

H 24/3790

110 Leslie Stone

MONASH UNIVERSITY
THESIS ACCEPTED IN SATISFACTION OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

ON..... 18 May 2004.....

.....

Sec. Research Graduate School Committee

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ERRATA

Page viii between the 9th and 10th lines, insert "AUFS absorbance units full scale"

Page 50 Section 2.6, heading: "Statistical" for "Statistic"

Page 55 para 1, 3rd line: "temperature" for "tmperature"

Page 55 para 1, 4th line: "different" for "differet"

Page 68 para 2, 1st line: "and" for "or"

Page 70 para 2, 3rd line: "it was found that pyrogallol" for "pyrogallol"

Page 71 para 2, 2nd line: "was" for "were"

Page 146 para 2, 1st line: "By using" for "Using"

Page 150 Table 5-21, 3rd line in the 3rd row: "pimelic" for "pPimelic"

Page 184 para 3, 1st line: "ratios" for "rations"

Page 190 para 1, 1st line: add "Figure 7-49," before "Figure 7-50"

Page 199 para 4, 4th line: "potassium" for "magnesium"

Page 202 para 3, 3rd line: "apparent" for "apparently"

**CHARACTERISATION OF ORGANIC AND
INORGANIC COMPONENTS IN PROCESS WATER
FROM A NOVEL LIGNITE DEWATERING PROCESS**

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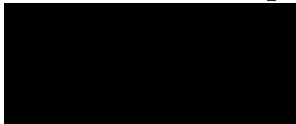
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2004

CERTIFICATE OF AUTHENTICITY

I hereby declare that the work presented in this thesis is my own, except where otherwise noted, and was carried out in the School of Chemistry, Monash University (Australia). To the best of my knowledge, this thesis contains no material which has been accepted for the award of any other degree or diploma in any university and contains no material previously published or written by another person, except where due reference is given.

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School of Chemistry
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2004

ABSTRACT

A novel lignite dewatering technique, Mechanical Thermal Expression (MTE), has been developed, investigated and shown to be energy efficient with potential for industrial application. Since water in the lignite is removed as a liquid during the process, a wastewater stream, containing both organic and inorganic impurities, is produced. Knowledge about the composition and nature of this process water is very important to provide an understanding of the water quality issues associated with this process and to evaluate the extent of remediation it may require. The objectives of this project were to develop appropriate methods for identification and quantitation of organic components in the MTE process water and to characterise both organic and inorganic components in the water as a function of processing conditions.

The solid phase extraction (SPE) method for sample preparation, with or without derivatisation, followed by gas chromatography-mass spectrometry (GC-MS) was selected and evaluated for the analysis of low molecular weight organic components in the MTE water. The PPL sorbent (Varian Bond Elut[®]) with ethyl acetate as the elution solvent demonstrated to be a suitable organic isolation method for quantitative analysis of mono-phenols in water samples at ppm levels using GC-MS. Derivatisation was not required. For simultaneous quantitation of mono-, di- and tri-phenols at lower concentrations, a two-step acetylation method was developed and validated. The method proved to be efficient and significantly improved the GC sensitivity for the phenolic compounds and reduced their detection limits to ppb levels. In order to analyse the otherwise undetectable carboxylic acids/carboxylates in the MTE water using GC-MS, a recently developed methylation method using trimethyloxonium tetrafluoroborate (TMO) to derivatise the polar carboxyl groups directly in the aqueous phase was quantitatively validated. The method was shown to be superior to non-aqueous phase methylation methods that were evaluated, especially for volatile compounds.

Utilising the SPE-GC-MS methods established in this study, low molecular weight organic components in the MTE process water could be identified and quantified. In the water removed from all the lignites investigated (including Victorian, South Australian and

German lignites), phenolic and carboxylic compounds were identified to be the major low molecular weight organic groups in the water with compounds containing carbonyl groups, such as cyclic ketones and furanones, also commonly present. Quantitatively, carboxylic acids were the most abundant low molecular weight compounds in the MTE water, accounting for over 95% of the total organic compounds identified using GC-MS.

The levels of organic carbon in the MTE water increased with processing severity and also directly correlated to the moisture reduction of the lignite. The levels of individual organic compounds followed a similar trend. For the same processing conditions, Victorian lignites generally released lower levels of organics than the South Australian lignites investigated.

The effects of MTE processing temperature and pressure on the removal of inorganic species were not as significant as for the organics. There was a tendency of increase of the removal with increasing moisture reduction of the lignite. Over 50% of the sodium and chlorine in all the lignites was removed in water soluble form during dewatering, whereas calcium and magnesium, being mainly present in an organically bound form, predominantly remained in the coal. Increasing the acidity of the coal water slurries to be dewatered considerably increased the extent of removal of all the inorganics from the lignite. Thus, MTE can be an efficient technique not only for moisture reduction but also for coal beneficiation.

PUBLICATIONS

The following publications have resulted from the studies undertaken for this degree:

Refereed papers:

Ying Qi and Alan L. Chaffee. Effects of processing conditions on the nature of product water from a novel coal drying process. In 'Proceedings of the 6th World Congress of Chemical Engineering'. Melbourne, Australia 24-27 September, 2001. ISBN 0 7340 2201 8.

International conference papers:

Ying Qi and Alan Chaffee. Characterisation of phenolic compounds in lignite dewatering product water using the SPE-GC-MS method. In 'Proceedings of the 12th International Conference on Coal Science'. Cairns, Australia. 3-6 November, 2003.

Thomas Wild, Ying Qi, Alan Chaffee and Karl Strauss. Analysis of organic and inorganic contents in product water from a novel low-rank coal dewatering process. In 'Nineteenth Annual International Pittsburgh Coal Conference Proceedings'. Pittsburgh, PA, USA. 23-26 September, 2002. ISBN: 1-890977-19-5.

Ying Qi and Alan L. Chaffee. Characterisation of organic and inorganic components in product water from a novel lignite drying process. In 'Eighteenth Annual International Pittsburgh Coal Conference Proceedings'. Newcastle, NSW. 3-7 December, 2001. ISBN 1-890977-18-7.

Ying Qi and Alan L. Chaffee. Effects of processing conditions on inorganic composition of product water from a novel coal drying process. In 'Proceedings of the 11th International Conference on Coal Science'. San Francisco, CA. 30 September-5 October, 2001. DOE/NETL-2001/1153.

National conference papers:

Ying Qi and Alan Chaffee. Characterisation of phenolic compounds in MTE wastewater using the SPE-GC-MS method. In 'Proceedings of the CRC for Clean Power from Lignite

Tenth Annual Conference'. CRC for Clean Power from Lignite, Monash University, Victoria. 12-13 June, 2003.

Ying Qi and Alan Chaffee. Removal of organic carbon and selective metal elements from lignites by the MTE dewatering. In 'Proceedings of the CRC for Clean Power from Lignite Ninth Annual Conference'. CRC for Clean Power from Lignite, Monash University, Victoria. 27-28 June, 2002, 159-164.

Ying Qi and Alan L. Chaffee. Effects of processing conditions on the nature of product water from a novel coal drying process. In 'Proceedings of CRC for Clean Power from Lignite Eighth Annual Conference'. CRC for Clean Power from Lignite, Monash University, Victoria, 28-29 June, 2001. 41-47.

Ying Qi and Alan L. Chaffee. Characterisation of organic and inorganic components in product water from novel coal drying process – background and methodology. In 'Proceedings of CRC for Clean Power from Lignite Seventh Annual Conference'. CRC for Clean Power from Lignite, University of Adelaide, SA. 22-23 June, 2000. 143-148. 2000.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my academic supervisor Dr Alan Chaffee. THANK YOU Alan for all your advice, guidance, constructive suggestions and helpful discussions, especially for your patience and extra efforts to bear with your non-English speaking student, through all these years. I am extremely lucky to have you as my supervisor and really appreciate everything you have done to help me through the whole time.

Also most importantly I would like to thank the CRC for Clean Power from Lignite for offering me this scholarship. Thanks to the CRC for all the financial and other support they provided so that I could have a 'luxury' PhD life. Special thanks to Dr Peter Jackson, my industrial supervisor, and to David, Malcolm, Howard and administration staff for all your help.

A special thank you to Dr Marc Marshall. Thank you very much Marc for helping me through the final stage of my PhD study, for proof reading my thesis with such scientific rigour and in such a timely manner. Marc, I wish you all the best. Please take good care of yourself.

Thank you to George, Tim and Ross for helping me with MTE experiments and making the hard task of working on the MTE stuff an enjoyable experience.

Thank you to Fei Yi and Tham for your friendship and help. The time we spent together has been so enjoyable. Thanks to Greg, Professor Roy Jackson (Prof.), Janine, Jason, Albert, Yuli and Tony and other Monash Coalies for making the group a pleasant and inspirational place to stay.

A special thank you to Sally and Victor for all your technical support with the GC-MS instrumentation and for your understanding of my desire to access the instruments.

Thank you to Laell for always being patient, answering my batches of questions and giving suggestions.

Thank you Mara in the Language service of the faculty for offering courses to non-native English speaking students and making me a better scientific writer.

Thank you to Maureen, Birute, Meryl in the office, Doug, Bob, Matthew in the store, Ashley in the Water Studies Centre and other staff at Monash Chemistry for your intensive assistance during my PhD.

Thank you to Professor Karl Strauss, Thomas, Christian and other people for your friendship and great support while I was living and doing collaborative research in your group in the Department of Chemical Engineering, University of Dortmund, Germany. Thank you all for giving me an enjoyable and unforgettable time in Germany.

THANK YOU to everybody in my family in China for all your love and great support through these years. Every year when I visit home, I feel like recharged with your love, your smile and your encouraging words. Knowing you are always there for me is my lifeline. Thank you to all my friends in Melbourne and Adelaide for your friendship and all your support. I cannot imagine my life in Australia without you guys.

LIST OF ABBREVIATIONS

AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
Al	aluminium
amu	atomic mass unit
ANOVA	analysis of variance
APHA	American Public Health Association
AR	analytical reagent
AS	Australian Standard
BF ₃	boron trifluoride
BM	Bowmans
BOD ₅	biological oxygen demand (five days)
bp.	boiling point
BSTFA	bis(trimethylsilyl)trifluoroacetamide
°C	degrees Celsius
Ca	calcium
Cl	chlorine or chloride
COD	chemical oxygen demand
CRC	the Cooperative Research Centre
daf	dry ash free
db	dry basis
dmif	dry mineral inorganic free
DOC	dissolved organic carbon
EPA	Environmental Protection Agency
ESMS	electrospray mass spectrometry
Fe	iron
FFF	field flow fractionation
FID	flame ionisation detector
FTIR	Fourier transform infrared spectroscopy
g	grams

GC	gas chromatography
GLC	gas liquid chromatography
GLM	general linear model
HB	Hambach
HCl	hydrochloric acid
HFBA	heptafluorobutyric anhydride
HPLC	high performance liquid chromatography
HRL	Herman Research Laboratory
HTD	hydrothermal dewatering
IC	ion chromatography
ICP	inductively coupled plasma
IR	infrared
K	potassium
kg	kilogram
kN	kilo Newton
KS	Kingston
L	Litres
LC	Lochiel
LHS	Lochiel High Sodium
LLE	liquid-liquid chromatography
LR	linear regression
LTA	low temperature ashing
LY	Loy Yang
m	meters
M	mole per Litre (mole/L)
Mg	magnesium
min	minute
mL	millilitres
mm	millimeters
MPa	mega pascals
MS	mass spectroscopy

MSD	mass spectrometric detector
MTE	mechanical thermal expression
MW	molecular weight or Morwell
MΩm	mega Ohm
Na	sodium
NMR	nuclear magnetic resonance spectroscopy
OC	organic carbon
P	pressure
PAH	polyaromatic hydrocarbons
PFBBBr	pentafluorobenzyl bromide
RSD	relative standard deviation
S	sulphur
SD	standard deviation
SECV	State Electricity Commission of Victoria
SPE	solid phase extraction
SRC	solvent refined coal
T	temperature
TIC	total ion chromatogram
TMO	trimethyloxonium tetrafluoroborate
TOC	total organic carbon
UBC	upgraded brown coal
μL	microlitres
μm	micrometers
wb	wet basis
WSC	the Water Studies Centre
YL	Yallourn

PREFACE

This thesis consists of eight chapters. The first chapter is the introduction. In the following chapter, materials and methodologies applied to this project are described, although some detailed experimental methodologies are introduced in individual chapters where necessary. Chapters Three to Five are dedicated to the organic analysis of MTE water. Chapter Three focuses on the development and evaluation of sample pre-treatment methods using SPE with and without derivatisation for identification and quantitation of major low molecular weight organic components by GC-MS. Chapter Four focuses on the discussion of identification results for major organic components present in the MTE process water. The fifth chapter outlines the effect of MTE processing conditions and lignite types on the amounts of major organic compounds and groups and of total organic carbon released into the MTE water. Chapter Six discusses the quantities of selected inorganic species in the process water as affected by processing conditions and the possible mechanisms of the removal of these inorganics during dewatering. The effects of introducing acids into the MTE system and the use of different heating methods on the organic and inorganic compositions of the MTE water are evaluated in Chapter Seven. The eighth chapter provides a conclusion and includes suggestions for future work. References are presented at the end of the thesis.

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CHAPTER ONE

INTRODUCTION

Southeast Australia's lignite deposits are very large and have provided the basis for a secure low-cost power supply over several decades. Due to the high moisture content (typically 50-70%) of these lignites, a drying process is the first and essential step in almost any process for lignite upgrading or utilization. Therefore, minimising the energy consumption of this drying step is critical to the economic viability of the overall process. Current coal dewatering technologies for power generation consume substantial amounts of energy in the evaporation of coal moisture.

Novel methods of water removal from low-rank coals have been developed and investigated [1-5]. Most of these dewatering techniques aim to reduce the moisture content by non-evaporative means so as to utilize the energy more efficiently. One of these dewatering processes is termed Mechanical Thermal Expression (MTE) [3, 6-8]. It involves the treatment of low-rank coal at elevated temperatures and pressures, whereby a coal product with lower moisture content and hydrophilicity can be produced. Due to its efficient moisture removal capability and low energy consumption, the MTE technique has potential for industrial application [9, 10].

In non-evaporative dewatering processes such as MTE, water is removed from coal in a liquid form. As elevated temperatures and pressures are often employed in these processes, both organic and inorganic impurities released from the coal are expected to appear in the water stream, thus presenting a potential environmental impact. Knowledge of the nature of this process water is necessary for the evaluation of water quality issues related to the process and the selection of future wastewater treatment approaches. The promising MTE technique has been developed and investigated for several years. Nevertheless, neither organics nor inorganics in the waste streams from this process have been previously characterised. This project aimed to characterise both the organic and inorganic components in the MTE process water from batch tests as a function of processing conditions.

As an introduction to the thesis, this chapter firstly gives an overview of the background information related to Australian low-rank coals and their high moisture content. Coal dewatering technologies are then introduced focusing mainly on non-evaporative processes, especially the novel MTE technique. Wastewater issues related to these processes are discussed and a need for characterisation of the MTE water is justified. The work on analysis of organics and inorganics in wastewater from low-rank coal dewatering as well as in other coal processing wastewaters is reviewed. Analytical approaches, with an emphasis on those for organics, are assessed to assist in choosing the methods to be applied in this project to the characterisation of the MTE water. Finally, the objectives of this project are stated.

1.1. Australian Low-rank Coal

Coal is a sedimentary rock formed principally from plant debris that was accumulated as peat and has been subjected to geological alteration, i.e. metamorphism. Coal is ranked as lignite, subbituminous coal, bituminous coal and anthracite [11]. The severity of the metamorphic changes, or the degree of coalification, determines the rank of the coal. Coalification progresses from peat to lignite/brown coal, to subbituminous coal, to bituminous coal and finally to anthracite [12].

Low-rank lignite or brown coal is an intermediate stage in the transformation over time of accumulated vegetable debris into hard or black coals and hence still has high residual moisture contents in the 30%-70% range [13], a low heat value of about 6 to 16 MJ/kg and a higher oxygen content [14] and lower aromaticity [15] than coals of higher rank. In the literature, both the terms lignite and brown coal have been used, depending principally on the common usage in the country being referred to. In this thesis, the word lignite is used in most contexts for consistency.

Large deposits of lignite occur in many countries, such as Germany, Australia and the USA, and their development has played an important part in the industrial growth of these countries [16]. Low-rank coal deposits in Australia are mostly located in the southern mainland states of Victoria, South Australia and Western Australia. Based on the International Commission of Coal Petrology Classification [17], the low-rank coals occurring in Victoria are classified as soft brown coals and hard brown coals, whereas the

American ASTM classification system designates all these coals as lignite B [18]. Low-rank coals occurring in South Australia and Western Australia are frequently referred to as lignite [18].

South Australian lignite resources are significant and widely distributed throughout the State, but only one deposit has been developed and is used exclusively in power stations [18]. The development of these resources is hindered by the water-saturated and unconsolidated overburden and interburden [19], the remote locations and/or coal quality [18]. A number of separate deposits of low-rank coal have been located in Western Australia and are not currently mined. Exploration has revealed problems related to remote locations and also coal quality [18].

Unlike the resources in Southern and Western Australia, Victorian lignite resources are vast by world standards and are concentrated in exceptionally thick seams under a relatively thin cover of overburden. They have been widely developed for decades and are the mainstay of the State economy, providing an estimated 94.7% of the non-renewable energy resources within the State [19]. Victorian lignite has the advantages of low levels of nitrogen, sulphur and inorganic impurities, but the disadvantages of high moisture content, ranging from 50% to 70%, and high oxygen content. Due to its importance to industry in the State and its unique properties, Victorian lignite has attracted intense interest from state governments, industry leaders and scientists. For these reasons, this investigation concentrated on Victorian lignites. A number of South Australian lignites and a German lignite were also studied for comparative purposes.

1.2. Low-rank Coal Dewatering Techniques

Although low-rank coals have been widely used in industry and have provided economic energy sources, the high moisture content has been a major impediment to their efficient utilisation. The emphasis on reducing production of greenhouse gases, particularly CO₂, in recent years has increased the importance of energy efficiency to give minimum CO₂ production per unit of energy produced. It has been recognised that there is an inverse relationship between the moisture content of Victorian lignite and the usable heat available from combustion of the coal [13]. Moreover, the high moisture content brings about disadvantages such as expensive transportation, difficult combustion and, consequently,

high capital costs (e.g. a brown coal boiler has to be about 1.5 times larger in linear dimensions than a black coal boiler of similar output [20]) and operation and maintenance costs. Therefore, efficient drying/dewatering processes are of enormous potential benefit and need to be selected to meet the specific requirement of an intended application. To efficiently utilise the low-rank coals, a number of dewatering techniques have been developed and some used over several decades.

From a technical perspective, coal dewatering processes can generally be grouped into three broad categories: evaporative (thermal), thermal non-evaporative and other non-evaporative processes [13].

1.2.1. Evaporative Dewatering

Evaporative dewatering technologies, in which heat is directly or indirectly applied to evaporate water from coal at atmospheric pressure, are the simplest and most common commercial processes. The heat transfer medium is usually hot flue gas (as currently utilised in the power stations burning lignite in the Latrobe Valley, Victoria) or steam. Technologies such as solar drying [21], microwave drying [22] and vapour recompression [23] have also been attempted in recent years, but none of them have progressed beyond the pilot plant stage.

Fluidised bed drying using hot air/flue gas or steam to fluidise a bed of coal to facilitate moisture removal has been developed over many years with a number of test units and demonstration plants built [24-27]. As mentioned by Couch [14], due to the relative complexities of the techniques involved, fluidised bed drying has not been used commercially on lignites.

Although there have been technical advances in some of these processes, the basic principles remain unchanged. Since water is removed by evaporation and thus the latent heat of vaporisation is expended, these techniques are generally energy inefficient. While the evaporative processes with simple or improved techniques are still largely in use, coal industries and scientists continue to seek more energy efficient drying techniques.

1.2.2. *Thermal Non-evaporative Dewatering*

Because of their improved energy efficiency compared to evaporative techniques, non-evaporative (thermal) processes, in which water is separated from coal in a liquid form using thermal energy, are potentially attractive and have been increasingly investigated. These processes involve heat treatment of the coal under pressure with steam or water at temperatures between 230°C and 350°C [14].

Non-evaporative (thermal) dewatering has been commercialised in a number of countries since the 1920's when the Fleissner process [28, 29] was developed in Austria. The Fleissner process involves batch treatment of lignite lumps in autoclaves with steam at temperatures of 230-280°C and under pressure high enough to prevent evaporative drying [13, 30]. A drier coal product is obtained as the water is removed as a liquid and separated by drainage.

Based on principles similar to those used in the Fleissner process, a series of non-evaporative dewatering processes have been developed but none of them has progressed beyond the pilot plant stage [30]. The Evans-Siemon process [31, 32], in which crushed coal is fed semi-continuously in water suspension to the reactor vessel and heated by high pressure steam, achieved improved thermal efficiency by avoiding the pressure cycling of the steam which occurs in the batch Fleissner system. Despite extensive further development by the (now defunct) SECV (State Electricity Commission of Victoria) [33-35], Evans-Siemon dewatering was considered far too complex and expensive [30] and was not progressed to a pilot plant.

Based on the same concept, a number of non-evaporative hydrothermal dewatering (HTD) processes have been developed, including a 100kg/h pilot plant in the Grand Forks Energy and Environmental Research Centre (EERC) – formerly Energy and Mineral Research Centre (EMRC) – in North Dakota, USA [36] and a 1 ton/h pilot plant built by the SECV Research and Development Department (now the Herman Research Laboratory – HRL) in Australia [4].

Another non-evaporative dewatering process is the upgraded brown coal (UBC) process, in which over 90% of the water in the coal can be replaced with a kerosene/asphalt mixture

when the mixture of coal and the oils is treated under temperature and pressure [5, 37]. However, economic evaluation of this process was not promising [37].

For the non-evaporative (thermal) processes, since water is removed as a liquid, there is a large saving in energy corresponding to the latent heat of vaporisation. However, due to the complexity of these processes and the cost of the additional pressurising facilities, the saving cannot significantly improve the overall economics of power generation. One of these processes, the HTD process, has been investigated by the Cooperative Research Centre (CRC) for Clean Power from Lignite [38]. Due to the high capital cost, the large electrical power consumption, the assumed large chemical energy loss from the coal during processing, the consumption of high pressure steam and the cost of wastewater disposal, it is not considered a viable technology [9].

1.2.3. *Other Non-evaporative Dewatering Processes*

Other non-evaporative dewatering processes include mechanical press dewatering, electro-dewatering, chemical dewatering and solvent dewatering [30]. Mechanical pressing has been practiced in Europe for generations on more fibrous drainable fuels, such as sugar cane bagasse and peat. In this process, raw material is mechanically compressed in a metal cylinder to a high pressure to expel the water in the material. Dewatering of lignite using the mechanical pressing technique has been extensively studied [39-43]. It has been concluded that the high pressures (10-50MPa) and long residence times (hours) required to produce significant dewatering together with the expense of equipment capable of undertaking this task inhibit the commercialisation of this technique [13, 44].

Electro-dewatering using electro osmosis has been investigated for dewatering of colloidal materials including coal washery wastes [45, 46]. A DC electric current applied to a slurry spread in an electrical field can dewater the immobile solid particles if they carry an electrostatic charge relative to the water in the slurry [30]. However, due to the un-encouraging outcome for coal dewatering [13], it is only considered as a supporting dewatering process to assist drainage, such as in solar drying, rather than as an independent drying process [30].

Chemical dewatering and solvent dewatering have been developed to the laboratory research stage [30] with no further progress identifiable in the open literature.

Due to the technical difficulties and high expense to realise adequate dewatering (such as in mechanical dewatering) and/or unsatisfying water removal outcomes, none of these dewatering processes has progressed to the pilot plant stage.

1.2.4. *A Novel Dewatering Technique – Mechanical Thermal Expression*

A novel dewatering process termed Mechanical-Thermal Expression (MTE) was first reported and patented by Professor K. Strauss' group in the Department of Chemical Engineering at the University of Dortmund, Germany [3, 47] and has been studied over recent years by this group [6, 7, 48] and by the CRC for Clean Power from Lignite, Australia [8, 49-52].

The MTE technique is a non-evaporative process combining the concepts of HTD and mechanical pressing. Water contained in the coal is removed in a liquid form by the application of both heat and mechanical force. To achieve a similar moisture removal, MTE requires less thermal energy than thermal dewatering (150-200°C for MTE versus >230°C for HTD) and considerably lower compression pressure (~6MPa) and shorter pressing time (minutes) than the mechanical dewatering (>10MPa and hours). Batch test results have shown that up to 80% of the original moisture content of Victorian lignite can be removed [49].

Therefore, proceeding under relatively mild conditions, the MTE technique has the advantages of low energy consumption, simple plant technology and short process time over the other non-evaporative processes and has very good prospects for utilisation in the power industry. Technical development and investigation are continuing in both Prof. Strauss' group in Germany and the CRC for Clean Power from Lignite in Australia. It has now progressed to the pilot plant stage in Germany with the commissioning of a quasi-continuous 2.6 ton/h pilot press unit at Rheinbraun AG's Sibylla research centre [6] and a 25 ton/h technical scale MTE unit at the RWE Energie's power plant [53]. A 1 ton/h pilot scale MTE rig in a different configuration has also been built and is under investigation at the CRC for Clean Power from Lignite [52].

1.3. Wastewater Issues with Non-Evaporative Dewatering Processes

The removal of coal water as liquid during the non-evaporative dewatering processes saves the latent vaporization energy and improves the efficiency of power generation. However, there is a disadvantage of this approach, i.e. the production of a wastewater stream. Since these processes usually employ elevated temperatures and/or pressures, the process effluents may contain significant amounts of organic contaminants as well as inorganics released from the coal. These present potential environmental impacts.

Analysis of wastewater from some non-evaporative processes has provided evidence for a sometimes heavily contaminated process effluent and thus a requirement for a wastewater treatment procedure. The analysis of process wastewater from a hydrothermal dewatering process development unit in North Dakota, USA [54] and from an HTD processing demonstration unit in Victoria, Australia [55, 56] has been reported. Table 1-1 summarises the analytical results for HTD water in the two reports and lists relevant water quality guidelines/criteria for comparison. The right three columns show data collected from the Australian and New Zealand guidelines for protection of aquatic ecosystems of freshwater [57, 58], for raw water for drinking purposes [57] and the EPA recommended water quality criteria [59], respectively.

Table 1-1. Results of water quality analyses of HTD wastewater compared with relevant water quality guidelines/criteria.

		EPRI result [60]		SECV result [55]	Guidelines for protection of aquatic ecosystem [57, 58]	Guidelines for raw water for drinking purposes [57]	EPA water quality criteria [59]
Processing conditions	lignite	Indian Head		Loy Yang			
	Processing temperature (°C)	330		300			
General parameters	pH	8.4	7.9	4.2	6.5-9.0	6.5-8.5	6.5-9
	TDS* (mg/L)	-	-	2460	<1000 (Salinity)	1000	250
Organics	TOC (mg/L)	3590	4230	1320	-	0.2 (organics**)	-
	BOD ₅ (mg/L)	1330	2270	1400	-	-	-
	COD (mg/L)	11100	12800	5300	-	-	-
	Phenol (mg/L)	20	20	15.4	0.085-1.2		-
	Ethanol (mg/L)	30	3	-	0.4-4.0	-	-
Inorganics & heavy metals	Sodium (mg/L)	973	1120	86	-	300	-
	Chloride (mg/L)	-	7	54	-	400	860
	Sulphate (mg/L)	100	140	190	-	400	-
	As (µg/L)	-	-	1.6	-	-	340
	Cd (µg/L)	-	-	0.07	-	-	4.3
	Pb (µg/L)	-	-	3.8	-	-	65
	Hg (µg/L)	-	-	<0.02	-	-	1.4

- not available/applicable

* total dissolved solids

** data obtained by CCE & CAE (carbon chloroform extraction and carbon alcohol extraction)

In evaluating the environmental impact of these wastewater sources, the organic contaminants are of prime importance because of their high levels in the effluents and their likely toxic characteristics. During a thermal dewatering process, organic structures of the coal can be decomposed to some extent, with the fragments dissolved in the water phase leading to increasing organic levels in the water. The analytical results shown in Table 1-1 indicate that the HTD wastewaters contained significant amount of total organic carbon (TOC) and corresponding high levels for chemical oxygen demand (COD) and biological oxygen demand (BOD). Phenols, as a major organic group often found in aqueous and non-aqueous liquids derived from coal [61-64] and mostly toxic in nature, were determined at a significant level in the HTD wastewaters, including two EPA priority pollutants – phenol and 2,4-dimethyl phenol [65]. Investigation proved that, in a fish killing incident caused by the effluent discharged from a coal gasification plant in China, 2,4-dimethyl phenol, 2-methyl phenol, 3-ethyl phenol and 2-ethyl phenol were among the major toxic compounds responsible for the total toxicity of the effluent [66]. These compounds were also detected in the HTD wastewaters [56, 65]. In summary, it is obvious that both the high levels and toxicity of the organic content in the HTD wastewaters cannot be accepted by natural water sources and, therefore, the process effluents cannot be disposed of directly to the water system without any treatment.

Compared to the environmental impact of organics, that of inorganics is of less concern for the HTD wastewaters. As shown in Table 1-1, heavy metals, which are a major environmental concern due to their toxicity, were present in the HTD water at levels far below the EPA water quality limits.

Like the HTD process, MTE employs elevated temperature (although lower than for HTD) and elevated pressure and produces a wastewater stream as a by-product. It would be expected to have similar environmental issues to the HTD process. For further development and study of MTE, information about water quality is therefore necessary, as discussed in more detail in Section 1.4.

1.4. Importance of Characterisation of Wastewater from Non-Evaporative Dewatering Processes

Prior analyses of the HTD wastewaters have led to an understanding that the effluents from non-evaporative dewatering processes may present an environmental impact, particularly to organic components. Consequently, wastewater cleanup will have to be considered when dealing with the whole dewatering strategy. Characterisation of the process wastewater is therefore imperative for the following reasons.

1.4.1. For Evaluation of Dewatering Techniques

An understanding of the nature of the effluent from a dewatering process such as MTE is necessary for the evaluation of the viability of the technique.

In general non-evaporative dewatering is considered energy efficient as the latent energy of vaporisation is saved. However, the overall process cannot be considered efficient and practical if the wastewater contains compounds which are difficult to remove and the concentrations of impurities are too high, as these often result in a high cost for wastewater treatment. Also, high levels of organics in the water imply a significant energy loss of the coal during processing. Detailed characterisation of organic compositions of HTD wastewaters indicated the presence of complex mixtures of hydrophilic and hydrophobic components [56, 65] and hence a requirement for a combination of water treatment techniques [55]. Comprehensive analyses of the technical and economic aspects of the HTD process, taking into account the important information provided by the water analysis, indicated that the process was not economical. Large energy loss due to organics in the wastewater and the high cost of wastewater disposal contributed significantly to this conclusion [9].

1.4.2. For Selection of Wastewater Cleanup Techniques

For a dewatering technique (such as MTE) that is proved to be practical and in the demonstration phase, knowledge of the nature of process effluents will help the selection of wastewater cleanup remedies.

Water treatment techniques are typically targeted at specific types of contamination. For example, reverse osmosis and electrodialysis are mainly used for the removal of dissolved inorganic salts, while biological processing is very efficient for removing organic matter in

wastewater [67]. Many physico-chemical water treatment techniques will only treat lipophilic components and leave the hydrophilics in solution, whereas biotreatment, on the other hand, is a possible approach to the removal of hydrophilic organics [55]. Hence, it is necessary that the composition of the process wastewater be characterised so as to help the design of appropriate water treatment schemes that facilitate the cleanup of different pollutant groups.

1.4.3. For Optimisation of Processing Conditions

Characterisation of the process water produced from non-evaporative dewatering under varied processing conditions will assist in optimisation of the process.

During the dewatering processes, both organic and inorganic species are removed from the coal. The removal of organic carbon, which is the energy source of the coal, is undesirable. Large energy loss by this path will reduce the coal combustion value and energy efficiency of the overall process. Therefore, in selecting the processing conditions the aim should be to minimize the organic carbon loss, consistent with other constraints (e.g. water content of the product).

On the other hand, the processing conditions should be selected to maximise the removal of inorganics, especially the volatile inorganics, consistent with other constraints, so as to minimise fireside fouling and corrosion problems during lignite combustion. Practical experience and laboratory studies on Victorian lignite have demonstrated that non-mineral inorganics in the coal contribute to the serious fireside ash fouling and corrosion problems experienced during combustion. The release of volatile inorganics is an important aspect of fly ash formation [68] and has been found to substantially influence the rate and severity of both fireside fouling/slugging [69, 70] and fireside corrosion of heat transfer surfaces [71]. The problems created by ash deposits and fly ash include reduced heat transfer, impedance of gas flow, corrosion of pressure parts and, thereby, additional maintenance costs for boiler operation [72, 73]. It is predicted that major volatile inorganics in Victorian lignite fired boilers at typical combustion temperatures (1300-1500K) are NaOH and NaCl with lesser quantities of Na_2SO_4 , Na and NaO [68]. Fireside bottom ash deposits are also related to non-mineral inorganic elements including Na, Ca, Mg, Fe, S and Si in Victorian lignite [74, 75]. Based on observations on the formation of deposits in experimental furnaces

burning a test coal under standard conditions, a general Fouling Index equation was developed by Garner [75] to predict the relative ash fouling behaviour of Victorian lignite:

$$\text{Fouling Index (all areas)} = 0.064 \text{ Si} + 0.132 \text{ Fe} + 0.085 \text{ Ca} + 0.438 \text{ Mg} + 0.570 \text{ Na} - 0.106$$

where the elemental compositions are expressed on a percentage dry coal basis. Although there are limitations on the validity of the Index for large scale boilers, the contribution of these elements to the formation of fireside deposits is definite. Hence, it will be of benefit if the processing conditions of dewatering can be chosen to improve the release of these inorganics to the water phase, in order to reduce fouling/corrosion problems.

For South Australian low-rank coals, the problems with the inorganics are even more serious. The lignites are utilised by industry only to a small extent mainly due to their very high concentrations of inorganic constituents, particularly sodium, chlorine and sulphur. Research on South Australian lignites has found problems due to inorganic salts in both coal combustion [76-78] and coal gasification processes [79]. It was concluded that sodium species, such as chlorides [79], sulphates and silicates [78], were likely to be the source of deposits on the equipment due to their low melting points.

In summary, optimisation of processing conditions should strive to identify (a) a balance between reducing organic removal and increasing inorganic removal from the coal as well as (b) a balance between higher coal moisture reduction and lower energy consumption. Quantitation of both organic and inorganic compositions of the process effluents as a function of processing conditions is necessary to achieve this.

This conclusion is also applicable to MTE. Although the MTE process investigated is carried out using laboratory batch test rigs, the results should be able to give an indication for future scaled-up processes, which are based on the same concept and mechanism.

1.5. Organics in Coal Processing Wastewater

As discussed in Section 1.3, wastewater issues related to the non-evaporative dewatering processes are closely associated with organic pollutants present in the water. The following review covers analytical work on organic components in wastewater from various coal processing sources including low-rank coal dewatering.

1.5.1. Analysis of Organics in Wastewater from Various Coal Processing Operations

For investigation of the nature of the effluents from low-rank coal dewatering processes, it is necessary to review the studies of wastewater streams from various coal processing operations, as the streams are likely to contain similar components derived from coal. Analytical approaches applied in earlier work may therefore help to identify the methods that can be used for characterising organic components in the MTE process water.

Many studies have originated from the evaluation of the environmental impact of liquid wastes from coal related operations or facilities, such as thermal power generating stations, coke ovens, coal conversion facilities as well as drying processes for low-rank coals and similar materials. Analytical approaches including gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) have often been employed.

Coal gasification is basically a process in which coal is gasified at high temperature and pressure with steam and air or oxygen. The organic content of gasification wastewater has attracted attention from water analysts [63, 80-82]. To characterise the wastewater from a gasification plant, Frucher and Petersen [63] developed a detailed analytical procedure involving solvent extraction and fractionation of organic analytes from the aqueous phase followed by GC-MS identification and quantitation of major components. Mohr and King [83] identified low-volatility and polar organic compounds in coal gasification condensate water. The analytical technique consisted of HPLC separation of the extracts followed by GC-MS analysis of the HPLC fractions.

Aqueous liquids from other coal conversion processes have also been of interest to researchers. The methods mentioned above developed by Frucher and Petersen [63] were used to analyse wastewater samples from an SRC (solvent refined coal) liquefaction plant. Olson et al [84] investigated a lignite liquefaction process in an aqueous system. They examined the reaction products using various instrumental approaches, including solid state ^{13}C NMR for residues, GC/FTIR/MS for solvent solubles and HPLC for catechols.

An important source of aqueous processing waste worthy of mention is the waste streams from drying processes for low-rank coals and coal-like materials such as peat and bark. Fagernäs and coworkers [85, 86] studied a fluidised-bed drying process for peat, bark and lignite and characterised the aqueous effluents using GC-MS, HPLC and GLC (gas liquid chromatography). HPLC was used for the analysis of water soluble and hydrophilic compounds [85]. Low molecular mass carboxylic acids (volatile hydrophilic acids) [85], other hydrophilic compounds [87] and lipophilic compounds were analysed by GLC, whereas the water solubles in acetone were separated and identified by GC-MS [86].

Non-evaporative dewatering techniques have been developed and some commercialised for decades. Characteristics of the organic composition of wastewater from these processes are expected to be more similar to that of the MTE process water than those of the processes discussed above. However, the information available in the literature is rather limited. Characterisation of organics from non-evaporative dewatering sources is carried out utilising similar techniques to that used for other coal processing wastewaters. As mentioned in Section 1.3, wastewaters from two HTD demonstration units in North Dakota, USA and Victoria, Australian were analysed [54-56]. GC-MS and NMR spectrometers were applied to characterisation of organics in wastewater from the North Dakota unit [54], while GC and GC-MS were used for the identification and quantitation of organics in wastewater from the Victorian HTD unit [56]. Racovalis [65] studied the organics in wastewater from HTD batch experiments using methods such as GC-MS, NMR and ESMS (electrospray-MS). The analytical approaches utilised in these studies provide options for the investigation of the MTE water.

1.5.2. Organic Composition of Low-rank Coal Processing Wastewater

The types of compounds or compound groups released to the wastewater during coal processing and their quantities may depend on the nature of the process, the materials processed and the severity of the processing conditions.

Organic compounds removed from operations processing high rank coals and processes employing severe conditions are more likely to be aromatic and hydrophobic. For example, in wastewater from a coal gasification process, Frucher and Petersen [63] found naphthalene as the major organic compound at about 10 ppm in gasifier quench water with

a variety of polyaromatic hydrocarbons (PAHs) also identified. Hydrophobic abietane, abietatriene, ferruginol and retene were identified to be the major components of the extractable fraction of organics from the scrub water.

Compared to the liquids derived from high rank coals during processing, those from lignite or peat are more likely to contain aliphatics and compounds containing oxygen functional groups, corresponding to the low aromaticity and high oxygen content of low-rank coals or peat (refer to Section 1.1). In a fluidised bed drying process of peat and bark, Alén and coworkers [85] identified the condensing organic materials to be mainly aliphatic carboxylic acids, aliphatic alcohols and aldehydes and carbohydrates. They also found that the amount and composition of organic components were markedly affected by drying temperature, with the amount increasing more than ten-fold when the drying temperature increased from 190 to 350°C. Analysis of wastewater from the Victorian HTD unit treating Loy Yang coal showed that major organic components present were aliphatics and oxygen-containing compounds including carboxylic acids, cyclopentenones, ketones, aldehydes, phenols and alcohols [55, 56]. Table 1-2 presents a list of the components, mostly oxygen-containing compounds, identified in the wastewater from HTD batch experiments by Racovalis [65].

Table 1-2. Components identified in wastewater from an HTD process [65].

Phenols	Alkanes	Substituted benzenes
phenol	4-propylheptane	1,2-benzenediol
2-methylphenol	2,6,8-trimethyldecane	3-methoxy-1,2-benzenediol
2-methoxyphenol	2,5,6-trimethyldecane	1,4-benzenediol
2-ethylphenol	2,6-dimethylheptadecane	2-methyl-1,4-benzenediol
4-methoxy-2-methylphenol	2,4,6-trimethyldecane	3-methyl-1,4-benzenediol
2-methoxy-4-methylphenol	3-methyltridecane	4-ethyl-1,3-benzenediol
2,4-dimethoxyphenol	Octacosane	1,2,3-trimethoxybenzene
3,4-dimethoxyphenol	2,6,10,14-tetramethylheptadecane	1,2-dimethoxybenzene
4-ethyl-2-methoxyphenol	5-methyltetradecane	1,4-diethylbenzene
2-methoxy-4-propylphenol	8-hexylpentadecane	1,2-diethylbenzene
2,5-methylphenol	4-methylhexadecane	1-methyl-(1-propenyl)benzene
4-methoxyphenol	1-tetradecene	1,2,4-triethylbenzene
2,6-dimethoxyphenol	pentatriacontane	1,3-dimethylbenzene
3-ethylphenol		1,3,5-triethylbenzene
4-methylphenol	<u>Cyclopentanones</u>	4,5-dimethyl-1,3-benzenediol
4-ethylphenol	2-hydroxy-3-methyl-2-cyclopentenon-1-one	2-methoxy-1,4-benzenediol
4,5-dimethoxy-2-methylphenol	2-methyl-2-cyclopenten-1-one	2-methyl-1,3-benzenediol
4,6-di[1,1-dimethylethyl]-2-methylphenol	2,3-dimethylcyclopent-2-en-1-one	4-methyl-1,2-benzenediol
2,6-bis[1,1-dimethylethyl]-4-ethylphenol	4,5-dimethylcyclopenten-1-one	3-methyl-1,2-benzenediol
2,4-dimethylphenol	2,3,4-trimethyl-2-cyclopenten-1-one	
2,6-dimethylphenol	3-methylcyclopent-2-enone	
2-ethyl-6-methylphenol	4-hydroxy-4-methyl-2-pentanone	<u>Others</u>
3,3,5-trimethylphenol	2-methylcyclopentenone	benzaldehyde
2-methoxy-6-(1-propenyl)-phenol		Vanillin
2-(propenyl)-phenol	<u>Acids</u>	spiro2,4heptan-4-one
1-[4-hydroxy-3-methoxyphenyl]-ethanone	tetradecanoic acid	3,3,5-trimethylcyclohexane
1-[4-hydroxy-3-methoxyphenyl]-2-propanone	hexadecanoic acid	2,3-dihydro-1H-inden-1-ol
1-(3-hydroxyphenyl)-ethanone	oleic acid	3,4-dimethyl-4-hexen-2-one
	octadecanoic acid	2,6-dimethylpyridine
	propanoic acid	
	2-methylpropanoic acid	

1.6. Strategies for Organic Analysis of MTE Process Water

Compared to the analysis of inorganics, analysis of organic compounds, which have more complex characteristics, is often more matrix dependent and requires cautious sample pre-treatment and sensitive analytical tools. On the one hand, approaches reported in the literature for organic analysis can be adopted and applied to the studies of similar water sources. On the other hand, differences in the nature of the water sources often require the establishment of analytical methods tailored for a particular analysis. This provides space for development and/or improvement of the analytical methods.

Therefore, with the expectation of establishing new methods and/or improving existing methods suitable for characterisation of the MTE process water, the analysis of organic components was the main focus of this project.

1.6.1. *Selection of Analytical Techniques*

1.6.1.1. For characterisation of organic compounds

As reviewed in Section 1.5.1, GC, GC-MS and HPLC, sometimes combined with FTIR and NMR, are the most common approaches applied to characterisation of organic compositions of effluents from coal processing including lignite dewatering. These techniques are in fact also the general analytical methods for organics in complex mixtures.

Infrared spectroscopy (IR) identifies functional groups present in the molecule and gives some indication of the presence of hetero elements – O, S, N, Si, halides – including their chemical environment. NMR identifies the type of hydrogen and carbon in organic molecules and also reveals the positions of functional groups in the molecule relative to each other. The limitations of the IR and NMR techniques are due to the fact that they usually cannot differentiate individual compounds present in complex mixtures. Furthermore, it is often difficult to obtain quantitative results for individual components or compound groups. For the characterisation of unknown organic mixtures in this project, these two techniques would not complete the task.

HPLC is often used for non-volatile, thermally labile and polar samples such as acids, bases, ionic compounds, surfactants and macromolecular compounds. Alén et al [85] used HPLC to characterise water soluble, hydrophilic compounds in peat and bark drying condensates. Although the water soluble compounds that accounted for 90-95% of the TOC in the condensates could be measured, the method was found not able to detect the volatiles easily. In addition to its weakness for volatile analysis, HPLC also has the disadvantages of low sensitivity and low separation efficiency. HPLC enabled Anthony et al [81] to perform analysis of phenols and organic nitrogen compounds in gasification liquors with a determination level down to about 1 ppm. However, it should be mentioned that the concentrations of the major compounds examined in the liquor were generally well above ppm levels with major phenols at 20-5000 mg/L and nitrogen compounds at 5-200 mg/L. The poor sensitivity of the technique compared to GC techniques is presumably not suitable for determining organics in the MTE water, which is produced under mild conditions and thus likely to contain low levels of organics.

GC is probably the most important single analytical technique used today, being able to analyse individual components both qualitatively and quantitatively. Coupled with various detection techniques, it provides an efficient separation technique and identification and quantitation method for volatile and low molecular weight organics with high sensitivity. Great progress has been made in interfacing GC with MS, IR and even NMR in recent years. Combining the ability of GC to separate components in complex mixtures and the power of MS to give information about the molecular weight and molecular structure of organics, the GC-MS method has the advantage over other measurements of being able to readily identify individual components in a complex matrix. Furthermore, the method has an important advantage over GC combined with other detectors; as MS can monitor selected ions, there is less interference from background or unseparated components.

With MS as a detector, usually GC is used for the initial screening procedure to determine the separation properties of the mixture and the MS detector is used to identify the compounds of interest. As demonstrated in Table 1-2, the power of GC-MS enabled about one hundred organic components to be identified in the wastewater from HTD batch experiments [65].

Thus, GC, especially when coupled with MS, has benefits over other analytical approaches for the purpose of developing a comprehensive understanding of volatile and semi-volatile components in wastewater. For identification and quantitation of these low molecular weight compounds in the MTE process water, which is produced under relatively mild conditions and hence expected to consist of organics at relatively low levels, GC-MS was selected as the preferred analytical approach.

1.6.1.2. For molecular weight distribution

GC techniques are usually superior for the analysis of volatile and semi-volatile organic compounds with low molecular weight. Due to the complexity of wastewater from coal processing in terms of its organic composition, supplementary information from other analytical approaches may be required to obtain a complete view, such as the surveys reported in the literature using HPLC, NMR, etc [65, 83, 85].

Organic compounds of molecular weight up to ~400 (Dalton) can usually be detected by GC techniques. Thus a method of obtaining the molecular weight distribution of the

organic constituents will provide an estimate of the proportion of organics detectable by GC, as well as giving useful general information about the organics in the wastewater.

Field-flow fractionation (FFF) is a relatively new separation method capable of high resolution fractionation of macromolecules, colloids and particles [88, 89] and, therefore, able to provide molecular weight distribution information. It is a chromatography-like elution technique but utilises physical separation mechanisms rather than chemical interactions [90, 91]. The sample is partitioned in an open, thin, ribbon-like channel by an externally applied field or gradient (e.g. electrical, magnetic, flow) due to different carrier velocities of sample components in the field [92].

Flow FFF, in which the driving force is a cross flow perpendicular to the channel, has been applied to characterisation of organic materials in effluents from various industrial processes including pulp and paper mills [89] and an HTD pilot plant [92]. Using the flow FFF method, Fonseka [92] was able to determine the molecular weight information about dissolved organic matter in the effluents from an HTD processing of the Latrobe Valley lignites.

In this project, as a supplemental approach to GC-MS characterisation, FFF was used to analyse the molecular weight distribution of organic matter in the MTE samples.

1.6.2. Sample Preparation Methods for GC Analysis

Prior to GC analysis, water samples often require pre-treatment, such as enrichment, extraction and fractionation, mainly for the following reasons:

- a) increasing the concentrations of the components which are present in the water at such low levels that otherwise they may not be detected by GC;
- b) isolating the components into a non-aqueous phase so that they can be analysed on GC columns, which may be damaged by water; and
- c) fractionating the components into different compound classes so that the sometimes complex mixtures can be effectively separated by GC.

The validity of an analytical method relies to a large extent on the efficiency of the sample pre-treatment procedures. Appropriate sample preparation methods can improve the

quality of a particular analysis considerably and *vice versa*. Since methods of utilising the GC technique for organic analysis are rather well-established, the development of new sample preparation methods and improvement of the existing methods for GC analysis have given scope for further exploration and have been a challenge for analytical chemists. Indeed, the development of improved sample preparation methods was a significant aspect of this project on MTE water characterisation.

A number of sample preparation methods have been investigated and applied over the years.

1.6.2.1. A conventional method – liquid-liquid extraction.

For decades, the most popular extraction and fractionation method was liquid-liquid extraction (LLE), in which organics are extracted from aqueous to organic phase with solvents, based on the solubility difference of the analytes in the two phases. Compound groups concentrated in the extract are determined by the selection of solvents and sometimes pH adjustments. This method was widely used for organic analysis of aqueous samples from various sources and provided a very useful tool before new sample preparation methods were introduced in recent years.

Serious weaknesses of LLE include the need for large volumes of samples and solvents, limited solvent selection range, emulsion formation between the two phases and lengthy preparation time and labour-intensive procedures. The use of large amounts of solvent results in the need to concentrate the extracts, leading to increased levels of interference from solvent impurities and possible analyte loss during the concentration step. Since LLE requires the solvents to be immiscible with water, this limits the use of polar solvents that could be used to extract polar and hydrophilic components. Moreover, multiple step extraction procedures require the use of a large amount of clean glassware, high grade (expensive and often toxic) solvents, intensive manpower as well as skilful personnel to achieve acceptable quantitative results.

To achieve improved extraction and separation efficiency, very complicated sample pre-treatment schemes, such as the one shown in Figure 1-1 used for organic analysis of coal gasification wastewater [80], are often necessary. The schemes usually include repeated steps of pH adjustment, extraction and back extraction of both aqueous phase and solvent

phase and cleaning of the extracts [93, 94]. Quantitatively, the repeated extraction and cleaning steps along with the emulsion problem are likely to result in the loss of the analytes, whereas unselective solvent extraction often leads to very complex mixtures that are difficult to separate by GC. It was found that the solvent fractionation technique applied to GC-MS analysis of the HTD wastewater did not partition organic species cleanly into different fractions [56]. The chromatograms of the extracts were found to be very complex and only about 7% of the over 60 compounds detected could be identified. Wang and Zhao [80] agreed that, for mixtures containing very complex organic compounds at high concentrations, LLE alone was inadequate for fractionation of the organics and had to be combined with other methods. After testing an LLE separation scheme for isolating organic components from HTD wastewater, Racovalis [65] pointed out that the LLE method was not suitable for the work and the solid phase extraction (SPE) method was chosen as an alternative.

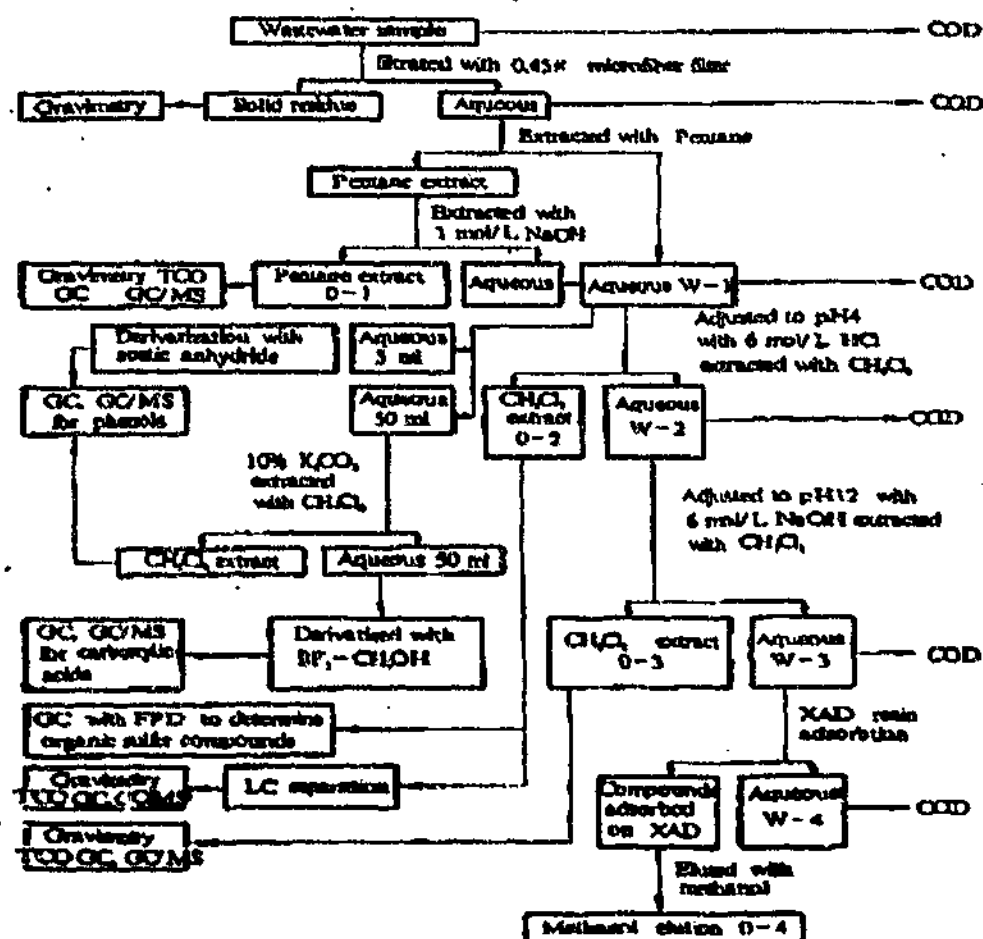


Figure 1-1. Separation scheme for GC-MS analysis of a gasification wastewater [80].

1.6.2.2. Solid phase extraction – SPE

SPE has become a very powerful tool for organic analysis of aqueous samples in recent years, as numerous solid phases have become commercially available. During the SPE process, analytes in a liquid matrix (aqueous or non-aqueous) are trapped in a solid sorbent and can be eluted in stages with solvents that have different affinities for certain compound groups. The various solid phases available – non-polar, polar, cation and anion exchange, etc – and the option of a variety of elution solvents – organic solvents of different polarities, acidic and basic buffers and ionic strength buffers – offer a great number of combinations to be optimised for a particular analysis. Therefore, compared to the LLE method, SPE has greatly enhanced separation and fractionation capabilities and there is scope for further improvement.

SPE as the sample pre-treatment method has been applied to wastewater analyses for years and its advantages over LLE have often been demonstrated [95-99]. There have been studies in which the drawbacks of LLE were substantially overcome with significantly

reduced usage of organic solvents, extraction time and labour when SPE was chosen as the preferred method [97, 99]. Compared to LLE, SPE proves to be less matrix dependent [97, 98] and offers better cleanup of complex samples and comparable or increased recoveries for analytes [97-99].

This method has been utilised for the analysis of organics such as phenols [100-103] and carboxylic acids [104, 105], which are often present in coal processing wastewater (see Section 1.5.2). For the purpose of extracting hydrophilic compounds in industrial wastewaters, Fiehn and Jekel [104] tested both silica based and polymer based SPE sorbents. Recovery studies found some polymer based sorbents to be powerful for the enrichment of hydrophilic aromatic substances, including carboxylic acids and phenols, with recovery rates mostly >80%. Grist et al [93] adopted an SPE method using C18 solid phase from Alltech® for the analysis of carboxylic acids in aqueous effluents from ozone bleaching pulps. Carboxylic acids eluted by serial addition of acetone, dichloromethane and methanol to the sorbent could be detected by GC-MS. Pissolatto et al [106] described a method of pre-concentrating contaminants in chlorinated phenolic pulp bleaching wastewater using SPE followed by GC analyses. The researchers applied the same method to extraction of phenols in coal gasification wastewater [82].

For characterisation of organics in wastewater from HTD batch tests treating Victorian lignite, SPE was evaluated as the sample pre-treatment method for GC-MS analysis [65]. A number of solid phases from Varian®, including C18, C8, CN and ENV, and elution solvents of different polarities were tested. Extraction of the water sample with C8 followed by successive elutions with dichloromethane and methanol was determined to be the most suitable. The extracts containing various compounds groups including phenols, cyclopentenones, alkanes and a few acids were successfully analysed by GC-MS (Table 1-2).

For GC-MS analysis of the MTE process water, SPE with all the advantages and successful applications in similar cases was selected as the sample preparation method. In order to achieve optimal results for the specific analysis of the MTE water, influential factors such as sorbents, elution solvents and extraction conditions were evaluated.

1.6.2.3. Derivatisation

GC is better adapted to the analysis of volatile and non-polar compounds than that of non-volatile and polar compounds. Derivatisation can be used to convert components with zero or low GC sensitivity to forms more suitable for GC analysis by reaction with selected derivatisation reagents. The main purposes of derivatisation are to increase the volatility of an analyte, to improve chromatographic characteristics of an analyte by decreasing its polarity and/or to increase the detector sensitivity of the analyte [107].

Most derivatisation reagents replace a labile hydrogen atom attached to a hetero-atom with a less polar, non-labile group [107]. Typical derivatisation reactions include silylation, alkylation/esterification and acylation for functional groups such as acids, alcohols, phenols, amines, aldehydes and ketones. As mentioned in Section 1.5.2, aqueous waste derived from coal often contains organics such as phenols, carboxylic acids and alcohols, which are generally polar and not very volatile. Derivatisation is often an essential step for the analysis of these compounds in wastewater from coal and coal-like materials to achieve satisfactory GC detection [80, 87, 93, 108].

In the water from the MTE process, which is carried out under relatively mild conditions, organics are likely to contain such polar functional groups as phenolics and carboxylic acids and are also expected to be present at low levels. Derivatisation would probably be required to improve the GC properties of these compounds.

It is worthy of mention that trimethylsilylation using reagents such as bis(trimethylsilyl)trifluoroacetamide (BSTFA) is a common derivatisation method for increasing the volatility and improving the GC characteristics of polar compounds [107] and has been often applied to characterisation of phenols and carboxylic acids in environmental samples [109-111]. However, the build-up of derivatisation reagents throughout the chromatographic system can lead to time-dependent in-situ trimethylsilylation of susceptible groups where derivatisation is not required. A dedicated GC instrument to perform analyses involving trimethylsilylation is recommended [107]. For this reason, in the present study, silylation methods were not considered as an option for MTE water analysis.

Further justification of the necessity of derivatisation for MTE water analysis and evaluation of the optional derivatisation methods are discussed in Chapter Three.

1.7. Analysis of Inorganics in Coal Processing Wastewater

1.7.1. *Inorganics in Lignite and Selection of Inorganics for Characterisation*

In high rank coals, inorganics are present mainly as minerals. Elements in the mineral species include major elements (such as Si, Al, Fe, Ca typically at a level of over 0.5%), minor elements (such as Mg, Na, K, Ti typically ranging from 0.02% to 0.5%) [112, 113] and trace elements (such as Zn, Ba, B, Zr, Sr, V, Pb, Cr, Ni, Cu, As, Co, U, Hg) [72] typically appearing in a range of parts per million (ppm) down to parts per billion (ppb) [114].

Unlike in the high rank coals, inorganics in lignites occur not only as discrete mineral particles, but also as elements distributed within macerals either chemically bound to organic functional groups, or dissolved as ionic species in coal water [68].

