Structural Determination, Identification and Removal of Bayer Liquor Organic Poisons

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Declaration of Originality

I hereby declare that the work contains herein is mine, and has not be submitted, in part or full, to any other university of institution for any award.

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Regina Elizabeth Maher
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Abbreviations and Acronyms

Al_2O_3	Alumina
$Al(OH)_3$	Aluminium Hydroxide
AMDIS	Automated Mass Spectral Deconvolution and Identification System
BSS	Between Sum of Squares
CI	Confidence Interval
DVB	Divinylbenzene
FA	Fulvic Acids
GC	Gas Chromatography
HA	Humic Acids
HPLC	High-Pressure Liquid Chromatography
HS	Humic Substances
IC	Ion-Chromatography
IS	Internal Standard
MS	Mass Spectrometry
MTBSTFA	*N*-*tert*-Butyldimethylsilyl-*N*-methyltrifluoroacetamide
MW	Molecular Weight
NOM	Natural Organic Matter
NPOC	Non-Purgeable Organic Carbon
OC	Organic Carbon
OM	Organic Matter
PA	Polyacrylate
PDMS	Polydimethylsiloxane
PolyDADMAC	Polydiallyldimethylammonium chloride
SEM	Scanning Electron Microscope
SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction
TIC	Total Ion Current Chromatogram
TOC	Total Organic Carbon
XIC	Extracted-Ion Chromatogram

Abstract

Large financial investments are required for the precipitation step of the Bayer Process to ensure moderate yields of gibbsite are recovered. This step is crucial for $Al(OH)_3$ production but unfortunately is subjected to inhibition caused by the presence of particular organic matter known as 'poisons'. Despite extensive research performed to mitigate these inhibiting effects, they have experience severe limitation.

The structure of the poisons is essential for understanding how inhibition is induced and consequently, how they can be removed. A new extraction and derivatisation method was developed using SPME with a polyacrylate fibre, coupled with MTBSTFA on-fibre derivatisation for analysing Bayer Liquor OM. As a result, 65 organic compounds were structurally characterised. Importantly, this OM identification process confirmed the absence model poisons, namely polyhydroxyls, within Bayer Liquor. A comparative study of Bayer Liquors organics, both pre and post gibbsite harvesting was used to identify the poisons. From this, 7 poisons were proposed with the inhibiting functionality identified.

To this end, a novel OM removal strategy was investigated which focused on transforming these highly polar poisons into volatiles. This removal strategy presents potential for mitigating inhibiting effect as some OM were successfully removed from the liquor in the form of pyrroles.

Chapter 1: Introduction

1.1. Preamble

Australia is the world's leading producer of the aluminium ore bauxite, representing 30% of the global production. Alumina is produced from bauxite on a commercial scale by the Bayer Process in which the mined bauxite undergoes hot caustic digestion to extract aluminium hydroxide into a solution leaving behind other metal and silicon oxide impurities. The aluminium hydroxide is subsequently precipitated out, where the yield and product crystal size distributions are determined. Unfortunately, bauxite is known to contain organic impurities which are co-extracted with the aluminium hydroxide during digestion, resulting in large financial losses, as the quality, yield and precipitation rates are all negatively affected by these organic impurities (1).

Research into understanding these organic impurities, which act as 'organic poisons', has grown extensively over the years to try resolve the huge financial burdens of this inefficiency. Many investigations have attempted to address the inhibiting effects of organic impurities on the aluminium hydroxide precipitation. However, no effective removal strategy for these organic impurities has been ascertained since the invention of the Bayer Process.

1.2. Australian Aluminium Production

For the first time in history, the consumption of the aluminium ore, bauxite, exceeded 200 million tonnes in 2007 making its production the largest of the nonfuel minerals (2, 3). Bauxite production continues to increase at a rate approximately equivalent to 6% per annum, constituting one of the largest financial influences in the mining industry (2). Australia is the world's largest producer and exporter of bauxite and the 5th largest aluminium producer. In 2013 Australia produced 77 million tonnes of bauxite, representing 30% of the global production (3, 4). Bauxite is the main source of aluminium and approximately 97% of all bauxite mined is used for the commercial production of aluminium (2). Bauxite is the name given to the aluminium oxide minerals gibbsite ($Al(OH)_3$), diaspore (α-AlO(OH)) and boehmite (γ-AlO(OH)), where the α and γ represent differing levels of mineral hardness. These minerals are highly abundant but are commonly accompanied by iron oxide impurities like goethite (FeO(OH)) and hematite (Fe_2O_3) (5).

The aluminium industry of Australia is a highly integrated sector comprised of mining, refining, smelting and semi-fabrication centres, making it of great economic importance on both

a national and global scale (4). In Australia, bauxite reserves are estimated to contain approximately 6 billion tonnes of raw mineral material. This amount represents the largest percentage of bauxite reserves, corresponding to 22% of the global resources (3). The high abundance of alumina resources in Australia provides a highly viable future for the Australian mining industry, providing financial security for the Australian economy. Bauxite deposits are found in almost all states and territories of Australia, however the majority of bauxite is primarily located in W.A. along the Darling Range, and the northern coast at Mitchell-Plateau and Cape, also the northern coast of Queensland at Weipa (4). The bauxite mining and aluminium industries are critical to the Australian economy and together they supply approximately 20, 000 jobs to Australians (4).

1.3. The Bayer Process

1.3.1. Outline of the Bayer Process

The Bayer Process is the commercial hydrometallurgy procedure for the production of aluminium hydroxide from bauxite. It is the first of the two major steps employed in alumina production (Equ. 1.3.1) and will be the major focus of this thesis. The Bayer Process was patented by Karl Josef Bayer in 1887 and is used for the refinement of bauxite into precipitated aluminium hydroxide ($Al(OH)_3$) which is subsequently calcinated to alumina (aluminium oxide; Al_2O_3) and then to aluminium by the Hall-Héroult Process which relies on the electrolytic reduction of alumina in molten cryolite (Na_3AlF_6) (6).

$$\text{Bauxite} \xrightarrow{\text{digestion+crystallisation}} Al(OH)_3 \xrightarrow{\Delta\ \text{calcination}} Al_2O_3 \qquad \textbf{Equ. 1.3.1}$$

The first step in the Bayer Process involves the milling of bauxites into fine particles followed by hot caustic digestion with ~5 M NaOH and/or $Ca(OH)_2$, in a high pressure reactor (7). The reactor temperature ranges are dependent on the type of ore, but are commonly 140 – 150 ^oC or 250 – 255 ^oC (7). The alkaline digestion liberates the gibbsite ($Al(OH)_3$) within the ore as soluble aluminate ($Al(OH)_4^-$) ions (Equ. 1.3.2) (8).

$$Al(OH)_3 + NaOH \rightarrow Al(OH)_4^- + Na^+ \qquad \textbf{Equ. 1.3.2}$$

The solution produced from this step is known as pregnant Bayer Liquor, as it is saturated with $Al(OH)_4^-$. Unfortunately, $Al(OH)_3$ is not the only alkaline soluble component of bauxite, and impurities, like silica, also become dissolved in the alkaline liquor, resulting in a saturated liquor containing both soluble and insoluble impurities and complexes. Typical insoluble impurities include iron oxides, lime solids and sodium aluminosilicates. These are able to be removed through filtration, before the liquor is cooled to 65 -75 ^oC. Many of the

soluble impurities are precipitated out upon the addition of precipitating reagents, like lime in the case of silica, also allowing them to also be removed during the filtration step (9). The mixture of the removed insoluble impurities is termed red mud and is typically discarded. Once cooled, the filtered pregnant Bayer Liquor is seeded with $Al(OH)_3$ to promote crystallisation of $Al(OH)_4^-$ as $Al(OH)_3$ (Equ. 1.3.3) (8). When adequate levels of $Al(OH)_3$ have been crystallised, they are removed from the Bayer Liquor to the second stage in the aluminium production, where $Al(OH)_3$ is subsequently calcinated to form Al_2O_3 (Equ. 1.3.4).

$$[Al(OH)_4^-] \xrightarrow{\text{seed with } Al(OH)_3} Al(OH)_3 + OH^- \qquad \textbf{Equ. 1.3.3}$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \qquad \textbf{Equ. 1.3.4}$$

The remainder of the Bayer Liquor is collected, concentrated and combined with new feed-stock before repeating the Bayer Process cycle. The recycling of the Bayer Liquor is financially beneficial as the liquor still contains uncrystallised $Al(OH)_4^-$ and valuable levels of NaOH. After the Bayer Liquor is sufficiently recycled, it is termed as spent Bayer Liquor and is subsequently discarded as the rates of $Al(OH)_3$ precipitation are no longer profitable. The inefficient precipitation rate is almost exclusively caused by the presence of organic matter (OM), derived from natural organic matter (NOM) (10).

1.3.2. Inefficiencies of the Bayer Process

Lateritic bauxites, from which $Al(OH)_3$ is refined, are found to contain varied amounts of OM, a portion of which are solubilised in the digestion step of the Bayer Process (11, 12). Due to the recycling of the Bayer Liquor, more OM is constantly introduced into the liquor and subsequently concentrated. There are several major concerns regarding the presence of OM in Bayer Liquor. These include the lowering of $Al(OH)_3$ yields, increased density, viscosity, specific heat and boiling points of the liquor, lowering red mud settling rates and generating excessive foam in liquor processes (12). However, the major concern for the alumina industry is the lowering of $Al(OH)_3$ yields.

Previously, quantification of the amount of unprecipitated $Al(OH)_3$ within spent Bayer Liquor was used to measure the extent of retention, possibly induced by OM (13). It was proposed that up to 50% of digested $Al(OH)_3$ cannot crystallise efficiently (13). Addressing the problems of OM in Bayer Liquor increases capital costs through installation of equipment and additional material usage, overall increasing the complexity of the refinement process (2). It was estimated in 2005 that the annual cost of OM to the Australian aluminium industry alone exceeds $500 million (1). This value would only have risen since and undoubtedly varies between countries due to the variation of bauxite formations and organic sources in their

reserves. Despite this, no significant advancements in OM removal have been made due to the severe analytical limitations of OM (14).

1.4. Inhibitors of the Bayer Process

1.4.1. Origin of Bayer Liquor Organic Matter

In order to investigate the OM which act as "organic poisons" within Bayer Liquor, it is essential to first understand the nature and complexity of their precursors, NOM. NOM is defined as a grouping of OM produced from the degradation of organisms which are ubiquitous in all natural environments. NOMs are an intrinsic part of the environment and are found to comprise ~1.58% of the Earth's crust (15-18). Structural characterisation of NOM has been limited due to their chemical complexity, as the natural arrangement of NOM is suggested to exist as supramolecular aggregates, as opposed to dissociated molecules (19). Strong evidence has been proposed to suggest that these aggregates are induced by hydrogen bonding, dipole interactions, micellar-type formation and chelation of biological-type molecules through metallic atoms, contributing to their analytical complexity (17, 18). Furthermore, the random condensation and polymerisation of these compounds makes their analysis almost impossible and thus it is not surprising that the work performed in this field is limited (15).

Humic Substances (HSs) are the most naturally abundant OM on Earth (15). The classification of HS, established by International Humic Substances Society (IHSS) is segregated into three main categories according to their properties of solubility and hydrophobicity. However, it is only the first two categories, Humic acids (20) and Fulvic acids (FAs), which are of interest to the Bayer Process. HAs are the fraction of HS which solubilise under neutral or alkaline conditions and precipitate under a pH level of 2 (19). FAs are the fraction of HS which remain soluble under all pH conditions. The high level of solubility exhibited by FA corresponds to higher proportions of carboxylic acid functional groups with lower aromatic content when compared to HA. The levels of aliphaticity, however, are generally similar between the two fractions (19, 21, 22).

Previously it has been shown that the distribution of organic compounds found within bauxite is significantly influenced by the recent history of the environment (23). From these studies, it was found that rainwater interacts with organic matter within the topsoil, resulting in rich solutions of HA and FA. Leaching of these rich solutions through the bauxite layers results in the adsorption of the acids onto the mineral surfaces, causing the formation of lateritic bauxites which are subsequently mined and processed for the production of aluminium (23). Unfortunately due to the alkaline solubility of HA and FA, they become readily solubilised in

the bauxite caustic digestion step of the Bayer Process, preventing complete extraction of $Al(OH)_3$. Due to the recycling of the liquor, the concentration of OM increases until an equilibrium concentration is reached (24).

It is important to recognise that the OM present during the precipitation step of the $Al(OH)_3$ is vastly different from the NOM which first entered the Bayer Process as a result of the caustic nature of the Bayer Liquor (25). Therefore, the OM found within Bayer Liquors are derived from the degradations of NOM (26-28).

1.4.2. Structural Characteristics and Inhibiting Mechanisms of Organic Poisons

There is a need to investigate how OM affects the yield, rate and quality of $Al(OH)_3$ crystallisation. Consequently, the structural characterisations and mechanisms of poisoning of Bayer Liquor OM have been of intense research interest for the last fifty years (2, 11). It was initially believed and confirmed to an extent that the concentration of OM influenced $Al(OH)_3$ crystallisation. Accordingly, many refineries perform routine monitoring of the most abundant OM, like oxalate (29). However, more recently model organic poisons were investigated in synthetic Bayer Liquor to try and understand how OM inhibits $Al(OH)_3$ crystallisation (11, 14, 30-40). For the first time it was demonstrated that the concentration of OM was not the only factor influencing $Al(OH)_3$ crystallisation nor was it the most prevalent one. The inhibition of $Al(OH)_3$ crystallisation was found to be greatly dependent on the chemical structure of the organic species. These mechanistic studies indicated that the majority of the carbon present within the Bayer Liquor may not have inhibiting properties (14, 41). Therefore, there is a need to identify which OM act as poisons.

1.4.2.1. Structural Characteristics of Organic Poisons

Organic poison models for Bayer Liquor have evolved from the need for information about their structure. Establishing a link between the structural characteristics of a poison and its ability to inhibit $Al(OH)_3$ crystallisation is a necessary step towards understanding how inhibition is induced. Such knowledge would enable identification of poisons from Bayer Liquor OM. Consequently, two key aspects need to be considered to fully understand the relationship between inhibition and structural characteristics of poisons; the functional groups of the organic species and the stereochemistry of those functionalities.

The foundation of many model poisons arose from investigations of hydroxyl groups and their ability to inhibit $Al(OH)_3$ crystallisation. The presence of at least one pair of vicinal hydroxyl group was found to increases a model's affinity to the gibbsite surface and so it was suggested that polyols or alditols could be potential poisons of Bayer Liquor (42, 43). However,

further investigation revealed that in addition to possessing at least one pair of vicinal hydroxyl groups, organic species which have one or more carboxylic acid groups adsorb more strongly that those without (43). Accordingly, it was found that the corresponding acid anions of the alditols and polyols exhibit stronger levels of inhibition than their non-acidic counterparts. The comparison between threitol and threonic acid highlights this relationship well, where threitol inhibits $Al(OH)_3$ precipitation by only 5%, whereas its acidic counterpart, threonic acid, inhibits crystallisation by 45%, revealing a difference of 40% inhibition between the pair (Figure 1.4.1) (44). Furthermore, it has been shown that with these inhibiting functionalities, inhibition strength increased with increasing length of carbon backbone. For example, mannitol (6 carbons) is known to inhibit precipitation by 41%, however erythritol (4 carbons) inhibits precipitation by only 9% (Figure 1.4.1) (41, 44, 45).

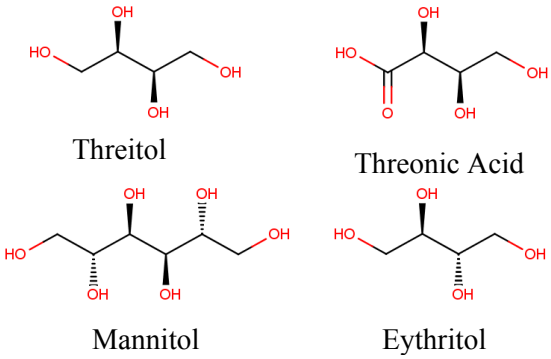


Figure 1.4.1. Threitol causes only 5% inhibition of $Al(OH)_3$ precipitation, whereas its acidic form, threonic acid, inhibits $Al(OH)_3$ precipitation by 45%. Mannitol inhibits precipitation by 41% whereas the shorter organic species, erythritol, inhibits precipitation by only 9% (45).

From these structural inhibition relationships, a common structural feature can be established namely multiple hydroxyl functionalities. Organic species containing this feature are known as polyhydroxyls and are considered the predominant poisons of Bayer Liquor, due to their unparalleled inhibiting strengths. However, variations in the inhibiting strength of polyhydroxyls, in some cases, have been shown to be independent of the carbon backbone length or number of vicinal hydroxyls, instead, being linked to the stereochemistry of the organic species.

A convincing study of polyols demonstrated that inhibiting strength can be increased by changing the stereochemistry of the vicinal hydroxyl groups. (40, 46). This is most clearly demonstrated in the example of stereoisomers, xylitol (*2R-3R-4S*), arabinitol (*2R-3R-4R*) and ribitol (*2R-3S-4S*), where xylitol inhibits crystallisation by 97%, whereas its stereoisomers arabinitol and ribitol, inhibit crystallisation by 28% and 11% respectively (39). The capability of chelating to aluminate ions within solution may be related to a poisons ability to inhibit crystallisation. Xylitol is able to form the strongest co-ordination with the aluminate ion compared to its stereoisomers, as the spatial arrangement of its vicinal hydroxyls are able to

form three co-ordination points with aluminate, whereas its stereoisomers are only able to form two (Figure 1.4.2) (30).

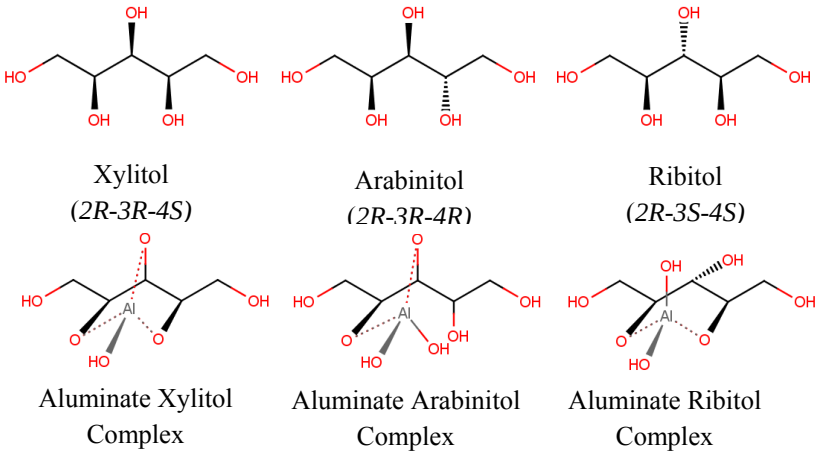


Figure 1.4.2. Inhibition between the stereoisomers of xylitol differ by 60-80%. (45)
Inhibition ability is described by the spatial arrangement of the vicinal hydroxyl groups and their ability to co-ordinate with the aluminate ion in a tetrahedral configuration. (32)

Structural knowledge of Bayer Liquor OM would greatly assist in the identification of poisons. The potential benefits of identifying these poisons has inspired many structural investigations in this area, unfortunately this type of information is limited for the full structural characterisation of both spent and pregnant Bayer Liquors OM.

1.4.2.2. Inhibiting Mechanisms of Organic Poisons

Investigations using gluconate to probe poisoning mechanisms revealed that rates of crystallisation drop to 0% with only 3.5% of the total crystal surface covered. These results indicate that inhibition is caused by a poison's tendency to absorb to active growth sites of the crystal, primarily at kinks in the crystal surface (33, 47-49). This finding is significant, as it indicates that only trace amounts of strong poisons need be present within the liquor to cause large inefficiencies in $Al(OH)_3$ growth (50). The blocking or deactivation of active growth sites cannot occur by poisons absorbing directly onto the crystal surface. Poisons exist as anions in the caustic conditions and are therefore unable to absorb onto the negatively charged gibbsite surface layer, as predicted by an electrostatic model of the gibbsite/solution interface (47). For that reason, two mechanisms of poisoning have been proposed to explain the presence of poisons only on active growth sites; the formation of an aluminate poison complex and the formation of a growth unit complex. The mode of inhibition is that both mechanisms are dependent on the structural functionality of the poison.

The study from xylitol and its isomers revealed that inhibition was related to the ability to complex to aluminate ions within solution. This complex formation, known as the aluminate poison complex can only occur between an aluminate ion and a polyhydroxyl poison, with the favourable release of water (Figure 1.4.2) (30). Formation of this complex results in the

stabilisation of the aluminate ion. The stronger the chelation, the more stable the aluminate ion becomes. From the electrostatic model of gibbsite, crystal growth occurs through the addition of aluminate ions onto the active sites. Aluminate ions must transform into an octahedral co-ordination from the tetrahedral co-ordination in order to become a part of the gibbsite crystal (47). However, when an aluminate ion is complexed to a poison, this transformation is inhibited from the induced stabilisation. The result, deactivation of the active site (45). This mechanisms explains the increased inhibiting strength of acidic polyhydroxyls as they are able to form stronger complexes to the aluminate ions (43, 51-53).

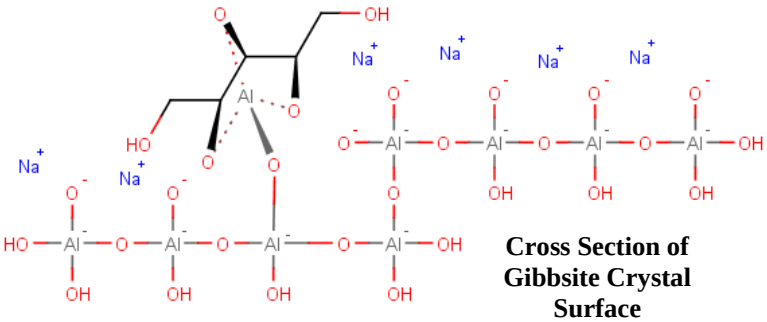
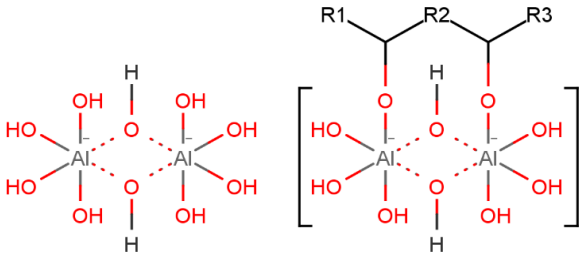


Figure 1.4.3. Schematic illustrating the concept of the aluminate poison complex inhibiting crystal growth (32) at active sites on the crystal surface after the escape of sodium ion by diffusion through the charged layer as described by the electrostatic $Al(OH)_3$ crystal growth model (16).

