Essential Readings in Light Metals: Alumina and Bauxite.
Edited by Don Donaldson and Benny E. Raahauge.

CHARACTERIZATION OF ORGANICS IN BAYER LIQUOR

J. D. Guthrie, P. J. The, and W. D. Imbrogno

Aluminum Company of America
Alcoa Technical Center
Alcoa Center, Pennsylvania 15069

Routine analytical methods have been developed for characterizing Bayer liquor. The methods consist of instrumental techniques, including gas chromatography for the low and intermediate molecular weight compounds and gel permeation chromatography for the high molecular weight material. Gas chromatography/mass spectrometry was used to identify several compounds in addition to those previously reported in the literature. Two spent liquor samples, together with corresponding lake water samples, were characterized to demonstrate applicability of the methods. Results of the analyses provided information for better understanding the nature of Bayer liquor.

Introduction

Organic matter found in bauxite is a composite of many substances described by such terms as humic, lignin, cellulose and protein. In the Bayer process, a portion of this organic matter is extracted into the liquor during digestion of the bauxite, and is decomposed to form soluble sodium organic compounds. To promote red mud settling, synthetic or natural flocculant, such as copolymers of acrylamide and sodium acrylate or starch is added to the liquor stream. Other materials which contribute small amounts to the organic content of liquor include anti-foaming agents and lubricants. With recycling of the liquor, the concentration of organics and their degradation products increases until an equilibrium concentration is reached.

It has been shown that the presence of a significant amount of organic material in Bayer liquor causes numerous process problems and lowers liquor productivity. Difficulties caused by organic impurities include lower alumina yield, generation of excessive fine aluminum trihydroxide particles, a higher impurities content in the alumina, colored liquor and aluminum trihydroxide, lower red mud settling rate, loss of caustic due to the formation of sodium organic compounds, increased liquor density, viscosity, boiling point and foaming of the liquor.

Numerous studies concerning the identification of organics in Bayer liquor have been reported (1-5). In general, the analytical methods employed were relatively long, thus limiting the number of samples which could be studied in detail.

The objective of the work reported here was to develop analytical techniques which were simple enough to allow characterization of organics in liquor on a routine basis. These techniques would facilitate studies related to control of organics in the Bayer process stream.

Methods incorporating three instrumental techniques were developed to characterize the organics. Gas chromatography (GC) under different sets of conditions was used to determine the low and intermediate molecular weight compounds. The high molecular weight materials were characterized by gel permeation chromatography (GPC). During development of the analytical methods, a gas chromatography/mass spectrometry (GC/MS) study was undertaken to identify compounds in the liquor in addition to those already reported in the literature.

To demonstrate the applicability of these methods, two spent Bayer liquor samples were characterized, along with the corresponding lake water for each sample. These samples were chosen because the organics in them were found to be different, even though the Bayer refining plants are quite similar.

Experimental Methods

Low Molecular Weight Compounds

To prepare a spent Bayer liquor sample for analysis, 1 ml was added to a 24 ml screw cap vial containing ~15mg of nonanoic acid (internal standard), and the mixture was cooled in an ice bath. To this, 1.5 ml of concentrated hydrochloric acid was carefully added with swirling until all of the alumina redissolved. Two milliliters of 1-butanol was added and the

mixture was vigorously shaken for 2 minutes. The sample was heated for 1 hour at approximately 70°C in a water bath. After cooling, the butanol layer was removed with a disposable Pasteur pipet, without removing any of the aqueous phase, and 1 µl of the solvent containing the butyl esters was injected into the GC.

To prepare a lake water sample for analysis, 20 ml was placed in a Petri dish and allowed to evaporate in a hood. One milliliter of 12% sodium hydroxide was used to rinse the air dried material into a 24 ml vial containing ~15mg of nonanoic acid as an internal standard. The remainder of the sample preparation procedure was the same as described for low molecular weight compounds in a liquor sample.

Samples were run on a Hewlett-Packard 5880 GC equipped with a flame ionization detector. The column was 1/8 in. O.D. x 10 ft. stainless steel packed with 10% SP-1000 on 100/120 mesh Chromosorb WAW (Supelco, Inc.). Chromatographic conditions were the following:

Injection port temp.	250°C
Detector temp.	350°C
Initial oven temp.	100°C
Time at initial temp.	5 min.
Program rate	10°/min.
Final oven temp.	250°C
Time at final temp.	5 min.
Carrier flow	30 ml/min.
Carrier	Helium
Attenuation	X512
Chart speed	0.5 cm/min.

A typical chromatogram of the low molecular weight compounds is shown in Figure 1. The compounds were quantified using an internal standard technique.

Organic acids were named as carboxylic acids, even though the compounds actually analyzed were butyl esters, silyl derivatives or a mixture of both, depending on the particular technique used. However, these compounds exist as sodium salts in the liquor.

Intermediate Molecular Weight Compounds

The liquor sample preparation procedure outlined for low molecular weight compounds was followed down to removal of the butanol layer from the 24 ml vial. At this point, the butanol layer was placed in a 30 ml beaker and allowed to evaporate overnight at room temperature in a hood. One milliliter of TRI-SIL silyl derivatizing agent (Pierce Chemical Company) was added to the dried sample. The sample and TRI-SIL were mixed, transferred to a 4 ml screw cap vial and centrifuged. One microliter of derivatized sample was injected into the GC.

To prepare a lake water sample for analysis, 20 ml was placed in a Petri dish and allowed to evaporate in a hood. One milliliter of 12% sodium hydroxide was used to rinse the dried material into a 24 ml vial. The remainder of the sample preparation procedure was the same as described for intermediate molecular weight compounds in a liquor sample.