Since there are many species of inorganics in lignite, it is impracticable and unnecessary to characterise all the species in the MTE process water. Only those most likely to be present in the water and those of interest for the purpose of evaluating the coal beneficiation effect of the process should be taken into consideration. For the selection of inorganic species for characterisation, there are three types of inorganics to choose from, i.e. the minerals, the non-mineral inorganics and possibly the trace elements. Mineral species, such as quartz (SiO_2), pyrite or marcasite (FeS_2) and a variety of clays in Victorian lignite [68], are not of interest since they are essentially water insoluble, although some major elements may be present in a relatively large amount. Trace elements including heavy metals occur in lignite at very low levels, as results for Victorian lignites have demonstrated [68]. Studies indicate that environmental concerns associated with the heavy metals in wastewater from lignite dewatering processes are negligible [55]. This group of inorganics can also be excluded from consideration. Therefore, the most interesting group of inorganics for investigation would be the non-minerals, as they include either water solubles that are most likely to be found in the aqueous phase from lignite dewatering or species that are known to contribute to the fouling and corrosion problems during lignite utilisation.

The most important non-mineral inorganics occurring in Victorian lignite are sodium, calcium, magnesium with smaller amounts of iron and aluminium as organically bound cations together with dissolved sodium chloride salts in the in-seam moisture [68, 115]. In South Australian lignites, calcium and magnesium are also the major organic associated elements, while sodium, chlorine and sulphur (as sulphate) are the most abundant water solubles [116].

Furthermore, as indicated in Section 1.4.3, non-mineral inorganics in lignite, such as sodium, calcium, chlorine and sulphur which may form volatile salts during combustion, are the major cause of fireside ash fouling/slagging and corrosion problems during lignite combustion. For the study of the potential beneficiation effect of the MTE treatment, the behaviour of these inorganic species during the dewatering process is also of importance.

Thus, elements including sodium, calcium, magnesium, iron and aluminium and non-metals chlorine and sulphur (as elements or as chloride and sulphate anions) were the major inorganics selected for quantitation in the MTE process water.

1.7.2. Inorganic Analysis of Aqueous Coal Derived Liquids and Selection of Analytical Approaches

Information in the literature on the analysis of inorganic matter in coal processing wastewaters is not as abundant as for the organics. The discussion below therefore covers studies of other aqueous coal derived liquids such as coal leachates. These analyses are usually for the purposes of studying mineral matter and elements in coal structures [117], ion exchange properties of the coal [118] and leaching behaviours of some elements [119]. Investigation of ash fouling or fireside deposit problems during coal utilization [120] and the environmental impact analysis of trace elements released from coal [121, 122] also require information provided by inorganic analysis.

The most commonly used analytical techniques for inorganics in coal derived water are atomic absorption spectroscopy and inductively coupled plasma methods.

1.7.2.1. Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) is probably the most frequently used method for quantitative elemental analysis of liquid samples, including those derived from coal [117,

119, 122-125]. AAS involves light absorption at specific wavelengths by free atoms. It is a reliable method of elemental analysis and is particularly useful for determination of trace metals in liquids. Most importantly, because samples are totally stabilised prior to analysis it is practically independent of the chemical forms of the element in samples.

AA analysis of aqueous coal processing streams and wastewater has provided useful information for understanding the processes and revealing potential environmental issues. AA was used for the analysis of Hg, As, Pb, Cd, Na, Li, K, Ca and V in the vapour phase of a gasification product stream [123]. The author concluded that defining the qualitative and quantitative nature of materials found in the product stream from the gasification test unit played an important role in developing the technology. An AA analysis determined that selected trace elements were present in some of the aqueous liquids from a coal Synthoil process in small quantities [122]. This supportive information enabled the researchers to conclude that the handling of wastewater streams from large Synthoil facilities should not be a serious problem with regard to the emission of these potentially toxic trace elements into the environment. Jimen / Carmona et al [119] proposed a novel subcritical water extraction method for the extraction of ash-forming elements from coal. An atomic spectrophotometer was used for the determination of Mg, Ca and Fe (in the absorption mode) and Na and K (in the emission mode) in water extracts. Concentrations of the analytes as affected by leaching conditions provided very important information for the establishment of optimum process conditions and for evaluation of this novel extraction method. AA was also used to provide quantitative information about Na, Ca, Mg and K in an HTD wastewater [126].

1.7.2.2. Inductively coupled plasma techniques.

In recent years emission spectroscopy, which usually denotes light emission by samples excited by electrical discharge, has been increasingly superseded by inductively coupled plasma (ICP) emission spectroscopy, which is much more reproducible and requires less skill to use. The ICP techniques have rapidly become much more important as a method of elemental analysis, providing a substantial degree of freedom from interferences and a capability of simultaneous multi-element determination [127]. Used for both qualitative

and quantitative analysis, this technique has very high sensitivities for the detection of both metals and non-metals.

The ICP techniques with high sensitivities have been utilised for elemental analysis of both aqueous and non-aqueous coal solutions. These include the commonly used ICP-AES (atomic emission spectroscopy) [120, 128, 129] and the more recently developed ICP coupled with mass spectrometry (ICP-MS) [120, 130].

1.7.2.3. Comparison of techniques for inorganic analysis.

Atomic spectroscopy is the most widely used technique for determining elements, especially the metallic ones, in almost every conceivable matrix. Commonly used methods are flame AAS and graphite furnace AAS. AA essentially determines one element at a time and thus cannot be used for a qualitative overall survey of the elements present. ICP emission spectroscopy is useful for the determination of basically all the metallic elements in the periodic table. The ICP techniques provide a very sensitive analytical approach for most of the trace elements. Major limitations of these techniques are related to the introduction system to ICP, i.e. matrix effects of solid materials dissolved in the sample and (for mass spectrometry) mass ion overlap. At this point, AA is a preferred method for quantitative analysis and ICP is suitable for qualitative analysis and multi-elemental analysis.

In view of the complementary advantages of the two methods, both the AA and ICP techniques were considered suitable for the inorganic analysis of MTE water. Since the analytical methods using these two approaches for common water samples are very well developed and many have long been standardised, the development of methods for inorganic analysis was not a focus of this project.

1.8. Project Objectives

In order to utilise low-rank coals of high moisture content more efficiently, more energy efficient and economic dewatering technologies are desirable. The MTE process, as one of the recent developed techniques, has proved to be promising for industrial application. A wastewater stream from the process is expected to contain both organic and inorganic contaminants released from the coal and presents potential environmental impact. The

object of this project was to characterise both organic and inorganic impurities in the MTE process water as a function of processing conditions. The specific research objectives were:

- a) to establish improved analytical methods for the characterisation of major organic components of MTE process water;
- b) to identify and determine typical levels for a range of organic and inorganic components in the MTE process water as a function of processing conditions and lignite types;

This will provide important information to assist the optimisation of MTE process conditions and inform the selection of appropriate waste management technologies.

CHAPTER TWO

MATERIALS AND METHODOLOGY

2.1. Introduction

This chapter introduces the materials and methodologies used in this project for producing, collecting and analysing the MTE process water. The validity of using different methods for the analyses of TOC and selected inorganic species by external laboratories is evaluated. For organic analysis, generic SPE sample preparation procedures and GC-MS conditions are described in this chapter, while the establishment and optimisation processes for the SPE methods with and without derivatisation are explained in detail in the following chapter, which specifically deals with method development issues.

2.2. Materials

2.2.1. Coals

Coals used in this project were lignites from Victoria, South Australia and Germany. Large quantities of run-of-mine coal samples collected were homogenised according to Australian Standard 4264.3 [131], ground to <6mm and stored in airtight containers to minimise oxidation and moisture loss. Properties of the lignites investigated determined by the Herman Research Laboratory (HRL) are presented in Table 2-3. Analytical methods used are listed in Section 2.5.

Table 2-3. Properties of lignites investigated.

Coal		Moisture %wb	Ash Yield %db	Volatile Matter %db	Fixed Carbon %db	C %daf	H %daf	O+N* %daf	S _{org} %daf
Victoria	Loy Yang A	57.4	1.04	51.4	47.6	69.4	5.0	25.4	0.27
	Loy Yang B	67.0	3.7	-	-	66.5	4.7	27.8**	0.40
	Morwell	57.2	2.1	50.7	47.2	68.7	4.9	26.1	0.25
	Yallourn	64.4	1.95	50.9	47.1	67.7	4.8	27.3	0.16
South Australia	Lochiel High Na	53.9	16.1	47.1	36.8	67.5	5.4	23.8	3.3
	Lochiel	57.5	14.3	47.1	38.6	68.1	5.1	22.9	3.8
	Bowmans A	51.4	13.1	48.5	38.4	65.2	4.9	25.0	4.8
	Bowmans B	55.3	16.3	-	-	67.1	5.3	23.6**	3.4
	Kingston	47.0	13.1	45.8	41.1	67.8	4.9	23.5	3.8
Germany	Hambach	53.9	5.3	-	-	67.6	4.8	26.5**	0.30

Coal		Element %db***						Acid Extractable %db***			
		Na	Ca	Mg	Fe _{tot}	Cl	S _{tot}	Na	Ca	Mg	Fe _{NP}
Victoria	Loy Yang A	0.09	0.05	0.06	0.07	0.10	0.28	-	-	-	-
	Loy Yang B	0.47	0.04	0.16	0.05	0.44	0.40	0.46	0.04	0.16	0.04
	Morwell	0.08	0.32	0.21	0.37	0.06	0.25	-	-	-	-
	Yallourn	0.07	0.14	0.18	0.61	0.05	0.20	-	-	-	-
South Australia	Lochiel High Na	1.41	0.68	0.84	0.18	0.59	2.85	-	-	-	-
	Lochiel	0.88	1.33	0.81	0.58	0.45	3.37	-	-	-	-
	Bowmans A	1.51	0.07	0.82	0.52	1.41	4.24	-	-	-	-
	Bowmans B	1.47	0.69	0.86	0.22	0.57	2.89	1.47	0.71	0.89	0.17
	Kingston	0.80	1.18	1.30	0.33	0.28	3.40	-	-	-	-
Germany	Hambach	0.23	1.23	0.46	0.41	0.04	0.30	0.23	1.14	0.47	0.40

* by difference

** oxygen only

*** error is 0.01%, db for values <0.1%, db and 0.02%, db for values >0.1%, db.

wb - wet basis; db - dry basis; daf - dry ash free basis; org - organic; tot - total; NP - non-pyritic

2.2.2. *Glassware*

For the analysis of low level organics in wastewater, glassware must be extremely clean so as to minimise interferences from contamination. In the present study, after being washed with detergent, rinsed thoroughly with tap water and dried, all the glassware used for organic analysis, including volumetric flasks, vials and pipettes, was soaked in a mixture of 3:1 (v/v) concentrated sulphuric acid and nitric acid for at least 48 hours. Tap water was used to thoroughly rinse and then soak the glassware for a minimum 24 hours. After being rinsed with tap water, distilled water and MilliQ water (ultra pure water), respectively, the glassware was dried at 105°C. Prior to use, the glassware was rinsed successively with HPLC grade methanol, dichloromethane and the solvent to be used in the subsequent tests.

2.2.3. *Standards and Reagents*

All standard organic chemicals used to prepare standard solutions for GC-MS analyses were GC or HPLC grade with purities between >97% and >99%, as specified by the manufactures.

To make a standard storage solution, the chemicals were weighed on an analytical balance and added into a dry clean volumetric flask. Methanol was used to dissolve the chemicals and dilute to the graduation. The series of standard solutions used for creating GC-MS calibration curves were prepared by diluting the storage solution in succession to the desired concentrations with ethyl acetate.

Aqueous standard solutions were used for method development purposes including recovery and derivatisation yield tests. Standard mixtures of different compositions were prepared by diluting corresponding standard storage solutions consecutively to the desired concentrations with MilliQ ultra pure water.

All organic solvents used in this study including methanol, dichloromethane and ethyl acetate were HPLC grade.

Reagents used in the sample preparation procedure, including hydrochloric acid, sodium carbonate, sodium bicarbonate, sodium hydroxide, acetic anhydride and acetyl chloride, were all analytical reagent (AR) grade. Methylation reagents, 13-15% boron

trifluoride/methanol complex and 98.5% trimethyloxonium tetrafluoroborate (TMO) solid, were purchased from Riedel-de Haën[®] and Aldrich[®], respectively.

2.2.4. *Water*

Water used in the MTE batch experiments was deionised water. Analysis of the water showed that all the items analysed for in the MTE water samples were present at levels below detection limits or negligible compared to that in the MTE water.

Water used to prepare standard solutions was ultra pure MilliQ water with a resistivity of 18M Ω m. Distilled water was used in all the blank tests for organic analysis, which followed the procedures established for the analysis of the MTE water samples. Impurities present in solvent extracts obtained from the blank tests are mentioned in Chapter Four.

2.3. **MTE Water Production**

Two MTE rigs for laboratory batch tests were utilised in this project. One is located in the Department of Chemical Engineering, Monash University, Australia and the other is in the Department of Chemical Engineering, University of Dortmund, Germany. The MTE apparatus at Monash University and experiments using this rig are described below and the results are discussed in Chapter Three to Chapter Six.

The MTE procedures and process water production using the MTE rig in Germany are introduced in Chapter Seven where the effects of introducing acids into the system and using different means of heating are evaluated.

2.3.1. *The MTE Process*

A photo and a schematic diagram of the MTE apparatus used in the laboratory batch experiments are shown in Figure 2-2 and Figure 2-3, respectively.

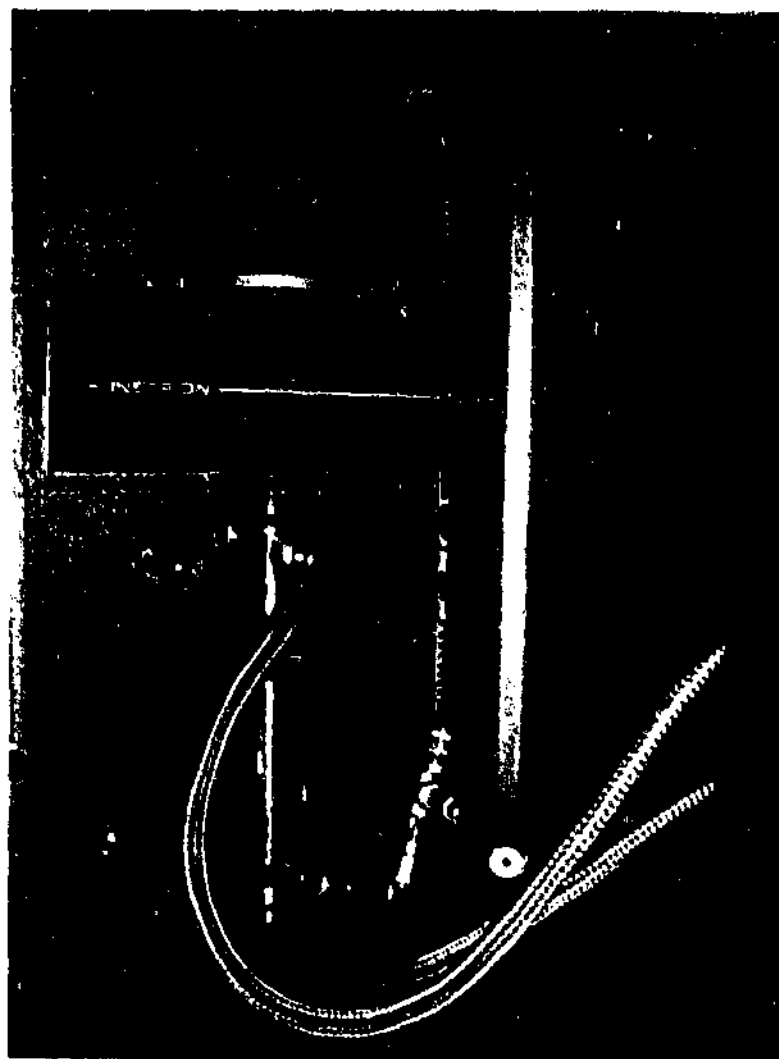


Figure 2-2. A photo of the MTE rig at Monash University.

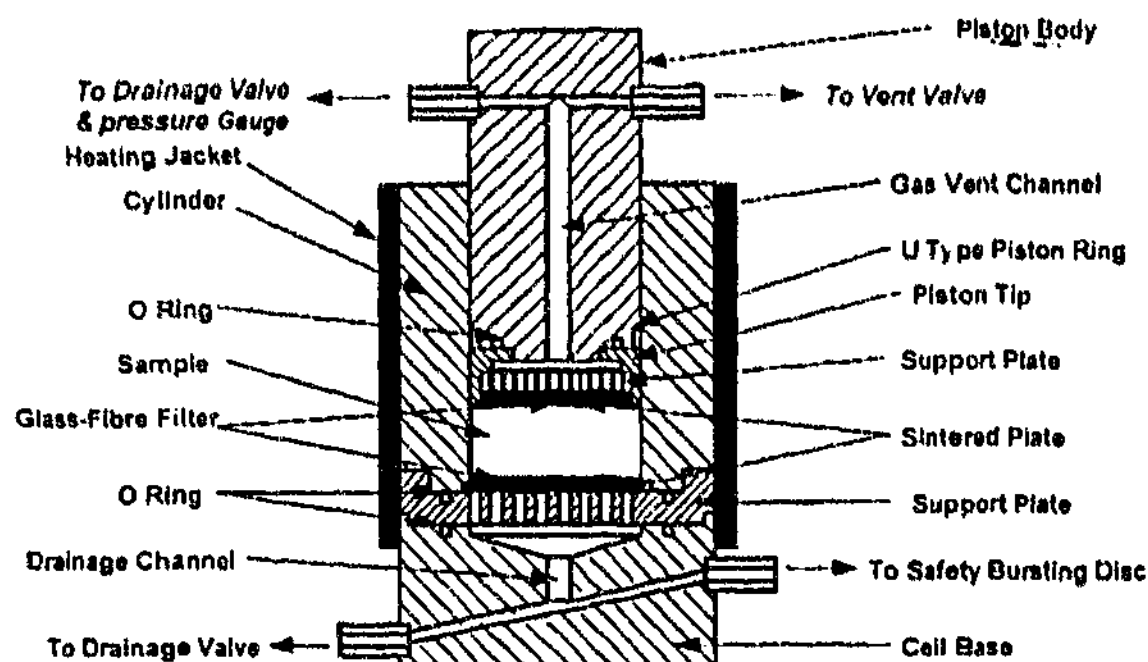


Figure 2-3. A schematic diagram of the MTE rig at Monash University [2].

The experimental apparatus used in the fundamental batch study is a compression-permeable cell which allows tests to be performed at temperatures up to 300°C [2] and pressures up to 25MPa. Throughout the whole process, the cell must be airtight to ensure dewatering is non-evaporative. The maximum operation temperature used in this study was 200°C and the maximum applied pressure was 25MPa.

The main body of the rig is the compression chamber, which includes a permeable sintered plate (40µm) at each end to allow air to be vented prior to compression and to facilitate water removal. Before each run, all the parts were washed with tap water, rinsed with deionised water and air-dried. To start an MTE run, the compression cell was loaded with a known weight (100.0g) of the coal sample and then filled with deionised water to create an air-free coal water slurry. After the piston was placed into the cylinder, more deionised water was added through the connected tubing to ensure the whole system was full of water and air-free so as to prevent water evaporation. The amount of water added was recorded. The piston was then lowered by an Instron mechanical press (Model 5569) to an initial force value of 1.2kN to further expel air in the system. The airtight chamber was then heated with an electrical heating jacket to the desired temperature. The final

temperature was then held for a certain period of time. The total time for heating and temperature holding prior to compression was pre-set to 30-40 min (the exact time depending on the final temperature) so that the holding time at the desired temperature was ~20 minutes. Once the desired temperature was reached, the Instron mechanical press was used to automatically increase the force on the cell loading (through the piston) at a constant rate to the desired pressing pressure. The applied force was maintained for 5 min by automatically adjusting the displacement of the piston. The piston position was then held for 10 min for stress relaxation. The pressure inside the system was always maintained above the water saturation pressure at the corresponding temperature to prevent evaporation.

2.3.2. *MTE Product Water Collection*

During the whole MTE process, a clean, dry, pre-weighed glass container was located at the water outlet to collect the water expelled. Following each experiment the system was allowed to cool to 25-30°C before the system pressure was released. The cell was then carefully detached, with all the excess water inside the chamber and connected tubing collected in the same container as the **product water**. The product coal pellet was also collected and double sealed in two plastic bags. All the parts of the system that had been in contact with coal and water during the process were thoroughly rinsed with deionised water and this **rinsing water** was collected in a separate container of known weight. Both the product water and rinsing water with containers were immediately weighed on a balance after the collection process.

The above procedure for operation and water collection was established following a number of MTE test runs. To check the validity of the water collection method, the system was rinsed for a second time for a number of MTE runs. Analytical results showed that all the analytes contained in the second-time rinsing water accounted for 1.7-6.5% of the total amounts present in the water phase. The single rinse method hence proved to be valid and efficient for the collection of all substances released to the water phase.

The collected product water and rinsing water samples were filtered with glass fibre filters (Whatman® GF/A 1.6µm) separately. The filter was air-dried and weighed and the weight of the coal residues was deducted from the total weight of the water samples. The pH of

each water sample was measured using a portable AORITEST1 pH meter (HANNA® Instruments). One portion of the filtered sample was sent for TOC analysis within 24-48 hours. Another portion of the sample was stored in clean dry plastic containers and sent for inorganic analysis. The rest of the sample was stored in clean dry glass containers for subsequent organic analysis. All portions were kept in a refrigerator at below 4°C.

2.4. MTE Water Analysis

2.4.1. *Total Organic Carbon Analysis*

Most of the TOC analysis of MTE water samples was carried out at the Water Studies Centre (WSC), Monash University using a Shimadzu TOC-5000 analyser and WSC test method 58 [132] based on APHA (American Public Health Association) method 5310B – the combustion-IR method [133].

This instrument at WSC broke down at the final stage of this study. Water samples were submitted to the Gribbles Analytical Laboratories for TOC tests using a Skalar TOC combustion IR analyser and the GAL method 242 [134] based on the same APHA method.

For water samples obtained from the MTE experiments completed at the University of Dortmund, Germany, TOC was determined using a DIMATOC 10C analyser and the same APHA method.

For comparison of the results obtained using the three different TOC analysers and calculation of system errors, a number of MTE water samples were analysed using different instruments. TOC concentrations of the samples and associated errors are listed in Table 2-4.

Table 2-4. Comparison of TOC results (g/L) obtained using different TOC analysers.

Sample No.	Shimadzu (WSC)	Skalar (Gribbles)	DIMATOC (Ger)	Error $\pm(A-B/2)$	Relative Error $\pm\%$	Interval (day)
1	1.4×10^{-1}	1.5×10^{-1}	-	0.05×10^{-1}	3.3	<2
2	1.3×10^{-1}	1.1×10^{-1}	-	0.10×10^{-1}	8.3	<2
3	3.0×10^{-2}	2.6×10^{-2}	-	0.20×10^{-2}	7.1	<2
4	2.7×10^{-2}	2.2×10^{-2}	-	0.25×10^{-2}	10	<2
5	4.1×10^{-1}	-	5.0×10^{-1}	0.45×10^{-1}	9.8	~40
6	1.5×10^{-1}	-	1.7×10^{-1}	0.10×10^{-1}	6.3	~40
7	1.1×10^{-2}	-	1.0×10^{-2}	0.05×10^{-2}	4.5	~40
8	1.9×10^{-2}	-	1.6×10^{-2}	0.15×10^{-2}	8.3	~40
9	$*3.5 \times 10^{-1}$	-	-	0.10×10^{-1}	2.9	28
10	$*4.2 \times 10^{-1}$	-	-	0.05×10^{-1}	1.2	23

* average of two analyses

Using the combustion-IR method, carbon in the materials is oxidised to carbon dioxide (CO_2) and the produced CO_2 measured by IR. Results in Table 2-4 indicate that differences between the TOC values (g/L) obtained using two different analysers were all less than 5 in the second decimal place and the relative errors were $\leq 10\%$. When the same instrument analysed the same sample at two times over 20 days apart, the difference was $<3\%$, implying that the TOC results would be still valid even if the delay before analysis was greater than the desired maximum 48hours.

In the following chapters, the TOC values are mainly used for comparison between the MTE runs within groups. As the TOC concentrations in the water samples in each group were analysed using the same TOC analyser, the differences between the TOC results acquired from different analysers can be regarded as acceptable.

2.4.2. Solid Phase Extraction (SPE) for Organic Analysis

2.4.2.1. Principles of SPE methods

The following descriptions about general principles of SPE methods are mainly summarised from an SPE handbook by Blevins et al [135].

An SPE process consists of five main steps: conditioning of the solid phase, extraction of the sample, washing out of the non-absorbed impurities, drying of the solid phase and

elution of the absorbed analytes. To achieve an efficient extraction for target analytes from the sample matrix using SPE, great caution should be exercised in each of the five steps:

- a) **Conditioning.** The purpose of the conditioning step is to solvate the sorbent creating a suitable environment for the isolates – the target analytes to be absorbed – to have adequate affinity to the solid phase and be retained on it. This step involves the use of solvents of suitable polarities to fully wet the solid sorbent followed by washing with a solvent that prepares the sorbent to receive the sample. The selection of the solvents used for conditioning and for washing the conditioning solvent should be based on the nature of the application and the sorbent selected. For aqueous samples, conditioning the solid phase with a polar organic solvent miscible with water followed by pure water or a buffer solution is usually the best approach.
- b) **Extraction.** Immediately after the last conditioning solvent has been applied, with the sorbent still fully wet, the samples should be applied to the sorbent bed for extraction. At this stage, components in the sample will either pass through or be retained on the sorbent. During operation, two factors are critical to the efficiency of the whole method. One is control of the rate at which the sample passes through the solid phase so that it is low enough for the analytes to have adequate contact with the sorbent. The other is keeping the flow of the sample continuous, i.e. ensuring that the solid phase never dries out until the extraction is complete.
- c) **Washing.** After the extraction step, not only are the isolates absorbed on the solid phase but non-absorbed impurities in the sample matrix may also be retained within the pores. Since the impurities may present interference if they enter the solvent extract, it is necessary to wash the sorbent with a solvent that is different in nature from the elution solvents and that will not disturb the absorbed isolates. This step is particularly important for the extraction of wastewater due to its complex matrix. For water samples, ultra pure water or buffer solutions can be selected as the washing solvents.

- d) Drying. For the extraction of aqueous samples, complete drying of the sorbent prior to solvent elution is necessary for optimum elution of the isolates and reduced water interference with the GC analysis. When more than one elution solvent is used, especially when the solvents used in two successive steps are immiscible, partial or complete drying of the sorbent between elution with the immiscible solvents is also preferable. Once the isolates have been retained on the sorbent, drying under air flow usually does not change the nature or amount of isolates retained, but excessive drying, e.g. with a strong air flow, at high temperature, extra long time, etc., should be avoided to prevent any possible loss or oxidation of the isolates.
- e) Elution. Elution is a process by which the isolates are removed from the sorbent bed by introducing a solvent(s) to which the isolates are more strongly attracted than they are to the sorbent. Elution with small aliquots of the elution solvent can enhance the recoveries compared to one elution using the same total volume of the solvent.

2.4.2.2. SPE optimisation

To develop a new SPE method or validate an existing method, the type and mass of the solid phase, volume of the sample to be extracted and the type and volume of the elution solvent(s) are all the key factors to be evaluated and optimised.

The most important factor is the selection of a suitable sorbent for a specific application. The selection strategy is to maintain a balance between maximum isolate retention and minimum elution solvent required, i.e. to ensure that the isolate-sorbent bond is, on the one hand, strong enough to retain maximum isolates and, on the other hand, able to be broken by a suitable elution solvent of minimum volume possible.

Selection of the elution solvent(s) is also critical for optimisation of a method. The most favourable elution condition is for the chosen elution solvent(s) to elute the isolates from the sorbent bed in the smallest volume possible.

Evaluation and selection of the sorbents and elution solvents were important aspects of the method development in this project. SPE as the selected sample preparation method for

GC-MS analysis of the MTE water was conducted using the Bond Elut[®] extraction columns from Varian[®]. Solid phases including silica-based C8 and polymer-based ENV and PPL were evaluated for extraction of samples without derivatisation. Acetylation yields achieved using C2, C8, C18 and PPL were assessed. Elution efficiencies using methanol, dichloromethane and ethyl acetate were compared. Evaluation experiments and results are discussed in detail in Chapter Three.

Sorbent mass and volumes of both the sample and elution solvent should be evaluated concurrently to achieve an optimal extraction result. The volume of the samples used for SPE was selected first taking into account the nature and volume of the MTE water samples available. Since the organics in MTE rinsing water samples as analysed as TOC were at a low level compared to that in the MTE product water, GC-MS characterisation of the organics was only carried out on the MTE product water samples. As the total volume of the product water from MTE laboratory batch runs was $\leq 200\text{mL}$ in most cases, less than 100mL of the sample was available for the GC-MS analysis of major organics including method development. Therefore, up to 10mL of the MTE sample was used for each extraction test.

With the sample volume determined, the selection of sorbent mass is based on the organic loading of the sample and sorbent capacity. Capacity is defined as the total mass of a strongly retained isolate that can be retained by a given mass of the sorbent under optimum conditions [135]. For silica-based sorbents, C2, C8 and C18, typical carbon loading is 5.6%, 12.2% and 17.4%, respectively, whereas for polymer-based sorbents such as ENV and PPL, capacity is even higher [136]. When determining the sorbent mass and the maximum amount of extractable sample, the retention not only of the analytes but also of the co-retained undesired components in the sample should be taken into consideration. Results show that TOC concentrations of all the MTE product water samples used in this study were $<1\text{g/L}$. The extraction of 10mL MTE sample then gives an organic carbon loading of $<10\text{mg}$ to the SPE sorbent. For all sorbents evaluated in this work, the lowest carbon loading capacity is 5.6% (C2). To accommodate a maximum 10mg organic carbon loading, a sorbent mass of 200mg should be sufficient. The use of higher mass of the sorbent for extraction of the same amount of the sample is unnecessary, as it will require larger volume of the elution solvent, resulting in more diluted final extracts.

The volume of an elution solvent(s) required is related to the bed volume of the sorbent. Bed volume is a unit of measurement commonly used to characterise retention and elution and is defined as the amount of solvent required to fill all the internal pores and interstitial spaces of the particles in a given size sorbent bed [135]. An optimal elution should require no more than 5 bed volumes of the solvent. For a 200mg sorbent mass, the bed volume is approximately 0.5mL. Elution with three to four bed volumes in aliquots proves to be sufficient and more efficient than one elution with the same total volume.

2.4.2.3. SPE procedures used in this project

The SPE procedures described in this section were utilised for the extraction of organic components in aqueous samples with and without derivatisation throughout the project wherever the use of SPE is mentioned in this thesis.

Figure 2-4 illustrates the method of using the Varian Bond Elut[®] columns in this study, in which positive pressure is applied, using a syringe, to force the eluant to pass through the column at a certain rate. It is one of the methods recommended by the manufacturer [137].

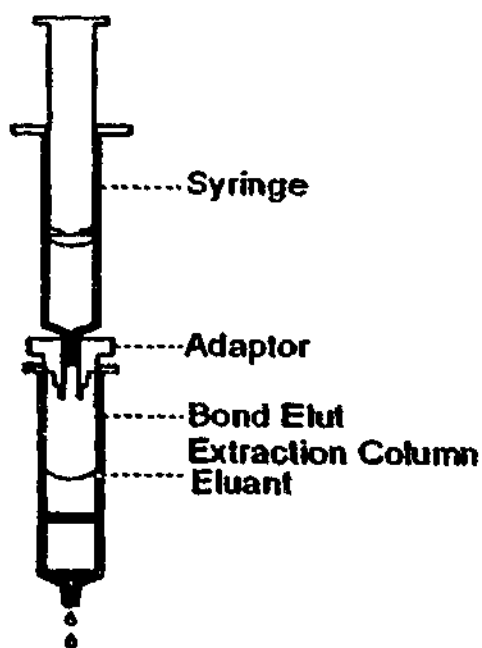


Figure 2-4. Method of using the Bond Elut[®] columns in this study [137].

Figure 2-5 shows a flow diagram of the procedure using SPE columns for water sample extraction. The procedure is described in detail below.

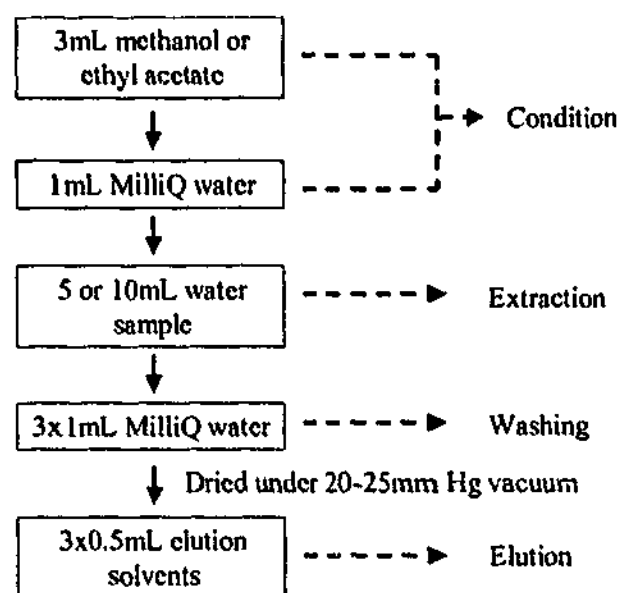


Figure 2-5. A flow diagram of the SPE procedure.

Firstly, the selected SPE column was conditioned by passing through 3mL of methanol or ethyl acetate followed by 1mL of ultra pure MilliQ water. The conditioning solvent was allowed to drain under gravity to ensure adequate wetting of the solid phase. Methanol was used when the elution solvents were dichloromethane or methanol, while ethyl acetate was selected when it was used as the elution solvent. For all sorbents, the rate at which ultra pure water passed through the column was controlled at approximately 1mL/min. When the experiments required the pH of the sample to be adjusted to 2-3, the pH of the MilliQ water was also adjusted to 2-3 using hydrochloric acid.

Next, 5mL (only in the case of methylation) or 10mL of the aqueous sample was forced through the SPE cartridge. For the solid phases other than PPL, the extraction rate was controlled at 0.3-0.5mL/min. For PPL, a rate of 1-1.5mL/min was possible under gravity or slightly positive pressure. After the bulk of the sample was transferred to the column, the sample vial was rinsed with the last conditioning solvent – ultra pure water or acidic ultra pure water – 3-4 times and the rinsing water was also passed through the solid phase. A continuous sample flow was maintained until the extraction step was complete.

The third step was to wash off the undesired impurities from the sorbent. 3x1 mL aliquots of ultra pure water or acidic ultra pure water were passed through the sorbent bed at a 1 mL/min rate. Excess water was removed by applying positive pressure using the syringe prior to drying.

Drying of the sorbent bed was realised by passing air through the column under vacuum of 20-25mm Hg. As the PPL solid phase could be dried easily, 20-30 minute drying time was adequate, whereas for other sorbents 45-60 minutes was preferred.

The final and a critical step was solvent elution. 3-4x0.5mL aliquots of the elution solvent were added to the dried column and drained under gravity or positive pressure at an estimated rate of 0.5-1mL/min. Approximately 1mL of the elution solvent was required for the first elution of PPL since an extra volume of the solvent was necessary for wetting the sorbent. The solvent extract was collected in a clean, dry and pre-weighed 2mL auto sampler vial. After the elution of each aliquot, excess solvent was forced out using the syringe and collected in the same vial. For quantitative analysis, the final solvent extract of 1-1.5mL was slowly concentrated under very gentle nitrogen flow to approximately 0.5-1mL and the vial was weighed prior to GC-MS analysis. The volume of the solvent extract could then be calculated based on the weight of the extract and solvent density.

2.4.3. *GC-MS Conditions*

GC-MS analysis of organics was carried out using an Agilent 6890 GC coupled with an Agilent 5973 mass selective detector (MSD). 1µl of the solvent extract or standard solution was injected using an Agilent 7683 automatic liquid sampler. The column was an Agilent HP-5MS of 30m length, 0.25mm internal diameter and 0.25µm film thickness with a constant helium flow of 1.2mL/min. A split/splitless injector was used and injector temperature was set at 230°C. To avoid column overloading, the analysis was carried out under split mode with a split ratio of 1:20 when analytes were present in high concentrations. The splitless mode was used when the samples were dilute.

Three GC oven temperature programs, A, B and C, were used for the analysis of different groups of organics and at different stages of the study. During the evaluation of SPE methods for samples without derivatisation and after phenol acetylation, different elution solvents including dichloromethane (bp. 40°C), methanol (bp. 64-65°C) and ethyl acetate (bp. 76-77°C) were used. To minimise solvent effect during GC analysis, it is preferred that the initial oven temperature be 10-25°C lower than the boiling point of the solvent. For the convenience of comparison, one common initial oven temperature of 40°C was chosen to accommodate the use of all three solvents. The oven temperature was programmed as

follows: initial temperature 40°C held for 2 minutes; first program rate at 2°C/min to 110°C immediately followed by the second program rate at 10°C/min to 280°C; final temperature held for 6 minutes. The total run time was 60min. This temperature program is named as Program A.

After method development, with ethyl acetate selected as the elution solvent, the temperature program B was utilised for the analysis of the samples without derivatisation: initial temperature 60°C held for 2 minutes; first program rate at 3°C/min to 170°C immediately followed by the second program rate at 6°C/min to 280°C; final temperature held for 3 minutes. The total run time was 60min.

The GC oven temperature program C was optimised for the analysis of carboxylic compound groups after methylation: initial temperature 60°C held for 2 minutes; program rate at 5°C/min to 280°C and the final temperature held for 4 minutes. The total run time was 50min.

The temperature of the transfer line connecting GC and MSD was set at 300°C – slightly higher than the maximum oven temperature. The MSD scanning mass range was 35-400 amu.

The Agilent ChemStation® software was used for all GC-MS data acquisition and data analysis.

2.4.4. *Molecular Weight Distribution – FFF*

The flow field-flow fractionation (FFF) method was applied to characterisation of the molecular weight distribution of organic matter in the MTE samples. The analysis was carried out by Postnova Analytics, Salt Lake City, Utah, USA.

Equipment and method used were as described by Assemi [138]. The carrier was a mixture of 1×10^{-2} M NaNO_3 and 2×10^{-5} M NaOH solution. Deionized water was used to prepare the carrier. NaOH was added to adjust the pH of the sample solution to 7.5. The detection was carried out using a UV detector set at 254nm and 0.02 AUFS. A 10 kDa regenerated cellulose acetate membrane was used in this analysis.

Standard calibration curves were obtained by plotting the molecular weight of a series of standard compounds against their elution time. Based on the standard calibration equation

and relevant information, molecular weight distribution of organic compounds in a sample could then be calculated.

2.4.5. *Analysis of Selected Inorganic Species*

For MTE experiments carried out at Monash University, inorganic analyses of water samples were contracted to external laboratories.

MTE water samples were submitted to WSC for the analysis of calcium (Ca), potassium (K), sodium (Na), magnesium (Mg), chloride (Cl^-) and sulphate (SO_4^{2-}). The metal elements were analysed on a Perkin Elmer atomic absorption spectrometer using WSC methods 10 to 13 [139-142], which are based on APHA method 3111B [143]. Chloride and sulphate were measured using flow injection colorimetric methods [144, 145] based on APHA methods 4500- Cl^- -G [146] and 4500- SO_4^{2-} [147], respectively.

At times when the AAS analytical service at WSC was not available, Na, Ca, Mg, K, iron (Fe), aluminium (Al), chlorine (Cl), and sulphur (S) in some MTE water samples were analysed at HRL on a SpectroFlame Module E ICPAES using methods based on APHA method 3120B [148]. Sulphate concentrations were calculated from the sulphur results assuming that all sulphur was present as sulphate in the water samples. The validity of the sulphur to sulphate calculation is discussed later in this section.

A Perkin-Elmer 1100B atomic adsorption spectrometry was used for the determination of Na, Ca, K, Mg and Fe concentrations in the MTE water samples acquired using the MTE rig at the University of Dortmund. The procedures used were based on APHA method 3111B [143].

To provide an internal check on the results obtained from different analytical laboratories, a number of representative comparisons are presented in Table 2-5.

Table 2-5. Comparison of analytical results for selected inorganics using different methods.

		Analytical result (mg/L)				Error %		
		Standard solution	MTE water #1	MTE water #2	MTE water #3	vs std	WSC vs HRL	HRL vs Ger
Na	Calculated concentration	183.43	-	-	-			
	AAS (WSC)	185±5*	270	-	-	1.1	8.9 (water#1)	0.3-3.6 (water #2-#3)
	ICPAES (HRL)	205±10*	323	172	439	12		
	AAS (Ger)	-	-	185	442			
Mg	Calculated concentration	37.24	-	-	-			
	AAS (WSC)	33±0*	64	-	-	11	4.5 (water#1)	1.3-3.2 (water #2-#3)
	ICPAES (HRL)	36±1*	70	15	39	2.7		
	AAS (Ger)	-	-	16	40			
SO ₄ ²⁻	Calculated concentration	147.16	-	-	-			
	AAS (WSC)	135±10*	420	17	110	8.2	1.4-5.1 (water #1-#3)	-
	ICPAES (HRL)	122±2*	408	18	108	17		

* average and error of duplicates.

In Table 2-5, error % between analytical methods is calculated using Equation 2.1.

$$\text{Error \%} = \frac{|A - B|/2}{(A + B)/2} \times 100 \quad \text{Equation 2.1}$$

where A and B are the concentrations of a selected component in the same sample determined by two different methods, or, in the case of the standard solution, B is the calculated concentration.

It can be seen that using the AAS method at WSC and the ICP method at HRL to analyse the standard solution, the errors are ≤17%. The relative errors between two different

analytical methods are all <9%. Therefore, all the above methods for the analysis of the selected inorganic species can be considered valid.

It should be noted that the results for the sulphate calculated from the sulphur values obtained using the ICPAES method are in good agreement with the sulphate results using the colorimetric method, as shown in Table 2-5. This demonstrates that the method of using ICPAES to analyse sulphur content then converting to sulphate values is valid for the sulphate analysis of the MTE water.

Due to the complexity of the matrix or low concentrations of some trace elements, sample pre-treatment prior to AA detection is sometimes required for elements such as Hg [123], As [149], Pb and Cd [123] using methods such as oxidation [122, 123], masking [123] and pre-concentration [122]. In the present study, comparison of the analytical results for Na, Ca and Mg in the MTE water samples with and without acid digestion demonstrated that direct measurement of the water samples was acceptable. Concentration results showed that the difference was <1 in the last significant digit.

2.5. Coal Analysis

Although detailed coal analysis was not included in the scope of this project, data for raw coals and MTE product coals are closely related to the characteristics of MTE water and therefore are beneficial for data analyses and discussion of the results.

The moisture content of all MTE coal products obtained using the MTE rig at Monash University and all the raw coals and product coals from the MTE runs carried out at University of Dortmund were determined by methods based on Australian Standard AS 2434.1 [150]. Approximately 10g of a representative sample, in duplicate or triplicate, was weighed and dried in the oven under nitrogen at 105°C for 3-6 hours. The moisture content was calculated from mass loss upon drying.

Analyses of the properties of the raw coals were carried out by HRL and the results are shown in Table 2-3. Moisture contents and ash yields of the raw coals was analysed using a Leco MAC Analyser according to HRL Method 1.6 [151]. Volatile matter was determined according to AS 2434.2 [152]. Carbon, hydrogen and nitrogen contents of the

raw coals were determined according to HRL Method 1.4 [153] using a Leco CHN600 analyser.

Total Fe, Ca, Na and Mg were determined on ash produced in the ash yield determination and the analyses were performed using a borate fusion-ICP method based on AS 1038.14.1 [154]. A combustion temperature of 600°C instead of 815°C was used to avoid the loss of sodium. Acid extractable elements, Fe, Ca, Mg and Na, in the raw coals used in the MTE experiments discussed in Chapter Seven were measured according to AS 2434.9 [155]. The chlorine content of the raw coal was determined based on AS 1038.8.2 [156] and the sulphur content was analysed based on AS 1038.6.3.2 [157] using a Leco SC32 sulphur analyser.

2.6. Statistic Analysis

Most of the MTE batch experiments were carried out in replicate. Therefore, the overall errors reported for the analytical results included not only the analytical errors associated with the measurement, but also the experimental errors from replicate runs. In order to distinguish the true effects of processing conditions on the removal of organics or inorganics without being misled by the errors, it is necessary to use statistic analysis. The SPSS® software package was used for all the statistic analyses reported in this thesis.

2.7. MTE Water Analysis Scheme

A summary of the MTE water analytical scheme is given in Figure 2-6. The analytical procedures included in this scheme are mainly described in this chapter except for that of acylation and methylation for phenolic and carboxylic compounds, which is detailed in Chapter Three.

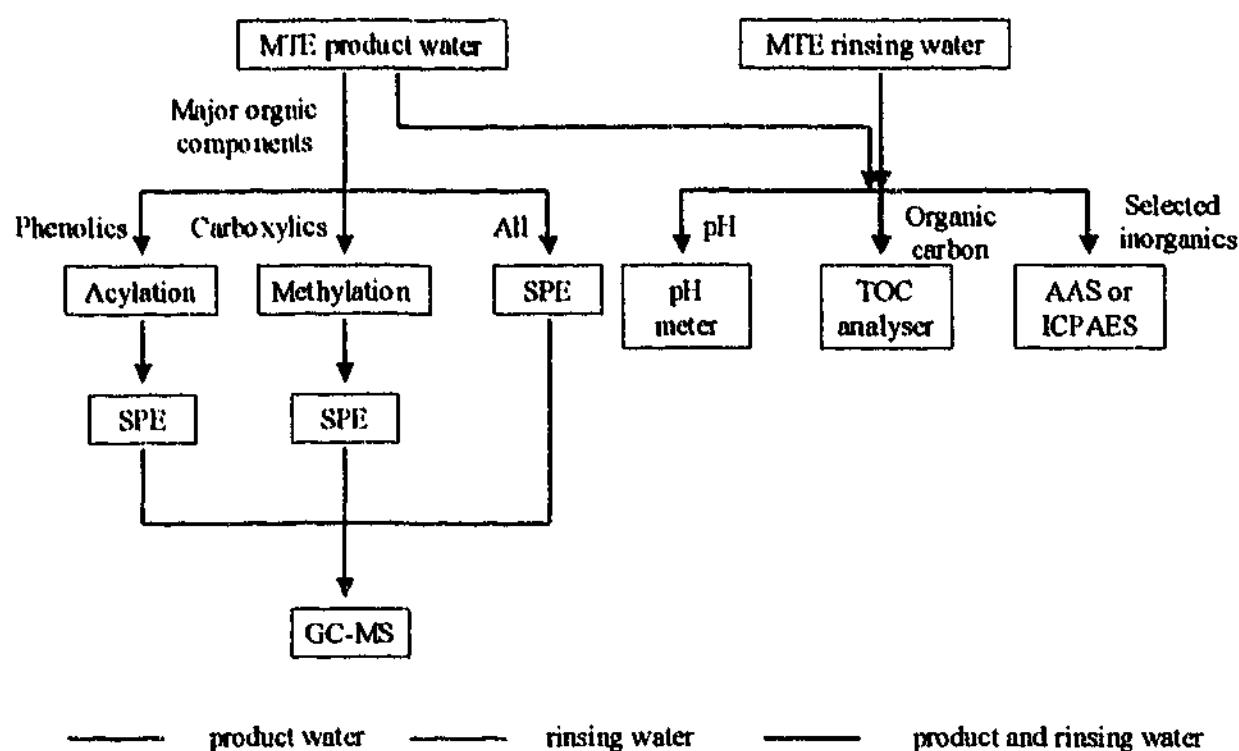


Figure 2-6. Scheme established for characterisation of MTE Water samples.

2.8. Acknowledgement

I would like to thank the following organisations and people for their assistances in conducting the work described in this chapter: the Water Studies Centre at Monash University, the Herman Research Laboratories and Gribbles Analytical Laboratories for providing analytical results for the raw coals, TOC and inorganic concentrations in MTE water samples; Mr T. Wild of the University of Dortmund for his assistance in analyses of moisture content of the MTE coal products, TOC and selected inorganics in water samples obtained at University of Dortmund; Dr T. Kealy of the Department of Chemical Engineering, Monash University, for his assistance in setting up MTE operation procedures; Mr R. Ellingham of the same organisation for producing MTE water samples and providing moisture content results of some MTE coal products; Dr G. Favas of the School of Chemistry, Monash University, for organising coal analyses at HRL; Dr S. Tadjiki of the Postnova Analytics, USA for completing FFF analysis of selected MTE water samples.

CHAPTER THREE

ESTABLISHMENT OF SPE-GC-MS METHODS FOR CHARACTERISATION OF ORGANIC COMPONENTS IN MTE PROCESS WATER

3.1. Introduction

This chapter is deals with the establishment of sample preparation methods for GC-MS characterisation of low molecular weight organic components in MTE water samples. It consists of three main sections besides this introduction. The first section is devoted to method development and validation using SPE for the analysis of organics in the water samples without derivatisation. The second section describes the acetylation-SPE method established for the analysis of phenolic compounds in water. The third section focuses on the methylation method established for the analysis of carboxylic compounds. Each section covers the method development process using standard solutions and method validation using standard-spiked MTE samples. A summary is given at the end of each section. Results of using these methods for the analysis of the MTE samples are summarised and discussed in next two chapters.

3.2. SPE without Derivatisation

As discussed in Section 1.6.2, the SPE method was chosen as the sample preparation method for GC-MS analysis of the MTE product water. Despite being effective for improving chromatographic properties of analytes, derivatisation implies at least one additional step in the sample preparation scheme. Furthermore, derivatisation reactions can produce side products that may interfere with the analysis [158]. Therefore, initially, SPE methods without derivatisation were evaluated.

3.2.1. *Aqueous Standard Solutions for Method Development*

In order to develop suitable SPE methods for GC-MS analysis of organics in the MTE product water, compounds that are likely to be present in the water should be selected to

prepare aqueous standard solutions that can be used for method development and validation.

Standard compounds were chosen based on the results of (a) preliminary analyses of the MTE product water and (b) previous studies of the HTD wastewater [54, 56, 65]. The selected compounds including phenolic compounds and carboxylic acids and their concentrations in the standard stock solution (~2000mg/L for the phenols and ~2500mg/L for the acids) are presented in Table 3-6. The nine phenols included phenol, five alkyl mono-phenols, one mono-phenol with an aldehyde group on the benzene ring (vanillin), one di-hydroxy phenol (catechol) and one tri-hydroxy phenol (pyrogallol). The carboxylic acids were three straight chain aliphatic di-acids, benzoic acid and one benzenetricarboxylic acid. Aqueous standard solutions used for method development and validation were the stock solution diluted with MilliQ water.

3.2.2. GC-MS Characterisation

Using the Agilent ChemStation® software for data processing, the base peak – the most abundant ion in the spectrum of a compound – is usually selected and integrated for quantitation of the compound. This ion is termed the **target ion**. The base peaks of all the phenols investigated were found to be their molecular ions, M^+ . **Qualifiers** are 1 or more ions in the spectrum used, together with the retention time, to confirm the presence of the compound.

The standard stock solution was diluted 10-fold with ethyl acetate. This diluted solution was analysed by GC-MS using the temperature program B described in Chapter Two. For each compound Table 3-6 lists the retention time in the total ion chromatogram (TIC) together with the target ion and qualifiers in the mass spectrum.

Table 3-6. Standard compounds for GC-MS analysis.

Chemical	Retention time (min)	Concentration (mg/L)	Target ion	Qualifier
phenol	7.99	1945	94	66
4-methyl phenol	11.29	1918	107	108, 77
2-methoxy phenol	11.80	2149	109	124, 81
2,4-dimethyl phenol	14.24	2030	122	107, 91
2-methoxy-4-methyl phenol	16.09	1985	138	123, 95
1,2-benzenediol (catechol)	16.37	2112	110	64
2,6-dimethoxy phenol	22.88	2080	154	139
1,2,3-benzenetriol (pyrogallol)	23.97	2230	126	108
4-hydroxy-3-methoxy benzaldehyde (vanillin)	24.78	2134	152	151
succinic acid (dicarboxylic acid C ₄)	-	2502	55	74, 100
benzoic acid (BZ)	14.82	2518	105	77, 122
pimelic acid (dicarboxylic acid C ₇)	-	2506	55	83, 124, 143
sebacic acid (dicarboxylic acid C ₁₀)	-	2483	55	98, 166, 185
1,2,4-benzenetricarboxylic acid (BT)	-	2497	148	166, 210

- undetectable at the selected concentration

All the phenolic compounds could to be detected at concentrations of ~200mg/L by GC-MS. In contrast, four of the five carboxylic acids analysed did not produce any signals at concentrations of ~250mg/L due to their poor chromatographic characteristics and, though the fifth, benzoic acid, did give a distinguishable peak in the TIC trace, the broad peak shape was unsuitable for quantitation. Hence for development of the SPE method without derivatisation, the further experiments discussed in this section were carried out with the phenolic compounds only.

Quantitation of the SPE extracts was accomplished using five or six point calibration for each component. Standard solutions of each concentration (in ethyl acetate) were injected onto the GC-MS and the response of the chosen target ion of each compound was plotted against the concentration.

Split mode injection (split ratio of 20:1) was used for analysis of all SPE extracts and standard solutions from recovery tests at high concentration (see Section 3.2.5) to avoid

column overloading. The highest concentration in the calibration curve for each component was ~200mg/L (1/10 of those listed in Table 3-6). The remaining concentrations corresponded to dilutions x2, x5, x10, x20 and x40. The temperature program A was used at this stage to facilitate the use of solvents with different boiling points, as discussed in Chapter Two.

For recovery tests at low concentration (see Section 3.2.6) and analyses of MTE water samples, GC-MS characterisation was carried out in a splitless mode and the standard calibration curves had points for five concentrations: ~2, ~4, ~8, ~20 and ~40mg/L, which were prepared by successive dilution of concentrated standard solutions. The temperature program B was used.

Examples of GC-MS calibration curves are shown in Figure 3-7. The relationship between MSD responses and concentrations of each compound can be successfully least-squares fitted by a linear equation of the form $y = bx \pm a$, where 'y' is the concentration, 'x' is the MSD response of the compound and 'a' and 'b' are the intercept on the y-axis and slope, respectively.

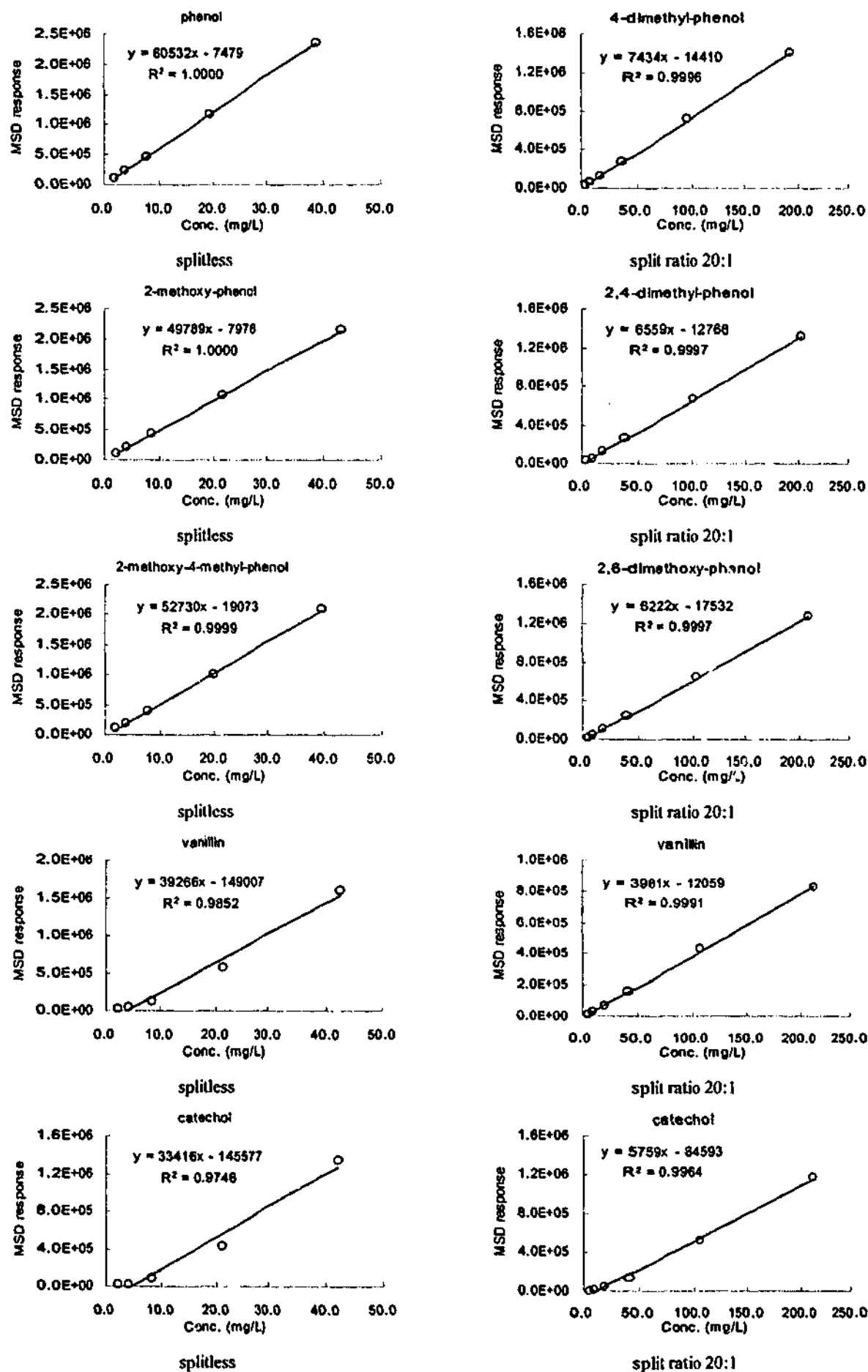


Figure 3-7. Standard calibration curves for selected compounds.

Most of the mono-phenols analysed exhibited a very good fit to a linear MSD response-concentration relationship with R^2 values >0.999 in both split and splitless modes. For vanillin and catechol, the compounds which have more than one functional groups attached to the benzene ring, the linear relationship for the splitless mode was not as good as for the split mode. At low concentrations, the peaks for catechol tended to be broad. Pyrogallol, the tri-hydroxy phenol, could not be detected at concentrations of 22 mg/L and lower.

By injecting the extract of an unknown sample onto the GC-MS under the same conditions as for the injection of the standard solutions, the abundances of the target ions of the selected compounds can be measured. Concentrations of the compounds in the extract can then be calculated according to the calibration equations and, hence, their concentrations in the corresponding water sample.

In recovery tests, as the concentration of a compound in the aqueous solution to be extracted is known, the recovery of the compound using the extraction method under test can be calculated as the percentage of the total amount of the component in solution detected in the extract.

Standard calibration was performed for each batch of analyses or every 24 hours when the analyses continued for more than one day.

3.2.3. *Sorbent Selection for Method Evaluation*

To establish a new SPE sample preparation method for a specific analysis, the first and essential step is sorbent selection. There are three general extraction mechanisms used in solid phase extraction: non-polar, polar and ion-exchange. Non-polar interactions occur between the carbon-hydrogen bonds of the sorbent functional groups and the carbon-hydrogen bonds of the isolates [135]. Since most organic molecules contain at least some non-polar structures, non-polar interactions are less selective than polar and ion-exchange extractions and, conversely, very effective for isolating groups of compounds with dissimilar structures. Therefore, when applications require the maximum possible number of isolates with different chemical properties to be extracted simultaneously, as for environmental samples, non-polar extractions are usually the technique of choice [135]. Since GC-MS analysis of the MTE product water aimed at screening and characterising all

the gas-chromatographable components, the non-polar extraction mechanism was the preferred option for the SPE preparation of the MTE water samples.