Other studies have questioned the aluminate poison complex stated above. It has been hypothesised that $Al(OH)_3$ crystal growth may not occur by addition of tetrahedral aluminate ions to active sites, but through addition of an octahedral dimer, known as a growth unit (Figure 1.4.4). The growth unit was proposed from molecular modelling and crystallographic considerations (33, 49) and was found to exist as the most prominent species in acidic conditions. However, in alkaline condition the aluminate ion is found to be the most prominent species (54) but exists in equilibrium with the growth unit (49). Inhibition of crystal growth by the growth unit is induced in a similar manner to the aluminate poison complex, where the growth unit forms a molecular complex with a poison with the release of two hydroxyls (49). The growth unit complex is able to dock onto the active site with the two remaining hydroxyls, leaving the poison facing outwards from the active site. This effectively deactivates the active growth site from further additions of growth units through steric hindrance (Figure 1.4.4). This mechanisms may also explain the observed relationship between increasing carbon backbone and increasing inhibition strength (Figure 1.4.1). It was found that organic species inhibiting crystal growth had matching inter-atomic distances between their hydroxyl groups to the inter-atomic distances of oxygen atoms in the growth unit (49). Furthermore, this mechanism is not limited to formation solely with polyhydroxyls, explaining why poisons without polyhydroxyl functionalities can also inhibit $Al(OH)_3$ crystallisation.



Growth **Growth Unit Complex**

Figure 1.4.4. Schematic illustrating the growth unit and the growth unit complex concept inhibiting crystal growth by docking onto the active growth site with the two free hydroxyls located at the bottom of the growth unit complex (50).

Given the uncertainties in the mechanisms of inhibition, the identification of the poisons from Bayer Liquor OM is crucial for the development of appropriate and cost effective removal strategies. Without the structural knowledge of Bayer Liquor OM, this cannot be ascertained.

1.5. Organic Matter of Bayer Liquor

1.5.1. Removal of Organic Matter from Bayer Liquor

Organic removal systems and technologies, whilst presenting large financial benefits through increasing liquor productivity, refinery output and lower capital cost per ton of alumina and caustic consumption, suffer from substantial economic and technical risks (55). Past approaches to increase the efficiency and economic viability of organic removal technologies and systems have experienced severe limitations in terms of their ability to work concurrently with the Bayer Process cycle. Despite extensive research and development work performed over the past five decades including over 60 patents, no effective, low cost organic removal strategy is currently being employed industrially to address the poisoning effects of OM (56). Presently, only a few patents developed from the early 80's are still in use, of these, the only patent controlling organic carbon (OC) species in Bayer Liquor is the sodium oxalate control (56). Whilst effective, this patent does not address any control or removal of the poisoning effects of OM. As such, no patents are currently employed in the Bayer Process to address the severe financial losses caused by organic impurities. From the sixteen systems designed to control organic poisons (44, 57-78), only three have been applied industrially, wet-oxidation, precipitation by polydiallyl-dimethylammonium chloride (polyDADMAC) additives and liquor calcination (56). While these methods are able to provide significant improvements to reducing levels of organics in synthetic Bayer Liquors, their inability to work effectively with the Bayer Process prevents them from being industrially viable.

To address the efficiency losses of $Al(OH)_3$ production, many alumina refineries (79) in conjunction with research bodies like CSIRO (78) worked to developed a novel OM removal strategy known as wet-oxidation. This OM removal strategy selectively targets model organic poisons through the introduction of molecular oxygen into the liquor under high temperatures

and pressures. This process results in the oxidative decay of organic species with multiple hydroxyls (44, 71, 80, 81). Wet-oxidation is highly effective in reducing concentrations of various polyhydroxyls, whilst simultaneously eliminating any inhibiting effects caused by these poisons in synthetic Bayer Liquors (44, 77). The effectiveness of this strategy inspired many engineering patents to be filed, allowing this method to be introduced directly into the Bayer Process. A German aluminium refinery, AOS, employed one of these patents, which concentrated on introducing wet-oxidation through digestion tubes (67, 82). The effects of oxygen addition at this plant were monitored over a two year period, where OC content was shown to slightly reduce over this time. However, despite the slight reduction in OC levels, $Al(OH)_3$ yield productivity was not improved, indicating that the poisoning effects were not being mitigated (82). The inability of wet-oxidation processes to mitigate the inhibiting effects of Bayer Liquor OM indicated that the targeted model poisons were not present within the liquor and are therefore are not the poisons of Bayer Liquor. Continual attempts have been made to achieve better economies with wet-oxidation processes. However, as the yield productivity showed no signs of improvement, the employment of this process was not considered economically justifiable (56).

In an attempt to further improve the economic viability of OM controls, more advanced technologies were developed with a focus towards limiting their processes to only one step. One such technology is liquid calcination. The application of a submerged plasma torch in combination with a draft tube to induce OM degradation presents several advantages, the most prominent of which is its ability to rapidly reduce OC levels (56). This process was shown to be highly effective in recovering alumina from spent Bayer liquor whilst keeping the high levels of NaOH. However, this technology was not able to work concurrently with the Bayer Process to remove the organics from pregnant Bayer Liquor. As a result, the implementation and operation of this technology was considered not economically viable (25, 83), as the yields of $Al(OH)_3$ production could not be directly improved during the Bayer Process.

Organic control through precipitation by polyDADMAC addition was designed to be incorporated into the Bayer Process cycle without additional engineering. This method focused on improving the quality of alumina through the removal of humate from Bayer Liquor. Humate constitutes a small portion of Bayer Liquor OM and is known to cause the lowering of alumina quality, in terms of particle size and whiteness (72). The precipitate produced from the polyDADMAC humate reaction is able to be removed during the filtration step of the Bayer Process. PolyDADMAC precipitation is a highly effective method of removing humate from both synthetic and spent Bayer Liquors, producing greater quality in particle size and whiteness

of product (69, 72). AOS in Germany also trialled the removal of Bayer Liquor OM by precipitation with polyDADMAC. However this process was discontinued as the tar-like products formed, blocked filter media decreasing red mud filtration rate considerably (82). Despite its ability to rapidly reduce humate levels and be incorporated into the Bayer Process cycle, its inability to work seamlessly and concurrently with the refineries engineering reduced its feasibility on both a practical and economic scale.

The economic viability of current organic control systems are limited in their success due to their inability to target organics responsible for poisoning and incorporate these technologies effectively into the recycling system of the Bayer Process, without additional engineering. Consequently, the financial cost of implementing and operating current removal technologies and strategies is too large. The key to overcoming these limitations lies in the structural information of Bayer Liquor OM. Unfortunately, this information is limited for both spent and pregnant Bayer Liquor.

1.5.2. Structural Characterisation of Bayer Liquor Organic Matter

OM in all environmental contexts, are notoriously challenging to characterise, especially for the structural characterisation of the molecular components. These challenges arise from the supramolecular nature of these complex mixtures, induced by their excessive hydrogen bonding and highly polar functionalities (19). Therefore it is not surprising that the progression of structurally characterising these compounds has been limited. The task of characterising the structure and nature of these complex compounds has been addressed by many analytical techniques in an attempt to overcome the analytical complexity experienced by Bayer Liquor OM (84).

Chromatographic separation techniques are commonly coupled with non-specific detection methods, like spectroscopic analysis, to attain the structural information of individual components of complex OM mixtures. Without the employment of separation techniques for analysis, structural characterisation performed on the individual component level could not be obtained (9, 15, 16, 19, 84-86). Unfortunately, the coupling of spectroscopic techniques with chromatographic techniques means that their analysis greatly relies on the characteristic elution times for specification. This aspect has its advantages, i.e. detection within a single chromatographic run, but is highly dependent on knowledge of identified compounds from calibrations or standards. The most successful of these cases was able to fully resolve and identify no more than ten organic species, all of which were aliphatic and aromatic carboxylic acids (Table 6.1.1). Therefore the coupling of chromatographic techniques with detection and identification techniques, like mass spectrometry (MS) greatly enhances the separation and

detection capabilities of the analysis, allowing simultaneous identification and quantification of individual components from complex mixtures like Bayer Liquor. For that reason, the most suitable technique for Bayer Liquor OM analysis has been shown to be gas chromatography – mass spectrometry (GC-MS) (87-89). By comparison, separation performed by GC provides the greatest resolution and is unsurpassed in that respect by any other separation technique. Unfortunately, the nature of OM means it is not directly amenable to GC due to the extensive polar functionalities and hydrogen bonds of OM. Therefore selective modifications like derivatisation, (7, 88, 90, 91) or reduction (92) are required to produce simpler and more volatile units of OM components.

Derivatisation provides the most structurally preserved approach and is therefore the preferred option. Three derivatisation approaches have been applied on Bayer Liquor OM, trimethylsilyl (TMS) (24), methylation (7, 88, 91) and/or butylation (91). Unfortunately, these techniques were limited in their success due to incomplete derivatisation, (24, 88) loss of low molecular weight species (93) and derivatisation of only carboxylic functionalities (91). Nonetheless, the TMS derivatisation was the most successful of the three, where 35 aliphatic and aromatic carboxylic acids were fully resolved, making it far superior to the latter two techniques which have only been able to fully resolve thirteen organic acids in the most successful case (Table 6.1.1) (91). Despite their likely formation during the bauxite digestion stage, none of these techniques were able to detect the presence of polyhydroxyls. Previously, only one polyhydroxyl, tartrate, has been detected within Bayer Liquors, (94, 95) however, the validity of its detection is questionable.

Recently, further work using TMS derivatisation resolved and characterised approximately 50 medium MW organic species, making this structural characterisation method far superior to others presented in literature (Table 6.1.1) (13). Interestingly, despite this method being validated for detecting polyhydroxyl compounds, only aliphatic and aromatic carboxylic acids were found within the Bayer Liquor (13). Unfortunately, the investigation only focused on characterising organic species from spent Bayer Liquor and not pregnant samples. Spent Bayer Liquor samples were chosen for analysis as it was believed that $Al(OH)_4^-$ was "trapped" within the liquor due to the presence of organic poisons. Therefore analysis of spent OM should provide a representation of OM causing the inhibition of $Al(OH)_3$ crystallisation (13). However, without a comparison to the OM present in pregnant liquor, this analysis was unable to identify any poisons from the characterised OM. This highlights the need for structural characterisation and quantification of Bayer Liquor OM pre and post gibbsite harvesting to determine which OM are the poisons of Bayer Liquor.

1.6. Project Objectives

Due to the large financial costs of organics to the aluminium industries and a lack of success for the mitigation and control of organics within Bayer Liquor, the following objectives for this research are proposed:

1. Perform full structural characterisation of OM from both pregnant and spent Bayer Liquors.
2. Determine the relative abundances of characterised OM present within the two Bayer Liquors.
3. Investigate the organic poisons of aluminium production by observing changes in OM between the two liquors Bayer Liquors.
4. Investigate a novel method for the removal of organic poisons from Bayer Liquors based on the identified poisons.

Chapter 2: Experimental

2.1. Samples and Reagents

The spent (Batch 36A) Bayer Liquor samples and pregnant (Batch 45) Bayer Liquor samples used were sourced from the Kwinana Refinery W.A. supplied by Alcoa World Alumina. Samples collected on 24.2.15.

N-Methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide (Sigma-Aldrich, 97.0%), Pyridine (Sigma-Aldrich, $H_2O \leq 0.05\%$, $\geq 99.8\%$), sodium hydroxide (Univar, 99.9%), aluminium hydroxide (BDH, 99.0%), nitric acid (AnalaR Normapur, 69.9%), sodium chloride (UNIVAR, 99.9%), sodium carbonate (AnalaR, 99.0%), and ammonia solution (BDH, 25%) were used without any further purification. All standards were sourced from Sigma-Alrich and were of a $\geq 99.0\%$ purity. Benzylnitrile (Ried el-de Haen) was purified by distillation. Chromic acid was prepared by dissolving sodium dichromate (Laboratory Chemicals, 98.0%, 5 g) in sulfuric acid (AnalaR Normapur, 98.6%, 100 mL).

2.2. Instrumentation

Gas-chromatography mass spectrometry (GC-MS) analysis was performed using a GC-17A, coupled with a quadrupole MS QP-5000 detector (Shimadzu). The mass spectrometer was run in full scane mode (40-500 *m/z* at 1000 amu/s). Chromatographic separation was achieved on a 5% phenyl/dimethyl polysiloxane (Rtx-5) column (30 m x 0.25mm x 0.25 µm film

thickness) using a helium carrier gas with a linear velocity of 40.0 cm sec^{-1}. For OM characterisation experiments the injector port and interface temperatures were 270 ^oC and 310 ^oC respectively. The injector was operated in splitless mode. The initial oven temperature was held at 30 ^oC for 3.5 minutes with an increasing rate of 8 $^oC\ min^{-1}$ to 310 ^oC. For OM removal experiments, the injector port and interface temperatures were 270 ^oC and 300 ^oC respectively. The injector was operated in split mode with a split ratio of 17. The samples were applied by the cold on-column technique at 10 ^oC. One minute after injecting the samples, the temperature of the oven was raised to 300^oC at a rate of 10 $^oC\ min^{-1}$.

2.3. Total Organic Carbon

The total organic carbon (TOC) was quantified in both pregnant and spent Bayer Liquor samples using a TOC-5000 analyser with ASI-5000 autosampler (Shimadzu). The instrument was calibrated using potassium hydrogen phthalate standard solutions in Milli-Q water (18.2 MΩ cm) over a concentration range of 15 – 80 mg C L^{-1}. A methanol standard (48 mg C L^{-1}) was used to assess the condition of the Pt catalyst. Both the pregnant and spent Bayer Liquor samples were acidified to pH 6.5 with HCl (2 M), where they were then centrifuged at 3000 rpm for 30 min to remove the precipitated $Al(OH)_3$. The precipitate was then washed in HCl (pH 6.5) four times. The supernatant was then filtered using 0.45 μM membrane filter (Sartorious), where it was collected as a clear, yellow solution. The filtered supernatant was then diluted by a factor of 50 where it was subsequently acidified to pH 4 using HCl (2 M). 5 mL aliquots were taken and purged with $N_{2\,(g)}$ for 5 minutes to remove any dissolved CO_2 prior to TOC analysis to avoid quantification of non-organic carbon.

2.4. Elemental Microanalysis of Bayer Liquor Aluminium Hydroxide

The pregnant and spent Bayer Liquor samples were left for a period of a few months to allow the extracted $Al(OH)_3$ to naturally precipitate out. The liquors were not seeded to promote $Al(OH)_3$ precipitation. The precipitate was collected and thoroughly washed with Milli-Q water (18.2 MΩ cm) and dried under vacuum for 12 hours at 40 ^oC. The samples were ground using an agate mortar and pestle to form a homogeneous mixture. The dried precipitates were then analysed using an Elemental Analyser PE2400 CHNS/O (PerkinElmer, Shelton, USA) with a PC based data system, PE Datamanager 2400 for Windows and a PerkinElmer AD-6 Ultra Micro Balance.

2.5. Characterisation and Quantification of Bayer Liquor Precipitate

A known volume of pregnant and spent Bayer Liquors were acidified to pH 6.5 with HCl (6 M). The acidified solutions were then centrifuged at 3000 rpm for 30 min to isolate the precipitated $Al(OH)_3$, which was collected and washed with HCl (pH 6.5) and subsequently died under vacuum at 50 ^oC for 10 hours. The precipitates were ground using an agate mortar and pestle to form a homogeneous powder, which was then calcinated in a furnace (CEMLS, Ceramic Engineering) for 15 hours at 1200 ^oC to yield a fine white powder. The powder was then weighed and characterised by X-ray florescence (XRF) spectroscopy (MiniPal QC, PAnalytical). A brown amorphous solid collected from the pregnant Bayer Liquor was also washed with HCl (pH 6.5) and died under vacuum at 50 ^oC for 10 hours. This material was then ground and mixed with the XRF Multi-mix PXR-200 in a 1:4 ratio. This mixture was characterised by XRF.

2.6. Characterisation of Bayer Liquor Organic Matter

Pregnant and spent Bayer Liquor samples were acidified to pH 6.5 with HCl (6 M) and centrifuged at 3000 rpm for 30 min to remove the precipitated $Al(OH)_3$. The supernatant was then accurately acidified to pH 2 using HCl (6 M). A 10 mL aliquot was transferred to a sample vial with the addition of the internal standard, cyclopentane carboxylic acid (105.3 mg L^{-1}) and NaCl (2 g). The protonated OM were extracted using solid-phase micro-extraction (SPME), dipping an 85 µm polyacrylate (PA) fibre into the solution for 10 minutes. SPME instrumentation was supplied by Supelco. Extraction was performed at room temperature (23 ± 3 ^oC). After the extraction, the fibre was immediately exposed to the headspace over MTBSTFA/Pyridine (7:3) derivatising reagent with a $N_{2\,(g)}$ atmosphere, heated at 70 ^oC for 10 minutes. The SPME needle was then directly inserted into the GC injection port at 270 ^oC and the fibre desorbed for 5 minutes. The derivatising step with MTBSTFA converts the polar, non-volatile organic matter to corresponding *tert*-butyl-dimethylsilyl ethers prior to GC-MS analysis.

2.7. Crystallisation of Gibbsite in Synthetic Bayer Liquors

Synthetic Bayer Liquor samples were prepared by dissolving $Al(OH)_3$ (15.5 g) in NaOH (6.5 M, 100 mL) solution at 190 ^oC. Five aliquots were taken from this synthetic liquor. In four of these aliquots *p*-hydroxybenzoic acid (11.09 x 10^3 mg L^{-1}), vanillic acid (11.07 x 10^3 mg L^{-1}), methylsuccinic acid (11.10 x 10^3 mg L^{-1}) and glutaric acid (10.85 x 10^3 mg L^{-1}) were

dissolved separately. The fifth aliquot was used as a blank. These solutions were then left to cool to room temperature, where they were subsequently dehydrated under vacuum at 45 ºC for 7 days. The crystals collected from each sample were washed with Milli-Q water (18.2 MΩ cm).

2.8. Ammonia Reactions with Bayer Liquor Organic Matter

Reactions with Bayer Liquors were performed in high-pressure reactors known as bombs. These bombs were comprised of two sections, an air tight 50 mL Teflon cylinder contained within a stainless steel pressure-tight cylinder. The Teflon cylinders are known to be porous, absorbing many organic impurities especially when heated. Therefore, the Teflon cylinders were cleaned before and after every use by heating chromic acid (20 mL) to 200 ºC for 1.5 hours continuously until the chromic acid remained brown. The Teflon bombs were then rinsed 3 times with distilled water. The Teflon bombs were then cleaned with nitric acid (2 M, 20 mL) which was heated to 200 ºC for 2.5 hours. The Teflon was then rinsed another 3 times with distilled water and dried at 120 ºC.

Aliquots of spent Bayer Liquor (40 mL) were transferred into the cleaned bomb along with frozen ammonium hydroxide solution (15 M, 10 mL). The ammonium hydroxide solution was frozen to slow the formation of ammonia gas once it comes into contact with the caustic Bayer Liquor. The bomb was then sealed and heated to 200 ºC for 14 hours, the duration of which it was continuously rotated.

An aliquot of the reacted liquor (20 mL) was transferred to a 40 mL sample vial. The internal standard, dimethylformamide (0.2 µL) was added to the liquor along with NaCl (2 g). The vial was then heated to 70 ºC for 10 minutes before extracting any volatile nitrogen species with SPME, by exposing an 85 µm carboxen/ polydimethylsiloxane (CAR/PDMS) coated fibre into the heated for 10 minutes. SPME instrumentation was supplied by Supelco. The SPME device was then directly inserted into the GC injection port at 270 ºC for analysis.

A separate aliquot of the reacted liquor (10 mL) was taken for OM characterisation, following the same procedure as described in section 2.6.

A blank analysis was also performed as described above but without the addition of the frozen ammonium hydroxide solution.

2.9. Wet-Oxidation of Bayer Liquor

Aliquots of spent Bayer Liquor (40 mL) were transferred into the cleaned bomb, where it was then purged with $O_{2\,(g)}$ for 2 minutes. The bomb was sealed with an oxygen atmosphere and heated to 200 ^{o}C for 14 hours, where it was continuously rotated.

An aliquot of the reacted liquor (20 mL) was transferred to a 40 mL sample vial. The internal standard, dimethylformamide (0.2 µL) was added to the liquor along with NaCl (2 g). The vial was then heated to 70 ^{o}C for 10 minutes before extracting any volatile species with SPME, by exposing an 85 µm carboxen/ polydimethylsiloxane (CAR/PDMS) coated fibre into the heated for 10 minutes. SPME instrumentation was supplied by Supelco. The SPME device was then directly inserted into the GC injection port at 270 ^{o}C for analysis.

A separate aliquot of the reacted liquor (10 mL) was taken for OM characterisation, following the same procedure as described in section 2.6.

2.10. Nitrile Stability Analysis in Spent Bayer Liquor

An aliquot of the blank ammonia reaction (20 mL) was transferred to a 40 mL sample vial. Benzyl cyanide (0.2 µL) was added to the liquor along with NaCl (2 g). The vial was then heated to 70 ^{o}C for 10 minutes before extracting any volatile species with SPME, by exposing an 85 µm carboxen/ polydimethylsiloxane (CAR/PDMS) coated fibre into the heated for 10 minutes. SPME instrumentation was supplied by Supelco. The SPME device was then directly inserted into the GC injection port at 270 ^{o}C for analysis. The vial was kept at 70 ^{o}C, where it was analysed 4 more times over a period of 4 hours to monitor the stability of the nitrile. This liquor was then taken for OM characterisation, following the same procedure as described in section 2.6.

A second aliquot was taken from the blank ammonia reaction (20 mL) was transferred to a 40 mL sample vial. Benzyl cyanide (0.2 µL) was added to the liquor along with NaCl (2 g). This vial was kept at 4^{o}C for 7 days. After this 7 day period, the vapours were analysed as stated above.

Chapter 3: Results and Discussion

3.1. Quantification of Total Organic Carbon

Determination of the total non-purgeable organic carbon (NPOC) was performed to provide accurate values of the TOC present within both spent and pregnant Bayer Liquor

samples, using a TOC analyser. The samples were acidified and purged with N_2 gas prior to TOC analysis to remove any non-organic carbon, such as dissolved CO_2 from the atmosphere. This analysis was performed in triplicate for each spent and pregnant Bayer Liquors samples provided, equating to 9 replicates for each liquor. These TOC results are tabulated below in with uncertainties reported at a 95% confidence intervals (CI).

