Identification of Organic Acids in Bayer Liquors by GC–MS: A Comparison Using Butylation and Methylation

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Abstract

Two well known derivatization methods, butylation and methylation, are compared by gas chromatography (GC)–mass spectrometry (MS) to identify organic acids in Bayer liquors. These two derivatization methods should be combined together for the determination of the carboxylic acids. Twenty-four organic acids are identified by GC–MS and 13 organic acids are firstly found in Bayer liquors. The retention times and the carbon number of these seven *n*-dicarboxylic acids (C_4–C_{10}) are fit into the linear relationship in Microsoft Excel.

Introduction

The Bayer process can be summarized as the digestion of bauxite with caustic liquor and the subsequent precipitation of hydrated alumina (1). Most bauxite contains organic matter in various amounts. The major source of organic matter that is introduced into the Bayer liquor is in the form of humic substances. During digestion, the organic matter is dissolved, degraded, and oxidized with the result that the liquors darken and notable amounts of oxalate and carbonate are formed.

Because of the acidic nature of the humic substances, more than 50% of the organic matter contained in the bauxite is extracted into the liquor. The principal degradation products are sodium oxalate and sodium carbonate. Depending upon the digestion conditions, typically 5–10% of the organic carbon is converted to sodium oxalate. Australian bauxites have conversion rates of two or three times higher (2,3).

In the Bayer process, the caustic liquor is recycled, and because of this, the organic matter builds up to an equilibrium level, typically to 10–30 g/L of organic carbon content, determined by the outputs and the inputs (4). Beside the bauxite input, some organic matters come from other sources, such as process water, grease, red mud flocculants, or antifoams. The outputs are through the adsorption on the red mud, or degradation to smaller molecular weight organics and carbonate, or adsorption on the product gibbsite.

Sodium oxalate has been shown to be very harmful with regard to alumina productivity and size (5,6). When sodium oxalate, if not controlled, builds up to a certain level of supersaturation, it precipitates out as fine needles in the hydrate precipitator tank. This co-precipitation affects the alumina product quality and the productivity in many ways.

The process is cyclical and, therefore, concomitant impurities present in the raw materials or reagents may accumulate unless periodically removed (7,8). From an analytical chemistry perspective, Bayer liquor is a most challenging matrix, consisting of alumina, sodium hydroxide, sodium carbonate, sodium chloride, sodium sulphate, sodium oxalate as well as unknown organic acid anions, all at varying concentrations (9–10). The rapid and reliable determination of organic compounds in Bayer liquor is of significant industrial importance because its presence has been implicated in the formation of small particle size hydrated alumina, which cannot efficiently be claimed and therefore must be recycled (11).

A variety of techniques have been utilized for the determination of sodium oxalate in Bayer liquors, including titrimetry (12), ion chromatography (13–17), capillary electrophoresis (17–21), flow injection analysis (22), high-performance liquid chromatograph (HPLC) (23–29), and gas chromatography (GC) (30–32). However, there are only a few reports focusing on the identification and determination of other organic acids in Bayer liquors. Baker et al. determined 13 organic acids by GC with derivatization (30). Whelan et al. (25) separated humics found in Bayer liquors on a Nova-Pak C18 column at a flow rate of 1.5 mL/min using tetrabutylammonium hydrogen sulfate as the ion-pairing reagent, and a gradient was used. But the quantitative determination was not performed because the separation was not excellent. Oxalate was the main organic component in Bayer liquor. In many factories, the oxalate was determined by titration with a standard potassium permanganate solution. This method often resulted in low precision and accuracy. Furthermore, it took a long time and required much reagents. The analysis of organic acids in Bayer liquors

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with HPLC systems is a difficult task because of the high ionic strength and pH. The aim of this work was to identify organic compounds and to optimize a derivatization method prior to GC–MS analysis.

