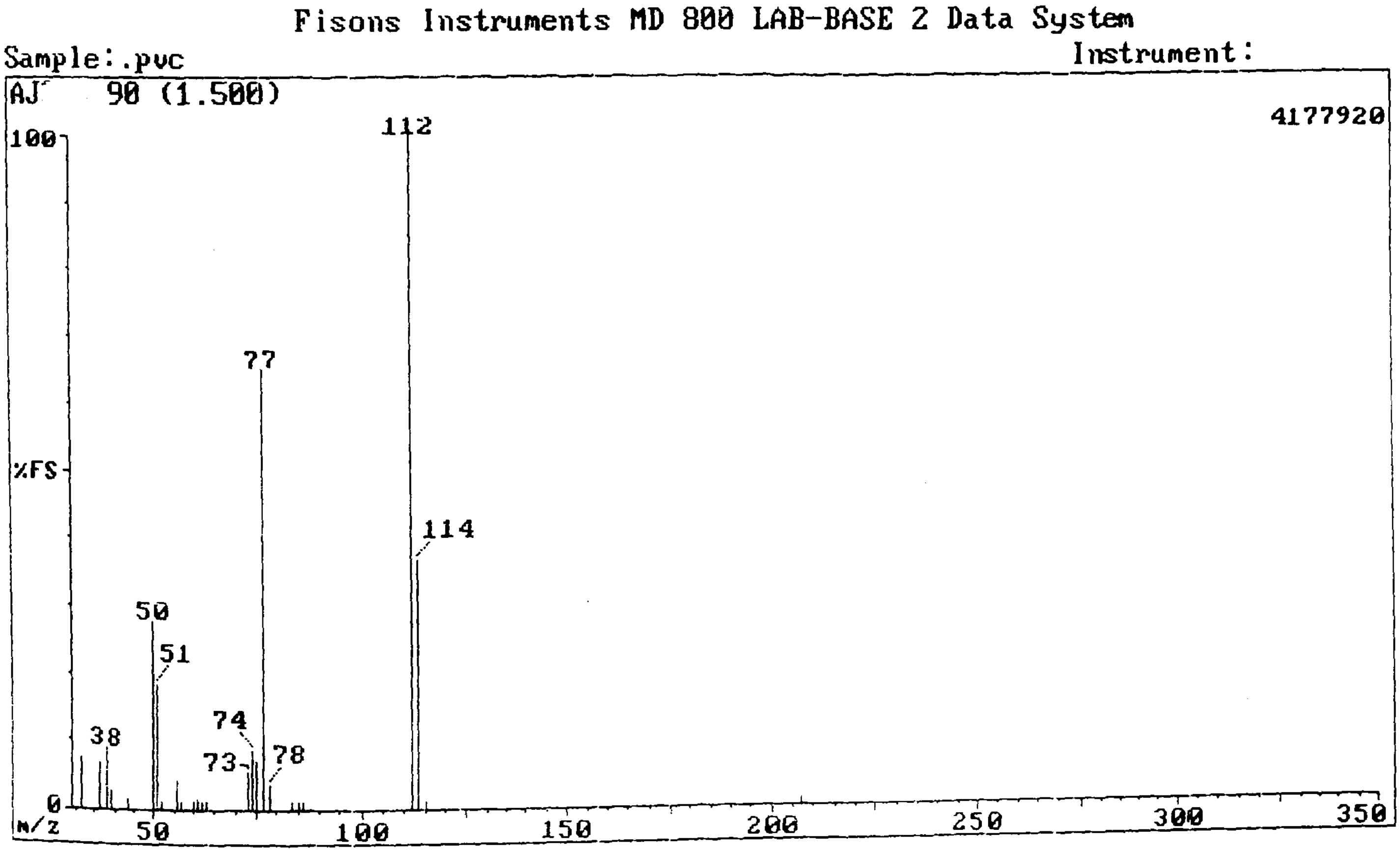


Figure 3-38: Mass spectrum of scan 128 (xylene)

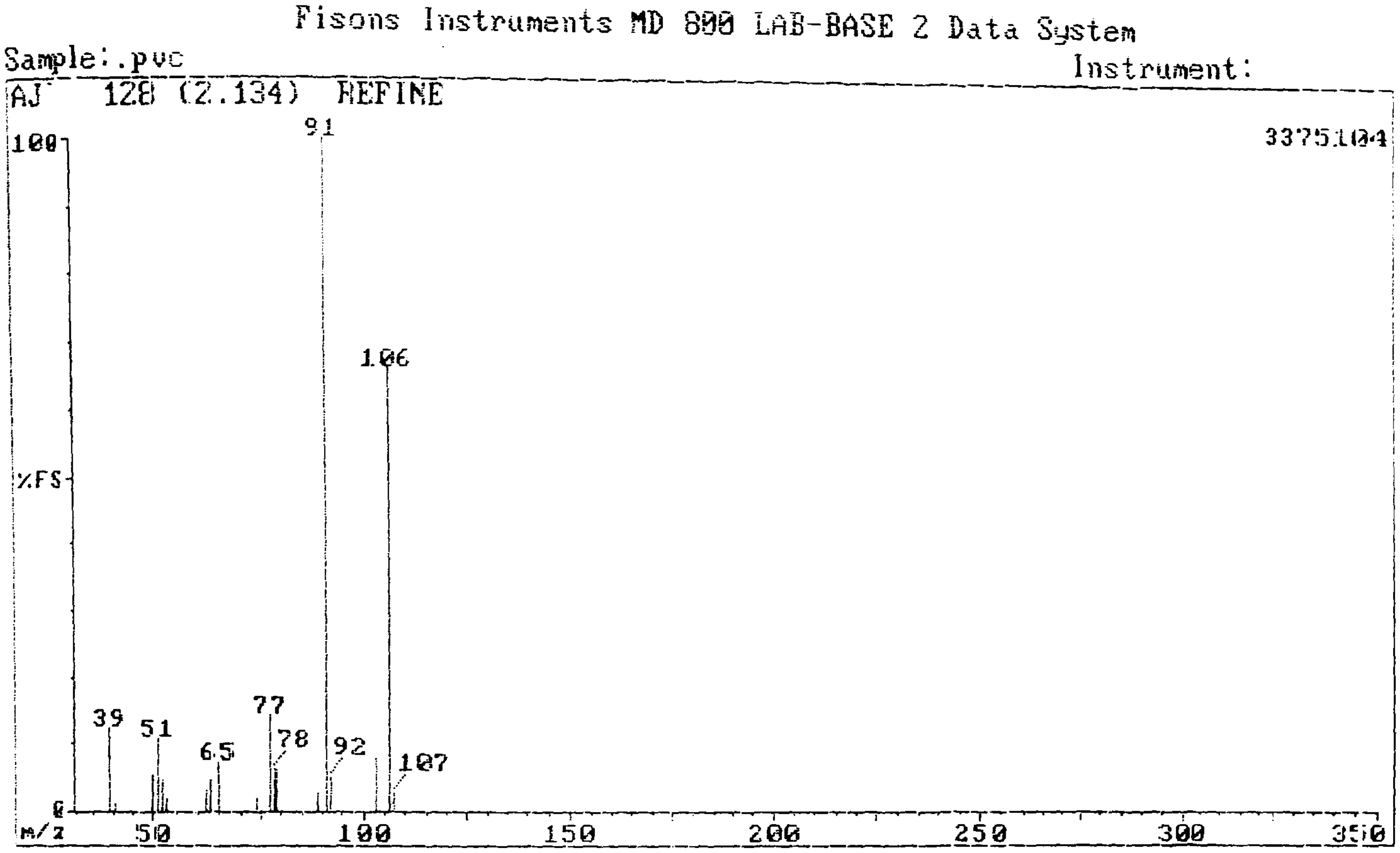


Figure 3-39: Mass spectrum of scan 309 (1,2 dichlorobenzene)

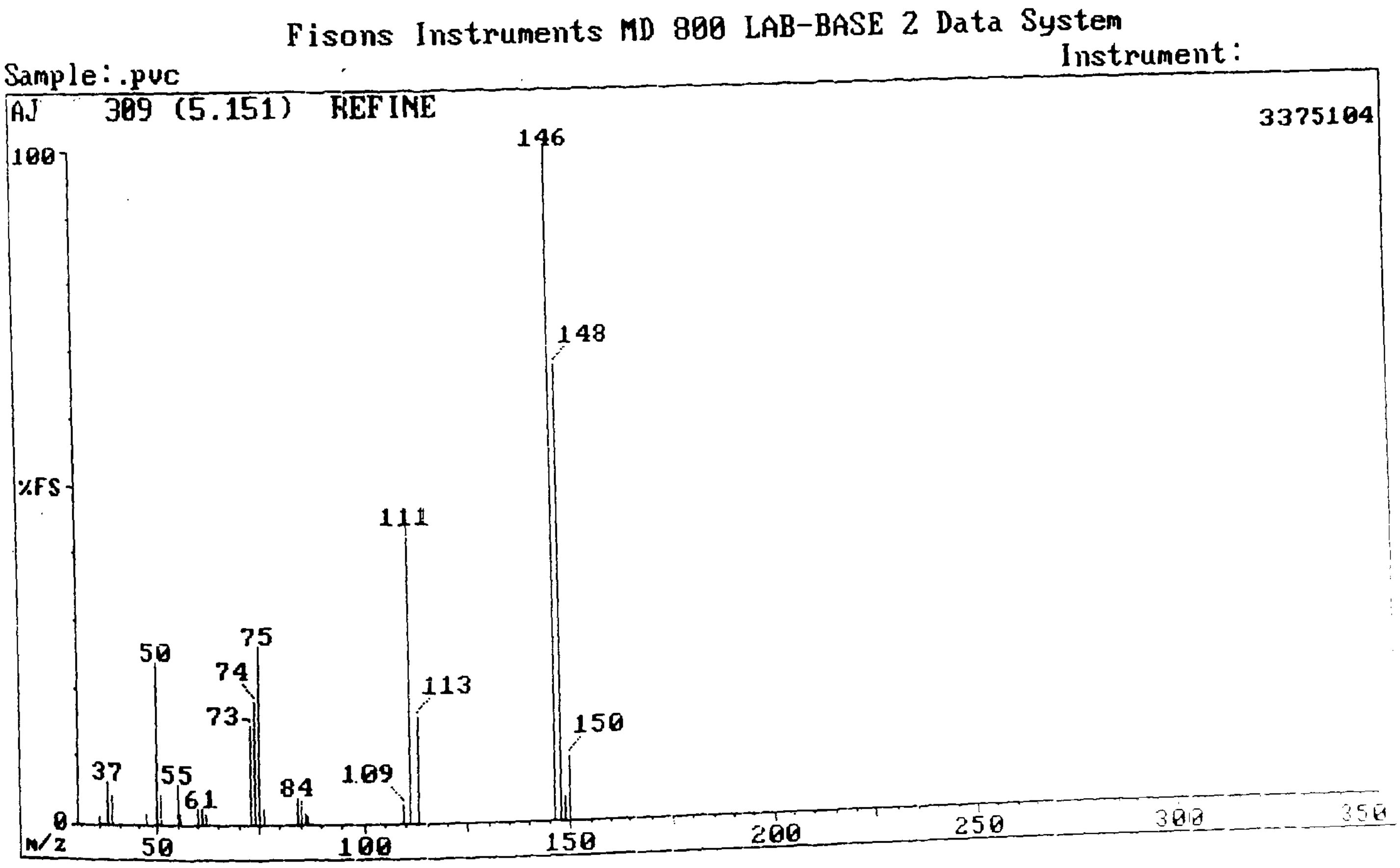


Figure 3-40: Mass spectrum of scan 614 (1,2,3 trichlorobenzene)

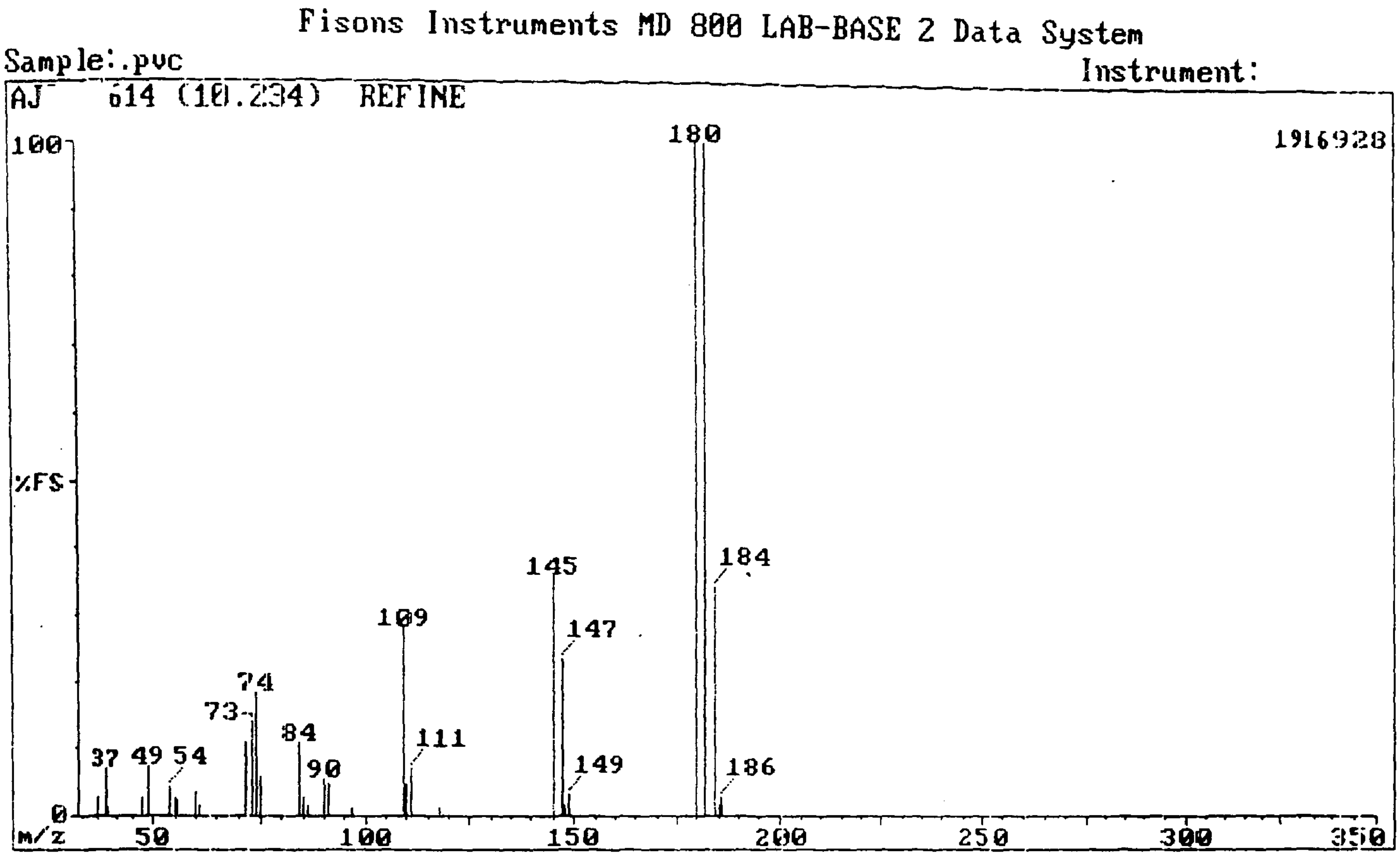


Figure 3-41: Mass spectrum of scan 639 (naphthalene)

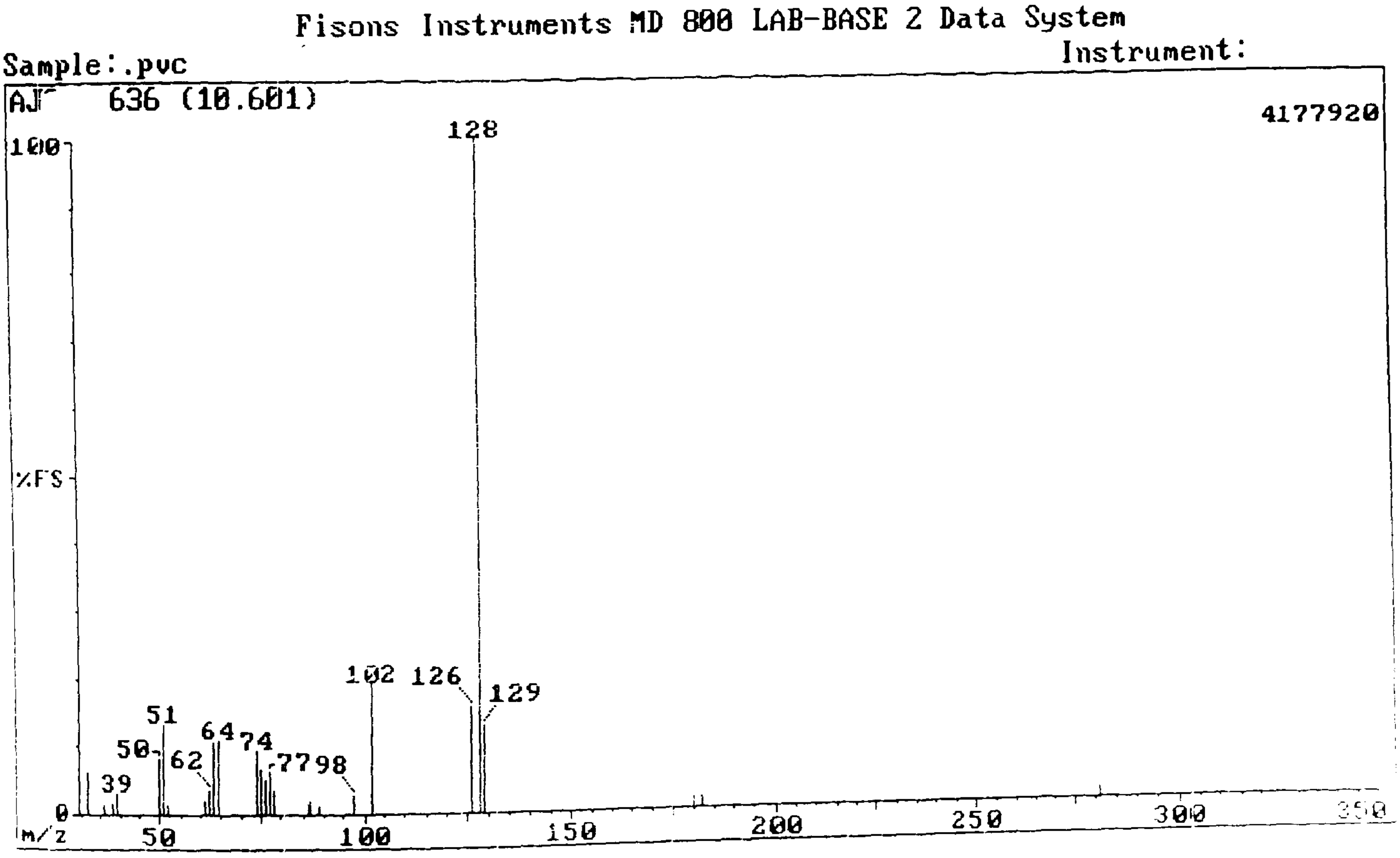


Figure 3-42: Mass spectrum of scan 869(1,2,3,5 tetrachlorobenzene)

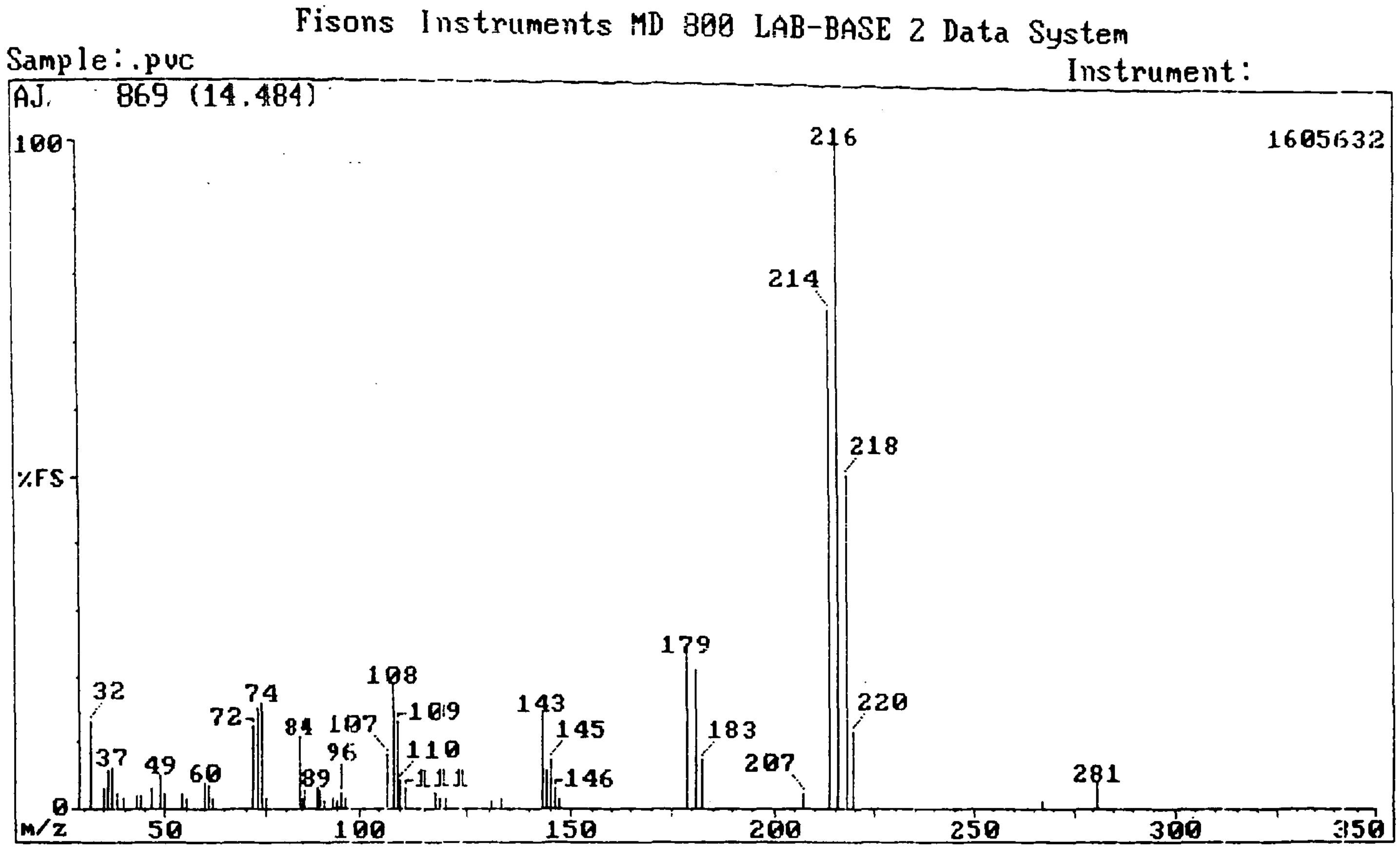
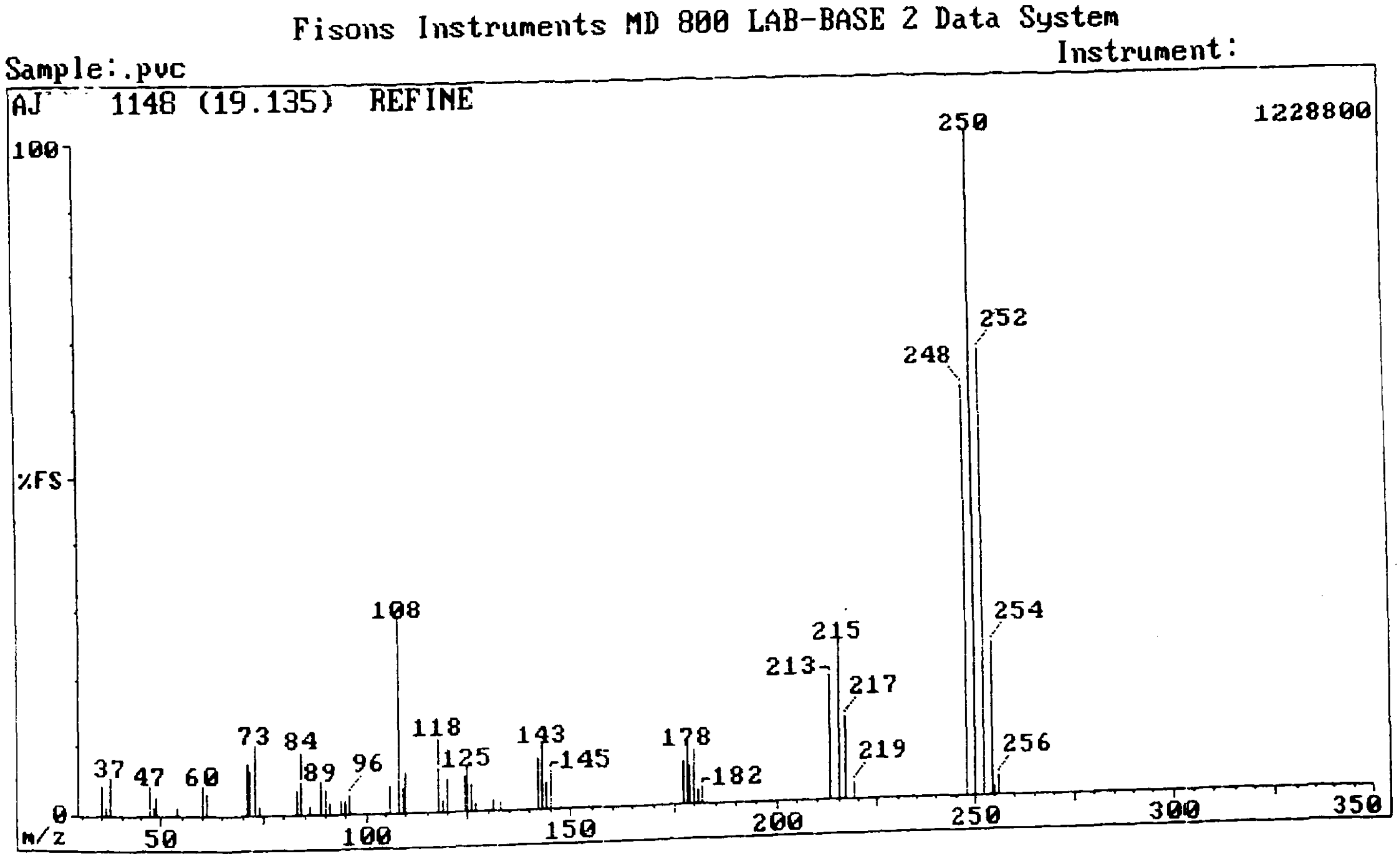


Figure 3-43: Mass spectrum of scan 1148 (pantachlorobenze)



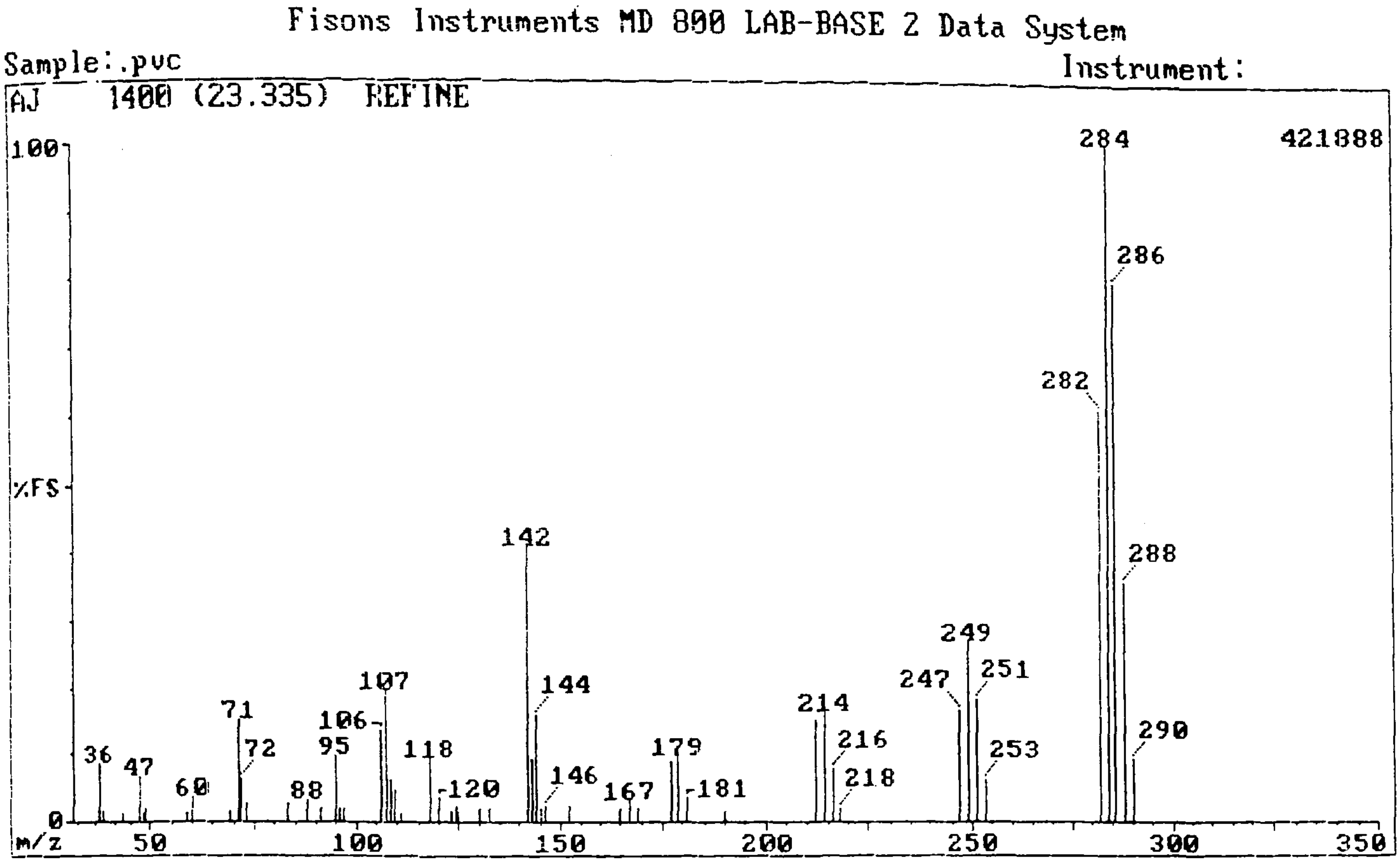


Figure 3-44: Mass spectrum of scan 1400 (hexachlorobenzene)

3.4 CONCLUSION:

The purpose of this research was to determine the effects of the presence of copper and copper compounds in thermal degradation of PVC

The beneficial effects of the presence of copper and copper compounds (especially cupric oxide) are: (1) an increase in the formation of short chain aliphatic hydrocarbons. (2) a decrease in the amount of the major aromatic hydrocarbon products formed and (3) a decrease in the amounts of HCl formed. A disadvantage of the presence of copper or copper compounds is an increase in the amount of dioxin formation.

