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

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TEXT

ABSTRACT

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21   Bayer process liquors present a difficult and complex matrix to the analytical chemist,

22   and the history of the application of modern analytical techniques to this problem is a

23   case study in innovation. All Bayer process liquors contain organic compounds, in

24   amounts varying from traces to several grams per litre. The total organic carbon

25   content of Bayer liquors may be less than 5 g/L up to as much as 40 g/L. The

26   presence of these organic impurities is of concern to Bayer technologists because they

27   can have significant impacts on the economics of the process and the quality of the

28   product. This review examines the history and current state-of-the-art of the analysis

29   of organics in Bayer process liquors, and provides guidance on the applicable

30   techniques matched to a comprehensive list of the compounds most likely to be

31   present.

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

36

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°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

83   of the process as well as being a key factor in the design of each specific plant. The

84   determination of organic impurities has been the subject of significant developmental

85   effort and continues to be an active area of research.

86   **2. Historical Perspective**

87   The presence of organic compounds in bauxite was recognised very early in the

88   history of the extraction of alumina from bauxite. Only 13 years after Bayer patented

89   his process [8], improvements patented by C M Hall included heating bauxite to burn

90   off organic matter prior to digestion [9]. A study of the processing of Urals bauxite

91   indicated the presence of soluble and insoluble organic matter [10], and that the

92   soluble organic matter was 58% carbon. Utley reported that Arkansas bauxite

93   contained 0.3 to 0.4% organic matter which was about 50% carbon [11]. Most of the

94   bauxite now being mined originates from lateritic deposits which are or have been

95   overlain by forests. Bauxite genesis relies on selective leaching of minerals by water

96   percolation, resulting in a layered profile as depicted schematically in Figure 1. In

97   such a profile the organic carbon content varies from a maximum in the order of 1%

98   in the overburden to a minimum of 0.1% or less in the clay floor of the deposit [1].

99

100   *Please place Figure 1 near here*

101

102   The soluble organics which enter Bayer process liquors impart a red-brown colour to

103   the liquor, the exact shade and intensity of which depends on both the bauxite source

104   and the processing conditions [12]. The significance of the presence of organics in

105   the liquor appears to have been first highlighted in the English-language literature in

106   Pearson's 1955 monograph on the aluminium industry [12], in which it was noted that

5

107 the organic matter in liquor originated mainly from the bauxite, and that it had a

108 number of negative influences on the operation and economics of refining operation,

109 and on the quality of the product. A more detailed account of the origins and effects

110 of organics in the Bayer process is given in the review by Solymár and Zsindely [13]

111 of bauxites then being processed in Hungary. The techniques available for the

112 investigation of organic compounds in highly alkaline liquors at that time involved

113 lengthy and complex wet chemical techniques [14], so the investigations in the

114 industry were probably limited to determination of total organic carbon (TOC) by

115 classical techniques such as permanganate titration [15, 16].

116

117 It has long been known that oxalate is formed in the Bayer process, because sodium

118 oxalate has limited solubility at high pH, and so can crystallize out if the organic input

119 to the refinery is sufficient [12, 17]. However, a deeper understanding of the nature

120 and reactions of organic compounds in Bayer liquors awaited the development of

121 instrumental techniques for organic determination. Specialised sample preparation

122 techniques also had to be developed for application to the highly concentrated and

123 complex matrix of Bayer liquors.

124

125 Table 1 summarises as a timeline the main innovations in analytical techniques and

126 their application to the analysis of Bayer liquors in the past 30 years. Details of the

127 application of these techniques to individual analytes are given in the Appendix.

128

129   *Please place Table 1 near here*

130

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

180   basis that this may result in losses of some organic compounds by adsorption to the

181   aluminium hydroxide surface. They recommend a 1:10 dilution followed by rapid

182   acidification to pH 1.5 with 1:1 HCl to precipitate the "humic" materials, which are

183   then separated by filtration, redissolved in NaOH and extracted onto a polar

184   adsorption resin (Amberlite XAD-7). The organics are subsequently washed from the

185   resin with deionized water to produce a neutral, salt-free solution containing the acid

186   forms of the "humic" materials. The collected dried solid humic material is then

187   extracted sequentially with diethyl ether, ethyl acetate, isopropyl alcohol and water

188   [26] .

189

190   Picard et al. [27] tested two separate extraction methods which were followed

191   directly by multidimensional chromatography and mass spectrometric analysis (see

192   section 5.1).

193

194   The first extraction method trialled was a liquid/liquid separation which used three

195   different solvents of increasing polarity in succession (ether, ether/n-butanol, and n-

196   butanol) to separate the organics on the basis of their polarity.

197

198   The second method was solid-phase extraction using a hydrophobic C18 stationary

199   phase. This was used to separate the organics into high, medium and low molecular

200   weight (HMW, MMW and LMW) fractions. The HMW fraction was defined as the

201   material which precipitated at low pH, the MMW as that which was soluble at low pH

202   and was retained on the C18 stationary phase, and LMW as the soluble fraction which

203   was not retained. On this basis, for samples taken from 10 different Bayer process

204   plants, it was found that the LMW fractions represented between 30 and 50% of the

205   TOC of the spent liquors analysed [27] .

206

207   Whelan and co-workers identified some anomalies from solvent extraction in which

208   compounds with a range of polarities were found in a particular solvent [26]. They

209   suggested that the solubility of humic materials may be controlled by association, in

210   which small molecules can aggregate by arranging their polar groups internally to

211   produce relatively hydrophobic micellular structures which are more soluble in less

212   polar organic solvents than might be expected. This phenomenon may be a function of

213   concentration as suggested, or it could be an artefact of the extraction procedure

214   which entails dissolving organic matter from concentrated Bayer humic material that

215   has been dehydrated and solidified.

216

217   Other approaches to the determination of molecular weight fractions are discussed in

218   the next section.

219

220   **3.3.   Fractionation by Molecular Weight and Size**

221   Separation of organic compounds into fractions based on apparent molecular weight

222   or molecular size by ultrafiltration (UF) or dialysis has been used to characterise the

223   organic matter present in Bayer liquor. Lever [21] used UF through membranes with

224   nominal molecular weight cutoff values (MW_{cutoff}) of 0.5, 1, 5 and 10 kDa. The

225   fractions collected were then evaporated and weighed to obtain a coarse apparent

226   molecular weight or size distribution. Dialysis into 1.2, 6, 12, 25, 50, 100, and 300

227   kDa MW_{cutoff} fractions has been described by Wilson et al. [25, 28].

228

229   Gel permeation chromatography (GPC), also known as size exclusion

230   chromatography (SEC), has been used to obtain a continuous apparent size

231   distribution of the organic matter present in Bayer liquor [29]. Separation has been

232   achieved on 500×7 mm x 140 Å and 100A Spherosil 100/200 porous silica bead

233   columns in series [21] or on 300 x 7.8 mm x 500 Å and 100 Å μ-Styragel columns in

234   series [22] with UV detection to obtain a molecular weight distribution of Bayer

235   liquor extracted with butanol. Each of these chromatograms was a continuum with no

236   discrete peaks.

237

238   It should be noted that SEC with UV detection underestimates saturated aliphatic

239   carboxylic anions, which are known to constitute a significant proportion of the total

240   organic carbon (TOC) in Bayer liquors but are not good absorbers of UV. A solution

241   to this could be to incorporate continuous TOC (or, more strictly, dissolved organic

242   carbon (DOC)) detection as well [30, 31], but application of this to Bayer liquors has

243   not yet been reported.

