IDENTIFICATION OF HYDRATE ACTIVE ORGANICS (HAO) PRESENT IN SPENT BAYER LIQUORS BY STATE-OF-THE-ART ANALYTICAL METHODS

Picard, F.[1]*, Audet, D.[2], Boily, H.[2] and Larocque, J.[1]
[1] *Alcan International Limited, Arvida Research and Development Centre, Jonquière, Québec, Canada*
[2] *Alcan International Limited, Banbury Laboratories, Banbury, England, United Kingdom*

Abstract

Considerable progress has been made over the last decade to identify organic compounds that hinder hydrate precipitation and certain polyfunctional entities, including mannitol, gluconate and tartrate have received particular attention. Using mass spectrometry detection liquid chromatography (LC/MS) and ion chromatography (IC/MS), we have undertaken an extensive identification of organic compounds present in Bayer liquor or adsorbed on aluminium trihydrate. These analytical techniques allow the identification of more than one hundred different compounds of low (<125 atomic mass units, a.m.u.), medium (125-300 a.m.u.) and high (>300 a.m.u.) molecular weights. Using these and other newly developed analytical methods, we have compared the concentration of specific organic compounds present in Bayer liquors with those found on washed hydrate. We found that compounds with adjacent chemical functions such as phthalate and salycilate had the highest affinity for hydrate surfaces. However, alditols, suspected earlier as HAO, were not detected in the liquors nor adsorbed on hydrate samples. Based on the analysis of samples from different alumina refineries, we are able to predict which thermally stable HAO's are likely to be present in high and low temperature Bayer liquors.

1. Introduction

Organic materials come in Bayer liquors from various sources: flocculent agents, anti-foaming agents, and crystal growth modifiers. However, humic matter, which constitutes between 0.05 and 0.5% in weight of bauxite, is the principal source of organic material in Bayer liquors. Based on its solubility properties, humic matter may be divided into three families: fulvic acids, soluble throughout the entire pH range; humic acids, insoluble in acids; and humine, insoluble at all pH [Stevenson, F.J., 1994]. Once introduced into the Bayer process, humic matter meets very aggressive conditions and is subject to many chemical modifications, particularly hydrolysis and oxidation. The very high molecular weight species (> 10 000 a.m.u.) are broken down into fulvic and humic acids and their degradation products stay in the liquor while larger insoluble fragments are eliminated along with red mud. After the digestion, up to 90% of the organics present in the bauxite will become solubilised in the liquor and 90% of the oxalate that will be formed in the next 24 hours is already present [Verghese, K.I., 1987]. Due to its high solubility and to the closed circuit nature of the Bayer process, the organic concentration increases with time until it reaches a steady state [Power, G.P., 1991] after a few years of operation under the same conditions. This increasing organic concentration has many negative effects on the process, including bound soda in alumina [Armstrong, L., 1993], liquor foaming, reduced classification performance, and decreasing hydrate yield and sizing yield [Power, G.P., 1991; Bird, R.D., 1983]. This is counter-balanced perhaps by an increase in COC (Critical Oxalate Concentration) [Lever, G., 1983] and by increasing hydrate solubility at digestion and filtration.

Research groups have tried to explain the nature of organic compounds that hinder most hydrate precipitation and they generally identify molecules with many functions to be the worst compounds [Armstrong, L., 1993; Coyne et al., 1994; Owen et al., 1999]. Among these compounds, mannitol, sodium gluconate and sodium tartrate have been the subject of much attention [Rossiter et al., 1999; Alamdari et al., 1993]. However, these studies have been carried out on synthetic liquors and none of the above-mentioned organics have been detected in plant liquors. Nevertheless, these communi-cations have enough merit to direct future studies in the direction of closely related molecules.