Table 3.1.1. Total organic carbon values for the spent and pregnant Bayer Liquors (± 95% CI $_{n=3}$), quantified using TOC analyser

Sample	TOC / g L^{-1}
Spent Bayer Liquor	8.2 ± 1.0
Pregnant Bayer Liquor	4.9 ± 1.2

As expected, the spent liquor was found to possess a higher TOC than the pregnant liquor, since the recycling of the Bayer Process introduces more OM with each new bauxite digestion.

In spent liquors, the organic content reaches a level of equilibrium, where the OM output rises to equal OM input, or OM input lowers to meet OM output (25). Poisoning mechanisms are one of the output sources of Bayer Liquor OM, as organic poisons are continuously removed during the gibbsite precipitation step through adsorption (14, 25). If an increase in this output source was observed with each new cycle, then poisons are slowly concentrating, causing rates of gibbsite precipitate to decrease. This indicates that these poisons may reach a critical level causing the liquor to exhaust its ability to recover gibbsite efficiently. Investigation into the amount of deposited carbon on precipitated gibbsite from both spent and pregnant liquors may indicate if this is occurring and therefore if this should be considered for identification of poisons.

3.2. Elemental Microanalysis of Bayer Liquor Aluminium Hydroxide

Determination of the percentage of carbon adsorbed onto precipitated gibbsite from both spent and pregnant Bayer Liquors was performed using a CHNS/O Elemental Analyser. Crystallisation of $Al(OH)_3$ was not induced as the liquors were not seeded. Alternatively, precipitation was prompted through aggregation processes, likely governed by Brownian diffusions and the attachment of colliding particles that are controlled by colloidal interactions (9, 96). Two distinct forms of precipitates were collected from the pregnant liquor: a hard brown amorphous layer and a white powder which was found underneath the first layer. However from the spent liquor, only a white powder was collected. The carbon weight percentages from the

washed and dried precipitates are tabulated in Table 3.2.1 with uncertainties reported at a 95% CI.

Table 3.2.1. Carbon weight percentage values of precipitate collected from spent and pregnant Bayer Liquors (± 95% CI $_{n=3}$), analysed using CHNS/O Elemental Analyser.

Sample	Carbon Weight Percentage / %
Spent White Precipitate	0.06 ± 0.2
Pregnant White Precipitate	0.01 ± 0.2
Pregnant Brown Precipitate	0.24 ± 0.2

The values tabulated in Table 3.2.1 are relatively small, indicating that only a small portion of organics absorb onto the precipitate. Interestingly, the comparison between the white precipitate values from the spent and pregnant liquors indicate that the rate of organic output via absorption onto precipitated $Al(OH)_3$ is equivalent for both spent and pregnant liquors at 95% CI. These results are not entirely surprising, as many organics are known to absorb readily to gibbsite surfaces, without inducing crystal growth inhibition (14, 49). Unfortunately, these results are therefore not indicative of the amount of poisons bound to the precipitated $Al(OH)_3$, but likely correspond to a variety of absorbed organics and poisons from the liquor. A recent survey performed at a BHP Billiton refinery revealed that the second largest HS removal step in the Bayer Process was through gibbsite precipitation (97). These findings suggest that organics are continuously removed from the liquor by gibbsite absorption and is not a trait unique to poisons as many investigations suggest (2, 14, 44, 78, 98).

Addressing the high carbon weight percentage of the brown amorphous solid collected from the pregnant liquor, it is apparent that the output of organics via precipitation is significantly greater in the pregnant liquor than the spent. The composition of this amorphous material will need to be determined to conclude whether organics are removed from the precipitation step solely by gibbsite adsorption or by adsorbing to another material within the liquor. Nonetheless, these results indicate that it is not the amount of organics adsorbed causing the decreased rates of gibbsite precipitated observed in spent liquors. Therefore, it becomes likely that the cause of spent liquor poisoning is through the increase production of particular poisons. The formation of these poisons must reach a level which is significantly large enough of outcompete other adsorbing poisons for active growth sites. Furthermore, these poisons must be forming at a rate greater than their increasing rates of removal. Assuming that the organic input from each new bauxite digestion has the same HS distribution, then the organic species present in the pregnant liquor must undergo chemical changes in the hot caustic conditions to produce the poisons at a greater rate than their removal.

3.3. Characterisation and Quantification of Bayer Liquor Precipitates

The amount of alumina present in both spent and pregnant liquors was quantified to determine the degree inhibition experience in spent liquor. For quantification, the recovered alumina from a known volume of liquor was weighed and characterised by XRF.

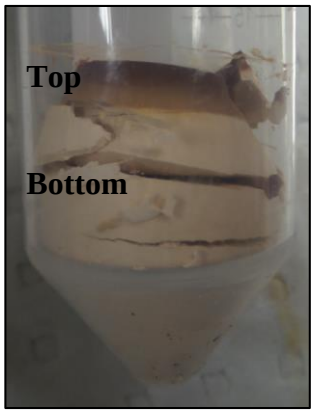


Figure 3.3.1. Picture of dried precipitated recovered from pregnant Bayer Liquor. Top: borwn amorphous layer. Bottom: pale powder

For alumina recovery, the liquors were acidified to pH 6.5, causing $Al(OH)_3$ to precipitate (99). The collected precipitates were washed and dried. Interestingly, as the precipitates dried, a hard brown amorphous solid began to form at the top of the precipitate (Figure 3.3.1), as observed in the naturally precipitated pregnant liquor mentioned in section 3.2. The pregnant precipitate formed a larger amount of the brown amorphous solid than the spent liquor.

The dried samples were homogenised, calcinated, weighed and characterised by XRF analysis, with the results tabulated in Table 3.3.1. A separate analysis of the brown amorphous solid, collected from the pregnant liquor was also characterised with results tabulated in Table 3.3.1.

Table 3.3.1. Summary of metal species with their precent composition present in pregnant and spent Bayer Liquors and a brown amorphous solid collected from pregnant Bayer Liquor. The metal species are assumed to exist as oxides due to calcination performed in an oxygen atmosphere.

Elemental Composition	Spent Liquor Concentration %	Pregnant Liquor Concentration %	Elemental Composition	Pregnant Brown Amorphous Solid Concentration %
Al_2O_3	98.199	98.621	Al_2O_3	90.514
K_2O	0.779	0.419	Cl	7.331
PO_4	0.461	0.536	Ga_2O_3	0.623
V_2O_5	0.194	0.146	CaO	0.443
Ga_2O_3	0.185	0.158	V_2O_5	0.434
CaO	0.065	0.068	MoO_3	0.339
CuO	0.064	0.013	As_2O_3	0.098
MoO_3	0.018	0.001	K_2O	0.058
Ag_2O	0.012	0.018	WO_3	0.048
			CuO	0.024
			Br	0.022
			Cr_2O_3	0.016

The XRF used in this analysis is incapable of detecting elements positioned above sodium in the periodic table of elements, therefore the amount of oxygen within the sample could not be directly analysed. As a result, the metals present in Table 3.3.1 were assumed and calculated as metal oxides, as the precipitate was calcinated in an oxygen atmosphere and would therefore likely exist as metal oxides.

Adjusting for compositions within the calcinated precipitates, the yield of alumina collected from the pregnant and spent Bayer Liquors were 129.9 g L^{-1} and 84.88 g L^{-1} respectively. The typical recovery yield of alumina collected during a cycle of the Bayer Process is 70 g L^{-1} (100). It is indicative that the induced inhibition seen in the spent liquor decreases efficiency to below 36%.

The compositional results from the brown amorphous solid revealed that it was a $Al(OH)_3$ crystal with a high levels of chloride. The high levels of chloride indicate that sodium chloride formed during the acidification which was performed with HCl. High levels of sodium in gibbsite crystals are known to rapidly increase the rates of gibbsite crystallisation (101). This may explain why only precipitated gibbsite with high levels of sodium crystallised during the drying process. The brown colour of this crystalline material may likely be attributed to the higher level of chromium present. Chromium provides the red colour seen in many other aluminium oxide gemstone like ruby.

3.4. Characterisation of Bayer Liquor Organic Matter

3.4.1. Extraction of Organic Species

To analyse the complex mixture of fulvic-type substances from a matrix as complicated as Bayer Liquor, pre-treatment procedures are required to provide a fraction rich with all target analytes, liberated from the other components of the matrix. There are a variety of sample preparation methods available for extraction and concentration of target analytes. However, the procedure has to preserve the structural integrity of the analyte whilst effectively removing the harsh liquor matrix. Traditional extraction techniques, namely solid-phase extraction often need large volumes of samples and solvents, contributing to time consuming and complex procedures (102). Additionally, the nature of these high-solvent techniques have been shown to introduce a bias with loss of low MW organics when extracted OM is dried under vacuum (13). Due to the high abundance and polar functionalities of low MW organics, they are of great interest to this investigation. Therefore, the analytical approach chosen to selectively isolate the fulvic-type substances from Bayer Liquor was solid-phase microextraction (SPME).

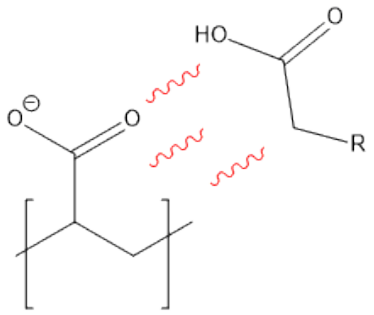


Figure 3.4.1. Polyacrylate (PA) fibre coating used to adsorb OM through hydrophobic, hydrogen bonding and dipole-dipole interactions, as represented by the squiggly lines and dashed lines respectively.

SPME is a solvent-free, one-step extraction method governed by a partition equilibrium of the analyte between the sample and the solid-phase fibre coating, known as the sorbent. (103) The fibre coating consists of an immobilised polymeric phase which can be altered to selectively target and extract different analytes from complex matrices (104). SPME has been extensively employed for volatile and semi-volatile, non-polar compound extraction using sorbents such as polydimethylsiloxane-divinylbenzene (PDMS-DVB), carboxen-PDMS and PDMS (104, 105). However, due to the nature of Bayer Liquor OM, SPME extraction must be performed using a polar sorbent like polyacrylate (PA), which is able to extract small to medium MW hydrophobic, transphilic and hydrophilic OM. PA fibre selectively extracts organics species through hydrogen bonding and dipole-dipole interactions between the acrylic group and the polar functionalities of the OM and hydrophobic interactions between the organic hydrophobic backbones and the alkane backbone of the polymer, Figure 3.4.1.

It is well known that interferences arising from the complexity of a sample matrix can contribute to poor extraction efficiencies using SPME (104). Removal of Bayer Liquor metallic species, like iron oxides and $Al(OH)_3$, can help to reduce the complexity of the liquor matrix. Therefore, the first step of the liquor pre-treatment procedure should involve removal of these metallic species to reduce the complexity and thus promote OM absorption onto the SPME sorbent. Aluminium is a strongly hydrolysing metal, however, it is relatively insoluble in the neutral range. At a pH of 6.5 the phase known to exhibit the lowest solubility, $Al(OH)_3$, becomes the dominant species (99). Accordingly, the first step employed in extraction of Bayer Liquor OM involved acidification of the liquor to pH 6.5, to neutralise the high causticity of the liquor, whilst simultaneously precipitating out $Al(OH)_3$. The precipitated $Al(OH)_3$ is removed from the acidified liquor through centrifugation, leaving a brown liquid, rich in OM.

It is necessary to reduce the liquors pH to increase the absorption of analytes to PA fibres (106-109). Extraction efficiencies of polar analytes dramatically improve at pH levels below the pK_a values of the analytes. The addition of sodium chloride is also able to increase the yields of extraction by increasing the ionic strength of the aqueous solution and ultimately enhancing the analytes affinity for the sorbent (106). Consequently, the liquor is further acidified to pH 2.00 with additions of NaCl (2 g), to promote the OM extraction efficiencies.

Acidification to pH 2.00 not only purges the solution of $CO_{2\,(g)}$ but also causes higher MW OM containing large alkane backbones with limited polar functionalities to crash out of solution (15). Previous studies have shown that these high MW organics constitute the smallest fraction of Bayer Liquor OM, comprising only of 4.3 – 9.2 % (w/w) of total TOC present in spent liquor (13). High MW organics do not exhibit inhibiting properties due to their low polar functionalities and are therefore not of interest in this analysis (14).

The second part of the extraction process involves directly immersing the PA fibre into the acidified liquor, where it is left for 10 minutes, long enough for a partition equilibrium to be reached between the sample and the fibre. Previous studies have shown rises in extraction temperatures worsen the extraction efficiencies of polar analytes onto PA fibres. Therefore, extraction was performed at room temperature (109). Once the fibre has extracted the OM from the water matrix, the fibre can be sheathed into its needle, awaiting analysis. SPME extraction is directly amendable to GC analysis, as adsorbed analytes can be subsequently desorbed and analysed by exposing the SPME fibre to a hot GC injector. Unfortunately, the OM adsorbed are not directly amendable to GC separations, due to their low volatility and/or stability from their excessive polar functionalities. Therefore, the next step required in the samples pre-treatment is derivatisation. The combination of SPME with a derivatisation step allows the determination of polar analytes by GC, thus enhancing both sensitivity and selectivity (109).

3.4.2. Derivatisation and Analysis of Extracted Organic Species

Chromatographic separation by GC provides the greatest level of resolution, allowing mixtures as complex as Bayer Liquor OM to be resolved. This chromatography technique, paired with MS ionisation techniques like electron ionisation (EI), enables important structural information to be obtained on the individual molecular components. It is therefore obvious that analysis by GC-MS is the most suitable analytical technique for structurally characterising Bayer Liquor OM. Additionally, SPME has the ability to be coupled with GC by directly desorbing the extracted organic species into the injector port. However, as the Bayer Liquor OM are highly polar compounds, transformation into more volatile compounds is required to enable GC analysis.

Derivatisation provides the most structurally preserved approach to increase the volatility of the OM. From the variety of derivatising reagents available, silyl derivatising reagents are considered to perform the most rapid, quantitative reactions which yield stable products with good chromatographic properties (103). Silyl derivatisation provides a one-pot reaction derivatising all carboxyl, hydroxyl, phenol and amino functionalities, as shown in Figure 3.4.2. Silyl derivatisation is far superior to other methylation/butylation techniques

where not all polar functionalities are simultaneously derivatised. Previously in literature, only TMS derivatising silyl reagents have been applied to Bayer Liquor OM, the most successful of these studies was able to structurally characterise 50 organic species. However, silyl derivatising reagents like *N*-*tert*-Butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) have been shown to be more robust approach, where other silyl reagents, namely TMS have limited stability with regard to hydrolysis, potentially affecting the derivatisation process (110). The large size of MTBSTFA produces tert-butyldimethylsilyl (t-BDMS) enables increased separation of conformers by rendering a larger structural difference between the derivatised conformers. This aspect is valuable for identification of chiral organic compounds which may have vicinal hydroxyls.

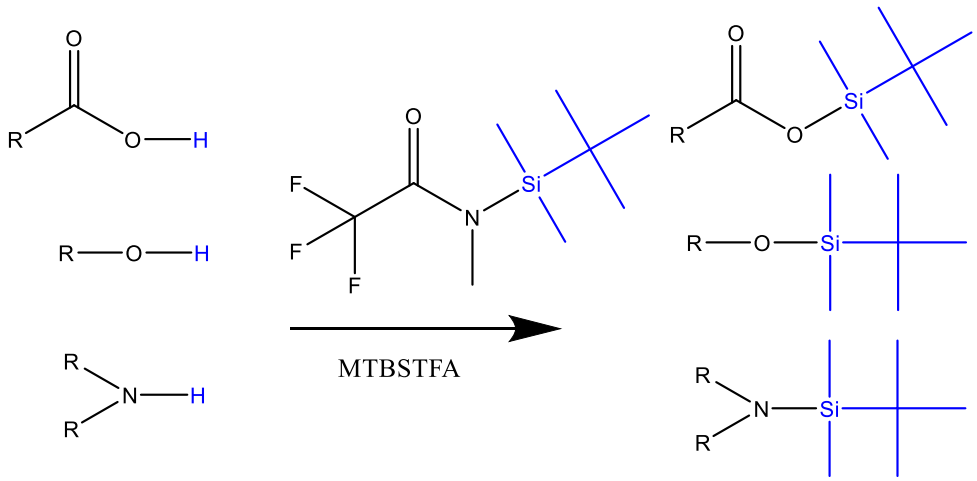


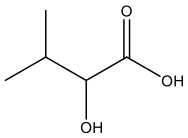
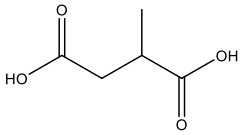
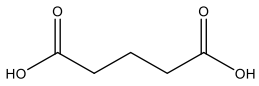
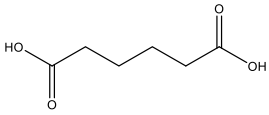
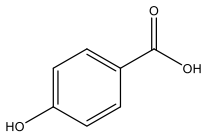
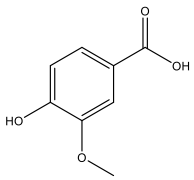
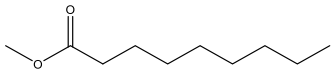
Figure 3.4.2. MTBSTFA derivatisation is a one-pot derivatisation that derivatise all polar functionalities into t-BDMS derivatives

The absence of solvents during SPME analysis gives a unique advantage for derivatisation, overcoming instabilities associated with water matrices. On-fibre derivatisation provides the successful combination of extraction and derivatisation for polar analyte analysis. Experimentally, on-fibre derivatisation is attained by exposing the fibre with extracted analytes to the headspace of a vial containing a small volume of the derivatising reagent. Preliminary studies were performed to optimise the conditions of derivatisation.

3.4.3. Preliminary Studies with Model Organic Species

The purpose of the preliminary study was to investigate the proficiency of the chosen extraction, derivatisation and detection techniques using model Bayer Liquor organics. Optimisation was required for the on-fibre derivatisation method. Additionally, the MS data collected from these standards were used to study the fragmentation patterns of *t*-BDMS derivatives under EI. The seven model organics chosen for this preliminary study with their corresponding concentrations are tabulated in Table 3.4.1.

Table 3.4.1. Model organics chosen for the preliminary investigation to study EI fragmentation patterns for *t*-BDMS derivatives, with their corresponding concentrations used in the study.

Name	Structure	Chosen Structural Features	Concentration / mg L^{-1}
2-Hydroxyl-3-methylbutyric Acid		- Carboxylic functional group - Alcohol functional group - α-Hydroxy carboxylic group (vicinal alcohols) - Sterically hindered hydroxyl	43.2
Methylsuccinic Acid		- Dicarboxylic functional group - Staggered aliphatic chain	43.2
Glutaric Acid		- Dicarboxylic functional group - Aliphatic chain	39.0
Adipic Acid		- Dicarboxylic functional group - Aliphatic chain	43.8
p-Hydroxybenzoic Acid		- Carboxylic functional group - Hydroxyl functional group - Aromatic	41.4
Vanillic Acid		- Carboxylic functional group - Alcohol functional group - Aromatic - Sterically hindered hydroxyl	40.8
Methyl Nonanoate		- Carbonyl - Aliphatic chain - No derivatisation required	10.8

The conditions chosen for the on-fibre derivatisation optimisation are tabulated in Table 3.4.2. Each derivatising chamber was prepared with a nitrogen atmosphere and 50 μL volume of derivatising reagent, where the ratio was varied in accordance to the chosen condition. The derivatisation time and temperature were carefully considered and selected to optimally detect

the wide range of OM present within Bayer Liquors. Each derivatising chamber was heated to the appropriate temperature for 10 minutes prior to analysis.

Table 3.4.2. Optimisation conditions tested for on-fibre derivatisation of model Bayer Liquor organics

Derivatising Reagents	Derivatising Temperature / ºC	Derivatising Time / min
MTBSTFA	50	5
MTBSTFA:Pyridine (7:3 ratio)	70	10
MTBSTFA:Pyridine (5:5 ratio)	90	20

Pyridine is an acid scavenger and is known to accelerate derivatisation reaction. The ratio of MTBSTFA:Pyridine (7:3) was shown to promote derivatisation, producing relatively good yields of derivatised products. In the absence of pyridine, poor yields were obtained. However, a higher ratio of pyridine lowered the yields, as the fibre began to absorb larger quantities of the solvent, thus outcompeting the organics on the fibre. Therefore 7:3 was chosen as the optimal ratio for the derivatising chamber.

The investigation of derivatising time and temperature proved difficult. Variations in these two parameters yielded vastly different results. Exposing the fibre to the derivatising chamber for a shorter periods of time, 5 minutes, favoured the response of smaller MW compounds, like 2-hydroxy-3-methybutyric acid, but provided little to no response for the larger and aromatic compounds as shown in Figure 3.4.3.

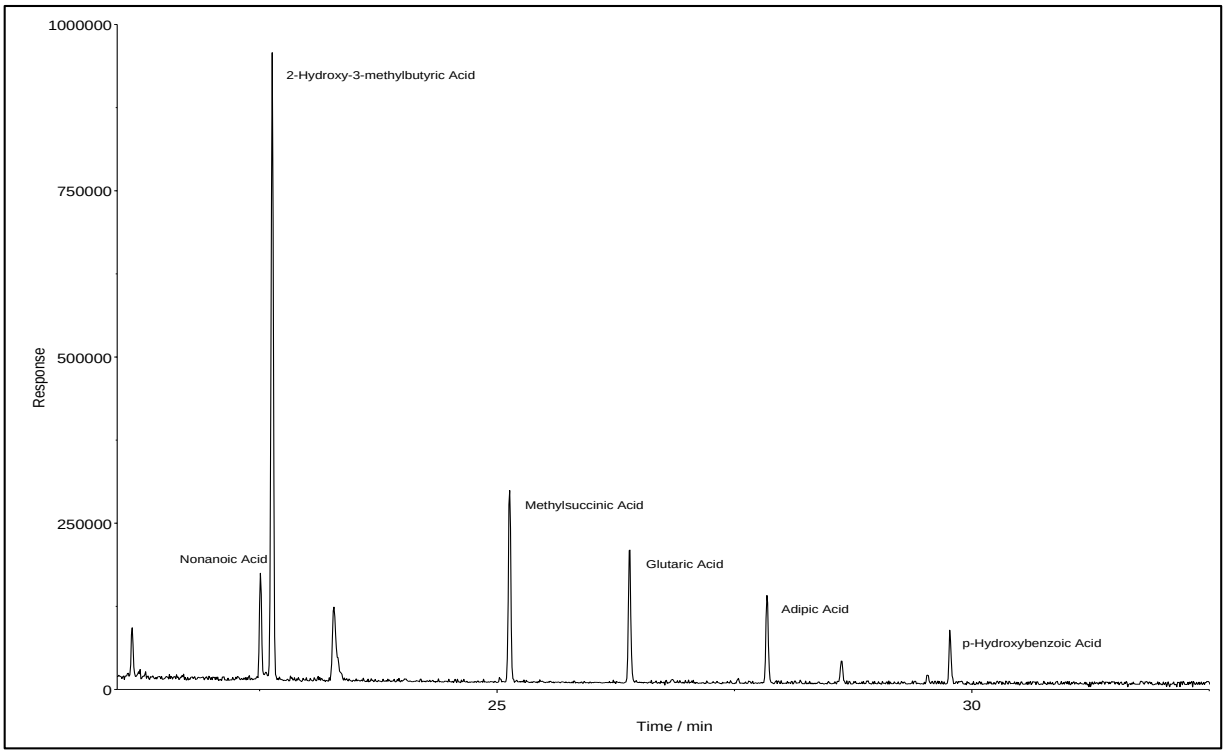


Figure 3.4.3. Derivatisation exposure time of 5 minutes of model Bayer Liquor organics, favouring the formation of lower MW species over larger, aromatic species.

