CHARACTERISATION OF GROUNDWATER IN MAINLY OLD AND CLOSED LANDFILL SITES

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

MEENU GAJREE

September 1999

Centre for Environmental Research

Department of Materials Engineering

Brunel University

Uxbridge

Middlesex

CONTENTS

ACKNOWLEDGEMENT

I am grateful to LB Hounslow (LBH) for funding this research work and I acknowledge encouragement and guidance by my supervisor Professor J. D. Donaldson and help by Dr. S. M. Grimes during the final stages of this research work. I am grateful to S. Brown, the Training Officer (LBH) for providing support and encouragement throughout the duration of this research work and my thanks to R. Wood (LBH) for his support and guidance. I am grateful to S. Stevens (LBH) for doing the GIS drawings.

I acknowledge technical support from The Centre for Environmental Research Group (CERG) at Brunel University, particularly Dr. S.J. Clark, H. Dee and B. Wheals. I also acknowledge help on Leaching Tests by D. Williamson.

I am grateful to the Landfill Team (LBH) for their support. I am particularly thankful to P. Robson, P. Thake and S. W. Moreby in Landfill Team of LBH and J. Burns, M. Hassan, N. Yasri and A. J. Jafari of CERG at Brunel University for their help with sampling groundwater.

My special thanks to Kamal for helping me out with IT problems. I am also grateful to my father Gp. Capt. Ved Kumar (Retd., IAF) for his inspiration to carry out this research work. Last, but not least, my thanks to my family Pran, Neesha and Kamal who have greatly supported this work and endured with patience my working on weekends and other non-working days such as annual holidays.

STATEMENT

Information contained in this thesis represents the research work of the author and the views and interpretations expressed are those of the author and not of LB Hounslow.

Meenu Gajree

ABSTRACT

A study is made of the use of chemical analysis of groundwater samples to assess groundwater quality. Samples from forty-seven boreholes within and around ten landfill sites in the London Borough of Hounslow were analysed. Most of the landfill sites studied were filled prior to the implementation of the Control of Pollution Act 1974 and were not designed with environmental protection in mind.

Boreholes were tested for methane, carbon dioxide and groundwater samples were analysed for electrical conductivity (EC), ammonium nitrogen (NH_4-N), COD, TOC, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, oxidation - reduction - potential (ORP) and pH. The first ten of these analytical parameters were considered for groundwater quality assessment and the most important selected for more detailed study namely CH_4, CO_2, EC, NH_4-N, COD and TOC.

Pollution ratings are allocated on the basis of single pollutant analytical data and averaged for each of the bore hole samples. Goodness of fit values between the single analyte values and the average data were calculated and no set of single analyte data was found to provide good groundwater quality assessment. A series of formulae combining the six analyte parameters was considered and the data evaluated by goodness of fit calculations to provide an effective means of assessing groundwater quality. The ratings obtained from the best formula are compared with historical broad band classification of landfill sites and show how sites must be assessed on the basis of samples taken from within the site and not around the perimeter.

The production of acetic acid in the acetogenic phase of landfill reactions will increase the leachability and mobility of many metal pollutants and particularly of lead. Studies on the leachability of lead in acetic acid media show how lead solubility is increased in acetic acid media by the formation of triacetatolead(II) species, $Pb(CH_3CO_2)_3^-$.

CHAPTER I - LIST OF CONTENTS

INTRODUCTION

Page Number

CHAPTER 1

INTRODUCTION

1.1 AIM

The aim of the work described in this thesis is to devise a method for the characterisation of groundwater for use as a management tool.

1.2 OBJECTIVES

The objectives of the research set out at the start of the project were

- To study groundwater characteristics at landfill sites in the London Borough of Hounslow by determining the levels of various components of the groundwater
- To include in the study landfill sites containing putrescible material and some virgin ground
- To use the data obtained to assess groundwater regime and the quality of groundwater in the Borough
- To relate data from borehole gas readings to groundwater quality
- To devise a means of predicting groundwater quality from gas monitoring data
- To measure the levels of dissolved acetates in groundwater and leachates from gassing landfill sites
- To relate the acetate levels in groundwater to the levels of gas emissions at landfill sites
- To study the effect of acetate concentrations on leaching of lead in the aqueous environment

1.3 INTRODUCTION AND BACKGROUND

Landfill has been defined by The International Solid Waste Association (ISWA) in 1992 as " The engineered deposit of waste onto and into land in such a way that pollution or harm to the environment is prevented and through restoration land provided which may be used for another purpose". Although this definition applies to more recent landfills, most old landfill sites were not designed or managed to protect the environment. Most of the landfill sites included in the present investigation were between 30 and 100 years old and, because little is known of their content and management, they provide an ideal situation for the study of the effects of landfill in groundwater.

Approximately 36 million tonnes of municipal solid waste are generated each year in the UK and 90% of that waste is and has been in the past disposed of to landfill. The principal inputs to landfill are the solid and liquid wastes generated by human activities. Table 1.1 gives an estimate of annual waste arisings in the United Kingdom. Although the mixture of household and commercial wastes commonly referred to as municipal solid waste forms less than 10% of total wastes it contains a high proportion of degradable materials that may decompose to produce organically strong leachates and landfill gas[1]. The typical overall composition of municipal solid waste and civic amenity waste as received at landfill is shown in the Table 1.2. About 50% of the materials consist of putrescible and cellulosic material, such as paper, wood, and garden waste and have the potential for microbial degradation in the short or long term.

Table 1.1

Estimate of Annual Waste Arisings in United Kingdom.

Waste Source	**Percentage of Total Arisings**	**Arisings-Million Tonnes Per Annum**
Household	5	20
Commercial	4	16
Industrial	17	68
Demolition and Construction	8	32
Sewage Sludge *,+	8	32
Agriculture	20	80
Mining and Quarrying	27	108
Dredging Spoils *	11	44
Total	100	400

* Dry Weight

+ Sewage Sludge is only a controlled waste when landfilled or incinerated but not otherwise.

Source: DOE, Waste Management Paper 26A, Landfill Completion, 1994.

Table 1.2

Typical Composition of Urban Collection and Civic amenity wastes as Delivered to Landfill

Constituent	**Weight % (as received)**
Paper	29.2
Putrescible	19.0
Unsorted fines	8.6
Glass	8.4
Ferrous metal	8.0
Misc. Combustible	5.8
Plastic - film	4.2
Misc. Non-combustible	4.0
Garden waste	3.8
Textile	3.0
Dense plastic	2,8
Wood	2.2
Non-ferrous metal	1.0

Source: DOE, Waste Management Paper 26A, Landfill Completion, 1994.

The moisture content of the waste is about 33% by weight, the bulk density of uncompressed waste is approximately 170 kg/m^3 and the gross and net calorific values of waste have been estimated as 9,260 kJ/kg and 7,630 kJ/kg respectively.

The amount of municipal waste generated has increased over the past 100 years. The composition of waste has been changing over that period, mainly caused by changes in regulations. Prior to the 1956 Clean Air Act, the waste consisted mainly, of ash and cinders and was therefore relatively inert. Since the 1960's the waste contained more putrescible material which has the potential to pollute the environment by generating landfill gas and leachate material.

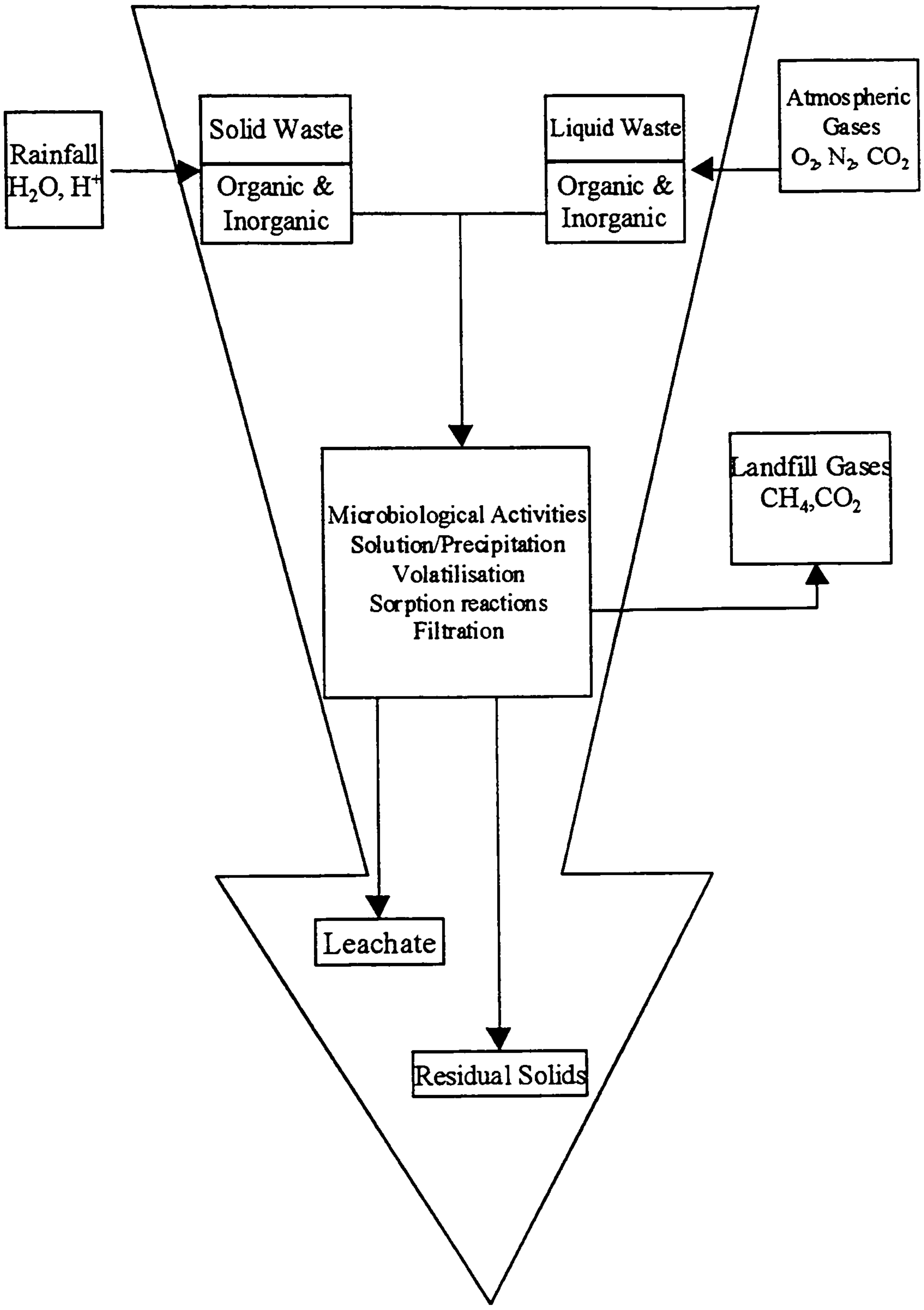
The landfill process is represented schematically in Figure 1.1. Inputs to landfill consists of solids (waste), liquid (rainfall) and gases (air). The waste undergoes changes due to microbial activity, solution/precipitation, volatilisation, sorption reactions and filtration to form the outputs, which are landfill gas, leachates, and residual solids. These processes are as shown in Figure 1.2 and described in greater detail below.

Within waste disposed to landfill, vegetable matter, paper, cardboard and to some extent textiles and other organic materials are potentially biodegradable. The overall breakdown of carbohydrates under anaerobic conditions can be represented by the equation:

$$\underset{\text{(carbohydrate)}}{C_6H_{12}O_6} \xrightarrow{\text{Micro-organisms}} CH_4 + CO_2 + \underset{\text{(bacteria)}}{\text{Biomass}} + \text{Heat}$$

The conversion of carbohydrate is a highly energy efficient process and the major product methane is a potential source of energy. The five stages in the decomposition of waste over a period of time to produce landfill gas and leachate are shown in Figures 1.3 and 1.4 respectively.

Figure 1.1 Landfill Processes



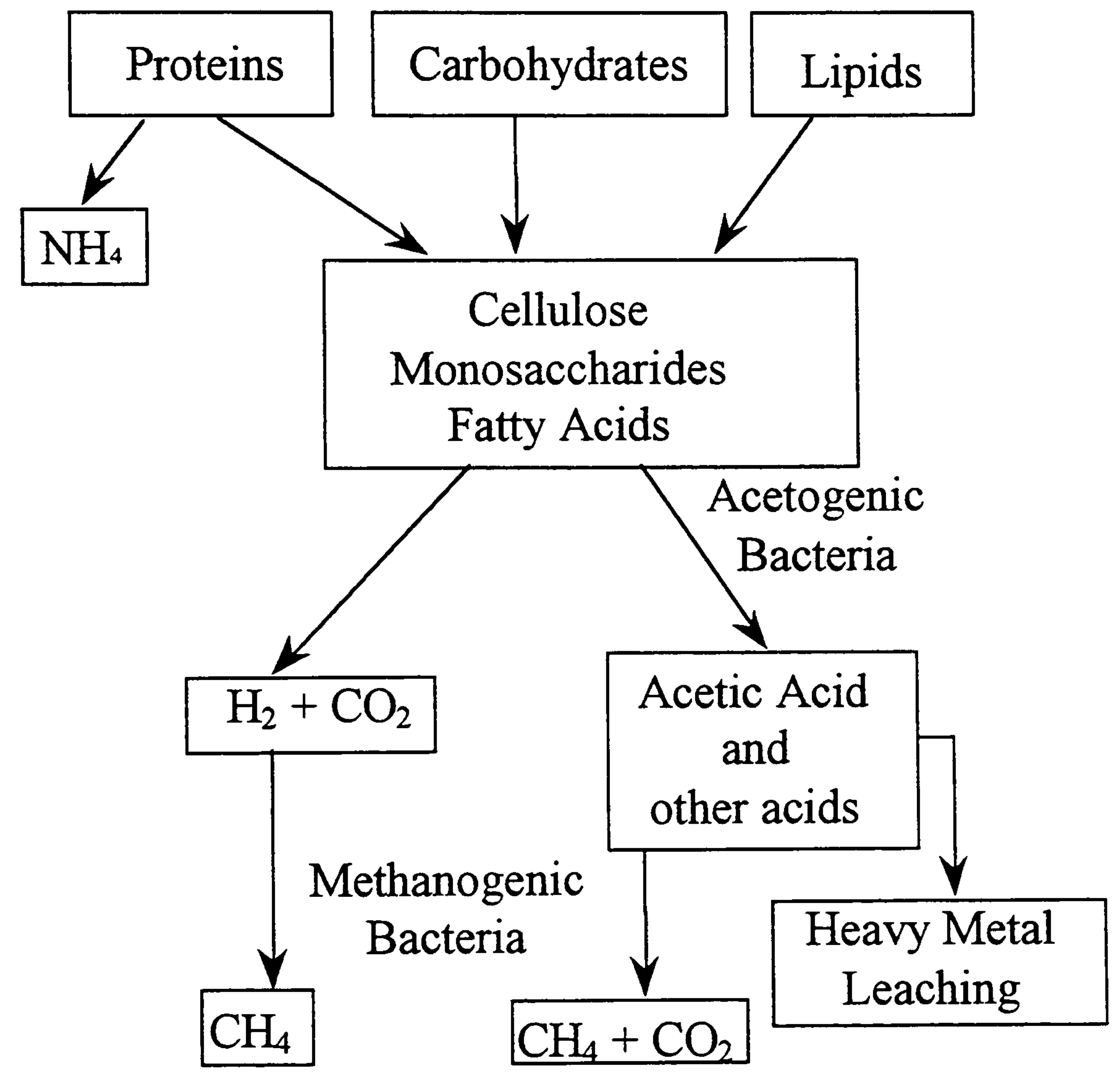
Adapted from: DoE, Waste Management Paper No. 26A, Landfill Completion, 1994.

The First Stage in the process is when organic waste is covered in landfill, initial stages of microbiological decomposition will be aerobic and the oxygen trapped in the waste will be utilised by micro-organisms with carbon dioxide and water being the main products. Oxygen is depleted rapidly and anaerobic micro-organisms, especially bacteria, start to take over the biodegradation.

The Second Stage is the hydrolytic stage, where proteins, carbohydrates, and lipids are hydrolysed to produce amino acids, simple sugars, glycerol and long chain fatty acids. The amino acids break down further with the formation of ammonium ions. As shown in Figure.1.4, the changes with time include: pH reduction, sharp increase in the heavy metal and chloride levels in the leachate, and an increase in hydrogen production. The carbon dioxide levels also increase sharply with time as shown in Figure 1.3. Waste compaction leads in time to maximum settlement in the ground, and the COD levels begin to increase rapidly in the leachate.

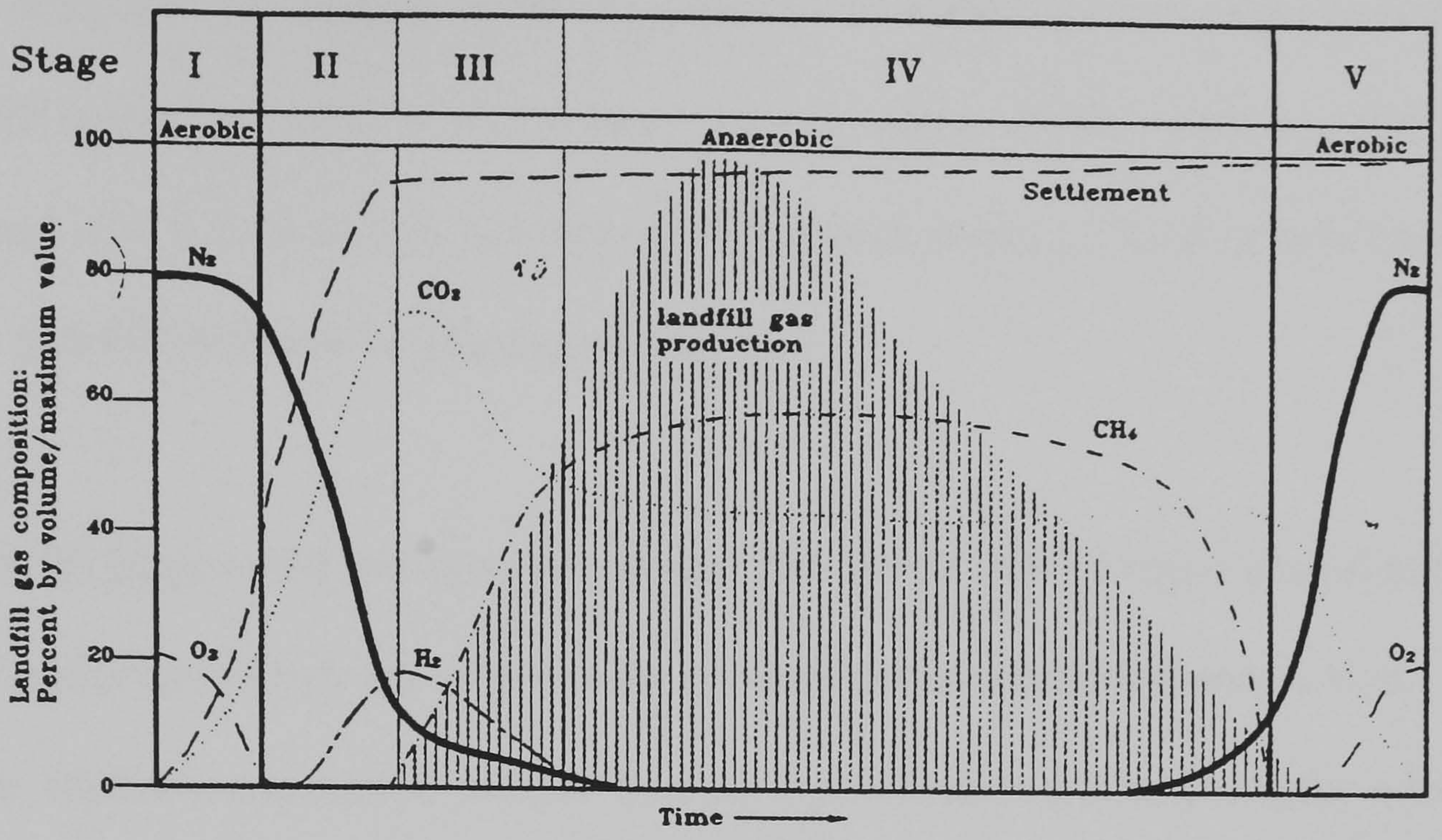
Figure 1.2

Stages in Degradation of Organic Waste



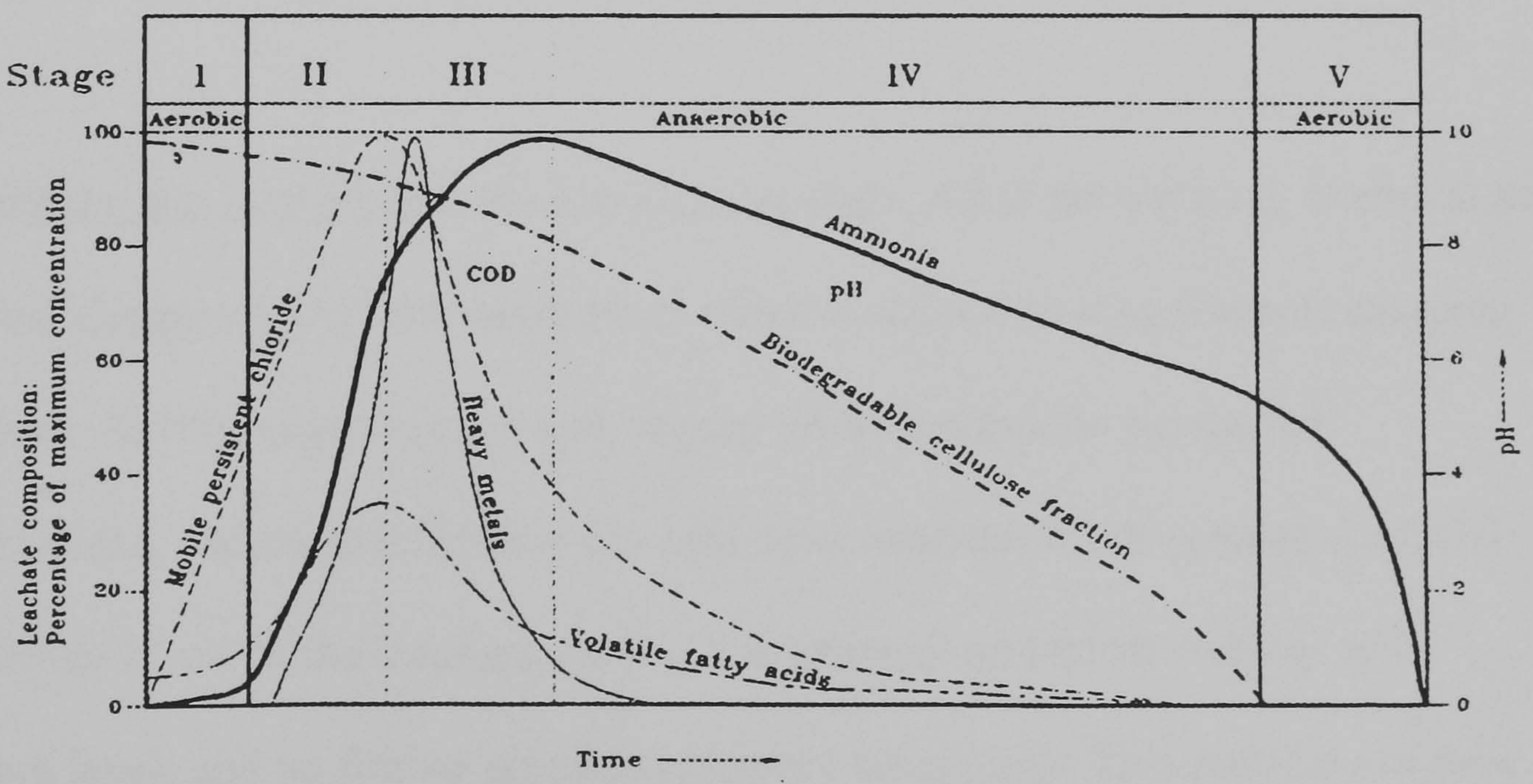
Adapted from: DoE, Waste Management Paper No. 27, Landfill Gas, 1991.

Figure 1.3 Changes in Composition of Landfill Gas



Source: DOE, Waste Management Paper 26B

Figure 1.4 Changes in Composition of Leachate



Source: DOE, Waste Management Paper 26B

In the Third Stage, the acetogenic stage, bacteria convert the organic products to acetates, hydrogen levels reduce sharply, methane production starts increasing, and carbon dioxide levels reduce. At this stage the COD reaches its maximum level due to increased organic content in the leachate. Concentrations of heavy metals also reach new maximum values rapidly and then start to reduce sharply. Chloride levels also reduce rapidly with time as this stage progresses.

The Fourth Stage is the methanogenic stage. This is one of the longest phases in the landfill stabilisation process where acetates break down to methane and carbon dioxide. Methane and carbon dioxide levels are produced at a steady rate for a few decades and this stage may last for many years as indicated by the fact that numerous landfill sites, more than 30 years old are still emitting methane gas. Ground settlement at this stage increases only slightly. The COD is sharply reduced in this stage as the organic content of the leachate becomes less because of the methanogenic stabilisation processes. Ammonia and chloride concentrations also reduce rapidly at this stage and the pH rises towards neutrality.

The Fifth and the final stage is the stabilisation stage, when the physical, chemical and biological changes within the waste are at minima and are tending towards stopping altogether. At this stage nitrogen and oxygen levels increase to normal air concentrations, carbon dioxide drops to near zero, methane is not present, the COD and chloride levels in the leachate are low and ammonium rapidly reduces to its minimum level, and no further ground settlement takes place. This process can take up to 60 years or more from the landfill completion. The rate of biodegradation processes can be retarded at any stage due to inhibition effects of certain chemicals, lack of moisture, and other factors.

1.3.1 Landfill Gas

In the methanogenic stage, landfill gas is produced at a steady rate for many years, possibly decades, giving approximately 66% methane and 33% carbon dioxide. Typical and maximum compositions of landfill gas are in Table 1.3 while typical compositions of other methane containing gases are in Table 1.4. Sometimes during site investigation it becomes necessary to determine the source of the methane gas in order to carry out appropriate remediation on site. A gas sample should then be collected and analysed in the laboratory to determine its composition.

Table 1.3

Typical Landfill Gas Composition

Component (%Volume)	Typical value (%volume)	Observed Maximum (%volume)
Methane	63.8	88.0
Carbon Dioxide	33.6	89.3
Oxygen	0.16	20.9
Nitrogen	2.4	87.0
Hydrogen	0.05	21.1
Carbon Monoxide	0.001	0.09
Ethane	0.005	0.0139
Ethene	0.018	-
Acetaldehyde	0.005	-
Propane	0.002	0.0171
Butanes	0.003	0.023
Helium	0.00005	-
Higher Alkanes	<0.05	0.07
Unsaturated Hydrocarbons	0.009	0.048
Halogenated Compounds	0.00002	0.032
Hydrogen Sulphide	0.00002	35.0
Organosulphur Compounds	0.00001	0.028
Alcohols	0.00001	0.127
Others	0.00005	0.023

Source: DOE, Waste Management Paper 26, 1986

Table1.4

Typical compositions of methane-containing gases

Source	Gas composition % by volume							
	CH_4	C_2H_6	C_3H_8	CO_2	CO	H_2S	N_2	O_2
Landfill gas	20-65			16-57	$<1\times10^{-4}$	2×10^{-5}	0.5-37	<0.3
Mine gas								
seam	80-95	8	4	0.2-6			2-9	
Pumped drainage	22-95	3	1	0.5-6	0-10		1-61	
Wetlands/ Peat lands								
Freshwater muds	3-86			0.3-13			16-94	
Saltwater muds	55-79			2-13				
Marsh gas	11-88						3-69	
Buried peats and Organic soils	45-97						1.6-54	
Mains natural gas	94	3.2	0.6	0.5			1.2	

Source: CIRIA Report 149, Protecting Development from Methane, 1995

1.3.1.1 Properties of landfill Gas.

Methane is a colourless, odourless, flammable gas with a density lighter than air. Carbon dioxide is also colourless and odourless, but is non-flammable and is denser than air, other main components of landfill gas at percentage levels are hydrogen, oxygen and nitrogen. When present, the later two gases are indicative of air ingress in a landfill. Nitrogen is inert and has little effect except to modify the explosive range for methane. However, the flammability of methane does depend upon the oxygen levels.

Explosive Nature of Landfill Gas: Both methane and hydrogen are flammable in the presence of oxygen. Methane is flammable in air within the range 5-15% by volume, while hydrogen is flammable within the range 4.1-75%. Hydrogen is mainly present in landfill in the early stages of waste stabilisation when the concentrations can reach levels of approximately 20% (v/v). Hydrogen is, however, seldom present in landfill gas at levels within the explosive range. The values of upper explosive limit (UEL) and lower explosive limit (LEL) depend on levels of gases such as carbon dioxide and nitrogen. For most purposes the flammable range of 5-15 %v/v methane is recognised and is the basis upon which methane gas control levels for adopting safety measures in and around landfill sites have been set. The emission of landfill gas within a landfill can cause underground fires, these can be difficult to extinguish and can lead to uncontrolled and unpredictable subsidence and production of smoke and toxic fumes.

Solubility of Landfill Gas. Gases are not always present in the ground in the gaseous state. They can be dissolved in the groundwater to an extent depending on the pressure, temperature and the concentration of other gases present and the dissolved mineral salt content of the water itself. Typical values of the solubility of methane and other gases in water are given in the Table 1.5

Table 1.5: Solubility of Landfill Gas

Gas	**Solubility at temperature 25°C and total pressure of 1 atm. (mg/l)***
Methane	21.5
Carbon dioxide	1510
Carbon monoxide	0.275
Hydrogen sulphide	3850
Hydrogen	1.6

Note * Total pressure is partial pressure of gas and water

Source: CIRIA Report 149, Protecting Development from Methane, 1995

Dissolved gases may be advected by groundwater and only when the pressure is reduced and solubility limit of the gas in water is exceeded, will they bubble out of solution and form a separate gaseous phase as follows

$$P_b = x_b \cdot K_b$$

Where P_b = partial pressure of the gas (dimensions of pressure)

x_b = mole fraction of solute (dimensionless)

K_b = Henry's Law constant (dimensions of pressure).

From this equation it is relatively simple to calculate the amount of methane or other gases dissolved in water if the pressure and composition of the associated gas phase is known. Henry's Law is valid for sparingly soluble gases. For carbon dioxide, however, Henry's Law holds at low pressures but significant deviations are found at high pressures due either to the fact that gas levels in solution are large because of the solubility of the gas or to the application of high-pressure situation. In case of carbon dioxide, equilibrium is set up between carbon dioxide, hydrogen carbonate and carbonate in solution as follows:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Table 1.6: Effect of pH on CO_2 in Solution

pH	4	5	6	7	8	9
%CO_2	99.5	95.4	67.7	17.3	2.0	0.2
% HCO_3^-	0.5	4.6	32.2	82.7	97.4	94.1
% CO_3^{2-}	0	0	0	0	2.6	5.7

From Table 1.6 it is clear that at low pH most of CO_2 remains in the gaseous form and only trace amount is present in the form of soluble bicarbonate ion. On the other hand at high pH most of CO_2 gas is present in the form of bicarbonate ion and only trace amount in a gaseous form. Therefore pH of a landfill will have an effect on the solubility of CO_2 gas from landfill processes.

Methane can be dissolved up to 3% by volume of water at 20°C and a pressure of 1 atm. And this is equivalent to a concentration of approximately 22 mg/l. The consequent migration of methane in groundwater over long distances followed by its release from solution to atmosphere can be a big problem.

1.3.1.2 Effects of landfill gas in Environment

Asphyxiation: Asphyxiation of humans, plants and animals due to landfill gas is found to be due more to its ability to displace oxygen from an environment rather than the presence of a particular gaseous species. For humans, oxygen concentrations below 10% v/v may result in permanent brain damage, and oxygen concentration should not be allowed to fall below 18% v/v at normal pressures. For plants, the lack of oxygen can cause vegetation 'die back', although carbon dioxide is also toxic to plant roots at elevated concentrations.

Toxicity: Toxic components of landfill gas include carbon dioxide and numerous trace gases to which both animals and plants may be sensitive.

Carbon dioxide: CO_2 acts as an asphyxiant by oxygen displacement and can cause death due to paralysis of the respiratory centres. The threshold limit value for carbon dioxide is 0.5% and concentrations above 5% results in laboured breathing, headaches and visual disturbances. The long term occupational exposure limit (OEL) for carbon dioxide is 0.5% and short term exposure limit (STEPL) is 1.5% by volume. In most cases toxicity will occur when concentration in an enclosed environment occurs. This would be accompanied by high levels of potentially risky methane. Guidance for dealing with such situations within a building structure is given in Waste Management Paper 27[2]. At levels above 20% carbon dioxide is also phytotoxic.

Hydrogen Sulphide: H_2S has a distinctive odour and is explosive in the range 4.4-45% by volume in air. It is normally present at low levels in landfill gases but can reach concentrations as high as 35% by volume[3]. H_2S is associated with the degradation of high sulphate containing waste such as plasterboard and gypsum containing materials. H_2S has an occupational exposure standard of 10ppm (8 hour average reference period), and a 15ppm short-term exposure limit (10 minute reference period).

Trace Components: The trace components of landfill gas mainly comprise alkanes and alkenes, and their oxidation products (aldehydes, ketones, alcohols, and esters). Waste Management Paper 26[3] lists 108 compounds found to be present in landfill gases. In most work place situations, significant dilutions occur as a result of mixing with air and the trace component levels would fall below Occupational Exposure (OEL) and Short-term Exposure (STEL) limits.

Global Warming or Greenhouse Effect: Warming of the earth's atmosphere can be caused by the accumulation within it of gases that absorb reflected solar radiation. These gases include methane, carbon dioxide, NO_x, SO_x and chlorofluorohydrocarbons. The long-term effects of this accumulation include climate change and a rise in sea level as a result of melting of polar ice. It is estimated that landfill gas contributes 20% of atmospheric methane emissions within the UK and that landfill gas methane contributes 1-2% to the annual rate of increase in radiation due to the accumulation of all 'greenhouse gases'. A steady increase in atmospheric methane has been identified over the period 1978-1988[4]. In this respect, Hadley Centre Climate Model predicts[5] that global temperatures will rise by about 3°C over the next century.

1.3.1.3 Landfill Gas Migration:

One of the effects of landfill gas production is its potential to migrate away from its source and affect the surrounding environment. For gas migration to occur, there must either be a concentration gradient to allow diffusion in the gaseous phase (diffusive flow), a pressure gradient (viscous flow) or a combination of both. The rate of diffusion for a gas is inversely proportional to the square root of its density. Thus a light gas like methane will migrate 1.65 times faster than the heavier carbon dioxide. When a suitable migration pathway is present e.g. fractured geological strata or highly permeable strata like sand and gravel, then the gas may migrate large distances. Landfill gas has been known to migrate 300-400 metres away from its source[2].

1.3.1.4 Changes to Landfill Gas During Migration

The composition of landfill gas changes as it migrates through a medium. It does not stratify into defined zones, but the mixture may concentrate in specific locations due to relative density differences with air or to the movement of air currents. Landfill gas generally has a similar density to that of air, but can also be heavier or lighter than air, depending on the detailed composition of its constituent gases. These can vary because of external factors such as methane oxidation, which will increase the carbon dioxide content making the gas heavier while dissolution of carbon dioxide in water will increase the methane concentration and make the gas lighter. These influences can change the composition of the gas from that measured within the landfill site. Other anomalous concentrations are caused by the mixing of landfill gas with other methane-rich mixtures such as mains or marsh gas before the gas reaches the ground surface. Such mixtures are difficult to interpret.

Several processes can affect gases as they flow through a medium. Some of the processes are listed below.

1. Adsorption and desorption will lead to different migration rates through a medium for each component of landfill gas. In the short term, this may cause pulses of single gas, especially carbon dioxide at the leading edge of the migrating body of gas[6].

2. Chemical reactions may take place between component gases and the medium which will disturb the make-up of the landfill gas. For example, carbon dioxide will react with calcium-containing water to produce calcium bicarbonate, reducing carbon dioxide levels within landfill gas.

3. Micro-organisms may alter the constituent gas concentrations. For example, some bacteria oxidise methane to carbon dioxide, rapidly changing the relative concentrations of these gases.

1.3.15 Controls on Old Landfill Sites to Protect its Environment and Nearby Developments

Controls can be imposed on old landfill sites which are not designed to protect the environment. These controls include venting trenches, venting wells, and gas and leachate barriers to protect sensitive receptors such as housing developments. New building structures can be incorporated with additional safety measures including venting systems under the floor along with a gas proof membrane. These measures can be imposed through Planning Regulations resulting, for example, from the Town and Country Planning Act 1990.

Gas Monitoring Programmes: Gas monitoring is an important aspect of the assessment of the environmental impact of landfill sites, especially old landfill sites. DoE has given guidance on this subject[2]. Boreholes can be installed around and within landfill sites. These should be deep enough (7 to 10 metres in Hounslow) to extract meaningful samples and should be logged and gas readings should be taken as the boreholes are installed. Old sites should be monitored regularly for at least 2 years to assess the landfill conditions properly. The equipment used should be serviced and calibrated regularly. The results can easily be misinterpreted if there is not sufficient understanding of the detection system of the equipment.

1.3.2 Landfill Leachate

It is well recognised by United States Environmental Protection Agency (US EPA) that leachate from landfills have the potential to pollute groundwater. The degree of environmental pollution caused by leachate would depend upon factors like local geology and hydrogeology, the nature of infilled waste and proximity of susceptible receptors. Groundwater flow rates can be very slow and are often measured in metres or tens of metres per year. As a result, an aquifer may only be identified as polluted long after the pollution has occurred, at which time remediation may not be possible, or if possible, very expensive.

1.3.2.1 Leachate Production

Leachate is water that has percolated through emplaced waste and in so doing has extracted suspended solids, soluble constituents of waste and soluble products of the waste degradation process. The composition of leachate depends on the stage of degradation and the type of waste within the landfill.

As shown in figure 1.4, leachates generated during the early stages of anaerobic degradation are characterised by high concentrations of volatile fatty acids, acidic pH, high BOD to COD ratio and high levels of both ammoniacal and organic nitrogen. Ammonia is largely generated as a result of the degradation of the proteinaceous materials. The low redox potential of this leachate facilitates the production of soluble reduced-state metals including chromium, iron and manganese. However, as the pH rises, these metals are precipitated as sulphides, hydroxides or carbonates depending upon the situation.

Following the onset of methanogenesis, many of the fatty acids responsible for the acidic pH and high BOD are converted to methane and carbon dioxide. Methanogenic leachates are characterised by low concentrations of fatty acids, neutral to alkaline pH, lower levels of ammoniacal nitrogen and low BOD to COD ratio. During the steady methanogenic stage, a dynamic equilibrium generally exists where organic compounds are consumed as fast as they are produced. The relationship between volatile fatty acids, cellulose degradation and gas production is illustrated in Figure 1.4.

An important factor affecting leachate generation is the absorptive capacity of the waste. This capacity may involve a combination of factors such as infiltration of surface water or rain water, groundwater ingress due to liner failure, generation of water by microbial processes and liquid input. Leachate generation can also occur long before the absorptive capacity has been exceeded as a result of channelling, the heterogenous nature of the waste or high-intensity rainfall event.

The absorptive capacity of waste varies according to its type, pre-treatment and degree of compaction. It has been demonstrated that the leachate production rate of a waste mass with a density greater than 0.7 tonnes/m^3, corresponds to 15-20% of the annual precipitation in comparison to 25-50% with similar waste, with density[7] less than 0.7 tonnes/m^3.

The amount of leachate generated at a landfill site can be determined by using the water balance equation[3]. The main factors contributing to water balance of a landfill site are

(a) water input including effective rainfall (precipitation minus run-off and evapo-transpiration), surface and groundwater infiltration and liquid waste disposal,

(b) surface area,

(c) nature of wastes,

(d) site geology, and

(e) surface liquid storage e.g. leachate balancing lagoons.

In estimating the amount of leachate likely to be generated each year from operational areas the following water balance equation may be used:

$L_o = I - E - aW$

Where

I = total liquid input (precipitation plus liquid waste plus any surface or groundwater inflow) (m^3/annum)

L_o = free leachate retained at the site (equivalent to leachate production minus leachate leaving the site) (m^3/annum)

E = evapotranspirative losses (evaporation plus minimal transpiration) (m^3 /annum)

a = absorptive capacity of the waste (m^3/tonne of waste as received)

W = weight of waste deposited (tonnes/annum)

Good landfill practice normally requires that the site is operated so that L_o is always negative or zero. A positive value for L_o implies leachate build-up in the site.

The equation requires modification to cover the position when final restoration has taken place. There may then still be some further absorptive capacity for liquid within the waste, (U) and an additional quantity (R) must be introduced to allow for surface water runoff. The revised water balance equation is then:

$L_T = I - E - R - U$

Where, L_T = leachate retained in the site after restoration.

Surface conditions which may affect leachate generation include vegetation, cover material (density, permeability, moisture content), surface topography and local meteorological conditions.

The refuse state will affect the “field capacity of waste”, which is defined as the maximum moisture content which a soil or solid material can retain in a gravitational field without producing continuous downward percolation. Each of the above factors can be measured with a varying degree of accuracy and inserted into a water balance equation, which will account for the total liquid inputs to and total water leaving the landfill.

1.3.2.2 Physico-Chemical Processes Affecting Leachate Migration and Attenuation

As the leachate moves through the unsaturated zone, there may be greater potential for chemical and biological attenuation. The main causes of removal of substances from groundwater are ion-exchange, precipitation and dissolution, generation of insoluble complexes and the generation of colloids, followed by flocculation and filtration. Most of these will be affected by the conditions of pH, temperature and redox potential amongst others. Adsorption, ion-exchange and precipitation tend to restrict leachate movement through strata, while complexation of heavy metals with organic materials may facilitate transport of metals through the aquifer. This aspect is studied in some detail in the present work in leaching experiments in acetate media as described in Chapter VI.

Table 1.7

Typical Composition of Leachates from Domestic Wastes at Various Stages of Decomposition. (All figures in mg/l except pH value)

Determinand	Fresh Wastes	Aged Wastes	Wastes with high Moisture content
pH	6.2	7.5	8.0
COD	23800	1160	1500
BOD	11900	260	500
TOC	8000	465	450
Volatile acids (as C)	5688	5	12
NH_3-N	790	370	1000
NO_3-N	3	1	1
Ortho-P	0.73	1.4	1.0
Cl	1315	2080	1390
Na	9601	300	1900
Mg	252	185	186
K	780	590	570
Ca	1820	250	158
Mn	27	2.1	0.05
Fe	540	23	2.0
Ni	0.6	0.1	0.2
Cu	0.12	0.03	-
Zn	21.5	0.4	0.5
Pb	0.40	0.14	

Source:DoE, Waste Management Paper 26A, Landfill Completion, 1994.

It should be possible to identify a series of redox zones in the groundwater in which different types of physico-chemical reactions take place. Close to a leakage point a strongly anaerobic zone develops with redox potential suitable for methane generation and several processes such as sulphate, iron, mangenese, and nitrate reduction. As the leachate enters an aerobic zone, where free dissolved oxygen is present leading to higher pH and conductivity a more effective attenuation of leachate would be facilitated as it flows from a landfill.

1.3.2.3 Biological Processes in leachate migration and attenuation

These processes are not well understood, but a realisation of the ability of micro-organisms to degrade many pollutants has stimulated research into this aspect of groundwater pollution. Microbiologically transformed pollutants may be more or less toxic than their source material and can have an important effect on the nature and extent of leachate pollution of groundwater. The importance of biological attenuation and the fate of some of the major pollutant groups in the sub surface region is considered below:

Nitrogen: The important biological process affecting nitrogen are ammonification – where the nitrogen in nitrogen containing organic compounds such as proteins in waste is converted to ammonia, and nitrification, where ammonium ion resulting from ammonia production is oxidised to nitrate. Both these processes usually occur above the water table and generally in the soil zone where organic matter and oxygen are abundant[4].

The transport and fate of ammonium ions involves a combination of processes of adsorption, cation exchange, incorporation into biomass and release to the atmosphere in gaseous form. Adsorption is possibly the main method of ammonium ion removal, and is particularly important under anaerobic conditions. With increasing pH, ammonium ion reacts to produce ammonia gas and can therefore be more easily released from the soil.

The negative valency of nitrate means that under normal soil and groundwater conditions there is little attraction to soil particles. Nitrates are therefore very mobile and can move through the sub-surface with minimal transformation and retardation.

Metals: The attenuation of metals by sorption especially through ion-exchange and precipitation can limit groundwater pollution by the leachate component. The four major metal attenuation processes are adsorption, ion-exchange, precipitation, and complexation with organic material. Complexation of metal such as lead with acetate which is expected to be present in gassing landfills is considered in the present study in ChapterVI. The important metals in terms of environmental hazards are the heavy metals and ion exchange is probably the most important process of fixation and removal of these metals. Precipitation reactions are greatly influenced by pH and are more common at neutral to high pH values and high redox potentials (oxidised metal species are usually less soluble than reduced varieties).

Organic Substances: The major processes which limit the mobility of organic substances are chemical precipitation, chemical degradation, volatilisation, biological degradation, biological uptake and adsorption. Many organic substances have extremely low solubilities in water which limit the possibility for appreciable migration in groundwater. However, many of these substances are toxic at very low concentrations and therefore can pose a hazard even at low concentrations.

1.4 Regulations and Guidance which Apply to Waste Management

1.4.1. Definition of Waste

Section 75 of the Environmental Protection Act 1990 (EPA) and the Controlled Waste Regulations 1992 defined waste as including

a) any substance which constitutes a scrap material or an effluent or other unwanted surplus substance arising from the application of any process; and

b) any substance or article which requires to be disposed of as being broken, worn out, contaminated or otherwise spoiled.

EPA has been amended by the Environment Act 1995 to reflect the new definition: "Waste" means any substance or object in the categories set out in Schedule 2B to this Act [i.e. EPA] which the holder discards or intends or is required to discard;...where as "Holder" is defined as the producer of the waste or the person who is in possession of it; and the "Producer" is anyone whose activities produce waste or any one who carries out pre-processing, mixing or other operations resulting in a change in the nature or composition of this waste.

Waste subject to the provisions of Control of Pollution Act 1974 (COPA) and EPA is known as "controlled waste" and includes wastes arising from domestic, industrial and commercial premises as well as "special waste" for which there are additional regulations.

- **Household waste**[8] includes waste from: premises occupied by a charity; land belonging to domestic property, caravan or residential home, or a private garage for a car; private (domestic) premises; moored houseboat; camp sites; prisons and penal institutions; public meeting halls; royal palaces;....
- **Industrial waste** includes waste from: commercial garages/maintenance premises (for vehicles, vessels, aircraft); workshops; dredging and tunnelling waste; clinical waste (other than from domestic property, residential home or house boat); aircraft vehicles, vessels not used for domestic purposes; leachate; poisons or noxious waste from certain processes (e.g. dry cleaning, paint mixing/selling, pesticide sales); premises for breeding, boarding stabling or exhibiting animals; waste oils,

waste solvent, scrap metals (except from domestic premises); waste imports and waste from ships.

- **Commercial waste** includes waste from: offices, showrooms; hotels; private garages (more than 25 sq m); club/social premises; markets or fairs; courts, government departments, local and central government premises; corporate bodies; tents on land other than camp sites.
- **Clinical waste** other than that from a private dwelling or residential home is classified as industrial waste for legislative purposes. Most clinical waste is also subject to Special Waste Regulation 1996.

1.4.2 Disposal of Waste to Land

Disposal of waste to land has the potential to cause severe environmental pollution and pose risks to human health, hence, management must ensure that as far as possible waste disposal is safe and acceptable. This century has seen a number of legislative improvements to reflect this and are mentioned below.

Section 92 of Public Health Act 1936 dealt with "Statutory Nuisance" aspects of waste disposal. Health and Safety at Work Act 1974[8] required safe working and employment conditions for landfill operators, and Town and Country Planning Act of 1970's required applicants to look into safe disposal by licensing of landfill developments. Introduction of the European "Groundwater Directive" – The Protection of Groundwater against Pollution Caused by certain Dangerous Substances – 80/68/EEC in 1980 (Appendix A) gives guidance on restriction on substances which should not be discharged in the groundwater. List 1 substances are the most potentially polluting substances and should be prevented from entering groundwater and only limited discharge of List 2 substances should be permitted to avoid pollution.

The first major regulations to prevent environmental pollution are Control of Pollution Act 1974. This affected landfill operations in three main ways. First, it required the disposal authority to prepare a Waste Disposal Plan for its area. Second, it required the site to be licensed before operations could commence. Third, the Act made provisions for the control of discharges to waters

The Environmental Protection Act 1990 (EPA1990) goes further than Control of Pollution Act 1974, it aims to prevent pollution of the environment, harm to human health or serious detriment to the amenity of the locality. The EPA1990, Section 74-Waste Management License Regulations 1994 introduced a new test of whether an applicant or holder is a "fit and proper person" to hold a license. Under this Act a proper aftercare of the sites is provided through control on the surrender of licences and requirement to comply with condition of a licence regardless of whether deposit of waste is taking place.

According to section 85 of Water Resources Act 1991, a person contravenes this regulation if he causes or knowingly permits any poisonous, noxious or polluting matter or solid waste matter to enter any controlled waters. Environment Agency (EA) since its formation has duties and powers with respect to pollution of the aquatic environment. These can be applied directly through the Water Acts of 1989/1991 (section 85 and 86 of WR91, indirectly through EPA1990 or Acts relating to the Planning Systems. The Environment Agency has special interest in contaminated land because it may represent a source or potential source of water pollution – surface and groundwater.

The functions, property etc of National Rivers Authority NRA were transferred to the Environment Agency as a result of the Environment Act 1995 (EA1995). This Act relates to the formation of Environment Agency and takes over the function under WRA1991 (Part III) which relates to control of pollution of water resources. EA1995 also takes over the functions of Waste Disposal Authority. The Waste Disposal Authority ensures proper waste management through Waste Licences on waste disposal activities.

Section 78A of the Environmental Act 1995 gives the responsibility to assess contaminated land and related groundwater and take remediation procedures where necessary. Although this part of the EA1995 is not implemented yet (it is expected to be implemented in the near future), it will fall on the local authority to carry out the assessment in order to decide on any remedial action. These changes form the main drivers for the research described in this work and the results should be important for local authorities.

Groundwater provides a proportion of the base flow for many rivers and water courses, it must affect the aquatic environment. In England and Wales approximately 75%[9] of all abstracted groundwater is used for public supply. If groundwater becomes polluted it can be difficult to rehabilitate. The slow rates of groundwater flow and limited microbiological activity mean that the self purification and flushing mechanism which takes place in surface water systems in days or weeks are likely to be measured in decades in groundwater and in sources of indirect discharges into or onto land (e.g. leachates from old landfill sites).

The Environment Agency has developed a policy to protect groundwater resources, which applies to protection of major water supplies, the document is called " Policy and Practice for the Protection of Groundwater".

High vulnerability to groundwater contamination is associated with thin permeable soil and shallow water table, because this would not allow significant interaction of contaminants with the soil particles in the unsaturated zone and with limited quantity of groundwater will cause relatively high concentrations of contaminants in the saturated zone. Low vulnerability is associated with thick clayey soil and deep water table. The proximity of an activity to a groundwater abstraction is important in assessing risk to contamination to that source. All types of groundwater sources require protection. 'Source Protection Zones I to III' are described below:

Zone I - Inner Source Protection is the area enclosed by a 50-day travel-time from any point below the water table to the source, but with a minimum radius of 50 metres. The 50-day travel time is based on the time it takes for biological contaminants to decay.

Zone II – Outer Source Protection Zone is the area enclosed by a 400-day travel-time from any point below the water table to the source or 25% of the recharge catchment area, whichever is larger. The travel time is based upon that required to provide delay and attenuation of slowly degrading pollutant.

Zone III – Source Catchment is the area required to support an abstraction from long-term annual groundwater recharge. For wells and boreholes the zone will be defined by calculations based on the authorised abstraction rate. The size of the zone depends on the volume abstracted and the effective rainfall and varies from tens to thousands of hectares.

The Local Authority's role in any aspect relating to contaminated land and groundwater pollution is stated in the Environment Act 1995. Section 57[10] states, "— 'Contaminated land' is any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances, on or under the land that-

(a) significant harm is being caused; or

(b) pollution of controlled water is being, or is likely to be caused;"

DoE's guidance on Licensing of Waste Management Facility is given in Waste Management Paper (WMP) 4, for landfilling Waste in WMP26 . Guidance on surrender of licence and criteria for Landfill Completion is given in WMP26A. Guidance on Landfill Gas Monitoring is given in WMP27.

1.4.3 Current EC and UK Policy on Waste Management – With Special Reference to Waste Disposal to Landfill

The concept of sustainable development as a policy came about in the UN Conference on Environment and Development (The Earth Summit) held in Rio de Janeiro in 1992. The Agenda 21 placed great emphasis on the need for all sectors of society to participate in the formation of effective national strategies for sustainable development. It is estimated[11] that between 1992 and 2012, demand for water supply is likely to have risen by around 10% in England and Wales. For this reason the protection of groundwater must also be a high priority over the next 20 years.

A Sustainable Framework for Waste Management is to minimise the amount of waste produced, to make best use of waste that is produced, and to minimise pollution from waste.

Current Trends Include: the increasing amount of waste; higher standards of environmental protection required by EC; and domestic waste management legislation. Growing public awareness and concern over some aspects of waste management, particularly recycling of household waste, siting of waste facilities and the disposal of hazardous_waste, and increasing cost of waste disposal creating pressure to minimise and recycle waste.

Problems and Opportunities

Most waste disposal in the UK is to landfill and there is considerable scope for waste reduction, recycling and energy recovery. Stricter control over emissions to air and water will alter the nature and contrary to Landfill Directive, increase the quantity of waste needing to be disposed off to land. Currently, the prices of the different waste management options do not accurately reflect their full environmental impacts. Cleaner technology needs to be further developed and information about it disseminated. There are adequate markets for reusable/recycled products and processes for energy recovered from waste need to be developed. New recovery/disposal routes also need to be developed for some wastes such as sewage sludge.

Current Responses

A framework of UK and EC regulations encourages minimisation of waste[11] and controls the management of waste in order to protect the environment and Government funds research, pilot projects, advice and information to industry, local authorities and community groups on waste reduction, re-use, recycling and energy recovery. Government has also set targets on waste recycling and is encouraging industry to set its own targets. The Non Fossil Fuel Obligation provides financial support for energy from waste plants and Government is considering a range of economic instruments to address distortions in the waste market – especially to help ensure that waste management options bear their full environmental costs and in turn, that the polluter pays.