The results with cupric oxide suggest that the presence of this material in the PVC combustion process could be used to control the nature of the pollutant emission. The use of cupric oxide and other metal oxide as potentially control additives for the PVC combustion described in chapter 4.

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CHAPTER 4-CONTROL OF EMISSIONS FROM THE COMBUSTION OF PVC

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4.1 INTRODUCTION:

With increasing pressure to reduce the amount of waste being landfilled incineration is becoming a more attractive means of disposal particularly if energy recovery is also involved. There is some concern, however, that incineration of waste produces pollutants which may cause more harm to the environment than other forms of waste disposal. The incineration of waste leads to the following residual emissions:

1) Pollutant emissions to the atmosphere

2) Contaminated waste water streams

3) Contaminated ash

Air pollution from waste incineration occurs in different forms including: [1, 2]

A) Odour, dust and litter problems from the discharge, storage and handling of waste

B) The gas stream passing through the combustion waste bed may extract ash, dust and char and carry them into the flue gas stream.

C) Metals and metal compounds may evaporate in the furnace to condense eventually in the colder parts of the flues and generate an aerosol of sub-micron particles.

D) If the waste being incinerated contains elements such as chlorine, fluorine, sulphur, nitrogen the generation of toxic or corrosive gases may result and, for example, nitrogen oxides may form at the high temperatures in the flame.

E) The pyrolysis products, arising during the thermal decomposition of waste, may be incompletely combusted to give CO, organic compounds such as polycyclic aromatic hydrocarbons, dioxins and furans, tar and soot particles.

In the previous chapter the nature of the emissions arising from the combustion of PVC alone and in the presence of copper and copper compounds was described. The purpose of the work described in this chapter is to develop a methodology to control of the combustion emissions including soot particulate.

4.1.1 Methods of Control

Control of pollutant emissions may be divided into control of material present in gas streams inside the process equipment and control of material arising in open or unconfined areas. Strategies for control include basic changes in procedures and materials, which eliminate or alter emissions, and the use of add-on or auxiliary equipment to remove pollutants prior to release of the inert carrier gas to the atmosphere.

Gas cleaning and atmospheric dispersion must be used as the final control step. Process operation, and system control is a means of minimising the quantities of substances entering clean up systems and, ultimately, being discharged to the atmosphere. Process operation and system control will concentrate contaminants in the smallest possible volume of air [3, 4, 5, 6].

Much consideration is being given to reducing pollution of the environment by dangerous substances and the bioaccumulation of pollutants in organisms has been identified for urgent action. In particular, legislation is being provided for controlling the release of such pollutants into the environment and methods for disposal or control are being developed for cases where their concentrations are above the legal limit.

The control of atmospheric emissions from a process will generally take one of three forms depending on the process, fuel, types and availability of control equipment, etc.

- Process change to a less polluting process.
- Fuel change
- Installation of control equipment between the point of pollutant generation and its release to the atmosphere.

4.1.1.1 Process change:

A process change can be either a change in operating procedures for an existing process or the substitution of a completely different process. In recent years this has been labelled "pollution prevention."

In some cases, the least expensive control is achieved by abandoning the old process and replacing them with new, less polluting ones. Any increased production and/or recovery of material may help offset a portion of the cost. It has, for example, proved to be cheaper to abandon old steel mills and to replace then with completely new furnaces than to modify old systems to meet pollution regulations. Kraft Pulp Mills found that the least costly method of meeting stringent regulations was to replace the old, high-emission recovery furnaces with a new furnace of completely different design. The Kraft mills have generally asked for, and received, additional plant capacity to offset partially the cost of the new furnace type.

4.1.1.2 Fuel Change:

In the past, for many air pollution control situations, a change to a less polluting fuel offered the ideal solution to the problem and fuel switching based on meteorological or air pollution forecasts was a common practice to reduce the air pollution burden at critical times. Some control agencies allowed power plants to operate on residual oil during certain periods of the year when pollution potential was low. For years some large utilities have followed a policy of switching from their regular coal to a more expensive, but lower-sulphur coal, when stagnation conditions were forecast.

Caution should, however, be exercised when considering any change in fuels to reduce emissions. This is particularly true considering today's fuel costs. Specific considerations might be the following:

1) What are current and potential fuel supplies? In many areas natural gas is already in short supply and it may not be possible to convert a large plant to use gas as a fuel because of current pipeline capacity.

2) Most large boilers use a separate fuel for auxiliary or stand-by purposes. One example is a boiler fired with wood residue as the primary fuel with residual oil as the standby where a change was made to natural gas as the primary fuel, with residual oil kept for standby. This change was made to lower particulate emissions and to achieve a predicted slightly lower cost. Because of gas shortages, this plant now operates on residual oil during most of the cold season, and the resulting particulate emissions greatly exceeds that of those previously found with wood fuel. In addition, an SO_2 emission problem exists with the oil fuel that was absent with wood and the overall costs have not been lowered because the most of the natural gas has increased since the conversion.

3) Strong competition exists for low-pollution fuels. If one area is using low sulphur fuel, it is probable that neighbouring areas are doing the same. Such a situation has resulted in extreme fuel shortages during cold spells in some large cities.

4.1.1.3 Pollution removal:

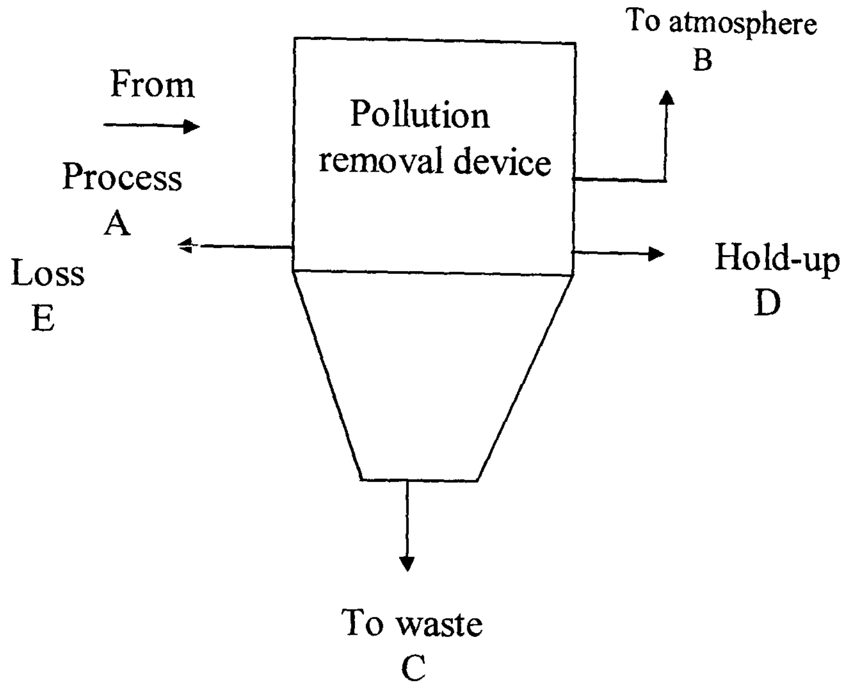
In many situations, sufficient control over emissions cannot be achieved by fuel or process changes. In cases such as these, the levels of the pollutants in the exhaust gases or process streams must be reduced to acceptable levels before they are released to the atmosphere.

Equipment for removal of pollutants includes hoods, ducting, controls, fans and disposal or recovery systems. The entire system should be engineered as a unit for maximum efficiency and economy. Many systems operate at less than maximum efficiency because a part of the system has been designed or adapted without consideration of the other parts. [7]

The efficiency of the control equipment is normally specified before the equipment is purchased. If a plant is emitting a pollutant at 500 kg/hr and the regulations allow an emission of only 25kg/hr, it is obvious that at least 95% efficiency is required in the pollution control system. This situation requires that achieved and the control regulation would also at least 95% removal on a weight basis of the pollutant is specify the test to be made to determine the efficiency of removal. Figure 4-1 shows the mass balance structure across a pollution removal device.

The information in Figure 4-1 can be expressed in terms of efficiency calculations.

Figure 4-1: The situation of a pollution removal device



The efficiency for the device shown in Figure 4-1 may be calculated in several ways:

Efficiency

$$\% = 100 \left(\frac{C}{A} \right) \quad \text{but since} \quad A = B+C$$

Efficiency

$$\% = 100 \left(\frac{C}{B+C} \right) \quad \text{or} \quad 100 \left(\frac{A-B}{A} \right)$$

The final acceptance test would probably be made by measuring two of the three quantities and using the appropriate equation. For a completely valid efficiency test the effect of hold-up (D) and loss (E) must also be taken into account.

To remove a pollutant from the carrying stream, some property of the pollutant that is different from the carrier must be exploited. The pollutant may have different size, inertia, electrical or absorption properties. Removal requires that the equipment be designed to apply the scientific principles necessary to perform the separation.

4.1.1.4 Disposal of pollutants:

If a pollutant is removed from the carring gas stream, disposal of the collected material becomes of vital concern. If the collected material is truly inert, it may be disposed of in a sanitary landfill. If it is at the other end of the scale, it is probably considered as toxic waste and strict laws will govern its disposal.

If a waste is designated as hazardous under the Resource Conservation and Recovery Act (RCRA) the resulting regulations apply to generators, transporters, and those who treat, store or dispose of that waste. [8]

The USEPA considers a substance hazardous if it exhibits one or more of the following characteristics [9].

1) Ignitable- the substance causes or enhances fires
2) Reactive- the substance reacts with others and many explode
3) Corrosive- the substance destroys tissues or metals
4) Toxic -the substance is a danger to health, water, food and air

Substances can be placed in any number of these categories, but placement in only one category is sufficient for the substances to be considered hazardous. Table 4-1 indicates the four main types of hazardous material, with examples of substances of each type [10]. In this table radioactive materials have not been included.

The general purpose of the ultimate disposal of hazardous waste is to prevent the contamination of susceptible environments. Surface water run-off, ground water leaching, atmospheric volatilisation and biological accumulation are processes that should be avoided during the active life of hazardous waste.

Table 4-1: The hazardous material types

Miscellaneous inorganic	Halogens and interhalogens	Miscellaneous organic	Organic halogen compounds
Metals	Bromine pentafluoride	Acrolein	Aldrin
Antimony	Chlorine	Dinitrophenol	Chlordane
Bismuth	Chlorine pentafluoride	Tetrazene	DDD,DDT
Cadmium	Chlorine trifluoride	Nitroglycerine	Dieldrin
Chromium	Fluorine	Nitroaniline	Endrin
Cobalt	Perchloryl fluoride	Chloroacetophenone	Heptachlor
Copper			Lindane
Lead			Parathion
Mercury			Methyl bromide
Nickel			Polychlorinated biphenyls (PCBs)
Selenium			Dioxin
Silver			
Tellurium			
Thallium			
Tin			
Zinc			
Non metallic			
Cyanide(ion)			
Hydrazine			
Phosgene			

4.1.2 Incineration (air emission and flue gas cleaning):

The combustion process in an incinerator breaks down the complex organic compounds of waste into more simple compounds and subsequently generates new compounds. Many of the compounds formed will be present in the flue gas. Carbon, hydrogen and sulphur will be converted to CO_2, H_2O and SO_2. Nitrogen will be converted to N_2 and NO_x. Chlorine will become HCl and may also be converted to complex organic chlorides. Inorganic substances will be oxidised and emitted as particles in the ash or as vapour in the flue gas. [1, 11, 12, 13, 14]

Typical pollutant content levels of raw flue gas from municipal solid waste incinerators are given in Table 4-2. [9] Flue gas typically contains 5 to 15 percent H_2O. Until recently, most attention was paid to the fly ash particulate matter and most flue gas cleaning consisted of fly ash removal by the use of cyclones, electric filters, bag filters or scrubbers. The most popular method has been electrostatic precipitation. The effect of filters on typical flue gases from incinerators is given in Table 4-3. [9]

In the last few years, attention has also been directed towards other elements in the flue gas, especially acid forming gases (HCl, HF), SO_2, heavy metals, (particularly Hg), dioxins and furans (PCDD and PCDF). The PCDD and PCDF compounds, together with polyaromatic hyrocarbons (PAH), can be limited by good incinerator design and efficient management. [1, 9,14] To reduce the emission of acid gases, new flue gas cleaning equipment has been developed. Two types of absorption can be used:

1. Absorption with lime
   - Dry absorption
   - Semi-dry absorption
2. Absorption in water
   - Scrubbing with added water
   - Condensation

Dry absorption works by the injection of dry $Ca(OH)_2$ to absorb HCl so forming $CaCl_2$ and water. The water will evaporate due to the heat in the flue gases, and a dry residue will remain. The dry residue, a mixture of $CaCl_2$ and fly ash, can then be separated in bag filters. Due to the high content of chloride salts there is a high leakage of chloride and also of heavy metals. Further treatment is to wash the material with water to encourage settling of heavy metals before discharging.

Table 4-2: Typical pollutant content levels of dry flue gas before cleaning and EU emission standard.

		Typical content:mg/Nm^3 at 9% CO_2		
		EC nominal capacity(t/h)		
Pollutant	**Typical untreated flue gas**	**Typical <1 t/h**	**1-3t/h**	**>3t/h**
Dust	1500-8000	200	100	30
SO_2	400	-	300	300
HCl	500	250	100	50
HF	5		4	2
NOx	300			
CO	100			150
Organic vapours	5			20
Hg vapours	0.05-0.5			0.2*
Ni+As+Pb+Cr+Cu +Mn	0.05-0.5			0.2
* total Hg and Cd				

Table 4-3: The effect of different filters on typical flue gases from incinerators .

Flue gases	Particle separation down to	Effectiveness %	Dust emission (mg/Nm^3)	Notes
Cyclone	10 µm	90	seldom less than 500	Low capital cost Big pressure loss (running costs)
Bag filters	0.3 µm	>99	<150	Lower capital cost than electric precipitation Large pressure loss than electric Required temperature less than 160°C
Electrostatic precipitation	0.3 µm	>99	<150	Expensive establishment Low pressure loss
Scrubber	1-2 µm	>95	<500	Low capital cost Big pressure loss (running costs) Cooling of flue gas

The semi-dry absorption process is similar to dry absorption with one exception. The Ca(OH$_2$) is injected in a water solution where the amount of water is balanced so that heat excess from the flue gas can evaporate the water. Scrubbing and condensation are normally positioned after a particle filter, often an electrostatic precipitator. When the acid gases (together with other pollutants) have been separated in water, further separation is achieved by treating the water. The water treatment process ends up with treated water of high chloride content to be discharged and a smaller amount of metal contaminated sludge that must be fixed with cement or fly ash before disposal in a landfill site.

4.1.2.1 Control of HCl from combustion of PVC

It is well known that thermal degradation of polyvinyl chloride evolves HCl, and that dehydrochlorination proceeds along the polymer chain resulting in the formation of a conjugated polyene which is responsible for the dark colour of the degraded polymer. [15,16]

The major source of HCl is regarded as PVC plastic. A direct relationship between HCl in the flue gas and PVC content of the waste for a municipal waste incinerator has been demonstrated. [17] PVC emits HCl by a gradual process of thermal decomposition which takes place between 180 and 600°C. Buekens and Schoeters[17], in laboratory studies of incineration, have shown that 60% of HCl is due to PVC, 36% to paper products, and 4% to grass and leaves.

A number of technologies are available for HCl removal; notably, spray towers, packed bed scrubbers, semi- dry scrubbers and dry scrubbers [18,19,20]. However, the efficiency of these technologies decreases with a shift from wet to dry scrubbing. Cory Environmental has chosen to rely on a semi-dry scrubber system for the removal of acid gases, not withstanding its slightly lower efficiency when compared to a spray tower or a packed bed scrubber. This is for a number of operational and environmental reasons. Wet scrubbing systems give rise to a wet exhaust gas which requires the deployment of a mist eliminator down stream. Wet systems also give rise to liquid effluent which require treatment. The EC Directive on the incineration of hazardous waste proposes [21] that the generation of liquid effluents from the operation of an incinerator should be minimised as far as possible. The flue gas leaves the boiler at approximately 230°C and enters the spray absorber through a top-mounted hot air inlet box. The latter is equipped with profiled baffle plates and adjustable vane rings which create the conditions necessary for the intimate mixing of the flue gas with the hydrate of-lime suspension used as the scrubber reagent. The HCl concentration of the clean gas is used to control the rate of hydrate-of-lime suspension added when the pollutant concentration in the flue gas is below the base load. For normal to maximum loads the hydrate-of-lime suspension is added at a constant rate.

The following reaction occurs when the atomised liquid comes into contact with the hot flue gas in the absorber:

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$$

4.1.3 Integrated Sampling for Particles:

An aerosol is a system consisting of airborne solid or liquid particles that are dispersed in a gas stream, usually the atmosphere. Dusts, smoke, soot, particles, mist, fumes and fog are all terms used to describe certain types of aerosols. Solid substances are defined as particles to distinguish them from liquid droplets.

4.1.4 Particles sampling:

Several methods are available for sampling of particulate, including, filtration, impingement, precipitation, gravity and centrifugal collection and diffusion. [22, 23, 24, 25, 26, 27]

4.1.4.1 Filtration:

Filters remove the particles from the air flow as a result of the operation of various mechanisms such as direct interception, impaction, diffusion and electric and gravitational forces. Direct interception occurs for particles with dimensions larger than the distance between the elements of the filter medium. Diffusion is the most efficient mechanism for the collection of very small particles; these particles are strongly affected by Brownian motion and diffuse through the air flow to the surface of the filter material where they adhere due to attraction forces. Particles with intermediate dimensions are preferably collected by impaction; as the air flow traverses the tortuous paths of the filter, where frequent directional changes encourage the deviation of particles from the air stream with consequent impingement on internal surfaces. Electrostatic forces may contribute to higher filtration efficiency if the filter and the aerosol are capable of acquiring static electrical charges.

The type of filter medium chosen for the sampling of a given particle depends upon several factors, such as price, availability, efficiency of filtration, the requirements of analytical techniques and the capacity of the filter to maintain its filtration characteristics and integrity in the sample conditions.

The efficiency of the filter in capturing various sized particles in a sampled air is frequently one of the most important factors in the selection of a filter medium. As the deposition of the particles over the filter substrate is dependent on several mechanisms it becomes obvious that the efficiency of sampling of an aerosol varies with the velocity of filtration, the size of the particles and the amount of material already collected. Low sampling velocities improve the collection of smaller particles due to the action of diffusion processes. An increase in the sampling velocity decreases the efficiency of diffusion but increases inertial forces with consequent collection by impaction. At very high flow rates the efficiency of collection may decrease due to the re-entrainment of particles previously deposited.

Every filter material contains chemical species, as major, minor or trace constituents, which are different in each type of filter. [28, 29] The filter medium used for the sampling and analysis of certain particulate compounds should be free from such compounds or contain them in quantities much smaller than the amounts collected. The filter material must also be inert to the atmospheric compounds of interest to avoid spurious results.

4.1.4.2 Impingement:

Impingement for the collection of particles consists of forcing the air flow through a jet which increases the velocity of the air stream, and thereby the momentum of associated particles, followed by collision of the air stream with an abrupt obstruction.

Because of their high momentum and the abrupt change in flow direction caused by the obstruction, the particles will tend to collect at the obstruction.

Impingers have been developed to operate either wet or dry. Wet impingers are used with the jet and collecting obstruction below the surface of a liquid (in which the particles must be insoluble). Dry impingers, as the name implies, have the jet and collecting obstruction dry, although an adhesive may be used to prevent the particles from becoming resuspended.

Because an impinger uses particle inertia for collection and that, in turn, depends upon the mass and velocity of the particles, the size collection efficiency of impingers depends on the flow rate.

The dependence of the particle size collection efficiency on jet velocity has been used to advantage in the design of cascade impactors. These are devices which use a series of sequential jets and collection plates with increasing jet velocities and/or decreasing gaps between the jet and the collecting plate. As the air stream progresses through the device smaller particles will be collected more efficiently. As a result, the cascade impactor fractionates the air sample to obtain a particle size distribution.

4.1.4.3 Precipitation:

Precipitation for the collection of aerosols depends upon exposing the air stream to either a thermal or electrostatic gradient.

In the former case, a sharp temperature gradient is created by a high temperature wire suspended across a cylindrical collection chamber. [26] The temperature gradient causes the particles to migrate towards the cooler collecting surface, apparently because gas molecules in contact with the hot wire acquire higher kinetic energy and, by impacting on particulates, that part of their momentum which has a larger component in the direction of cooler regions. These devices are extremely efficient for particle sizes from 5 μm down to 0.01 μm and possibly smaller, but the basic instrument is limited to a relatively low flow rate (0.007 to 0.02 litre min^{-1}). The thermal precipitator is recommended primarily for specialised research studies where efficient collection of particles for microscopic investigation is required, but not for general aerosol sampling usage.

In the case of electrostatic precipitation, a high voltage potential (12kV, DC. or 20kV, AC.) is maintained across the plates of a capacitor with the air to be sampled flowing between the capacitor plates. The ionising potential created by the electrostatic field produces ions in the gas stream which, in turn, tend to collide with particles and charge them. The charged particles then migrate under the influence of the electrostatic field to the collecting electrode. This device has been found to be virtually 100% efficient for a wide range of particles sizes at flow rates up to 85 $lmin^{-1}$ [30].

4.1.4.4 Gravity and centrifugal collection:

Gravity and centrifugal collection depends upon the action of an external remote force on the particles to cause their movement toward a collecting surface. In the case of the former, the gravitational attraction of the particle mass towards the earth causes particles to settle at a rate dependent on the fluid drag forces counteracting gravity. For smaller particles the settling rate is small in relation to air movements with the effect that small (less than 7 μm) particles remain suspended.

In the case of centrifugal collection, the air stream is made to follow a spiral pathway in a cyclone, with the resulting centrifugal action on the particles causing them to move outward to a collecting surface. Both collection methods are limited to larger particles than are collected by other collection mechanisms and their use is aimed primarily at preliminary separation of larger particles prior to a secondary collector.

4.1.4.5 Diffusion:

The motion of suspended particles in the submicrometer range is strongly affected by random collisions with gas molecules. These particles traverse a random irregular path, their position at any given time being dependent on their most recent collisions with molecules. This movement is called Brownian diffusion and is, at a given temperature, dependent on particle dimensions. Smaller particles with less momentum are more strongly affected by collisions with molecules and present higher diffusion velocities than larger particles.

Brownian diffusion is the mechanism used for the fractionation and collection of aerosols smaller than 0.3µm, particles for which gravitational, centrifugal and impaction mechanisms are inefficient.

The fractionation of particles smaller than 0.3µm is achieved with the diffusion battery which is an assembly of equally spaced circular tubes or holes, through which the air flow containing the aerosol passes. Due to Brownian motion the particles diffuse to the walls where they stick and are removed from the airborne state since, upon physical contact, surface adhesive forces dominate. At the boundary of every the tube internal surface the particle concentration is nil and a gradient of aerosol concentration exists along the tube radius and tube axis. Smaller particles, having larger diffusion coefficients, are collected preferentially, the sampled air becoming enriched in larger particles. Fractionation of aerosol mass according to diameter can be achieved with a cut-off diameter dependent on the length of the diffusion tubes. Several lengths can be obtained by an assemblage of smaller units in series.

4.2 Experimental work

4.2.1 Control of HCl:

Pure PVC without any additives was used as a reference material for experiments and experiments were conducted with mixtures of PVC and CuO, PVC and Al_2O_3, PVC and Fe_2O_3, PVC and ZnO and PVC and MoO_3.

The decomposition of PVC and PVC in the presence of CuO, Al_2O_3, Fe_2O_3, ZnO or MoO_3 was investigated in an electric furnace with temperature programming from room temperature to 600 °C, with a constant heating rate of 10C° min^{-1}, under air atmosphere with a flow rate 50 ml min^{-1}.

The combustion was carried out were run in a flow reactor consisting of a silica tube (110 cm length, 5 cm ID) located in a furnace. The sample, 2mg PVC or 2mg PVC with 0.2mg, 2mg and 6mg of one of the above metal oxides, was held in a silica combustion boat.

The HCl gas from the combustion was trapped by drawing the gases through a series of two bubblers, each containing 30 ml of absorption solution (0.00075M $NaHCO_3$ and 0.0022 M Na_2CO_3) while the second bubbler was a fritted bubbler.

A Dionex Ion Chromatograph model 2010i with a conductivity detector was used for analysis of HCl and chloride.

4.2.1.1 Results:

Table 4-4 shows the concentration of HCl from combustion of PVC and PVC in the presence of CuO, MoO_3, Fe_2O_3, ZnO and Al_2O_3 at different concentrations of metal oxide. The results show that the production of HCl in the presence of metal oxide is less than from the combustion of pure PVC and that the levels of HCl decrease with an increase in the amount of metal oxide present.

Table 4-4: Concentration of HCl (ppm) from combustion of PVC and PVC in presence of some metal oxide at different concentrations (% wt)

Sample	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	10950	-	_	_
[illegible]	-	6500	1050	680
[illegible]	-	7820	1130	730
[illegible]	-	11000	4018	2536
[illegible]	-	9100	2210	1700
[illegible]	-	7950	1270	850

HCl produced during the degradation process autocatalyzes the HCl elimination reaction. The HCl elimination from the polymer causes conjugation of the polyene linkages which grow until the chain is stabilised by the resonance energy. HCl once produced, however, can interact with the double bond of the polyene linkage, thus reducing the effective size of the polyene linkage. When the size of polyene linkage is reduced, chlorine becomes destabilised and HCl is further eliminated. This catalytic effect of HCl has been confirmed by various workers. [31, 32, 33]

The effect of cupric oxide, zinc oxide, molybdenum trioxide, ferric oxide and aluminium oxide on reducing the catalytic effect of HCl produced is also shown in Table 4-4 in the present study.

Chlorine can also react with some metal oxides to produce metal chloride as in the following reaction:

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

4.2.2 Control of aromatic and chlorinated aromatic hydrocarbons:

The results in chapter 3 described an investigation of the thermal degradation of PVC and mixtures of PVC with $CuCl_2$, CuO and copper. The results show that the thermal degradation of PVC occurs in two stages and emission of chlorinated aromatic hydrocarbons and aromatic hydrocarbons in the presence of cupric oxide is less than emissions from pure PVC and other mixtures. The effect of several metal oxides on the pyrolysis of PVC has been receiving increased attention, because of the potential interest in these materials as fire retardants and smoke suppressants. Brauman [33] investigated the effect of iron (III) pyromellitate, zinc pyromellitate and molybdenum trioxide on the thermal decomposition of rigid PVC. She found that the iron compound decreased the amount of pure aromatics formed against a control formulation containing no additive. Blazso and Jakab [34] investigated the effect of some metals (aluminium, iron and zinc), metal oxides (aluminium, titanium, copper and iron) and carboxylates (zinc and tin) on the thermal decomposition processes of PVC. They found benzene formation was hindered by the metals, metal oxides and carboxylates. Their results showed increased benzene evolution on alumina (and to a lower extent on titanium dioxide). Lida and Goto

[35] found a decreased amount of aromatic volatiles, but an increased amount of alkylaromatic volatiles among the thermal decomposition products of PVC in the presence of copper and iron oxides. Muller [36] investigated the formation of aromatics during pyrolysis of PVC in the presence of metal chlorides.

4.2.2.1 Experimental:

To study the effect of metal oxide on the combustion of PVC, a electric furnace with a silica tube was used (chapter 3 section 3.3.2.1).

In this study the combustion of pure PVC was used as control and mixtures of PVC powder and CuO, ZnO, Fe_2O_3, MoO_3 and Al_2O_3 were studied samples for comparison. The samples were placed as a thin layer in a silica combustion boat and fed to the furnace via a gate. For combustion, the samples were heated at a rate of 10C° from room temperature to 600°C and kept there for 15 minutes. The production of aromatic and some chlorinated aromatic hydrocarbons was studied in samples consisting of 2mg pure PVC or 2mg PVC and 0.1, 0.2 and 0.4mg metal oxide while for the determination of 2,3,7,8-TCDD, 100 mg samples of pure PVC or 100 mg PVC and 5, 10 or 20 mg metal oxide were used.

Sampling and analysis methods for chlorinated aromatic hydrocarbon and 2,3,7,8-TCDD were the same as those described in chapter 3 section 3.3.5. Some short chain linear hydrocarbons were also analysed by the methods described in Chapter 3 section 3.3.4.

4.2.2.2 Results:

Tables 4-5, 4-6, 4-7, 4-8 and 4-9 show the concentrations of some aromatic and chlorinated aromatic hydrocarbons from the combustion of PVC and PVC in the presence of CuO, ZnO, Fe_2O_3, MoO_3 and Al_2O_3 at 600°C with different ratios of PVC and metal oxide. The concentration of most emission gases decreases with increasing metal oxide. It is clear that some metal oxides, MoO_3, ZnO, CuO, strongly reduce the production of the emission gases.

It is clear that there is a huge difference between the concentration of aromatic and chlorinated aromatic hydrocarbon emissions from combustion of PVC and PVC in presence of these metal oxides. These results prove that aromatic hydrocarbons and chlorinated aromatic hydrocarbons are more easily released from the PVC than from PVC in the presence of metal oxides.