244

245   All separations based on molecular size should be treated with caution when applied

246   to Bayer liquor extracts. Membranes and size exclusion gels have long been used for

247   the fractionation of proteins and peptides, for which purpose they are calibrated with

248   particles of known size which are uniform, spherical, non-polar and relatively

249   chemically inert. The technique has been extended to the characterization of natural

250   organic matter (NOM), but the interpretation of results becomes more complex

251   because separation is no longer purely on the basis of molecular size, and there are no

252   universally applicable calibration standards [32, 33]. Interpreting the information

253 obtained from molecular size separation methods in such systems is therefore not

254 straightforward, and can lead to gross errors when specific chemical and physical

255 interactions between the analytes and the stationary phase are significant [34, 35].

256 Bayer liquor organics contain a high proportion of highly polar groups, in particular

257 carboxylic acids. Electrostatic effects and hydrogen bonding can therefore be

258 expected to play an important, even dominant, role in the retention behaviour, so

259 correlations of retention times with molecular size alone are unlikely to be valid, and

260 aggregation of small molecules into micellular structures noted in Section 3.2 can

261 cause them to behave as if they have a much higher molecular weight than is in fact

262 the case [28] .

263

264 Notwithstanding these complications, separations using membranes and columns of a

265 variety of types are an important aspect of the sample preparation methodologies

266 available for investigating the nature of Bayer liquor organics.

267 ## 3.4.   Consolidated Sample Preparation Strategy for

268 ## Determination of the High Molecular Weight Fraction

269 Using the experience outlined in the previous sections, a preparation method suitable

270 for the determination of the high molecular weight fractions of Bayer liquors is that

271 developed by Wilson et al. [25] . To enable this quite complex scheme to be

272 appreciated visually, we have prepared a flow-sheet representation of it (Figure 2). It

273 consists of the following seven main elements:

274   1. dilution

275   2. acidification to precipitate humics

276   3. redissolution in NaOH

277   4. extraction on XAD-7 resin

278   5. washing and elution

279   6. acidification on Amberlite 120 resin

280   7. filtration and aliquot preparation/storage.

281

282   *Please put Figure 2 near here*

283

284   This scheme enables quantitative separation of the high molecular weight organics

285   from the liquor, to produce a stock solution of the organics in acid form, free from

286   aluminate and other salts. The stock solution may be sub-sampled for size separation

287   and/or other determinations, or freeze-dried for storage.

288

289   *Please put Figure 1 near here*

290   # 4. Chromatographic Separation

291   ## 4.1.   Gas Chromatography (GC)

292   According to the published literature, the first significant advance in the application of

293   modern chromatographic techniques to the determination of organic compounds in

294   Bayer liquors was the work of Lever in the 1970s [21], in which capillary GC was

295   used to analyse species with low to medium molecular weights (40 to 350 Da). The

296   method relied on methylation and butylation of methanol extracts using diazomethane

297   or diazobutane in ether to produce volatile compounds suitable for separation by gas

298   chromatography. Using these methods, Lever was able to confirm the identity and

299   quantify the amounts of five key degradation products already believed to be present:

300   formate, acetate, lactate, oxalate and succinate. He was also able to identify a range

301   of previously unidentified molecules, in particular a comprehensive range of mono-

302 aromatic carboxylic acids from the degradation of humic molecules [21]. The low

303 molecular weight molecules were identified and quantified by comparing their

304 responses in the flame ionization detector (FID) to known standards.

305

306 GC quickly became the basis of a variety of methods for the investigation of low to

307 medium molecular weight organic compounds in Bayer liquors. The differences in

308 the methods used by various workers were at first mainly in the sample preparation

309 techniques used, but later developments in column technology and detection methods

310 have also had a significant influence.

311

312 The main variants in the derivatization methods are as follows:

313 • Methylation of a methanol extract using diazomethane in ether [21, 36], or by

314   direct application to Bayer liquor using acidified tris(hydroxymethyl)

315   aminomethane in chloroform and methanol [37];

316 • Methylation of an aqueous solid phase alkaline extract using

317   tetrabutylammonium hydroxide added at pH 8.5 [38], or of a Bayer liquor

318   butanol extract using acidified methanol [39];

319 • Butylation. Lever [21] derivatized dried neutralised Bayer liquor using

320   acidified butanol. Baker et al. [40] derivatized butanol extracts using acidified

321   butanol in a microwave oven, Guthrie et al. [22] and Wellington and Valcin

322   [41] derivatized Bayer liquor directly using acidified butanol, while Xiao [39]

323   derivatized acidified, solvent extracted Bayer liquor using acidified butanol

324   followed by hexane extraction.

325

326   Caution must be exercised in the use of derivatization techniques and in the

327   interpretation of the results obtained. For example, Wilson et al. [38] found that the

328   methyl ester did not form quantitatively for some compounds and that some methyl

329   esters were non-volatile. Xiao [39] found that losses of low molecular weight acids

330   could occur due to evaporation during concentration procedures. He also found that

331   butylation could result in dibutyl ether artefacts, that it was difficult to identify

332   unknowns from their butyl derivatives, and that butylation was not useful for high

333   molecular weight acids. Xiao therefore recommended that methylation and

334   butylation be used in combination to optimise recoveries and improve the confidence

335   in the identification of analytes.

336

337   Guthrie et al. [22] derivatized the butanol extracts with Tri-Sil for the determination

338   of low and intermediate molecular weight aliphatic and aromatic acids. Silylation

339   (using hexamethyldisilazane and trimethylchlorosilane) was also used by Ellis et al.

340   [42] to analyse plant extracts and digested plant extracts. Using this procedure, it was

341   possible to determine low and intermediate molecular weight mono-, di- and tri-

342   carboxylic aliphatic and aromatic acids, aliphatic and aromatic hydroxy carboxylic

343   acids, polyhydric alcohols, alkanes, carbohydrates and furans. According to Eyer

344   [43], Alcoa World Alumina has developed a GC method based on methylation

345   followed by chloroform extraction for the routine determination of oxalate, malonate

346   and succinate. It was found that the method could be extended to include benzene as

347   an analyte directly, but it was necessary to use butanol to derivatize acetate and

348   formate for determination. Tardio [44] used a similar method to determine formate,

349   acetate, butyrate, oxalate, malonate, succinate, glutarate, lactate, malate and fumarate

350   as the methyl esters.

351

352 The advent of GC with mass spectrometry detection (GC-MS) in place of or in

353 addition to non-specific detection by FID brought a major advance in analytical

354 capability by enabling the identification of individual compounds, for example

355 according to the scheme illustrated in Figure 3 [22].

356

357 *Please put Figure 3 near here*

358

359 The complexity of the mixture of organic compounds in Bayer liquor is illustrated by

360 the GC trace in Figure 4 for compounds in the MW range 90 to 300 Da. The

361 numbered peaks were identified by MS [22]. The addition of modern multi-

362 dimensional mass spectrometry has since demonstrated the potential for the

363 identification of many hundreds of compounds [27] . To date however, a total of only

364 85 individual compounds, all of which have molecular weights below 350 Da, have

365 been specifically identified in the literature as being present in Bayer liquors [1].