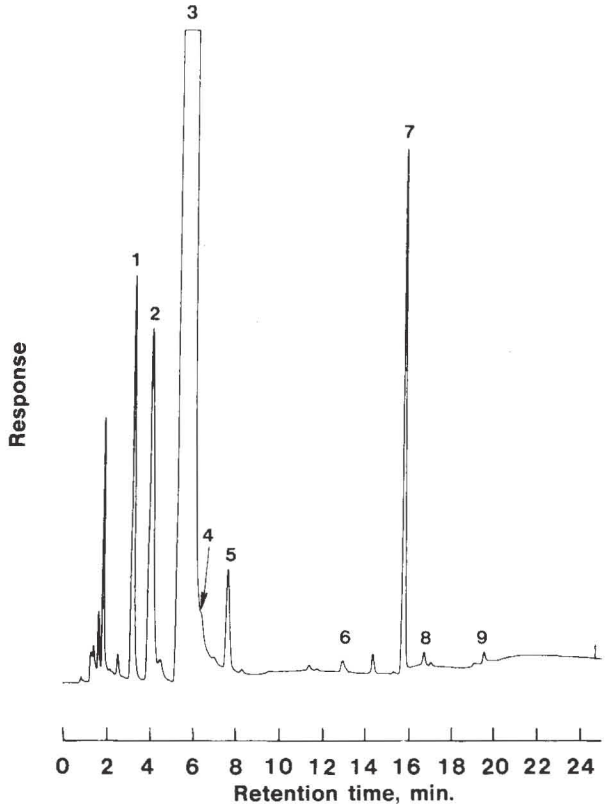

Figure 1 Gas Chromatogram of Low Molecular Weight Compounds in Bayer Liquor. Peak 1 = Formic, 2 = Acetic, 3 = Butanol, 4 = Propionic, 5 = Butyric, 6 = Lactic, 7 = Nonanoic (IS), 8 = Oxalic, 9 = Succinic.

Samples were run on a Hewlett-Packard 5880 GC equipped with a capillary column inlet and a flame ionization detector. The column was a 0.25 mm I.D. x 30 m DB-5 fused silica capillary (J&W Scientific, Inc.). Chromatographic conditions were the following:

Injection port temp.	300°C
Detector temp.	350°C
Initial oven temp.	50°C
Final oven temp.	325°C
Program rate	10°/min.
Time at final temp.	5 min.
Injection type	Splitless
Carrier flow	30 cm/sec.
Carrier	Helium
Attenuation	X32
Chart speed	1 cm/min.

A typical capillary GC chromatogram is shown in Figure 2.

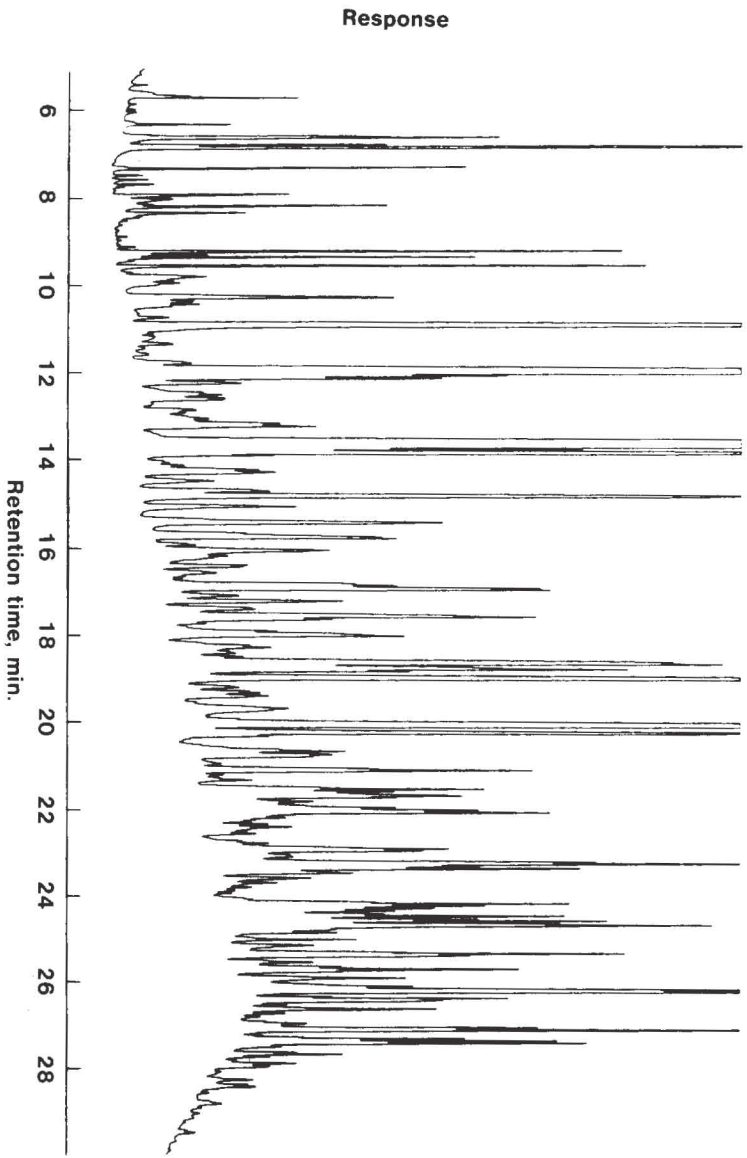

Figure 2 Gas Chromatogram (Capillary Column) of Intermediate Molecular Weight Compounds in Bayer Liquor

The same liquor sample shown in Figure 2 was run on a packed column for comparison (see Figure 3). The column used was 1/8 in. O.D. x 6 ft. stainless steel packed with 3% SP-2250 on 100/120 mesh Supelcoport (Supelco, Inc.). A 2 µl injection was used with the following conditions:

Injection port temp.	300°C
Detector temp.	350°C
Initial oven temp.	50°C
Final oven temp.	325°C
Program rate	10°/min.
Time at final temp.	5 min.
Carrier flow rate	20 ml/min.
Carrier	Helium
Attenuation	X64
Chart speed	1 cm/min.

Individual compounds can be quantified using an internal standard technique. However, when comparing two or more samples, visual inspection of the chromatograms for comparison of peak areas or peak heights may provide sufficient information and be more practical than attempting to quantify a large number of peaks.

