# A review of the determination of organic compounds in Bayer process liquors

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## TEXT

# ABSTRACT

Bayer process liquors present a difficult and complex matrix to the analytical chemist, and the history of the application of modern analytical techniques to this problem is a case study in innovation. All Bayer process liquors contain organic compounds, in amounts varying from traces to several grams per litre. The total organic carbon content of Bayer liquors may be less than 5 g/L up to as much as 40 g/L. The presence of these organic impurities is of concern to Bayer technologists because they can have significant impacts on the economics of the process and the quality of the product. This review examines the history and current state-of-the-art of the analysis of organics in Bayer process liquors, and provides guidance on the applicable techniques matched to a comprehensive list of the compounds most likely to be present.



**Keywords:** Organics analysis; Bayer process; Review

# FIGURE CAPTIONS

**Figure 1: Schematic representation of a typical lateritic bauxite profile (diagram reproduced with the permission of BHP Billiton Worsley Alumina) [1].**

**Figure 2: Sample preparation scheme for the separation of high molecular weight organics from Bayer liquors, derived from the descriptions given by Wilson et al. [25].**

**Figure 3: Example of a determination scheme using GC-MS and GPC(SEC), adapted from Guthrie et al. [22].**

**Figure 4: LC trace for medium MW (90-300 Da) compounds in a Bayer liquor from Guthrie et al.. The numbered peaks were identified by MS [22].**

**Figure 5: IC trace for low MW compounds in a Bayer liquor from Picard et al. showing assignments by MS [27].**

**Figure 6: Multidimensional determination sequence adapted from Whelan et al. [61] showing GPC-UV fractionation followed by LC-MS operated in full scan mode and LC-MS/MS operated in product ion mode.**

# 1. Introduction

The Bayer process, by which bauxite is treated with strong sodium hydroxide to refine alumina, is applied to about 97% of the over 200 million annual tonnes of bauxite mined globally. The organic compounds present in bauxite are primarily complex, water-insoluble materials derived from plant and animal matter, and include humic and fulvic matter, lignins and cellulose. Relatively minor amounts of organic compounds enter the liquor from other sources which include various chemical additives such as flocculants (in some cases starch but predominantly synthetic flocculants), dewatering aids, crystal modifiers and water treatment chemicals [1].

The organic carbon content of bauxite is generally in the range 0.02 to 0.50 % (w/w, carbon basis) [1]. Bauxite digestion is usually carried out at temperatures in the range 135 to 245$^{o}$C at sodium hydroxide concentrations in the region of 3.5 to 5 molar [2]. Under these conditions a significant proportion of the organic matter present in the bauxite is extracted into the liquor [1] or released through the formation of volatile organic compounds [3]. The compounds extracted into the liquor undergo alkaline degradation reactions which lead to a predominance of low to medium molecular weight compounds at steady-state, with typically 90% of compounds in the molecular weight range 90 to 500 Da [1].

The presence of organic impurities in the liquor has significant implications for all aspects of the Bayer process, including process yield, product quality [4, 5], scale formation [6] and environmental emissions [7], all of which affect the overall viability

of the process as well as being a key factor in the design of each specific plant. The determination of organic impurities has been the subject of significant developmental effort and continues to be an active area of research.

## 2. Historical Perspective

The presence of organic compounds in bauxite was recognised very early in the history of the extraction of alumina from bauxite. Only 13 years after Bayer patented his process [8], improvements patented by C M Hall included heating bauxite to burn off organic matter prior to digestion [9]. A study of the processing of Urals bauxite indicated the presence of soluble and insoluble organic matter [10], and that the soluble organic matter was 58% carbon. Utley reported that Arkansas bauxite contained 0.3 to 0.4% organic matter which was about 50% carbon [11]. Most of the bauxite now being mined originates from lateritic deposits which are or have been overlain by forests. Bauxite genesis relies on selective leaching of minerals by water percolation, resulting in a layered profile as depicted schematically in Figure 1. In such a profile the organic carbon content varies from a maximum in the order of 1% in the overburden to a minimum of 0.1% or less in the clay floor of the deposit [1].

*Please place Figure 1 near here*

The soluble organics which enter Bayer process liquors impart a red-brown colour to the liquor, the exact shade and intensity of which depends on both the bauxite source and the processing conditions [12]. The significance of the presence of organics in the liquor appears to have been first highlighted in the English-language literature in Pearson's 1955 monograph on the aluminium industry [12], in which it was noted that

the organic matter in liquor originated mainly from the bauxite, and that it had a number of negative influences on the operation and economics of refining operation, and on the quality of the product. A more detailed account of the origins and effects of organics in the Bayer process is given in the review by Solymár and Zsindely [13] of bauxites then being processed in Hungary. The techniques available for the investigation of organic compounds in highly alkaline liquors at that time involved lengthy and complex wet chemical techniques [14], so the investigations in the industry were probably limited to determination of total organic carbon (TOC) by classical techniques such as permanganate titration [15, 16].

It has long been known that oxalate is formed in the Bayer process, because sodium oxalate has limited solubility at high pH, and so can crystallize out if the organic input to the refinery is sufficient [12, 17]. However, a deeper understanding of the nature and reactions of organic compounds in Bayer liquors awaited the development of instrumental techniques for organic determination. Specialised sample preparation techniques also had to be developed for application to the highly concentrated and complex matrix of Bayer liquors.

Table 1 summarises as a timeline the main innovations in analytical techniques and their application to the analysis of Bayer liquors in the past 30 years. Details of the application of these techniques to individual analytes are given in the Appendix.

*Please place Table 1 near here*

# 3. Sample Preparation and Fractionation

The methods of sample preparation for the analysis of Bayer liquors range from a simple dilution in water to complex preparation procedures, depending on the information required and the analytical methods to be used. The following sections summarise the most important methods, in order of complexity.

## 3.1. Dilution, Neutralization and Acidification

Dilution in water has been found to be satisfactory for the determination of the most prevalent organic anions present in Bayer liquor by a number of analytical techniques. This has the advantages of simplicity and speed, which are particularly important for routine applications. In addition, the risk of artefacts due to incomplete extraction or adsorption, losses encountered during fractionation or evaporation, and so on, are avoided. However, the dilutions required are often quite high (at least 1:200, and often 1:1000 or more [18, 19]), which limits both the sensitivity and the variety of compounds that can be analysed by the analytical technique that follows, such as ion chromatography (IC) or capillary electrophoresis (CE). Nevertheless, simplicity of sample preparation was one of the key reasons for the early adoption of IC as a routine method for the determination of oxalate and other important anions in Bayer liquors [20], and remains the method of choice for analysis in that application.

Lever [21] used $CO_2$ to reduce the alkalinity of the liquor and remove the aluminate content prior to determination under conditions favourable to the formation of a mixture of dawsonite (sodium aluminium carbonate) and aluminium hydroxide, which were then removed by filtration. This procedure has the advantage of removing most of the aluminate from solution without adding mineral acid anions. The solution was

155 then passed through a cation exchange resin to ensure that all of the organic
156 compounds were in their acid forms to facilitate derivatization, neutralized with
157 NaOH, and evaporated to dryness prior to being butylated for determination by gas
158 chromatography (GC) with a flame ionization detector.
159
160 Guthrie et al. [22] used a simpler procedure in which concentrated HCl was added
161 directly to a liquor sample in an ice bath until the precipitated aluminium hydroxide
162 was redissolved. The resulting solution was butylated and analysed for low molecular
163 weight compounds by GC. To analyse intermediate molecular weight compounds,
164 these authors evaporated the butanol extracts to dryness and reacted the residues with
165 "Tri-Sil" (dimethyl-(trimethylsilylamino)Si) to produce the silyl derivatives for GC
166 analysis. Others [21, 23] have used methylation for this purpose.

167 ## 3.2. Precipitation and liquid or solid phase extraction

168 The preparation for determination of the high molecular weight ("humic") fractions of
169 Bayer liquor generally involves first precipitating the "humic" material by
170 acidification to a pH of 2 or less, as is the practice in the analysis of soils [24].
171 Lever's approach was to extract the precipitated organics with n-butanol and
172 neutralize the extract with NaOH, followed by water-washing and ultrafiltration to
173 produce a salt-free aqueous extract which could be separated into nominal molecular
174 weight fractions by membrane filtration [21]. Alternatively, Guthrie et al. [22] kept
175 the initial steps of the sample preparation the same as described in section 3.1 for GC
176 analysis, and used tetrahydrofuran (THF) as the solvent for the butyl esters.
177
178 Wilson et al. [25] cautioned against the precipitation of aluminium hydroxide in the
179 preparation of liquors for determination of high molecular weight compounds on the

basis that this may result in losses of some organic compounds by adsorption to the aluminium hydroxide surface. They recommend a 1:10 dilution followed by rapid acidification to pH 1.5 with 1:1 HCl to precipitate the “humic” materials, which are then separated by filtration, redissolved in NaOH and extracted onto a polar adsorption resin (Amberlite XAD-7). The organics are subsequently washed from the resin with deionized water to produce a neutral, salt-free solution containing the acid forms of the “humic” materials. The collected dried solid humic material is then extracted sequentially with diethyl ether, ethyl acetate, isopropyl alcohol and water [26] .

Picard et al. [27] tested two separate extraction methods which were followed directly by multidimensional chromatography and mass spectrometric analysis (see section 5.1).

The first extraction method trialled was a liquid/liquid separation which used three different solvents of increasing polarity in succession (ether, ether/n-butanol, and n-butanol) to separate the organics on the basis of their polarity.