The Way Forward

Government will be influenced by the extent to which businesses and consumers recognise the need to adopt sustainable practices towards waste and will continue to fund research, advice and pilot projects and provide an appropriate framework of regulation and market instruments to encourage sustainable waste management practices[11]. Businesses can make a particularly significant contribution by taking greater responsibility for the wastes they produce, agreeing and achieving recycling targets, and investing in processes to reduce or re-use waste material. The waste industry will need to invest in increased reclamation/reprocessing capacity and facilities for energy recovery from incineration/landfill, and individuals will need to take more care to minimise the amount of household rubbish they dispose of, accept less packaging and the increased use of re-usable or recyclable products.

Landfill remains the predominant route for waste disposal in the UK[11]. Modern UK practice is to encourage biological processes within the mass of landfilled waste which degrade, neutralise, and stabilise the harmful component of the waste. Over a period of time, typically several decades, the waste ceases to present any significant threat to the environment. Landfill in principle, would then be an environmentally sustainable process.

Contaminated Land: The objective for the future is to prevent or to minimise further contamination through pollution control and market mechanisms[11]. But land which is already contaminated should be dealt with where there is risk of threatening health, safety or the environment where practical, it should be brought back into beneficial use, so helping to minimise pressures on greenfield sites.

Dealing with contaminated land is a considerable economic burden and raises important issues of priorities for national resources. The Government approach is that threats should be dealt with on the basis of a realistic set of priorities related to risk. Land should be treated where it is necessary or worthwhile to cure or to control the problem. The goal is to bring land to a standard where it is suitable for its actual or intended use.

There can be problems in applying the polluter pays principle to contaminated land. With historic pollution, the polluter may no longer exist or may be unable to meet the costs; ownership of the site may have changed; and contamination may sometimes remain on a site for many years with no harmful effects until activities or other changes many years later lead to a problem.

There are difficult questions to address here, with no easy answers. The Government has therefore set up a review of the powers and duties of public authorities related to identification, assessment and appropriate treatment of contaminated land and liabilities. This relates to the Environment Act 1995, and guidance is expected from the Government in the near future.

The UK Government has recently published a draft waste strategy for England and Wales "A Way with Waste" prior to producing a National Waste Strategy (NWS) implementing the EC Directive on the Landfill of Waste is due early in year 2000.

The present Government's vision is to achieve substantial increases in recycling and energy recovery; engagement of the public in increased re-use and recycling of household waste; and a long-term framework with challenging targets underpinned by realistic programmes. There is a strong emphasis on waste minimisation, creative use of economic incentives, and increased public involvement in decision making.

Government would encourage waste minimisation, reuse of materials and products and recycling. Government would also encourage incineration with energy recovery. With regard to landfill, Government is committed to reducing reliance on landfill by introducing progressively diminishing limits on the landfill of biodegradable municipal waste and to requiring all wastes to be treated before they are landfilled.

This would eventually lead to only relatively 'inert' wastes going to landfill, and would minimise the potential for environmental pollution through production of gas and leachate containing species derived from organic materials. This is in accord with the EU Landfill Directive.

Landfill Tax. The recent introduction of the landfill tax should create an incentive to avoid landfilling of waste. Since October 1996, a tax on waste disposal to landfill has been levied at £7 per tonne for active waste which includes household waste and £2 per tonne for inactive waste. The Chancellor announced in the Budget on 17 March 1998 that the rate for active waste would be increased to £10 per tonne from April 1999. Active waste Landfill Tax will increase at a rate of £1 per year until it reaches £15[12]. This tax would indirectly pay towards environmental protection and improvement.

Chapter II describes the landfill sites in London Borough of Hounslow (LBH); Chapter III describes the Methodology used for sampling and analysing groundwater samples and Chapter IV reports the Results of groundwater analysis.

1.5 References

1. DoE, Waste Management Paper No. 26A, Landfill Completion, 1994.
2. DoE, Waste Management Paper No. 27, Landfill Gas, 1991.
3. DoE, Waste Management Paper No26, Landfilling Wastes, 1986.
4. Westlake K., "Landfill Waste Pollution and Control", Chichester, Albion, 1995.
5. DETR, "Global Warming", Global Atmosphere Research Programme 96/97.
6. Institute of Waste Management, Monitoring Landfill Gas, 1990.
7. HMSO, Waste Management Paper No. 26B, Landfill Design Construction and Operation Practice, HMSO, 1995.
8. Pollution Handbook, National Society for Clean Air and Environmental Protection, 1999.
9. NRA, Policy and Practice for Protection of Groundwater, 1992.
10. Environment Act 1995, Part II, Contaminated Land and Abandened Mines, 1995.
11. HMSO, Sustainable Development, The UK Strategy, 1994.
12. Wood R. N., LB Hounslow, Personal Communication, 1999.

CONTENTS - CHAPTER II

LONDON BOROUGH OF HOUNSLOW AND LANDFILL SITES

Page Numbers

CHAPTER II

LONDON BOROUGH OF HOUNSLOW AND LANDFILL SITES

2.0 Introduction and Background

LB Hounslow is situated in the west of London and east of Heathrow Airport. The Borough covers 5658 ha (57km^2). The geology of the area is mainly sand and gravel up to approximately 7 metres and then London Clay. During the last 50 years or so some of the land was worked for minerals (sand and gravel), the resulting pits were back-filled with waste. It is estimated that there is a total of 962 ha (17%) of landfill sites and made ground, of which 750 ha (13%) is covered by landfill sites and the remaining by made ground[1]. This is illustrated in Figure 2.1. Landfill sites in LB Hounslow are sites are formed by back filling pits created by mineral extraction, these are roughly 4 to 7 metres in depth. Made grounds are sites where there is 3 metres depth or less of fill. Most of these contaminated land sites are located towards the west of the Borough. The old landfill sites in the LB Hounslow are not engineered to protect the environment, hence, the areas in the vicinity of the sites are highly vulnerable to contamination from landfill gas and leachates. The Borough Council started to monitor these sites for landfill gas in 1989 as a result of the Department of Environment requirement under the guidance contained in Waste Management Paper 27. As a result of this over 400 boreholes have been installed in the Borough, these go down 0.5 to 1 metre into the London Clay as shown in Figure 3.1 and provide a means for sampling groundwater and gas emissions.

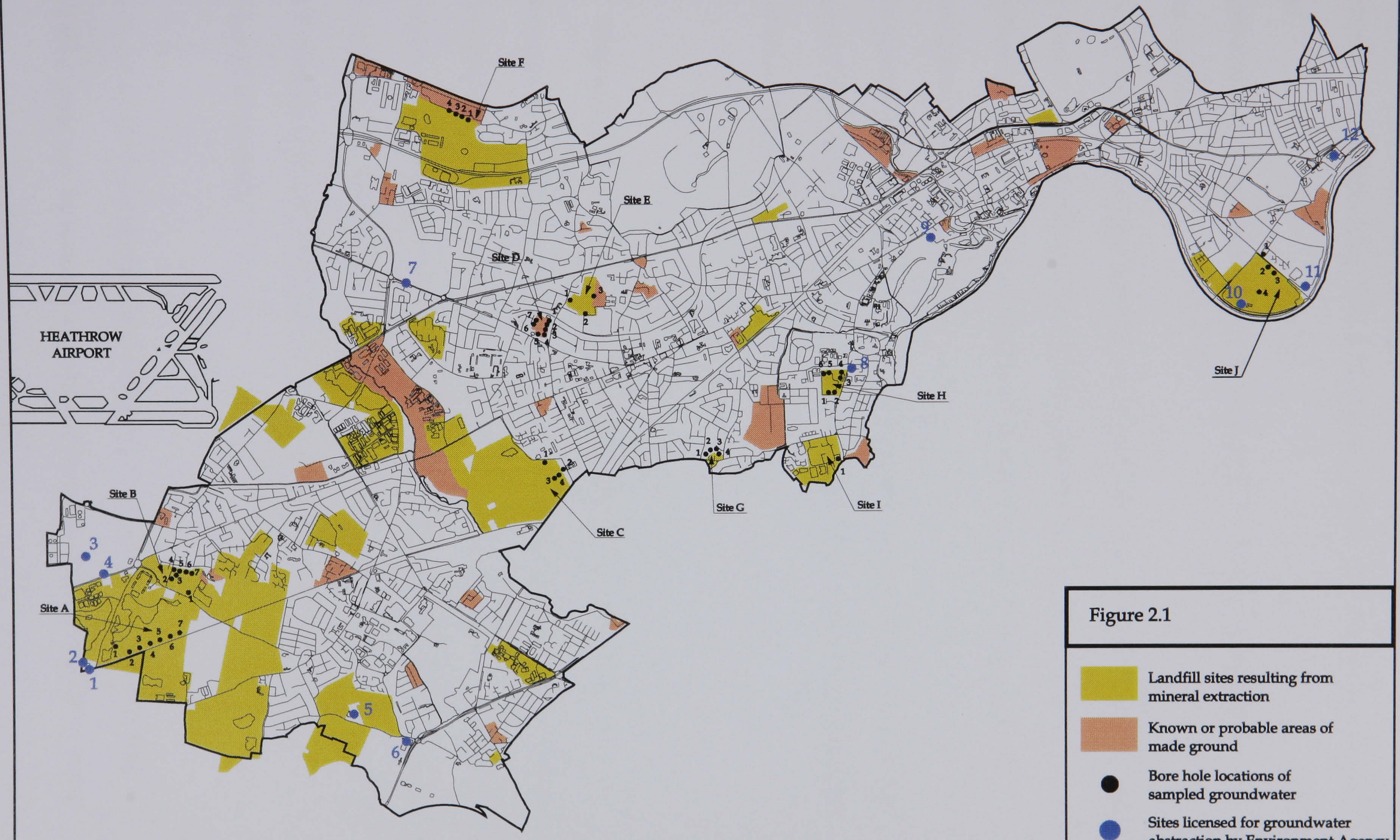


Figure 2.1

🟨 Landfill sites resulting from mineral extraction

🟧 Known or probable areas of made ground

● Bore hole locations of sampled groundwater

🔵 Sites licensed for groundwater abstraction by Environment Agency

The information presented on this map is based on records held by or provided to the L B Hounslow. No responsibility can be accepted for the accuracy of this information.

2.1 Geology of the Borough

The geology of the Borough can easily be related to the Environment Agency's Groundwater Vulnerability Map. This is illustrated in Figure 2.2 and is described as follows:

1. The hatched area is approximately 3m of brick earth on sand and gravel and it overlies London clay.
2. Area marked in blue is approximately 7m of sand and gravel over London Clay and acts as a major aquifer because of its extensive areal extent.
3. Area marked in brown is a minor aquifer of limited areal extent. This is made of sand and gravel over London Clay.
4. Area marked in green is mainly London Clay, therefore a non-aquifer. London clay strata in LB Hounslow has a 100m thickness and overlies thin Woolwich and Reading Beds of some 20m upon the chalk strata.

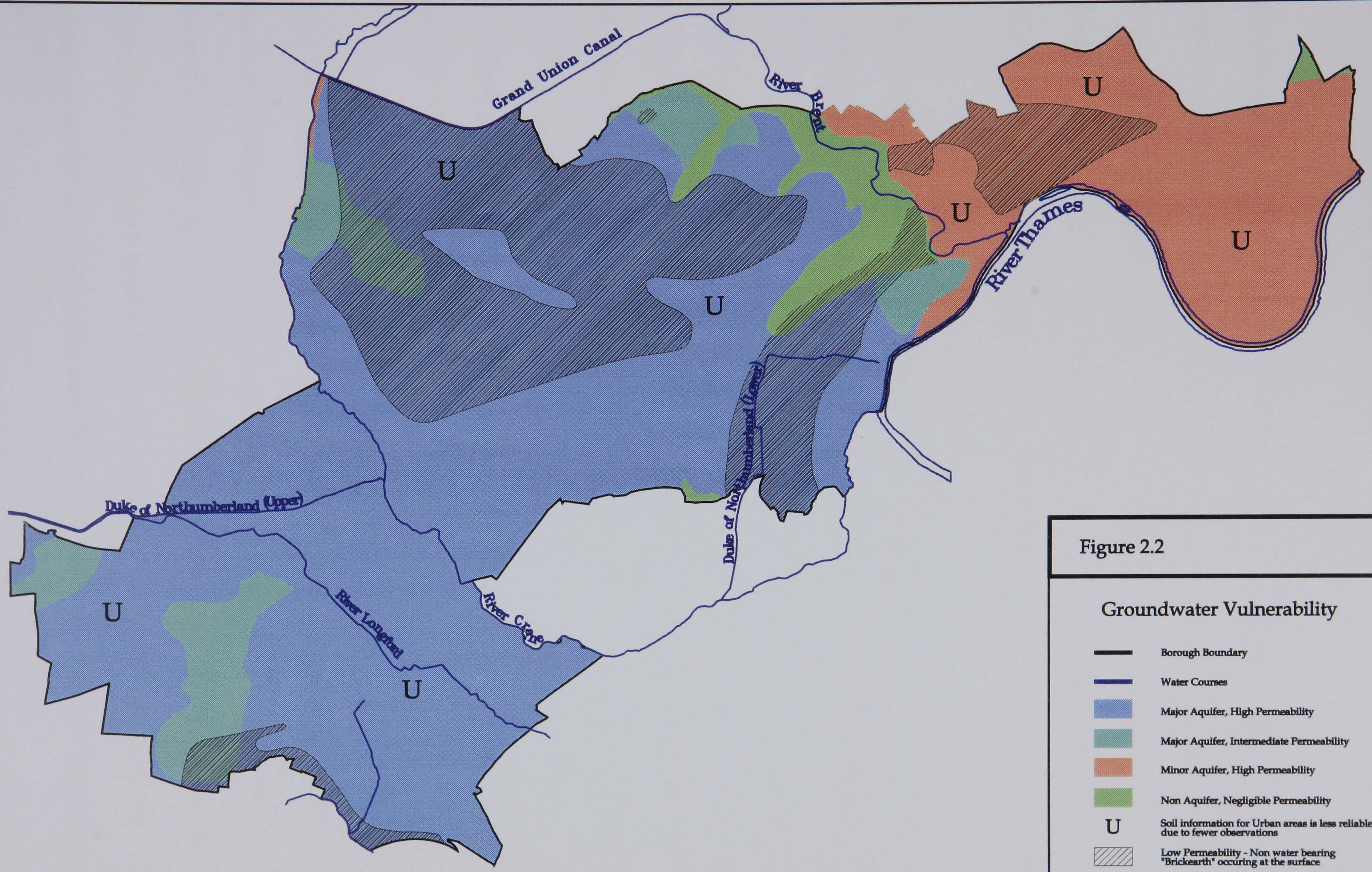
2.2 Major Aquifers in Hounslow and Groundwater Flow

Aquifers may be classified into two principal types; unconfined and confined aquifers. An *Unconfined Aquifer* is a geological unit and it is porous, permeable and saturated, from which water may be removed and in which the upper surface of water is open to the atmosphere. The water surface is called the water table. The sand and gravel strata in LB Hounslow is an aquifer of this type and the groundwater from this strata is investigated in this study.

A *Confined Aquifer* is a geological unit which is porous, permeable and saturated from which water may be removed and which is bounded above and below by strata

Figure 2.2

Groundwater Vulnerability



The information presented on this map is based on records held by or provided to the L B Hounslow. No responsibility can be accepted for the accuracy of this information.

of significantly lower permeability. The groundwater from chalk strata below the London clay is not considered in this study.

The London clay strata is highly impermeable to water, it may absorb water but not transmit it in sufficient quantities. To be considered as an aquifer, the geological strata must be capable of storing and releasing water. The ability to store water is related to the porosity of the material and it is the function of grain size. The volume of water which will drain freely from an unconfined aquifer is termed the *specific yield.*

Sand and gravel, the main geological strata in the virgin grounds of the LB Hounslow, have been quoted[2] to have porosity of between 28% (gravel) to 38% (sand); with specific yield of 23% (gravel) to 38% (sand); whereas clay has porosity of 42% and specific yield of only 3%. Hence, the clay strata at 5 to 9 metres below ground level, forms a good impermeable strata below the highly permeable and vulnerable sand and gravel strata in the L B Hounslow. Classification of mineral grains in soil is according to its size. The size of clay particles is <0.002 mm diameter; silt is >0.002 mm and <0.075 mm diameter; sand particle is >0.075 mm and < 2 mm diameter and gravel has >2 mm and < 75 mm diameter.

The aquifers in the Borough are considered to be highly permeable major aquifers by the Environment Agency. In general, the groundwater in the Borough flows towards the River Thames, that is, North West to South East, although, the local trends may be different depending on any nearby tributaries, where the flow would be towards the tributaries. A nearby landfill area may alter the groundwater flow, but a detailed study of these has not been possible at this stage because there are insufficient groundwater level monitoring points.

It is understood that the groundwater flows very slowly which does not allow the contaminants to disperse quickly, hence, the contaminants can build up easily in an area and these could be quite localised. It has been estimated[3] that the cost of decontamination of a site may range from £110,000 per hectare for minor remediation to £1.5 million per hectare plus landfill tax for a major project. This includes the cost of remediating groundwater where necessary. The levels of these costs show that the present study of groundwater assessment is important.

2.3 Groundwater Abstraction Points in Hounslow

In the Borough there are 12 groundwater abstraction points, most of these are extracted from the gravel strata and are used for agricultural and industrial purposes[4]. These are illustrated in the Figure 2.1 and details are in Table 2.1. From Table 2.1 it is clear that there is no major abstraction for public water supplies, hence, Source Protection Zones do not apply to LB Hounslow.

2.4 Possible Implications of Groundwater Contamination

Contaminated groundwater can affect the environment in various ways, for example,

a) Leachate from a landfill not designed to protect the environment has the potential to migrate well away from its origin and produce methane and other contaminants. This could affect the rivers or developments well away from its source.

b) Inorganic contaminants like chloride, sulphide and sulphate have the potential to attack the building structure.

c) Organic contaminants like phenols and chlorinated solvents have the potential to attack and deteriorate the services and affect the water supplies.

d) Ammonia can kill the fish if present in significant concentration.

e) Low dissolved oxygen can affect the quality of water and result in high COD, BOD and TOC.

Table 2.1 Details of Groundwater Abstraction in LB of Hounslow

Source of all of the abstractions is the sand and gravel strata.

No.	Site Name & Location	Purpose	Depth	Authorised Quantity per Annum (Cubic Metres)
1	St George's Nursery Clockhouse La.	Spray irrigation	10 ft	2,906
2	Bridge Farm Nursery	Spray Irrigation under glass	10 ft.	5,448
3 & 4	T P Steel & Sons Mayfield Farm	Spray Irrigation	15 ft.	22,700
5	LB Hounslow Feltham Rd. Allotments	Agricultural	20 ft.	2,043
6	Unigate Dairies Ltd. Sunbury Way, Hanworth	Industrial Process (Dairy Washing)	12 ft.	54,480
7	Rectory Farm, Bath Rd., Cranford	Spray irrigation	8.2m	6,818
8	Garvin House, Isleworth	Cooling	7.6m	11,365
9	Syon Park, Brentford	Agricultural & Spray irrigation	6.1m	273 & 8,819
10	Dukes Meadow	Spray Irrigation	12m	8,000
11	Riverside Racquets	Spray irrigation	4.8m	6,000
12	Griffin Brewery, Chiswick	Cooling	9 m	81,828

Source: Information provided by Environment Agency.

2.5 Categories of Sites and Boreholes Sampled for Gas and Leachate for this Study

A total of 47 boreholes in 4 categories of sites, in relation to landfill sites in Hounslow have been sampled for gas and groundwater for this study. The borehole logs for each category are described in Appendix B. The four categories of sites are described in Table 4.1 in Chapter IV.

Chapter III deals with ‘Methodology’, and includes details of borehole design which are used for sampling groundwater, method of groundwater sampling, choice of parameters tested and analytical techniques used for groundwater analysis

---

2.6 References

1 London Borough of Hounslow, State of the Environment Report, 1994.

2 Spence I., Groundwater-Pollution, Prevention and Remediation, Seminar, (Groundwater Hydraulics, University of Abertay, Dundee), 1997.

3 Harris E C., Local Authority Waste & Environment, Counting the Cost of Decontamination, 7 September 1997.

4 Environment Agency, Personal Correspondence, 1998.

CHAPTER III - LIST OF CONTENTS

METHODOLOGY

Page Numbers

CHAPTER III

METHODOLOGY

This chapter describes the details of methods adopted to carry out the practical work related to this study. The topics described are under the headings:

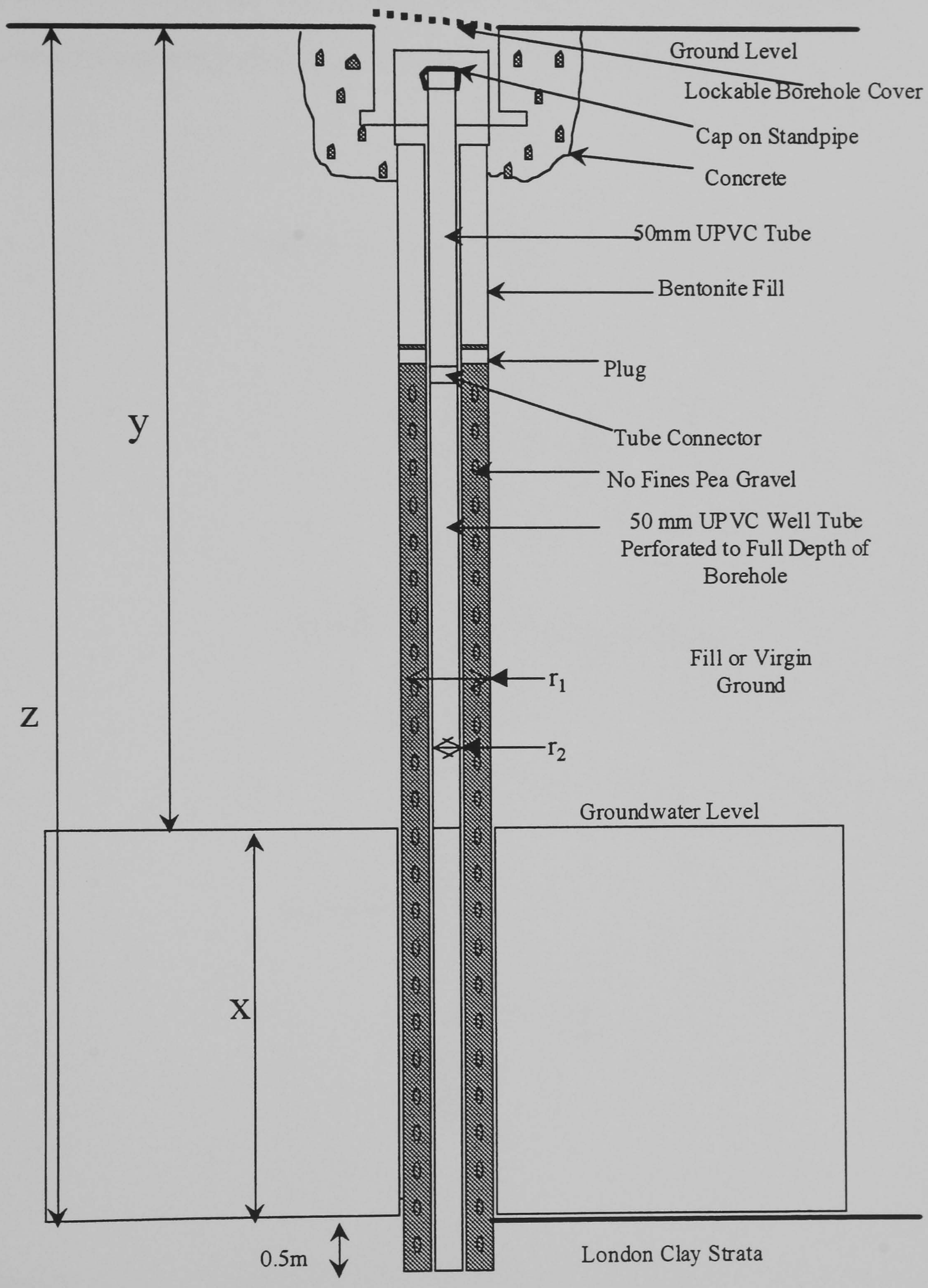
1. Design of the boreholes and method of groundwater sampling.
2. Choice of the water parameters tested.
3. Analytical Techniques used for groundwater analysis.

3.1 Design of the Boreholes and Groundwater Sampling

The boreholes used for groundwater sampling are generally 7 metre deep and they go down not less than 0.5m into the impermeable strata – the London Clay. The design of the borehole is shown in figure 3.1, the outer casing of the boreholes are 150mm and the inner standpipes are 50 to 55mm. The inner standpipe is surrounded by no-fines pea gravel media. The standpipe is perforated from 1 metre below ground level with a minimum of four 5 mm diameter perforations at 150 mm intervals. The top 1 metre standpipe is not perforated. At nearly ground level the standpipe is capped. The top 1 metre of the standpipe surround is sealed with bentonite and finished at the ground level with concrete. The standpipe is boxed in a lockable cover. This borehole design ensures that soil gas from depth would penetrate the inner standpipe and air ingress from atmosphere is minimised by the use of bentonite seal from the top of the borehole surrounding area.

3.1.1. Design of the Boreholes

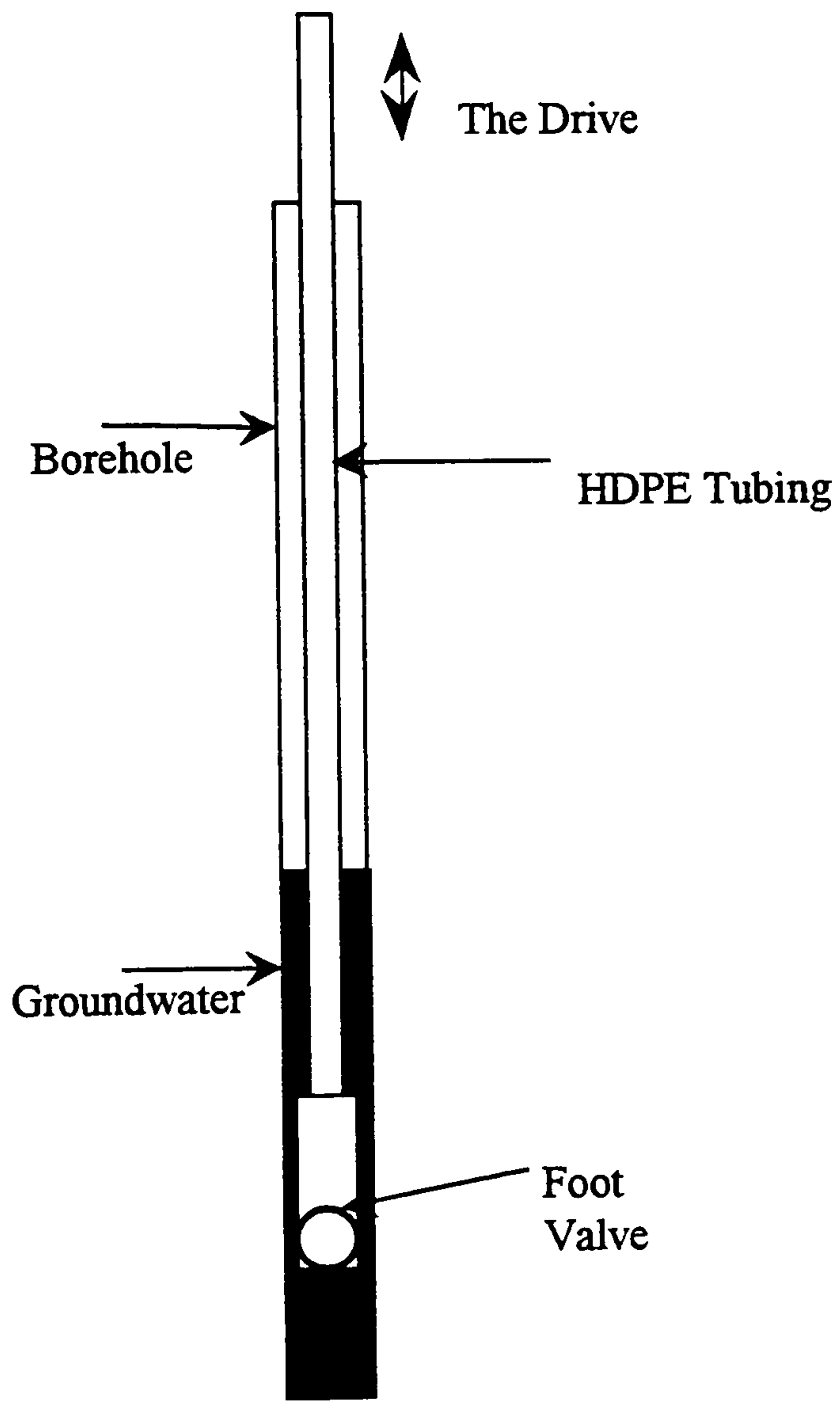
Figure 3.1 **Borehole Design**



Method of Groundwater sampling.

A Waterra manual groundwater sampling pump was used for drawing the water from the boreholes. This is a High Density Poly Ethylene (HDPE) tubing with a foot valve at the end as shown in the figure 3.2. The equipment is placed inside the borehole and it is operated manually to pump the groundwater out of the borehole.

Figure 3.2



Waterra Groundwater Sampler

Sampling is carried out by lowering the tubing and valve assembly below the groundwater level in the borehole. The sampling cycle is

a) The water level inside the tubing rises to the level of water in the borehole.
b) A rapid upstroke closes the foot valve and lifts the water column.
c) When this cycle is repeated the water rises in the tube and discharges at the ground level.
d) The groundwater is collected in a graduated bucket, an estimated volume of water is purged and discarded before it was collected in clean glass or HDPE bottles.

At the end of groundwater sampling from a borehole, the groundwater sampling device is rinsed with deionised water to prevent any cross contamination between the boreholes

The groundwater level is determined by using a dipmeter with audio-visual indicator. The level of base of the borehole is recorded from the borehole logs. In reality the base of the borehole has been much higher than the borehole logs possibly due to silting of the boreholes.

The groundwater in most of the cases was purged between one and three times to ensure the collection of a representative sample. The volume of groundwater required to be purged before sample collection was calculated and is shown in section 3.1.3.

3.1.3 Calculations to Estimate the Minimum Amount of Water Required to be Purged From a Borehole

From Figure 3.1 if:

x = length of the water column in the standpipe in cm

y = depth to water level reading (dip meter reading) in cm

z = depth of borehole in cm, (from borehole log or determined by using dip metre)

$x = z - y$

r_1 = radius of the borehole annulus

r_2 = radius of the stand-pipe within the borehole annulus.

1. Volume of water in the borehole standpipe

$$= \pi r_2^2 x$$

$$= 3.14 \times 2.7 \times 2.7 \times x \text{ (cm}^3\text{)}$$

$$= 23 x \text{ (cm}^3\text{)}$$

2. Volume of annulus in groundwater

$$= \pi r_1^2 x$$

$$= 3.14 \times 7.5 \times 7.5 \times x$$

$$= 177 x \text{ (cm}^3\text{)}$$

3. Volume of annulus in groundwater and around the standpipe

$$= 177 x - 23 x \text{ (cm}^3\text{)}$$

$$= 154 x \text{ (cm}^3\text{)}$$

It is estimated[2,3] that pea gravel occupies roughly 75% of the volume and 25% volume is occupied by groundwater.

Therefore volume of groundwater around the stand pipe is

$= (154 \times 25/100)\ x\ (\text{cm}^3)$

$= 38.5\ x\ (\text{cm}^3)$

4. Total volume of water in the borehole

   $= 23\ x + 38.5\ x\ (\text{cm}^3)$

   $= 61.5\ x\ (\text{cm}^3)$

5. Therefore for every 10 cm length of water column (i.e., x = 10 cm) there is at least/approximately 620 cm^3 of water in the borehole.

   Or

Approximately 0.62 litres of water for every 10 cm of water column

This result was used for estimating minimum amount of water required to be purged before collecting a groundwater sample for analysis.

The change in the concentrations of various parameters on purging the boreholes was studied, the results and discussion on the results are in Chapter IV, Section 4.7.

3.2 Choice of the Groundwater Parameters Tested

The choice of water quality parameters tested is based on discussions with the Environment Agency and Hounslow Council. In very broad terms, there are four main categories of water parameters, based on the origins of water from waste within landfill sites. These are described in Table 3.1.

Table 3.1

Water Quality Parameters Tested and Their Possible Origins from Waste in Landfill Sites.

Water Quality Parameter Tested	Possible Origins in Landfill Sites	Effect on Environment in case of Pollution
Temperature	Underground fires, high rate of biodegradation of waste	Unstable ground, flammable and explosive landfill gas production
Conductivity, chloride, sulphate	Natural geological surroundings, general inorganic contamination	Possible damage to building structure
TOC, COD, and ammonia	Organic waste, sewage	Oxygen depletion in water courses, toxic to fish and other organisms
Nickel, copper, lead, cadmium	Industrial waste, sewage	Toxic to plants and humans through bio-accumulation in fish and plants.

Tests for all these parameters were used in this work and are described in Chapter IV

3.3 Analytical Techniques Used For Groundwater Analysis

The techniques used in this work for groundwater analysis are:

1) Ion Chromatography,
2) Chemical Oxygen Demand,

3) Total Organic Carbon, and

4) Atomic Absorption Spectroscopy. These are described in detail in the following sections.

3.3.1. Ion Chromatography (IC)

3.3.1.1. Introduction

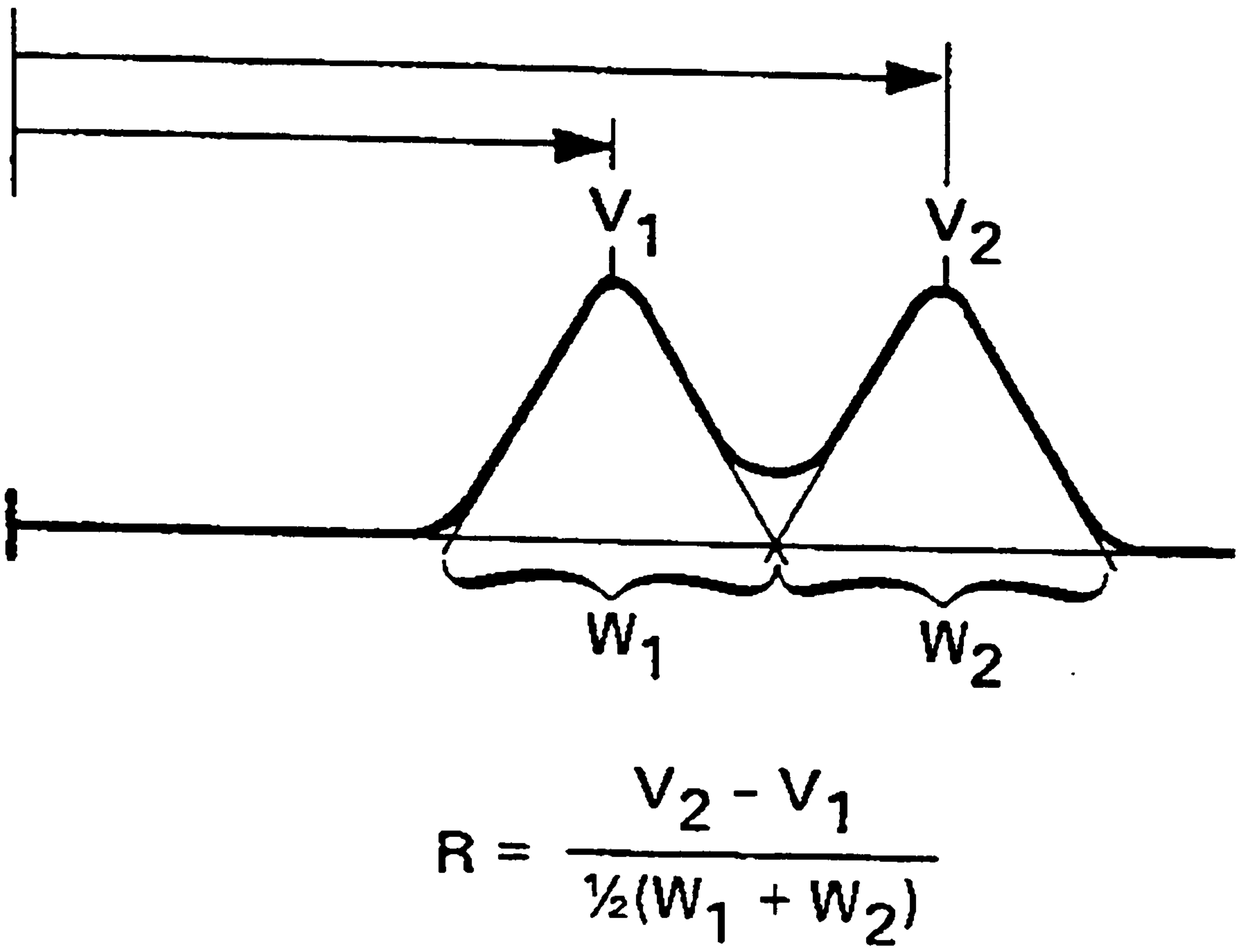
Chromatography involves separation due to differences in the equilibrium distribution of sample components between two different phases, a mobile phase and a stationary phase. The analyte component of the samples migrates through the chromatographic system only when in the mobile phase. The velocity of migration of a component is a function of the equilibrium distribution. The components having distributions favouring the stationary phase migrate slower than those having distributions favouring the mobile phase, separation then results from different velocities of migration as a consequence of difference in equilibrium distributions.

3.3.1.2. Column Theory

Figure 3.3 illustrates the separated peaks found in a typical chromatogram.
Where R is Resolution and is a means of measuring the degree of separation of a two component system. It is defined as the distance between the peak centres of two peaks divided by the average base width of the peaks[3]. V_1 and V_2 are the Retention Time (RT) of component 1 and 2 respectively. (RT is proportional to retention volume).

'R', is a function of three fundamental parameters in chromatographic separation, these are selectivity (α), efficiency (N) and capacity (K').

Figure 3.3 Resolution and Separation of Peaks in IC Chromatogram



Source: Dionex, Ion Chromatography, Training Manual.

Selectivity, Efficiency, Capacity

The Resolution can be expressed as a function of selectivity, efficiency and capacity as follows:

$$R = 1/4\underbrace{\left(\frac{\alpha - 1}{\alpha}\right)}_{\text{Selectivity}}\underbrace{\left(\sqrt{N}\right)}_{\text{Efficiency}}\underbrace{\left(\frac{K'}{1 + K'}\right)}_{\text{Capacity}}$$

Selectivity

Selectivity is the net retention time ratio for 2 components and is equal to the ratio of equilibrium distribution coefficients. When $\alpha = 1$, resolution is 0. The larger the value of α, the better the selectivity and easier the separation. V_0 denotes elution or retention volume of a non-retained peak.

$$\alpha = \frac{V_2 - V_0}{V_1 - V_0} = \frac{k'_2}{k'_2} = \frac{K_2}{K_1}$$

Efficiency or Theoretical Plates

Efficiency is expressed in terms of theoretical plates (*N*), given by the formula:

$$N = 16\left(\frac{t_R}{W}\right)^2 = 5.5\left(\frac{t_R}{W_{1/2}}\right)^2$$

Where

t_R is the retention time of the retained component measured at the peak maximum.

$W_{1/2}$ is the peak width at ½ height

The number of theoretical plates *(N)*, is a measure of band dispersion throughout the chromatographic system. The smaller the band dispersion, the higher the value of N. Thus efficiency is a measure of how well or how poorly a column is packed. Other factors that affect theoretical plates of a column are:

a) the size of particles,. The smaller the particle size, the greater the efficiency of separation because of shorter diffusion paths which minimises band diffusion.

b) particle size distribution. Greater the uniformity of particle size and packing, the greater is a column efficiency.

c) whether the particles are porous or pellicular.

In a separation column, each solute molecule interacts with the column packing and is continuously transferred into and out of the stationary phase. When it is retained in the column it falls behind the sample band centre as it migrates down the column. When in mobile phase, it moves with the mobile phase, with a velocity faster than the band centre. Since there is a flow in the mobile phase, the actual concentration of solute in the mobile phase is always in non-equilibrium with the adjacent stationary phase. The dispersion of the peak is minimised by choosing conditions such that non-equilibrium is reduced and the rate of exchange is maximised. Sometimes this can be carried out by raising the column temperature.

The number of theoretical plates is proportional to the column length. In general, longer columns have more plates. Efficiency of columns can be measured independent of column length in terms of measuring height equivalent to theoretical plates, i.e. HETP. Assuming the columns have the same internal diameters

$$HETP = \frac{L(mm)}{N}$$

Where,

L, is the length of the column in mm

N is the number of theoretical plates in the column

Efficiency measures the ability of the column to maintain the sample band without allowing it to spread.

The factors affecting column efficiency are:

'μ', linear velocity. Lower μ gives higher value of N. N is in the range of velocity above 0.05cm/sec

'dp', particle size, smaller particle size gives higher N

'L', column length, N is proportional to L

Mobile phase viscosity. Lower values give higher value of N

'T' temperature. High value reduces viscosity

Volumes outside column – N is decreased as volume increases

Sample amount and size- increasing sample size decreases N

Capacity Factor: *k'*

The capacity of column is described by *k'*, the capacity factor

$$k' = \frac{V_1 - V_0}{V_0}$$

k' can be thought of as the retention of a component in terms of column volumes

V_0 is the elution or retention volume of a non retained peak.

V_1 is the retention time of the retained component measured at the peak maximum

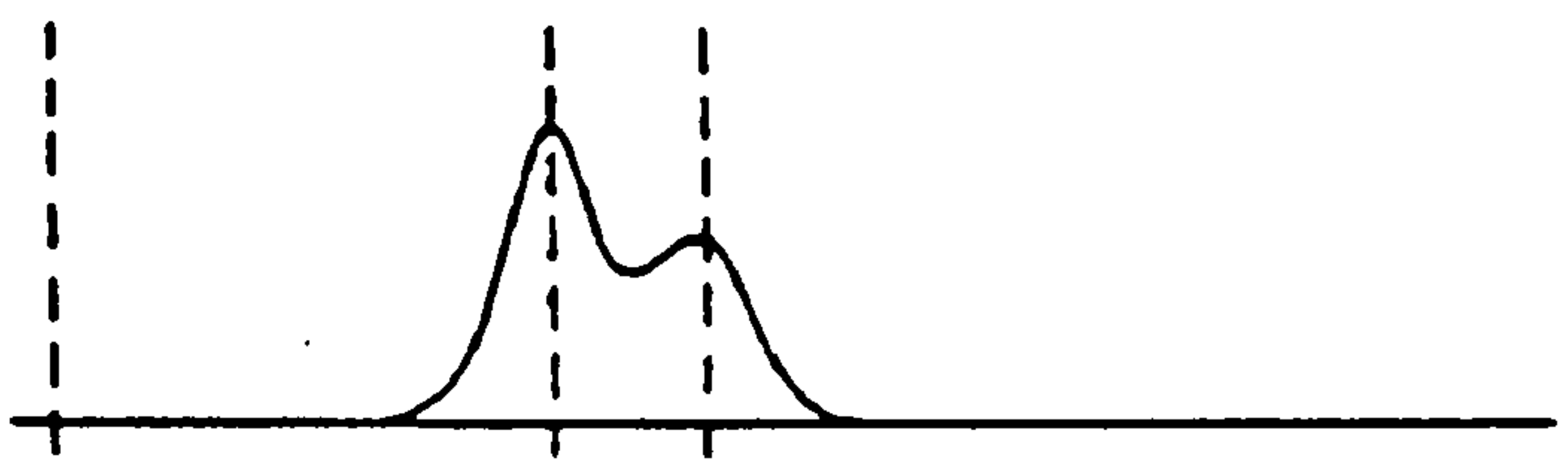
k' measures the retained component in terms of column volumes.

The greater the capacity factor the longer a peak will be retained.

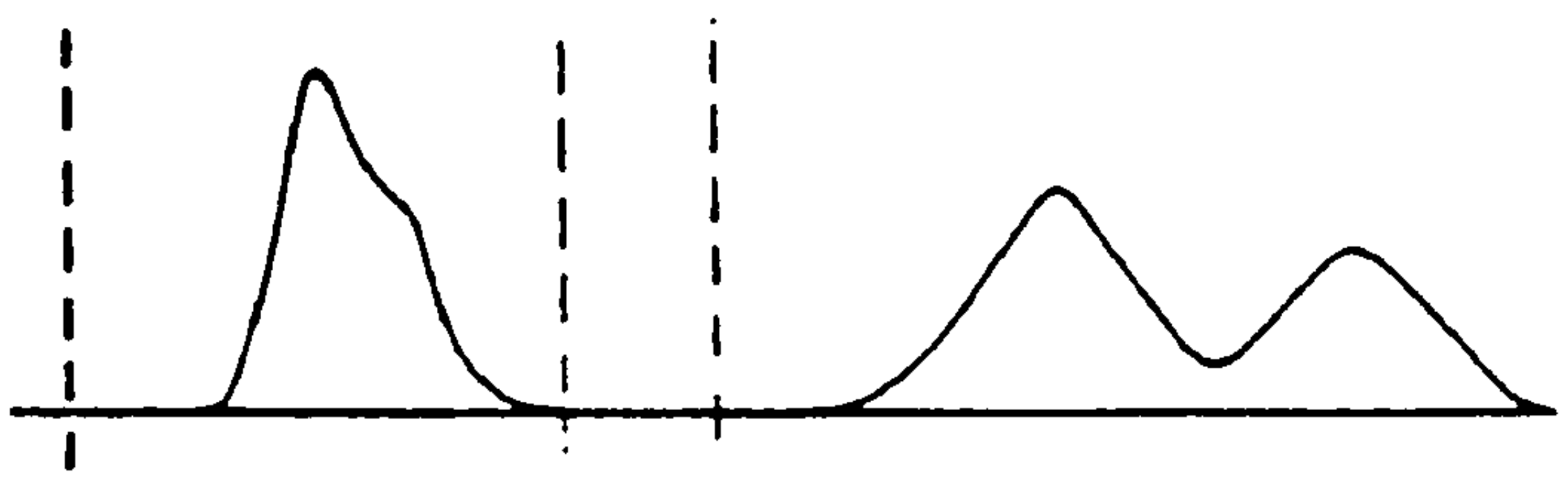
The changes in α, N and k' affects the resolution as illustrated in Figure 3.4.

Figure 3.4 Effect of k', N and α on Resolution

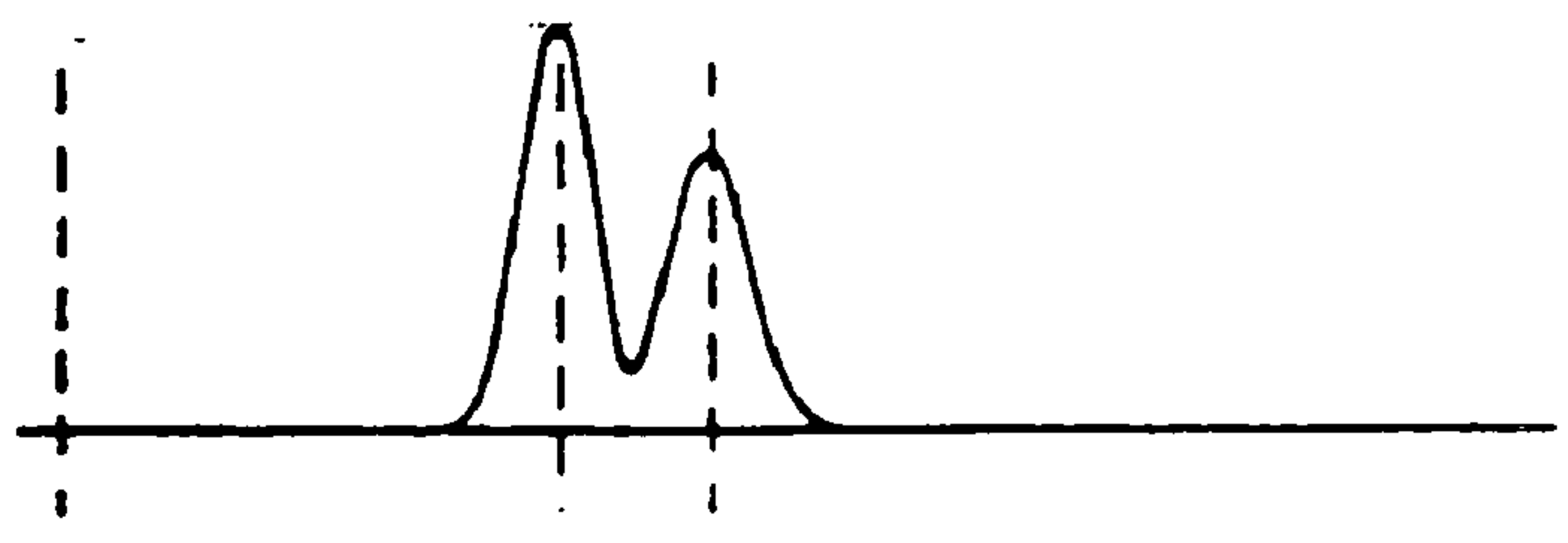
Initial Resolution of Peaks



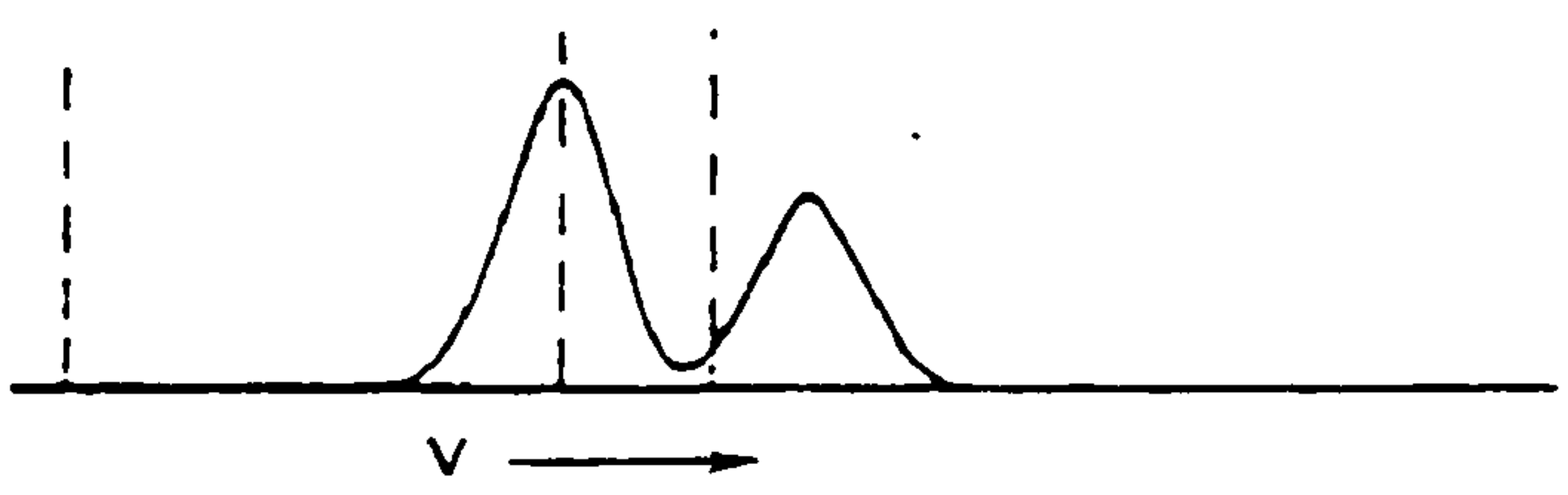
Change In Resolution on Varying k' (Capacity Factor)



Change In Resolution on Varying N (Theoretical Plates or Efficiency)



Change In Resolution on Varying α (Separation Factor or Selectivity)



Adapted from Dionex, Ion Chromatography Training Manual

From Figure 3.4 it is clear that increasing selectivity has the greatest effect on resolution.

Ion Chromatograph.

The concept of ion chromatograph is shown schematically in Figure3.5.

Pump: The mobile phase or eluent in IC is a liquid. The pump propels it constantly and precisely through the column. The equipment has a constant pressure/ constant flow pump.

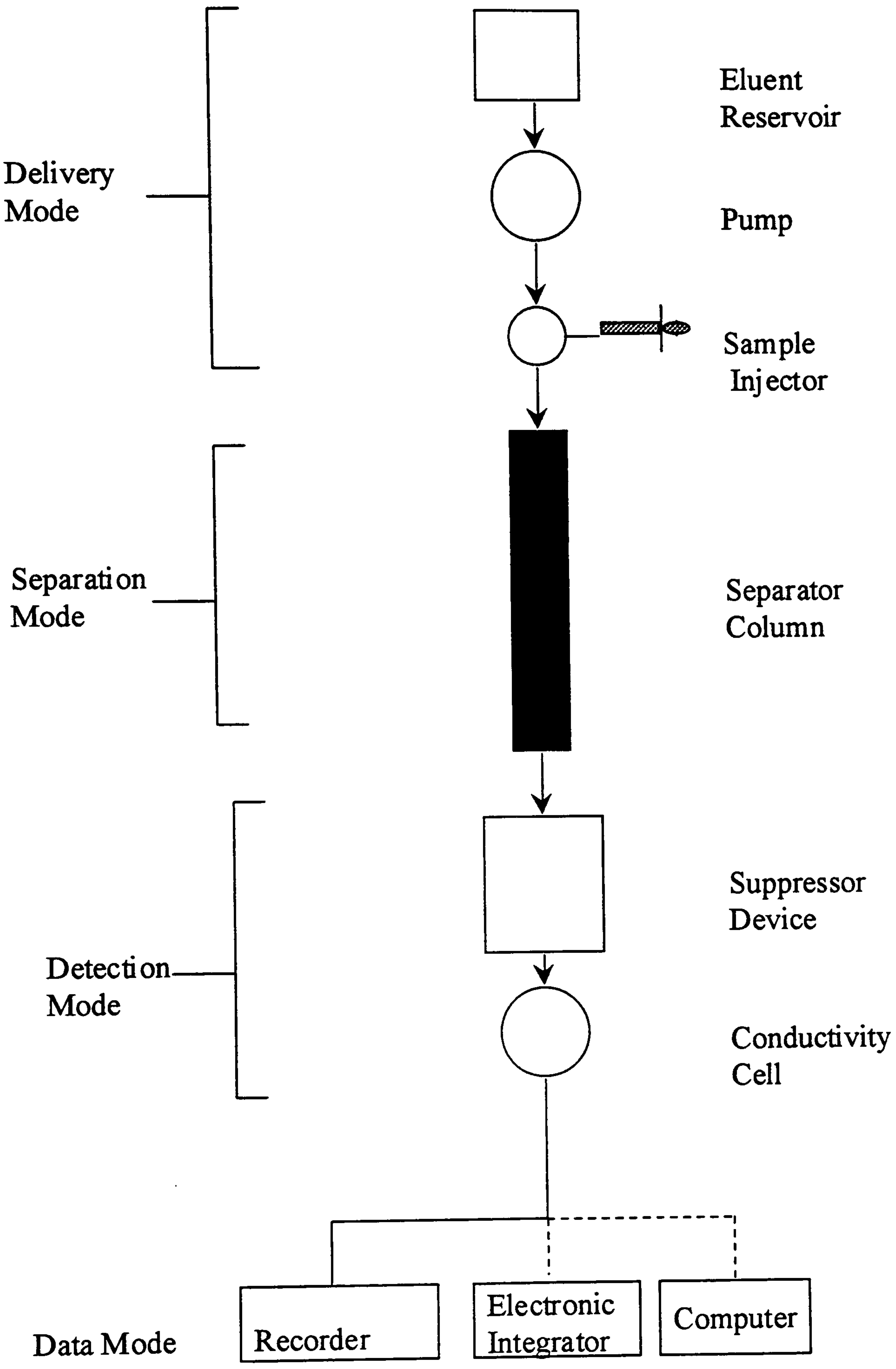
Injector: A loop valve injector was used in the analysis. When the valve is actuated the sample in the loop is swept into the flowing eluent stream and into the column.