These results indicate that larger or more chemically hindered compounds need longer exposure time to derivatise efficiently. Both vanillic acid and *p*-hydroxybenzoic acid have alcohol groups para to a carboxylic acid group. Carboxylic acids functionalities are known to be deactivating and alcohols are electron donating. Therefore, derivatisation at the para hydroxyl group might have been hindered and consequently required longer exposure time to derivatise efficiently. Accordingly, when the derivatising time was increased to 20 minutes the responses of the aromatic species improved. However, the increased time caused response in the lower MW compounds to significantly reduce with little to no change seen in the aliphatic acids, as shown in Figure 3.4.4.

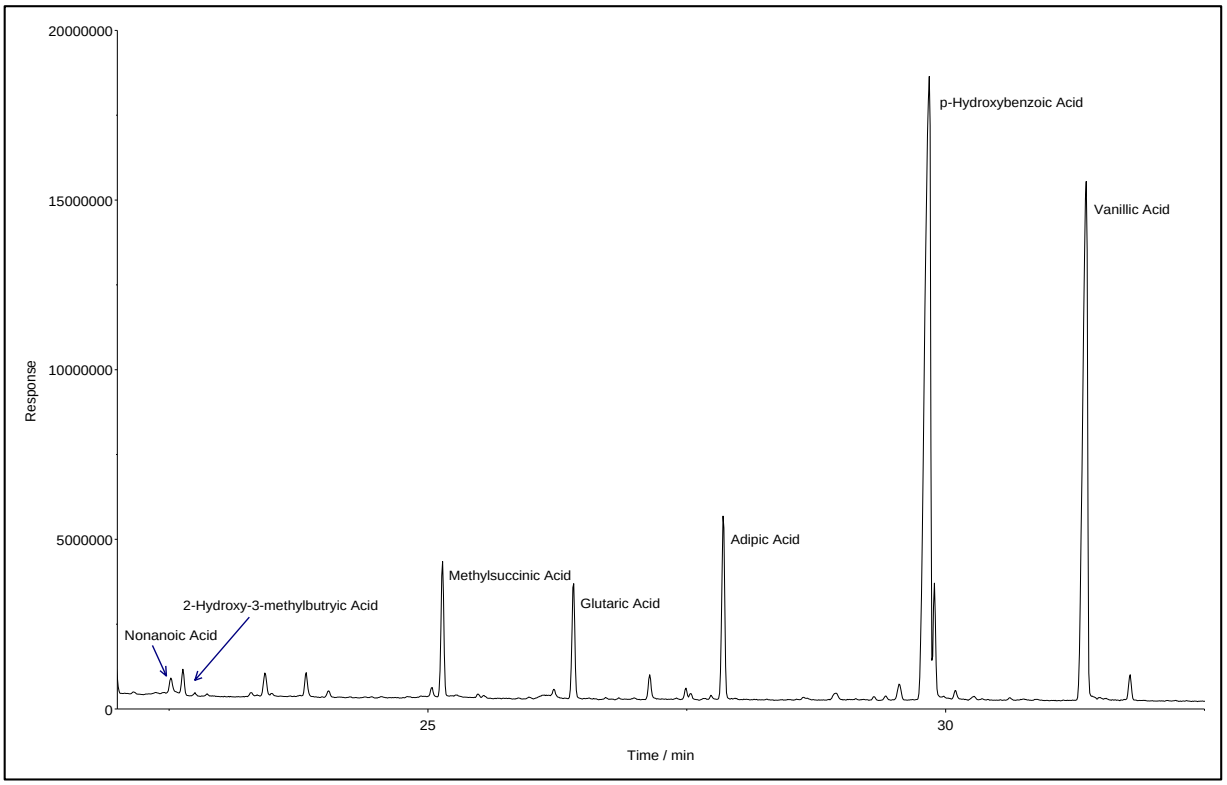


Figure 3.4.4. Derivatisation exposure time of 20 minutes of model Bayer Liquor organics, favouring the formation of larger, aromatic species over lower MW aliphatic species.

Derivatised *t*-BDMS esters are significantly less polar than their underivatised counterparts. Therefore, compounds which derivatise quickly, like low MW organics, desorb off the fibre when exposed to the derivatising chamber for too long as their affinity to the polar fibre has decreased. 10 minutes derivatising time yielded the most favourable responses for the aliphatic and low MW organics, without completely jeopardising the aromatic species, as seen in Figure 3.4.5. Therefore, 10 minutes was selected as the most appropriate derivatising time to incorporate the extensive range of organics in Bayer Liquor.

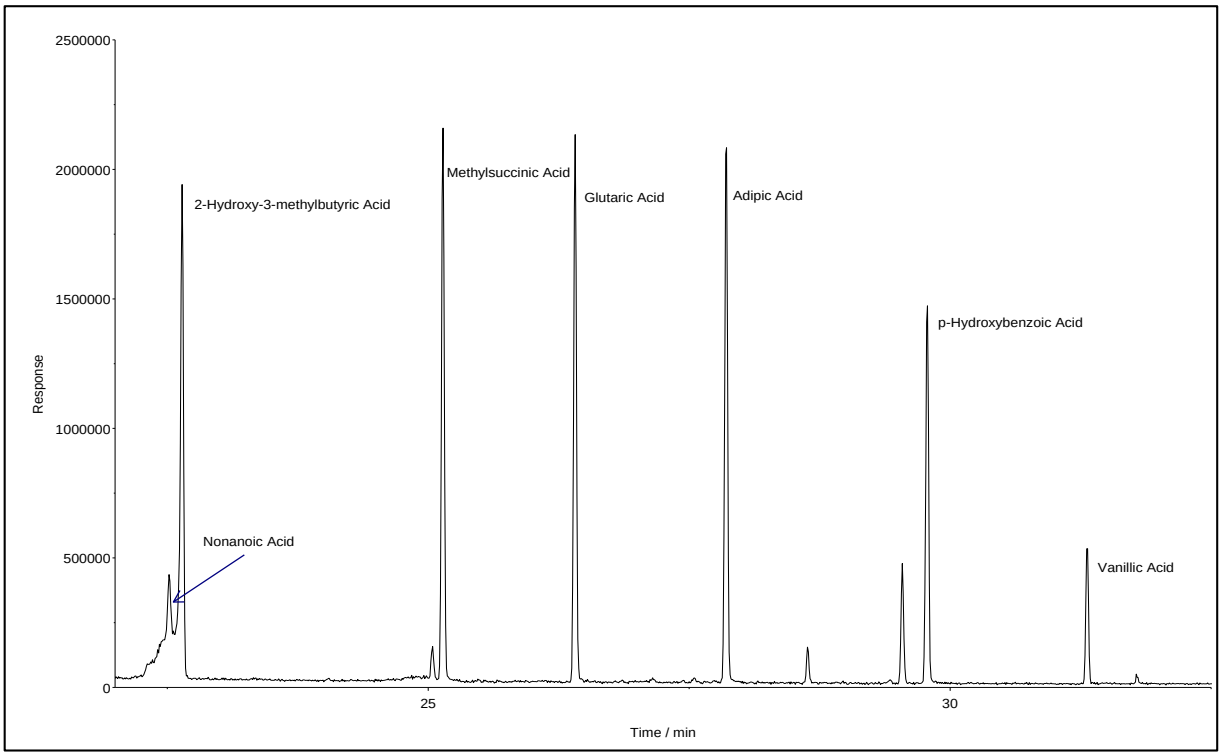


Figure 3.4.5. Derivatisation exposure time of 10 minutes of model Bayer Liquor organics, favouring the formation of larger, aromatic species over lower MW aliphatic species.

Derivatising temperatures were investigated in conjunction with the changing derivatising times. More non-polar compounds and fast derivatising compounds are more susceptible to decrease at higher temperatures, as rate of desorption are promoted. However, at lower temperatures more chemically hindered analytes are unable to derivatise efficiently (106). Consequently, the derivatisation temperature chosen was 70 ºC and this produced the highest yielding responses across the range of organic species analysed.

Initially, the yields of recovery were calculated using the methyl nonanoate ester as the internal standard (IS). However, each replicate showed an increase in the response factor for all standards, indicating that the IS was slowing hydrolysing in the acidified conditions. Evidence of the hydrolysis was revealed by the decreasing peak area of the IS which was accompanied by an increasing peak are of the IS acidic counterpart, as shown in Figure 3.4.3. As a consequence, a new IS needed to be chosen for the characterisation and relative abundance calculations of Bayer Liquor organics.

Two key features were considered when choosing an appropriate IS; structural similarity to model Bayer Liquor organics and retention time. The retention time was of particular importance to avoid co-elution and consequently accurate measurements of peak areas. The structural features of the IS must resemble model Bayer Liquor organics but also must be unique enough to not exist within the liquor. Therefore, cyclopentane carboxylic acid was chosen as the new IS.

The MS data collected from each standard was studied to understand how *t*-BDMS derivatives behave and fragment under EI. This information was then used as a method of analysis for characterising the detected Bayer Liquor organics.

3.4.4. Mass Spectral Fragmentation and Analysis

During the silylation reaction, all groups with active hydrogens are converted into their corresponding *t*-BDMS ethers or ethers via an S_N2 substitution reaction, producing a single derivative for each compound (111). Derivatised OM were analysed by EI to obtain the fragmentation pattern of each compound. Characterisation of each analytes was first addressed by comparison to NIST MS libraries. However, due to limited matching library hits, further steps needed to be taken to identify the derivatised analytes.

The observed ions of *m/z* 73 (TMS), 75 (DMS-OH) and 147 (TMS-O-DMS) have been previously used as internal reference or diagnostic ions of *t*-BDMS ethers (112, 113). These ions are a product of rearrangement processes from MTBSTFA derivatives. The rearrangement fragments *m/z* 73 and 75 are known to appear in almost all *t*-BDMS mass spectres. MTBSTFA derivatives can therefore be selectively targeted by extracting *m/z* 73 and 75 ion chromatograms from the total ion current chromatogram (TIC). The *m/z* 73 and 75 extracted-ion chromatograms (XIC) mirrored that of the TIC, indicating that almost all peaks appearing on the TIC were derivatised analytes. Extraction of less general ions corresponding to more specific structural characteristics can be used to deduce more structural information. The fragment *m/z* 147 is one such ion. Analytes containing two or more active oxygen functionalities, alcohol or carboxylic groups, are able to produce the rearrangement fragment *m/z* 147. This ion can be extracted to deduce analytes containing these functionalities. The intensity of this ion can also provide a general guide for the proximity of these functional groups and in some cases distinguish between isomer of aromatic analytes.

In the mass spectra of *t*-BDMS derivatives, the fragmentation ion $[M-57]^+$ is generally the most abundant ion. The stability of the *tert*-butyl radical (M = 57 amu) favours the cleavage of this moiety over the fragmentation of the total *t*-BDMS group, hence giving rise to the prominent $[M-57]^+$ ion (112). The assignment of the $[M-57]^+$ was used as the first step of the identification procedure, assuming the most abundant signal to be the $[M-57]^+$ ion. In a few cases, the detection of the molecular ion, or the less intensive ions $[M-15]^+$ and $[M-131]^+$ (*t*-BDMS + H_2O), assisted in this identification process. Aromatic compounds are known to exclusively produce the $[M-57]^+$ as the base peak (112, 114) and this was so assumed in most aromatic identification processes.

The next step for characterising aromatic analytes involved the identification of aromatic substituents. This was achieved by targeting common fragmentation ions like benzyl (*m/z* 91, 65 and 39), benzoyl (*m/z* 105, 77 and 51) or phenol (*m/z* 94 and 65). From this information, blueprint structures of aromatic analytes were proposed. For aliphatic acids, homologous series were used to help identify compounds of the same structure, but differing by one carbon length.

More specific steps were required to minimise the number of possible structures when identifying analytes. EI fragmentation pathways and mechanisms for prominent *m/z* ions in the spectra were proposed to explicate each analytes structure. Isotopic peak patterns, calculated using Automated Mass Spectral Deconvolution and Identification System (AMDIS) were used to determine the elemental composition and consequently the molecular formula of the suspected structures. This was extensively used to verify proposed structures for *t*-BDMS derivatives.

Once a structure was proposed for a derivatised analyte, retention indices were compared to literature values provided in the NIST MS library. Retention indices were calculated by running a linear alkane standard (C_{12}-C_{44}, Supleco) under the same chromatographic conditions used for the derivatised OM. An error of 5% between literature and experimental retention indices was used as a guide for identification. Eighteen of the characterised OM were directly validated by co-injection with known standards.

3.4.5. Structurally Characterised Bayer Liquor Organics

Based on the analysis of low to medium MW hydrophobic/hydrophilic/transphilic OM isolated and derivatised from both pregnant and spent Bayer Liquors, 65 organic species were characterised. The organic species of this fraction are dominated by aliphatic and aromatic organic acids. This is consistent with previous studies which have detailed Bayer Liquor OM (2). A summary of the characterised organic species with their corresponding chromatograms are presented in Table 3.4.3, Figure 3.4.6 and Figure 3.4.7 for pregnant and spent liquors respectively.

Table 3.4.3. Compound table for characterised organic matter from Bayer Liquor

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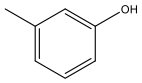
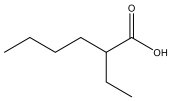
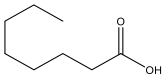
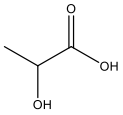
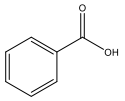
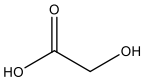
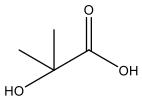
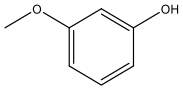
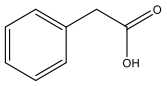
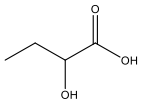
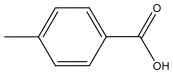
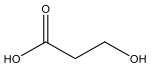
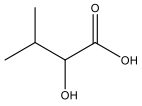
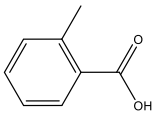
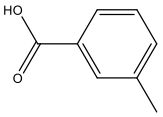
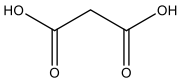
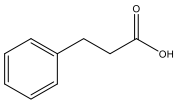
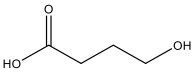
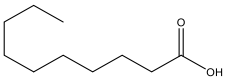
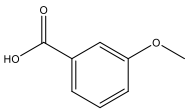
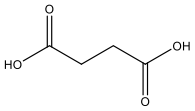
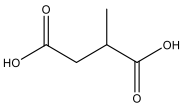
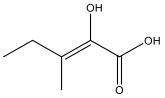
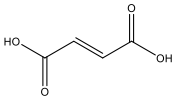
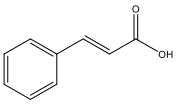
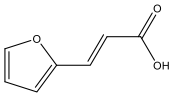
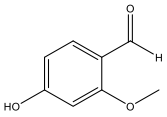
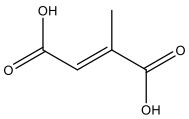
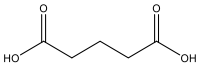
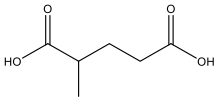
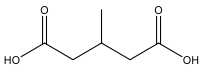
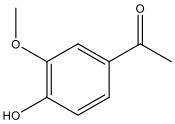
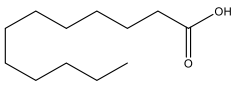
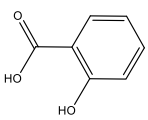
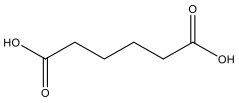
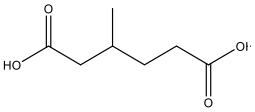
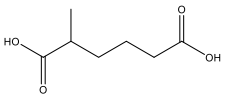
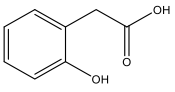
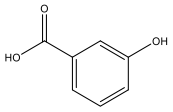
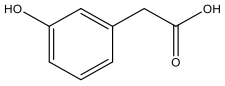
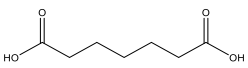
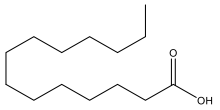
1		2		3	
4		5		6	
7		8		9	
10		11		12	
13		14		15	
16		17		18	
19		20		21	
22		23		24	
25		26		27	
28		29		30	
31		32		33	
34		35		36	
37		38		39	
40		41		42	

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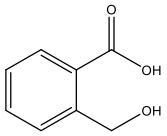
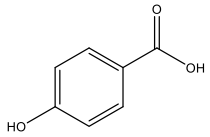
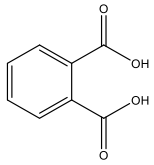
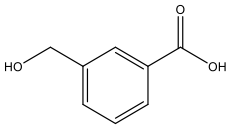
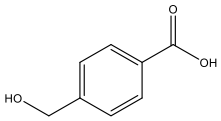
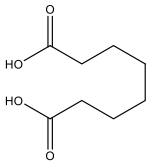
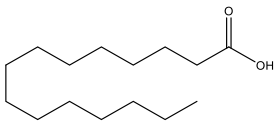
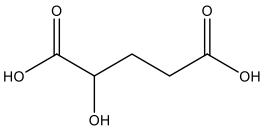
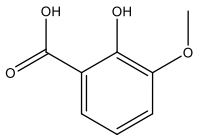
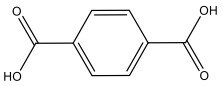
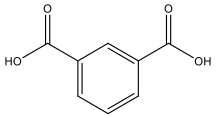
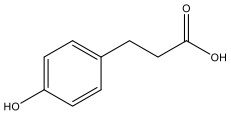
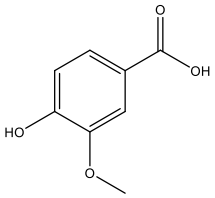
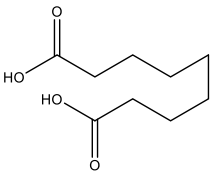
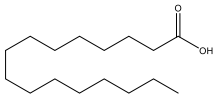
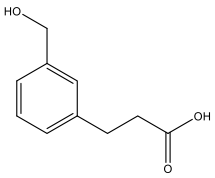
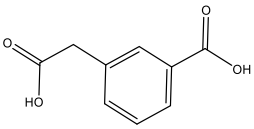
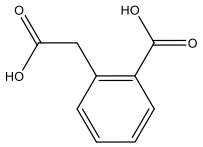
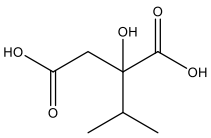
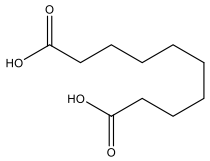
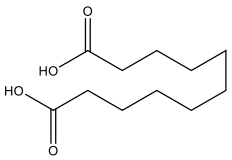
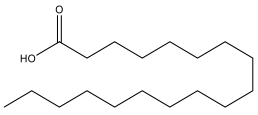
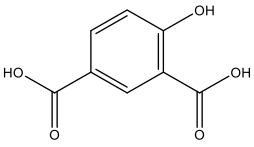
43		44		45	
46		47		48	
49		50		51	
52		53		54	
55		56		57	
58		59		60	
61		62		63	
64		65			

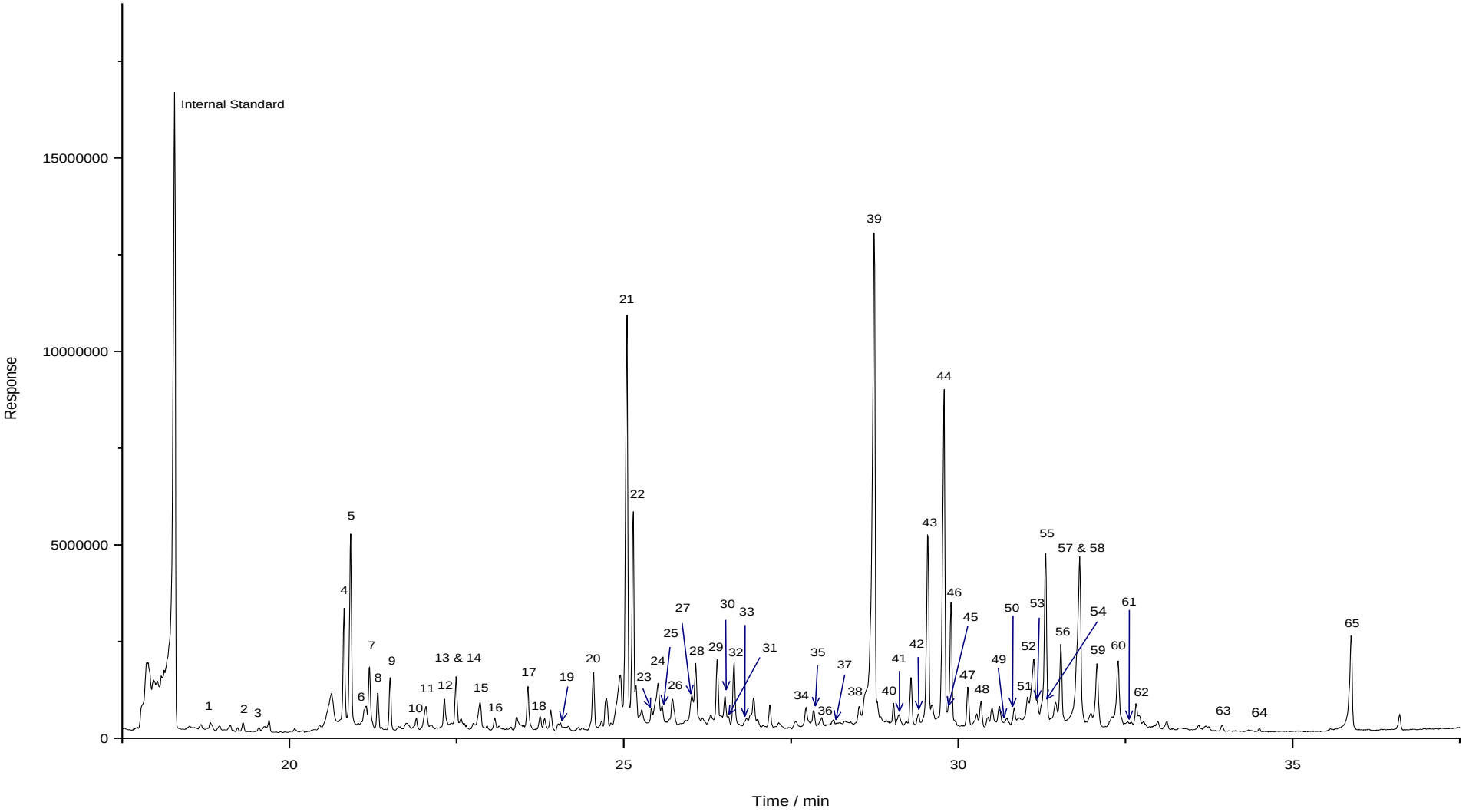


Figure 3.4.6. Detailed GC TIC of pregnant Bayer Liquor organic matter analysed as t-BDMS derivatives. The numbered peaks correspond to organic species listed in Table 3.4.3