366

367 Most of the compounds that have been found in Bayer liquors are organic acid anions

368 [1]. For example, Xiao [39] was able to analyse more than twenty mono- and di-

369 carboxylic acids using a combination of methylation and butylation; Picard et al. [27]

370 claim to have identified over a hundred acids, but they cite only those corresponding

371 to the twenty most intense peaks in the mass spectra. On the other hand, Wellington

372 and Valcin [41] found more than 15 non-acid compounds including alkenes, phenols,

373 pyrolidinones, quinolines and pyrroles in a Bayer liquor using butylation.

374

375 According to Eyer [43], Alcoa World Alumina has applied GC-MS to the

376 determination of a range of low molecular weight (C_3-C_{20}) hydroxycarboxylic acids

377 extracted from Bayer liquors and analysed as the trimethylsilate esters.

378

379 Pyrolysis-GC-MS, in which the products of the pyrolysis of a sample in an inert

380 atmosphere at various temperatures are analysed by GC-MS, has been used to

381 characterise the high molecular weight material in Bayer process liquors [25, 28] .

382 This method enables the material to be characterised in terms of its main functional

383 constituents, and provides evidence for their likely origins. Because of the large

384 number and complexity of the pyrolysis products, however, it has not been possible to

385 identify specific starting compounds with any confidence by this method.

386 ## 4.2.   Ion Chromatography (IC)

387 Ion chromatography relies on the separation of ions on an ion exchange column, after

388 which the solution is passed through a "suppressor" column. In the case of anion

389 determination, the suppressor removes the sodium ions from the solution and replaces

390 them with hydrogen ions that react with the corresponding hydroxide ions to form

391 water. This suppresses the bulk conductivity of the solution, so that the remaining

392 anions can be detected by their conductivity. This method, which was developed in

393 the 1970s, can be applied to both cations and anions, but was the first method to

394 become available for routine determination of multiple anions using a single, simple

395 detection technique [45]. The key to the method is the suppressor, which must be

396 regularly regenerated for continuous use, and maintenance of suppressor performance

397 is crucial to ensuring ongoing sensitivity, accuracy and precision of determination.

398

399 The advent of IC provided for the first time a rapid method requiring minimal sample

400 preparation for the simultaneous determination of many of the low molecular weight

401 organic acids of most interest to Bayer process technologists. Generally, the only

402 sample preparation required is dilution in water prior to introduction to the analytical

403 system. This method therefore lends itself to automation, and is suitable for high

404 volume, routine use.

405

406 Nevertheless, the nature of Bayer liquor places restrictions on the application of IC for

407 determination. The high ionic strength and pH of the liquor mean that samples

408 require significant dilution (typically at least 500:1) prior to determination, which

409 limits the sensitivity of the method. Interferences between the many organic and

410 inorganic anions present is also a limiting factor [18]. In addition, the high aluminate

411 content and the insolubility of aluminate between pH 5 and 10 means that eluents

412 outside this pH range must be used, or else the solution must be stabilised by the

413 addition of a complexing agent, such as tartrate or gluconate [18]. Alumina fouling of

414 the suppressor is a key issue, even with alumina complexants in the eluant, and this

415 generally requires regular flushing with strong acid (e.g. 1 M HCl) [46]. Some

416 workers have overcome this problem by pre-treating the samples with an ion

417 exchange resin to remove the aluminate ions prior to determination [47, 48], but this

418 increases the complexity of the method and is a disadvantage for high volume routine

419 use.

420

421 Since the 1980s, oxalate and other low molecular weight aliphatic acids in Bayer

422 liquor have been analysed directly by ion chromatography with anion exchange

423 columns and alkaline mobile phases using conductivity detection [48, 49]. Oxalate is

424 currently measured in this way in key process streams in many Bayer plants on a daily

425 or more frequent basis [19, 20].

426

427 Detection by UV absorbance was found to be more satisfactory for aromatic acids

428 because their lower pK_a values made conductivity detection difficult [48]. Xiao et al.

429 [47] have recently reported a method for the rapid determination of the organic anions

430 formate, acetate, propionate, oxalate, succinate and glutarate, as well as the inorganic

431 anions fluoride, chloride and sulphate, with a single injection providing good

432 accuracy and precision. The chromatographic run time was 33 minutes, but pre-

433 treatment of the samples by ion exchange is required to achieve this.

434

435 Brindel and Lectard [48] used GC-MS to identify 9 benzene carboxylates separated

436 by IC from a Bayer liquor, and identified 11 other compounds by comparison with

437 standard compounds. Picard et al. [27] used IC followed by MS detection to separate

438 and identify 11 low molecular weight aliphatic and aromatic acids present in Bayer

439 liquor, as illustrated in Figure 5. The solution from the IC separation was introduced

440 to the MS via electrospray ionization, a "soft" ionization method which enables the

441 formation of ions without fragmentation of the parent molecules. They then used this

442 technique to survey the liquors from 10 different plants, and found that the four most

443 prevalent compounds, formate, acetate, oxalate and succinate, accounted for between

444 15 and 40% of the TOC in the Bayer liquors studied.

445

446 *Please put Figure 5 near here*

447

4.3. Capilliary Zone Electrophoresis (CZE)

448

449 Applying an electric field gradient to ions in a solution causes ion migration in the

450 direction of the field. The rate and direction of the migration are determined by the

451 charge and hydrodynamic radius of the ions. This effect is the basis of the separation

452 of ions by CZE, commercial instruments for which became available around 1990.

453 CZE is now an active field of research in its own right, and may be found in a very

454 wide range of analytical applications [50]. Detection is usually by UV absorption,

455 often by indirect detection using an added chromophore [51], sometimes called the

456 "probe" [52]. The mobile phase may include various electroosmotic flow and

457 selectivity modifiers [53]. The first analyses for anions in Bayer liquor used chromate

458 as the probe with indirect detection at 254 or 245 nm [18, 19, 52, 54]. These analyses

459 were successful for the determination of oxalate in Bayer liquor, but peak shape and

460 resolution of other aliphatic acids was usually poor, even under apparently optimal

461 conditions.

462

463 Breadmore and co-workers [55] investigated various complex mixtures of different

464 reagents and were able to separate 14 low molecular weight aliphatic acids, with

465 separation selectivity and resolution able to be changed substantially by varying the

466 electrolyte conditions. Only formate, acetate and oxalate were found in actual Bayer

467 liquor by this method.

468

469 To remove the issues associated with the use of toxic chromate reagents, Chovancek

470 et al. [56] introduced the use of molybdate as the probe with detection at 214 nm.

471 Under these conditions, 5 low molecular weight aliphatic acids were rapidly separated

472 in Bayer liquor with good resolution and peak shapes.

473

474   CZE has a number of advantages over IC in the areas of selectivity, speed of

475   determination, peak separation and sample volume requirements. Although it did

476   initially suffer from less stable retention times, poor peak shapes and a much higher

477   detection limit [18, 19], it appears these problems have been largely overcome, so that

478   CZE now has excellent reproducibility, peak shapes, linearity and limits of detection

479   for many of the low molecular weight acids of interest in Bayer liquor [56]. CZE has

480   recently been applied to the determination of 18 carboxylic acids for the monitoring

481   of bioreactors, and it is reasonable to suppose that similar advances could be made in

482   the analysis of Bayer process solutions using this approach [57].

483

484   **4.4.   High Performance Liquid Chromatography (HPLC)**

485   HPLC, sometimes known as high *pressure* liquid chromatography, can be operated in

486   a number of different modes and with stationary phases of different chemistries, and a

487   variety of mobile phases and additives. As such, it is a very flexible technique for the

488   determination of a wide variety of types and sizes of organic compounds in a range of

489   matrices. HPLC can also be used to investigate the fundamentals of adsorption as

490   shown by the work of Bouchard et al. [58] who used it to determine dynamic

491   adsorption isotherms of organic compounds with the potential to inhibit the

492   precipitation step of the Bayer process.