Column: The HPIC analytical columns used in this work have internal diameter of 4mm, where as the HPICE Ion Exclusion column is 9mm in diameter.

Detectors: These sense the presence and measure the amount of sample component in the column eluent. A good IC detector exhibits high sensitivity, low noise and a wide linear response to all types of ions.

Figure 3.5

SCHEMATIC ILLUSTRATION OF AN ION CHROMATOGRAPH



A conductivity detector was used for analysis in this research work. Conductivity is a universal property of ionic species in solution and shows simple dependence on species concentration. However, the conductivities from the sample ions may be 'masked' by that from the much more abundant eluent ions. This detection problem is alleviated by using chemical suppression which reduces the background conductivity of the fluent to a low or negligible level. The chemical suppression is accomplished by using a suppression device (ion exchange resin or ion exchange membrane) in the suppressor column.

Data Handling: An electronic integrator automatically measures peak area / height and retention times. Retention times from the chromatograms are used for qualitative analysis and the peak area/height are proportional to concentration of species. Therefore, this effectively allows quantification of the ionic species.

3.3.1.3. Modes of Separation

IC utilises multiple modes of separation and detection and quantification of ionic species at very low concentration. In all cases, IC separation are due to differences in the equilibrium distribution of sample components between the mobile phase and stationary phase. The stationary phase is the key to IC separations since the column is the heart of the whole process.

There are three main modes of separation.

1. Mobile Phase Ion Chromatography (MPIC). This phase is used for the separation of hydrophobic ions such as alkyl and aryl sulfonates and sulphates, quaternery

amines, I^-, SCN^-, ClO_4^-, BF_4^- and metal cyanide complexes. This mode has not been used in this research work.

2. High Performance Ion Chromatography (HPIC). This mode is used for separating common inorganic ions such as F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}etc.
3. High Performance Ion Chromatography Exclusion (HPICE) is used for separating organic and amino acids as well as group separation of inorganics from organics. This mode of separation has been used for determination of acetates in the groundwater samples.

Table 3.2 Ion Exchange Capacity of the 3 types of Resins

	Type of Resin For Analysis	**Ion Exchange Capacity (meq/g)**
1.	MPIC- no fixed ion exchange capacity	0
2.	HPIC- moderately low fixed ion exchange capacity	0.01-0.05
3.	HPICE-high fixed ion exchange capacity	3-4

The mechanism for separation in MPIC is adsorption and/or ion pairing. In the case of HPIC, the separation involves the use of low capacity pellicular ion exchange resin. In this case the separation mode is dominated by ion exchange. HPICE utilises totally functionalised high capacity exchange resin. The separation mode in this case is dominated by Donnan Exclusion.

The Properties of Resin in ion exchange chromatography are dependent upon a) the material, (b) the extent of cross linking, (c) the particle size, (d) the functional group identity, and (e) the capacity.

a) Material, The resin in the separation column consists of polymers of styrene and divinyl benzene (DVB). The rigidity or strength of the resin bead depends upon the amount of DVB in the resin.

b) Cross-linking, the higher the cross-linking, the less a resin will swell in a liquid environment. The higher the cross-linking the lower is the total pore volume of resin and consequently less separation is obtained. Resins containing less than 6% DVB are not pressure–stable [4] and cannot be regarded as HPLC (High-Performance Liquid Chromatography) materials. Rigid polystyrenes are true high performance materials. They are highly cross-linked and hence do not swell and are stable up to 350 bar.

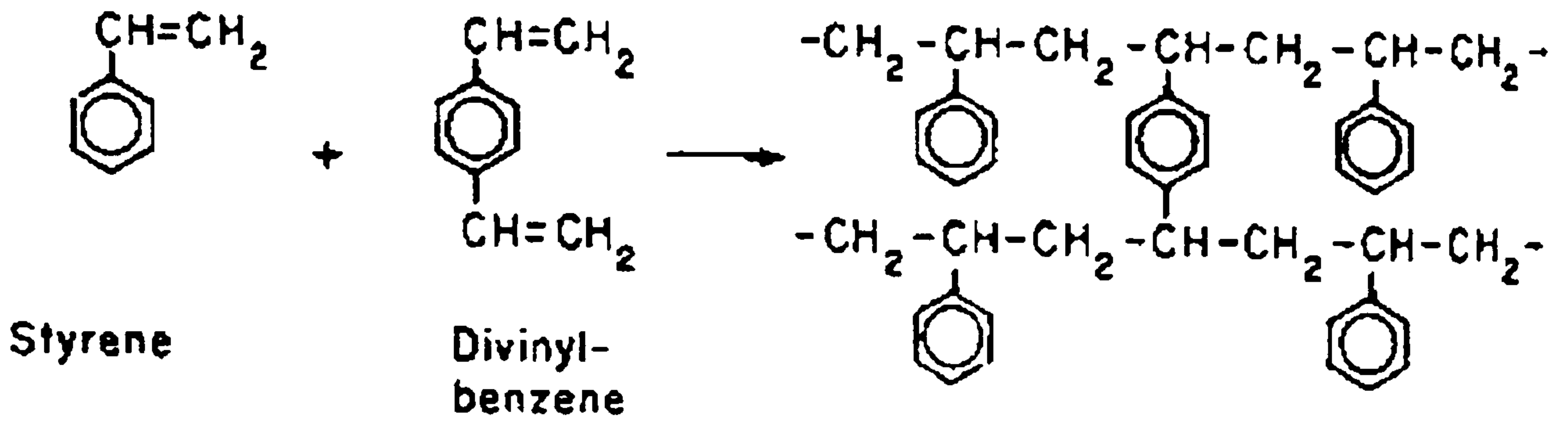
c) Particle size: The smaller the resin particle the greater the efficiency of separation because the smaller the particles the shorter the diffusion paths and the band dispersion is minimised.

d) Functional Group Identity: Sulphonic acid and quaternary amine type resins are the most commonly used resin functional groups. Resin having functional groups throughout the bead are termed "porous", as in HPICE. Resins with group limited to the bead surface are called "pellicular" resin, as in HPIC.

e) Capacity: The capacity of an ion exchange resin is defined as the number of functional groups per unit volume or mass. Ion exchange capacity is usually defined in terms of milli equivalent per gram (meq/gm). The higher the capacity of a particular resin, the longer the retention of solutes and stronger the mobile phase necessary for a time-efficient separation.

High Performance ion Chromatographs

The HPIC resins for cation Ion Chromatography employ an inert hydrophobic core, the surface of which contains sulphonic acid groups. These functional groups are covalently bonded to the copolymer. The resin core is hydrophobic, largely due to the hydrophobic nature of styrene and DVB.



Styrene-divinylbenzene resin.

This produces high efficiency due to the fact that no functional groups are present in the core enhances its hydrophobicity. By limiting functional groups to the surface, the diffusion paths to these exchange sites are shortened. This produces high efficiencies with moderately low capacities. Pictorial representation of Cation and Anion Separator Resins is illustrated in Figure 3.6.

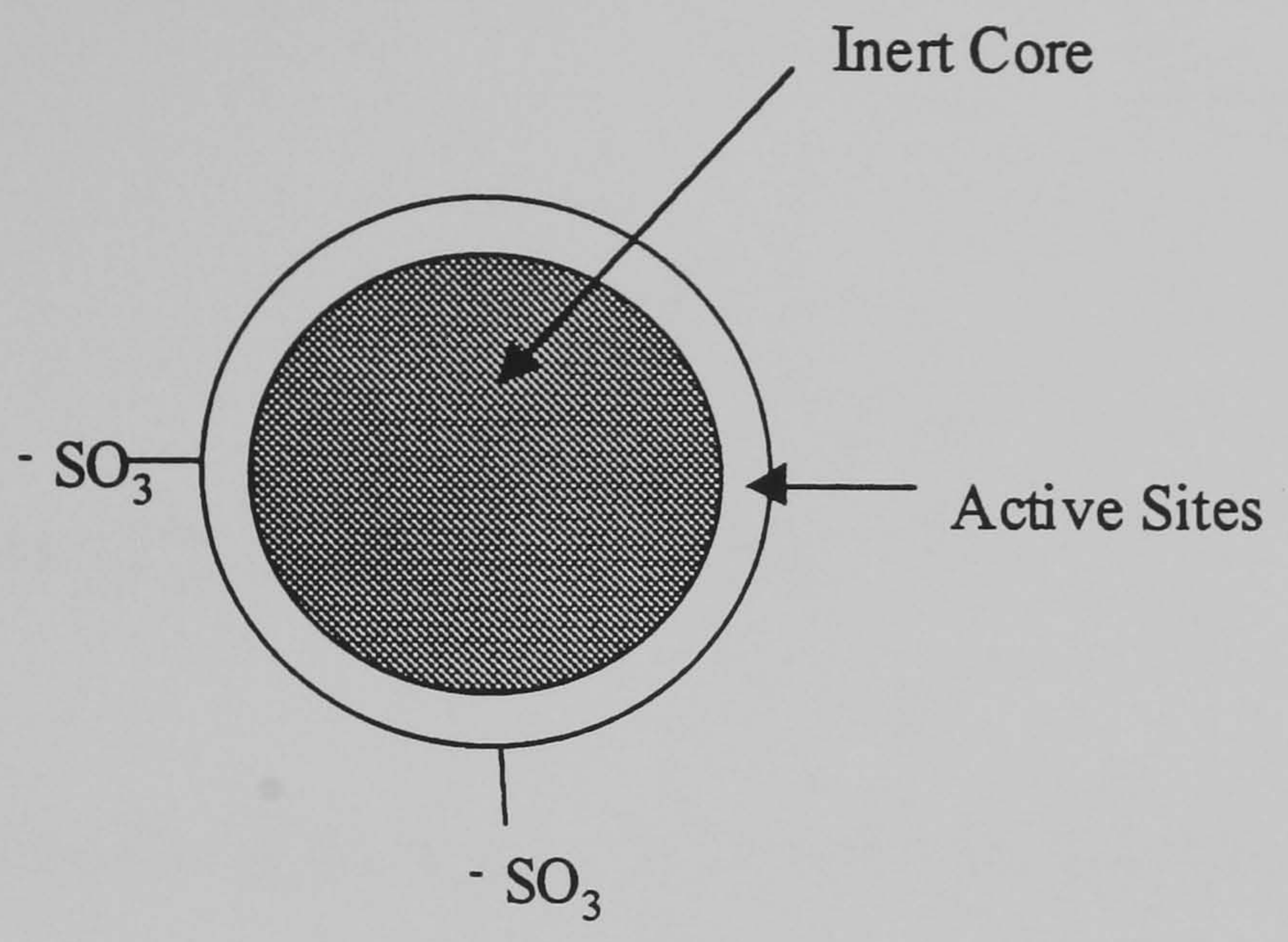
The Anion Separator resin is similar to the cation resin. This again has an inert PS/DVB core with sulphonic groups attached to the surface of the beads. The sulphonic groups provide a means to attach the small totally porous anion exchange beads to the surface-sulphonated PS/DVB bead. The aminated beads are strongly held to the surface by coulombic forces. van der Waals forces hold the PS/DVB matrix of the animated bead and the PS/DVB resin of the surface sulfonated substrate. For geometric reasons not all of the SO_3H^- sites are occupied with aminated particles, but generally this does not cause a problem.

The small anion exchange particles attach to the surface of the pellicular inner core provides the anion separating capability of the resin. The anions in solution compete for the cationic sites. Because ions have different affinities for the fixed exchange sites, it is possible to separate mixtures of ionic compounds.

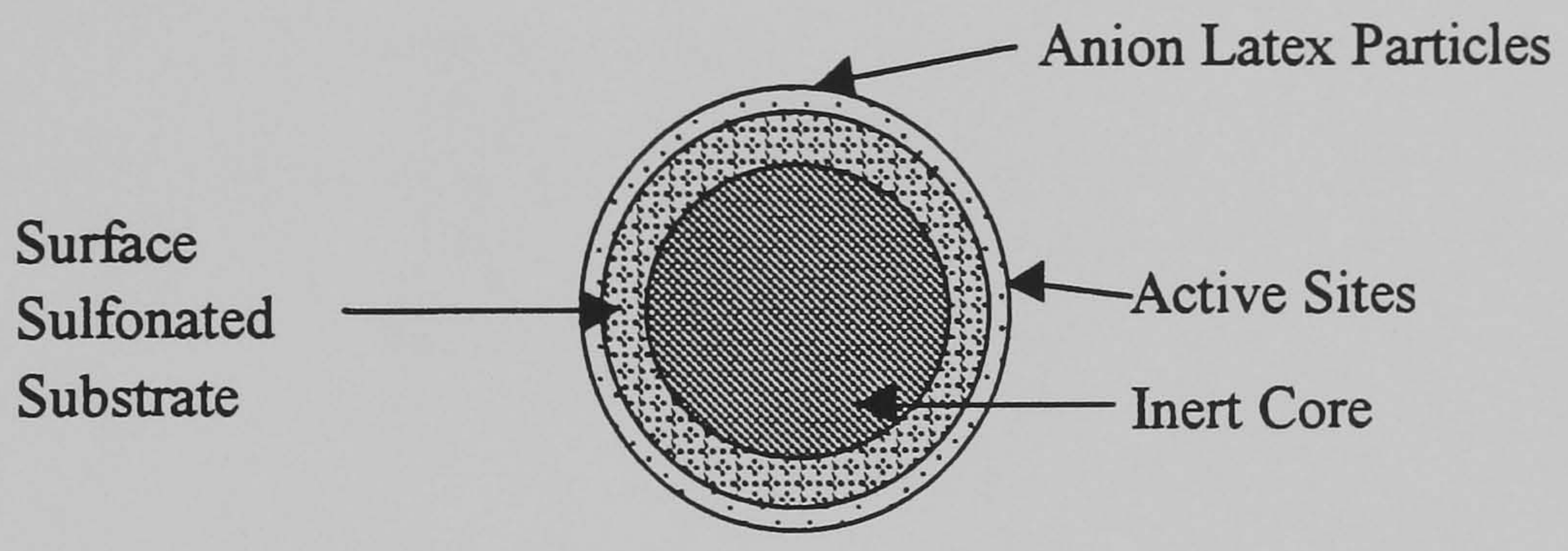
Equilibria for anion and cation exchange processes are illustrated in the following equations.

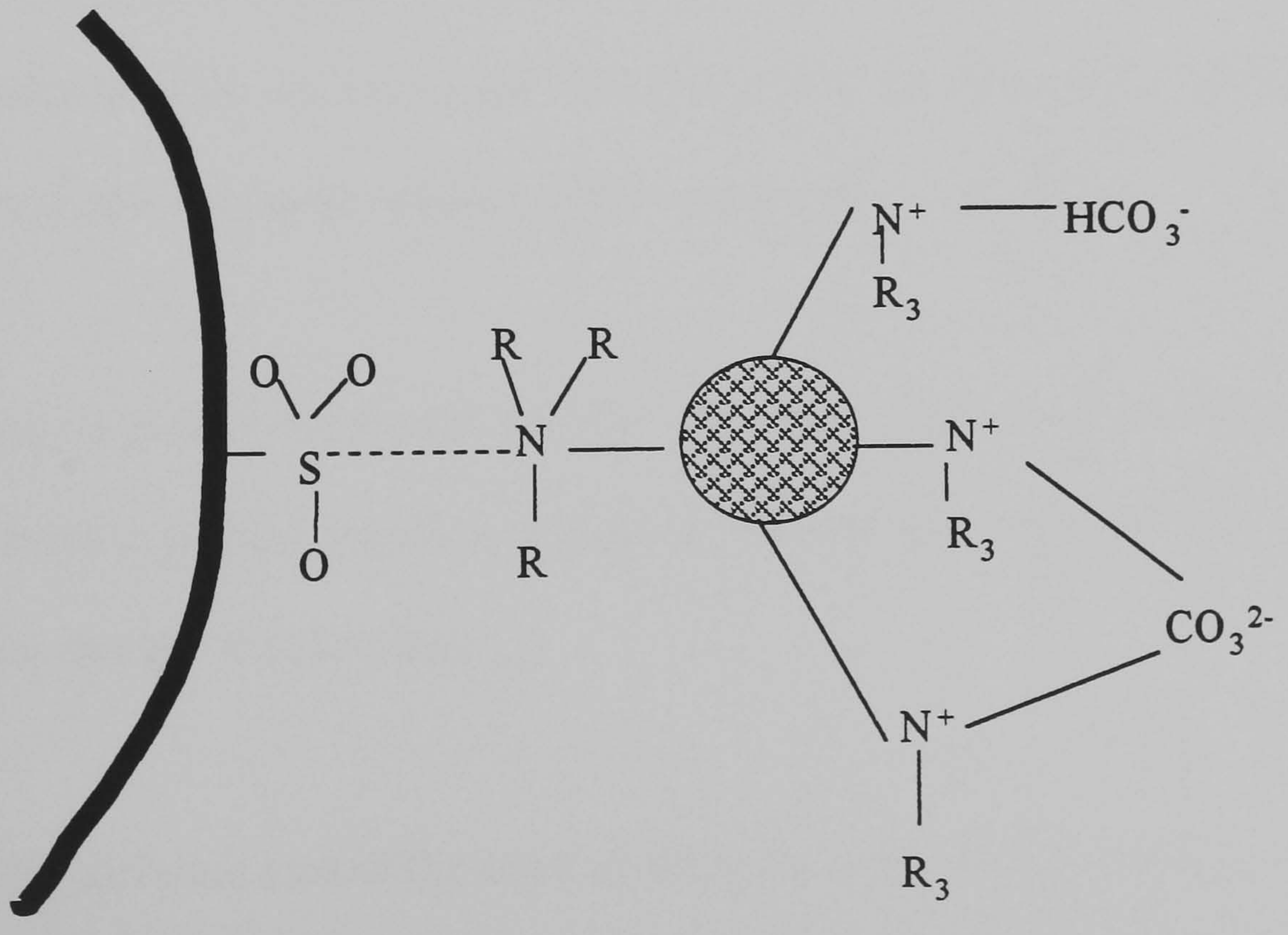
Figure 3.6 Pictorial Representation of Cation and Anion Separator Resin

Cation Separator Resin



Anion Separator Resin





Anion Exchange

$$X^- + HCO_3^-\ {}^+NR_4\text{—Resin} \rightleftharpoons X^-\text{—}{}^+NR_4\text{—Resin} + HCO_3^-$$

(Solute) (Eluent)

Cation Exchange

$$M^+ + H^+\ {}^-O_3S\text{—Resin} \rightleftharpoons M^+\ {}^-O_3S\text{—Resin} + H^+$$

M^+ = Solute Cation

The equilibrium for Anion Exchange is given by the following equation:

$$K = \frac{\overset{\text{Resin}}{[R_4N^+}\ \overset{\text{Solute}}{X^-]}\ \overset{\text{Eluent}}{[HCO_3^-]}}{\underset{\text{Resin}}{[R_4N^+}\ \underset{\text{Eluent}}{HCO_3^-]}\ \underset{\text{Solute}}{[X^-]}}$$

The higher the value of the distribution coefficient 'K', the more strongly the ionic solute interacts with the ion exchanger. The distribution coefficient is a function of ionic charge, ionic size, ionic strength of the eluent, pH and resin type.

Ionic Charge In general the greater the valence of the sample ion, greater the affinity for the ion exchange sites, therefore, the typical elution order is first monovalent, then divalent and last trivalent ions.

Ionic Size For different ions of the same valence, the larger the ionic radius, the more polarisable is the ion, and the more it is strongly attracted to an ion exchange site.

Therefore the elution order of the halides is F^-, Cl^-, Br^- and I^- which corresponds to increasing ionic size.

Adsorption Affects ions having strong adsorption interactions with the stationary phase will have long retention times under standard analysis conditions.

pH. Eluent pH affects the distribution of multivalent ions. The affinity of an ion is a function of ionic charge, and is also function of the pH of the mobile phase. For example, phosphate will elute after NO_2^- followed by NO_3^- and sulphate. At higher pH (〉11) it will elute after SO_4^{2-}.

Resin Type The selectivity of an ion exchange resin plays a major role in HPIC in separations since it directly affects the equilibrium distribution of both the sample ions and eluting ions. The elution characteristics of ions can be changed by changing the selectivity of the resin. This can be accomplished by varying cross-link, the size or the functional group of the anion exchange material.

It is possible to obtain large changes in the analytical conditions by changing flow rates and eluent concentrations.

HPIC Guard Columns are used primarily to protect the analytical column. This is a short version of the analytical column. It filters particulate matter from the solutions and the strongly retained ions could lead to `poisoning` of the analytical columns. The guard columns selectivity matches the separator column.

3.3.1.4. Modes of Detection

There are a variety of detection modes employed in the ion chromatographic techniques, e.g., conductivity and UV. In this research work the method of detection in all of the experiments has been by the conductivity mode. Conductivity mode of detection utilises suppressed conductivity. This provides a wide linear range, high sensitivity, high selectivity, and ease of operation. This also provides a system capable of analysing a wide variety of ions, ions with pK_A or pK_B less than 7.

Chemical Suppression. In this method the conductivity of the eluent is chemically suppressed using ion exchange techniques (packed columns or fibres) prior to detection by conductivity. Suppresser devices change the concentration of highly conductive eluent ions to species which are significantly less conductive. In addition, solute ions are converted to their corresponding acids or hydroxides as they pass through the suppresser. The exceptionally high mobilities of H^+ and OH^- ions in water increase the conductivity of most species, resulting in increased detection sensitivity. Reduction of the background eluent conductivity also increases detector sensitivity.

Conventional chemical suppression is accomplished by placing a second ion exchange device downstream from the analytical column. For example, in anion exchange chromatography, the suppressor is a cation exchange device in the H^+ form. The suppressor converts the carbonate eluent to weakly ionised carbonic acid while converting the solute ion into its more conductive acid form as shown in the reactions below.

1. $2\,(H^+—Resin) + Na_2CO_3 \rightarrow 2\,(Na^+——Resin) + H_2CO_3$

$(H^+ — Resin) + NaHCO \rightarrow 3\,(Na^+— Resin) + H_2CO_3$

2. $(H^+$——Resin) + Cation——$X^- \rightarrow$ Cation ——Resin + $H^+ X^-$

In the case of suppression of background ions in the eluent stream of a cation exchange system, in the analysis of Na^+, NH_4^+, and K^+. Dilute HCl is pumped through the analytical column. Ion exchange occurs as H^+ ions compete with the sample ions for the sulphonic acid exchange sites. After the ions are separated, they exit at various times from the bottom of the column in a background of HCl eluent.

When this mixture of sample ions and eluent enters the suppressor device containing a strong base ion exchange material in the OH^- form, two main reactions take place:

1. HCl is removed by the device as follows:-

   HCl + Resin—— OH $\rightarrow$ Resin —— Cl + H_2O

2. The alkali metal/ ammonium chlorides are converted to their hydroxides.

   M^+Cl^- + Resin—— OH $\rightarrow$ Resin ——Cl + M^+OH^-

Thus highly conducting HCl ions from the eluent are removed. Only the deionised water containing the three separated metal hydroxides passes into the conductivity cell where the cations are identified by measuring retention times

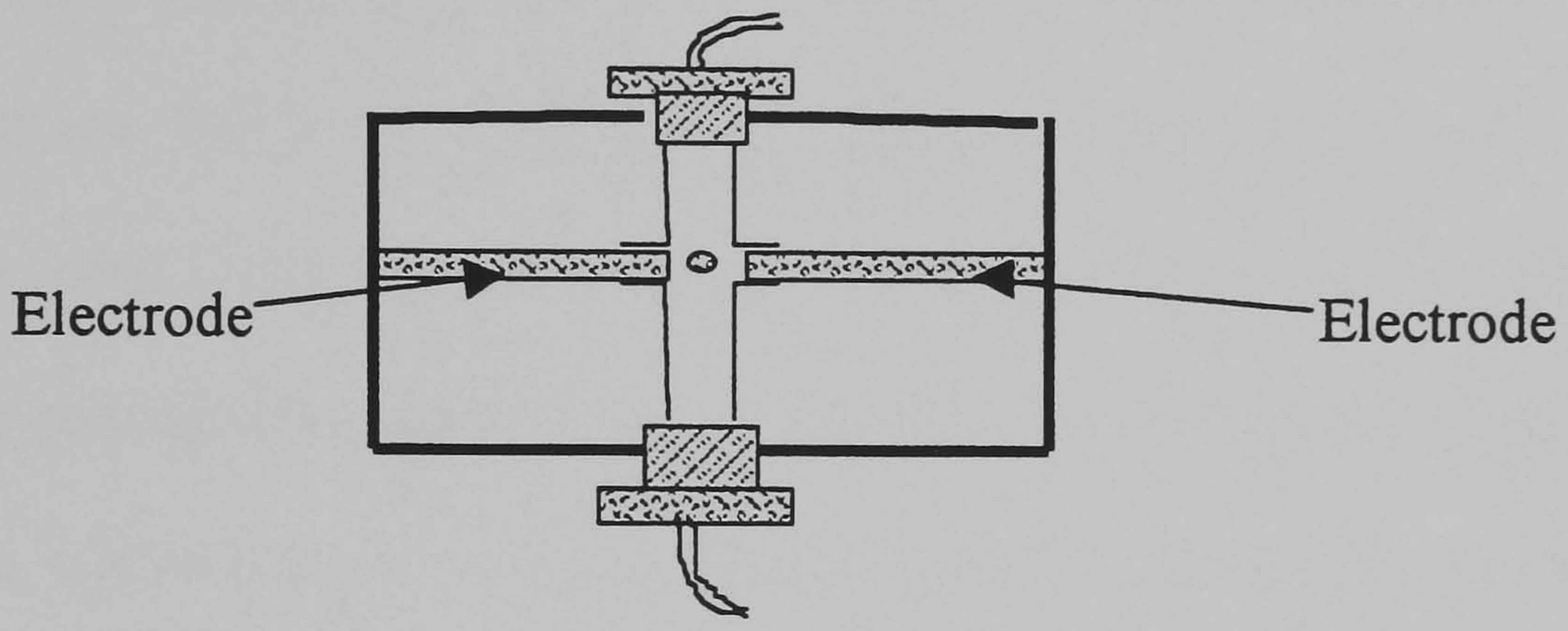
Fibre suppressors are better for analysis especially when anions are being determined, because, due to Donnan Exclusion phenomenon, weak acids like HNO_2 and H_2CO_3 are retained by the column thereby causing broadening of the peaks and interference with the peak areas and heights of the ions being determined. This is particularly the case for fluoride and chloride via an automatic integrator.

3.3.1.5 Conductivity Detection.

This is based upon the electrical conductivity of an ionic solution when placed between two oppositely charged electrodes. The two electrodes are mounted in the cell body as shown in Figure 3.7.

Figure 3. 7

Conductivity Detection



The presence of ions in the solution allows electrical current to flow between the electrodes, completing the circuit. At low concentrations, conductivity is directly proportional to the concentration of conductive species in the solution. The total ionic concentration of the solution in the cell and the temperature of that solution affect the linearity of this relationship.

Effect of Concentration: The electrical conductance of a solution depends upon the type and concentration of all the ions present. Ideally, conductance increases linearly as the total ionic concentration increases. This linearity is limited by the degree of dissociation, the mobility of ions in solution and the formation of ion pairs in the solution.

For weak electrolytes (e.g. weak acids and bases) the primary factor limiting detection linearity is the degree of dissociation or ionisation. Weak electrolytes are not completely ionised in solution. As the concentration increases, the ratio of ionised to non ionised species decreases, therefore concentration of detected ions is less than the total concentration of the species in solution. Hence, this causes deviation in detector linearity at high concentrations.

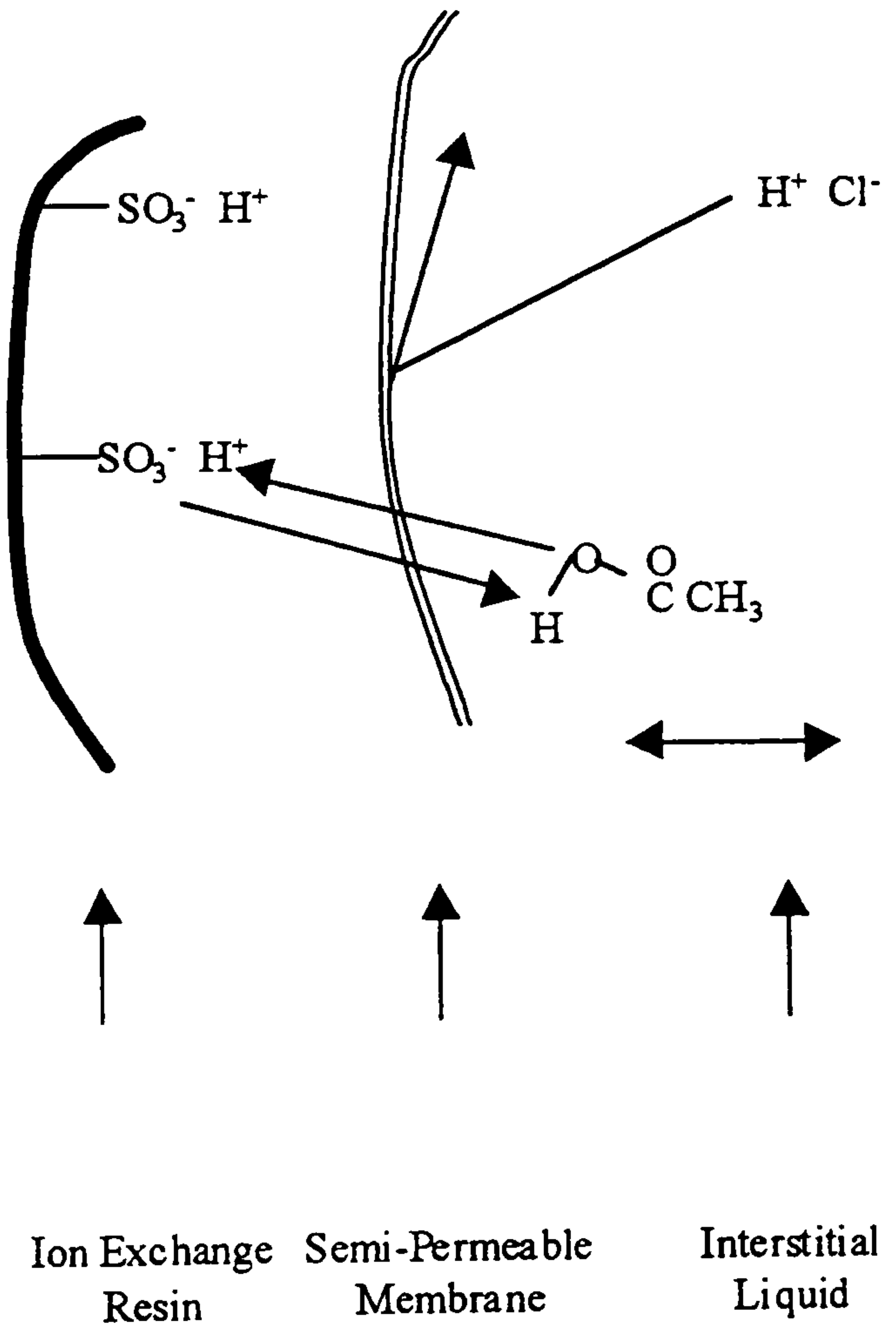
For strong electrolytes (e.g. strong acids, bases and their salts), these dissociate completely in solution. The primary factor limiting detection linearity is ionic mobility. Ionic mobility is defined as the migration velocity of an ion in an electric field in which the potential changes/volt cm^{-1} in the direction of the field. The higher the ionic mobility, higher is the conductivity. Factors affecting ionic mobility are the degree of dissociation of the ions in solution and the charge density of the hydrated ions. Ions of high charge density exhibit high mobility. At higher concentrations the degree of dissociation of a strong electrolyte decreases, resulting in lower ionic mobility and a non-linear detector response.

Effect of Temperature: Conductivity of solution is directly affected by its temperature. A change in temperature causes a change in the solution conductivity. As the solution conductivity increases, the effect of temperature changes become more pronounced. This is observed as a regular baseline that is directly related to the room temperature. The change may in turn affect the reproducibility and linearity of a determination. In the present work care was taken to ensure that the results reported were from within the linear range to ensure accuracy.

3.3.1.6 High Performance Ion Chromatography Exclusion (HPICE)

This separation mode employs closely sized, totally sulphonated cation exchange resin of controlled cross-link. The technique makes use of the Donnan Exclusion phenomenon. This phenomenon limits the ability of a charged species i.e., an anion to move into the pore volume of the resin. However, non-ionised species are not subject to Donnan Exclusion and may permeate into the pores of the resin. The Donnan Exclusion concept is illustrated in Figure3.8.

Figure 3.8 Donnan Exclusion Principle



Source: Dionex, Ion Chromatography Training Manual

The functional groups of the resin tend to form a semi-permeable membrane between the interstitial liquid (the eluent) of the resin particles and the occluded liquid inside the resin pores. A highly ionised species such as SO_4^{2-} cannot penetrate the membrane, therefore no retention of such anions occurs. Such highly ionised anions in solutes elutes in the void volume of the system. A non-ionised or weak anion e.g. CH_3COO^- can penetrate the ionic membrane and reach the volume within the pores. Retention then becomes a function of total pore volume and surface area of the resin. An analyte like CH_3COO^- elutes at some volume greater than the excluded volume.

Ionisation of a weak acid like acetic acid would depend upon pH of the eluent. The higher the pH greater the ionisation and consequently the less is the retention by an ion exclusion mode. Chromatographic separation is principally dependent upon the distribution of the species between the occluded resin pore liquid (stationary liquid) and the interstitial liquid (mobile phase).

HPICE separation depends upon the following factors:-

1. Solute pKa – the larger the pK, longer the retention time.
2 Temperature – elevated temperature will increase ionisation and decrease retention.
3 Concentration of Solute – ionisation is a function of concentration.
4 Eluent pH – the lower the pH, larger the retention of a weak electrolyte.
5 Cross-linking of resin – the higher the cross-linking, the lower the pore volume and less separation obtained on the column.
6 Nature of the resin.

7 Flow rates – Since separation is diffusion dependent, slow flow rates (approximately 0.8 mL/min.) are desirable.

3.3.1.7.Qualitative and Quantitative Analysis

Qualitative Analysis: Constituents in a sample can be identified by comparing the retention times or distance on a chromatogram to those of a standard. Operating conditions like flow rate, temperature and eluent strength must remain constant for the comparison to be valid.

Quantitative Analysis: Once constituents have been separated and identified, quantification in most cases was performed by comparing detector response for the sample with that of a standard.

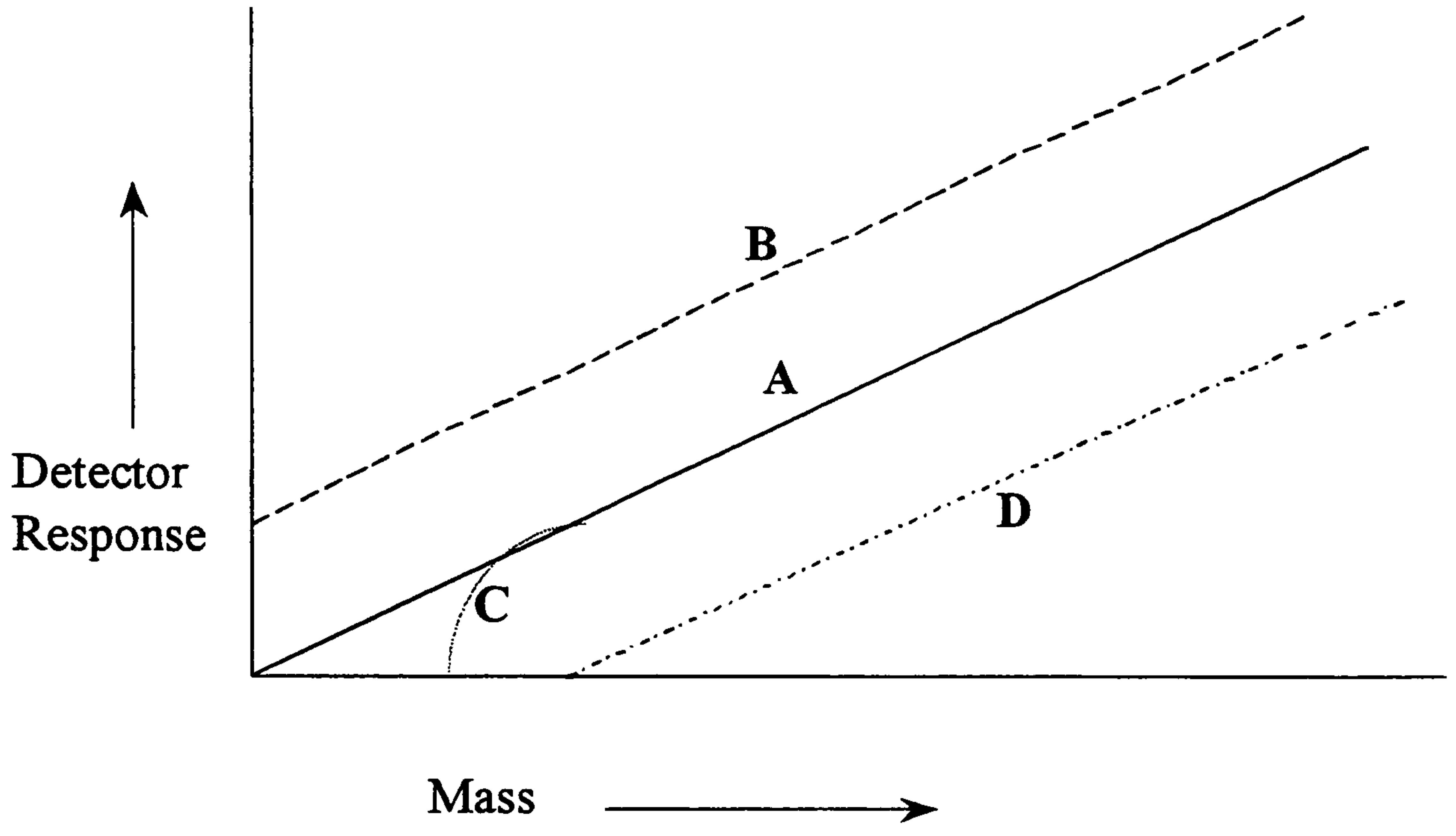
Separation of peaks can be optimised to assure accurate quantification by weakening or changing the eluent and tailing of peaks can be caused by sample overload and or adsorption effects. These can be improved by diluting the sample.

Physical Measurement: Detector response was measured by using either peak height or more often by measuring peak area. This was automatically worked out by the integrator of a computer.

For each chromatographic analysis, precision of results was checked by running at least one sample 5 times and at least every other sample run in duplicate to keep a check on the reliability of the results.

<u>Calibration Curves:</u> Calibration curves can be of the types described in the Figure 3.9.

Figure 3.9 Calibration Curves

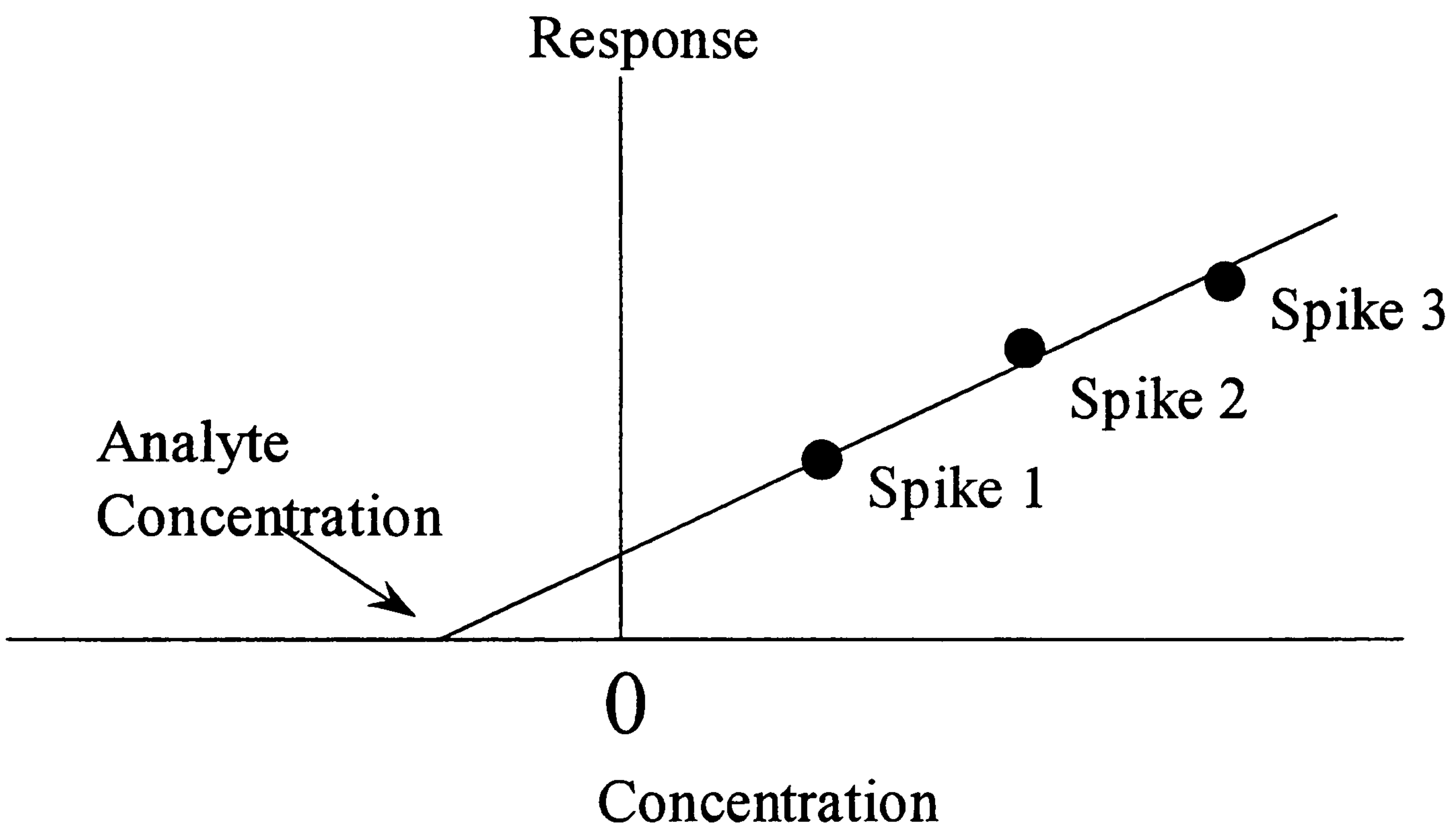


Where ‘A’ is the desired type of calibration curve. ‘B’ is obtained when there is an unresolved peak and during the standard addition method, while, ‘C’ occurs when column or suppressor adsorbs trace amounts of analyte, and ‘D’ is obtained due to sample loss during preparation and serial dilutions.

Calibration curves were obtained for each experiment by running at least three sets of standards. The sample dilutions were adjusted to fall within the linear range of detection. Concentrations of each analyte were read from the calibration graph and the results obtained by multiplying the measurements by the dilution factor.

Standard Addition Method: This method was used for determining acetates in the groundwater samples. The advantage of using this method is that a number of interferences can be overcome. An example of acetate determination is given in Figure 3.10.

Figure 3.10

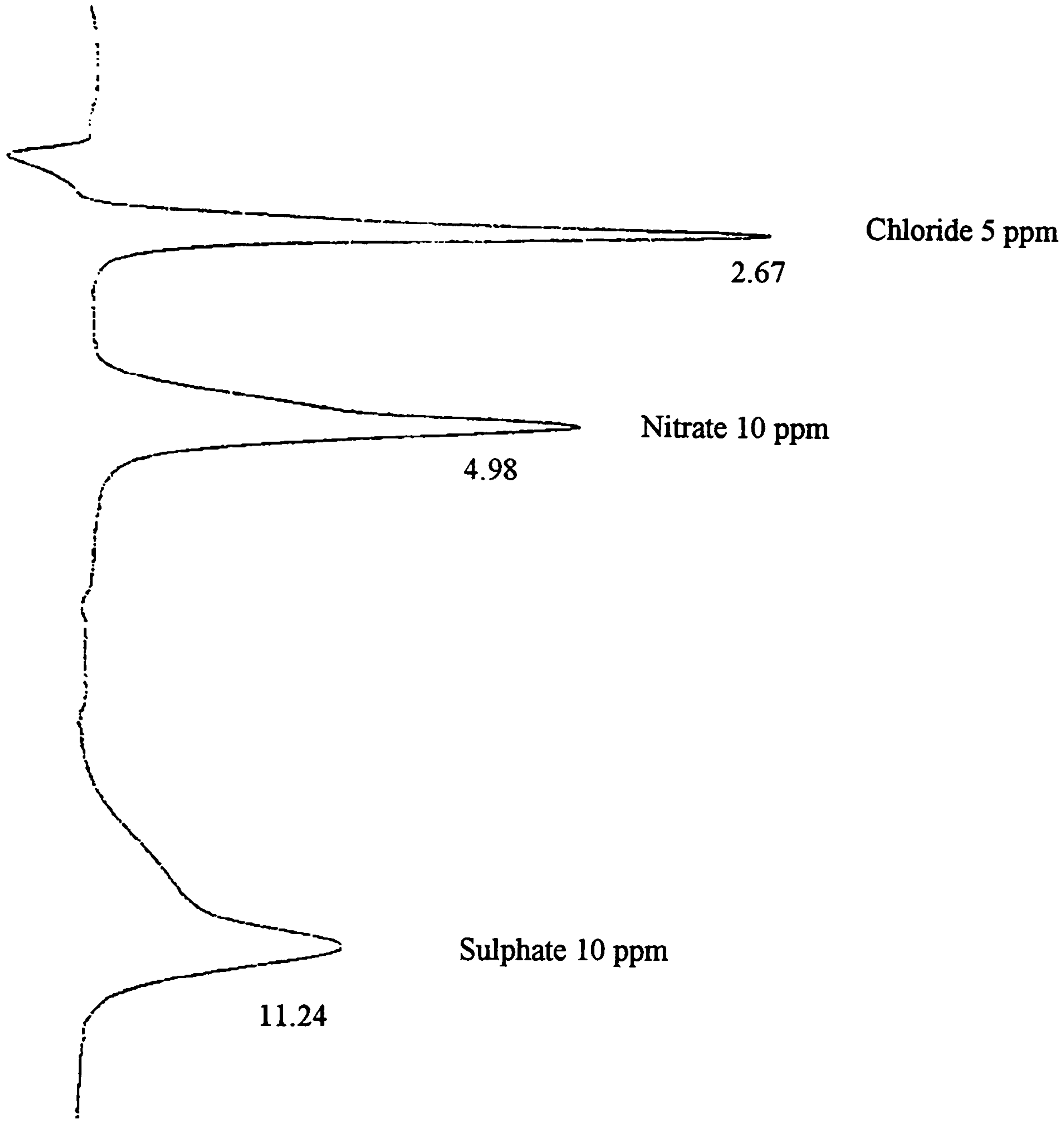


Care was taken to ensure that all the dilutions were made to the same final volume. This ensures that any possible interferent would be present at the same concentration in all solutions and affect the analyte anion equally in all the chromatographic runs.

Examples of chromatograms used for IC analysis are presented in Figures 3.11 to 3.14. The results of peak areas from standard solutions were used for producing calibration lines and these are shown in figures 3.15 to 3.17. The resulting calibration graphs were used for calculating analyte concentrations in the groundwater samples.