Tables 4-10, 4-11 and 4-12 show the concentrations of short chain linear hydrocarbons arising from PVC combustion in the presence of different concentrations of metal oxide. The results show that the presence of metal oxides increases the concentration of short chain linear hydrocarbons and with increasing metal oxide the concentration of short chain linear hydrocarbons slightly increases.

Table 4-5: Amount of some aromatic and chlorinated aromatic hydrocarbons (μg) from combustion of PVC and PVC in the presence of different concentration of CuO

Product	0%	5%	10%	20%
Benzene	500	59	45	49
Toluene	68	24	20	18
o-Xylene	0.9	0.38	0.2	0.19
Naphthalene	3.65	0.36	2.55	0.25
Chlorobenzene	1.22	0.71	0.7	0.69
Ethylbenzene	4.05	2.8	2.8	2.8
p-Dichlorobenzene	0.35	0.1	0.08	0.08
o-Dichlorobenzene	8.56	1.9	1.8	1.7
1,2,5-Trichlorobenzene	1.2	0.64	0.62	0.6
1,2,4-Trichlorobenzene	5	2.7	2	1.97
1,2,4,5-Tetrachlorobenzene	6.2	2.35	2.2	2.1
Pentachlorobenzene	3.8	1.1	1.1	1.0
Hexachlorobenzene	4	1.5	1.4	1.25
2,3,7,8-TCDD	8 ng	15.5 ng	16 ng	17 ng

Table 4-6: Amount of some aromatic and chlorinated aromatic hydrocarbons (μg) from combustion of PVC and PVC in the presence of different concentrations of ZnO

Product	0%	5%	10%	20%
Benzene	500	28	25	24
Toluene	68	36.4	31.2	27.5
o-Xylene	0.9	0.18	0.11	0.11
Naphthalene	3.65	0.67	0.54	0.51
Chlorobenzene	1.22	0.42	0.35	0.31
Ethylbenzene	4.05	1.9	1.7	1.5
p-Dichlorobenzene	0.35	0.06	0.05	0.05
o-Dichlorobenzene	8.56	1.1	1.05	1.03
1,2,5-Trichlorobenzene	1.2	0.38	0.37	0.37
1,2,4-Trichlorobenzene	5	1.5	1.3	1.2
1,2,4,5-Tetrachlorobenzene	6.2	1.6	1.5	1.4
Pentachlorobenzene	3.8	0.6	0.5	0.48
Hexachlorobenzene	4	0.9	0.9	0.8
2,3,7,8-TCDD	8 ng	9 ng	10 ng	12 ng

Table 4-7: Amount of some aromatic and chlorinated aromatic hydrocarbons (μg) from combustion of PVC and PVC in the presence of different concentrations of Al_2O_3

Product	0%	5%	10%	20%
Benzene	500	420	360	310
Toluene	68	50.6	47.3	42.8
o-Xylene	0.9	0.79	0.64	0.41
Naphthalene	3.65	3.2	2.52	0.08
Chlorobenzene	1.22	0.98	0.85	0.73
Ethylbenzene	4.05	3.81	3.2	2.7
p-Dichlorobenzene	0.35	0.32	0.29	0.21
o-Dichlorobenzene	8.56	7.3	6.89	5.5
1,2,5-Trichlorobenzene	1.2	1.02	0.98	0.55
1,2,4-Trichlorobenzene	5	4.4	3.86	2.2
1,2,4,5-Tetrachlorobenzene	6.2	6.3	6.8	7
Pentachlorobenzene	3.8	4.15	4.7	4.8
Hexachlorobenzene	4	4.2	4.9	4.7
2,3,7,8-TCDD	8 ng	6.3 ng	4 ng	3.5 ng

Table 4-8: Amount of some aromatic and chlorinated aromatic hydrocarbons (μg) from combustion of PVC and PVC in the presence of different concentration of MoO_3

Product	0%	5%	10%	20%
Benzene	500	22	20.0	18.5
Toluene	68	24.5	21.1	18.9
o-Xylene	0.9	0.23	0.21	0.18
Naphthalene	3.65	0.28	0.25	0.21
Chlorobenzene	1.22	0.3	0.3	0.28
Ethylbenzene	4.05	0.17	0.16	0.14
p-Dichlorobenzene	0.35	0.01	0.01	-
o-Dichlorobenzene	8.56	0.45	0.4	0.38
1,2,5-Trichlorobenzene	1.2	0.22	0.2	0.19
1,2,4-Trichlorobenzene	5	0.41	0.39	0.34
1,2,4,5-Tetrachlorobenzene	6.2	5.9	5.7	5.5
Pentachlorobenzene	3.8	0.25	0.21	0.20
Hexachlorobenzene	4	0.27	0.23	0.20
2,3,7,8-TCDD	8ng	9ng	11ng	13ng

Table 4-9: Amount of some aromatic and chlorinated aromatic hydrocarbons (μg) from combustion of PVC and PVC in the presence of different concentration of Fe_2O_3

product	0%	5%	10%	20%
Benzene	500	230	170	160
Toluene	68	37.6	33.8	29.9
o-Xylene	0.9	0.62	0.41	0.34
Naphthalene	3.65	1.7	1.387	1.22
Chlorobenzene	1.22	0.87	0.68	0.55
Ethylbenzene	4.05	2.9	2.1	1.6
p-Dichlorobenzene	0.35	0.23	0.17	0.14
o-Dichlorobenzene	8.26	7.6	7.2	7.0
1,2,5 Trichlorobenzene	1.2	0.9	0.65	0.47
1,2,4-Trichlorobenzene	5	3.9	3.1	2.72
1,2,4,5-Tetrachlorobenzene	6.2	5.3	4.72	3.84
Pentachlorobenzene	3.8	3.1	2.9	2.6
Hexachlorobenzene	4	3.2	2.82	2.48
2,3,7,8-TCDD	8 ng	8.1 ng	10 ng	15 ng

Table 4-10: Concentration of some short chain hydrocarbons from the combustion in air of PVC and PVC in the presence of 10% metal oxide (ppm)

Sample	Methane	Ethylene	Ethane	Propylene	Propane	N-butylene
PVC	17000	4300	5520	1250	600	3050
PVC + CuO	27500	5600	12200	3000	2400	7800
PVC + MoO_3	47600	12040	15456	3500	2900	7930
PVC + ZnO	51765	13095	17388	3806	3160	8505
PVC + Fe_2O_3	49300	12470	16560	3625	3010	8100
PVC + Al_2O_3	21000	4900	5980	1400	1100	3980

Table 4-11: Concentration of some short chain hydrocarbons from the combustion in air of PVC and PVC in the presence of 5% metal oxide (ppm)

Sample	Methane	Ethylene	Ethane	Propylene	Propane	N-butylene
PVC	17000	4300	5520	1250	600	3050
PVC + CuO	23100	4480	10736	2040	5850	4588
PVC + MoO_3	33320	9261	11040	2500	1830	5164
PVC + ZnO	43868	10733	14400	3198	2184	7145
PVC + Fe_2O_3	42869	6927	14153	3072	2528	6864
PVC + Al_2O_3	17948	4083	3147	1270	611	3344

Table 4-12: Concentration of some short chain hydrocarbons from the combustion in air of PVC and PVC in the presence of 2% metal oxide (ppm)

Sample	Methane	Ethylene	Ethane	Propylene	Propane	N-butylene
PVC	17000	4300	5520	1250	600	3050
PVC + CuO	16500	2986	8258	1457	4500	3529
PVC + MoO_3	21752	6830	82314	1287	1187	3829
PVC + ZnO	3988	9872	11350	2873	1883	5812
PVC + Fe_2O_3	40322	6535	13200	2523	1837	4735
PVC + Al_2O_3	16325	3171	2372	989	532	2931

4.2.3 Control of soot:

Polyvinyl chloride has intrinsic fire retardant properties. When it is forced to burn, however, it behaves like most organic material and evolves smoke. The combustion of benzene and other aromatic hydrocarbons is known to be an important source of smoke. A large number of chemical compounds have been reported as smoke retarders for PVC.

Saracco et al.. [37] controlled soot emission from diesel by catalytic traps. These traps are made from a ceramic foam coated with catalysts suitable for soot reduction and based on mixtures of KCl with different vanadates. Van Setten-Baal et al. [38] developed a satisfactory support for a promising catalytic phase based on eutectic mixtures of Cs_2O, V_2O_5 and MoO_3 for the oxidation of diesel soot. They found that low porous, high temperature, high strength ceramics are good supports for a molten salt soot oxidation catalyst. Jelles et al.[39] found that molten salt catalysts are highly active compared to solid single oxide catalysts, probably as a result of the increased contact area due to wetting of the soot by the mobile catalyst. Noirot et al. [40] described control of soot emissions by filtration and post combustion while Xlong et al. [41] studied the effect of ionic additives on aerosol coagulation and found that ionic additives can result in narrow size distributions and small average soot particle sizes. Chung and Tsang [42] studied the control of soot during the combustion of polystyrene. They studied the effect of various metallic additives as soot suppressants and found that soot yield could not be significantly reduced by controlling the oxidiser (air) flow rate but that the soot yield could be greatly reduced by adding small amounts of air into the pyrolysis zone of the flame. They also compared the salts of Na, K, Ca and Ba in the combustion. Ca salts were found to be the least effective in reducing soot, K and Na were nearly equally effective but Ba was found to be much more effective than all of the others with its effectiveness strongly dependent on its addition rate. Ballistreri at el. [43] studied the amount of smoke suppression induced in PVC by some metal oxides measured as a function of temperature. Panaglotou and Levendis [44] studied the combustion characteristics of four commonly encountered plastics, poly(styrene), PVC, poly(ethylene) and poly(propylene). They found that PVC exhibited the highest soot volume fraction in its flame and observed that the rate of burning was highest for PVC particles and the lowest for poly(ethylene).

The purpose of the work described here is to study the use of metal oxides to control particulate emissions from PVC combustion.

4.2.3.1 Control of soot:

The combustion chamber consists of a furnace and a flask made of silica placed in a oven equipped with an appropriate thermocouple and temperature control system. An outside air or nitrogen source, with a suitable rotameter, admit gas near to the sample at a controlled rate of 1 l min^{-1}.

The temperature is pre-set at 600°C or 800 °C. Samples consisted of 200 mg PVC powder or a mixture of 200mg PVC and a metal oxide (Fe_2O_3, Al_2O_3, CuO, MoO_3 and ZnO). The weight of metal oxide was 2%, 5% or 10% of the PVC weight. The sample was placed into a porcelain crucible which was placed into the flask through the stopper at the top of the chamber.

4.2.3.1.1 Sampling and analysis of soot:

A 37mm fibre glass filter paper or cellulose filter paper was used for the collection of soot which was drawn on to the filter by a small vacuums pump at a flow rate of 1 $lmin^1$.

Two methods were used for the measurement of soot. Firstly, calculation of the difference between weight before and after the sample was collected on the 37mm fibre glass filter paper. The filter paper was left in an oven at 110 °C for 24 hours before and after sampling because filter paper can absorb moisture from the atmosphere. Secondly, the sample was collected on the 37mm filter paper and Dunedin photo-electric cell was used to measure the soot optical density on the filter.

4.2.3.2 Results:

Tables 4-13, 4-14 and 4-15 show the amount of soot obtained from the combustion of PVC or PVC in the presence of a metal oxides. The results show that the addition of metal oxides considerably reduces the smoke evolution from PVC combustion.

The amount of soot generated in the combustion at different temperatures, is reported for pure PVC and PVC in the presence of Fe_2O_3, CuO, ZnO, MoO_3 or Al_2O_3 in this study. The results show amount of soot generated at 600 °C is higher that at 800 °C.

The results also show the amount of soot from the combustion of pure PVC and PVC in the presence of metal oxides at 2% wt, 5% wt and 10% wt. At 10% wt metal oxide the effect of cupric oxide on the control of soot is the best followed by the effects MoO_3, Fe_2O_3, Al_2O_3 to ZnO which has the smallest effect. It is clear that for molybdenum trioxide that increasing the loading from 2 to 10% reduces smoke formation.

Table 4-13: Amount of soot (g) from the combustion of PVC or PVC in the presence of 2% metal oxide

Sample	600 °C	800 °C
PVC	0.016	0.007
PVC + Fe_2O_3	0.0083	0.0047
PVC + CuO	0.0053	0.0033
PVC +ZnO	0.014	0.008
PVC + MoO_3	0.013	0.008
PVC + Al_2O_3	0.013	0.006

Table 4-14: Amount of soot (g) from the combustion of PVC or PVC in the presence of 5% metal oxide

Sample	600 °C	800 °C
PVC	0.016	0.007
PVC + Fe_2O_3	0.0072	0.004
PVC + CuO	0.005	0.0032
PVC +ZnO	0.0127	0.0071
PVC + MoO_3	0.0097	0.0073
PVC + Al_2O_3	0.0128	0.0056

Table 4-15: Amount of soot (g) from the combustion of PVC or PVC in the presence of 10% metal oxide

Sample	600 °C	800 °C
PVC	0.016	0.007
PVC + Fe_2O_3	0.0068	0.0039
PVC + CuO	0.0051	0.0031
PVC +ZnO	0.0099	0.057
PVC + MoO_3	0.007	0.0.004
PVC + Al_2O_3	0.0122	0.0053

In case of ZnO, although zinc oxide does not vaporise below 1000°C, the presence of reducing gases (combustion products) could provide a lower temperature volatilisation route. In this route, free zinc metal could be an intermediate phase, and zinc oxide aerosols or particles would be counted by a photometer as smoke or weight by balance. Tables 4-16, 4-17 and 4-18 show the reflection of light measured by a photo-electric cell for samples of soot on the filter paper in different concentrations of metal oxide and at different temperature.

The results show optical density for soot from combustion of pure PVC is higher than with metal oxide and with increase in temperature the density of soot decreased.

Table 4-16. Optical density of soot from combustion of PVC or PVC in the presence of 10% metal oxide

Sample	600 °C	800 °C
PVC	3.7	1.2
PVC + Fe_2O_3	1.7	0.6
PVC + CuO	1.5	0.5
PVC +ZnO	3	1.5
PVC + MoO_3	1.7	0.6
PVC + Al_2O_3	3.1	1

Table 4-17: Optical density of soot from combustion of PVC in the presence of 5% metal oxide

Sample	600 °C	800 °C
PVC	3.7	1.2
PVC + Fe_2O_3	1.9	0.7
PVC + CuO	1.6	0.5
PVC +ZnO	2.9	1.3
PVC + MoO_3	2.4	1.1
PVC + Al_2O_3	3.2	1.1

Table 4-18: Optical density of soot from combustion of PVC in the presence of 2% metal oxide

Sample	600 °C	800 °C
PVC	3.7	1.2
PVC + Fe_2O_3	2	0.7
PVC + CuO	1.6	0.5
PVC +ZnO	2.1	0.3
PVC + MoO_3	3.1	2
PVC + Al_2O_3	3.3	1.1

4.2.4 Solid residue:

The residue from PVC combustion in the presence of metal oxides was measured by introducing the sample (2g) into an electric furnace heated to fixed temperature under air at a flow rate of 1 l. min^{-1}. The samples were 2g PVC or mixture of 2g PVC and metal oxide (iron oxide, cupric oxide, zinc oxide, molybdenum oxide or aluminium oxide) at a concentration of 2% or 5% or 10%. After a fixed time about 5 minutes the crucible was withdrawn and cooled under N_2 (to avoid further decomposition or oxidation), and weighed.

4.2.4.1 Results:

Tables 4-19, 4-20 and 4-21 show the percent of solid residue from the combustion of pure PVC and PVC in the presence of Fe_2O_3, CuO, ZnO, MoO_3 or Al_2O_3 in air.

The results show that the solid residue increased from combustion of PVC in the presence of those metal oxide.

Table 4-19: per cent of solid residue from combustion of PVC and PVC in the presence of 2% metal oxide

Sample	450 °C %R	600 °C %R
PVC	14	9
PVC + Fe_2O_3	15	11
PVC + CuO	22	18
PVC +ZnO	30	24
PVC + MoO_3	21	17
PVC + Al_2O_3	19	14

Table 4-20: per cent of solid residue from combustion of PVC and PVC in the presence of 5% metal oxide

Sample	450 °C %R	600 °C %R
PVC	14	9
PVC + Fe_2O_3	17	12
PVC + CuO	25	21
PVC +ZnO	33	27
PVC + MoO_3	23	19
PVC + Al_2O_3	20	16

Table 4-21: per cent of solid residue from combustion of PVC and PVC in the presence of %10 metal oxide

Sample	450 °C %R	600 °C %R
PVC	14	9
PVC + Fe_2O_3	22	14
PVC + CuO	29	25
PVC +ZnO	32	27
PVC + MoO_3	27	22
PVC + Al_2O_3	24	18

4.3 SUMMARY:

Based on this study the following overall observations can be made:

A) Metal oxides specially transition metal oxides promote crosslinking of decomposing PVC chains to yield char as a residue.

B) Formation of aromatic hydrocarbons and chlorinated aromatic hydrocarbons are hindered by metal oxides in combustion of PVC.

C) The levels of HCl emissions from the combustion of PVC in the presence of metal oxides are less than its in the absence of metal oxide. The reduction occurs when HCl reacts with the metal oxide to form chlorides and is resulted to the concentration of metal oxide.

E) The concentration of metal oxides present is important in the control of aromatic hydrocarbons and chlorinated aromatic hydrocarbons. With increasing concentration of metal oxide from 0% to 5% the emission of chlorinated aromatic hydrocarbons and aromatic hydrocarbons decreased while emissions of the short liner hydrocarbons increases.

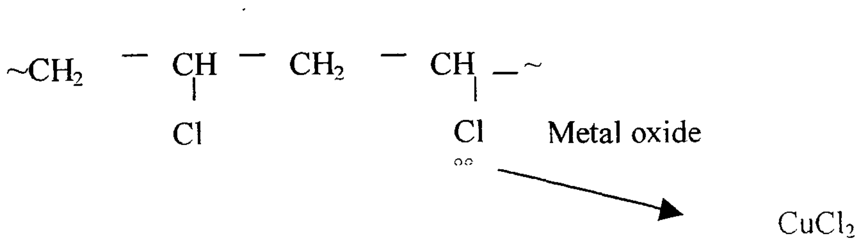
4.4 DISCUSSION

Consequent interaction of the organic free radical product can lead to cyclisation in the final steps (V and VII) of benzene formation (scheme 4-2).

The fact that the amount of aromatics are decreased and the amount of short linear hydrocarbon molecules emitted are increased means that most of this final stage is suppressed in the present of Cu or CuO.

There are two possible mechanisms by which this could be achieved.

1) The $CuCl_2$ formed in the process is a Lewis acid and formed complex easily in the case of PVC. The complexes are likely to be formed with the Cl donor atoms in the PVC fragments, for example:



$$\sim CH_2 - \underset{Cl}{CH} - CH_2 - \underset{\underset{\circ\circ}{Cl}}{CH} - \sim \xrightarrow{\text{Metal oxide}} CuCl_2$$

Complex formation affects the nature of the reaction in the system, thus suppressing the formation of the precursor to the aromatic molecules and at the same time providing more short linear hydrocarbon fragments.

2) Cu and CuO could catalyse either or both of the following reactions:

- Crosslinking by free radical reaction
- Reaction at double bonds

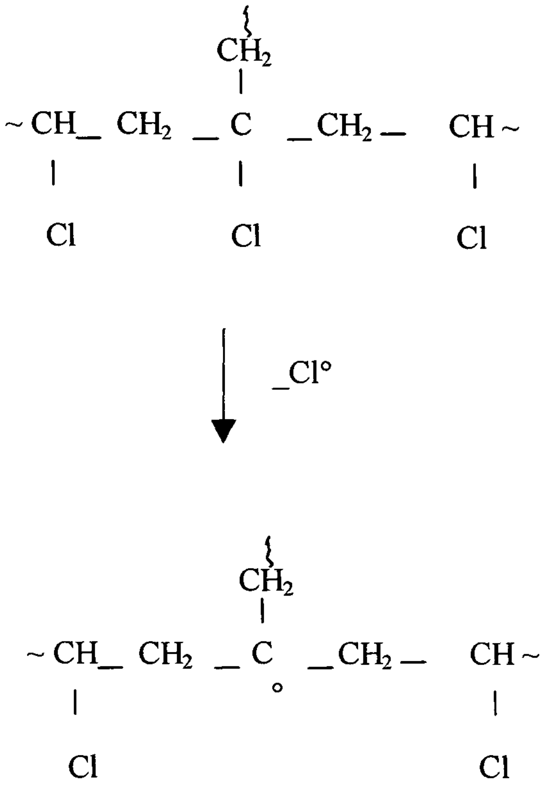
Either catalysis process would lead to the observed decrease in emission of aromatic molecules.

Other metal species depend upon:

1) ability to react with HCl

2) Lewis acid properties of metal chloride

3) effect of the relevant catalyst mechanism for the individual molecules.



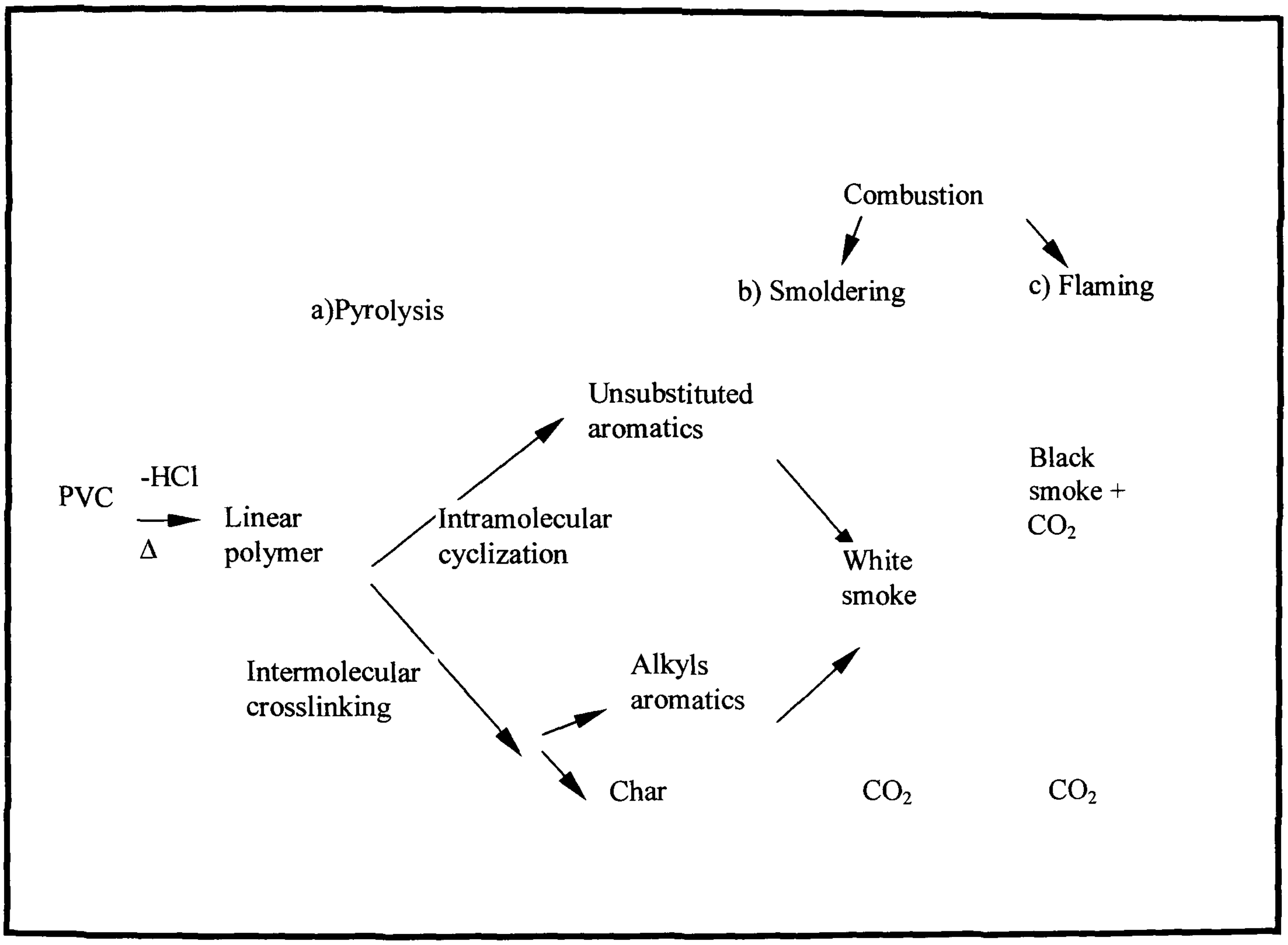
The reaction of the Cl° radical will be with H° radical also formed in the process to give HCl. The amount of HCl emitted from the system will, however, be reduced by reaction with metal or metal oxide, for example:

$$CuO \quad + \quad 2HCl \longrightarrow CuCl_2 + H_2O$$

A large amount of smoke is produced from the combustion of PVC by producing aromatic hydrocarbons. (scheme 4-1)

Lewis acid promoted pathways have been proposed for the thermal decomposition of PVC in the presence of metal oxide. These routes are summarised in scheme 4-1.

Looking at the whole process in the pyrolytic stage, metal oxides catalyse the crosslinking reaction of the polyene chains formed in the primary step, thus causing a reduction in the aromatic hydrocarbons evolved. Some worker has shown an increase in char residue when PVC is heated in the absence of oxygen. According to present results mainly unsubstituted aromatic hydrocarbons are suppressed because metal oxides catalyse the intermolecular crosslinking reaction at the intermolecular reaction which lead to polyene rearrangement.



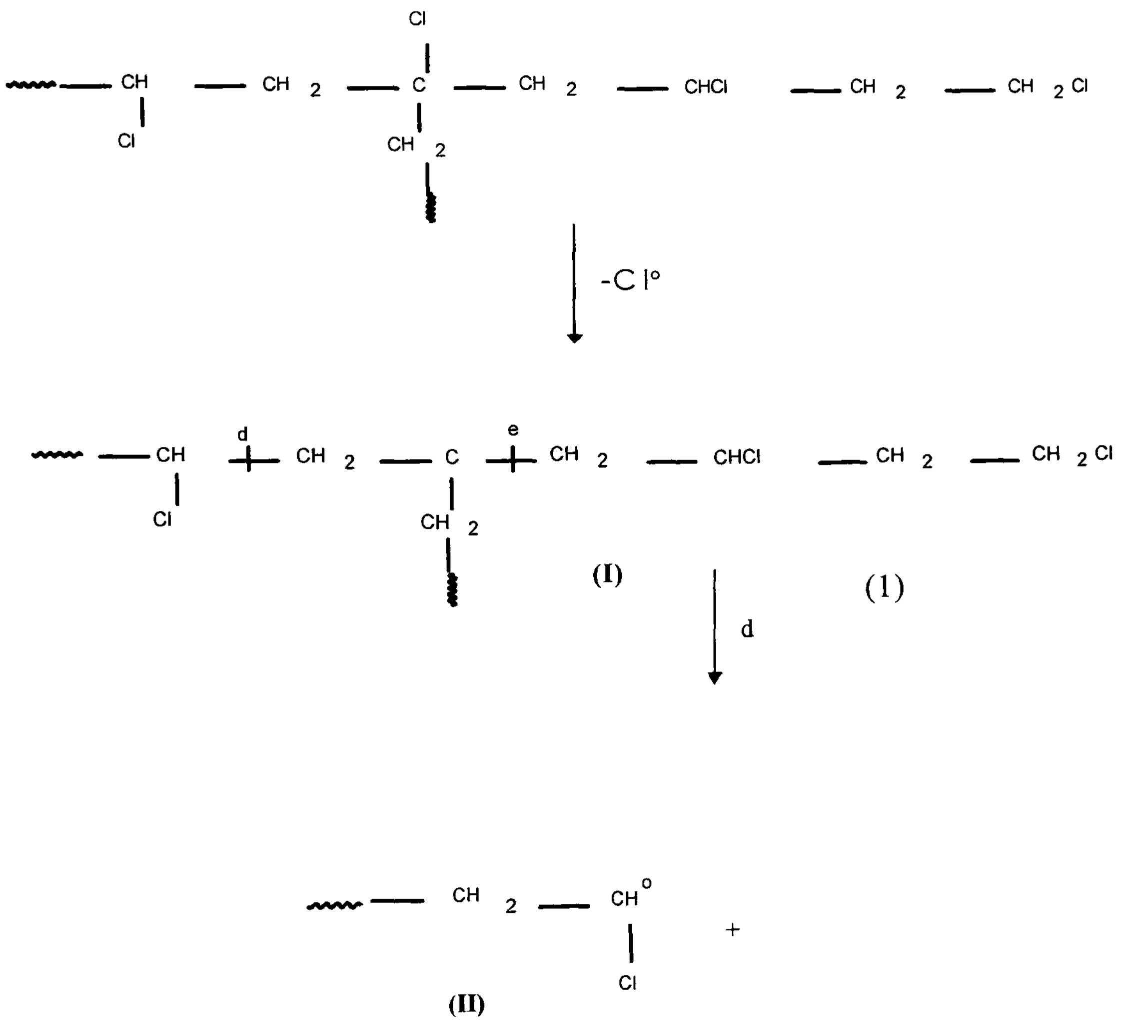
Scheme 4-1: The thermal decomposition of PVC

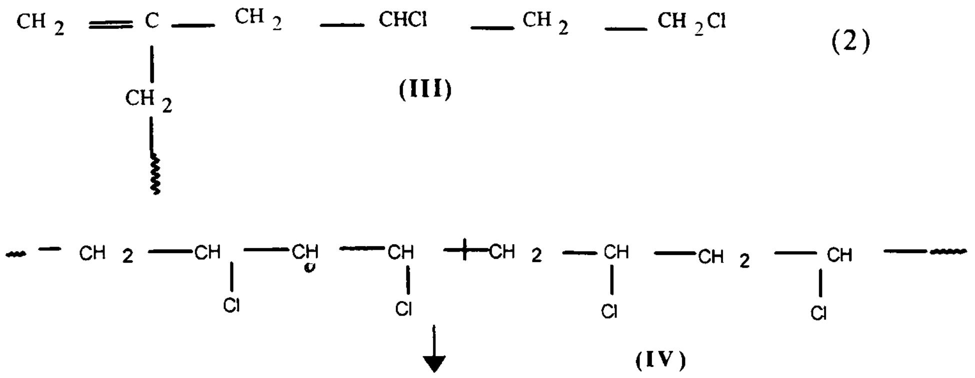
Smoke evolution is suppressed because of fuel reduction. Once this stage has been completed the same additives catalyse the char oxidation to CO_2 and cause a decrease in the combustion residue. At higher temperature the combustion becomes flame and the fuel evolution of CO_2.