493

494   The first reported use of HPLC for analysing Bayer liquors was by Salomon who was

495   able to identify a range of degradation products from the digestion of bauxite in

496   alkaline liquors [29]. Roumeliotis and co-workers [59] used it for the separation,

497   identification and quantification of carboxylic acids. They investigated reverse phase,

498   ion pair, ion exchange and ligand exchange separation techniques using 67 different

499   combinations of stationary and mobile phases with variable or fixed (254 nm)

500   wavelength UV detection. Nineteen low molecular weight aliphatic and aromatic

501   mono-, di-, tri, tetra- and penta-carboxylic acids were identified. However, despite

502   careful optimisation of the HPLC setup and conditions, many of the peaks were broad

503   and poorly resolved. Using semi-preparative reverse phase chromatography, they also

504   isolated aromatic carboxylic acids in a number of fractions from a 90 minute

505   chromatographic run for further characterisation and identification by MS.

506

507   Susic et al. [60] used HPLC on a reverse phase (RP) column with an ammoniacal

508   mobile phase and fluorescence detection to measure the "humic acid" concentration in

509   Bayer liquor, without separating it into its constituents.

510

511   Wilson and co-workers [26] applied HPLC to the analysis of the so-called "humic"

512   material (see Power and Loh [1] for a discussion of the meaning of "humic" in this

513   context) which had been separated from a Bayer liquor sample by acidification,

514   precipitation, solid-phase extraction and evaporation. The extracted solids were

515   redissolved in a water/methanol mixture and analysed using a variety of HPLC

516   methods of increasing complexity. It was found that RP chromatography alone was

517   inadequate, because the majority of the Bayer liquor humic material eluted in the first

518   20 minutes, with insufficient peak separation. Operating in ion-suppression mode, in

519   which the ionization of strong acids (and bases) is suppressed by the presence of a

520   buffer, resulted in better separation. The method was further improved by using ion-

521   pair mode, in which improved control of retention and selectivity is achieved by

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

523   phase.

524

525   The most successful technique was reverse phase ion-pair chromatography with a

526   mobile phase consisting of acetonitrile, water, formic acid and tetrabutylammonium

527   hydrogen sulfate [26] . Best results were achieved by applying the ion-pairing reagent

528   in a controlled time-dependent ratio (gradient) with acetonitrile. This enabled small

529   molecules to be resolved at the beginning of the chromatogram while allowing the

530   larger molecules to elute within a practical time period. The separation was achieved

531   on a C18 column of dimensions 150 x 3.9 mm x 4 µm and with a pore size of 60 Å,

532   using a diode array UV detector with wavelengths between 190 and 400 nm.

533   Chromatography times were long (100-650 minutes), but it was possible to resolve a

534   large number of individual small molecules within the first 200 minutes. At longer

535   elution times, material of higher molecular weight and lower polarity was eluted. It is

536   claimed that this is the first time that Bayer "humic" materials had been separated into

537   groups of different polarities. In addition, the material did not elute as a continuum,

538   but as clusters of peaks. This was interpreted as evidence for the existence of

539   micellular clusters for which only certain configurations are stable. No individual

540   compounds present in the Bayer liquor were identified in this developmental work,

541   but the methodology appears to have great potential for separating the "humic"

542   material into smaller and simpler fractions which could then be further separated by

543   LC for determination by mass spectrometry (MS) for example. This concept was

544   subsequently developed and applied to Bayer liquors to produce a multi-dimensional

545   separation and determination method which could revolutionise the determination of

546   such complex mixtures [61] (see section 7).

547

548 Xiao and co-workers have described the determination of oxalate, tartarate, acetate,

549 succinate, glutarate, malonate, adipate and butene dicarboxylate in Bayer liquor using

550 a C18 reverse phase column with a methanol/potassium dihydrogen phosphate mobile

551 phase and UV detection at 215 nm [62, 63]. Separation was relatively rapid (less than

552 10 minutes) but the retention times for the same compounds under apparently

553 identical conditions were found to be variable. Peaks were broad and detection limits

554 were also rather high (1-10 mg/L) for compounds other than oxalic acid.

555

556 Machold et al. [64] report the determination of 21 low molecular weight aliphatic and

557 aromatic carboxylic acids in 6 M NaOH using a reverse phase organic acid column

558 after dilution and acidification to pH 2, with a run time of only 9 minutes. Two

559 different mobile phases (potassium dihydrogen phosphate and potassium dihydrogen

560 phosphate/acetonitrile) were used, with UV detection at either 215 or 254 nm.

561

562 **5. Detection Methods and Spectroscopy**

563 Conventional chromatographic separation techniques employ non-specific detection

564 methods such as conductivity and UV absorption, relying on the characteristics of the

565 separation (e.g. elution time) as an indicator of speciation. This has the great

566 advantage of enabling a series of different compounds to be detected and quantified in

567 a single chromatographic run, but it generally relies on knowledge of the identity of

568 the compounds from calibrations with known compounds or separate analysis of each

569 peak.

570

571   The advent of techniques which provide identification as well as detection, in

572   particular mass spectrometry (MS), greatly increases the usefulness of the basic

573   separation by providing the ability to simultaneously identify and quantify the

574   components of complex unknown mixtures such as Bayer liquors.

575   ## 5.1.   Mass Spectrometry (MS)

576   The first published application of MS to the analysis of Bayer liquors is the work of

577   Guthrie et al. [22], who applied it to detect and identify compounds following

578   separation by GC. This enabled the identification of 35 compounds, several of which

579   had not been previously reported in Bayer liquor. MS has since been used by a

580   number of workers in investigations related to Bayer liquors, generally to provide

581   definitive identifications of the components present after separation by a variety of

582   chromatographic techniques. Niemela and Grocott [65] used GC-MS for a detailed

583   examination of the organics in Bayer liquor, which revealed the presence of more than

584   350 individual compounds. The authors claim to have identified over 200 of these,

585   but revealed the identities of only 14 compounds listed as examples of the successful

586   use of GC-MS.   However, without naming individual compounds, they reported the

587   presence of: 45 hydroxymonocarboxylic acids, 6 oxo-dicarboxylic acids, 10

588   tricarboxylic acids, 7 hydroxy tricarboxylic acids, 4 tetracarboxylic acids, 13 fatty

589   acids, 23 aromatic monocarboxylic acids, 18 aromatic di- or poly-carbosylic acids, 20

590   neutral (mainly phenolic) compounds, and various miscellaneous acids. GC-MS has

591   also been used to identify the compounds that were adsorbed onto aluminium

592   hydroxide from a Bayer liquor [38], to identify the components of water-soluble

593   extracts of plant remains in bauxites [42] and to identify the products of alkaline

594   leaching of plant materials related to bauxite digestion [6].

595

596 GC-MS has been used extensively by Niemela and co-workers in studies related to

597 the digestion of a range of natural materials, including woods and bark, cellulose,

598 starch and humic materials [66-74].