Figure 3.11

Calibration for Anion Determination by IC - Chromatogram



Chromatographic Conditions for Anion Analysis

- Column - HPIC AS4A / AG4A
- Eluent - HCO_3^- / CO_3^{2-}
- Regenerant - 0.025N H_2SO_4
- Flow of Eluent - 1 ml / min
- Pressure 670 psi
- Background Conductivity - 15 µs / cm

Figure 3.12

Chromatogram - Anion Determination by IC in Sample D7 (10 Times Diluted)

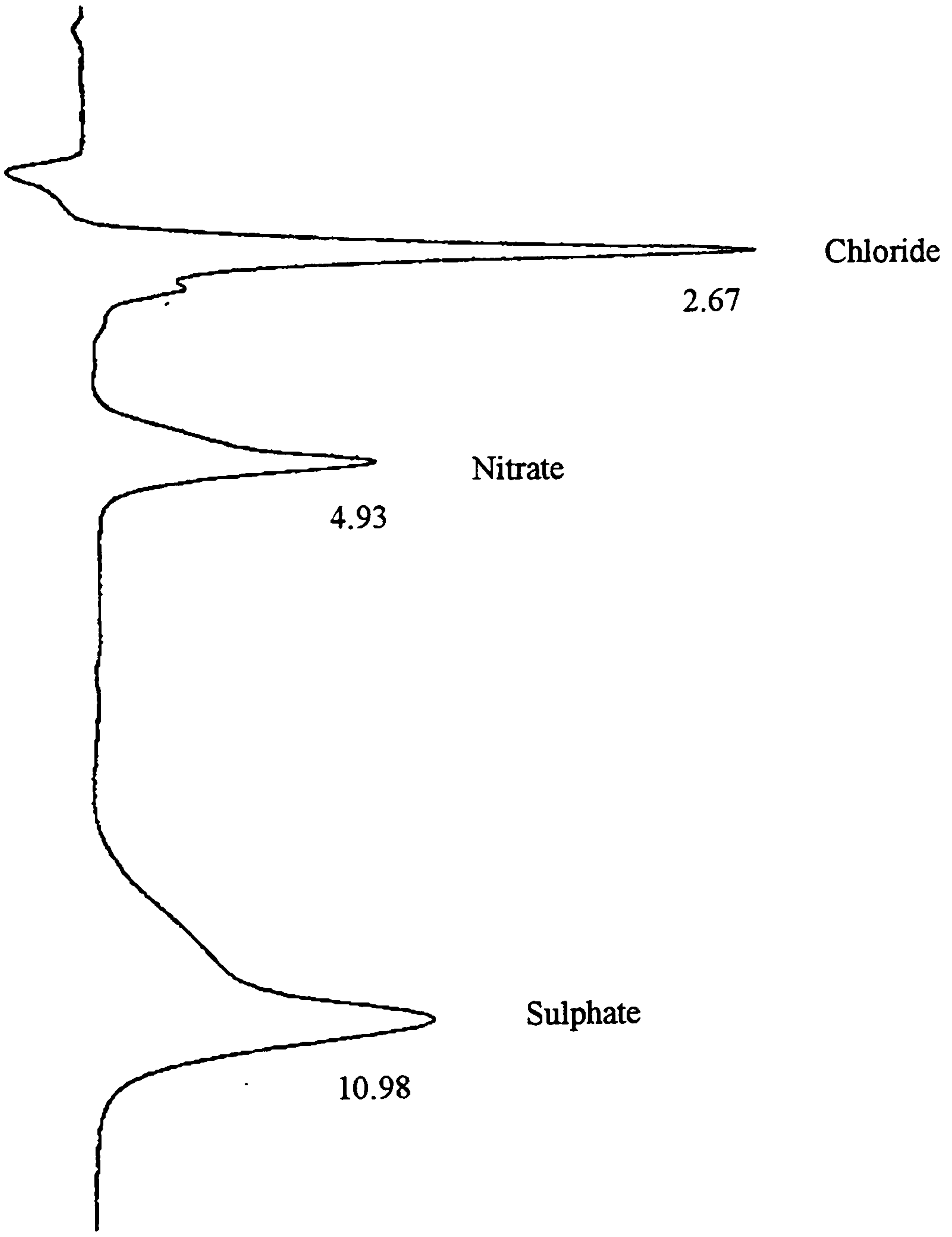
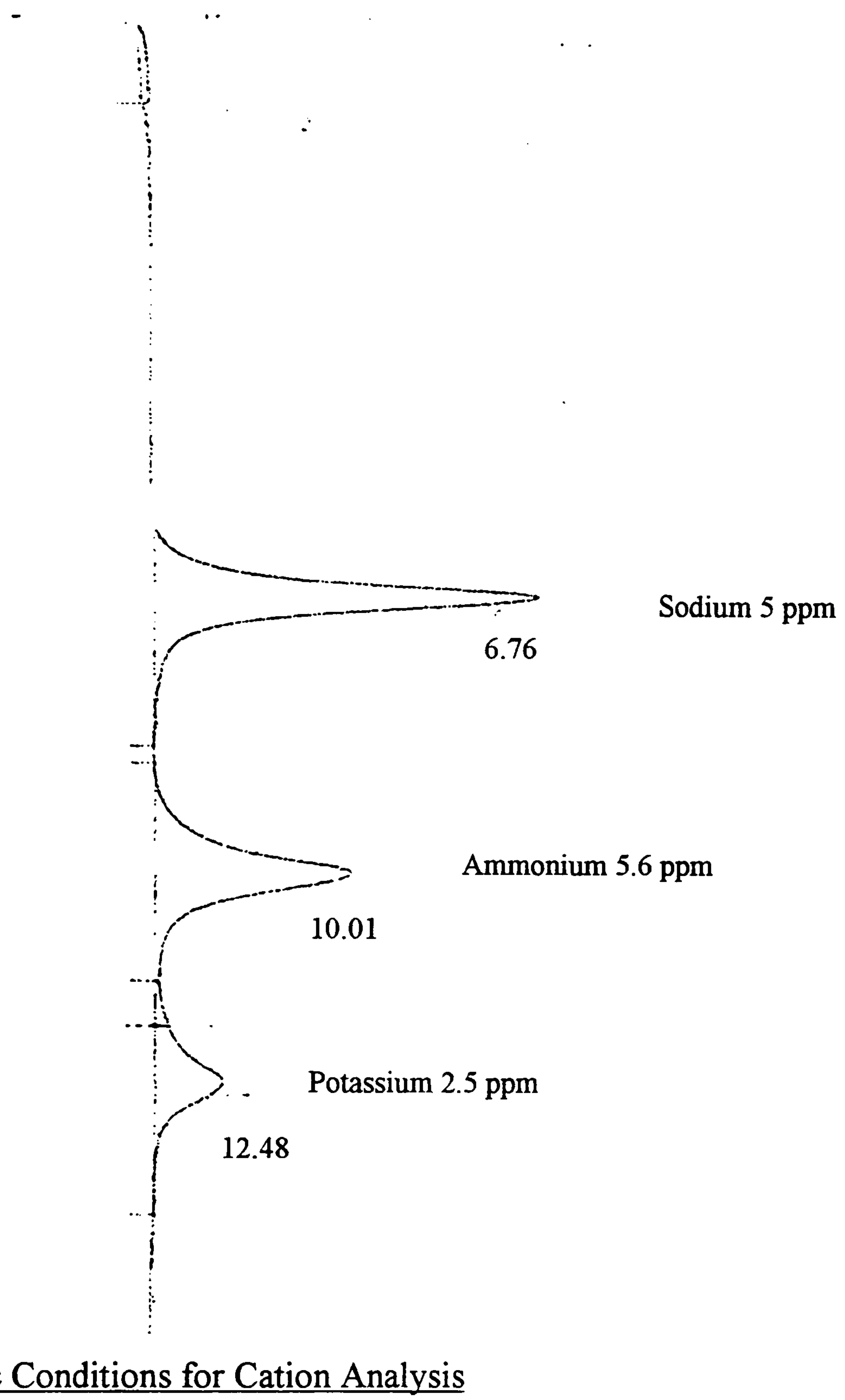


Figure 3.13

Chromatogram - Calibration for Cations (Na, NH_4, and K) by IC



<u>Chromatographic Conditions for Cation Analysis</u>

- Column - CS2 with CG2 (guard column)
- Eluent - 5 mM HCl
- Regenerant - 0.04 M TMOH
- Flow of Eluent - 1.5ml / min
- Pressure - 890 psi
- Background Conductivity - 3.93 µs / cm

Figure 3.14

Determination of Cations in Sample B3 (10 Times Diluted) by IC

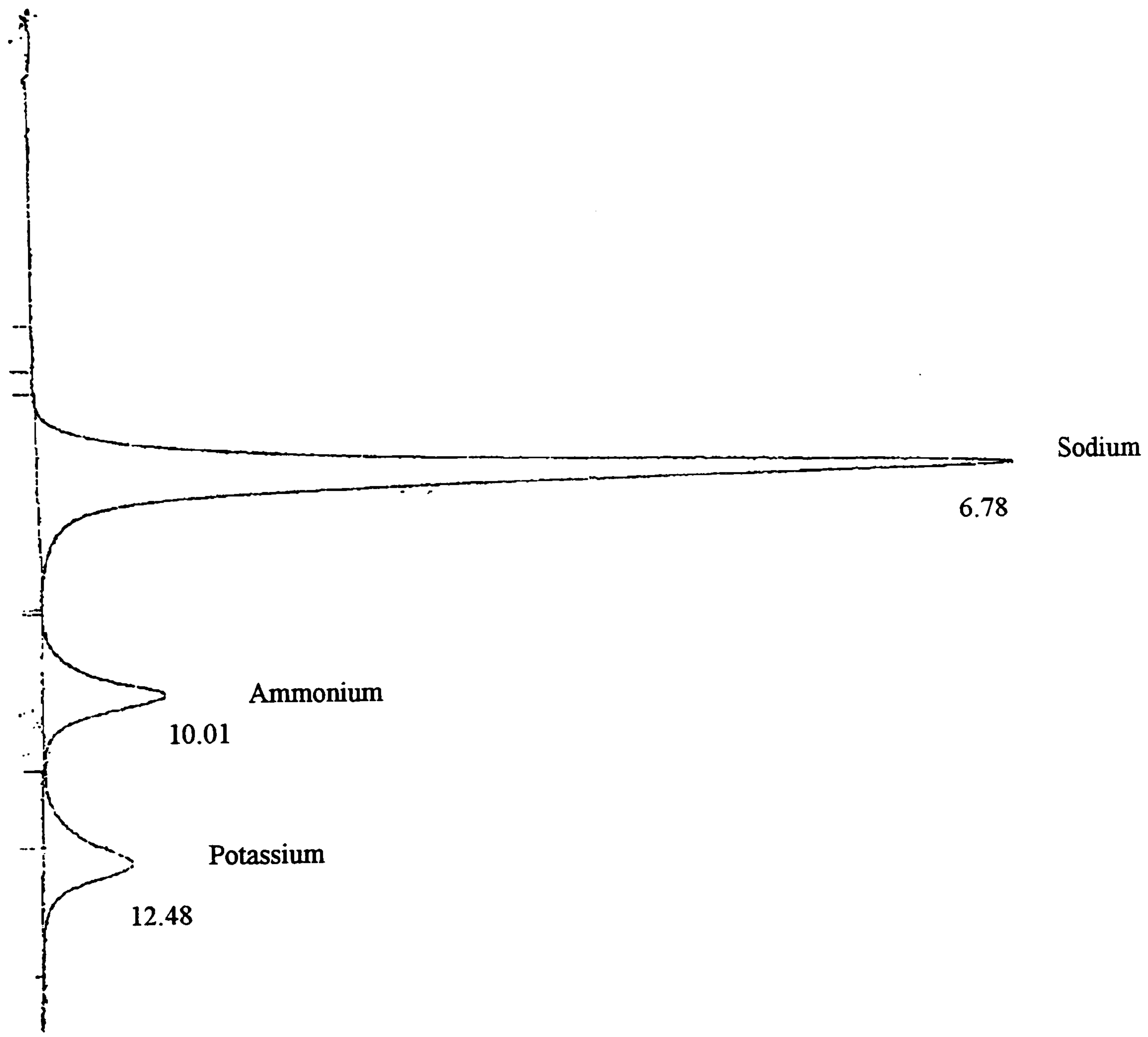
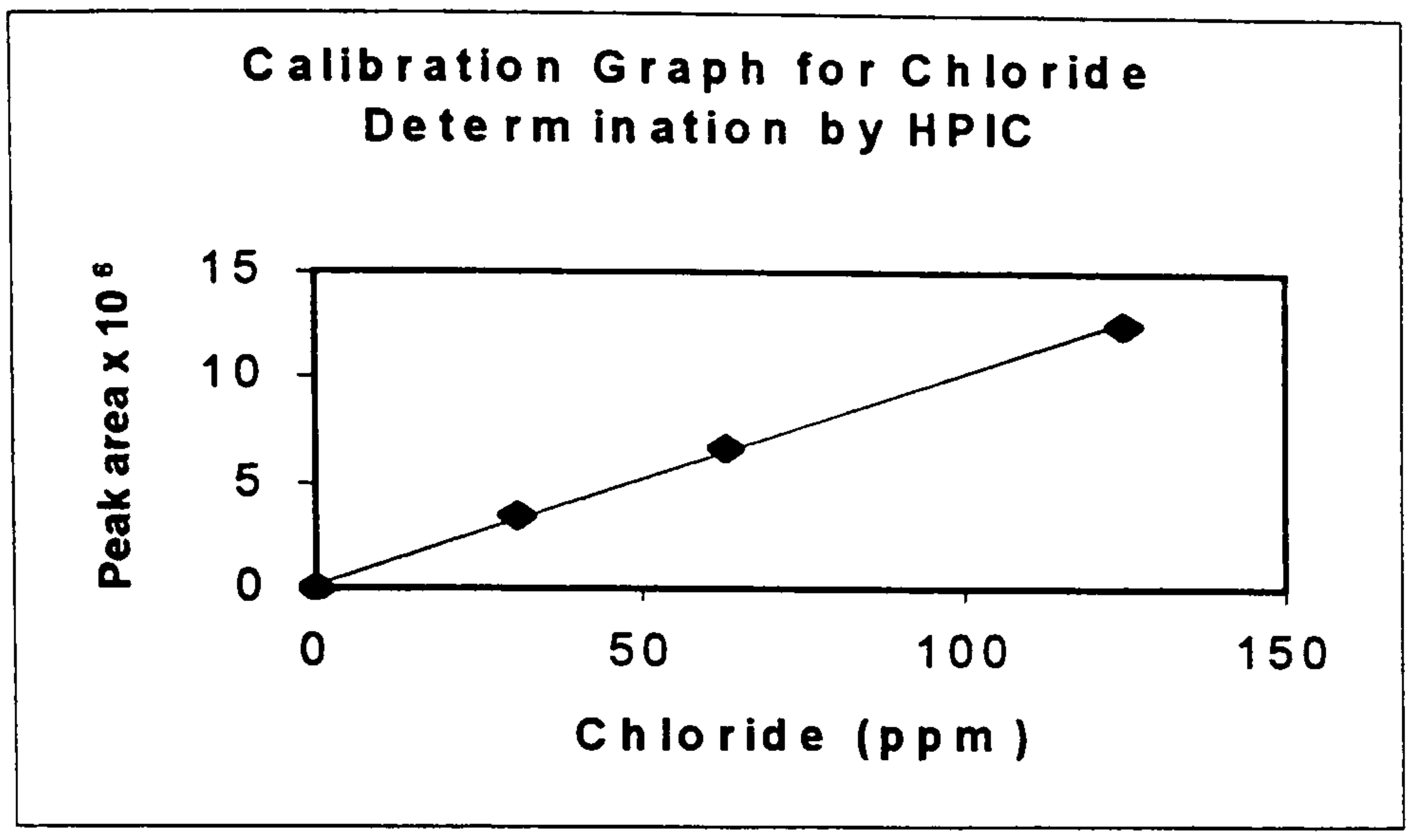
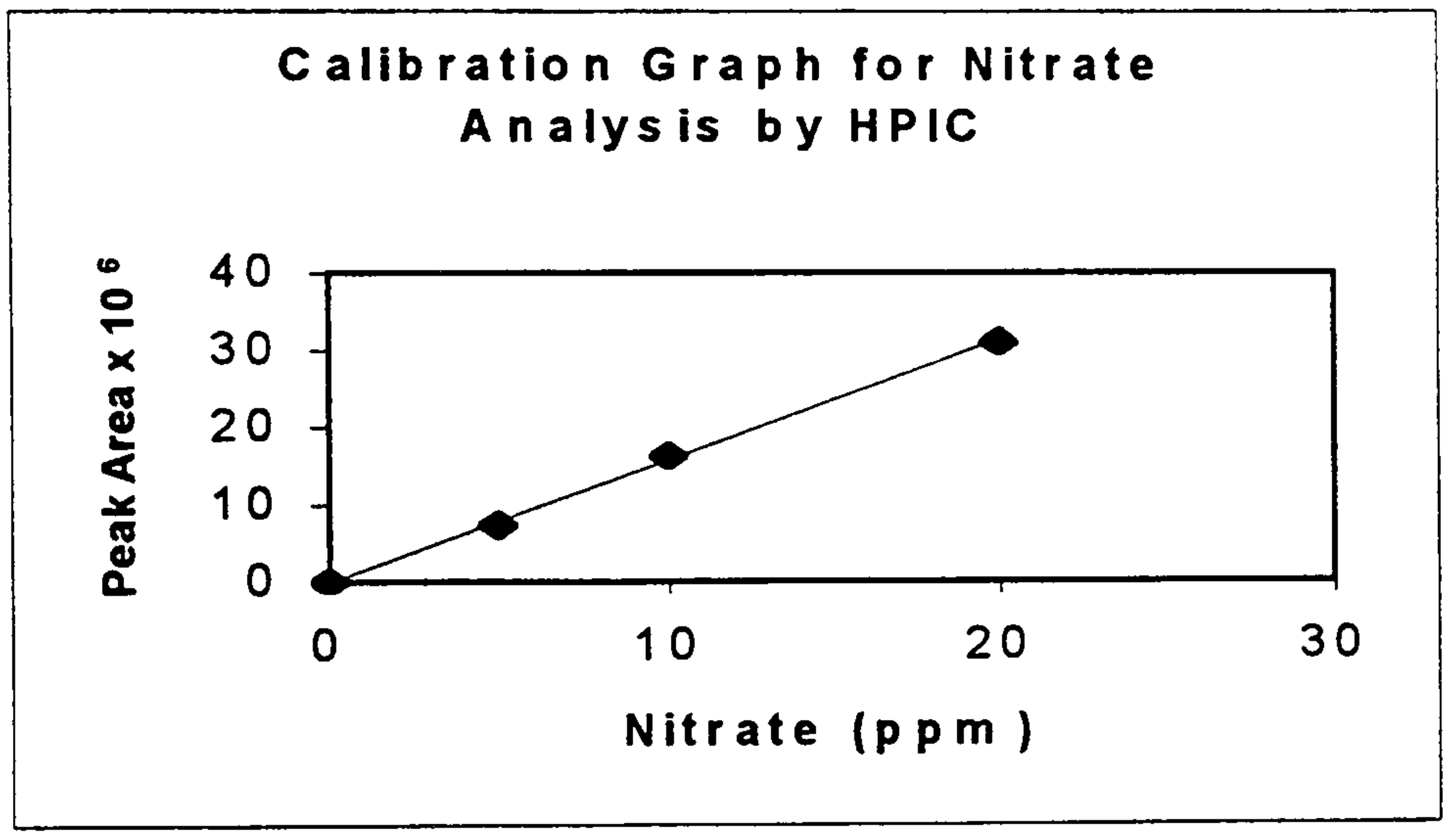


Figure 3.15 Calibration Graphs for Anions (Chloride, Nitrate and Sulphate)





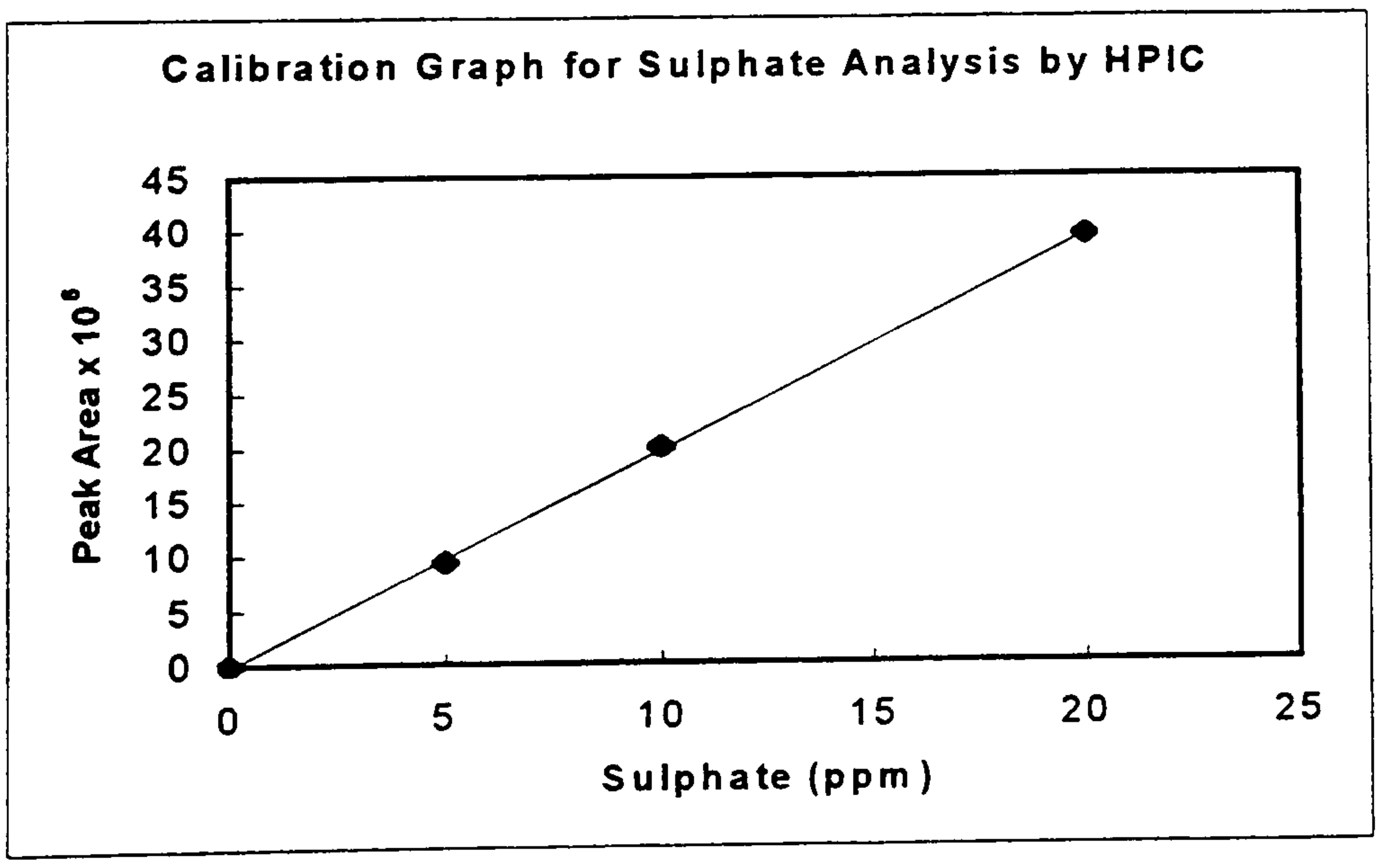
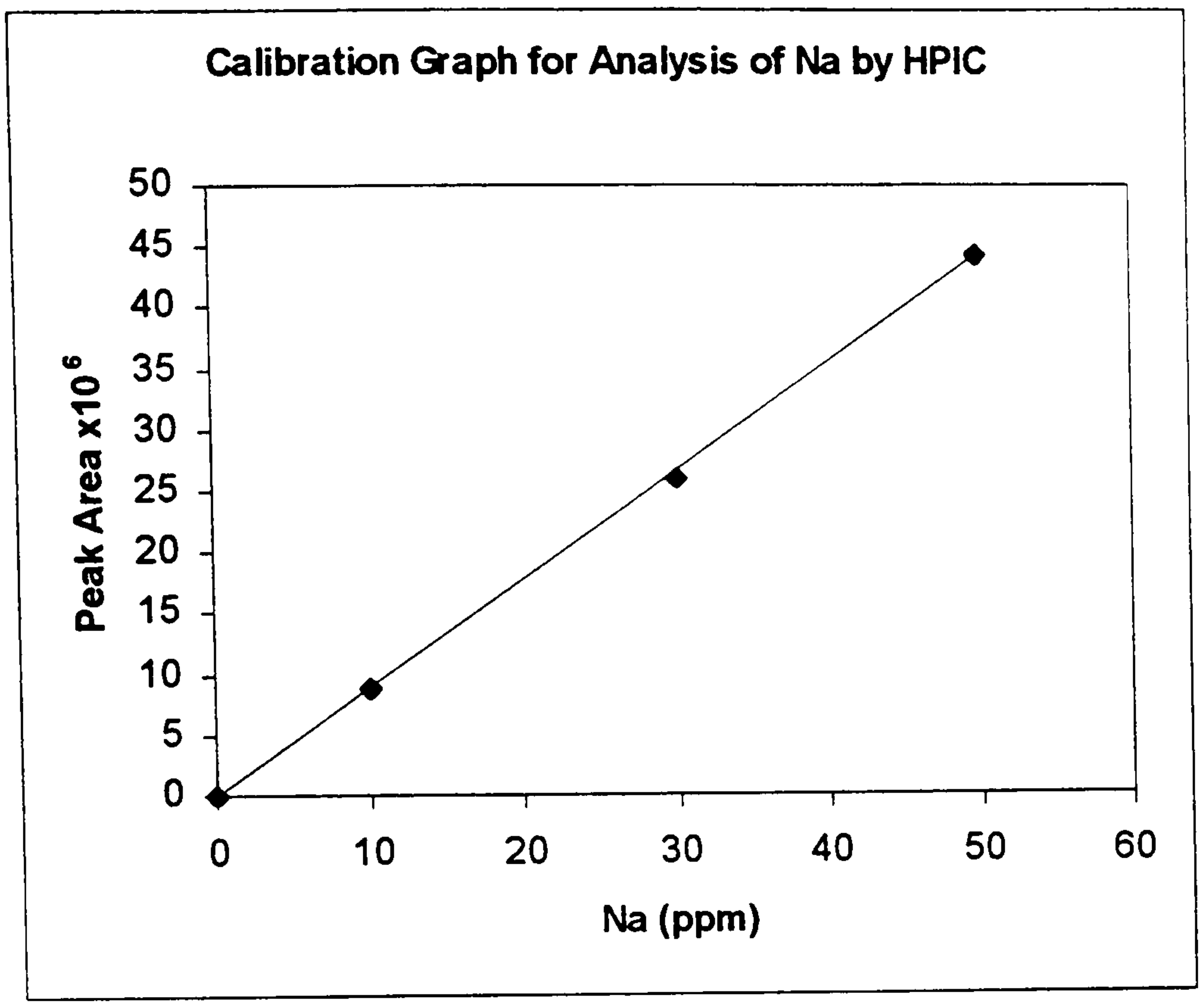


Figure 3.16 Calibration Graph for Sodium and Potassium



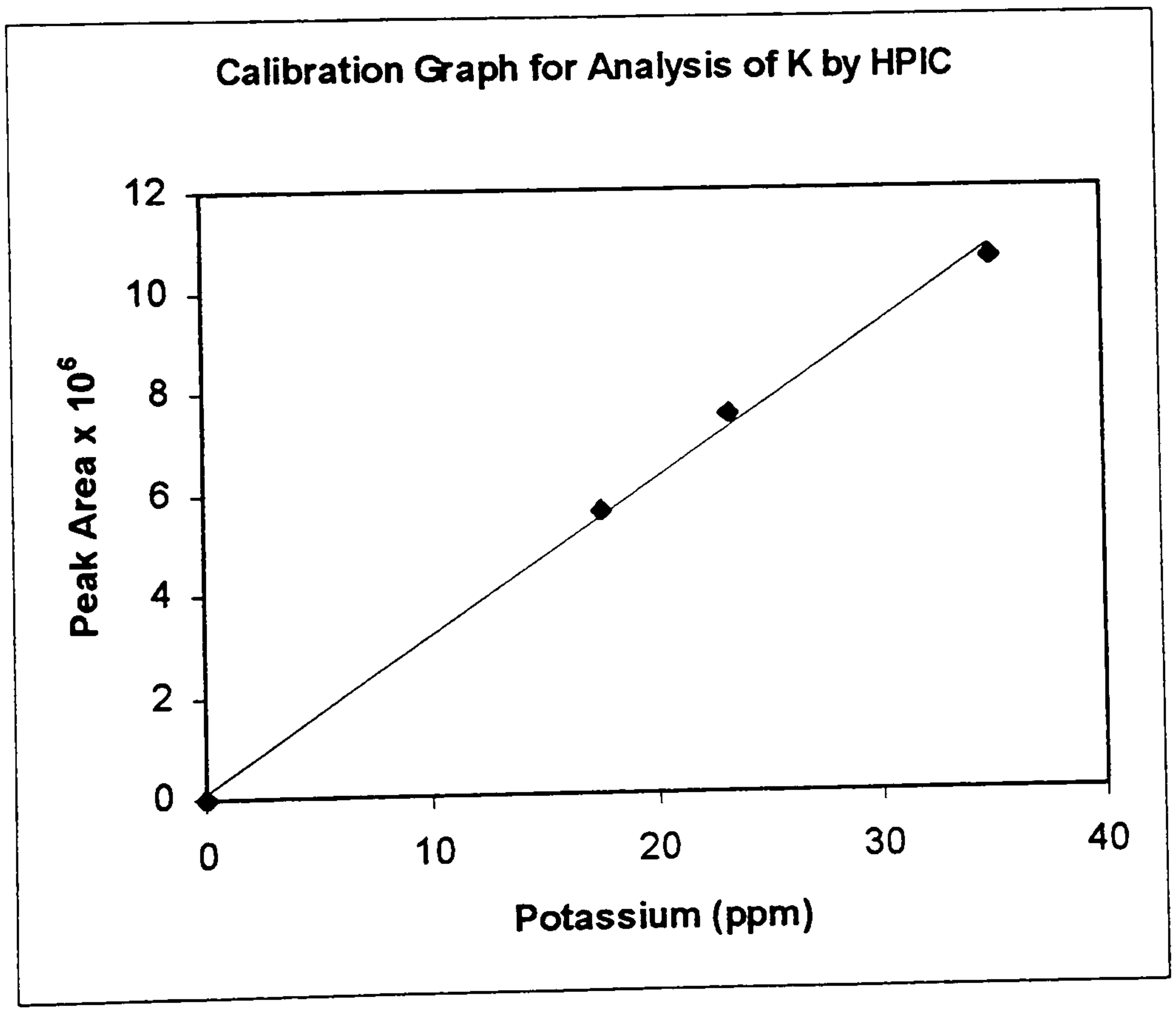
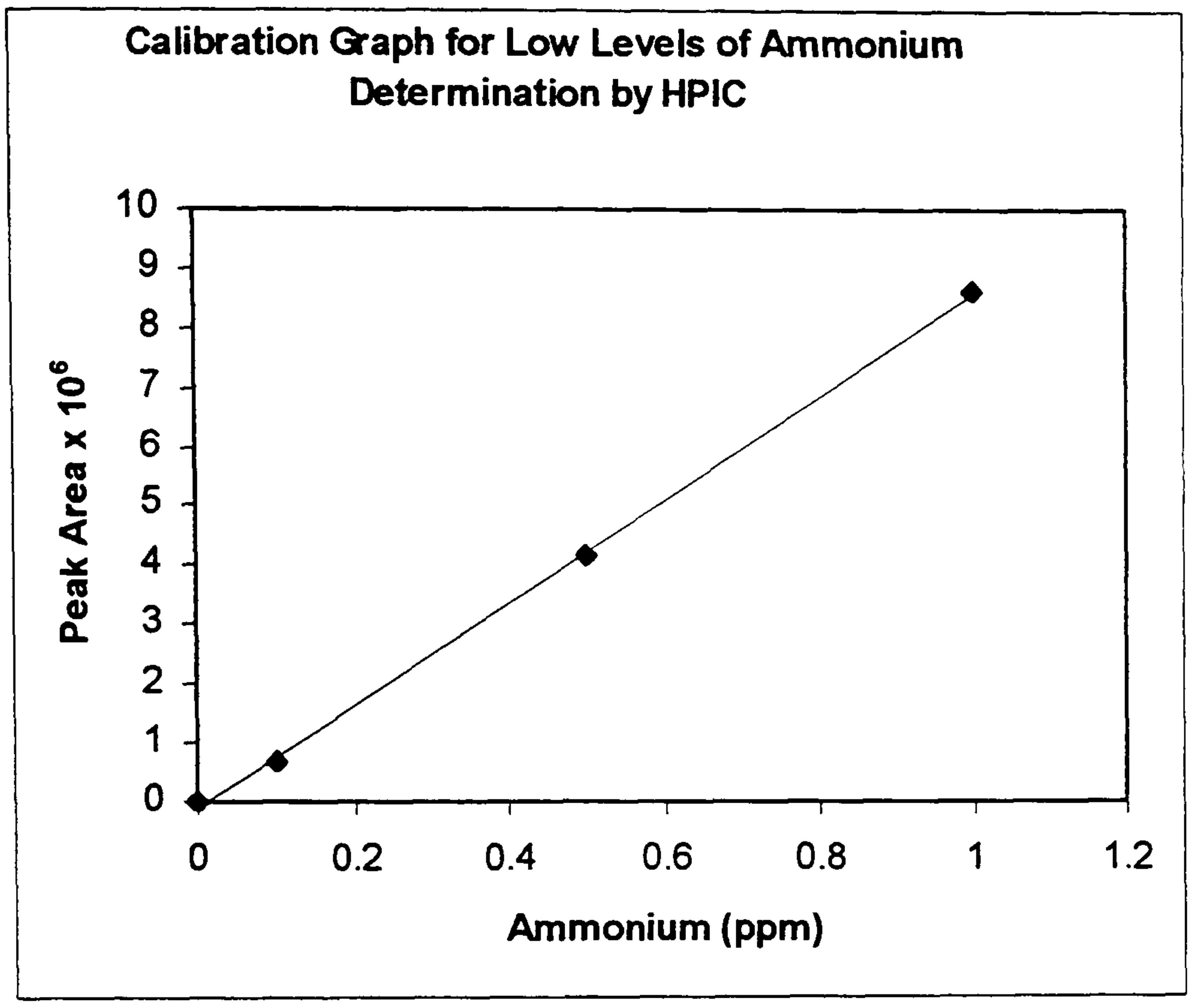
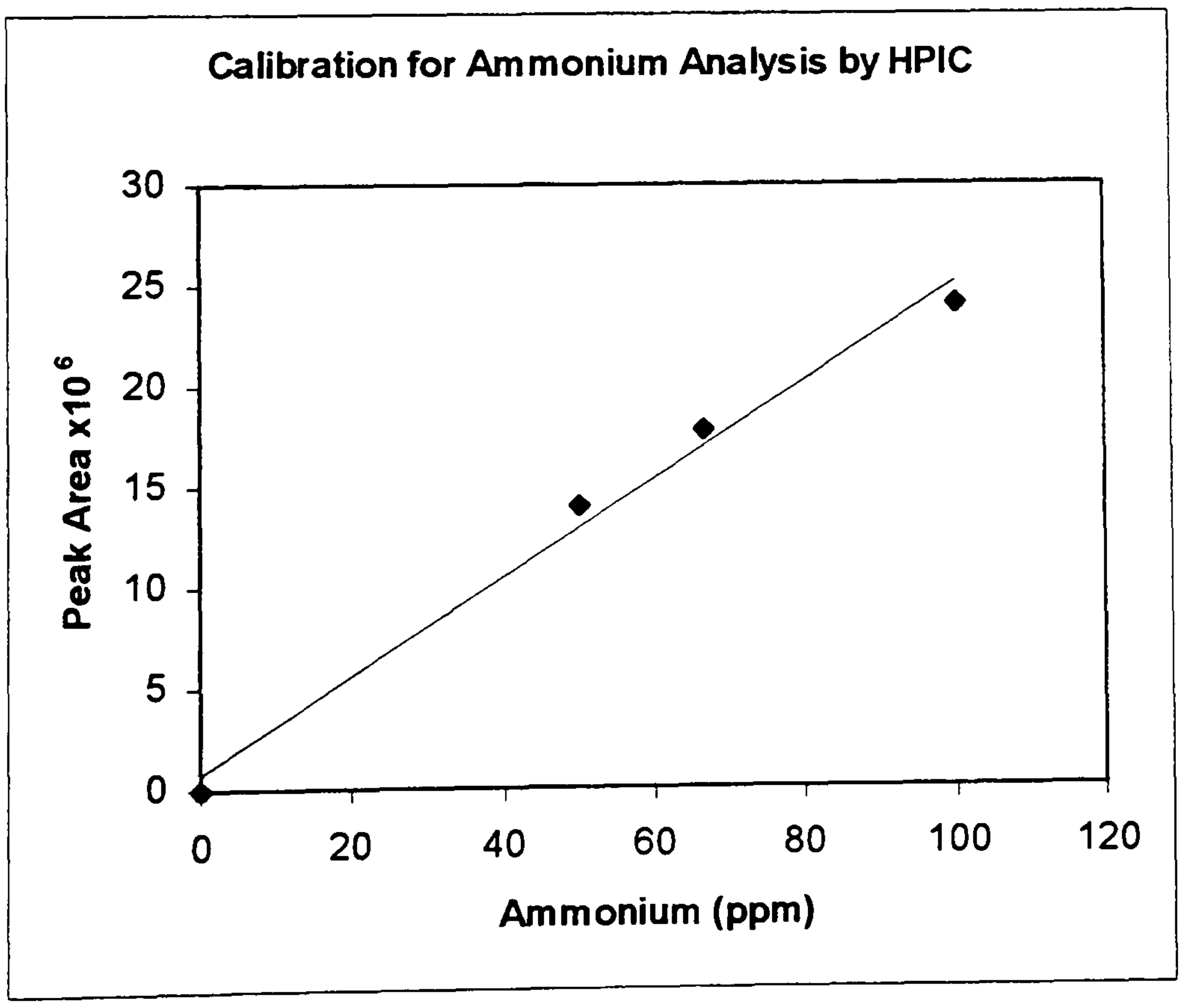


Figure 3.17 Calibration Graph for Low Levels and High Levels of Ammonium





3.3.2. Chemical Oxygen Demand (COD)

COD measurement is of great importance in water quality. COD level gives an indication of the amount of organic matter present in the system and the quantity of oxygen required for its stabilisation.

The COD is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant such as dichromate. COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies. The test for COD is non-specific in that it does not identify the oxidisable material present, similarly, it does not indicate the total organic carbon present since some organic compounds are not oxidised by dichromate method where as some inorganic compounds are oxidised. Nevertheless, COD is a useful indicator of pollution in water.

Principle of Method: The hexavalent chromium in a potassium chromate solution in sulphuric acid is reduced to the green trivalent chromium ion by the oxidisable substances contained in water in the presence of a suitable catalyst. The COD level is determined by measuring the colour intensity of CrIII at 585nm which is directly related to concentration.

Reaction

$Cr_2O_7^{2-} + 8H^+ \rightarrow 2Cr^+ + 4H_2O + 3O$

Procedure: Prefilled reagent test tubes containing acidified potassium dichromate and catalyst was used for COD determination. The digestion unit was pre set at 148°C. 2

ml of groundwater sample was pipetted into the pre-filled reagent bottles. The bottles were shaken well before being placed in the digestion unit for a period of 2 hours. After 2 hours the test tubes were removed from the digestion unit and cooled down to room temperature. It was ensured that the solutions were clear before analysis. Intensity of colour was read directly on photometer at 585nm. A blank correction was applied by using a 'reference blank' in the photometer. The average of a number of readings on replicate measurements gave the COD values.

Interferences

1. Turbidity effects may lead to higher COD values being recorded.
2. Sample should contain less than 1000 ppm chloride
3. Ammonium ion is not oxidised in this test unless chloride is present in sufficient amounts to cause interference.

3.3.3. Total Organic Carbon (TOC)

TOC is a measure of organic carbon and is converted to carbon dioxide by oxidation after inorganic carbon has been removed.

TOC in this work was determined by the measurement of carbon dioxide released by chemical oxidation of the organic carbon in the sample. In the results obtained by this method volatiles were not included because these were purged along with the inorganic carbon before oxidation of the residual organic carbon in the sample. This method is accepted by the EPA and by standard methods[5].

The equipment, Model 700 Total Organic Carbon Analyser, is controlled by a microprocessor and is used to regulate temperatures, central-timing sequences and perform calculations. Since the equipment has a linearised infrared analyser, a single point calibration is used for the determination of TOC. The sampling is by means of a sample loop.

The sample is first acidified with 5% phosphoric acid and purged with Nitrogen gas of Total Inorganic Carbon (TIC), then 10% potassium persulphate ($K_2S_2O_8$), a strong oxidiser is added. The oxidant quickly reacts with organic carbon in the sample at 100°C to form carbon dioxide. When the oxidation reaction is complete, the carbon dioxide is purged from the solution, concentrated by trapping, then desorbed and carried into a non-dispersive infra-red analyser which is calibrated to directly display the mass of carbon dioxide detected. The resulting carbon mass in the form of CO_2 is equivalent to the mass of dissolved organic carbon originally in the sample. The infra-red analyser used in the equipment is a single beam sensitised to carbon dioxide.

Method

1. The calibrated equipment is operated with deionsed and low carbon water for approximately 30 minutes until consistent readings are obtained.
2. A standard carbon solution (5 or 10 ppm carbon) was analysed to confirm reliability of results and then samples were analysed in duplicate.
3. At the end of all the sample runs, the standard was again run, followed by cleaning by operating with de-ionised and low carbon water.

3.3.4. Atomic Absorption Spectroscopy (AAS)

Theory of Atomic Spectrometry: Each line in line spectra for atomic transitions can be considered as 'monochromatic' radiation. Because of the wave character of light, each line in the spectrum is characterised in terms of its wavelength (λ);

$$\lambda = c/\nu$$

c is the velocity of light and ν is frequency in Hertz (Hz) or cycles s^{-1}. Spectra can also be presented as a function of the wave number $\bar{\nu}$

$$\bar{\nu} = 1/\lambda \text{ (units cm}^{-1}\text{)}$$

The recommended unit of wavelength is nanometer ($1\text{nm} = 10^{-9}\text{m}$). In Atomic Spectrometry the wavelength region from 190nm in the UV region to 850nm in the infrared plays an important part.

According to atomic theory only discrete and characteristic energy transitions are possible between discrete atomic energy levels. Absorption or emission of radiation is a result of a transition between two energy levels of the atom. Planck showed that there is the following relationship between the energy and frequency of a particular radiation:

$$E = h\nu = hc\bar{\nu}$$

Where E is the energy and h is the Planck's constant (6.6×10^{-34} Js). The frequency of radiation (ν) corresponds with the difference between two levels of energy E_m and E_n;

$$\nu_{mn} = (E_m - E_n)/h$$

The lowest energy level is called the ground state and is the state in which each atom will normally exist. Any other level of higher energy corresponds to an excited state. An atom can emit radiation only if it is in an excited state. Then energy will be released and the atom will return to a state of lower energy (either the ground state or an intermediate state). At room temperature most of the atoms are in the ground state.

The absorption spectrum can be obtained when the atoms are irradiated with radiation of the correct wavelength (corresponding to the energy difference between excited states and the ground state).

This principle is applied to determine the concentration of metal ions in the groundwater samples. A large number of metals can be analysed accurately by atomic spectrometry.

Atomic absorption spectroscopy (AAS) AAS is the measurement of absorption of radiation by free atoms. The total amount of absorption depends on the number of free atoms present and the degree to which the free atoms absorb the radiation. The basic components of an atomic absorption spectrometer are shown in figure 3.18 and 3.19.

1. The radiation source (a hollow cathode) emits a sharp line spectrum characteristic of the analyte element.
2. The emission beam from the radiation source is modulated.
3. The modulated signal passes through the atomic vapour where the atoms of the analyte absorb radiation of the line-like radiation source.
4. The desired spectral line is selected by the monochromator.
5. The isolated analyte line falls on to the detector, a photomultiplier where the light signal is converted into the electric signal.
6. The modulated signal is amplified by a selective amplifier.
7. The signal is finally recorded by a readout device[6].

Figure 3.11

Components of AAS

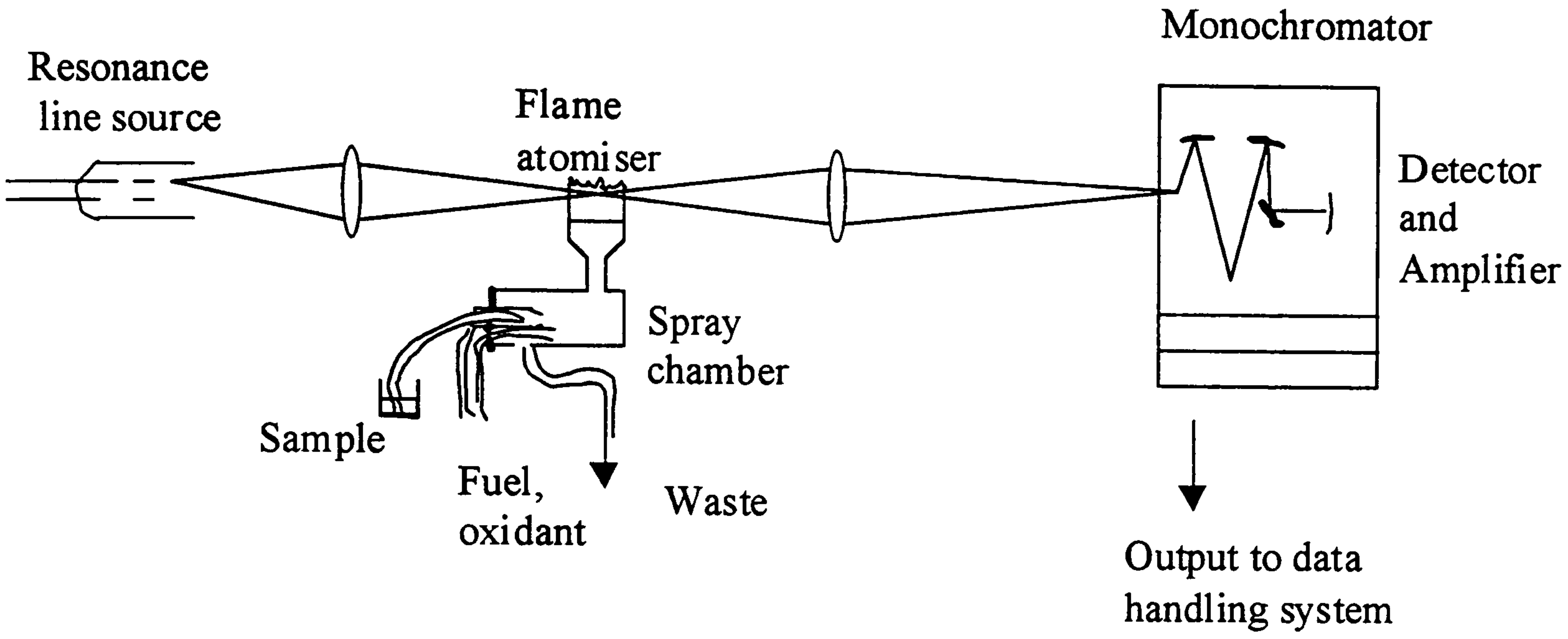
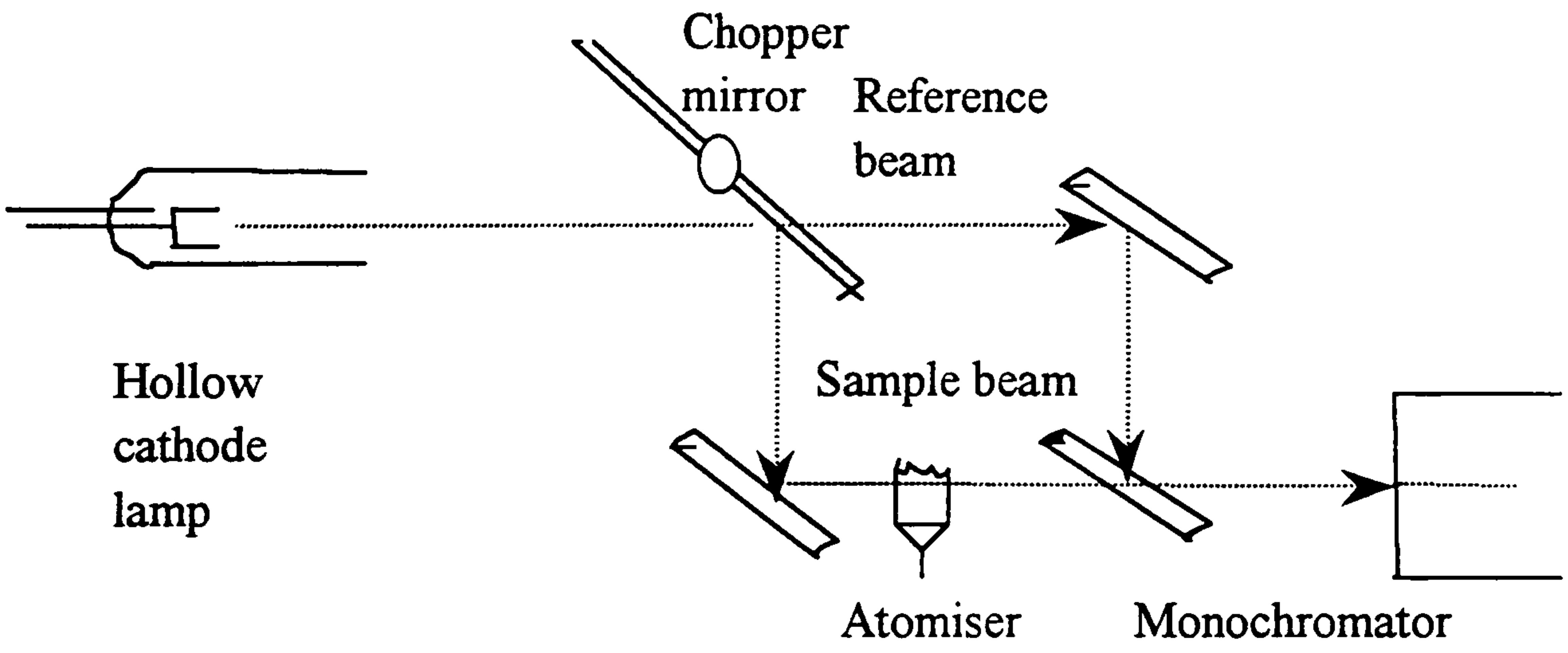


Figure 3.12

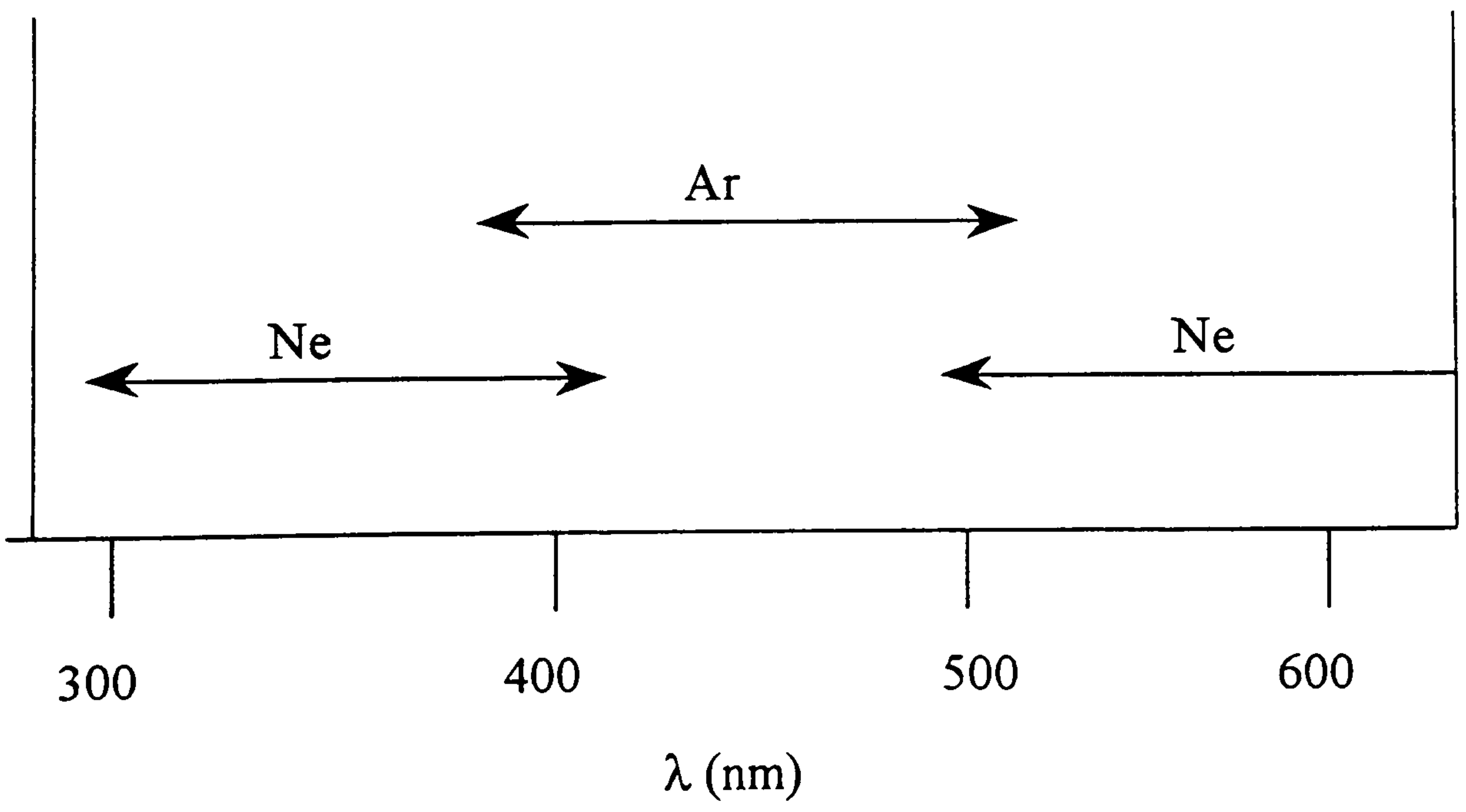
Light path in double-beam AAS instrument



The most important radiation sources in AAS are the hollow cathode lamps.

Hollow Cathode Lamps: consist of a glass cylinder and an anode and a cathode. The cylindrical cathode is either made of the analyte element or filled with it. The diameter of the cathode is 3 to 5 mm. The anode is in the form of a thick wire and usually made of tungsten, nickel, tantalum or zirconium. The glass tube is first evacuated and then filled with an inert gas (argon or neon). The pressure of the inert gas is about 0.5 to 1.3 kPa. The choice of the inert gas depends upon two factors. Firstly, emission lines of the filler gas must not coincide with the resonance lines of the analyte element. The filler gas used in the hollow cathode lamp is easy to detect by the colour of the emission beam of lamp. Argon gives a blue and neon an orange discharge. Secondly, the relative ionisation potentials of the inert gas and cathode metal must be taken into account. The ionisation potential of neon is much higher than that of argon. Neon is therefore used in lamps of metals with high ionisation potential.

Figure 3.20 Main emission regions of Argon and Neon.



The kinetic energy of ions hitting the surface of the cathode must be higher than the energy of the metal bonds. Normally the emission intensity of the lamp can be increased by raising the applied current. This increases the number of metal atoms excited by filler gas ions in the gas phase.

The lifetime of a hollow cathode lamp depends especially on the consumption of the filler gas and the purity of the cathode material. Filler gas will be adsorbed on metal deposited on the tube walls and the resulting decrease of the filler gas depends upon the applied current and voltage. The cathode must be made from purest metal available in order to get pure emission spectrum. Pure metals are manufactured by electrolytic deposition and during the process hydrogen may be absorbed into the metal. Hydrogen in the cathode material will diminish the emission intensity in the UV region. To get rid of these difficulties lamps are kept in vacuum at a high temperature during their manufacture.

The electrodes are shielded by ceramic materials and mica plates to avoid energy losses. The discharge is limited to occur inside the cathode openings. By using shielding materials, the intensity of the resonance lines increases with respect to the intensities of the lines of ions and filler gas and the broadening of the lines decreases.

Monochromator: The function of this is to isolate the measured line (resonance radiation) from other emission lines of the cathode material and lines of the filler gas. AA is a very selective method when an element specific radiation source is used. It is practically free of spectral interferences caused by overlapping atomic lines of other elements. The monochromator consists of two slits (an entrance slit and an exit slit) and a dispersing component (a prism or a grating). A prism or diffraction grating is used to disperse the radiation into individual wavelengths. The dispersion of a prism is high in the UV region, but decreases rapidly with increasing wavelengths. The prisms are quite useful in AAS as the majority of resonance lines lie in the UV region.

Detector: Photomultiplier tubes (PMT) are used in the detector in AAS. A photomultiplier contains a photo-emissive cathode and several anodes (dynodes) in a vacuum. The cathode is coated with an easily ionised material such as alloys of alkali metals with antimony, bismuth, and / or silver. The spectral sensitivity of a PMT depends primarily on the coating material of the photoemissive cathode. Practically, the lowest measurable wavelength is 193.7nm (As) and the highest one is 852.1 nm (Cs).

A photon falling on the surface of the cathode causes the emission of an electron, provided the photon is sufficiently energetic to ionise the material. The signal is amplified by the process of secondary emission. This results in high amplification of the original current.

Modulation of the Signal; - The optical signal falling upon the detector consists of the resonance line radiation and emission from the atomizer. The emission originated from the flame consists of molecular band emission and scatter from small particles. Only the resonance signal of the radiation source is required since other radiation falling on the detector diminishes the absorbance value that can be recorded. The output of the radiation source is therefore coded by modulation and an amplifier placed after the detector is tuned to the same modulated frequency. In mechanical modulation, the radiation beam is interrupted using a rotating sector (chopper) before the atomizer. The chopper splits the light beam into sample and reference beams at a fixed frequency. A beam of regularly varying intensity is produced which will generate an alternating signal at the detector. An AC amplifier is tuned to amplify signals only at the same frequency as the beam modulation. Thus all the noise at other frequencies is rejected and the signal-to-noise ratio improves.

Read Out Device :- hard copy of analytical results were made as a printer read out.

Calibration: AAS is a relative method, quantitative results were obtained by comparison of sample solutions with standard solutions. In the present work care was taken to ensure that the solutions were within the linear range of detection.

The Lambert-Beer Law: Lambert-Beer Law relates the absorbance to the concentration of metal in the test solution. This is derived in the following way. The intensity of a monochromatic radiation emitted from the radiation source is I_0, passing through the atomizer with a length b. The intensity of light will decrease to the value I. The reduction of the light intensity in the length db is -dI which is directly proportional to the light intensity I, to the length db, and to the number of absorbing atoms N. The number of atoms is in turn directly proportional to the concentration of the metal in test solution (c)

$$- dI = k I c db$$

where k is the relative coefficient. Lambert-Beer Law is obtained by integrating over the whole length of the atomizer:

$$-\int_{I_0}^{I} dI/I = kc\int_{0}^{b} db$$

$$\log I_0/I = k' \, c \, b$$

The Lambert-Beer Law is normally written as:

$$A = a \, b \, c$$

Where A is the absorbance [$\log I_0 / I$] and a is the absorption coefficient. In a series of measurements b is constant and determines, together with the absorption coefficient, the slope of the calibration graph, i.e. the sensitivity of the method.

Between absorbance and transmittance (T) is the following relationship

$$A = \log (I_0 / I)$$

$$= \log (1 / T)$$

The output of the detector is determined by the energy falling on it, and is directly proportional to the transmittance. The transmittance values are then converted to absorbance.

Optimization of operating Parameters: The fundamental function of atomizers in AAS is to produce atoms. The basic steps carried out continuously in flame atomisation are: 1. Nebulisation (conversion of sample into droplets leaving small particles), 2. Desolvation (removal of solvent); 3.Atomization (thermal or chemical breakdown of solid particles); 4. Measurement (interaction with radiation); 5. Condensation of reaction products (residue removed by exhaust flame gases).

A number of instrumental parameters will affect precision and sensitivity in these atomization techniques. Bandpass (slit width) and lamp current must be optimised. In AAS other operating parameters are burner height, burner alignment, fuel flow, flame type and impact bead adjustment.

Flame Atomization: The atomization technique in AAS is spraying of the sample solution into a flame.

Flames: In the flame atomization technique the sample is sprayed into the flame in the form of an aerosol generated by means of a nebulizer. Flames employed in AAS may be divided into two groups: the combustion flames and diffusion flames. In fuel-oxidant mixtures, the temperatures of the flame varies generally from 2000 to 3000K. Air and dinitrogen oxide (N_2O) are the most widely used oxidants and acetylene, propane, and hydrogen are the most common fuel gases. The most widely used flame is the air-acetylene flame. For about 30 elements it offers a suitable environment and a temperature suitable for the quantitative determination. The flame is transparent over a wide spectral range and shows only noticeable radiation absorption below 230nm.

The metal ions in groundwater samples analysed by AAS are calcium, nickel, copper, cadmium and lead. All the results of groundwater analysis are in Chapter IV and these are discussed in Chapter VI.

3.4 References

1. Dionex, Ion-Chromatography. Training Manual,
2. Robson P., FGS, LB Hounslow, Private Communication.
3. Spence I., "Groundwater - Pollution, Prevention and Remediation", Seminar. (Groundwater Hydraulics, University of Abertay, Dundee), 1997.
4. Meyer V. R., "Practical High Performance Liquid Chromatography", Wiley, Chichester, 1994.
5. Operating Procedures and Service Manual, Model 700, Total Organic Carbon Analyser.
6. Lajunen L. H. J., "Spectrochemical Analysis by Atomic Absorption and Emission", Royal Society of Chemistry, Cambridge, 1992.