High Molecular Weight Compounds

Sample preparation for GPC analysis was the same as described for GC analysis for intermediate molecular weight compounds down to the addition of TRI-SIL. In place of the TRI-SIL, 1 ml of uninhibited tetrahydrofuran (THF) was added, the solution was transferred to a 4 ml screw cap vial and centrifuged. Ten microliters of solvent containing butyl esters was injected into the GPC. The samples were run at two wavelengths, 254 nm and 400 nm. For the 254 nm run, the sample was diluted 1:20.

The lake waters were prepared by placing 20 ml of sample in a Petri dish and allowing them to evaporate in a hood. One milliliter of 12% sodium hydroxide was used to rinse the dried sample into a 24 ml vial. The remainder of the GPC sample preparation procedure was the same as described for the liquor sample above.

The GPC analysis was performed on a Hewlett-Packard 1080B liquid chromatograph equipped with a variable wavelength detector. The columns were 7.8 mm I.D. x 30 cm, 500A and 7.8 mm I.D. x 30 cm, 100A µ Styragel (Waters Associates) in series. Chromatographic conditions were as follows:

Eluent	Tetrahydrofuran (uninhibited)
Flow rate	1 ml/min.
Detector	400 nm and 254 nm
Chart speed	0.5 cm/min.
Attenuation	X128 for 254 nm run
	X64 for 400 nm run

Chromatograms resulting from runs at 254 nm and 400 nm are shown in Figures 4 and 5.

A calibration standard for the humic material determined at 400 nm was prepared in the following way. Five hundred milliliters of Bayer liquor was mixed with 500 ml of water and 30 g of powdered activated carbon (Nuchar, Kodak) for 16 hours at 50°C. The mixture was then filtered

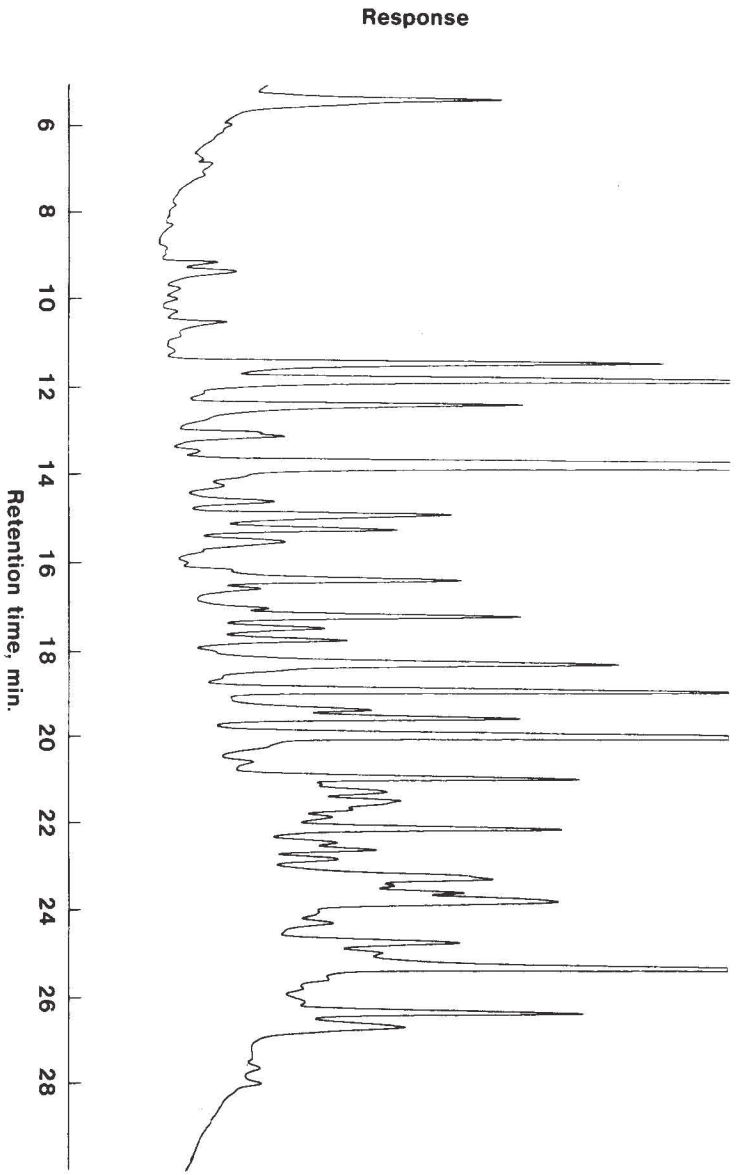

Figure 3 Gas Chromatogram (Packed Column) of Intermediate Molecular Weight Compounds in Bayer Liquor