4.4.1 Mechanism of the formation of some aromatic hydrocarbons:

4.4.1.1 Benzene:

Benzene is the most abundant aromatic compound formed during the pyrolysis of PVC, and considerable efforts have been made to elucidate the mechanism of its formation. [45,46] Intramolecular cyclization of polyene sequences to form benzene has been considered several times, and O'Mara proposed that this process might involve the formation of a vinyl or polyene radicals by chain scission. [26] The cyclization reaction would then occur by a depropagation process, with subsequent splitting off of benzene and regeneration of the radical end [45 46, 47, 48] The scheme 4-2 shows the mechanism of benzene formation initiated by tertiary Cl scission.

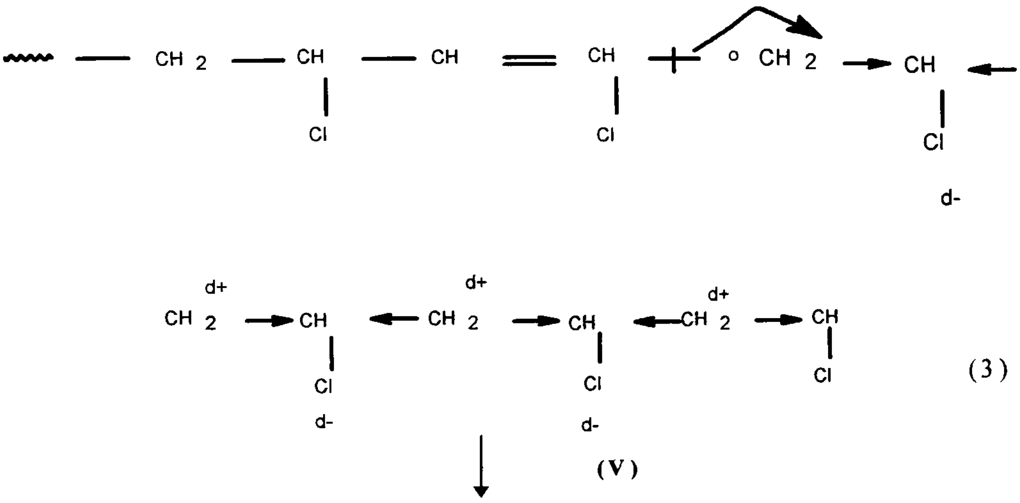




(III)

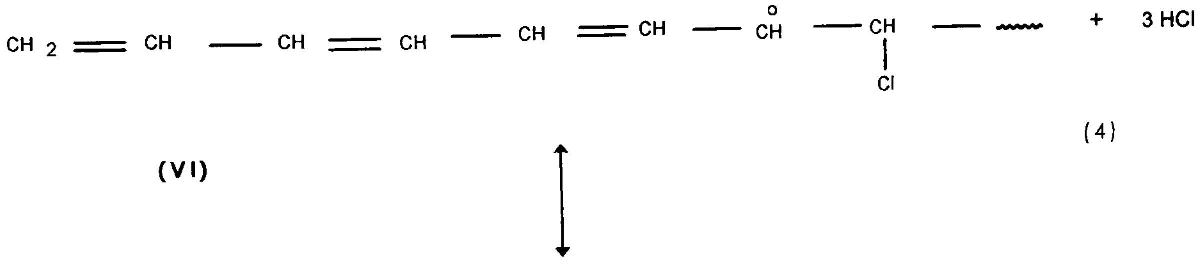
(IV)

(2)



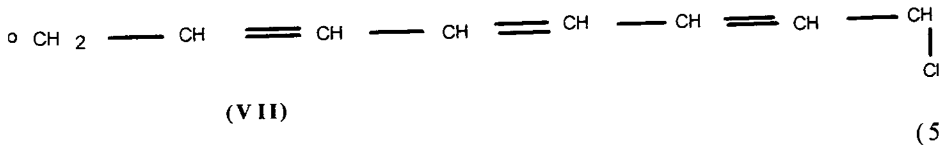
(V)

(3)



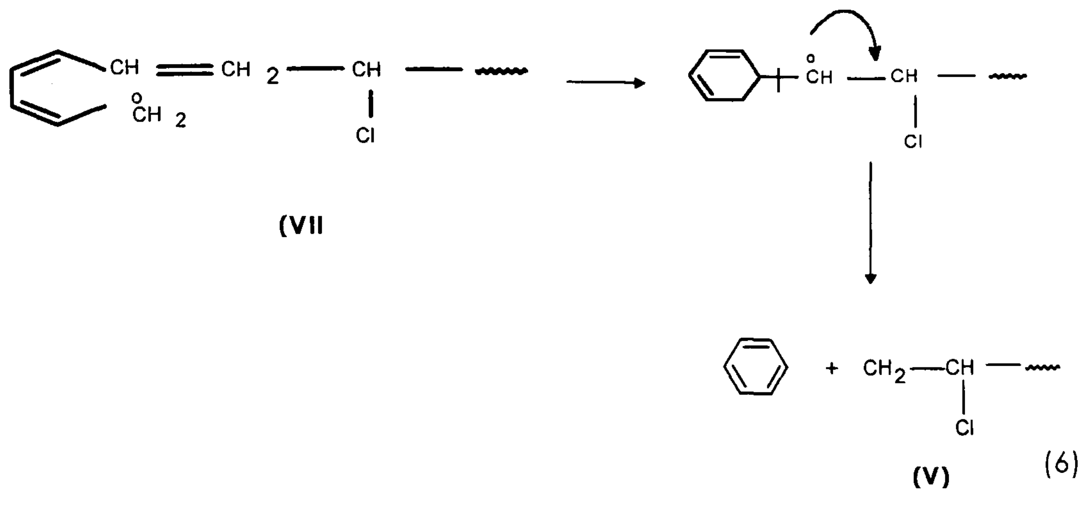
(VI)

(4)



(VII)

(5)



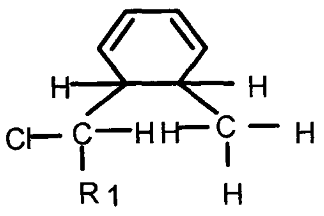
Scheme 4-2: Benzene formation initiated by tertiary Cl scission

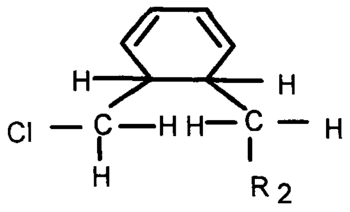
The macroradical I formed through tertiary Cl scission (reactionl) would usually split in position d with formation of macroradical II and macromolecule III (reaction2). Its main reaction route in the absence of monomer is likely to be H atom abstraction from another chain or from its own chain (back biting at the fifth C atom).

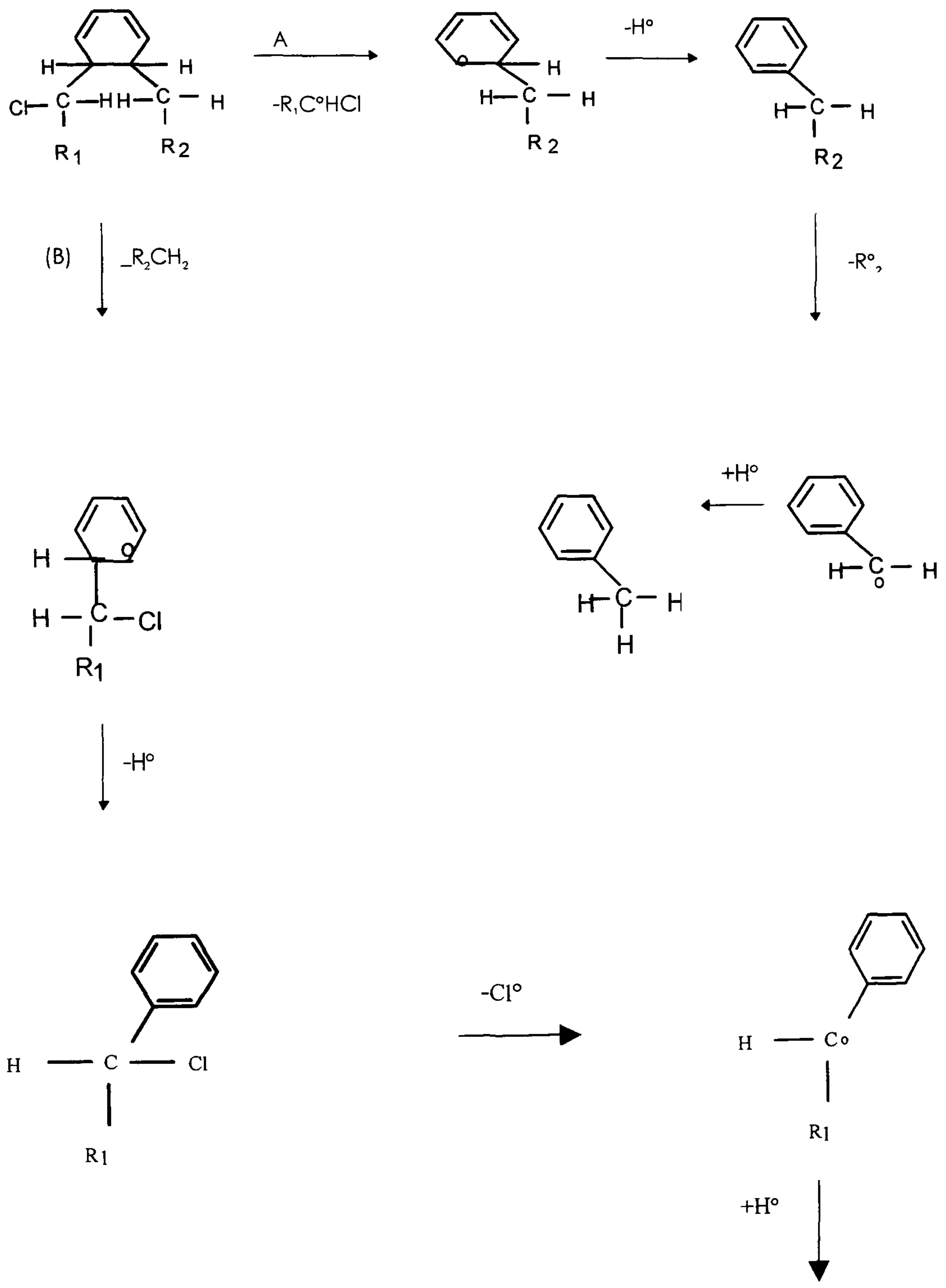
The Cl atom expelled in reaction (1) will give a random attack on any macromolecule. The affinity of Cl atom for the CH_2 group would lead to H abstraction through which radical IV is formed. Radical IV can split (reaction 3) leading to radical V which has a structure more favourable to zip dehyrochlorination. The electron withdrawing effect of Cl polarises the bonds in radical V by which radical VI results after three double bonds have been formed (reaction 4). Radical VI has a resonance form VII. It is proposed that radical VII attacks the double bond at the sixth C atom closing a cyclohexadiene ring then split the bond to the ring as this bond is weakened by the withdrawing effect exerted by the Cl atom on the radical. The scission is followed by aromatisation and H atom rearrangement so that no H transfer from other molecules is needed.

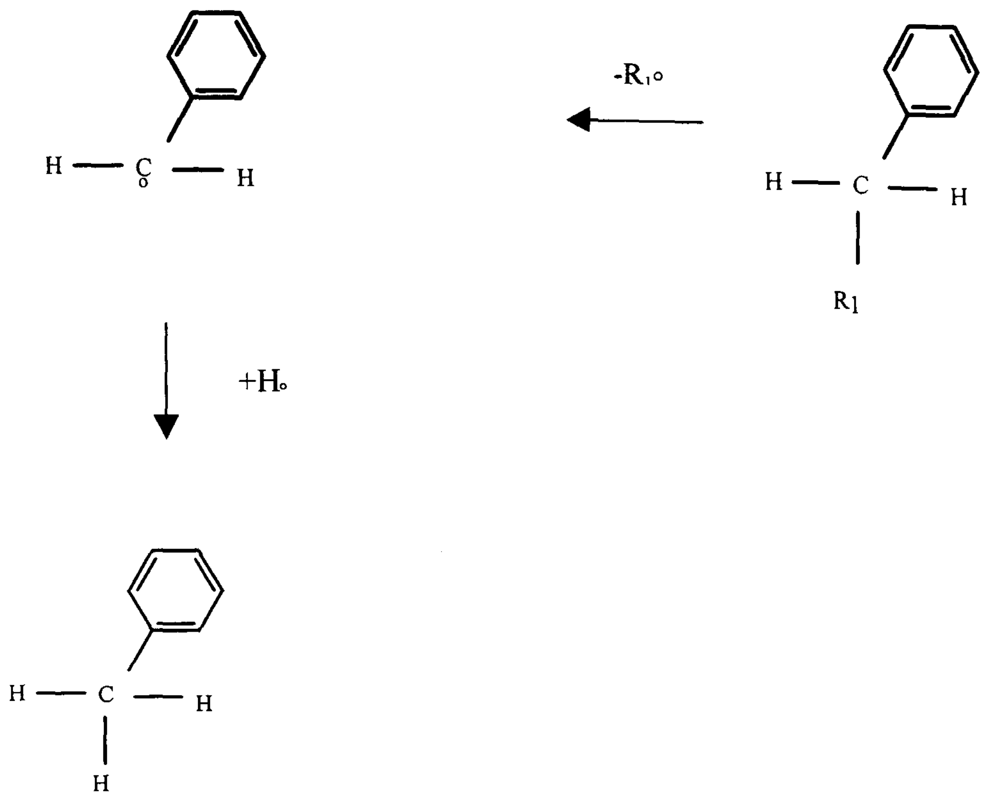
4.4.1.2 Toluene:

An alternative to scheme 4-2 would be the formation of intermediates in which methyl groups attached to cyclohexadiene rings are “preformed” in the early stages of polymer decomposition. The same cyclohexadiene intermediate (VI) would be the precursor to yield intermediates:





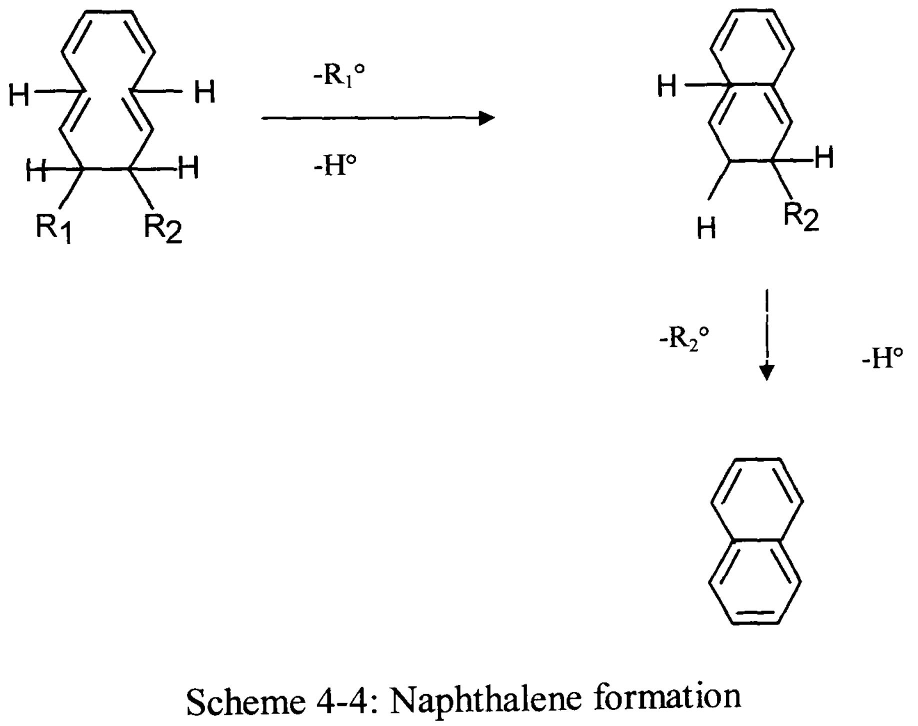




Scheme 4-3: Toluene formation

4.4.1.3 Naphthalene:

Scheme 4-4 suggests a cyclodecate triene intermediate for naphthalene; other close variations of scheme 4-4 also can be drawn.

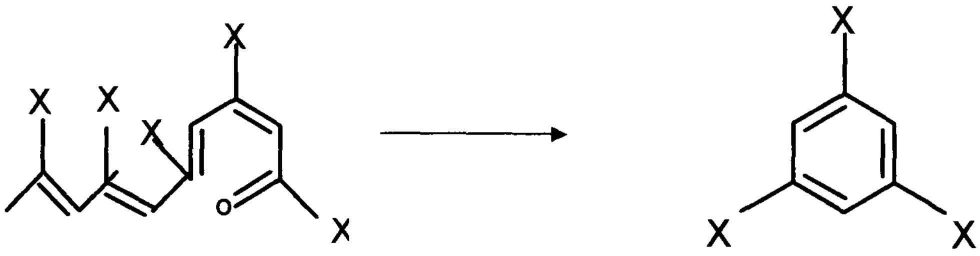


Scheme 4-4: Naphthalene formation

4.4.1.4 Halogenated Aromatic Hydrocarbon:

Unsubstituted aromatics may be produced equally well by intramolecular cyclization of the polyene. radicals, starting from opportunely folded chains, as shown in schemes 4-2 and 4-3. It can be seen that the mechanism proposed is quite homogeneous and accounts for the simultaneous evolution of unsubstituted aromatic in the pyrolysis of PVC.

In fact, the cyclization of halogenated polyene radical explains nicely the formation of the halogenated condensed aromatics. (scheme 4-5)



Scheme 4-5: Trichlorobenzene formation

4.5 CONCLUSION:

The presence of cupric oxide and other metal oxides used alters the course of all of the reactions described in this section. The nature of the interaction will vary with details of the reaction mechanism, but the removal of chlorine from the system as copper chloride must have a major effect on direct reactions with HCl and free radical reactions involving Cl° radical and free radical. Since metal oxide can also act as heterogeneous catalysts, it is also possible that they affect the course of crosslinking and addition reactions at double bonds.

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CHAPTER FIVE: APPLIED FIELD CONTROL OF SOOT PARTICULATE EMISSIONS IN THE COMBUSTION OF LIQUID AND GASEOUS FUELS

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5.1 Introduction:

The five principal classes of pollutants from combustion sources are carbon monoxide, nitrogen oxides, sulphur oxides, organic compounds (unburned and partially burned hydrocarbons) and particulate (soot, fly ash and aerosols).

The emission levels from specific combustion devices depend on the interaction between physical and chemical processes occurring within the device.

Most previous studies on soot have been directed towards examination of the mechanism of soot formation and the measurement of soot concentration in a flame. Ayachiet et. al [1] measured the soot concentration and the diameter of particles in the combustion chamber of a diesel engine. They reported that the diameters of soot particles were about 200 nm and the particle density reached 10^{15} particles / m^3. Other workers [2] have studied the temperature and soot particles on the centre line of axisymmetrical laminar diffusion flames and Arai et. al. [3] have reported that the maximum soot concentration in the turbulent diffusion flame increases with increasing temperature of the soot formation zone in the flame. Weinberg et al [4, 5, 6] have suggested that the growth of soot particles in a flame is related to the presence of charged species.

There have been a few studies on the effects of magnetic field on combustion. The first investigation on the effects of applying a magnetic field to a flame in the atmosphere was reported by Faraday [7] who found that diamagnetic gases such as nitrogen and hydrogen made a detour around the magnetic poles in air. The effects of magnetic fields on the combustion of alcohol and hydrocarbons in the presence of platinum catalysts has been studied to simulate, in part, the oxidation of organic matter in the living body and it has been found that combustion velocity and temperature are influenced by magnetic fields. The combustion temperature of alcohol decreased within a range 100-200°C when the combustion site was exposed to gradient magnetic fields in a range 20-200 T under 0.5-1.4 T. [8]

Cozens et. al [9] have commented that any electric force generated by polarisation in the flame is too small to be an action force and that the laminar flame is bent because the pressure exerted by a magnetic field is larger than the pressure drop in the flow.

H. Tanaka et. al [10, 11] found the deformation of the diffusion flame in a magnetic field was a consequence of the pressure acting on the interface between the flame and air.

N.I. Wakayama [12, 13] showed that the action of magnetic force on paramagnetic oxygen gas can be expressed as:

$$F = \frac{1}{2} pO_2 \, (\text{susc}) \, O_2 \, H^2$$

where (susc) O_2 is the magnetic susceptibility of O_2 gas and pO_2 is its partial pressure and H is the magnetic field strength. He also found the flame temperature could be increased by up to 120°C in an applied field and explained this effect in terms of inhomogeneous magnetic fields that promote combustion reactions in a diffusion flame because a homogeneous field does not have any effect. [14]

The effect of an alternating electric field on the radiation spectrum of a smoking flame has been studied.[15] The soot formation, nucleation and growth in laminar acetylene / air diffusion flames in applied field have been investigated by Faeth et al. [16,17] They reported that soot formation began when the temperature was about 980°C and that the decomposition yielded acetylene. Du et al. [18] reported the effects of various gaseous additions on the soot particle in a strained diffusion flame and found the addition of H_2 increases flame temperature.

Saito et al [19] found the shape of the flame changes remarkably in an electric field and varies with applied voltage and electrode gap and that at an applied voltage over 8kV, the flame temperature reached above 2000°C for acetylene. Kono et al [20] showed that the sooting tendency of diffusion flames changes with the frequency of applied alternating electric field. Some workers have explained such changes of flame shape and area in terms of ionic wind.

5.1.1 Definition of combustion

Combustion is the rapid exothermic oxidation reaction with the ability to propagate through a suitable medium. The rapid reactions produce gradients that transport processes convert into heat and species fluxes that speed the reactions. Under suitable conditions, almost everything that can undergo a rapid exothermic oxidation can burn.[21]

Flames produced from a single initial reactant are called decomposition flames. More commonly, however, combustion involves a pair of reactants. Complex mixtures can burn, but reactants can usually be classified as either fuels or oxidisers.

The traditional flame has two reactants, a fuel and an oxidiser. A majority of the elements and their compounds are considered fuels relative to oxygen. Combustion results in direct emissions of reactive or unreactive gases and aerosols. The composition and relative abundance of products emitted are primarily related to the fuel composition itself and, to a significant extent, to the physical characteristics of the combustion process. Fuels are mainly of a carbonaceous nature, so combustion produces primarily CO_2 and H_2O:

$$(C_xH_yO) + O_2 \longrightarrow xCO_2 + 1/2y\,H_2O$$

The chemical composition of combustion plumes is, however, more complex. A principal important parameter is the presence in the fuel matrix of other elements such as S, N or trace elements. It is also important to consider the physical conditions of the combustion process which determine deviations from the " ideal" combustion case and hence formation of more reduced species. There is a vast array of reduced carbonaceous species which may be produced in the atmosphere by combustion, either as gases (CO, CH_4, hydrocarbons, organic gases, volatile organic compounds) or aerosols.

Following Goldberg [22] formation of aerosols may be explained by the dismutation of carbon monoxide through the reaction:

$$2CO \longleftrightarrow C + CO_2$$

or by polymerisation /dehydrogenation of the fuel (R_iH) under the oxidative action of the hydroxyl radical or any oxidant:

$$R_iH + OH^\circ \longrightarrow R_i^\circ + H_2O$$

$$2R_i^\circ + CO \longrightarrow R_iCO + R_h^\circ$$

$$CO + OH^\circ \longleftrightarrow H^\circ + CO_2$$

$$H_2 + OH^\circ \longrightarrow H^\circ + H_2O$$

$$R_h + R_iH \longrightarrow R_{h+i}H \quad \text{(Polymerisation)}$$

Fresh combustion-derived particles may be presented as a carbonaceous matrix with inclusions of various trace elements. The relative importance of non-carbon atoms in combustion aerosol is related to several important determining factors. These include: the initial composition of the fuel matrix, the volatilisation capability of a given element in derived products and the mode of production of particles (primary vs. secondary production).

Finally, aerosols evolve in the atmosphere by interactions with other species, and upon entering cloud systems they undergo major coagulation and chemical reaction. Ageing phenomena severely affect the surface of particles and thus "old" combustion particles are probably different from "fresh" ones. On average, old combustion particles are heterogeneous particles consisting of a carbonaceous core covered by a coating of organic materials and electrolytes among which sulphate is often the most important component from the environmental viewpoint.

5.1.1.1 Diffusion flames

If the fuel and oxidiser are introduced separately and the flow is laminar, the combustion is usually limited by diffusional mixing of the reactants. [23] Diffusion flame geometry is controlled by diffusion, as the name suggests.

5.1.1.2 Turbulent flame:

Turbulent flames dominate most commercial combustion processes. The most obvious effect is the increase in effective flame speed or volumetric heat release rate. Much of this may be geometric in origin rather than fundamental mechanism changes. [23]

5.1.1.3 Soot:

Most of the early work on soot formation under premixed conditions was conducted with air as the oxidiser. It can be concluded that ethane has a greater sooting tendency than ethene or acetylene with the general order being:

aromatics > alkanes> alkenes> alkynes

The most extensive early data of sooting under laminar diffusion flame conditions, as measured by the smoke-height method, were obtained by Schalla and co-workers [24] who confirmed the general sooting tendency order.

Upon comparison, the trends of the alkyl compounds in the premixed case revealed an inconsistency with the oxidation reaction mechanism of ethane under fuel rich conditions: It was found that the alkane was rapidly converted first to alkene and then to the alkyne.[23, 25, 26] Thus one would expect the alkynes to exhibit the greatest sooting propensity under premixed conditions. Milliken found that the cooler the flame, the greater the tendency to soot and that when two competing rate processes were occurring in the sooting flame viz. the pyrolysis rate of the fuel and the rate of oxidative (hydroxyl radical, OH°) attack on the precursors. Both rates increase with temperature, but the oxidative rate increases faster. Other studies [27, 28] verified Milliken's calculations and extended the concept by showing that in diffusion flames, where there is no oxidative attack on the precursors, the soot volume fraction created increases with temperature.

Harris and Weiner [29, 30] have contributed much to the study of soot particle history in premixed flames. They used laser light scattering and extinction measurements to determine particle size, number density and volume fraction in experiments with flat flame burners stabilised by a water-cooled porous plug.

5.1.1.3.1 Chemical mechanisms of soot formation :

The chemistry of fuel pyrolysis, and hence fuel structure, plays an important role in sooting diffusion flames. The identical chemical character of the soot formed from diffusion or premixed controlled systems seem to suggest a commonality in the chemical mechanism for soot formation. Apparently, there is an underlying fuel-independent general mechanism that is modified only with respect to alternative routes to intermediates. These routes are simply affected by the combustion system temperature and the general character of the initial fuel. Essentially, this concept implies that the relative propensity of one fuel to form soot compared to another is primarily determined by a difference in the initial rate of formation of the first and second aromatic ring structures.

5.1.2 Analysis of organic (OC) and black(BC) carbon aerosols:

The total carbon (TC) content of aerosols is determined after removal of carbonates, by burning particles accumulated on carbon-free collection surfaces (glass, quartz or silver fibre filters). The amount of carbon is obtained by a carbon analyser using infrared, chromatographic or coulometric detection of CO_2. The limiting factor of the analytical protocol, especially for OC analyses, is the filter blank which is of the order of $1.5 \pm 1 \mu gC\ cm^{-2}$.

The black carbon (BC) content of aerosols is determined by a wide variety of methods, [31, 32] all techniques being based on an operational definition of BC. The main concern is to ensure a sufficient overlap of results using different methods which remains difficult even for methods of the same type. [33]

- **Optical methods:**

In optical methods, BC is considered to be the most effective absorbent of the aerosol for visible atmospheric radiation. Methods are based on the degree of attenuation of a reflected or transmitted light beam. Particles are analysed as a filter deposit by instruments such as the aethalometer. [34] In this device, reflection on the filter surface or multi- scattering by the particle deposit [35] are artefacts that should be taken into account.

If a fibre filter is used, multi-reflections inside the fibrous matrix enhances the measurements sensitivity. A more sophisticated technique, the "integrating sphere", has been described by Heintzenberg. [36] In this procedure, aerosols are dispersed in a liquid and are supposed to be closer to their atmospheric state than when deposited on a filter and the multiple reflections on the sphere walls also ensure a satisfactory sensitivity. Furthermore, all the light scattered is integrated, ensuring more reliable measurements than with other methods such as the integrating plate method. [37]

Optical determinations of BC contents are very sensitive and may permit on-line measurements.

5.1.2.1 Optical microscopy

Optical microscopy is most often used for the examination of particles from about 3μm to 1mm. The theoretical lower limit is approximately 0.2μm but the diffraction halo around the particle gives a gross over estimation of particle size. The most severe limitation of this method is the small depth of focus so that, for a sample having a wide range of sizes, only a few particles are in focus in any field of view. The surface of particles larger than about 5μm can be studied by reflected light, but only transmission microscopy is suitable for smaller particles.

5.1.2.2 Electron microscopy:

Transmission electron microscopy (TEM) is used for the direct examination of particles in the 0.001-5μm size range. The TEM operates by flooding the sample with an electron beam, most commonly at 100-200 kV, and generating an image on a fluorescent screen or a photographic plate. Analyses can be performed directly on the screen images, but this ties down the instrument for long periods of time. Hence it is more usual to analyse the photographic images.

TEMs operate in the magnification range from about 600 X to 1000000X. Some TEMs have a closed circuit television system fitted so that the image can be fed directly to an automatic image analysis system.

Specimens for TEM are often deposited on or in a thin membrane which rests on a grid. These grids are usually made of copper and form a support for the sample.