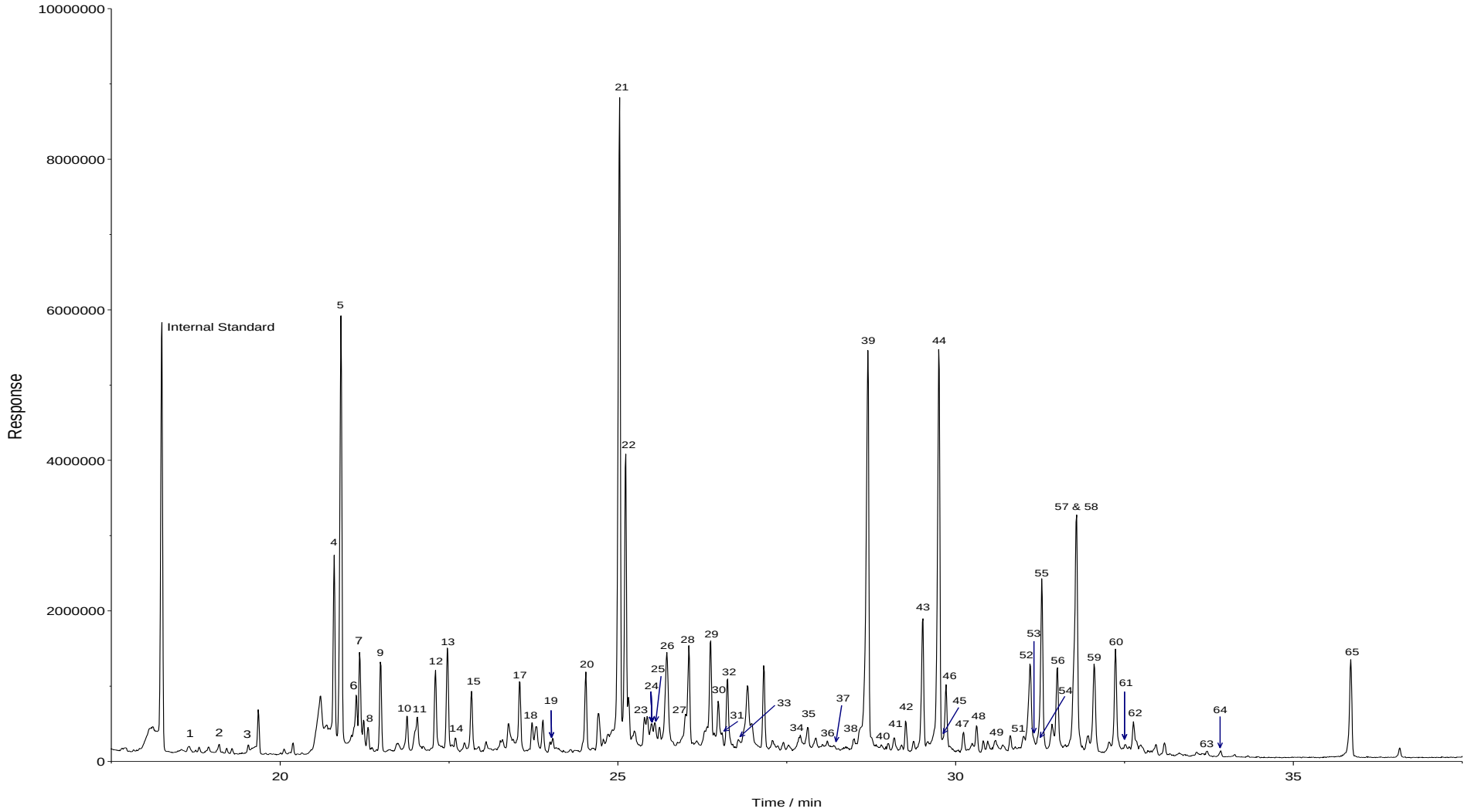


Figure 3.4.7. Detailed GC TIC of spent Bayer Liquor organic matter analysed as t-BDMS derivatives. The numbered peaks correspond to organic species listed in Table 3.4.3

The progressive formation of these relatively smaller organic molecules from NOM in the highly caustic liquor can be envisaged by considering a number of possible reactions. The "humic type structure" shown in Figure 3.4.8 a) is considered a hypothetical structure humic acid originated from soil and will be used in conjunction with structures of model FA in Figure 3.4.8 b) and lignin to help explain the observed Bayer Liquor organics and their relative abundances.

These large HA are commonly comprised of aromatic moieties with multiple polar functionalities. Exposed amide, ester or ether linkages and sidechains may be subjected to possible hydrolysis, oxidisation, cleavage or rearrangement reactions in caustic conditions. Increasing temperatures and causticity progressively increases the degree of degradation of large humic molecules, producing complex mixtures of simpler, smaller and more stable compounds. As, the digestion conditions of the Bayer Process are relatively severe at temperatures above 145 ^{o}C and caustic concentration of approximately 5 mol L^{-1}, aromatic linkages are mostly destroyed, resulting in a wide range of mono-aromatic compounds with simple substituents. Under mild conditions it is unlikely that aromatic moieties are directly attacked. However, under the severe digestion conditions of the Bayer Process, the opening of benzene rings followed by condensation to form larger aliphatic compounds may be possible, though no direct evidence for this has been presented in literature. The range of organic species detected in both Bayer Liquors can be seen from the caustic degradation of HA, as shown in Figure 3.4.8. However, not all the predicted degradation products are observed. Each degradation product must exhibit a high level of stability to withstand these severe conditions. Recent studies of model Bayer Liquor organics revealed that phenols, aromatic and aliphatic carboxylic acids are stable in high caustic conditions even with temperatures raised to 180 ^{o}C (27, 28). Therefore the stability of these small organic acids explains why they are the dominating organics found within both liquors. Whilst stable and likely to form, no amines or amides were detected within the characterised OM from either liquors. These findings indicate that these products are relatively volatile and are lost from the hot liquor through emissions.

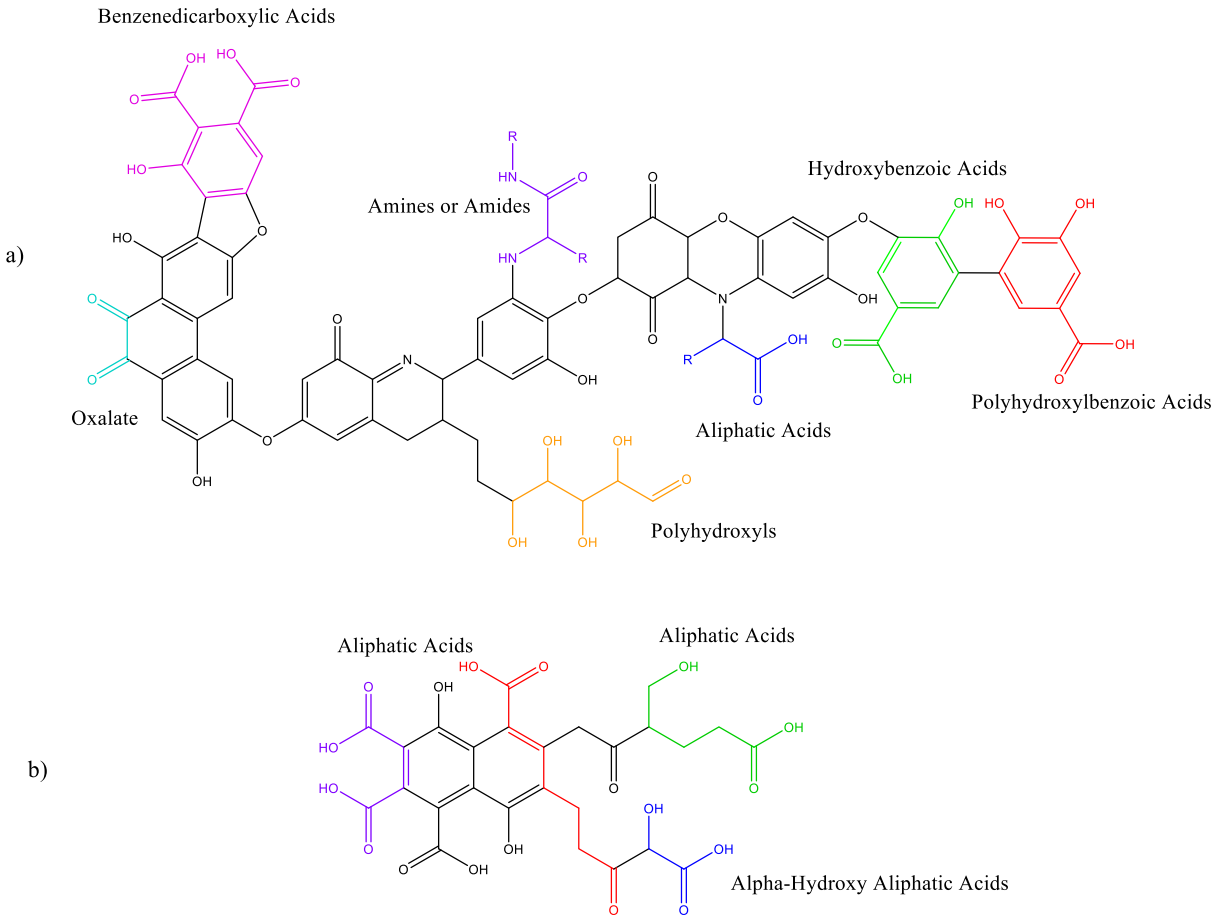


Figure 3.4.8. a) Hypothetical structure of soil HA b) model of soil FA, illustrating how some compounds observed in Bayer Liquor could originate from the breakdown of humic molecules.

Woody material is another primary source of OM in bauxite and is manly derived from root systems and degraded leaf litter and branches. Lignins and polysaccharides are major components of woody material. There are many structural similarities between humates and lignins, indicating that many of the degradation products from this material would resemble that of HA. However, the β-O-4 linkage shown in Figure 3.4.9 is a unique structural feature of lignins. This linkage is readily broken in alkaline solutions to produce polyhydroxyls as illustrated in Figure 3.4.10.

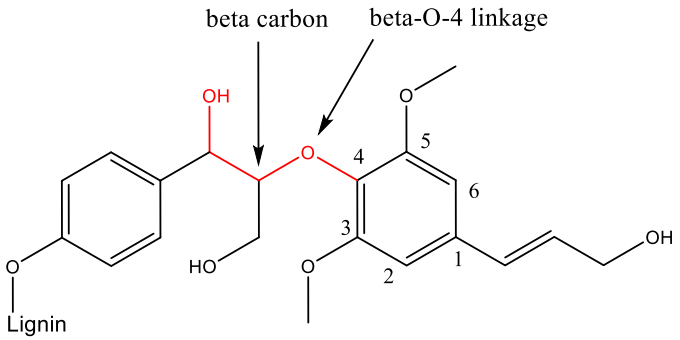


Figure 3.4.9. A schematic illustrating the unique structural feature of lignins known as β-O-4 linkage with adjacent hydroxyls.

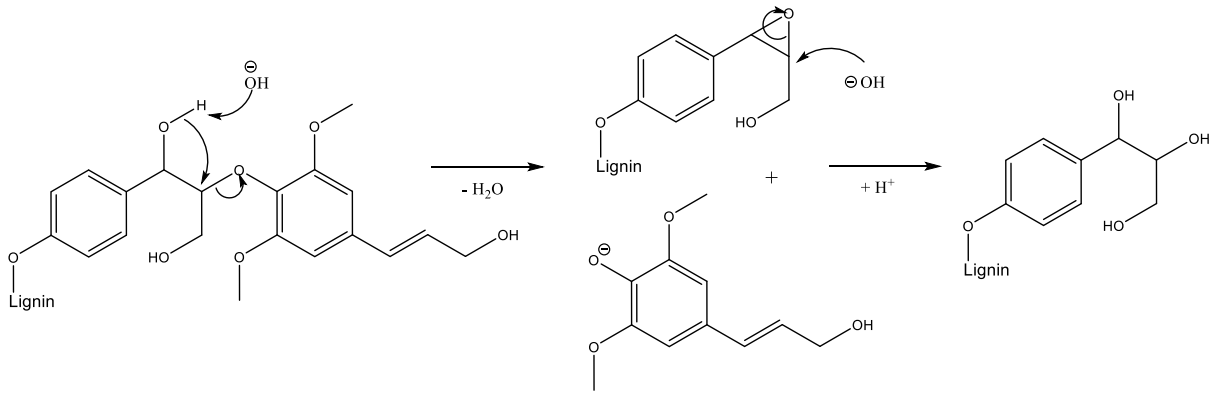


Figure 3.4.10. Alkaline induced breakage at beta-O-4 linkage (26).

As discussed previously, the most distinct features of all model organic poisons are vicinal hydroxyls, commonly as polyhydroxyls or α-hydroxy carboxylic acids. The formation of polyhydroxyls is of great interest and has been shown to be produced in alkaline breakdown of bauxite NOM such as lignins, Figure 3.4.10 (26) and HA Figure 3.4.8. However, no polyhydroxyls were identified amongst the analysed OM from either the pregnant and spent liquors, with only 8 short-chained aliphatic α-hydroxy carboxylic acids detected.

The lack of polyhydroxyls detected in either liquor is not entirely unsurprising and has been noted in other investigations (24). Their lack of recovery has been previously interpreted as evidence that they are the poisons of Bayer Liquor, due to their continual removal from the liquor through poisoning mechanisms (14). However, from the results obtained in section 3.4, it was concluded that adsorption is not a property unique to poisons. Other investigations have questioned the existence of polyhydroxyls in Bayer Liquor and have explored their instability as a possible explanation to why none have been recovered. NOM degradation products require a high level of stability to exist and concentrate within Bayer Liquors. Recently it was reported that aliphatic polyhydroxyls, low MW carboxylic acids and aliphatic carboxylic acids with hydroxyl groups readily degraded at 90 ^{o}C in NaOH (6 mol kg^{-1}). This means that at temperatures even below digestion conditions, it is possible for organics with reactive functional groups to cleave or undergo decomposition reactions, forming short-chained organics and low MW carboxylic acids. Clearly, the instability of polyhydroxyls explains why none were detected within the liquor. Therefore, it can also be assumed that polyhydroxyls could not possibly be responsible for poisoning the spent liquor, as their rates of formation could not increase to exceed or reach their rapid rates of degradation.

3.4.6. Bayer Liquor Organic Poison Identification

The purpose of structurally characterising the organics from both pregnant and spent liquors was to identify the poisons responsible for the inhibition of gibbsite crystallisation in

spent liquors. Comparing the organic species present within the two liquors should indicate whether inhibition is caused by the introduction of a new organic species within the spent liquor, or by existing poisons reaching critical concentrations.

To observe any changes in the detected organic species present within both liquors, their relative abundances needed to be determined. Each characterised organic species was normalised to the IS, as shown in Figure 3.4.11 and Figure 3.4.12 for pregnant and spent liquors respectively with uncertainties reported at a 95% CI. These relative abundances are not representative of their actual abundances within the liquor. SPME and on-fibre derivatisation cannot provide absolute quantification as the extraction and derivatisation processes introduce bias through loss of highly volatile species and increases in higher absorbing organics, resulting in some to appear more abundant than others. Therefore, only changes between the relative abundances can be used for this assessment. The change between the two liquors cannot be evaluated by directly subtracting one from the other, as this does not account for the increased TOC levels of the spent liquor, so almost all species will have increased to some extent. Therefore, between sum of squares (BSS) calculations were performed to measure each organic species variation between the two liquors, as summarised in Figure 3.4.13.

An example of the BSS calculations to determine variance between liquor organics is shown below.

The results obtained for the relative abundance of butyric acid from both pregnant and spent liquors are shown in the following table.

Parameter	Spent Liquor Normalise Value	Pregnant Liquor Normalised Value
Mean	3.0	0.29
SD	1.0	0.14

The grand mean can be obtained from:

$$\bar{\bar{x}} = \sum_{l} \left(\frac{N_l}{N}\right) \bar{x}_l$$

$$\bar{\bar{x}} = \left(\left(\frac{5}{10}\right) \times 3.0\right) + \left(\left(\frac{5}{10}\right) \times 0.29\right) = 1.6$$

The between-liquors sum of squares was obtained by

$$BSS = n \sum_{i} (\bar{x}_i - \bar{\bar{x}})^2$$

$$BSS = 5 \times ((3.0 - 1.6)^2 + (0.29 - 1.6)^2) = 18$$

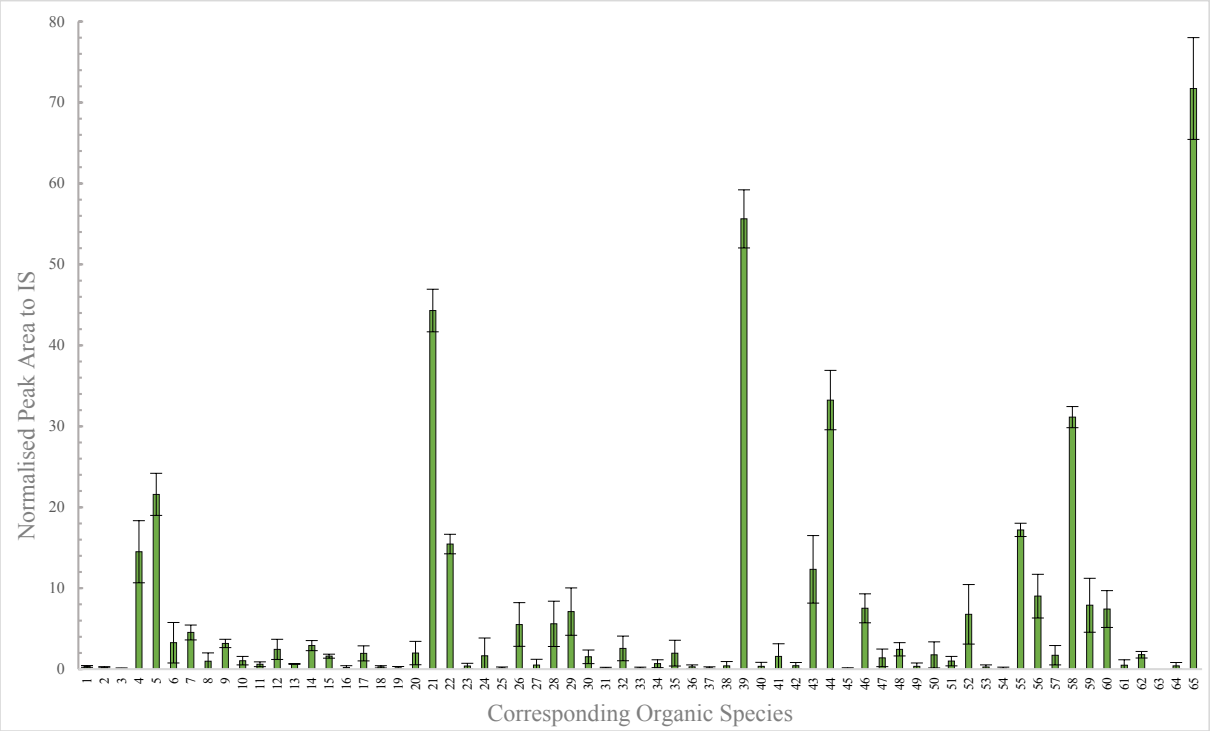


Figure 3.4.11. Peak areas (± 95% CI $_{n=5}$) of characterised organic species found in pregnant Bayer Liquor normalised to the IS (105.3 mg L^{-1}). Corresponding organic species are tabulated in Table 3.4.3.

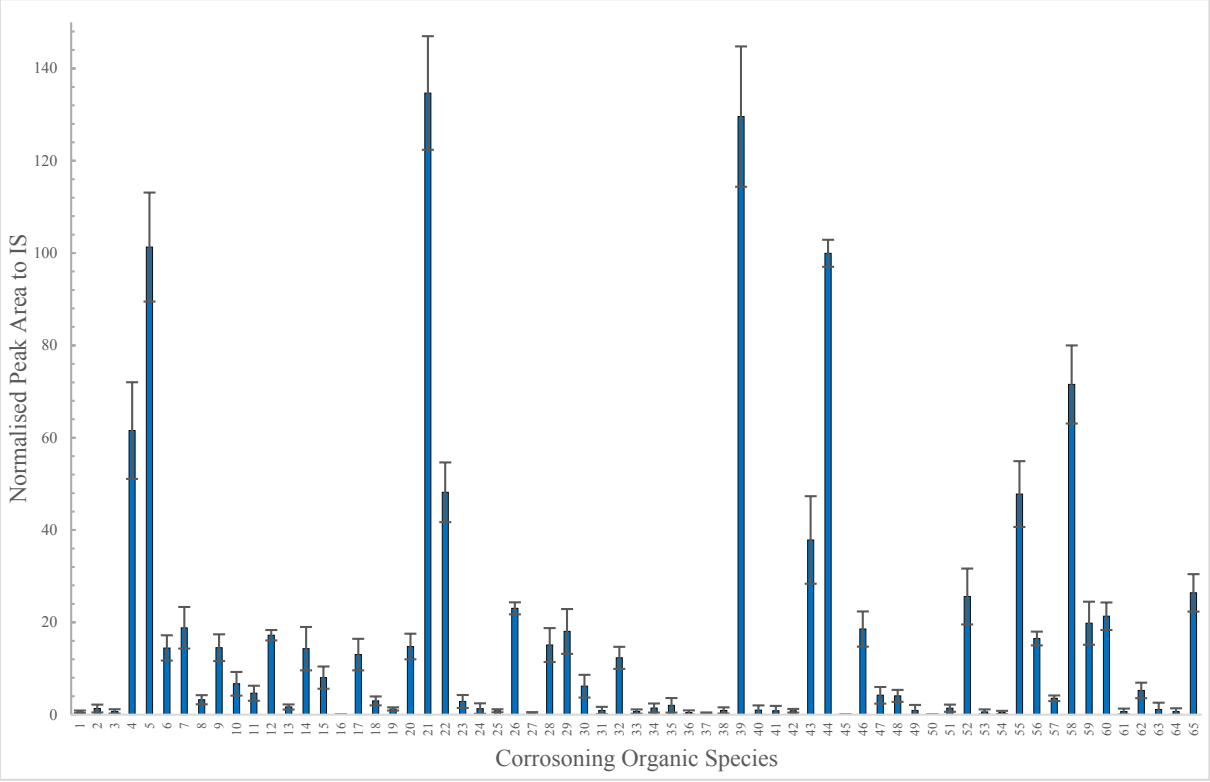


Figure 3.4.12. Peak areas (± 95% CI $_{n=5}$) of characterised organic species found in spent Bayer Liquor normalised to the IS (105.3 mg L^{-1}). Corresponding organic species are tabulated in Table 3.4.3.