CHAPTER IV - LIST OF CONTENTS

RESULTS

CHAPTER IV

RESULTS

4.1 Classification of Boreholes and Method of Numbering Samples

Gas and groundwater results from four categories of sites in the London Borough of Hounslow are reported in this chapter. The boreholes (BH) tested are either in virgin ground around landfill sites or within the perimeter of old and relatively recently filled landfill sites. A total of 47 boreholes in 4 categories of sites, in relation to landfill sites in Hounslow have been sampled for gas and groundwater for this study.

Section.4.7 contains results to show the effect of purging on tested parameters in Class I, III and IV of borehole. Validity of Results is reported in Section 4.8. The borehole logs for each category are in Appendix 1, and the classification of boreholes is as following

Table 4.1 Classification of Boreholes

Class	Type of Fill or Type of Site Location of BH
Class I	Boreholes in the perimeter of landfill sites more than 50 years old or in virgin ground.
Class II	Boreholes within landfill sites with waste filled more than 50 years ago.
Class III	Boreholes in the perimeter of actively gassing landfill sites and with waste filled less than 50 years ago.
Class IV	Boreholes within actively gassing landfill sites with waste filled less than 50 years ago.

4.1.1 Method Adopted for Numbering Samples Analysed for this Study

The sites investigated for this study are labelled alphabetically 'A' to 'J'. In each of these sites the boreholes are numbered 1,2, etc. These sites and borehole location are as shown in Figure 4.1. Therefore, each sample is designated by its site reference that is 'A' to 'J' along with the borehole number 1,2, etc.

4.2 Results of Class I Boreholes.

These boreholes are in the perimeter of landfill sites filled more than 50 years ago or in virgin ground.

The analytical data for class I sites are in Table 4.2 (methane and carbon dioxide); Table 4.3 (Field Tests: pH indices, electrical conductivity (EC), oxidation-reduction potential (ORP), ammonium nitrogen (NH_4-N), chemical oxygen demand (COD) and total organic carbon (TOC); Table 4.4 (chloride, nitrate, sulphate, sodium, potassium, calcium, nickel, copper, cadmium, and lead).

4.2.1 Landfill/Soil Gas Results

Highest Steady Landfill/Soil Gas Readings ever Recorded and Highest Readings in the Last 3 Years are presented in Table 4.2.

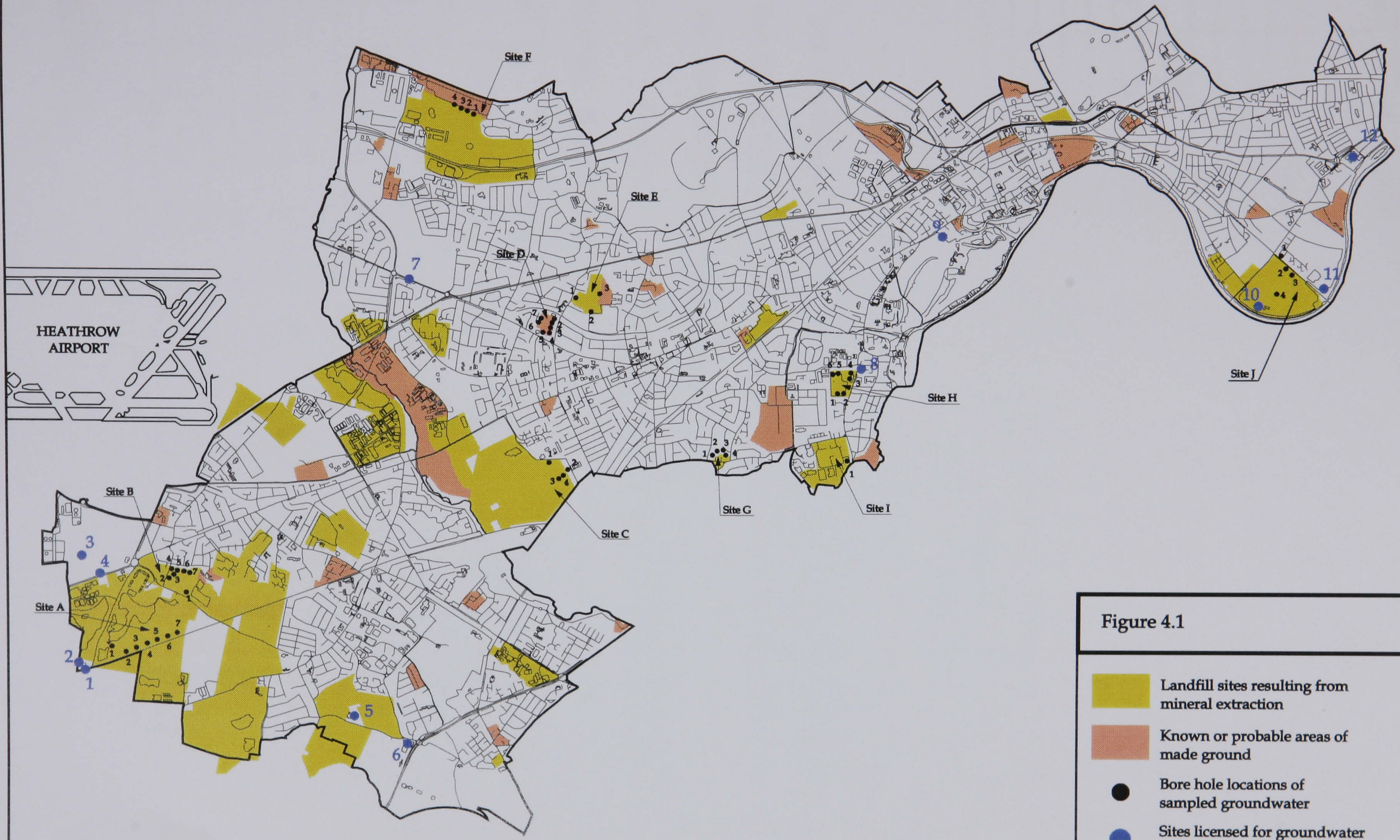


Figure 4.1

🟨 Landfill sites resulting from mineral extraction

🟧 Known or probable areas of made ground

● Bore hole locations of sampled groundwater

🔵 Sites licensed for groundwater abstraction by Environment Agency

The information presented on this map is based on records held by or provided to the L B Hounslow. No responsibility can be accepted for the accuracy of this information.

Table 4.2 Landfill/Soil Gas Results from Class I Boreholes

All gas readings in % volume

LF Site No.	Age of The Site (years)	BH No.	Lab. Sample No.	CH_4 Highest Recorded	CH_4 Highest in last 3 years	CO_2 Highest Recorded	CO_2 Highest In last 3 years
27	-	B94033	C2	0	0	3.3	1.8
40	68	B93039	G4	0	0	2.6	1.3
O8	-	B93019	D7	0	0	2.7	2.5
O8	-	B93028	D6	0	0	2.5	1.7
40	68	B93042	G1	0	0	2.2	0.3
40	68	B93044	G2	0	0	2.5	0.9
40	68	B93045	G3	0	0	1.8	0.2
O8	-	B93022	D5	0	0	3.4	1.5
O8	-	B93023	D4	0	0	2	0.9
O8	-	B93024	D3	0	0	0.9	0.8
O8	-	B93025	D2	0	0	2.1	2.1
O8	-	B93026	D1	0	0	0.8	0.8

4.2.2 pH, Conductivity, ORP, NH_4 - N, COD, and TOC in Class I boreholes

Field Test Results (pH, Conductivity, and ORP) and Lab. Test Results (NH_4 - N, COD, and TOC) are presented in Table 4.3.

Table 4.3 Field Test Results (pH, Conductivity, and ORP) and Lab. Test Results (NH_4 - N, COD, and TOC)

Sample No.	Field Tests			Lab Tests (ppm)		
	pH	EC (µs/cm)	ORP (mv)	NH_4-N	COD	TOC
C2	6.7	377	0	0.6	36	11
G4	6.8	385	15	0.05	<10	10
D7	7.4	682	109	0.2	<10	5
D6	6.6	418	100	0.2	<10	5
G1	7.4	461	106	<0.05	59	5
G2	-	526	60	<0.05	67	6
G3	6.2	449	116	<0.05	88	5
D5	7	587	-	0.6	72	8
D4	7.2	552	-	0.05	52	3
D3	7.6	405	-	0.12	63	3
D2	7.4	605	-	0.2	65	3
D1	6.7	731	-	-	65	4

4.2.3 Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} in Class I Boreholes

Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+ Determined by Ion Chromatography; Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} by Atomic Absorption Spectroscopy are presented in Table 4.4.

Table 4.4 Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}.

All the results are in unit 'ppm'

Sample No.	Cl	NO_3	SO_4	Na	K	Ca	Ni	Cu	Cd	Pb
C2	49	2	72	14	4	62		0.01	0.001	
G4	21	44	80	14	5	87	<0.1	<0.1	<0.03	<0.2
D7	49	52	117	26	4	113	<0.01	<0.1	<0.003	<0.02
D6	37	12	82	17	2	73	<0.01	<0.1	<0.003	<0.02
G1	25	75	85	14	4	64	0.12	<0.1	<0.03	<0.2
G2	26	69	93	23	3	79	0.14	<0.1	<0.03	<0.2
G3	20	78	90	20	5	54	0.18	<0.1	<0.03	<0.2
D5	40	48	149	27	2	81	<0.1	<0.1	<0.03	<0.2
D4	40	52	130	25	2	78	<0.1	<0.1	<0.03	<0.2
D3	28	48	87	11	-	56	0.13	<0.1	<0.03	<0.2
D2	52	42	100	35	6	88	<0.1	<0.1	<0.03	<0.2
D1	55	42	126	35	7	104	0.13	<0.1	<0.03	<0.2

4.3 Results of Class II Boreholes.

Class II samples are from boreholes in landfill sites filled more than 50 years old.

The analytical data for Class II sites are in Table 4.5 (methane and carbon dioxide); Table 4.6 (pH indices, electrical conductivity, oxidation-reduction potential, ammonium nitrogen, chemical oxygen demand and total organic carbon); Table 4.7 (chloride, nitrate, sulphate, sodium, potassium, calcium, nickel, copper, cadmium and lead).

4.3.1 Landfill/Soil Gas Results in Class II Boreholes

Highest steady landfill gas readings ever recorded and highest in the last 3 years are presented in Table 4.5.

Table 4.5 Landfill/Soil Gas Results in Class II Boreholes

All gas readings are in % volume unit

LF Site No.	Age of The Site (years)	BH No.	Lab. Sample No.	CH_4 Highest Recorded	CH_4 Highest in last 3 years	CO_2 Highest Recorded	CO_2 Highest In last 3 years
37	67	B92001	H5	0	0	2.1	1.5
37	67	B92002	H6	0	0	5.7	2.6
37	67	B92004	H1	0	0	5.7	3
37	67	B92005	H2	0	0	5.1	3.7
37	67	B92007	H3	0	0	8.9	0.1
37	67	B92008	H4	0.1	0	5.8	3
32	51	B93001	E2	1	0	11.0	3.2
32	51	B93013	E1	0	0	7.5	0
32	51	B93018	E3	0	0	7.6	4
41	51	B95005	J1	0	0	2.2	2.2
41	51	B00038	J2	0	0	7.6	3.3
41	51	B00037	J3	2.6	1.2	5.6	5.4
41	51	B00042	J4	0	0	7.5	7.5

4.3.2 pH, Conductivity, ORP, NH_4 - N, COD, and TOC in Class II Boreholes

Field Test Results (pH, Conductivity, ORP) and Lab. Test Results (NH_4 - N, COD, and TOC Determined by Ion Chromatography) are presented in Table 4.6.

Table 4.6 pH, Conductivity, ORP, NH_4 - N, COD, and TOC

Sample No.	Field Tests			Lab Tests (ppm)		
	pH	EC (µs/cm)	ORP (mv)	NH_4-N	COD	TOC
H5	7.3	1223	116	0.5	19	9
H6	6.9	806	100	0.04	<10	5
H1	6.8	1500	9	1.6	46	23
H2	6.9	1573	-60	2.7	28	18
H3	6.9	1803	-166	9	67	32
H4	6.8	1720	-110	1.2	28	17
E2	6.6	1867	-147	9.5	50	25
E1	7	1312	-86	2.8	65	30
E3	7.3	1934	-31	1.7	14	10
J1	6.8	1704	130	<0.04	<10	38
J2	5.9	1634	-34	2	47	21
J3	7.4	947	-187	8.2	75	30
J4	6.7	1594	-95	3.4	41	20

4.3.3 Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} Results in Class II Boreholes.

Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+ Determined by Ion Chromatography; Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} by Atomic Absorption Spectroscopy are presented in Table 4.7.

Table 4.7 Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} Results.

Results in ppm

Sample No.	**Cl**	**NO_3**	**SO_4**	**Na**	**K**	**Ca**	**Ni**	**Cu**	**Cd**	**Pb**
H5	143	14	440	103	23	243	<0.1	<0.1	NR	NR
H6	35	15	240	26	8	193	<0.1	<0.1	<0.03	<0.2
H1	25	1	730	33	53	415	<0.1	<0.1	<0.03	<0.2
H2	28	<0.5	825	37	36	434	0.1	<0.1	<0.03	<0.2
H3	58	<0.5	575	42	33	431	<0.1	<0.1	<0.03	<0.2
H4	33	9	650	-	-	350	<0.1	<0.1	<0.03	<0.2
E2	28	9	1050	43	19	606	<0.1	<0.1	<0.03	<0.2
E1	39	<0.5	610	34	2	312	0.1	<0.1	<0.03	<0.2
E3	15	<0.5	1600	31	25	476	0.1	<0.1	<0.03	<0.2
J1	86	5	600	63	36	260	<0.1	<0.1	<0.03	<0.2
J2	32	0.5	595	44	37	409	<0.1	<0.1	<0.03	<0.2
J3	40	0.5	<5	79	29	133	<0.1	<0.1	<0.03	<0.2
J4	46	<0.5	960	68	43	365	<0.1	<0.1	<0.03	<0.2

4.4 Results from Class III Boreholes

Class III boreholes are in the perimeter of actively gassing landfill sites filled less than 50 years ago. The analytical data for Class III sites are presented in Table 4.8 (methane, and carbon dioxide); Table 4.9 (pH indices, conductivity, oxidation-reduction potential, ammonium nitrogen, chemical oxygen demand and total organic carbon) and Table 4.10 (chloride, nitrate, sulphate, sodium, potassium, calcium, nickel, copper, cadmium and lead).

4.4.1 Landfill/Soil Gas Readings in Class III Boreholes

Landfill gas readings with highest ever recorded and highest in the last 3 years gas results are presented in Table 4.8.

Table 4.8 Landfill/Soil Gas Readings

All the gas Result are in % volume unit

LF Site No.	Age of The Site (years)	BH No.	Sample No.	CH_4 Highest Recorded	CH_4 Highest in Last 3 years	CO_2 Highest Recorded	CO_2 Highest in Last 3 Years
3	32	B00001	B4	6	0.1	8.4	4.8
3	32	B93178	B2	0	0	2.1	0.4
3	32	B00003	B5	30	2.5	25.2	15.5
3	32	B00004	B6	17.5	3.9	20.7	13.8
3	32	B00005	B7	30	6.2	33	18.2
3	32	B93184	B1	0	0	4.6	2.7
27	25	B94039	C4	12.5	0	12.5	12.3
27	25	B93225	C1	0.9	0	4.2	4.2
33	31	B00024	F4	0	0	12	8.9
33	31	B00025	F3	14	6.1	1.5	0.8
33	31	B00026	F2	24	2.7	23	10.6
33	31	B00027	F1	0	0	4	2.8
38	31	B00051	I1	24.2	8.5	5.3	4.4

4.4.2 pH, Conductivity, ORP, NH_4-N, COD, and TOC Results from Class III Boreholes

Field Test Results (pH, Conductivity, ORP) and Lab. Test Results (NH_4-N Determined by Ion Chromatography; COD, and TOC) Results are presented in Table 4.9.

Table 4.9 pH, Conductivity, ORP, NH_4-N, COD, and TOC

Sample No.	Field Tests			Lab. Tests (ppm)		
	PH	EC (µs/cm)	ORP (mv)	NH_4-N	COD	TOC
B4	6.6	1725	13	92	174	94
B2	6.8	1581	60	58	325	110
B5	6.6	1448	128	57	73	24
B6	6.7	808	183	6	59	12
B7	6.6	1263	144	21	79	20
B1	6.4	986	159	<1.0	35	43
C4	6.4	1518	33	10	122	93
C1	-	-	-	2	119	72
F4	-	-	-	8	47	51
F3	-	-	-	16	232	51
F2	6.7	1355	73	14	205	33
F1	6.9	1498	43	12	120	77
I1	7.6	810	-	5.8	73	40

4.4.3 Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}in Class III Samples

Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+ Determined by Ion Chromatography; Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} by Atomic Absorption Spectroscopy are presented in Table 4.10.

Table 4.10 Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} Results

All the Results are in ppm units

Sample No.	Cl	NO_3	SO_4	Na	K	Ca	Ni	Cu	Cd	Pb
B4	80	-	54	-	-	158	-	<0.1	<0.03	<0.2
B2	97	27	180	-	-	-	-	<0.1	<0.03	<0.2
B5	56	ND	77	68	44	200	<0.1	<0.1	<0.03	<0.2
B6	22	-	90	24	17	130	<0.1	<0.1	<0.03	<0.2
B7	50	ND	61	53	24	210	<0.1	<0.1	<0.03	<0.2
B1	57	117	200	-	-	92	-	<0.1	<0.03	<0.2
C4	25	<0.3	1970	28	22	351	-	0.03	0.006	-
C1	25	<0.3	870	29	20	460	-	0.03	0.007	-
F4	11	26	580	-	-	376	-	-	-	-
F3	58	26	119	-	-	146	-	-	-	-
F2	55	20	96	-	-	291	-	-	-	-
F1	40	16	248	-	-	227	-	-	-	-
I1	60	11	262	27	20	-	-	-	-	-

4.5 Results from Class IV Boreholes

Class IV boreholes are in actively gassing landfill sites with less than 50 years old waste.

The analytical data for Class IV sites are in Table 4.11 (methane and carbon dioxide); Table 4.12 (pH indices, conductivity, oxidation-reduction potential, ammonium nitrogen, chemical oxygen demand, total organic carbon); Table 4.13 (chloride, nitrate, sulphate, sodium, potassium, calcium, nickel, copper, cadmium, and lead).

4.5.1 Landfill Gas Readings from Class IV Boreholes

Landfill gas results with highest recorded gas results and highest results in the last 3 years are presented in Table 4.11.

Table 4.11 Landfill Gas Readings from Class IV Boreholes

All Gas Readings in '% volume' units

LF Site No.	Age of The Site (years)	BH No.	Sample No.	CH_4 Highest Recorded Results	CH_4 Highest in Last 3 Years	CO_2 Highest Recorded Results	CO_2 Highest in Last 3 Years
3	32	B00018	B3	30.9	25.5	30.5	18
BL	17	J15	A2	48	48	5	5
BL	17	J14	A3	47	47	13	13
BL	10	M-302	A1	63.4	57.2	32.2	26.2
BL	17	A7	A7	30.4	30.4	17	17
BL	17	A6	A6	46.2	31.1	12.5	12.5
BL	17	A5	A5	19	19	15	15
BL	17	J13	A4	69.1	69.1	6.9	6.9
27	25	B93226	C3	26.1	17.4	15.5	15.5

4.5.2 Field Test Results (pH, Conductivity, ORP) and Lab. Test Results (NH_4-N, COD, and TOC) in Class IV Boreholes.

Field Test Results (pH, Conductivity, ORP) and Lab. Test Results (NH_4-N, Determined by Ion Chromatography; COD, and TOC) are presented in Table 4.12.

Table 4.12 **Field Test Results (pH, Conductivity, ORP) and Lab. Test Results (NH_4-N, COD, and TOC)**

Sample No.	Field Tests			Lab. Tests (ppm)		
	PH	EC (μs/cm)	ORP (mv)	NH_4-N	COD	TOC
B3	6.8	1957	_159	43	197	32
A2	6.5	1560	_157	30	119	27
A3	5.8	1960	_103	113	135	47
A1	5.5	2930	_125	27	229	80
A7	6.4	1823	_50	26	287	67
A6	6.4	2200	_155	118	191	56
A5	6.7	1962	_166	75	177	32
A4	8	1789	_134	45	201	54
C3	6.7	1912	_140	12	119	119

4.5.3 Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} in Class IV Boreholes

Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+ were determined by Ion Chromatography and Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} by Atomic Absorption Spectroscopy. The Results are presented in Table 4.13.

Table 4.13 **Results of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}**

All Results in ppm

Sample No.	Cl	NO_3	SO_4	Na	K	Ca	Ni	Cu	Cd	Pb
B3	175	ND	25	157	44	280	<0.1	<0.1	<0.03	<0.2
A2	37	ND	585	76	37	310	<0.1	<0.1	<0.03	<0.2
A3	225	26	10	136	77	250	<0.1	<0.1	<0.03	<0.2
A1	360	ND	276	280	51	320	<0.1	<0.1	<0.03	<0.2
A7	101	<0.5	<5	105	38	302	0.28	<0.1	<0.03	<0.2
A6	103	<0.5	<5	130	70	260	<0.1	<0.1	<0.03	<0.2
A5	147	0.5	55	113	56	267	0.41	<0.1	<0.03	<0.2
A4	133	0.5	130	136	45	254	0.25	<0.1	0.2	<0.2
C3	38	<0.3	950	121	40	454	-	0.02	0.008	-

4.6 Variation in Concentrations of Various Groundwater Parameters Tested in the Four Categories of Sites / Boreholes.

From the results in sections 4.2 to 4.5, variations in analyte concentrations in Class I to Class IV site boreholes are presented in Table 4.14.

Table 4.14 Variation in Concentrations of Analyte Concentrations in Four Class of Sites

Tested Parameter	Units	Class I	Class II	Class III	Class IV
Methane	**% vol.**	0	0 - 2.6	0 -24	19 - 69
Methane in Last 3 Yrs.	,,	0	0 - 1.2	0 - 8	17 - 69
CO_2	,,	0.8 - 3.4	2 - 11	2 - 25	5 - 32
CO_2 in Last 3 Yrs	,,	0.2 - 2	0 - 7.5	0.4 - 15	5 - 26
pH		6.2 - 7.6	5.9 - 7.3	6.4 - 7.6	5.5 - 8
EC	**µs/cm**	377-682	806-1934	808-1725	1560-2930
ORP	**mv**	_15 - +116	_187 - +130	_183- +159	_50- _166
NH_4-N	**ppm**	<0.05 - 0.6	<0.04 - 9.5	<1 - 92	12 - 118
COD	,,	<10 - 88	<10 - 75	35 - 232	119 -287
TOC	,,	3 - 11	5 - 38	12 - 110	27 - 80
Cl	,,	25 - 49	15 - 143	11 - 97	37 - 360
NO_3	,,	2 - 78	<0.5 - 15	<0.3 - 27	<0.5 - 26
SO_4	,,	72 - 149	<5 - 1600	54 - 1970	<5 - 950
Na	,,	11 - 35	26 - 103	24 - 68	76 - 280
K	,,	2 - 7	2 - 53	17 - 44	37 - 70
Ca	,,	54 - 104	133 - 606	92 - 460	250 - 454
Ni	,,	<0.01-0.18	<0.1 - 0.1	<0.1	<0.1 - 0.41
Cu	,,	<0.1	<0.1	<0.1	<0.1
Cd	,,	<0,03	<0.03	<0.03	<0.03-).2
Pb	,,	<0.2	<0.2	<0.2	<0.2

4.7 Effect of Time Sampling on the Tested Analytes in Groundwater Samples from Class I, Class III and Class IV boreholes .

4.7.1 Effect of Time Sampling on Class I Boreholes

The change in concentrations of the analytes in borehole D7 as the borehole is purged is reported in Table 4.15.

Table 4.15 Effect of Time Sampling on Sample D7

BH No.	Sample Type	COD (ppm)	TOC (ppm)	NH4-N (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
D7	Pre-purge	<10	7	0.2	26	5	42	69	137
D7	Purged	<10	5	0.2	26	4	49	52	117
D6	Pre-purge	<10	5	<0.04	17	2	35	36	82
D6	Purged	<10	5	0.2	17	2	37	12	82

4.7.2 Effect of Time Sampling on Class III Boreholes.

The change in concentrations of the analytes in borehole B7 as the borehole is purged is reported in Table 4.16.

Table 4.16 Effect of Time Sampling on sample B7

BH No.	Sample Type	COD	TOC	NH4-N	Na	K	Cl	SO4
B7	Pre-purge	81	28	24	58	25	52	64
B7	Purged	79	20	21	53	24	50	61

4.7.3 Class IV Borehole B3

The change in concentrations of the analytes in borehole B3 as the borehole is purged is reported in Table 4.17.

Table 4.17 Effect of Time Sampling on Sample B3

Vol. Purged (L)	COD (ppm)	TOC (ppm)	NH4-N (ppm)	Na (ppm)	K (ppm)	Cl (ppm)	SO4 (ppm)
5	231	34	40	85	52	110	315
35	195	32	45	145	47	173	95
40	194	31	36	157	38	217	61
45	189	32	40	157	43	199	56
50	197	31	43	157	44	175	25

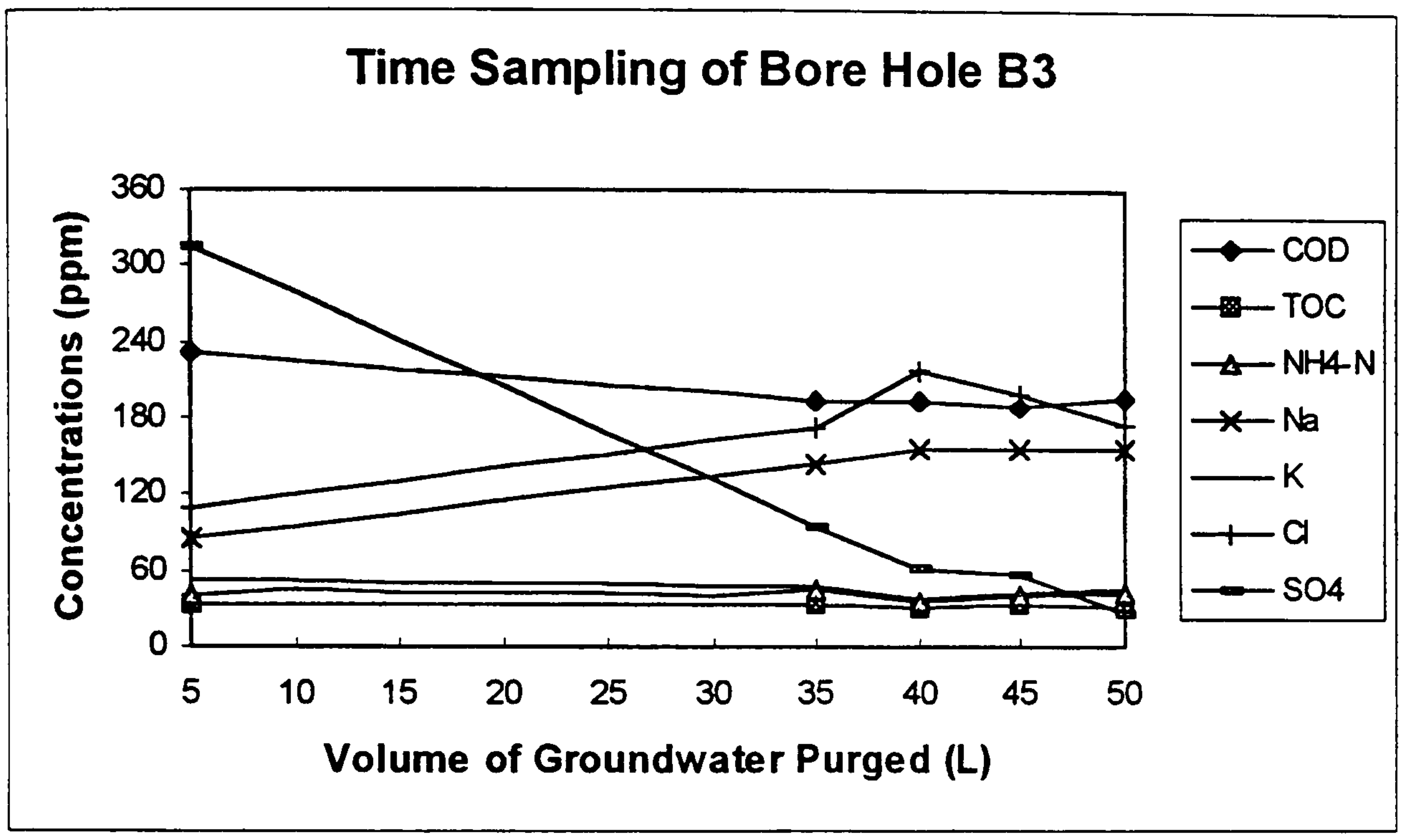
4.7.4. Effect of Time Sampling on Analyte Concentrations

Class I Site Boreholes: The results for these tests are reported in Table 4.15. The results do not show any significant change in the concentration of the analytes in pre-purge and purged samples.

Class III Site Boreholes: The results for these tests are reported in Table 4.16. In this case also, the results in pre-purge and purged samples do not show any significant change.

Class IV Site Borehole: Class IV boreholes are highly gassing boreholes in relatively active landfill sites. Landfill environment in this case can be expected to be different from Class I and III sites. Such sites are highly anaerobic and have a typical landfill environment. In this case there was change in concentrations of some of the analytes. As reported in Table 4.17, Na^+ ion levels increased from 85 to 157 ppm as the groundwater was purged; Cl^- levels increased from 110 to 175. The reason for an increase in Na^+ and Cl^- ions is not clear at this stage. The most remarkable change was noticed in SO_4^{2-} concentrations. Sulphate levels dropped from 315 ppm in the pre-purge sample to 25 ppm in the final purged sample. This drop in concentration is due to the reason that borehole environment is relatively more open to air, hence is more aerobic than its surrounding areas. Sulphides are more readily oxidised to sulphate than other reduced forms such as methane, hence, a sharp drop in the levels of sulphate as the groundwater is purged. It was surprising to see that there was no significant change in the levels of COD, TOC, K^+ and NH_4-N on purging the boreholes.

Figure 4.1 Effect of Time Sampling on Borehole B3 in Class IV Site



4.8 Validity of Results

Standard Deviation (SD) for each analyte determined for this study is presented in Table 4.18

Table 4.18

Analyte	**COD**	**TOC**	**NH_4-N**	**Na^+**	**K^+**
S D	0.9	0.5	0.06	0.1	0.2
Analyte	**Cl^-**	**NO_3**	**SO_4**	**EC**	**Acetate**
S D	0.1	0.05	0.04	0.3	1.2

The results of Class I to Class IV boreholes are used for assessing groundwater quality in Chapter V under the heading 'Data Handling' and the results are discussed in Chapter VII under the heading 'Discussion of Borehole Quality Results'.

CHAPTER V - LIST OF CONTENTS

DATA HANDLING AND GROUNDWATER QUALITY ASSESSMENT

Page Numbers

CHAPTER V

DATA HANDLING AND GROUNDWATER QUALITY ASSESSMENT

5.0 Introduction and Background

This chapter considers results from Chapter IV to devise a means to characterise each borehole sample according to its level of contamination and finally makes use of the best method to test some blind samples collected and analysed by an external organisation.

From Table 4.14, it is clear that the analytes follow as expected a general trend in the level of concentrations of each analyte in the four classes of sites. Generally, there is an increase in pollutant concentrations from a Class I site to Class IV site. The two analytes which do not follow such a trend are sulphate and nitrate ions. Hence, these are not considered in this assessment. The ten parameters considered for borehole assessment are CH_4, CO_2, electrical conductivity (EC), ammonium nitrogen (NH_4-N), COD, TOC, Cl^-, Na^+, K^+, and Ca^{2+}. With regard to heavy metal results (Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}), these are not present in any significant concentrations, and are below the detection level in the groundwater samples, hence, these were not considered in this assessment.

Three methods are used to characterise borehole samples. In the first method all of the ten parameters are considered separately to characterise single borehole contamination. In the second method only six of the factors are considered separately as a means of assessing single borehole contamination. In the third method, a combination of the same six parameters is weighted and a set of nine formula based on them are considered as a means of characterising borehole contamination. Each of these methods is discussed in the following sections.

The results of the ten parameters obtained from borehole samples as described in Chapter IV are used in the work described in this chapter and are listed in Table 5.1.

5.1 Site Assessment Method by Considering 10 Parameters

5.1.1 Assignment of Ratings to the Ten Considered Parameters.

The data in Table 5.1 for each of the considered parameters were divided into 15 ratings and based on ranges of contaminant concentration a rating of 1 to 15 was assigned to each result. For example, in the case of electrical conductivity (EC), from table 5.1 the EC values range from 377µs/cm to 2930µs/cm, the difference between the lowest and highest value is

2930-377 = 2553µs; 2553 is divided into 15 ratings,

2553/15 = 170.2;

each rating value increases by 170.

Starting with the lowest value 377, rating 1 ranges from 377 to 377+170 = 547.

Rating 2 is worked out by adding 548 to 170 = 718; and the range of rating 2 is 548 to 718 etc.. The values for 15 ratings are worked out and are listed in the Table. 5.2.

In this way ranges of values for each of the ratings for the ten parameters is calculated and listed in Table 5.3.

Table 5.1 Results used for Groundwater Quality Assessment

Sample	CH_4	CO_2	EC	NH_4-N	COD	TOC	Cl	Na	K	Ca
C2	0	3.3	377	0.6	36	11	49	14	4	62
G4	0	2.6	385	0.05	<10	10	21	14	5	87
D7	0	2.7	682	0.2	<10	5	49	26	4	113
D6	0	2.5	418	0.2	<10	5	37	17	2	73
G1	0	2.2	461	<0.05	59	5	25	14	4	64
G2	0	2.5	526	<0.05	67	6	26	23	3	79
G3	0	1.8	449	<0.05	88	5	20	20	5	54
D5	0	3.4	587	0.6	72	8	40	27	2	81
D4	0	2	552	0.05	52	3	40	25	2	78
D3	0	0.9	405	0.12	63	3	28	11	2*	56
D2	0	2.1	605	0.2	65	3	52	35	6	88
D1	0	0.8	731	0.2*	65	4	55	35	7	104
H5	0	2.1	1223	0.5	19	9	143	103	23	243
H6	0	5.7	806	0.04	<10	5	35	26	8	193
H1	0	5.7	1500	1.6	46	23	25	33	53	415
H2	0	5.1	1573	2.7	28	18	28	37	36	434
H3	0	8.9	1803	9	67	32	58	42	33	431
E1	0	7.5	1312	2.8	65	30	39	34	2	312
E3	0	7.6	1934	1.7	14	10	15	31	25	476
J1	0	2.2	1704	<0.04	<10	38	86	63	36	260
J2	0	7.6	1634	2	47	21	32	44	37	409
J4	0	7.5	1594	3.4	41	20	46	68	43	365
B2	0	2.1	1581	58	325	110	97	48*	25*	162*
B1	0	4.6	986	<1.0	35	43	57	48*	25*	92
F4	0	12	1355*	8	47	51	11	59*	25*	376
F1	0	4	1498	12	120	77	40	59*	25*	227
H4	0.1	5.8	1720	1.2	28	17	33	59*	30*	350
E2	1	11	1867	9.5	50	25	28	43	19	606
B4	0.1	4.8	1725	92	174	94	80	48*	25*	158
B5	2.5	15.5	1448	57	73	24	56	68	44	200
B6	3.9	13.8	808	6	59	12	22	24	17	130
J3	2.6	5.6	947	8.2	75	30	40	79	29	133
C1	0.9	4.2	1573	2	119	72	25	29	20	460
B7	6.2	18.2	1263	21	79	20	50	53	24	210
C4	12.5	12.5	1518	10	122	93	25	28	22	351
F3	14	1.5	1355*	16	232	51	58	59*	25*	146
F2	24	23	1355	14	205	33	55	59*	25*	291
I1	24.2	5.3	810	5.8	73	40	60	27	20	240*
A5	19	15	1962	75	177	32	147	113	56	267
C3	26.1	15.5	1912	12	119	119	38	121	40	454
A7	30.4	17	1823	26	287	67	101	105	38	302
B3	30.9	30.5	1957	43	197	32	175	157	44	280
A3	47	13	1960	113	135	47	225	136	77	250
A6	46.2	12.5	2200	118	191	56	103	130	70	260
A2	48	5	1560	30	119	27	37	76	37	310
A1	63.4	32.2	2930	27	229	80	360	280	51	320
A4	69.1	6.9	1789	45	201	54	133	136	45	254

'*' These figures are averages from nearby borehole analysis.

Table 5.2

Range of Values in each of the 15 Ratings For Analyte EC

Rating	**Range of Value in Analyte EC (μs)**
1	377 - 547
2	548 - 718
3	719 - 889
4	890 - 1060
5	1061 - 1231
6	1232 - 1402
7	1403 - 1573
8	1574 - 1744
9	1745 - 1915
10	1916 - 2086
11	2087 - 2257
12	2258 - 2428
13	2429 - 2599
14	2600 - 2770
15	2771 - 2941

In the case of methane a slightly different approach was taken. Since the presence of methane in concentrations above 1% is considered to pose a significant risk, methane concentrations 0 to <1 were rated as 1, for concentrations 1% volume and greater than 1%v, the same method for assigning a rating was followed as for EC.

5.1.1.1Range of Values in Ratings 1 to 15 for the Ten Considered Parameters

Range of values for 1 to 15 ratings for the ten parameters are in Table 5.3

Table 5.3

Rating	CH_4	CO_2	EC	NH_4	COD	TOC	Cl	Na	K	Ca
1	0-<1	0-3	0-547	0-7	0-20	0-10	0-33	0-28	0-6	0-90
2	1-5	4-5	548-718	8-15	21-41	11-18	34-56	29-46	7-11	91-127
3	6-10	6-7	719-889	16-23	42-62	19-26	57-79	47-64	12-16	128-164
4	11-15	8-9	890-1060	24-31	63-83	27-34	80-102	65-82	17-21	165-201
5	16-20	10-11	1061-1231	32-39	84-104	35-42	103-125	83-100	22-26	202-238
6	21-25	12-13	1232-1402	40-47	105-125	43-50	126-148	101-118	27-31	239-275
7	26-30	14-15	1403-1573	48-55	126-146	51-58	149-171	119-136	32-36	276-312
8	31-35	16-17	1574-1744	56-63	147-167	59-66	172-194	137-154	37-41	313-349
9	36-40	18-19	1745-1915	64-71	168-188	67-74	195-217	155-172	42-46	350-386
10	41-45	20-21	1916-2086	72-79	189-209	75-82	218-240	173-190	47-51	387-423
11	46-50	22-23	2087-2257	80-87	210-230	83-90	241-263	191-208	52-56	424-460
12	51-55	24-25	2258-2428	88-95	231-251	91-98	264-286	209-226	57-61	461-497
13	56-60	26-27	2429-2599	96-103	252-272	99-106	287-309	227-244	62-66	498-534
14	61-65	28-29	2600-2770	104-112	273-293	107-114	310-332	245-262	67-71	535-571
15	66-70	30-32	2771-2941	113+	294+	115+	333+	263+	72+	572+

5.1.1.2 Assignment of Ratings to Each Considered Analyte

The ratings assigned to each of the considered parameters, viz CH_4, CO_2, electrical conductivity (EC), ammonium nitrogen (NH_4-N), COD, TOC, Cl^-, Na^+, K^+, and Ca^{2+} are in Tables 5.4 to 5.13.

Tables 5.4 to 5.13

Ratings Assigned to each Result of CH_4, CO_2, EC, NH_4-N, COD, TOC, Cl^-, Na^+, K^+ and Ca^{2+}.

Table 5.4

Rating	Sample No.	CH4 (%v)
1	C2	0
1	G4	0
1	D7	0
1	D6	0
1	G1	0
1	G2	0
1	G3	0
1	D5	0
1	D4	0
1	D3	0
1	D2	0
1	D1	0
1	H5	0
1	H6	0
1	H1	0
1	H2	0
1	H3	0
1	E1	0
1	E3	0
1	J1	0
1	J2	0
1	J4	0
1	B2	0
1	B1	0
1	F4	0
1	F1	0
1	H4	0.1
1	B4	0.1
2	C1	0.9
2	E2	1
2	B5	2.5
2	J3	2.6
2	B6	3.9
3	B7	6.2
4	C4	12.5
4	F3	14
5	A5	19
6	F2	24
6	I1	24.2
7	C3	26.1
7	A7	30.4
8	B3	30.9
11	A6	46.2
11	A3	47
11	A2	48
14	A1	63.4
15	A4	69.1

Table 5.5

Rating	Sample No.	CO2 (%v)
1	D1	0.8
1	D3	0.9
1	F3	1.5
1	G3	1.8
1	D4	2
1	D2	2.1
1	H5	2.1
1	B2	2.1
1	G1	2.2
1	J1	2.2
1	D6	2.5
1	G2	2.5
1	G4	2.6
1	D7	2.7
1	C2	3.3
1	D5	3.4
2	F1	4
2	C1	4.2
2	B1	4.6
2	B4	4.8
2	A2	5
2	H2	5.1
2	I1	5.3
3	J3	5.6
3	H6	5.7
3	H1	5.7
3	H4	5.8
3	A4	6.9
3	E1	7.5
3	J4	7.5
4	E3	7.6
4	J2	7.6
4	H3	8.9
5	E2	11
6	F4	12
6	C4	12.5
6	A6	12.5
6	A3	13
7	B6	13.8
7	A5	15
7	B5	15.5
7	C3	15.5
8	A7	17
9	B7	18.2
11	F2	23
15	B3	30.5
15	A1	32.2

Table 5.6

Rating	Sample No.	EC (μs)
1	C2	377
1	G4	385
1	D3	405
1	D6	418
1	G3	449
1	G1	461
1	G2	526
2	D4	552
2	D5	587
2	D2	605
2	D7	682
3	D1	731
3	H6	806
3	B6	808
3	I1	810
4	J3	947
4	B1	986
5	H5	1223
6	B7	1263
6	E1	1312
6	F2	1355
6	F4	1355
6	F3	1355
7	B5	1448
7	F1	1498
7	H1	1500
7	C4	1518
7	A2	1560
7	H2	1573
7	C1	1573
8	B2	1581
8	J4	1594
8	J2	1634
8	J1	1704
8	H4	1720
8	B4	1725
9	A4	1789
9	H3	1803
9	A7	1823
9	E2	1867
9	C3	1912
10	E3	1934
10	B3	1957
10	A3	1960
10	A5	1962
11	A6	2200
15	A1	2930

Table 5.7

Rating	Sample No.	NH4-N (ppm)
1	J1	0
1	G1	0
1	G2	0
1	G3	0
1	B1	0
1	H6	0.04
1	G4	0.05
1	D4	0.05
1	D3	0.12
1	D1	0.2
1	D7	0.2
1	D6	0.2
1	D2	0.2
1	H5	0.5
1	C2	0.6
1	D5	0.6
1	H4	1.2
1	H1	1.6
1	E3	1.7
1	J2	2
1	C1	2
1	H2	2.7
1	E1	2.8
1	J4	3.4
1	I1	5.8
1	B6	6
2	F4	8
2	J3	8.2
2	H3	9
2	E2	9.5
2	C4	10
2	F1	12
2	C3	12
2	F2	14
3	F3	16
3	B7	21
4	A7	26
4	A1	27
4	A2	30
6	B3	43
6	A4	45
8	B5	57
8	B2	58
10	A5	75
12	B4	92
15	A3	113
15	A6	118

Table 5.8

Rating	Sample No.	COD (ppm)
1	G4	0
1	D7	0
1	D6	0
1	H6	0
1	J1	0
1	E3	14
1	H5	19
2	H2	28
2	H4	28
2	B1	35
2	C2	36
2	J4	41
3	H1	46
3	J2	47
3	F4	47
3	E2	50
3	D4	52
3	G1	59
3	B6	59
4	D3	63
4	D2	65
4	D1	65
4	E1	65
4	G2	67
4	H3	67
4	D5	72
4	B5	73
4	I1	73
4	J3	75
4	B7	79
5	G3	88
6	C1	119
6	C3	119
6	A2	119
6	F1	120
6	C4	122
7	A3	135
9	B4	174
9	A5	177
10	A6	191
10	B3	197
10	A4	201
10	F2	205
11	A1	229
12	F3	232
14	A7	287
15	B2	325

Table 5.9

Rating	Sample No.	TOC (ppm)
1	D4	3
1	D3	3
1	D2	3
1	D1	4
1	D7	5
1	D6	5
1	G1	5
1	G3	5
1	H6	5
1	G2	6
1	D5	8
1	H5	9
1	G4	10
1	E3	10
2	C2	11
2	B6	12
2	H4	17
2	H2	18
3	J4	20
3	B7	20
3	J2	21
3	H1	23
3	B5	24
3	E2	25
4	A2	27
4	E1	30
4	J3	30
4	H3	32
4	A5	32
4	B3	32
4	F2	33
5	J1	38
5	I1	40
6	B1	43
6	A3	47
7	F4	51
7	F3	51
7	A4	54
7	A6	56
9	A7	67
9	C1	72
10	F1	77
10	A1	80
12	C4	93
12	B4	94
14	B2	110
15	C3	119

Table 5.10

Rating	Sample No.	Cl (ppm)
1	F4	11
1	E3	15
1	G3	20
1	G4	21
1	B6	22
1	G1	25
1	H1	25
1	C1	25
1	C4	25
1	G2	26
1	D3	28
1	H2	28
1	E2	28
1	J2	32
1	H4	33
2	H6	35
2	D6	37
2	A2	37
2	C3	38
2	E1	39
2	D5	40
2	D4	40
2	F1	40
2	J3	40
2	J4	46
2	C2	49
2	D7	49
2	B7	50
2	D2	52
2	D1	55
2	F2	55
2	B5	56
3	B1	57
3	H3	58
3	F3	58
3	I1	60
4	B4	80
4	J1	86
4	B2	97
4	A7	101
5	A6	103
6	A4	133
6	H5	143
6	A5	147
8	B3	175
10	A3	225
15	A1	360

Table 5.11

Rating	Sample No.	Na (ppm)
1	D3	11
1	C2	14
1	G4	14
1	G1	14
1	D6	17
1	G3	20
1	G2	23
1	B6	24
1	D4	25
1	D7	26
1	H6	26
1	D5	27
1	I1	27
1	C4	28
2	C1	29
2	E3	31
2	H1	33
2	E1	34
2	D2	35
2	D1	35
2	H2	37
2	H3	42
2	E2	43
2	J2	44
3	B2	48
3	B1	48
3	H4	48
3	B4	48
3	B7	53
3	F4	59
3	F1	59
3	F3	59
3	F2	59
3	J1	63
4	J4	68
4	B5	68
4	A2	76
4	J3	79
6	H5	103
6	A7	105
6	A5	113
7	C3	121
7	A6	130
7	A3	136
7	A4	136
9	B3	157
15	A1	280

Table 5.12

Rating	Sample No.	K (ppm)
1	D6	2
1	D5	2
1	D4	2
1	E1	2
1	G2	3
1	C2	4
1	D7	4
1	G1	4
1	G4	5
1	G3	5
1	D2	6
2	D1	7
2	H6	8
4	B6	17
4	E2	19
4	C1	20
4	I1	20
5	C4	22
5	H5	23
5	B7	24
5	E3	25
6	J3	29
7	H3	33
7	H2	36
7	J1	36
8	J2	37
8	A2	37
8	A7	38
8	C3	40
9	J4	43
9	B5	44
9	B3	44
9	A4	45
10	A1	51
11	H1	53
11	A5	56
14	A6	70
15	A3	77
1	D3	2
5	B2	25
5	B1	25
5	F4	25
5	F1	25
6	H4	30
5	B4	25
5	F3	25
5	F2	25

Table 5.13

Rating	Sample No.	Ca (ppm)	Rating	Sample No.	Ca (ppm)	Rating	Sample No.	Ca (ppm)
1	G3	54	3	B4	158	7	A2	310
1	D3	56	3	B2	162	7	E1	312
1	C2	62	4	H6	193	8	A1	320
1	G1	64	4	B5	200	9	H4	350
1	D6	73	5	B7	210	9	C4	351
1	D4	78	5	F1	227	9	J4	365
1	G2	79	6	I1	240	9	F4	376
1	D5	81	6	H5	243	10	J2	409
1	G4	87	6	A3	250	10	H1	415
1	D2	88	6	A4	254	11	H3	431
2	B1	92	6	J1	260	11	H2	434
2	D1	104	6	A6	260	11	C3	454
2	D7	113	6	A5	267	11	C1	460
3	B6	130	7	B3	280	12	E3	476
3	J3	133	7	F2	291	15	E2	606
3	F3	146	7	A7	302			

5.1.2 The Goodness of Fit and Residual Calculations on the Ratings for each Analyte Sample.

The ratings in tables 5.4 to 5.13 are used to work out Goodness-of-fit and 'R'. For each sample, assessment was of the goodness of fit of the measured data for each analyte. This was obtained by calculating a residual 'R'

$$R = \frac{\sum_{i=1}^{i=n} |X_m - X_i|}{\sum_{i=1}^{i=n} X_i}$$

$\sum Xi$

is the sum of 47 ratings for an analyte. X_i is the rating for each of the analyte and is shown in the Tables 5.3 to 5.13 and in 5.14

X_m is the mean rating of a sample as shown in table 5.14

$|X_m - X_i|$

is the modulus of the deviation of the rating for each analyte from the mean rating of a sample. These are listed for each analyte in Table 5. 15.

Table 5.14 Ratings and Average of Ten Ratings for Each Sample

				Ratings (X_i)						(X_m)
Sample	CH_4	CO_2	EC	NH4-N	COD	TOC	Cl	Na	K	Ca	Av
D6	1	1	1	1	1	1	2	1	1	1	1.1
D7	1	1	2	1	1	1	2	1	1	2	1.3
G4	1	1	1	1	1	1	1	1	1	1	1.0
H6	1	3	3	1	1	1	2	1	2	4	1.9
H5	1	1	5	1	1	1	6	6	5	6	3.3
E3	1	4	10	1	1	1	1	2	5	12	3.8
C2	1	1	1	1	2	2	2	1	1	1	1.3
J1	1	1	8	1	1	5	4	3	7	6	3.7
D4	1	1	2	1	3	1	2	1	1	1	1.4
H2	1	2	7	1	2	2	1	2	7	11	3.6
H4	1	3	8	1	2	2	1	3	6	9	3.6
G1	1	1	1	1	3	1	1	1	1	1	1.2
D3	1	1	1	1	4	1	1	1	1	1	1.3
D2	1	1	2	1	4	1	2	2	1	1	1.6
D1	1	1	3	1	4	1	2	2	2	2	1.9
G2	1	1	1	1	4	1	1	1	1	1	1.3
J4	1	3	8	1	2	3	2	4	9	9	4.2
D5	1	1	2	1	4	1	2	1	1	1	1.5
H1	1	3	7	1	3	3	1	2	11	10	4.2
B1	1	2	4	1	2	6	3	3	5	2	2.9
J2	1	4	8	1	3	3	1	2	8	10	4.1
G3	1	1	1	1	5	1	1	1	1	1	1.4
B6	2	7	3	1	3	2	1	1	4	3	2.7
E1	1	3	6	1	4	4	2	2	1	7	3.1
E2	2	5	9	2	3	3	1	2	4	15	4.6
F4	1	6	6	2	3	7	1	3	5	9	4.3
H3	1	4	9	2	4	4	3	2	7	11	4.7
J3	2	3	4	2	4	4	2	4	6	3	3.4
B7	3	9	6	3	4	3	2	3	5	5	4.3
B5	2	7	7	8	4	3	2	4	9	4	5.0
C1	2	2	7	1	6	9	1	2	4	11	4.5
F1	1	2	7	2	6	10	2	3	5	5	4.3
I1	6	2	3	1	4	5	3	1	4	6	3.5
C4	4	6	7	2	6	12	1	1	5	9	5.3
B4	1	2	8	12	9	12	4	3	5	3	5.9
F3	4	1	6	3	12	7	3	3	5	3	4.7
F2	6	11	6	2	10	4	2	3	5	7	5.6
A5	5	7	10	10	9	4	6	6	11	6	7.4
C3	7	7	9	2	6	15	2	7	8	11	7.4
A2	11	2	7	4	6	4	2	4	8	7	5.5
B3	8	15	10	6	10	4	8	9	9	7	8.6
B2	1	1	8	8	15	14	4	3	5	3	6.2
A3	11	6	10	15	7	6	10	7	15	6	9.3
A7	7	8	9	4	14	9	4	6	8	7	7.6
A6	11	6	11	15	10	7	5	7	14	6	9.2
A4	15	3	9	6	10	7	6	7	9	6	7.8
A1	14	15	15	4	11	10	15	15	10	8	11.7

Table 5.15 Residual Results by Considering Ten Analytes

Residual		0.61	0.46	0.30	0.77	0.38	0.45	0.66	0.42	0.29	0.27
	(X_m)				mod. X_m-X_i						
Sample	**Av**	**CH4**	**CO2**	**EC**	**NH4**	**COD**	**TOC**	**Cl**	**Na**	**K**	**Ca**
D6	1.1	0.1	0.1	0.1	0.1	0.1	0.1	0.9	0.1	0.1	0.1
D7	1.3	0.3	0.3	0.7	0.3	0.3	0.3	0.7	0.3	0.3	1.0
G4	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H6	1.9	0.9	1.1	1.1	0.9	0.9	0.9	0.1	0.9	0.1	1.0
H5	3.3	2.3	2.3	1.7	2.3	2.3	2.3	2.7	2.7	1.7	1.0
E3	3.8	2.8	0.2	6.2	2.8	2.8	2.8	2.8	1.8	1.2	1.0
C2	1.3	0.3	0.3	0.3	0.3	0.7	0.7	0.7	0.3	0.3	0.3
J1	3.7	2.7	2.7	4.3	2.7	2.7	1.3	0.3	0.7	3.3	1.0
D4	1.4	0.4	0.4	0.6	0.4	1.6	0.4	0.6	0.4	0.4	0.4
H2	3.6	2.6	1.6	3.4	2.6	1.6	1.6	2.6	1.6	3.4	1.0
H4	3.6	2.6	0.6	4.4	2.6	1.6	1.6	2.6	0.6	2.4	1.0
G1	1.2	0.2	0.2	0.2	0.2	1.8	0.2	0.2	0.2	0.2	0.2
D3	1.3	0.3	0.3	0.3	0.3	2.7	0.3	0.3	0.3	0.3	0.3
D2	1.6	0.6	0.6	0.4	0.6	2.4	0.6	0.4	0.4	0.6	0.6
D1	1.9	0.9	0.9	1.1	0.9	2.1	0.9	0.1	0.1	0.1	1.0
G2	1.3	0.3	0.3	0.3	0.3	2.7	0.3	0.3	0.3	0.3	0.3
J4	4.2	3.2	1.2	3.8	3.2	2.2	1.2	2.2	0.2	4.8	1.0
D5	1.5	0.5	0.5	0.5	0.5	2.5	0.5	0.5	0.5	0.5	0.5
H1	4.2	3.2	1.2	2.8	3.2	1.2	1.2	3.2	2.2	6.8	1.0
B1	2.9	1.9	0.9	1.1	1.9	0.9	3.1	0.1	0.1	2.1	0.9
J2	4.1	3.1	0.1	3.9	3.1	1.1	1.1	3.1	2.1	3.9	1.0
G3	1.4	0.4	0.4	0.4	0.4	3.6	0.4	0.4	0.4	0.4	0.4
B6	2.7	0.7	4.3	0.3	1.7	0.3	0.7	1.7	1.7	1.3	2.0
E1	3.1	2.1	0.1	2.9	2.1	0.9	0.9	1.1	1.1	2.1	1.0
E2	4.6	2.6	0.4	4.4	2.6	1.6	1.6	3.6	2.6	0.6	2.0
F4	4.3	3.3	1.7	1.7	2.3	1.3	2.7	3.3	1.3	0.7	1.0
H3	4.7	3.7	0.7	4.3	2.7	0.7	0.7	1.7	2.7	2.3	1.0
J3	3.4	1.4	0.4	0.6	1.4	0.6	0.6	1.4	0.6	2.6	0.4
B7	4.3	1.3	4.7	1.7	1.3	0.3	1.3	2.3	1.3	0.7	3.0
B5	5.0	3.0	2.0	2.0	3.0	1.0	2.0	3.0	1.0	4.0	1.0
C1	4.5	2.5	2.5	2.5	3.5	1.5	4.5	3.5	2.5	0.5	2.0
F1	4.3	3.3	2.3	2.7	2.3	1.7	5.7	2.3	1.3	0.7	1.0
I1	3.5	2.5	1.5	0.5	2.5	0.5	1.5	0.5	2.5	0.5	1.0
C4	5.3	1.3	0.7	1.7	3.3	0.7	6.7	4.3	4.3	0.3	4.0
B4	5.9	4.9	3.9	2.1	6.1	3.1	6.1	1.9	2.9	0.9	2.9
F3	4.7	0.7	3.7	1.3	1.7	7.3	2.3	1.7	1.7	0.3	1.7
F2	5.6	0.4	5.4	0.4	3.6	4.4	1.6	3.6	2.6	0.6	5.2
A5	7.4	2.4	0.4	2.6	2.6	1.6	3.4	1.4	1.4	3.6	1.4
C3	7.4	0.4	0.4	1.6	5.4	1.4	7.6	5.4	0.4	0.6	7.0
A2	5.5	5.5	3.5	1.5	1.5	0.5	1.5	3.5	1.5	2.5	0.0
B3	8.6	0.6	6.4	1.4	2.6	1.4	4.6	0.6	0.4	0.4	1.6
B2	6.2	5.2	5.2	1.8	1.8	8.8	7.8	2.2	3.2	1.2	3.2
A3	9.3	1.7	3.3	0.7	5.7	2.3	3.3	0.7	2.3	5.7	3.3
A7	7.6	0.6	0.4	1.4	3.6	6.4	1.4	3.6	1.6	0.4	0.6
A6	9.2	1.8	3.2	1.8	5.8	0.8	2.2	4.2	2.2	4.8	3.2
A4	7.8	7.2	4.8	1.2	1.8	2.2	0.8	1.8	0.8	1.2	1.8
A1	11.7	2.3	3.3	3.3	7.7	0.7	1.7	3.3	3.3	1.7	3.7

5.1.3 Calculation of Residual 'R' for Analyte - EC

From table 5.15 and formula for R in section 5.1.2

For example, R for EC is worked out first of by adding all the Mod X_m - X_i

For EC for the 47 samples is 84.