5.1.3 Particle size:

The images seen in a microscope are projected areas whose dimensions depend on the orientation of particles on the slide. Particles in stable orientation tend to present their maximum area to the microscope, hence the sizes measured by microscopy tend to be greater than those measured by other methods; that is, the smallest dimension of the particles are neglected. Any one particle has an infinite number of linear dimensions hence, if a chord length is measured at random, the length will depend upon the particle orientation on the slide. These orientation dependent measurements are known as statistical diameters, acceptable only when determined in such numbers as to typify a distribution. They are measured parallel to some fixed direction and are acceptable only when orientation is random; i.e., the distribution of diameters measured parallel to some other direction must give the same size distribution.

5.1.3.1 Acceptable statistical diameters

Acceptable statistical diameters are:

- Martin's diameter (d_m) being the length of the line which bisects the area of the projected area of the particle. The line may be in any direction, but must be maintained constant throughout the analysis. [38]

- Feret's diameter (d_F) is the distance between two tangents on opposite sides of the particle parallel to some fixed direction. [38]

- The projected area diameter (d_a) [38] takes into account both dimension of the particle in the measurement plane, being the diameter of a circle having the same projected area as the particle. It is necessary to differentiate between this diameter and the projected area diameter for a particle in random orientation (d_p) since, in this case, the third and smallest dimension of the particle is also included.

5.1.3.2 Particle size analysis by image analysis:

Whenever a sample is prepared for particle size analysis, it should be examined by microscopy. Such an examination allows an estimate of the particle size range of the powder under test and its degree of dispersion.

Microscopy is often used as an absolute method of particle size analysis since it is the only method in which the individual particles are observed and measured.

A size analysis by number is simpler to perform than an analysis by mass since, in the former, the statistical reliability depends solely on the number of particles measured.

Light microscopy is suitable for the measurement of particles in the size range from 3 μm to 1mm. For the range under 3 μm scanning electron microscopy (SEM) or TEM can be used.

5.1.4 Definition of a magnet:

Magnetic phenomena were first observed at least 2500 years ago in fragments of magnetised iron ore found near the ancient city of Magnesia. Permanent magnets were found to exert forces on each other as well as on pieces of iron that were not magnetised. Before the relation of magnetic interactions to moving charges was understood, the interactions of permanent magnets and compass needles were described in terms of magnetic poles.

The concept of magnetic poles may appear similar to that of electric charge and north and south poles may seem analogous to positive and negative charges. But the analogy can be misleading. While isolated positive and negative charges exist, poles always appear in pairs.

5.1.4.1 Magnetic field:

The space in which magnetic forces act is called a magnetic field. Magnetic field is a vector field, that is, a vector quantity associated with each point in space.

If a 1μC charge and a 2μC charge move through a given magnetic field with the same velocity, the force on the 2μC charge is twice as great as that on the 1μC charge. The magnitude of the force is also proportional to the magnitude, or " strength", of the field. If the magnitude of the field becomes doubled changing the charge or its velocity, the force doubles.

The magnetic force also depends on the velocity of a moving particle. The magnitude F of the forces is found to be proportional to the component of V perpendicular to the field; when that component is zero (that is, when V and B (magnetic field) are parallel or antiparallel), the force is zero. [39, 40]

The following equation shows the magnetic force on a moving charged particle force on a charge q moving with velocity V in a magnetic field B

$$F = qV \times B$$

This equation is valid for both positive and negative charges.

From this equation the units of B must be the same as the units of F/qV. Therefore the SI unit of B is equivalent to 1 N.S/C.m, or since one ampere is one coulomb per second (1A=1C/S), 1N/A.m. This unit is called the Tesla(T). The cgs unit of B, the gauss($1G=10^{-4}$ T), is also in common use.

5.1.5 Electric field:

The ancient Greeks discovered as early as 600 B.C. that when they rubbed amber with wool, the amber could then attract other objects. Now the amber has acquired a net electric charge or has become charged. Electric charge, like mass, is one of the fundamental attributes of the particles of which matter is made. The interactions responsible for the structure and properties of atoms and molecules are primarily electric interactions between electrically charged particles.

The negative charge of the electron has exactly the same magnitude as the positive charge of the proton. The number of protons or electrons in a neutral atom of an element is called the atomic number of the element. If one or more electrons are removed, the remaining positively charged structure is called a positive ion. A negative ion is a atom that has gained one or more electrons.

The electric force between two point charges also depends on the quantity of charge on each body, which is denoted by q. The magnitude of the electric forces between two point charges is directly proportional to the product of the charges and inversely proportional to the square of the distance between them. In mathematical terms, the magnitude F of the force that each of two point charges q_1 and q_2 at distance r apart exerts on the other can be expressed as: [39,40]

$$F = K \frac{|q_1.q_2|}{r^2}$$

where K is a constant whose numerical value depends on the system of units used, q is char point and r is distance . This equation is called Coulomb's Law.

When a charged particle (body A) exists, an electrical field around of this particle produce, for example, at point P. This electric field is present at P even if there is no other charge at P; it is a consequence of the charge on body A only. If a point charge q_o is then placed at point P, it experiences the force F_o. Then it is clear that the electric force on a charged body is exerted by the electric field created by other charged bodies. The force is equal to the electric field E produced at that point by charges other than q_o, multiplied by the charge q_o :

$$F = q_o. E$$

The charge q_o can be either positive or negative.

The magnitude E of the electric field at P is:

$$E = \frac{1}{4\pi\varepsilon_o} . \frac{|q|}{r^2}$$

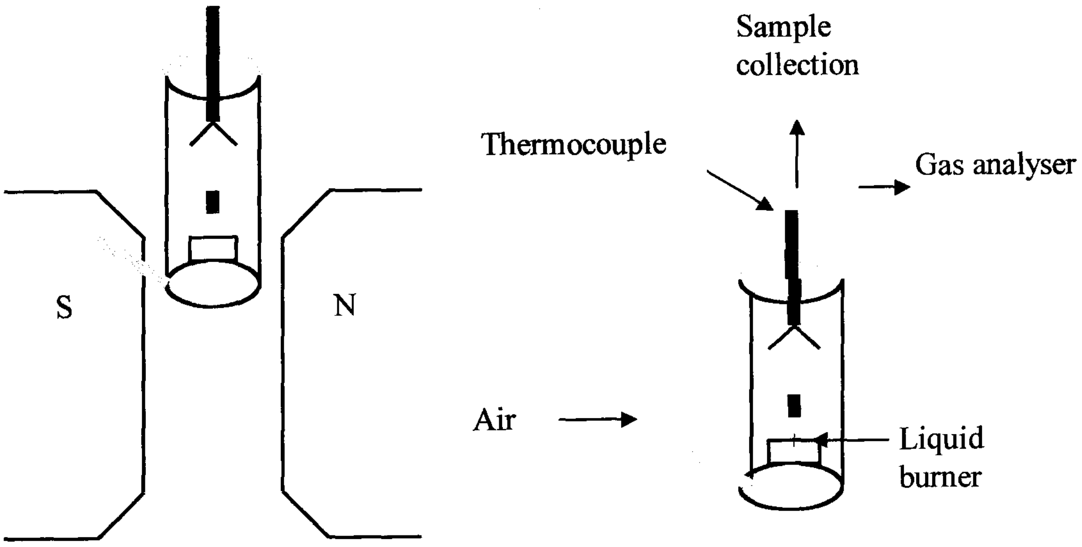
where r is the distance from the source point, ε_o is permittivity.

5.2 EXPERIMENTAL WORK:

5.2.1 Effect of magnetic field

In the present study a glass alcohol burner was used in the first set of experiments. Two rectangular permanent magnets with an intensity of 9500G and 18000G in the middle were placed on opposite sides of the burner. The area of each magnetic pole was 10cm x 15cm and the distance between the magnetic poles was 15cm. The burner nozzle was placed at the mid-point between the two magnetic poles. The burner was placed into a cylindrical glass tube and air passed into this container from a tube at the back. The sample of soot was collected 15cm from the top of the flame. Air flow was set at 7 l min^{-1} , 14 l min^{-1}, 21 l min^{-1} or 28 l min^{-1}. The size of wick for all experiments was 4mm. Fuel was 25ml paraffin or a mixture of 15ml paraffin and 10 ml benzene. Figure 5-1 is a schematic diagram of the apparatus.

Figure 5-1: A schematic diagram of the apparatus for experiment with liquid flame



Two methods were used for sampling soot emission.

(1)-A 37mm fibre glass filter paper held in a holder with a small vacuum pump collected the sample. Before sampling soot the collected filter paper was heated at 110°C in an oven for 24 hours and weighed. After sampling, it was held under the same conditions before being weighed. The sampling time used was 5 min at a flow rate of 0.51 min^{-1}.

(2)-In the other method a 37mm cellulose filter paper held in a disc filter holder with a vacuum pump was used to collect the sample.

To evaluate the soot a smoke stain reflectometer model 43 (Diffusion System Ltd) was used. For size measurement and morphology of the soot, a light microscope and a JEOL 2000 FX TEM were used. For microscopy work the sample was collected on a membrane filter paper. The membrane filter was made transparent by adding a few drops of immersion oil to the upper side of the filter. In preparing for TEM each sample was coated with carbon and then cut into several small pieces. Each piece was placed on a copper mesh. Each sample was placed, film side up, on a section of metal mesh on the bottom of a Petri dish. Dimethylformide was poured into the dish until the filter squares were wetted by capillary action. The Petri dish was covered. After 24 hours the soot particles had settle on the undissolved copper mesh. After drying, the specimens were used for TEM examination. For measuring particle size a Cambridge Counatimeter 520 was used.

To examine the flame behaviour under magnetic field, the flame was photographed with a digital camera and the flame length measured. The flame surface temperatures were measured with a thermocouple.

Other experiments were performed with a gas burner where fuel and oxidiser were premixed. Air was used as oxidiser and the fuel was methane or acetylene. In these cases sampling time for collection of soot was 2 hours at a flow rate of 11 min^{-1}.

5.2.1.1 Results:

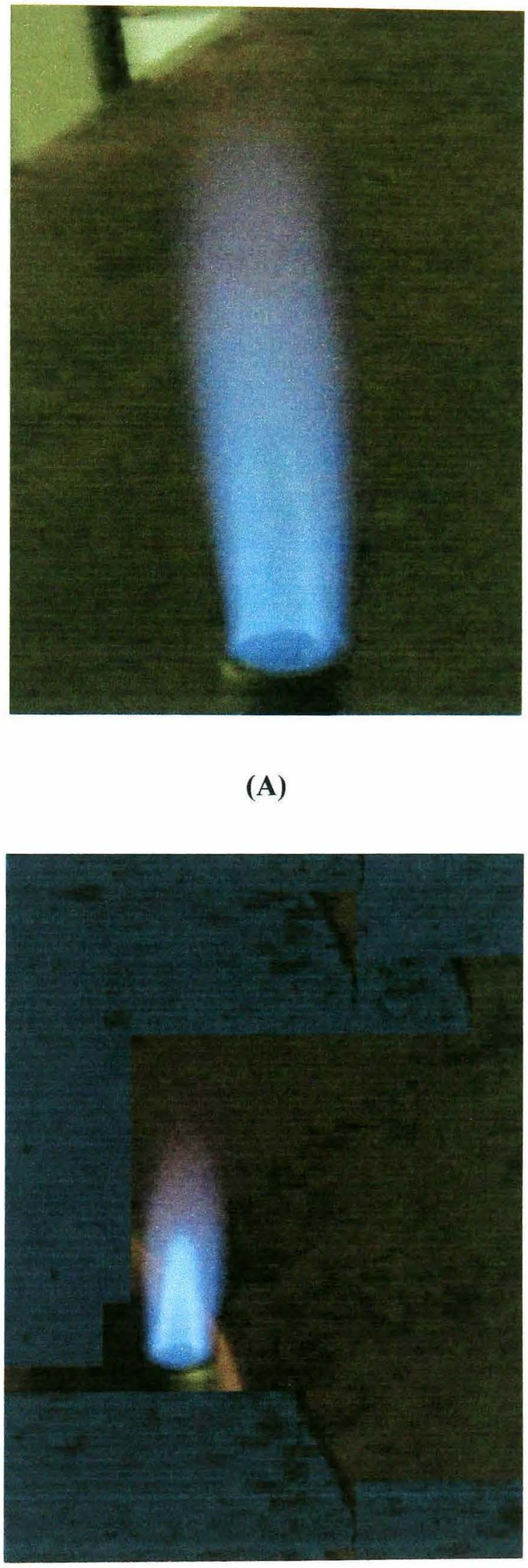
Figures 5-2 and 5-3 show the shape of the flame with and without magnetic field for both liquid and gas burners. The results show that when the permanent magnets were installed, the flame had quite different behaviour. The flame from both burners looks more brilliant, the surface area decreases with increasing magnetic field and the flame becomes smaller and narrower when the field is applied.

Figure 5-2: The effect of magnetic field on shape of a paraffin flame A) without magnetic field, B) with magnetic field

(A)

(B)

Figure 5-3 The effect of magnetic field on shape of a acetylene flame. A) without magnetic field , B) with magnetic field



(A)

(B)

Tables 5-1, 5-2, 5-3 and 5-4 show the effects of magnetic field on the flame temperature and flame length. The results show that for all experiments the length of flame becomes shorter and the flame temperature increases with increasing magnetic field strength.

Tables 5-5, 5-6, 5-7 and 5-8 show the amount of soot from liquid and gas burners with zero and applied magnetic fields. It is clear that with the increase of temperature of the flame in the magnetic field situation that the formation of soot decreases and that the flame has smaller length.

Tables 5-9 and 5-10 show the effect of magnetic field on soot size emission from the combustion of acetylene, methane, paraffin and a mixture of paraffin and benzene.

Electron microscope photographs of soot formed in the paraffin flame are shown in Figure 5-4 and for the acetylene flame in Figure 5-5. All samples showed chains, consisting of the smallest particles and domains formed from these chains when combustion was carried out in a magnetic field.

Table 5-1: The effect of magnetic field on the length and temperature of methane flame.

Magnetic field (G)	Temperature °C	Flame length cm
0	800	5
9500	850	4.1
18000	910	3.3

Table 5-2: The effect of magnet field on the length and temperature of acetylene flame.

Magnetic field (G)	Temperature °C	Flame length cm
0	1800	4.6
9500	1870	3.5
18000	1965	2.7

Table 5-3: The effect of magnetic field on the length and temperature of a paraffin flame at different air flow rates.

Magnetic field (G)	Flow l min^{-1}	Temperature °C	Flame length cm
0	7	600	6.5
	14	625	4.5
	21	630	3.5
	28	647	3
9500	7	624	5.7
	14	651	4
	21	676	3.25
	28	681	2.75
18000	7	650	5
	14	673	3.5
	21	702	3
	28	710	2.5

Table 5-4: The effect of magnetic field on the length and temperature of a mixture of paraffin and benzene flame at different air flow rate.

Magnetic field (G)	Flow l min^{-1}	Temperature °C	Flame length cm
0	7	570	6.8
	14	590	4.9
	21	621	3.7
	28	629	3.2
9500	7	593	5.9
	14	625	4.3
	21	640	3.5
	28	651	3
18000	7	608	5.4
	14	631	3.8
	21	657	3.3
	28	673	2.8

Table 5-5: The effect of magnetic field on the soot emission of a methane flame

Magnetic field (G)	Optical density of soot (%)	Soot- mg
0	62	3×10^{-3}
9500	83	1.3×10^{-3}
18000	95	9×10^{-4}

Table 5-6: The effect of magnetic field on soot emission of an acetylene flame

Magnetic field (G)	Optical density of soot (%)	Soot- mg
0	67	2.7×10^{-3}
9500	88	1.2×10^{-3}
18000	97	7×10^{-4}

Table 5-7: The effect of magnetic field on soot emission of a paraffin flame at different air flow rates.

Magnetic field (G)	Flow air l min^{-1}	Optical density of soot (%)	Soot- mg
0	7	53.25	3.8×10^{-3}
	14	67	2.6×10^{-3}
	21	75	1.9×10^{-3}
	28	83.75	1.4×10^{-3}
9500	7	69	2.1×10^{-3}
	14	73	1.79×10^{-3}
	21	80	1.39×10^{-3}
	28	82	1.17×10^{-3}
18000	7	75	1×10^{-3}
	14	79	8×10^{-4}
	21	85	6×10^{-4}
	28	86	4×10^{-4}

Table 5-8: The effect of magnetic field on soot emission from a mixture of paraffin and benzene flame at different air flow rates.

Magnetic field (G)	Flow air l min^{-1}	Density of soot (%)	Soot- mg
0	7	68	4.9 x 10^{-3}
	14	49.5	3.7 x 10^{-3}
	21	55	2.7 x 10^{-3}
	28	68	2.1 x 10^{-3}
9500	7	45	3.02 x 10^{-3}
	14	44.25	2.26 x 10^{-3}
	21	51.25	1.63 x 10^{-3}
	28	61.5	1.28 x 10^{-3}
18000	7	42.5	1.56 x 10^{-3}
	14	43.75	1.2 x 10^{-3}
	21	53.25	8.1 x 10^{-4}
	28	56	4.5 x 10^{-4}

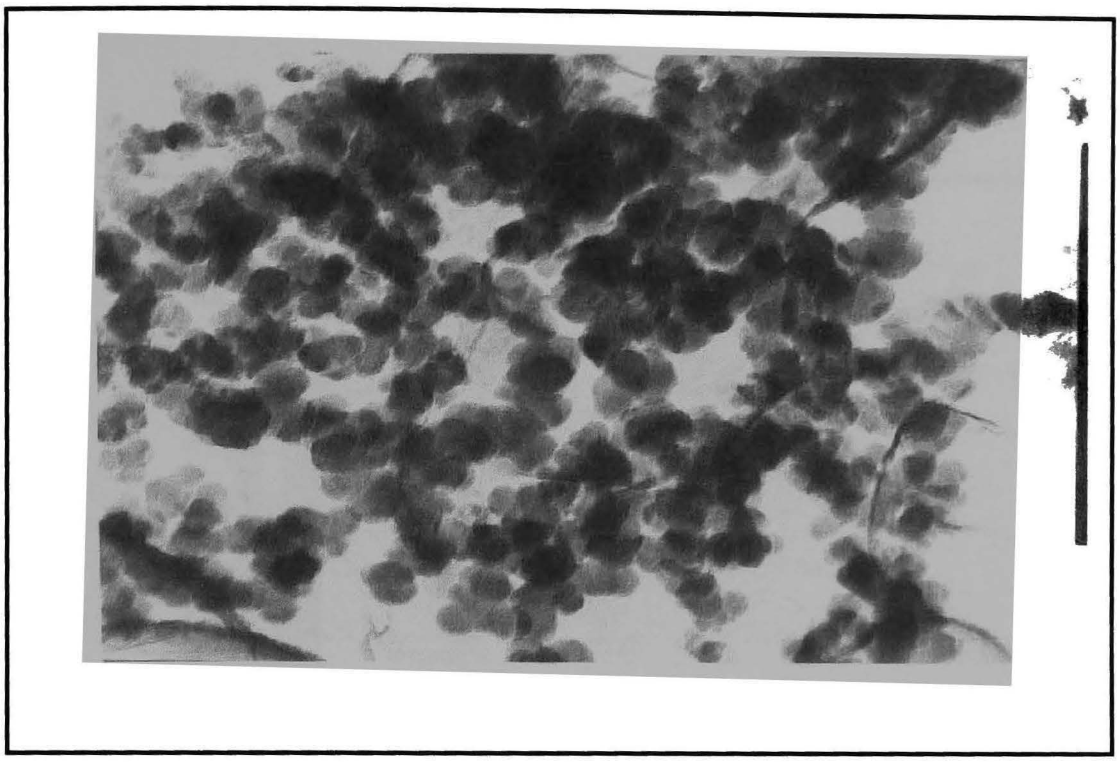
Table 5-9: Effect of magnetic field on soot size emission from acetylene and methane flame.

Magnetic field (G)	Acetylene		Methane	
	Particle (nm)	Chain (μm)	Particle (nm)	Chain (μm)
0	5	1	7	2
9500	3	2.5	5	3.2
18000	2	4	3	4.8

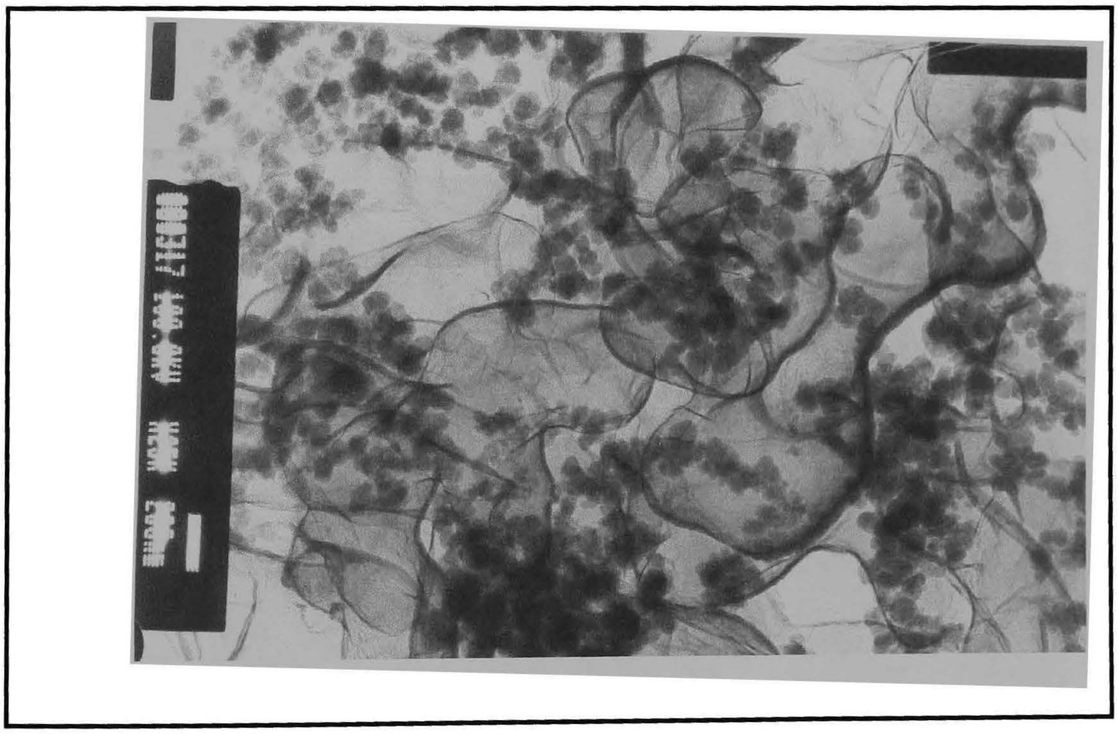
Table 5-10: Effect of magnetic field on soot size emission from the combustion of a paraffin or a mixture of paraffin and benzene at different air flow rate.

Magnetic field (G)	Air flow (l min^{-1})	Paraffin		Paraffin +benzene	
		Particle (nm)	Chain (μm)	Particle (nm)	Chain ((μm)
0	7	20	7	28	10
	14	18	6	22	8.5
	21	14	4.5	18	7.2
	28	13	4	15	6
9500	7	16	11	21	13
	14	14	8.3	18	10.7
	21	11	7	15	8.9
	28	10	6.3	12	7.5
18000	7	13	12.2	19	17
	14	11	9.1	15	14.2
	21	7	8.3	11	13
	28	6	7.1	9	11.8

Figure 5-4: The effect of magnetic field on particle size and morphology of soot from a paraffin flame :A) without magnetic field, b) with magnetic field 18000G

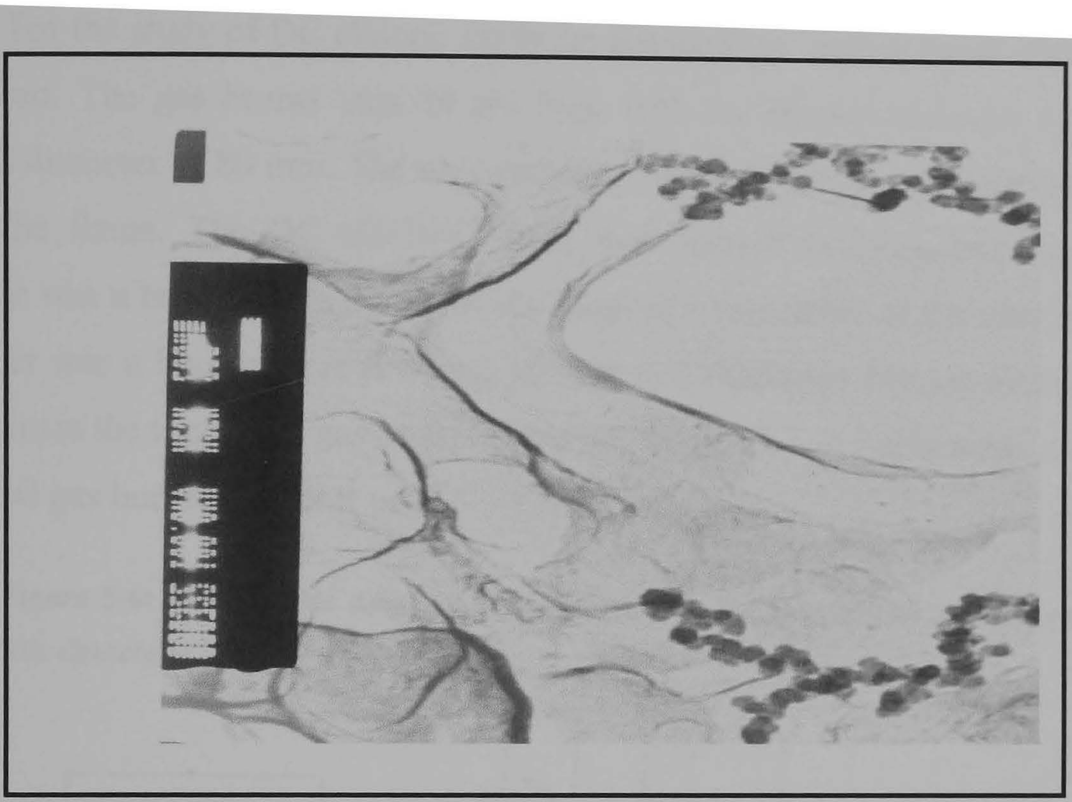


(A) — is 200 nm

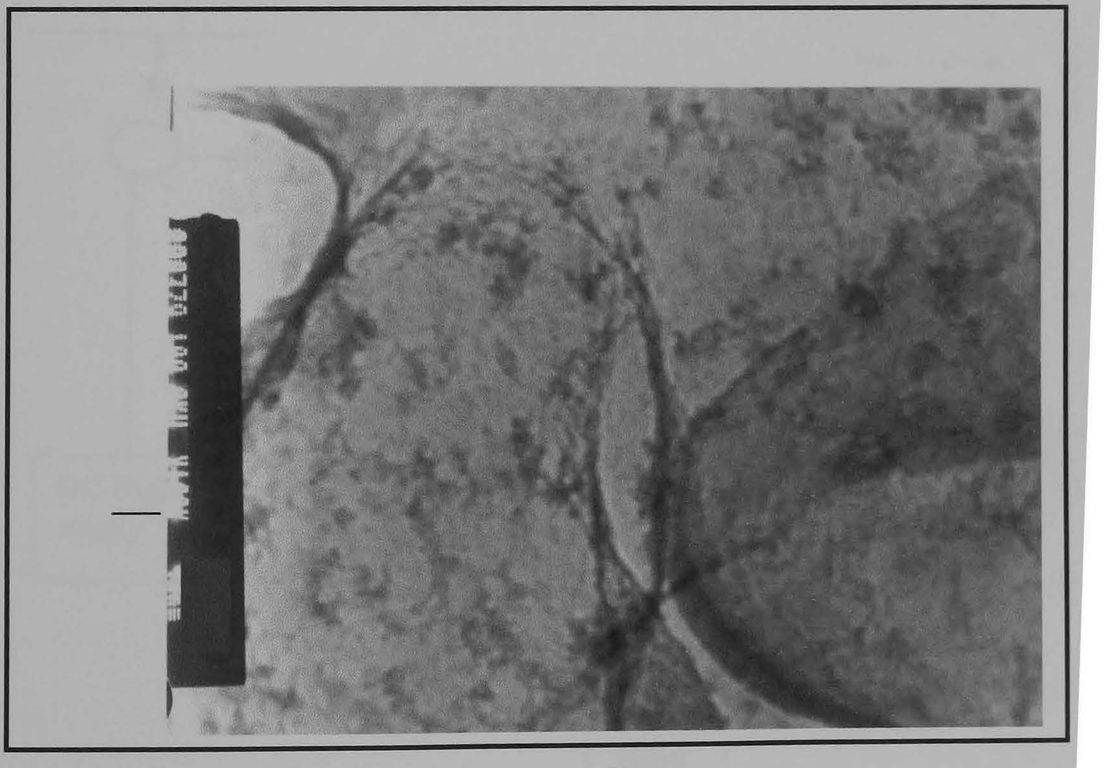


(B) — is 200 nm

Figure 5-5: The effect of magnetic field on particle size and morphology of soot from a acetylene flame: A) without magnetic field B) with magnetic field of 18000G