599

600 Despite these developments, there are surprisingly few reports in the literature of the

601 use of GC-MS for the direct identification of compounds present in Bayer liquors,

602 although it has been used extensively to identify pyrolysis products of liquor fractions

603 from a range of preparation and separation techniques [6, 25, 42, 75]. One reason for

604 this is that GC-MS is limited in its ability to provide information on the highly polar

605 compounds of high molecular weight that are of interest in Bayer liquors [27]. To

606 address this issue, Picard et al. [27] developed methods based on separations by

607 HPLC and IC, coupled with detection and identification by MS. Identification was

608 facilitated by using tandem mass spectrometry (i.e. MS-MS), in which a second stage

609 of MS is used to provide detailed structural information on ions separated in the first

610 stage of MS [76]. The same authors also used MS-MS directly to analyse the

611 components of liquid-liquid extracts from Bayer liquors. These analyses enabled

612 definitive identifications to be made of the compounds present in the highly complex

613 mixtures extracted from Bayer liquors, and led to the identification of over 100

614 individual compounds (although only the 20 most significant are named in the

615 publication) [27].

616

617 MS was also used as the detector in a multi-dimensional separation technique

618 developed by Whelan et al. [61] for Bayer liquor analysis, which is discussed further

619 in Section 7. Extension of the use of MS-MS in combination with new forms of

620 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

646   with hydrogen peroxide in the presence of Fe-TAML (tetra-amidato macrocyclic

647   ligand) catalyst. Low colour ratios are primarily associated with humic acids, while

648   high colour ratios and a stronger dependence of absorbance on wavelength are more

649   characteristic of fulvic acids.

650

651   A fundamental study of the UV spectra of pure sodium aluminate liquors [85]

652   confirmed the previously held belief that the UV absorbance of Bayer liquors is

653   entirely due to the presence of organic compounds.

654

655   ## 5.3.   IR Spectroscopy

656   Fourier transform infrared (FTIR) spectroscopy has been used by Wilson and co-

657   workers to characterise solid samples including bauxite, red mud, scale, precipitate,

658   organic matter, lignin and evaporated Bayer liquor extracts [2, 28, 86]. While not

659   able to identify specific compounds, FTIR spectroscopy was capable of distinguishing

660   the aromatic and aliphatic constituents, as well as C-O and C=O functional groups.

661   FTIR can also be used to quantify the total organic carbon (TOC) content, and a

662   number of other chemical and physical parameters, of Bayer liquor by correlating the

663   IR spectrum of the liquor with the spectra of known standards [87].

664

665   Hind et al. [88, 89] used FTIR spectroscopy to investigate the nature of the surfaces of

666   solids in contact with highly alkaline solutions.

667   ## 5.4.   NMR Spectroscopy

668   The use of NMR spectroscopy for the determination of organic compounds in Bayer

669   liquors was pioneered by Wilson and co-workers, who subsequently used it

670 extensively in investigations of liquors and solids associated with the Bayer process.

671 Wilson's first paper on this subject used ^{1}H NMR to investigate the composition of

672 humic substances from a number of sources, one of which was Bayer liquor [90]. The

673 NMR data clearly showed formate, acetate and succinate, which had previously been

674 identified [21], but also revealed the presence of smaller concentrations of propionate,

675 lactate, tartrate, o-phthalate and a number of other benzene carboxylic acids and

676 phenolic acids, which were attributed to the degradation of humic substances in the

677 bauxite, and possibly of starch which was added to the liquor as a flocculant [38].

678 The advent of effective water suppression techniques substantially improved the

679 sensitivity of the method in aqueous media such as Bayer liquor [91].

680

681 Ellis et al. [92] were able to quantitatively analyse glucose, formate, acetate, lactate,

682 glycolate and ethanol directly in simulated Bayer liquor using a 300 MHz instrument.

683 Beach et al. [84] used a 500 MHz instrument with a built-in pulse program for solvent

684 suppression by presaturation and SpinWorks software to quantitatively analyse

685 formate, mannitol, sorbitol, xylitol, gluconic acid, adonitol and/or dulcitol when

686 added to sodium hydroxide solutions and mannitol when added to diluted Bayer

687 liquor.

688

689 Machold et al. [64] used ^{1}H NMR operating at 300 MHz to assist in the

690 identification of compounds analysed by HPLC in studies of the degradation of

691 individual organic compounds in 6 M sodium hydroxide over extended times. The

692 compounds determined were formate, acetate, oxalate, succinate, lactate, malonate,

693 glutarate, adipate, pimelate, malate, tartrate, gluconate, benzoate, phthalate,

694 terephthalate, salicylate, 4-hydroxybenzoate and gallate.

695

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.

710

^{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.

719

720   ^{13}C NMR has also been used in a number of investigations related to Bayer liquor and

721   associated materials, particularly by Wilson et al. [25] , who have developed specific

722   methods tailored for the complex mixtures involved. Solution ^{13}C NMR has been used

723   to characterise Bayer liquor and solid state [13]C Cross Polarization Magic-Angle

724   Spinning NMR (^{13}C CP/MAS NMR) has been used to characterise Bayer-derived

725   solids and evaporated Bayer liquor extracts. This is illustrated by Wilson et al. [38] in

726   the determination of methyl derivatized extracts from aluminium hydroxide cake from

727   an alumina refinery. They were able to assign chemical shifts to alkyl, alcoholic,

728   aromatic, oxalate, and carboxylate functionalities, but were not able to identify

729   specific compounds.

730

731   Smith et al. [94] used ^{13}C NMR to investigate polyols in relation to their interactions

732   with aluminate ions in solution and their role in the inhibition of gibbsite

733   crystallization.

734

735   Baker et al. [95] and Wilson and co-workers [6, 25, 26, 28, 38, 86] used ^{13}C CP/MAS

736   NMR to examine solid material such as bauxite, red mud, scale, precipitated

737   aluminium hydroxide, organic matter, lignin and evaporated Bayer liquor extracts.

738   Although the instrument was capable of 200 MHz, best results were obtained at 50

739   MHz. It was not possible, even in Bayer liquor sequentially extracted with diethyl

740   ether, ethyl acetate, isopropyl alcohol and water, to identify individual compounds,

741   but the presence of different types of carbons were inferred. These included carbonyl,

742   aromatic and aliphatic carboxylic acids, salts and esters, aromatic and aliphatic carbon

743   with and without substituted electron-donating groups, including methyl, methylene

744 and methyne carbon, alkoxy including methoxy carbon, di-alkoxy, oxalate, formate

745 and acetate carbonyl and acetal carbon.

6. Thermal Analysis

6.1. Solution Oxidation and Combustion

748 The simplest form of thermal analysis is combustion to determine the total organic

749 carbon (TOC) content. Solution oxidation methods have been used for this, but the

750 early methods based on, for example, dichromate oxidation, were found to under-

751 estimate the more refractory compounds, and so have largely been replaced by

752 combustion techniques [6, 25, 26, 28, 38]. Nevertheless, improvements in solution

753 oxidation using a combination of persulphate and UV light resulted in the

754 development of instruments with much better recoveries [96, 97]. Determination of

755 TOC by solution oxidation or combustion usually relies on detection of evolved CO_2

756 with an infra-red (IR) detector. This method requires correction for, or simultaneous

757 determination of, the inorganic (carbonate) content [98], and catalysts are generally

758 used to facilitate quantitative combustion [43, 99]. Considerable progress has been

759 made in the design of automated instruments for this method [100].