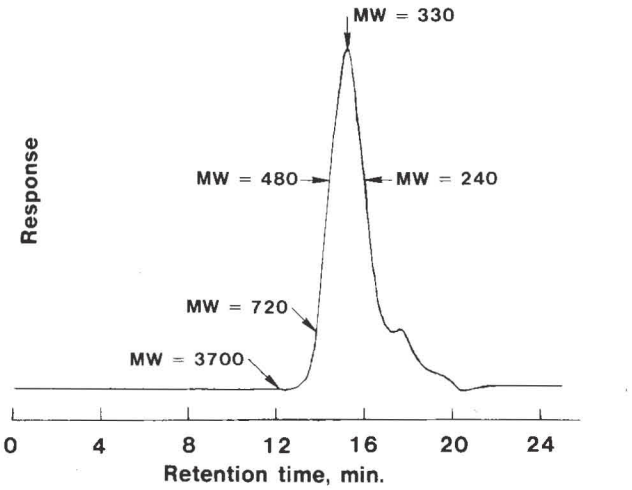

Figure 4 GPC Chromatogram of Organics in Bayer Liquor, Detector Set at 254 nm

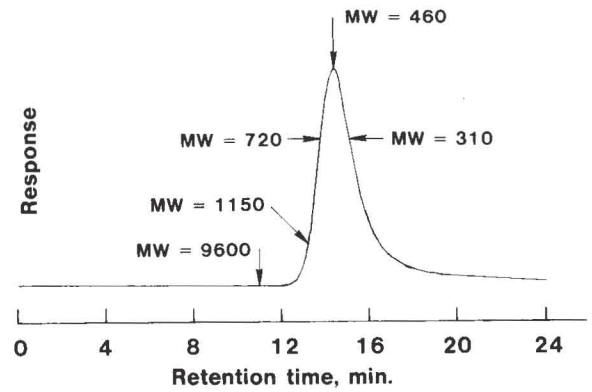

Figure 5 GPC Chromatogram of Organics in Bayer Liquor, Detector Set at 400 nm

through number 1 paper and washed with 100 ml of cold water. The organics were desorbed by mixing the carbon with 100 ml of 50% sodium hydroxide for 4 hours at 80°C. The carbon was filtered and washed with 500 ml of hot water, and the filtrate was acidified with concentrated hydrochloric acid to pH 1. The solution was allowed to stand overnight and the humics were filtered on a 1.2 micron membrane filter.

The organic carbon content of the dried humic material was 45%. A sample was prepared for GC (intermediate molecular weight compounds) and GPC analysis as described above. The gel permeation chromatogram showed a peak similar in molecular weight range to the peak obtained from liquor samples. The GC analysis showed a relatively clean chromatogram, indicating the sample separated by this technique was essentially high molecular weight material.

A molecular weight versus retention time calibration curve was prepared by running polystyrene standards with molecular weights of 9000, 4000, 2000, and 800. A fifth standard, di-n-butyl succinate (MW = 230), was also run. The calibration curve is plotted in Figure 6.

It should be pointed out that the standards used for the molecular weight calibration curve are structurally different from the humic type substances being analyzed. Therefore, the molecular weights reported for the samples should be used only to compare samples and should not be taken as absolute.

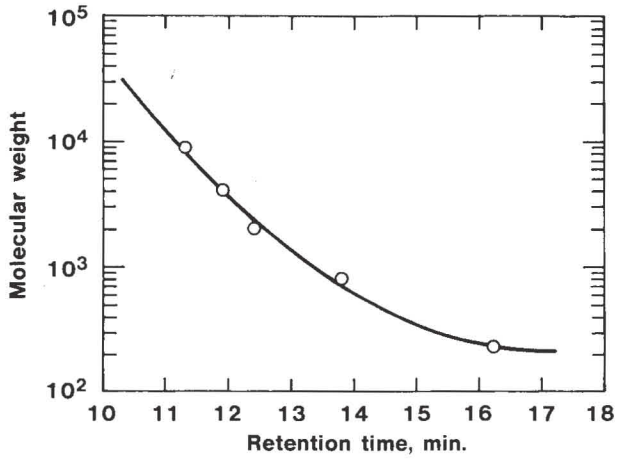

Figure 6 Gel Permeation Chromatography Calibration Curve

Gas Chromatography/Mass Spectrometry

A sample for GC/MS analysis was prepared by placing 1 ml of liquor in a 24 ml screw cap vial and carefully adding 1.5 ml of concentrated hydrochloric acid with swirling to redissolve the alumina. Two milliliters of 1-butanol was added to the acidified sample, followed by shaking. The lower aqueous phase was removed and 5% sodium hydroxide was added dropwise with shaking until the color transferred from the butanol back to the aqueous phase. This aqueous phase was separated and acidified to a pH <2 with concentrated hydrochloric acid and the water was allowed to evaporate overnight at room temperature. One milliliter of TRI-SIL was added to the dried sample, followed by centrifuging.

The sample was run on a Hewlett-Packard 5985 GC/MS, and the resulting chromatogram identifying the compounds by number is shown in Figure 7. Table I lists the compounds identified. The GC conditions were the same as those described for the intermediate molecular weight compounds using a capillary column. The mass spectrometer was equipped with an electron impact source set at 70 electron volts.

Results

Spent Bayer liquor and lake water samples from two low temperature digestion plants (A and B) were analyzed by the techniques described in the experimental methods section. The bauxite used by the plants was mined from different sites of the same deposit. Table II lists typical compositions for these four samples.

TABLE II

Compositions of Samples from Plants A and B

	Plant A		Plant B	
	Liquor	Lake Water	Liquor	Lake Water
Al_2O_3 (g/L)	72.0	4.8	70.7	3.7
Total Caustic (g/L Na_2CO_3)	192.9	8.0	205.6	4.4
Total Alkali (g/L Na_2CO_3)	241.7	14.5	248.0	10.0
Total Organic Carbon (g/L)	17.1	1.3	17.9	0.8
NaF (g/L)	3.3	0.3	2.4	0.2
NaCl (g/L)	13.5	1.0	10.3	0.7
Na_2SO_4 (g/L)	6.3	0.6	5.3	0.5

The gas chromatograms for the low molecular weight compounds were similar to the chromatogram in Figure 1. The comparison of formic and acetic acids are listed in Table III.

Gas chromatograms representing the intermediate molecular weight compounds in the four plant samples are shown in Figures 8 through 11. Selected peaks in samples A and B were compared by calculating the concentration of a component in B relative to the same component in A (peak areas in sample A were assigned a concentration of 100%). The results are listed in Table IV.