The second method was solid-phase extraction using a hydrophobic C18 stationary phase. This was used to separate the organics into high, medium and low molecular weight (HMW, MMW and LMW) fractions. The HMW fraction was defined as the material which precipitated at low pH, the MMW as that which was soluble at low pH and was retained on the C18 stationary phase, and LMW as the soluble fraction which was not retained. On this basis, for samples taken from 10 different Bayer process

plants, it was found that the LMW fractions represented between 30 and 50% of the TOC of the spent liquors analysed [27] .

Whelan and co-workers identified some anomalies from solvent extraction in which compounds with a range of polarities were found in a particular solvent [26]. They suggested that the solubility of humic materials may be controlled by association, in which small molecules can aggregate by arranging their polar groups internally to produce relatively hydrophobic micellular structures which are more soluble in less polar organic solvents than might be expected. This phenomenon may be a function of concentration as suggested, or it could be an artefact of the extraction procedure which entails dissolving organic matter from concentrated Bayer humic material that has been dehydrated and solidified.

Other approaches to the determination of molecular weight fractions are discussed in the next section.

## 3.3. Fractionation by Molecular Weight and Size

Separation of organic compounds into fractions based on apparent molecular weight or molecular size by ultrafiltration (UF) or dialysis has been used to characterise the organic matter present in Bayer liquor. Lever [21] used UF through membranes with nominal molecular weight cutoff values ($MW_{cutoff}$) of 0.5, 1, 5 and 10 kDa. The fractions collected were then evaporated and weighed to obtain a coarse apparent molecular weight or size distribution. Dialysis into 1.2, 6, 12, 25, 50, 100, and 300 kDa $MW_{cutoff}$ fractions has been described by Wilson et al. [25, 28].

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), has been used to obtain a continuous apparent size distribution of the organic matter present in Bayer liquor [29]. Separation has been achieved on 500 × 7 mm x 140 Å and 100A Spherosil 100/200 porous silica bead columns in series [21] or on 300 x 7.8 mm x 500 Å and 100 Å μ-Styragel columns in series [22] with UV detection to obtain a molecular weight distribution of Bayer liquor extracted with butanol. Each of these chromatograms was a continuum with no discrete peaks.

It should be noted that SEC with UV detection underestimates saturated aliphatic carboxylic anions, which are known to constitute a significant proportion of the total organic carbon (TOC) in Bayer liquors but are not good absorbers of UV. A solution to this could be to incorporate continuous TOC (or, more strictly, dissolved organic carbon (DOC)) detection as well [30, 31], but application of this to Bayer liquors has not yet been reported.

All separations based on molecular size should be treated with caution when applied to Bayer liquor extracts. Membranes and size exclusion gels have long been used for the fractionation of proteins and peptides, for which purpose they are calibrated with particles of known size which are uniform, spherical, non-polar and relatively chemically inert. The technique has been extended to the characterization of natural organic matter (NOM), but the interpretation of results becomes more complex because separation is no longer purely on the basis of molecular size, and there are no universally applicable calibration standards [32, 33]. Interpreting the information

obtained from molecular size separation methods in such systems is therefore not straightforward, and can lead to gross errors when specific chemical and physical interactions between the analytes and the stationary phase are significant [34, 35]. Bayer liquor organics contain a high proportion of highly polar groups, in particular carboxylic acids. Electrostatic effects and hydrogen bonding can therefore be expected to play an important, even dominant, role in the retention behaviour, so correlations of retention times with molecular size alone are unlikely to be valid, and aggregation of small molecules into micellular structures noted in Section 3.2 can cause them to behave as if they have a much higher molecular weight than is in fact the case [28] .

Notwithstanding these complications, separations using membranes and columns of a variety of types are an important aspect of the sample preparation methodologies available for investigating the nature of Bayer liquor organics.

### 3.4. Consolidated Sample Preparation Strategy for Determination of the High Molecular Weight Fraction

Using the experience outlined in the previous sections, a preparation method suitable for the determination of the high molecular weight fractions of Bayer liquors is that developed by Wilson et al. [25] . To enable this quite complex scheme to be appreciated visually, we have prepared a flow-sheet representation of it (Figure 2). It consists of the following seven main elements:

1. dilution
2. acidification to precipitate humics
3. redissolution in NaOH
4. extraction on XAD-7 resin

5. washing and elution
6. acidification on Amberlite 120 resin
7. filtration and aliquot preparation/storage.

*Please put Figure 2 near here*

This scheme enables quantitative separation of the high molecular weight organics from the liquor, to produce a stock solution of the organics in acid form, free from aluminate and other salts. The stock solution may be sub-sampled for size separation and/or other determinations, or freeze-dried for storage.

*Please put Figure 1 near here*

# 4. Chromatographic Separation

## 4.1. Gas Chromatography (GC)

According to the published literature, the first significant advance in the application of modern chromatographic techniques to the determination of organic compounds in Bayer liquors was the work of Lever in the 1970s [21], in which capillary GC was used to analyse species with low to medium molecular weights (40 to 350 Da). The method relied on methylation and butylation of methanol extracts using diazomethane or diazobutane in ether to produce volatile compounds suitable for separation by gas chromatography. Using these methods, Lever was able to confirm the identity and quantify the amounts of five key degradation products already believed to be present: formate, acetate, lactate, oxalate and succinate. He was also able to identify a range of previously unidentified molecules, in particular a comprehensive range of mono-

aromatic carboxylic acids from the degradation of humic molecules [21]. The low molecular weight molecules were identified and quantified by comparing their responses in the flame ionization detector (FID) to known standards.

GC quickly became the basis of a variety of methods for the investigation of low to medium molecular weight organic compounds in Bayer liquors. The differences in the methods used by various workers were at first mainly in the sample preparation techniques used, but later developments in column technology and detection methods have also had a significant influence.

The main variants in the derivatization methods are as follows:

- Methylation of a methanol extract using diazomethane in ether [21, 36], or by direct application to Bayer liquor using acidified tris(hydroxymethyl) aminomethane in chloroform and methanol [37];
- Methylation of an aqueous solid phase alkaline extract using tetrabutylammonium hydroxide added at pH 8.5 [38], or of a Bayer liquor butanol extract using acidified methanol [39];
- Butylation. Lever [21] derivatized dried neutralised Bayer liquor using acidified butanol. Baker et al. [40] derivatized butanol extracts using acidified butanol in a microwave oven, Guthrie et al. [22] and Wellington and Valcin [41] derivatized Bayer liquor directly using acidified butanol, while Xiao [39] derivatized acidified, solvent extracted Bayer liquor using acidified butanol followed by hexane extraction.

Caution must be exercised in the use of derivatization techniques and in the interpretation of the results obtained. For example, Wilson et al. [38] found that the methyl ester did not form quantitatively for some compounds and that some methyl esters were non-volatile. Xiao [39] found that losses of low molecular weight acids could occur due to evaporation during concentration procedures. He also found that butylation could result in dibutyl ether artefacts, that it was difficult to identify unknowns from their butyl derivatives, and that butylation was not useful for high molecular weight acids. Xiao therefore recommended that methylation and butylation be used in combination to optimise recoveries and improve the confidence in the identification of analytes.

Guthrie et al. [22] derivatized the butanol extracts with Tri-Sil for the determination of low and intermediate molecular weight aliphatic and aromatic acids. Silylation (using hexamethyldisilazane and trimethylchlorosilane) was also used by Ellis et al. [42] to analyse plant extracts and digested plant extracts. Using this procedure, it was possible to determine low and intermediate molecular weight mono-, di- and tri-carboxylic aliphatic and aromatic acids, aliphatic and aromatic hydroxy carboxylic acids, polyhydric alcohols, alkanes, carbohydrates and furans. According to Eyer [43], Alcoa World Alumina has developed a GC method based on methylation followed by chloroform extraction for the routine determination of oxalate, malonate and succinate. It was found that the method could be extended to include benzene as an analyte directly, but it was necessary to use butanol to derivatize acetate and formate for determination. Tardio [44] used a similar method to determine formate, acetate, butyrate, oxalate, malonate, succinate, glutarate, lactate, malate and fumarate as the methyl esters.

The advent of GC with mass spectrometry detection (GC-MS) in place of or in addition to non-specific detection by FID brought a major advance in analytical capability by enabling the identification of individual compounds, for example according to the scheme illustrated in Figure 3 [22].

*Please put Figure 3 near here*

The complexity of the mixture of organic compounds in Bayer liquor is illustrated by the GC trace in Figure 4 for compounds in the MW range 90 to 300 Da. The numbered peaks were identified by MS [22]. The addition of modern multi-dimensional mass spectrometry has since demonstrated the potential for the identification of many hundreds of compounds [27] . To date however, a total of only 85 individual compounds, all of which have molecular weights below 350 Da, have been specifically identified in the literature as being present in Bayer liquors [1].

Most of the compounds that have been found in Bayer liquors are organic acid anions [1]. For example, Xiao [39] was able to analyse more than twenty mono- and di-carboxylic acids using a combination of methylation and butylation; Picard et al. [27] claim to have identified over a hundred acids, but they cite only those corresponding to the twenty most intense peaks in the mass spectra. On the other hand, Wellington and Valcin [41] found more than 15 non-acid compounds including alkenes, phenols, pyrolidinones, quinolines and pyrroles in a Bayer liquor using butylation.

According to Eyer [43], Alcoa World Alumina has applied GC-MS to the determination of a range of low molecular weight ($C_3$-$C_{20}$) hydroxycarboxylic acids extracted from Bayer liquors and analysed as the trimethylsilate esters.