(A) — is 50 nm



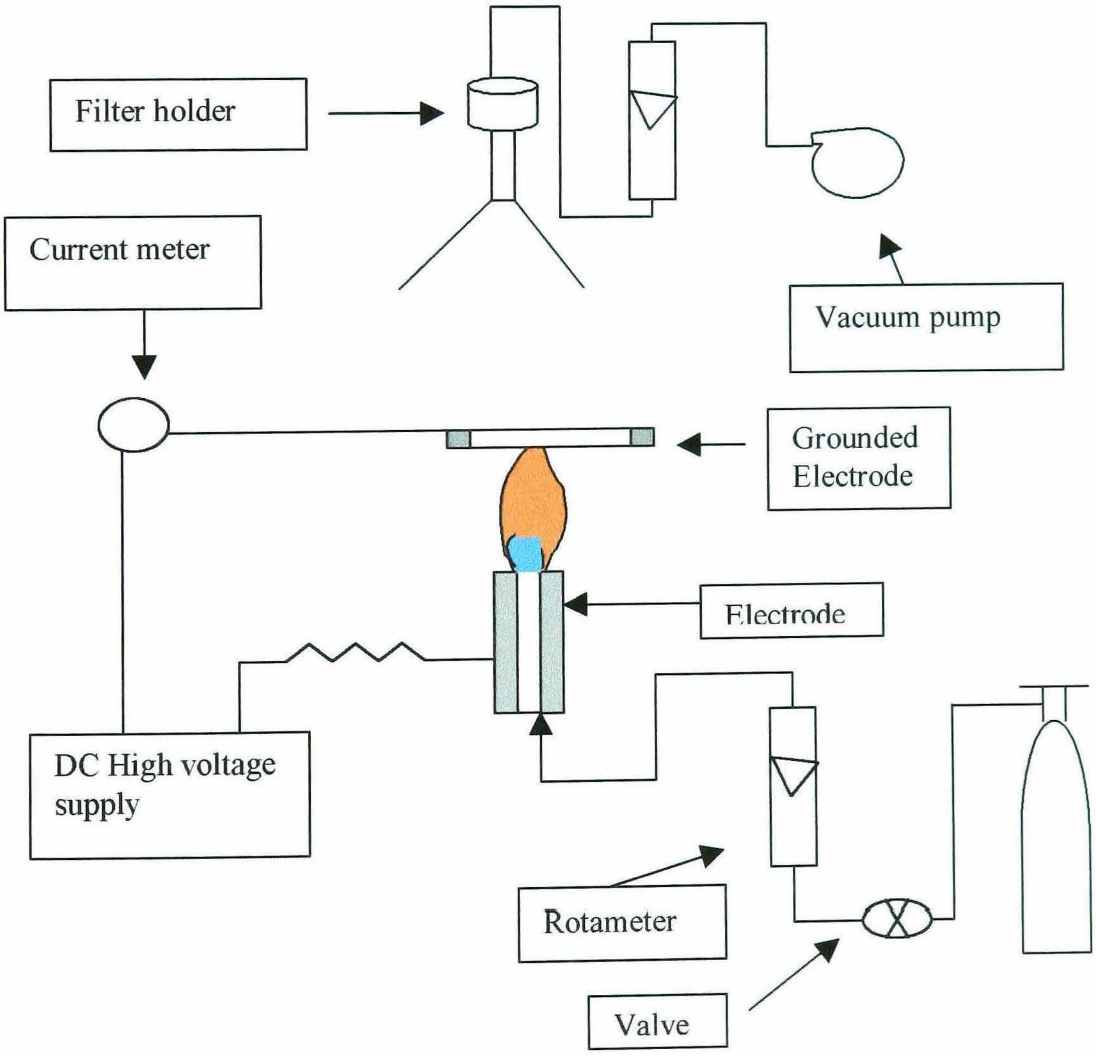
(B) — 50nm

5.2.2 Effect of DC Electric field on combustion and control of soot in a diffusion flame:

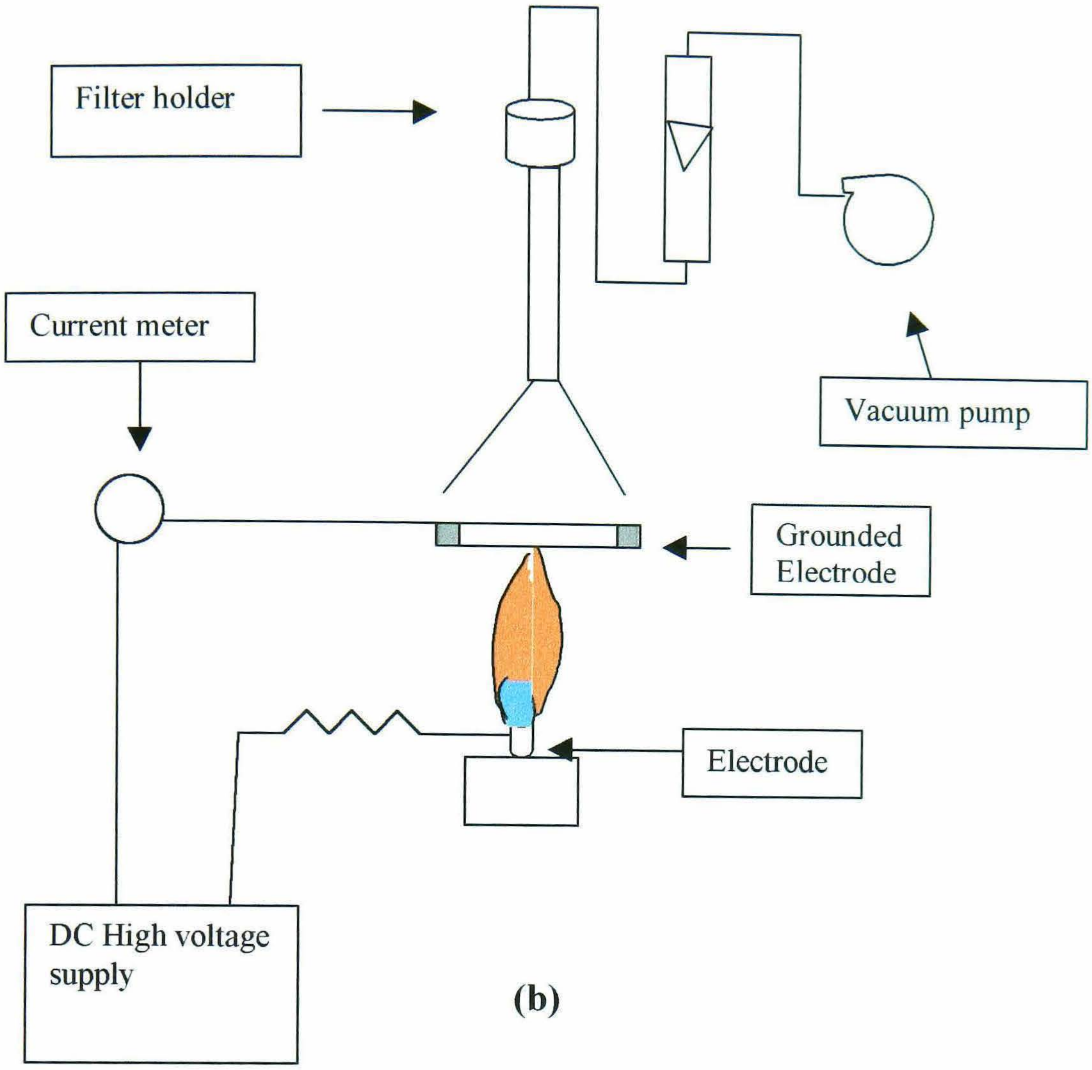
5.2.2.1 Experimental:

For the study of DC electric fields on combustion, both a liquid and a gas burner were used. The gas burner was 10 cm high with an internal diameter of 60 mm and external diameter of 80 mm. The soot emission from the flame was determined at 15 cm above the flame. The DC electrical field was formed between two electrodes, one electrode was a brass nozzle on top of the glass alcohol burner or the tube of gas burner. The other was a brass ring (o.d. 7mm, id.5mm and thickness 10mm) situated 20 mm or 40 mm from the top of the gas or liquid burner. Figure 5-6 is a schematic diagram of the liquid and gas burners systems used.

Figure 5-6: A schematic diagram of the apparatus for experiment with A) gas or B) liquid burner with electrodes



(a)



(b)

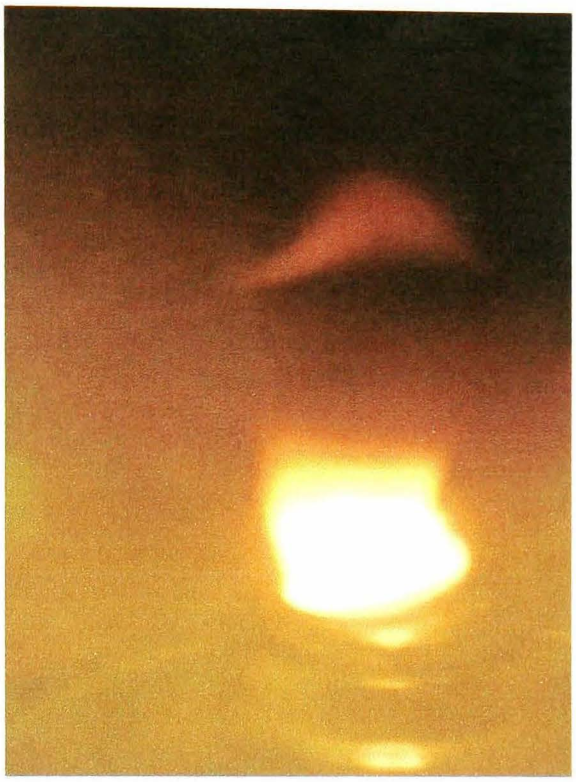
The sampling method for soot emissions was the same as that described in section 5.2.1. The changes of soot particle characteristics during the application of an electric field were investigated by light microscopy and TEM. Soot samples were photographed after collection on a membrane filter. For light microscopy, each filter was prepared by cutting it into two sections and placing the filter treated with immersion oil (so the membrane filter became transparent) on a glass slide.

5.2.2.1.1 Results:

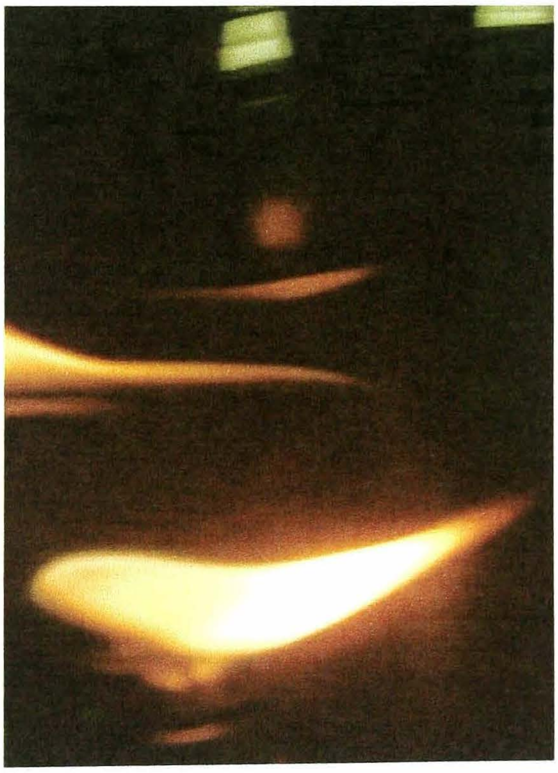
5.2.2.1.1.1 Effect of electric field on flame shape:

Figure 5-8, 5-9 and 5-10 show the flame shapes with increasing voltage for paraffin and acetylene with 5kV and 15kV.

Figure 5-8: The effect of electric field on the shape of a paraffin flame: A) with 5KV applied voltage, B) with 15KV applied voltage



(A)



(B)

Figure 5-10: The effect of electric field on the shape of an acetylene flame. a) with 5kV applied voltage, b) with 15kV applied voltage

(A)

(B)

The length of flame with and without electric field was measured. The results are shown in Table 5-11. The flame length became shorter with electric field and decreased with decreasing distance between the two electrodes.

Table 5-11: The effect of electric field on length of flame when second electrode held at 20 mm and 40 mm.

Sample	Voltage (kV)	Length of flame 20mm	 40mm
Acetylene	0	4	4
	5	4	4
	10	3.5	2.5
	15	2.7	2.2
Methane	0	4.2	4.2
	5	4.2	4.2
	10	3.6	12.8
	15	2.9	2.2
Paraffin	0	6	6
	5	5.8	5.8
	10	4.7	4.3
	15	3.4	3.1

5.2.2.1.1.2 Effect of electric field on electric current:

Without any flame between two electrodes, the electric current was zero for a wide range of voltages tested. Figure 5-11, 5-12 and 5-13 show the electric current measured with a flame between the two electrodes for acetylene, methane and paraffin.

The results show current increased linearly for all experiments with electric field because of the electric conductivity of the hot burned gases and the flame which contains carbon particles and ionic species.

Figure 5-11: Relationship between electric field and electric current for acetylene

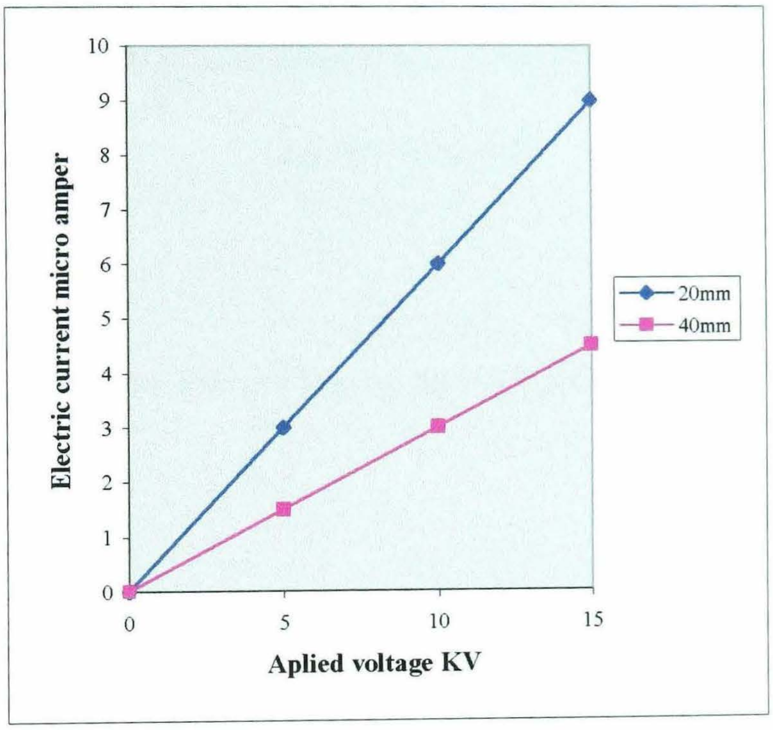


Figure 5-12: Relationship between electric field and electric current for methane

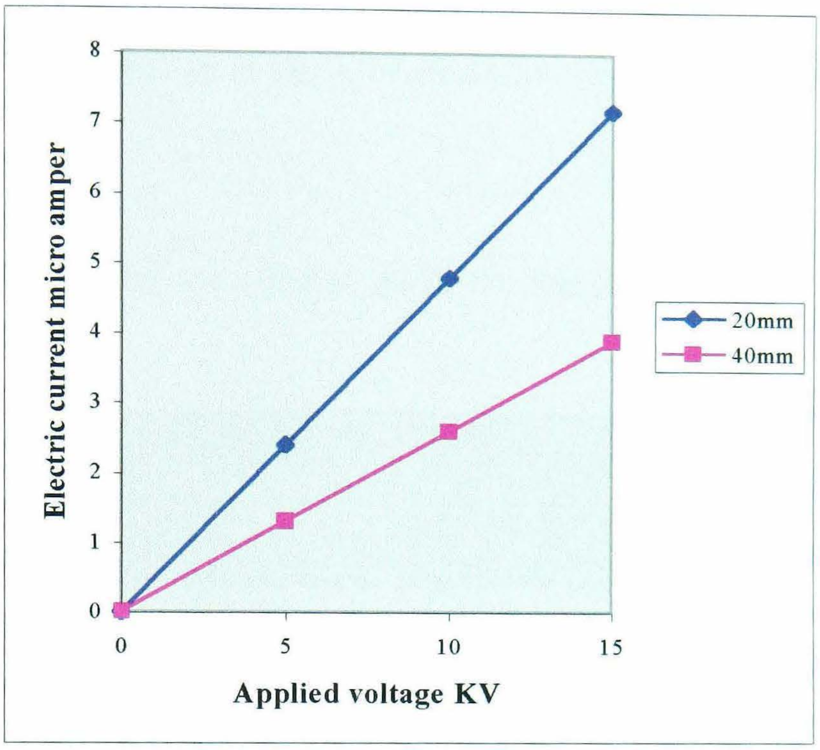
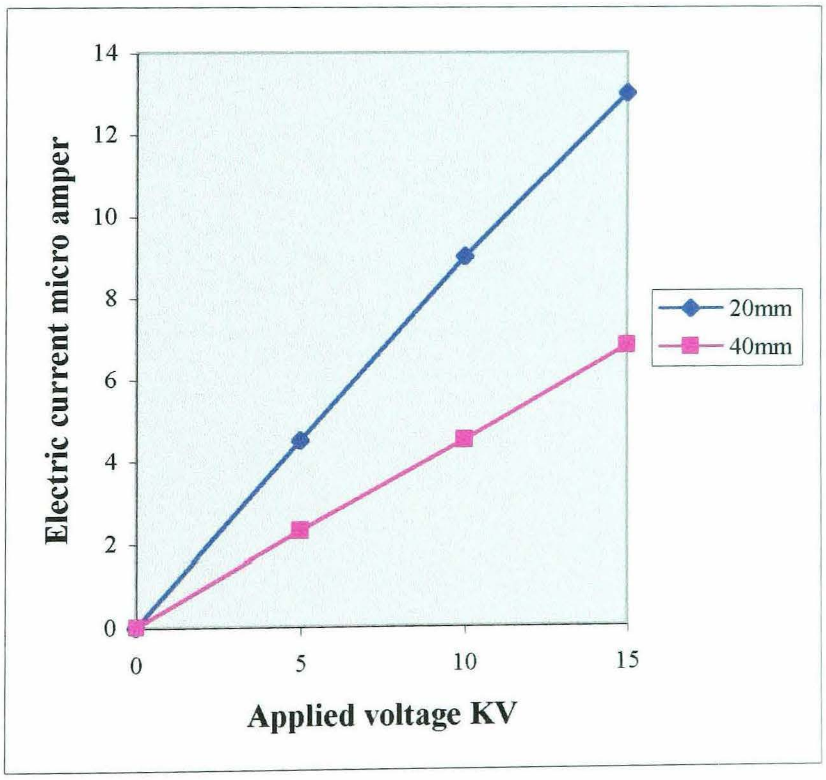


Figure 5-13: Relationship between electric field and electric current for paraffin



5.2.2.1.1.3 Flame temperature:

The measured flame temperatures for acetylene, methane and paraffin with and without electric field are shown in Table 5-12. The results show that with increasing electric field, the flame temperature in all experiments increased.

Table 5-12: The effect of electric field on flame temperature of acetylene, methane and paraffin

Sample	Applied voltage (kV)	Temperature (°C)
Acetylene	0	1800
	5	1850
	10	1900
	15	1950
Methane	0	830
	5	868
	10	905
	15	940
Paraffin	0	630
	5	650
	10	671
	15	698

5.2.2.1.1.4 Effect of applied voltage on soot emission:

The effects of the electric field on soot emissions from the acetylene, paraffin and methane flames are shown in Figures 5-14, 5-15 and 5-16. The soot emissions were defined as the ratio of the mass of soot emission with and without electric field (Ms/ Mso). The value Ms/ Mso was used to evaluate the efficiency of soot reduction by electric field. It is clear that the soot emission decreases when the electric field is greater than about 2kV. For example the value of Ms/Mso reached 0.1 for acetylene which means a 90 % efficiency of soot reduction. The figures also show the efficiency of soot reduction decreased with increasing distance between the two electrodes.

Table 5-13 shows the effect of electric field on the particle size of soot formed in acetylene, methane and paraffin flames. The results show a particle size decrease and also length of chain decrease with increasing voltage. Electron microscope photographs of soot formed in the paraffin flame with different voltage are shown in Figure 5-17 and for the acetylene flame in Figure 5-18.

Figure 5-14: The effect of electric field on soot emission from an acetylene flame

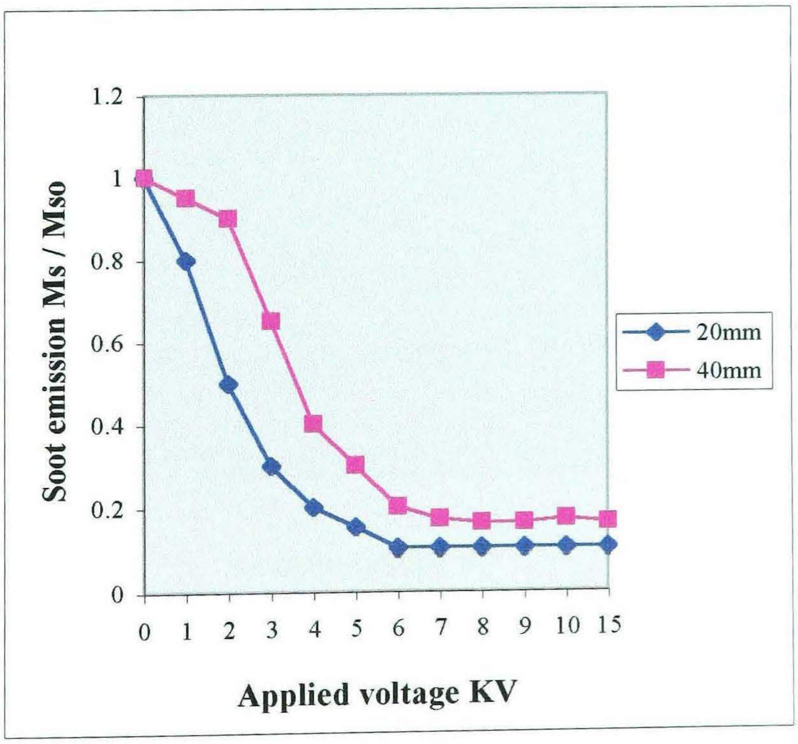


Figure 5-15: The effect of electric field on soot emission from a paraffin flame

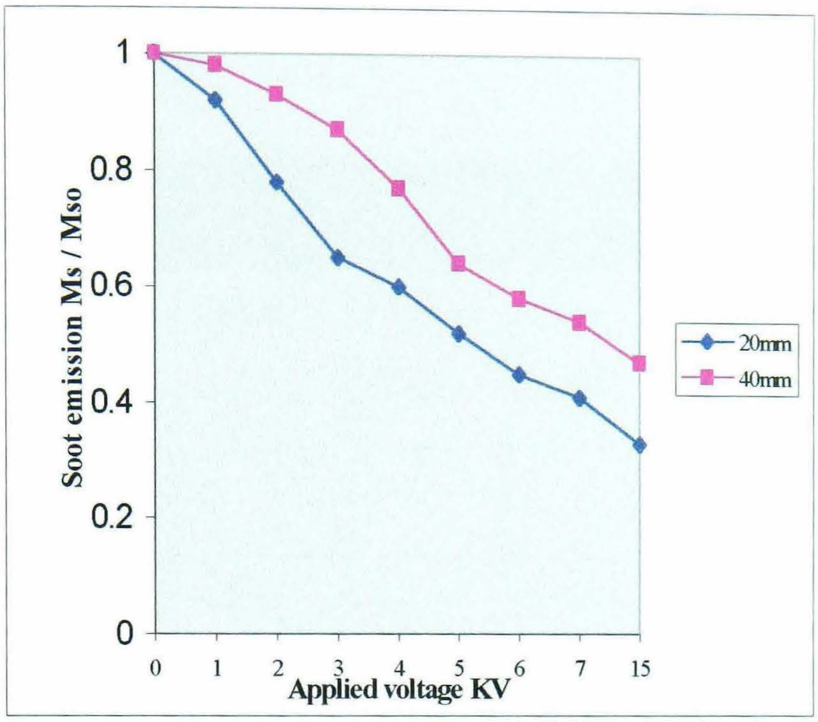


Figure 5-16: The effect of electric field on soot emission from a methane flame

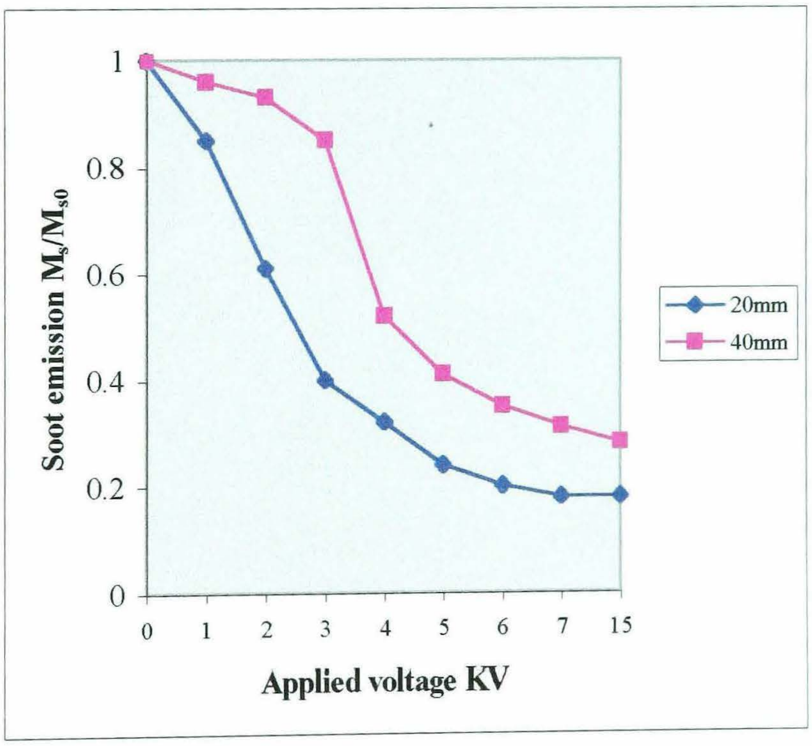
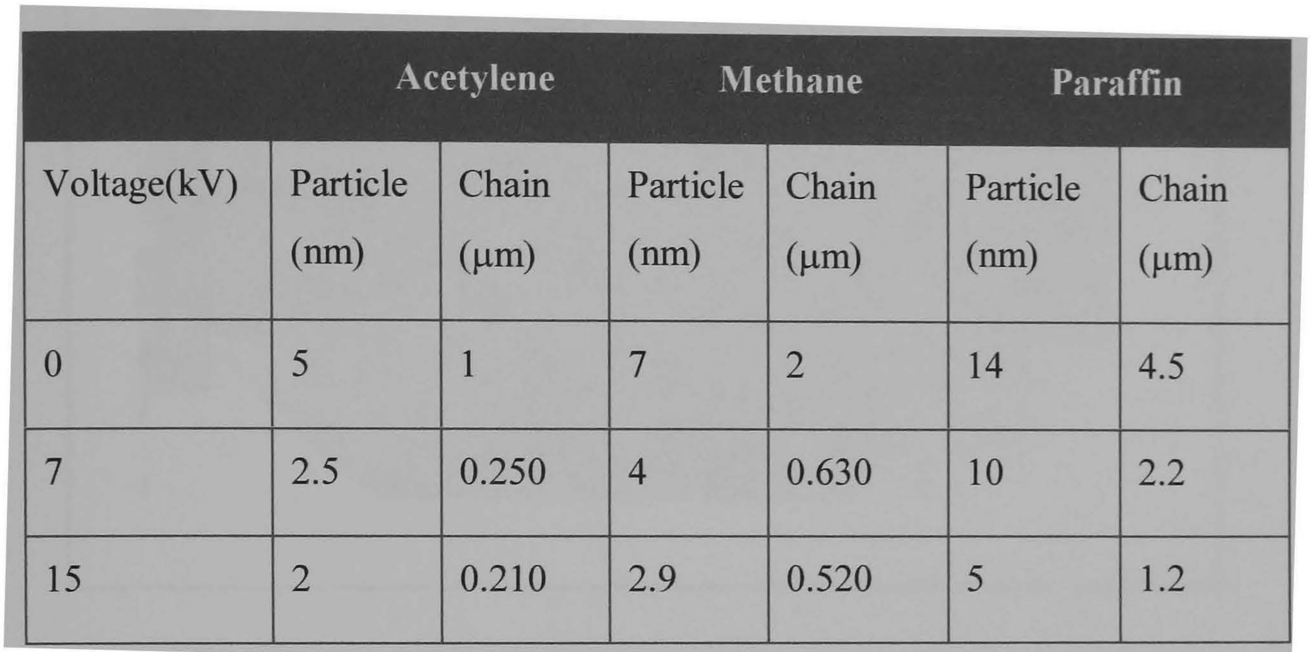
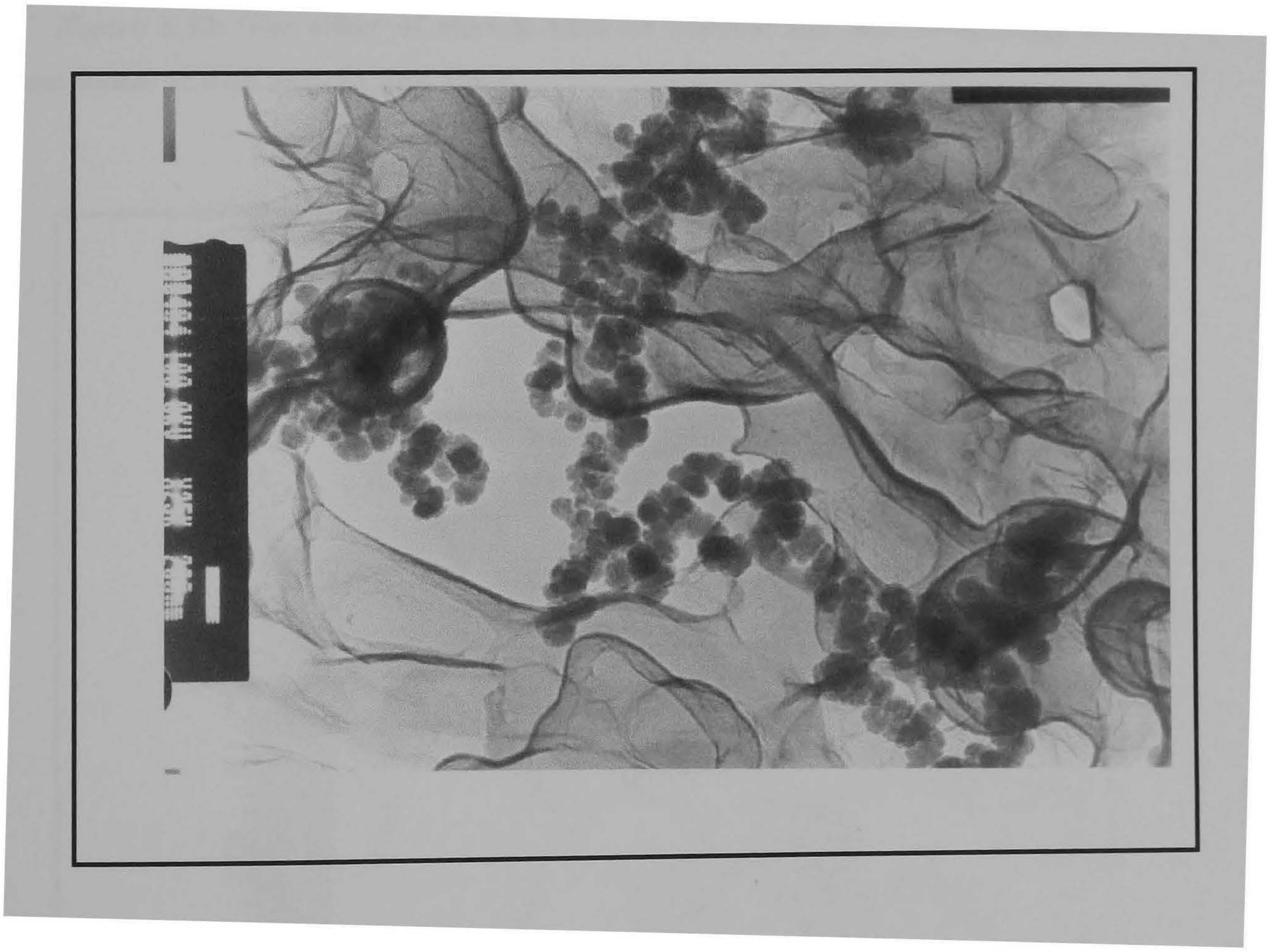