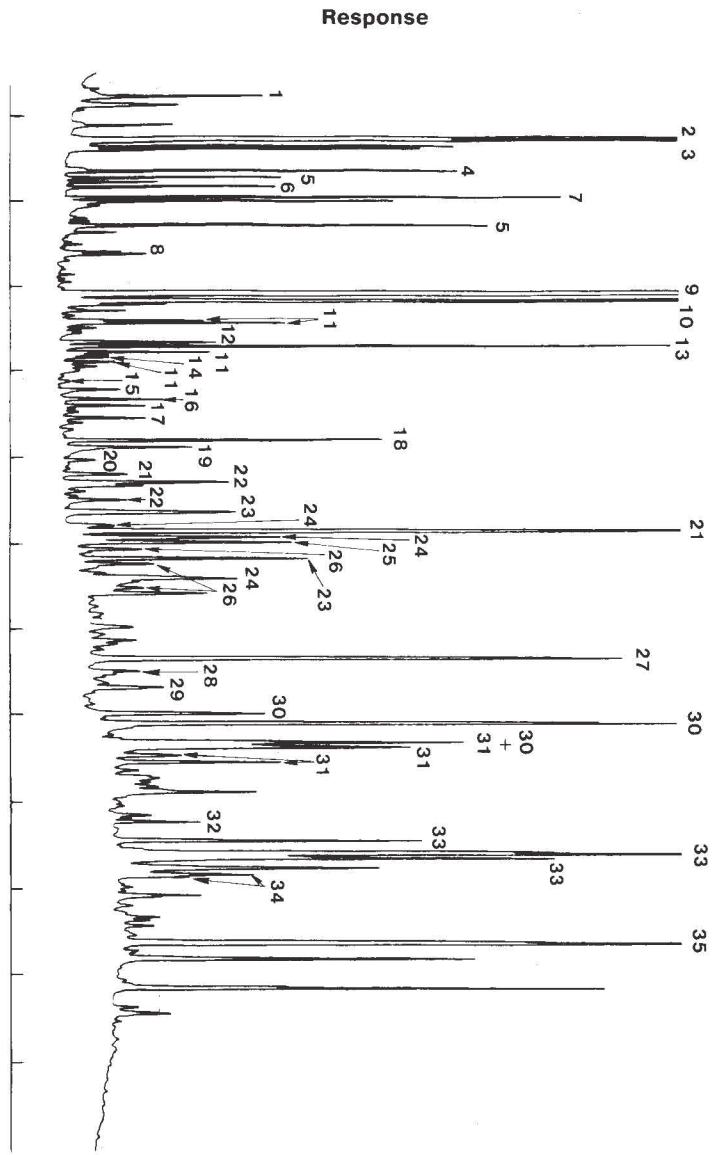

Figure 7 GC/MS Chromatogram Identifying Compounds in Bayer Liquor

Table I

Compounds Identified by GC/MS

1. Hydroxypropanoic (lactic)*
2. Ethanedioic (oxalic)*
3. Ethanolamine
4. Butanolamine
5. Hydroxybutanoic
6. Hydroxypropanoic
7. Propanedioic (malonic)*
8. Benzenecarboxylic (benzoic)
9. Butanedioic (succinic)*
10. Methylbutanedioic (methyl succinic)
11. Dimethylbutanedioic (dimethyl succinic)
12. Methylbutenedioic
13. Pentanedioic (glutaric)*
14. Dimethylpentanedioic (dimethyl glutaric)
15. Hydroxypropanedioic (hydroxy malonic)
16. Hydroxybutanedioic (hydroxy succinic, malic)
17. Hexanedioic (adipic)
18. Hydroxybenzoic (salicylic)
19. Hydroxypentanedioic (hydroxy glutaric)
20. Heptanedioic (pimelic)
21. Propanetricarboxylic (tricarballylic)*
22. Ethanetricarboxylic
23. Benzenedicarboxylic
24. Butanetricarboxylic
25. Propenetricarboxylic
26. Methylbenzenedicarboxylic
27. Hydroxybenzenedicarboxylic
28. Hexadecanoic (palmitic)
29. Butanetetracarboxylic
30. Benzenetricarboxylic (trimersic/trimellitic/hemimellitic)
31. Methylbenzenetricarboxylic
32. Hydroxydiphenylethanoic (benzilic)
33. Benzenetetracarboxylic (pyromellitic/prehnitic/mellophanic)
34. Methylbenzenetetracarboxylic
35. Benzenepentacarboxylic

*Indicates which compounds were confirmed by comparing GC retention time and mass spectral data with a known compound.