Experimental

Chemicals

Analytical grade methanol, *n*-butanol, ethyl acetate, hexane, and petroleum ether were purchased from Hanbon Company Limited (Huaiyin, Jiangsu, China). Analytical grade HCl, H_2SO_4, and $NaHCO_3$ were used for the acidification of the process liquors and neutralization of the derivatives. The Milli-Q water was purified by passage through a Compact Milli-RO and Milli-Q water system from Millipore (Milford, MA). Working standard solutions were prepared daily by dilution with Milli-Q water. Potassium dihydrogenphosphate, sodium hydrogen carbonate, and hydrochloric acid (HCl) were analytical-reagent grade and supplied by Shanghai (Shanghai, China). The samples were filtered through cellulose membrane filters (0.45 µm, Whatman, Clifton, NJ). The eluention was filtered with membrane filters (0.45 µm, AFO-0504, Phenomenex, Torrance, CA).

Apparatus

GC–MS analysis was performed on an Agilent system consisting of a model 6890 GC, a model 5973 mass selective detector, and an Agilent ChemStation data system (Palo Alto, CA). The GC column was an HP-5ms fused silica capillary (30 m × 0.25 mm, 0.25 µm). A PHS-3C pH meter (Shanghai) was also used.

Sample preparation

Extraction

A 10-mL amount of Bayer liquor was dissolved in 20 mL of Milli-Q water. The pH was adjusted to approximately 7.50 using 8M HCl, and the mixture was stirred for 15 min using a magnetic stirrer. The pH was then adjusted to approximately 2.00 using 0.1M HCl. The mixture was transferred to a 100-mL volumetric flask with Milli-Q water, filled up to the mark, and stirred. A 10-mL volume of this solution was filtered through a 0.45-µm cellulose acetate membrane. The solid-phase extraction (SPE) procedure involved an ion-exchange cartridge (100 × 4.6 mm I.D., particle size 40 µm, Hanbon Science & Technology, Huaiyin, Jiangsu, China), which was activated with 10 mL of sodium hydroxide solution 0.1M (percolation rate 3.0 mL /min). A 10-mL volume of Bayer liquor solution was passed through at a flow-rate of 0.5 mL/min. The cartridge was washed with 10 mL of water (3 mL/min) and organic acids were eluted with 20 mL of HCl 0.1M (0.5 mL/min). This solution was shaken with 20 mL *n*-butanol for 10 min.

Butylation

After settling, 1 mL H_2SO_4 (1:1, v/v) was added to 10-mL

Table I. GC–MS Results of Butylation Derivatives

No.	t_R* (min)	Compounds	Formula	Match (%)	Relative content (%)
1	3.377	4-Heptanone	$C_7H_{14}O$	92	1.245
2	3.525	*n*-Butyl ether	$C_8H_{18}O$	96	89.167
3	3.634	2,4-Dimethyl-3-pentanol	$C_7H_{16}O$	91	0.424
4	3.925	Propanoic acid, butyl ester	$C_7H_{14}O_2$	93	0.302
5	4.268	3-Methyl-4-heptanone	$C_8H_{16}O$	95	1.732
6	4.697	2-Methyl-propanoic acid, butyl ester	$C_8H_{16}O_2$	90	0.108
7	5.463	Butanoic acid, butyl ester	$C_8H_{16}O_2$	95	3.234
8	6.291	2-Methyl-butanoic acid, butyl ester	$C_9H_{18}O_2$	90	0.185
9	6.371	3-Methyl-butanoic acid, butyl ester	$C_9H_{18}O_2$	89	0.247
10	7.189	Pentanoic acid, butyl ester	$C_9H_{18}O_2$	80	0.164
11	8.798	Hexanoic acid, butyl ester	$C_{10}H_{20}O_2$	80	0.176
12	9.778	1,1-Dibutoxybutane	$C_{12}H_{26}O_2$	93	1.756
13	11.292	Oxalic acid, dibutyl ester	$C_{10}H_{18}O_4$	90	0.299
14	11.527	Benzoic acid, butyl ester	$C_{11}H_{14}O_2$	81	0.355
15	13.852	Succinic, dibutyl ester	$C_{12}H_{22}O_4$	88	0.287
16	15.019	Glutaric acid, dibutyl ester	$C_{13}H_{24}O_4$	80	0.081
17	18.276	1,2-Benzenedicarboxylic, dibutyl ester	$C_{16}H_{22}O_4$	95	0.221

* t_R = Retention time.