Table 5-13: Effect of electric field on soot size emission from acetylene, methane and paraffin flames

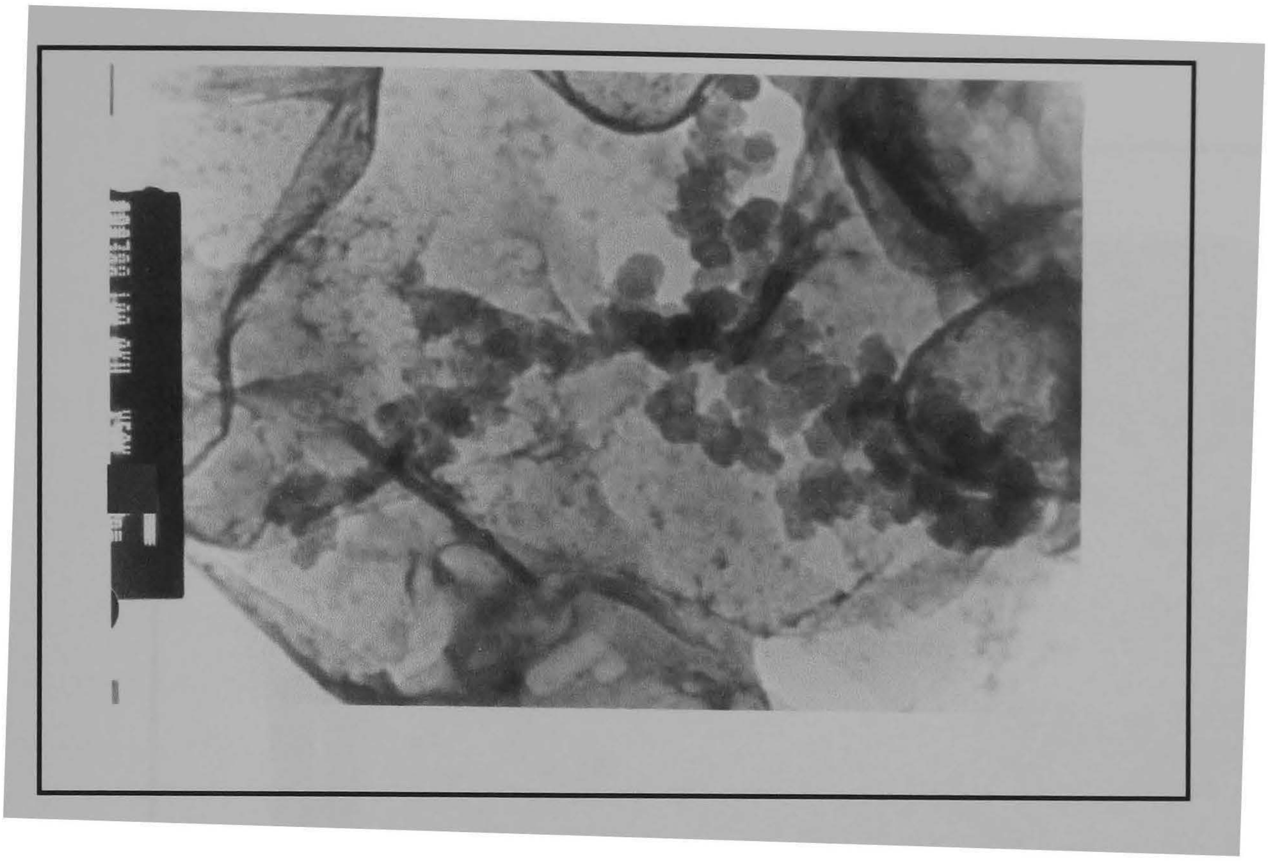


	Acetylene		Methane		Paraffin	
Voltage(kV)	Particle (nm)	Chain (μm)	Particle (nm)	Chain (μm)	Particle (nm)	Chain (μm)
0	5	1	7	2	14	4.5
7	2.5	0.250	4	0.630	10	2.2
15	2	0.210	2.9	0.520	5	1.2

Figure 5-17: The effect of electric field on particle size and morphology of soot from a paraffin flame. a) with 5kV, b) with 15kV

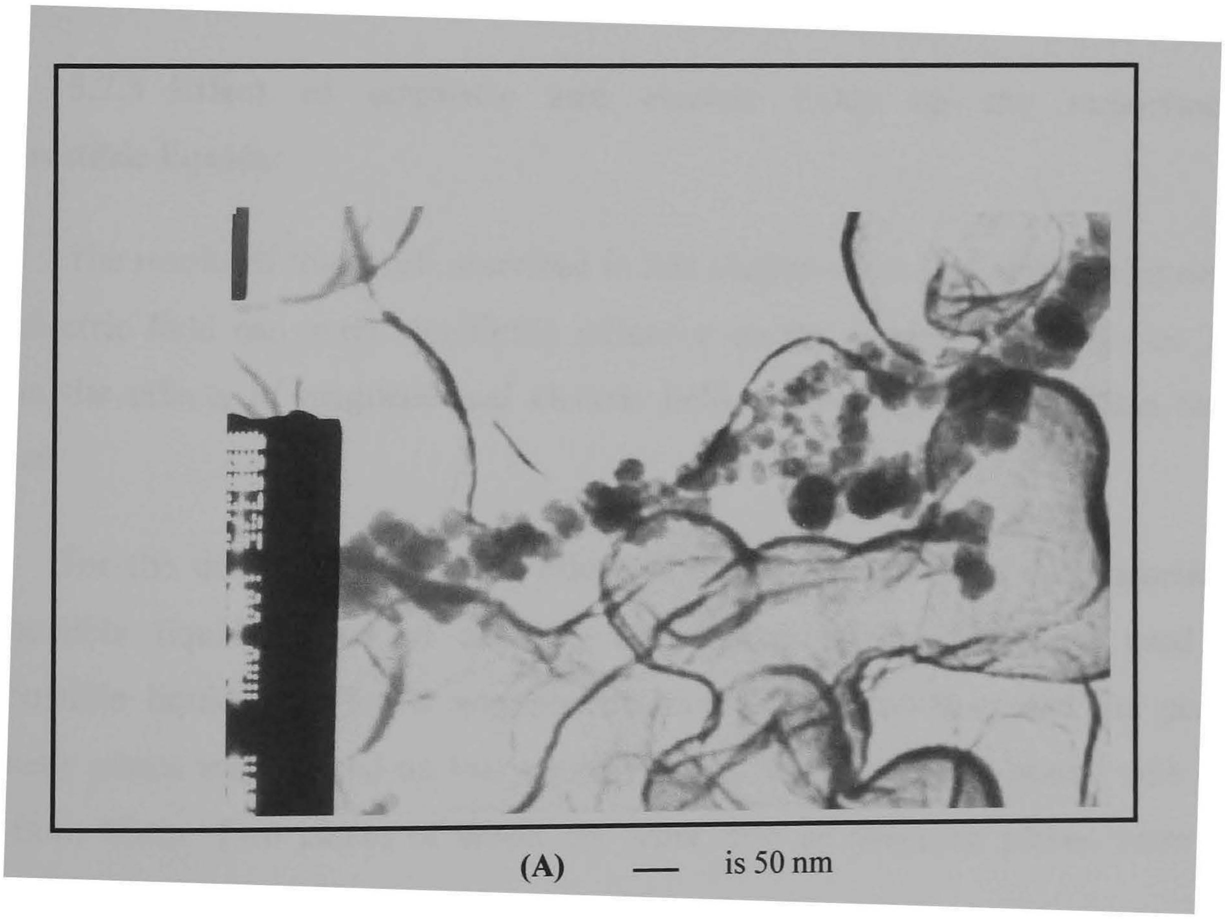


(A) — is 200nm

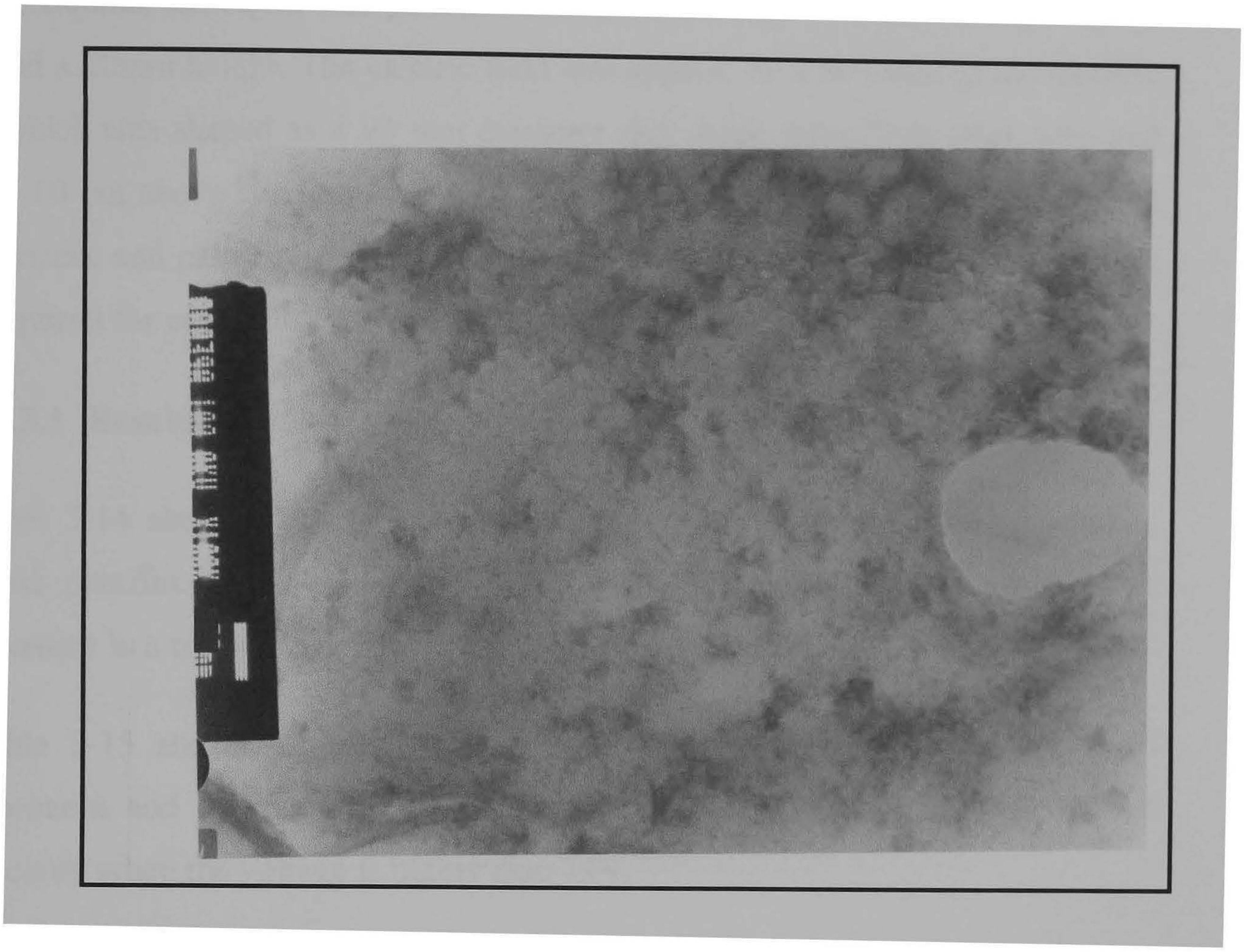


(B) — is 50 nm

Figure 5-18: The effect of electric field on particle size and morphology of soot from a acetylene flame. a) with 5kV, b) with 15kV



(A) — is 50 nm



(B) ——— is 50 nm

5.2.3 Effect of magnetic and electric fields on the vaporisation of combustible liquids:

The results of this work described in this chapter show that applied magnetic field and electric field can exert significant influence on the combustion processes. For this reason the effects of magnetic and electric field on the liquid vaporisation rate were studied.

For the determination of the effect of a magnetic field on the vaporisation of combustible liquids, 25ml of acetone, or benzene or paraffin were used as the combustible liquid. The liquid was poured into a glass container and the permanent magnetic plates were placed on two opposite sides. The liquid was heated with a heater gun from 20cm. Two pieces of wood, the same size as magnetic plates, were used in control experiments.

For the determination of an electric field's effect on the vaporisation of combustible liquids, the liquid was poured into a grounded metallic cell having a 40mm diameter and a 20mm height. The electric field was applied by a potential to the metallic electrode which was shaped as a 90 mm diameter ring made from 2mm thick wire and was placed 10 cm above the upper edge of liquid container sample. In this experiment acetone, benzene and paraffin were used. The mean liquid vaporisation time was taken as the time required for complete evaporation.

5.2.3.1 Results:

Table 5-14 shows the effect of magnetic field on the vaporisation of acetone, benzene and paraffin. As is evident from table, the evaporation rate of combustible liquids increases in a magnetic field.

Table 5-15 shows the effect of applied electric field on the vaporisation of acetone, benzene and paraffin. It is clear that vaporisation rate increases with electric field, especially when the voltage is higher than 7kV.

Table 5-14: The effect of magnetic field on the vaporisation time of acetone, benzene and paraffin

Magnetic fields (G)	Vaporisation time (min)		
	Acetone	Benzene	Paraffin
0	3.50	5.45	15
9400	2.35	4.30	11.42
18000	1.50	3.15	9.10

Table 5-15: The effect of applied electric field on the vaporisation time of acetone, benzene and paraffin.

Voltage(KV)	Vaporisation time (min)		
	Acetone	Benzene	Paraffin
0	3.56	5.55	16.3
3	2.10	4.15	12.34
7	1.05	3.35	10.15
15	0.47	2.25	8.32

5.2.4 Evaluation of heat flux from the flame to the liquid :

Another experiment was designed to evaluate electric behaviour in the heat flux from the flame to the liquid surface with a corresponding increase, or decrease, in the burning rate.

In this test a grounded metallic cell of 20mm diameter and 50mm high was used as a combustible liquid container. A thermocouple was placed at the bottom of the metallic container and an electrode was placed 100 mm above the upper container edge.

5.2.4.1 Results:

Figures 5-19, 5-20, and 5-21 show the typical time variation of the samples temperature at the container bottom during the burning process with and without an electric field. The results show that the heating of the liquid is significantly accelerated compared with the reference sample without electric field.

Figure 5-19: Typical time variations of the thermocouple signal during the application of a 3kV applied voltage and without the field for benzene.

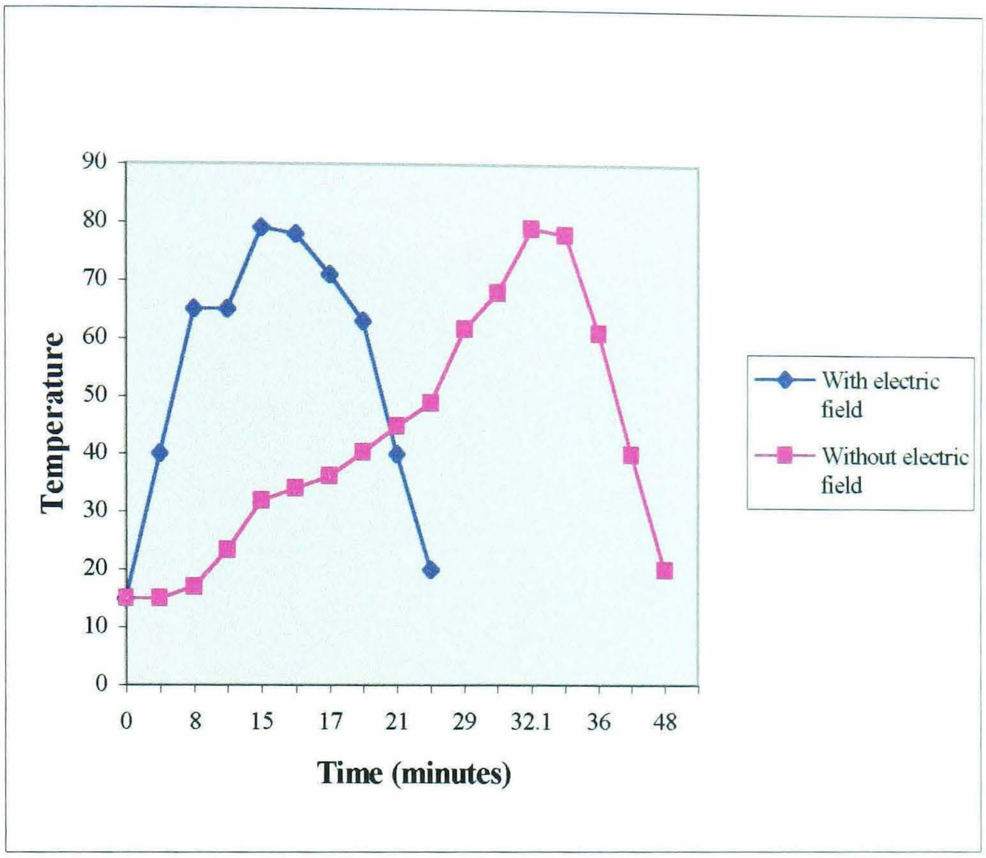


Figure 5-20: Typical time variations of the thermocouple signal during the application of a 3kV applied voltage and without the field for paraffin.

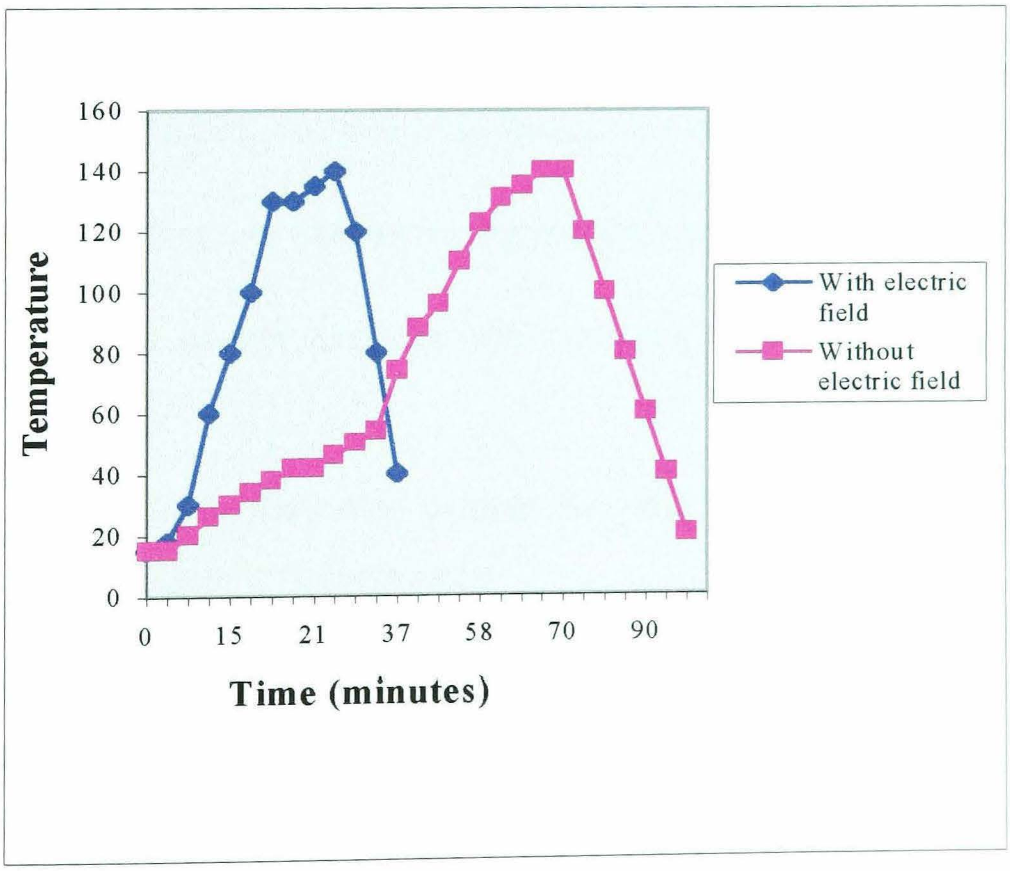
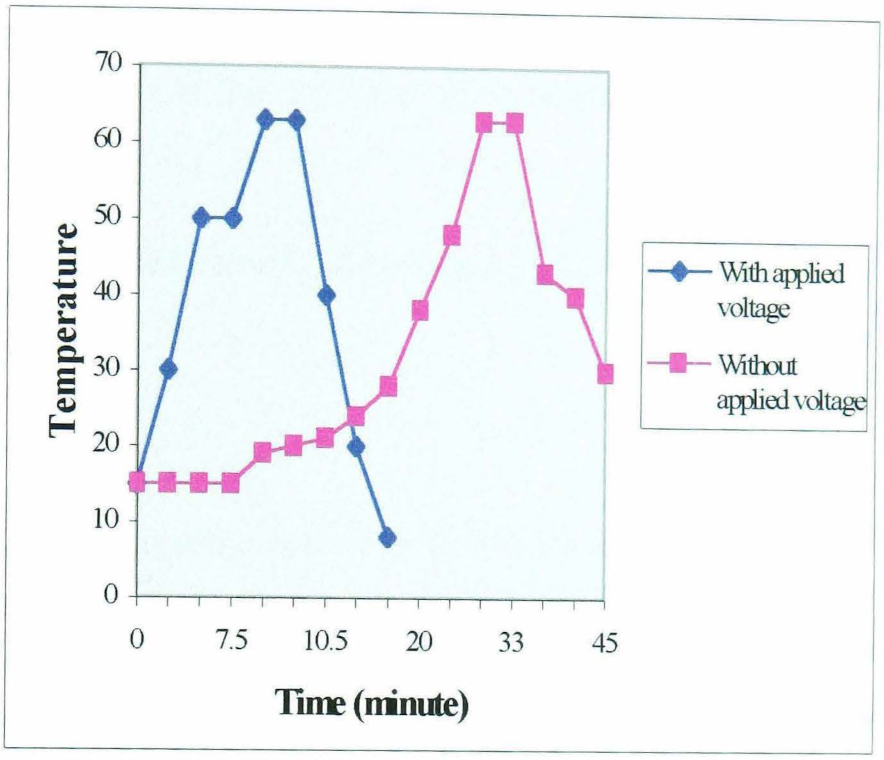


Figure 5-21: Typical time variations of the thermocouple signal during the application of a 3kV applied voltage and without the field for acetone



5.3 RESULTS SUMMARY:

The effect of magnetic and electric fields on the control of soot from liquid and gaseous combustion was studied. The following results were obtained:

1- Soot emissions decrease with increasing magnetic or electric field strength.

2- The particle size of soot decreases with increasing magnetic field strength but the chain length increased.

3- Microscopic results show that particle size and chain length of soot both decreased with increasing electric field strength.

4- Flame temperature in all experiments performed in magnetic and electric fields increases with increasing magnetic field strenth and electric field.

5-The length of flame decreases with increasing magnetic field strength and electric field.

6-Both applied magnetic and electric fields increase the vaporisation rate of combustible liquid, the effect increasing with increasing magnetic field strength or electric field.

7- The magnitude of heat flux from the flame liquid surface increases in a positive applied field strength..

8-The results show that electric current increased linearly in all experiments with electric field.

5.4 Discussion:

It is clear from the results described in this chapter that applied magnetic and electric fields have a profound effect on the combustion of liquid and gas fuels. The previous work in the Centre for Environmental Research [41, 42] has shown that there are many other examples of the effects of applied magnetic fields in the behaviour of charged species in fluids. The direct interaction of applied fields on charged species has been shown to cause major changes in behaviour in systems involving free-radical reactions, ion-pair, controlled reactions, precipitation reaction and crystallisation flocculation dispersion processes.

To interpret the combustion results from this work it is necessary to consider the nature of the charged species that are present in the system.

1) In liquid fuels the molecules are held together by weak electrostatic interactions and in the case of a crystallisation system, for example, it has been shown that the growth of hydrocarbon and carbohydrate complexes is changed when they are crystallised in magnetic fields.

In gaseous fuels it is possible that molecules such as methane can form clusters either with themselves or with other molecules giving a situation similar to that in liquid hydrocarbons.

2) The oxygen molecule is paramagnetic and will be influenced by applied fields.

3) Water vapour from the atmosphere or from the combustion process is a diamagnetic molecule and could be affected by the applied fields.

4) In the combustion process itself that are a number of charged species that could interact with the applied field. These include free radicals, ionic species and particulates that will have a high surface charge to bulk ratio.

The overall effects on combustion could arise from combustion of interaction between the applied field and these charged species.

The results in the rate of evaporation of liquid fuels prior to combustion clearly show that the fields do have a weakening effect in the small electrostatic charge holding the molecules in the liquid and provide a further example of this type of direct effect. Consistent with this observation are the results obtained for studies on the transfer of heat to liquids which is shown to be more rapid in applied fields. Weakening of the interaction between the molecules of the fuel will increase their freedom to vibrate and therefore aid the heat transfer process.

It is possible that the increase in flame temperature observed in applied fields could also be due to the increase in evaporation of fuel molecules but it is more likely that this of effect more swamped by other fuel, charged spices interaction in the flame.

The increase in flame temperature could arise from the following interactions with an applied field in the flame.

a) Increase in the reactivity of the oxygen molecules because of paramagnetic interaction

b) Increase in the reactivity of free radicals by the magnetokinetic effect

c) The effects of generating electric currents in the flame, which are shown to increase with increasing applied field strength.

d) Increase in surface reaction with particulates because of the effects of fuel – surface charge interactions.

The consequences of the increase in flame temperature and of the increased reactivity of species in the flame should be the reduction in particulate emission observed in this work.

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CHAPTER SIX: SUMMARY OF RESEARCH AND CONCLUSION

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6.1 INTRODUCTION:

Man-made sources of pollutants can be conveniently classified as stationary combustion, transportation, industrial processes and solid waste disposal sources. The principal pollutant emissions from stationary combustion processes are particulate pollutants, such as fly ash and smoke, sulphur and nitrogen oxides, hydrocarbons and sometimes inorganic acids. The combustion process is responsible for generation of a wide range of pollutants.

Waste incineration has been employed since 1895 for its" historical purpose", that of reducing the volume of waste while transforming it into hygienically safe residues. But modern waste incineration technology has even more to offer. PVC is a common polymer in solid waste specially medical waste, recycling of car components and recycling of power cable etc.

The overall aims of this work were to develop techniques for sampling and analysis of chlorinated aromatic hydrocarbons specially 2,3,7,8-TCDD, to identify pollutants from pyrolysis and combustion of PVC alone and PVC in the presence of some metal compounds, to develop methods of pollutant control and to study the effect of magnetic field and electric field on combustion of liquid or gas.

6.2 Objectives:

The current standard methods available for extraction and analysis of chlorinated aromatic hydrocarbons, such as TCDD, are based on solvent extraction. These take a long time to prepare and can introduce experimental errors.

One of the common methods of controlling air pollution is pollutant removal. For pollutant removal to be accomplished, the polluted carrier gas must pass through a control device or system, which collects or destroys the pollutant and releases the cleaned carrier gas to the atmosphere. It is clear that this method is very expensive and requires regular attention and maintenance by a qualified technician.

The purpose of the research described in this thesis is to develop methods of analysis and control of some pollutant emissions from combustion of PVC, liquid and gas.

The objectives of this work were:

1- to have obtained a novel method for sampling and analysis of chlorinated aromatic hydrocarbons.

2- to have measured some harmful emissions from combustion and pyrolysis of PVC

3- to have investigated the thermal decomposition of PVC in the presence of some metal compounds.

4- to have developed a method for control of pollutant emission from combustion of PVC at source

5- to have developed a novel method for control of soot emissions from combustion of liquid and gas

6.3 Deliverables from this work:

A) The focus in chapter two was to obtain a method for sampling and analysis of chlorinated aromatic hydrocarbons in air. The summary of this chapter is the following:

A novel method has been developed for the sampling and analysis of chlorinated aromatic hydrocarbons and 2,3,7,8-TCDD with solid sorbent and thermal desorption GC-MS. The capacity of the sorbent used, the breakthrough value and percentage recovery of the analyte from the sorbent are reported. A high resolution GC-MS was used for the analysis of 2,3,7,8-TCDD and the thermal desorption unit was also used to transfer compounds from the Carbotrap to GC-MS. A 30 metre capillary column, coated with poly (5% diphenyl, 95% dimethyl siloxane), was used to separate the chlorinated hydrocarbons. A 60 metre capillary column, coated with cyanosilicone resin, was used to separate the 2,3,7,8 TCDD. The results are presented for mixed sorbent tubes because single bed sorbent tubes are not capable of sampling for a wide range of compounds.

A summary of optimum conditions is shown in Table 6-1.