Non-polar sorbents can be classified into two categories: bonded silica sorbents, such as C18 and C8, and polymer-based sorbents, such as Varian[®] PPL and ENV. C8 is a common non-polar sorbent selective for aromatic rings and alkyl chains and was chosen by Racovalis [65] for GC-MS characterisation of organic components in HTD wastewater. As the MTE and HTD processes are similar, it would be expected that the organic components of the process water would also be similar, so that the C8 sorbent was selected as one of the SPE sorbents evaluated for the analysis of the MTE product water. PPL and ENV are two polymer-based sorbents that, according to the manufacturer, are ideal for the extraction of polar organic species such as phenols [159], which would be expected to be important constituents of the MTE water (see Section 3.2.1). Therefore, they were also evaluated in this study.

As the extraction mechanism for all selected sorbents is non-polar, the extraction condition (e.g. pH) should be selected to reduce the polarity of the analytes for an optimum result. For phenolic compounds, the polarity would be reduced at a low pH. According to the manufacturer the optimal extraction pH for PPL is 2. Therefore, in this work, the pH of the water samples was adjusted to 2 ± 0.5 prior to extraction using the PPL and ENV sorbents. Extractions of the water samples with and without pH adjustment (i.e. pH=2 vs 4-5) using the C8 sorbent did not exhibit significant difference. Since pH=2 is the lower end of the pH stable range for C8 (pH=2-9) [160], slightly higher pH (3 ± 0.5) was used for all the extractions using C8.

3.2.4. *Elution Solvent Selection for Method Evaluation*

Selection of elution solvents is also critical for sufficient recovery of the analytes extracted. Methanol (MeOH) and dichloromethane (methylene chloride – MC) were both selected by Racovalis [65] for the elution of organics in HTD wastewater after extraction. Methanol and ethyl acetate (EA) are both among the most commonly used elution solvents for non-polar extraction and the latter is the recommended elution solvent for the PPL sorbent by the manufacturer. In this study, the above three solvents were all assessed for the elution of different sorbents.

3.2.5. *Results of Recovery Tests*

Extraction recovery experiments were carried out in triplicate for each condition using different SPE sorbents (C8, ENV and PPL) and elution solvents (MC, MeOH and EA). 10mL of an aqueous standard mixture with each compound present at ~2mg/L was extracted. Average recoveries and relative standard deviations (RSD) are shown in Table 3-7.

Table 3-7. Results of recovery tests using different sorbents and elution solvents.

Chemical		C8			ENV		PPL	
		MC	MeOH	EA	MeOH	EA*	MeOH	EA
phenol	Recovery (%)	55	23	82	66	82	62	100
	RSD (%)	1.6	4.4	0.85	1.3		0.29	0.99
4-methyl phenol	Recovery (%)	80	61	91	70	80	64	99
	RSD (%)	3.0	2.3	0.92	1.6		0.17	0.86
2-methoxy phenol	Recovery (%)	66	20	88	66	81	63	100
	RSD (%)	1.9	19	0.88	2.4		0.35	1.5
2,4-dimethyl phenol	Recovery (%)	82	64	89	70	81	64	98
	RSD (%)	1.8	0.24	0.66	2.2		1.6	1.6
2-methoxy-4-methyl phenol	Recovery (%)	79	62	90	68	81	65	99
	RSD (%)	1.9	0.82	0.65	2.0		1.5	1.5
catechol	Recovery (%)	39	53	37	82	55	73	70
	RSD (%)	2.4	2.2	1.1	3.0		5.9	3.1
2,6-dimethoxy phenol	Recovery (%)	83	69	78	79	77	74	98
	RSD (%)	1.7	2.1	0.93	3.6		8.5	3.6
pyrogallol	Recovery (%)	-	-	-	-	-	-	-
	RSD (%)	-	-	-	-	-	-	-
vanillin	Recovery (%)	89	54	87	71	82	59	101
	RSD (%)	1.4	0.96	1.8	6.8		14	0.54

* no replicate

- undetectable

As can be seen in Table 3-7, extraction recoveries of the phenolic compounds were very dependent on the sorbent-solvent combination selected. In most cases, using methanol for elution of the three solid phases gave recoveries between 50 and 80%, whereas elution of

the same solid phases with ethyl acetate remarkably increased the recoveries to more than about 80%. An exception was catechol. Since the compound is fairly polar, it is perhaps not surprising that the more polar methanol appeared to be a better elution solvent than the less polar ethyl acetate. For elution of C8, dichloromethane gave comparable recoveries as ethyl acetate for most of the phenols.

Of the three solid phases, the polymer-based PPL and ENV sorbents gave higher recoveries of the phenols than C8 when eluted with methanol. Using ethyl acetate as the elution solvent, the overall performance of the solid phases for phenol extraction was in the order PPL>C8>ENV. Over 98% of all the phenols, except catechol, were recovered when extracted using the PPL-ethyl acetate combination. It should be noted that none of the extraction recoveries for catechol was over 90% and that the tri-hydroxy phenol – pyrogallol – was not detected in any of the extracts.

Extraction of the phenol-containing water samples using the PPL solid phase with ethyl acetate as the elution solvent clearly provided the best extraction yields overall. Most of the compounds investigated could be almost fully recovered from the water phase with very good reproducibilities. Therefore, this method was the sample preparation method chosen for direct extraction of phenolic components from the water samples.

3.2.6. *Validation of Selected Extraction Method*

For the recovery tests, water samples extracted were mixtures of the standard compounds in MilliQ water. Real water samples are often far more complex, containing organic components of different concentrations and nature as well as inorganic impurities. A valid sample preparation method should be able to give comparable results when it is applied to standard samples with water as matrix and to real samples with a more complex matrix.

Validation of the selected PPL-ethyl acetate extraction method in this study was conducted by recovery tests using standard mixtures of different concentrations and standard-spiked MTE water samples. Recoveries of the phenols from the spiked MTE samples can be calculated using the equation below:

$$\text{Recovery\%} = \frac{(Q_{\text{total}} - Q_{\text{mte}})}{Q_{\text{added}}} \times 100$$

Equation 3.2.

where Q_{total} is the total amount of a compound detected in a spiked MTE sample, Q_{mte} is the amount of the compound found in the MTE water sample averaged from three repeat analyses and Q_{added} is the known quantity of the component added to the MTE sample.

Method validation results are provided in Table 3-8.

Table 3-8. Results of validation of the direct SPE method.

	Recovery%±SD			
	Standard mixture			Standard-spiked MTE sample
	~2mg/L	~0.4mg/L	~0.2mg/L	~0.2mg/L
phenol	100±1	98±2	95±3	105±9
4-methyl phenol	99±1	97±2	98±4	99±2
2-methoxy phenol	100±1	97±2	94±3	104±4
2,4-dimethyl phenol	98±2	95±2	94±2	96±2
2-methoxy-4-methyl phenol	99±1	95±2	98±2	95±1
catechol	70±3	52±5	*	*
2,6-dimethoxy phenol	98±4	91±4	96±1	90±10
vanillin	101±1	98±2	91±6	105±0

* detected but not quantifiable

The results in Table 3-8 reveal that >90% of all the mono-phenols at concentrations between 0.2 and 2mg/L could be recovered from the standard water solutions using the PPL-ethyl acetate method. While complete extraction of the mono-phenols at 2mg/L was achieved, recoveries of the phenols at lower concentrations were slightly lower.

Extraction of the MTE water sample and the same sample spiked with ~0.2mg/L standard phenols showed that >90% of all the mono-phenols could be recovered from an MTE water matrix. The higher standard deviations in some cases compared to those in the recovery tests using standard solutions were probably due to the effect of the complex sample matrix.

Due to their greater polarity, the multi hydroxy phenols were not extracted as efficiently as the mono-phenols. Catechol could be detected at concentrations as low as 0.2mg/L in water. However, in the low concentration range, quantitation results are prone to error since the GC-MS calibration curve of catechol is not as linear as for the mono-hydroxy

phenols, especially when the splitless mode was used as was necessary for low concentration extracts (refer to Figure 3-7). Pyrogallol was not detected in any of the SPE extracts of the standard solutions (~0.2, 0.4, 2mg/L). This outcome is mainly due to its very low GC-MS sensitivity (undetectable at concentrations of ~20mg/L or below) and, possibly, low extraction yield.

3.2.7. *Summary*

Method evaluation and validation have demonstrated that extraction of the MTE water samples using PPL with ethyl acetate for elution without derivatisation is a valid sample preparation method for GC-MS quantitation of the mono-phenols when their concentrations are around 0.2mg/L or higher in MTE water. The PPL solid phase with high capacity and flow properties is optimised for the extraction of polar species from large volume water samples [159]. GC-MS quantitation of mono-phenols at lower concentrations in larger volume water samples would be achievable using this extraction method.

Nevertheless, for the particular case of GC-MS analysis of the MTE product water from batch experiments with limited water volume, when the concentrations of these components were below the GC quantitation range, this method would not be suitable and reliable. Methods of increasing the GC sensitivity and/or extraction recoveries of the components rather than increasing the extraction volume should be considered for optimising the analysis.

Moreover, the compounds with multi-hydroxy groups generally exhibited poor chromatographic properties and/or low extraction recoveries due to their polar characteristics and could only be quantitated or detected at relatively high concentrations. Thus, the direct SPE method was inappropriate or inapplicable for the extraction and analysis of these compounds.

For the analyses of low concentration phenols and multi-hydroxy phenols in the MTE water samples, derivatisation methods that can improve the chromatographic performance and/or SPE extraction efficiency of these compounds are required.

Due to their high polarity and poor chromatographability, the selected carboxylic acids, in their underivatised form, could not be detected by GC-MS even at very high

concentrations ($\sim 250\text{mg/L}$). Thus, it appeared necessary to reduce the polarity of these compounds using methods such as derivatisation in order to extract and analyse these compounds in water samples effectively.

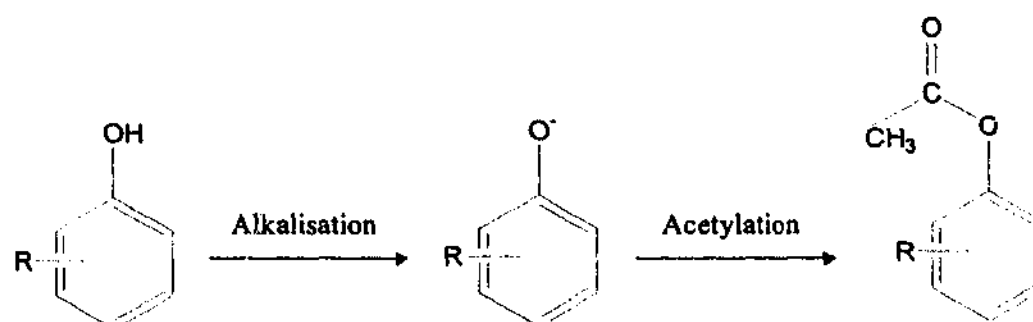
3.3. Phenol Acetylation-SPE

Sample pre-treatment methods, involving derivatisation and extraction of derivatised products, were established and validated for GC-MS characterisation of phenolic compounds in MTE water. The experiments and results are introduced in this section.

3.3.1. Selection of Phenol Derivatisation Method

Commonly used phenol derivatisation reactions include alkylation with diazoalkanes [161-163], pentafluorobenzoylation using pentafluorobenzyl bromide (PFBBR) [164-166] and acylation/acetylation using heptafluorobutyric anhydride (HFBA) [167] or acetic anhydride. Diazoalkanes esterify not only phenols but also alcohols [168] and carboxylic acids [169, 170] and, hence, the reaction is not selective. Another disadvantage is that it involves isolation of the organics from the water phase [161, 169]. The PFBBR method gives derivatives of high GC sensitivity but also often requires a non-aqueous environment [164, 171, 172], heating and long reaction time [164]. In addition, the high GC sensitivity is likely to result in high background during detection.

Acetylation is a commonly used derivatisation method for the determination of phenolic compounds [158]. The reaction with acetylation reagents is simple and can be realised under alkaline conditions directly in aqueous solution at room temperature. Acetylates of the polar phenols can then be isolated by extraction methods such as SPE. The mechanism of phenol acetylation can be expressed in the following manner:



The most frequently used acetylation reagent is acetic anhydride, which is readily available, inexpensive, non-hazardous and, most importantly, does not interfere with the

phenols in wastewater from treatment of coal and similar materials. Grist et al [93] used acetic anhydride acetylation for quantitative analysis of chlorophenols in aqueous ozone bleaching effluents of pulps. Wang and Zhao [80] indicated that di-hydroxy phenols in coal gasification wastewater could only be detected after derivatisation using the acetic anhydride method. In pulp bleaching wastewater, phenols, including phenol, 2-methoxy phenol, catechol and vanillin that were also detected in the MTE product water in preliminary tests (refer to Section 3.2.1), were determined by Pissolatto and coworkers [82] using this method.

Acetylation using acetic anhydride was therefore chosen as the derivatisation method evaluated for the analysis of phenolic compounds in MTE water in this study.

A flow diagram for the acetylation SPE-GC-MS method for the analysis of phenolic compounds in water samples is shown in Figure 3-8. Derivatisation, extraction and GC-MS characterisation are the three major steps.

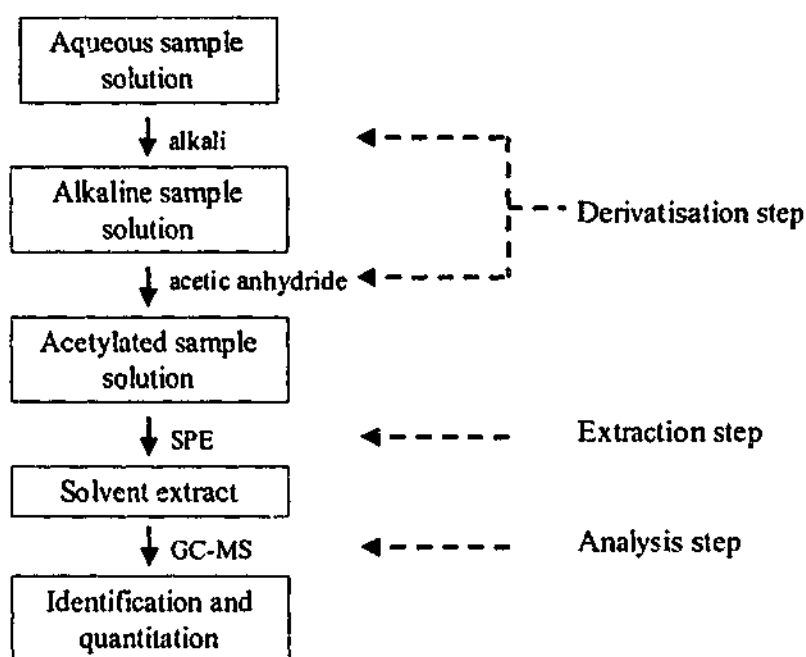


Figure 3-8. Procedure of phenol acetylation-extraction and GC-MS analysis.

To establish and validate the acetylation-extraction method for GC-MS analysis of phenols in the MTE water, firstly a number of derivatisation and extraction parameters were evaluated and optimised using standard phenols of known concentrations in aqueous solutions. Secondly, standard calibration curves were prepared by analysing a series of standard aqueous solutions of different concentrations following the optimised procedure. Finally, the selected phenols in an MTE water sample and a standard-spiked MTE sample were quantitated for validation of the method.

3.3.2. *Evaluation of SPE Conditions*

As shown in Figure 3-8 derivatisation is the first of the three main steps in the general procedure for phenol analysis. It is very important that evaluation of the derivatisation method be based on optimised extraction conditions and GC conditions. Therefore, prior to the evaluation of the derivatisation method, the extraction conditions were optimised by comparing a number of solid phases and elution solvents for extraction of the acetylated phenols in aqueous solutions.

3.3.2.1. *Experimental*

Derivatisation was carried out using a mixture of nine phenolic compounds (as listed in Table 3-6) each at a known concentration of ~2mg/L in MilliQ water. At this stage the

phenol acetylation method utilised by Wang and Zhao [80] for the analysis of coal gasification wastewater was adopted with modification.

Prior to acetylation 1mL of 10% (w/v) sodium carbonate solution was added to 10mL of the ~2mg/L standard solution to make it alkaline. Immediately after the addition of 0.3mL acetic anhydride the mixture was stirred on an electro-magnetic stirrer for 5 minutes using a Teflon-coated magnetic stir bar to promote reaction and the removal of carbon dioxide produced. The solution was then subjected to SPE using a series of solid phases and elution solvents followed by GC-MS analysis of the extract using a split mode injector and the temperature program A described in Chapter Two.

3.3.2.2. Results and discussion

SPE sorbents tested were C18, C8, C2 and PPL. C18 is the most hydrophobic silica-based sorbent available and very popular because of its extremely high retention of non-polar compounds (typical carbon loading 17.4% [135]). It has previously been used for the extraction of acetylated phenols in water samples [173]. C8 and C2 are less retentive and often used as a replacement of C18 when the molecules are retained too strongly on the latter. The polymer-based sorbent PPL is suitable for the extraction of polar species such as phenols as demonstrated in Section 3.2. It was also chosen for the extraction of acetylated phenols as a comparison with the silica-based sorbents. Both dichloromethane and ethyl acetate were used as elution solvents for C18 and C8, whereas C2 and PPL were eluted with ethyl acetate only.

The final volume of the SPE extracts for GC-MS analysis varied between 0.5 and 1mL (calculated from the weight of the extracts and solvent densities as mentioned in Chapter Two). For comparison purposes the GC-MS responses were normalised to an extract volume of 1mL. The normalised MSD responses of each compound in the extracts using different sorbents and elution solvents are illustrated in Figure 3-9. Error bars represent the standard deviations from three repeat tests. Abscissa labels are names of the sorbents (C18, C8, etc.) and elution solvents (dichloromethane – MC and ethyl acetate – EA) tested. Under the derivatisation conditions employed in this part of the study, the GC-MS responses of pyrogallol were, in all cases, very low. Hence the results are not included.

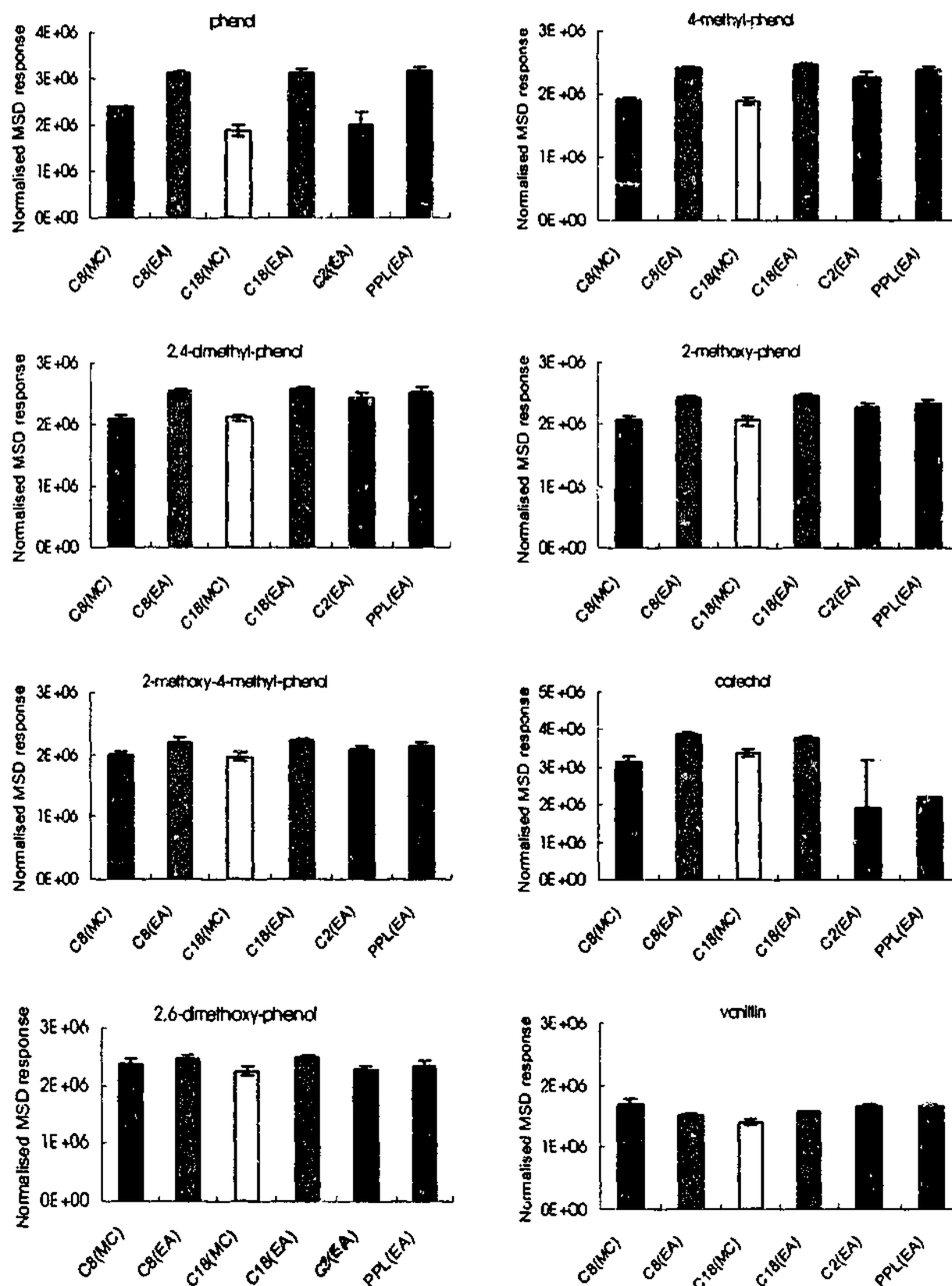


Figure 3-9. Comparison of different SPE sorbents and elution solvents for extraction of acetylated phenols.

For the C18 and C8 solid phases, ethyl acetate was apparently more efficient than dichloromethane as the elution solvent. Eluted with the same solvent – ethyl acetate – all

the sorbents investigated achieved comparable extraction yields for most of the phenol acetates. Their overall extraction performances roughly followed the order C18>C8>PPL>C2. Relative standard deviations were <5% with only a few exceptions, indicating good reproducibilities.

Thus, both the C18 or C8 sorbents, with ethyl acetate as the elution solvent, were shown to be acceptable choices for the extraction of phenolic compounds from water after acetylation. C18 was used in all further phenol acetylation experiments considering its higher carbon loading capacity than C8.

3.3.3. *Evaluation of Derivatisation Conditions*

For method development purposes, a number of factors including alkalisation conditions, the amount of the acetic anhydride and reaction time were assessed and optimised.

3.3.3.1. Amount of acetylation reagent and reaction time

Sodium/potassium carbonates are the most commonly used salts for alkalisation prior to acetylation using acetic anhydride. It has been suggested that the molar ratio between the carbonate and the acetic anhydride is an important factor that affects phenol acetylation yields [174, 178]. However, such an effect was observed, by Lyytikäinen and Pellinen [179], only for catechols but not for mono-hydroxy chlorophenols. It was found that the ratio 4:100 (v/v) of the acetic anhydride to 0.1M potassium carbonate was sufficient for acetylation of catechols [179]. The authors proposed that two competitive reactions – the acetylation reaction and the degradation of acetic anhydride by carbonate producing acetic acid and carbon dioxide – both consume acetic anhydride. Hence, they suggested a need to provide a sufficient amount of the acetic anhydride, rather than a specific molar ratio, in order to ensure complete derivatisation of the phenols. Louter et al [180] found that 0.05mL acetic anhydride was sufficient to derivatise 5mL aqueous sample containing six chlorophenols each at 1mg/L and they used 0.1mL to provide a safety margin. Wang and Zhao [80] applied 0.2 to 0.5mL of the reagent to 5mL coal gasification wastewater sample containing >7g/L phenols in total. Alberici and coworkers [181] found that 0.05mL was sufficient to derivatise phenols at total concentrations up to 1g/L in water.

In the present study, TOC levels in the MTE product water were <1g/L. For method development, the highest concentrations in the standard solutions was ~2mg/L for each of

the nine phenols. Based on reports by other researchers, acetic anhydride volumes of 0.3 and 0.5mL were evaluated (using 1mL 10% sodium carbonate) – approximately equivalent to the ratios of 3:100 (v/v) and 5:100 (v/v) of acetic anhydride to 0.1M sodium carbonate.

The acetylation of phenols by acetic anhydride is fast. According to Lyytikäinen and Pellinen [179] the reaction was completed within three minutes and several reports in the literature indicated a reaction time of five minutes [175, 177, 182]. Some groups preferred longer reaction times, such as 15-20 minutes [80, 173]. The observation that after three hours the acetates formed started to degrade at low pH [179] suggests that excessive long reaction times should be avoided.

In this study the SPE method was used for post-derivatisation enrichment. It usually takes 20 to 30 minutes to extract 10mL water samples using the silica-based sorbents. Hence it is important to ensure that the phenol derivatives did not degrade during the whole pre-treatment period. For evaluation purposes, reaction times of 5, 30 and 90 minutes prior to SPE were examined, leading to roughly 30, 60 and 120 minutes of total derivatisation-extraction time, respectively.

Figure 3-10 presents the MSD responses of 2,4-dimethyl phenol after acetylation using different amounts of the acetic anhydride for different reaction times. The results from two repeat tests under each condition are both shown.

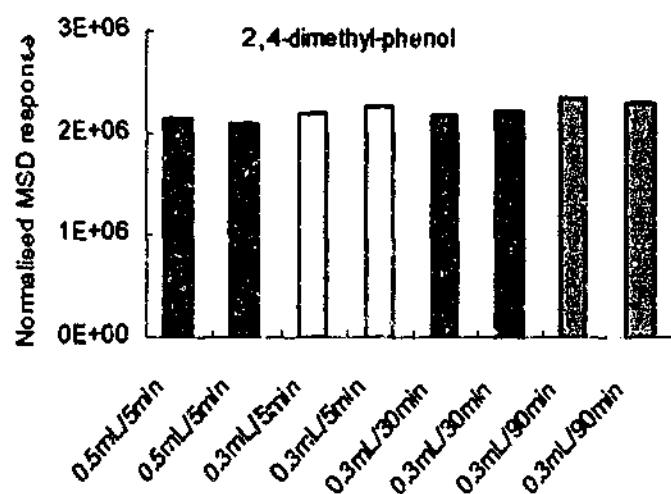


Figure 3-10. Effects of the amount of acetic anhydride and reaction time on phenol acetylation yields.

It can be seen that the acetylation yields of 2,4-dimethyl phenol did not vary much with the amount of the acetic anhydride and reaction time. Similar effects were observed for the other phenols investigated. This outcome suggests that under the selected buffering condition 0.3mL acetic anhydride was sufficient for acetylation of the phenols. The reaction was substantially complete after five minute reaction plus extraction time. Longer reaction time did not lead to significant increase of the acetylation yields. Degradation of the acetates did not appear to occur over the time examined.

3.3.3.2. Effect of pH in aqueous phase – Development of a two-step acetylation method

The issue. During the evaluation of SPE conditions and acetylation parameters described above, the derivatisation method used by Wang and Zhao [80] was adopted. Using this method, pyrogallol gave very low derivatisation-extraction yields, as indicated in Section 3.3.2.2, suggesting that these conditions were inappropriate for acetylation of the tri-hydroxy phenol. Although similar alkalisation conditions have been used for phenol acetylation in a number of prior studies [80, 176, 181], none of them involved tri-hydroxy phenols.

If, as suggested by Lyytikäinen and Pellinen [179], multi-hydroxy phenols require higher acetic anhydride to carbonate ratios, the low acetylation yield of pyrogallol under alkaline conditions should be increased by increasing the amount of the acetic anhydride with the amount of carbonate remaining constant. In this study, however, the acetylation yield of pyrogallol was not improved when 0.5mL rather than 0.3mL of acetic anhydride was used. Moreover, a larger amount of the acetic anhydride leads to a reduction in the pH of the water solution. This lowering of pH could occur very quickly after the addition of the acetic anhydride [177] and would be likely to result in increased degradation of the phenol acetates over a longer period of time [179]. Since the SPE step after derivatisation required 20-30min in the present study, increasing the amount of acetic anhydride was not considered to be an appropriate solution for the low acetylation yield of pyrogallol.

Effect of pH. Generally, the aqueous solution is buffered at a high pH prior to the addition of acetic anhydride to stabilise the phenolate anions for acetylation [174]. Sodium hydroxide [180], sodium/potassium carbonate [80, 82, 177, 181] and sodium/potassium

hydrogen carbonate [174, 182-184] have all been used to alkalise the aqueous samples for phenol acetylation. It should be noted, however, that in most of these applications the description of the alkalisation step often focuses on the type and amount of the alkali used without indicating the pH of the solutions. Very few reports in the literature have mentioned the effect of pH on phenol acetylation yields [177, 179, 185].

In order to determine the optimal alkalisation conditions for all the phenols investigated, a variety of previously reported alkalisation methods were examined and the pH prior to acetylation was measured for each case. These included 1mL 10% sodium carbonate (pH $\approx$ 10.5-11) as used by Wang and Zhao [80], 0.5mL 4% (1M) sodium hydroxide (pH $\approx$ 11.5-12) following Louter et al [180] and 0.1g solid sodium hydrogen carbonate (pH $\approx$ 8.5-9) calculated from the amounts used by Boyd [182] and Coutts et al [174]. Additions of 0.5mL 10% sodium carbonate (pH $\approx$ 9.5-10) and 0.05g sodium hydrogen carbonate (pH $\approx$ 7.5-8) were also evaluated. Normalised MSD responses of each compound in SPE extracts obtained after derivatisation under different alkalisation conditions were compared.

Figure 3-11 illustrates the effect of pH on the acetylation yield for a selection of the standard phenols employed in this study.

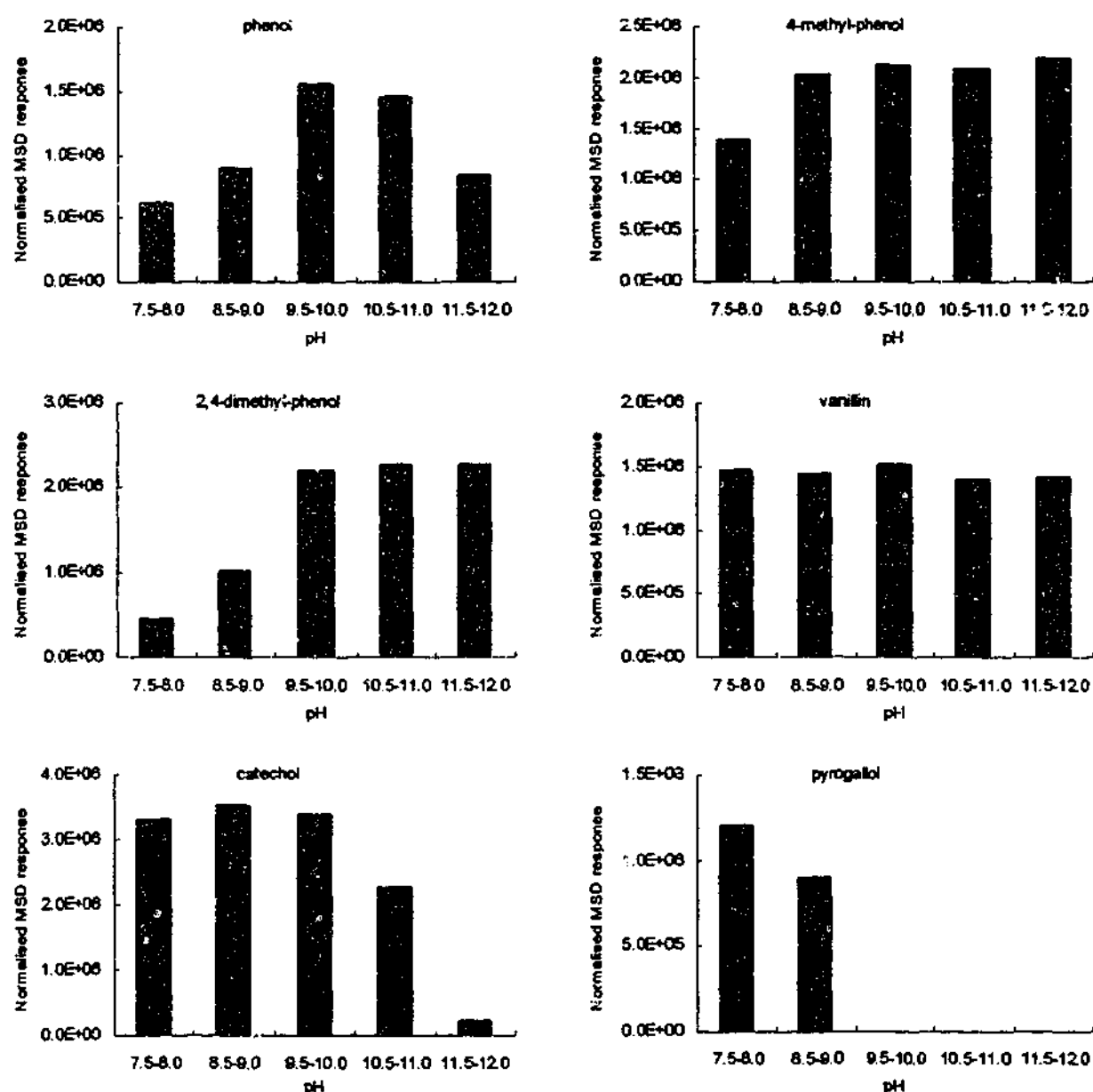


Figure 3-11. Relationship between acetylation yield and pH.

It was found that the pH of the water solutions prior to acetylation was the factor that most affected the derivatisation reaction of the phenols. The plots demonstrate that the effect of pH on acetylation yield varied significantly with phenol types. For vanillin, the pH appeared to have little influence on its derivatisation over the pH range investigated. The derivatisation yields of most of the phenols increased with pH to reach a constant level when the pH was $\geq 8.5-9$ (4-methyl phenol) or $\geq 9.5-10$ (2,4-dimethyl phenol). The behaviour of 2-methoxy phenol, 2-methoxy-4-methyl phenol and 2,6-dimethoxy phenol (all not shown) was virtually identical to that of 2,4-dimethyl phenol. In contrast, the acetylation yields of the two multi-hydroxy phenols significantly decreased at high pH. This explains why pyrogallol showed very low GC-MS response when 1mL 10% sodium

carbonate (pH=10.5-11) was used (Section 3.3.2). The pH effect on catechol acetylation is different from that observed by Boyd [182], who found that di-hydroxy phenols were only partially acetylated (one hydroxy group) when too little sodium bisulphate was added. An optimum pH existed for phenol acetylation (pH=9.5-10) and the acetylation yield was lower at pH below or above this value. Similar behaviour was observed by Li [185] for 4-nitro-phenol and pentachlorophenol; both achieved the highest yield at pH=5.

The reason for the low acetylation yield of catechol and pyrogallol at high pH could be that the acetylation of the phenolate ions of these compounds (multi-hydroxy phenols) is relatively slow compared to that of their protonated forms. Also, at high pH the acetic anhydride may be destroyed by hydrolysis before the acetylation process is completed, as suggested by Renberg and Lindström [177]. A similar effect was observed by Bengtsson [167] during heptafluorobutylation of phenols.

Although the acetylation method using acetic anhydride has been extensively applied to the analysis of alkyl-, chloro- and nitro-phenols including di-hydroxy phenols, as reviewed in Section 3.3.1, there has been little work covering a combined series of mono-, di- and tri-hydroxy phenols using this method. Boyd [182] was able to derivatise and analyse all three types of the phenols, adding 8g sodium hydrogen carbonate per litre water sample for alkalisation. Although the author did not mention the pH after alkalisation, it is likely to be relatively low. As demonstrated in the present study, under this condition the acetylation of pyrogallol can be significant but the yields for some of the mono-phenols, particularly phenol, will be low (refer to Figure 3-11).

In summary, phenol and pyrogallol showed to be the most pH-sensitive of the phenols investigated in terms of acetylation; that is, the maximum acetylation occurred only in a narrow pH range. There was no common pH at which both compounds were acetylated to a large extent. The current method with one pH adjustment has the disadvantage of seriously sacrificing the yield of majority of the phenols when operated in neutral or weak basic conditions or else that of pyrogallol and phenol when operated in strongly basic conditions. Bao et al [173] adjusted the pH of water samples to 11 using potassium carbonate for acetylation of a number of alkyl, chloro- and bromo-phenols. While they obtained recoveries >90% for most of the phenols, only 57% of phenol itself could be

acetylated. The low recovery they reported for phenol is very likely due to a low acetylation yield at this pH, as identified in the present study.

In order to analyse mono-, di- and tri-hydroxy phenols simultaneously, there is a need to improve the extent of pyrogallol acetylation without sacrificing the yield of the other phenols.

Two-step acetylation – The principle. pH was identified to be the key factor that affects the phenol acetylation yield. Seeing that there was no common pH at which all the phenols were optimally acetylated, the idea of a two-step derivatisation, involving two pH adjustments and acetylation, was put forward. First, instead of increasing the amount of the acetic anhydride to accomplish the acetylation of pyrogallol, the concentration of the protonated form of pyrogallol can be increased by lowering the pH of the aqueous phase so that the acetylation rate is increased and the competitive degradation of the acetic anhydride reduced. In a second step, the acetylation of the other phenols, which is favoured at high pHs, can be achieved by alkalising the water solution prior to their acetylation.

Two-step acetylation – Experimental. Various combinations of first and second buffering pHs were examined. In the first buffering-derivatisation step, intended to acetylate pyrogallol at a lower pH, the pH of the 10mL sample solution was adjusted using hydrochloric acid and/or 10% sodium carbonate to the desired value. After the addition of 0.1mL acetic anhydride a reaction time of five minutes was allowed. The second step followed the same procedure as the previous one-step derivatisation (Section 3.3.2.1) except that solid sodium carbonate was used to adjust the pH with the 10% sodium carbonate solution for fine adjustment. As large quantities of the sodium carbonate were required to alkalise the sample at this step, the solid salt was used to avoid excessive sample dilution and large extraction volumes. Following the addition of 0.3mL acetic anhydride and five minute reaction, the derivatised sample was subjected to SPE and GC-MS in the normal way.

Two-step acetylation – Results and discussion. Normalised MSD responses of each compound after two-step acetylation under different conditions are compared in Figure 3-12 for representative compounds. The two figures in each abscissa label refer to the buffering pH values for the first and second acetylation steps, respectively.

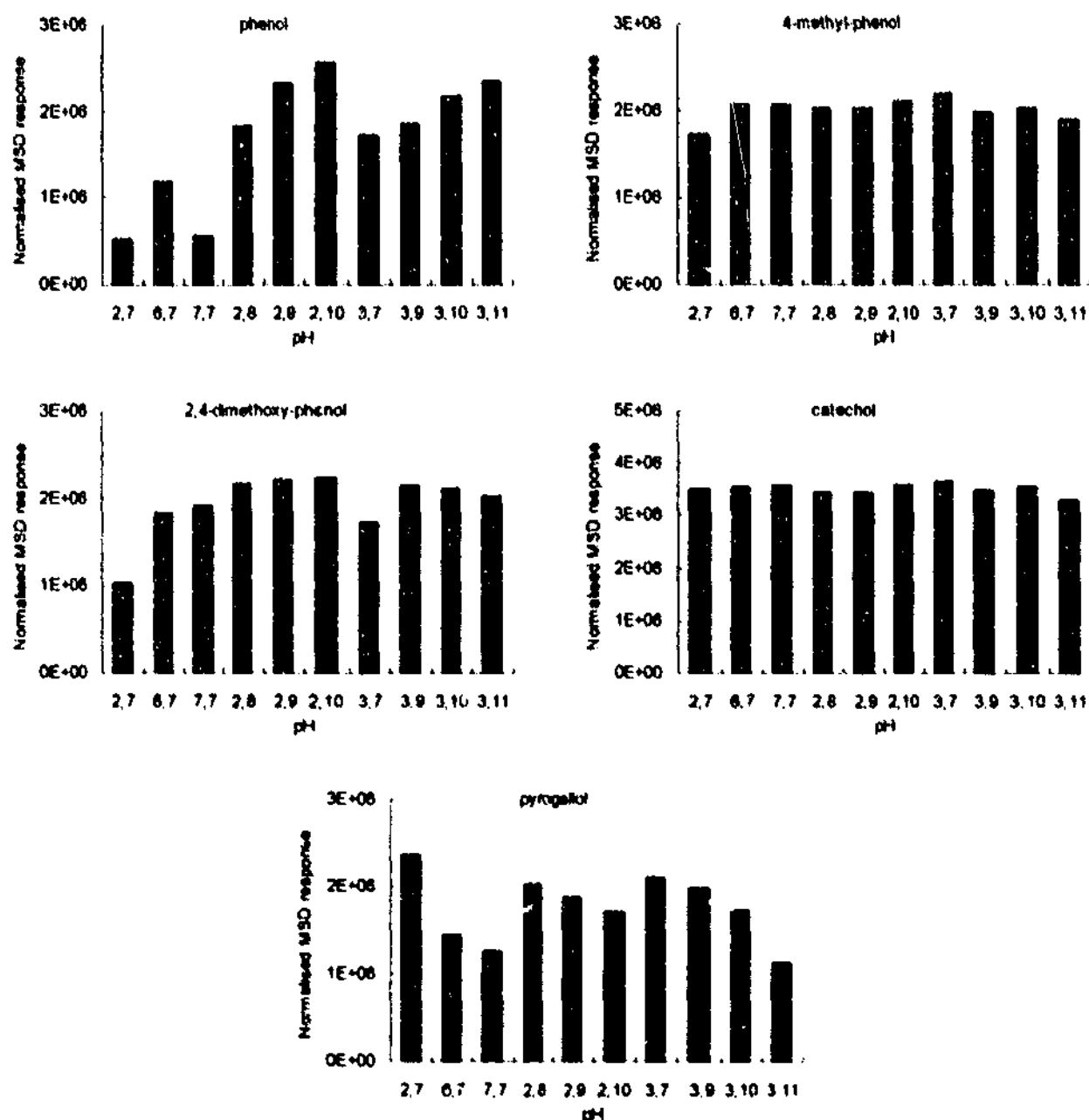


Figure 3-12. Effect of two-step pH adjustment on phenol acetylation yield.

It can be seen that the phenols exhibited different acetylation behaviours during the two-step acetylation. The acetylation of catechol and vanillin (not shown) did not seem to be correlated to the buffering condition. The yield for 4-methyl phenol did not depend on the pH combination except for the low yield at pH=2,7. The behaviours of 2-methoxy phenol and 2-methoxy-4-methyl phenol (both not shown) were very similar to the case of 4-methyl phenol. 2,4-dimethoxy phenol and 2,6-dimethoxy phenol (not shown) both required the second pH to be above 8 for the yields to reach a maximum level. For all these

compounds, there were a number of common pH combinations, at which their acetylation yields were at a maximum level.

On the other hand, the acetylation of phenol and pyrogallol exhibited strong pH-dependence. Their acetylation yields varied with slight pH changes. Therefore, the selection of buffering condition that facilitates the acetylation of both these compounds was the most critical factor in fixing the conditions to be used for routine analyses. Since the relationship between pH and derivatisation yield of the two compounds essentially followed opposite trends, the optimum condition should be the one under which both compounds exhibited near maximum acetylation. Thus, pH=2 and 9 were selected as the first and second acetylation pH, respectively. This condition was then used for the rest of the experiments discussed in this section, including the preparation of standard calibration curves and the analyses of the MTE water samples.

3.3.4. *GC-MS Characterisation and Standard Calibration Curves*

A benefit of the phenol acetylation method for GC-MS characterisation is that the mass spectra of the phenol acetates are very similar to those of the corresponding phenols with the same ion as the base peak. The acetylation of each hydroxy group adds a mass of 42 to the phenol molecule. The presence of M^+-42 , M^+-84 and M^+-126 as base peaks in the spectra is characteristic of mono-, di- and tri-hydroxy phenol acetates, respectively. The mass spectra of phenol, catechol and pyrogallol and their acetates are presented in Figure 3-13.

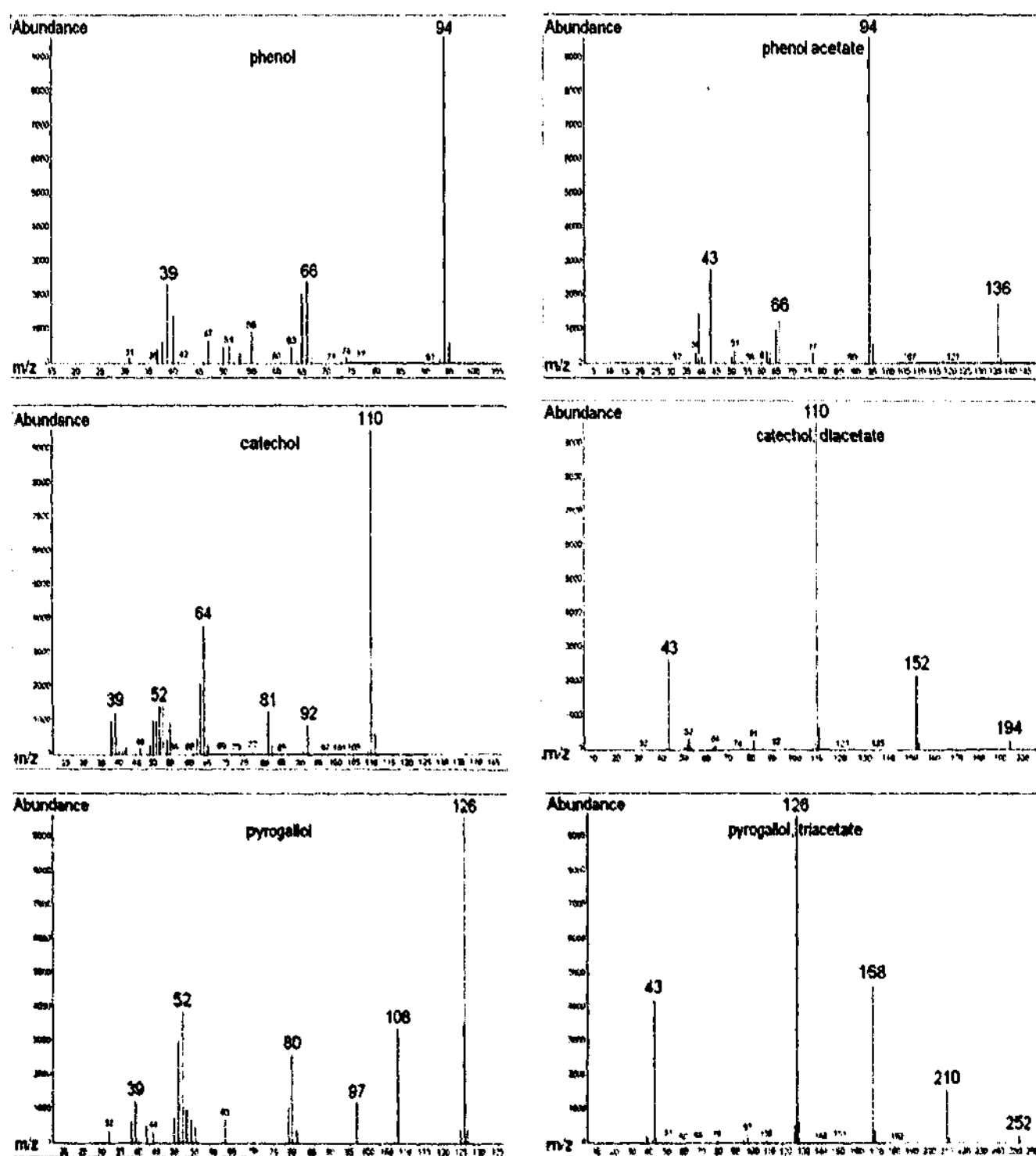


Figure 3-13. Mass spectra of selected phenols and their acetates

As shown in the figure, the molecular ions 94, 110 and 126 of the mono-, di- and tri-hydroxy phenols respectively, are the most abundant peaks in the spectra of both the phenols and their acetates. An ion with a mass of 136 appears in the spectrum of phenol acetate indicating the presence of one hydroxy group in the structure. The ions 152 and 194 for catechol and 168, 210 and 252 for pyrogallol, with abundance decreasing with

increasing mass number, characterise the acetylation of two and three hydroxy groups on the benzene rings, respectively.

The GC-MS calibration curves for quantitation were prepared by acetylating standard phenols of different concentrations in water under the optimised conditions and analysing the SPE extracts on GC-MS. A great advantage of this method over the use of standard phenol acetates for calibration is that the errors due to incomplete derivatisation-extraction are minimised or eliminated. When derivatisation is carried out under optimised conditions, it is not necessary to determine the absolute derivatisation yield. Using the standard calibration curves for quantitation, the concentrations of the phenols in water samples can be directly determined.

Concentrations of the standard solutions for derivatisation were ~800, ~200, ~100, ~40, ~10, and ~4 µg/L from successive dilution of concentrated standard solutions (refer to Table 3-6) using MilliQ water. The selection of a broad range of concentrations for calibration was due to the potential broad range of phenol concentrations in different MTE water samples. The concentrations in unknown samples can then be calculated by selecting different calibration ranges according to the level of the GC-MS response. Figure 3-14 presents examples of the standard linear calibration curves employed, together with the derived equations and R^2 values. The plots 'phenol (b)' and 'vanillin (b)' are the calibration curves in a lower concentration range of the two compounds. The least-squares-fit trendlines were drawn based on the average MSD responses of three replicates for each concentration. Relative standard deviations for the replicates are <10% in most cases.

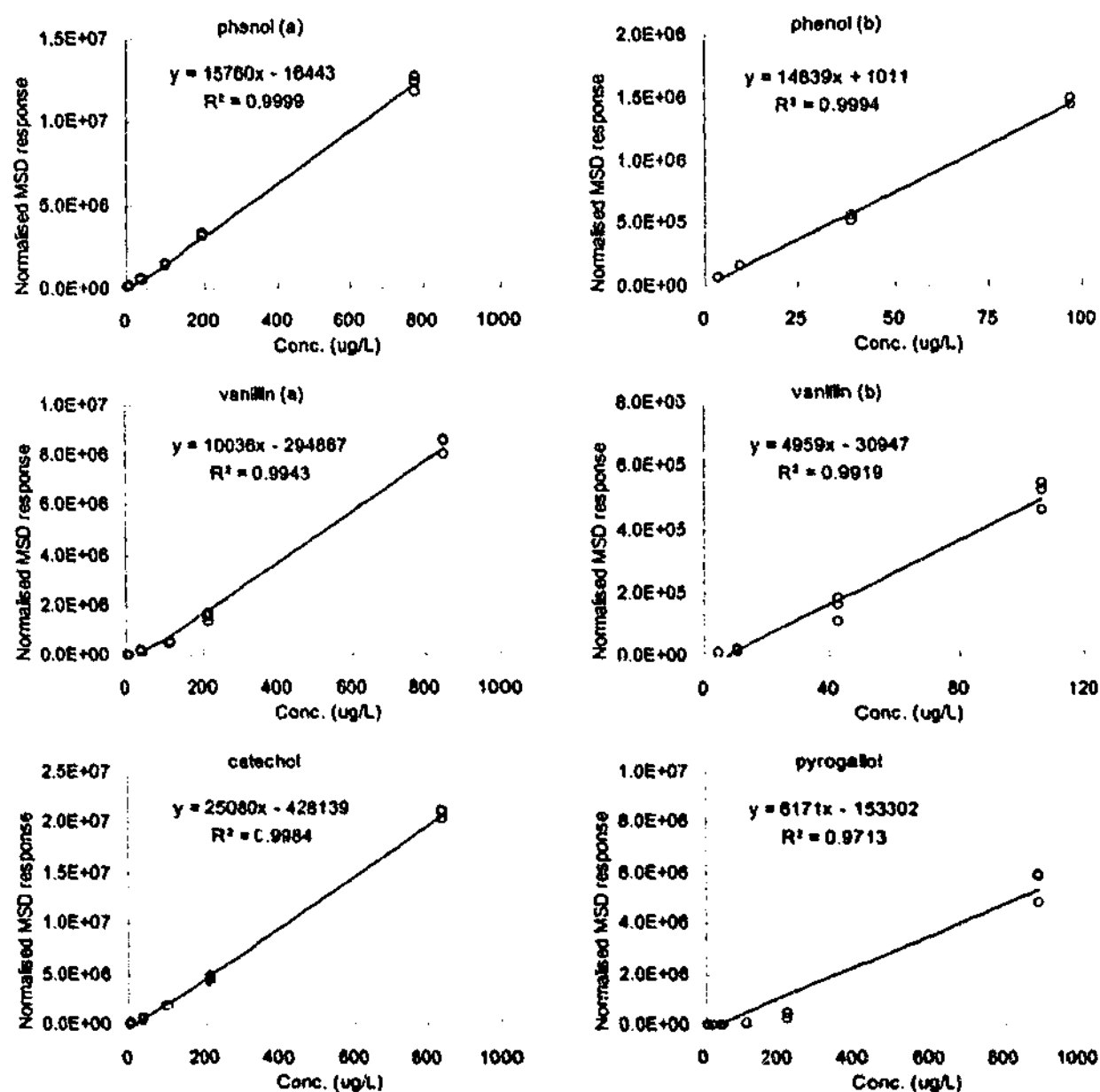


Figure 3-14. Standard calibration curves of selected phenol acetates.

The R^2 values of the linear least-squares calibration curves for all the mono-phenols and catechol are >0.99 in a broad concentration range from 4 to 800 $\mu\text{g/L}$ including the lower concentration range from 4 to 100 $\mu\text{g/L}$ as shown by the plots 'phenol (b)' and 'vanillin (b)'. The calibration curve for pyrogallol exhibits a linear MSD response-concentration relationship but the R^2 value, though acceptable, is not as good as for the other phenols. Concentrations of the phenols in a water sample were calculated using calibration curves of different concentration ranges accordingly.

3.3.5. Validation of the Two-step Acetylation Method

In a similar manner to the approach applied to the validation of the SPE method without derivatisation (Section 3.2.6), the two-step phenol derivatisation method was validated by

analysing an MTE water sample with and without spiking using known amounts of the standard phenols. Concentrations of the phenols in both spiked and unspiked samples were determined using the standard calibration curves for each component. Recoveries were calculated using Equation 3.2. The method validation results are shown in Table 3-9. Errors are standard deviations of three replicates.

Table 3-9. Results of validation of the two-step acetylation-SPE method

	Amount in MTE sample ($\mu\text{g/L}$)	Amount added ($\mu\text{g/L}$)	Total amount in spiked MTE sample ($\mu\text{g/L}$)	Recovery	
				%	RSD%
phenol	76 $\pm$ 1	195	280 $\pm$ 16	105	7.9
4-methyl phenol	3.6 $\pm$ 0.3	192	208 $\pm$ 3	106	1.4
2,4-dimethyl phenol	0.89 $\pm$ 0.03	203	212 $\pm$ 2	104	0.92
2-methoxy phenol	89 $\pm$ 3	215	321 $\pm$ 1	108	0.24
2-methoxy-4-methyl phenol	3.5 $\pm$ 0.1	199	215 $\pm$ 0	107	0.17
catechol	627 $\pm$ 19	211	824 $\pm$ 17	93	8.7
2,6-dimethoxy phenol	43 $\pm$ 1	208	244 $\pm$ 16	97	8.0
vanillin	118 $\pm$ 5	213	345 $\pm$ 29	107	13
pyrogallol	92 $\pm$ 5	223	240 $\pm$ 14	67	9.7

The results show that all the phenols, except pyrogallol, attained >90% recoveries from the MTE water matrix. Even catechol, which could not be quantified using the direct SPE method without derivatisation, was quantitatively recovered. For pyrogallol, the recovery was low compared to the mono- and di-hydroxy phenols, very likely due to the fact that derivatisation of this component was very pH sensitive. A slight increase of the pH in the second acetylation step could result in notable reduction of the acetylation yield as shown in Figure 3-12. With the limited amount of water samples used (10mL), it proved difficult to buffer the solutions to a very consistent pH.

Table 3-9 quotes recoveries for some compounds that are >100%, a circumstance that has previously been recorded in the literature (up to 120% in some cases) [173, 175, 185]. It is possible that the sample matrix may have a positive effect on the recoveries. Furthermore, some of the phenols were present in the MTE water sample and spiked sample at concentrations of different magnitudes (e.g. 3.6 $\mu\text{g/L}$ vs 208 $\mu\text{g/L}$ for 4-methyl phenol;

Table 3-9). Errors could have arisen when calculating the concentrations using calibration curves of different concentration ranges.

In conclusion, the analysis of the standard-spiked MTE water sample confirmed that the two-step acetylation-SPE method is an improvement over current methods and is appropriate for the analysis of mono- and di-hydroxy phenols in water samples with complex matrix. Derivatisation of pyrogallol is still problematic, but identification and quantitation of the compound at relatively high concentrations is achievable with careful buffering.

The optimised and validated two-step acetylation method was then applied to the characterisation of phenolic compounds in selected MTE water samples.

3.3.6. *Comparison of SPE Methods with and without Acetylation for Phenol Analysis*

The outcome achieved in this study further proves that acetylation of the polar hydroxy groups on a benzene ring can remarkably improve the chromatographability of the compounds and the sensitivity for GC-MS detection. Table 3-10 compares the SPE methods with and without acetylation using the abundance of target ions, detection limits and concentration results of a real MTE sample.

Table 3-10. Comparison of SPE methods with acetylation (A) and without acetylation (B) for phenol analysis.

	Abundance of target ion		Detection limit (µg/L)		Analytical result for MTE sample (µg/L)	
	A	B	A	B	A	B
phenol	3.1×10^6	1.1×10^6	0.13	7	17	31
4-methyl phenol	2.6×10^6	1.0×10^6	0.64	12	12	34
2,4-dimethyl phenol	2.9×10^6	1.0×10^6	0.091	13	4.2	-
2-methoxy phenol	2.8×10^6	1.0×10^6	0.86	7	3.37×10^2	4.4×10^2
2-methoxy-4-methyl phenol	2.8×10^6	9×10^5	1.4	19	7.4	-
catechol	4.5×10^6	1×10^5	2.2	94	1.67×10^1	1.9×10^1
2,6-dimethoxy phenol	3.4×10^6	9×10^5	1.2	61	1.53×10^2	2.0×10^2
vanillin	1.5×10^6	2×10^5	3.6	77	4.75×10^2	4.0×10^2
pyrogallol	1.5×10^5	-	13	2.1×10^1	1.3×10^2	-

- undetected

That the base peaks in the spectra of the phenols and their acetates are from the same ions allows the comparison of the two methods using abundance of the same ions. For the phenols, the abundance data in Table 3-10 are the MSD responses of the phenols each at ~2mg/L in a standard solution. For the phenol acetates, the data correspond to the MSD responses of a 1mL extract obtained from acetylation and extraction of a 10mL, ~0.2mg/L phenol solution. Assuming the acetylation-extraction yields were all 100%, the concentration of each acetate in the extract was approximately 2mg/L. The actual concentrations were probably lower due to incomplete acetylation-extraction.

Comparison of the two sets of abundance data shows that the acetylation method gives substantially higher GC-MS responses for each of the phenols listed. Catechol and pyrogallol exhibit the most significant improvements.

The lowest concentration at which a compound can be confidently quantified should be the lowest concentration that falls within the linear response-concentration relationship, i.e. the lowest concentration used to prepare the calibration curves. For the mono-phenols and catechol, the lowest quantitation concentration was 50-100µg/L without derivatisation and ~4µg/L after derivatisation. Quantitation of pyrogallol was only achievable at concentrations above ~20µg/L after derivatisation.