6.2. Thermogravimetry and Calorimetry

761 Thermal analysis has been used to investigate the combustion behaviour of samples of

762 organics extracted from Bayer liquors and separated into molecular weight fractions

763 [25, 28]. This information was used to draw conclusions regarding the general nature

764 of the organic compounds in the various fractions. The loss of mass (9-18%,

765 depending on fraction) up to 200^oC was attributed to loss of surface and bound water

766 and volatile organics trapped in a macromolecular matrix. Further mass loss from 200

767 to 350°C was attributed to carboxylic acids and aliphatic biopolymers, and the

768 remainder of the humic matter was combusted by 500°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] .

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

791   Nevertheless, the technique has proved very useful in developing an understanding of

792   the overall chemistry of the materials analysed by enabling estimation of

793   aromatic/aliphatic ratios and allowing the proportions of alkyl, carboxylic acid,

794   carbonyl, phenoxy and nitrogen-containing groups to be determined [6].

795   **7. Multi-dimensional Methods**

796   The analysis of complex mixtures can often be simplified by the use of multi-

797   dimensional separation and determination methods, in which an initial separation by,

798   for example LC, is then followed by a secondary separation by the same or another

799   technique such as MS. The use of LC-MS-MS by Picard et al. [27] described in

800   Section 5.1, in which over 100 individual compounds were identified (although only

801   the 20 most significant are named), is an example of this. It has been pointed out that

802   to take full advantage of the improved separation offered by multidimensional

803   systems, the number of system dimensions should equal the number of definable

804   sample attributes [103].

805

806   Whelan et al. [61] developed a powerful multi-dimensional technique for the analysis

807   of Bayer extracts in which the fractions from solid-phase extraction were separated

808   into ninety 200 µL sub-fractions by GPC (see section 3.3) which were then analysed

809   by LC. Peaks from the LC output were then introduced into a triple quadrupole MS

810   via electrospray ionisation for identification of components. Product ion spectra were

811   then further resolved by a second stage of MS operating with collision-induced

812   fragmentation. This allowed the identification of a small proportion of the isolated

813   compounds, but most compounds were not identified. The analysis sequence is

814   illustrated in Figure 6.

815

Please place Figure 6 near here

817

818 This example provides an insight into the possibilities offered by this concept. A very

819 large amount of very high quality information can be generated by experiments of this

820 nature, requiring a great deal of expertise and data analysis for proper interpretation.

821 Nevertheless, further development of multi-dimensional methods, in particular LC-

822 MS-MS with electrospray ionization, offers the potential for a step-change

823 improvement in knowledge of the nature of organics in Bayer liquors. For example, it

824 should be possible to confirm or otherwise the presence of compounds predicted to

825 form from the initial degradation of natural organic matter in the digestion process

826 [61].

827

8. Summary of Analytical Methods

829   A summary of the compounds that have been detected in Bayer liquors, and the

830   methods that have been used to detect them, is provided in the Appendix. The table is

831   in two parts: Table A1 lists the compounds that have been reported more than once in

832   the literature, and which are on that basis designated to be "generally present" in

833   Bayer liquors [1]; Table A2 is a list of compounds that have been reported only once

834   in the literature, giving a list that is indicative of some of the additional compounds

835   that may be present in any given Bayer liquor.

9. Summary and Future Directions

837   The application of increasingly sophisticated analytical techniques to the

838   determination of organics in Bayer process liquors has led to significant advances in

839   the knowledge of the nature, reactions and impacts of organics in the Bayer process

840   over the past 40 years. This knowledge has enabled significant advances in

841   processing technology which have benefited the industry in terms of costs of

842   production, product quality and environmental impacts. GC and IC methods for the

843   determination of the main low molecular weight anions, which account for the

844   majority of the organic carbon in Bayer liquors, are well established as routine

845   methods. CZE has emerged as a potentially more rapid, cost-effective and flexible

846   method, and promises to replace the established methods and to enable the inclusion

847   of a larger number of analytes.

848   The main challenge remains in the determination of the high molecular weight

849   compounds, where despite considerable efforts to date there remains a significant

850   knowledge gap. Techniques which are now available or are in development, in

851 particular multi-dimensional methods based on LC-MS-MS with "soft" ionization,

852 offer the prospect of rapid progress in the generation of knowledge about the high

853 molecular weight compounds. With the aid of these techniques it should be possible

854 to "unlock the genome" of Bayer liquor organics which could lead to a quantum

855 improvement in the capability of technologists to interpret and manipulate the organic

856 chemistry of Bayer liquors.

10. Acknowledgements

857

858

865 **TABLES and APPENDIX**

866

867

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

875

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

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

878

Compound	MW	CAS No.	Analytical Method					Citations
			GC	IC	CZE	HP LC	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]

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Table A2: Additional Compounds Discovered in Individual Bayer Liquors

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

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]