$\sum Xi$

From Table 5.14 is the sum of ratings for EC for 47 samples. This is calculated to be 278

R = 84/278

= 0.30

In this way, the residual, R, for CH_4 is 0.61; CO_2 is 0.46, NH_4-N is 0.77, COD is 0.38, TOC is 0.45, Cl is 0.66, Na is 0.42, K is 0.29, Ca is 0.27. All these results are in Table 5.20. The smaller the value of R the better is the goodness-of-fit.

5.2 Groundwater Quality Assessment Using Six Main Factors

The second method in assessing the level of contamination in a borehole is by considering only six factors rather than ten. The parameters not considered are Ca, Na, K and Cl^-. The reason for taking this approach is because it was assumed that the above four parameters are taken into consideration twice, once by the analyte EC and once by considering each analyte concentration separately. It is possible that it accounts for a proportion of error in the assessment. The six main factors taken into consideration in this method are CH_4, CO_2, EC, NH_4-N, COD, and TOC.

The same method as above is adopted for calculating the value of R, except that the average ratings are those of the above mentioned six main factors. The Table 5.16 has the data for X_i, X_m, and modulus X_m-X_i, expressed as X_m - X_i, and the values for goodness-of-fit 'R'.

Table 5.16 Residual 'R' by Considering Six main Factors

	AV Main Factors	CH4		CO2		EC		NH4		COD		TOC	
Residual			0.58		0.454		0.31		0.715		0.30		0.407
Sample	X_m	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i
D6	1.000	1	0.000	1	0.000	1	0.000	1	0.000	1	0.000	1	0.000
D7	1.167	1	0.167	1	0.167	2	0.833	1	0.167	1	0.167	1	0.167
G4	1.000	1	0.000	1	0.000	1	0.000	1	0.000	1	0.000	1	0.000
H6	1.667	1	0.667	3	1.333	3	1.333	1	0.667	1	0.667	1	0.667
H5	1.667	1	0.667	1	0.667	5	3.333	1	0.667	1	0.667	1	0.667
E3	3.000	1	2.000	4	1.000	10	7.000	1	2.000	1	2.000	1	2.000
C2	1.333	1	0.333	1	0.333	1	0.333	1	0.333	2	0.667	2	0.667
J1	2.833	1	1.833	1	1.833	8	5.167	1	1.833	1	1.833	5	2.167
D4	1.500	1	0.500	1	0.500	2	0.500	1	0.500	3	1.500	1	0.500
H2	2.500	1	1.500	2	0.500	7	4.500	1	1.500	2	0.500	2	0.500
H4	2.833	1	1.833	3	0.167	8	5.167	1	1.833	2	0.833	2	0.833
G1	1.333	1	0.333	1	0.333	1	0.333	1	0.333	3	1.667	1	0.333
D3	1.500	1	0.500	1	0.500	1	0.500	1	0.500	4	2.500	1	0.500
D2	1.667	1	0.667	1	0.667	2	0.333	1	0.667	4	2.333	1	0.667
D1	1.833	1	0.833	1	0.833	3	1.167	1	0.833	4	2.167	1	0.833
G2	1.500	1	0.500	1	0.500	1	0.500	1	0.500	4	2.500	1	0.500
J4	3.000	1	2.000	3	0.000	8	5.000	1	2.000	2	1.000	3	0.000
D5	1.667	1	0.667	1	0.667	2	0.333	1	0.667	4	2.333	1	0.667
H1	3.000	1	2.000	3	0.000	7	4.000	1	2.000	3	0.000	3	0.000
B1	2.667	1	1.667	2	0.667	4	1.333	1	1.667	2	0.667	6	3.333
J2	3.333	1	2.333	4	0.667	8	4.667	1	2.333	3	0.333	3	0.333
G3	1.667	1	0.667	1	0.667	1	0.667	1	0.667	5	3.333	1	0.667
B6	3.000	2	1.000	7	4.000	3	0.000	1	2.000	3	0.000	2	1.000
E1	3.167	1	2.167	3	0.167	6	2.833	1	2.167	4	0.833	4	0.833
E2	4.000	2	2.000	5	1.000	9	5.000	2	2.000	3	1.000	3	1.000
F4	4.167	1	3.167	6	1.833	6	1.833	2	2.167	3	1.167	7	2.833
H3	4.000	1	3.000	4	0.000	9	5.000	2	2.000	4	0.000	4	0.000
J3	3.167	2	1.167	3	0.167	4	0.833	2	1.167	4	0.833	4	0.833
B7	4.667	3	1.667	9	4.333	6	1.333	3	1.667	4	0.667	3	1.667
B5	5.167	2	3.167	7	1.833	7	1.833	8	2.833	4	1.167	3	2.167
C1	4.500	2	2.500	2	2.500	7	2.500	1	3.500	6	1.500	9	4.500
F1	4.667	1	3.667	2	2.667	7	2.333	2	2.667	6	1.333	10	5.333
I1	3.500	6	2.500	2	1.500	3	0.500	1	2.500	4	0.500	5	1.500
C4	6.167	4	2.167	6	0.167	7	0.833	2	4.167	6	0.167	12	5.833
B4	7.333	1	6.333	2	5.333	8	0.667	12	4.667	9	1.667	12	4.667
F3	5.500	4	1.500	1	4.500	6	0.500	3	2.500	12	6.500	7	1.500
F2	6.500	6	0.500	11	4.500	6	0.500	2	4.500	10	3.500	4	2.500
A5	7.500	5	2.500	7	0.500	10	2.500	10	2.500	9	1.500	4	3.500
C3	7.667	7	0.667	7	0.667	9	1.333	2	5.667	6	1.667	15	7.333
A2	5.667	11	5.333	2	3.667	7	1.333	4	1.667	6	0.333	4	1.667
B3	8.833	8	0.833	15	6.167	10	1.167	6	2.833	10	1.167	4	4.833
B2	7.833	1	6.833	1	6.833	8	0.167	8	0.167	15	7.167	14	6.167
A3	9.167	11	1.833	6	3.167	10	0.833	15	5.833	7	2.167	6	3.167
A7	8.500	7	1.500	8	0.500	9	0.500	4	4.500	14	5.500	9	0.500
A6	10.000	11	1.000	6	4.000	11	1.000	15	5.000	10	0.000	7	3.000
A4	8.333	15	6.667	3	5.333	9	0.667	6	2.333	10	1.667	7	1.333
A1	11.500	14	2.500	15	3.500	15	3.500	4	7.500	11	0.500	10	1.500

5.2.1 Calculations for Residual for Analyte EC

In this method, the residual for EC is calculated by first obtaining the sum of mod X_i-X_m,, where X_i is the rating of analyte. For example, in the case of EC for each of the 47 samples tested, the sum of mod X_{EC}-X_m is 86.5, and the sum of all the X_{EC}, (sum of 47 EC rating values) is 278;

Goodness-of-fit 'R' is = 86.5/278

= 0.31

Residual for EC considering only the 6 main factors is worked out as 0.31.

In this way the residual for the 6 main factors considered are calculated. Residual for CH_4 is 0.58, for CO_2 is 0.45, for EC is 0.31, for NH_4-N is 0.72, for COD is 0.30, and for TOC is 0.41. All the results for R are in Table 5.20. Goodness-of-fit R for EC is nearly the same by using the second method, but generally all of the other parameters have lower residual value compared to taking all the 10 factors into consideration. Therefore, this method is better for borehole quality assessment.

5.3 Borehole Contamination Assessment by 'Weighting' certain Factors and Combining the Six Main Factors

In the previous section the goodness-of-fit is considered for each of the measured parameters. This section deals with the combination of all six parameters to provide a pollution assessment.

In this third method for assessing the level of contamination in a borehole, greater weighting is given to CH_4 concentrations because methane is considered to have significant hazard risks associated with low concentrations. For example, If methane were to accumulate in confined spaces it would have the potential to cause an explosion (between 5 and 15% volume in air). Methane in concentrations more than 1% inside the buildings is considered to be risky according to the DoE guidance in Waste Management Paper 27. Nine combinations of the six main measured parameters are considered for the assessment and these are

Formula 1: $1CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 2: $2CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 3: $3CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 4: $4CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 5: $5CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 6: $6CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 7: $7CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 8: $8CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

Formula 9: $9CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$

5.3.1 Calculation Method for the Values for Each of the 9 Formulae

For example using formula 3, i.e. $3CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$, and from table5.1, using the figures for sample A1, the value for the formula is

$$3 \times 63.4+32.2+2930/100+27+229+80$$

$$= \quad 587.7$$

In this way values for all of the 47 samples using formulae 1 to 9 was calculated and the results are in table 5. 17.

Table 5.17 Range of Values for Each Sample Using Formula with 1 to 9 CH_4

	Formulae with 1 to 9 CH_4 combinations								
Sample	1 CH_4	2 CH_4	3 CH_4	4 CH_4	5CH_4	6 CH_4	7 CH_4	8 CH_4	9 CH_4
D6	12	12	12	12	12	12	12	12	12
D7	15	15	15	15	15	15	15	15	15
G4	17	17	17	17	17	17	17	17	17
H6	19	19	19	19	19	19	19	19	19
H5	43	43	43	43	43	43	43	43	43
E3	53	53	53	53	53	53	53	53	53
C2	55	55	55	55	55	55	55	55	55
J1	57	57	57	57	57	57	57	57	57
D4	63	63	63	63	63	63	63	63	63
H2	70	70	70	70	70	70	70	70	70
H4	69	69	69	70	70	70	70	70	70
G1	71	71	71	71	71	71	71	71	71
D3	70	70	70	70	70	70	70	70	70
D2	76	76	76	76	76	76	76	76	76
D1	77	77	77	77	77	77	77	77	77
G2	81	81	81	81	81	81	81	81	81
J4	88	88	88	88	88	88	88	88	88
D5	90	90	90	90	90	90	90	90	90
H1	91	91	91	91	91	91	91	91	91
B1	92	92	92	92	92	92	92	92	92
J2	94	94	94	94	94	94	94	94	94
G3	99	99	99	99	99	99	99	99	99
B6	103	107	111	114	118	122	126	130	134
E1	118	118	118	118	118	118	118	118	118
E2	115	1167	117	118	119	120	121	122	123
F4	132	132	132	132	132	132	132	132	132
H3	135	135	135	135	135	135	135	135	135
J3	131	133	136	139	141	144	146	149	152
B7	157	163	169	176	182	188	194	200	207
B5	187	189	191	194	196	199	201	204	206
C1	214	215	216	216	217	218	219	220	221
F1	228	228	228	228	228	228	228	228	228
I1	156	181	205	229	253	277	302	326	350
C4	265	278	290	303	315	328	340	353	365
B4	382	382	382	382	383	383	383	383	383
F3	328	342	356	370	384	398	412	426	440
F2	313	337	361	385	409	433	456	481	505
A5	338	357	376	395	414	433	452	471	490
C3	311	337	363	389	415	441	467	493	520
A2	245	293	341	389	437	485	533	581	629
B3	353	384	415	446	477	508	538	569	600
B2	511	511	511	511	511	511	511	5119	511
A3	375	422	469	516	563	610	657	704	751
A7	446	476	506	537	567	598	628	658	689
A6	446	492	538	584	630	677	723	769	815
A4	394	463	532	601	670	739	808	878	947
A1	461	524	588	651	714	778	841	905	968

5.3.2 Assignment of Ratings 1 to 15 to each of the 47 Samples Using Formulae with $1CH_4$ to 9 CH_4

For example using formula 3, that is considering 3 times methane in the combination of the main factors, from Table 5.17, the value for the 3 x methane combination ranges from 11.88 to 587.7;

1. The difference between the lowest and highest value is 587.7 - 11.88

   = 575.8

2. Divide 575.8 by 15; i.e. 575.8/15 = 38.4

   which is approximately 38

2. For range of rating 1, start with the lowest value, i.e.12, and add 38 = 50;

   Therefore, range for rating 1 is 12 to 50.

3. For rating range 2, add 51 to 38 = 89;

   Therefore, range for rating 2 is from 51 to 89.

In this way the range of values is calculated for formula with combination with 3 times methane and the range is presented in Table 5.18

4. Ratings 1 to 15 were assigned to the 47 samples analysed using $1CH_4$ to $9CH_4$ combination formulae. These ratings are presented in Table 5.19

5.3.3. Calculation Method for 'R'

Residual is calculated according to the formula for R:

$$R = \frac{\sum_{i=1}^{i=n} \left| X_m - X_i \right|}{\sum_{i=1}^{i=n} X_i}$$

For example, in case of using formula with 3CH$_4$ combination, the sum of all the ratings of 47 samples is 248, and sum of all the 47 mod X_m-X_i results is 64.8;

Table 5.18 Range of Values in each of 15 Ratings Using 3CH$_4$ Formula

Range of values for formula with 3 times methane concentration

Rating	Range of 3CH$_4$ Formula values
1	12 - 50
2	51 - 89
3	90 - 128
4	129 - 167
5	168 - 206
6	207 - 245
7	246 - 284
8	285 - 323
9	324 - 362
10	363 - 401
11	402 - 440
12	441 - 479
13	480 - 518
14	519 - 557
15	558 - 596

R = 64.8/258

= 0.26

In this way residual for all of the 9 combinations were worked out

5. The results of residual are shown in Tables 5.19 and 5.21

Note: in table 5.19,

X_m denotes mean rating for a sample considering six main factors;

X_i is rating of a sample using combination formula;

X_m-X_i denotes modulus X_m-X_i

Table 5.19 Results of 'R' using Each of the Nine Fomulae

Residual		0.27		0.27		0.26		0.28	
		$1CH_4$		$2CH_4$		$3CH_4$		$4CH_4$	
Sample No	Av. (X_m)	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i
D6	1.000	1	0.000	1	0.000	1	0.000	1	0.000
D7	1.167	1	0.167	1	0.167	1	0.167	1	0.167
G4	1.000	1	0.000	1	0.000	1	0.000	1	0.000
H6	1.667	1	0.667	1	0.667	1	0.667	1	0.667
H5	1.667	1	0.667	1	0.667	1	0.667	1	0.667
E3	3.000	2	1.000	2	1.000	2	1.000	1	2.000
C2	1.333	2	0.667	2	0.667	2	0.667	2	0.667
J1	2.833	2	0.833	2	0.833	2	0.833	2	0.833
D4	1.500	2	0.500	2	0.500	2	0.500	2	0.500
H2	2.500	2	0.500	2	0.500	2	0.500	2	0.500
H4	2.833	2	0.833	2	0.833	2	0.833	2	0.833
G1	1.333	2	0.667	2	0.667	2	0.667	2	0.667
D3	1.500	2	0.500	2	0.500	2	0.500	2	0.500
D2	1.667	2	0.333	2	0.333	2	0.333	2	0.333
D1	1.833	2	0.167	2	0.167	2	0.167	2	0.167
G2	1.500	3	1.500	2	1.500	2	0.500	2	0.500
J4	3.000	3	0.000	3	0.000	2	1.000	2	1.000
D5	1.667	3	1.333	3	1.333	3	1.333	2	0.333
H1	3.000	3	0.000	3	0.000	3	0.000	2	1.000
B1	2.667	3	0.333	3	0.333	3	0.333	2	0.667
J2	3.333	3	0.333	3	0.333	3	0.333	2	1.333
G3	1.667	3	1.333	3	1.333	3	1.333	3	1.333
B6	3.000	3	0.000	3	0.000	3	0.000	3	0.000
E1	3.167	4	0.833	4	0.833	3	0.167	3	0.167
E2	4.000	4	0.000	3	0.000	3	1.000	3	1.000
F4	4.167	4	0.167	4	0.167	4	0.167	3	1.167
H3	4.000	4	0.000	4	0.000	4	0.000	3	1.000
J3	3.167	4	0.833	4	0.833	4	0.833	3	0.167
B7	4.667	5	0.333	5	0.333	5	0.333	4	0.667
B5	5.167	6	0.833	6	0.833	5	0.167	5	0.167
C1	4.500	7	2.500	6	2.500	6	1.500	5	0.500
F1	4.667	7	2.333	7	2.333	6	1.333	6	1.333
I1	3.500	5	1.500	5	1.500	5	1.500	6	2.500
C4	6.167	8	1.833	8	1.833	8	1.833	7	0.833
B4	7.333	12	4.667	11	4.667	10	2.667	9	1.667
F3	5.500	10	4.500	10	4.500	9	3.500	9	3.500
F2	6.500	10	3.500	10	3.500	9	2.500	9	2.500
A5	7.500	10	2.500	10	2.500	10	2.500	9	1.500
C3	7.667	10	2.333	10	2.333	9	1.333	9	1.333
A2	5.667	8	2.333	11	2.333	9	3.333	9	3.333
B3	8.833	11	2.167	11	2.167	11	2.167	11	2.167
B2	7.833	15	7.167	15	7.167	13	5.167	12	4.167
A3	9.167	11	1.833	12	1.833	12	2.833	12	2.833
A7	8.500	14	5.500	14	5.500	13	4.500	13	4.500
A6	10.000	14	4.000	14	4.000	14	4.000	14	4.000
A4	8.333	12	3.667	13	3.667	14	5.667	14	5.667
A1	11.500	14	2.500	15	2.500	15	3.500	15	3.500

Table 5.19 continued

Residual	0.27		0.27		0.27		0.29		0.29	
	$5CH_4$		$6CH_4$		$7CH_4$		$8CH_4$		$9CH_4$	
Sample	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i	X_i	X_m-X_i
D6	1	0.000	1	0.000	1	0.000	1	0.000	1	0.000
D7	1	0.167	1	0.167	1	0.167	1	0.167	1	0.167
G4	1	0.000	1	0.000	1	0.000	1	0.000	1	0.000
H6	1	0.667	1	0.667	1	0.667	1	0.667	1	0.667
H5	1	0.667	1	0.667	1	0.667	1	0.667	1	0.667
E3	1	2.000	1	2.000	1	2.000	1	2.000	1	2.000
C2	1	0.333	1	0.333	1	0.333	1	0.333	1	0.333
J1	1	1.833	1	1.833	1	1.833	1	1.833	1	1.833
D4	2	0.500	2	0.500	1	0.500	1	0.500	1	0.500
H2	2	0.500	2	0.500	2	0.500	1	1.500	1	1.500
H4	2	0.833	2	0.833	2	0.833	1	1.833	1	1.833
G1	2	0.667	2	0.667	2	0.667	1	0.333	1	0.333
D3	2	0.500	2	0.500	2	0.500	1	0.500	1	0.500
D2	2	0.333	2	0.333	2	0.333	2	0.333	2	0.333
D1	2	0.167	2	0.167	2	0.167	2	0.167	2	0.167
G2	2	0.500	2	0.500	2	0.500	2	0.500	2	0.500
J4	2	1.000	2	1.000	2	1.000	2	1.000	2	1.000
D5	2	0.333	2	0.333	2	0.333	2	0.333	2	0.333
H1	2	1.000	2	1.000	2	1.000	2	1.000	2	1.000
B1	2	0.667	2	0.667	2	0.667	2	0.667	2	0.667
J2	2	1.333	2	1.333	2	1.333	2	1.333	2	1.333
G3	2	0.087	2	0.333	2	0.333	2	0.333	2	0.333
B6	3	0.000	3	0.000	3	0.000	2	1.000	2	1.000
E1	3	0.167	3	0.167	3	0.167	2	1.167	2	1.167
E2	3	1.000	3	1.000	3	1.000	2	2.000	2	2.000
F4	3	1.167	3	1.167	3	1.167	2	2.167	2	2.167
H3	3	1.000	3	1.000	3	1.000	3	1.000	2	2.000
J3	3	0.167	3	0.167	3	0.167	3	0.167	3	0.167
B7	4	0.667	4	0.667	4	0.667	4	0.667	4	0.667
B5	4	1.167	4	1.167	4	1.167	4	1.167	4	1.167
C1	5	0.500	5	0.500	4	0.500	4	0.500	4	0.500
F1	5	0.333	5	0.333	4	0.667	4	0.667	4	0.667
I1	6	2.500	6	2.500	6	2.500	6	2.500	6	2.500
C4	7	0.833	7	0.833	6	0.167	6	0.167	6	0.167
B4	8	0.667	8	0.667	7	0.333	7	0.333	6	1.333
F3	8	2.500	8	2.500	8	2.500	7	1.500	7	1.500
F2	9	2.500	9	2.500	9	2.500	8	1.500	8	1.500
A5	9	1.500	9	1.500	9	1.500	8	0.500	8	0.500
C3	9	1.333	9	1.333	9	1.333	9	1.333	8	0.333
A2	10	4.333	10	4.333	10	4.333	10	4.333	10	4.333
B3	10	1.167	10	1.167	10	1.167	10	1.167	10	1.167
B2	11	3.167	10	2.167	10	2.167	9	1.167	8	0.167
A3	12	2.833	12	2.833	12	2.833	12	2.833	12	2.833
A7	12	3.500	12	3.500	12	3.500	11	2.500	11	2.500
A6	14	4.000	14	4.000	13	3.000	13	3.000	13	3.000
A4	15	6.667	15	6.667	15	6.667	15	6.667	15	6.667
A1	15	3.500	15	3.500	15	3.500	15	3.500	15	3.500

5.4 Results of Residual

From Tables 5.15, 5.16, and 5.19, the results of Residual 'R' calculated are presented in Tables 5.20 and 5.21

5.4.1 Results of Residual (Goodness of Fit) Using Individual Factors

The results of residual of individual factors are presented in Table 5.20

Table 5.20 Results of Residual R by Considering Single Factors

	CH_4	CO_2	EC	NH_4	COD	TOC	Cl	Na	K	Ca
R - All Factors	0.61	0.46	0.3	0.77	0.38	0.45	0.66	0.42	0.29	0.27
R-Main Factors*	0.58	0.45	0.31	0.71	0.3	0.41				

'R' represents Residual

* Main factors taken into consideration are CH_4, CO_2, EC, NH_4-N, COD, and TOC. All Factors include Cl^-, Na^+, K^+ and Ca^{2+}.

From Table 5.20 it is clear that when only the main factors are taken into consideration the residual figures are lower, hence, this is a better method of assessing a borehole contamination.

5.4.2 Results of Residuals Using Nine Combinations of the Main Factors

Table 5.21 is of 'R' values calculated by using formula 1 to 9, which relates to 1 to 9 times CH_4 and in each case $+CO_2+EC/100+NH_4$-N+COD+TOC values as described in section 5.3

Table 5.21

Results of residual values using 9 combinations of the main factors.

Formula	1	2	3	4	5	6	7	8	9
	$1CH_4$	$2CH_4$	$3CH_4$	$4CH_4$	$5CH_4$	$6CH_4$	$7CH_4$	$8CH_4$	$9CH_4$
Residual	0.27	0.27	0.26	0.28	0.27	0.27	0.27	0.29	0.29

Table 5.21 gives the lowest residual figures, or best 'goodness of fit', therefore this method is the best way of assessing site contamination. The formula using $3CH_4$ is the best means of characterising groundwater or site for contamination.

5.5 Characterisation of the 47 Samples Analysed

From table 5.21 the best method of characterising groundwater samples for contamination is by rating them 1 to 15 using combination formula $3CH_4 + CO_2 + EC/100 + NH_4\text{-}N + COD + TOC$.

From table 5.19, the 47 samples are rated 1 to 15 using $3CH_4$ formula. The ratings of 47 groundwater samples analysed are in Table 5.22

Table 5.22 Characterisation and Rating of Each Sample Analysed

Sample No.	Rating	Class	Sample No.	Rating	Class
D6	1	I	F4	4	III
D7	1	I	H3	4	II
G4	1	I	J3	4	II
H6	1	II	B7	5	III
H5	1	II	B5	5	III
E3	2	II	C1	6	III
C2	2	I	F1	6	III
J1	2	II	I1	5	III
D4	2	I	C4	8	III
H2	2	II	B4	10	III
H4	2	II	F3	9	III
G1	2	I	F2	9	III
D3	2	I	A5	10	IV
D2	2	I	C3	9	IV
D1	2	I	A2	9	IV
G2	2	I	B3	11	IV
J4	2	II	B2	13	III
D5	3	I	A3	12	IV
H1	3	II	A7	13	IV
B1	3	III	A6	14	IV
J2	3	II	A4	14	IV
G3	3	I	A1	15	IV
B6	3	III			
E1	3	II			
E2	3	II			

5.6 Testing of the Groundwater and Borehole Assessment Scale

Formula with $3CH_4$ combination method was found to be the best option for assessment for contamination in a borehole. The method was put to test when blind results where samples were collected and analysed by an external organisation was used for site categorisation. The rating of results for samples SA, SB, SC, SD, SF, SH, SI and SK were assessed according to $3CH_4$ combined formula. The rating for these samples are described in Table 5.23

Table 5.23 Site Assessment of Blind Samples Using 3CH$_4$ Formula

Assessment for the level of contamination in samples SA, SB, SC, SD, SF, SH, SI and SK are as shown in table 5.23

Sample Ref.	CH4 (%)	CO2 (%)	EC (us/cm)	TOC (mg/l)	COD (mg/l)	NH4-N (ppm)	3CH4Formula	Rating
SC	0	1.3	835	2.1	0.0001	0.00002	12	1
SF	0	10.2	1015	2.4	28	0.00022	51	1
SK	0	5.4	840	5.9	36	0.04	56	2
SD	0	1.6	1210	18.3	28	0.00001	60	2
SB	1.2	11.2	645	11.6	48	0.005	81	2
SA	20.5	4.8	1120	14.9	48	0.0046	140	4
SI	23.7	11.4	1990	19	6	8.3	136	4
SH	17.7	16.5	4900	92	260	0.397	471	12

These results are discussed in detail in Chapter VII

CHAPTER VI

ACETATE MEDIUM IN LANDFILL LEACHATE AND LEACHABILITY TESTS

Page Number

CHAPTER VI

ACETATE MEDIUM IN LANDFILL LEACHATE SAMPLES AND A STUDY OF ITS EFFECT ON LEACHING HEAVY METALS - WITH PARTICULAR REFERENCE TO LEAD

Evidence was found for the presence of acetic acid or acetate ions in leachate samples from highly gassing landfill sites in the LB of Hounslow. This chapter contains details of a study of the effects of acetate on the leachability of heavy metals and particularly of lead. Section 6.1 relates to determination of acetate in leachate samples and section 6.2 relates to leachability experiments on lead salts.

6.1 Acetate in Landfill Leachate

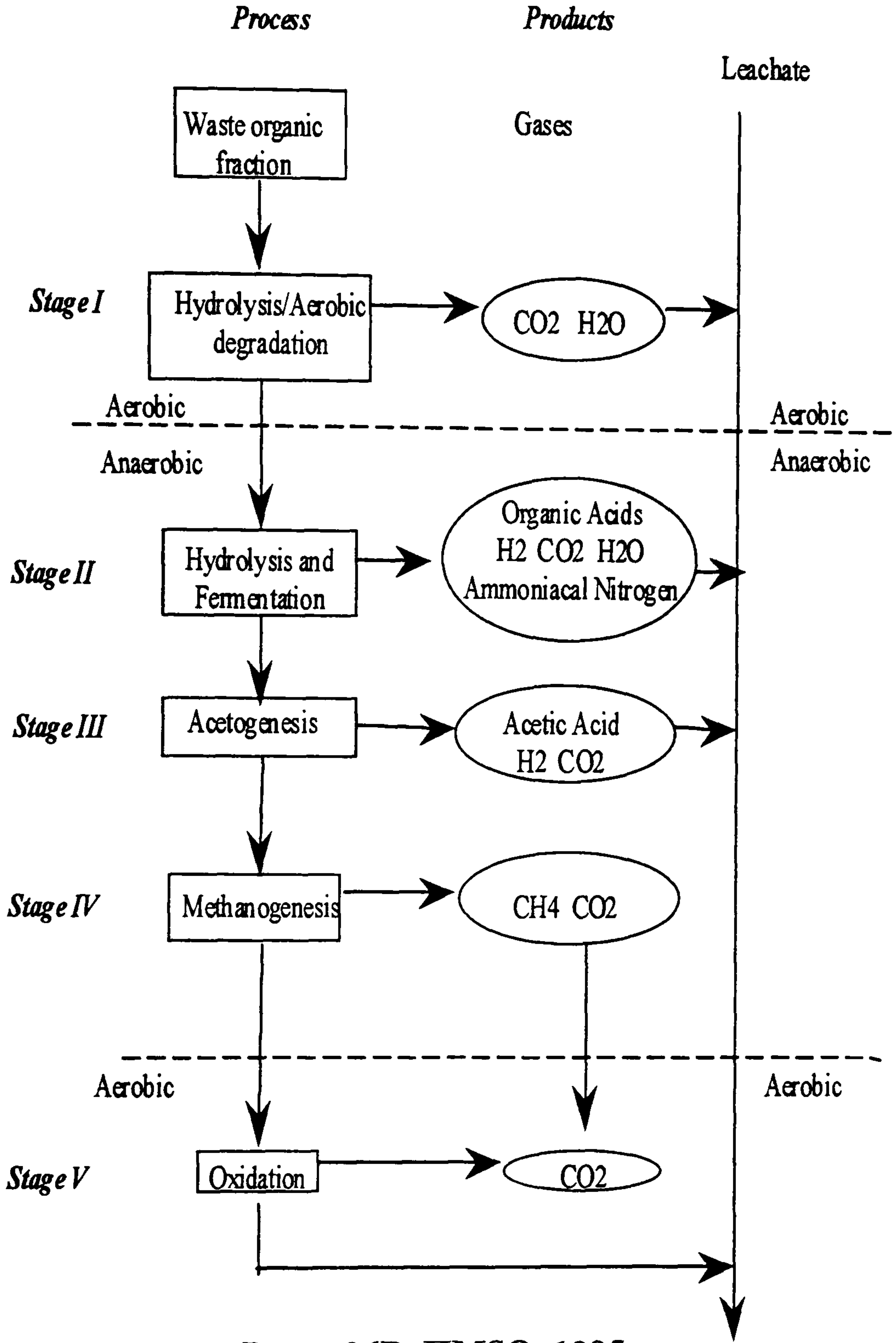
6.1.1 Background on Acetates in Landfill Leachates

Figures 1.3 and 1.4 illustrate the five major stages in the decomposition of organic waste in landfill. These five stages in decomposition of organic waste are considered in further detail with special reference to the micro-organisms involved in these processes. Figures 6.1 and 6.2 illustrate these stages.

<u>Stage I- Aerobic Phase</u>: This phase involves aerobic degradation of the waste. As soon as the waste in landfill is covered, oxygen in the waste is used up by the organic fractions of the waste and hydrolysis of polymers, such as cellulose, proteins, and lipids takes place to form simpler organic products and carbon dioxide and water.

Figure 6.1

Major Stages of Waste Degradation[1]



Source: DoE, Waste Management Paper 26B, HMSO, 1995.

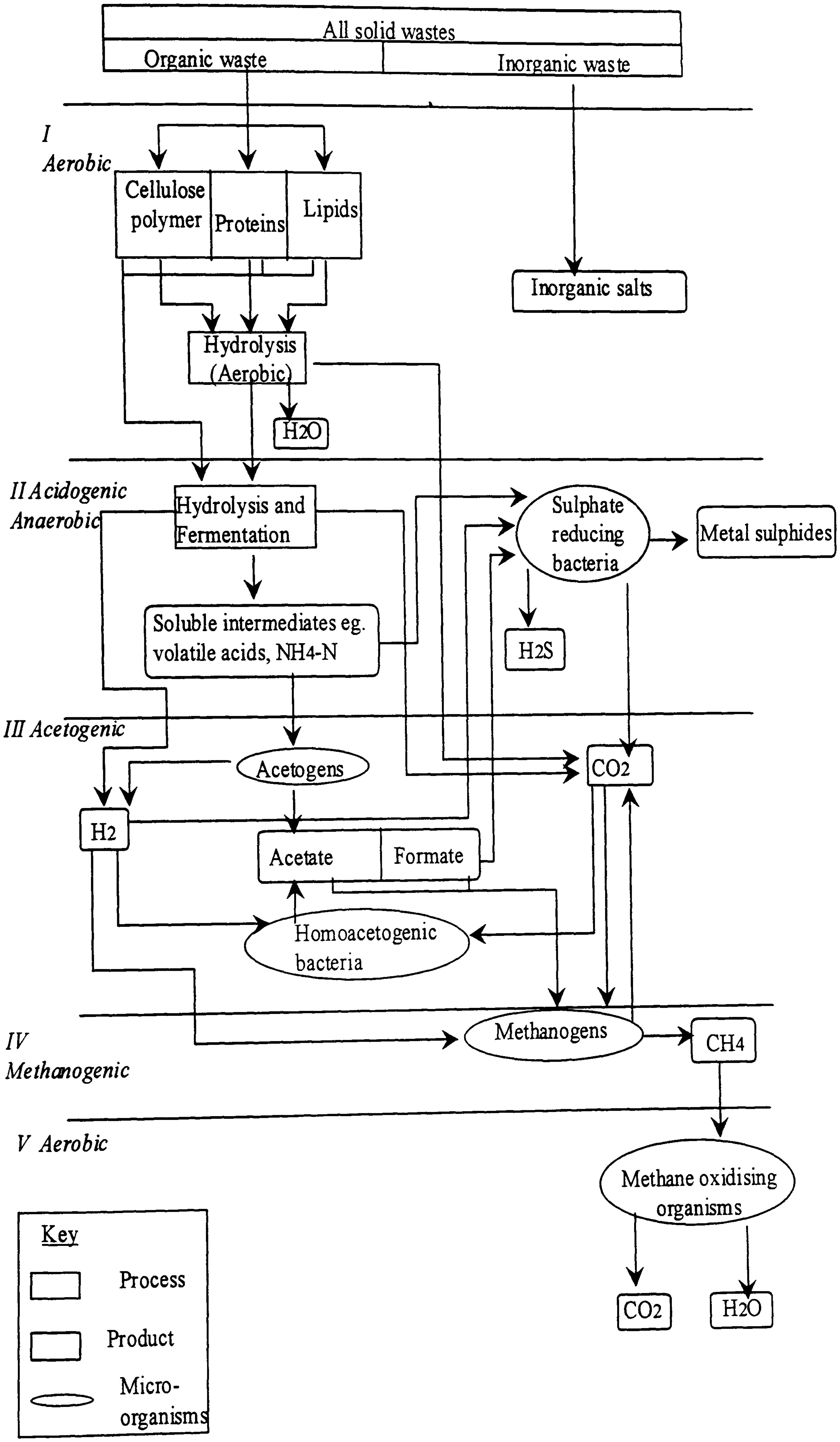
<u>Stage II - Acidogenic Anaerobic Phase:</u> When all the oxygen is consumed by the waste, the landfill environment changes and becomes favourable for anaerobic bacteria to act on organic polymers to produce products such as butyrate, propionate, lactate, succinate, ethanol, acetate, hydrogen and carbon dioxide. The last three form the methanogenic substrate and are produced in the initial fermentation steps.

The microorganisms known to act in the anaerobic fermentation stage are *Clostridium, Bacteroides, Peptostreptococcus, Peptococcus, Eubacterium, and Lactobacillus*[2].

Under experimental conditions[3], this phase was characterised by accumulation of carboxylic acids and a decrease in pH from 7.5 in fresh refuse to between 5.7 and 6.2. The accumulation of acidic fermentation intermediates can be attributed to the fact that there is insufficient levels of oxygen and nitrate in the fresh refuse to achieve complete sugar oxidation; due to carbon dioxide dissolution; and due to low acid consuming activities of acetogenic and methanogenic bacteria.

Stage III- Acetogenic Phase: At this stage, the acetogenic bacteria use the hydrogen and volatile fatty acids produced in stage II as substrate to form acetic acid, hydrogen and carbon dioxide. This results in an increase in the pH and decrease in the volatile fatty acids. Under experimental conditions, this phase was characterised by a decrease in the accumulation of carboxylic acids concurrent with increasing rate of methane production. At this stage the pH of the refuse increases from 6.2 to 7.9 and the methanogen microorganism population increases. Most notably, the cellulolytic and acetogen microorganism population increases in the third phase of refuse decomposition above the numbers measured in fresh refuse[3].

Figure 6.2 Stages of Waste Degradation in Detail[1]. Source:DoE.



Experiments on capacities of prairie soil to form and consume acetate under anaerobic conditions have shown that propionate, formate, butyrate and hydrogen were trace products detected in soil suspensions; of these trace products propionate accumulated to levels approximating to 1% that of the major product acetate[4]. It is understood that equilibrium is set up in the bio-degradation processes where the rate of acetate formation is in equilibrium with the rate of acetate utilisation, for example in methane formation.

Some of the known acetogens are: *Syntrophomonas, Acetobacterium, Syntrophobacter, Acetobacterium*. These microorganisms use butyrate, propionate, lactate, succinate, and ethanol as substrate to produce acetate, hydrogen and carbon dioxide[2].

Homoacetogenic bacteria are organisms from genus *Clostridium*; *C. formicoaceticum, C. thermoaceticum, C. acidiciurici; C. cylindrosporum* . These organisms can transfer the hydrogen equivalents liberated in the initial oxidation of substrate only to carbon dioxide to produce acetate[5]. Acetic acid is formed according to equation:

$$8[H] + 2CO_2 \rightarrow CH_3 - COOH + 2H_2O$$

<u>Stage IV- Methanogenic Phase:</u> At this stage, methanogenic bacteria act on acetate, H_2 and CO_2 to form CH_4 and CO_2. The acetate generated is in equilibrium with the rate of methane generation, hence, pH remains near neutral and excesses of volatile fatty acids are not present in the landfill leachate. There is a steady decrease in the

level of biodegradable cellulose in the waste and steady generation of landfill gases i.e. CH_4 and CO_2.

In this phase, micro organisms such as *Methanosarcina, Methanothrix* act on substrate acetate, H_2 and HCO_3^- to form products: CH_4 and CO_2; where as *Methanobrevibacter, Methanomicrobium, Methanogenium, Methanobacterium, Methanococcus, and Methanospirillum* act on substrate H_2 and HCO_3^- to form CH_4.

Under experimental conditions[3] the pH of refuse increases from 6.2 to 7.9 in this phase. The methanogenic bacteria appeared to reach a critical level; acetate and H_2 consumption improved conditions for conversion of butyrate and propionate to acetate, this resulted in an increase in the pH of the ecosystem. As the pH increased, the acetogen population increased which allowed for additional carboxylic acid consumption and a further increase in CH_4 production.

Sulphate Reducing Bacteria: These bacteria are strictly anaerobic and have the ability to use sulphate and other oxidised sulphur compounds as electron acceptors during anaerobic respiration and reduce the sulphate to hydrogen sulphide according to equation:

$$SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O$$

Microorganisms known to use sulphate as substrate are *Desulfovibrio* and *Desulfotomaculum.* The refuse ecosystem has the capacity to reduce high concentrations of sulphate and sulphate-reducing bacteria are reported to outcompete methanogens for hydrogen[3]. Thus in a hydrogen-limited environment, sulphate will inhibit methane production.

Stage V Aerobic Phase is the final stage in landfill stabilisation when the landfill environment becomes aerobic once again. The landfill site does not undergo any further anaerobic biodegradation, hence, no further methane production and ground settlement takes place. In this phase methylotrophic bacteria from family *Methylococcaceae* (genera *Methylococcus and Methylomonas,* which use methane and other reduced one carbon compounds as their sole carbon and energy sources under aerobic or microaerobic (low oxygen) conditions, where as methanotrophs use methane exclusively as their carbon and energy source to form products: CO_2 and H_2O.

A landfill site can take a number of decades to stabilise. In Hounslow some of the landfill sites which are more than 40 years old are still producing methane. It may be assumed that a gassing landfill may take up to 50 years to reach a stabilisation stage, i.e., stage V.

6.1.2 Methodology for Acetate Determination

Acetate in groundwater samples was determined by High Performance Ion Chromatography Exclusion (HPICE) system. The principle behind the separation of acetates by HPICE column and system is described in Section 3.3.1.6. The basis for acetate separation in the column is due to the fact that undissociated acetate gets adsorbed on the column resin, hence it is retained by the column. Whereas other anions such as, Cl^-, NO_3^-, and SO_4^{2-} are not retained by the column, this results in the separation of acetates from strong anions.

Deionised water was used as eluent on the HPICE column. The separation of anions and acetates was tested under various conditions, such as, flow rate of eluent from 1.5 ml/min. down to 0.9 ml/min. The most suitable flow rate was found to be 0.9 ml/min. Various standard solutions of acetates were analysed to determine the detection limit of acetate and the linear range of acetate detection. The detection limit of acetate was found to be 0.1ppm and linear range of acetate detection was found to be from 5ppm to 20ppm. Standard solutions of chloride, nitrate and sulphate were run separately and then with standard acetate solution to establish the retention time of various analytes separately. In each run a peak was noticed well after the acetate peak, which was due to carbonate as impurity in the standard solution, possibly due to dissolved CO_2 from air.

A standard solution of formate, acetate and propionate was run separately to establish their retention times and characterise their separation in the chromatographic column. Retention time (RT) was 4.68 minutes for formate; 5.88 minutes for acetate; and 6.45 minutes for propionate.

An undiluted groundwater sample was analysed in the HPICE system but this gave a massive unresolved peak. It was established that the best separation of acetate in a groundwater sample took place when it was diluted five times with deionised water. In this way there was a clear separation of the acetate peak as detected by ion chromatography.

The best conditions for determining acetate was found to be the following:

HPICE-AS1 column; deionised water as eluent; no regenerant; flow of eluent was best at 0.9ml/min; groundwater samples were diluted 5 times before preparing solutions for analysis to obtain best results; the pressure in the system was 520 psi. In each chromatographic run, a broad peak appeared at RT 9 to 9.5 minutes that was confirmed to be due to carbonate. Examples of chromatograms obtained by using standard Acetate solution and diluted groundwater samples spiked with standard acetate solution are as shown in Figures 6.3 and 6.4 respectively. Figure 6.5 shows the calibration graph for acetate under the above experimental conditions. Results for acetates in the three leachate samples analysed are reported in Section 6.3.

6.2 Leachability Tests on Lead Salts.

This section looks into the possible effects of acetate on leaching lead from landfill waste into the aqueous environment

6.2.1 Background

The study of leachability of lead is important to understand the behaviour of any lead in waste containing a high organic content. High concentrations of acetate may cause mobilisation of lead into the aqueous environment, this would then have the potential to contaminate rivers and surface waters.

6.2.1.1.Occurrence of Lead

Lead occurs chiefly as sulphide in galena, which is one of the most widely distributed of the metal sulphides. In the British Isles lead is generally obtained from veins in carboniferous rocks. The ore has some zinc and about 3ozs of silver per ton. The lead content of the ore as mined varies, generally it is more than 5%. The average concentration in rocks is 13mg kg^{-1} and in soils is 20 mg kg^{-1}. Natural mobilisation of lead into the environment occurs principally from

Figure 6.3

Chromatogram - Calibration for Acetates

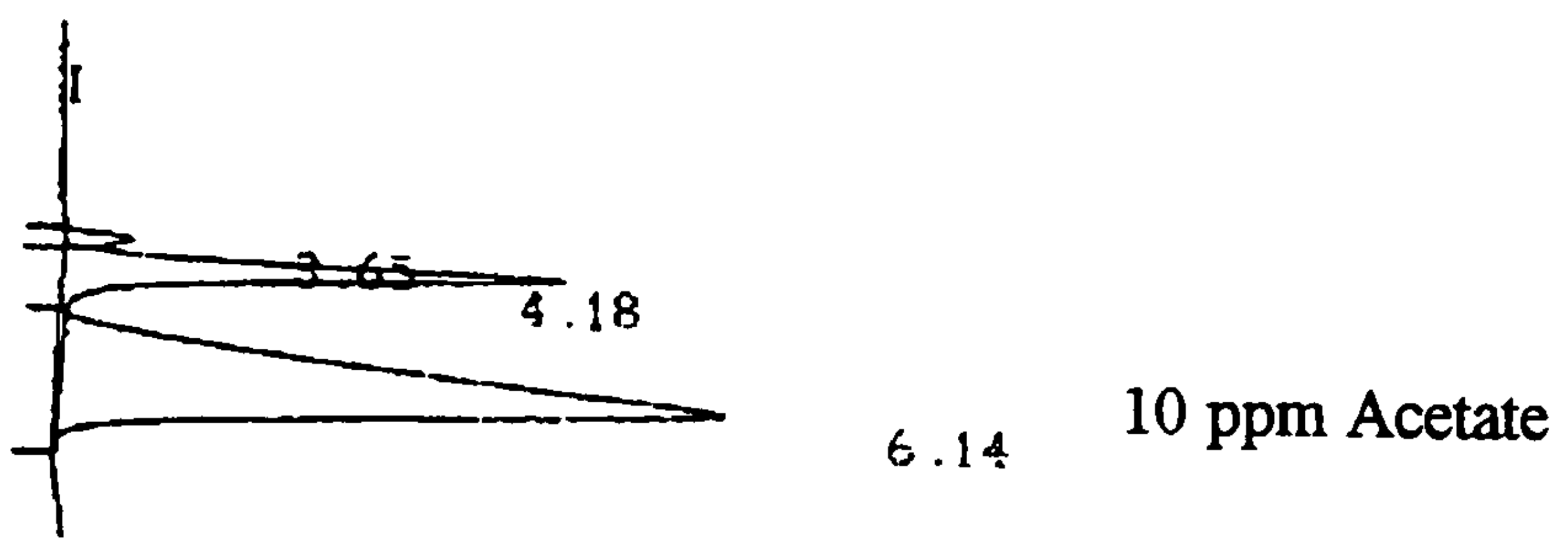


Figure 6.4

Chromatogram - 5 Times Diluted Sample A1 with 10 ppm Acetate Standard

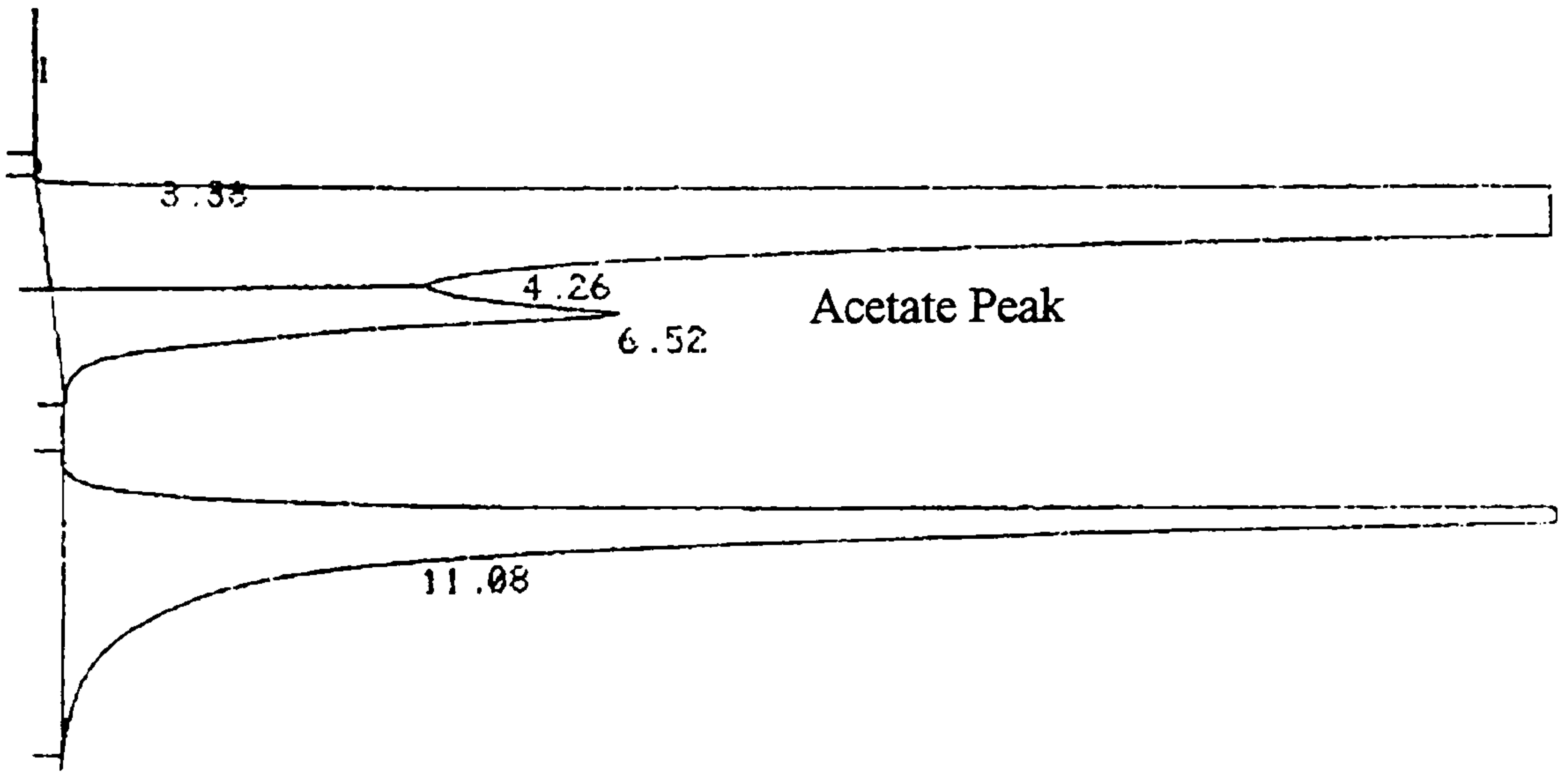


Figure 6.5 The graph below is calibration for acetate determination.