Detection limits are the lowest concentration of a compound detectable by a method. They will be generally lower than the lowest quantitation concentration. Usually the detection limit of a GC analytical method is calculated using the signal to noise ratios (S/N) in chromatograms. In the present study, since the GC-MS identification and quantitation were carried out using the GC-MS responses of the target ion, interferences from the baseline noise were found to be essentially zero. Therefore, the method using signal to noise ratios to calculate detection limits was not applicable. During data processing, the abundance of the smallest peaks appearing in the chromatograms was generally 5000 area counts. This number was therefore used to calculate the detection limits. In the calibration equation $y = bx \pm a$, when 'y' equals 5000, the concentration 'x' in the SPE extracts (using the SPE method without derivatisation) or in water (using the acetylation-SPE method) can be calculated. Data presented in Table 3-10 assume a concentration factor of 20, i.e. a 10mL water sample concentrated to a 0.5mL extract.

It can be seen in the table that the detection limit is inversely correlated to the target ion abundance. Using the acetylation method the detection limits of the phenols increase by one to two magnitudes. Comparison of the two methods shows that the sensitivity of the GC-MS detection for the phenols can be greatly improved by derivatisation.

Analytical results for the MTE water sample confirmed that, for the analysis of the mono-hydroxy phenols and catechol at relatively high concentrations, the results obtained using both methods were comparable. For the components present at low concentrations (e.g. phenol and 4-methyl phenol) which were below the valid quantitation range of the direct SPE method, the two methods gave different results. The components, such as pyrogallol, which could not be detected without derivatisation since their concentrations were lower than the detection limits of the method, could be identified and quantified after acetylation.

Advantages of the two-step acetylation-SPE method over the SPE method without derivatisation can be summarised as follows:

- a) Improved chromatographic characteristics. The peaks of phenol acetates in TIC are narrower and sharper than those of the phenols – features that are preferred for GC-MS identification and quantitation;

- b) Improved identification confidence. The selectivity of the acetylation reaction for phenolic groups with the presence of the M^+-42 ion in the spectra provides improved confidence in assignment of phenol identities. This is particularly important for the analysis of complex mixtures containing various organic compound groups;
- c) Improved GC-MS sensitivity. Most importantly, the sensitivity of GC-MS detection can be remarkably improved, especially for the multi-hydroxy phenols, which without derivatisation could not be quantified (e.g. catechol) or even detected (e.g. pyrogallol) under most circumstances. More phenols, therefore, can be identified and quantified without the need for larger sample quantities or further concentration of the extracts;
- d) Improved extraction efficiency. The extraction efficiency of the phenols, especially for the multi-hydroxy phenols, is improved. Without derivatisation, the maximum extraction recoveries of catechol using C8 were <40%. After derivatisation and extraction using C18, the acetylation-extraction recovery of catechol increased to >90%; and
- e) Improved quantitation reliability. Experimental errors due to incomplete acetylation and extraction during work-up can be minimised, because the conditions for the analysis of water samples are the same as that for preparing the standard calibration curves. Quantitation results are thus more precise and reliable.

3.3.7. Summary

The pH in water solutions prior to acetylation was identified as the critical factor that affects phenol acetylation yields. A two-step acetylation-SPE method was developed and optimised for the analysis of mono-, di- and tri-hydroxy phenols in water samples. Validation of the method showed that near quantitative derivatisation and extraction would be simultaneously achieved for mono- and di-hydroxy phenols. Even the simultaneous detection and quantitation of pyrogallol (a tri-hydroxy phenol) was achievable.

Compared to the SPE method without derivatisation, the acetylation method significantly improved the sensitivity of GC-MS detection of the phenols and proved to be suitable for the analysis of MTE water samples.

3.4. Carboxylic Acid Methylation-SPE

Carboxylic groups in the aqueous phase can be present either as carboxylic acid (at low pH) or as carboxylate ions (at high pH). For simplicity, the term 'carboxylic acid' is used to refer to both forms in this thesis (unless specified otherwise).

Investigations discussed in Section 3.2 revealed that derivatisation of carboxylic acids was imperative for identification and quantitation of these compounds using the current GC-MS methods. This section introduces the experiments and results of evaluation and validation of methylation-SPE methods for the analysis of the carboxylic acids in MTE water samples.

3.4.1. Introduction

Esterification, particularly methylation, is a very common derivatisation method for the analysis of carboxylic acids [186-188]. Important advantages of methyl esters over silyl esters are that they are more stable, particularly with respect to moisture, and that their mass spectra are often easier to interpret [189].

Methylation with diazomethane is probably the most facile analytical derivatisation [158] with the advantages of rapid, experimental easy and minimal by-products [107]. However, the preparation and use of this reagent involves certain risks due to its carcinogenic and explosive properties. [158, 189]. Although this method has been used to determine organic acids in wastewater from processing of coals and similar materials [93, 190], it was not considered as an option in this study.

Boron trifluoride (BF_3)/methanol is a common reagent frequently used to alkylate organic acids for determination in various environmental samples [191-194]. It has been employed for the analyses of carboxylic acids in wastewater from processing of coals and similar materials [65, 80, 195]. Wang and Zhao [80] were able to identify mono- and di-carboxyl acids and aromatic acids in a coal gasification effluent after methylation with BF_3 /methanol complex. Using the reagent to methylate aliphatic carboxylic acids in oil

shale retort water prior to GC-MS characterisation, Riley et al [195] proposed that this technique in combination with other derivatisation methods could be used for analysis of water soluble organic components in aqueous process wastes and other environmental samples. In this study BF_3 /methanol complex was evaluated as one of the methylation reagents for GC-MS characterization of carboxylic acids in MTE product water.

Acetyl chloride in alcohols, such as methanol, *n*-butanol, propanol, has been applied to derivatisation of organic acids in natural water [196], municipal wastewater [197] and biological samples [198]. Lepage and Roy [198] found that this reagent is more efficient and water tolerant than BF_3 /methanol for methylation of fatty acids in bio-specimens. For the analysis of the MTE water, acetyl chloride/methanol was assessed for comparison with the BF_3 method.

Most of the reactions between methylation reagents and carboxyl groups require a non-aqueous medium since hydrolysis of the reagents is far more rapid than the methylation reaction. Therefore, isolation of the organics from the water phase prior to methylation is often necessary for the analysis of aqueous samples. Water drying under a nitrogen stream [65, 80] and extraction by LLE [194, 197] or SPE [188, 199] are the two frequently used acid isolation methods. In the present work, both the nitrogen drying and SPE methods for acid isolation prior to methylation were evaluated.

The acid isolation step prior to methylation is generally a time-consuming process with a significant probability that the analytes will be lost by volatilisation and/or incomplete extraction. Methods that can directly methylate the acids in the presence of water are desirable. A new method that allows this has recently been developed by Liebich and coworkers [189, 200]. They achieved direct methylation of organic acids in the aqueous phase using trimethyloxonium tetrafluoroborate (TMO).

TMO was first synthesised by Meerwein et al [201, 202] and has been utilised as one of the esterification reagents for methylation of carboxyl groups [203-206]. The feature that TMO (i.e. Me_3OBF_4 , Figure 3-15) does not react with water as fast as with acid anions enables the directly methylation of organic acids in the aqueous phase [200]. Sample preparation for the analysis of organic acids in water samples can thus be simplified by omitting the lengthy drying or extraction step. The method proved to be reliable for

profiling organic acids in native urine samples by Liebich and coworkers [189, 200], who considered TMO as a good replacement for hazardous diazomethane.

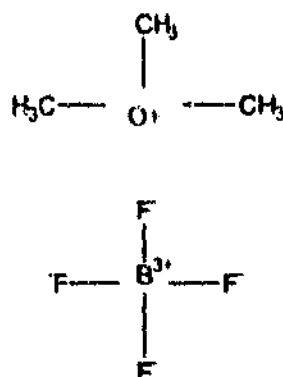


Figure 3-15. Formula of TMO.

Since the original development of the direct TMO methylation method, there have been very few subsequent reports of its application to the identification or quantitation of organic acids. Furthermore, the work of Liebich et al [189, 200] was qualitative in nature and did not involve method validation or quantitation. Therefore, it is important to develop an in-depth understanding of the TMO methylation method for the determination of organic acids in aqueous samples. Thus, this method was investigated and compared with the non-aqueous phase methylation methods.

In summary, the sample preparation strategies investigated in this work included acid isolation by nitrogen drying and SPE, non-aqueous phase methylation using acetyl chloride/methanol and BF_3 /methanol and direct methylation using TMO.

3.4.2. Comparison of Acetyl Chloride/methanol and BF_3 /methanol for Methylation

In this section, methylation efficiency of the two methylation reagents for carboxylic groups are compared. The experiments were carried out using organic solvent solutions of the selected standard acids instead of aqueous solutions to eliminate any effect of the acid isolation step.

3.4.2.1. Experimental

In the literature, methods reported using BF_3 /methanol for methylation varied in terms of the amount of the reagent, reaction temperature and time employed. The use of 1-2mL 10-14% BF_3 /methanol achieved sufficient methylation in a number of studies [80, 193, 194]. The reaction time used was between 3-5 minutes [65, 193, 194] and 20-30 minutes [80,

207]. Reactions were conducted at 70°C by Casado et al [193, 194] and by Rotzsche [207], while Lepage and Roy [198] reportedly used 100°C. Some reports described the use of a hot water bath or flux without recording the precise temperature [65, 80].

The conditions utilised in the current work were selected based on the methods mentioned above. 1mL of the 13-15% BF₃/methanol complex was added to a 1mL standard methanol solution with each acid at ~10mg/L (refer to Table 3-6) in a 10mL vial. The vial was then sealed with a crimp top cap and heated in a water bath for 30 min at 75-80°C. 5mL MilliQ water was added to remove excess BF₃/methanol reagent after the contents of the vial had cooled to room temperature, since any residues of BF₃ can cause irrecoverable damage to the GC column. The aqueous solution was then subjected to SPE followed by GC-MS analysis of the extract.

Using acetyl chloride as the derivatising reagent, the method described by Lepage and Roy [198] for the analysis of fatty acids in human milk was adopted. A 5:100 (v/v) acetyl chloride/methanol solution was freshly prepared prior to use. 1mL of the solution was added to a 10mL vial containing the 1mL standard acid solution (~10mg/L of each acid in methanol). Methylation reaction took place in the sealed vial in a 100°C water bath for 1 hour. After the contents had cooled to room temperature, 5mL MilliQ water was added to create an aqueous matrix for extraction using SPE.

The C18 sorbent with ethyl acetate as the elution solvent – the chosen SPE condition optimised for the extraction of phenol acetylation products as described in last section – was applied to the extraction of methylated derivatives. The selection was based on a consideration of the similar non-polar characteristics of phenol acetates and methyl esters and the extremely good retention for non-polar compounds that C18 achieves [208].

The temperature program C described in Chapter Two was applied to GC-MS characterisation of the methyl esters.

3.4.2.2. Results and discussion

Figure 3-16 compares the MSD responses of the five methyl esters in the extracts, normalised to a 1mL basis, after acid methylation-SPE using acetyl chloride/methanol

(AC) and BF_3 /methanol (BF). Abscissa labels are abbreviations of the carboxylic acids (refer to Table 3-6). Error bars are the standard deviations from three repeat experiments.

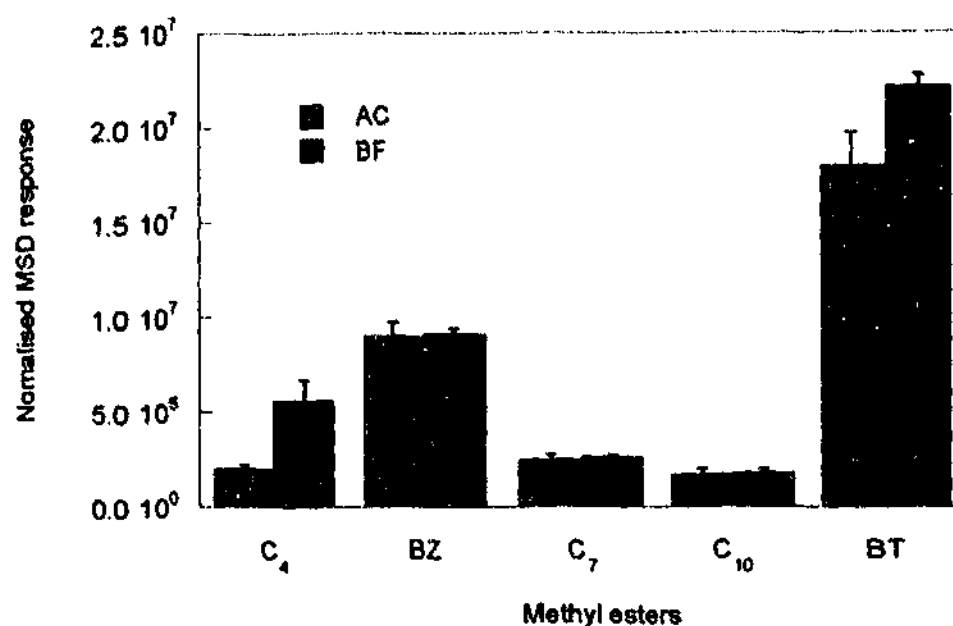


Figure 3-16. Comparison of acetyl chloride (AC) and BF_3 (BF) for methylation of carboxylic acids

The results show that the use of both reagents gave comparable methylation yields for benzoic acid (BZ) and the C_7 and C_{10} dicarboxylic acids, whereas the yields of the C_4 acid and 1,2,4-benzenetricarboxylic acid (BT) were substantially higher when using BF_3 /methanol.

Acetyl chloride/methanol was found by Lepage and Roy [198] to be advantageous over BF_3 /methanol for the analysis of fatty acids in biological samples, as its methylation performance was not affected by moisture up to 10%. However, for the analysis of water samples this should not be of much benefit. In addition, using acetyl chloride requires longer reaction time to achieve complete methylation even for water samples [196].

Thus, for evaluation of acid isolation methods, BF_3 /methanol, with its higher methylation efficiency for all the acids studied, was chosen as the methylation reagent.

3.4.3. *Evaluation of Acid Isolation Methods*

In this section, two acid isolation methods – drying under a nitrogen stream and acid extraction using SPE – are compared for the methylation of standard acids in aqueous solutions.

3.4.3.1. Experimental

Water samples treated were 5mL standard solutions containing the five carboxylic acids each at ~2mg/L (i.e. 1/1250 of the concentrations shown in Table 3-6).

To remove water with nitrogen, the sample in a 10mL vial was subjected to a gentle nitrogen flow through a Teflon tube. To bring the sample to dryness, 8-10 hours were generally required. The dried sample was then subjected to methylation using BF_3 /methanol.

Using the SPE method to separate the organic acids from the water phase, C18, C8 and PPL were evaluated. The selection of these three solid phases was based on a high carbon loading capacity for C18 and C8 and a superior retention for polar compounds for PPL. The same SPE procedure described in Chapter Two was applied except that the extract was collected in a 10mL crimp top vial instead of a 2mL auto sampler vial. Acids isolated in the extracts were then methylated using the BF_3 /methanol method.

The acid methylation method using BF_3 /methanol followed the procedures described in Section 3.4.2.1. Methyl esters in water were then extracted using C18 followed by elution with ethyl acetate. The extracts were characterised using GC-MS.

3.4.3.2. Results and discussion

Normalised MSD responses of the methyl esters obtained from BF_3 /methanol methylation following acid isolation by SPE using C18 (C18- BF_3 in the figure), C8 (C8- BF_3) and PPL (PPL- BF_3) and nitrogen drying (N_2 - BF_3) are illustrated in Figure 3-17 in Section 3.4.4. Error bars in the plots are the standard deviations of triplicates. In order to demonstrate the influence of nitrogen drying on the reproducibility of results for volatile compounds, the results from four replicates instead of the average for succinic acid (C_4) are presented in the plot.

It can be seen that the three SPE sorbents gave similar acid extraction yields except that for 1,2,4-benzenetricarboxylic acid, a significantly higher extraction yield was achieved using PPL.

In most cases, the SPE method was not able to isolate a sufficient amount of the acids from the water phase for methylation. The acid isolation yield of all the acids, except benzoic acid, using the SPE method was considerably lower than that using nitrogen drying.

The nitrogen drying method, on the other hand, exhibited poor reproducibilities for the volatile acids, i.e. the C_4 acid and benzoic acid. The loss of the low molecular weight acids due to evaporation under nitrogen flow (even gentle flow) over a long period of time is predictable. For the analysis of MTE water samples, this could lead to unreliable results. Comparison between the MTE samples containing organics of different characteristics would be inappropriate.

Clearly, acid isolation is a critical point in the whole methylation-extraction process. To achieve optimal methylation yield, consideration should focus on either the selection of more efficient acid isolation methods or elimination of the isolation step, i.e. using direct methylation in the aqueous phase.

3.4.4. *Direct Methylation in Aqueous Phase Using TMO*

In this section, the newly developed direct aqueous phase methylation method using TMO is compared with the non-aqueous methylation methods. Results of validation of this method for the analysis of MTE water samples are also discussed.

3.4.4.1. Experimental

The direct TMO methylation procedures described below are based on the method developed by Liebich and Gesele [189, 200] and used for profiling organic acids in urine samples.

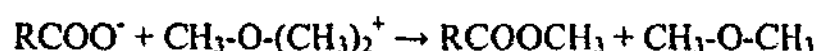
A 10mL glass vial containing a 5mL aqueous standard solution of the acids, each at ~2mg/L, and a Teflon-coated magnetic stir bar were placed on an electro-magnetic stirrer. After the stirrer was turned on, about 20 mg of solid sodium carbonate were added to alkalise the sample. Methylation using the TMO solid was then performed in five steps, each involving the addition of a 30mg TMO solid into the water sample.

The first three steps were identical. For each step, a total of 30mg of solid TMO was added with a spatula in five aliquots over four minutes, allowing one minute of reaction after the addition of each aliquot. After the addition of the last aliquot, a further one minute of

reaction was allowed before the solution was neutralised using 15 mg solid sodium hydrogen carbonate. In the fourth step, addition of 30mg TMO solid was similarly carried out in five aliquots except that, after the addition of the last aliquot and one minute of reaction, 20 mg sodium carbonate was added instead of 15 mg sodium hydrogen carbonate to alkalis the sample solution to pH $\approx$ 8. In the fifth (last) step 30 mg TMO was again added to the solution in five aliquots following the same procedure except that 20 mg sodium hydrogen carbonate was used to neutralise the reaction mixture at the end of the step. The stirrer was then stopped and the vial was sealed with a crimp top cap and incubated for two minutes in a water bath at 100°C. The two minute incubation was to remove any remaining reagents, especially BF₃ by-product, to avoid any damage to the GC column [200]. The cooled aqueous solution was then subjected to SPE using C18-ethyl acetate and the solvent extract was characterised on GC-MS using the temperature program C described in Chapter Two.

3.4.4.2. Results and discussion

In the presence of the carboxylic acids, TMO methylates the carboxyl group, particularly the carboxylate ion, to form methyl ester [189]:



Due to the occurrence of the competitive reaction between water and TMO, in order to achieve optimum methylation, it is very important to promote the reaction between TMO and the carboxyl group while inhibiting the water-TMO reaction. On the one hand, since the reactivity of the carboxylate ion is higher than that of the undissociated acid, the reaction with carboxyl group should be favoured by creating an alkali environment. Since the hydrolysis of the tetrafluoroborate ion increases the acidity of the reaction solution [189], it is necessary to neutralise the mixture with sodium hydrogen carbonate and/or to alkalis with sodium carbonate after the addition of TMO. On the other hand, during the course of methylation, TMO should be added in small portions and the reaction should be conducted at room temperature so as to minimise its reaction with water. In addition, it is preferable to use a small volume of the water sample. Results of the present study showed significantly reduced methylation yields when using 10mL of water sample instead of 5mL.

Figure 3-17 presents the results of direct methylation using TMO (TMO in the figure) as a comparison with the non-aqueous methylation methods. Error bars are the standard deviations from three replicate experiments.

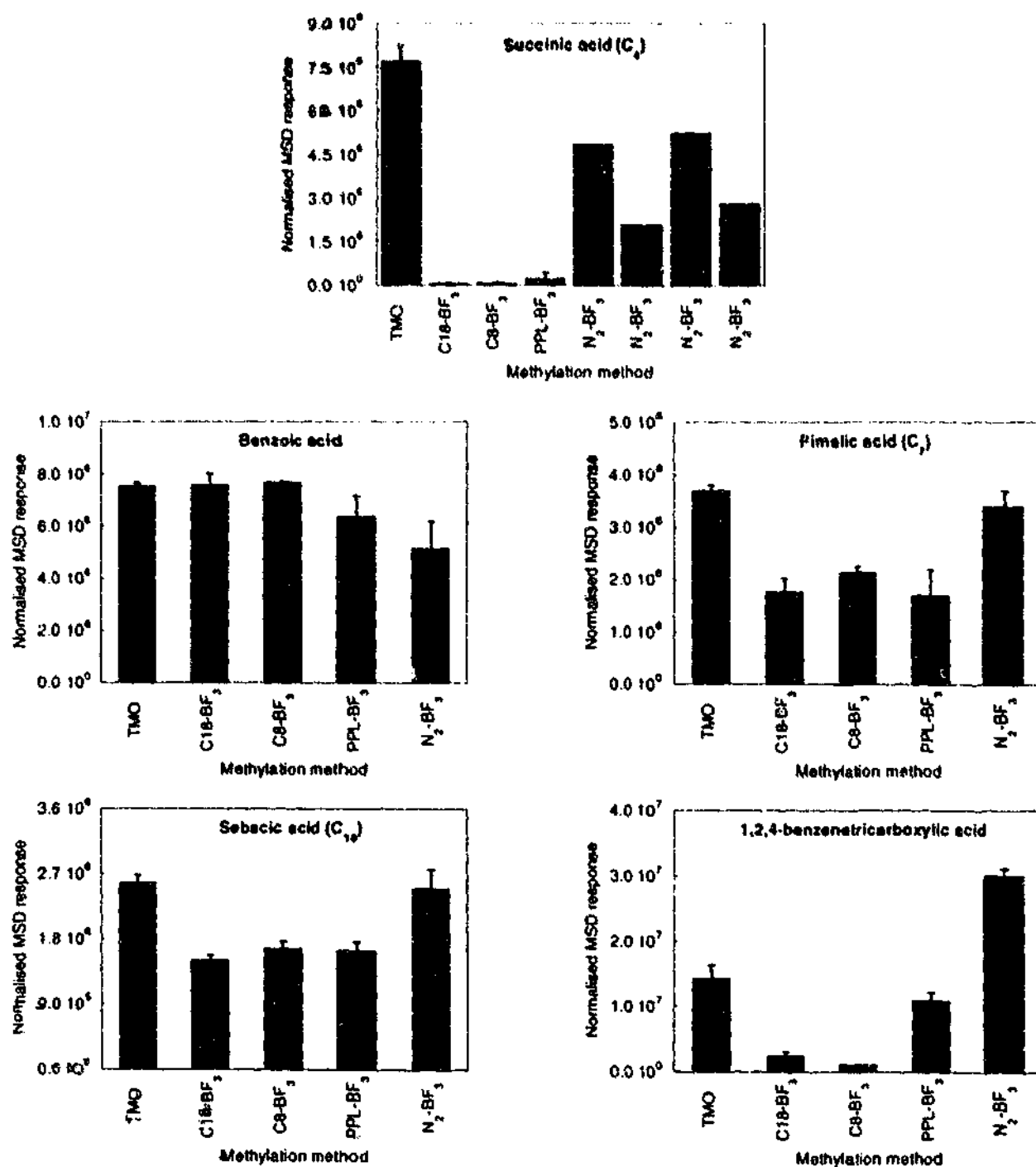


Figure 3-17. Comparison of different acid isolation and methylation methods.

It can be seen that, among the methylation methods investigated, the TMO aqueous phase methylation was undoubtedly superior to the N₂-BF₃ method for the two lower molecular weight acids – C₄ and benzoic acid – in terms of both the methylation yield and reproducibility. For the C₇ and C₁₀ acids, the two methylation methods achieved

comparable results. This outcome is in agreement with that observed by Liebich and Roy [189] that the two methods were equally effective for methylation of fatty acids. They also found that the yields using both methods were comparable with those obtained using diazomethane.

However, for 1,2,4-benzenetricarboxylic acid, the methylation yield using the TMO method was less than half of that using the N_2 - BF_3 method. This finding is different from that observed by Liebich and Roy [189]. The researchers found that methylation yields of acids with the carboxyl group located directly at the aromatic ring using TMO were ca. 100% of that using diazomethane, compared to 50% using the BF_3 method.

Despite the low yield for 1,2,4 benzenetricarboxylic acid using TMO, the direct methylation method exhibited the following advantages over the other methods evaluated:

- a) First and foremost, the lengthy acid isolation step using nitrogen drying or solvent extraction was avoided. The total time and labour were substantially reduced;
- b) Both the methylation yield and reproducibility for low molecular weight acids were significantly improved compared to the methylation methods that require nitrogen drying; and
- c) Methylation efficiency for the aliphatic acids was generally comparable or higher than that using the other methods.

Hence, the direct TMO methylation appears to be an attractive method for the analysis of carboxylic acids in water samples. However, it should be noted that the use of BF_3 /methanol, after nitrogen drying, can be a suitable methylation method for carboxylic acids of low volatility and is especially efficient for benzenetricarboxylic acids.

In this study, for identification and quantitation of carboxylic acids in the MTE water, the TMO method was validated and the results are discussed below.

3.4.5. *GC Characterisation and Standard Calibration Curves*

Table 3-11 presents the molecular ions and base peaks in the spectra of the five carboxylic acids and molecular ions, target ions and qualifiers in the spectra of their methyl esters. Since identification and quantitation were not carried out using the acids, the term 'base

peak' is used instead of 'target ion' – a term which is particularly used for quantitation as mentioned in Section 3.2.2.

Table 3-11. Characteristics of spectra of selected carboxylic acids and their methyl esters.

	Acid		Methyl ester		
	Molecular ion	Base peak	Molecular ion	Target ion	Qualifier
succinic acid (C ₄)	118	55	146	115	55, 114
benzoic acid	122	105	136	105	136
pimelic acid (C ₇)	160	55	188	115	125, 157
sebacic acid (C ₁₀)	202	55	230	74	125, 199
1,2,4-benzenetricarboxylic acid	210	148	252	221	252

Unlike the spectra of phenol acetates which are very similar to that of the phenols, the spectra of the methyl esters of carboxylic acids differ from those of the acids as illustrated in Figure 3-18. The presence of an abundant ion $M^+ - 31$ in the spectra is characteristic of methyl esters of the acids (e.g. ions 199 and 221 for sebacic acid and 1,2,4-benzenetricarboxylic acid, respectively, as shown in Figure 3-18). Generally, in the spectra of aromatic acid methyl esters, this ion is the most abundant peak, with a less intense molecular ion also present in the spectra. For aliphatic acids and their methyl esters, molecular ions are usually not present in their spectra.

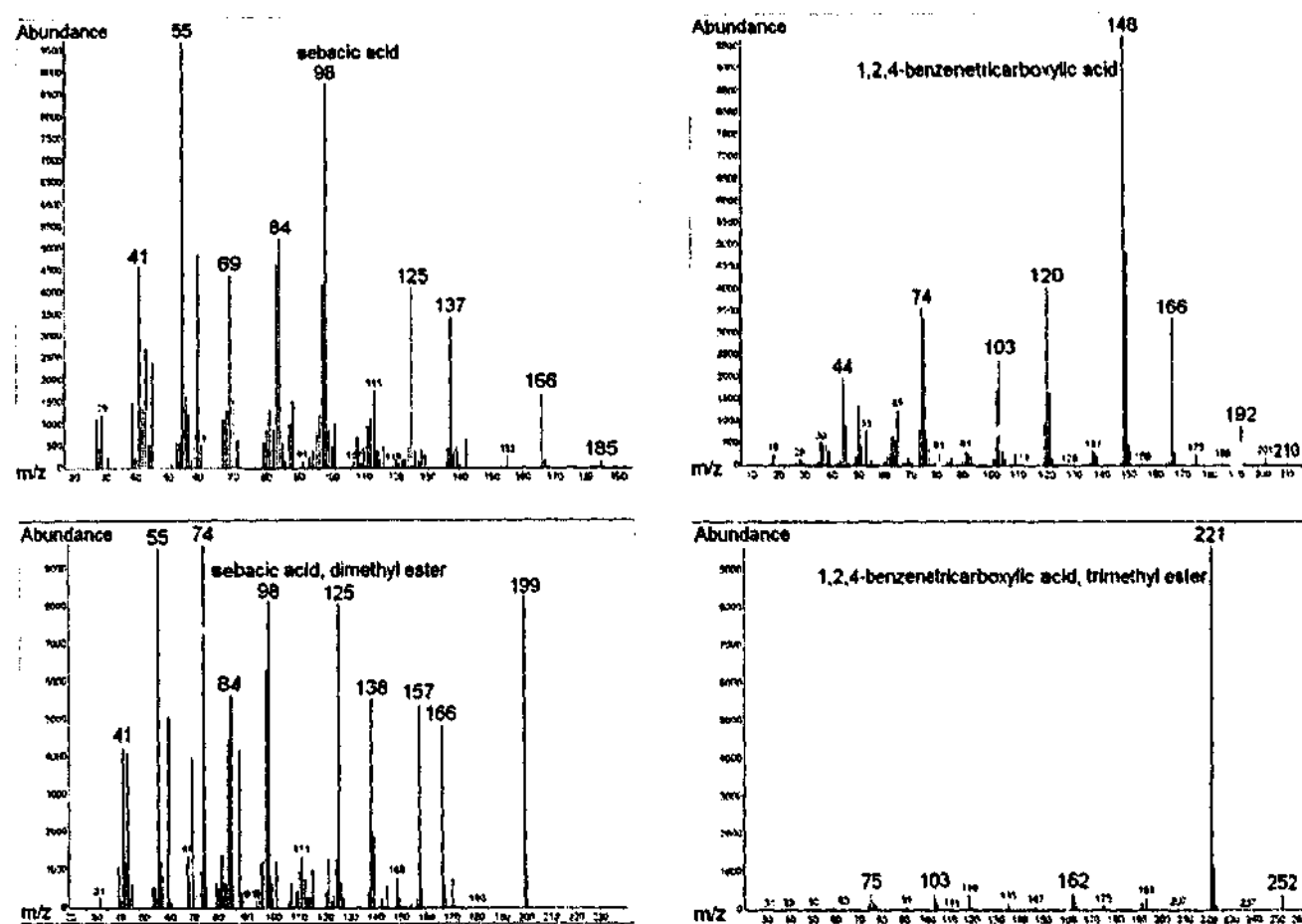


Figure 3-18. Spectra of selected carboxylic acids and their methyl esters

A method similar to that used for preparing the standard calibration curves of phenol acetates was applied to standard calibration of the acids. A series of 5mL aqueous acid solutions of different concentrations were methylated in triplicate using TMO following the procedures described in Section 3.4.4.1 with the concentrations of each acid at 0.050, 0.10, 0.20, 1.0, 2.0 mg/L, respectively. The normalised MSD response of the methyl esters is plotted against the concentration (Figure 3-19). The linear least-squares trendlines for each compound were drawn based on the average MSD responses of triplicate analyses.

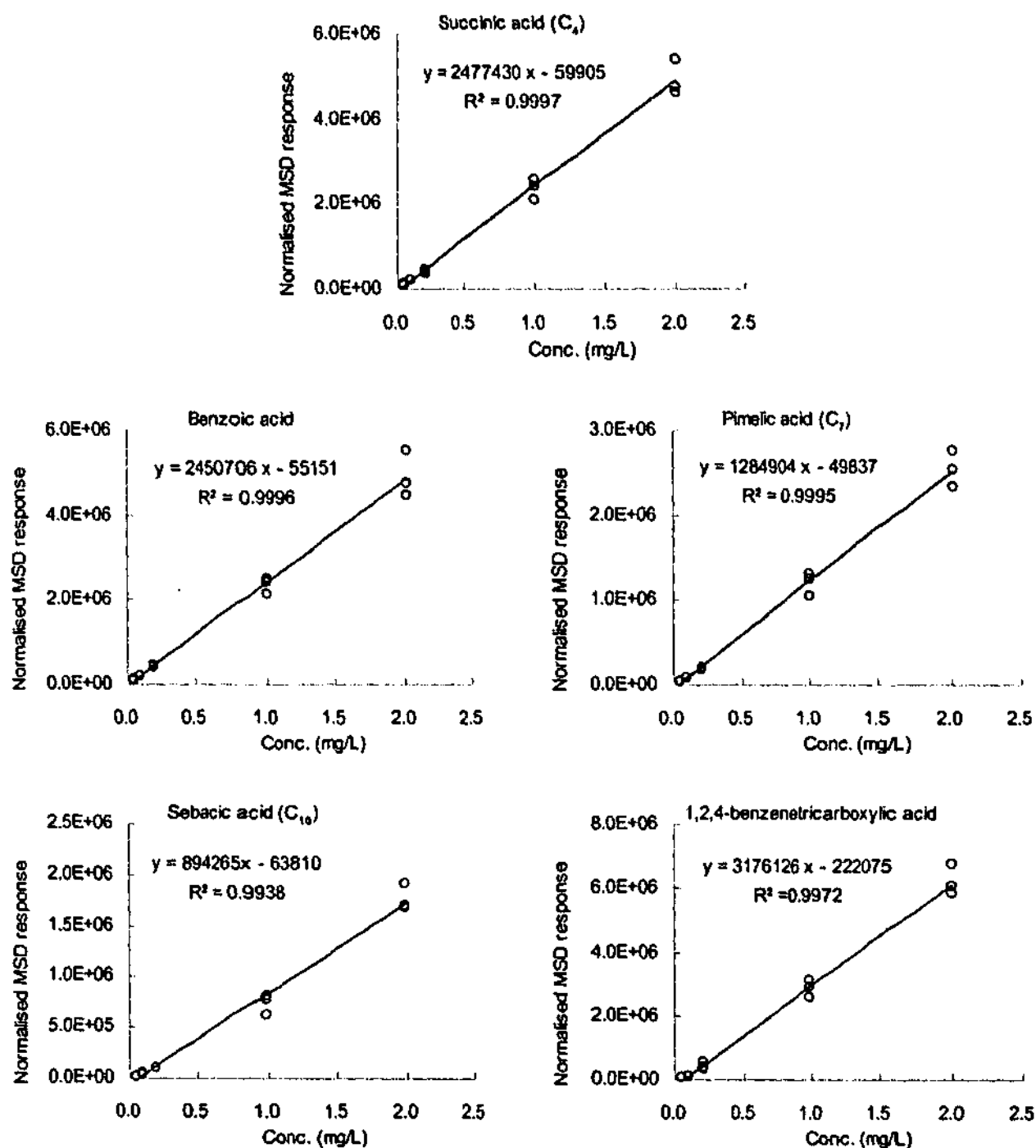


Figure 3-19. Standard calibration curves of carboxylic acids after methylation.

All the methyl esters showed a good least-squares linear MSD response-concentration relationship with $R^2 > 0.99$ and relative standard deviations between 2 and 17% for individual concentrations. Using the equations $y = bx \pm a$ fitted by least-squares to the methyl ester calibration curves, the concentrations of the corresponding acids in water samples could be directly calculated.

3.4.6. *Validation of the TMO Methylation Method*

To validate the TMO methylation method, an MTE water sample of 5mL and the same sample spiked with known concentrations of the standard acids were both derivatised and quantified following the procedures detailed in Section 3.4.4.1. Recoveries of each acid after methylation and extraction were calculated using Equation 3.2. The method validation results are shown in Table 3-12. Standard deviations and relative standard deviations were calculated from three repeat experiments.

Table 3-12. Validation results for the TMO methylation method.

	Amount in MTE sample (mg/L)	Amount added (mg/L)	Total amount in spiked MTE sample (mg/L)	Recovery		Detection limit (μ g/L)
				%	RSD%	
succinic acid (C ₄)	12 $\pm$ 0	0.20	12 $\pm$ 0	-	-	3.3
benzoic acid (BZ)	0.13 $\pm$ 0.02	0.20	0.34 $\pm$ 0.02	103	7.6	2.0
pimelic acid (C ₇)	0.27 $\pm$ 0.02	0.20	0.46 $\pm$ 0.02	98	12	10
sebacic acid (C ₁₀)	0.15 $\pm$ 0.01	0.20	0.35 $\pm$ 0.01	103	4.2	13
1,2,4- benzenetricarboxylic acid (BT)	1.4 $\pm$ 0.1	0.20	1.6 $\pm$ 0.0	94	13	13

Since the concentration of the added succinic acid was negligible compared to its concentration in the MTE sample, the recovery of succinic acid could not be calculated. Nevertheless, the rest of the acids all achieved >90% recoveries. Since the unknown samples were analysed under identical conditions to the standard solutions used for calibration, errors due to incomplete methylation or extraction were minimised. Although the methylation yield for 1,2,4-benzenetricarboxylic acid using the TMO method was low relative to the BF₃ method, its concentration could still be quantitatively determined in the spiked sample. In other words, the performance of the TMO methylation method was quite consistent and not significantly influenced by the sample matrix.

Detection limits for the acids were calculated using the same method as for the phenols determined by the two-step acetylation-SPE method (see Section 3.3.6). The data presented in Table 3-12 are for the analysis of a 5mL water sample concentrated as a

0.5mL extract. Results showed that using the TMO direct methylation method, carboxylic acids at ppb levels in the water samples could be detected.

It is worth mentioning that in the water phase TMO reacts not only with the carboxyl groups of the acids but also with phenolic groups (i.e. to form methoxy groups). For the analysis of real water samples, methylation of the phenolic groups may lead to difficulties in distinguishing between phenolic compounds and methoxy substituted aromatics. This is also the reason that this method could not be used for derivatisation of both carboxylic acids and the phenols. In this study, since the same MTE water sample was both acetylated and methylated, any methylated phenolic groups could be distinguished by comparing the methylation results with the acetylation results. Furthermore, at the method development stage, the presence of standard phenols during methylation of the carboxylic acids had little impact on the methylation results of the acids, except for the occurrence of methylated phenols.

3.4.7. *Summary*

A recently developed methylation method using TMO directly derivatises carboxylic acids in the aqueous phase so that the acid isolation step can be eliminated. Compared to the BF_3 /methanol method which requires a non-aqueous environment, the TMO method proved to be superior or equally effective in terms of both methylation yield and reproducibility, except for a benzenetricarboxylic acid.

The method was validated for quantitative analysis of organic acids in water samples for the first time. Results showed that methylation using TMO gave quantitative recoveries for the carboxylic acids investigated and that the method was suitable for the identification and quantitation of carboxylic acids in the MTE water.

3.5. **Conclusion**

Sample preparation methods for GC-MS characterisation of major low molecular weight organic compounds in the MTE water were established and validated.

Evaluation of the SPE method without prior derivatisation of the analytes showed that the PPL solid phase, using ethyl acetate as the elution solvent, provided quantitative recoveries of the mono-hydroxy phenols at ppm levels. However, this method was not as efficient for

the quantitation of the mono-phenols at lower concentrations or for the multi-hydroxy phenols.

A two-step phenol acetylation method was developed and proved to be effective for the quantitative SPE-GC-MS analysis of mono- and multi-hydroxy phenols in water samples. This method provided considerably improved GC-MS sensitivity for the phenolic compounds, especially the multi-hydroxy phenols, allowing identification and quantitation in the ppb range.

Carboxylic acids are not easily detected and quantified by GC-MS, even at high concentrations due to their polar nature. A novel qualitative method using TMO as the reagent for direct methylation of carboxylic acids in the aqueous phase was validated for quantitative analysis. The time-consuming acid isolation step necessary with other methylation reagents, such as acetyl chloride and BF_3 in methanol, could be omitted. Complete methylation, similar to that obtained using the BF_3 /methanol method with nitrogen drying, was achieved.

CHAPTER FOUR

IDENTIFICATION OF ORGANIC COMPONENTS IN MTE PROCESS WATER

4.1. Introduction

This chapter presents the results of identification of low molecular weight organic species in MTE process water using the SPE-GC-MS methods established in Chapter Three. First, strategies applied to the identification of the organic components in chromatograms are introduced. Second, the major low molecular weight compounds identified in the water are summarized. Third, the origins of major organic structures present in the MTE water are discussed.

4.2. Interpretation of Mass Spectra and Identification of Compounds

For each selected MTE water sample the chromatograms of three SPE extracts (without derivatisation, after acetylation and after methylation) were examined for the presence of major organic compounds. Identification of the major peaks in the chromatograms was based on the following procedures and strategies.

- a) Identification of the nine phenolic compounds and five carboxylic acids which were selected for quantitation (refer to Table 3-6) was based on the match for both the retention time and the mass spectra of the peaks relative to those for the standard compounds.
- b) Generally, library searches for the spectrum of 'pure' peaks in the total ion chromatograms (TICs) (i.e. peaks composed of only one component as identified by the 'peak purity analysis' function of the ChemStation[®] software) gave high quality matches (e.g. >90%) with standard spectra of one or more compounds. In cases where only one high quality library match was obtained, the identity of the peak could generally be confirmed. In cases

where more than one high quality match was obtained, this provided only an indication of structural features of components that were possibly present.

For many aliphatic compounds, e.g. straight chain mono- and di-carboxylic acids, the library search generally gave high quality matches with one compound, so that it was nearly certain that the 'pure' peak was actually due to the matched compound. However, for compounds belonging to a set of isomers or to a set of compounds with similar structural features (e.g. isomeric alkyl aromatics), the spectra of all the compounds in the set were often similar. Library searching could only provide information about the likely structural features of these compounds.

- c) For peaks which did not give high quality library matches, due to interference from background, the use of the 'spectrum subtraction' function in the software usually reduced the interference, improved the library search quality and thus helped to identify possible library matches.
- d) Using the 'peak purity analysis' and 'spectrum subtraction' functions, the identification of multiple components from peaks that were not well-separated was often possible.

It is common to find unseparated peaks in chromatograms of complex mixtures such as the SPE extracts of the MTE water samples. A peak in TIC, as shown by Figure 4-20 (a), might easily be identified as arising from one component with a complex spectrum and lead to false or poor library matches. However, using the peak purity analysis, the existence of two different components in the peak could be clearly distinguished (Figure 4-20 (b)). By subtracting the spectrum of the less abundant component (ions 152 and 137) from that of the main component (ions 151 and 180) and vice versa, it was possible to obtain good library matches for both components and assign their structures.

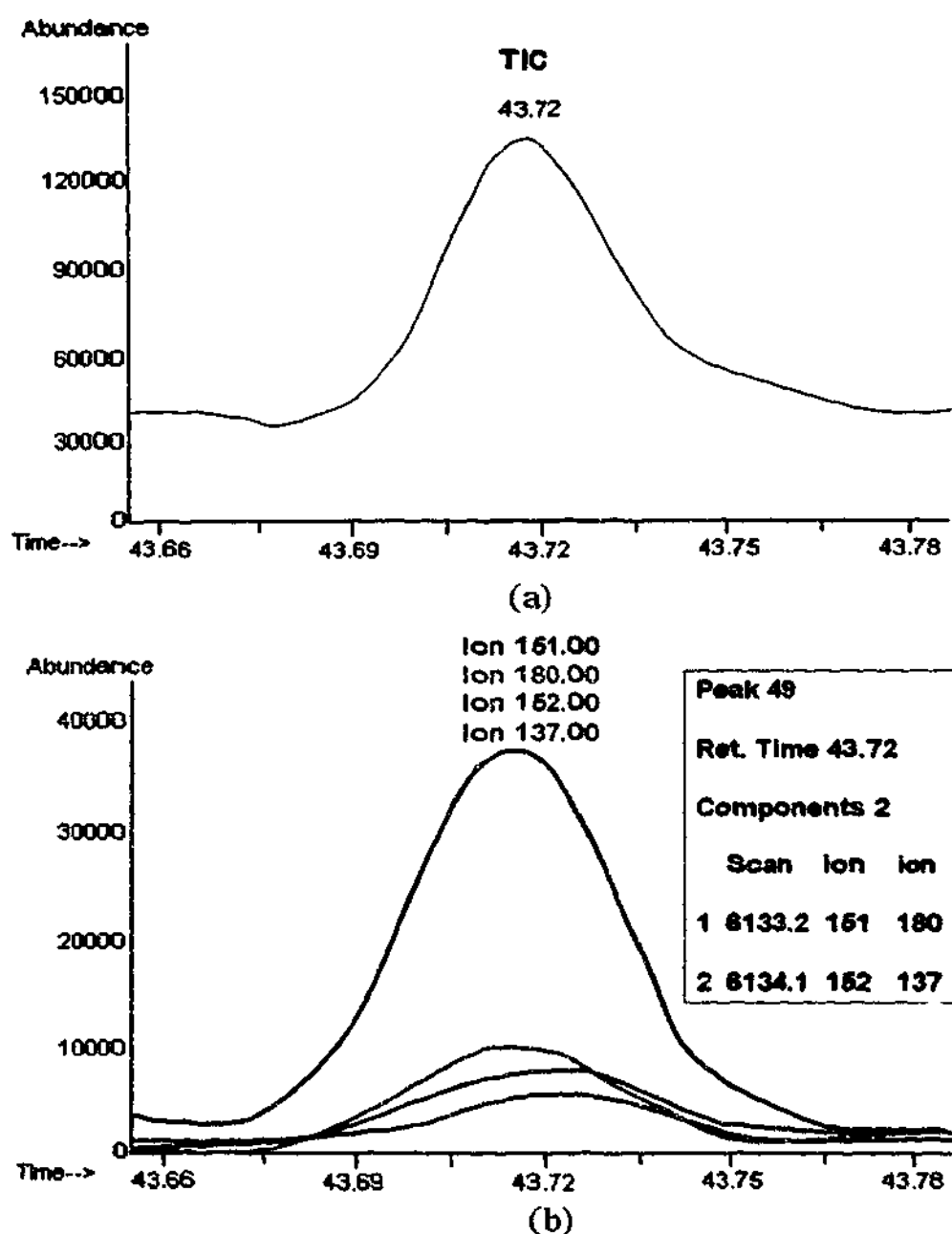


Figure 4-20. Identification of components in an unseparated peak.

- e) Some ions in the spectra are characteristic of certain classes of compounds. The presence of two or more such ions may help to define the class of compound and, thus, to justify or confirm the library search results.

The molecular ions of aromatic compounds can almost always be observed and are usually intense, whereas in the spectra of aliphatic compounds the molecular ions are often weak or absent. Table 4-13 summarizes the major characteristic ions [209] of some compound groups that were typically found in the MTE process water.

Table 4-13. Characteristic ions of typical compound groups in MTE process water.

m/z	Compound type	Example*
91, M-1, M	methylphenols	4-methyl phenol (107, 108)
91, M-15, M	dimethylphenols, methoxyphenols	2,4-dimethyl phenol (107, 122), 2,6-dimethoxy phenol (139, 154)
43, M-126, M-84, M-42, M	phenol acetates	phenol acetate (94, 136), pyrogallol triacetate (126, 168, 210, 252)
M-29, M-1, M	benzaldehydes	4-hydroxy-3-methoxy benzaldehyde (vanillin) (123, 151, 152)
M-29, M-28, M-R, M	alkyl (R) cyclic ketones	3-methyl-2-cyclopenten-1-one (67, 81, 96)
74, 87, M-59, M-43, M-31	methyl esters of aliphatic mono carboxylic acids (C ₄ -C ₂₆)	decanoic acid, methyl ester (C ₁₀) (74, 87, 143, 155)
55, 59, M-73, M-63, M-31	dimethyl esters of aliphatic dicarboxylic acids	heptanedioic acid, dimethyl ester (C ₇) (59, 115, 125, 157)
M-59, M-31, M	methyl esters of aromatic carboxylic acids	2,4-dimethyl benzoic acid, methyl ester (105, 133, 164)

* The numbers in brackets give the m/z values of the prominent peaks of the compound.

The use of characteristic ions to assist in confirming assignments is illustrated in the following example. Figure 4-21 shows two almost identical spectra of substituted phenols (acetylated). The spectrum library search found higher quality matches (>90%) for both a 1-methylethyl phenol and a hydroxyphenyl ethenone. The characteristic ion information helped confirm the difference between the spectra. In the first spectrum the presence of the ion $m/z=91$, which is characteristic of alkyl phenols, provided support for the assignment to a methylethyl phenol. In the other spectrum the ion at $m/z=93$ was more abundant than the ion at $m/z=91$ and was likely due to the loss of the $-C(O)CH_3$ group (43) from an acetylated phenol molecule (136). Hence, the two spectra could be confidently distinguished as an acetylated methylethyl phenol and an acetylated hydroxyphenyl ethanone, respectively. However, the information was not sufficient to identify the precise geometric arrangement of the substituents (i.e. *ortho*, *meta* or *peta*), since the mass spectra of such isomeric compounds are very similar (see below).

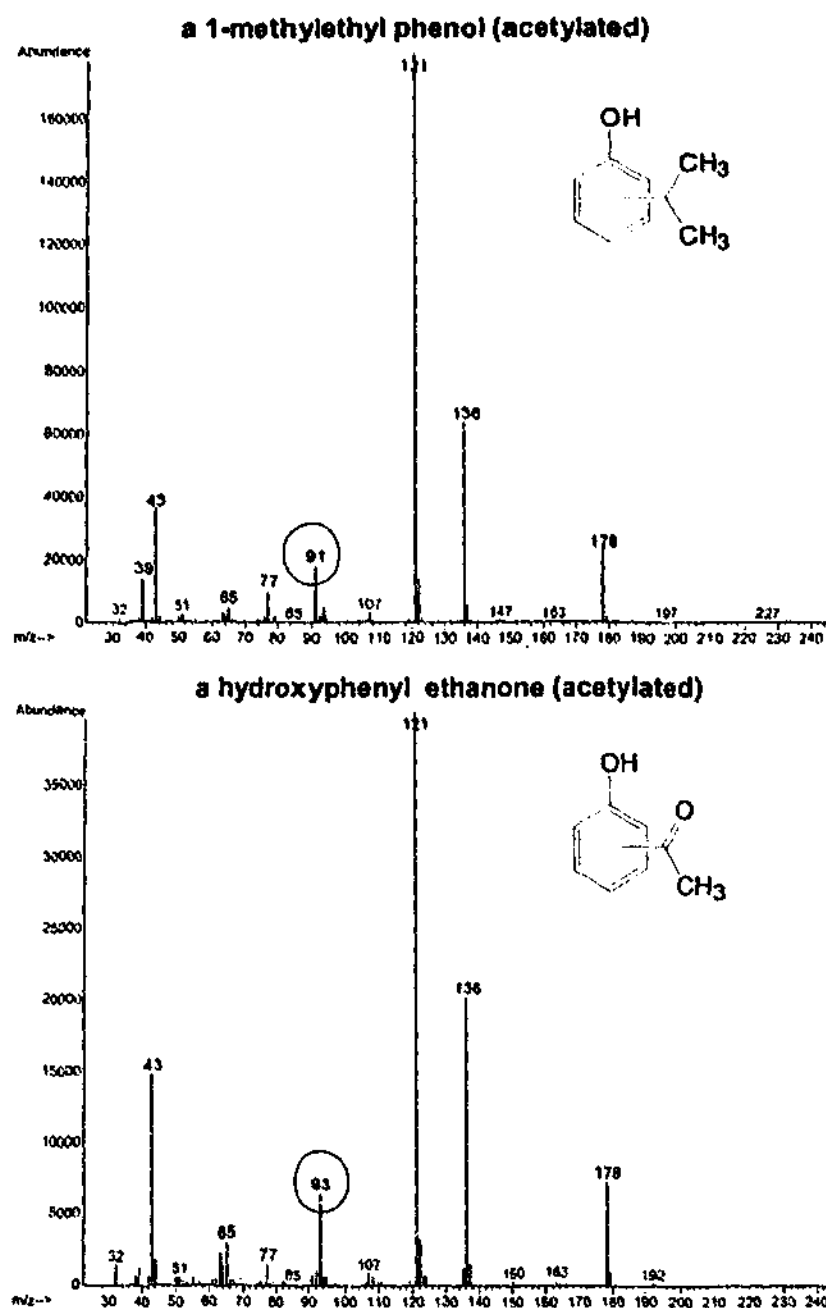


Figure 4-21. Comparison of similar spectra to illustrate the importance of characteristic peaks.

- f) The existence of a series of aliphatic compounds, with a mass difference of 14 ($-\text{CH}_2-$) or 28 ($-\text{C}_2\text{H}_4-$) between successive members, could be confirmed by the regularly distributed peaks found using the 'extracted ion chromatogram' function of the software to extract their common characteristic ions. Series of compounds identified in the MTE water using this approach included the aliphatic mono- and di-carboxylic acids.

Using the 'extracted ion chromatogram' function, the responses of one or more ions in the spectrum could be extracted from the TIC and shown as a single ion chromatogram. Figure 4-22 demonstrates a TIC and the extracted ion chromatograms for ions at $m/z=55$, 59, 74 and 87 of the same sample.

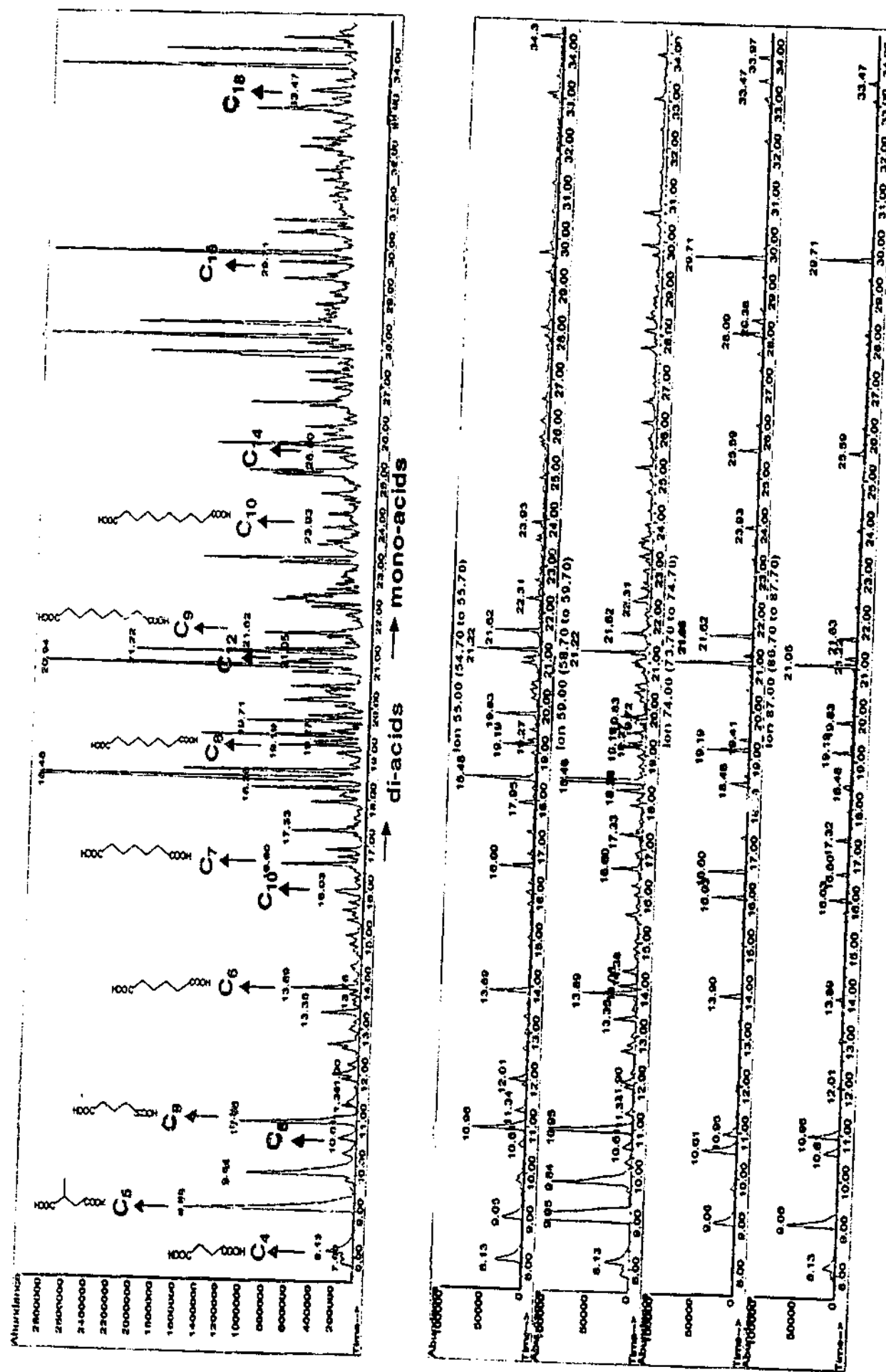


Figure 4-22. Presence of aliphatic carboxylic acids (methyl esters) as shown by TIC and extracted ion chromatograms.

These four ions are commonly present in the spectra of methyl esters of aliphatic carboxylic acids ($C \geq 4$). Ions with $m/z=74$ and 87 are characteristic of the methyl esters of aliphatic mono-acids, whereas ions with $m/z=55$ and 59 are only prominent in the TIC of methyl esters of di-acids. The difference in retention times between successive peaks of the straight-chain acids in each of the two series is approximately constant, so that homologous series can easily be distinguished. In the di-acid series all homologues between C_4 and C_{10} could be observed, whereas in the mono-acid series only the even carbon number chain homologues C_8 - C_{18} were observed. The peaks possessing the same characteristic ions that were located at retention times between those of the peaks from straight-chain compounds were likely to be branched-chain acids. Branched-chain compounds are known to elute prior to the straight chain isomer with the same carbon number [210], such as in the case of the peak eluting at 9.05 min shown in Figure 4-22 as being due to methyl butanedioic acid (dimethyl ester), which eluted before the peak at 10.95min due to pentanedioic acid (dimethyl ester).

- g) A similar approach was used to locate the peaks of series of aromatic compounds, such as phenols and benzoic acids. Since the molecular ions of these compounds are usually intense. The molecular ions to extract could be calculated by adding mass of likely substituent groups (e.g. 14 for methyl, 28 for ethyl, 30 for methoxy, etc) to the mass of the basic molecular structures, e.g. phenol (94) and benzoic acid (122). This method was also applicable to the corresponding derivatives of these compounds, i.e. the phenol acetates and the benzoic acid methyl esters. However, in these cases the characteristic ions would not be the molecular ions of the derivatives (M) but rather the M-42 and M-31 ions, respectively.

For example, ions at $m/z=108$, 122, 136 and 150 were obtained by successively adding a mass of 14 to the mass 94, the base peak, M-42, of phenol acetate and also, coincidentally, the molecular ion of phenol. Figure 4-23 shows the extracted ion chromatograms of these ions and an overlaid extracted ion chromatogram of an SPE extract after acetylation.