Pyrolysis-GC-MS, in which the products of the pyrolysis of a sample in an inert atmosphere at various temperatures are analysed by GC-MS, has been used to characterise the high molecular weight material in Bayer process liquors [25, 28] . This method enables the material to be characterised in terms of its main functional constituents, and provides evidence for their likely origins. Because of the large number and complexity of the pyrolysis products, however, it has not been possible to identify specific starting compounds with any confidence by this method.

## 4.2. Ion Chromatography (IC)

Ion chromatography relies on the separation of ions on an ion exchange column, after which the solution is passed through a "suppressor" column. In the case of anion determination, the suppressor removes the sodium ions from the solution and replaces them with hydrogen ions that react with the corresponding hydroxide ions to form water. This suppresses the bulk conductivity of the solution, so that the remaining anions can be detected by their conductivity. This method, which was developed in the 1970s, can be applied to both cations and anions, but was the first method to become available for routine determination of multiple anions using a single, simple detection technique [45]. The key to the method is the suppressor, which must be regularly regenerated for continuous use, and maintenance of suppressor performance is crucial to ensuring ongoing sensitivity, accuracy and precision of determination.

The advent of IC provided for the first time a rapid method requiring minimal sample preparation for the simultaneous determination of many of the low molecular weight organic acids of most interest to Bayer process technologists. Generally, the only sample preparation required is dilution in water prior to introduction to the analytical system. This method therefore lends itself to automation, and is suitable for high volume, routine use.

Nevertheless, the nature of Bayer liquor places restrictions on the application of IC for determination. The high ionic strength and pH of the liquor mean that samples require significant dilution (typically at least 500:1) prior to determination, which limits the sensitivity of the method. Interferences between the many organic and inorganic anions present is also a limiting factor [18]. In addition, the high aluminate content and the insolubility of aluminate between pH 5 and 10 means that eluents outside this pH range must be used, or else the solution must be stabilised by the addition of a complexing agent, such as tartrate or gluconate [18]. Alumina fouling of the suppressor is a key issue, even with alumina complexants in the eluant, and this generally requires regular flushing with strong acid (e.g. 1 M HCl) [46]. Some workers have overcome this problem by pre-treating the samples with an ion exchange resin to remove the aluminate ions prior to determination [47, 48], but this increases the complexity of the method and is a disadvantage for high volume routine use.

Since the 1980s, oxalate and other low molecular weight aliphatic acids in Bayer liquor have been analysed directly by ion chromatography with anion exchange columns and alkaline mobile phases using conductivity detection [48, 49]. Oxalate is

currently measured in this way in key process streams in many Bayer plants on a daily or more frequent basis [19, 20].

Detection by UV absorbance was found to be more satisfactory for aromatic acids because their lower $pK_a$ values made conductivity detection difficult [48]. Xiao et al. [47] have recently reported a method for the rapid determination of the organic anions formate, acetate, propionate, oxalate, succinate and glutarate, as well as the inorganic anions fluoride, chloride and sulphate, with a single injection providing good accuracy and precision. The chromatographic run time was 33 minutes, but pre-treatment of the samples by ion exchange is required to achieve this.

Brindel and Lectard [48] used GC-MS to identify 9 benzene carboxylates separated by IC from a Bayer liquor, and identified 11 other compounds by comparison with standard compounds. Picard et al. [27] used IC followed by MS detection to separate and identify 11 low molecular weight aliphatic and aromatic acids present in Bayer liquor, as illustrated in Figure 5. The solution from the IC separation was introduced to the MS via electrospray ionization, a “soft” ionization method which enables the formation of ions without fragmentation of the parent molecules. They then used this technique to survey the liquors from 10 different plants, and found that the four most prevalent compounds, formate, acetate, oxalate and succinate, accounted for between 15 and 40% of the TOC in the Bayer liquors studied.

*Please put Figure 5 near here*

## 4.3. Capilliary Zone Electrophoresis (CZE)

Applying an electric field gradient to ions in a solution causes ion migration in the direction of the field. The rate and direction of the migration are determined by the charge and hydrodynamic radius of the ions. This effect is the basis of the separation of ions by CZE, commercial instruments for which became available around 1990. CZE is now an active field of research in its own right, and may be found in a very wide range of analytical applications [50]. Detection is usually by UV absorption, often by indirect detection using an added chromophore [51], sometimes called the "probe" [52]. The mobile phase may include various electroosmotic flow and selectivity modifiers [53]. The first analyses for anions in Bayer liquor used chromate as the probe with indirect detection at 254 or 245 nm [18, 19, 52, 54]. These analyses were successful for the determination of oxalate in Bayer liquor, but peak shape and resolution of other aliphatic acids was usually poor, even under apparently optimal conditions.

Breadmore and co-workers [55] investigated various complex mixtures of different reagents and were able to separate 14 low molecular weight aliphatic acids, with separation selectivity and resolution able to be changed substantially by varying the electrolyte conditions. Only formate, acetate and oxalate were found in actual Bayer liquor by this method.

To remove the issues associated with the use of toxic chromate reagents, Chovancek et al. [56] introduced the use of molybdate as the probe with detection at 214 nm. Under these conditions, 5 low molecular weight aliphatic acids were rapidly separated in Bayer liquor with good resolution and peak shapes.

CZE has a number of advantages over IC in the areas of selectivity, speed of determination, peak separation and sample volume requirements. Although it did initially suffer from less stable retention times, poor peak shapes and a much higher detection limit [18, 19], it appears these problems have been largely overcome, so that CZE now has excellent reproducibility, peak shapes, linearity and limits of detection for many of the low molecular weight acids of interest in Bayer liquor [56]. CZE has recently been applied to the determination of 18 carboxylic acids for the monitoring of bioreactors, and it is reasonable to suppose that similar advances could be made in the analysis of Bayer process solutions using this approach [57].

## 4.4. High Performance Liquid Chromatography (HPLC)

HPLC, sometimes known as high *pressure* liquid chromatography, can be operated in a number of different modes and with stationary phases of different chemistries, and a variety of mobile phases and additives. As such, it is a very flexible technique for the determination of a wide variety of types and sizes of organic compounds in a range of matrices. HPLC can also be used to investigate the fundamentals of adsorption as shown by the work of Bouchard et al. [58] who used it to determine dynamic adsorption isotherms of organic compounds with the potential to inhibit the precipitation step of the Bayer process.

The first reported use of HPLC for analysing Bayer liquors was by Salomon who was able to identify a range of degradation products from the digestion of bauxite in alkaline liquors [29]. Roumeliotis and co-workers [59] used it for the separation, identification and quantification of carboxylic acids. They investigated reverse phase,

ion pair, ion exchange and ligand exchange separation techniques using 67 different combinations of stationary and mobile phases with variable or fixed (254 nm) wavelength UV detection. Nineteen low molecular weight aliphatic and aromatic mono-, di-, tri, tetra- and penta-carboxylic acids were identified. However, despite careful optimisation of the HPLC setup and conditions, many of the peaks were broad and poorly resolved. Using semi-preparative reverse phase chromatography, they also isolated aromatic carboxylic acids in a number of fractions from a 90 minute chromatographic run for further characterisation and identification by MS.

Susic et al. [60] used HPLC on a reverse phase (RP) column with an ammoniacal mobile phase and fluorescence detection to measure the “humic acid” concentration in Bayer liquor, without separating it into its constituents.

Wilson and co-workers [26] applied HPLC to the analysis of the so-called “humic” material (see Power and Loh [1] for a discussion of the meaning of “humic” in this context) which had been separated from a Bayer liquor sample by acidification, precipitation, solid-phase extraction and evaporation. The extracted solids were redissolved in a water/methanol mixture and analysed using a variety of HPLC methods of increasing complexity. It was found that RP chromatography alone was inadequate, because the majority of the Bayer liquor humic material eluted in the first 20 minutes, with insufficient peak separation. Operating in ion-suppression mode, in which the ionization of strong acids (and bases) is suppressed by the presence of a buffer, resulted in better separation. The method was further improved by using ion-pair mode, in which improved control of retention and selectivity is achieved by

adding a water-soluble organic compound (the ion-pairing reagent) to the mobile phase.

The most successful technique was reverse phase ion-pair chromatography with a mobile phase consisting of acetonitrile, water, formic acid and tetrabutylammonium hydrogen sulfate [26] . Best results were achieved by applying the ion-pairing reagent in a controlled time-dependent ratio (gradient) with acetonitrile. This enabled small molecules to be resolved at the beginning of the chromatogram while allowing the larger molecules to elute within a practical time period. The separation was achieved on a C18 column of dimensions 150 x 3.9 mm x 4 μm and with a pore size of 60 Å, using a diode array UV detector with wavelengths between 190 and 400 nm. Chromatography times were long (100-650 minutes), but it was possible to resolve a large number of individual small molecules within the first 200 minutes. At longer elution times, material of higher molecular weight and lower polarity was eluted. It is claimed that this is the first time that Bayer "humic" materials had been separated into groups of different polarities. In addition, the material did not elute as a continuum, but as clusters of peaks. This was interpreted as evidence for the existence of micellular clusters for which only certain configurations are stable. No individual compounds present in the Bayer liquor were identified in this developmental work, but the methodology appears to have great potential for separating the "humic" material into smaller and simpler fractions which could then be further separated by LC for determination by mass spectrometry (MS) for example. This concept was subsequently developed and applied to Bayer liquors to produce a multi-dimensional separation and determination method which could revolutionise the determination of such complex mixtures [61] (see section 7).