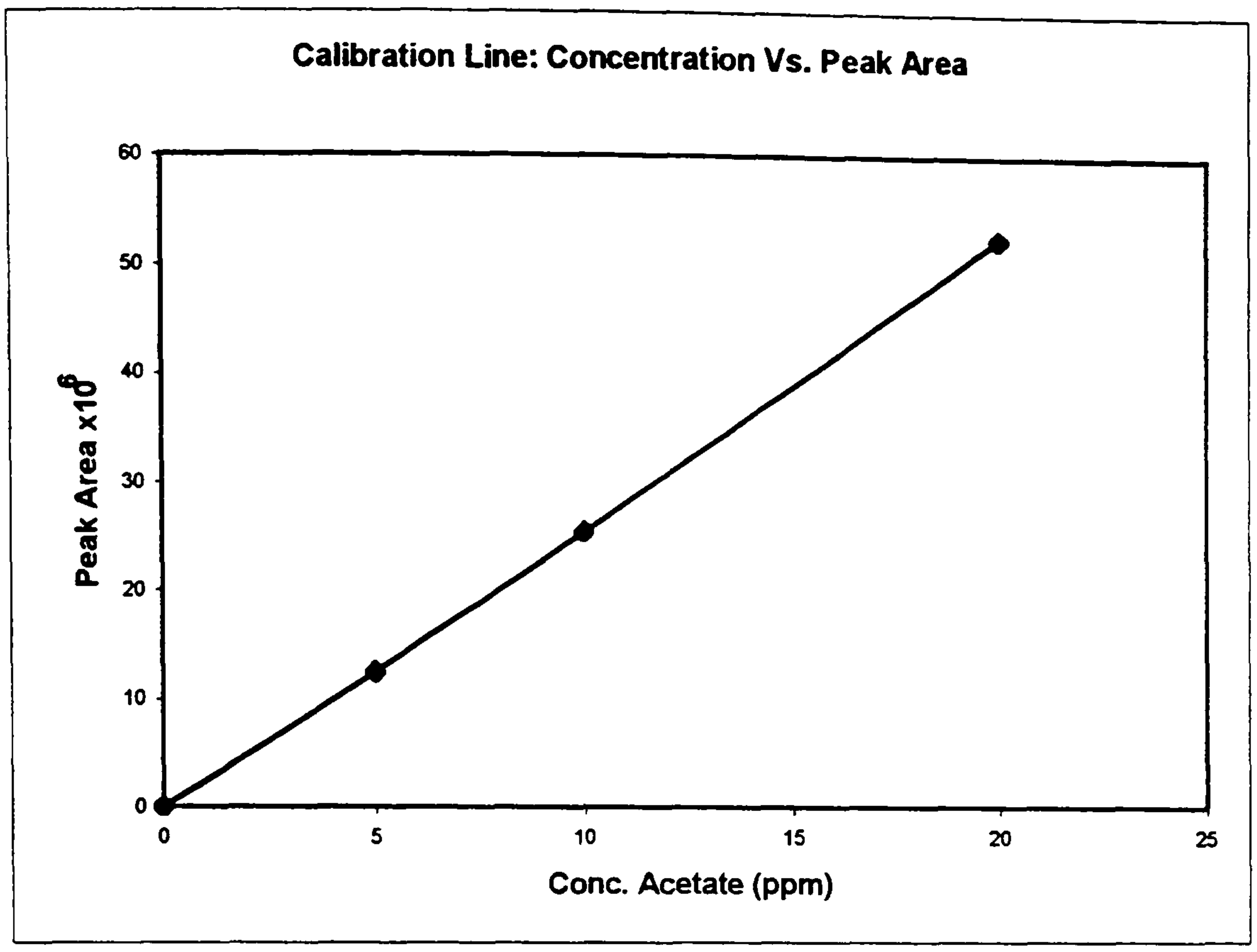
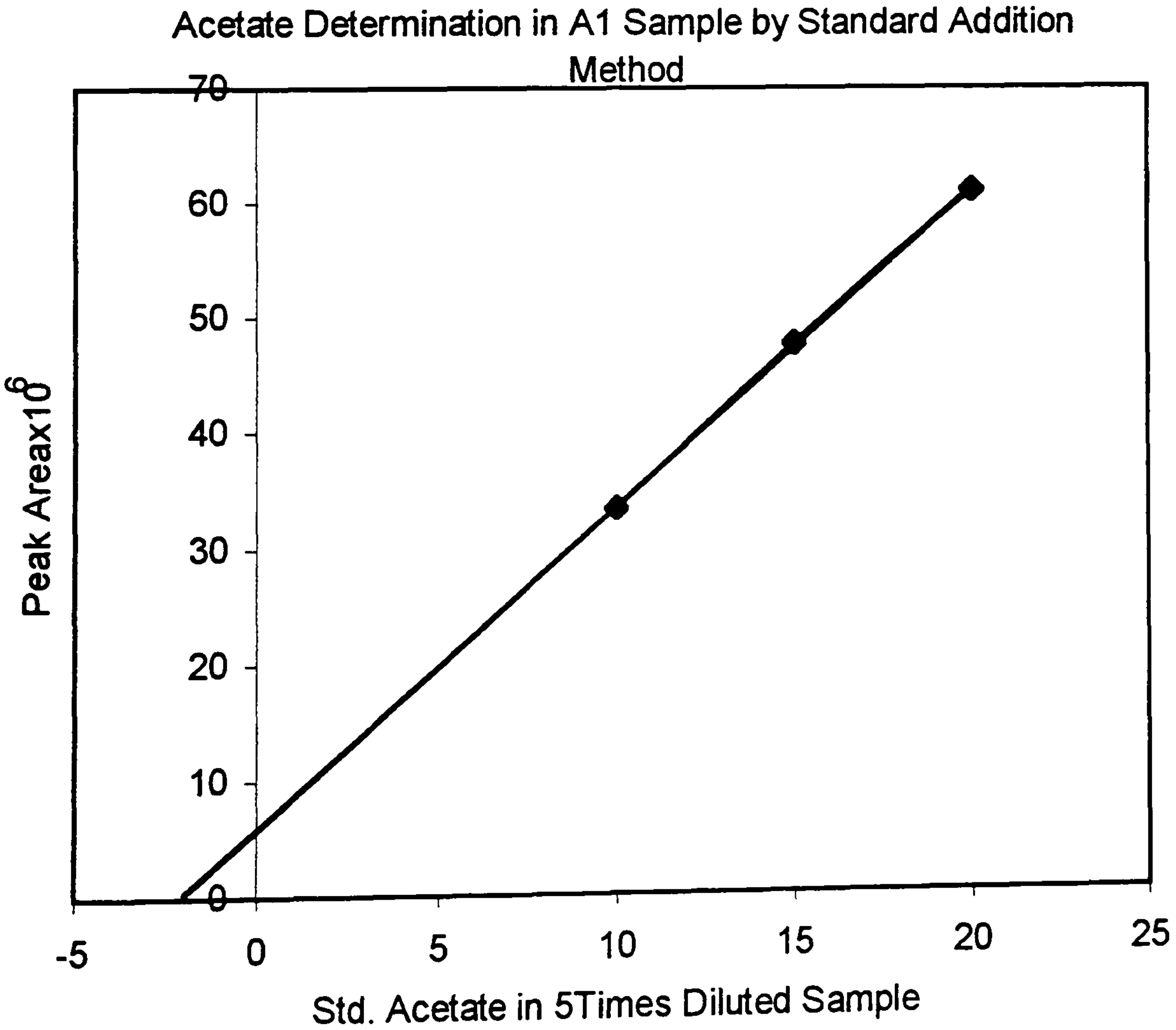


Figure 6.6



the erosion of lead-containing rocks and through gaseous emissions during volcanic activity.

6.2.1.2.Uses of Lead

Lead was first used to produce water pipes in Roman times, and until the 1950's was still used extensively in the UK. Since then lead pipes have been largely replaced by copper ones. At pH greater than 7, lead pipes obtain protection against dissolution of lead by the formation of lead, calcium and magnesium carbonates protective coating.

6.2.1.3.Toxicity of Lead

Lead is a cumulative poison. About 90% of the lead[6] retained in the body enters the bones, from which it can be remobilised. WHO recommends a maximum intake of 3mg lead per person per week. Children and infants should have intakes of less than 1 mg lead per week. The average rate of absorption of dietary lead is about 8%, but about 40% of the fine particulate lead retained in the lungs are absorbed. The absorbed lead enters the blood stream where over 90% is bound to the red blood cells with a mean residence time of 1 month. Bones act as the major reservoir for lead in the body and the residence time is 40-90 years in adult.

Lead binds strongly to a large number of molecules, such as amino acids, haemoglobin, many enzymes, RNA, and DNA, it thus disrupts many metabolic pathways. The effects of lead toxicity are very wide ranging and include impaired blood synthesis, hypertension, hyperactivity and brain damage.

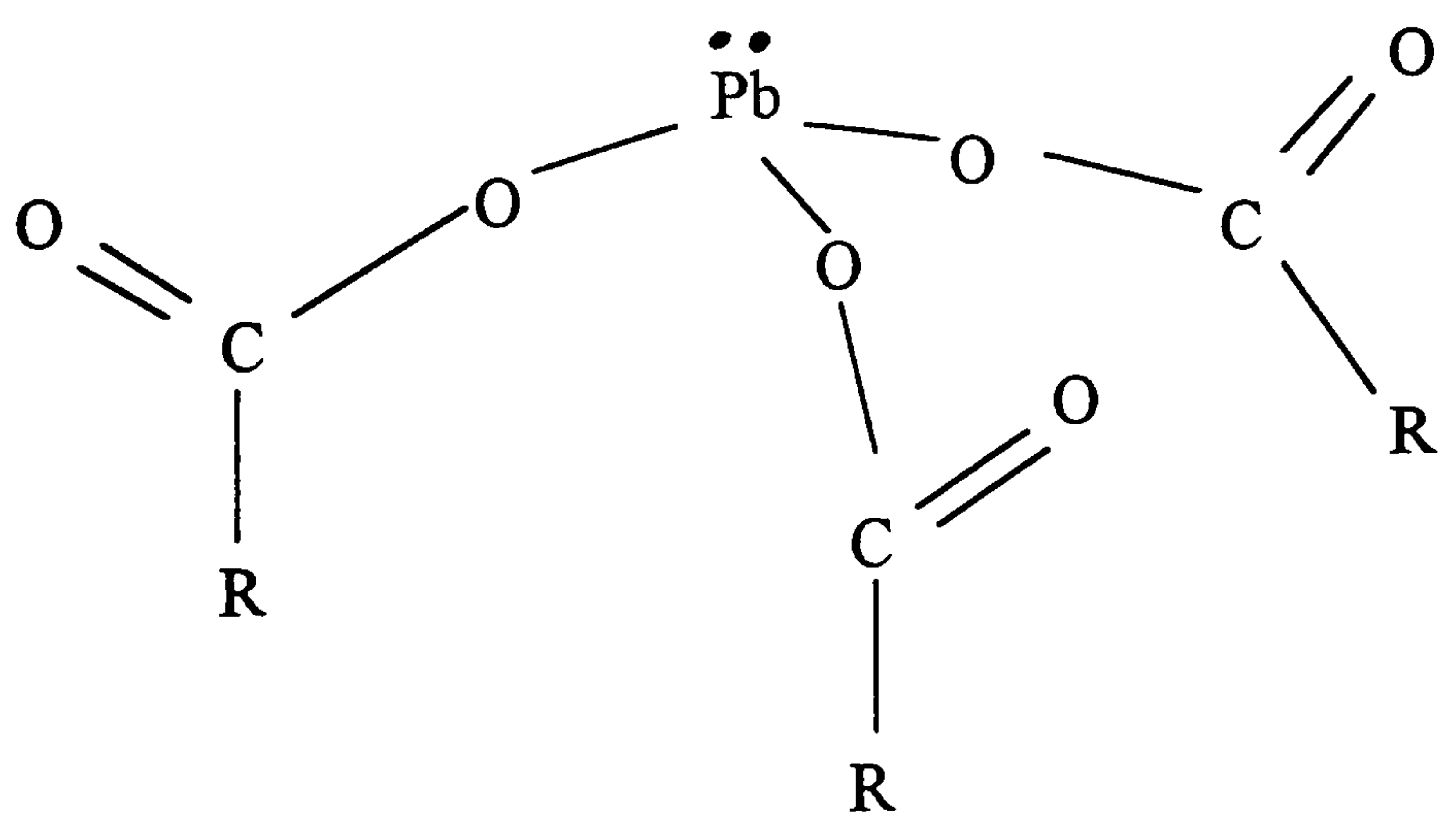
6.2.1.4.Limits of Lead in Water

The EC limit for lead in drinking water is 50μg dm^{-3}, but, the WHO recommends[6] that the limit should be reduced to 10μg dm^{-3}

6.2.2. Chemical Properties of Lead

The metal resists the action of sulphuric and hydrochloric acids and yet it is readily attacked by weak organic acids - like acetic acid. It is slowly dissolved by water and is very susceptible to corrosion by the action of moist air. Lead - Pb, is a metal and is commonly available. It has oxidation states II and IV. The II state is the stable oxidation state, the IV state of lead is strongly oxidising. Under many conditions lead has low mobility in the environment and particularly in soil. The reason for this is the very low solubility of most compounds of lead including oxide, carbonate, sulphate, phosphate and basic lead salt that result from preparation of complex hydroxide ions such as $Pb_4(OH)^{4+}$. The only situation in which lead can be readily mobilised in the environment is when weak organic acid anions such as acetate are present. Under these conditions lead forms the very stable and very soluble tricarboxylatolead[7] (II) ion $Pb(R.CO_2)_3^-$.

Structure of $Pb(R.CO_2)_3^-$ Ion



For this reason it is important to study the effect of acetate in landfill leachate on lead mobility.

6.2.3. Methodology - Leachability Tests

The procedure followed for this experiment is based on 'Leachability Test Method for Solid Waste Materials' - a Canadian method by Brian Smith, Natural Resources Canada - Private communications (Appendix C). The adopted method is modified version of the above method and it is as follows:

The groundwater sample used for this experiment was taken from borehole B3, a Class IV borehole. The analytical results for the groundwater are in Tables 4.11 to 4.13.

10 g of the lead compound were weighed and placed in a 250ml capacity HDPE sample bottle. 160 ml of groundwater were added to the solid material and the bottle shaken for 15 minutes before the pH was measured using a pH meter calibrated at pH4 and pH7 whilst the sample was stirred. The pH was adjusted to within ±0.02 of that required (pH5.5, 6.0, 6.5, 7.0 and 7.5) with 2M acetic acid or sodium acetate. The sample was then shaken using a mechanical shaker for a further 24 hours. The pH of each sample was measured at intervals after the start of 1, 3, 6 and 22 hours and adjusted again if necessary.

After 24 hours, the groundwater was added to make up to 250 ml in a volumetric flask. The sample of leachate liquor was then filtered and it was kept refrigerated until analysed. Each compound was sampled in triplicate and the method repeated for pH 5.5, 6.0, 6.5, 7.0, and 7.5. Blank solutions of groundwater with no lead compound added were also prepared for each pH and run along side each of the three compounds.

The compounds investigated were lead carbonate, freshly precipitated, the first basic salt to be precipitated from a solution of lead nitrate on the addition of sodium hydroxide and lead oxide.

Preparation of lead carbonate

A 1 mol dm^{-3} solution of lead II nitrate in de-ionised water was prepared and mixed in equal quantities with a 1 mol dm^{-3} sodium carbonate solution in deionised water. The white precipitate formed was filtered off and dried in an oven at 50°C. The lead carbonate was then ground to a fine powder before it was used.

Preparation of Basic Salt from Lead Nitrate

The first precipitate obtained from a lead (II) nitrate solution on the addition of sodium hydroxide has been identified as $[Pb_4(OH)_4]\ [NO_3]_4$. The precipitate was prepared according to the procedure[8]. A 1 mol dm^{-3} solution of lead nitrate in deionised water was prepared and a 1 mol dm^{-3} sodium hydroxide solution added to it gradually whilst the pH was measured. Sodium hydroxide was added until the pH reached and stabilised at pH 5.25. The precipitate was filtered off, washed with absolute ethanol and dried in an oven at 80°C. The $[Pb_4(OH)_4][NO_3]_4$ was then ground into fine powder before it was used for the leachability test.

Determination of Lead in Solutions: Lead in the leachate liquor was determined by Atomic Absorption Spectroscopy. The procedure is described in Section 3.3.4

6.3. Results

6.3.1. Results of Acetate in Groundwater Samples

The results of acetate in Class IV groundwater samples are presented in Table 6.1.

Table 6.1 Acetate Concentrations in Groundwater Samples

Sample No.	Acetate Concentration (ppm)
A1	11
A2	7.5
B3	6.25

These results are discussed in chapter VII.

6.3.2. Results of Leachability Tests of Lead Salts in Acetic Acid Medium from pH 5.5 to 7.5

The lead concentrations in various test solutions are presented in Tables 6.2 to 6.4. The results from 'blank' test samples indicate the background levels of lead in leachate samples.

In order to compare each set of results, the amount of lead leached into the groundwater sample is converted to percentage of lead leached from each lead salt. The graph in figure 6.11 shows the effect of pH on the amount of lead leached from the three compounds tested.

6.3.2.1 Lead Carbonate - $2PbCO_3.Pb(OH)_2$ Results

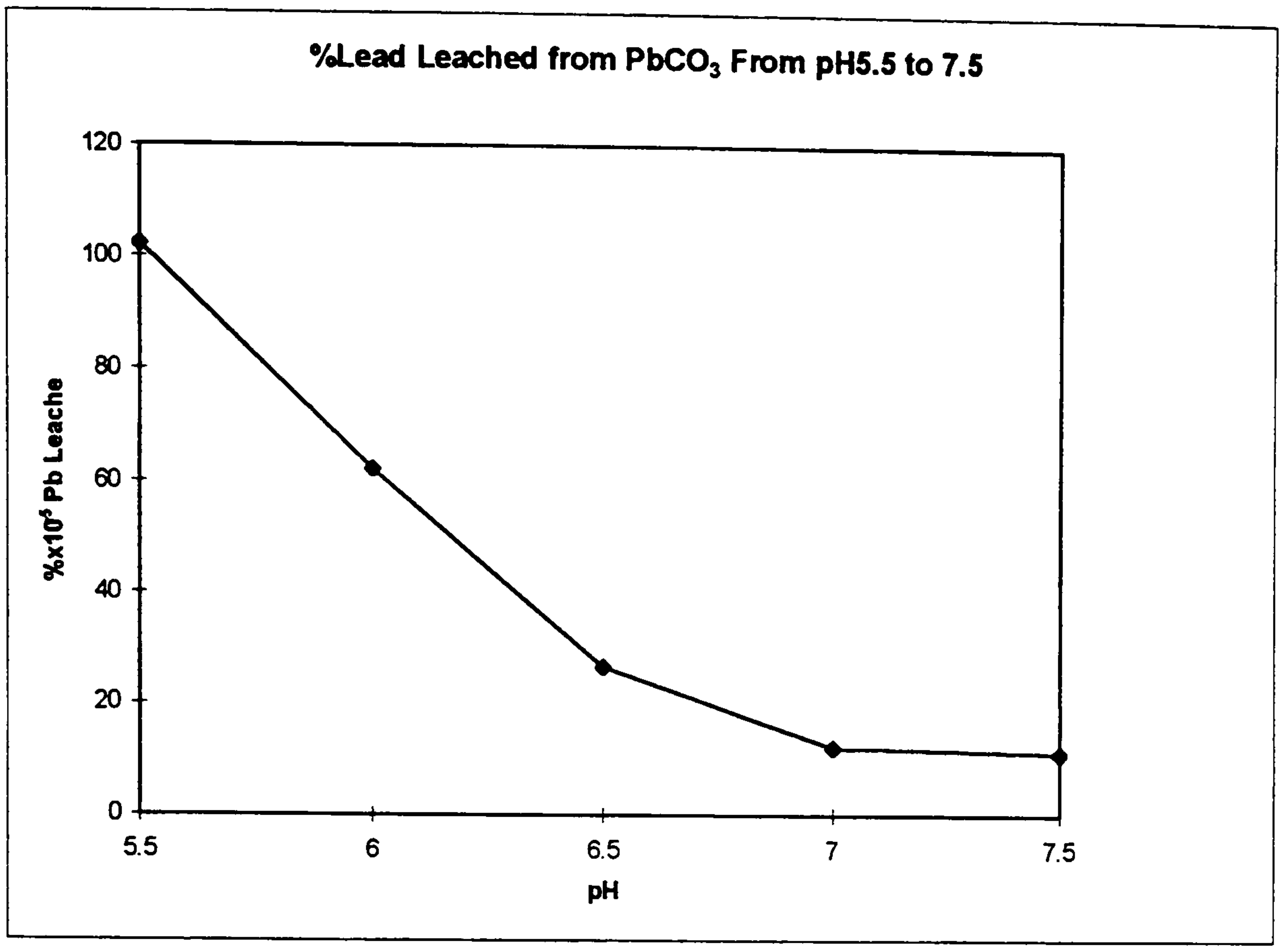
Results of leaching experiment using lead carbonate and groundwater at pH 5.5, 6, 6.5, 7 and 7.5 are presented in Table 6.2

Table 6.2 Results of Leaching Experiments Using Lead Carbonate

Sample Number	Weight of Lead carbonate (g)	pH	Pb in Leachate (ppm)	Pb in leachate less blank (ppm)	Mean Pb in Leachate (ppm)	% Pb Leached $x10^{-5}$	Mean% Pb leached $x10^{-5}$
1	10.0028	5.5	0.53	0.4	0.31	133.33	102.2
2	10.0039		0.37	0.24		79.97	
3	09.9994		0.41	0.28		93.34	
Blank	-		0.13	-			
4	10.0004	6.0	0.33	0.19	0.19	63.33	62.2
5	10.0013		0.37	0.23		76.66	
6	10.0078		0.28	0.14		46.63	
Blank	-		0.14	-			
7	10.0023	6.5	0.20	0.08	0.08	26.66	26.6
8	10.0061		0.22	0.1		33.3	
9	10.0009		0.18	0.06		19.99	
Blank	-		0.12	-			
10	10.0017	7.0	0.15	0.03	0.04	16.66	12.2
11	10.0039		0.17	0.05		10.0	
12	10.0042		0.15	0.03		6.66	
Blank	-		0.12	-			
13	10.0072	7.5	0.13	0.02	0.03	6.66	11.1
14	10.0061		0.14	0.03		9.99	
15	10.0023		0.16	0.05		16.66	
Blank	-		0.11	-			

The graph in Figure 6.7 illustrates the percentage of $PbCO_3$ leached from pH 5.5 to 7.5.

Figure 6.7 Percentage of Pb Leached from $PbCO_3$ from pH 5.5 to 7.5



6.3.2.2 Basic Lead Nitrate $[Pb_4(OH)_4][NO_3]_4$ Results

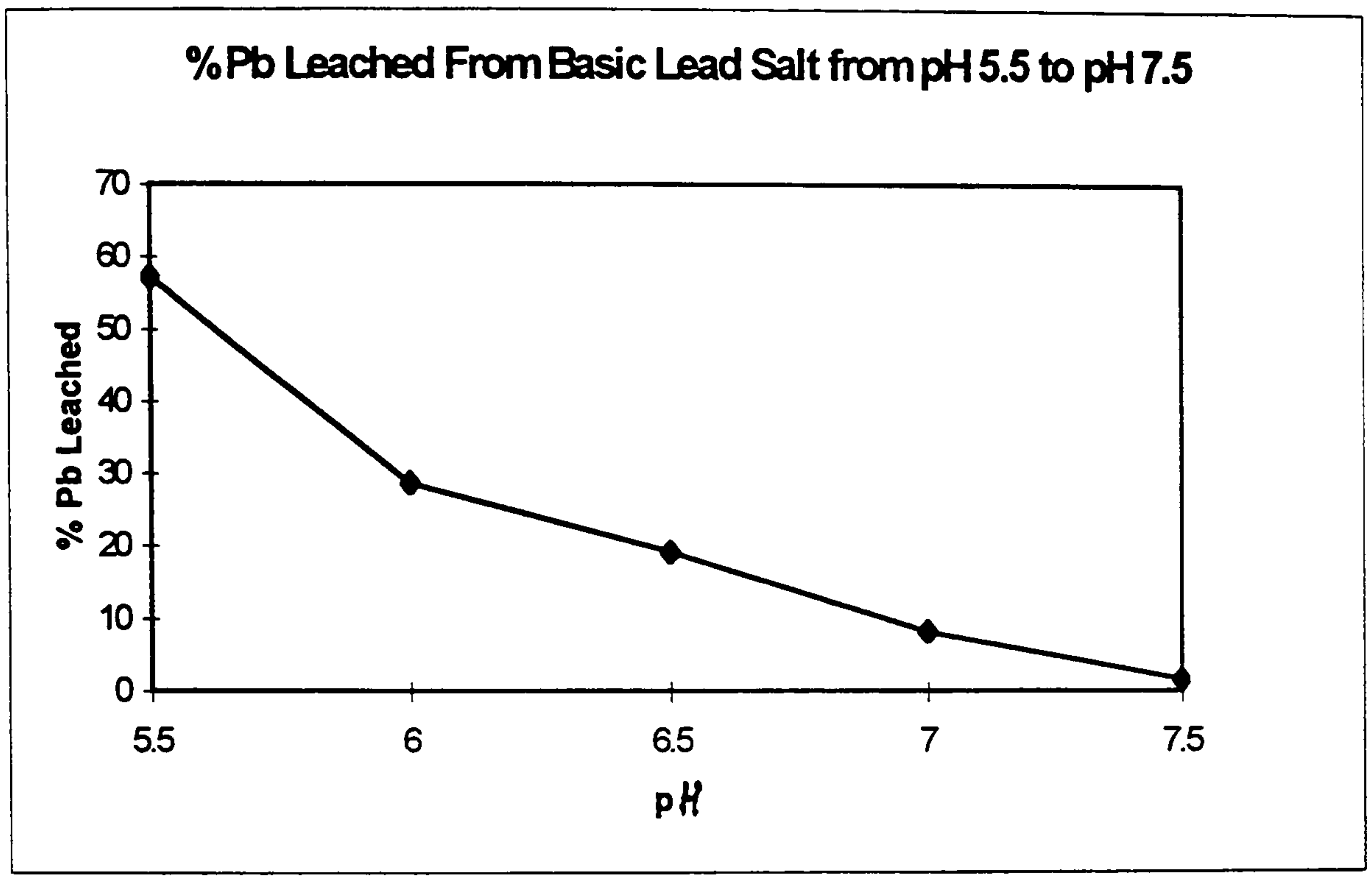
Results of leachability experiment using basic lead salt from lead nitrate from pH 5.5 to 7.5 are presented in Table 6.3.

Table 6.3 Results of Leachability Experiments using Basic Lead Salt

Sample Number	Weight of Basic Lead Salt (g)	pH	Pb in Leachate (ppm)	Pb in leachate less blank (ppm)	Mean Pb in Leachate (ppm)	% Pb Leached	Mean% Pb leached
16	10.0021	5.5	16420	16419.85	16609.8	56.6940	57.4
17	9.9993		16800	16799.85		58.0230	
Blank	-		0.15				
18	10.0007	6.0	7280	7279.87	8309.9	25.1398	28.7
19	10.0044		9340	9339.87		32.2416	
Blank	-		0.13				
20	10.0016	6.5	5800	5799.88	5549.9	20.0272	19.2
21	10.0041		5300	5299.88		18.2960	
Blank	-		0.12				
22	10.0018	7.0	2400	2399.88	2379.9	8.2870	8.2
23	10.0025		2360	2359.88		8.1483	
Blank	-		0.12				
24	10.0060	7.5	512	511.86	456.5	1.7670	1.6
25	10.0034		401.2	401.06		1.3851	
Blank	-		0.14				

The graph in Figure 6.8 illustrates the percentage of lead leached from basic lead salt from pH 5.5 to 7.5.

Figure 6.8 Percentage of Pb Leached from Basic Lead Salt from pH 5.5 to 7.5.



The graph in figure 6.9 illustrates the percentage of lead leached from lead oxide from pH 5.5 to 7.5, and the graph in figure 6.10 illustrates the amount of lead leached from PbO from pH 6 to 7.5.

6.3.2.3 Lead Oxide Test Results

Results of leachability experiments using lead oxide from pH5.5 to 7.5 are presented in Table 6.6

Table 6.6 Leaching Experiments using Lead Oxide from pH 5.5 to 7.5

Sample Number	Weight of Lead Oxide (g)	pH	Pb in Leachate (ppm)	Pb in leachate less blank (ppm)	Mean Pb Leached (ppm)	% Pb Leached	Mean% Pb leached
26	9.9971	5.5	22300	22299.89	24773.2	60.07	66.7
27	10.0093		26860	26859.89		72.27	
28	9.9974		25160	25159.89		67.77	
Blank	-		0.11				
29	10.0087	6.0	0.51	0.39	0.48	104.94x10^{-5}	129.3x10^{-5}
30	9.9970		0.60	0.48		129.31x10^{-5}	
31	9.9971		0.69	0.57		153.55x10^{-5}	
Blank	-		0.12				
32	10.0059	6.5	0.31	0.17	0.15	45.76x10^{-5}	40.4x10^{-5}
33	10.0061		0.30	0.16		43.06x10^{-5}	
34	10.0009		0.26	0.12		32.31x10^{-5}	
Blank	-		0.14				
35	9.9986	7.0	0.26	0.13	0.10	35.01x10^{-5}	27.8x10^{-5}
36	10.0037		0.19	0.06		16.15x10^{-5}	
37	10.0076		0.25	0.12		32.30x10^{-5}	
Blank	-		0.13				
38	10.0044	7.5	0.09	-0.02	0.003	0.0	2.7x10^{-5}
39	9.9985		0.11	0.0		0.0	
40	10.0070		0.14	0.03		8.1x10^{-5}	
Blank	-		0.11				

Figure 6.9 illustrates the percentage of lead leached from pH 5.5 to 7.5 and Figure 6.10 illustrates the percentage of lead leached from PbO from pH 6 to 7.5.

Figure 6.9 Percentage of Pb leached from Lead Oxide from pH 5.5

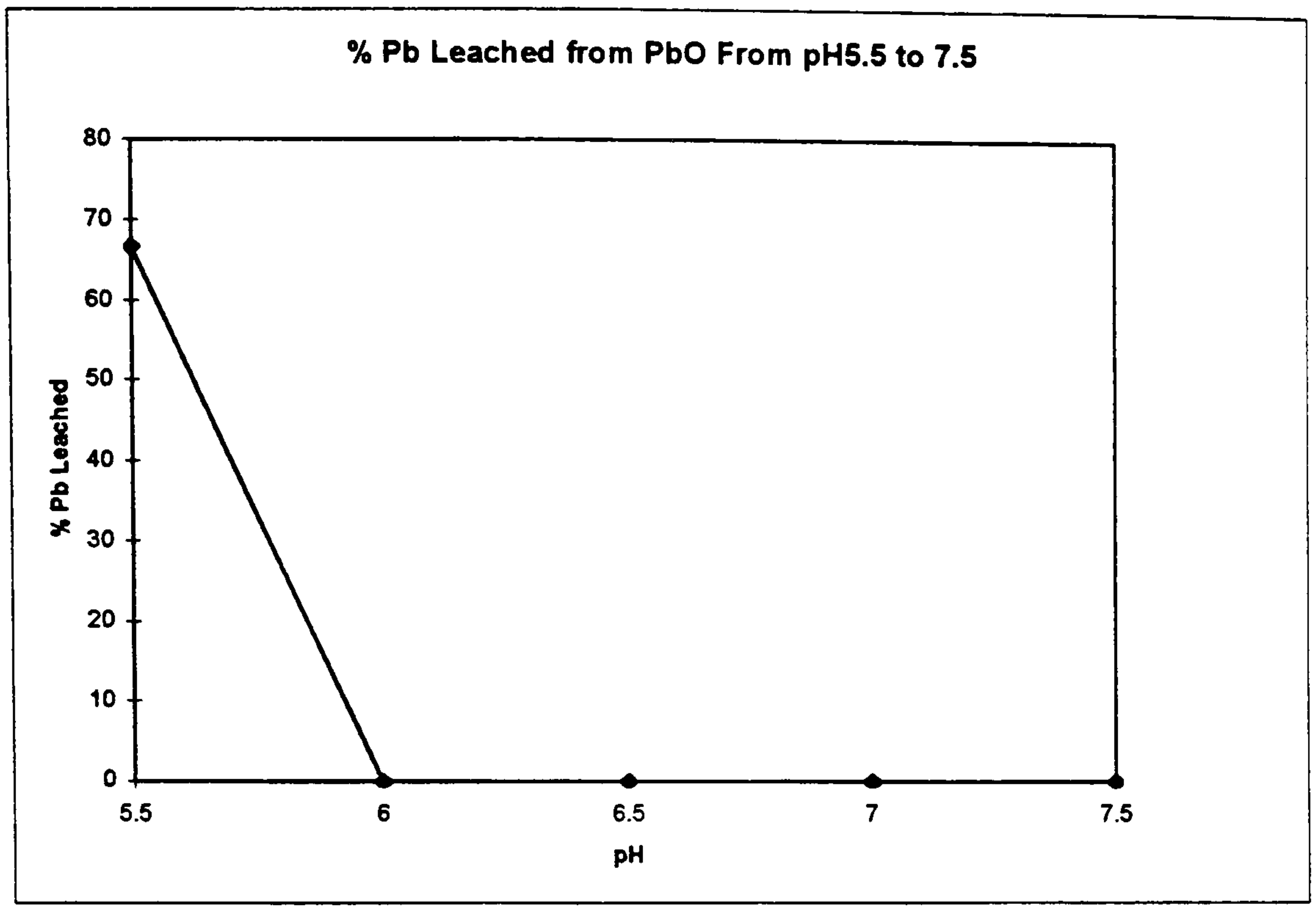
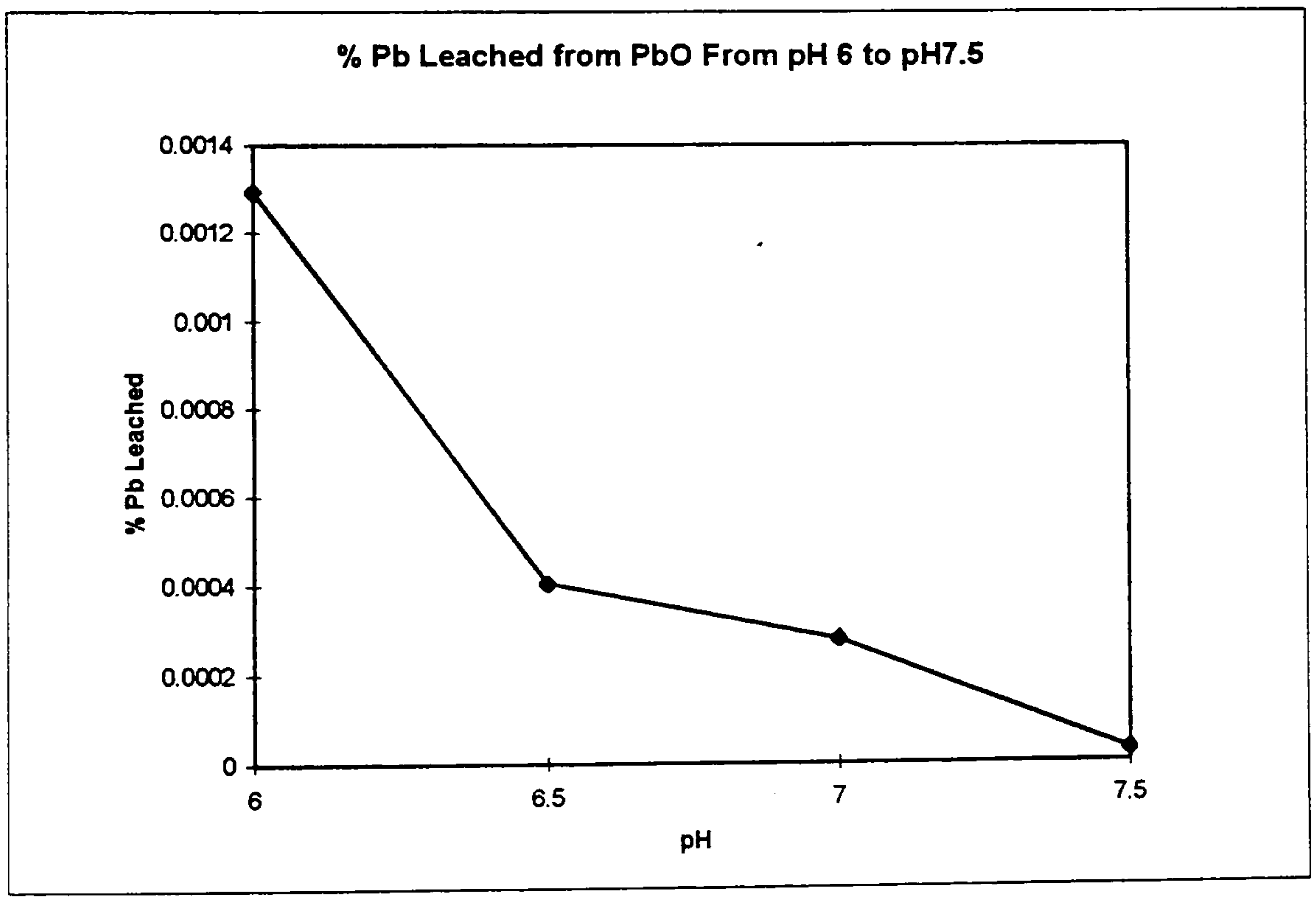
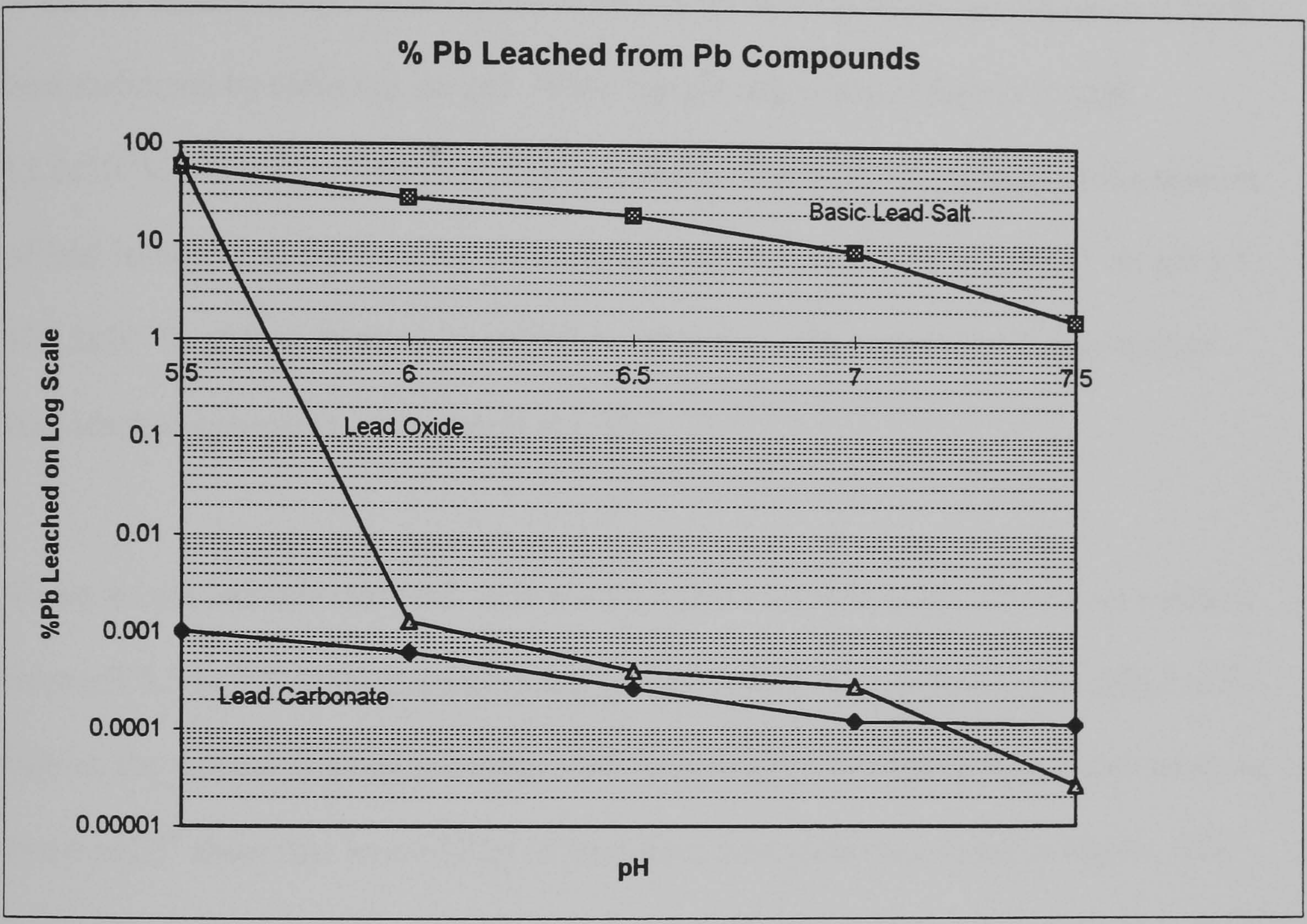


Figure 6.10 Percentage of Pb Leached from pH 6 to 7.5



The graph in Figure 6.11 shows the percentage of lead leached from the three lead compounds tested.

Figure 6.11



6.3.3 Discussion of Results on Leaching Experiments with Acetic Acid using Lead Salts:

6.3.3.1 Lead Carbonate

Figure 6.7 illustrates that the maximum amount of lead leached from lead carbonate at pH 5.5 was only 102.2x10^{-5}%. Although only a trace amount, it is clear from the graph in Figure 6.7 that the percentage of lead leached into the aqueous medium increased as the pH of groundwater was reduced by adding acetic acid. At pH 7.5 only 11.1x10^{-5} % lead leached into the groundwater. At pH7 12.2x10^{-5}% of lead leached into the groundwater sample. This is only an increase of 10% in the amount of lead leached when the pH of the test solution was decreased from pH 7.5 to pH7. At a lower pH of 6.5, 26.6x10^{-5}% of lead leached into the aqueous medium; this is relatively significant increase (increase by 118%) in the amount of lead leached from lead carbonate by reducing the pH. When the pH was reduced further to pH6, 62.2x10^{-5}% of lead leached from lead carbonate. This is 134% increase in the amount of lead leached into the aqueous medium compared to the result at pH 6.5. At pH 5.5 102.2x10^{-5}% of lead leached from $PbCO_3$. This is a 64% increase in the amount of lead leached compared to the result at pH6.

These results indicate that lead carbonate is quite insoluble in the acetic acid medium from pH 5.5 to 7.5. Only trace amounts of lead from $PbCO_3$ is leached at pH5.5 to 7.5 values, the amount leached increases with reducing pH. Recent similar experiments at lower pH 5[9] show that leachability of lead from lead carbonate is much higher. 310 mg/L of lead leached into aqueous medium, where as at pH5.5 in this work only 0.31 ppm lead leached into the leachate solution.

6.3.3.2. Basic Lead Nitrate $[Pb_4(OH)_4] [NO_3]_4$

Figure 6.8 illustrates that solubility of basic lead nitrate is quite high in the groundwater at landfill pH, i.e., 5.5 to 7.5. The solubility of salt increases tremendously as the pH reduces from 7.5 to 5.5.

At pH 7.5 only 1.6% of the Basic Lead Nitrate dissolves in the groundwater. The amount of Basic Lead Nitrate dissolved increases to 8.2% at pH 7. This is as an increase by 412% from solubility at pH 7.5. At pH 6.5, the solubility of basic lead nitrate increased to 19.2%. This is an increase by 134% in the solubility of basic lead nitrate compared to the value at pH7. On further reducing the pH of the groundwater to pH 6, the solubility of basic lead nitrate increased to 28.7%, which is an increase by 49% from the value at pH6.5. At pH5.5 the amount of basic lead nitrate dissolved in groundwater increased to 57.4%. In this case the amount of basic lead nitrate leached into the groundwater increased by 100% compared to the value at pH6.

Basic lead nitrate is highly mobile under the groundwater conditions between pH 5.5 to 7.5. If lead is present in the form of basic lead nitrate in landfill waste, or if conditions were right for basic lead nitrate to be formed under the landfill waste conditions, then lead would easily leach into the aqueous medium to affect the environment.

6.3.3.3 Leachability Experiments with Lead Oxide

Figures 6.9 and 6.10 illustrates that the maximum amount of lead leached was from PbO at pH 5.5 when 66.7% of lead leached into the groundwater. From pH 6 to pH7.5 only trace amounts of lead leached into the solution. The increase in the amount of lead leached as pH reduced from pH7.5 to 5.5 is as follows.

As the pH of the groundwater test solution was reduced from pH7.5 to pH7, the amount of lead leached from PbO increased from $2.7\text{x}10^{-5}\%$ to $27.8\text{x}10^{-5}\%$. This amounts to an increase by 930% in the amount of lead leached compared to the value at pH7.5. On further reducing the pH of the test solution to pH6.5, the amount of lead leached from PbO increased to 40.4×10^{-5}%. This is an increase by 45% in the amount of lead leached compared to the value at pH7. On further reducing the pH from 6.5 to 6, the amount of lead leached increased from 40.4×10^{-5}% to 129.3×10^{-5}%. This is an increase by 220% in the amount of lead leached compared to the value at pH6.5. On reducing the pH further to pH 5.5, the amount of lead leached increased to 66.7%. This is an increase by 52×10^{5}% in the amount of lead leached.

These results indicate that if Lead Oxide is present in the landfill waste at pH5.5, 66.7% of lead would leach from the PbO and it could cause significant contamination in the aqueous environment. At pH more than 5.5 only trace amounts of lead would leach from PbO, therefore the lead would be quite immobile and would not affect the environment.

From the graph in figure 6.11, it is clear that lead in the form of lead carbonate is fairly insoluble from pH5.5 to 7.5. It dissolves only in trace amounts in landfill environment from pH5.5 to 7.5. However, recent experiments[9] carried out at pH 5 show that lead from $PbCO_3$ in acetic acid medium is highly mobile. For example, at pH 5, 310 mg/L of Pb leached into the aqueous phase. This indicates that Pb in the form of carbonate would have the potential to leach from waste containing high organic content in the Stage III or Acetogenic Phase of waste biodegradation.

PbO would leach into the landfill leachate in the presence of high amounts of acetic acid at pH5.5, because under the experimental conditions, 67% of Pb leached into the leachate solution. This is the maximum amount of lead leached under the experimental conditions in the leaching experiments. From pH6 to pH7.5 only trace amounts of lead from PbO is leached, hence, at pH 6 to pH7.5 range in landfill environment PbO would be quite immobile and is not expected to pose any risk hazard on the aqueous environment.

Basic Lead Salt, $[Pb_4(OH)_4]\,[NO_3]_4$, if present or formed in the landfill waste would have greatest impact on contaminating groundwater at landfill pH range from pH5.5 to pH7.5; PbO at pH5.5 and Lead Carbonate at pH5 would have the greatest implications on contaminating environment through groundwater pathways. It could target surface and river waters and would have the potential to contaminate the potable water supplies. Lead could also be taken up by plants and hence could target the human food source through contaminated plants and vegetables.

6.3.4 Conclusions of Leachability Tests.

Although lead salts are fairly insoluble, in a landfill situation where the waste contains mixed waste with high proportions of putrescible and organic content, and the landfill is in the Acetogenic Phase or Stage III of waste biodegradation, then one may expect high concentrations of organic acids, such as acetic acid. Under such conditions soluble lead acetate as $Pb(CH_3CO_2)_3^-$ is formed and the mobility of lead is expected to be high. This situation would have the implications of contaminating the groundwater with heavy metals such as lead.

6.4 References

1. DoE, Waste management Paper 26B, "Landfill Design, Construction and Operational Practice", HMSO, London, 1995.
2. Prescott L. M., Harley J. P., Klein D. A., "Microbiology" Fourth Edition, Mc Graw Hill 1999.
3. Barlaz M. A., Schaefer D. M., Ham R. K., Bacterial Population Development and Chemical Characteristics of Refuse Decomposition in a Simulated sanitary landfill, *Applied and Environmental Microbiology,* 1989, **55**,(1), 55-65.
4. Wagner C., Griebhammer A., Drake H. L., Acetogenic Capacities and the Anaerobic Turnover of Carbon in a Kansas Prairie Soil, *Applied and Environmental Microbiolgy,* 1996, **62**, 494-500.
5. Schlegel H. G., "General Microbiology", Cambridge University Press 1986.
6. O'Neill P., "Environmental Chemistry", Second Edition, Chapman and Hall, London, 1993.
7. Donaldson J. D., Grimes S. M., Reviews on Silicon, Germanium, Tin and Lead Compounds, *A Quarterly Review, Lone pair Effects in Tin (II) Chemistry,* Freund Publishing House Ltd., Tel.Aviv, Israel, 1984, **VIII**, (1), 1-132.
8. Grimes S. M., Johnston S. R., Abrahams I., Characterisation of the Predominant Low-pH Lead (II)-Hydroxo Cation, $Pb_4(OH)_4^{4+}$; Crystal Structure of $[Pb_4(OH)_4][NO_3]_4$ and the Implications of Basic Salt Formation on the Transport of Lead in the Aqueous Environment, *J. Chem. Soc. Dalton Trans.* 1995, 2081-2086.
9. Hussain Z., PhD Thesis, Brunel University, 1999.

CHAPTER VII

DISCUSSION OF BOREHOLE QUALITY RESULTS

CHAPTER VII

DISCUSSION OF BOREHOLE QUALITY RESULTS

7.0 Discussion of Results

The results described in Chapters IV and V are discussed in this chapter in terms of borehole characterisation under the headings:

- Relationship between Historical Site Knowledge and Pollutant Concentration.
- Groundwater Quality Assessments.
- Groundwater Quality Assessment Scale and Characterisation of the Borehole Samples.
- Testing of Groundwater Quality Assessment Scale.
- Relationship between Landfill Gas and Groundwater Quality.
- Proportion of sites in LB Hounslow with Low, Moderate and High Level of Contamination.
- Risk assessment of High Contamination Rating (15) Boreholes by Comparing COD Results with Results from Elsewhere in the Country
- Risk Assessment Using 'Source - Pathway - Target' Framework.

7.1 Relationship between Historical Site Knowledge and Pollutant Concentration

The historical site classifications i.e. Class I, II, III and IV Sites are defined in chapter IV with Class I sites being the least polluted. The results in table 4.14 indicate that there is a definite increase in concentrations of the tested analytes from Class I samples to Class IV samples. Each of the analytes is considered separately.

Methane: Methane results show that in Class I Sites (virgin ground and perimeter of more than 50 years old landfill sites), no methane was detected in the last 3 years. In Class II sites (boreholes within more than 50 years old landfill sites), methane levels ranged from 0 to 1 % by volume. In Class III sites (boreholes in the perimeter of highly gassing and more recent landfill sites), up to 24% methane was detected; and in Class IV sites (boreholes within highly gassing landfill sites), the methane concentrations up to 69% volume were detected.

Carbon dioxide: CO_2 levels in Class I sites range from 0.2% to 2%v; up to 7.5% v in Class II Sites; up to 15% in Class III Sites and up to 26% in Class IV Sites. An increase in the levels of carbon dioxide from Class I to Class IV sites is clearly evident.

Carbon dioxide can originate from sources other than landfill gas, such as oxidation of organic materials in soil, respiration of living animals and plants (roots etc.) in the soil. High levels of carbon dioxide in landfills with low levels of methane can signify that a landfill has nearly stabilised. This is particularly true of Class II landfill sites where high levels of carbon dioxide with low levels of methane are noticed.

pH: pH generally remained near neutral, except in two samples where pH was found to be low. Sample A1 has pH 5.5 which is from a recently filled site (10 years old) and it is possibly in the pre or early methanogenic stage, hence a low pH is to be expected. Sample J2 has pH5.9 and it is from the perimeter of a landfill site and is more than 60 years old. It is possible that low pH is due to a more local contamination rather than the landfill. Most of the landfill sites in Hounslow are more than 30 years old, therefore, near neutral pH is as expected of old landfill sites in either Stage IV (methanogenic) or Stage V (aerobic) of landfill biodegradation.

Conductivity: is up to 682 µs/cm in Class I sites; 806 to 1934 µs/cm in Class II sites; up to 1725 µs/cm in Class III sites and 1560 to 2930 µs/cm in class IV sites. There is a clear trend in conductivity increase from class I to class IV sites. Conductivity levels relate to inorganic contamination, hence, it is a straightforward method of getting an indication of the level of inorganic contamination by using portable equipment.

ORP: ORP (Oxidation-Reduction Potential) was found to be lowest in Class IV sites, it was -166mv in sample number A5. The ORP readings were found to be generally positive to slightly negative in old landfill sites, and highly negative in Class IV sites where the landfill environment is anaerobic. This is again an easy method of getting an indication of the level contamination on site.

Ammonium-Nitrogen, (NH_4-N): NH_4-N was low, that is up to 0.6ppm in Class I sites; up to 9.5ppm in class II sites; up to 92ppm in class III sites and up to 118 ppm in class IV sites. High levels of ammonia would indicate the presence of proteinaceous material in the fill. Ammonia in groundwater could also be derived from sewage contamination.

Chemical Oxygen Demand (COD): the trend of COD levels from Class I to Class IV shows that the level of COD is up to 88 ppm in Class I samples and up to 287 ppm in Class IV sites. COD is a good indicator of organic contamination in a water sample as described in section. The 'R' value for COD indicates that it is a fairly good single criteria to assess the level of contamination on site when considered on its own.

Total Organic Carbon (TOC): TOC relates to organic carbon in groundwater and is a good indicator of organic contamination in water samples. It is clear from Table 4. 14 that TOC is low in Class I sites, the results in this case range from 3 to 11 ppm. In Class II samples, the TOC results range from 5 to 38 ppm; in Class III results the TOC results range from 12 to 110 ppm and in Class IV samples the results range from 27 to 80 ppm. Abnormally high TOC results can be obtained due to other than landfill contamination, such as, sewage and hydrocarbon contamination i.e., from petroleum products such as fuel oils and industrial solvents from industries such as dry cleaning and car repairs and others. But no abnormally high values were found for the Hounslow boreholes.

Other Anions and Cations: Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2-} are generally lower in Class I and high in Class IV but do not bear a good relation to the class of site. The levels of anions and cations in groundwater samples would depend upon the level of contamination and also the surrounding natural environment. In the final assessment in this work, anions and cations are taken to be represented by electrical conductivity for the groundwater quality assessment.

Heavy Metals: The groundwater samples were tested for Ni^{2+}, Cu^{2+} Cd^{2+}, and Pb^{2+}. Significant levels of the metals were not detected. There may be a number of reasons for these. For example, a) the heavy metals may be present in an insoluble form in the solids and sediments of the site; b) the pH levels are not low enough to extract the metals into the aqueous environment; c) heavy metals are not present in significant quantities in the landfill environment. Further investigations need to be carried out in the landfill sediments to understand this aspect of landfill contamination.

7.2 Groundwater Quality Assessment

A methodology for using the analysis of groundwater samples was developed where a 'Goodness-of-Fit' or 'R' value is worked out using 1 to 15 rating for the results of 47 samples analysed. The goodness of fit between the average ratings and the individual analyte ratings was then determined as a residual function 'R'. The calculations make use of the average rating for each sample. For example, in the case of methane, the 'R' value obtained by using an average of 10 analytes (CH_4, CO_2, EC, NH_4-N, COD, TOC, Cl, Na, K and Ca) is 0.61. But when an average of only 6 main analytes are considered (CH_4, CO_2, EC, NH_4-N, COD, TOC), the 'R' value for methane improved to 0.58.

On using the value for methane in various combinations (nine) with other main analytes, the 'R' value reduced even lower, i.e. in the range from 0.26 to 0.29. The best Goodness-of-Fit value was obtained by using the formula with $3CH_4$, i.e. $3CH_4(\%v) + CO_2(\%v) + EC(\mu s/cm)/100 + NH_4\text{-}N(ppm) + COD(ppm) + TOC\ (ppm)$. Hence, using the formula with 3CH4 is the best means of assessing a borehole for contamination.

Groundwater Quality Assessment by Considering Single Analyte/Factor: It is clear that if a single factor has to be taken into consideration to assess groundwater quality, then, electrical conductivity and COD are fairly good criteria for getting an indication of groundwater quality because these have relatively low 'R' values, 0.3.

If possible, it is better to categorise a site by considering more than one factor or analyte, because numerous factors contribute towards the contamination of a site. Anomalies in high ratings can arise due to contamination from sources other than landfill. For example, a site near a landfill may not be gassing but due to other reasons may be significantly contaminated, as in sample numbers B4 and B2. These two boreholes have no significant landfill gas readings, but ammonia levels are high and this results in a high rating for these boreholes.