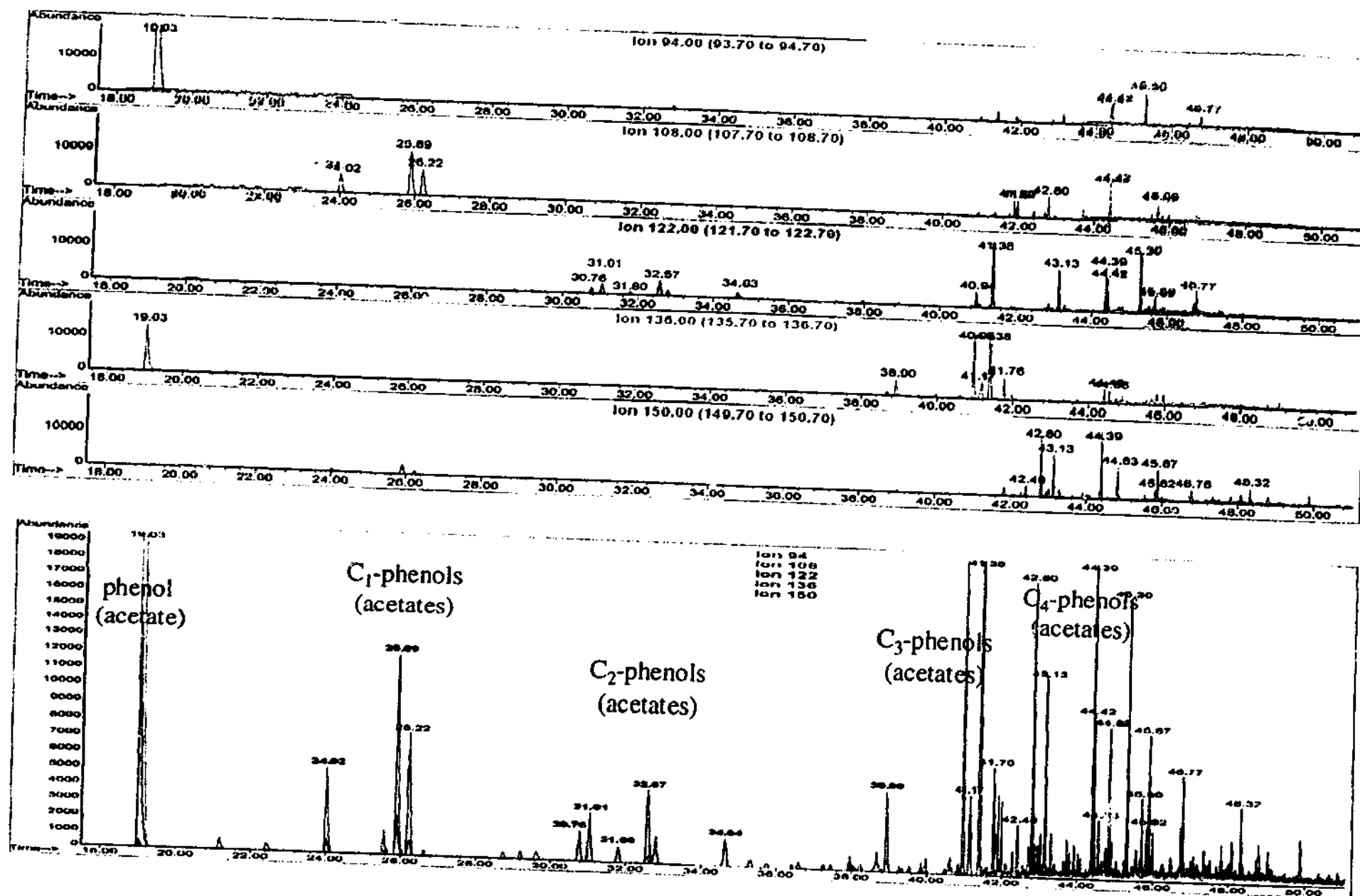


Figure 4-23. Individual and overlaid extracted ion chromatograms of phenol acetates.

However, unlike the aliphatic acids where the addition of a mass unit simply means another alkyl group (e.g. 14 for a methyl group and 28 for an ethyl group), the aromatic compounds may have a variety of substituent groups attached to the aromatic rings, sometimes with the same nominal mass. For example, the addition of 28 mass units can correspond to the addition of two methyl groups, one ethyl group or one carbonyl group ($C=O$). One substitution by a methoxy group adds the same mass (30) as substitutions, together, by one hydroxy and one methyl group. The mass addition of 42 mass units can correspond to three methyl groups, one methyl and one ethyl group, or one propyl group (including a number of isomeric possibilities in each case).

Hence, identification of these aromatic compounds was more complicated. Detailed spectrum interpretation was not sufficient. Supplementary information would be required.

- h) Where library searches turned up more than one closely matched compounds (due to the similar spectra of some organic compounds), peak assignment sometimes required not only careful inspection of the spectra but also other available information. For example, published information regarding the polarity, boiling point (bp.) or elution order of similar compounds could be very helpful.

For isomers or compounds with very similar structural features, their polarities are typically similar. Therefore, their elution order is generally in the same order as the corresponding boiling points. Information on boiling points was obtained using SciFinder Scholar® database. For example, as illustrated in Figure 4-23, following the peak of phenol acetate at 19.03 min there was a group of three peaks at 24.02, 25.89 and 26.22 min. The nearly identical spectra showed an intense ion peak at $m/z=108$ with a less abundant ion peak at $m/z=107$ and an ion $m/z=150$. This is indicative of a methyl phenol with one acetylated hydroxy group (refer to Table 4-13). Library searching identified high quality matches for the three peaks as acetates of 2-, 3- and 4-methyl phenols. Since the polarities of the three compounds are similar, boiling point is an important factor in determining the elution order of these compounds. The peak at 26.22 min was confirmed as 4-methyl phenol acetate (bp. = 212.1°C) by its retention time and spectrum matches with the standard compound. The boiling points of the acetates of 2- and 3-methyl phenols are

207.2°C and 211.4°C, respectively. Thus, it was almost certain that the peaks at 24.02 and 25.89 min represented acetylated 2-methyl phenol and 3-methyl phenol, respectively. This elution order of the methyl phenol acetates is in agreement with that observed in previous studies using similar GC columns [80, 82].

Analyses of the organic compounds in similar water sources reported in the literature may also provide supportive information for identification of the peaks. Spectra of the five peaks at 30.76, 31.01, 31.80, 32.57 and 34.63 min in the chromatogram shown in Figure 4-23 all gave abundant ions of $m/z=122$, 107 and 164, which suggests they were acetylated dimethyl or ethyl phenols. The peak at 31.01 min was definitively identified as acetylated 2,4-dimethyl phenol (bp.=226.4°C) using the standard compound (see strategy 'a'). Based on spectrum search and boiling point information, the peaks at 30.76, 32.57 and 34.64 min were probably acetylated 2,5-dimethyl phenol (bp.=224.9°C), 2,3-dimethyl phenol (bp.=230.6°C) and 3,4-dimethyl phenol (bp.=235.2°C), respectively. This elution order is in agreement with that of the four phenol acetates observed by Wang and Zhao [80] and also that of the underivatised phenols (with a similar boiling point order as their acetates) observed by Giabbai et al [211] in coal gasification wastewater on similar GC columns. Library searching confined the peak at 31.80 min (between the peak for 2,4-dimethyl phenol acetate and that for 2,3-dimethyl phenol acetate) to be an acetylated ethyl phenol, however, these still allowed three possibilities, namely acetylated 2-ethyl (bp.=238.0°C), 3-ethyl (bp.=208.4°C) and 4-ethyl (bp.=233.7°C) phenols. For underivatised phenols, Giabbai et al [211] confirmed (using standard compounds) that a peak contained 4-ethyl phenol (bp.=219.0°C) was eluted after the mixed peak due to both 2,4-dimethyl phenol (bp.=210.9°C) and 2,5-dimethyl phenol (bp.=211.1°C) but before the peak due to 2,3-dimethyl phenol (bp.=216.9°C). This elution order suggests that an ethyl phenol (e.g. 4-ethyl phenol, bp.=219.0°C) may elute before a dimethyl phenol with slightly lower boiling point (e.g. 2,3-dimethyl phenol, bp.=216.9°C). Taking into consideration all the above information, the peak at 31.80 min was more likely to be due to 4-ethyl phenol acetate than 3-ethyl phenol acetate.

- i) The probabilities of the occurrence of a particular structure in the lignite should also be taken into consideration when assigning identities of the peaks

with similar spectra, since the relatively mild conditions employed by MTE were likely to lead to the release of organic compounds that resemble the original lignite structure.

For example, research on lignitic structures indicates that a 1,2,4-substituted benzene ring is more likely to be present than a 1,3,5-substituted structure (refer to Section 4.4.3.1). Although the identities of the peaks between 30.76 and 34.63 min in Figure 4-23 as acetylated dimethyl phenols or ethyl phenols were difficult to establish definitively unless standard compounds were used, the presence of acetylated 3,5-dimethyl phenol was therefore relatively unlikely.

- j) With help from supplementary information as discussed strategies 'h' and 'i', identification of some isomers was possible. However, in many cases, a definite choice from a set of compounds with near identical mass spectra was not possible, as mass spectrometry alone cannot determine the position of aromatic substitutions [212] and any supplementary information may be inadequate. In these cases, tentative identities (e.g. 'a trihydroxy phenol' or '?-methoxy-?,?-benzenediol') were sometimes assigned to the components.

For large aromatic compounds, the number of isomeric possibilities can be substantial. Supplementary information such as boiling point was inadequate to fully resolve the identity of such compounds. The peak at 41.17 min in Figure 4-23 gave a nearly identical spectrum to the one shown in Figure 4-21 (a) for the methylethyl phenol acetate. Possible identities included not only the acetates of methylethyl phenols (three isomers) but also those of some trimethyl phenols and phenols substituted by one ethyl and one methyl group. Two possible identities chosen from the library matches with the highest qualities were assigned to the peak, which was hence labelled as the acetate of 2,3,5-trimethyl phenol OR 4-[1-methylethyl] phenol.

- k) The spectra of some peaks could not provide sufficient information about their structures. However, the presence of some characteristic ions in their spectra allowed the peaks to be identified as belonging to a certain compound group. These compounds were not considered as identified components but

were included in the quantitation of the corresponding organic compound groups.

For example, the presence of an intense M-42 peak and a less abundant M peak in an unidentified spectrum implies that the component may be an acetylated mono-hydroxy phenol. Similarly, an intense M-31 peak and a less abundant M peak suggest the presence of a methylated aromatic acid (refer to Table 4-13).

- l) A few compounds containing hetero-elements, such as chlorophenols and thiophenes, were identified. The presence of chlorine in a compound is revealed by a pair of ions in the spectrum, separated by 2 mass numbers, where the abundance of the higher mass ion is about one third that of the lower mass ion. This is due to the natural abundance of chlorine isotopes 35 and 37, respectively. Sulphur-containing compounds also exhibit this feature, where ions separated by 2 mass numbers are clearly present. However, in this case, the abundance of the higher mass ion is only 4.4% of the abundance of the lower mass ion. The ion 97 is the characteristic fragment from alkyl thiophenes.
- m) Compounds such as dimethyl phthalates (163, 194), diethyl (or larger alkyl group) phthalates (149), butylated hydroxytoluene (205, 220) and siloxanes (207, 281, etc) are common impurities due to contamination of the samples (from plastic) or the GC system (e.g. septum or column bleeding). They were present in the chromatograms of the extracts from blank tests and were frequently found in TICs of the sample extracts and thus excluded from any further interpretation.

Using the strategies outlined above, a majority of the peaks in the chromatograms could be assigned specific or tentative identities. Of course, for complex organic mixtures such as extracts of the MTE water, it is impossible for all the organic components to be fully identified. There are limitations due to incomplete separation of GC-MS peaks and the presence of 'unknowns' for which there are no library spectra.

The unidentified peaks were frequently appeared in the high temperature range of the chromatograms, such as the peak at 48.32min in the overlayed extracted ion chromatogram shown in Figure 4-23.

4.3. Organic Components in the MTE Water

Major organic compounds identified in the MTE water by GC-MS, as introduced in this chapter, are a summary of the results from analyses of the chromatograms of all three extracts (i.e. without derivatisation, after acetylation and after methylation) for each sample. Although, as expected, the number of phenolic compounds identified in the underivatised extracts was smaller than in the acetylated extracts, the results from the former could not be discarded for two main reasons. First, some polar compounds, such as furancarboxylic acids and thiophenecarboxylic acids, were identified only in the underivatised PPL. This may be because these acids were not captured by the non-polar C18 sorbent (used for sample extraction after derivatisation) or because they became volatile after methylation and were lost during the work up procedure. Second, where individual components were present in their original forms in the underivatised PPL extracts as well as in derivatised forms in the acetylated or methylated extracts, this assisted confirmation of their identity.

Figure 4-24 shows an example of the TIC of an acetylation-SPE extract. Identified structures (some are tentative identities) are illustrated for major peaks that can be conveniently labelled.

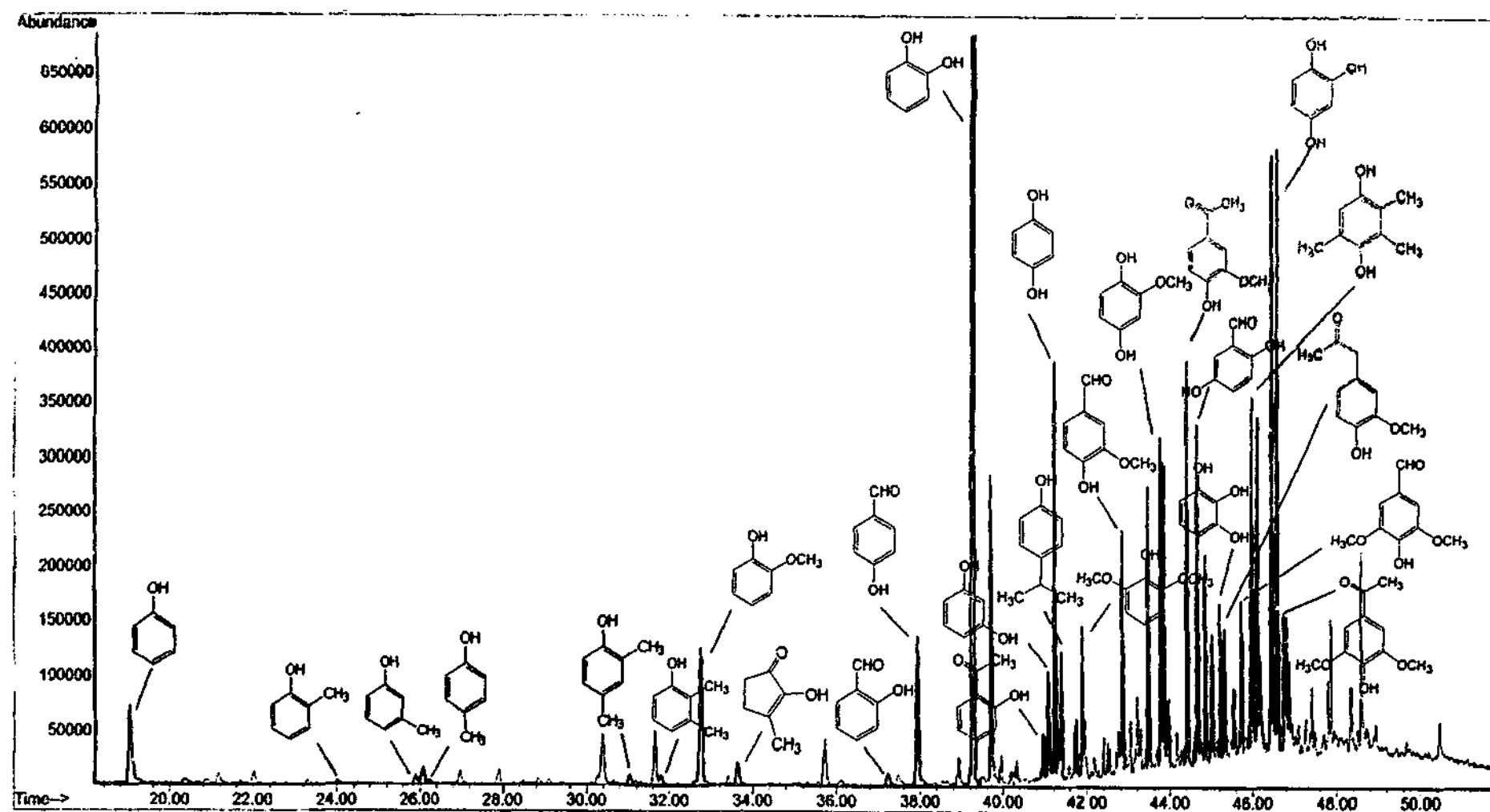


Figure 4-24. Total ion chromatogram (TIC) of an acetylation-SPE extract of an MTE water sample (Loy Yang, 200°C, 25MPa)

4.3.1. *Major Organic Compounds Identified by GC-MS*

Organic compounds in the water released from seven different lignites (Loy Yang A, Morwell, Yallourn, Bowmans A, Lochiel, Kingston and Lochiel High Sodium), respectively, by MTE treatment at 200°C, 6MPa were identified. Only those compounds found in the water from four or more lignites are listed in Table 4-14 to Table 4-16. The tentative identifications of some compounds are also noted in the tables.

The grouping of the compounds as shown in the following tables was based mainly on functional groups. Since in some cases more than one functional group is present, the following prioritisation scheme for functional group classification was used: hetero-element containing compounds (sulphur, chlorine, nitrogen, etc), furans, cyclic ketones > carboxylic acids > phenolics (PhOH) > aldehydes (O=C-H), etc. For example, benzoic acids with hydroxy groups attached on the benzene ring were grouped as carboxylic acids, whereas hydroxy substituted benzaldehydes were listed together with the phenols.

Table 4-14. Major phenols identified in four or more MTE water samples.

Mono-hydroxy phenols			
Alkyl phenols		Methoxy phenols	Phenolic ketones
phenol	4-[1-methylethyl]phenol	2-methoxy phenol	1-[2-hydroxyphenyl]-ethanone
2-methyl phenol	2-methyl-5-[1-methylethyl]-phenol	4-methoxy phenol	1-[3-hydroxyphenyl]-ethanone
3-methylphenol	5-methyl-2-[1-methylethyl]-phenol	2-methoxy-4-methyl phenol	1-[4-hydroxyphenyl]-ethanone
4-methyl phenol	2,4-bis[1-methylethyl]-phenol	2-methoxy-4-ethyl phenol	1-[4-hydroxy-3,5-dimethoxyphenyl]-ethanone
2,4-dimethyl phenol	4-[1-methylpropyl]phenol	2,6-dimethoxy phenol	1-[4-hydroxy-3-methoxyphenyl]-2-propanone
2,5-dimethyl phenol	2- or 4-[2-methylpropyl] phenol	2,4-dimethoxy phenol	Phenolic benzaldehydes
2,3-dimethyl phenol	?-methyl-?-propyl phenol	1-[4-hydroxy-3-methoxyphenyl] ethanone	2-hydroxy benzaldehyde
3-ethyl phenol	4-[1,1-dimethylpropyl] phenol 4-[3-methyl-2-butenyl]-phenol		3-hydroxy-benzaldehyde 4-hydroxy benzaldehyde 4-hydroxy-3-methyl benzaldehyde 4-hydroxy-3-methoxy benzaldehyde (vanillin) 4-hydroxy-3,5-dimethoxy-benzaldehyde
Di-hydroxy phenols			
1,2-benzenediol (catechol)	?-dimethyl-1,3-benzenediol	1-[2,4-dihydroxyphenyl]-ethanone	1-[2,4-dihydroxy-3-methylphenyl]-propanone
1,3-benzenediol	2,3,5-trimethyl-1,4-benzenediol	1-[2,5-dihydroxyphenyl]-ethanone	2,4-dihydroxy benzaldehyde
1,4-benzenediol	a methoxy benzenediol	1-[2,4-dihydroxyphenyl]-propanone	2,5-dihydroxy benzaldehyde
2-methyl-1,4-benzenediol		1-[2,5-dihydroxyphenyl]-propanone	3,4-dihydroxy benzaldehyde
a methyl benzenediol			?,?-dihydroxy-4-methoxy-benzaldehyde
Tri-hydroxy phenols*			
1,2,3-benzenetriol (pyrogallol)	1,2,4-benzenetriol	1,3,5-benzenetriol	a tri-hydroxy phenol (MW=182)

* in water from three lignites

Table 4-15. Major carboxylic acids identified in four or more MTE water samples.

Aliphatic di-acids		
Unsaturated acids	Straight chain acids	Branched chain acids
2-butenedioic acid 2-pentenedioic acid 2,3-dimethyl-2-butenedioic acid 2,4-hexadienedioic acid	butanedioic (succinic) acid (C ₄) pentanedioic acid (C ₅) hexanedioic acid (C ₆) heptanedioic (pimelic) acid (C ₇) octanedioic acid (C ₈) nonanedioic acid (C ₉) decanedioic (sebacic) acid (C ₁₀)	methyl-butanedioic acid 2-methyl-pentanedioic acid 3-methyl-pentanedioic acid 3,3-dimethyl-pentanedioic acid 2-methyl-hexanedioic acid
Aliphatic mono-acids		
Unsaturated acids	Straight chain acids	Ketonic acids
2-pentenoic acid octadecenoic acid	octanoic acid (C ₈) decanoic acid (C ₁₀) dodecanoic acid (C ₁₂) tetradecanoic acid (C ₁₄) hexadecanoic acid (C ₁₆) octadecanoic acid (C ₁₈)	4-oxo-pentanoic acid 7-oxo-octanoic acid
		Aldehyde acids
		9-oxo-nonanoic acid
Aliphatic tri-acids		
ethane-1,1,2-tricarboxylic acid 2-methoxy-propane-1,2,3-tricarboxylic acid	propane-1,2,3-tricarboxylic acid	butane-1,2,4-tricarboxylic acid
Aromatic acids		
Benzeneacetic acids	Benzoic acids	
benzeneacetic acid	benzoic acid	4-hydroxyl-3-methoxy-benzoic acid
4-methoxy-benzeneacetic acid	4-methyl-benzoic acid	?-hydroxyl-?-methoxy-benzoic acid
3,4-dimethoxy-benzeneacetic acid	4-methoxy benzoic acid	4-hydroxy-2-methoxy-3,5,6-trimethyl benzoic acid
4-hydroxy-3-methoxy-benzeneacetic acid	3-methoxy-4-methyl-benzoic acid	2,4-dihydroxy-3,6-dimethyl-benzoic acid
Benzenedicarboxylic acids	2,4-dimethoxy-6-methyl-benzoic acid	3,4,5-trihydroxy benzoic acid
4-methyl-1,2-benzenedicarboxylic acid	?,?-dimethoxy-?-methyl benzoic acid	
4-methyl-1,3-benzenedicarboxylic acid	3-ethoxy-benzoic acid	
?-methyl-?,?-benzenedicarboxylic acid	2-hydroxy benzoic acid	
benzenetricarboxylic acids		
1,2,4-benzenetricarboxylic acid	1,3,5-benzenetricarboxylic acid	5-methyl-1,2,4-benzenetricarboxylic acid

Table 4-16. Other major components identified in four or more MTE water samples.

Cyclic ketones		
3-methyl-2-cyclopenten-1-one	2,3-dimethylcyclopent-2-en-1-one	2-hydroxy-3-methyl-2-cyclopenten-1-one
4,4-dimethyl-2-cyclopenten-1-one	3-ethylcyclopent-2-en-1-one	3-methyl-2-cyclohexen-1-one
4,5-dimethyl-2-cyclopenten-1-one	2,3,4-trimethyl-cyclopent-2-en-1-one	2,3-dihydro-1H-inden-1-one
Benzaldehydes		Ethanones
4-[1-methylethyl] benzaldehyde	acetophenone (phenyl ethenone)	1-[2,5-dimethylphenyl]-ethanone
4-ethoxy benzaldehyde	1-[4-methylphenyl]-ethanone	1-[4-[1,1-dimethylethyl]phenyl]-ethanone
Furans and related structures		
2,4-furandicarboxylic acid	2[3H]-benzofuranone (2-coumaranone)	2,3-benzofurandione
2,5-furandicarboxylic acid	1[3H]-isobenzofuranone	4-methyl-1,3-isobenzofurandione
3,4-dimethyl-2,5-furandione	5-methyl-3[2H]-isobenzofuranone	5,6-dimethyl-1,3-isobenzofurandione
3-ethyl-4-methyl-2,5-furandione	5-methyl-1[3H]-isobenzofuranone	3,4-dihydro-2H-1-benzopyran-2-one
Hetero-element-containing compounds		
2-[1,1-dimethylethyl] thiophene	2,3-pyridinedicarboxylic acid	
3-methyl-2-thiophenecarboxylic acid	2,5-pyridinedicarboxylic acid	

Organic compound groups present in MTE water samples released from different lignites treated under the same conditions were similar. Phenolic and carboxylic compounds were particularly common groups identified. Other types of compounds commonly present were those containing carbonyl groups (C=O), such as cyclic ketones and furanones. Alcohols were not observed, whereas a small number of sulphur and nitrogen containing compounds were identified. Chlorophenols were also found in the water samples from one or two lignites.

Most of these compound groups have been detected in aqueous effluents from various operations processing lignites or similar materials, in which phenolic and carboxylic compounds are usually the two most common groups observed, as in this study. Carboxylic compounds including mono- and di- aliphatic acids were the major groups in condensates from a peat and bark drying process (with a few benzoic acids) [85, 86] and in effluents from an HTD process [56]. They were also found in wastewater from sources such as coal gasification [80] and pulp bleaching [93]. Phenols, as the major compound

group, were identified in the aqueous phase of low-rank coal hydrothermal dewatering (HTD) systems [65, 213, 214] as well as in wastewater from coal gasification processes [66, 81, 82].

Cyclic ketones, mainly cyclopentanones and cyclopentenones, have been reported to be a common compound group present in the aqueous phase after various lignite hydrothermal treatment processes [56, 65, 84], while furans and/or aldehydes were found in condensates from processes such as wood gasification [215] and peat drying [85, 86].

Mainly owing to the detailed nature of this study, utilising various sample pre-treatment methods, the lists of compounds identified in the MTE water samples are more extensive (despite their relatively low concentrations) than those reported from other similar water sources.

Utilising an SPE method followed by GC-MS, Racovalis [65] was able to identify a large number of phenolic compounds but only a few carboxylic acids in wastewater from HTD bench tests (refer to Table 1-1). However, carboxylic acids were identified as one of the major compound groups present in the wastewater from an HTD pilot plant [56]. It is possible that the researcher identified relatively few acids (and no tri-hydroxy phenols) because the water samples were not derivatised before analysis. In the present study these carboxylic acids and tri-hydroxy phenols were generally found only after acetylation or methylation.

In the MTE water, a variety of hetero-element-containing compounds, including sulphur or nitrogen containing carboxylic acids, chlorophenols and thiophenes, were detected. These compounds have not commonly been reported in similar process water, such as effluents from HTD processing of lignite [56, 65] or peat and lignite drying [85, 86].

Thus, the compound identification results shown in this chapter further demonstrate that the SPE-GC-MS schemes developed in this study provide a useful tool for more comprehensive understanding of low molecular weight organic components in the MTE water and were advantageous relative to methods previously utilised for similar samples.

4.3.2. *Effects of Processing Conditions and Lignite Sources on Types of Organic Compounds in MTE Water*

For a given lignite treated under different MTE temperatures and pressures, the major compound groups present in the process water were similar. Individual organic components identified and their relative abundances in the water were also very similar, although there were substantial differences in concentration. That is to say, fewer organic compounds were identified in the water released under milder conditions. However, many of the compounds that were not initially observed actually did appear in the chromatograms after the solvent extracts were further concentrated. That the types of organic species in process water produced at different temperatures were similar was also observed by Racovalis [65] for wastewater from the HTD process.

In MTE water removed from different lignites treated under the same conditions, the major compound groups identified were similar, as mentioned in last section. Nevertheless, the individual compounds present did vary with lignite types. In general, Loy Yang A and Yallourn lignites (from Victoria) released the smallest number of phenolic species amongst the coals investigated, followed by Lochiel High Sodium lignite (from South Australia). However, fewer tri-hydroxy phenols were found in the water removed from all the South Australian lignites. Unlike the phenolic compounds, the carboxylic compounds observed in the water were very similar for all lignites.

These differences between organic components released from different lignites were also reflected in quantitation results, as discussed in detail in the next chapter.

4.4. **Origins of Organic Components in MTE Water**

4.4.1. *Organic Fragments Derived from Lignite*

Organic components present in liquid products from physical and/or chemical treatment of the coal are actually (a) fragments of coal structure that have formed via decomposition of the original coal polymer with possibly subsequent further reactions [216] or (b) low molecular compounds trapped in the coal matrix [217, 218]. The former should possess characteristics of the original coal structures from which they derive. This is the concept that many coal structural studies are based upon. These studies include partial or controlled

breakdown achieved by solvolysis (i.e. solvent extraction), hydrogenolysis and oxidation that can give information on the skeletal structure of the coal [219-222].

Researchers have observed the presence of organic components related to lignitic structures in various liquid products from processing Australian lignites [223-227].

As organic compounds derived from lignite are likely to be structurally related to the coal, an understanding of the lignite structures is necessary for studying the origins of organic compounds present in the MTE water.

4.4.2. *Lignite Constituents*

The mechanism of coalification is believed to be exceedingly complicated and the final product, coal, possesses a complicated and chemically heterogeneous structure [228]. Therefore, it is rather difficult to precisely describe the chemical changes that occur during coalification and to fully determine the coal chemical structure.

Though a wide range of coalification theories has been propounded in attempts to define the parent materials of the coal and the mechanisms of coalification [15, 228], it is commonly agreed that coal has originated from plant debris and is composed of a series of macerals, which are related to various components of the original plant matter and which can be observed visually under the microscope.

The constituents of plants which could possibly give rise to coal and commonly associated structures include cellulose, protein, waxes, resins, terpenes, sterols, flavonoids, tannins, lignins and alkaloids [228]. In the course of coalification, buried plant materials undergo a series of transformation processes from peat to lignite to coal and to anthracite [229]. Some of the plant structures are selectively preserved, while some are chemically transformed and/or gradually lost.

As put by Hatcher and coworkers [230]:

“...the organic portion of peat is initially composed of a mixture of (1) vascular plants containing lignin, with other labile organic compounds such as cellulose, and (2) non-vascular plants containing these paraffinic macromolecules as well as carbohydrates and proteins. As the peat forms and is buried anaerobically, the labile

constituents, carbohydrates (cellulose) and proteins, are decomposed and lost. The more resistant lignin and paraffinic macromolecules are selectively preserved..."

Coal structural studies have indicated that, from peat to coal via lignite, plant materials such as cellulose were gradually lost and the preservation and transformation of lignin structures occurred [231-237]. Therefore, lignite, as the product of aging peat, can be considered as a mixture of structural types such as carbohydrates (cellulose), lignin, paraffins and, possibly, resins [230, 238].

The main hetero-atom functional groups in lignites have been well defined by previous studies. In Victorian lignite, the carboxylic and phenolic groups account for most (50-55%) of the total oxygen present [239]. The next most abundant oxygen groups is carbonyl (15-20%) [240]. Alcoholic groups are found to be present in some Victorian coals such as Yallourn and Morwell at low levels (accounting for 10% oxygen) [239]. Nitrogen and sulphur contents in Victorian lignites are generally low [239]. Nitrogen is mainly present in basic form such as pyridines [241], while the dominant form of sulphur compounds is as thiophenes [239].

In view of the discussion in Section 4.4.1, it would be expected that many of the organic compounds in the MTE process water should be structurally related to these chemical moieties in lignite, and that the oxygen functional groups they possess should be similar to the more polar functional groups in coal (Hence they are likely to be water soluble compounds).

4.4.3. *Origins of Major Compound Groups in MTE Water*

4.4.3.1. *Aromatic compounds*

Aromatic compounds in MTE process water include phenolic compounds, aromatic carboxylic acids, benzaldehydes and other compounds containing benzene rings.

As mentioned in Section 4.4.2, lignin is one of the main wood components that selectively survives early degradation in peat during coalification [233, 242, 243]. It is commonly agreed that the lignin structure is the primary source of aromatic structures in lignite [231, 237, 244-246]. Thus, it provides the origin of aromatic compounds in lignite [233, 235, 247] and therefore of the aromatic compounds in MTE water.

A long history of lignin chemistry, as reviewed by Adler [248], provided the foundation for chemical structure studies of low-rank coals by Hatcher and coworkers [235, 245, 249]. The basic building unit of lignin structure is the guaiacyl nucleus (i.e. a single phenolic ring with an *ortho* methoxy group) substituted with an oxygenated C_3 sidechain in the *para* position. The examples of guaiacyl building units are illustrated in Figure 4-25.



Figure 4-25. Examples of guaiacyl building units of lignin structure [228, 248].

A structural model of modern gymnosperm lignin is shown in Figure 4-26. It was proposed by Hatcher [249] after modification of an earlier published model of softwood lignin [248]. Figure 4-27 illustrates a structural model of a partially degraded gymnosperm wood from lignite, prepared by Hatcher [249] based on analytical data from Australian lignites [249, 250].

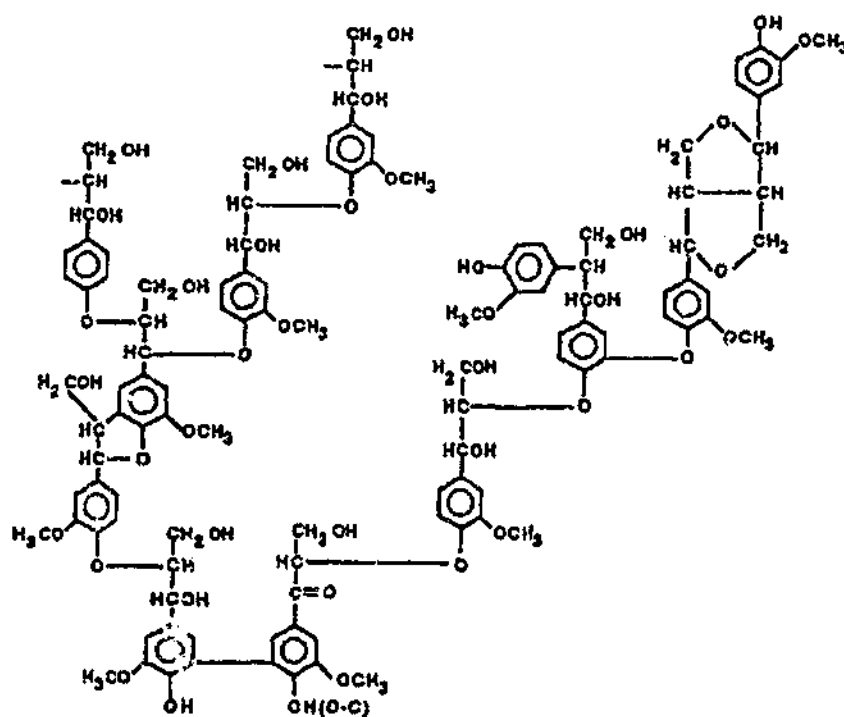


Figure 4-26. A structure model of lignin by Hatcher [249] modified from a lignin model by Adler [248].

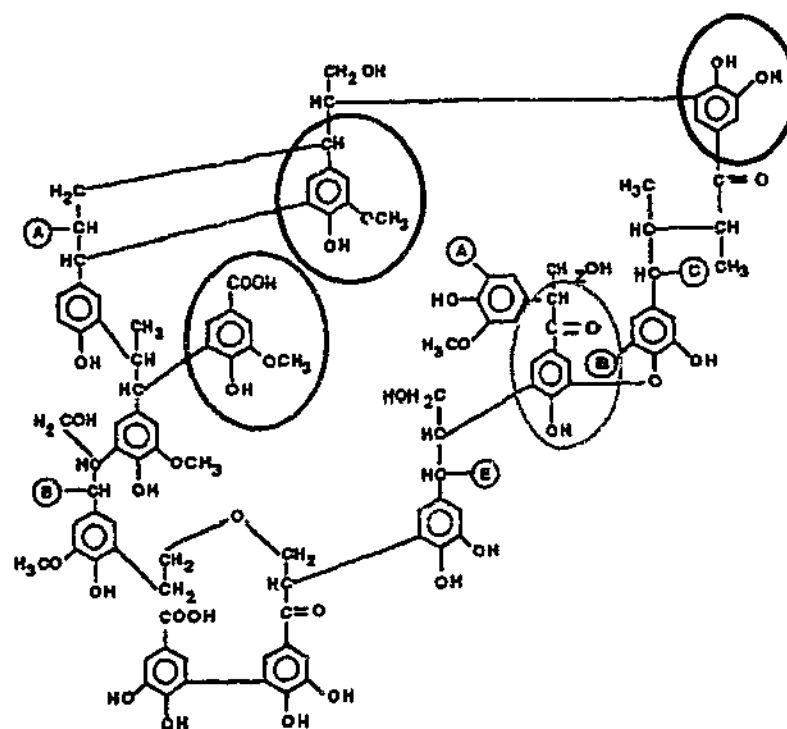


Figure 4-27. A structural model for lignitic wood by Hatcher [249]. (Circled letters indicate cross-linking sites).

The main differences between the lignite model and the lignin model are: (a) the demethylation of methoxy groups on some aromatic rings leaving hydroxy groups instead; (b) an increase in carbon substitution of the aromatic rings and (c) the presence of carboxyl groups and the addition of more carbonyl groups.

The aromatic structures in lignin that the aromatic compounds in MTE process water were likely to originate from can be readily recognised in the structural model (Figure 4-27). Substituted mono-hydroxy phenols, di-hydroxy phenols (catechols), substituted benzoic acids and phenolic ketones can be seen as the fragments or reaction products derived from structures such as those circled in green, blue, red and pink, respectively. Other aromatic compounds such as the tri-hydroxy phenols, aromatic acids and benzaldehydes may also find their origins in such lignin structures. Thus, the aromatic compounds present in the MTE water may simply be the fragments from lignin structures that were cleaved during the thermal treatment that was part of MTE processing.

It is also clear why 1,2,4-substituted aromatics were considered to be more likely to occur in MTE process water than 1,3,5 substituted fragments, since the latter substitution pattern is not part of the original lignite structure (See Section 4.2).

4.4.3.2. Aliphatic carboxylic acids

Aliphatic carboxylic acids identified in the MTE water include saturated and unsaturated mono- and di-acids, short chain tri-acids, etc. as shown in Table 4-15.

Fatty acids (aliphatic monocarboxylic acids) are commonly found in natural compounds such as lipids and waxes [251, 252], which are widely distributed in plants and woods and are important plant materials contributing to coal deposition [15, 228]. Branched monocarboxylic acids are characteristic constituents of microbes, while branched dicarboxylic acids are probably the oxidation products of the microbial branched mono-acids [252]. Tricarboxylic acids (such as those identified in the MTE process water and in lignite hydrolysis products [252]) resemble citric acid, which is the metabolic intermediate product in the Krebs cycle – one of the fundamental biochemical cycles [228, 252]. It is believed that the cycles are continued under the influence of micro-organisms and their enzymes even after the death of the plants [228].

Observations of the release of aliphatic carboxylic acids as reaction products from treatment of plant materials may provide clues about another route by which these compounds can be produced from coal structures. Both mono- and di-carboxylic acids have been identified as the main degradation products during thermal treatment of plant cellulose under alkaline conditions [253, 254]. Closely similar structures occur in lignite. The presence of cellulose has been mentioned in Section 4.4.2.

The carboxylic acids derived from lipids and waxes need not have been present as such in the original plants. Like the cellulose, the lipids, waxes, etc. in the coal may release aliphatic acids during coalification reactions. Hayatsu et al [236] suggested that kerogen-like aliphatic-rich materials contained in lignite may be derived from lipids (e.g. hydrocarbons, waxes, terpenoids and steroids). Oxidation of lignite was found to release abundant aliphatic dicarboxylic acids with a similar distribution pattern to those released from kerogen oxidation [236]. Free form acids can be found physically absorbed in the micropores of the coals [251, 255]. It is suggested that the free fatty acids are liberated due to hydrolysis of plant materials such as lipids during the initial stage of plant accumulation and coalification [251, 252]. This hypothesis is supported by the results of a study by Komori et al [252], who observed that the hydrolysis products of solvent insoluble lignite

residues gave fatty acid distributions similar to those present in the solvent extracts. This implies the same origin for both groups of fatty acids.

Therefore, unlike the aromatic compounds that originate from lignin structures, the aliphatic acids are more likely derived from aliphatic structures in lignite, such as cellulose or lipids from plant materials. Aliphatic acids found in the MTE water were mostly short chain homologues (<C18). It is probably because these acids are more water soluble, as they possess, proportionally, much smaller hydrophobic hydrocarbon chains.

4.4.3.3. Cyclic ketones

Cyclic ketones observed in the MTE water are mainly alkyl substituted 2-cyclopentenones. These compounds may not be as common as phenolics and carboxylics but they are often found in the effluents of lignite processing, as mentioned in Section 4.3.1.

A number of studies provide evidence for cellulose as the main origin of cyclic ketones. In the oil conversion products of cellulose, wood and lignin, a number of alkyl-substituted cyclopentanones were identified, with the relative abundance decreasing from cellulose to wood to lignin [256]. This is an indication that cellulose rather than lignin is the precursor of these compounds. Thermochemical treatment of cellulose materials under alkaline conditions was also found to form a number of cyclopentanones and cyclopentenones, besides releasing large numbers of carboxylic acids as degradation products [253, 254, 257].

It has been proposed that the alkyl cyclopentanones and cyclopentenones are formed during thermal reactions of reactive carbonyl compounds in carbohydrate materials (e.g. cellulose) via intra-molecular cyclisation [254, 258].

Thus, it is probable that the cyclic ketonic structures are derived from cellulose-like materials in lignite.

4.4.3.4. Furans and related structures

In the MTE water, furans and related structures detected are mainly furanones, furancarboxylic acids and benzofuranones.

These non-phenolic oxygen-containing heterocyclic structures (e.g. furans and benzofurans) have been sometimes found in coal derived products though generally

present only at low levels. A series of furancarboxylic acids was detected in the oxidation products of lignites [236]. Benzofurans and similar structures were also found in solvent extracts of brown coals (lignite) [259] and bituminous coals [260].

Furan and its tetrahydro derivatives are known to be present as one of the structural units in lignans and lignins [236]. In lignite coal, the abundant aromatic-rich lignin-derived materials is considered to be the major source of the oxygen-containing heterocyclic structures found in the structures of coal macromolecules [236, 261]. The lignin origin of these structures is supported by laboratory evidence that lignin can be transformed by oxidation into lignin-like polymers containing oxygen-containing heterocyclic structures, such as furan, benzofuran, dibenzofuran and xanthone [261].

The furans and similar oxygen-containing cyclic compounds in the MTE water therefore probably originate from the lignin structures in lignite.

4.4.3.5. Sulphur and nitrogen containing compounds

Organic sulphur in coal is considered to have similar chemistry to oxygen and is present in similar functional groups such as thiophenols and thiophenes [13]. In the MTE water, a number of thiophenes and thiophenecarboxylic acids were identified in both Victorian (low sulphur content) and South Australian lignites (high sulphur content).

Research has shown evidence for the important role that bacteria, and perhaps algae, may play in the formation of organic sulphur in coal. A study of high sulphur coals indicated that a large proportion of sulphur in the high-sulphur coals has a bacterial origin [262]. Investigation of low sulphur coals showed that organic sulphur was derived from a combination of original plant sulphur and secondary, ^{34}S -depleted sulphur probably produced from bacterial reduction of sulphate [263]. Isotopic studies by Westgate and Anderson [264] led to similar conclusions, that most of the organic sulphur in high-sulphur coals was derived from post-depositional reactions with a ^{34}S -depleted source, probably related to bacterial reduction of dissolved sulphate, whereas organic sulphur in the low-sulphur coals reflects the original plant sulphur.

Mechanisms of the incorporation of sulphur into organic matter have also been investigated. Casagrande et al [265] demonstrated the reaction of H_2S with peat to produce organic sulphur, which is incorporated rapidly into the humin and humic acid fractions. A

possible origin of polycyclic thiophenes in coal was proposed by White and coworkers [266], who suggested that these compounds may have slowly formed during coalification via reaction of polycyclic aromatic hydrocarbons (PAHs) with sulphur, pyrite, and/or H_2S by insertion of a sulphur bridge into the starting PAH [266].

In the present study, only a small number of nitrogen containing compounds, pyridines, were observed in the MTE water. Nitrogen in coal originates from the proteins of plants and microorganisms. However, most of these proteins or their products of hydrolysis have been transformed by reactions into different types of nitrogen compounds during coalification [267], mainly as pyridine or pyrrolic type rings [15]. The pyridine structure in lignite is probably the origin of the nitrogen containing compounds found in the MTE process water.

4.5. Summary

Application of the SPE-GC-MS methods, established in Chapter Three, led to the identification of major low molecular weight organic compounds in MTE water produced from different lignites under a range of conditions.

The major organic compound groups present in the MTE water for different lignites and for different processing conditions were similar. The most abundant compound groups were phenolic and carboxylic compounds, with compounds containing carbonyl groups (e.g. cyclic ketones and furanones) also significant.

Individual components and their relative abundance observed in the water from different processing severities were similar, but their occurrence did vary somewhat for different lignites.

The major organic compound groups released from the lignites during MTE treatment can be related to origins in the lignitic structures, in which aspects of the structure of the original plant materials are preserved during the coalification process. Aromatic compounds (e.g. phenols and aromatic acids) and furan related structures (e.g. furanones and benzofuranones) may be derived from the aromatic lignin structures in lignite, while aliphatic acids and cyclic ketones are probably related to the aliphatic materials, such as lipids and cellulose, in the coal.

CHAPTER FIVE

QUANTITATION OF ORGANIC COMPOSITION OF MTE PROCESS WATER

5.1. Introduction

The quantities of organics in the MTE process water and the effects of both processing conditions and lignite type are presented in this chapter. The first part of the chapter discusses the total organic carbon released to the process water. The second part mainly summarises GC-MS quantitation results for major organic components in selected MTE water samples. The molecular weight distribution of organic components in the MTE water is also discussed.

5.2. Quantities of Organic Carbon In MTE Water

The effects of MTE processing conditions, including temperature, pressure, compression rate and the use of kneaded coal, were investigated using Loy Yang A lignite. Morwell and Lochiel High Sodium were also treated at certain temperatures or pressures for comparison. A fuller range of lignites were treated under identical process conditions to investigate the effect of source material.

5.2.1. *Concepts and Calculations*

While the total organic carbon (TOC) in water is defined as all carbon atoms covalently bonded in organic molecules, the standard definition of dissolved organic carbon (DOC) is the fraction of TOC that passes through a 0.45µm filter [268]. In the present study, MTE water samples analysed for TOC were filtered through glass fibre filters (1.6µm). Very fine coal particles might have passed through the filters. Therefore, the term TOC, as used in this thesis, includes DOC plus any fine particulate organic carbon that might have passed through the glass fibre filters.

Since the volume of process water produced from different MTE batch runs varied, the determined TOC concentrations, in g/L, were not suitable for direct comparison. Instead,

the total amounts of organics released from the coal were recalculated as grams of organic carbon (OC) removed per kilogram of dry coal, as shown in Equation 5.3.

$$OC = \frac{(C_p \times V_p + C_r \times V_r)}{M_{coal} \times (1 - f_{mo})} \quad \text{Equation 5.3}$$

where:

- OC is the organic carbon in the MTE process water released from the coal (g/kg coal, db);
- C_p and C_r are the concentrations of TOC in MTE product water and rinsing water samples, respectively (g/L);
- V_p and V_r are the total volumes of MTE product water and rinsing water, respectively (mL);
- M_{coal} is the mass of the raw coal used in each run (g, wb); and
- f_{mo} is the fraction of water in the raw coal on a wet basis (g/g coal, wb).

5.2.2. *Effect of Processing Temperature and Pressure*

The first variables examined were temperature and pressure. In this batch of experiments, MTE processing conditions investigated included temperatures of 120, 150, 180 and 200°C and applied pressures of 6, 12 and 25MPa.

5.2.2.1. *Loy Yang A*

The organic carbon removal from Loy Yang A is plotted in Figure 5-28 as a function of MTE processing temperature at different pressures. For comparison purposes, the moisture removal results for the same runs are shown in Figure 5-29.

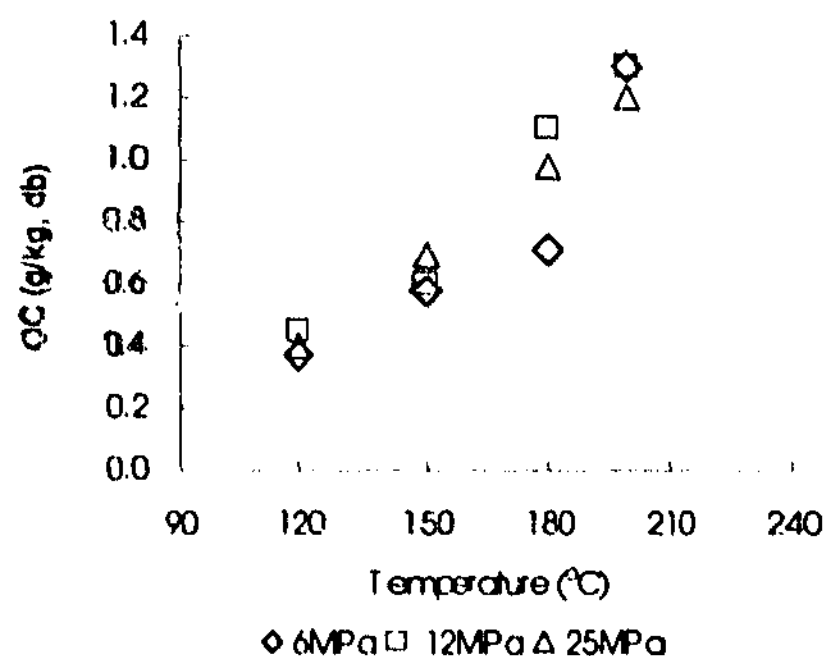


Figure 5-28. Organic carbon removal versus processing temperature at different pressures – LYA.

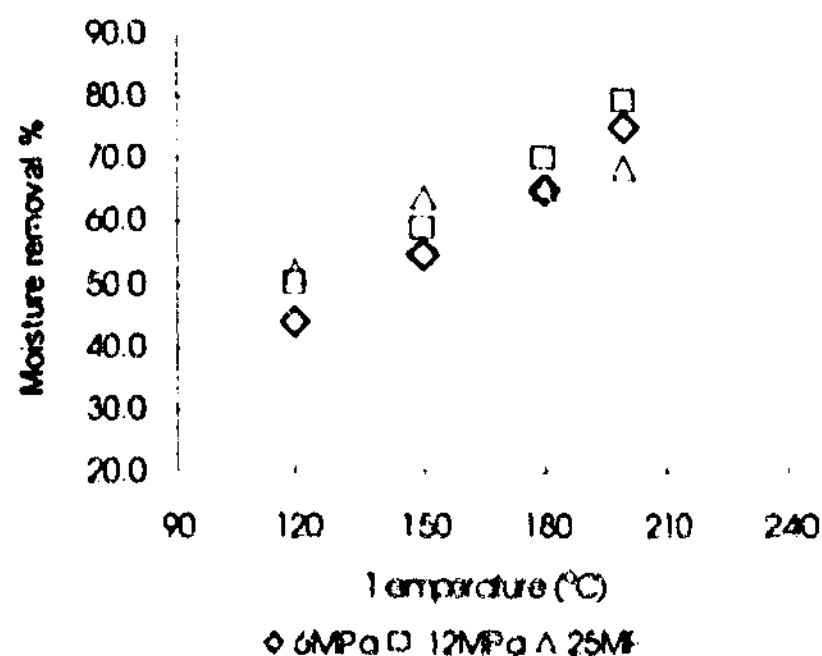


Figure 5-29. Moisture removal versus processing temperature at different pressures – LYA.

The data points shown in the figures are averages of replicates. Table 5-17 presents statistical details (number of replicates, means and standard deviations) related to individual data points.

Table 5-17. Means and standard deviations (SD) determined for organic carbon and moisture removal from Loy Yang A lignite.

MTE processing condition		OC (g/kg, db)		Moisture removal %	
		Number of replicates	Mean±SD	Number of replicates	Mean±SD
120°C	6MPa	1	0.37	1	44.0
	12MPa	2	0.45±0.07	2	50.4±2.3
	25MPa	1	0.4	1	52.1
150°C	6MPa	4	0.58±0.16	3	54.8±4.0
	12MPa	6	0.60±0.11	6	59.1±3.5
	25MPa	3	0.69±0.04	3	63.8±3.8
180°C	6MPa	2	0.71±0.07	2	65.1±4.0
	12MPa	3	1.1±0.1	2	70.3±0.5
	25MPa	3	0.98±0.19	3	65.7±3.8
200°C	6MPa	2	1.3±0.0	2	75.2±12.4
	12MPa	3	1.3±0.4	3	79.4±6.1
	25MPa	5	1.2±0.6	4	68.7±9.3

There is a notable increase in organic carbon removal as the processing temperature increased (Figure 5-28). The percentage moisture removal follows a similar trend as shown in Figure 5-29.

The effect of processing pressure does not appear to be as significant as that of temperature within the range of conditions investigated. As shown in Figure 5-28 and Figure 5-29, the data points at 12MPa are, in most cases, higher than those at 6MPa. The data points at 25MPa are lower at the higher temperatures (180, 200°C); but the differences are within the limits of error or only just outside them.

The preceding observations are based on average results from replicate MTE runs. It can be seen in Table 5-17 that the errors in some cases are quite high. As mentioned in Chapter Two, in this case, a more searching statistical analysis (using SPSS[®]) is desirable to uncover the probable effect of processing conditions taking into account experimental errors.

The general linear model (GLM) is the most widely used statistical model. It assumes that independent variables (e.g. temperature and pressure) affect dependent variables (e.g. OC

and moisture removal) in a linear fashion [269]. The analysis of variance (ANOVA) and linear regression (LR) are special cases of the GLM model. In the context of this study, ANOVA investigates whether the changes in moisture removal and OC with temperature and pressure are significant in a statistical sense, i.e. greater than can be explained by the experimental error. LR obtains the best (in a least-squares sense) linear relation between the observed response (e.g. OC or moisture removal) and the so-called explanatory variables (e.g. temperature and pressure) and checks whether the linear relation is significant, compared to the experimental error [270]. The statistical techniques make certain assumptions about the data, but are 'robust' in the sense that they give meaningful answers even if the assumptions are violated to some extent [270]. Therefore, ANOVA and LR are suitable tools for statistic analysis of the effect of processing temperature and pressure. Table 5-18 presents the results of the ANOVA analyses.

Table 5-18. ANOVA analysis of the effects of processing temperature (T) and pressure (P) on organic carbon (OC) and moisture removal.

	p-value (all data)			p-value (exclusive of data at 25MPa)			p-value (exclusive of data at 200°C)		
	T	P	T*P	T	P	T*P	T	P	T*P
OC	0.000	0.254	0.980	0.018	0.171	0.600	0.003	0.070	0.794
Moisture removal	0.004	0.567	0.240	0.001	0.034	0.905	0.017	0.494	0.168

T*P – interaction between the two factors.

The p-values give the probability that a large difference between two populations (e.g. OC at lower and higher temperatures) would occur by chance [269]. When the value is small (i.e. <0.05), the effect of the independent variable on the dependent variable can be regarded as significant.

All the p-values for the temperature effect are <0.05 (Table 5-18), so that despite the variability between replicates at specific conditions, the MTE processing temperature did significantly affect the organic carbon and moisture removal. Linear regression analysis for the means of organic carbon versus temperature at 6, 12 and 25MPa gave R^2 values of 0.8324, 0.9568 and 0.9993, respectively. R^2 values for moisture removal versus temperature at 6, 12 and 25MPa are 0.9939, 0.9915 and 0.8758, respectively.

The effect of pressure was much smaller than that of temperature. Results in Table 5-18 show that, across the whole range of temperatures and pressures investigated, the pressure effect was insignificant (p -value is much greater than 0.05). However, when the pressure effect in the range of 6 to 12MPa was evaluated, i.e. excluding data at 25MPa, a significant effect (p -value=0.03) of pressure on moisture removal was revealed. For organic carbon removal, when the pressure effect was analysed at lower temperature range, i.e. excluding data at 200°C, the pressure effect became almost significant (p -value=0.07).

The standard deviations results in Table 5-17 provide an explanation for the observation that the pressure effect was insignificant at higher temperatures or pressures. In the cases of severe conditions (especially high temperatures), the standard deviations are higher than for the milder conditions investigated. This is probably due to difficulties in maintaining constant pressure inside the MTE experimental rig when used at high temperature. In other words, when the deviations are large in proportion to the data values, the effect of the factor, i.e. pressure, will be statistically evaluated as insignificant. At lower temperatures and pressures, the pressure effect appears to be significant since the deviations are now small in proportion to the data values.

Results in Table 5-18 also show that across the range of conditions investigated, the interaction between temperature and pressure effects ($T \cdot P$) is insignificant. This means that processing temperature and pressure affected both the dewatering efficiency and the release of the organics independently.

Two conclusions can be derived from these observations. First, under the conditions investigated in this study, the removal of organic species as well as moisture increased with the severity of the MTE processing conditions. Second, temperature caused a more significant impact than pressure on the amounts of organics and water removed from the lignite. That the MTE processing temperature has a greater influence than pressure on moisture reduction was also observed by Guo et al [271] for temperatures between 20 and 280°C and for pressures between 3 and 12MPa.

Increases in the concentration of organics in the aqueous condensates or wastewater as a function of process temperature have been observed for a number of fuel drying processes [54, 86, 272, 273]. A linear relationship between the organic carbon released to wastewater

and the drying temperature was present for HTD treatment of Indian Head lignite in the range of 270-330°C by HTD, although the effect was not stated in the report [54]. Racovalis et al [273] found that TOC concentrations in the HTD wastewater from batch autoclave experiments increased logarithmically with increasing temperature in the range of 250-350°C.

5.2.2.2. Other lignites

Studies of the effect of MTE processing temperature and pressure on organic carbon removal were also carried out using Morwell lignite from Victoria and Lochiel High Sodium lignite from South Australia. The organic carbon removed from Morwell at 200°C and different pressures and from Lochiel High Sodium at 6MPa and different temperatures are presented in Figure 5-30 and Figure 5-31, respectively. The error bars, where present, represent the standard deviations of data from two and four replicate runs for Morwell and Lochiel High Sodium lignites, respectively.

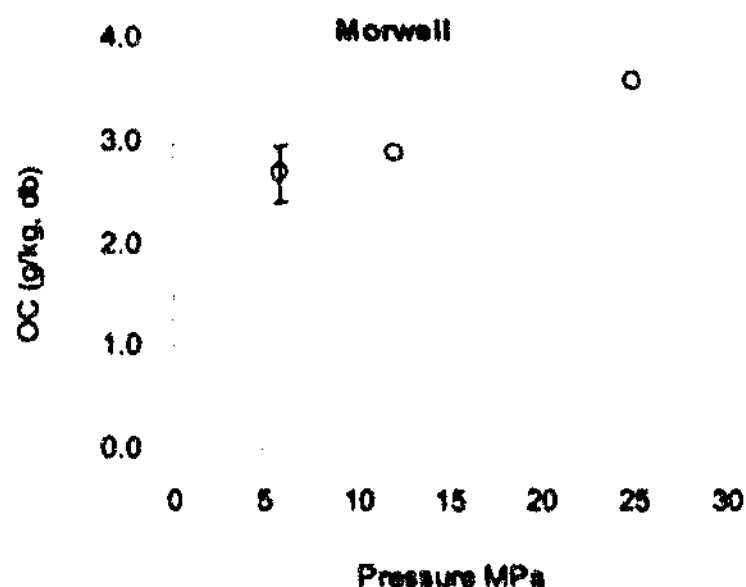


Figure 5-30. Organic carbon removal versus pressure (200°C) - MW.