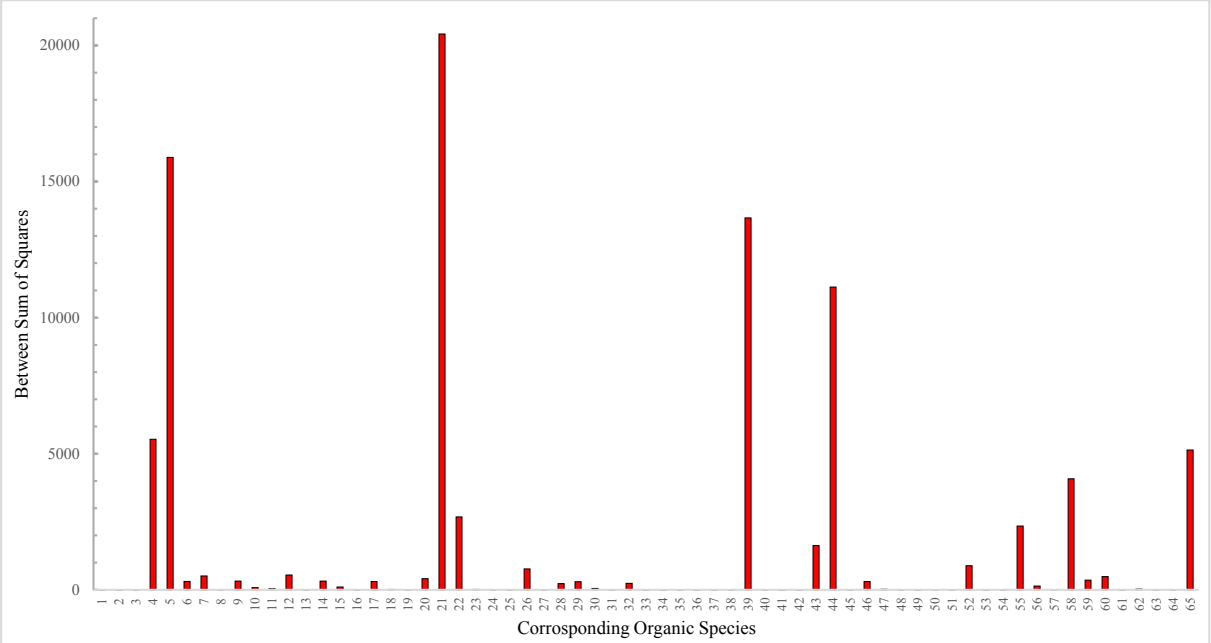


Figure 3.4.13. Between-liquor sum of square calculations to measure which organic species detected significantly differ between the two Bayer Liquors. Corresponding organic species are tabulated in Table 3.4.3.

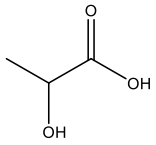
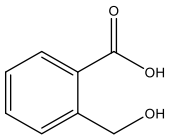
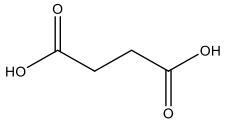
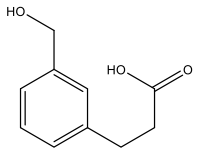
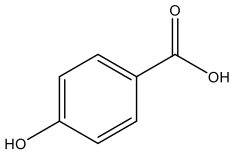
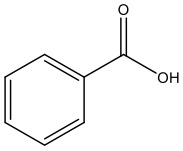
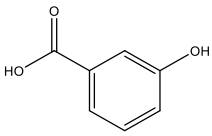
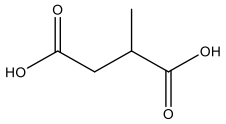
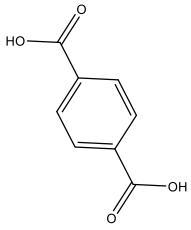
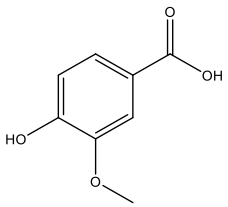
Interestingly, the comparison of organic species present between the two liquors revealed that all the organic species detected within the spent liquor were also all found within the pregnant liquor, with the exception of α-hydroxypentanedioic acid which was found to only exist within the pregnant liquor. These findings suggest that the poisoning of spent liquor is not induced by the formation of new poisons, but by an increased abundance of existing poisons.

As rates of organic removal are constant between the spent and pregnant liquors, poisons need to exist in a significantly greater concentration in the spent liquor to outcompete other absorbing organics, consequently preventing the recovery of gibbsite. Accordingly, organics that significantly increase between the two liquors would be indicative of potential poisons. Certainly, some organics may have inhibiting properties which do not accumulate, however, in order for inhibition to increase, so must the poisons. Therefore all organic species which do not significantly accumulate overtime, despite their potential inhibiting properties will not be considered as the poisons of spent Bayer Liquor. Naturally, some organics will concentrate more than other organics. Therefore, this feature alone cannot be used to identify which organics are poisons. Various inhibiting structural features must also be considered in conjunction with changes in OM abundance for the proposal of suspected poisons.

From the BSS calculations shown in Figure 3.4.13, only 11 organic species demonstrated significant differences between the two liquors. However, compound 65 will not be considered as a potential poison as its variation decreased across the liquors and therefore

does not fit the proposed criteria for inhibiting poisons. A summary of the organic species which significantly increased in between the two liquors is presented in Table 3.4.4.

Table 3.4.4. Organic species which significantly increase in relative abundance between the two liquors, as determined from between-liquor sum of square calculations.

Organic Species with Significant Variation between Pregnant and Spent Liquors				
				
Lactic acid	2-Hydroxymethyl benzoic	Succinic acid	3-(Hydroxymethyl) phenyl propanoic acid	*p*-Hydroxybenzoic acid
				
Benzoic acid	*m*-hydroxybenzoic acid	Methylsuccinic acid	1,4-Benzenedicarboxylic acid	Vanillic acid

Only one of the organic species showing significant variation between the two liquors has vicinal hydroxyls groups. This feature alone highlights its potential as a strong inhibitor. Lactic acid along with succinic acid have been shown to be major degradation products of model Bayer Liquor organics (28) and have been previously reported to cause significant effects of both the yield and particle size distribution of gibbsite under conditions of unseeded precipitation (115). However, no inhibiting effects from these two acids have been reported for seeded precipitation. These two aliphatic acids along with methyl succinic acid will be considered as likely poisons based on previous studies.

For assessing the inhibiting abilities of the remaining 7 aromatic acids, the net charge of the carboxylic oxygens will be considered. Carboxylic groups are known to induce inhibition. The strength of the oxygens net charge is often a reflection of that species inhibiting strength, increasing the net charge in turn increases inhibition. In aromatic systems, the net charge of the carboxylic oxygen can be influenced by the presence of other substituents. Electron-withdrawing substituents can induce a deactivating effect when located para or ortho to the carboxylic group, reducing its net charge and thus its inhibiting ability. This is evident in the comparison between benzoic acid and 1,4-benzenedicarboxylic acid. Benzoic acid is known to inhibit gibbsite growth, however with the addition of a second carboxylic acid para to the first, no inhibition is observed (116, 117). Electron-donating substituents, when positioned para

to the carboxylic group increases the inhibiting strength by increasing the net charge of the carboxylic oxygen (117). Whilst ortho substituents can also increase net charges when electron donating, inhibition is often found to decrease for ortho substituted acids due to steric hindrance (117).

From this information, it can be inferred that 2-hydroxymethyl benzoic acid is unlikely to be a poison. The hydroxymethyl group is not only deactivating, but is located ortho to the carboxylic acid, overall lowering the net charge of the carboxylic oxygen whilst sterically hindering the carboxylic group. This compound can therefore be ruled out as a potential poison. In the case of 3-(hydroxymethyl)phenyl propanoic acid, the hydroxy methyl substituent would not affect the net charge of the carboxylic oxygen as the system is not conjugated. However, as the carboxylic group lies on the aliphatic chain, its ability to inhibit would likely be governed by the characteristics of aliphatic acids not aromatic acids. Previous studies have shown that aliphatic acids containing only one carboxylic acid are unable to inhibit gibbsite growth (14). Therefore, it is also unlikely for 3-(hydroxymethyl)phenyl propanoic acid to exhibit inhibiting properties and therefore will also not be considered as a potential poison.

The meta and para isomers of hydroxybenzoic acid demonstrate potential inhibiting abilities. *p*-hydroxybenzoic acid possesses an electron-donating hydroxyl para to its carboxylic group, increasing the net charge of the carboxylic oxygen. However, *m*-hydroxybenzoic acid would likely exhibit an inhibiting strength similar to that of benzoic acid, as the hydroxyl lies meta to the carboxylic group and therefore is unlikely to contribute to any electronic effects. Controversy, o-hydroxybenzoic acid is known to not inhibit gibbsite growth. However, this may be due to an imposed steric hindrance. A similar assessment can be made for vanillic acid in that a hydroxyl lies para to the carboxylic group.

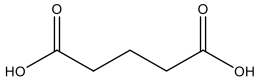
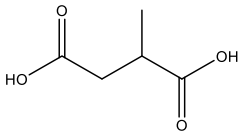
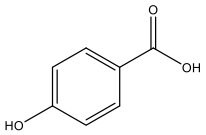
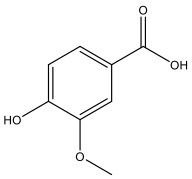
The evaluations made for the identification of spent Bayer Liquor poisons have led to the proposal of 7 likely poisons; lactic acid, succinic acid, methyl succinic acid, benzoic acid *p*-hydroxybenzoic acid, *m*-hydroxybenzoic acid and vanillic acid. The major structural feature shared between these species is the carboxylic acid group and not vicinal hydroxyls. Accordingly, this feature will be considered as a potential target for the OM removal design.

3.4.7. Crystallisation of Gibbsite in Synthetic Bayer Liquor using Identified Poisons

To expand on the results obtained from the BSS calculations and structural assessments, a more detailed examination of the crystallisation was undertaken to eliminate the uncertainties associated with poison identification. Crystallisation of gibbsite in the presence of 3 of the proposed poisons from section 3.4.6 was performed, as tabulated in Table 3.4.5. These poisons were accompanied by glutaric acid, an organic species which did not show any significant

change between the two liquors and is known to not inhibit gibbsite growth. This compound was included within the study to monitor how crystallisation would occur in the presence of non-inhibiting organics. Lactic acid, benzoic acid and succinic acid were not investigated as previous studies have detailed their inhibiting abilities.

Table 3.4.5. List of organic species chosen for gibbsite crystallisation in synthetic Bayer Liquor. Three of these species are proposed poisons, where their structural features will be assessed for inhibition.

Name	Structure	Chosen Structural Features
Glutaric Acid		Not suspected poison Dicarboxylic acids separated by 3 carbons.
Methylsuccinic Acid		Suspect poison Dicarboxylic acids separated by 2 carbons.
p-Hydroxybenzoic Acid		Suspect poison Carboxylic functional group para to a hydroxyl functional group
Vanillic Acid		Suspect poison Carboxylic functional group para to a hydroxyl functional group. Meta methoxy group to carboxylic functionality

This investigation aimed to assess the inhibiting abilities of the identified poisons and in turn, the structural features responsible for this inhibition. When a poison adsorbs to an active growth site causing it to deactivate, the crystal morphology alters (36, 50). Therefore, evaluating changes in the crystal morphology will indicate if the organic species is truly a poisons. Comparisons to the blank and glutaric acid crystals will be used to help identify whether the crystal morphology is altered in the presence of these "inhibiting" organics.

Each synthetic Bayer Liquor sample was prepared in the presence of one organic species from Table 3.4.5, excluding the blank. The synthetic liquors were then dehydrated in a vacuum oven to promote crystallisation. The crystallisation process was continuously monitored over a 7 day period. Interestingly, crystals from the glutaric acid sample began to immediately crash out of solution as the solutions were cooled to room temperature, whereas the blank sample only began to produce crystals within the first day. The remaining 3 samples began to slowly crystallise over the next 3 days. After the 7 day period, the crystals were removed and washed to remove any excess organic material which had not absorbed to the crystals surface. However, as the crystal were washed, the ones grown in the presence of the three poisons began to redissolve. This occurrence was not observed for the blank or the glutaric acid crystals. The

suspect poison crystals continuously redissolved during the washing step, indicating that no true gibbsite crystals were forming and crystallisation was therefore inhibited by the presence of these suspect poisons.

From these results, it was determined that inhibition is induced by electron-donating substituents para to a carboxylic acid group in aromatic systems and that carbon-chains longer than 4 carbons are unable to inhibit growth for aliphatic acids.

3.5. Bayer Liquor Organic Poison Removal

3.5.1. Development of a Novel Organic Poison Removal Strategy

The development of a novel OM removal strategy for the Bayer Process must address four main goals. First, the developed strategy must target the organics known to cause inhibition. Second, the strategy needs to work with the conditions of the Bayer Process, allowing it to be directly imbedded into the cycle. Third, the strategy needs to be simple, limited to only one step. Lastly, the targeted OM must be removed from the Bayer Liquor without additional refinery engineering. Unfortunately, no current OM removal strategy or technology found within literature accomplishes all four goals to a satisfactory level.

Carboxylic acid groups are the structural feature causing inhibition, as observed from the identified organic poisons as detailed in section 3.4.6. Targeting this functionality for removal should result in the removal of identified inhibitors. The transformation of carboxylic acids into a less polar more volatile functionality would be the most practical approach for removal. As such, the transformation of carboxylic acids into nitriles (or amides) via an ammonia reaction was investigated.

The reaction of carboxylic acids into nitriles involves the nucleophilic attack by ammonia on the carbonyl carbon to produce an amide intermediate. This amide can subsequently be dehydrated to further produce a nitrile with the favourable release of water. Whilst high yielding in acidic and neutral conditions, transformation of carboxylic acids into nitriles have never been investigated in caustic conditions where carboxylic acids will be anions. As anions, carboxylic functional groups lack two features required for this reaction within the caustic liquor; a stable leaving group and an electrophilic carbonyl carbon.

As no polyhydroxyls were detected within the liquor, inhibition via the aluminate poison complex becomes unlikely. Attention therefore has to be drawn to structural arrangement of the growth unit complex, which accommodates inhibition through carboxylic acid groups. In the growth unit complex, the carboxylic oxygens of poisons are complexed to aluminium atoms within the growth unit. In this formation, the carbonyl carbon becomes more electrophilic as

the oxygen is no longer anionic. Additionally, the growth unit is able to act as a highly stable leaving group, promoting the nucleophilic attack. The result, transformation of inhibiting poisons into nitriles whilst simultaneously liberating the growth unit from inhibiting, as shown in Figure 3.5.1.

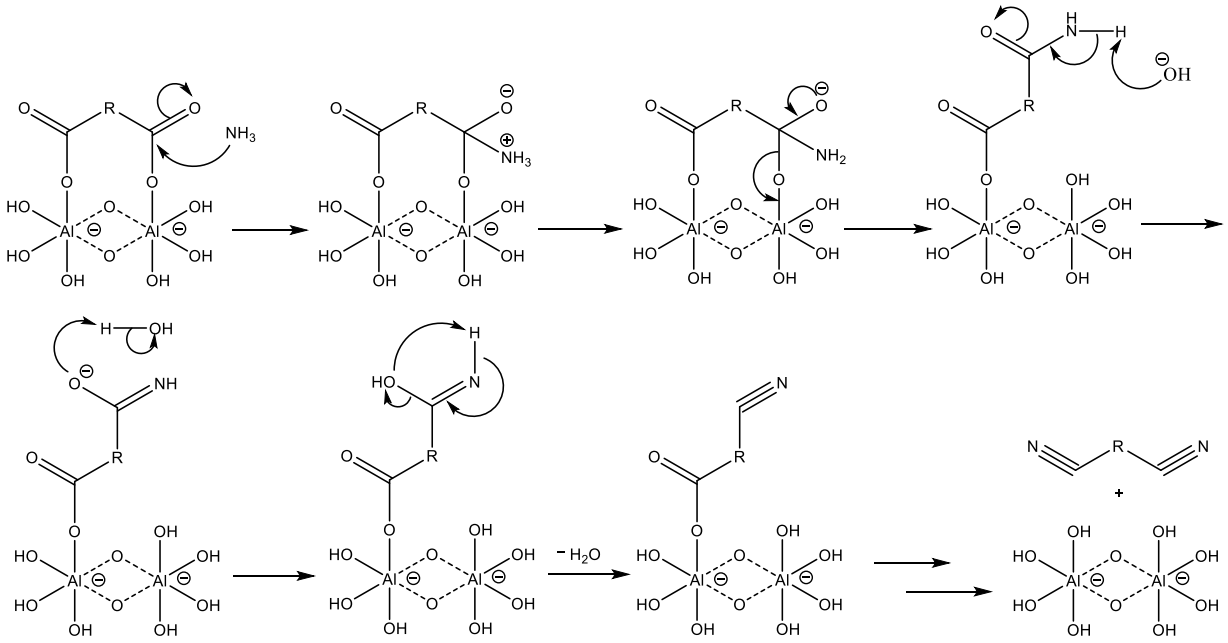


Figure 3.5.1. The proposed mechanisms for carboxylic acid removal via an ammonia reaction. When inhibiting poisons are complexed to the growth unit they can become more susceptible to nucleophilic attack, resulting in the release of the growth unit from the formation of a nitrile.

In caustic conditions, the formation of the amide intermediate lies in equilibrium with the carboxylic acid (Equ. 3.5.1). In accordance with Le Chatelier's principle, formation of the amide is promoted in high pressures, as equilibrium will shift the reaction forward to reduce any ammonia present. Therefore, the formation of the amide intermediate could be promoted if performed during the digestion step of the Bayer Process, which operates under high temperatures and pressures. The favourable formation of water in the final step should push the reaction to completion.

$$2\mathrm{R(COO^-)_2} + 2\mathrm{NH_3} \rightleftharpoons 2\mathrm{R(CONH_2)_2} + 2\mathrm{OH^-} \rightleftharpoons 2\mathrm{R(CN)_2} + 2\mathrm{H_2O} \qquad \textbf{Equ. 3.5.1}$$

This one-step reaction has the potential to work concurrently with the Bayer Process without additional engineering, allowing all known inhibiting poisons to be transformed into volatile organics which can be subsequently lost through vapour emissions. Properly executed, the proposed OM removal strategy would address all four goals to a satisfactory level.

3.5.2. Experimental Design and Analysis of Ammonia Reactions

The formation of nitriles from organic acids will be examined in conditions mirroring the extreme temperatures and pressures of the Bayer Process digestion step. Depending on the

quality of bauxite ore, digestion temperatures operate at either 140 – 150 ºC or 250 – 255 ºC (7). To compensate for both ranges, the temperature chosen for the ammonia reactions was 200 ºC. Simulating the high pressures of the digestion step was achieved by performing the reaction in a high-pressure reactors known as bombs.

Due to the impracticality of liquor purging under pressurised confinement, the ammonia was introduced in the form of ammonium hydroxide solution. To prevent the loss of ammonia upon the addition of ammonium hydroxide solution to the caustic liquor, the ammonium hydroxide solution was frozen. This successfully slowed the generation of ammonia gas, allowing the bomb to be assembled without the loss of ammonia. Once assembled, the bomb was subjected to heating for 14 hours, the duration of which it was continuously rotated to enable optimal interaction between the ammonia gas and the liquor.

To measure the success of this OM removal strategy, the volatiles and the relative abundances of the characterised OM remaining within the liquor need to be analysed. Comparing the relative abundances of each characterised organic species pre and post ammonia reaction will confirm which organic species reacted, with particular interest drawn to the identified poisons. If successful, the production of nitriles from ammonia treatment should be detected from the liquor vapour emissions. Consequently, a new method to detect these volatile products was investigated.

For volatile analysis, SPME offers a highly simple and sensitive approach, allowing non-polar organics to be sampled in the gaseous phase above a solution through headspace sampling. Traditionally, the extraction of volatile organic species has been achieved using SPME with fibre coatings of PDMS-DVB, carboxen-PDMS and PDMS (104, 105). Carboxen-PDMS was the fibre chosen to sample the nitrogen volatile products, as this fibre demonstrates the greatest sensitivity for low MW volatiles and acidic compounds, allowing both nitriles and potential amide intermediates to be detected (118).

In headspace sampling mode, the fibre is placed in the headspace above an equilibrated sample. Two forms of equilibrium take place during headspace extraction: the between sample and gaseous phases ($K_{\text{sample – air}}$) and the fibre and the air ($K_{\text{fibre – air}}$). Compounds possessing high $K_{\text{fibre – air}}$ values absorb more to the fibre than those with smaller values. This equilibrium constant cannot be altered to increases rates of absorption, however $K_{\text{liquid – air}}$ can be manipulated to cause the species of interest to favour the gaseous state. Techniques like heating and increasing ionic strength of the sample causes non-polar organics to increase their rates of emissions to favour the headspace sampling. Accordingly, the liquor after the ammonia reaction was treated with NaCl before heating to 70 ºC.

When choosing an appropriate IS for the volatile analysis, 4 key points need to be considered so the $K_{\text{sample}-\text{air}}$ and $K_{\text{fibre}-\text{air}}$ values are similar to the expected nitrile products. In order to match the $K_{\text{liquid}-\text{air}}$ values, the IS must be soluble in aqueous solutions but have a similar volatility as the expected products, so its absorption does not over or under saturate the headspace. Additionally, the compound must contain a nitrogen but not be basic, so its absorption to the fibre is similar to that of the products. Ideally, to match all these requirements a nitrile compound would be most appropriate. However due to the range of organic acids detected within the liquor, it is likely that there would be an extensive range of nitriles produced, so another nitrogen containing species must be considered. Therefore, dimethylformamide was chosen, as it is the closet matching compound which is not a nitrile.