Borehole A2 is in a landfill which is approximately 30 years old and is reported to have very high methane readings, but maximum carbon dioxide is reported to be only 5%. This is not a typical landfill gas mixture proportion. There will probably be other factors contributing towards contamination on site. In such instances measuring gas flow rates would have given a good indication of the rate of landfill gas generation, hence, contamination due to landfill sources. By considering numerous factors associated with site contamination, a site can be better categorised with respect to contamination on site.

7.3 Groundwater Quality Assessment Scale and Characterisation of the Groundwater Samples:

The range of values for the formula with $3CH_4$ in ratings 1 to 15 is given in table 7.1. Using this criteria 47 samples analysed were graded 1 to 15 and the results are presented in Table 8.1. This method is found to be the best means for assessing the site for contamination. The values for ratings 1 to 15 are presented in Table 7.1 and this forms a scale against which level of contamination at a site or borehole can be assessed.

Table 7.1

Range of Values for $3CH_4$ Formula, i.e. $3CH_4+CO_2+EC/100+NH_4\text{-}N+COD+TOC$ in Ratings 1 to 15.

Rating	Range of values for $3CH_4$ Formula
1	12 – 50
2	51 – 89
3	90 – 128
4	129 – 167
5	168 – 206
6	207 – 245
7	246 – 284
8	285 – 323
9	324 – 362
10	363 – 401
11	402 – 440
12	441 – 479
13	480 – 518
14	519 – 557
15	558 – 596

7.4 **Testing of Groundwater Quality Assessment Scale:**

Some blind results from an external source and from boreholes in Hounslow were provided by a colleague to assess the level of contamination. From section 5.11 and table 5.21 and using formula with $3CH_4$, the samples SA, SB, SC, SD,SF, SH, SI, and SK were rated 4,2,1,2,1,12,4, and 2 respectively. Each one of these samples is considered separately.

Sample SA: This sample is from a site which is on the perimeter of a landfill site marked No. 38 on LB Hounslow (LBH) plan. This site was filled 33 years ago, the fill consists of black clay fill with brick and concrete to a depth of 4m. The sample is rated 4 using formula 3 value of 140.4. This is the same borehole as sample number I1 in this study. Sample I1 is rated 5. This rating is only slightly higher than the results from sample SA. There could be various reasons for this, the most appropriate one is that a number of venting systems have been installed near the borehole to protect the near by housing development. This may have oxidised the organic materials on site. This also means that the remedial measures are working. There may be other reasons for variation in ratings such as changes in analyte concentrations due to seasonal changes of rainfall.

Sample SB: is from a site number 36, Thornbury Park. This sample is rated 2 and formula 3 value is 80.8. The site is approximately 50 years old which has taken waste such as, ash, stone, brick, clay and wood. The site is fairly clean because it has inert and old fill. The rating obtained for this site is appropriate according to the history of the site.

Sample SC: This sample is from borehole B93121, site number A6 on LBH plan, the borehole has fill up to 0.6m and the fill consists of top soil over brick earth. The site is more of made ground than landfill. Using formula 3, it has a value of 11.7 and it is rated 1. This rating is appropriate with the type of fill.

Sample SD: This borehole is in Site number 17. The sample is rated 2 with formula3 value 10. The borehole log shows that there is no fill on site. This rating is also appropriate for the site.

Sample SF: The borehole is in site marked AP1 on LBH plan, borehole number B93102. This site is a 50 years old site which has 3m of fill consisting of soil, brick, concrete, and ash. The borehole is rated 1 with formula 3 value of 50.7. The rating 1 is appropriate for the type of site and its history.

Sample SH: This site is marked O14 on LBH plan, the borehole number is B93171. The site is made ground due to filling of sewerage works. There is 3.8m of fill and fill consists of brick earth, soft dark grey silty clay. The site is 37 years old, it is rated 12 with formula 3 value of 471. The rating is appropriate with the site details because it is contaminated due to its past use as sewage works. Sample SI: This borehole is in the perimeter of a highly gassing site, site number 33, borehole number B00026. Site 33 is 32 years old. The borehole sampled has fill up to 2.6m which consists of firm grey clay, brick, concrete, and black clay. This borehole is the same as F2 analysed for this study. Sample SI is rated 4 using formula 3 it has a value of 135.7. In this study the same borehole is rated 9 which is much higher than the rating from externally analysed results. The reason for this is that numerous venting systems have been installed in the area to protect the nearby housing development. This also indicates that the remedial measures are effective.

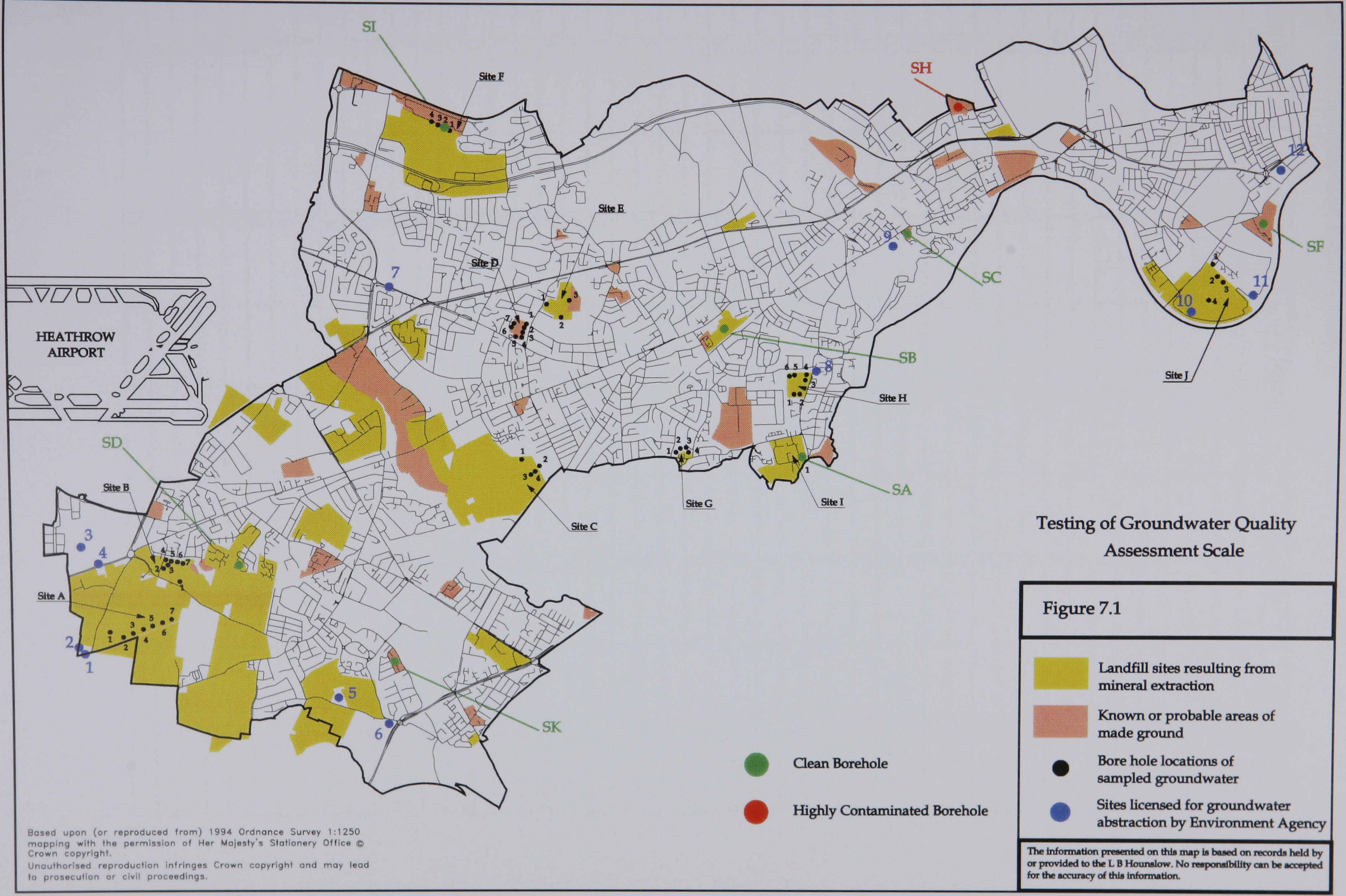
Sample SK: This sample is from site marked A11 on LBH plan. The borehole number is B93147. The site A11 is 38 years old which has 0.7m of fill consisting of dark brown brick earth. The borehole is rated 2 using formula 3 (value 55.7). This rating is appropriate for the type of site and fill.

Using these blind results and analysing the ratings obtained by using formula 3 (3 CH_4 formula), it is confirmed that the formula with 3 CH_4 works effectively to assess the groundwater contamination in and around landfill areas in sand and gravel aquifers. The locations of these samples are shown in Figure 7.1.

7.5 Relationship between Landfill Gas and Groundwater Quality: Results from the four classes of sites are considered against their ratings and methane and carbon dioxide (landfill gas) to see if there is a direct relationship between landfill gas and groundwater quality.

Table 7.2 lists the ratings of the samples analysed along with the highest methane and carbon dioxide recorded in the last 2 to 3 years and the class of site (I to IV). Table 7.3 relates the Class I to Class IV sites with the highest landfill gas readings recorded in these sites in the last 2 years and the range of ratings assigned to the corresponding sites. It is clear from Tables 7.2 and 7.3 that in class I sites (boreholes in virgin ground or perimeter of landfill sites more than 50 years old), where no methane is recorded in the last 2 years, the site will have a rating of 1 to 3. In class II sites (boreholes in landfill sites more than 50 years old), where maximum methane is less than 3%v and carbon dioxide is a maximum 11% volume, in such sites the rating may be predicted to be up to a maximum of 4. Such low rating (1 to 5) sites are considered to be relatively 'clean'.

From Table 7.2, it appears that all boreholes with methane readings more than 30%v could be predicted to have ratings 9 to 15, which has relatively high contamination.



Testing of Groundwater Quality
Assessment Scale

Figure 7.1

Based upon (or reproduced from) 1994 Ordnance Survey 1:1250 mapping with the permission of Her Majesty's Stationery Office © Crown copyright.
Unauthorised reproduction infringes Crown copyright and may lead to prosecution or civil proceedings.

The information presented on this map is based on records held by or provided to the L B Hounslow. No responsibility can be accepted for the accuracy of this information.

Table 7.2: Relationship between Historical Classification of Site, its Pollution Rating and Landfill Gas Concentration

Sample No	Class	Rating	CH_4 (%v)	CO_2 (%v)
D6	I	1	0	2.5
D7	I	1	0	2.7
G4	I	1	0	2.6
H6	II	1	0	5.7
H5	II	1	0	2.1
E3	II	2	0	7.6
C2	I	2	0	3.3
J1	II	2	0	2,2
D4	I	2	0	2
H2	II	2	0	5.1
H4	II	2	0	5.8
G1	I	2	0	2.2
D3	I	2	0	0.9
D2	I	2	0	2.1
D1	I	2	0	0.8
G2	I	2	0	2.5
J4	II	2	0	7.5
D5	I	3	0	3.4
H1	II	3	0	5.7
B1	III	3	0	4.6
J2	II	3	0	7.6
G3	I	3	0	1.8
B6	III	3	3.9	13.8
E1	II	3	0	7.5
E2	II	3	1	11
F4	III	4	0	12
H3	II	4	0	8.9
J3	II	4	2.6	5.6
B7	III	5	6.2	18.2
B5	III	5	2.5	15.5
C1	III	6	0.9	4.2
F1	III	6	0	4
I1	III	5	24.2	5.3
C4	III	8	12.5	12.5
B4	III	10	0.1	4.8
F3	III	9	14	1.5
F2	III	9	24	23
A5	IV	10	19	15
C3	IV	9	26.1	15.5
A2	IV	9	48	5
B3	IV	11	30.9	30.5
B2	III	13	0	2.1
A3	IV	12	47	13
A7	IV	13	30.4	17
A6	IV	14	46.2	12.5
A4	IV	14	69.1	6.9
A1	IV	15	63.4	32.2

Table 7.3: Range of Ratings, CH_4 and CO_2 in Class I to IV Sites

Class of Site	Range of Ratings	CH_4 (%v)	CO_2 (%v)
I	1 to 3	0	Up to 3.4
II	1 to 4	Up to 2.6	2 to 11
III	3 to 13	0 to 24	2 to 23
IV	9 to 15	19 to 69	5 to 32

There is no direct relationship between the levels of landfill gas and site contamination. In order to carry out a thorough site assessment, groundwater should be analysed for contamination. Some samples may have a high rating due to contamination from sources other than landfill. In such cases high methane results would not be present, for example, in borehole B4 and B2. Therefore, it is important to analyse groundwater samples in order to assess a site properly for level of contamination.

7.6 Percentage of Sites in LB Hounslow with Low, Moderate and High level of Contamination.

Site ratings 1 to 5 represents low contamination; ratings 6 to 10 represents moderate level of contamination; and ratings 11 to 15 represents high level of contamination. Assuming that the 47 groundwater samples analysed represent the proportion of the types of landfill sites and areas around landfill sites in the Borough, the Table 7.4 shows the results of percentage of low, moderate and high levels of contaminated sites in LB Hounslow.

Table 7.4: % of Sites with Low, Moderate and High Level of Contamination

Rating	No. of Samples Out of Total 47	% of Total Samples	Site Contamination & % of Total
1	5	10.6	**Low** 63.7%
2	12	25.5	
3	8	17	
4	3	6.4	
5	2	4.2	
6	2	4.2	**Moderate** 18.9%
8	1	2.1	
9	4	8.4	
10	2	4.2	
11	1	2.1	**High** 14.7%
12	1	2.1	
13	2	4.2	
14	2	4.2	
15	1	2.1	

From this deduction,

- 64% of potentially contaminated landfill sites in Hounslow have low contamination, with ratings 1to 5. These may be considered 'clean'.
- 19% of potentially contaminated landfill sites in Hounslow have moderate contamination, with ratings 6 to 10.
- 15% of potentially contaminated landfill sites have high contamination, with ratings 11 to 15.

Boreholes with low, moderate and high level of contamination are shown in Figure 8.1.

7.7 Risk Assessment of High Contamination Rating (15) Borehole.

The landfill sites and boreholes investigated for this study are mainly old landfill sites (pre 1974 Control of Pollution Act). Hence, such sites may be considered to be 'Dilute and Disperse' type of landfills. The advantage of such landfill sites, particularly in the highly permeable sand and gravel aquifers are that the leachate is in continuity with the surrounding groundwater. The leachate, is therefore being continuously diluted and any potential contaminants do not remain in high concentrations after they leave the site.

The landfill sites investigated have between 5 to 7 metres deep waste, unlike some of the licensed sites elsewhere in the country where the landfill sites can be expected to be much deeper, therefore these would have larger volumes of waste per unit area and possibly have taken waste with high proportions of organic waste. From Table 1.7, the results under 'Aged Waste' and 'Fresh Waste' is compared with the results of 15 rating sample from this study, and these are considered below.

In the case of non-availability of all the factors for using formula with 3 CH_4 for site assessment, (from the R values in Table 5.20) COD and EC are the best single criteria for site/borehole assessment due to its relatively low goodness-of-fit and R value result. COD result for a typical leachate from 'aged' domestic waste is quoted as 1160 mg/l, and the highest COD result from this study is 325 ppm. The unit ppm may be taken to be the same as mg/l. Hence, the COD result quoted in Table 1.7 is compared the highest result from this study, which is 3.5 times greater than the highest COD result from this study. From this deduction, the landfill leachates/groundwater investigated in this study are at least 3.5 times cleaner than the aged waste results (quoted in Table 1.7) from elsewhere in the country.

Using the same reasoning as above, the COD result from fresh waste is quoted in Table 1.7 as 23800mg/l. This works out as 73 times higher than the highest COD result from this study. Therefore, the most contaminated leachate investigated in this study is 73 times cleaner than fresh waste results quoted from elsewhere in the country (Table 1.7).

The level of leachate contamination in this study is therefore at least 3.5 times cleaner than leachates from aged waste from elsewhere in the country and at least 73 times cleaner than fresh waste results from elsewhere in the country.

7.9 Risk assessment Using 'Source - Pathway - Target' Framework.

Source: Source for contamination in this case is landfill sites with high rating boreholes.

Pathway: is groundwater and vegetation on high contamination rating sites.

Targets: Target for landfill leachate may be a) groundwater abstraction points for potable uses; b) sensitive developments near the sites which could be affected by landfill gas and c) uptake of groundwater by edible plants and vegetables. These aspects are considered separately below.

a) There are no groundwater abstraction points for potable use licensed by Environment Agency in the LB Hounslow area (Table 2.1). Therefore, there is no risk of contamination of potable waters.

b) Sensitive Developments near Landfill sites: Some of the high contamination rating groundwater samples are A3 (rating 12), A7 (rating 13), A6 (rating 14), A4 (rating 14), and A1 (rating 15). All these samples are from an area which is a Country Park, the filled areas near the housing developments have been remediated by excavation of waste and by filling any putrescible waste away from any sensitive development in specially designed cells with leachate and gas control measures.

Most of the park is surrounded by gas venting and gas barrier systems. Hence these sites have a low risk of affecting any sensitive developments.

Borehole B3 is within a gassing landfill. This area is partly surrounded by housing developments and a school. The site has been remediated by installing a gas barrier and venting trench along the perimeter with the sensitive developments, thereby intercepting the pathway to sensitive targets.

c) Site A has mainly grassed areas, therefore any risk due to use of edible plants is minimum. Site B is waste ground therefore risk due to ingestion of contaminated plants is also minimum.

<u>Moderately Contaminated Sites:</u> The moderately contaminated sites investigated are with ratings 6 to 10, and these are borehole samples C4, C3, A2, A5, F3, F2, B4, B2, B3. These boreholes are considered one at a time. C4 is in the middle of a school playground. This site has been remediated with venting wells and boreholes installed nearer to the school building structures. Borehole C2 with rating 1 is one of such boreholes. This indicates that sites nearer to the building structure are 'clean' and the building is not at risk.

B4 and B2 are in the perimeter of a gassing landfill site. Although high levels of landfill gas have not been detected in these boreholes, there is high level of contamination due to ammonia in the groundwater. This may be due to a leaking sewer and needs to be investigated further.

C3 is within a waste ground area, which is well away from any developments. Boreholes nearer to developments such as, C2 in the same area has a rating 2. Therefore, contamination in C3 does not pose a significant risk to the nearby buildings.

A2 and A5 are within the Country Park area and is discussed above. These sites do not pose a risk to any sensitive targets. F3 and F2 are boreholes in the perimeter of a highly gassing landfill site with housing development within 50m of the site. This area has been remediated with venting systems and boreholes installed nearer to building structure. The borehole nearer to the building structure is assessed to have no significant levels of landfill gas on site. This shows that the areas of building structures are not affected by contamination from the nearby contaminated site.

Most of the moderately contaminated boreholes do not pose any significant risk to any sensitive targets, except for boreholes B4 and B2. These need to be investigated further for the source of contamination, particularly ammonia.

CHAPTER VIII - LIST OF CONTENTS

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH WORK

Page Numbers

CHAPTER VIII

CONCLUSIONS

8.1 Methodology for Borehole Groundwater Quality Assessment

The borehole groundwaters studied in this work were characterised by analysis for CH_4, CO_2, pH, Electrical Conductivity (EC), Oxidation-Reduction Potential (ORP), NH_4-N, COD, TOC, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}. Ten of the analytes were considered in detail for characterising borehole samples namely CH_4, CO_2, EC, NH_4-N, COD, TOC, Cl^-, Na^+, K^+, Ca^{2+}.

The range of compositions for each of these analytes was divided into fifteen equal portions and assigned a rating of single analyte contamination of 1 to 15 on this basis. An average of the ten analyte ratings for each borehole sample was calculated and this average compared with the individual analyte ratings. The goodness-of-fit between the average ratings and the individual analyte ratings was then determined as a residual function. The results showed that no single measured component of the groundwater could be used to characterise the borehole quality.

A second average rating was calculated using the data for only six analytes - CH_4, CO_2, EC, NH_4-N, COD, and TOC, but again a goodness-of-fit calculation based on this average did not identify a single analyte as being capable of characterising borehole qualities.

A number of combinations of the six parameters were then taken into consideration and the best formula to describe groundwater quality (that is the one with the best goodness-of-fit residual) was determined to be $3CH_4+CO_2+EC/100+NH_4$-

N+COD+TOC. The units for CH_4 and CO_2 are in %volume, EC in µs/cm and NH_4-N, COD and TOC in ppm.

The range of values for the formula for all the samples was divided into 15 portions of rating 1 to 15 and the same procedure was followed to work out goodness-of-fit residual function. Residual for this formula was the best for assessing groundwater quality.

The ratings for the 47 samples analysed along with the historical classification of sites are in Table 8.1. From Table 8.1, the range of ratings in class I to class IV sites are in Table 8.2. Boreholes with low, moderate and high level of contamination are shown in Figure 8.1.

Table 8.2 shows that boreholes in Class I and Class II sites have low ratings (1 to 4) and are considered to be clean sites. Boreholes in class IV sites have high ratings (9 to 15) and are clearly contaminated. In the case of Class III sites, the samples have a wide range of ratings (3 to 13) which range from 'clean' to 'high' level of contamination. For this reason to characterise groundwater samples it is important to sample groundwater from within a landfill site. For the same reason, for planning permission purposes it is important that Class III sites where sensitive development is proposed, such as housing, is thoroughly investigated for contamination to decide on safety measures to be adopted on site.

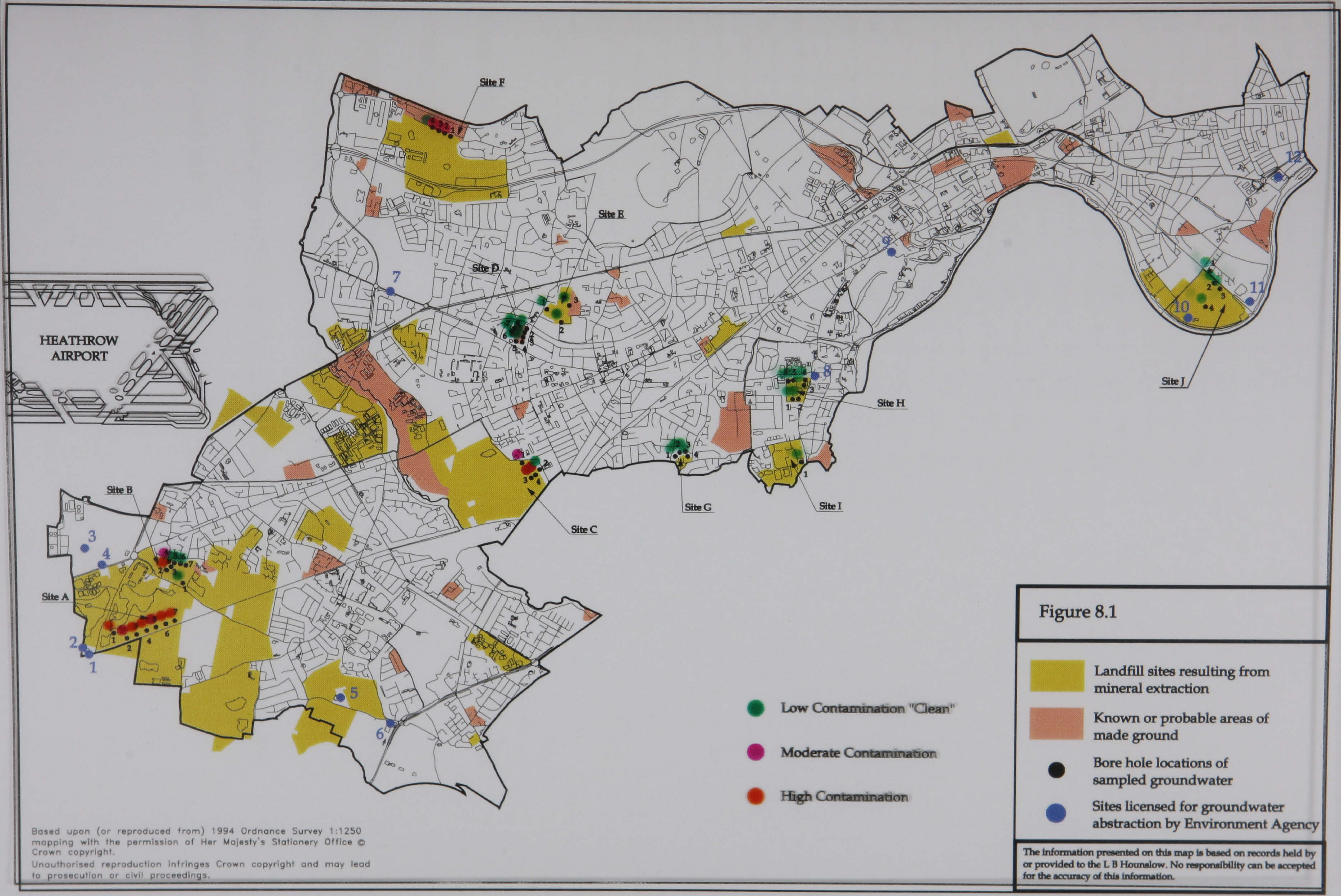


Figure 8.1

The information presented on this map is based on records held by or provided to the L B Hounslow. No responsibility can be accepted for the accuracy of this information.

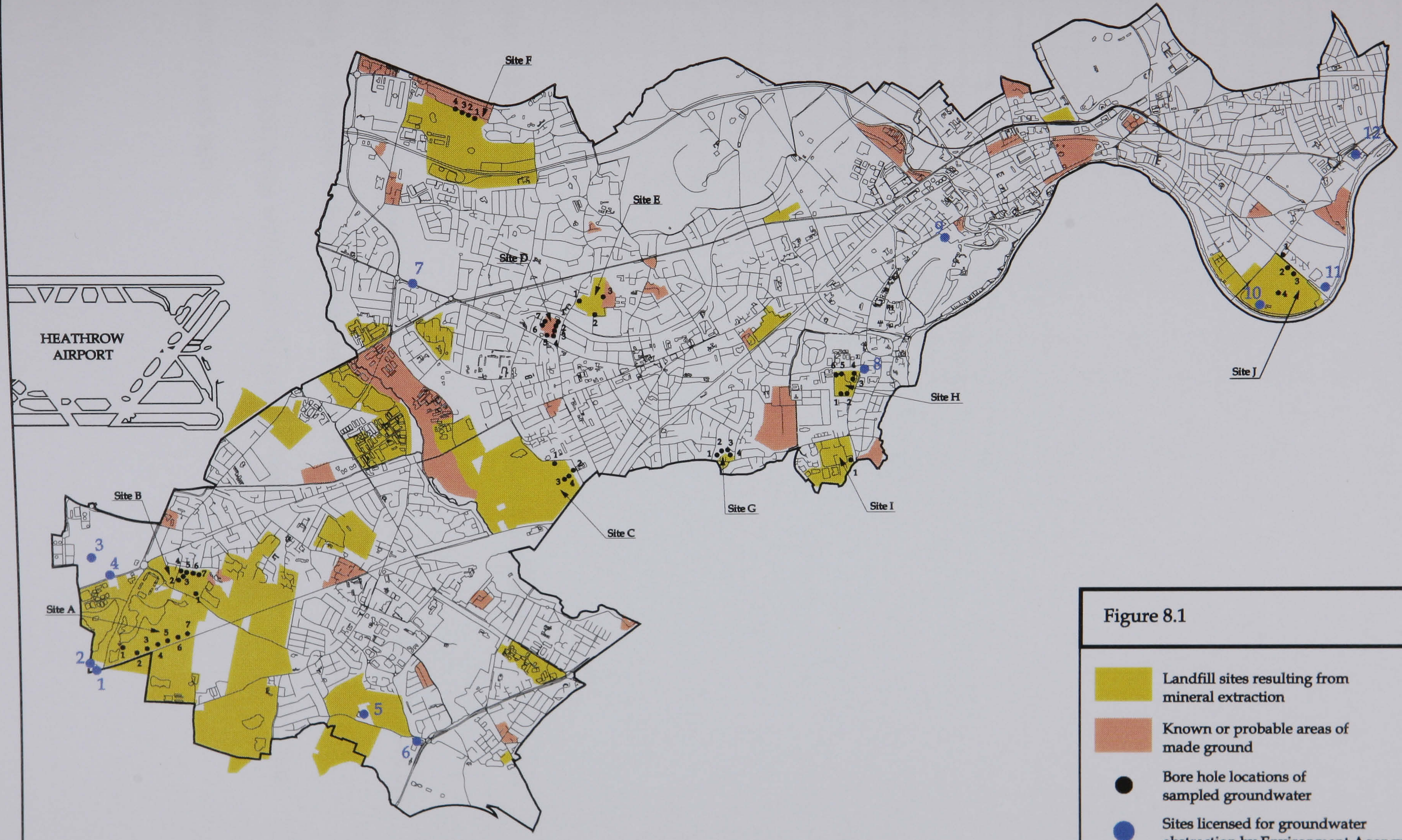


Figure 8.1

🟨 Landfill sites resulting from mineral extraction

🟧 Known or probable areas of made ground

● Bore hole locations of sampled groundwater

● Sites licensed for groundwater abstraction by Environment Agency

The information presented on this map is based on records held by or provided to the L B Hounslow. No responsibility can be accepted for the accuracy of this information.

Table 8.1 **Characterisation of the 47 Samples Analysed**

Sample No.	Rating	Class*	Sample No.	Rating	Class*
D6	1	I	B7	5	III
D7	1	I	B5	5	III
G4	1	I	I1	5	III
H6	1	II	C1	6	III
H5	1	II	F1	6	III
E3	2	II	C4	8	III
C2	2	I	F3	9	III
J1	2	II	F2	9	III
D4	2	I	C3	9	IV
H2	2	II	A2	9	IV
H4	2	II	B4	10	III
G1	2	I	A5	10	IV
D3	2	I	B3	11	IV
D2	2	I	A3	12	IV
D1	2	I	B2	13	III
G2	2	I	A7	13	IV
J4	2	II	A6	14	IV
D5	3	I	A4	14	IV
H1	3	II	A1	15	IV
B1	3	III			
J2	3	II			
G3	3	I			
B6	3	III			
E1	3	II			
E2	3	II			
F4	4	III			
H3	4	II			
J3	4	II			

*

- Class I- Boreholes in the perimeter of landfill sites more than 50 years old or in virgin ground;
- Class II - Boreholes within landfill sites with waste filled more than 50 years ago;
- Class III- Boreholes in the perimeter of actively gassing landfill sites;
- Class IV- Boreholes within actively gassing landfill sites with waste filled less than 50 years ago.

Table 8.2

Range of sample ratings in Class I to Class IV sites.

Class	Ratings
I	1 - 3
II	1 - 4
III	3 - 13
IV	9 - 15

8.2 Acetate Medium in Landfill Leachates and Study of Leachability of Lead in Acetate Medium.

The presence of acetic acid arising from microbial activity in landfill boreholes has the potential to increase the leaching and mobility of heavy metals in the landfill. Although the LB Hounslow sites show little evidence of leaching effect of acetate on metals, a study of the mobility of heavy metals in acetate media was carried out to investigate the process which relates to highly active mixed waste landfill in the Acetogenic Stage of landfill biodegradation.

Acetate concentrations in three leachate samples from highly gassing boreholes A1, A2 and B3 were determined to be 11, 7.5 and 6.25 ppm respectively.

From the leachability tests it is clear that although lead salts are fairly insoluble, in a landfill situation where there is mixed waste with high proportions of putrescible and organic content, and when the landfill is in the Acetogenic Phase or Stage III of waste biodegradation, then mobility of heavy metals such as lead can be expected to be significant due to formation of $Pb(CH_3COO)_3^-$ ions which would have the potential to contaminate groundwater.

8.3 Recommendations for Further Research Work

Further research work should deal with the study of

- Sediments and solids in the four classes of sites.
- The leachability tests to be carried out using landfill solids from the highly gassing landfill sites using a) landfill leachate, b) deionised water, in both cases, at various pH conditions in acetic acid medium.
- Levels of acetic acid to be determined in leachate samples from waste containing high proportions of organic and putrescible waste from elsewhere in the country.

LIST OF APPENDICES

Page Number

APPENDIX A

Circular 20/90
(Department of the Environment)
Circular 34/90
(Welsh Office)

Joint Circular from the

Department of the Environment
2 Marsham Street, London SW1P 3EB

Welsh Office
Cathays Park, Cardiff CF1 3NQ

29 October 1990

EC Directive on Protection of Groundwater Against Pollution Caused by Certain Dangerous Substances (80/68/EEC): Classification of Listed Substances

1. This circular provides further guidance and information on the classification of certain chemicals as List I or List II for the purposes of EC Directive 80/68/EEC ("the directive"). It replaces the advice given in paragraphs 6 to 8 of DoE Circular 4/82 and Welsh Office Circular 7/82 of 1 March 1982, covering the scope of the directive. In particular, it provides a revised and more specific procedure for determining those substances as belonging to List I or List II. The replacement paragraphs are given in Appendix 1. The circular is addressed to the waste disposal authorities (WDAs) in England and Wales.

2. When referring to DoE Circular 4/82 and Welsh Office Circular 7/82 the following changes should be noted:

(i) Reference throughout the earlier circular to "water authorities" should now be interpreted as referring to the National Rivers Authority (NRA);

(ii) wherever Part II of the Control of Pollution Act 1974 was mentioned or relevant before, then Part III of the Water Act 1989 now applies; and

(iii) the disposal authorities are the current disposal authorities which are not necessarily those which were operational in 1982. The same applies to the mineral planning authorities.

Action Required

3. As a result of the revised advice, WDAs should review those disposal licences for landfill sites involving the disposal of wastes containing substances within List I of the groundwater directive. In this respect WDAs should note that following recent correspondence with the European Commission, the Government has agreed that on the basis of their intrinsic characteristics the three pesticides bromoxynil, bromoxynil octanoate and chlorpyrifos should be regarded as List I substances for the purpose of this directive. WDAs should seek the advice of the NRA as to the effect these sites may have on groundwater.

4. Where the NRA advises that discharges from a landfill site are liable to affect groundwater adversely and that such water is not permanently unusable, then the disposal licence should be reviewed. The deposit of all wastes containing List I substances should be prohibited where the concentrations and the amounts would lead to a discharge of these substances into groundwater. In cases of uncertainty over the classification of listed substances, further advice can be obtained from the appropriate regional headquarters of the National Rivers Authority (see Appendix 4). A consultation paper on a proposed national scheme for the classification of substances for the purpose of the directive is being issued by the Department and Welsh Office at about the same time as this circular.

5. Any queries on this circular should be directed in England to Tony Sheils, Department of the Environment, Water Environment B Division, Room A414, Romney House, 43 Marsham Street, London SW1P 3PY (tel: 071–276 8268) and in Wales to John Saunders, Welsh Office, Environment Division, Room 2117, Cathays Park, Cardiff CF1 3NQ (tel: 0222 823178).

D L H ROBERTS, *Head of Water Environment B Division, Department of the Environment.*

A H H JONES, *Head of Environment Division, Welsh Office*

The Chief Executive
  County Councils in England
  (for information in Wales)
  District Councils in Wales
  (for information in England)
  London and former metropolitan area waste authorities
The Town Clerk
  City of London (for information)
The Director
  Her Majesty's Inspectorate of Pollution (for information)
The Chief Executive
  National Rivers Authority
  (for information)

Scope and Purpose of the Directive

Following the same paragraph numbering as in DOE Circular 4/82, Welsh Office Circular 7/82:

6. The general purpose of the directive is to prevent the pollution of groundwater by the substances listed in the Annex to the directive—see Appendix 2 of this circular. More specifically, Member States are obliged to take the necessary steps:

(a) to prevent substances in List I from entering groundwater; and

(b) to limit the introduction of List II substances into groundwater so as to avoid pollution.

"Groundwater" is defined for the purposes of this directive as "all water which is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil". Although this is narrower than that in Part III of the Water Act 1989 which also covers underground waters in the unsaturated zone, it is the wider definition of "ground waters" in S.103 of the Water Act 1989 that should be applied when implementing this circular. "Pollution" is defined for the purpose of the directive as "the discharge by man, directly or indirectly, of substances or energy into groundwater, the results of which are such as to endanger human health or water supplies, harm living resources and the aquatic ecosystem or interfere with other legitimate uses of water".

7. The Annex to the directive specifies the families and groups of substances which belong to List I and List II. However, the introductory paragraphs to List I note that some individual substances belonging to the families or groups may be inappropriate to List I on the basis of low risk of toxicity, persistence and bioaccumulability. For a substance from the List I families or groups of substances to be classified as inappropriate to List I it is necessary for the competent authority to be satisfied that it represents a low risk on the basis of each of its intrinsic characteristics of toxicity, persistence and bioaccumulation. An assessment procedure to be carried out by competent authorities when considering whether a substance is inappropriate to List I is attached as Appendix 3 to this circular.

8. Exceptions from the general scope of the directive are made in Article 2. These state that the directive shall not apply to:

(a) discharges of domestic effluent from isolated dwellings not connected to a sewerage system and outside areas protected for the abstraction of water for human consumption;

(b) discharges found to contain substances in List I or II in a quantity and concentration so small as to obviate any future danger of deterioration in the quality of the receiving water;

(c) discharges of matter containing radioactive substances.

In addition, under Articles 4.2 and 4.3 the following may be authorised after prior investigation:

(d) discharges of List I substances into groundwater which is found to be permanently unsuitable for other uses, especially domestic or agricultural, provided that other aquatic systems or ecosystems cannot become polluted by these substances and that mineral exploitation is not impeded;

(e) discharges due to reinjection into the same aquifer of water used for geothermal purposes, water pumped out of mines and quarries or water pumped out for civil engineering purposes;

and under Article 6:

(f) aquifer recharge for the purpose of groundwater management may be carried out subject to special authorisation provided that there is no risk of the groundwater becoming polluted.

In the light of the above, the Secretaries of State consider that exception 8(b) should be interpreted as applying only to discharges where the amounts of listed substances present are so small as to enable unimpaired use of water from the aquifer without necessitating any significant change in its treatment where this is given. The same criterion should be applied even where the aquifer is not currently in use, except where an aquifer is permanently unusable. Exact interpretation in individual cases would be a matter for the judgement of the competent authority concerned—in consultation with the NRA as appropriate—but the protection of groundwater resources should be the prime consideration. WDAs should provide the NRA with all necessary relevant information.

With respect to 8(d) above, this provision recognises that there is little point in attempting to protect groundwater which is already permanently unusable. Even in these cases the directive requires direct discharges to be authorised, but makes it unnecessary to impose any restrictions on the authorisation other than to ensure that all technical precautions are taken so that List I substances cannot reach other aquatic systems.

APPENDIX 2

ANNEX FROM GROUNDWATER DIRECTIVE 80/68/EEC

List I of Families and Groups of Substances

List I contains the individual substances which belong to the families and groups of substances enumerated below, with the exception of those which are considered inappropriate to List I on the basis of a low risk of toxicity, persistence and bioaccumulation.

Such substances which with regard to toxicity, persistence and bioaccumulation are appropriate to List II are to be classed in List II.

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment.
2. Organophosphorus compounds.
3. Organotin compounds.
4. Substances which possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment(1).
5. Mercury and its compounds.
6. Cadmium and its compounds.
7. Mineral oils and hydrocarbons.
8. Cyanides.

List II of Families and Groups of Substances

List II contains the individual substances and the categories of substances belonging to the families and groups of substances listed below which could have a harmful effect on groundwater.

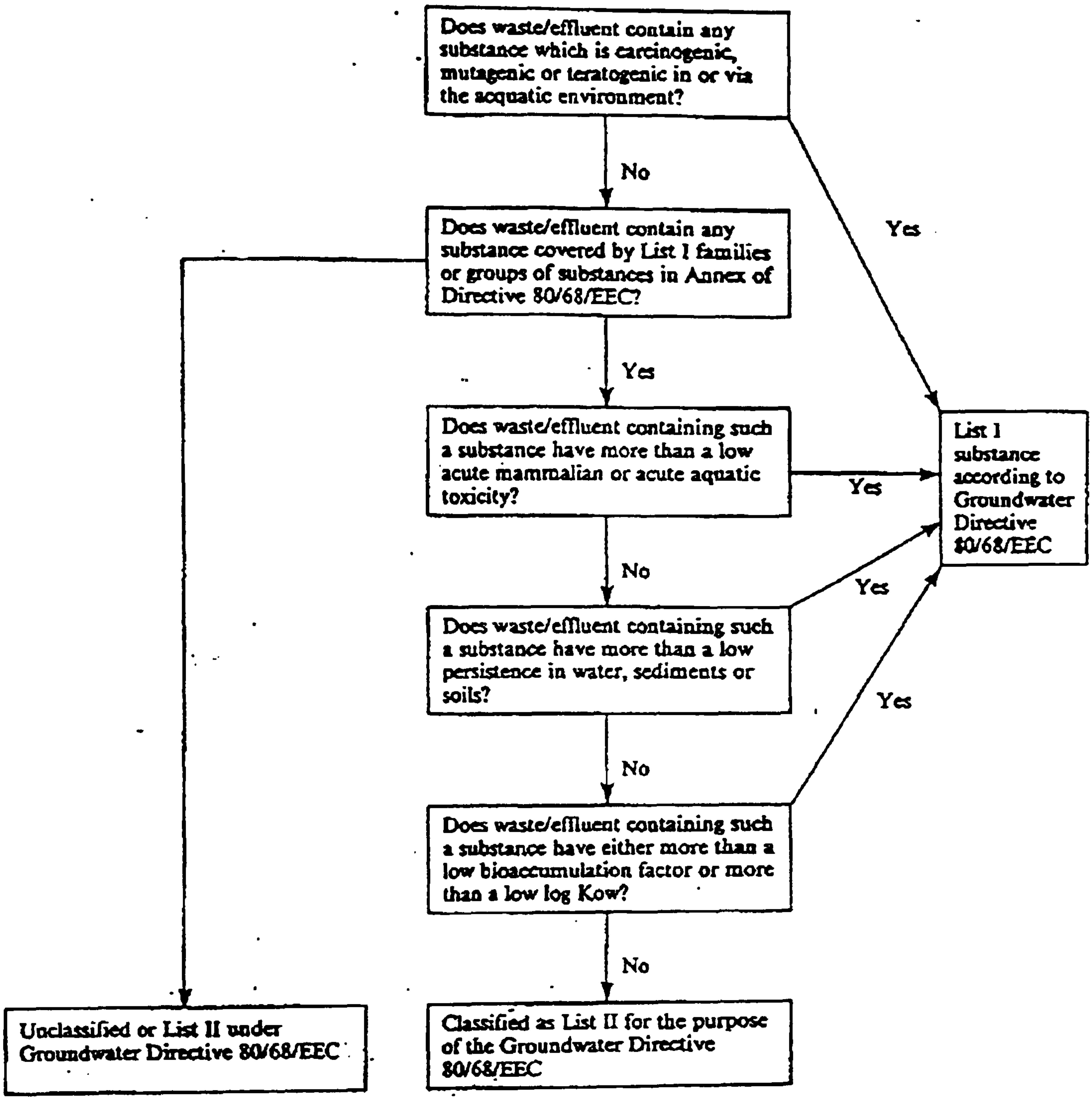
1. The following metalloids and metals and their compounds:
    1. Zinc
    2. Copper
    3. Nickel
    4. Chrome
    5. Lead
    6. Selenium
    7. Arsenic
    8. Antimony
    9. Molybdenum
    10. Titanium
    11. Tin
    12. Barium
    13. Beryllium
    14. Boron
    15. Uranium
    16. Vanadium
    17. Cobalt
    18. Thallium
    19. Tellurium
    20. Silver
2. Biocides and their derivatives not appearing in List I.
3. Substances which have a deleterious effect on the taste and/or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption.
4. Toxic or persistent organic compounds of silicon, and substances which may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.
5. Inorganic compounds of phosphorus and elemental phosphorus.
6. Fluorides.
7. Ammonia and nitrites.

---

(1) Where certain substances in List II are carcinogenic, mutagenic or teratogenic they are included in category 4 of List I.

APPENDIX 3

Assessment Procedure Diagram as an Aid for Determination of Listing Status



Does waste/effluent contain any substance which is carcinogenic, mutagenic or teratogenic in or via the acquatic environment?

Does waste/effluent contain any substance covered by List I families or groups of substances in Annex of Directive 80/68/EEC?

Does waste/effluent containing such a substance have more than a low acute mammalian or acute aquatic toxicity?

Does waste/effluent containing such a substance have more than a low persistence in water, sediments or soils?

Does waste/effluent containing such a substance have either more than a low bioaccumulation factor or more than a low log Kow?

List I substance according to Groundwater Directive 80/68/EEC

Unclassified or List II under Groundwater Directive 80/68/EEC

Classified as List II for the purpose of the Groundwater Directive 80/68/EEC

The above represents a logical approach to the assessment of a waste's/effluent's status for the purpose of the Groundwater Directive 80/68/EEC: the order in which the questions appear does not imply any grading of importance, but will usually provide the quickest reasoned decision.

APPENDIX B

BOREHOLE LOGS

Class I Boreholes

Boreholes (BH) in Virgin Ground/Clean Fill

BH No.	Lab. No	BH Log		'Fill' Details
		Depth (m)	Strata	
B94033	C2	0.0	Topsoil	No fill recorded
		0.4	Silty clay	
		0.7	Claybound gravel	
		1.5	Sand & gravel	
		6.9	Clay	
		8.0	Extent of BH	
B93039	G4	0.0	Fill	Brick, gravel
		0.7	Gravel, sand&clay	
		1.2	Sand	
		1.9	Sand & gravel	
		4.6	Clay	
		6.0	Extent of BH	
B93019	D7	0.0	Top soil	No fill recorded
		0.2	Silty clay	
		1.2	Sand & gravel	
		6.1	Clay	
		7.0	Extent of BH	
B93028	D6	0.0	Top soil	No fill recorded
		0.1	Silty sandy clay	
		1.2	Clay & gravel	
		2.4	Sand & gravel	
		7.1	Clay	
		7.6	Extent of BH	
B93042	G1	0.0	Top soil	Gravel & soil fill
		0.25	Fill	
		0.8	Clay & gravel	
		1.2	Sand & gravel	
		1.8	Silty clay	
		2.0	Sand & gravel	
		5.7	Clay	
		6.5	Extent of BH	
B93044	G2	0.0	Top soil	Soil with traces of bric
		0.15	Fill	
		0.6	Clay & gravel	
		1.1	Sand	
		2.9	Sand & gravel	
		3.9	Clay	
		6.0	Extent of BH	

B93045	G3	0.0	Top soil	Silty sandy stoney clay
		0.1	Fill	Fill
		0.9	Sand	
		1.1	Sand & gravel	
		4.2	Clay	
		6.0	Extent of BH	
B93022	D5	0.0	Top soil	No fill recorded
		0.2	Silty sandy clay	
		2.4	Sand and gravel	
		5.3	Clay	
		6.0	Extent of BH	
B93023	D4	0.0	Top soil	No fill recorded
		0.25	Silty sandy clay	
		1.1	Sand & gravel	
		5.2	Clay	
		6.0	Extent of BH	
B93024	D3	0.0	Top soil	No fill recorded
		0.2	Silty sandy clay	
		1.7	Sand and gravel	
		5.4	Clay	
		6.0	Extent of BH	
B93025	D2	0.0	Top soil	No fill recorded
		0.2	Silty sandy clay	
		1.4	Sand and gravel	
		5.3	Clay	
		6.0	Extent of BH	
B93026	D1	0.0	Top soil	No fill recorded
		0.25	Clay & gravel	
		1.2	Sand & gravel	
		5.8	Clay	
		7.0	Extent of BH	

Class II Sites Borehole Logs

Table4 Boreholes (BH) in Old Fill

BH No.	Lab. No.	BH log		'Fill Details'
		Depth (m)	Strata	
B92001	H5	0.0	Top soil	Stones, brick, rubble, Clay and 'fill'
		0.7	Fill	
		4.0	Sand & gravel	
		6.4	Clay	
		7.0	Extent of BH	
B92002	H6	0.0	Top soil	Brown clayey brick rubble fill
		0.1	Fill	
		4.0	Sand & gravel	
		6.10	Clay	
		7.0	Extent of BH	
B92004	H1	0.0	Top soil	Brick, black ash, clay, rubble
		0.8	Fill	
		6.0	Sand & gravel	
		7.0	Clay	
		7.5	Extent of BH	
B92005	H2	0.0	Top soil	Clay, brick, stone with black staining
		0.5	Fill	
		5.9	Sand & gravel	
		6.9	Clay	
		8.0	Extent of BH	
B92007	H3	0.0	Fill	Loose black ash, clay, Brick and stone fill
		7.5	Sand & gravel	
		8.5	Clay	
		9.0	Extent of BH	
B92008	H4	0.0	Top soil	Brick, rubble, ash, stone & clay fill
		0.6	Fill	
		7.0	Sand & gravel	
		7.6	Clay	
		8.10	Extent of BH	
B93001	E2	0.0	Top soil	Clay, brick, stone, sand
		0.2	Fill	
		4.9	Clay	
		6.0	Extent of BH	
B93013	E1	0.0	Top soil	Clay, brick, ash silt, sand
		0.1	Fill	
		6.0	Sand & gravel	
		7.4	Clay	
		8.0	Extent of BH	
B93018	E3	0.0	Top soil	Brown sandy clay fill
		0.15	Fill	
		3.6	Sand & gravel	
		5.75	Clay	
		6.5	Extent of BH	

B95005	J1	0.0	Fill/made ground	Soil, brick, concrete, Clay fill
		1.8	Silty sandy clay	
		3.5	Sand & gravel	
		8.3	Clay	
		9.0	Extent of BH	
B00037	J3	0.0	Top soil	Loose black clay, brick, ash, sand
		0.3	Fill	
		8.6	Clay	
		9.10	Extent of BH	
B00038	J2	0.0	Top soil	Firm black clay, brick, Coal, wood and gravel
		0.3	Fill	
		8.5	Clay	
		9.5	Extent of BH	
B000042	J4	0.0	Fill	Black gravel, clay with brick, glass and wood
		9.9	Clay	
		10.5	Extent of BH	

Class III Boreholes

Table6 Boreholes in the Perimeter of Gassing Landfill Sites

BH No.	**Lab. No.**	**Borehole Log**		**'Fill' Details**
		Depth (m)	**Strata**	
B00001	B4	0.0	Fill	Loose ash, brick, pebbles, Clay Black sand
		0.55	Sandy clay	
		0.80	Sand & gravel	
		6.25	Clay	
		7.30	Extent of BH	
B93178	B2	0.0	Top soil	No fill encountered
		0.30	Silty sandy clay	
		0.90	Sand & gravel	
		5.50	Clay	
		6.0	Extent of Bh	
B00003	B5	0.0	Top soil	Domestic refuse, builders rubble, black gravel, brick
		0.15	Fill	
		6.60	Clay	
		7.60	Extent of BH	
B00004	B6	0.0	Fill	Builders Rubble, domestic refuse
		6.45	Clay	
		7.50	Extent of BH	
B00005	B7	0.0	Top soil	Builders rubble, domestic refuse
		0.3	Fill	
		4.9	Sand & gravel	
		6.2	Clay	
		7.2	Extent of BH	
B93184	B1	0.0	Fill	Top soil, clay, ash, brick fill
		1.0	Sandy clay	
		1.5	Sand & gravel	
		7.5	Silty clay	
		8.0	Extent of BH	

B93225	C1	0.0 3.6 3.9 5.0	Fill Sand & gravel Clay Extent of BH	Concrete, wood, paper, brick etc.
B00024	F4	0.0 4.10 6.0	Fill Clay Extent of BH	Clay, bricks, concrete, stones, brown/black clay
B00025	F3	0.0 4.2 6.0	Fill Clay Extent of BH	Clay, brick and rubble fill
B00026	F2	0.0 2.6 4.2 6.0	Fill Sand & gravel Clay Extent of BH	Firm grey clay, brick, concrete, black clay
B00027	F1	0.0 1.5 4.0 6.0	Fill Sand & gravel Clay Extent of BH	Brick and stones
B94039	C4	0.0 0.15 2.10 2.40 2.60 7.50 8.10	Top soil Fill Sand & gravel Silty, sandy clay Sand & gravel Clay Extent of BH	Brick, wood, clay, concrete, paper
B00051	I1	0.0 4.0 7.0 8.0 8.5	Fill Sandy clay Sand & gravel Clay Extent of BH	Black clay fill with brick and concrete

Class IV Sites Boreholes

Table5 Boreholes in Highly Gassing Sites

BH No	Lab. No.	Borehole Log		'Fill' Details
		Depth (m)	Strata	
B93226	C3	0.0 8.3 9.0	Fill Clay Extent of BH	Clay, bricks, wood, paper, Gravel
B00018	B3	0.0 6.5 7.5	Fill Clay Extent of BH	Ash. Domestic refuse, builders Rubble
M302	A1	>10m	Putrescible waste	Exact details not known
J10	A7	Not known	Not known	Not known
J11	A6	” ”	” ”	” ”
J12	A5	” ”	” ”	” ”
J13	A4	” ”	” ”	” ”
J14	A3	” ”	” ”	” ”
J15	A2	” ”	” ”	” ”

APPENDIX C

Proposed Leachability Test Methods for Solid Waste Materials

Sample Preparation.

Weigh accurately 10g of sample into a dish or basin and dry overnight at 110°C, reweigh to determine the weight loss. Perform analysis in duplicate.

On the dried material, if necessary reduce the particle size to fit into the size range required (jaw crusher, mortar or cutting) then identify the size range :

(a) Massive	> 1 mm
(b) Semi-dispersible	0.1-1.0 mm (100-1000 microns)
(c) Dispersible	<0.1 mm (< 100 micron)

Once the dry weight is determined and a weight fraction identified use the following extraction methods on **fresh** dewatered material. All analyses are to be carried out in duplicate.

Canadian Method (modified).

(Brian Smith, Natural Resources Canada, Private Communication)

1) Place the equivalent of 10g dry mass of material in a 250 ml conical flask and add 160 ml of fresh DI water (less the moisture content of the sample).

2) Shake for 15 minutes before measuring the pH using a meter calibrated at pH 4.1 and pH 7. The solution must be stirred during the pH measurement.

3) If the pH is greater than 5.2 add sufficient 0.5M acetic acid to reduce the pH to 5.0 ± 0.2. **Note** No more than 4 ml of 0.5M acetic acid may be added per gram material (40ml) during the whole extraction.

4) Shake the sample for 24 hours at room temperature, taking samples and monitoring the pH as follows.
   4a) After 1, 3, 6 hours from the start remove a 5 mL sample for immediate analysis (store refrigerated if it cannot be analysed at once). Check the pH and adjust to pH 5 if the pH is above 5.2.
   4b) If the pH is below 4.8 after 6 hours add a further 40 mL of DI water and adjust pH as before.
   4c) After 22 hours check the pH again and reduce if necessary.
   4d) After 24 hours add sufficient water to make the total volume 250 mL.

5) Separate the solid and liquid phases by centrifuge and filtration to obtain approx 100 mL of solution for analysis.

6) Determine the concentrations of the Basel elements in the total leachate as mg extracted/gram dry weight and mg extracted/gram wet weight.

7) Carry out the same procedure in parallel on a blank solution.

8) Repeat for each size fraction.