Xiao and co-workers have described the determination of oxalate, tartarate, acetate, succinate, glutarate, malonate, adipate and butene dicarboxylate in Bayer liquor using a C18 reverse phase column with a methanol/potassium dihydrogen phosphate mobile phase and UV detection at 215 nm [62, 63]. Separation was relatively rapid (less than 10 minutes) but the retention times for the same compounds under apparently identical conditions were found to be variable. Peaks were broad and detection limits were also rather high (1-10 mg/L) for compounds other than oxalic acid.

Machold et al. [64] report the determination of 21 low molecular weight aliphatic and aromatic carboxylic acids in 6 M NaOH using a reverse phase organic acid column after dilution and acidification to pH 2, with a run time of only 9 minutes. Two different mobile phases (potassium dihydrogen phosphate and potassium dihydrogen phosphate/acetonitrile) were used, with UV detection at either 215 or 254 nm.

## 5. Detection Methods and Spectroscopy

Conventional chromatographic separation techniques employ non-specific detection methods such as conductivity and UV absorption, relying on the characteristics of the separation (e.g. elution time) as an indicator of speciation. This has the great advantage of enabling a series of different compounds to be detected and quantified in a single chromatographic run, but it generally relies on knowledge of the identity of the compounds from calibrations with known compounds or separate analysis of each peak.

The advent of techniques which provide identification as well as detection, in particular mass spectrometry (MS), greatly increases the usefulness of the basic separation by providing the ability to simultaneously identify and quantify the components of complex unknown mixtures such as Bayer liquors.

## 5.1. Mass Spectrometry (MS)

The first published application of MS to the analysis of Bayer liquors is the work of Guthrie et al. [22], who applied it to detect and identify compounds following separation by GC. This enabled the identification of 35 compounds, several of which had not been previously reported in Bayer liquor. MS has since been used by a number of workers in investigations related to Bayer liquors, generally to provide definitive identifications of the components present after separation by a variety of chromatographic techniques. Niemela and Grocott [65] used GC-MS for a detailed examination of the organics in Bayer liquor, which revealed the presence of more than 350 individual compounds. The authors claim to have identified over 200 of these, but revealed the identities of only 14 compounds listed as examples of the successful use of GC-MS. However, without naming individual compounds, they reported the presence of: 45 hydroxymonocarboxylic acids, 6 oxo-dicarboxylic acids, 10 tricarboxylic acids, 7 hydroxy tricarboxylic acids, 4 tetracarboxylic acids, 13 fatty acids, 23 aromatic monocarboxylic acids, 18 aromatic di- or poly-carbosylic acids, 20 neutral (mainly phenolic) compounds, and various miscellaneous acids. GC-MS has also been used to identify the compounds that were adsorbed onto aluminium hydroxide from a Bayer liquor [38], to identify the components of water-soluble extracts of plant remains in bauxites [42] and to identify the products of alkaline leaching of plant materials related to bauxite digestion [6].

GC-MS has been used extensively by Niemela and co-workers in studies related to the digestion of a range of natural materials, including woods and bark, cellulose, starch and humic materials [66-74].

Despite these developments, there are surprisingly few reports in the literature of the use of GC-MS for the direct identification of compounds present in Bayer liquors, although it has been used extensively to identify pyrolysis products of liquor fractions from a range of preparation and separation techniques [6, 25, 42, 75]. One reason for this is that GC-MS is limited in its ability to provide information on the highly polar compounds of high molecular weight that are of interest in Bayer liquors [27]. To address this issue, Picard et al. [27] developed methods based on separations by HPLC and IC, coupled with detection and identification by MS. Identification was facilitated by using tandem mass spectrometry (i.e. MS-MS), in which a second stage of MS is used to provide detailed structural information on ions separated in the first stage of MS [76]. The same authors also used MS-MS directly to analyse the components of liquid-liquid extracts from Bayer liquors. These analyses enabled definitive identifications to be made of the compounds present in the highly complex mixtures extracted from Bayer liquors, and led to the identification of over 100 individual compounds (although only the 20 most significant are named in the publication) [27].

MS was also used as the detector in a multi-dimensional separation technique developed by Whelan et al. [61] for Bayer liquor analysis, which is discussed further in Section 7. Extension of the use of MS-MS in combination with new forms of sample presentation, such as electrospray ionization (ESI), have been used to good

621 effect in the investigation of humic and fulvic matter [77, 78], and have already been
622 used to some extent in the analysis of Bayer liquors [27, 61].
623
624 The use of these techniques will undoubtedly find increased application to the
625 analysis of Bayer liquors in the future. For example, the development of high
626 resolution MS instruments in combination with LC and a range of ionization
627 techniques has enabled major progress in the analysis of complex environmental
628 systems [79]. The use of instruments with very high mass resolution (>30,000) and
629 mass accuracy (<5 ppm), coupled with single-stage and multi-stage ion fragmentation
630 and sophisticated software, enables more reliable determination of target compounds
631 and the possibility of screening for suspected analytes and unknowns without
632 reference standards. The high resolving power and high spectral accuracy available in
633 state-of-the-art instruments could be expected to enable significant advances in
634 knowledge if applied to Bayer liquors.

635 ## 5.2. UV-Visible Spectroscopy

636 UV-Visible spectroscopy is a standard method of detection used in conjunction with
637 LC and IC separation [18, 46-48, 64, 80], and is the usual (albeit indirect) detection
638 method for CZE determination [51].
639
640 UV absorbance measurements have been used directly to estimate the amounts of
641 highly coloured compounds, loosely termed “humates” present in Bayer liquors [81-
642 83]. However, it has been shown that the “humate” fraction of Bayer liquors is
643 substantially different from the parent humate present in the bauxite [1]. Beach and
644 co-workers [84] used the colour ratio, Q4/6 = (absorbance at 400 nm) / (absorbance at
645 600 nm), to characterise the type of organic matter being removed from Bayer liquor

with hydrogen peroxide in the presence of Fe-TAML (tetra-amidato macrocyclic ligand) catalyst. Low colour ratios are primarily associated with humic acids, while high colour ratios and a stronger dependence of absorbance on wavelength are more characteristic of fulvic acids.

A fundamental study of the UV spectra of pure sodium aluminate liquors [85] confirmed the previously held belief that the UV absorbance of Bayer liquors is entirely due to the presence of organic compounds.

## 5.3. IR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy has been used by Wilson and co-workers to characterise solid samples including bauxite, red mud, scale, precipitate, organic matter, lignin and evaporated Bayer liquor extracts [2, 28, 86]. While not able to identify specific compounds, FTIR spectroscopy was capable of distinguishing the aromatic and aliphatic constituents, as well as C-O and C=O functional groups. FTIR can also be used to quantify the total organic carbon (TOC) content, and a number of other chemical and physical parameters, of Bayer liquor by correlating the IR spectrum of the liquor with the spectra of known standards [87].

Hind et al. [88, 89] used FTIR spectroscopy to investigate the nature of the surfaces of solids in contact with highly alkaline solutions.

## 5.4. NMR Spectroscopy

The use of NMR spectroscopy for the determination of organic compounds in Bayer liquors was pioneered by Wilson and co-workers, who subsequently used it

extensively in investigations of liquors and solids associated with the Bayer process. Wilson's first paper on this subject used $^{1}$H NMR to investigate the composition of humic substances from a number of sources, one of which was Bayer liquor [90]. The NMR data clearly showed formate, acetate and succinate, which had previously been identified [21], but also revealed the presence of smaller concentrations of propionate, lactate, tartrate, o-phthalate and a number of other benzene carboxylic acids and phenolic acids, which were attributed to the degradation of humic substances in the bauxite, and possibly of starch which was added to the liquor as a flocculant [38]. The advent of effective water suppression techniques substantially improved the sensitivity of the method in aqueous media such as Bayer liquor [91].

Ellis et al. [92] were able to quantitatively analyse glucose, formate, acetate, lactate, glycolate and ethanol directly in simulated Bayer liquor using a 300 MHz instrument. Beach et al. [84] used a 500 MHz instrument with a built-in pulse program for solvent suppression by presaturation and SpinWorks software to quantitatively analyse formate, mannitol, sorbitol, xylitol, gluconic acid, adonitol and/or dulcitol when added to sodium hydroxide solutions and mannitol when added to diluted Bayer liquor.

Machold et al. [64] used $^{1}$H NMR operating at 300 MHz to assist in the identification of compounds analysed by HPLC in studies of the degradation of individual organic compounds in 6 M sodium hydroxide over extended times. The compounds determined were formate, acetate, oxalate, succinate, lactate, malonate, glutarate, adipate, pimelate, malate, tartrate, gluconate, benzoate, phthalate, terephthalate, salicylate, 4-hydroxybenzoate and gallate.

In complex solutions such as Bayer liquor, it has not been possible to specifically identify more than few of the most prevalent compounds present using $^{1}$H NMR. It is nevertheless possible to identify specific organic functional groups, and to estimate their relative proportions. Whelan et al. [26] used a 300 MHz NMR instrument with field gradient coils to record $^{1}$H spectra of Bayer liquor extracts in deuterated dimethyl sulfoxide (DMSO-$d_6$). This enabled the detection of formate and acetate, and demonstrated the presence of a number of structural classes, including aromatic rings containing ether and hydroxyl groups, alkenes, and ether and alkoxyl groups attached to humic molecules. $^{1}$H-$^{1}$H homonuclear correlation (COSY) NMR spectroscopy, a two-dimensional technique, was also used. This enabled the presence of a number of additional features to be inferred, including carboxylic acid and methyl ketone groups. Specific compounds including 4-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 1,2-benzene dicarboxylic acid, and 1,4-benzene dicarboxylic acid were also identified.