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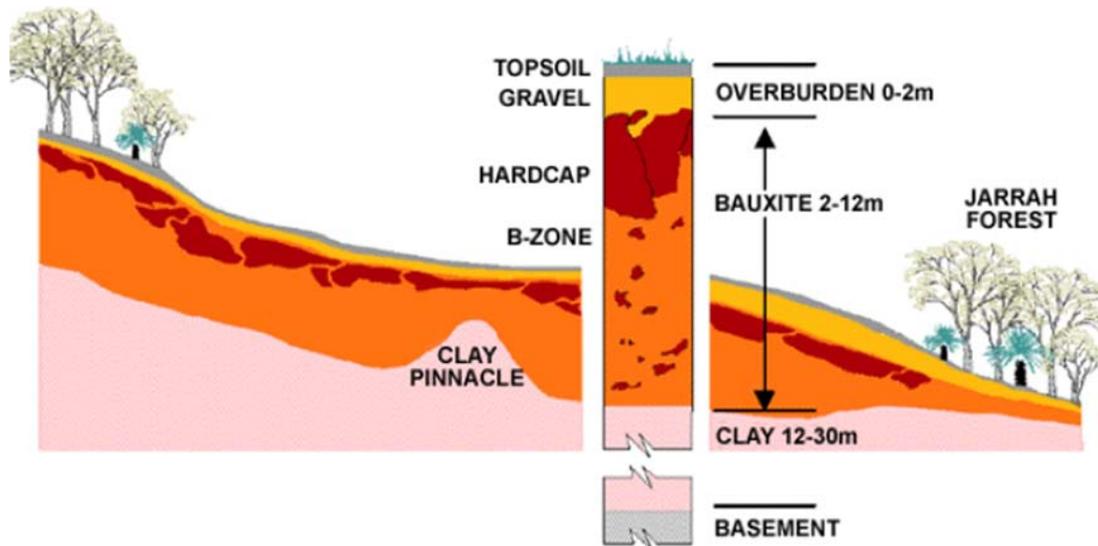893
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903 **Figure 2: Schematic representation of a typical lateritic bauxite profile (diagram reproduced with the permission of BHP Billiton**
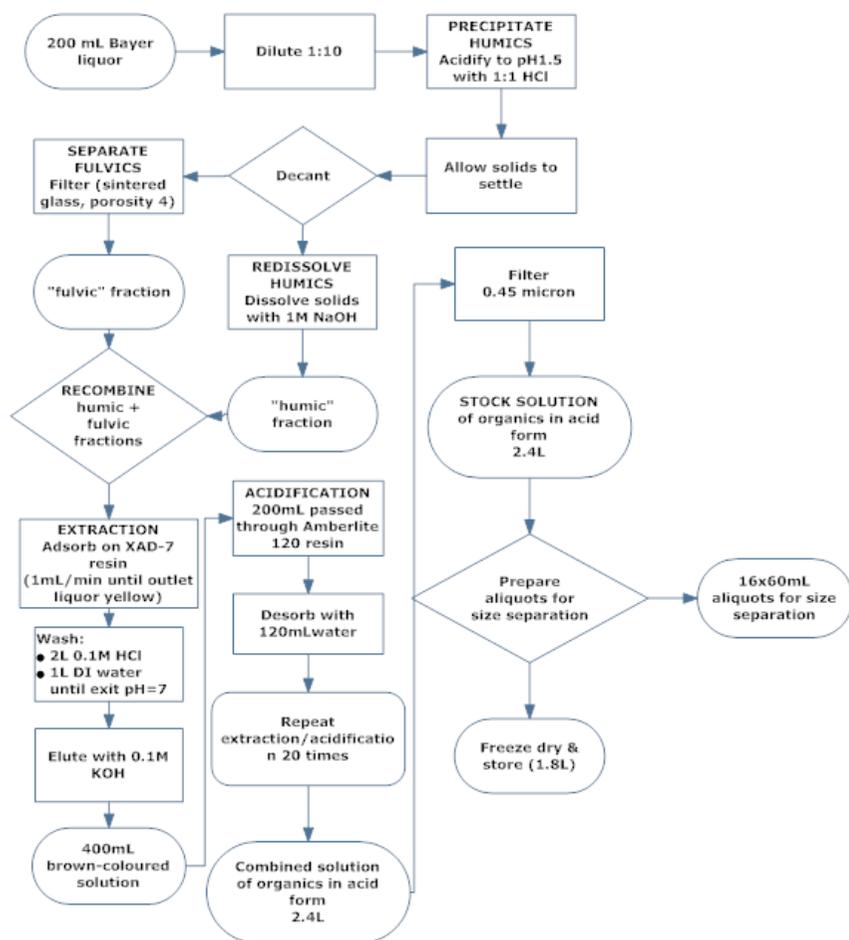
904 **Worsley Alumina) [1].**
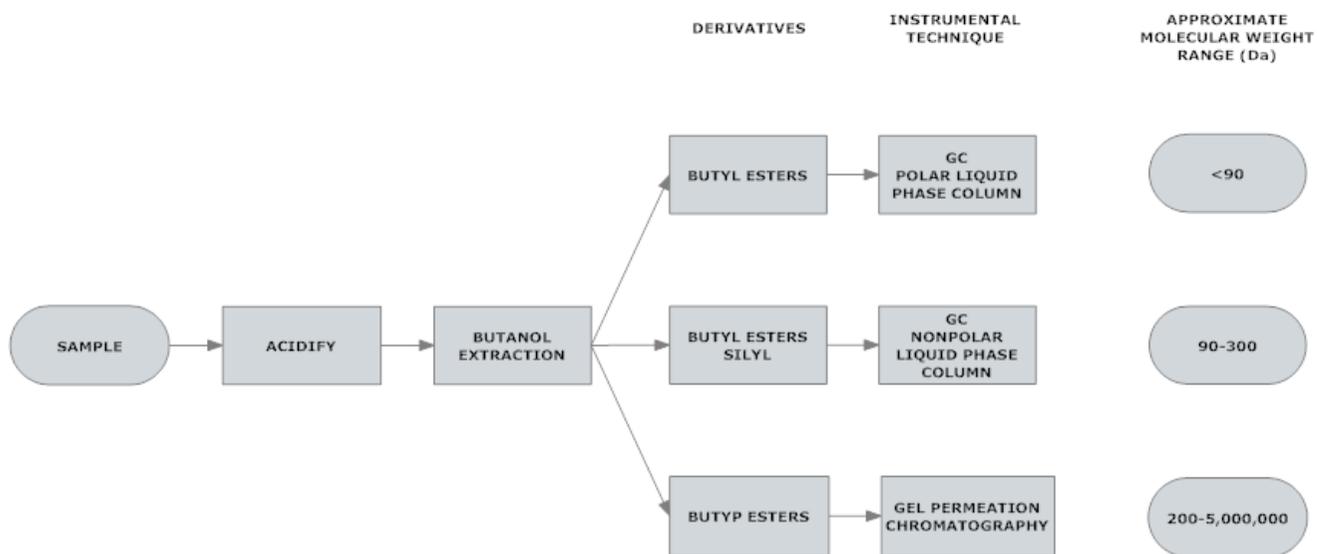
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Figure 2: Sample preparation scheme for the separation of high molecular weight organics from Bayer liquors, derived from the

descriptions given by Wilson et al. [25].

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918   **Figure 3: Example of a determination scheme using GC-MS and GPC(SEC), adapted from Guthrie et al. [22].**
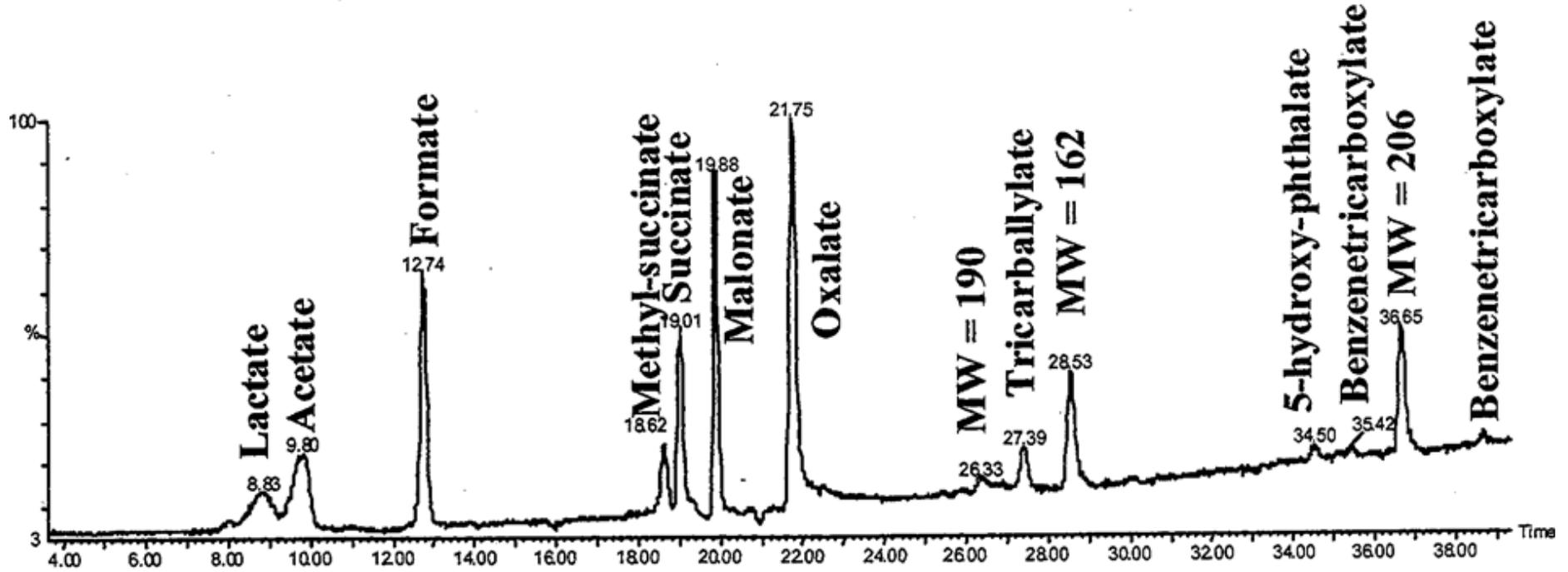
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927 **Figure 4: LC trace for medium MW (90-300 Da) compounds in a Bayer liquor from Guthrie et al.. The numbered peaks were**