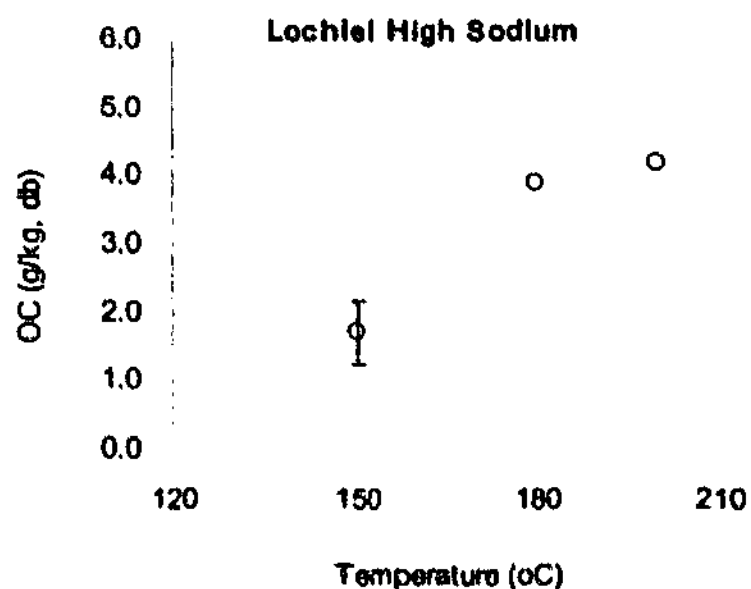


Figure 5-31. Organic carbon removal versus temperature (6MPa) – LHS.

As can be seen in the plots, the organic carbon removal from Morwell lignite increased moderately with increasing processing pressure, whilst the increase with temperature for Lochiel High Sodium was much larger. Statistical analyses indicated that the correlation between organic carbon removal and pressure for Morwell was almost significant (p -value=0.07), whereas the correlation between organic carbon removal and temperature for LHS was significant (p -value<0.05).

It can be concluded that, despite differences in the absolute amounts of organic carbon removed from these lignites during MTE, the effects of process severity were similar to the case of Loy Yang A. That is, increasing temperature generally increased the amounts of organic carbon removed to the water phase, whereas the increase with pressure was almost significant.

5.2.3. *Effect of Compression Rate and Use of Kneaded Coal*

5.2.3.1. *Compression Rate*

The compression rate is the rate at which the piston travels downwards to apply mechanical force onto the coal (and water) loaded inside the compression chamber until the desired final pressure is reached. A series of experiments were undertaken to see if the compression rate had any impact on the amount of organic carbon removed during MTE processing.

Figure 5-32 shows a plot of organic carbon removal versus compression rate at 150°C, 12MPa for Loy Yang A. Since the rate covers a broad range from 10 mm/min to 500mm/min, a logarithmic scale is used on the X-axis. The percentage moisture removal is also illustrated on the same graph. The error bars represent the standard deviations of data from six replicate runs.

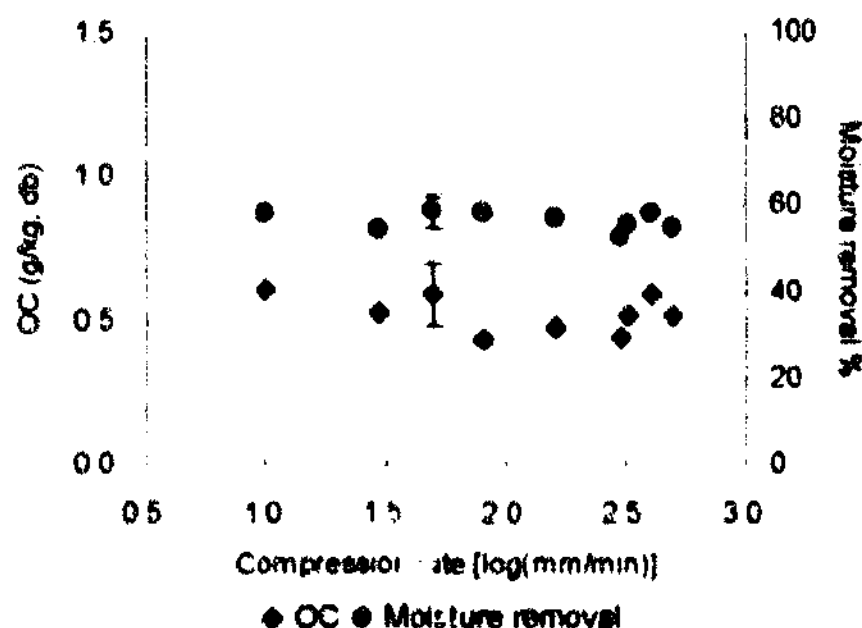


Figure 5-32. Organic carbon removal versus compression rate – L.Y.A.

It can be seen that, across the broad range of compression rates, both the organic carbon removal and moisture reduction remained steady within variations due to experimental error.

The purpose of the compression rate tests was to optimise the rate as one of the operational variables for maximising moisture removal. During compression, there was an axial hydraulic pressure gradient. Increasing the compression rate led to a rapid increase in gradient resulting in an effective reduction in the average compression pressure applied. Hence, a decrease of the moisture removal might be expected. However, prior studies on laboratory scale [271] and pilot scale [3, 6] MTE processes demonstrated that, if 5-20min holding time was allowed following compression, the moisture content of the final products reached essentially the same level, despite the different compression rates applied. This finding implies that, given an adequate time for pressure redistribution and stress relaxation, any effect of the initial compression rate on moisture removal is

overcome and the final moisture content is independent of its compression history. Thus, it appears that for the procedure used in the present study – holding the pressure for five minutes, then holding the piston position for ten minutes – was sufficient to give moisture removal independent of compression rate.

The organic carbon removal was observed to follow a similar trend and was also independent of the compression rate*.

5.2.3.2. Kneading Time

The effect of using kneaded coal was investigated by kneading the raw coal at 10rpm for different periods of time in an IKA "Ika Visc HDK 0.6" kneader prior to loading the material into the MTE cell.

Kneading the coal produced a paste-like material. The effect of kneading on the physical properties (e.g. pore sizes, surface areas, etc.) of the coal is unclear, but analysis of the kneaded coal showed that kneading generally did not affect the amount of water retained in the coal structure.

The effect of kneading on organic carbon removal for Loy Yang A lignite is illustrated in Figure 5-33. The corresponding results for moisture removal are shown in Figure 5-34. The error bars are standard deviations based on repeat runs.

* Since these experiments were carried out early in the sequence of work, a compression rate of 50mm/min was selected and used for all other MTE batch experiments described.

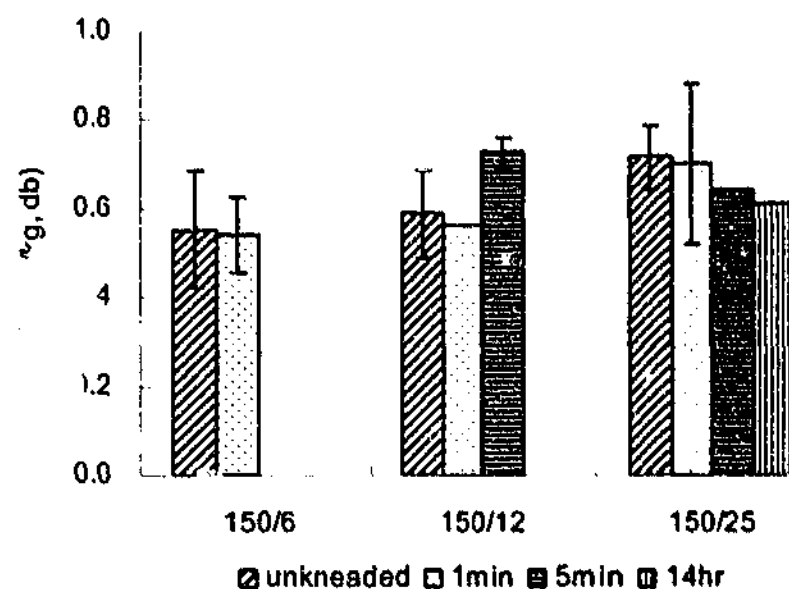


Figure 5-33. Organic carbon removal versus kneading time – LYA*.

*The labels on the abscissa give MTE temperature (°C)/pressure (MPa).

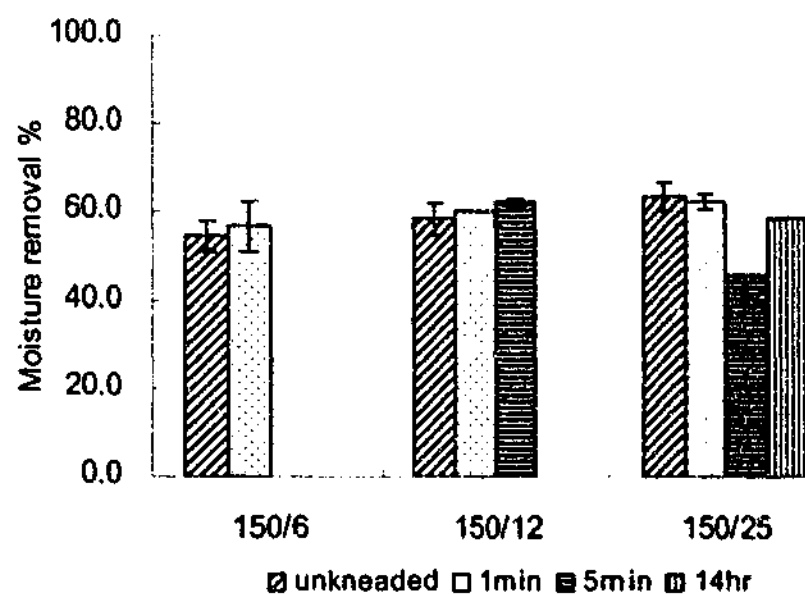


Figure 5-34. Moisture removal versus kneading time – LYA*.

*The labels on the abscissa give MTE temperature (°C)/pressure (MPa).

After considering the errors, it can be seen that, for the same processing temperature and pressure, there was little variation in moisture removal, or for organic carbon removal.

The results indicate that coal kneading did not have a significant impact on the efficiency of the dewatering or on the release of organic matter into the aqueous product stream.

5.2.4. Coal Water Removal and Organic Carbon Removal

As discussed in Section 5.2.2, both the removal of organic carbon and of moisture followed a similar trend as the MTE processing conditions varied. In order to glean a better understanding of the relationship between the removal of organic matter and coal water, the amount of organic carbon removed under various processing conditions (e.g. different temperatures, pressures, compression rates, etc.) is plotted against the corresponding percentage moisture removal, as shown in Figure 5-35 (Loy Yang A).

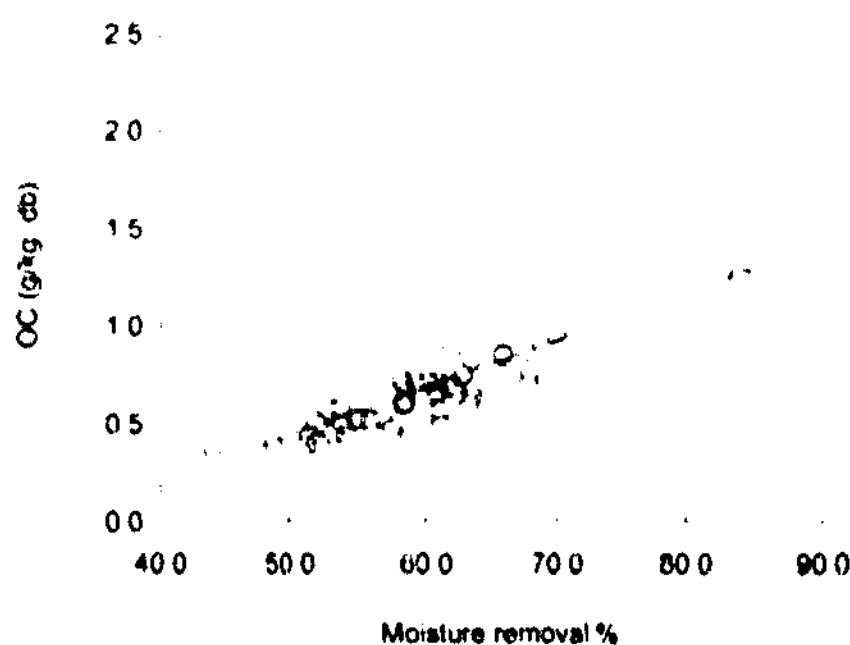


Figure 5-35. Organic carbon removal versus moisture removal – LYA.

The plot shows that, despite some scatter, there was a good increasing trend in organic carbon removal with the amount of water removed from the coal. Statistical analysis indicated that the direct correlation between organic carbon and moisture removal was significant at the 0.05 level (i.e. 95% confidence level).

The mechanisms of the water removal from lignite during dewatering can be related to the manner in which water is physically held within the lignite structure. The interpretation of water sorption isotherms of low-rank coals indicates that various forms of water can be distinguished as follows [13]:

- a) free or bulk water admixed with the coal and contained in macropores and interstices;

- b) water condensed in coal capillaries;
- c) multilayer water, i.e. weakly hydrogen bonded water on top of monolayer water, and
- d) monolayer water hydrogen bonded to oxygen functional groups on the coal surface.

These various forms of water in lignite are illustrated in Figure 5-36.

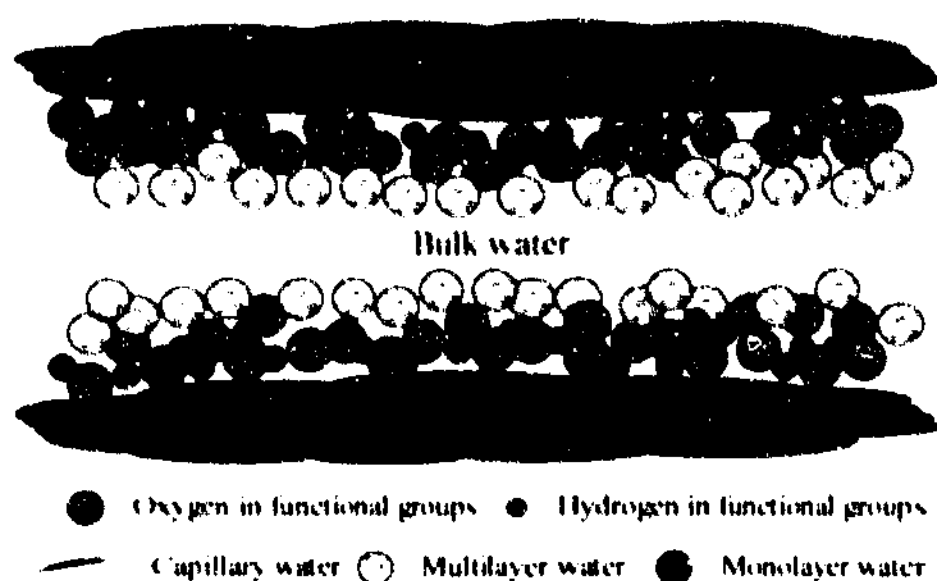


Figure 5-36. Water in lignite

During non-evaporative thermal dewatering, evolved water comes from (a) shrinkage of coal particles, reducing the volume of pores, interstices, etc. available for holding water; (b) thermal expansion of water so that a smaller mass can be accommodated per unit pore volume available and (c) water forced out from the pores by carbon dioxide, which results from thermal decomposition of the functional groups [13]. In a study by Murray and Evans [34] on HTD dewatering, water removal from lignite was related to thermal decomposition of carboxyl groups releasing carbon dioxide during hydrothermal dewatering. However, since MTE dewatering is carried out at relatively low temperatures ($\leq 200^\circ\text{C}$), at which thermal decomposition of oxygen functional groups is insignificant [13], the removal of coal water via mechanism (c) during MTE is unlikely. It was observed by Favas et al [51] that the moisture reduction of lignite by MTE treatment was rather accompanied by

macropore reduction and that both moisture and macropore reduction correlated directly with the processing severity.

As mentioned in Chapter Four, organic matter released from lignite thermal treatment is either organic fragments from thermal decomposition of the lignite structure or free organic species absorbed onto the coal matrix [216-218]. Therefore, the thermal decomposition of functional groups, possibly accompanied by other thermal reaction, will have the effect of liberating fragments of the lignite structure. It is reasonable to expect that these processes will proceed to a greater extent and/or more rapidly at higher temperature leading to more organic materials being released and/or dissolved in the pore water. As the water removal proceeds to a greater extent with increasing process severity, an increase of the organic level in the removed water should be expected.

5.2.5. Organic Carbon Removed from Different Lignites

In order to compare the organic carbon released from different lignites, Loy Yang A (LYA), Morwell (MW) and Yallourn (YL) from Victoria and Bowmans A (BMA), Lochiel (LC), Kingston (KS) and Lochiel High Sodium (LHS) from South Australia were all treated by MTE at 200°C, 6MPa. The results are presented in Table 5-19. The carbon contents of the raw coals are also listed for reference.

Table 5-19. Comparison of organic carbon removed from different Australian lignites at 200°C, 6MPa.

		Victorian			South Australian			
		LYA	MW	YL	BMA	KS	LC	LHS
OC (g/kg, db)		1.3±0.4	2.7±0.2	3.3±0.1	3.8	3.3	3.7	4.2
Raw coal	C % daf	69.4	68.7	67.7	65.2	67.8	68.1	67.5

daf – dry ash-free basis

The data indicate that Loy Yang A released the smallest amount of organic carbon. The organic carbon losses for the other coals were between 3 and 4g/kg (db). The South Australian lignites released larger amounts of organics than the Victorian lignites under the same conditions. In other words, the process water from MTE treatment of Loy Yang A was the 'cleanest' in terms of organic contamination.

It is interesting to observe that, in most cases, the raw coals with higher carbon content (daf) tended to release less carbon during dewatering.

5.2.6. Organic Carbon in Wastewater – Comparison of MTE with Other Drying Processes

In the laboratory batch MTE runs, 100g of raw coal and approximately 150-200mL of water – a coal to water ratio between 0.5 and 0.67 – were used producing ~200mL process water with a maximum organic carbon concentration of ~0.4 g/L for Loy Yang A. The treatment of Morwell, Yallourn and the South Australian lignites gave water with higher organic carbon levels – up to 0.8 g/L (~5 g/kg dry coal).

Table 5-20 compares the MTE data with data for a range of lignite drying processes reported in the literature. These data are organic carbon levels in process wastewater from non-evaporative thermal processes (e.g. HTD and steam drying) and in aqueous condensates from an evaporative drying process – fluidised bed drying.

Table 5-20. Comparison of organic carbon level in process waters from different lignite drying processes.

	MTE (present study)	Batch HTD [273]	Pilot HTD in USA [54]	Pilot HTD in Victoria [55]	Steam drying [272]	Fluidise- bed drying [86]
Temperature °C	120-200	250-350	270-330	300	182-222	250
Lignite	Loy Yang	Loy Yang	Indian Head	Loy Yang	Loy Yang	Rhenish
TOC (g/L)	0.08-0.4	0.3*-7	1.66-4.23	1.32	-	-
OC (g/kg dry coal)	0.4-2.2	2*-50*	-	-	0.1*-2.3	3

* estimated from charts presented in the papers.

- not available

In spite of the fact that different lignites and drying processes are compared, the effect of processing temperature on the removal of organics is clearly evident. For those processes employing higher temperatures, e.g. the HTD process, the organic carbon levels in the process water are significantly higher. In batch HTD experiments using a Loy Yang lignite [273], the treatment of 40g of a 3:1 water:coal slurry, at temperatures of 250-350°C, produced wastewater with TOC concentrations up to 7g/L (~50g/kg, db). Even at 250°C –

the lowest temperature employed in that study, the TOC level was approximately 0.3-0.8 g/L (estimated from the chart presented).

It can be seen that the MTE process investigated in the present study produced water with lower organic carbon loadings than any of the other listed processes. This can be attributed to the relatively low temperature employed.

Thus, it can be concluded that, in terms of the organic carbon loading that lignite non-evaporative drying processes emit to the process water stream, MTE might be seen to be more environmental friendly than other drying processes, such as HTD.

5.3. Quantities of Major Organic Components in MTE Water

Quantitative results discussed in this section include only those from the GC-MS analyses of the SPE extracts after acetylation or methylation for each MTE sample. The effects of process severity and type of lignite on the quantities of major organic components and compound groups are discussed.

5.3.1. *Calculation and Estimation*

Using the SPE-GC-MS methods described in Chapter Three, the concentrations of nine selected phenols and five selected carboxylic acids (refer to Table 3-6) in representative MTE product water samples were determined.

In order to compare quantitative results for individual compounds between MTE runs, it is convenient to convert concentrations of the compounds (g/L) to proportions of dry coal charge using an equation similar to Equation 5.3, which was used for the OC calculation. Since the GC-MS analysis of major organic components was only carried out for the product water samples (refer to Chapter Two), the amounts of these components in the rinsing water samples had to be estimated to enable calculation of the total amounts removed to the water phase. Assuming that the proportion of each individual compound present in the product water and rinsing water samples is the same as that of the total organic carbon, the total amount of the compound released to the water phase was calculated using the equation below:

$$M_i = \frac{C_i \times V_p \times \left(1 + \frac{C_r \times V_r}{C_p \times V_p}\right)}{M_{\text{coal}} \times (1 - f_{\text{H}_2\text{O}}\%)}$$

Equation 5.4

where:

- M_i is the mass of a compound i released to the MTE process water from the coal (mg/kg coal, db);
- C_i is the concentration of the compound i in MTE product water (mg/L);
- C_p and C_r are the concentrations of TOC in MTE product water and rinsing water samples, respectively (g/L);
- V_p and V_r are the total volumes of MTE product water and rinsing water samples, respectively (mL);
- M_{coal} is the mass of the raw coal used in each run (g, wb); and
- $f_{\text{H}_2\text{O}}$ is the fraction of water in the raw coal on a wet basis (g/g coal, wb).

Using the quantitation results for the 14 selected major components, the total amounts of phenolic and carboxylic compounds in the samples could be estimated. The estimation of the total amount of phenolic compounds was carried out in four steps:

- a) Calculating the conversion factor relating concentration to peak area.

As described in Section 3.3.4, standard calibration curves for the nine selected phenols were carried out by plotting the normalised MSD response of the target ions against concentration in standard solutions. This gave linear calibration curves of the form $y = bx \pm a$, where 'y' is the normalised MSD response and 'x' is the phenol concentration in the solutions. In order to calculate the total amount of the phenolic compounds, a similar approach was used but the total ion current peak area was used for each phenol instead of the area of the target ion. In this case, the intercept, 'a', was generally small and could be neglected. Thus, the concentration equation could be expressed as $x = f^*y$, where 'f' equals '1/b' and can be understood as a factor relating concentration to total peak area. For the eight mono- and di-hydroxy phenols, f was between 2×10^{-5} and 4×10^{-5} ($\mu\text{g/L}$ per area count). For pyrogallol, as its calibration curve was not perfectly linear for the whole

concentration range (refer to Figure 3-14), f was determined to be 2×10^{-4} and 6×10^{-5} ($\mu\text{g/L}$ per area count) in the lower ($<200 \mu\text{g/L}$) and higher ($200\text{--}800 \mu\text{g/L}$) concentration ranges, respectively.

b) Summing the total peak areas for phenolic compounds.

The peak areas for all phenolic compounds identified in the TICs of the acetylated extracts were integrated and summed. Peaks that could not be confidently assigned a specific identity but that were identified as phenolic compounds were included in the calculation. For components that were present at very low levels or that were poorly separated from impurities (e.g. unidentified peaks, column bleedings, etc.) in the chromatograms, peak areas were estimated as follows. As indicated in Section 3.3.6, the smallest peak area of the target ions appearing in the chromatograms was generally 5000 count units. For all the nine standard phenols, the ratio of total peak area to target ion peak area was approximately 2:1. Hence, 10000 counts were used as the peak area of these compounds (i.e. present at very low concentrations or mixed with impurities). Since the relative abundance of non-phenolic compounds (e.g. cyclic ketones and furanones) identified in the acetylation-SPE extracts was small ($<10\%$ of the peak area in most cases) and since no standard compounds of this type were used as standard calibrants, these compounds were included in the summation for the mono- and di-hydroxy phenol group. The peak areas of tri-hydroxy phenols were summed separately.

c) Calculating the total concentration of phenolic compounds.

The total concentration of phenolic compounds in an MTE sample was calculated using the equation $x = f \cdot y$ (Step (a)), where 'y' is the sum of the peak areas for all identified phenolic compounds (from Step (b)). To simplify the calculation, the factor f for phenol (3×10^{-5} $\mu\text{g/L}$ per area count) was used to estimate the concentration of the total mono- and di-hydroxy phenols. The factors for pyrogallol in the lower ($<200 \mu\text{g/L}$) and higher ($200\text{--}900 \mu\text{g/L}$) concentration ranges (2×10^{-4} and 6×10^{-5} $\mu\text{g/L}$ per area count, respectively) were used to estimate a range of concentration of the tri-hydroxy phenols.

d) Calculating the total amount of phenolic compounds.

The concentration of the phenolic compounds (mg/L) was converted to proportion of dry coal charge using an equation similar to Equation 5.4 with the concentration and amount of a compound replaced by those of the total phenols.

To estimate the amount of total carboxylic acids, a similar method was applied. The factors, f , for the five acids were between 8×10^{-8} and 3×10^{-7} (mg/L per area count). The factors for succinic acid (2×10^{-7} mg/L per area count) and benzoic acid (3×10^{-7} mg/L per area count) were used to estimate the concentrations of total aliphatic acids and aromatic acids, respectively. Acids with the carboxylic functional groups on both the benzene ring and side chains (e.g. benzene acetic acids) were taken to be aromatic acids. As the ratios of total peak area to target ion peak area of the five acids varied from 1.3 to 14, the averaged ratio for succinic acid and benzoic acid, 1.5 (corresponding to 7500 area counts), was used to define the minimum peak area included for components present at very low concentration or as unresolved peaks.

In other words, the equation $x = f \cdot y$ used to estimate the total concentration of the phenols or carboxylic acids can be expressed as:

$$C_{total} = f \times A_{total} \quad \text{Equation 5.5}$$

where:

- C_{total} is the estimated total concentration of phenols or acids ($\mu\text{g/L}$ for phenols and mg/L for acids);
- f is the conversion factor relating concentration to peak area ($\mu\text{g/L}$ per area count for phenols and mg/L per area count for acids);
- A_{total} is the sum of the peak areas for all identified phenols (including non phenols) or acids (peak count units).

In order to compare the mass of different organic species and determine the proportions of each group of compounds to organic carbon (OC as in Equation 5.3), the amount of each compound group was converted to the corresponding mass of carbon by using the molecular weights of phenol, pyrogallol, succinic acid and benzoic acid to facilitate the conversion. Equation 5.6 details the calculation procedure.

$$I\% = \frac{M_{total} / MW_r \times k}{OC} \times 100 \quad \text{Equation 5.6}$$

where:

- $I\%$ is the proportion of a compound group to total organic carbon (OC) as a percentage;
- M_{total} is the estimated total amount of a compound group - (g phenol/kg, db), (g pyrogallol/kg, db), (g succinic acid/kg, db) and (g benzoic acid/kg, db) for mono- & di-hydroxy phenols, tri-hydroxy phenols, aliphatic acids and aromatic acids, respectively;
- MW_r is the molecular weight of the four reference compounds for each group - 94 (phenol) for mono- and di-hydroxy phenols, 126 (pyrogallol) for tri-hydroxy phenols, 118 (succinic acid) for aliphatic acids and 122 (benzoic acid) for aromatic acids;
- k is the molecular weight of the carbons in the reference compound - 6×12 for mono- and di-hydroxy phenols, 6×12 for tri-hydroxy phenols, 4×12 for aliphatic carboxylic acids and 7×12 for aromatic acids (note that the carbon numbers of the reference compounds are 6, 6, 4, 7, respectively); and
- OC is the total amount of organic carbon in a sample (g /kg, db).

5.3.2. *Effect of Processing Conditions*

The effects of processing conditions on the concentrations of the 14 selected compounds (quantitative determinations) and on the estimated concentrations of the major compound groups in MTE water are presented in Table 5-21. Organic carbon levels (OC) are also presented as a reference. Table 5-22 details the relative abundance of each compound group to the total quantity of identified organics. It should be noted that the units for the quantities of individual compounds and phenolic groups listed in Table 5-21 are mg/kg, whereas for the total acids it is g/kg.

Table 5-21. Amounts of selected organic components and major groups in MTE water produced under different conditions – LYA and MW.

	Loy Yang A				Morwell	
	150°C 25MPa	200°C 6MPa	200°C 25MPa	200°C 6MPa	200°C 6MPa	200°C 25MPa
Phenols (mg/kg, db)	phenol	0.075	0.0081	1.3	0.50	0.72
	4-methyl phenol	0.027	0.014	0.13	0.035	0.050
	2,4-dimethyl phenol	0.0053	0.0095	0.053	0.011	0.017
	2-methoxy phenol	0.021	0.42	1.1	0.69	0.91
	2-methoxy-4-methyl phenol	0.015	0.026	0.096	0.030	0.035
	1,2-benzenediol	0.024	0.033	4.9	2.9	3.9
	2,6-dimethoxy phenol	0.013	0.18	0.52	0.34	0.42
	vanillin	0.040	0.058	2.3	1.7	1.8
	1,2,3-benzenetriol (pyrogallol)	0.038	0.069	0.96	0.16	0.14
Acids (mg/kg, db)	succinic acid (C4)	0.30	11	46	59	41
	benzoic acid	0.40	1.4	0.39	0.38	0.34
	pimelic acid (C7)	0.099	0.60	4.5	4.1	4.2
	sebacic acid (C10)	0.60	0.62	1.8	1.8	1.7
	1,2,4-benzenetricarboxylic acid	6.8	18	21	25	30
Total mono- & di-hydroxy phenols (mg phenol/kg, db)		0.31	3.0	13	18	22
Total tri-hydroxy phenols* (mg pyrogallol/kg, db)		0.038	0.26-0.85	0.32-1.1	0.89-3.0	1.0-3.4
Total aliphatic acids (g succinic acid/kg, db)		0.091	0.43	0.65	0.83	0.74
Total aromatic acids (g benzoic acid/kg, db)		0.070	0.19	0.38	0.47	0.54
Total identified compounds (g/kg, db)		0.16	0.62	1.0	1.3	1.3
OC (g/kg, db)		0.71	1.3	2.2	2.5	2.9

* The range of tri-hydroxy phenols is calculated using factors *f* for lower and higher concentration ranges (see Section 5.3.1).

Two water samples from the MTE treatment of Morwell lignite under identical conditions (200°C, 6MPa) were analysed to examine reproducibility of the approach. These results are

also shown in the tables and demonstrate that reasonably good reproducibility was obtained. The relative differences for the analysis of individual compounds are between 2 and 43%. The biggest percentage difference relates to the result for 2,4-dimethyl phenol with a concentration as low as 2-3 μ g/L in water. For all the estimated results, differences between the two samples are $\leq 20\%$. It should be noted that these differences are influenced both by analytical errors from the GC-MS quantitation and the experimental errors in the production of MTE water samples.

It can be seen in Table 5-21 that both the amounts of the 14 selected components and the estimated amounts of major compound groups in the MTE water increased with increasing process temperature and with pressure, with just a few exceptions such as phenol and 4-methyl phenol in the Loy Yang A case. The results are consistent with the effect of processing conditions on the amount of organic carbon (OC) present in the water (refer to Section 5.2.2). Thus, not only did the OC in the MTE water increase with process severity, but so did the amounts per unit coal charge of many individual phenols and carboxylic acids and the total amounts of these compound classes. That the release of individual organic components and compound groups increases with process temperature has previously been observed for lignite in the HTD process [54] and for peat in a fluidised-bed drying process [86].

The results in Table 5-21 also show that the extent of the increase for different components and compound groups with processing severity were different in some cases. Generally, the amounts of individual di- and tri-hydroxy phenols (e.g. catechol and pyrogallol) increased more than those of mono-hydroxy phenols. The increase for phenols was generally more significant than that for the acids, although the phenols were present at much lower levels (mg/kg vs g/kg). This can be seen more clearly by the relative abundance data in Table 5-22.

Table 5-22. Percentages of major compound groups in total identified organics in MTE water produced under different conditions – LYA and MW.

	Loy Yang A				Morwell	
	150°C 25MPa	200°C 6MPa	200°C 25MPa	200°C 6MPa	200°C 6MPa	200°C 25MPa
Mono- and di-hydroxy phenols %	0.19	0.48	1.2	1.4	1.7	2.6
Tri-hydroxy phenols %	0.024	0.042- 0.14	0.031- 0.11	0.067- 0.23	0.077- 0.26	0.28- 0.94
Total phenols %	0.22	0.52- 0.62	1.3-1.4	1.4-1.6	1.8-1.9	2.8-3.5
Aliphatic acids %	56	69	62	63	57	64
Aromatic acids %	43	30	36	36	41	33
Total acids %	100	99	99	99	98	97

The results shown in Table 5-22 demonstrate that the phenolic compounds were always present as a very small proportion of the organic compounds detected by GC-MS. More than 97% of the identified organic compounds were those containing carboxylic functional groups. Similar observations have been made for GC characterisation of organics released during other lignite drying processes [56, 86]. Fagerås et al [86] found that organic species determined by GC methods in the condensate from fluidised-bed drying of lignite were predominantly monocarboxylic acids and other organic acids. In the wastewater from HTD treatment of Loy Yang lignite, volatile fatty acids and acids detected in the hydrophilic fraction were present in the largest proportions (>400mg/L in total) with the phenolics at only 22mg/L [56].

One of the reasons for the large proportions of carboxylic acids present in the water phase may be that free aliphatic acids can be found physically absorbed on the lignite matrix or weakly bound to it [251, 255]. Thus, they may be liberated more readily to the aqueous phase than any phenols in covalently bound structures. It should be noted that aliphatic acids accounted for a larger proportion than any other compound group in the MTE water (Table 5-22). A second possible reason for the abundance of carboxylic acids is that, due to their polar and hydrophilic properties, any carboxylic acids decomposed from the lignitic structure or trapped in the matrix [218] may be preferentially dissolved in water during MTE processing as compared to the less hydrophilic phenolic compounds.

Another possible reason for the relative abundance of carboxylic acids is the mild conditions employed by MTE. Although research has found that the carboxyl groups in lignite are thermally unstable and can be largely decomposed to form carbon dioxide and water [274-276], this does not occur to a significant extent at 200°C or below [13]. As the MTE process was conducted under relatively mild conditions ($\leq 200^\circ\text{C}$), the carboxyl groups in lignite should substantially persist and, thus, could be released to the process water. In fact, even for processes like HTD, which are carried out at temperatures as high as 300°C, carboxylic acids were still found to be prominent in the process water, as reported by SECV [56].

5.3.3. *Variation between Lignites*

Quantitation results for the 14 selected compounds and major compound groups in the MTE water from treatment of different lignites at 200°C, 6MPa are presented in Table 5-23. The relative abundances of the compound groups are shown in Table 5-24.

Table 5-23. Amounts of selected organic components and major groups in MTE water from different lignites produced at 200°C and 6MPa.

	Victorian			South Australian			
	LYA	MW*	YL	BMA	KS	LC	LHS
Phenols (mg/kg, db)	phenol	0.0081	0.61	0.012	0.93	0.49	0.12
	4-methyl phenol	0.014	0.043	0.010	0.055	0.077	0.014
	2,4-dimethyl phenol	0.0095	0.014	-	0.016	0.019	0.014
	2-methoxy phenol	0.42	0.80	0.015	0.58	1.3	1.7
	2-methoxy-4-methyl phenol	0.026	0.033	0.020	0.027	0.028	0.034
	1,2-benzenediol	0.033	3.4	0.042	0.030	0.034	0.029
	2,6-dimethoxy phenol	0.18	0.38	0.20	0.039	0.18	0.11
	vanillin	0.058	1.8	0.077	1.2	0.87	0.064
	1,2,3-benzenetriol (pyrogallol)	0.069	0.15	0.14	-	-	-
Acids (mg/kg, db)	succinic acid (C4)	11	50	3.2	86	110	8.6
	benzoic acid	1.4	0.36	0.41	0.36	4.0	2.2
	pimelic acid (C7)	0.60	4.2	0.51	6.6	3.7	2.7
	sebacic acid (C10)	0.62	1.8	-	1.7	1.7	1.1
	1,2,4-benzenetricarboxylic acid	18	28	34	30	27	12
Total mono- & di-hydroxy phenols (mg phenol/kg, db)							
3.0 20 3.3 9.9 14 29 11							
Total tri-hydroxy phenols** (mg pyrogallol/kg, db)							
0.26-0.85 0.95-3.2 0.56-1.9 0.036-0.12 0.45-1.5 0.22-0.73 -							
Total aliphatic acids (g succinic acid/kg, db)							
0.43 0.79 0.70 0.94 1.0 0.80 0.78							
Total aromatic acids (g benzoic acid/kg, db)							
0.19 0.51 0.38 0.35 0.46 0.75 0.18							
Total identified compounds (g/kg, db)							
0.62 1.3 1.1 1.3 1.5 1.6 1.0							
OC (g/kg, db)							
1.3 2.7 3.2 3.8 3.3 3.7 4.2							

* average of duplicate

** The range of tri-hydroxy phenols is calculated using factors *f* for lower and higher concentration ranges (see Section 5.3.1).

- undetected

The data in Table 5-23 show that the quantities of individual components and compound groups released to the MTE water varied with lignite type. Some trends can be identified

from the results. Firstly, among all the lignites investigated Loy Yang A was the 'cleanest' coal in terms of its release of organics to the MTE process water. The amounts of most of the individual compounds and compound groups released from Loy Yang A were the lowest – as they were for the organic carbon (refer to Table 5-19).

Secondly, the quantities of the phenolic compounds varied considerably (by a factor of more than 10 for the two classes of mono-/di-hydroxy phenols and tri-hydroxy phenols) with lignite type. In general, the Victorian lignites released lower levels of the mono- and di-hydroxy phenols (except for Morwell), but higher levels of the tri-hydroxy phenols than the South Australian coals.

Thirdly, the quantities of the carboxylic acids and total identified compounds varied less than that of the phenols. The variation of the amounts of aliphatic acids released from different lignites was little more than a factor of 2.

Finally and interestingly, the coals which released larger amounts of the aromatic acids, namely Morwell, Kingston and Lochiel, also released larger amounts of the phenols. Both classes are aromatic compounds.

Table 5-24. Percentages of major compound groups in total identified organics in MTE Water from Different Lignites produced at 200°C and 6MPa.

	Victorian			South Australian			
	LYA	MW*	YL	BMA	KS	LC	LHS
Mono- and di-hydroxy phenols %	0.48	1.6	0.30	0.76	0.95	1.8	1.1
Tri-hydroxy phenols %	0.042-0.14	0.072-0.25	0.052-0.18	0.003-0.009	0.031-0.10	0.014-0.046	-
Total phenols %	0.52-0.62	1.6-1.8	0.36-0.48	0.76-0.85	1.0-1.1	1.9	1.1
Aliphatic acids %	69	60	65	72	68	51	80
Aromatic acids %	30	39	35	27	31	47	19
Total acids %	99	99	100	99	99	98	99

* average of duplicates

It can be seen in Table 5-24 that for all the lignites investigated phenolic compounds accounted for very small proportions of the total identified compounds released (<2%). It is also apparent that the proportions of the aromatic acids were substantially smaller than

those of the aliphatic acids. As discussed in Section 5.3.2, the presence of free (absorbed) aliphatic acids (released to the process water), the higher polarity and hydrophilicity of the acids and the mild MTE conditions, are all factors that may help to explain these observations.

Comparing the lignites, Loy Yang A and Yallourn lignites from Victoria released the smallest proportions of the phenolic compounds. The largest proportions of the phenols were released from Lochiel. Although the proportions of both aliphatic acids and aromatic acids varied considerably with lignite types, total acids accounted for 98-100% of the total identified compounds for all the coals investigated.

5.3.4. *Molecular Weight Characteristics of Organic Composition of MTE Water*

Field-flow fractionation (FFF) is an effective fractionation method which can provide molecular weight distribution information about organic materials in aqueous solutions. Representative MTE samples were analysed using this method. A typical molecular weight distribution pattern of the organic matter in MTE water samples is illustrated in Figure 5-37.

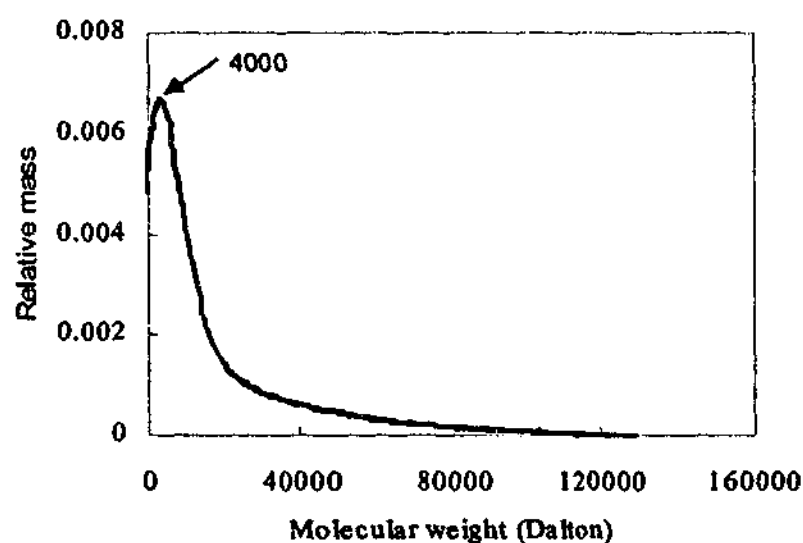


Figure 5-37. Molecular weight distribution of organics in an MTE water sample produced at 200°C, 6MPa – LYA.

Although a limitation with the FFF analysis is that it does not resolve low molecular weight components, it gives information about molecular weight distribution of high molecular weight components and their relative mass. The typical plot in Figure 5-37

suggests that a high proportion of the organic material in MTE water was of high molecular weight. For all the MTE samples analysed, the peak of the molecular weight distribution was observed at 4000-5000 Dalton. Based on this approach, compounds with molecular weight >700 appeared to account for 80-90% of the total mass. Also, the molecular weight of ~90% of the mass appeared to be less than 50,000 Dalton, but there was a very long tail extending to ~150,000 Dalton.

Observations from the present study provide some indication of the polar nature of the high molecular weight organics in MTE process water. The MTE water samples were from yellow to brown in colour, with a darker colour generally implying a higher TOC concentration. Most of the material adsorbed on the SPE sorbent and eluted by non-polar solvents was of relatively light colour; strongly coloured material could be in part washed off the sorbent with water and most was soluble in methanol, implying it was relatively polar. GC analysis of the methanol fraction using either polar or non-polar columns did not produce meaningful peaks, suggesting these polar molecules were of high molecular weight and, hence, a major source of the high molecular weight material detected by FFF.

Studies of high molecular weight substances in similar water sources may give some clues to the characteristics of the large molecules in MTE water particularly the strongly light-absorbing ones. In pulp bleaching effluents, the chromophore groups were found to be mainly aromatic and quinonoid moieties, with the coloured molecules varying from 400 to 150,000 Dalton in size [92]. These chromophore groups in effluents from pulp and paper mill industries generally come from lignin degradation and commonly bear phenolic, hydroxyl and weak acidic functional groups [92]. As discussed in Section 4.4.2, the lignin component of the original wood is known to be preserved through the early stage of coalification [247, 277]. Thus, there could be some similarity between the water from lignite processing and that from pulp and paper processing so that the coloured high molecular weight compounds in the MTE water could likewise include lignin degradation products with various oxygen functional groups.

FFF analyses of effluents from HTD processing of Victorian lignites have also revealed the presence of abundant high molecular weight materials (i.e. of the order of 4000-5000 Dalton) [55, 92]. Fulvic acids were found to be the most abundant organic species with

lesser amount of humic acids and neutral substances [92]. The most abundant molecular weight of the fulvic acid and humic acid fractions was 3000-4000 Dalton, as for the MTE process water analysed here.

5.3.5. *Evaluation of the GC-MS Methods Used*

Analysis using the SPE-GC-MS methods described in Chapter Three excluded at least two groups of organic compounds in MTE water from the quantitation results.

The first group includes compounds which gave GC-MS peaks, but were excluded from the quantitation or estimation. This group includes unidentified components in derivatisation-SPE extracts and those which were only identified in underivatised SPE extracts. Analytical results in this study indicated that these compounds were present in MTE water at relatively low levels. For example, the unidentified peaks in the chromatograms of derivatised extracts typically accounted for <10% of the total peak areas (A_{total} in Equation 5.5). Also, at the method development stage, SPE sorbents and solvents of different properties were tested for extraction of MTE water samples. Only a few components identified in these underivatised extracts (e.g. furancarboxylic acids) were not detected in the derivatised extracts and, thus, remained unquantified. The quantities and proportions of such compounds were small, as suggested by their low peak areas relative to those of the phenols in the same chromatograms and the small proportions of the phenolic compounds in the total identified organics.

The second group excluded from quantitation includes compounds that could not be detected by the SPE-GC-MS methods utilised. This includes volatiles and high molecular weight species.

Volatile compounds, methanol, ethanol and acetone, were found at high concentrations (3-500mg/L) in process water from HTD treatment of Indian Head lignite [54]. In this study, preliminary tests of the MTE water confirmed the presence of such low molecular weight volatiles. Compounds including methanol, ethanol, acetone and, probably, propanol were detected by a headspace-GC method. However, with the GC-MS methods used in this study, these compounds, if not lost during sample preparation, would elute before or with solvents from the GC column and thus could not be detected, unless a solvent-free method (e.g. a headspace GC system) was employed.

High molecular weight compounds are another group of compounds that could not be detected using the SPE-GC-MS methods used. In the MTE water, the highest molecular weight of the organics identified by GC-MS was ~350 Dalton. In similar water sources, the presence of organic compounds with molecular weight up to ~400 Dalton has been identified using other analytical approaches. Using electro-spray mass spectrometry (ESMS) to characterise organic components in the wastewater from HTD batch tests, Racovalis [65] observed some peaks of >400 Dalton. Alén et al [85] applied HPLC and GLC (gas-liquid chromatography) techniques to characterisation of organic compounds in condensates from fluidised-bed drying of peat and detected a number of high molecular weight components with molecular weight >400 Dalton. HPLC provides the means of high resolution analysis of compounds with molecular weight up to 600 Dalton [278]. However, in the present study, attempts using HPLC followed by ESMS to analyse an MTE water sample with the highest TOC level of all MTE water samples (TOC=0.9g/L) failed to give any meaningful information about the presence of polar or high molecular weight organics.

The proportions of the identified compounds in total organic carbon calculated using Equation 5.6 for a range of MTE water samples are shown in Table 5-25. Results from FFF analysis of some MTE water samples are also presented.

Table 5-25. Carbon content of organics in MTE water quantitatively estimated by GC-MS as a proportion of total organic carbon (OC) compared to FFF results.

	Loy Yang A			Morwell			
	150°C 25MPa	200°C 6MPa	200°C 25MPa	200°C 6MPa	200°C 6MPa	200°C 25MPa	
Total phenols (as carbon) in OC %	0.037	0.23	0.48	0.62	0.65	1.4	
Total acids (as carbon) in OC %	12	24	24	27	23	28	
Total identified organics (as carbon) in OC %	12	24	24	27	24	29	
	Victorian (200°C 6MPa)			South Australian (200°C 6MPa)			
	LYA	MW*	YL	BMA	KS	LC	LHS
Total phenols (as carbon) in OC %	0.23	0.64	0.11	0.20	0.35	0.61	0.20
Total acids (as carbon) in OC %	24	25	17	16	22	23	11
Total identified organics (as carbon) in OC %	24	26	17	17	23	23	11
Relative mass% by FFF (MW<700 Dalton)	17	-	13	-	-	17	12

* averages of duplicate
- undetermined

Comparison of the GC-MS quantitation results with the molecular weight distribution results from FFF analysis aids the evaluation of the GC-MS methods applied in the present study. The total identified organic compounds (mainly acids) accounted for approximately 10-30% of the total organic carbon in all MTE water samples examined (Table 5-25). FFF results indicated that roughly 10-20% of the organics in MTE water were low molecular weight components (MW<700 Dalton). Furthermore, the proportion of low molecular weight components as determined by FFF and of GC-MS identified compounds (as carbon in OC) were well correlated with each other. Hence, the results from the two analyses were in reasonable good agreement.

Two conclusions can be drawn from these results. First, the GC-MS unidentified organics were mainly high molecular weight components that cannot be detected by GC-MS. Second, the GC-MS methods utilised in this study are valid and very efficient for

identification and quantitation of the chromatographable components with low molecular weight.

The proportions of the GC detectable organics (as carbon in OC) were, generally, slightly higher than the proportions of low molecular weight compounds as determined by FFF. This difference could be due to the time delay between the GC-MS analysis and the FFF analysis, which was carried out several months after the GC-MS analysis. Polymerisation due to aging of the samples could have occurred, leading to an increase in the proportion of large molecules in the water.

5.4. Summary

For identification and quantitation of the low molecular weight organic components that are chromatographable, the SPE-GC-MS methods developed in this study proved to be valid and efficient.

The GC detectable organic compounds accounted for a small proportion (10-30%) of the total organic carbon in the MTE water. Molecular weight distribution analysis by FFF indicated that unchromatographable high molecular weight components accounted for most of the compounds not detected by GC-MS.

Restricting attention to GC-MS detectable compounds, in all cases examined (varying process severity and lignite type), phenolic compounds were present in the MTE water at very low levels compared to the carboxylic compounds. Carboxylic compounds accounted for >97% of the total chromatographable organics. Aliphatic carboxylic acids were generally more abundant than aromatic acids.

For a given lignite, the overall organic levels in MTE process water tended to increase with processing severity. Increasing the temperature had a bigger effect on organic carbon removal into the process water than did the pressure. The removal of individual organic components and compound groups also increased with increasing temperature and pressure. Changes in other operation parameters, such as compression rate and the physical state of the coal charge (kneaded vs unkneaded), did not significantly affect the release of total organic carbon from the lignites.

Under the same MTE processing conditions, the quantities of organic carbon removed from Victorian lignites were generally lower than from the South Australian coals. The abundances of individual components and compound groups varied with lignite.

CHAPTER SIX

COMPOSITION OF INORGANICS IN MTE PROCESS WATER

6.1. Introduction

This chapter deals with inorganic components present in MTE process water. Results for the amount of selected inorganics released to the water from different lignites under different conditions are summarised in two sections. An in-depth discussion of the mechanisms of inorganics removal during MTE processing is then presented.

6.2. Quantitation and Calculation

Concentrations of one alkali metal element – sodium – and two alkaline-earth metals – calcium and magnesium were determined for each MTE product water and rinsing water sample. Potassium, iron and aluminium in the water samples were only quantified at an early stage of this work. Results showed that these elements, in most cases, were present at very low levels (marginally above detection limits or undetectable). It is inappropriate to compare their abundance in different water samples due to the large analytical errors and low concentrations involved. Chloride and sulphate, as the major inorganic anions in the water, were also determined. The contents of these inorganics in the original lignites investigated are given in Table 2-3.

To enable comparison between the results from different MTE runs, the same method used to convert organic carbon concentrations (g/L) in the MTE water to absolute amounts of organic carbon removed from the coal (g/kg, db coal) (Equation 5.1) was applied to the calculation of the amounts of selected inorganics released, to give Equation 5.3.

$$M_j = \frac{(C_{jp} \times V_p + C_{jr} \times V_r)}{M_{coal} \times (1 - f_{H_2O})} \quad \text{Equation 6.7}$$

where:

- M_j is the amount of an inorganic component j released to the MTE process water from the coal (g/kg coal, db);

- C_{jp} and C_{jr} are the concentrations of the component j in MTE product water and rinsing water samples, respectively (g/L);
- V_p and V_r are the total volumes of MTE product water and rinsing water samples, respectively (mL);
- M_{coal} is the mass of the raw coal used in each run (g, wb); and
- f_{H_2O} is the fraction of water in the raw coal on a wet basis (g/g coal, wb).

6.3. Effect of Processing Conditions

This section discusses the release of selected inorganic species in the MTE water produced under different processing conditions. Most of the experiments were carried out using Loy Yang A lignite. Morwell and Lochiel High Sodium were also used for some comparisons.

6.3.1. Loy Yang A

6.3.1.1. Sodium (Na)

The amounts of Na removed from Loy Yang A lignite at different MTE temperatures and pressures are plotted in Figure 6-38. For a clearer view, the data in the plot are averages from replicate runs. Detailed results including the number of replicates and standard deviations are shown in Table 5-17.

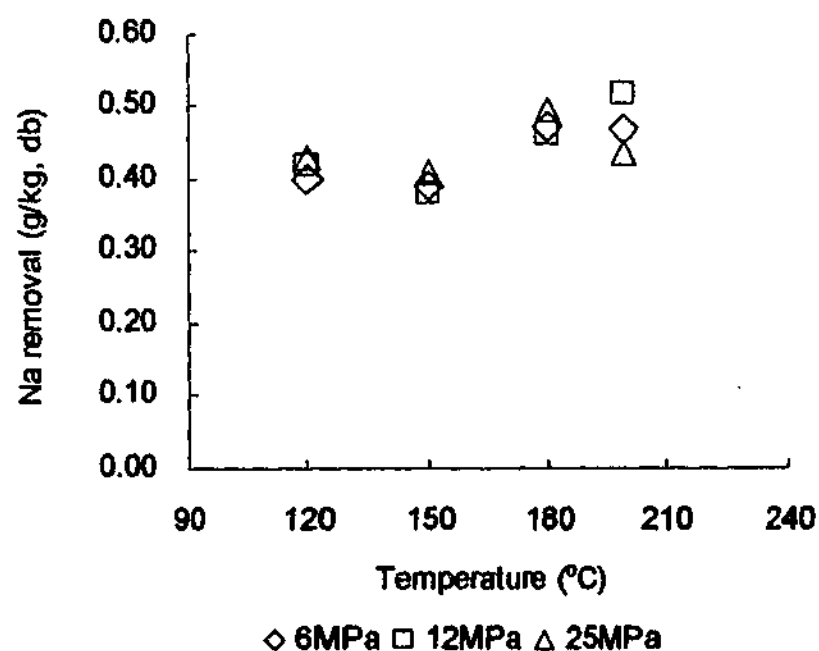


Figure 6-38. Na removal versus MTE processing temperature at different pressures – LYA*.

*Na content in raw coal=0.9±0.1 g/kg, db

Table 6-26. Means and standard deviations (SD) of Na removal and Mg removal from Loy Yang A in MTE process water.

MTE processing condition		Number of replicates	Na (g/kg, db) Mean±SD	Mg (g/kg, db) Mean±SD
120°C	6MPa	1	0.40	0.069
	12MPa	2	0.42±0.01	0.066±0.008
	25MPa	1	0.43	0.080
150°C	6MPa	?	0.39±0.07	0.072±0.010
	12MPa	6	0.38±0.06	0.077±0.012
	25MPa	3	0.41±0.02	0.078±0.005
180°C	6MPa	3	0.47±0.03	0.076±0.006
	12MPa	3	0.46±0.03	0.078±0.016
	25MPa	2	0.50±0.01	0.085±0.006
200°C	6MPa	2	0.47±0.00	0.086±0.006
	12MPa	3	0.52±0.12	0.084±0.007
	25MPa	4	0.44±0.07	0.064±0.007

The data shown in Figure 6-38 suggest that the Na content of the MTE water (i.e. the Na removal from the coal) at 180°C and 200°C was higher than at 120°C and 150°C and that

there were no trends with pressure. Statistical analysis indicated that the direct correlation between the Na removal and temperature was significant (p -value=0.03) at 12MPa and was almost significant (p -value=0.06) at 6MPa, but insignificant at 25MPa. The pressure effect was not significant in all cases.

Analyses of the results for Na removal showed that using different compression rates and kneaded coals did not significantly affect the Na removal.

In order to gain a deeper understanding of the Na removal as affected by MTE conditions, Na removal is plotted against the percentage moisture removal for all processing conditions, including different temperatures, pressures, compression rates and the use of kneaded coals (Figure 6-39).

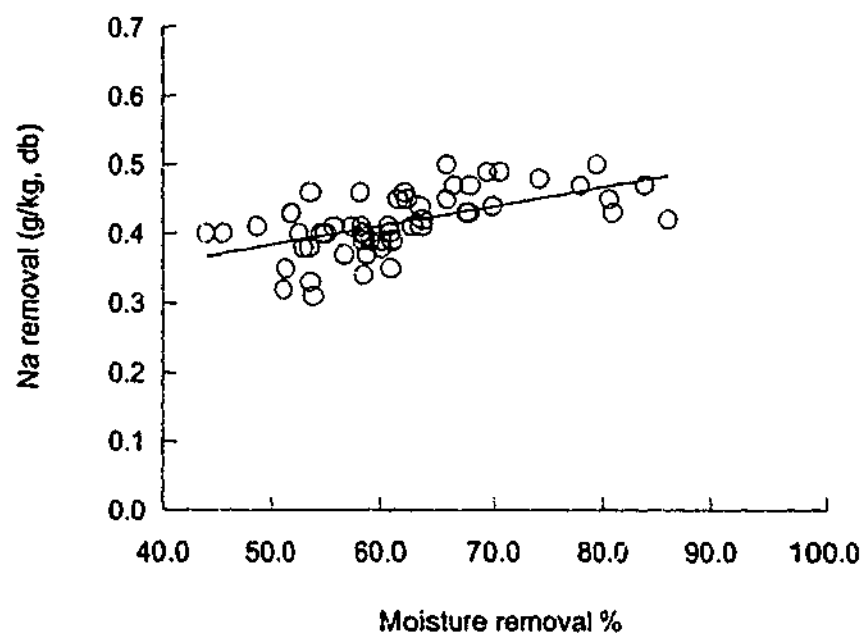


Figure 6-39. Na removal versus moisture removal under different MTE processing conditions – LYA.

It can be seen that there was an increasing trend for the Na removal with increasing moisture removal. Statistical analysis indicated that this correlation was significant (p -value $\ll$ 0.05).

Other studies on the MTE process have also found a direct correlation between the Na removal and moisture reduction [50, 51]. As concluded in Chapter Five and observed in previous studies on MTE [3, 7, 8, 48-51], reduction of the moisture content in lignite by MTE treatment increases with increasing processing severity, particularly the temperature.

Therefore, it is reasonable to expect that the Na removal would, to some extent, increase with increasing processing severity. The reason that the pressure effect on Na removal was identified to be statistically 'not significant' in the present study may be due to the fact that the increase in moisture removal with pressure was marginal (refer to Section 5.2.2) and, thus, the increase in Na removal (correlated with moisture removal) with increasing pressure, if any, may be less than the experimental scatter.

The correlation between the Na removal and moisture reduction of the lignite suggests that the Na removed during MTE treatment was present as dissolved Na in the water in the original lignite. This is discussed in detail in Section 6.5.

6.3.1.2. Magnesium (Mg) and calcium (Ca)

Figure 6-40 and Figure 6-41 plot the Mg removal versus processing temperature at different pressures and versus the percentage moisture removal (for all MTE processing conditions), respectively. The data presented in Figure 6-40 are the averages from replicate runs. Detailed results including the number of replicates and standard deviations are shown in Table 5-17.

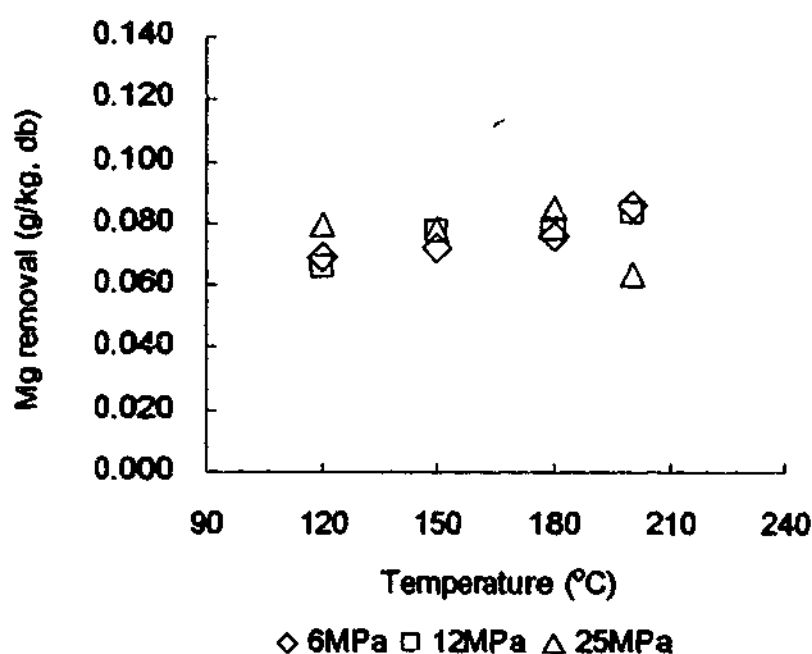


Figure 6-40. Mg removal versus MTE processing temperature at different pressures - LYA*.