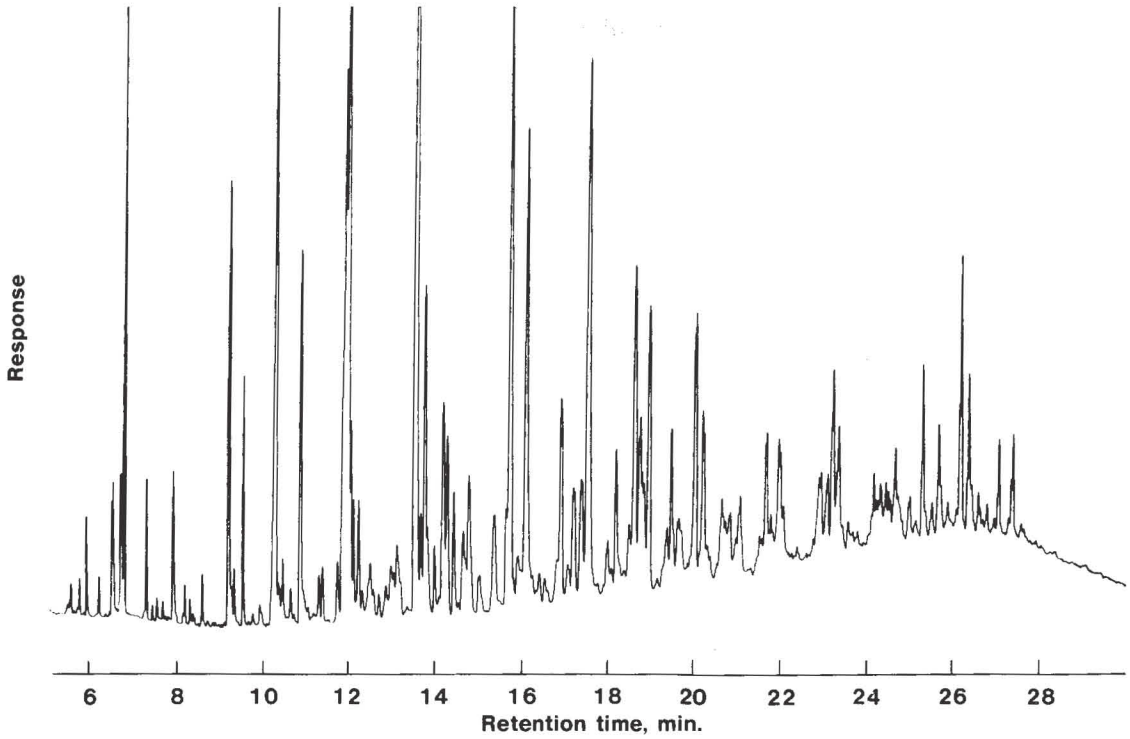

Figure 9 Intermediate Molecular Weight Compounds from Liquor B

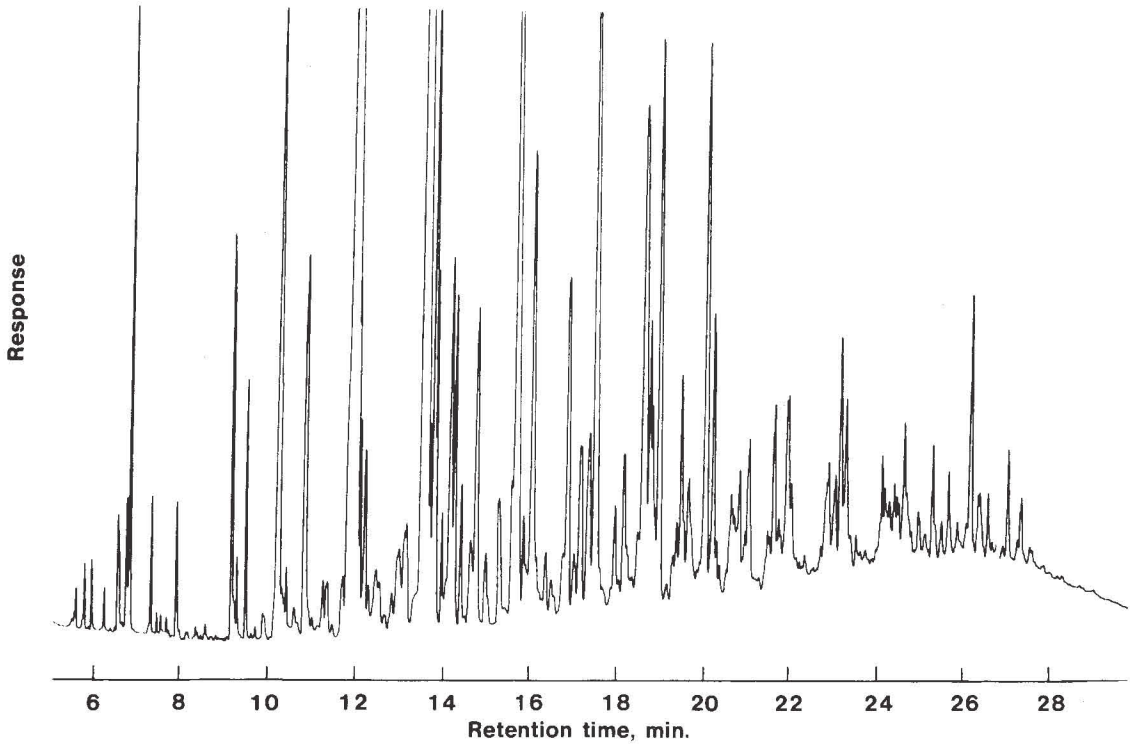

Figure 8 Intermediate Molecular Weight Compounds from Liquor A

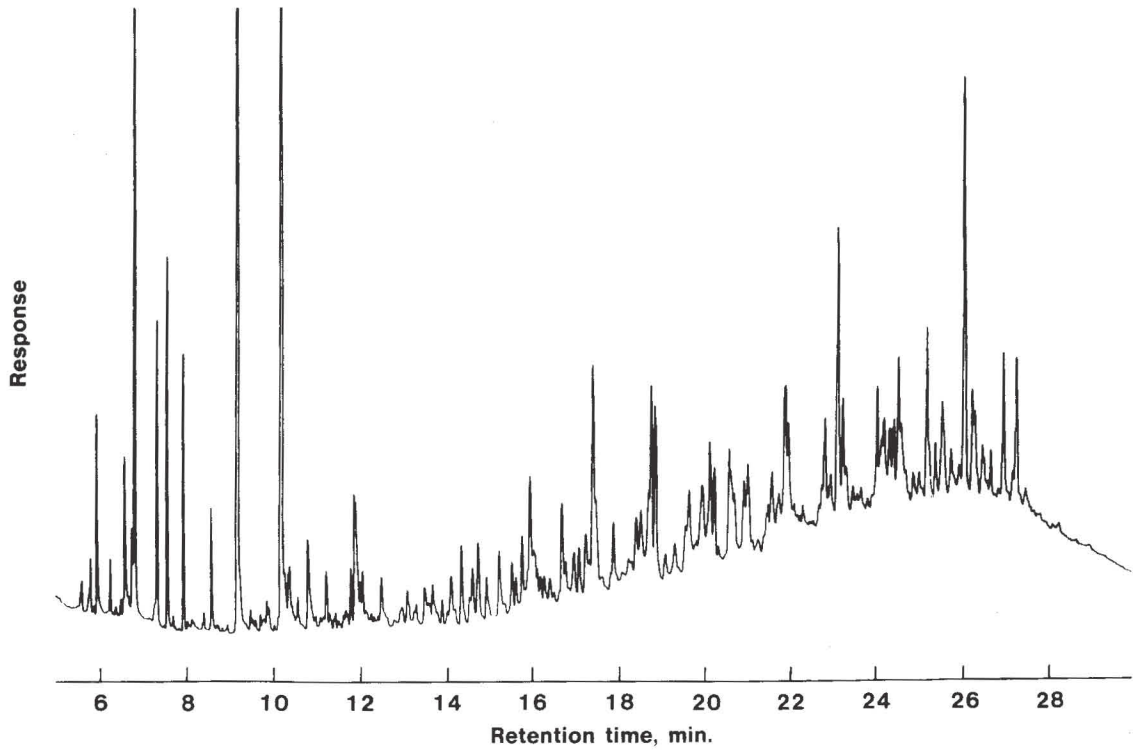

Figure 11 Intermediate Molecular Weight Compounds from Lake Water B

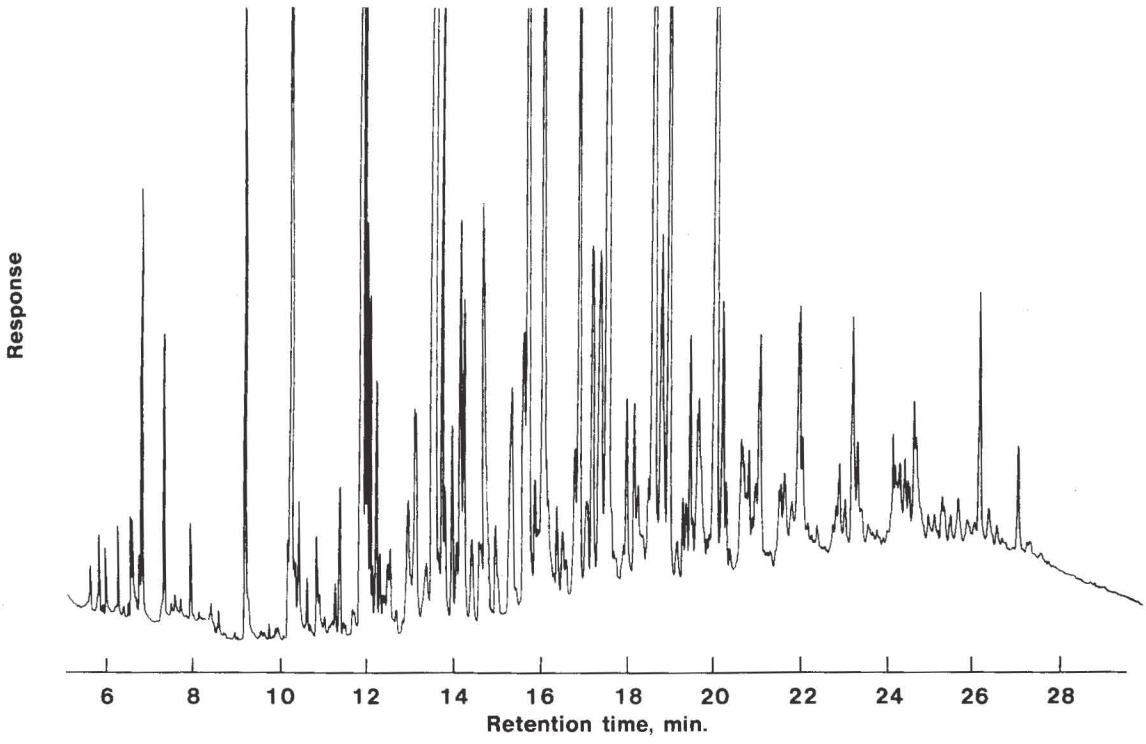

Figure 10 Intermediate Molecular Weight Compounds from Lake Water A

TABLE III

Comparison of Low Molecular Weight Compounds in Plant Samples

Sample	Formic (g/L)	Acetic (g/L)
Liquor A	5.9	11.0
Liquor B	3.4	6.1
Lake Water A	0.2	1.1
Lake Water B	None Detected	0.1

TABLE IV

Comparison of Intermediate Molecular Weight Compounds in Plant Samples

Sample	Oxalic	Succinic	Propane Tricarboxylic	Benzene Tetracarboxylic
Liquor A	100%	100%	100%	100%
Liquor B	80	32	41	54
Lake Water A	100	100	100	100
Lake Water B	70	1	17	79

The GPC peaks of the high molecular weight compounds resulting from the analysis of samples A and B were similar in shape to those in Figures 3 and 4. Table V lists the concentration of humic material, along with the molecular weights at the peak maxima for the 400 nm and 254 nm runs. An appropriate standard was not available for the peak at 254 nm, since this peak includes all compounds which absorb UV light at this wavelength. However, a column has been included in Table V showing the concentration of material in B absorbing at 254 nm relative to A.

TABLE V

Comparison of High Molecular Weight Material in Plant Samples

Sample	400 nm (Humic)	Molec. wt. at peak max.	254 nm	Molec. wt. at peak max.
Liquor A	3.1 g/L	604	100%	396
Liquor B	6.3	631	134	404
Lake Water A	0.06	571	100	394
Lake Water B	0.10	665	109	410

Discussion

Analytical Methods

The complexity of the mixture of organic material in Bayer liquor dictates the use of a combination of instrumental techniques to obtain a complete picture of the organics present. Figure 12 summarizes the sample preparation procedure, instrumental method and the approximate molecular weight range covered by each technique.