Table 6-1: The optimum conditions for thermal desorption

Sample	Group I*	2,3,7,8 TCDD
Flow rate for desorption	2-2.5	2.5-3
Temperature for desorption	330	350
Length of time for desorption	4	6
Flow rate for preparation	13-15	25
Length of time for preparation	14	17
Valve temperature	220	220
Transfer line temperature	220	250

---

* Group I compounds includes: toluene, chlorobenzene, dichlorobenzene, tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene and tetrachloroethylene.

B) The focus in chapter three was to investigate the thermal degradation of PVC alone and PVC in the presence of copper, copper chloride or cupric oxide and to measure some emissions. The summary of this work is the following:

The thermal stability of the samples under study is less under conditions of combustion in comparison to pyrolysis conditions. The stability of the sample under condition of combustion is in the order PVC + CuO > PVC + Cu > PVC + $CuCl_2$ > PVC and under pyrolysis conditions is PVC + Cu > PVC + $CuCl_2$ > PVC + CuO ≥ PVC.

FT-IR tests made on the solid residue following combustion or pyrolysis show a change in position and absorbance of peaks assigned to C-Cl and C-H bands after the first step weight loss for PVC and PVC in the presence of copper or cupric oxide but only after the second step weight loss for PVC in the presence of copper chloride. As the temperature was increased the shape and position of the peaks changed with the greatest change occuring at high temperature alone.

Combustion or pyrolysis of PVC also and PVC in the presence of copper, copper chloride and cupric oxide at different temperatures have been successfully achieved. The main inorganic volatile is HCl. The concentration of HCl in gaseous emission from PVC in the presence of CuO is less than other samples while the concentration of HCl in the presence of $CuCl_2$ was more than in the other samples. The concentration of HCl is greater under combustion conditions than under pyrolysis conditions.

Benzene is the major volatile organic compound formed under pyrolysis and combustion conditions. The thermal degradation of PVC alone and PVC in the presence of copper compounds produces a large number of chlorinated aromatic hydrocarbon, aromatic hydrocarbons and short chain hydrocarbons.

The results show that the thermal degradation of PVC in the presence of copper, copper chloride and especially cupric oxide leads to the formation of more short chain linear gases, but fewer aromatic hydrocarbons and chlorinated aromatic hydrocarbons than from PVC alone.

2,3,7,8-TCDD is produced in the combustion of PVC in the presence of these copper compounds and also in the pyrolysis of PVC in the presence of CuO.

C) The aim for chapter 4 was to obtain a method for controlling the amount of HCl, aromatic hydrocarbons, and soot formed. The summary of this work is:

1-The presence of metal oxides, CuO, Fe_2O_3, ZnO, Al_2O_3, MoO_3, promote crosslinking of the decomposing PVC chain.

2-The formation of aromatic hydrocarbons and chlorinated aromatic hydrocarbons is hindered by the presence of metal oxides in combustion of PVC.

3-The concentration of HCl emission from combustion of PVC is reduced in the presence of metal oxides. HCl formation is depressed in the presence of the metal oxides because of ability to react with the metal oxide to form metal chlorides.

4-The concentration of metal oxides is important for control of aromatic hydrocarbons and chlorinated aromatic hydrocarbons. An increase in the concentration of metal oxide from 0% to 5% leads to a decrease in the concentration of hydrocarbons and aromatic hydrocarbons but an increase in short linear hydrocarbons. When the concentration of metal oxide is high (15% and 20% of metal oxide), however, the difference in the concentration of pollutants formed is less significant.

D) The focus in chapter five was to investigate the effect of applied fields on liquid and gas combustion processes for control of soot emissions. The summary of this work is:

1-Soot emissions decrease with increasing magnetic or electric field strength.

2-The particle size of soot decreases with increasing magnetic field strength but the chain length increased.

3-The microscopic results show that particle size and chain length of soot both decreased with increasing electric field strength.

4-The flame temperature in all experiments carried out in the presence of magnetic and electric fields increase with increasing field strength.

5-The length of flame decreases with increasing field strength.

6-Both magnetic fields and electric fields increase the vaporisation rate of combustible liquid with the effect increasing as field strength is increased.

7-The magnitude of heat flux from the flame liquid surface increases in positive applied field strength.

8-The results show that electric current increased linearly in all experiments with electric field.

APPENDIX A: TOXICOLOGY OF DIOXIN

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1 INTRODUCTION

The term “dioxins” is commonly used to refer to a family of compounds comprising around 75 dioxins and 135 related furans. The number and position of chlorine atoms on the molecule differ for each of the 210 compounds, and this also has a considerable effect on their relative toxicity. Only 17 of them are recognised as being highly toxic and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is the most dangerous. These compounds are shown in Table A-1.

Intensive studies of dioxins have confirmed that they acts as a powerful “growth dysregulator”, an “environmental hormone” that interferes with normal growth and development in fish, birds, reptiles, amphibians and mammals, including humans.

Dioxin disrupts the central nervous system, the immune system, the hormone (endocrine) system and the reproductive system, preventing normal growth and development of young and causing a variety of cancers.

Table A-1: 2,3,7,8-TCDD Toxicity equivalent factors for polychlorinated dibenzodioxins and dibenzofurans:

Number	Compound	TEQ*
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8- PeCDD	0.50
3	1,2,3,6,7,8-HxCDD	0.10
4	1,2,3,7,8,9-HxCDD	0.10
5	1,2,3,4,7,8-HxCDD	0.10
6	1,2,3,4,6,7,8-HpCDD	0.01
7	1,2,3,4,6,7,8,9-OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8- PeCDF	0.5
11	1,2,3,6,7,8-HxCDF	0.1
12	1,2,3,7,8,9-HxCDF	0.1
13	1,2,3,7,8-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	1,2,3,4,6,7,8,9-OCDF	0.001

---

* TEQ =Toxic equivalent concentration

2 BIOCHEMICAL EFFECTS OF 2,3,7,8-TCDD

2,3,7,8-TCDD is the most potent form of a broad family of xenobiotics that bind to an intracellular protein known as the Ah (aromatic hydrocarbon) receptor. Other members of this family include halogenated hydrocarbons such as the biphenyls, naphthalenes, and dibenzofurans, as well as non-halogenated species such as 3-methylcholanthrene and β-naphtaflavone.

The aromatic hydrocarbon (Ah) receptor was discovered almost 25 years ago and achieved notoriety as the front-line site of action of highly toxic environmental chemicals such as halogenated dioxins and polychlorinated biphenyls. [1]

Many of the known biological activities of PCDD`s and PCDF`s appear to follow their rank order binding affinity of the congeners and analogues to the aryl hydrocarbon receptor (AhR). This rank order holds for toxic responses such as acute toxicity and teratogenicity and for changes in concentration of several hepatic proteins including the induction of cytochromes P-450IA1 and IA2 and the modulation of the oestrogen receptor and epidermal growth factor receptor (EGFR).

The relationship between AhR binding and carcinogenicity of TCDD is less clear. However, TCDD is a carcinogen in several strains of laboratory animals (mice, rats, hamsters, fish) and the tumour sites include liver, thyroid and the respiratory tract, as well as others.

The binding of TCDD to AhR is similar, although not necessarily identical, to the interaction of many steroid hormones with their intracellular receptors.[2]

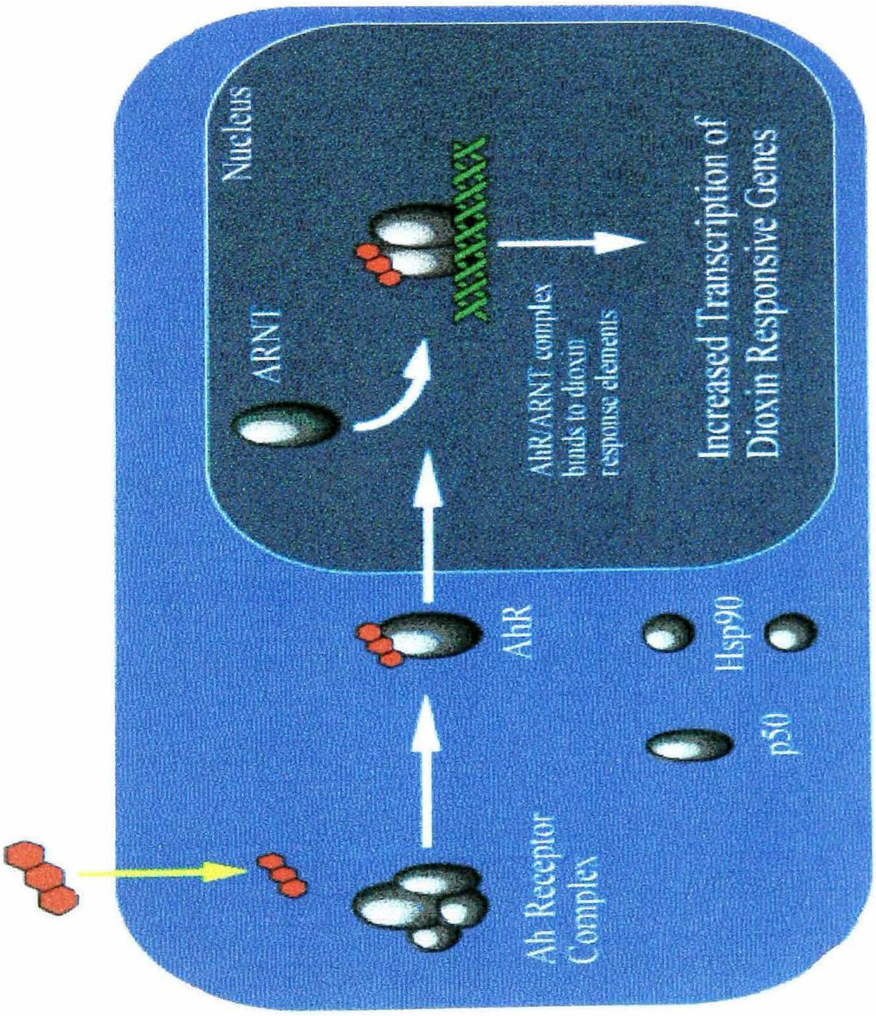
The binding of TCDD to AhR is reversible. Subsequent events, however, seem to reduce the likelihood of dissociation of the ligand: receptor complex with another macromolecule, the so-called ARNT (AhR nuclear transport) protein. [3] There may be a family of ARNT proteins that differ by cell types, which could account in part for the diversity of actions of TCDD in different tissues. The relationship between TCDD concentration and nuclear Ahr- TCDD concentration appears to be linear [4] indicating that, at low ligand concentrations, ARNT is not a rate-limiting factor. In the case of transcriptional activation of the CYP1A1 gene, the Ahr-ARNT-TCDD complex (activated TCDD complex) associates with specific elements in the genome called the xenobiotic (or dioxin) responsive elements (XREs or DREs).

As schematic representation of one mechanism whereby TCDD can modulate gene expression is shown in Figure A-1.

2.1 Thyroid hormones:

TCDD decreases circulating thyroid hormones and this is thought to be due to an increase in hepatic glucuronosyltransferase which metabolise these hormones and increase their elimination. Van Birgelen[5] determined total and free plasma thyroxin concentration and hepatic tyroxin glucuronidation (T4UGT) in rats exposed to TCDD for 90 days in the diet.

Figure A-1: A schematic of one mechanism of TCDD in cell



2.2 Vitamin metabolism

TCDD alters vitamin homeostasis in several species.[6] Reduction in hepatic storage of vitamin A is consistently observed in several species.[7] Although the importance of altered vitamin A homeostasis in the toxicity of dioxins is poorly understood, several studies have reported interactive effects of vitamin A and TCDD.[8]

3 NEUROLOGICAL AND BEHAVIOURAL TOXICOLOGY

The neurotoxic effects of the dioxins and related compounds have not received much attention, in comparison to other target organs, despite a number of clinical and semi-anecdotal reports of neurotoxic signs and symptoms in exposed humans. [9]

TCDD may be neurotoxic through indirect actions that affect the nervous system function and development. Low level, single dose exposures of pregnant rats results in offspring with significant alterations in sexual behaviour, characterised by demasculinization and feminization of male rats.[10, 11, 12] However, male hamsters exposed perinatally to TCDD do not exhibit alteration in sexual behaviour at doses of TCDD that reduce epididymal and ejaculated sperm.[13] In addition, feminization of sexual behaviour was not observed in male long Evans rats prenatally exposed to 1g TCDD /kg.[13]

Several reports have considered the effect of prenatal exposure on non-sexual behaviour. Peri- and postnatal exposure to TCDD was claimed to alter locomotor activity and learning behaviour in Wistar rats. [14] Perinatal exposure to TCDD also alters the auditory function in rats, which may be mediated by decreases in thyroid hormones.

4 TERATOLOGICAL AND DEVELOPMENTAL TOXICOLOGY

4.1 Cleft palate

TCDD produces structural malformation and developmental toxicity in several species. In mice, increase in the incidence of cleft palate is a well characterised phenomenon.[7, 15, 16] The doses required to produce cleft palate in mice are well below doses that produced maternal toxicity or foetal mortality .

Cleft palate in rats [17, 18] and hamsters [19] is induced at doses that result in significant maternal toxicity and foetal mortality. The induction of cleft palate is between 10% and 20%. However, in the mouse, cleft palate can reach 100% incidence before any foetal mortality or maternal toxicity is demonstrated. These data indicate that the mouse is extremely sensitive to this response. In vitro studies [20] indicate that humans may be much less sensitive than mice (1000 x) to TCDD mediated increases in cleft palate and similar to the rat.

4.2 Hydronephrosis

In mice, hydronephrosis is also produced by TCDD following prenatal exposure at doses that do not produce foetal mortality. [21] Postnatal exposure prior to day 4 can also produce hydronephrosis in mice.[22] The hyronephrosis induced by TCDD is due to occlusion of the ureter by epithelial cells.[23]

At present, there is no evidence that indicates humans are as sensitive as mice to these effects. The only available data comparing the sensitivity of foetal tissue demonstrate that human and rat foetal tissues are equally sensitive to the effects of TCDD.[20] These data suggest that sublethal exposure to TCDD may not result in frank terata of kidney. The relative effective doses for noncancer endpoints in studies with single dose administration are shown in Tables A-2 and A-3

4.3 Thymic and splenic atrophy

Prenatal exposure to TCDD produces thymic atrophy in all species tested and occurs at doses well below those that cause maternal or foetal toxicity. [20] Thymic atrophy occurs at similar doses in rats, guinea pigs and hamsters exposed prenatally despite a 5000 fold difference in LD_{50} in the adult animals. [19] The sensitivity and interspecies consistency of this response indicate that prenatal exposure to TCDD may result in thymic atrophy in humans.

In adult animals, TCDD induced thymic atrophy occurs at higher doses compared to animals exposed in utero. Thymic atrophy occurs at doses which result in overt toxic effects such as weight loss and lethality.[19]

Table A-2 - Relative effective dose for noncancer endpoints in studies with single dose administration

Study description	Dose regime[1]	Endpoint	shape parameter[2]	1%extra effect[3]	lower conf. bound[1]	upper conf.bound[1]	Data[4]	Fit type[5]
Kitchin & Woods, 1979 female S-D rats	Single	Liver cytochrome p-450	0.53	0.46	0.00	34.77	W	H
	3 days	liver benzopyrene hydroxlase	1..37	1.03	0.54	2.11	W	H
Abraham, et al., 1988 femal Wistar rats	Single	liver cytochrome p-450	0.72	1..93	0.52	12.50	W	H
	7 days	liver EROD	0..97	0.16	0.09	0.30	W	H
Narasimhan et al. 1994 female B6c3F1 mice	Single,	liver EROD	0..97	1.15	0.00	72.81	W	H
	24 hrs	liver Cyp1A1	1.00	0.22	0.00	33.67	W	H
		liver Cyp1A2	3.88	141.50	0.00	828.39	W	H
		Total Ah receptor binding	3.85	168.16			UW	H
Davis & Safe 1988 maleC57Bl/6N mice	S,4days	Spleen PFC/10 cells	2.60	13.50	0.02	44.91	UW	H
		Spleen PFC/10 cells	3..96	211.01	182.15	294.32	UW	H
Olson , et al., 1980 male golden syrian hamsters	Single	Thymus weight	1..37	11323.50	0.45	83368.89	W	H
	50 days	spleen weight	5.75	294389.3	-[6]	-	W	H
Mably, et al., 1992 preg.female,male offspring, HoltmanS-Drat	single	Sperm morph.-day 120	4.20	99.22	28.33	371.99 *	W	H
		Fertility index	23.06	350.53	-	-	W	H
		Cauda Sperm count day 63	0.86	0.43	0.01	1.95	W	H
		Cauda sperm count -day 120	0.97	1.19	0.13	6.62	W	H
		Cauda sperm count/g-day 120	1.50	4.80	0.00	17.92	W	H

1- Dose regime :Single dose indicated ,lenghth of time until sacrifice.

2-Shape of the dose-response curve expressed as exponent in hill equation or power law fit to the data.

3-Doses are in ng/kg body wt.(single doses).

4-Data types used in analyses :W-group means weighted by inverse of standard or power law fit to the data.

5-Type of fit :H-Hill equation fit ,P-power law fit.

6- A dash indicates where a quantity could not be computed .

* limited by domain of search

Table A-3. Relative effective dose for noncancer end points in studies with single dose administration

Study description	Dose[1] regime	Endpoint	Shape parameter[2]	10% extra effect[3]	Lower conf.bound[1]	Upper conf.bound[1]	Data[4]	Fit type[5]
Kitchin & Woods, 1979 femaleS-D rats	Single	Liver cytochrome p-450	0.53	41.31	4.24	372.19	W	H
	3 days	liver benzopyrene hydroxlase	1..37	5.56	3.53	11.27	W	H
Abraham, et al., 1988 femal Wistar rats	Single	liver cytochrome p-450	0.72	52.46	26.89	141.60	W	H
	7 days	liver EROD	0..97	1.69	1.14	2.62	W	H
Narasimhan et al. 1994 female B6c3F1 mice	Single,	liver erod	0..97	12.36	0.09	242.64	W	H
	24 hrs	liver Cyp1A1	1.00	2.21	0.00	255.56	W	H
		liver Cyp1A2	3.88	257.63	2.55	1872.92	UW	H
		Total Ah receptor binding	3.85	306.37	-[6]	-		
Davis & Safe 1988 maleC57Bl/6N mice	S,4days	Spleen PFC/10 cells	2.60	34.23	1.25	74.70	UW	H
		Spleen PFC/10 cells	3..96	387.31	377.23	429.23	UW	H
Olson, et al.,1980 male golden syrian hamsters	Single	Thymus weight	1..37	6520.74	250.15	239129.80	W	H
	50 days	spleen weight	5.75	470125.8	-	-	W	H
Mably,etal.,92 preg.female ,male offspring, HoltmanS-Drat	single	Sperm morph.-day 120	4.20	180.93	109.61	386.96*	W	H
		Fertility index	23.06	396.85	-	-	W	H
		Cauda Sperm count day 63	0.86	7.09	1.19	16.01	W	H
		Cauda sperm count -day 120	0.97	15.35	5.30	31.24	W	H
		Cauda sperm count/g-day 120	1.50	27.44	0.15	49.53	W	H

1- Dose regime :Single dose indicated ,lenghth of time until sacrifice.
2-Shape of the dose-response curve expressed as exponent in hill equation or power law fit to the data.
3-Doses are in ng/kg body wt.(single doses).
4-Data types used in analyses :W-group means weighted by inverse of standard or power law fit to the data.
5-Type of fit :H-Hill equation fit ,P-power law fit.
6- A dash indicates where a quantity could not be computed .

* -limited by domain of search

5 REPRODUCTIVE TOXICITY

5.1 Female reproductive toxicity

Several studies have demonstrated that TCDD affects female reproductive function in mice, rats and monkeys. TCDD reduces fertility, litter size, and uterine weights. TCDD also alters menstrual and oestrus cycling in monkeys, mice and rats. Uterine weight and menstrual oestrus cycling are regulated by oestrogens. These data indicate that TCDD has antioestrogenic effects that could impair female reproductive functioning.The antioestrogenic effects of TCDD are, however, tissue specific as well as developmental state specific.[24, 25]

The antioestrogenic actions of TCDD could be mediated either by changes in circulating oestradiol, qualitative changes in oestrogen metabolism or through decreases in oestrogen receptors. In mice, TCDD does not alter serum oestradiol levels and the antioestrogenic actions of TCDD are associated with decreases in uterine cytosolic and nuclear oestrogen receptor protein. [24] Similarly, TCDD decreases the binding capacities of rat hepatic and uterine oestrogen receptor [25] but does not affect serum oestradiol levels.

5.2 Male reproductive toxicity

When administered to adult rats, TCDD decreases testis and sex organ weights, decreases spermatogenesis and reduces fertility.[26, 27, 28] These effects are associated with decreases in plasma testosterone.[26] The decreases in circulating androgens are due to decreased testicular responsiveness to luteinizing hormone and increased pituitary responsiveness to feed back inhibition by androgens.[28, 29, 30]

In contrast to the adults, the developing male reproductive system is very sensitive to effects of TCDD. In male rats, prenatal exposure to TCDD produces persistent decreases in sex organ weight, and permanent decreases in cauda epodidymal sperm and ejaculated sperm counts.[10, 11, 12] In addition, similar effects were observed in hamsters exposed to 2g/kg of TCDD in vitero.[31] The effects on sperm counts in rats occurs at a single dose as low as 64ng/kg (Mably). Initial reports suggested that prenatal exposure to TCDD produced demasculinization and feminization of male sexual behaviour in Holtzman rats.[11]

6 RELEVANCE OF ANIMAL DATA FOR PREDICTING HUMAN TOXICITY:

Although the reliability of using animal data to estimate human risks has been questioned, as human data are limited it does appear that animal models are generally appropriate for estimating human risks. Many of the biochemical effects produced by TCDD in animals also occur in humans. Data on effects of TCDD and its analogues in humans are based on in vitro (i.e. in cell culture) as well as epidemiological studies.

In vitro systems such as keratinocytes or thymocytes in culture have clearly shown that human cells possess Ah receptors and that they respond similarly to cells derived from rodents. Several reports in the literature suggest that exposure of humans to TCDD and related compounds may be associated with cancer at many different sites, including malignant lymphomas, soft tissue sarcomas, hepatobiliary tumours, hematopoietic tumours, thyroid tumours and respiratory tract tumours.[32, 33, 34, 35, 36, 37]

Several noncarcinogenic effects of PCDDs show good agreement between laboratory species and humans. [38] For example, in laboratory animals, TCDD causes altered intermediary metabolism manifested by changes in lipid and glucose levels. Consistent with these results, workers exposed to TCDD during the manufacture of trichlorophenol showed elevated total serum triacylglycerides and cholesterol with decreased high density lipoprotein.[39] The results of a statistical analysis of serum TCDD analysis and health effects in Air Force personnel following exposure to Agent Orange were reported.[40] Significant associations between serum TCDD levels and several lipid related variables were found (percent body fat, cholesterol, triacylglycerols). Another interesting finding of these studies was a positive relationship between TCDD exposure and diabetes.

The human to experimental animal comparison is confounded by at least two factors:

1-For most toxic effects produced by dioxin, there is marked species variation. An outlier or hightly susceptible species for on effect (i.e. guinea pigs for lethality or mice for teratogenicity) may not be an outlier for other responses .

2-Human toxicity testing is based on epidemiological data comparing "exposed" to "unexposed" individuals. However, the "unexposure" cohorts contain measurable amounts of background exposure to PCDDs, PCDFs and dioxin-like OCBs. Also, the results of many epidemiological studies are hampered by small sample size, and in many cases the actual amounts of TCDD and related compounds in the human tissues were not examined.

7 HUMAN RESPONSE:

Human data always present difficulties for dose-response assessment. Unlike laboratory studies, there are a variety of confounding factors which are difficult to control: there is also the possibility of disease misclassification and usually weak measures of dose. Risk studies in human populations do not, however, require assumptions concerning species extrapolation and as such, should be used maximally in study dose- response.

7.1 Lung cancer and cancer combined:

Data from five retrospective occupational cohorts provide evidence of the human carcinogencity of dioxin. All showed increased mortality from respiratory system cancer; the two largest cohorts [35, 38] showed increases in mortality from soft tissue sarcoma and four cohorts [34, 35, 36, 41, 42] showed increased mortality from all cancer types showing significance only for the high-exposure, long latent period subcohort. The largest study with 18,000 workers from 20 cohorts in 10 countries [37] showed no increase in overall cancer mortality, but these authors, unlike the others, have not presented the data allowing for a latent period, thus inclusion of person years at risk during early years following start of exposure may bias the estimates toward the null.

Further more, the Saracci et al. [37] and Becher et al [43] studies, unlike the other three, provide no way to quantitatively estimate TCDD exposure to their cohorts. The Becher et al [43] analysis of four phenoxy herbicide production plants in Germany (2,479 workers) found statistically significant increased mortality from all cancers, respiratory cancers and non-Hodgkin`s lymphoma. The largest of these four plants was, however, previously studied by Manz et al [35] who, unlike Becher et al,[43] provided sufficient information on TCDD levels for dose -response modelling.

Fingerhut et al [34] studied of more than 5000 U.S. workers from 12 U.S. plants producing chemicals contaminated with TCDD. Of the 1520 workers exposed to TCDD contaminated processes for at least 1 year with a more than 20 years latency, mortality was significantly increased for both lung cancer (standard mortality ratio [SMR] =142) and for all cancer combined (SMR=146).

Lu et al [44] have shown that both RA (retinoic acid) and TCDD elicit a number of common responses in MCF-7 human breast cancer cells, including inhibition of oestrogen- induced cell proliferation and [H-3] thymidine uptake, inhibition of nuclear oestrogen receptor [ER] ligand binding, and interactions with a consensus oestrogen-responsive element in a gel mobility shift assay. RA and TCDD also decrease steady - state ER mRNA levels in a time dependent manner.

An industrial accident in Seveso, Italy, in 1976, caused contamination of the residential community with 2,3,7,8-TCDD. Cancer occurrence was investigated in the first post-accident decade (1977-1986) among nearly 20,000 subjects aged 0-19 years by Pesatori et al.[45] They have shown a suggestive increase for Hodgkin's lymphoma (relative risk [RR] =2.0,95% confidence interval (CI)=0.5-7.6). Myeloid leukaemia showed a clear, but not statistically significant increase (RR=2.7,95% CI= 0.7-11.4). The most prominent result concerned thyroid cancer, not just for the magnitude of the increase (two cases RR=4.6,95%CI=0.6-32.7) The authors say any conclusive interpretation would be premature because of the short time since initial exposure, ecological definition of exposure status and limited number of events.

Bertazzi et al.[33] examined cancer mortality from 1976 to 1991 among residents of Seveso, Italy, after the same industrial accident. The area was divided into zones with decreasing exposure to dioxin (A) highest, (B) lower, (R) lowest. The population of a surrounding non contaminated area was used as a reference group. In zone A they saw a moderate increase in mortality from digestive cancer among women (relative risk RR= 1.5,95% confidence interval CI= 0.5-3.5). In zone B, women had an increased mortality from stomach cancer (RR=2.4,95% ,CI=0.8-5.7) and men had increased mortality from rectal cancer (RR=6.2,95%,CI=1.7-15.9).The highest risk seen in zone B was for leukaemia (RR=3.1,95%CI=0.4-11-9 in men and RR 6.5, 95% CI =0.7-23.5 in women). Soft tissue sarcoma was elevated only among zone R males (RR=2.1,95%, CI =0.6-5.4).

7.2 Non -cancer effects of dioxin

Pokrovsky, et al.[46] have shown a relationship between AIDS an dioxin exposure. The primary observation made in this study is as follows:

"In MT-4 cell culture infected by HIV-1 virus and increase of virus production after a treatment of cells with 2,3,7,8-TCDD has been revealed."

Schecter[53] reported elevated levels of dioxins and dibenzofurans, known immunosuppressants, in clinically symptomatic AIDS patients as compared with asymptomatic but human immunodeficiency virus (HIV) infected patients who had below - average dioxin levels.

Ralpff, [48] has shown smokers infected with HIV-1 tend to develop AIDS more quickly than non-smokers. Some scientists have also observed that dioxin like compounds foster the proliferation of the AIDS virus in cultured cells.

Tsyrlov [49] has shown 2,3,7,8-TCDD is an inducer of microsomal benzo(a)pyrene hydoxylase (AHH) and 7-ethoxyresorulin o-diethylase (EROD) in MT -4 human lymphoid cell culture.

Two other effects of dioxin can be as following:

A)- Development and other biological signalling molecules. Dioxin can alter the growth differentiation and viability of cells. These processes are particularly important during development from a single fertilised egg to a complete organism. During this time, cells grow and differentiate into body tissues. There is an increasing amount of evidence suggesting that in the biochemical systems affected by dioxin the molecular receptor and the genes and proteins it regulates may play some important role in this process.

Blankenship [50] has shown the developing organism may be particularly sensitive to the effect of dioxin. This appears to be true for the male reproductive system in the rat. These results are generally consistent with observations of psychomotor developmental delay in children of human mothers exposed to mixtures of dioxin-like and non dioxin-like compounds. The children of relatively highly exposed women who consumed rice oil contaminated with polychlorinated dibenzo furans and PCBs exhibited learning problems and behavioural disorders.[51] These children also suffered abnormal skin pigmentation, deformed nails, early tooth growth and smaller size .

However, humans may not be as prone to dioxin-induced cleft palate as mice.

B) - Immune system impacts

The immune system has to recognise and eliminate foreign substances from the body, including microorganisms that it first met decades before or that it has never encountered and avoid reacting againt itself. Errors in either direction are problematic: an over- reactive immune system may lead to autoimmune disease, while suppression may lead to increased susceptibility to disease and cancer. Proper functioning of the immune system involves delicate control over growth and maturation of immune system cells and the hormone-like compounds which regulate them. Perturbation of the immune system may be one of the most sensitive effects of dioxin. Children of mothers who lived in dioxin-contaminated Times Beach, Missouri during and after pregnancy had elevated rates of bronchitis.[52]

A recent Dutch study suggests hormonal changes in the general population. Levels of certain thyroid hormones in 38 healthy new-born infants depended significantly on the concerntrations of dioxin-equivalents in the breast milk of their mothers.[53]

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