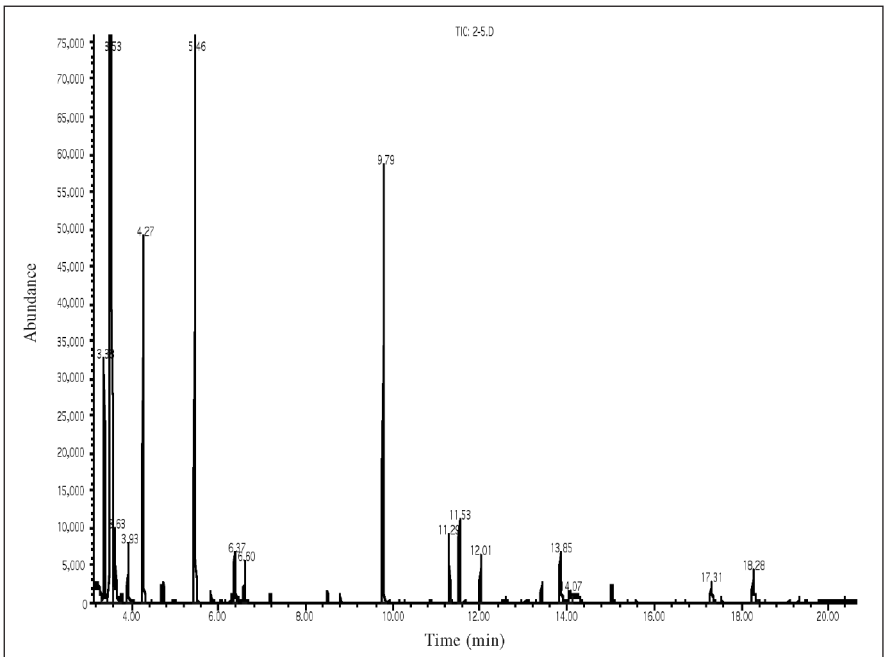

Figure 1. Total ion chromatogram of butylation derivatives.

n-butanol phase, and esterification of the acids was accomplished in a water bath with the temperature of 80°C for a day. After cooling to room temperature, a 2 mL derivative was removed and neutralized with $NaHCO_3$, and then it was shaken with 10 mL hexane. The organic acids present were identified by injection of 1 µL of the hexane fraction into the GC–MS.

Methylation

Another 10-mL *n*-butanol phase was evaporated to dryness by a rotary-evaporator. Then ethyl acetate was used to wash out the acids inside the flask. The ethyl acetate fraction was filtrated and evaporated, and 10 mL methanol and 1 mL H_2SO_4 (1:1, v/v) were added. The vessel was sealed, and esterification of the acids was accomplished in a water bath with the temperature of 55°C for a day. After cooling to room temperature, a 2 mL derivative was removed and neutralized with $NaHCO_3$, then was shaken with 10 mL hexane. The organic acids present were identified by an injection of 1 µL of the hexane fraction into the GC–MS.

Table II. GC–MS Results of Butylation Derivatives

No.	t_R* (min)	Compounds	Formula	Match (%)	Relative content (%)
1	5.440	Succinic acid, dimethyl ester	$C_6H_{10}O_4$	85	1.178
2	6.148	Benzoic acid, methyl ester	$C_8H_8O_2$	90	1.912
3	6.588	Glutaric acid, dimethyl ester	$C_7H_{12}O_4$	81	1.118
4	7.303	2,5-Dimethyl-benzaldehyde	$C_9H_{10}O$	76	4.662
5	7.486	Hexanedioic acid, dimethyl ester	$C_8H_{14}O_4$	88	0.495
6	8.246	Heptanedioic acid, dimethyl ester	$C_9H_{16}O_4$	84	0.369
7	8.600	3-Methyl-hexanedioic acid, dimethyl ester	$C_9H_{16}O_4$	80	0.997
8	8.835	3-Hydroxy-benzoic acid, methyl ester	$C_8H_8O_3$	72	0.417
9	8.949	Octanedioic acid, dimethyl ester	$C_{10}H_{18}O_4$	78	0.506
10	9.075	1,2-Benzenedicarboxylic, dimethyl ester	$C_{10}H_{10}O_4$	89	1.556
11	9.372	1,3-Benzenedicarboxylic acid, dimethyl ester	$C_{10}H_{10}O_4$	85	1.043
12	9.595	Nonanedioic acid, dimethyl ester	$C_{11}H_{20}O_4$	72	0.861
13	10.201	Decanedioic acid, dimethyl ester	$C_{12}H_{22}O_4$	74	0.459
14	10.629	Tetradecanoic acid, methyl ester	$C_{15}H_{30}O_2$	81	1.145
15	11.812	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	85	5.471
16	12.915	9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	66	0.835
17	13.098	Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	77	2.037