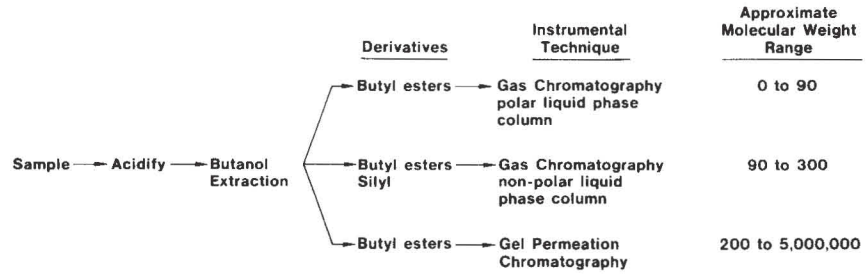

Figure 12 Analysis Scheme for Characterizing Organics in Liquor

Extraction of acidified Bayer liquor with 1-butanol served the dual purpose of separating the organics from the inorganics in the sample and esterifying the carboxylic acids as shown in reaction (1), making the compounds easier to analyze by gas chromatography.

$$RCOOH + R'OH \xrightarrow[\Delta]{H^+} RCOOR' + H_2O \qquad (1)$$

However, for the intermediate molecular weight compounds, a second derivatizing step was needed to convert the remaining polar groups (OH, SH and NH) into non-polar functionalities, again to make the chromatography easier. This was accomplished by preparing silyl derivatives as shown in reaction (2).

$$ROH + R'_3SiX \longrightarrow ROSiR'_3 + HX \qquad (2)$$

Thus, the GC chromatograms obtained by this sample preparation technique are mixtures of butylated and silylated compounds. Compounds which are only partially esterfied, and would not normally chromatograph, are also silylated, making the chromatograms (e.g. Figure 2) appear more complex

than is really the case. The chromatogram in Figure 8, which consists of only silyl derivatives of the compounds, represents a more realistic picture of the complexity of the intermediate molecular weight compounds.

Although capillary GC is more difficult than packed column GC, comparison of Figures 2 and 3 shows the additional effort is beneficial in the case of the intermediate molecular weight compounds. Several peaks on the packed column were found to be more than one compound through the additional resolution provided by the capillary column.

The high molecular weight organic material present in Bayer liquor suggests the application of gel permeation chromatography as a means of characterizing this portion of the organics. Initially, porous silica size exclusion columns were used which were compatible with an aqueous system. However, several problems developed, including short column life and difficulty with reproducibility. The second approach to this problem was to employ a sample preparation technique similar to the one developed for the gas chromatographic samples. This method allowed the use of μ Styragel (styrene divinylbenzene copolymer) columns with the sample dissolved in solvent. In addition, the butanol extraction preparation technique removed inorganics from the sample, resulting in a cleaner sample for introduction into the GPC instrument. The esterification step also eliminated the problem of adsorption of the carboxylic acids on the column packing.

The identification of organic compounds by GC/MS is often facilitated by the preparation of silyl derivatives. From the mass spectra of these derivatives, the molecular weight of the compounds can usually be determined (6). To simplify the GC/MS identification, the butyl esters, resulting from the butanol extraction, were hydrolyzed back to the acids before preparing the silyl derivatives. The compounds were identified using a combination of GC retention time, molecular weight and mass spectral library searches. The compounds in Table I marked with an asterisk were confirmed by comparison of GC and MS data with reference compounds. The mass spectra of isomers is usually quite similar, requiring GC retention data to identify which isomer is present. When several isomers of a compound were found, as indicated by the same molecular weight, the parent compound was listed in Table I, and the isomers shown in the chromatogram were all given the same number, corresponding to the parent compound.

Results From Plant Samples

Although plants A and B operate under similar conditions, comparison of liquor and corresponding lake water samples by the methods outlined in the experimental methods section indicates that the organics are quite different.

Table III shows that liquor A has approximately twice the concentration of low molecular weight compounds as liquor B. Lake water A also has a higher concentration of these compounds than lake water B. A similar trend was observed for the intermediate molecular weight compounds, with a lower concentration of organics in plant B than in plant A samples. Comparison of GC retention times in Figures 8 through 11 shows that the same intermediate molecular weight compounds are present in all four samples. The results for the high molecular weight material shown in Table V are opposite those of the low and intermediate molecular weight compounds. Here, the organic material in the samples from plant B is approximately twice the concentration found in the samples from plant A. In addition, the molecular weight of the humic type material in plant B is higher than in plant A.

The results from characterization of these four samples indicate that the high molecular weight material in liquor A has degraded to a greater extent to low and intermediate molecular weight compounds than has the high molecular weight material in liquor B. The GC profile of the intermediate molecular weight compounds is very similar for both liquors, indicating no depletion or production of specific compounds in one liquor versus the other. However, this is not true for the lake water samples. The GC profile of the intermediate molecular weight compounds in lake water A is different from liquor A and the GC profile of lake water B is different from liquor B. These observations, together with comparison of GC retention times, indicate that the organics are undergoing changes in the lakes, and that these changes are primarily in relative concentrations of compounds, not in types of compounds. The shift in molecular weight distribution of the high molecular weight material between the liquor and lake water samples suggests that a change in the humic material is also occurring in the lakes. It is also possible that changes may occur between the time the organics leave the liquor and arrive at the lake. This would provide a second possible explanation for the results reported here. Further study is needed to determine if this is the case.

Acknowledgements

The authors would like to thank W. C. McGrew for his GC/MS work, J. P. Auses for his assistance in developing the GPC technique and D. J. Binet and M. E. Sumich for their helpful consultation throughout this project.

References

1. Gordon Lever, "Identification of Organics in Bayer Liquor," Light Metals, 2 (1978) pp. 71-83.

2. Pierre Salomon, "Contribution a l'analyse des substances organiques contenues das les bauxites etles liqueurs d'aluminate du cycle 'Bayer.' Oxydation par l'oxygene," Ph.D. thesis presented at L'Institute National Polytechnique De Grenoble, July, 1982.

3. Z. G. Szabo, M. Orban and I. Perl, "Some Fundamental Research for Alumina Industry in Hungary," ICSOBA Conference, Athens, Greece, (1978) pp. 422-436.

4. P. Roumeliotis and K. K. Unger, "Possible Uses of HPLC for the Separation, Isolation, Identification and Quantitative Determination of Substances from Complex Mixtures - Illustrated by Carboxylic Acid and Sodium Aluminate Liquors from the Bayer Process of Aluminum Recovery," Chromatographia, 15 (2) (1982) pp. 107-116.

5. K. Yamada, T. Harato and H. Kato, "Oxidation of Organic Substances in the Bayer Process," Light Metals, (1980) pp. 117-128.

6. Alan E. Pierce, Silylation of Organic Compounds, Pierce Chemical Company, Rockford, Illinois, 1968.