



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

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## 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.

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## 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 0.02–0.50% (w/w, carbon basis) [1]. Bauxite digestion is usually carried out at temperatures in the range 135–245 °C at sodium hydroxide concentrations in the region of 3.5–5 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 90–500 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 0.3–0.4% 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 Fig. 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].

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

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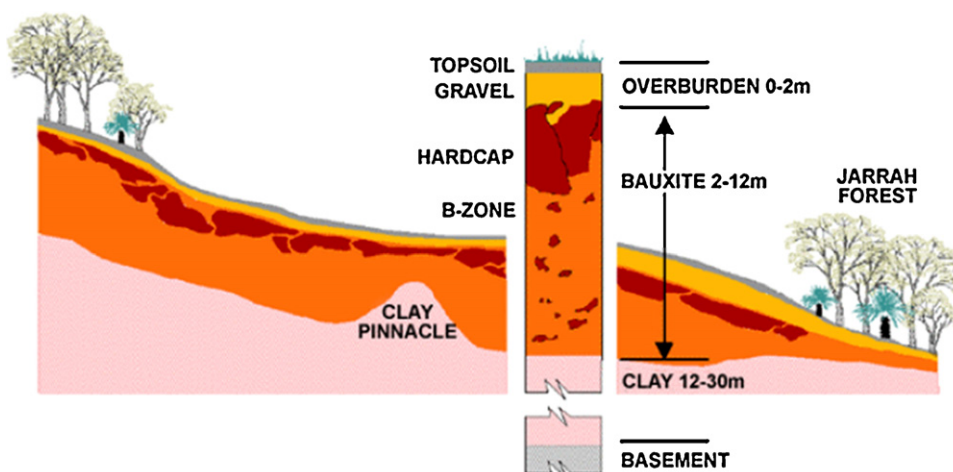


Fig. 1. Schematic representation of a typical lateritic bauxite profile from Western Australia (diagram reproduced with the permission of BHP Billiton Worsley Alumina) [1].

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 Appendix A.

### 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 zone elec-

trophoresis (CZE). 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  $\text{CO}_2$  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 then passed through a cation exchange resin to ensure that all of the organic compounds were in their acid forms to facilitate derivatization, neutralized with NaOH, and evaporated to dryness prior to being butylated for determination by gas chromatography (GC) with a flame ionization detector.

Guthrie et al. [22] used a simpler procedure in which concentrated HCl was added directly to a liquor sample in an ice bath until the precipitated aluminium hydroxide was redissolved. The resulting solution was butylated and analysed for low molecular weight compounds by GC. To analyse intermediate molecular weight compounds, these authors evaporated the butanol extracts to dryness and reacted the residues with “Tri-Sil” (dimethyl-(trimethylsilylamino)Si) to produce the silyl derivatives for GC analysis. Others [21,23] have used methylation for this purpose.

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

The preparation for determination of the high molecular weight (“humic”) fractions of Bayer liquor generally involves first precipitating the “humic” material by acidification to a pH of 2 or less, as is the practice in the analysis of soils [24]. Lever’s approach was to extract the precipitated organics with n-butanol and neutralize the extract with NaOH, followed by water-washing and ultrafiltration to produce a salt-free aqueous extract which could be separated into nominal molecular weight fractions by membrane filtration [21]. Alternatively, Guthrie et al. [22] kept the initial steps of the sample preparation the same as described in Section 3.1 for GC analysis, and used tetrahydrofuran (THF) as the solvent for the butyl esters.

Wilson et al. [25] cautioned against the precipitation of aluminium hydroxide in the 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 precip-

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