* The compounds are listed in order of retention time.

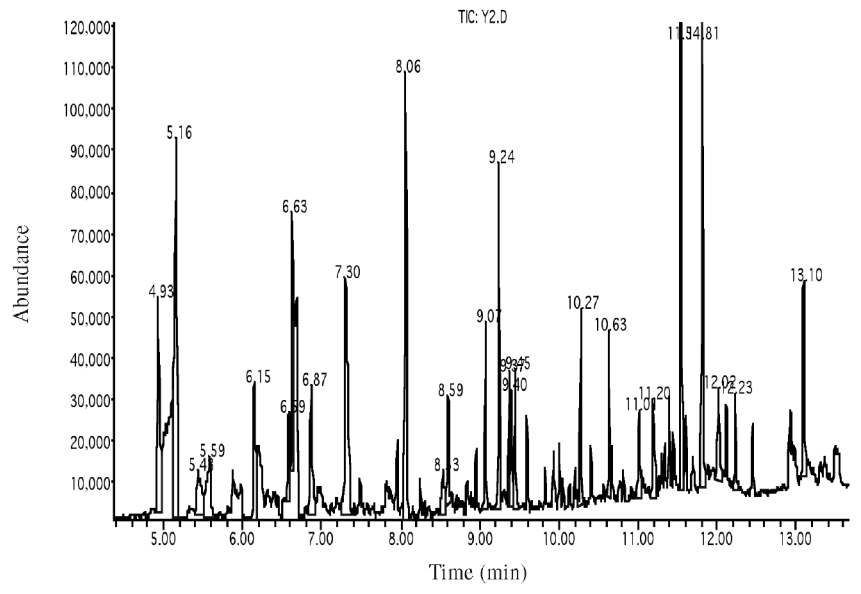

Figure 2. Total ion chromatogram of methylation derivatives.

GC–MS

GC–MS analysis was performed on an Agilent system consisting of a model 6890 GC, a model 5973 mass selective detector, and an Agilent ChemStation data system. The oven temperature was programmed at 60°C for 5 min, and then increased to 250°C at a rate of 5°C /min. Injector and detector temperatures were 250°C and 265°C, respectively. The carrier gas, helium, was adjusted to a linear velocity of 30 cm/s. The hexane extract (1.0 µL) was injected into the GC–MS (without any further dilution) using the split mode with a split ratio of 1:60. The ionization energy was 70 eV with a scan time of 5 scans/s and mass range of 40–540 amu. The percentages of compounds were calculated by the area normalization method without considering response factors. The components were identified by comparison of their mass spectra with those of a computer library (2000 NIST database). Data obtained were conformed to compare data published in the literature.

Results and Discussion

Butylation

From Figure 1 and Table I, 12 organic acids were identified by butylation, namely propanoic, 2-methyl-propanoic, butanoic, 2-methyl-butanoic, 3-methyl-butanoic, pentanoic, hexanoic, benzoic, oxalic, succinic, glutaric, and 1,2-benzenedicarboxylic. Among the 12 organic acids, only four were dicarboxylic acids. The butylation derivatives analyzed showed a high level of *n*-butyl ether (accounting for 89.167%), a volatile compound, which previously was never found in Bayer liquor. *n*-Butyl ether was formed during butyl esterification by condensing 2 equiv. of *n*-butanol. If *n*-butyl ether was removed, propanoic, pentanoic, hexanoic, benzoic, and butanoic acids were major constituents identified after butyl esterification (accounting for 52.32%).