*Mg content in raw coal = 0.6 ± 0.1 g/kg, db

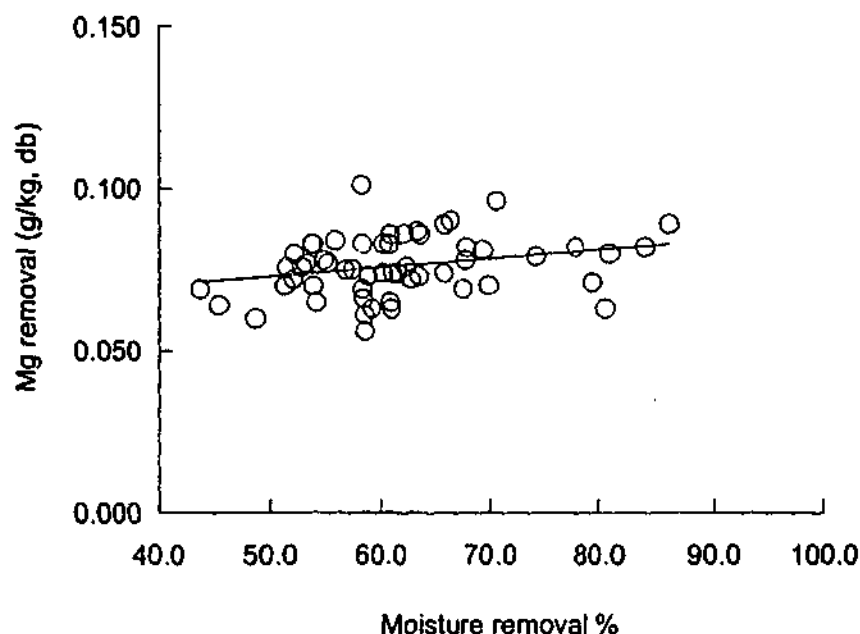


Figure 6-41. Mg removal versus moisture removal under different MTE processing conditions – LYA.

Mg removal did not show any obvious consistent trend with increasing temperature or pressure (Figure 6-40). Statistical analysis showed that the correlation between Mg removal and processing temperature or pressure was not significant. However, Figure 6-41 shows that there was a weak correlation of the Mg removal with moisture reduction. Statistical analysis indicated that this correlation was significant ($p\text{-value}=0.04$).

The plots of Ca removal versus processing temperature at different pressures and versus moisture removal (not shown) are very similar to the corresponding cases of the Mg removal. However, statistical analysis did not show significant correlation of the Ca removal with either processing severity or moisture removal. A possible reason could be the data scattering relative to the generally low concentrations of Ca in all MTE water samples.

The amounts of Ca and Mg removed from Loy Yang A were approximately 10 and 5 fold lower, respectively, than the amount of Na removed, though the three elements, Na, Ca and Mg, were present at similar levels (0.09, 0.05 and 0.06%, db, respectively) in the original lignite. Therefore, the big difference between the amount of Na removed and those of Ca and Mg was obviously not due to their different concentrations in the lignite. It suggests that the removal of the latter two elements was more difficult than that of the Na, possibly

due to larger proportions of Ca and Mg being present in non-removable forms in the lignite.

6.3.1.3. Chloride and sulphate

The chloride removal (data averaged from replicates) is plotted against MTE processing temperature at different pressures in Figure 6-42. Figure 6-43 gives a plot of the chloride removal versus percentage moisture removal (for all MTE processing conditions).

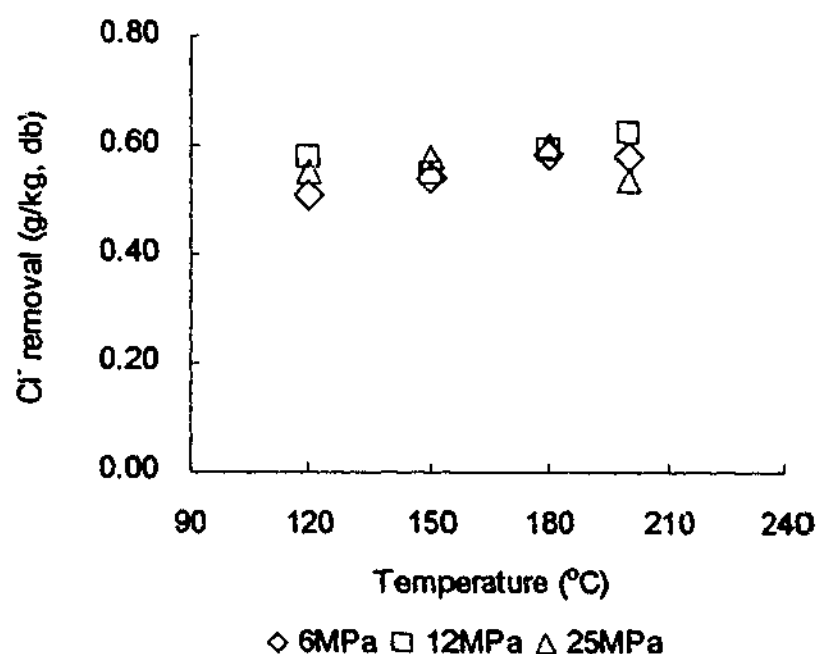


Figure 6-42. Chloride removal versus MTE processing temperature at different pressures – LYA*.

*Cl content in raw coal = 1.0 ± 0.2 g/kg, db

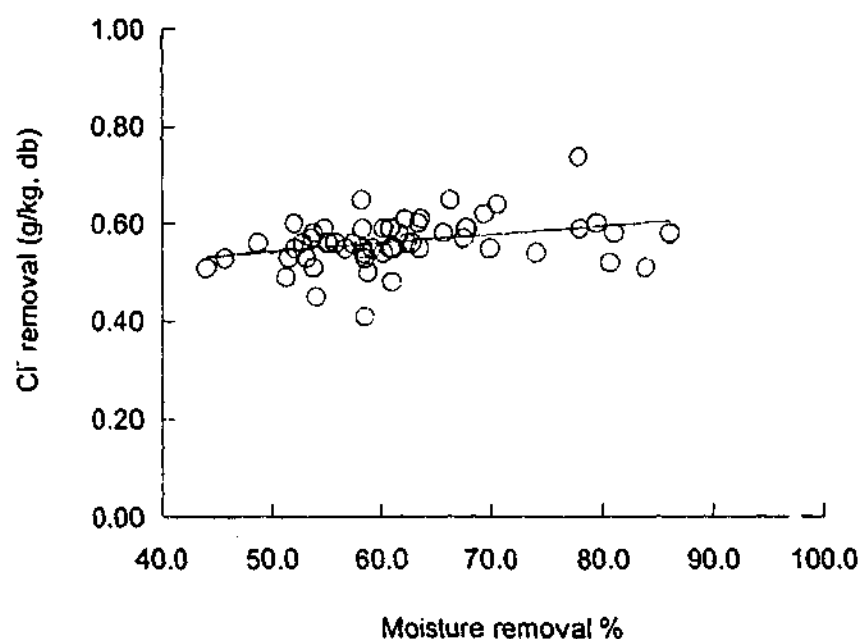


Figure 6-43. Chloride removal versus moisture removal under different MTE processing conditions – LYA.

The effect of processing severity on chloride removal was not significant, as suggested by Figure 6-42 and confirmed by statistical analysis. Like the cases of Na and Mg, chloride removal also increased weakly with moisture removal (Figure 6-43). Statistical analysis revealed a significant correlation ($p\text{-value}=0.03$) between chloride removal and moisture removal.

The removal of sulphate showed similar relationship with the processing severity or moisture removal to the removal of chloride. That is, the effect of processing severity on sulphate removal was not significant, but there was a statistically significant increasing trend of sulphate removal with moisture removal.

The amount of chloride or sulphate in the water was in the same range as that of Na, i.e. 0.3-0.6g/kg.

6.3.2. *Morwell and Lochiel High Sodium*

In addition to the extensive experiments carried out using Loy Yang A lignite, some runs to investigate effects of processing conditions were also conducted using Morwell (MW) lignite from Victoria and Lochiel High Sodium (LHS) lignite from South Australia. Morwell lignite was subjected to MTE at 200°C and different pressures (6, 12 and 25MPa).

Lochiel High Sodium was dewatered by MTE at 6MPa and various temperatures (150, 180 and 200°C).

Figure 6-44 and Figure 6-45 show the plots of the Na removal from Morwell lignite versus processing pressure at 200°C and versus corresponding moisture removal, respectively. For Lochiel High Sodium lignite, the plots of Mg removal versus processing temperature at 6MPa and versus corresponding moisture removal are shown in Figure 6-46 and Figure 6-47, respectively. The plot of Na removal from Lochiel High Sodium lignite versus moisture removal is shown in Figure 6-48. Error bars present are standard deviations for two and four replicate runs for Morwell and Lochiel High Sodium cases, respectively.

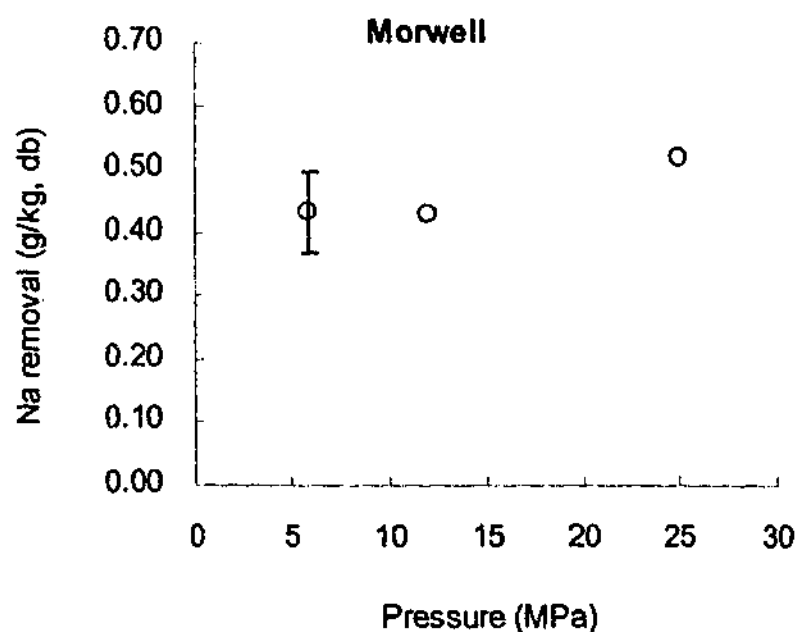


Figure 6-44. Na removal versus MTE processing pressures (200°C) – MW*.

*Na content in raw coal=0.8±0.1g/kg, db

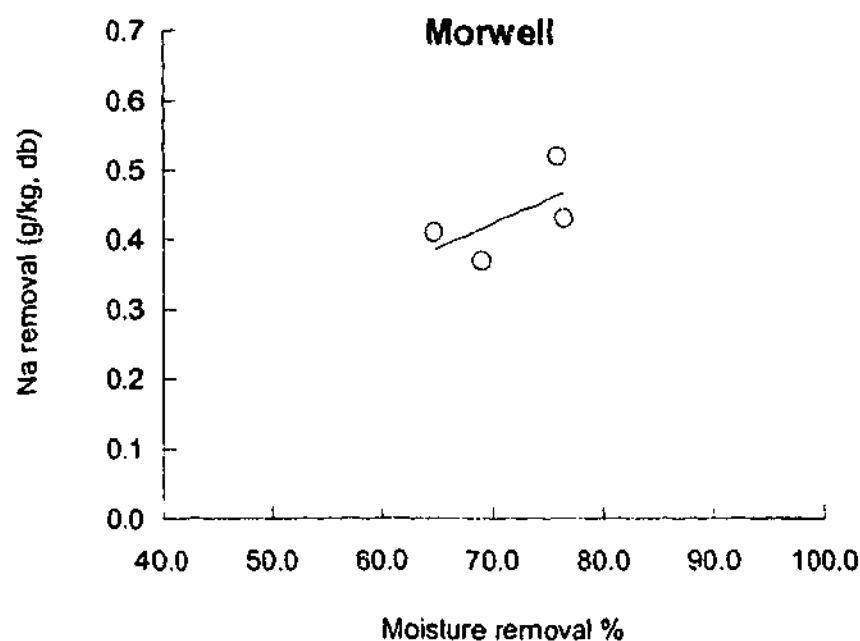


Figure 6-45. Na removal versus moisture removal at different MTE processing pressures (200°C) – MW.

For Morwell lignite, the plots show that the Na removal increased with increasing processing pressure and moisture removal (Figure 6-44 and Figure 6-45). The plots of chloride and sulphate removal versus moisture removal (not shown) also exhibited an increasing trend. No trends could be identified in the plots of the Ca and Mg removal versus either processing pressure or moisture removal. However, statistical analysis indicated that only the increase in Na removal with increasing pressure was significant. The removal of other selected inorganic components from Morwell lignite did not significantly correlate to either processing pressure or moisture removal.

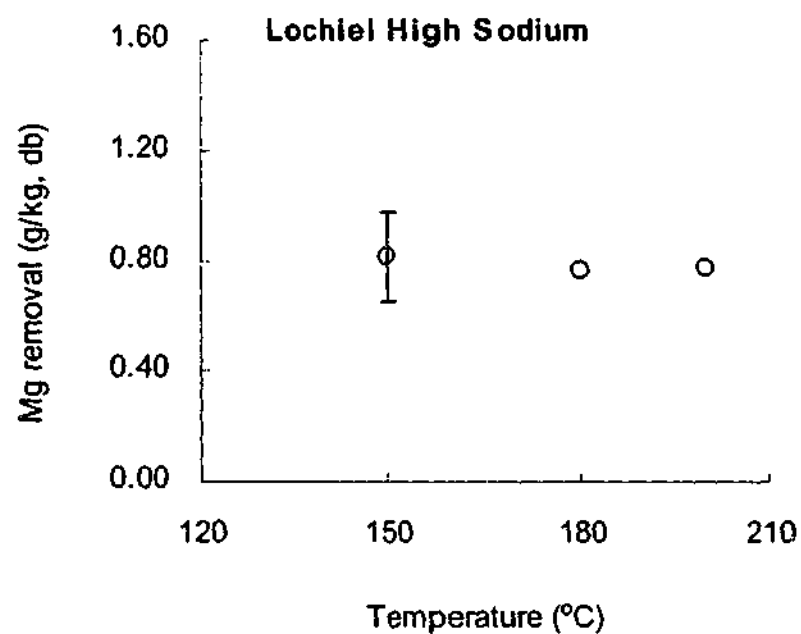


Figure 6-46. Mg removal versus MTE processing temperature (6MPa) – LHS*.

* Mg content in raw coal = 8.4 ± 0.2 g/kg, db

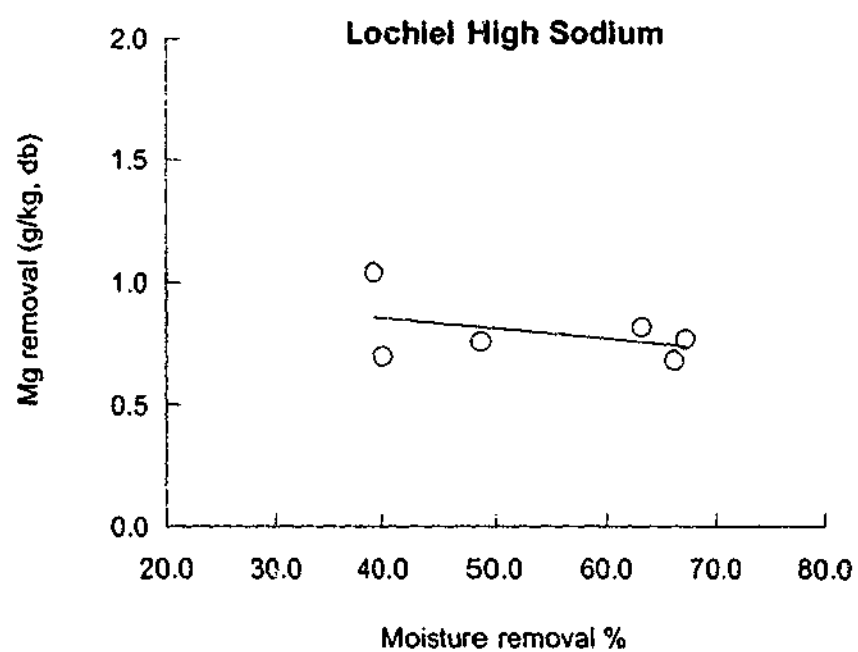


Figure 6-47. Mg removal versus moisture removal at different MTE processing temperature (6MPa) – LHS.

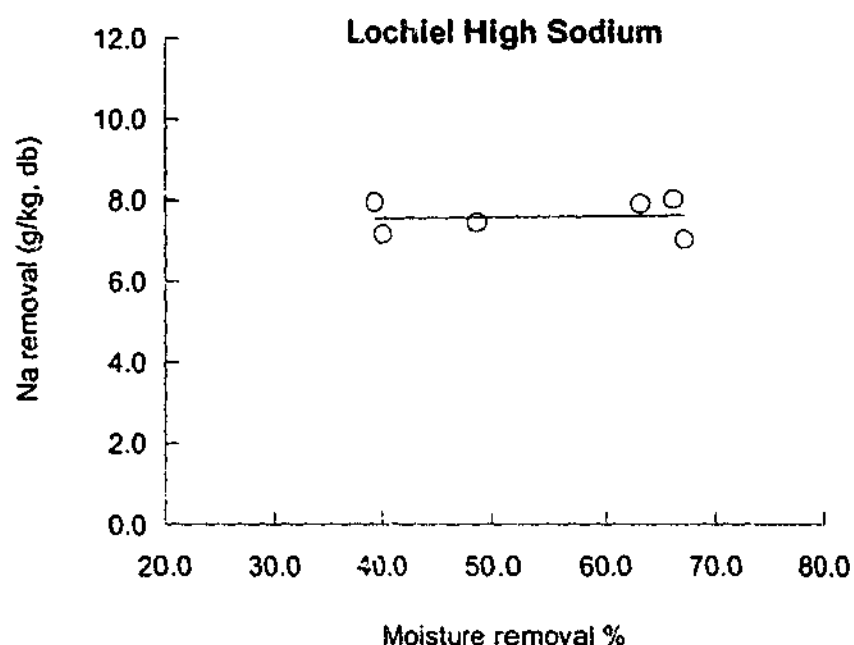


Figure 6-48. Na removal versus moisture removal at different MTE processing temperature (6MPa) – LHS*.

* Na content in raw coal = 14.1 ± 0.2 g/kg, db

For Lochiel High Sodium lignite, linear regressions of the plots for selected inorganics versus processing temperature or versus moisture removal suggested either no apparent trends (as seen in Figure 6-46 and Figure 6-48) or even a decrease with moisture removal (Figure 6-47). However, statistical analysis (ANOVA) indicated that there was no significant correlation of the removal of selected inorganic components with either processing temperature or moisture removal.

The reason that the removal of selected inorganic components from Morwell and Lochiel High Sodium did not show significant correlation with either processing severity or moisture removal may be that the effect of the MTE processing severity or the increasing trend with moisture removal, if any, was marginal (as observed in the Loy Yang A case). When only a few replicate experiments were carried out using Morwell and Lochiel High Sodium lignites, any correlation between the removal of the inorganics and processing severity or moisture removal could not be identified due to natural data scatter in the results of the experiments. This scatter is probably in large part a consequence of the addition of a variable amount of water at the start of an MTE experiment and the procedures used (gentle shaking and tapping) to remove air bubbles from the coal. As a

result, variable mixing of this added water with the original coal water and consequently the transfer of inorganics to the added water probably varied between runs. This would lead to variation in the proportion of inorganics removed, even for runs conducted under otherwise identical conditions.

6.4. Comparison between Lignites

In order to compare the extent of the removal of inorganics from different lignites, Loy Yang A (LYA), Morwell (MW) and Yallourn (YL) from Victoria and Bowmans A (BMA), Kingston (KS), Lochiel (LC) and Lochiel High Sodium (LHS) from South Australia were all subjected to MTE processing under the same conditions – 200°C, 6MPa.

The amounts of the inorganics in the raw coals investigated together with the amounts and proportions released to the MTE process waters are summarised in Table 6-27.

Table 6-27. Comparison of the removal of selected inorganics from different lignites (200°C, 6MPa).

	Lignite	Na	Ca	Mg	Cl	S*
Content in raw coal (% db)	LYA	0.09	0.05	0.06	0.10	0.28
	MW	0.08	0.32	0.21	0.06	0.25
	YL	0.07	0.14	0.18	0.05	0.20
	BMA	1.51	0.07	0.82	1.41	4.24
	KS	0.80	1.18	1.30	0.28	3.40
	LC	0.88	1.33	0.81	0.45	3.37
	LHS	1.41	0.68	0.84	0.59	2.85
Amount in MTE water (g/kg db)	LYA**	0.47±0.00	0.043±0.002	0.086±0.006	0.58±0.07	0.15±0.00
	MW**	0.39±0.02	0.082±0.005	0.13±0.01	0.34±0.04	0.11±0.01
	YL**	0.33±0.02	0.050±0.001	0.12±0.00	0.27±0.00	0.098±0.002
	BMA	9.6	0.64	3.3	14	5.6
	KS	3.9	0.22	0.31	3.3	1.7
	LC	6.0	0.59	1.3	5.4	3.3
	LHS	7.0	0.26	0.77	6.0	2.9
% in MTE water	LYA	52	8.6	14	58	5.4
	MW	49	2.5	6.2	56	4.2
	YL	47	3.6	6.7	54	4.9
	BMA	64	91	40	98	13
	KS	49	1.9	2.4	119	5.0
	LC	69	4.4	16	120	9.7
	LHS	50	3.8	9.2	101	10

* The data for the raw coals are total sulphur content and for the MTE water are sulphur converted from sulphate (SO_4^{2-}).

** average of duplicates

As shown in Table 6-27, the levels of the selected elements present in the three Victorian lignites were similar. The contents of Na and S in the South Australian lignites were more than ten fold greater than in the Victorian lignites. The other three elements were also present in higher amounts in the South Australian coals with only one exception – Ca in Bowmans A.

In the water removed from different lignites, Na and Cl were the two most abundant elements. Ca was the least abundant, followed by Mg (or S in the cases of Morwell and

Yallourn). All the inorganics in water removed from the South Australian lignites were present at substantially higher levels than in the cases of the Victorian lignites, corresponding to their higher concentrations in the original lignites. The results for the South Australian lignites are similar to those reported in a previous study by Quast and Readett [116], who also found large amounts of Na, Cl and S (as sulphate ion) with lesser amounts of Ca and Mg in water extracts of Bowmans, Lochiel and Kingston lignites and lowest levels of water soluble inorganics from Kingston.

The percentage removal data provide a clearer view regarding the behaviour of these inorganics. Compared to the sometimes big differences between the absolute amounts of an element in the MTE process water from different lignites, the proportions of a given element removed were similar in most cases. For the three Victorian lignites, approximately 50% of the Na and Cl were removed by the MTE treatment, whilst the South Australian coals lost 50-70% of the Na and (within limits of error) all their chlorine. The proportions of the other three elements extracted into the water phase were much smaller, i.e. less than 10% in most cases. Loy Yang A released the largest proportions of the Ca and Mg among the Victorian lignites, whereas, for the South Australian lignites, the smallest proportions of these two elements were removed from Kingston.

There are two observations worthy of special mention. First, exceptionally large proportions of the Ca and Mg were removed from Bowmans A (91% and 40%, respectively). This may imply that the predominant forms of Ca and Mg in this coal were different from those in the other lignites, i.e. more water soluble. Second, the proportions of the Cl removal were unrealistically high (>100%) for Kingston and Lochiel. It should be noted that the data were calculated from the results of coal analysis using ICPAES (errors= $\pm 0.02\%$, db) and water analysis using a colorimetric method or ICPAES (errors%=12% in the case of Cl in LYA and MW as shown in Table 6-27). A systematic error in either or both techniques could give rise to the impossible percentages; the high proportions may be due to either a systematically high analytical result for Cl in the water samples or a low result for the Cl content of the coals. However, such errors were unlikely to affect comparisons between lignites so that the results suggest that a greater fraction of the Cl was indeed removed by MTE treatment from the South Australian lignites.

For all the lignites studied, 50% or higher proportions of the Na and Cl could be removed by MTE treatment. Ca, Mg and S were also removed to a lesser extent (except for the high Ca removal from BMA). These elements are known to contribute to fouling/slugging and corrosion problems during lignite utilisation [68, 74, 75, 279]. Therefore, the removal of these inorganic species via MTE treatment is of potential significance for the beneficiation of these lignites.

6.5. Removal Mechanisms of Inorganics during MTE

6.5.1. *Removal of the Elements from Lignite*

The results of this study revealed that the sodium in lignites behaved differently to calcium and magnesium during MTE treatment. It also showed that elements like iron and aluminium were only present in MTE process water at very low levels (see Section 6.2). The different behaviours of these elements during MTE processing suggest that they were originally present in different chemical forms.

The extent of removal of the elements during MTE processing can be related to the forms in which they are present in the lignite. In general, inorganic constituents in coals occur either (a), in mineral form, as discrete minerals or (b) as non-minerals distributed throughout the macerals chemically bound to organic functional groups or dissolved as ionic species in water within the pores [112, 280].

Unlike high-rank coals, in which minerals constitute almost all the non-carbonaceous fraction, low-rank coals contain reasonable amounts of non-mineral inorganics that mainly exist in two forms: as free ions present in the water associated with the coal and as cations exchanged onto functional groups (e.g. carboxyl, phenolic, etc.) forming part of the organic coal substance [68, 116]. For the study of the behaviour of the inorganic elements that can be leached into the water phase during dewatering, the non-mineral inorganics are therefore clearly of more importance.

In Victorian lignites, it has been confirmed that almost all the calcium and magnesium occurs as exchangeable cations associated with the carboxyl functional groups [115, 281, 282]. However, sodium is not only organically bound to functional groups but also dissolved, mainly as chloride, in the in-seam moisture [115, 281, 283]. For the South

Australian lignites, generally, water-soluble inorganics consist of predominantly sodium, chlorine and sulphur (as sulphate ion) with lesser amounts of calcium and magnesium [116].

Since large proportions of the original sodium in these lignites were dissolved in pore water, apparently, the soluble proportion of the sodium was preferentially removed during MTE processing. Therefore, the removal of this element was in proportion to the water removed from the lignites (see Section 6.3.1.1).

For Victorian lignites, the presence of calcium and magnesium in these lignites almost exclusively as organically bound elements has been recognised in previous studies [115, 281, 282]. If any removed calcium and magnesium were originally present as dissolved salts in the pore water, this proportion would be very small. If this be so, the major proportion of calcium and magnesium removed in the MTE process water could come from different sources. It is indicated that, during high temperature non-evaporative thermal treatment of the lignite, organically bound inorganic cations (e.g. calcium and magnesium) can be released due to thermal decomposition of carboxylate functional groups [13]. During MTE dewatering, the removal of calcium and magnesium in conjunction with carboxylate decomposition is less likely due to the relatively low temperatures employed. However, the calcium and magnesium in lignite might be associated with the organic acids leached into the water phase. This mechanism has been proposed for the removal of calcium and magnesium during water extraction of Victorian lignites [281, 284]. Durie [281] suggested that the small amounts of water-soluble calcium – <5% and ~15% – extracted from Morwell and Yallourn lignites, respectively, were probably organically bound and associated with the colloidal humic suspension in the extracts. In this study, the pH of all MTE product water from the Victorian lignites investigated was between 4 and 5. In this weakly acidic environment, the removal of calcium and magnesium as organically associated cations quite possibly occurred. For the South Australian lignites, the small proportions of calcium and magnesium present in the MTE process water (except for Bowmans A) were compatible with a similar removal mechanism; though, in these cases, due to a lack of previous work, the possibility that the calcium and magnesium removed during MTE were simply dissolved as inorganic salts in the pore water cannot be totally excluded.

Non-mineral iron and aluminium in Victorian lignite can be present as exchangeable cations [68, 285] or as a monovalent cationic hydroxy complexes, i.e. (Fe complex)⁺ and (Al complex)⁺, bound to the carboxylate groups [115]. The low water solubility of the forms of these elements present in lignites may explain their very low levels in the MTE water analysed. The result in this study is in agreement with that of Bou-Raad et al [284], who also found the two elements as ions in aqueous extracts of some Victorian lignites to be at very low or undetectable levels. During hydrothermal dewatering of South Australian lignites including Bowmans, Lochiel and Kingston, these two elements were also found to be essentially fully retained in the coals [286].

6.5.2. *Cations and Anions in the Water Phase*

Although the methods used to measure the concentrations of the sodium, calcium and magnesium in MTE water (AAS and ICPAES) cannot determine the forms of these elements, it is likely that these elements are in fact present in their most stable form in the aqueous phase, i.e. as cations.

Chlorine and sulphur in the MTE water were analysed both as elements by ICPAES and as chloride and sulphate anions by a colorimetric method (refer to Chapter Two). The results for chlorine and chloride were very similar. Also, when the total sulphur determined by the ICP method was expressed as sulphate ions, the results were in good agreement with those from the colorimetric determinations.

For the purpose of further understanding the mechanisms of the removal of the inorganics during MTE processing, this section discusses the behaviour of the selected inorganics as ionic species in the water phase.

6.5.2.1. *Sulphur and sulphate*

A possible special effect of the behaviour of sulphur in lignites during MTE processing requires that a whole subsection of discussion be dedicated to this element.

As discussed above, sulphur in MTE water was predominantly, if not entirely, present as sulphate. In South Australian lignites, sulphur can be present in significant portion as soluble sulphate [116]. Thus, the sulphate sulphur in these lignites could be the main source of the sulphate in the MTE water. Nevertheless, studies indicate that, in Victorian

lignites, the proportion of sulphur in sulphate form is small and that it occurs mostly as organic sulphur [281] and may also occur in mineral form as pyrite or marcasite [68], neither of which is water soluble. The sulphur content of the MTE process water from Victorian lignites (Table 6-27) translated to 0.01-0.02wt%, db sulphate sulphur in the original coal, which would be close to the limit of detection, thus the results could be consistent with sulphate sulphur in the original coal as the main source of the sulphur in the MTE water for the Victorian coals.

However, results from sulphur fixation during ashing, particularly low temperature ashing of lignite, indicate that a conversion of organic-form sulphur to soluble sulphate during MTE processing, with possibly some involvement of inorganic cations, cannot be excluded as a source of sulphur in MTE water.

During lignite ashing at high temperature ($>370^{\circ}\text{C}$), different forms of sulphur in lignite can be fixed to form sulphates in the ash [281, 287]. The important role that the ion exchangeable cations play in this process was recognised as early as 1965 by Darie and Schafer in their unpublished work introduced by Schafer [239]. Indeed, the amount of fixed sulphur was found to depend on the calcium to sulphur ratio, but not on the original form of sulphur [239].

Low temperature ashing (LTA) involves ashing at a low temperature utilising an electronic device with radio frequency or microwave producing gases in excited states [288-290]. The temperature for LTA varies between $<60^{\circ}\text{C}$ [289] and $150\text{-}200^{\circ}\text{C}$ [290, 291], but is typically about 150°C [292-294].

A sulphur fixation effect has been observed particularly for low-rank coals during LTA. Miller et al [287] described a new method to determine the mineral matter in coal by LTA and discovered that side reactions including the fixation of organic sulphur as sulphate led to a higher-than-expected measured mineral content for low-rank subbituminous coals and lignites and affected the suitability of LTA for these coals. The involvement of cations associated with carboxyl groups was also recognised. Morgan et al [295] found that it was the interaction of exchangeable calcium with sulphur and oxygen that contributed to the existence of significant quantities of anhydrite (CaSO_4) in ash of the lignites from LTA. Similarly, during LTA of a series of low-rank coals at 125°C , bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$)

was detected as one of the major mineral phases in some of the lignite samples [296]. The researchers suggested that the formation of this hemihydrated calcium sulphate was due to the fixation of organic sulphur by organically bound calcium cations that were not completely removed by the ion exchange procedure employed. The fixation of organic sulphur as sulphate during LTA was also observed for Australian lignites [294].

In summary, in low-rank coals such as lignites, even if the sulphates are not originally present, they may be formed by reactions between sulphur in any forms and exchangeable cations at temperatures as low as $<150^{\circ}\text{C}$. The amount of the sulphate formed is likely to be associated with the concentration of the exchangeable cations in the lignite.

The temperatures employed in the MTE processes in this study were between 120°C and 200°C – a level that is comparable with that in LTA situations where sulphur fixation occurs. Thus, it is possible that a similar sulphur transformation effect occurred so that sulphate ions could occur in the MTE water from lignites that were unlikely to originally have contained soluble sulphate salts. Furthermore, if this process was actually occurring, the amount of the sulphate ions would be expected to correlate with that of the exchangeable cations, sodium, calcium and magnesium, just as if the sulphur had been present in the original coal as sulphate.

6.5.2.2. Relative abundance of selected cations and anions in MTE water

The molar abundance of individual ions and the relative abundance ratios for selected cations and anions in different combinations were calculated to provide further insight into the origin and fate of the ions during MTE processing. The average results for each condition are presented in Table 6-28. The data with numerical values close to 1 are marked in bold.

Table 6-28. Average charge equivalence ratios of selected cations to anions released to MTE water from different coals.

MTE temperature	Lignite	$\text{Na}^+ : \text{Cl}^-$	$\text{Na}^+ : (\text{Cl}^- + \text{SO}_4^{2-})$	$(\text{Ca}^{2+} + \text{Mg}^{2+}) : \text{SO}_4^{2-}$	$(\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}) : (\text{Cl}^- + \text{SO}_4^{2-})$
		A	B	C	D
120°C		1.2	0.75	0.86	1.1
150°C	LYA	1.1	0.75	1.2	1.1
180°C		1.2	0.81	0.98	1.1
200°C		1.3	0.80	0.93	1.1
	MW	1.8	1.1	2.0	1.9
	YL	1.9	1.1	2.1	2.0
200°C	BMA	1.1	0.57	0.87	0.98
	KS	1.8	0.85	0.34	1.0
	LC	1.7	0.74	0.66	1.1
	LHS	1.8	0.88	0.42	1.1

For Loy Yang A lignite, at lower temperatures, the average ratios of sodium to chloride (ratio A) are close to 1. This suggests that, in these cases, the sodium in the MTE water came mainly from sodium chloride dissolved in the pore water of the original coal. This result is consistent with the report that soluble sodium is predominantly present as sodium chloride in Victorian lignites [115, 281]. At all temperatures, the relatively low sodium to anion ratios (ratio B) and the value close to 1 for ratio C suggest that indeed calcium and magnesium were important in determining the sulphate content of the MTE water, because either sulphates of these elements were dissolved in the pore water or calcium and magnesium assisted in a transformation of sulphur to sulphate during MTE processing (refer to Section 6.5.2.1).

For the Bowmans A case, the ratios are very similar to the cases of Loy Yang A at low temperatures, except for the ratio B. This suggests that the removal of the sodium was also predominantly as sodium chloride. However, unlike the case of Loy Yang A, in which calcium and magnesium were almost exclusively present as organically bound cations and were difficult to remove during MTE processing, for the Bowmans A lignite, the large proportions of calcium and magnesium removed into the water during MTE processing (91% and 40%, respectively) suggest they were, to a large extent, present as soluble salts

in the original lignite. Sulphur in South Australian lignites can be present as soluble sulphate ions, as indicated by Quast and Readett [116]. The very low ratio B (sodium to chloride and sulphate) and a ratio C not far from 1 may suggest that significant proportions of calcium and magnesium were possibly released as sulphates from Bowmans A.

The behaviours of the ionic species in the other three South Australian lignites were very similar. The major differences between these cases and the Loy Yang A case are the much higher ratio A and the much lower ratio C. Since the ratio D (total cations to total anions) is nearly one, it implies that sodium and the two alkali-earth elements were distributed between the two anions – either as chloride or as sulphate or as both. In these cases, it is likely that sodium was not only associated with chloride but also with sulphate. The presence of the sulphate-associated sodium would lead to a high ratio A (sodium to chloride), whereas the presence of the sodium-associated sulphate would result in a low ratio C (calcium and magnesium to sulphate), both observed for the three lignites.

For Loy Yang A and the South Australian lignites, the ratios of all cations to all anions (ratio D) is close to 1, suggesting that the cations and anions selected for quantitation have accounted for most of the major ionic species present in the water. Other anions, such as anions of the organic acids (refer to Chapter Five), apparently were only a relatively minor contributor to the charge balance.

The behaviours of the ions in Morwell and Yallourn were different from all the other lignites investigated. The ratios of all combinations of cation to anion are approximately 2, except for the ratio B (sodium to chloride and sulphate), which is close to 1. Apparently, the removal of the sodium in these coals was associated with the removal of both chloride and sulphate anions. That all the ratios of cation to anion are very high suggests that significant portions of anions present in the water were not accounted for during quantitation. A similar effect was observed by Bou-Raad et al [284], who examined major cations and anions in aqueous soxhlet extracts of Morwell and obtained high cation to anion ratios if only chloride and sulphate were accounted for. The authors attributed this effect to the release of significant levels of carbon based anions such as acetate, carbonate and oxalate, with oxalate as the predominant organic anion. In the present study, the release of carboxylic compounds (carboxylic acids and/or carboxylates) has been

confirmed by the results of characterisation of organic species as introduced in Chapter Four and Five. The results for Morwell and Yallourn suggest a possibility that carbon based anions or other anions, as well as chloride and sulphate, may contribute to the charge balance in the water from the two lignites.

6.6. Summary

For Loy Yang A lignite, the release of selected inorganics (except for calcium) significantly correlated with moisture removal of the lignite during MTE processing. However, unlike the removal of organic materials, which was significantly affected by MTE processing severity, the removal of the selected inorganic species from the lignite exhibited non-significant correlation with the processing severity, except for the significant or almost significant effect of temperature on sodium removal at low pressures. Such a correlation would be expected for components contained in the pore water.

For Morwell and Lochiel High Sodium lignites, the removal of selected inorganics did not show significant correlation with either the processing severity or moisture removal. This is possibly because the experimental uncertainty (data scatter) from replicate runs was too great relative to the expected trends.

The South Australian lignites generally released higher levels of the inorganics than the Victorian lignites during MTE treatment. However, the proportions of the inorganics removed from different lignites were similar. For all the coals investigated, over 50% of the sodium and even larger portions of the chloride could be removed by MTE processing. Approximately 80-90% of the calcium, magnesium and sulphur still remained in the lignites, except for calcium and magnesium in Bowmans A, where 91% and 40% were removed, respectively.

The removal of the inorganic species during the MTE process could be correlated to the forms of these species present in the lignites. In all the lignites investigated, significant proportions of the sodium were present as soluble salts and, thus, were readily removed ($\geq 50\%$) associated with chloride and/or sulphate anions. In the Victorian lignites, almost all the calcium and magnesium were present as organically associated exchangeable cations. Small proportions of these elements were nevertheless removed to the MTE water likely due to thermal decomposition of carboxylate functional groups releasing the bound

cations or together with associated organic anions; for two Victorian lignites (Morwell and Yallourn) removal of calcium and magnesium other than as soluble inorganic salts was almost certainly significant. For the South Australian lignites (except Bowmans A), the removal of small proportions of the calcium and magnesium was also consistent with removal of organically bound cations, but dissolved sulphates could contribute. For the Bowmans case, it appears likely that the large proportions of calcium and magnesium removed during MTE processing were present in sulphate form. Sulphate sulphur in the original lignites could be the main source of sulphate in MTE water. However, for the Victorian lignites, a transformation of organic sulphur to sulphate during the MTE treatment could not be fully excluded.

CHAPTER SEVEN

EFFECT OF ACIDIFICATION AND MEANS OF HEATING ON THE NATURE OF MTE PROCESS WATER

7.1. Introduction

The results discussed in Chapter Six reveal that the MTE treatment of Victorian and South Australian lignites resulted in the removal of a significant amount of sodium and smaller amounts of calcium and magnesium from the lignites.

An important contribution of sodium, calcium and magnesium to fouling problems during combustion has been identified for Victorian lignites [75]. The presence of sodium-containing inorganic species in lignite, which become volatile during utilisation, has been recognised as a very important factor in the formation of ash deposits for both Victorian and South Australian lignites [68, 78, 79, 282]. It was also noted that it was the exchangeable calcium cations rather than mineral calcium that was involved in the formation of carbonate minerals during hydrogenation of low-rank coals, causing serious operation difficulties in the reactor system [282]. Therefore, a reduction of the inorganic content of lignite by MTE treatment could be of benefit to the lignite utilisation industry.

A large proportion of these inorganic elements is present in lignite as organically bound exchangeable cations [115, 281]. A feature of ion exchangeable cations in lignite is that they can be exchanged by hydrogen when the acidity of the environment is raised [68, 297, 298]. Therefore, an increase in the acidity of the coal water mixture during dewatering would be expected to promote this ion exchange process, leading to a reduction of these inorganic elements in the dewatered products. Furthermore, some minerals in the coal are acid soluble and may be therefore released to the water phase under acidic conditions.

Therefore, one of the aims of this study was to investigate the effect of increasing the acidity of the coal water slurries on the removal of selected elements during MTE dewatering. Such an investigation may also assist in deepening our understanding of the removal mechanisms of these elements from lignites.

Hydrochloric acid and carbon dioxide in the water phase have both been employed as means of removing inorganic matter from coal. Treatment with hydrochloric acid for demineralisation of low-rank coals was studied as early as in 1937 by Sustmann and Lehnert [299, 300]. It has been demonstrated that using hydrochloric acid for mineral removal from coals [301-303] and lignites [304] is an efficient approach. Carbon dioxide (as carbonic acid in the presence of water) has also been utilised for coal beneficiation and shown to be an effective method for demineralisation [305]. Thus, these two methods were selected in this study for investigating demineralisation effects during MTE.

In order to develop a better understanding of the relationship between the forms of the inorganic species and the mechanisms of the removal of inorganics by MTE treatment, water and acid extractions of the lignites were also carried out.

Another aim of the study was to compare two methods of providing the process heat. At an early stage of MTE development, the laboratory-scale rigs for batch tests were heated electrically [49, 306]. As the technique progressed to larger scales, steam at high temperature and pressure was used to supply the thermal energy for the process [6, 7, 52, 53]. This study investigated the effect of using hot water preheating followed by steam heating instead of electrical heating on the constituents of the MTE process water.

7.2. Experimental

7.2.1. *MTE Processing and Water Production*

7.2.1.1. The lignites

The feed coals used in the experiments were 'run of mine' samples homogenised and ground to <10mm. They were Loy Yang B and Bowmans B from Australia and Hambach from Germany. Properties of the coals are given in Table 2-3.

Since one of the aims of this investigation was to understand the potential for removal of the inorganics by the MTE treatment, Loy Yang B and Bowmans B, with higher ash content (inorganic matter) than Loy Yang A and Bowmans A, respectively, were specifically chosen for this work. Hambach, with higher ash content than Loy Yang B, from the Rhenish lignite district located west of Cologne, Germany, was selected as a comparison.

7.2.1.2. The apparatus

Figure 7-49 to Figure 7-51, respectively, show a photo, a schematic diagram of the compression vessel and a flow chart of the MTE rig, located in the Department of Chemical Engineering, University of Dortmund, that was utilised for this work.



Figure 7-49. Photo of the MTE rig located in the University of Dortmund [307].

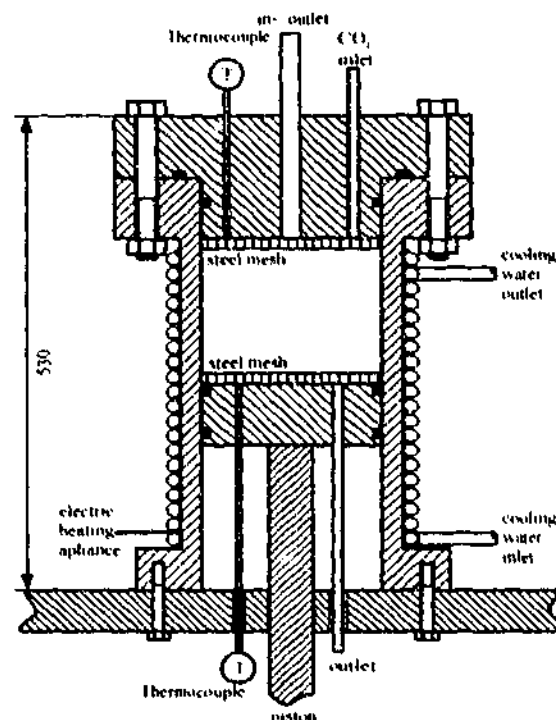


Figure 7-50. Schematic diagram of the pressure vessel [307].

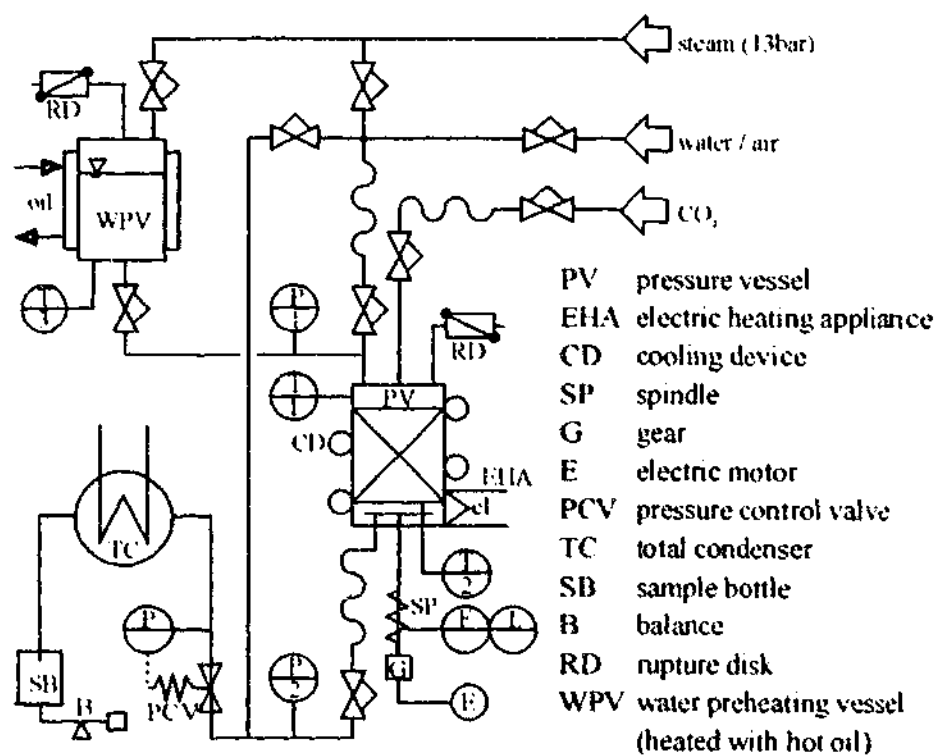


Figure 7-51. Flow chart of the experimental set-up [307].

The experimental rig consists of a high quality steel cylinder (Figure 7-50 and PV in Figure 7-51) with an inner diameter of 125mm. It can be adapted to either electrical heating or steam heating. A compression force of up to 150 bars (15MPa) can be applied

onto the load inside the cylinder (i.e. coal water slurries) by means of an electrically powered piston (SP, G, E in Figure 7-51) inserted at the bottom of the cylinder. The water that is squeezed out leaves the vessel through orifices at both the top and bottom. With the assistance of a cooling device (CD) mounted outside the vessel, it is possible for the system to be cooled to ambient temperature quickly after each run. To avoid solid loss during compression, two stainless steel mesh plates were located at each end of the cylinder to hold the load.

This rig arrangement allows the injection of pressurised carbon dioxide (CO_2) to the sealed compression vessel. A 'weak' acidic environment could therefore be realised through the injection of CO_2 to the system. The system is also designed to accommodate preheating of the coal by hot water flushing followed by heating with pressurised steam.

7.2.1.3. The conditions

A list of the experiments undertaken and the corresponding conditions is given in Table 7-29. Each of the three selected lignites was treated under each of the five listed conditions. The Hambach lignite was also treated at 200°C in order to characterise major organics in the product water.

The experiments discussed in this chapter were not replicated due to time constraints. Errors (shown as error bars in the figures) are calculated from the analytical errors of each measurement (some are too small to show). Previous work using the same MTE apparatus was found to provide reliable and reproducible results [308]. Moreover, the main concern of the work discussed in this chapter was to identify trends between different lignites and different processing conditions. Absolute precision with respect to the extent of dewatering and demineralisation was a secondary concern.

Table 7-29. MTE conditions employed in the experiments

Code	Temperature (°C)	Net pressure (MPa)	Cell load	Prior to heating	Heating means
EW (electrical/water)	150	12	650g coal/650ml distilled water	-	electrical
EC (electrical/CO ₂)	150	12	650g coal/650ml distilled water	CO ₂ injection	electrical
EA (electrical/acid)	150	12	650g coal/650mL 0.05M HCl	-	electrical
SF (steam/fresh water)	130-160	12	650g coal	~300ml 180°C distilled water flushing	steam
SR (steam/recycled water)	130-160	12	650g coal	~300ml 180°C recycled water flushing	steam

For convenience of discussion, the five conditions are coded as shown in the first column of Table 7-29. The EW condition is the 'standard condition' since these experiment was carried out under similar conditions to those used for the MTE rig at Monash University. The net pressure, 12MPa, was the actual mechanical force supplied by the piston, 14MPa, minus the fluid pressure inside the vessel, 2MPa. This was slightly higher than the pressure employed in comparable experiments with the rig at Monash University. In the latter cases the net pressure was the applied pressure, 12MPa, minus 0.5MPa (the maintained fluid pressure inside the MTE cell).

7.2.1.4. The process

In the EW experiments, the compression cell was loaded with a known weight (650g) of raw coal and distilled water (650mL). The coal and water were stirred in-situ to form a slurry in order to expel any trapped air and to ensure homogeneous heat transfer within the cell during the experiments. When sealed, the vessel was heated by electrical heating coils (EHA in Figure 7-51) to the desired temperature, which was held for 20-30 minutes before mechanical compression using an engine-driven spindle began (SP, G, E in Figure 7-51). During the compression stage, the hydraulic pressure was maintained using the pressure control valve (PCV in Figure 7-51), at a level higher than the saturation steam pressure to avoid water evaporation. When the desired compression pressure was attained, it was

maintained for approximately 1.5 hours, during which time the hydraulic pressure was maintained at 20MPa. After chilling in a condenser (TC in Figure 7-51), the expelled water was collected in a preweighed glass container (sample bottle) located on a weighing balance (SB, B in Figure 7-51). Following each experiment the pressure vessel was cooled using a cooling coil (CD in Figure 7-51) until the temperature in the vessel was below 60°C. Then the hydraulic pressure was released, the vessel was detached and the coal pellet and product water were collected and weighed. The system was thoroughly rinsed with distilled water. The rinsing water was collected separately and weighed.

Experiments EC and EA were carried out under similar conditions to EW, except that, for the EC experiments, after the pressure vessel was sealed, CO₂ gas (at 30 bars or 3MPa) was continuously injected into the slurry for approximately one hour prior to heating. In the EA experiments, the coal water slurry was prepared using 650mL 0.047M hydrochloric acid solution (replacing the distilled water).

The pH of the distilled water added to the EW experiments was around 6, while that of the 0.047M hydrochloric acid solution used in the EA runs was 1.3. In the EC cases, as the system was sealed for injection of CO₂, the pH of the coal slurries could only be estimated. Assuming that the dissolution of CO₂ in the water was close to equilibrium after continuous injection under 30 bars for one hour, the concentration of CO₂ was approximately 1kg/L (20°C, 30 bars) [309]. Based on the equilibrium constant of dissolved CO₂, the pH of the coal water slurries inside the cylinder was estimated to be 2.5. Therefore, the acidity of the coal-water slurries in the experiments increased in the order EW<EC<EA.

Steam was used as an alternative means of heating (with hot water flushing) to simulate the conditions of larger scale MTE runs. ~300mL distilled water (in SF experiments) or 'recycled water' from the SF run using the same coal (in SR experiments) was preheated to ~180°C in a separate vessel (WPV in Figure 7-51) before each run. After the pressure vessel was loaded with coal (only) and sealed, this hot water was forced by pressurised steam to pass through the coal in the vessel. As soon as the hot water was used up (signalled by steam emerging from the water outlet), steam was conducted directly to the cylinder until the temperature inside the vessel increased to the intended value (~150°C).

The steam supply was then cut off and the mechanical compression force applied. It should be noted that, in the steam heating experiments, it was difficult to control the temperature precisely and the temperature decreased gradually by 20-30°C over the compression period.

For all the experiments, the temperature, fluid pressure, applied mechanical force and position of the piston were measured as a function of time and recorded.

For each run, the masses of raw coal and dewatered product coal were measured and their water contents determined. Both the product water and rinsing water samples were filtered using 0.45µm Teflon filters. Samples were stored below 4°C for subsequent use.

The methods used for the water analysis are described in Chapter Two. There were some small differences for the work reported in this chapter. Since the water samples were filtered with 0.45µm filters, the total organic carbon determined by a DIMATOC 100 TOC analyser could be directly equated to dissolved organic carbon (DOC) (see Section 5.2.1). Sodium, potassium, calcium, magnesium and iron in the water samples were quantified using a Perkin-Elmer 1100B atomic adsorption spectrometry (AAS). Chloride and sulphate were measured at the Water Studies Centre, Monash University, using a flow injection colorimetric method.

7.2.2. *Water and Acid Extraction of Lignites*

The purpose of the extraction experiments was to remove the inorganics in their original state so as to reflect and further the understanding of their behaviour during MTE treatment, rather than determining the total water/acid extractables. Therefore, the raw lignites (not dried) were used for both water and acid extraction experiments and the extraction was carried out using only one batch of water or acid.

The three lignites were subjected to extraction using distilled water and dilute hydrochloric acid (HCl). The lignites were ground to very fine particles and the moisture content was measured prior to use. Two 10g portions of each coal were placed each in a plastic conical flask. Plastic rather than glass flasks were used to prevent extraction of sodium, etc. from the glass material. One portion was mixed with 50mL distilled water and the other with

50mL 2M HCl. The flasks were then sealed and fixed on an electrical mixer. The water and acid extractions were continued for ~48 hours at room temperature.

After extraction, the contents of the flasks were filtered with a filter paper followed by a 0.45µm Teflon filter. The filtrates were analysed for sodium, potassium, calcium, magnesium and iron using an AAS.

Water extraction of the three lignites was also carried out using slurries with different coal to water ratios (Table 7-30). Different amounts of each coal were each added to 50mL of distilled water and the slurries extracted for ~48 hours. The extracts were filtered and analysed as above. The selection of a maximum 30g Hambach lignite sample instead of the maximum 50g used for the other two lignites was because the coal absorbed so much of the added water in the 50/50 (w/v) coal water mixture that there was little residual water to allow effective extraction.

7.3. Inorganics Removed by Water and Acid Extraction

In this section, the results of the removal of inorganics from lignite by water and acid extraction are discussed.

7.3.1. Water Extraction of Different Amounts of Coal

For all the elements analysed, their concentrations in the water extracts increased as the ratio of coal to water increased (except for iron in Loy Yang B and Bowmans B where concentrations were very low and the variation could be ascribed to analytical error). However, when the data were recalculated as percentage removal of the total amount of the elements in the raw coal, the trends were different, as shown in Table 7-30 (errors $< \pm 1$ in the last significant figure).

Table 7-30. Percentage removal of selected inorganics by water extraction.

	Coal/water (g, wb/mL)	pH	Na%	K%	Ca%	Mg%	Fe%
Hambach	0.5/50	~6	40	16	0.1	0.09	0.1
	1/50	~6	24	10	0.1	0.1	0.2
	10/50	~6	13	5.7	0.06	0.08	0.07
	30/50	~6	10	4.1	0.07	0.1	0.04
Loy Yang B	0.5/50	~6	62	12	9.9	0.7	1.1
	1/50	~6	60	13	3.2	1.8	0.5
	10/50	4-5	55	14	3.8	10	0.06
	50/50	4-5	55	13	5.8	18	0.02
Bowmans B	0.5/50	~6	61	42	0.4	0.5	0.2
	1/50	~6	62	47	0.4	0.9	0.2
	10/50	4-5	60	39	2.1	3.7	0.03
	50/50	4-5	54	33	1.8	4.3	0.005

It is assumed that water extraction of lignite mainly removes water soluble inorganics (usually present in 'salt' form) that are physically contained within, or dissolved in, the pore water of lignite and possibly some organically bound cations dissociated from the surface functional groups [310]. The removal of small proportions of calcium and magnesium as organically bound cations by water extraction has been suggested by studies on Victorian lignites [281, 284]. Therefore, the inorganics that remain in the coal after water extraction include non-soluble minerals, most of the organically bound cations and/or the water solubles that could not be extracted under the conditions employed.

It can be seen in Table 7-30 that, in most cases, the water extraction removed a large proportion of the sodium, a smaller proportion of potassium, much smaller proportions of calcium and magnesium and very little iron. The large proportions of sodium and potassium removable by water extraction suggest that significant proportions of these elements were present in the lignites as soluble salts in pore water. The results that small proportions of the calcium and magnesium and even smaller proportions of the iron were removed by water extraction imply that these elements were mainly present in the lignites in water insoluble forms, either as exchangeable cations or in mineral forms. These observations are consistent with the results for inorganics removal by MTE treatment of

some Victorian and South Australian lignites discussed in Chapter Six and those of previous investigations on Australian lignites [115, 116]. In the Hambach lignite, small proportions of major elements in dissolved form were previously observed for this coal [53].

The percentage removal of sodium and potassium generally decreased with increasing coal to water ratios, except for that of the potassium in Loy Yang B which varied within error (Table 7-30). It should be noted that the extraction of lignite using a certain amount of water is not expected to continue until all the water soluble inorganics are in the aqueous phase; rather, an equilibrium will eventually be reached, with inorganic elements distributed between the coal and aqueous phases. Therefore, the extent of the removal of inorganics depends not only on the form of the inorganics present in the coal, but also on the length of the extraction period [130, 284] and the coal to water ratio of the slurry [311]. For water soluble inorganics, it is expected that equilibrium would be reached more rapidly, giving more inorganics in the aqueous phase for smaller coal to water ratios. Given ~48 hours of extraction, with sufficient water and only a small amount of coal (0.5/50 and/or 1/50 w/v), the removal of the water soluble portions of sodium and potassium may be considered complete. This means 40% and ~60% of the sodium in Hambach and the two Australian lignites, respectively, may be present as soluble salts in coal water. Likewise, 16%, 12-13% and 42-47% of the potassium in Hambach, Loy Yang B and Bowmans B may be present as soluble salts. As the coal to water ratios increased, significant proportions of the sodium could still be extracted from the two Australian lignites (>50%), whereas only ~10% of the sodium was removed from Hambach. This is possibly because the water extraction of Hambach at high coal to water ratios was not as efficient as for the other coals due to the smaller amount of free water available for extraction because more water was absorbed by the coal (refer to Section 7.2.2).