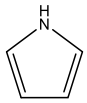
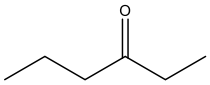
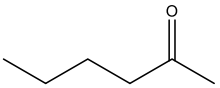
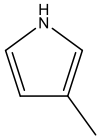
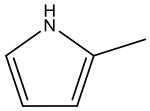
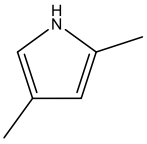
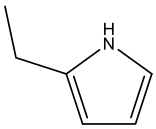
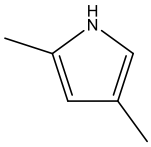
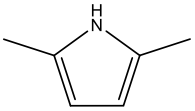
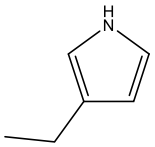
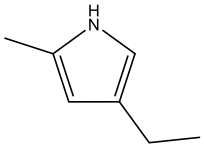
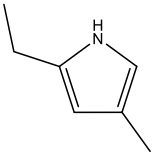
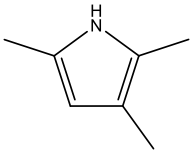
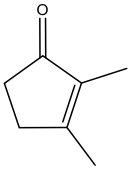
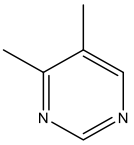
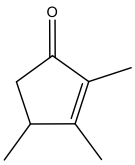
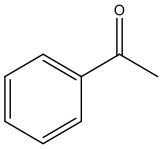
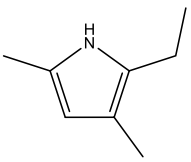
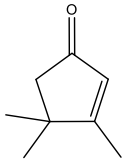
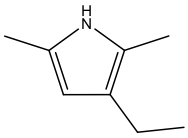
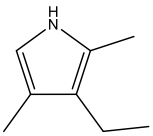
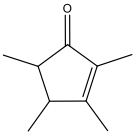
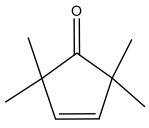
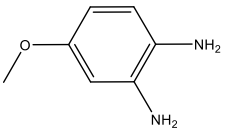
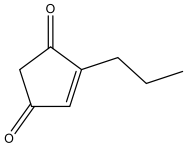
3.5.3. Volatile Analysis Post OM Removal

A comparative study was performed to assess the developed OM removal strategy against current methods found in literature. Wet-oxidation was chosen for the comparison due to the high level interest it has received in literature.

The blank from the ammonia reaction was analysed to observe what volatiles are produced naturally from heating the spent Bayer Liquor. Interestingly, a distribution of cyclopenten-1-one alkyl isomers were detected along with a few aliphatic ketones. These volatiles are likely produced from the further breakdown of HA and NOM still remaining within the liquor. However, a recent study of volatile products from the degradation of organic in synthetic Bayer Liquor reported that a series of cyclopentane products were identified and were likely due to the degradation of furanoate (119).

Surprisingly, the volatile analysis of the spent liquor post ammonia reaction revealed that instead of the predicted nitrile products, the vapour emissions were dominated by a distribution of alkyl pyrrole isomers. A summary of the detected volatiles are presented in Table 3.5.1. These results were unexpected, as the conditions of the Bayer Liquor were considered to be not reducing enough to produce aromatic nitrogen species. Production of these aromatic species are most likely a result of a rearrangement or cyclisation processes with subsequent dehydration. To confirm this, the initial reagents need to be identified. Unfortunately, from these products it is unclear which organics were the original reagents as the structural integrity was likely lost during these reactions. Therefore, to understand the reducing processes occurring, the remaining Bayer Liquor organics need to be analysed.

Table 3.5.1. Detected volatile organics from the post ammonia reaction of the spent Bayer Liquor. Sampled through headspace analysis with carboxen/PDME SPME and analysed by GC-MS.

Peak Number	Structure	Peak Number	Structure	Peak Number	Structure
1		2*		3*	
4		5		6	
7		8		9	
10		11		12	
13		14*		15	
16*		17*		18	
19*		20		21	
22*		23*		24	
25*					

* Organics detected within the blank

The oxidative breakdown of polyhydroxyl species, namely tartaric acid, are known to produce oxalate, formic acid, acetic acid, 3-hydroxypropanoic acid and ultimately CO_2 as degradation product. High levels of CO_2 should indicate the oxidative breakdown of any

organics containing vicinal hydroxyls. Accordingly, CO_2 levels from the wet-oxidation sample were compared to the blank sample. However, no distinct differences in CO_2 levels were observed between the wet-oxidation and the blank vapour emissions. Unsurprisingly, the volatile analysis of the wet-oxidation mirrored the blank, with no additional volatiles detected. Targeting the degradation products oxalate, formic acid, acidic acid and 3-hydroxypropanoic acid during the Bayer Liquor organic analysis will be used to confirm any oxidative decay.

3.5.4. Characterisation of Organics Post OM Removal

The purpose of structurally characterising the organics from both OM removal samples was to measure the success of these processes by identifying the organics removed. In comparison to the original organic distribution from the spent liquor, both the ammonia and wet-oxidation samples demonstrated a significant depletion in organic species. Interestingly, the relative abundances between the two samples are equal. The difference between the organics from the OM removal samples and the original spent liquor organics are shown in Figure 3.5.2.

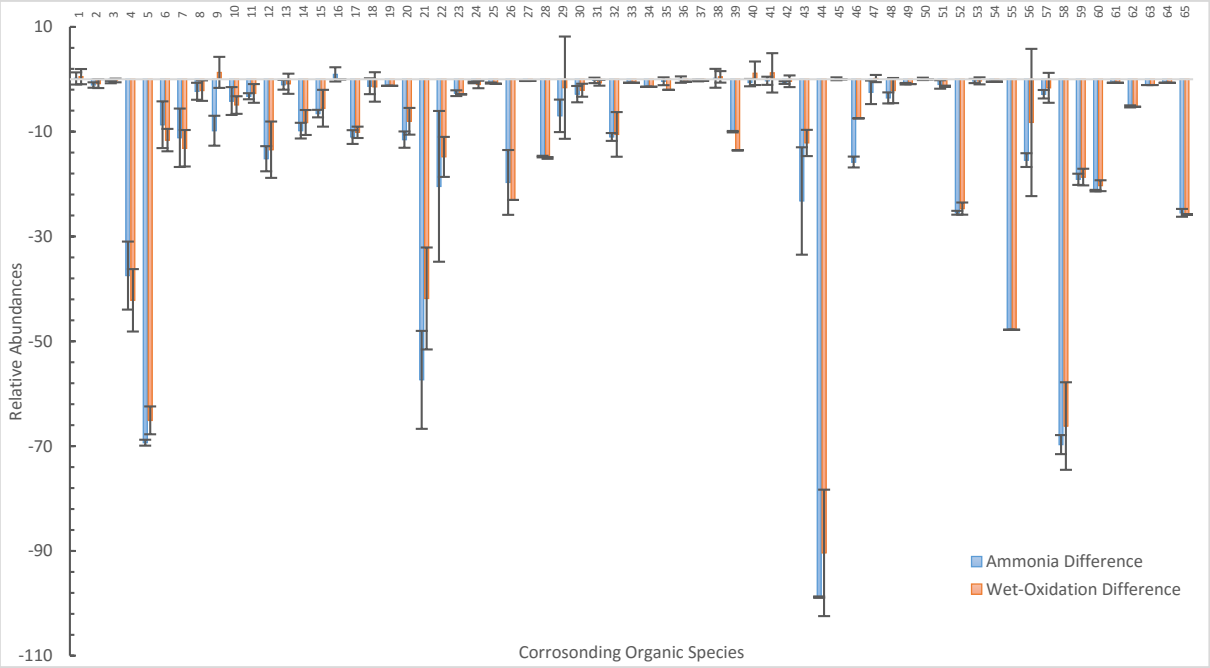


Figure 3.5.2. Difference in relative abundance (± 95% $CI_{n=2}$) of characterised organic species between both wet-oxidation or ammonia OM removal strategies and the original spent Bayer Liquor organics. Negative values indicate higher relative abundance within the original spent liquor. Positive values indicate higher relative abundance within OM removal strategy samples. Peaks normalised to the IS (105.3 mg L-1). Corresponding organic species are tabulated in Table 3.4.3.

It is unconvincing that these results are a reflection of the OM removal strategies, as both demonstrate the same distribution, but target different organic species. Similarly, it is unlikely that the observed depletion is caused by thermal degradation, as the organics species within Bayer Liquor are considered stable. Therefore to determine if the observed changes are

a feature of the experimental setup or from the removal strategies themselves, these samples will be compared to the organics from the blank sample.

The organic analysis from the blank sample showed the same levels of depletion as the OM removal samples. As these depletions were consistent across all samples, it can be concluded that it is a feature of the experimental setup. The Teflon bombs used for the reactions are hydrophobic and can become highly porous when heated. Therefore, it is likely that the organics were extracted into the Teflon lining from the aqueous liquor through a solid-phase extraction process. Consequently, this extraction process may have hindered the extent of the ammonia reduction reaction. Therefore, the information obtained from the organic analyses cannot be used to assess the extent or success of the developed OM removal strategy. Nonetheless, a degree of reduction was observed from the production of the pyrrole isomers.

3.5.5. Nitrile Stability Investigation

To investigate the results obtained from the volatile ammonia analysis, a more detailed examination of nitriles stability in the caustic liquor was undertaken to understand why a series of pyrrole isomers were produced in place of the predicted nitriles. Nitrile stability was examined by addition of benzyl cyanide into the blank liquor, where it was subsequently heated to 70 ^{o}C and continuously analysed for 4 hours. Analyses taken at 0, 1 and 2 hours are shown in Figure 3.5.3, Figure 3.5.4 and Figure 3.5.5 respectively.

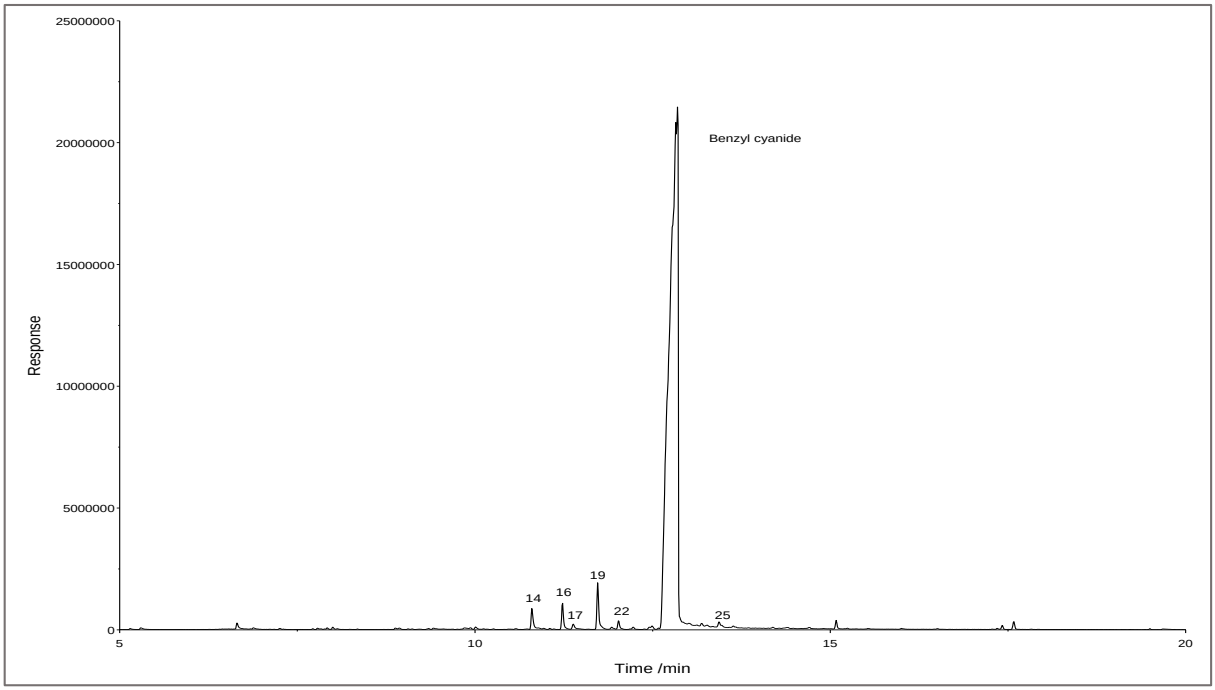


Figure 3.5.3. Detailed GC TIC of volatiles from the blank ammonia sample spike with benzyl cyanide (10.1 mg L^{-1}), measured at 0 hours. The numbered peaks correspond to volatiles tabulated in Table 3.5.1.

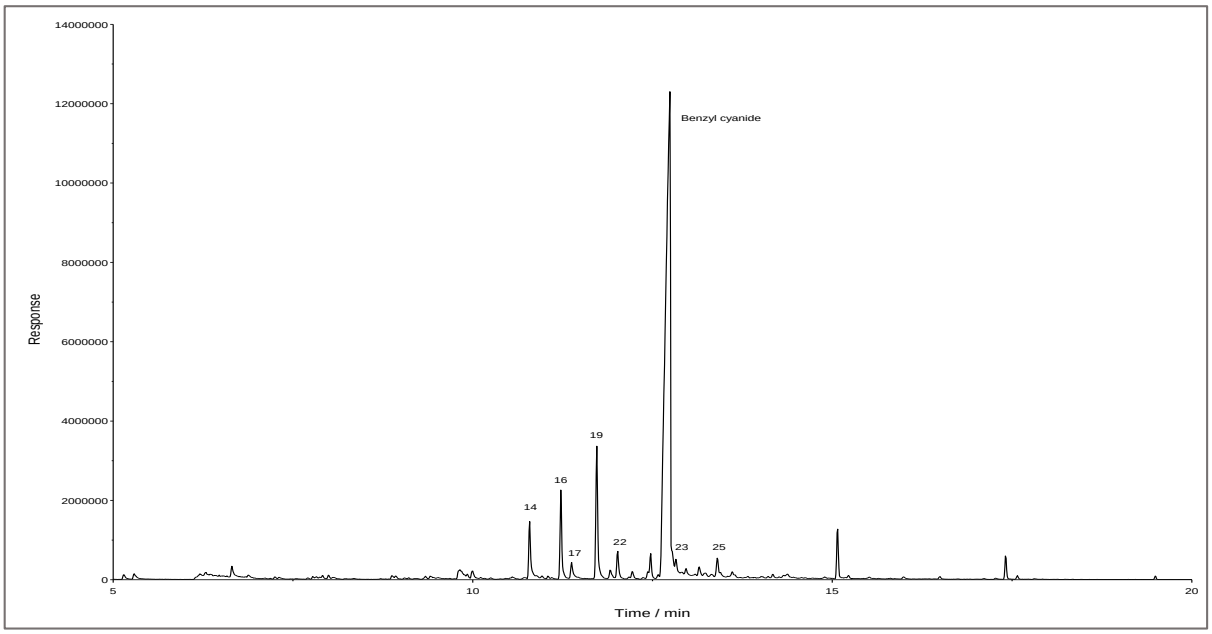


Figure 3.5.4. Detailed GC TIC of volatiles from the blank ammonia sample spike with benzyl cyanide (10.1 mg L^{-1}), measured at 1 hour. The numbered peaks correspond to volatiles tabulated in Table 3.5.1.

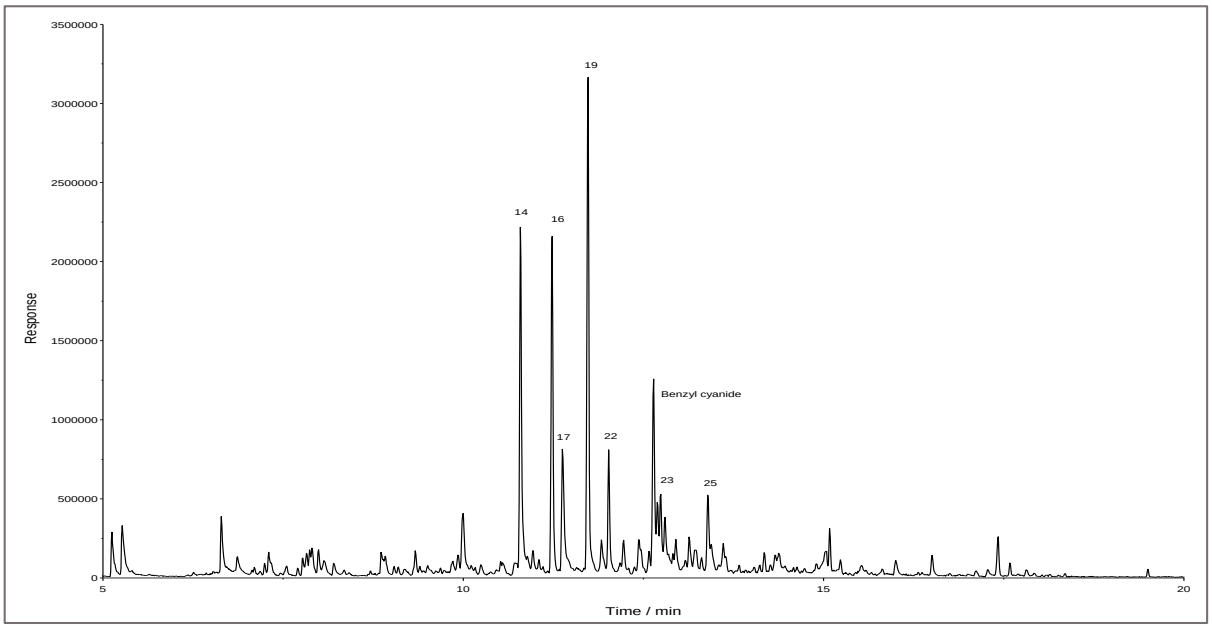


Figure 3.5.5. Detailed GC TIC of volatiles from the blank ammonia sample spike with benzyl cyanide (10.1 mg L^{-1}), analysed at 2 hours. The numbered peaks correspond to volatiles tabulated in Table 3.5.1.

These results show a rapid depletion in benzyl cyanide concentration over a two hour period, indicating that the nitrile is hydrolysing in the caustic liquor. However, hydrolysis only appears to occur when the liquor is heated, as the results from the liquor kept at 4 ^{o}C for 7 days showed no signs of hydrolysis.

As nitriles are subjected to hydrolysis even at mild temperatures in the caustic conditions, it is likely that the amide intermediate is the favoured state. Therefore, it is possible that the pyrroles formed from a subsequent rearrangement or cyclisation reaction from the amide intermediate. Consequently the following Hofmann-type rearrangement mechanism

shown in Figure 3.5.6 is proposed to explain the formation of pyrroles from organic acids with α-hydroxyls. Although the compound used in this mechanism was not detected within the spent liquor from section 3.4.5, similar compounds with shorter chains were detected within the liquor. This compound therefore was likely produced from the breakdown of remaining HA and NOM. This is a reasonable assumption given the larger molecules are likely not susceptible to extraction, causing them to become subjected to thermal degradation as the liquor is heated. Furthermore, the organic distribution for the blank yielded the same abundances as the ammonia samples, indicating that the pyrroles were not formed from those organics.

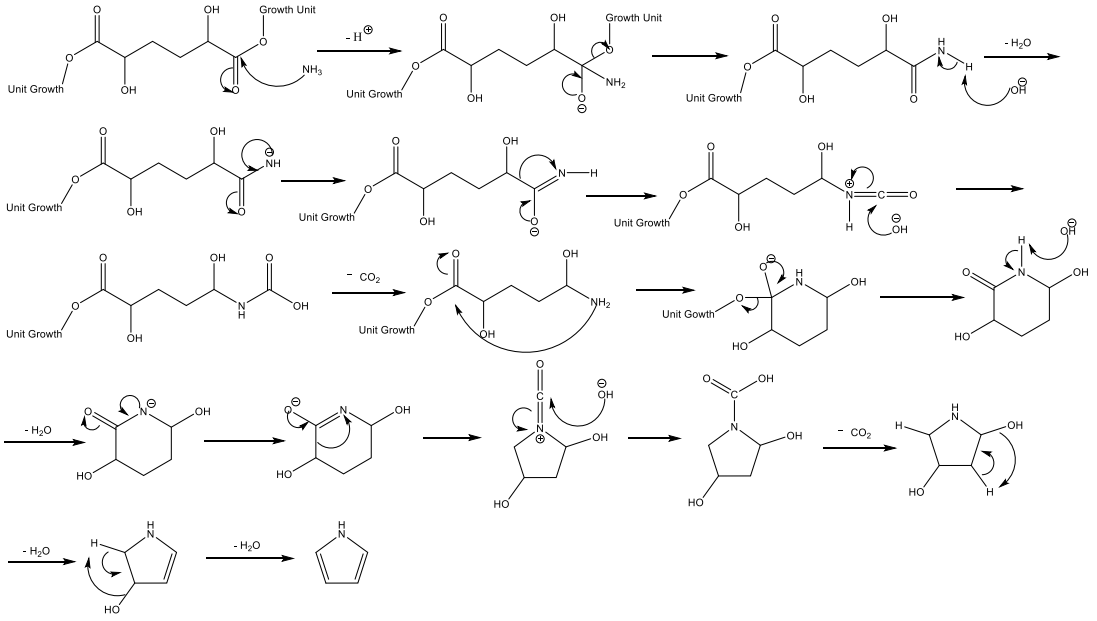


Figure 3.5.6. Hofmann-type rearrangement reaction mechanisms to produce pyrroles from aliphatic acids and ammonia.

Evidence of this Hofmann-type rearrangement mechanisms was found in the organic analysis of the blank solution which was initially spiked with benzyl cyanide. Initially, the amide intermediate was thought be the final product of the hydrolysed benzyl cyanide. However, the rearrangement product of the amide, benzylcarbamic acid, was detected within the liquor. The mechanism for this rearrangement product is shown in Figure 3.5.7. Interestingly, only the rearranged product was observed and not the decarboxylated amine. As the temperatures were only raised to 70 ^{o}C, it is likely that higher temperatures are required for the decarboxylation step.

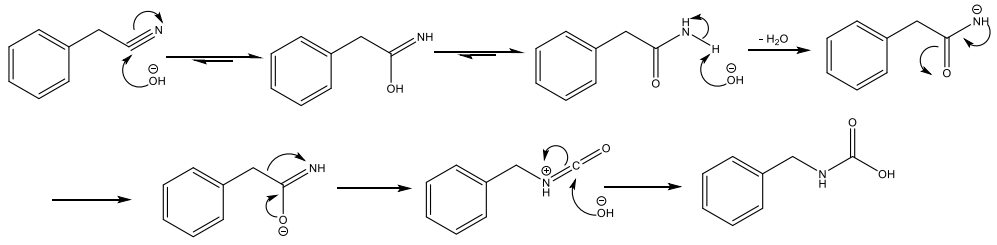


Figure 3.5.7. Hydrolysis of benzyl cyanide into its amide, followed by a Hofmann-type rearrangement mechanism, resulting in benzylcarbamic acid.