Methylation

The methylation does not need, a priori, any purification step before injection into the GC, but in order to increase the partition coefficient during hexane extraction of the esters, it is necessary to add $NaHCO_3$ to neutralize the derivatives. From Figure 2 and Table II, 16 organic acids were identified, namely: succinic, benzoic, glutaric, hexanedioic, heptanedioic, 3-methyl-hexanedioic, octanedioic, 1,2-benzenedicarboxylic, 1,3-benzenedicarboxylic, nonanedioic, decanedioic, tetradecanoic, hexadecanoic, 9,12-octadecadienoic, octadecanoic, and 3-hydroxy-benzoic acids. However, among the 16 organic acids, 10 were dicarboxylic acids.

GC–MS analyses

Analytical methods to identify and quantitatively measure these compounds in water involve their extractions into a suitable solvent followed by chromatographic analysis. The extraction methods mostly include liquid–liquid extractions (LLE) or SPE. The compounds in the extract are determined by GC using an electron capture detector, HPLC, GC–MS, or capillary electrophoresis. Derivatization of these acids, usually to their ester derivatives, is often required to improve the chromatographic separation and obtain better sensitivity.

The percentages of compounds were calculated by the area normalization method, without considering response factors. The components were identified by comparison of their MS with those of a computer library (2000 NIST database). Several literature reports have previously identified organic acids in Bayer liquors (13–32), and these results were helpful in identifying organic acids in Bayer liquors. Ten dicarboxylic acids were found in the methylation derivatives. The retention times (y) and the carbon number (x) of these seven n-dicarboxylic acids were fit to the linear relationship in Microsoft Excel. Calibration plots were expressed as regression lines: $y = 2.6321 + 0.7771x$ ($R^2 = 0.9991$). From this point, the HP-5ms fused silica capillary column was excellent for the separation n-dicarboxylic acid esters. In addition, tentative identification of the components was accurate.

Table III. Comparison of Different Derivatization Methods

	Butylation	Methylation
Acid	Relative content (%)	Relative content (%)
Mono	84.03 (8)	57.93 (6)
Dicarboxylic	15.97 (4)	42.07 (10)

Comparison of different derivatization methods

Two derivatization procedures were compared in order to find the best result for the identification of organic acids in Bayer liquor (Table III). In butylation, a low level of dicaboxylic

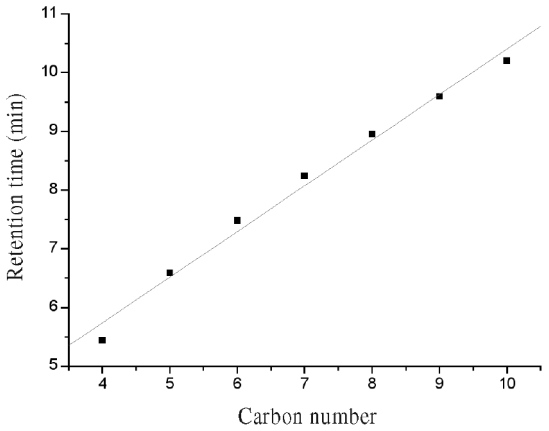

Figure 3. Calibration of retention times in GC to the carbon number of n-dicarboxylic esters.

Table IV. Concentrations of Organic Acids Reported in Bayer Liquors

	Concentration reported in the literature (g/L)						
Acid	Jackson et al. (17)	Haddad et al. (19)	Harakuwe et al. (20)	Barnett et al. (22)	Xiao et al. (28)	Baker et al. (30)	Lever et al. (33)
Formic		1.4–1.5				2.57–2.83	2.3
Acetic		4.7–5.0			0.2–23.7	2.92–3.00	4.4
Propanoic						0.06	
Butanoic						0.02–0.04	
Pentanoic						–*	
Lactic						0.27–0.35	
Oxalic	1.71.78–4.61	0.8–0.9	3.37	1.7–6.7	0.1–1.79		2.5
Malonic						0.75–0.84	
Succinic					1.4–7.8	1.1	1.4
Glutaric					0.1–8.0	0.1	0.9
Methylsuccinic						0.14	
Benzoic						0.01	