$^{13}$C NMR has been used in relatively simple matrices to analyse specific organic compounds in solution. For example, Ellis et al. [92, 93] used a Bruker DRX300 spectrometer, inverse gated and operating at 75.4 MHz, to quantitatively analyse glucose, formate, acetate, lactate, glycolate, carbonate and ethanol in 3.5 M sodium hydroxide solutions. In this work, the decomposition of D-glucose labelled with $^{13}$C at the 1 and 6 positions, and lactate labelled at the 1 position, were studied in order to understand the mechanisms of carbon exchange in the alkaline degradation of glucose.

$^{13}$C NMR has also been used in a number of investigations related to Bayer liquor and associated materials, particularly by Wilson et al. [25] , who have developed specific methods tailored for the complex mixtures involved. Solution $^{13}$C NMR has been used to characterise Bayer liquor and solid state $^{13}$C Cross Polarization Magic-Angle Spinning NMR ($^{13}$C CP/MAS NMR) has been used to characterise Bayer-derived solids and evaporated Bayer liquor extracts. This is illustrated by Wilson et al. [38] in the determination of methyl derivatized extracts from aluminium hydroxide cake from an alumina refinery. They were able to assign chemical shifts to alkyl, alcoholic, aromatic, oxalate, and carboxylate functionalities, but were not able to identify specific compounds.

Smith et al. [94] used $^{13}$C NMR to investigate polyols in relation to their interactions with aluminate ions in solution and their role in the inhibition of gibbsite crystallization.

Baker et al. [95] and Wilson and co-workers [6, 25, 26, 28, 38, 86] used $^{13}$C CP/MAS NMR to examine solid material such as bauxite, red mud, scale, precipitated aluminium hydroxide, organic matter, lignin and evaporated Bayer liquor extracts. Although the instrument was capable of 200 MHz, best results were obtained at 50 MHz. It was not possible, even in Bayer liquor sequentially extracted with diethyl ether, ethyl acetate, isopropyl alcohol and water, to identify individual compounds, but the presence of different types of carbons were inferred. These included carbonyl, aromatic and aliphatic carboxylic acids, salts and esters, aromatic and aliphatic carbon with and without substituted electron-donating groups, including methyl, methylene

and methyne carbon, alkoxy including methoxy carbon, di-alkoxy, oxalate, formate and acetate carbonyl and acetal carbon.

# 6. Thermal Analysis

## 6.1. Solution Oxidation and Combustion

The simplest form of thermal analysis is combustion to determine the total organic carbon (TOC) content. Solution oxidation methods have been used for this, but the early methods based on, for example, dichromate oxidation, were found to under-estimate the more refractory compounds, and so have largely been replaced by combustion techniques [6, 25, 26, 28, 38]. Nevertheless, improvements in solution oxidation using a combination of persulphate and UV light resulted in the development of instruments with much better recoveries [96, 97]. Determination of TOC by solution oxidation or combustion usually relies on detection of evolved $CO_2$ with an infra-red (IR) detector. This method requires correction for, or simultaneous determination of, the inorganic (carbonate) content [98], and catalysts are generally used to facilitate quantitative combustion [43, 99]. Considerable progress has been made in the design of automated instruments for this method [100].

## 6.2. Thermogravimetry and Calorimetry

Thermal analysis has been used to investigate the combustion behaviour of samples of organics extracted from Bayer liquors and separated into molecular weight fractions [25, 28]. This information was used to draw conclusions regarding the general nature of the organic compounds in the various fractions. The loss of mass (9-18%, depending on fraction) up to 200$^{o}$C was attributed to loss of surface and bound water and volatile organics trapped in a macromolecular matrix. Further mass loss from 200

767 to 350$^{o}$C was attributed to carboxylic acids and aliphatic biopolymers, and the
768 remainder of the humic matter was combusted by 500$^{o}$C. It was found that the lower
769 molecular weight fractions contained the higher proportions of volatile matter [25,
770 28].
771
772 Further investigations using differential scanning calorimetry (DSC) revealed a
773 number of additional aspects of the nature of the organic fractions. As expected, the
774 DSC results were consistent with an increase in polymerization with combustion
775 temperature, but also provided data interpreted to indicate the existence of water and
776 small organic molecules bound within a macromolecular matrix [25, 28] .

## 777 6.3. Pyrolysis

778 Anaerobic pyrolysis followed by GC separation and MS detection (Py-GC-MS) has
779 been used extensively by Wilson and co-workers to analyse the organic components
780 of Bayer liquors and related materials (including bauxite, red mud, scale and
781 precipitated aluminium hydroxide) from a variety of sources and under a range of
782 conditions [25, 28]. This technique is in principle capable of providing a great deal of
783 information on the nature of complex materials by examination of their pyrolysis
784 products. The results obtained are, however, somewhat technique-dependent, so a
785 good knowledge of the exact methodology employed is essential [25, 28, 101].
786 Furthermore, the relationships between the compounds detected and the parent
787 compounds that were present in the original material are generally not
788 straightforward. The presence of oxidizing agents or catalysts, such as the iron oxide
789 present in bauxites and red muds, may also have an influence on the results [102].
790

Nevertheless, the technique has proved very useful in developing an understanding of the overall chemistry of the materials analysed by enabling estimation of aromatic/aliphatic ratios and allowing the proportions of alkyl, carboxylic acid, carbonyl, phenoxy and nitrogen-containing groups to be determined [6].

# 7. Multi-dimensional Methods

The analysis of complex mixtures can often be simplified by the use of multi-dimensional separation and determination methods, in which an initial separation by, for example LC, is then followed by a secondary separation by the same or another technique such as MS. The use of LC-MS-MS by Picard et al. [27] described in Section 5.1, in which over 100 individual compounds were identified (although only the 20 most significant are named), is an example of this. It has been pointed out that to take full advantage of the improved separation offered by multidimensional systems, the number of system dimensions should equal the number of definable sample attributes [103].

Whelan et al. [61] developed a powerful multi-dimensional technique for the analysis of Bayer extracts in which the fractions from solid-phase extraction were separated into ninety 200 µL sub-fractions by GPC (see section 3.3) which were then analysed by LC. Peaks from the LC output were then introduced into a triple quadrupole MS via electrospray ionisation for identification of components. Product ion spectra were then further resolved by a second stage of MS operating with collision-induced fragmentation. This allowed the identification of a small proportion of the isolated compounds, but most compounds were not identified. The analysis sequence is illustrated in Figure 6.

*Please place Figure 6 near here*

This example provides an insight into the possibilities offered by this concept. A very large amount of very high quality information can be generated by experiments of this nature, requiring a great deal of expertise and data analysis for proper interpretation. Nevertheless, further development of multi-dimensional methods, in particular LC-MS-MS with electrospray ionization, offers the potential for a step-change improvement in knowledge of the nature of organics in Bayer liquors. For example, it should be possible to confirm or otherwise the presence of compounds predicted to form from the initial degradation of natural organic matter in the digestion process [61].

# 8. Summary of Analytical Methods

A summary of the compounds that have been detected in Bayer liquors, and the methods that have been used to detect them, is provided in the Appendix. The table is in two parts: Table A1 lists the compounds that have been reported more than once in the literature, and which are on that basis designated to be “generally present” in Bayer liquors [1]; Table A2 is a list of compounds that have been reported only once in the literature, giving a list that is indicative of some of the additional compounds that may be present in any given Bayer liquor.

# 9. Summary and Future Directions

The application of increasingly sophisticated analytical techniques to the determination of organics in Bayer process liquors has led to significant advances in the knowledge of the nature, reactions and impacts of organics in the Bayer process over the past 40 years. This knowledge has enabled significant advances in processing technology which have benefited the industry in terms of costs of production, product quality and environmental impacts. GC and IC methods for the determination of the main low molecular weight anions, which account for the majority of the organic carbon in Bayer liquors, are well established as routine methods. CZE has emerged as a potentially more rapid, cost-effective and flexible method, and promises to replace the established methods and to enable the inclusion of a larger number of analytes.

The main challenge remains in the determination of the high molecular weight compounds, where despite considerable efforts to date there remains a significant knowledge gap. Techniques which are now available or are in development, in

particular multi-dimensional methods based on LC-MS-MS with “soft” ionization, offer the prospect of rapid progress in the generation of knowledge about the high molecular weight compounds. With the aid of these techniques it should be possible to “unlock the genome” of Bayer liquor organics which could lead to a quantum improvement in the capability of technologists to interpret and manipulate the organic chemistry of Bayer liquors.