928 **identified by MS [22].**
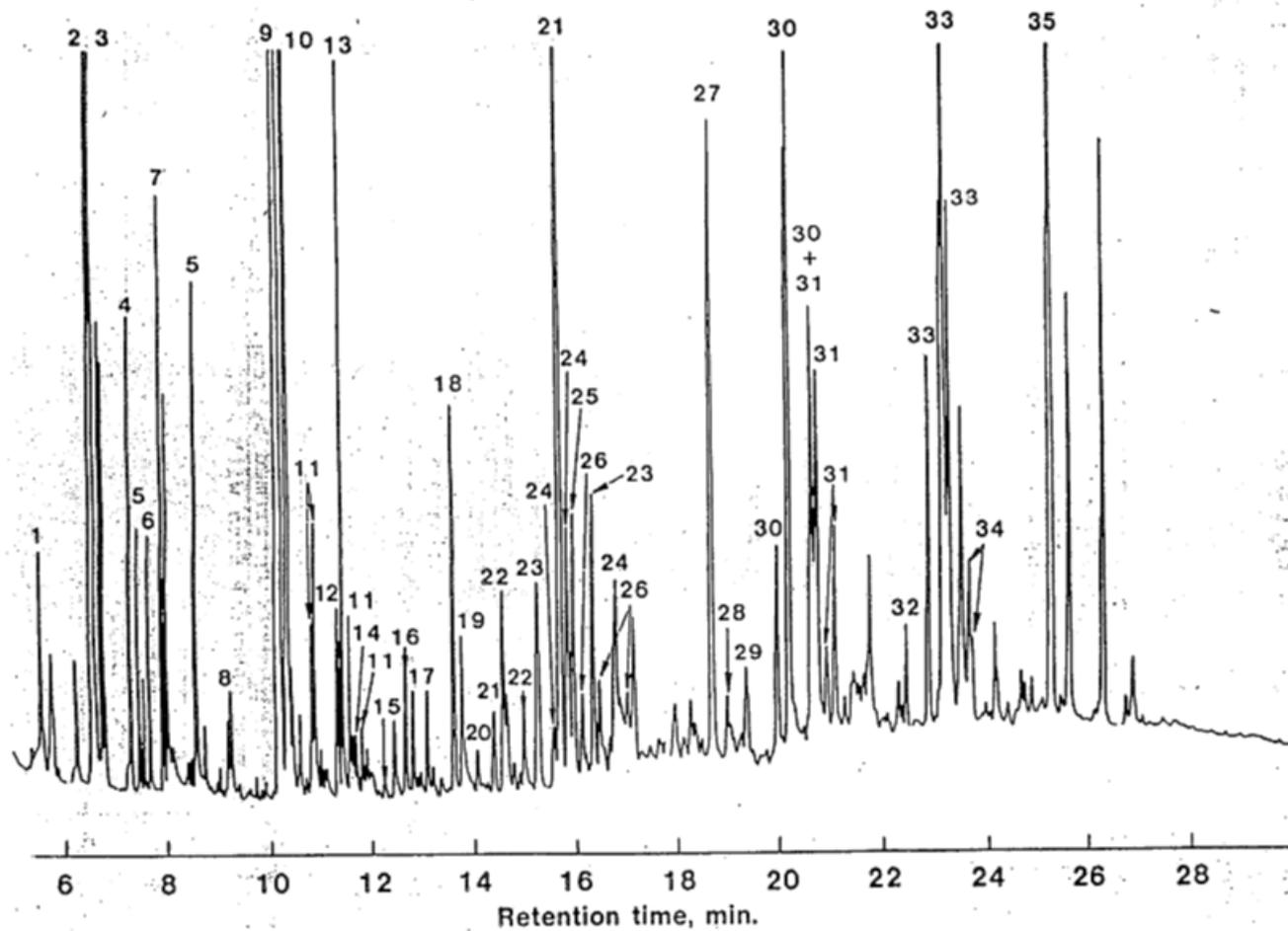
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930 **Figure 5: IC trace for low MW compounds in a Bayer liquor from Picard et al. showing assignments by MS [27].**
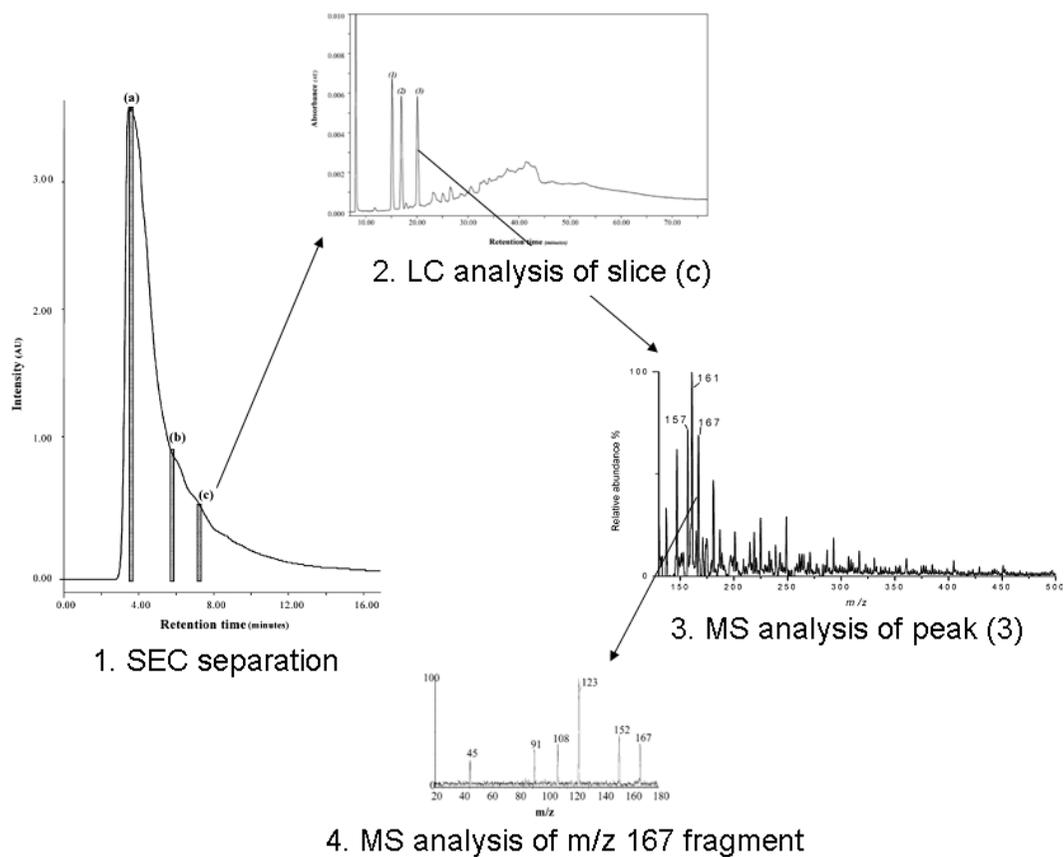
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937 **Figure 6: Multidimensional determination sequence adapted from Whelan et al. [61] showing GPC-UV fractionation followed by LC-**

938 **MS operated in full scan mode and LC-MS/MS operated in product ion mode.**

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2. LC analysis of slice (c)

1. SEC separation

3. MS analysis of peak (3)

4. MS analysis of m/z 167 fragment

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