It is likely that ammonia can still be used as an effective OM removal strategy. This is evident with the production of pyrroles from these preliminary results, despite the loss of organics into the Teflon liner during the reaction. The production of pyrroles provides a more effective route for poison removal due to their greater levels of volatility. Whilst this method demonstrated that some organics were reduced and subsequently removal from the liquor, it could not be determined if the poisons were effectively targeted during this reaction. Based on the above mechanism, it is likely that the identified poisons were not transformed into the observed pyrroles. However, this is more likely due to their extraction into the Teflon liner and not due to their reactivities. Further investigations of this reduction process will need to be performed to fully observe and understand the extent of this novel OM removal strategy.

3.6. Future Directions

Based on the current investigation, the following are suggested for further investigations into the organic poisons of Bayer Liquor.

1. To date, research into poisoning mechanisms and effects of the dominant aromatic and aliphatic acids tabulated in Table 3.4.3 are limited in literature. Accordingly, a more extensive study into these processes will be investigated for many of the identified organics and poisons. Crystallisation investigations will be used to study the effects of these acids. Crystal morphologies will be assess using X-ray powder diffraction techniques. From these investigations, a criteria of structural features will be developed to help identify future poisons.
2. Development of an industrialised analytical tool to identify and quantify the presence of the identified poisons within the liquor using advanced novel technologies.
3. Due to the potential success observed from the ammonia investigation for the removal of OM, further investigations into developing and analysing this strategy will be taken.
4. Investigations into alternate OM removal strategies will also be investigated if the ammonia reaction is unable to target the identified poisons.

Chapter 4: Conclusion

This project aimed to investigate the organic poisons responsible for inhibiting the efficient recovery of gibbsite from spent Bayer Liquor, with the intent of designing a novel OM removal strategy which not only effectively targets the identified poisons, but is able to work concurrently with the Bayer Process.

The quantification of organics adsorbed onto precipitated gibbsite revealed that rates of organic removal from absorption are equivalent between the two liquors. From this it was concluded that adsorption is not a trait unique to poisons. Therefore, in order for inhibiting rates to increase, the poisons need to significantly concentrate to outcompete other adsorbing organics.

Due to limitations experienced in previous characterisation methods, an alternate analytical method was applied for detailing the organic component structures. A one-step extraction technique was employed to isolate a fraction rich with all target analytes, liberated from the complex matrix. This extraction technique was coupled with an optimised derivatisation step. As a result, 65 organic compounds were characterised from both spent and pregnant Bayer Liquors, proving to be the most successful characterisation study currently in this area. Importantly, this OM identification process confirmed the absence of model poisons, namely polyhydroxyls. A comparative study between the pregnant and spent liquor organics was performed to identify the poisons of spent Bayer Liquor. Crystallisation experiments confirmed the inhibiting abilities of the identified poisons. From these findings, 7 poisons were proposed with the inhibiting functionality identified.

A novel method for poison removal was investigated, targeting the carboxylic functionality. The transformation of carboxylic acids into less polar, more volatile nitriles was explored as a potential strategy. However, the volatile analysis from the ammonia treated liquor detected a series of alkyl pyrrole isomers and not the intended nitriles. The organic analysis post ammonia reaction was performed to identify which organics were reduced, only to reveal that the majority of the organics were extracted from the liquor during the reaction. Nitrile stability investigations revealed that the reaction to form nitriles stops at the amide intermediates, only to undergo a Hoffman-type rearrangement followed by decarboxylation and dehydration.

Although no direct evidence was obtained to determine the success of the investigated OM removal strategy, the production of pyrroles is evident that organic acids are able to be transformed into volatile species in the caustic liquor.

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Chapter 6: Appendix

6.1. Structurally Characterised Bayer Liquor Organics

Table 6.1.1. Bayer Liquor organics detected in Literature. Compounds reported in Bayer Liquor, listed in order of MW. Presented with characterisation method, their systematic and common name and their reference(s).

Systematic Name	Common Name	MW	Characterisation Method	References
Methanoic acid	Formic acid	46	IC after Solid-Phase Extraction, Butylation Derivatisation GC& CZE	(120-122)
Ethanoic acid	Acetatic acid	60	Butylation Derivatisation GC, RP-HPLC after Solid-Phase Extraction, CZE, IC after Solid-Phase Extraction	(95, 120-122)
2-aminoethanol	Ethanolamine	61	TMS Derivatisation GC-MS	(24)
Propionic acid	Propanoic acid	74	Butylation Derivatisation GC, IC after Solid-Phase Extraction, RP-HPLC after Solid-Phase Extraction	(120, 121, 123)
4-amino-1-butanol	Butanolamine	75	TMS Derivatisation GC-MS	(24)
2-hydroxy ethanoic acid	Glycolic acid	76	TMS Derivatisation GC-MS	(13)
Butyric acid	Butanoic acid	88	Butylation Derivatisation GC, RP-HPLC after Solid-Phase Extraction	(121, 123)
2-methyl propionic acid	Isobutyric acid	88	RP-HPLC after Solid-Phase Extraction	(123)
Ethanedioic acid	Oxalic acid	90	TMS Derivatisation GC-MS, RP-HPLC after Solid-Phase Extraction, CZE, IC after Solid-Phase Extraction	(24, 95, 120, 122, 123)
2-hydroxy propanoic acid	Lactic acid	90	TMS Derivatisation GC-MS, Butylation Derivatisation GC	(13, 24, 121)
3-hydroxypropanoic acid	3-hydroxypropionic acid	90	TMS Derivatisation GC-MS	(13)
N-methyl pyrrolidinone	N-methyl-2-pyrrolidinone	99	IC & GC-MS	(124)
3-methyl butanoate	Isovalerate	101	Butylation Derivatisation GC, RP-HPLC after Solid-Phase Extraction	(121, 123)
2-methyl butanoic acid		102	RP-HPLC after Solid-Phase Extraction	(123)
Pentanoic acid	Valeric acid	102	Butylation Derivatisation GC	(121)
2-hydroxybutanoic acid	β-hydroxybutyric acid	104	TMS Derivatisation GC-MS	(13, 24)
Propanedioic acid	Malonic acid	104	TMS Derivatisation GC-MS, Butylation Derivatisation GC, CZE	(13, 24, 121, 122)
2-hydroxy-2-methylpropanoic acid		104	TMS Derivatisation GC-MS	(13)
2-hydroxy butanoic acid	Butane dioate	104	TMS Derivatisation GC-MS	(24)
3-methylphenol	*m*-Cresol	108	IC & GC-MS	(124)

Table 6.1.1. Continued.

Systematic Name	Common Name	MW	Characterisation Method	References
(1H-pyrrol-2-yl) ethanone	2-acetyl pyrrol	109	IC & GC-MS	(124)
4-heptanone	Dipropyl ketone	114	RP-HPLC after Solid-Phase Extraction	(123)
Butenedioic acid	Fumaric acid	116	TMS Derivatisation GC-MS	(13)
Hexanoic acid	Caproic acid	116	RP-HPLC after Solid-Phase Extraction	(123)
2,4-dimethyl-3-pentanol	Diisopropylcarbinol	116	RP-HPLC after Solid-Phase Extraction	(123)
4-hydroxy-3-pentenoic acid		116	TMS Derivatisation GC-MS	(13)
Butanedioic acid	Succinic acid	118	TMS Derivatisation GC-MS, Butylation Derivatisation GC, RP-HPLC after Solid-Phase Extraction	(13, 24, 95, 121)
2-hydroxy-2-methylbutanoic acid	2-hydroxy-2-methylbutyric acid	118	TMS Derivatisation GC-MS	(13)
2-hydroxypentanoic acid	2-hydroxyvaleric acid	118	TMS Derivatisation GC-MS	(13)
2-methyl-propanedioic acid	Methylmalonic acid	118	TMS Derivatisation GC-MS	(13)
2-hydroxypropanedioic acid	Tartronic acid	120	TMS Derivatisation GC-MS	(24)
Benzenecarboxylic acid	Benzoic acid	122	TMS Derivatisation GC-MS	(13, 24)
2,4-dimethylphenol	*o*-Xylenol	122	IC & GC-MS	(124)
3-methyl-4-heptanone	Butyl propyl ketone	128	RP-HPLC after Solid-Phase Extraction	(123)
Dibutyl ether		130	RP-HPLC after Solid-Phase Extraction	(123)
2-methylene-butanedioic acid		130	TMS Derivatisation GC-MS	(13)
2-methyl-2-butenedioic acid	Mesaconic acid	130	TMS Derivatisation GC-MS	(13, 24)
1,5-pentanedioic acid	Glutaric acid	132	TMS Derivatisation GC-MS, Butylation Derivatisation GC, RP-HPLC after Solid-Phase Extraction	(13, 24, 95, 121, 123)
2-ethyl-propanedioic acid	Ethylmalonic acid	132	TMS Derivatisation GC-MS	(13)
2-methylbutanedioic acid	Methylsuccinic acid	132	TMS Derivatisation GC-MS, Butylation Derivatisation GC	(13, 24, 121)
Hydroxy butanedioic acid	Malic acid	134	TMS Derivatisation GC-MS	(13, 24)
2,5-dimethyl benzaldehyde		134	RP-HPLC after Solid-Phase Extraction	(123)
2-hydroxyphenyl ethanone	Acetophenone	136	IC & GC-MS	(124)
Phenylacetic acid		136	TMS Derivatisation GC-MS	(13)

Table 6.1.1. Continued.

Systematic Name	Common Name	MW	Characterisation Method	References
4-hydroxy-*α*-methylene-benzenemethanol		136	TMS Derivatisation GC-MS	(13)
2-hydroxy benzoic acid	Salicylic acid	138	TMS Derivatisation GC-MS	(24)
3-hydroxy benzoic acid	*m*-salicylic acid	138	TMS Derivatisation GC-MS, RP-HPLC after Solid-Phase Extraction	(13, 95, 123)
5-hydroxy benzoic acid	*p*-salicylic acid	138	TMS Derivatisation GC-MS	(13)
4-hydroxyphenethyl alcohol		138	TMS Derivatisation GC-MS	(13)
5-oxo-3-methyl-3-hexanpic acid		142	TMS Derivatisation GC-MS	(13)
1,6-hexanedioic acid	Adipic acid	146	TMS Derivatisation GC-MS, CZE, RP-HPLC after Solid-Phase Extraction	(13, 24, 122, 123)
2,2-dimethyl butanedioic acid	2,2-dimethyl succinic acid	146	TMS Derivatisation GC-MS	(13)
2,3-dimethyl butanedioic acid	2,3-dimethyl succinic acid	146	TMS Derivatisation GC-MS	(13)
2-methylpentanedioic acid	2-methylglutaric acid	146	TMS Derivatisation GC-MS	(13)
3-methylpentanedioic acid	3-methylglutaric acid	146	TMS Derivatisation GC-MS	(13)
2-hydroxypentanedioic acid	Hydroxy glutaric	148	TMS Derivatisation GC-MS	(13, 24)
2-hydroxy-2-methylbutanedioic acid	Citramalic acid	148	TMS Derivatisation GC-MS	(13)
4-hydroxy-2-methyl acetophenone		150	IC & GC-MS	(124)
2,3-dihydroxy butanedioic acid	Tartaric acid	150	RP-HPLC after Solid-Phase Extraction, CZE	(94, 95, 122)
4-hydroxy-benzeneacetic acid	4-hydroxyphenylacetic acid	152	TMS Derivatisation GC-MS	(13)
3-methoxy benzoic acid	*m*-anisic acid	152	HPLC	(7)
4-methoxy benzoic acid	*p*-anisic acid	152	HPLC	(7)
Dimethylpentanedioic	Dimethyl glutaric acid	160	TMS Derivatisation GC-MS	(24)
Heptanedioic acid	Pimelic acid	160	TMS Derivatisation GC-MS, RP-HPLC after Solid-Phase Extraction	(13, 24, 123)
3-methyl hexanedioic acid	3-methyladipic acid	161	TMS Derivatisation GC-MS, RP-HPLC after Solid-Phase Extraction	(13, 123)
2-hydroxyhexanedioic acid	*α*-hydroxyadipic acid	162	TMS Derivatisation GC-MS	(13)

Table 6.1.1. Continued.

Systematic Name	Common Name	MW	Characterisation Method	References
Ethane tricarboxylic acid	Ethane-1,1,2-tricarboxylic acid	162	TMS Derivatisation GC-MS	(24)
1-(2,4-dihydroxy) phenyl-1-propanone		166	GC-MS	(88)
1,2 benzene dicarboxylic acid	Phthalic acid	166	TMS Derivatisation GC-MS	(13, 24)
1,3 benzene dicarboxylic acid	Isophthalic acid	166	TMS Derivatisation GC-MS	(13)
1,4 benzene dicarboxylic acid	Terephthalic acid	166	TMS Derivatisation GC-MS	(13)
4-(1-hydroxyvinyl)-2-methoxyphenol		166	TMS Derivatisation GC-MS	(13)
4-hydroxy-3-methoxybenzoic acid	Vanillic	168	TMS Derivatisation GC-MS	(13)
1-propene-1,2,3-tricarboxylic acid	Aconitic acid	174	TMS Derivatisation GC-MS	(13, 24)
1,6 hexane dicarboxylic acid	Octanedioic acid	174	RP-HPLC after Solid-Phase Extraction	(123)
Propane-1,1,2-tricarboxylic acid		176	TMS Derivatisation GC-MS	(13, 24)
Propane-1,2,3-tricarboxylic acid	Tricarballylic acid	176	TMS Derivatisation GC-MS	(13)
2-carboxy phenylacetic acid	Homophthalic acid	180	TMS Derivatisation GC-MS	
Benzene-4-methyl-1,3-dicarboxylic acid	4-hydroxyisophthalic acid	180	TMS Derivatisation GC-MS	(24)
Benzene-4-hydroxy-1,2-dicarboxylic acid		180	TMS Derivatisation GC-MS	(13)
2-hydroxy-1,2-benzene dicarboxylic acid	4-hydroxyphthalic acid	182	TMS Derivatisation GC-MS	(24)
Nonanedioic acid	Azelaic acid	188	TMS Derivatisation GC-MS, RP-HPLC after Solid-Phase Extraction	(13, 123)
Butane tricarboxylic acid	Butanetrioic acid	190	TMS Derivatisation GC-MS	(24)
2-hydroxypropanetricarboxylic acid	Citric acid	192	TMS Derivatisation GC-MS, CZE	(13, 122)
2,3,4,5,6-pentahydroxy hexanoic acid	Gluconic acid	196	CZE	(122)
1,8-octane dicarboxylic acid	Sebacic acid	202	Butylation & Methylation Derivatisation GC-MS	(91)
1,1-dibutoxybutane		202	Butylation & Methylation Derivatisation GC-MS	(91)
1,2,3,-benzene tricarboxylic acid	Hemimellitic acid	210	TMS Derivatisation GC-MS	(24)
1,2,4-benzene tricarboxylic acid	Trimellitic acid	210	TMS Derivatisation GC-MS	(24)

Table 6.1.1. Continued.

Systematic Name	Common Name	MW	Characterisation Method	References
1,3,5-benzene tricarboxylic acid	Trimesic acid	210	TMS Derivatisation GC-MS	(24)
Hydroxy(diphenyl)acetic acid	Benzilic acid	228	TMS Derivatisation GC-MS	(24)
Tetradecanoic acid	Myristic acid	228	Butylation & Methylation Derivatisation GC-MS	(91)
Butanetetracarboxylic acid		234	TMS Derivatisation GC-MS	(24)
3,5-di-tert-butyl-4-hydroxybenzaldehyde		234	HPLC	(7)
1,2,4,5-benzene tetracarboxylic acid	Pyromellitic acid	254	TMS Derivatisation GC-MS	(24)
Hexadecanoic acid	Palmitic acid	256	TMS Derivatisation GC-MS, RP-HPLC after Solid-Phase Extraction	(24, 123)
9,12-octa decadienoic acid	Linoleic acid	280	Butylation & Methylation Derivatisation GC-MS	(91)
Octadecanoic acid	Stearic acid	284	RP-HPLC after Solid-Phase Extraction	(123)
Benzene-1,2,3,4,5-pentacarboxylic acid	Benzene pentacarboxylic acid	298	TMS Derivatisation GC-MS	(24)
2,3,10,15,19,23-hexamethyltetracosa-2,6,10,14,18,22-hexane	Squalene	410	HPLC	(7)

CZE (Capillary Zone Electrophoresis), GC (Gas-Chromatography), MS (Mass Spectrometry), IC (Ion-Chromatography) HPLC (High-Pressure Liquid Chromatography) and RP-HPLC (Rapid Phase - HPLC)

Table 6.1.2. Compound table for detected Bayer Liquor organic matter. Literature retention indicates were obtained from NIST MS library

Peak Number	Identified Compound	Mean Retention Index	Literature Retention Index	Derivation in Retention Index Pregnant / %	NIST MS Library Comparison
1	m-Cresol	1457.2	-	-	Yes
2	2-Ethylhexanoic Acid	1468.0	-	-	Yes
3	Heptanoic Acid	1472.0	-	-	Yes
4	Lactic Acid	1528.8	1484.4*	2.99	Yes
5	Benzoic Acid	1532.4	-	-	Yes
6	Glycolic Acid	1540.7	1542.1	-0.09	Standard
7	α-Hydroxyisobutyric Acid	1542.4	1498.9*	2.90	Yes
8	3-Methoxyphenol	1546.9	1512.4*	2.28	Yes
9	Benzeneacetic Acid	1553.5	1534.7*	1.22	Yes
10	2-Hydroxybutanoic Acid	1567.5	-	-	Yes
11	4-Methyl Benzoic Acid	1572.9	-	-	Yes
12	Propanoic Acid	1582.5	1583.9	-0.09	Standard
13	2-Hydroxy-3-Methylbutyric Acid	1590.7	1594.0	-0.21	Standard
14	2-Methyl Benzoic Acid	1588.8	-	-	Yes
15	3-Methyl Benzoic Acid	1601.7	-	-	Yes
16	Malonic Acid	1617.0	1616.4	0.04	Standard
17	Benzenepropanoic Acid	1627.1	-	-	Yes
18	Butyric Acid	1633.8	-	-	Yes
19	Decanoic Acid	1642.1	-	-	Yes
20	Methoxybenzoic Acid	1662.1	-	-	-
21	Succinic Acid	1679.7	-	-	Yes
22	Methylsuccinic Acid	1683	1683.6	-0.03	Standard

Table 6.1.2. Continued.

Peak Number	Identified Compound	Mean Retention Index	Literature Retention Index	Derivation in Retention Index Pregnant / %	NIST MS Library Comparison
23	2-Hydroxy-3-methylpent-2-enoic Acid	1693.4	1737.9*	-2.56	Yes
24	Fumaric Acid	1697.2	1698.4	-0.07	Standard
25	Cinnamic Acid	1699.1	-	-	Yes
26	2-(Furan-2-yl) acrylic Acid	1704.8	-	-	-
27	4-Hydroxy-2-Methoxybenzaldehyde	1714.3	-	-	Yes
28	Mesaconic Acid	1716.8	1823.0*	-5.83	Yes
29	Glutaric Acid	1728.2	1728.9	-0.04	Standard
30	2-Methylglutaric Acid	1732.4	-	-	-
31	3-Methylglutaric Acid	1734.4	-	-	Yes
32	4-Hydroxy-3-methoxyacetophenone	1738.1	-	-	Yes
33	Dodecanoic Acid	1744.7	-	-	Yes
34	2-Hydroxybenzoic Acid	1775.6	-	-	Yes
35	Adipic Acid	1779.8	1779.5	0.02	Standard
36	3-Methyladipic Acid	1786.2	-	-	Yes
37	2-Methyladipic Acid	1789.8	-	-	Yes
38	2-Hydroxyphenylacetic Acid	1814.6	-	-	Yes
39	3-Hydroxybenzoic Acid	1841.8	-	-	-
40	3-Hydroxyphenylacetic acid	1881.6	-	-	Yes
41	Pimelic Acid	1893.5	1895.6	-0.11	Standard
42	Myristic Acid	1929.0	1931.9	-0.15	Standard
43	2-Hydroxymethyl benzoic Acid	1946.7	-	-	-

Table 6.1.2. Continued.

Peak Number	Identified Compound	Mean Retention Index	Literature Retention Index	Derivation in Retention Index Pregnant / %	NIST MS Library Comparison
44	4-Hydroxybenzoic Acid	1977.2	1990.5	-0.67	Standard
45	1,2-Benzenedicarboxylic Acid	1985.3	-	-	Yes
46	3-(Hydroxymethyl) Benzoic Acid	1991.3	-	-	-
47	4-(Hydroxymethyl) Benzoic Acid	2024.5	-	-	-
48	Octanedioic Acid	2049.3	2047.4	0.09	Standard
49	Pentadecanoic Acid	2083.7	2181.2*	-4.47	Yes
50	α-Hydroxypentanedioic Acid	2102.8	-	-	Yes
51	2-Hydroxy-3-Methyoxybenzoic Acid	2138.5	2142.0*	-0.16	Yes
52	1,4-Benzenedicarboxylic Acid	2151.5	-	-	Yes
53	1,3-Benzenedicarboxylic Acid	2157.5	-	-	-
54	3-(4-Hydroxyphenyl) Propionic Acid	2166.0	2236.9*	-3.17	Yes
55	Vanillic Acid	2173.5	2180.9	-0.34	Standard
56	Nonanedioic Acid	2202.9	2200.3	0.12	Standard
57	Hexadecanoic Acid	2233.3	2230.5	0.13	Standard
58	3-(Hydroxymethyl) phenyl Propanoic Acid	2239.8	-	-	-
59	3-(Carboxymethyl) Benzoic Acid	2273.1	-	-	-
60	2-(Carboxymethyl) Benzoic Acid	2313.9	-	-	-
61	Isopropylmalic Acid	2328.9	-	-	Yes
62	Decanedioic Acid	2448.2	2346.7	4.32	Standard
63	Undecanoic Acid	2464.9	2465.5*	-0.03	Yes

Table 6.1.2. Continued.

Peak Number	Identified Compound	Mean Retention Index	Literature Retention Index	Derivation in Retention Index Pregnant / %	NIST MS Library Comparison
64	Octadecanoic Acid	2485.1	2482.8*	0.09	Yes
65	4-Hydroxyisophthalic Acid	2672.0	-	-	-

- Not provided in literature or different stationary phase used for GC column, * VF-5ms column 30 m x 0.25 µm x 0.25 µm