## 10. Acknowledgements

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# TABLES and APPENDIX

868

869

870 **Table 1: 30-year timeline for the development and application of modern**

871 **analytical methods to Bayer liquors**

872

| Year | Method | Species Determined | First Citation |
|---|---|---|---|
| 1978 | Gas chromatography with flame ionization detection (GC) | Oxalate & other small organic anions | [21] |
| 1982 | Gel permeation chromatography with UV detection (GPC) | High molecular weight organic compounds | [29] |
| 1982 | Liquid chromatography with UV detection (LC) | Products of degradation of high molecular weight compounds | [29] |
| 1983 | Ion Chromatography with UV detection (IC) | Oxalate & other small organic anions, as well as chloride, sulphate & fluoride | [48] |
| 1984 | Gas chromatography - mass spectrometry (GC-MS) | High molecular weight organic compounds | [22] |
| 1986 | UV absorbance | "Humates" | [82] |
| 1990 | Thermal decomposition | Total organic carbon (TOC) | [20] |
| 1992 | Capillary Zone Electrophoresis with conductivity detection (CZE) | Oxalate & other small organic anions, as well as chloride, sulphate & fluoride | [19] |
| 1996 | UV-catalysed persulphate oxidation | Total organic carbon (TOC) | [99] |
| 1997 | Infra-red spectroscopy (IR) including Fourier transform IR (FTIR) | Structure & composition of the solid/liquid interface | [88] |

| | | | |
|---|---|---|---|
| 1998 | $^{13}$C NMR | Functional groups of organic compounds | [38] |
| 1998 | Differential thermal analysis (DTA) & differential scanning calorimetry (DSC) | General organic substances | [38] |
| 1999 | Pyrolysis gas chromatography mass spectrometry (py-GC/MS) | Type of high molecular weight organic compounds | [25] |
| 2002 | Liquid chromatography-tandem mass spectrometry (LC-MS/MS) | Variety of organic compounds | [27] |
| 2003 | $^{1}$H NMR | Functional groups of organic compounds and quantitative determination of small organic anions | [92] |
| 2005 | Multi-dimensional high performance liquid chromatography with UV detection (HPLC) | Potentially variety of high molecular weight organic compounds | [61] |
| 2006 | Fourier Transform Infra-Red spectroscopy (FTIR) | Total organic carbon (TOC) and other solution parameters | [87] |

873

# APPENDIX

## Table A1: Analytical Methods Summary: Compounds Generally Present in Bayer Liquors

Named as anions, listed in order of MW (of acid form).

| Compound | MW | CAS No. | Analytical Method | | | | | Citations |
|---|---|---|---|---|---|---|---|---|
| | | | GC | IC | CZE | HPLC | GC-MS | |
| formate | 46 | 64-18-6 | ✓ | ✓ | ✓ | | | [21, 27, 40, 47, 52, 98, 99, 104, 105] |
| acetate | 60 | 64-19-7 | ✓ | ✓ | ✓ | ✓ | | [21, 22, 27, 40, 47, 52, 98, 99, 105, 106] |
| propanoate | 74 | 79-09-4 | ✓ | ✓ | | | ✓ | [40, 47, 62, 98, 99, 104, 105] |
| butanoate | 88 | 107-92-6 | ✓ | | | | ✓ | [40, 62, 98, 99, 104] |
| iso-butyrate | 88 | 79-31-2 | | | | | ✓ | [23, 104] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| oxalate | 90 | 144-62-7 | ✓ | ✓ | ✓ | ✓ | ✓ | [19, 21-23, 27, 47, 54, 62, 63, 80, 98, 99, 104-106] |
| lactate | 90 | 598-82-3 | ✓ | ✓ | | | ✓ | [21, 22, 27, 40, 105] |
| isovalerate | 101 | 503-74-2 | ✓ | | | | | [23, 40, 104] |
| valerate | 102 | 109-52-4 | ✓ | | | | | [23, 40, 98, 99] |
| malonate | 104 | 141-82-2 | ✓ | | ✓ | ✓ | ✓ | [22, 27, 40, 52, 62] |
| 2-hydroxybutanoate | 104 | 600-15-7 | ✓ | | | | ✓ | [22, 38] |
| succinate | 118 | 110-15-6 | ✓ | ✓ | | ✓ | ✓ | [19, 21-23, 27, 38, 40, 47, 52, 62, 63, 80, 98, 99, 104-106] |
| benzoate | 122 | 65-85-0 | ✓ | | | | ✓ | [22, 23, 26, 27, 40, 62, 104] |
| glutarate | 132 | 110-94-1 | ✓ | ✓ | | ✓ | ✓ | [21-23, 38, 40, 62, 63, 80, 98, 99, 104, 106] |
| salicylate | 138 | 69-72-7 | ✓ | | | | ✓ | [21, 22, 27, 38] |
| m-salicylate | 138 | 99-06-9 | | | | | ✓ | [23, 27, 38, 62] |
| adipate | 146 | 124-04-9 | | | | ✓ | ✓ | [22, 23, 26, 52, 62, 98, 99, 104] |
| methyl-succinate | 146 | 498-21-5 | ✓ | ✓ | | | ✓ | [22, 27, 40] |
| tartrate | 150 | 87-69-4 | | | ✓ | ✓ | | [19, 52, 63, 80] |
| pimelate | 160 | 111-16-0 | ✓ | | | | ✓ | [21, 22, 62, 99] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ethane-1,1,2-tricarboxylate | 162 | 922-84-9 | | | | | ✓ | [22, 27] |
| phthalate | 166 | 89-99-3 | ✓ | | | | ✓ | [26, 27, 38, 40, 98, 99, 104] |
| isophthalate | 166 | 121-91-5 | | | | | ✓ | [22, 27, 62] |
| terephthalate | 166 | 100-21-0 | | | | | ✓ | [26, 27, 38] |
| octanedioate | 174 | 505-48-6 | ✓ | | | | ✓ | [21, 26, 62] |
| tricarballate | 176 | 99-14-9 | | | | | ✓ | [22, 27] |
| propane-1,1,2-tricarboxylate | 176 | NA | | | | | ✓ | [27, 65] |
| 4-hydroxyphthalate | 183 | 610-35-5 | ✓ | | | | ✓ | [21, 27, 65] |
| 5-hydroxyisophthalate | 183 | NA | ✓ | ✓ | | | ✓ | [27, 38, 65] |
| azelate | 188 | 123-99-9 | | | | | ✓ | [23, 26, 47] |
| citrate | 192 | 77-92-9 | | | ✓ | | ✓ | [44, 52, 65] |
| hemimellitate | 210 | 569-51-7 | | | | | ✓ | [22, 27, 98, 99, 104] |
| trimellitate | 210 | 528-44-9 | ✓ | | | | ✓ | [21, 22, 27, 98, 104] |
| trimesate | 210 | 554-95-0 | ✓ | | | | ✓ | [27, 98, 99] |
| pyromellitate | 254 | 89-05-4 | ✓ | | | | ✓ | [21, 27, 36, 38, 98] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| palmitate | 256 | 57-10-3 | | | | | ✓ | [22, 23, 26] |
| stearate | 284 | 57-11-4 | | | | | ✓ | [23, 26] |
| benzene pentacarboxylate | 298 | NA | ✓ | | | | ✓ | [21, 27, 36] |
| mellitate | 342 | 517-60-2 | ✓ | | | | ✓ | [21, 27] |

879

880

881 **Table A2: Additional Compounds Discovered in Individual Bayer Liquors**

882 Compounds with only one citation, sorted by molecular weight. Named as acids, following convention of cited papers.

883

| Compound | MW | CAS No. | Method | Citation |
|---|---|---|---|---|
| ethanolamine | 60 | 141-43-5 | GC-MS | [22] |
| butanolamine | 75 | 13325-10-5 | GC-MS | [22] |
| methyl-2-pyrrolidinone | 99 | 872-50-4 | GC-MS | [41] |
| 2-methyl butanoic | 102 | 116-53-0 | GC-MS | [23] |
| 3-methylphenol | 108 | 108-39-4 | GC-MS | [41] |
| (1H-pyrrol-2-yl)ethanone | 109 | 1073-83-9 | GC-MS | [41] |
| 4-heptanone | 114 | 123-19-3 | GC-MS | [23] |
| hexanoic acid | 116 | 142-62-1 | GC-MS | [23] |
| 2,4-dimethyl-3-pentanol | 116 | 600-36-2 | GC-MS | [23] |
| 2,4-dimethylphenol | 122 | 105-67-9 | GC-MS | [41] |
| 3-methyl-4-heptanone | 128 | 15726-15-5 | GC-MS | [23] |
| dibutyl ether | 130 | 142-96-1 | GC-MS | [23] |

| | | | | |
|---|---|---|---|---|
| propane-2,3-dicarboxylic acid | 131 | NA | GC-MS | [27] |
| malic acid | 134 | 6915-15-7 | GC-MS | [22] |
| 2,5-dimethylbenzaldehyde | 134 | 5779-94-2 | GC-MS | [23] |
| 2-hydroxyphenylethanone | 136 | 582-24-1 | GC-MS | [41] |
| 4-methyl benzoic acid | 136 | NA | GC-MS | [27] |
| butane-2,3-dicarboxylic acid | 146 | NA | GC-MS | [27] |
| 4-hydroxy-2-methylacetophenone | 150 | 875-59-2 | GC-MS | [41] |
| 3-methoxy benzoic acid | 152 | 586-38-9 | GC-MS | [26] |
| 3-methyl salicylic | 152 | 200-068-3 | GC-MS | [27] |
| 4-methoxy benzoic acid | 152 | 202-818-5 | GC-MS | [26] |
| 3-hydroxy-4-methyl benzoic acid | 152 | NA | GC-MS | [27] |
| butane-2-methyl-2,3-dicarboxylic acid | 160 | NA | GC-MS | [27] |
| 3-methyl hexanedioic | 161 | 623-82-5 | GC-MS | [23] |
| 1-(2,4-dihydroxy) phenyl-1-propanone | 166 | NA | GC-MS | [38] |
| propane-1,1,2-tricarboxylic acid | 176 | NA | GC-MS | [65] |
| propane-1,1,2-tricarboxylic acid | 176 | NA | GC-MS | [65] |
| homophthalic acid | 180 | 85-51-0 | GC-MS | [27] |