Unlike the percentage removal of sodium and potassium, the percentage removal of calcium and magnesium from Bowmans B and of magnesium from Loy Yang B increased substantially as the coal to water ratio increased. In Hambach, the proportions of calcium and magnesium extracted by water did not vary significantly with coal to water ratio. As calcium and magnesium in lignites are often largely present in water insoluble forms, one of the mechanisms of removal for these elements would probably be exchange of

organically bound cations for hydrogen ions in a weak acidic environment. The values of pH in the water extracts were consistent with the occurrence of such a process. When extracting small amounts (i.e. 0.5g and 1g) of the Loy Yang B and Bowmans B lignites, the pH in the water extracts was ~6, as in the distilled water used. When larger amounts of these two coals (i.e. 10g and 50g) were added, the pH of the extracts decreased to 4-5 (See Table 7-30). Ion exchange process with hydrogen ions would be promoted in the more acidic environment in the cases of the Australian lignites, leading to the removal of larger proportions of these elements. In the Hambach cases, the pH of all the water extracts was about 6, so that no effect on ion exchange would be expected.

The concentration of the iron in all water extracts was very low, so that any apparent differences were smaller than experimental error and no valid comparisons could be made. The very small proportions of the iron in all the cases suggest that this element was present in all three lignites predominantly in water insoluble forms.

7.3.2. *Comparison of Water Extraction with Acid Extraction*

Table 7-31 presents the percentage removal of selected inorganics by water extraction and acid extraction (coal:water 10g:50mL). Calculated errors are $\leq \pm 1$ in the last significant figure.

Table 7-31. Percentage removal of selected inorganics by water extraction and acid extraction.

		Na%	K%	Ca%	Mg%	Fe%
Hambach	water	13	5.7	0.06	0.08	0.07
	acid	102	58	102	94	74
Loy Yang B	water	55	14	3.8	10	0.06
	acid	84	33	19	92	39
Bowmans B	water	60	39	2.1	3.7	0.03
	acid	89	99	58	92	56

*10g coal (wb) : 50mL water or 2M HCl.

Acid extraction removes not only the water soluble portions of the inorganics but also cations originally bound to the organic matrix and dissolves acid soluble minerals (such as hydrous oxides and carbonates) and some cations associated with clay minerals [116, 312, 313]. The inorganic components not leached from the coal after acid extraction are

supposed to be mainly incorporated in acid insoluble minerals, particularly clays, quartz and pyrite [314] and may also include acid extractable minerals and exchangeable cations that could not be removed under the extraction conditions.

Under the same conditions (Table 7-31), acid extraction removed significantly larger proportions of all the five inorganic elements from all lignites than water extraction. Comparison of the results for the three lignites shows that the removal of all five elements increased most for Hambach. Although the additional removed material may include water solubles that were not removed by water extraction, the considerably bigger difference between the proportions of acid extractables and water extractables for all the elements for Hambach than for the two Australian lignites suggests that larger proportions of these elements were present as exchangeable cations and/or acid soluble minerals in Hambach than in the Australian lignites.

Comparison between the water and acid extractable fractions confirms that, for calcium, magnesium and iron, exchangeable cations and/or acid soluble minerals accounted for significantly larger proportions of these elements in all three lignites than the water solubles.

After acid extraction, sodium and calcium in Hambach and potassium in Bowmans were almost fully extracted. >90% of the magnesium was removed from all three lignites. However, substantial proportions of some elements still remained, such as calcium and magnesium in Loy Yang B lignite. Raw coal analysis (Table 2-3) indicates that all five elements in these three lignites are almost totally acid extractable, as defined by the standard analytical method. The results suggest that the method is only a rough guide to what can be extracted in a more practical situation such as the extraction conditions employed in this work.

7.4. Water Removal by MTE Processing

The moisture contents of all the MTE products were between 28% and 38% (wb). For Hambach, Loy Yang B and Bowmans B with initial moisture contents of 54%, 67% and 55% respectively, the average moisture removal was 63%, 74% and 60%, respectively. The lignite with the highest initial moisture content (i.e. Loy Yang B) lost more water during MTE processing. Cavallaro and Quast [315] noticed a similar effect during

mechanical dewatering; the lignites with a higher initial moisture content underwent greater dewatering than the drier coals.

Figure 7-52 shows the percentage moisture removal from the three lignites under different MTE processing conditions.

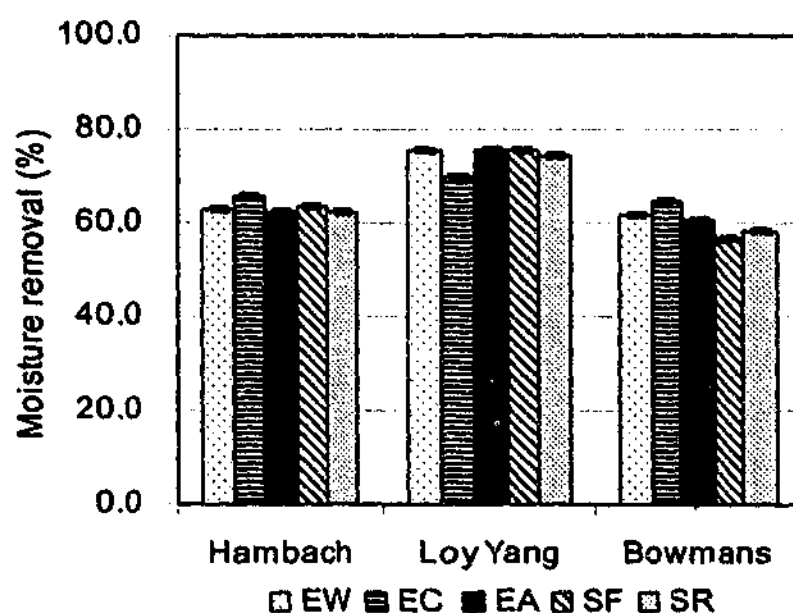


Figure 7-52. Percentage removal of the initial water in different lignites by MTE*.

*For key to conditions refer to Table 7-29.

The percentage moisture removal from the lignites during MTE was essentially independent of the process conditions investigated in this work (Figure 7-52). Small differences could be due to experimental errors such as small temperature deviations.

Thus, it can be concluded that, at constant processing temperature and pressure, the dewatering effect of MTE was not significantly influenced by the conditions investigated, e.g. injection of CO₂, use of hydrochloric acid or heating with steam.

7.5. Organics in MTE Process Water

In this section, the removal of organics as dissolved organic carbon (DOC) from the lignites under different conditions is compared. Results of GC-MS characterisation of major organic components in the MTE water removed from Hambach at 200°C are also summarised.

7.5.1. Organic Carbon Removal by MTE processing

In the discussion in this chapter, variations of MTE processing conditions refer to either different acidities of the coal water slurry (i.e. processing medium) in EW, EC and EA runs or to the use of different heating methods in comparisons between the EW, SF and SR runs.

7.5.1.1. Effect of the acidity of processing medium

Figure 7-53 shows the loss of organic matter (as DOC) to MTE process water from the lignites for processing media of different acidities.

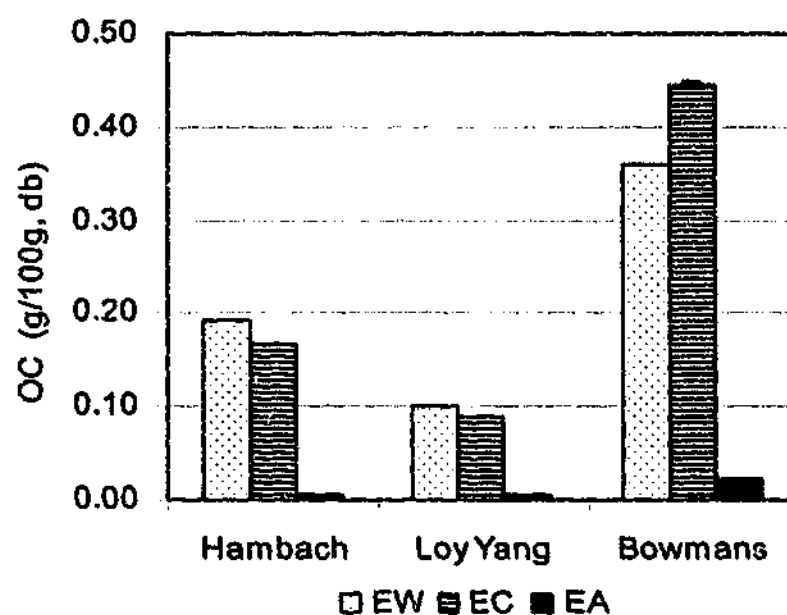


Figure 7-53. Organic carbon removal versus MTE processing medium*.

*For key to conditions refer to Table 7-29.

Figure 7-53 shows that, for all three lignites, the organic carbon removal decreased as the acidity of the coal water slurry was raised, with the only exception being the Bowmans B case under the weak-acid condition (EC). The use of 'strong' acid (EA) instead of water (EW) significantly reduced the amount of organics removed from these lignites by MTE treatment. The injection of CO₂ (EC) only slightly reduced the organic carbon removal from Hambach and Loy Yang B. In all three cases (EW, EC and EA), Bowmans B exhibited the greatest tendency to release organics to the water phase followed by Hambach then Loy Yang B.

The decreased release of organic species into MTE water with increasing acidities of the coal water slurry could be related to the effect of pH on the proportion of ionised and non-ionised forms of organic functional groups. Oxygen functional groups in lignite are present either in ionised forms, such as carboxylates or phenolates associated with exchangeable cations, or in non-ionised forms associated with hydrogen. During MTE treatment in an acidic environment, as the pH decreased, the proportion of the non-ionised carboxylic acid or phenol form would increase at the expense of the ionised (carboxylate or phenolate) form (refer to Figure 7-54). The non-ionised forms, being less polar, would be expected to be less soluble than the ionised forms, so that the solubility of the organic material would indeed be expected to decrease with decreasing pH, as observed.

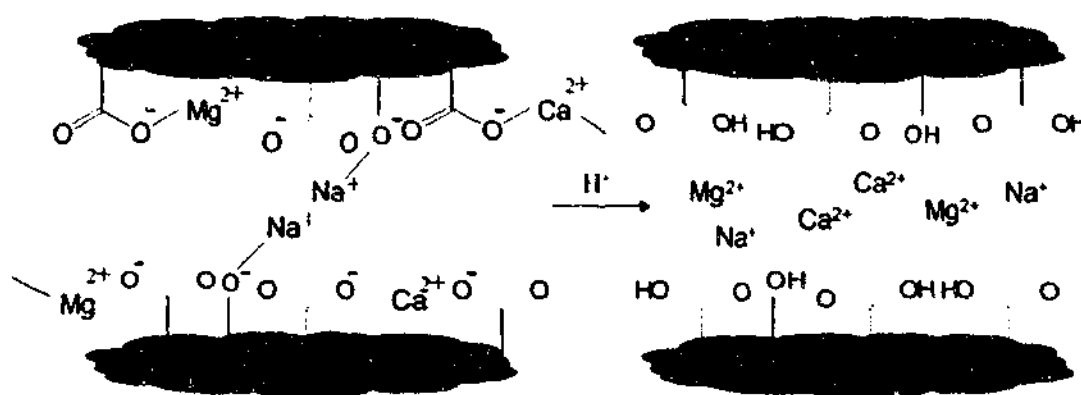


Figure 7-54. Change in state of acidic functional groups in lignite in an acidic environment.

The proceeding argument also shows why, as observed in a number of studies [316-318], the treatment of lignites with aqueous hydrochloric acid can improve the solubility of lignite in organic solvents.

The above argument could not explain why organic carbon removal from Bowmans B in the EC case was higher than in the EW case. The reason for this apparently anomaly is unclear.

7.5.1.2. Comparison of heating methods

In Figure 7-55, organic carbon removal under the standard condition (EW) is compared with that from the processes using steam for heating and hot distilled water (SF)/‘recycled’ water (SR) for preheating.

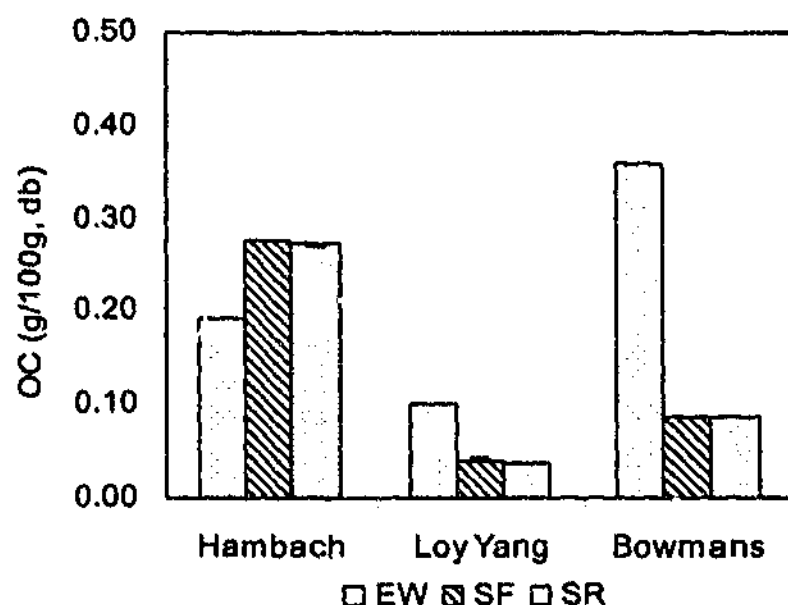


Figure 7-55. Organic carbon removal versus MTE heating methods*.

*For key to conditions refer to Table 7-29.

Figure 7-55 shows that there was a significant decrease in organic carbon removal from Loy Yang B and Bowmans B when using steam/hot water (SF and SR) instead of electrical heating (EW). However, an increase was observed in the case of Hambach. Organic carbon in the MTE water from SF and SR runs was present at similar levels.

The effect of using different heating methods on organic carbon removal may be related to the different temperature control processes during the runs. Over the course of the SF and SR runs, there was a temperature reduction of 20-30°C (compared to the constant temperature in the EW runs). As concluded in Chapter Five, processing at lower temperatures leads to reduced removal of organic carbon. In addition, in the EW experiments, the time required for heating the coal inside the chamber to the desired temperature was much longer than in the SF and SR cases (~3hr vs <0.5hr). Over the much longer time at elevated temperature, thermal decomposition of the organic structures and dissolution of the fragments, which contribute to the organic carbon level in the water phase, might proceed to a greater extent. Therefore, the lower temperature and much shorter heating time may be the two main reasons that much smaller amounts of organic carbon were removed from Loy Yang B and Bowmans B during the SF and SR runs.

It is not clear why the organics released from Hambach exhibited an opposite trend. It is worthy of mention that, in the steam/hot water processes, samples of the two Australian

lignites in the chamber were not pre-compressed prior to heating, as attempts of pre-compression failed to allow hot water and steam to efficiently pass through the coal bulk. However, pre-compression was applied to the Hambach lignite, resulting in a more compact coal bulk which would probably allow more efficient thermal conduction than for the Australian lignites.

It is notable that organic carbon in the 'recycled' water carried over from the SF run did not lead to an increase of the total organic carbon level in the water from that for the corresponding SR run.

7.5.2. *Characterisation of Organic Composition of MTE Water from Hambach*

GC-MS identification and quantitation of major organic components was only carried out on the product water from the MTE treatment of Hambach at 200°C, 12MPa. All SPE-GC-MS experimental methods and calculation methods introduced in Chapters Three and Four were applied to the identification and quantitation of organic components in this water sample.

In general, major organic components identified in the water from Hambach were very similar to those identified in the water from other lignites treated at 200°C, 6MPa (refer to Table 4-14 to Table 4-16). Only a few compounds, such as 3,4,4-trimethyl-2-cyclopenten-1-one and 2,6-chlorophenol, were not identified in the water from other lignites. Carboxylic acids, phenols, cyclic ketones, furanones and benzofuranones were the major compound groups present in this water, as for the MTE water from Australian lignites.

Table 7-32 lists the amounts of selected organic compounds and compound groups in the MTE water from Hambach (200°C, 12MPa). Results (from Chapter Five) for Loy Yang A and Lochiel, which released the lowest and highest levels, respectively, of most of the identified organic components and compound groups at 200°C, 6MPa are also shown in the same table for comparison. The unit for individual compounds and total phenolic compounds is mg/kg. The unit for total acids and organic carbon is g/kg.

Table 7-32. Amounts of selected organic components and major groups in MTE water from Hambach (HB) compared with Australian lignites.

		HB	LYA	LC
		200°C/12MPa	200°C/6MPa	200°C/6MPa
Phenols (mg/kg, db)	phenol	0.23	0.0081	1.1
	4-methyl phenol	0.13	0.014	0.14
	2,4-dimethyl phenol	0.047	0.0095	0.042
	2-methoxy phenol	5.0	0.42	6.9
	2-methoxy-4-methyl phenol	0.033	0.026	0.11
	1,2-benzenediol (catechol)	0.030	0.033	0.036
	2,6-dimethoxy phenol	0.015	0.18	0.89
	vanillin	0.090	0.058	0.12
Acids (mg/kg, db)	1,2,3-benzenetriol (pyrogallol)	-	0.069	-
	succinic acid (C4)	0.065	11	19
	benzoic acid	0.52	1.4	4.2
	pimelic acid (C7)	0.93	0.60	7.1
	sebacic acid (C10)	0.29	0.62	2.5
	1,2,4-benzenetricarboxylic acid	3.5	18	37
Total mono- & di-hydroxy phenols (mg phenol/kg, db)		24	3.0	29
Total tri-hydroxy phenols (mg pyrogallol/kg, db)		-	0.26-0.85	0.22-0.73
Total aliphatic acids (g succinic acid/kg, db)		0.69	0.43	0.80
Total aromatic acids (g benzoic acid/kg, db)		0.61	0.19	0.75
Total identified compounds (g/kg, db)		1.3	0.62	1.6
OC (g/kg, db)		4.7	1.3	3.7

- undetected

It can be seen that the results for Hambach are comparable with the cases of the Australian lignites using a different MTE rig and treated at lower pressures. The major difference of the results is that the five selected carboxylic acids (but not total acids) were present in the water from Hambach at lower levels. These results indicate that although the relative

abundance of individual components might be different, the abundance of major compound groups and total identified compounds present in the water from Hambach was not significantly different from that in the other cases.

Table 7-33. Relative abundance of major compound groups in total identified organics and organic carbon in MTE Water from Hambach.

		HB	LYA	LC
		200°C/12MPa	200°C/6MPa	200°C/6MPa
% in total identified compounds	Mono- and di-hydroxy phenols %	1.8	0.48	1.8
	Tri-hydroxy phenols %	-	0.042-0.14	0.014-0.046
	Total phenols %	1.8	0.52-0.62	1.9
	Aliphatic acids %	52	69	51
	Aromatic acids %	46	30	47
	Total acids %	98	99	98
% identified compounds (as carbon) in OC		15	24	23

Relative abundance results in Table 7-33 also demonstrate that major organic compound groups in the MTE water from Hambach were present in similar proportions as in the water from the Australian lignites (nearly identical to the Lochiel case). Phenolic compounds accounted for very small proportions of the total identified compounds. 98% of the GC-MS detectables were carboxylic acids. Components identified by GC-MS estimated to account for 15% of the total organic carbon.

That the organic constituents in the MTE water from Hambach were similar to those identified for the Australian lignites is possibly due to similarities in the distribution of oxygen containing functional groups in these lignites. The oxygen content in Hambach (26%) is similar to that in the Australian lignites investigated (refer to Table 2-3). Rhenish lignite has a high oxygen content (23.4-27.8%); carboxyl groups are the most important oxygen-containing functional group followed by hydroxyl groups and/or ethers and ketones with small proportions of methoxy groups [319]. A similar distribution of oxygen containing functional groups is present for Victorian lignites [239, 274], and the behaviour of South Australian lignites suggests similarities in their composition also (Chapter Five).

7.6. Inorganics in MTE Process Water

The discussion in this section focuses on the behaviours of monovalent sodium and divalent calcium and magnesium during MTE processing. The concentrations of potassium and iron in some cases were too low to permit meaningful comparison and discussion.

The levels of the inorganics in the MTE water from the various lignites were quite different. In order to compare the results for the three lignites in the same graph, the data are expressed as percentage removal of the total amount of the respective species present in the raw coals (refer to Table 2-3).

7.6.1. *Comparison of MTE Treatment to Water Extraction*

In contrast to the water extraction experiments, the MTE treatment was carried out at elevated temperatures; in a notably shorter period of time (2-4 hours vs >48 hours); under pressure and without agitation of the coal water slurry. In the following discussions where the results from the two types of treatment (MTE vs extraction) are compared, it should be kept in mind that some aspects of the MTE conditions might benefit the removal of inorganics from the lignites, such as the elevated temperature and pressure. In particular, Jiménez-Carmona et al [119] observed that extraction of the cations in coal was achieved in a much shorter time at high temperature (300°C) than at low temperature (180°C) during subcritical water extraction. Other aspects would inhibit inorganics removal, such as the shorter period of time and the absence of agitation. The observed behaviours would be the consequence of the combined effects of all factors.

Table 7-34 summarises the percentage removal of sodium, calcium and magnesium by the standard MTE treatment (EW) and the water extraction experiments (errors $\leq \pm 1$ in the last significant figure).

Table 7-34. Percentage removal of selected elements by MTE and water extraction*.

	Treatment	Coal : water (w/w)	Na%	Ca%	Mg%
Hambach	Extraction	1:100	40	0.1	0.09
		1:1.7	10	0.07	0.1
	MTE (EW)	1:1	31	0.2	1.3
Loy Yang B	Extraction	1:100	62	9.9	0.7
		1:1	55	5.8	18
	MTE (EW)	1:1	54	19	14
Bowmans B	Extraction	1:100	61	0.4	0.5
		1:1	54	1.8	4.3
	MTE (EW)	1:1	54	3.8	8.0

* For MTE conditions refer to Table 7-29; For water extraction conditions and data refer to Table 7-30.

For sodium, results show that the water extraction of a small amount of coal (coal:water 1:100) removed a larger proportion of this element than MTE and water extraction using large amount of coal (coal:water=1:1). Comparing the latter two cases, for the two Australian coals, the proportions of the sodium removed by MTE and water extraction were similar, whilst, for Hambach, the MTE treatment improved the sodium removal compared to the water extraction.

The sodium removed by water extraction was probably mainly present in a water soluble form in the lignites investigated (see Section 7.3.1) and the fact that less sodium was removed by MTE (EW) than by water extraction of small amount of coal (1:100) implies this was also true for sodium removed during the EW process. For the two Australian lignites, the MTE treatment at elevated temperature in a shorter time achieved similar results for sodium removal compared to the water extraction at 1:1 coal to water ratio. Assuming that the water extraction of lignites at the low coal to water ratio (1:100) removed all water soluble sodium from the three lignites (see Section 7.3.1), both the MTE and water extraction were able to remove a majority (~90%) of the water soluble sodium from these two lignites. In the Hambach case, as mentioned in Section 7.3.1, water extraction of Hambach at high coal to water ratios was inefficient due to the little free water available for extraction. The MTE treatment employing elevated temperature

enabled the removal of larger proportions of the sodium from this coal, i.e. ~80% of the total water soluble sodium.

The behaviour of calcium and magnesium during MTE and water extraction was significantly different from that of the sodium. In all cases, the percentage removal of these elements was much lower than that of the sodium for the same lignite. However, the MTE treatment involving relatively severe conditions did facilitate a further removal of these elements from all three lignites (except for magnesium in Loy Yang B).

As discussed in Chapter Six and Section 7.3 in this chapter, calcium and magnesium in the Victorian lignites investigated were largely present as organically bound ions. During water extraction at room temperature, the removal of elements in these forms is likely to be a result of ion exchange process (by hydrogen), which is related to the low pH of the coal water environment, as suggested in Section 7.3.1. Nevertheless, during the MTE dewatering processes, the organically bound cations may be released into water associated with carbon based organic anions (e.g. carboxylates) in Victorian lignites (refer to Section 6.5.2.2 dealing with charge balance). An observation in the Hambach case may provide evidence for the removal of the organically associated elements during MTE related to processes other than ion exchange. The pH of the MTE process water from Hambach in the EW case was ~6 – the same level as in the water extracts of this coal, so that the further removal of both calcium and magnesium by MTE treatment was apparently not due to an effect of lower pH. That the MTE treatment removed larger proportions of the calcium and magnesium from all three lignites (except for magnesium in Loy Yang B) than the water extraction suggests a removal mechanism related to the more severe conditions of temperature and pressure, e.g. release of cation-organic complexes (carboxylates, etc.) from the coal structure.

7.6.2. *Effect of Acidity of Processing Medium*

7.6.2.1. Sodium

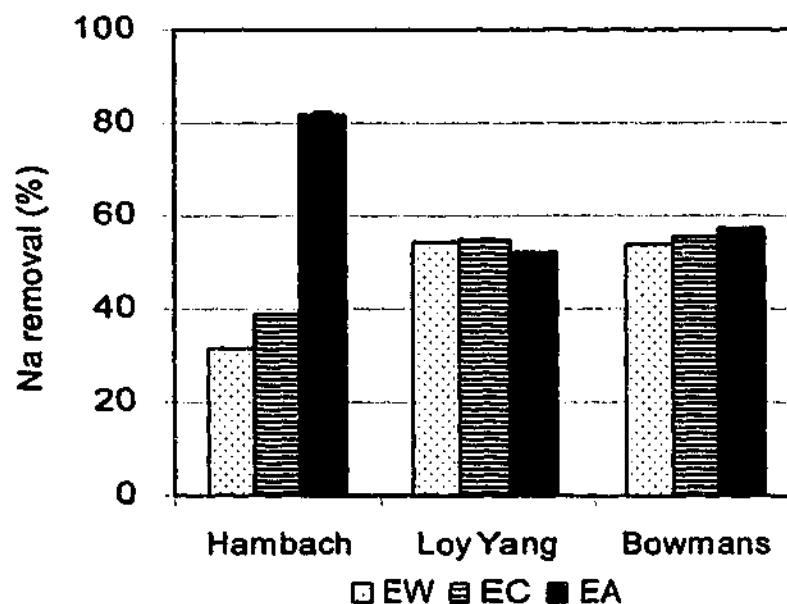


Figure 7-56. Percentage removal of Na versus MTE processing medium.

As shown in Figure 7-56, sodium removal from the Australian lignites was nearly independent of the acidity of the processing medium, whereas the removal from Hambach increased considerably with increasing acidity of the coal water slurries (from 30% to >80%), especially in the 'strong acidic' (EA) case. A greater effect of acid on sodium removal from Hambach lignite was also noted for ordinary acid extraction (Table 7-31).

The above observations further support the proposal that the 50-60% sodium removed by MTE treatment from the two Australian lignites were originally present as water soluble salts. Hence, the extent of sodium removal was not affected by the acidity of the coal water slurries. It also suggests that under the MTE conditions employed, only the water soluble portions of the sodium in the two lignites could be removed. In the Hambach case, the substantially greater proportions of the sodium removed during the EA runs suggest that the element was originally present in either an organically bound form or in an acid soluble mineral form.

Compared to the results from acid extraction, by which >80% and ~100% of the sodium in the Australian lignites and Hambach, respectively, could be removed, MTE processing

removed smaller proportions of the sodium. This is likely due to the still weak acidic condition employed by MTE (0.047M vs 2M HCl for acid extraction).

In the case where the water insoluble portions of the sodium was removed (e.g. EA Hambach case), the removal of the sodium as exchangeable cations might have occurred, (in addition to any dissolution of the sodium as acid soluble minerals). As illustrated in Figure 7-54, when acid was introduced during MTE processing, any sodium cations exchanged onto the functional groups (such as carboxyl and phenolic groups) might be at least partially replaced by hydrogen as the acidic functional groups re-associated. This would lead to a further release of organically associated sodium into the water phase.

7.6.2.2. Calcium and magnesium

The behaviours of the two alkaline-earth metals during the MTE treatment were again similar in most cases and are therefore discussed together. The percentage removal of calcium and magnesium in coal water slurries of different acidities is shown in Figure 7-57 and Figure 7-58, respectively.

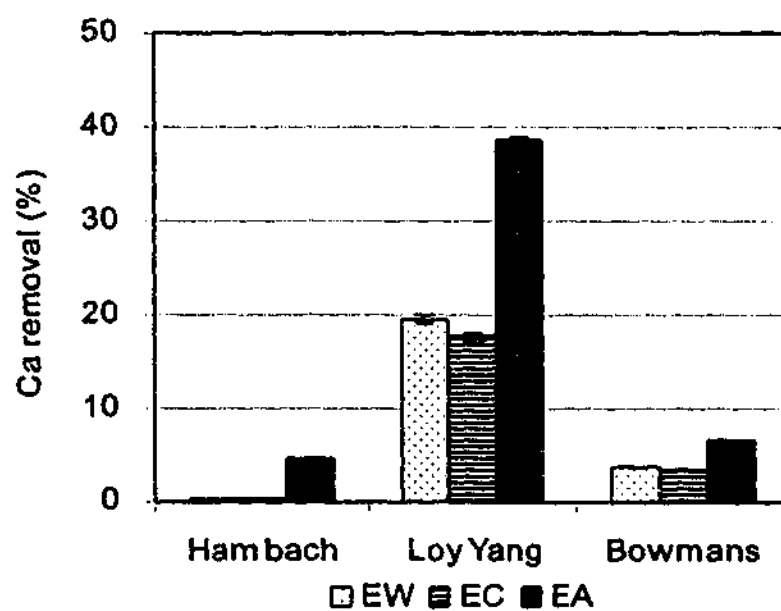


Figure 7-57. Percentage removal of Ca versus MTE processing medium.

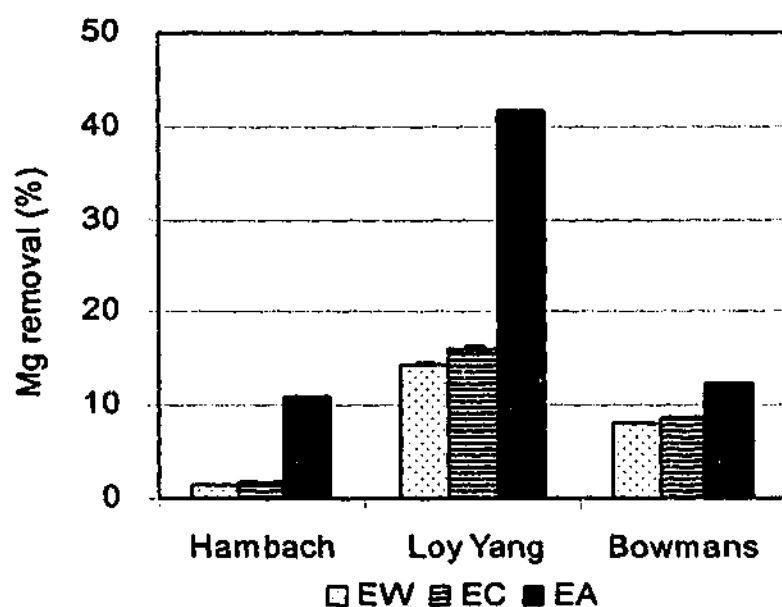


Figure 7-58. Percentage removal of Mg versus MTE processing medium.

Under the same condition, the proportions of calcium and magnesium removed from different lignites varied significantly. Loy Yang B released the largest proportions of both elements, while Hambach released the smallest proportions, with Bowmans B in between. This ordering of the magnitude is consistent with the results obtained from the water extraction experiments at similar coal to water ratios (Table 7-30). It can be deduced that the removal of these elements from Loy Yang B was more facile than from the other two lignites. However it is also the case, for all the lignites, that major proportions of the calcium and magnesium remained in an insoluble form.

For a given lignite, MTE treatment in the hydrochloric acid environment (EA) significantly improved the removal of the calcium and magnesium. The extent of the improvement in the Hambach case was the greatest (as for acid extraction), whereas the removal of both elements from Bowmans B only slightly increased. As calcium and magnesium in lignites were present mainly in water insoluble forms, the further removal of the elements under acidic conditions may be a result of either an ion exchange process removing the exchangeable cations (refer to Figure 7-54) or dissolution of acid soluble minerals. An increase in the pH of the MTE process water from all EA experiments (pH=2.5-4) relative to the pH of the hydrochloric acid solutions (pH=1.3) added prior to each EA runs may be

considered evidence for the occurrence of the exchange of cations with hydrogen, leading to reduced hydrogen ion concentrations.

The use of the CO₂/water system for removal of inorganics in lignite involves not only the coupling of water with carbon dioxide generating a weakly acidic solution that would be beneficial [305], but also penetration of carbon dioxide into the coal [320] along fault lines of mineral inclusion possibly resulting in the separation of the mineral matter from the coal matrix [305].

However, comparing the EC cases with the EW cases, the percentage removal of the calcium and magnesium from all three lignites was only slightly different. Although the variations were beyond analytical error (as shown by the error bars in the figures), the possibility that they were due to small variations in process conditions could not be excluded. The effect of injecting CO₂ to the MTE system on the removal of these elements could be concluded to be not significant.

7.6.2.3. MTE for coal beneficiation

Coal beneficiation involves the separation of mineral and inorganic matter from the combustible portion of the coal [321]. The removal of inorganic species by the MTE treatment recognised in the present work is expected to be of benefit for lignite utilisation. In this study, the two demineralisation methods using the carbon dioxide/water system and hydrochloric acid solution were combined with the MTE treatment. The efficiency of these treatments for overall removal of inorganics in lignite is discussed in this subsection.

It should be noted that the number of inorganic species selected for quantitation in this study was very limited relative to the numerous species that would be present in the MTE process water. Therefore, for the evaluation of the beneficiation efficiency (i.e. removal of total mineral matter) of the MTE treatment, it is more appropriate to use the data from ash analysis. Percentage ash removal by MTE in different processing media is shown in Figure 7-59.

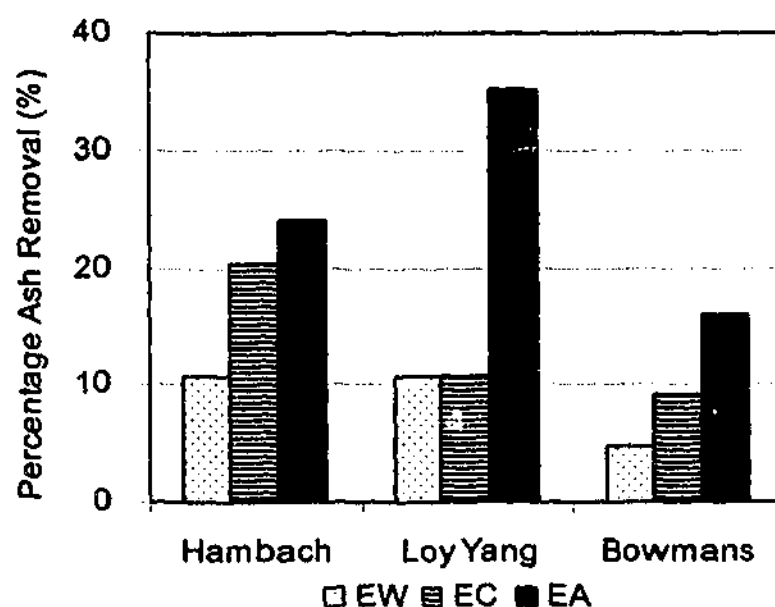


Figure 7-59. Percentage ash removal by MTE in different processing media.

Initial ash yields of the raw Hambach, Loy Yang B and Bowmans B lignites were 5.3, 3.7 and 16.3% (db), respectively. Under the same processing condition, the MTE treatment removed the largest quantities of ash from Bowmans B among the three lignites. However, as Bowmans B has the highest ash level, the proportion of the ash removed from this coal was the smallest.

In the EW cases, i.e. the MTE treatment without any demineralisation assistance, over 10% of the total ash from Hambach and Loy Yang B and 5% from Bowmans B could be removed. This outcome offers an additional benefit of MTE besides its moisture removal capability.

In the EC cases, the de-ashing effect of the carbon dioxide/water system can be seen more clearly when the reduction of ash yields in the MTE coal products, rather than the levels of individual elements present in the MTE water, is examined. For Hambach and Bowmans B, the EC treatment led to noticeable further ash removal relative to EW treatment. The further reduction was 9.4% and 4.3% of the total ash yield in the two lignites, respectively. The results were comparable with the 5-15% ash reduction obtained by Sapienza et al [305], who utilised a pressurised carbon dioxide/water system for bituminous coal beneficiation. The ash removal from Loy Yang B was not affected by the introduction of CO₂ in the system. It is likely that the inorganic species removed from Loy Yang B in the

EW and EC cases were originally mainly present in water soluble forms. Therefore, the removal was not affected by slightly increased acidity of the coal water slurries.

An increase of the acidity of the coal water slurries using hydrochloric acid solutions (i.e. the EA cases) significantly increased the ash reduction from all three lignites. Up to 35% of the total ash from Loy Yang B, 24% from Hambach and 16% from Bowmans B were removed.

7.6.3. *Comparison of Heating Methods*

Besides two major differences between the EW experiments and the SF and SR experiments – higher temperature and longer heating period in the former cases – which affected the removal of organic carbon from the lignites, there were two factors that might influence the behaviours of the inorganics during these runs. First, the total quantities of water entered the system in the SF and SR cases were larger than for the EW experiments. Second, the coal water slurries during the EW treatment were left motionless inside the compression vessel, while in the SF and SR cases the flows of water and steam condensate continuously flushed the coal bulk prior to compression.

Therefore, the removal of the inorganics in different cases was not only affected by the forms of these inorganics present in lignites but also by the differences in processing conditions.

7.6.3.1. *Sodium*

The percentage removal of sodium in the experiments using steam for heating is shown in Figure 7-60. The results from the runs using 'standard condition' (EW) are shown in the same figure for comparison.

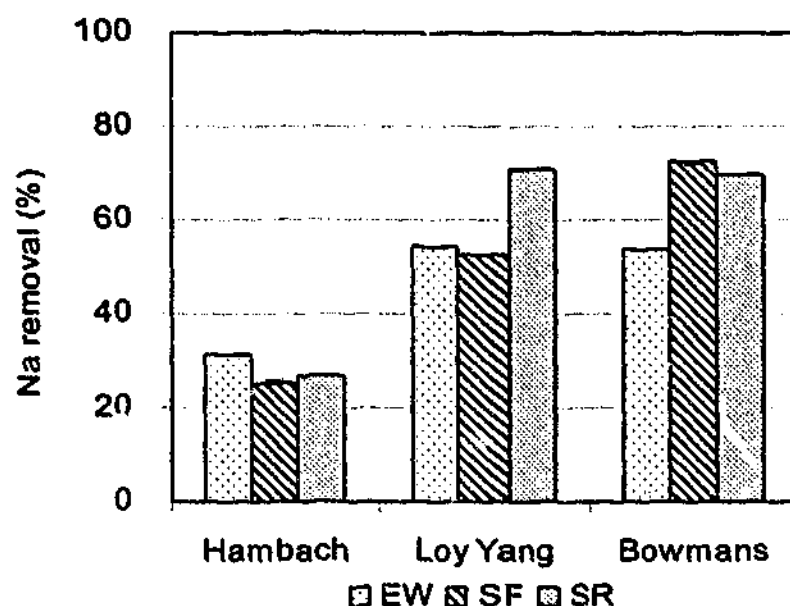


Figure 7-60. Percentage removal of Na versus MTE heating methods.

MTE treatment using steam for heating removed smaller proportions of the sodium from Hambach but larger proportions from the Australian lignites, except for the SF case of Loy Yang B (Figure 7-60).

MTE treatment with no increase in the acidity of the processing medium mainly removed the water soluble portions of the sodium from the lignites (see Section 7.6.1). Therefore, the extent of the removal largely depended on the ratios of coal to water, as discussed in Section 7.3.1 and 7.6.1. In the EW runs, the ratio of coal to water was 1:1 (650g/650mL). For the SF and SR experiments, the added water was from two sources: (a) hot water for preheating and (b) steam condensate. Since the condensation of steam continued until the temperature was high enough, the final volumes of the product water from the SF and SR treatment of Hambach, Loy Yang B and Bowmans B were approximately 400mL, 1000mL and 700mL more than those from the corresponding EW experiments, respectively. Moreover, during the heating period, the hot water and steam condensate flushed through the coal bulk continuously, equivalent to an agitation effect. This period was longer for the Australian lignites as it was more difficult for the water to pass through these lignites than in the Hambach case. Therefore, during the SF and SR runs, both the presence of a larger amount of water and the water flushing effect would be expected to increase the removal of the sodium compared to the EW case. This was observed for the two Australian lignites.

Sodium removal from Hambach was affected by different factors. For this coal, the removal of sodium at high coal to water ratios was very difficult, as shown by the water extraction experiments (Section 7.3.1). The MTE treatment at elevated temperature enabled further removal of the sodium in these cases (refer to Table 7-34). In the SF and SR runs, the further addition of 400mL water resulted in a coal water slurry of 1:1.6, similar to the highest coal to water ratio case of water extraction and therefore of little help in this connection. Thus any effect of heating method on the removal of sodium from Hambach would be due principally to temperature and possibly to the processing time. Since the SF and SR treatments were at temperatures 20-30°C lower and for a much shorter time than the EW treatment, it would be expected that SF and SR would tend to remove less sodium from Hambach, as observed.

7.6.3.2. Calcium and magnesium

The results for calcium and magnesium in the EW, SF and SR experiments are shown in Figure 7-61 and Figure 7-62, respectively.

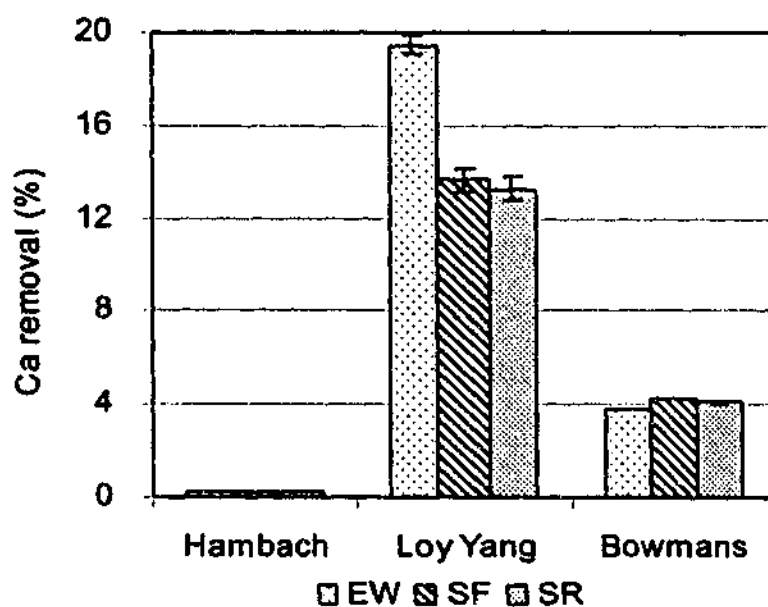


Figure 7-61. Percentage removal of Ca versus MTE heating methods.

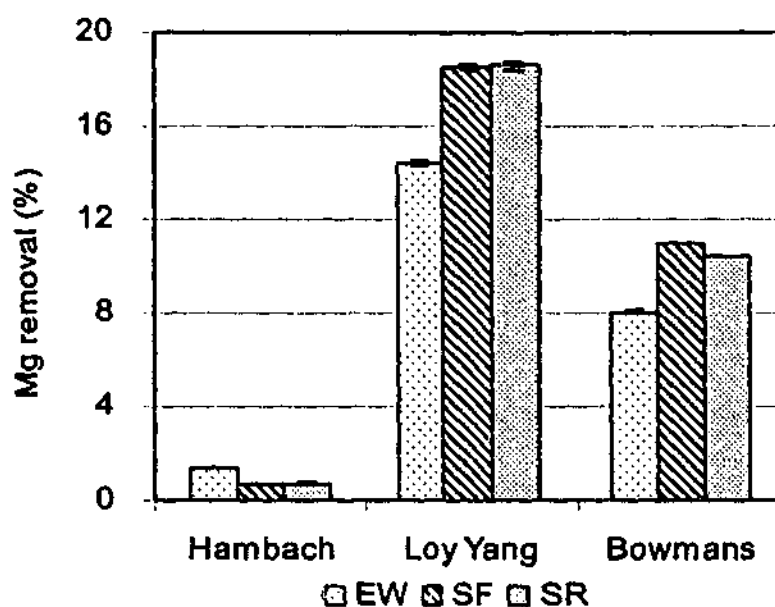


Figure 7-62. Percentage removal of Mg versus MTE heating methods.

In the case of calcium, as can be seen in Figure 7-61, very small proportions of the element were removed from Hambach and Bowmans B (~0.3% and ~4%, respectively). For these two lignites, the calcium removal was basically independent of the different heating methods employed during MTE treatment. This is likely due to the difficulty of removing calcium from these lignites. Any variations of the processing conditions were not significant enough to affect the calcium removal from these two lignites.

In the case of Loy Yang B, calcium was removed in much larger proportions compared to the cases of the other two lignites. Using steam for heating, its removal was significantly reduced. As this element was present mainly in water insoluble form in lignites and its removal could be associated with organic anions during MTE treatment (Section 6.5.2.2), it appears that the higher temperature and much longer heating time in the EW case would assist the removal of this element.

Results in Figure 7-62 show that the effect on removal of the magnesium from Hambach of different heating methods was similar to that for removal of calcium from Loy Yang B. The effect can again be explained by the lower temperature and shorter heating time employed in the SF and SR cases.

However, for the two Australian lignites, magnesium removal increased when using steam for heating in the SF and SR cases. This behaviour of magnesium in these cases was

similar to that of the sodium in the two Australian lignites, although the removal mechanisms of magnesium, which was present in lignites mainly in water insoluble forms, were likely different from those for sodium. The observation could not be explained by the effect of temperature or different heating time. Using the information available at present, this effect could not be explained.

7.6.3.3. Use of the 'recycled' water

As can be seen in Figure 7-60 to Figure 7-62, in most cases, the two types of MTE treatment (SF vs SR) achieved similar results in terms of the removal of selected elements.

The only difference between the SF and SR experiments was that the SR runs used about 300mL of the product water from the corresponding SF runs containing certain levels of 'contaminants' removed from the same coal. The amounts of selected elements contained in the reused water were ~15-20% of the total amounts of the respective elements in the water from the SR runs. As the proportions of the elements present in the water from the SF and SR runs were at the same level, it appears that the presence of certain amounts of the 'contaminants' in the added water actually reduced further removal of the inorganics during the SR treatment.

The consequence of using the 'contaminated' water during MTE may be related to a process similar to extraction equilibrium. Under a certain extraction condition, concentrations of the dissolved species in the water may reach a level when no further dissolution from the coal could occur. As the SF and SR experiments were carried out under nearly identical conditions, it is likely that the two processes reached a similar equilibrium state at which the inorganics could not be further removed. This would result in the same levels of the inorganics present in the water phase, despite the use of 'recycled' water.

7.6.4. *Cations and Anions in the MTE Process Water*

It is useful to compare the relative abundance of various anions and cations in the MTE water to gain a further insight into the behaviour or removal mechanisms of the inorganic elements during MTE processing.

Table 7-35 presents the charge equivalence ratios of selected cations to anions in the MTE water averaged from the data from the EW, SF and SR runs. The results from the EC and EA runs were not included as the charge balance in these cases involved considerable amounts of carbonate and chloride that were not originally present in the system. The data with values that are close to 1 are marked in bold. For comparison purposes, the results for Loy Yang A and Bowmans A, discussed in Chapter Six, are also listed in the table.

Table 7-35. Average charge equivalence ratios of selected cations to anions released to MTE water.

		Na : Cl	Na : (Cl+SO ₄ ²⁻)	(Ca+Mg) :SO ₄ ²⁻	(Na+Ca+Mg) :(Cl+SO ₄ ²⁻)
		A	B	C	D
Hambach	200°C/12MPa	4.8	3.6	2.7	4.3
Loy Yang B	200°C/12MPa	0.90	0.80	1.7	0.98
Bowmans B	200°C/12MPa	1.7	0.91	0.39	1.1
Loy Yang A	150°C/6MPa	1.1	0.75	1.2	1.1
Loy Yang A	200°C/6MPa	1.3	0.80	0.93	1.1
Bowmans A	200°C/6MPa	1.1	0.57	0.87	0.98

For the assessment of this table, two basic points must be remembered. First, besides the major inorganic species selected for quantitation in this work, a far greater number of both organic and inorganic ions may be present. Second, whatever ionic species are present in the water, the net charge must be zero.

The results for Loy Yang B are very similar to those for Loy Yang A at low temperature. The ratio A is close to 1, which suggests the removal of the sodium mainly as soluble chloride salts. Since the contents of sodium and chlorine in Loy Yang B were much higher than in Loy Yang A (refer to Table 2-3), it seems that, in the Loy Yang B case, the process of sodium removal associated with chloride occurred predominantly even at high temperature.

Comparing the Bowmans B case to Bowmans A case shows that ratio B in the former case is close to 1 instead of the ratio A in the latter case. This suggests that the removal of the sodium from Bowmans B was associated with both chloride and sulphate ions. In the Bowmans A case, very large proportions of the calcium and magnesium were removed and

the removal was likely to be associated with sulphate ions (refer to Section 6.5.2.2). For Bowmans B, smaller proportions of these two elements were removed. As significant portion of the removed sulphate ions was associated with the sodium removal, leading to a low ratio C, the presence of the sulphate associated sodium, therefore, resulted in a high ratio A.

For both Loy Yang B and Bowmans B lignites, ratio D (sodium, calcium and magnesium to chloride and sulphate) is close to 1. This suggests that the selected cations were released into the aqueous phase mainly associated with chloride and sulphate anions and that all major ionic species contributing to charge balance in the MTE water were accounted for during quantitation. This result is similar to the cases of most Victorian and South Australian lignites investigated in this study (refer to Chapter Six).

For the Hambach case, though, the situation is very different. All calculated ratios are much larger than 1 indicating that considerably large number and/or quantities of anions other than chloride and sulphate must have been released to the water phase and were not accounted for during quantitation. The information available did not allow clarification of the nature of these ions. Carbonate and organic anions may be important.

7.7. Summary

The effects of increasing the acidity of the coal water slurries for MTE treatment and use of different heating methods on the removal of both organic and inorganic components from lignites were investigated.

The removal of moisture from Hambach, Loy Yang B and Bowmans B was not influenced by either variation of acidity of MTE processing medium or use of different heating methods. About 55-75% of the original water content in the coals could be removed at 150°C, 12MPa.

Organic compounds in the MTE process water from the Hambach lignite, as identified by GC-MS, were very similar to those removed from the Australian lignites investigated. GC-MS methods identified only small proportions (~15%) of the organic carbon present in MTE process water, among which 98% were carboxylic acids with very small proportions of phenolic compounds.

The introduction of hydrochloric acid during MTE processing considerably reduced the release of organic matter to the water phase. The treatment improved the sodium removal from the Hambach lignite but did not substantially affect its removal from the Australian lignites. However, the removal of both calcium and magnesium from all lignites during MTE processing was increased significantly by the acid addition. MTE treatment in the 'strong' acidic environment significantly improved the beneficiation efficiency of the MTE process, as shown by the reduction of ash yields of the MTE coal products.

The injection of gaseous CO₂ marginally reduced the release of the organic carbon during MTE, but did not show any significant impact on the removal of sodium, calcium or magnesium. However, a further ash reduction in the MTE coal products by this treatment compared to the standard MTE processing shows that the 'weak acidic' environment was still beneficial in terms of the desired inorganics removal.

MTE processing using two heating methods (electrical vs steam/hot water) affected the removal of organic carbon and inorganic components differently for the three lignites. MTE treatment using steam for heating reduced the removal of organic carbon but improved the removal of sodium and magnesium from the two Australian lignites. In the Hambach cases, the removal of organic carbon increased by the MTE processing using steam, while the removal of sodium and magnesium decreased. Only a small proportion of the calcium was removed and this was not significantly affected by the use of different heating methods. The use of 'recycled' water instead of distilled water for preheating did not affect the proportions of either organic carbon or selected inorganics present in the water phase.

7.8. Acknowledgement

The work described in this chapter was carried out in the Department of Chemical Engineering, University of Dortmund.

I would like to thank everybody in Professor Strauss' group for their strong support of this work. Particularly, I would like to thank Mr T. Wild for all his assistance in completing this work.

CHAPTER EIGHT

CONCLUSIONS AND FUTURE WORK

An understanding of the nature and composition of the water from MTE dewatering is essential for the purpose of process evaluation. It will assist process optimisation and will also inform the development of water reuse and waste management strategies. This work characterised both organic and inorganic constituents present in the process water and examined the effects of processing conditions and lignite type on their nature and concentration. The project achieved three main goals. Firstly, a variety of analytical protocols suitable for the isolation, identification and quantitation of major low molecular weight organic components ($MW < 400 \text{amu}$) in MTE process water were established. These were based on solid phase extraction and GC-MS detection. Secondly, the major low molecular weight organic components in the MTE process water were identified and quantified. The effects of MTE processing conditions on the organic carbon content and on the distribution of major organic components and compound groups in the MTE water were investigated. Thirdly, the effects of processing conditions on the behaviour of inorganic species during MTE treatment were determined and compared for lignites from Victoria, South Australia and Germany.

8.1. Method Development for Organic Analysis

The major low molecular weight organic components in MTE water were identified and quantified using the GC-MS technique. Sample pretreatment schemes were developed utilising the SPE method both with and without derivatisation. Phenols and carboxylic acids were recognised as the two major organic compound groups present in the MTE water.

Direct extraction of water samples using the polymer based PPL solid phase with ethyl acetate as the eluent proved to be unsuitable for the analysis of phenols and acids at low concentrations in the MTE water. Nevertheless, it was shown that the approach can be utilised for the analysis of mono-phenols at sub-ppm levels with high recoveries and good reproducibility. The method is simple, fast and the elution solvent is non-hazardous. The

sorbent is optimised for the extraction of highly polar species from large volume water samples [159]. The detection of some polar phenols and carboxylic acids (including some not detected in the derivatised extracts) demonstrated that, where large volumes of water are available (e.g. effluents from MTE pilot plants), the selectivity for polar compounds, the high adsorption capacity and the compatibility with high volume flows may allow the use of this approach to the analysis of these polar organics without the need for derivatisation.

A two-step acetylation method using acetic anhydride, following pH adjustment of the sample, was developed for phenol analysis. The method was shown to provide improvement over the commonly used one-step method and was capable of simultaneous determination of mono- and multi-hydroxy phenolic compounds at ppb levels. The acetylation of phenolic functional groups considerably improved the GC sensitivity and lowered the detection limits for these compounds, especially the di- and tri-hydroxy phenols, and significantly increased the number of phenolic components identified in the MTE water samples.

A novel methylation method involving direct aqueous phase derivatisation of carboxylic acid groups was quantitatively evaluated and validated. This method, based on the use of trimethyloxonium tetrafluoroborate (TMO), eliminated the time consuming acid isolation step and was shown to be more efficient than non-aqueous methylation methods based on the use of boron trifluoride/methanol and acetyl chloride/methanol. Using TMO, large numbers of polar carboxylic acids, most of which were not detected via other approaches, could be identified and quantified.

The SPE-GC-MS methods established in the present study enabled the development of a reasonably comprehensive understanding of the organic composition of MTE water. It is likely that they can be applied to the identification and quantitation of organic compounds in other aqueous samples of similar or related origin.

GC coupled with MS proved to be an excellent tool for both identification and quantitation of low molecular weight organic compounds ($MW < 400 \text{ amu}$). The highly efficient separation capability of GC enabled the identification of individual components by MS. In addition, the use of advanced data analysis software, with functions such as identification

and quantitation using *target ions*, *peak purity analysis* and *single ion extraction* has greatly improved the efficiency of GC-MS identification and quantitation.

8.2. Nature of MTE Water

8.2.1. *Organic Constituents of MTE Water*

The amount of organic carbon extracted into the water from lignite during MTE processing increased with processing temperature and pressure. Compression rate and the use of kneaded coal appeared to have little impact on the organic carbon content of the MTE water. The quantities of individual components and compound groups present in the MTE water also generally increased with increasing processing severity.

The major compound classes identified in the water removed from different lignites under all conditions were similar. They included carboxylic acids, phenolic compounds, cyclic ketones, furans and related compounds as well as some nitrogen, sulphur and chlorine containing compounds. The number and relative abundance of individual components in the water varied with the lignite.

Phenolic compounds accounted for very small proportions (<2%) of the total GC-MS identified organics. Low molecular weight compounds identified by GC-MS were predominantly carboxylic acids. High molecular weight organic materials not identified by GC-MS accounted for >70% of the total organic carbon in the MTE water.

Concentrations of the organics in MTE water were lower than in the process water from other lignite dewatering processes. This finding, along with MTE's other features such as its significant moisture reduction and energy saving capabilities, supports the view that MTE is a promising approach to lignite dewatering. Nevertheless, the presence of organic impurities, particularly toxic phenolic compounds, implies that careful consideration of appropriate remediation strategies will be necessary.

8.2.2. *Inorganic Species in MTE Water*

The removal of sodium into the water increased significantly with increasing processing temperature at low pressures. The effect of processing severity on other selected inorganics was generally not significant. Nevertheless, the removal of major inorganic components was significantly correlated with moisture removal from the lignite during MTE

processing. Increasing the acidity of the coal water slurries was found to significantly improve the removal of major inorganic elements.

The behaviour of the inorganic elements during MTE processing depends on the forms in which they are originally present in the lignite. In the Victorian lignites investigated, a large proportion of the sodium occurs as water soluble salts and, therefore, was more readily removed by the MTE treatment than calcium and magnesium, which tend to occur in the lignites as organically bound cations. The organically bound cations could be in part exchanged with hydrogen when the acidity of the coal water slurries increased and, thus, could be transferred into the water phase. Chloride and sulphur (in the form of sulphate) were also removed into the MTE process water. The same considerations explain the behaviour of the South Australian and German lignites investigated.

In terms of the reduction of inorganic species from the coal, the MTE treatment can be regarded as an efficient coal beneficiation process. The removal of more than 50% of the sodium and reasonable proportions of other inorganics, in most cases, implies that MTE can produce not only a drier but also 'cleaner' coal product that may help to reduce fouling problems during lignite utilisation.

8.3. Suggestions for Future Work

8.3.1. *Organic Analysis*

GC-MS coupled with the SPE sample pretreatment method proved to be a very effective approach for characterisation of organic species in the MTE water. Compounds which could be analysed using this method are of low molecular weight with estimated boiling point $>100^{\circ}\text{C}$ and molecular weight <400 . The MTE water contains many organic species outside these ranges of boiling point and molecular weight, as discussed below.

Volatile compounds such as methanol and ethanol were found in MTE water samples in preliminary tests in this study and in similar water sources [54]. Headspace techniques coupled with GC-MS may be the method of choice for the identification and quantitation of these volatile materials. Methods for applying headspace and GC-MS techniques, after esterification of water samples, for the analysis of volatile carboxylic acids are also available in the literature [108]. Molecular weight distribution analysis by FFF suggested

that a large proportion of the organic species in the MTE water are very high molecular weight compounds/polymers not characterisable by GC-MS.

Therefore, to gain a more comprehensive understanding of the organic composition of the MTE process water, further research is required to analyse both the very volatile components and the polar, high molecular weight components. Further understanding of the nature of these substances, particularly of the high molecular weight compounds, is probably important for the purpose of selecting appropriate water treatment techniques.

8.3.2. Water Reuse and Waste Management

The presence of some toxic phenolic and other organic impurities implies that the MTE process water cannot be discharged without cleanup. During the selection of MTE water treatment techniques, a major concern would be these organic contaminants. The focus of future work in this area could involve testing different water treatment approaches for cleanup of organic impurities found in the MTE water. Solutions may include a combination of processes such as filtration, adsorption, membrane technologies and biodegradation.

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