*Reported, but not quantitated.

acid was found. The butylation is easier to perform, but it is possible to induce interfering by-products such as *n*-butyl ether. The derivatives are also not easily identified by GC–MS according to their mass spectra, which are available in the software library. Moreover, this methodology does not require any evaporation step and, hence, does not induce any compound losses. The methylation is not easily carried out because of the evaporation step. During the process of evaporation, some low molecular weight organic acids in the Bayer liquor were lost. Therefore, less low molecular weight organic acids were found among the methylation derivatives. Among the butylation derivatives, only monoacids with a low-boiling point up to hexanoic acid were found; however, there are only high-boiling monoacids, such as hexadecanoic and octadecanoic acid, in methylation derivatives. In conclusion, these two derivatization methods should be combined together for the analysis of carboxylic acids.

Among all the esterifying agents that were used in this study to convert the acids in the solvent extract to their ester derivatives, methanol showed a distinct advantage over *n*-butanol. Under the experimental conditions, the yield of butyl esters was much smaller, especially for the dicaboxylic acids, than the yield of methyl esters obtained from methanol. In addition, similar peaks on the chromatogram were also detected in the butylation derivatives, the major products being *n*-butyl ether (accounting for 89.167% of total content). On the other hand, butyl ester formed much smaller amounts.

Comparison with literature data

Some literature reports have identified and quantitated organic acids previously in Bayer liquors (Table IV). Baker et al. (30) determined 13 organic acids by GC with butanol derivatization. Formic, acetic, propanoic, butanoic, lactic, 3-methylbutanoic, pentanoic, benzoic, malonic, succinic, methylsuccinic, glutaric, and 1,2-benzenedicarboxylic acids were identified and determined by GC. A previous report focused more on determining oxalic acid, which was abundant in Bayer liquors. However, only a low level of oxalic acid in Bayer liquors (Table I) was found. In addition, from the results of GC–MS, 24 organic acids were identified, namely oxalic, succinic, glutaric, hexanedioic, heptanedioic, 3-methyl-hexanedioic, octanedioic, 1,2-benzenedicarboxylic, 1,3-benzenedicarboxylic, nonanedioic, decanedioic, propanoic, 2-methyl-propanoic, butanoic, 2-methyl-butanoic, 3-methyl-butanoic, pentanoic, hexanoic, benzoic, tetradecanoic, hexadecanoic, 9,12-octadecadienoic, hexanedioic, octadecanoic, and 3-hydroxy-benzoic acids. Among these organic acids, heptanedioic, 3-methyl-hexanedioic, octanedioic, 2-methyl-butanoic, 1,2-benzenedicarboxylic, 1,3-benzenedicarboxylic, nonanedioic, decanedioic, hexanedioic, hexadecanoic, 9,12-octadecadienoic, octadecanoic, and tetradecanoic acids were firstly identified in Bayer liquors.

Conclusion

In the present investigation, the authors have focused on a simple approach to modify a known method to routinely analyze organic acid in Bayer liquors by GC–MS. Two derivatization methods were investigated in the study. In this method, the Bayer liquors were first extracted with SPE and then acidified. The organic acids were partitioned from water into the butanol phase. For methylation, the butanol phase was evaporated to dryness by a rotary-evaporator. Methanol was then added to the extract with one drop of 1:1 H_2SO_4. The organic acids were converted into their methyl esters. This method avoided the use of any costly or hazardous derivatizing agent and seems to be simple and straightforward in approach and practical application.

Because different methods of derivatization yield different efficiencies, it is important to combine different methods together to identify the unknown compounds. In this work, two derivatization procedures were used. Twenty-four organic acids were identified by GC–MS and 13 organic acids were firstly found in Bayer liquors. It merits future studies to determine the contents of organic acid in Bayer liquors from different factory and to study how to remove these compounds.

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