| | | | | |
|---|---|---|---|---|
| benzene-4-methyl-1,3-dicarboxylic acid | 180 | NA | GC-MS | [27] |
| 2-hydroxyisophthalic acid | 183 | NA | GC-MS | [65] |
| Isocitric acid | 192 | 320-77-4 | GC-MS | [65] |
| 1-hydroxy-1,1,2-propane tricarboxylic acid | 192 | NA | GC-MS | [65] |
| 1-hydroxy-1,1,3-propane tricarboxylic acid | 192 | NA | GC-MS | [65] |
| butane-1,1,4-tricarboxylic acid | 194 | NA | GC-MS | [65] |
| butane-1,2,4-tricarboxylic acid | 194 | NA | GC-MS | [65] |
| decanedioic | 202 | 111-20-6 | GC-MS | [23] |
| 2-hydroxy-1,2,4-butane tricarboxylic acid | 206 | NA | GC-MS | [65] |
| 1,1-dibutoxybutane | 202 | 5921-80-2 | GC-MS | [23] |
| pentane-1,3,5-tricarboxylic acid | 204 | NA | GC | [21] |
| ethane-1,1,2,2-tetracarboxylic acid | 206 | NA | GC-MS | [27] |
| benzene-1,3,4-tricarboxylic acid | 210 | NA | GC-MS | [27] |
| benzene-2-hydroxy-1,4,5-tricarboxylic acid | 226 | NA | GC-MS | [27] |
| tetradecanoic acid | 228 | 544-63-8 | GC-MS | [23] |
| 3,5-di-tert-butyl-4-hydroxybenzaldehyde | 234 | 1620-98-0 | GC-MS | [26] |
| benzene-1,2,3,5-tetracarboxylic acid | 254 | 89-05-4 | GC | [21] |

| | | | | |
|---|---|---|---|---|
| 9,12-octadecadienoic | 280 | 60-33-3 | GC-MS | [23] |
| benzene hexacarboxylic acid | 342 | 517-60-2 | GC | [21] |
| squalene | 410 | 111-02-4 | GC-MS | [26] |

**Figure 2: Schematic representation of a typical lateritic bauxite profile (diagram reproduced with the permission of BHP Billiton Worsley Alumina) [1].**

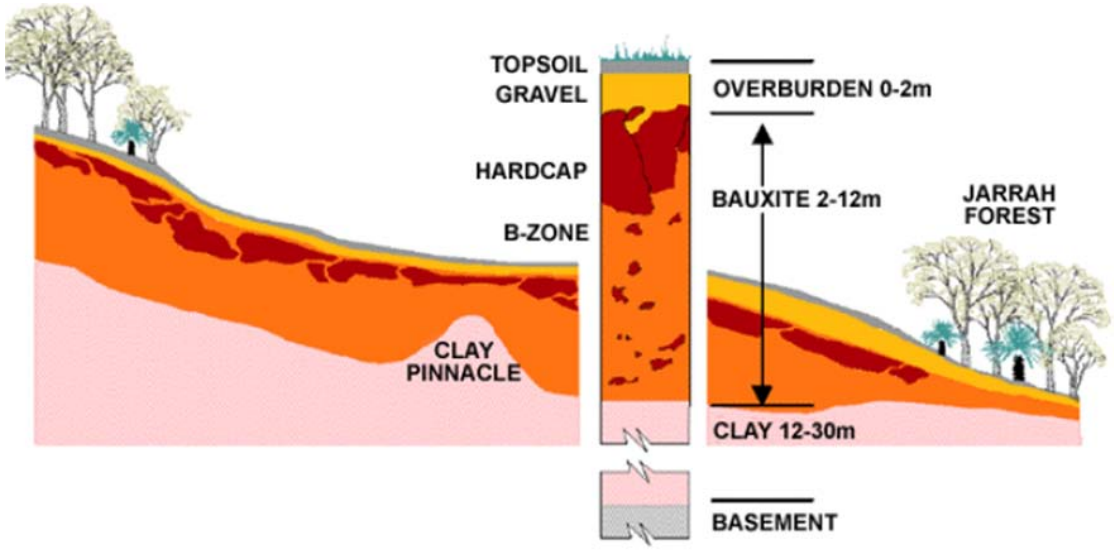


**Figure 2: Sample preparation scheme for the separation of high molecular weight organics from Bayer liquors, derived from the descriptions given by Wilson et al. [25].**

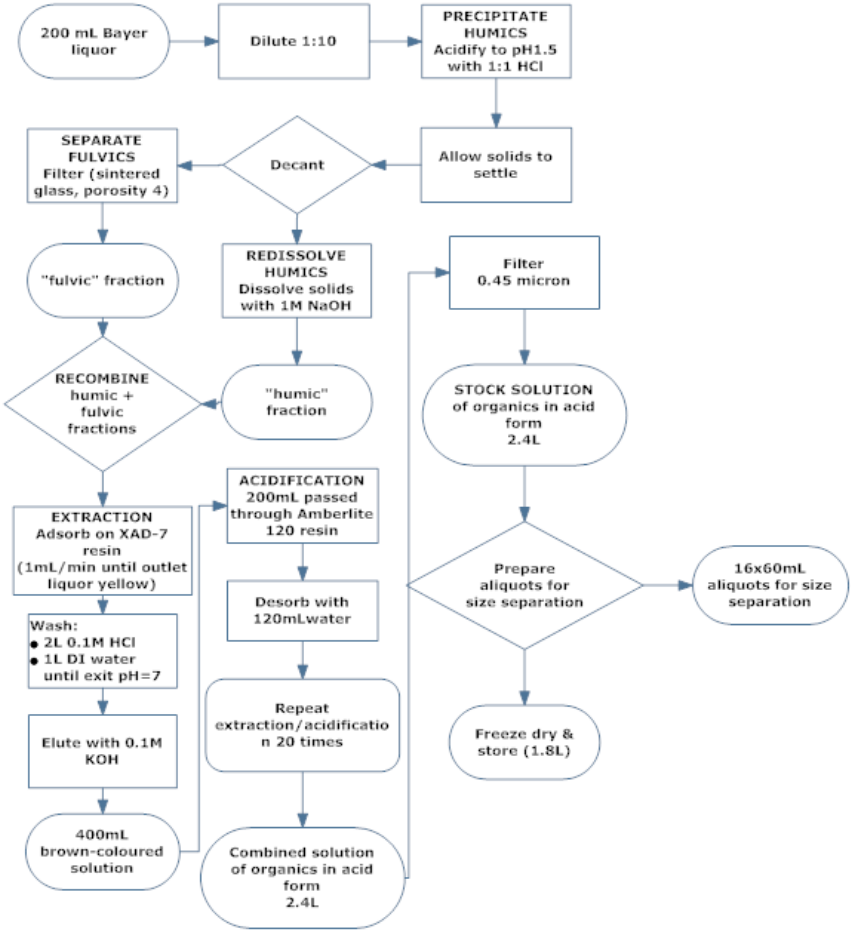


**Figure 3: Example of a determination scheme using GC-MS and GPC(SEC), adapted from Guthrie et al. [22].**

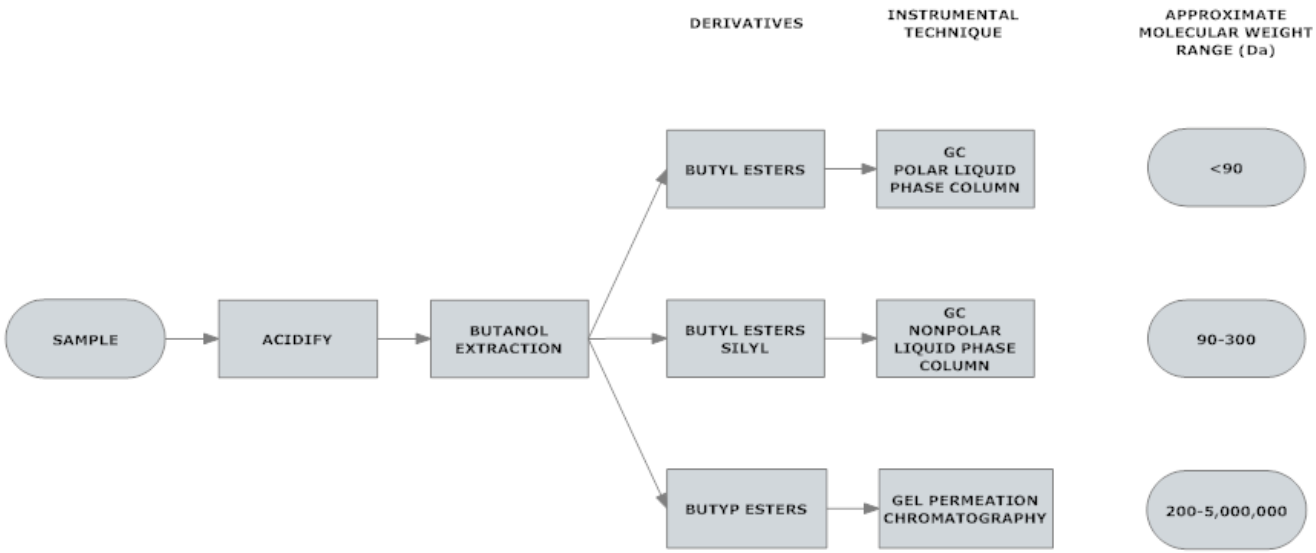


**Figure 4: LC trace for medium MW (90-300 Da) compounds in a Bayer liquor from Guthrie et al.. The numbered peaks were identified by MS [22].**

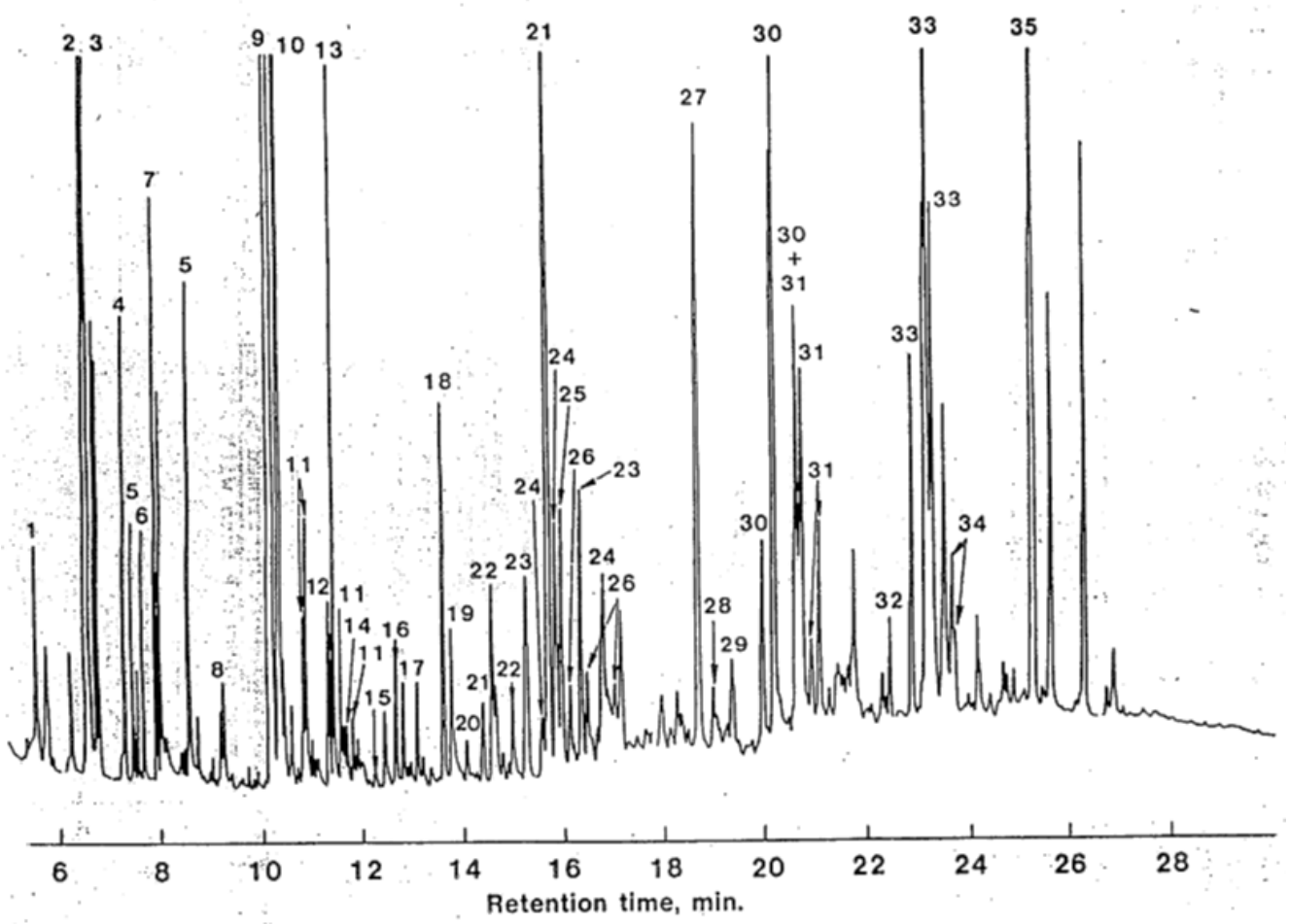


**Figure 5: IC trace for low MW compounds in a Bayer liquor from Picard et al. showing assignments by MS [27].**

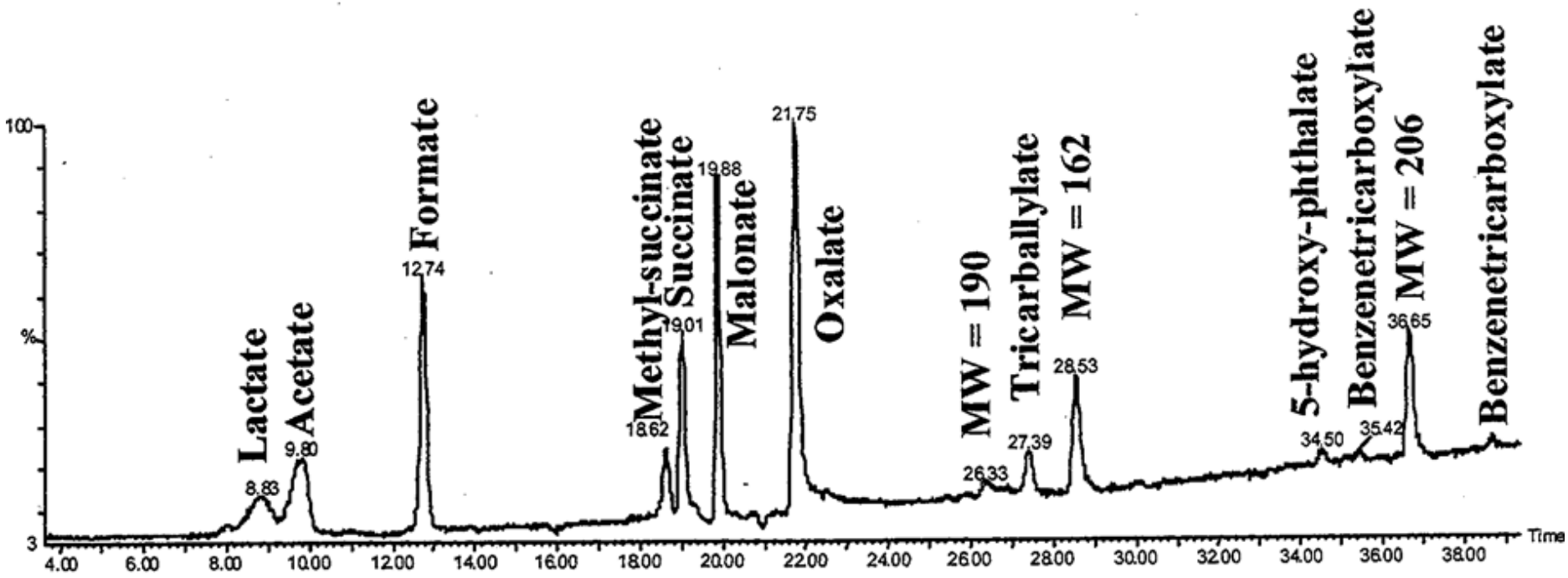
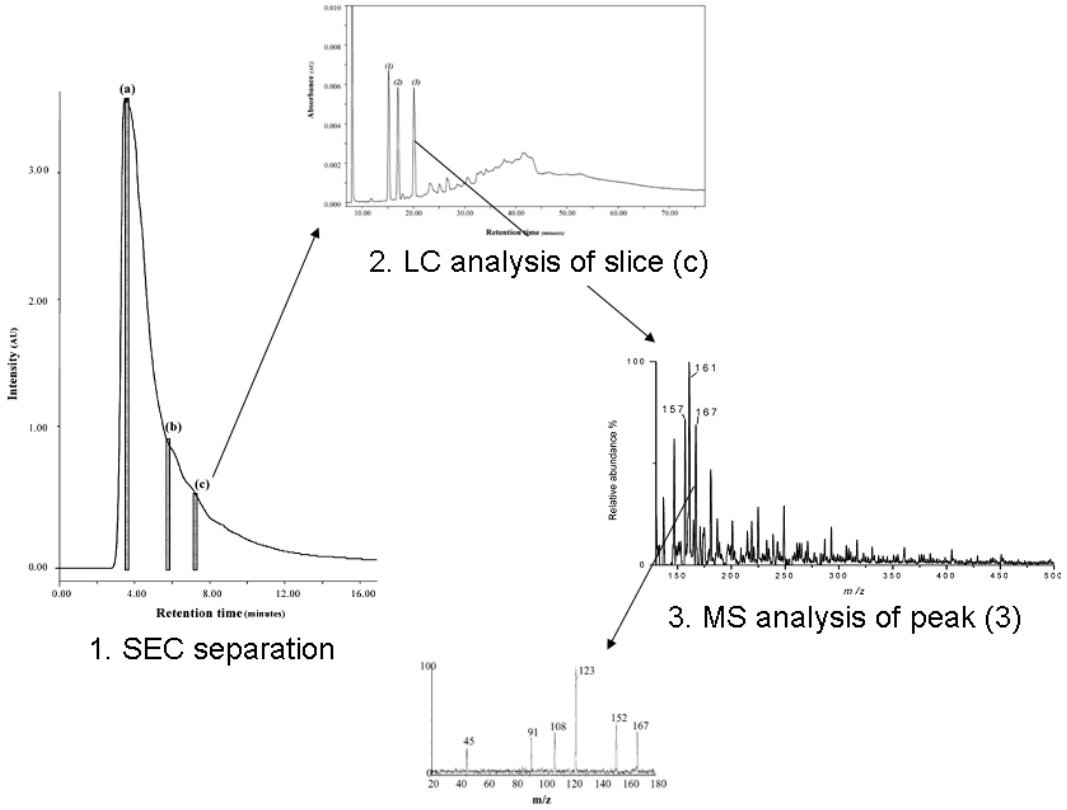


**Figure 6: Multidimensional determination sequence adapted from Whelan et al. [61] showing GPC-UV fractionation followed by LC-MS operated in full scan mode and LC-MS/MS operated in product ion mode.**



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