The understanding and fine-tuning of newly developed liquor treatments are based on an adequate analytical support. However, until now, research groups have suffered a cruel lack of precise analytical methods in that domain. Only a few robust methods exist, such as Total Organic Carbon analysis (TOC) and sodium oxalate dosage by ion chromatography (IC). There is also gas chromatography (GC) that could give more specific information. In the last 20 years, refinements of GC methods, developed by Lever [Lever, G., 1978], have been realised by many research groups [Guthrie et al., 1984; Wilson et al., 1998; Solymár et al., 1996] but without any breakthrough. The presence of high amounts of various inorganic species renders the direct analysis of the liquors impossible. For that reason, the application of these methods requires sample preparations based on liquid-liquid extraction. Chloroform and ether extract only a small quantity of the organics, which is why n-butanol was introduced [Lever, G., 1978]. In literature, the authors affirm that this solvent would extract humic acids from the liquor [Lever, G., 1978; Guthrie et al., 1984]. Based on this affirmation, sample preparation methods have been developed at Alcan, that successively use solvents of increasing polarity, followed by gravimetric analysis to partition the organics into different families. However, GC/MS fails to give information on the organic compounds present in the more polar fractions, due to their high molecular weights and to their high polarity.

Another option to consider in the analysis of high molecular weight organics and very polar organics is High Performance Liquid Chromatography (HPLC). HPLC has seldom been applied to Bayer plant liquors. Polycarboxylic acids found in Bayer liquor have been analysed by normal

KEY WORDS: HAO, poison, ion chromatography, mass spectrometry, sodium acetate, humic matter

[Susic et al., 1990] and reverse [Roumeliotis et al., 1982] phase HPLC. When combined with the very specific mass spectrometry (MS) detection, the versatility of HPLC gives rise to a very powerful technique. In January 2000, an LC/MS instrument was commissioned at Alcan Arvida R&D Centre to better understand the fate and behaviour of Bayer liquor organics and to support the development of new organic destruction and removal processes.

This paper deals with the development of two sample preparation methods that allow the partition of organics into different fractions, based on their chemical properties. This organic partition into families can yield an organic "signature" for each Bayer liquor. These fractions were then analysed by LC/MS in order to determine their composition and to establish differences between the organic composition of the various plants. A novel IC method with MS detection was used to determine the concentrations of the highly soluble salts, including sodium formate, sodium acetate and sodium succinate. In the last section of this paper, the application of these developments to study the effects of temperature on the organic composition and the identification of Hydrate Active Organics (HAO) will be shown.

2. Experimental methods

2.1 *Sample preparation*

Liquor and the washed hydrate samples were obtained from eight low digestion temperature plants and two from high digestion temperature plants. All liquor samples were heated to 90°C for 24 hours, upon arrival, in order to render precipitated salts soluble again.

Two extraction methods have been used, one based on liquid-liquid extraction and the second based on solid-phase extraction (SPE). The liquid-liquid extraction method uses successively three different solvents of increasing polarity (ether, a mixture of ether and n-butanol, and n-butanol). The solid-phase extraction method was developed to fractionate the organics in Bayer liquor into families. As developed, this method allows partition into three organic families, the high molecular weight (HMW), the medium molecular weight (MMW) and the low molecular weight (LMW) organics. HMW organics precipitate at acidic pH and are removed from samples by filtration. The LMW organics are not retained on a hydrophobic C-18 SPE cartridge. MMW organics are retained on this cartridge and can be recovered by elution with a NaOH solution or an organic solvent like DMF. For ion chromatography, a simple dilution of the samples was done.

2.2 *Chromatographic and spectrometric analysis*

The signal from both HPLC and IC were recorded on a Quattro LC mass spectrometer from Micromass in negative electrospray mode. HPLC analyses were done by reverse-phase elution on a 2.1-mm C_{18} LC-PAH column from Supelco using a water-acetonitrile (10 mM formic acid) linear gradient elution. The IC experiments were done on the same HPLC instrument from Waters but using a 4-mm AS11-HC column from Dionex and a NaOH linear gradient elution.

3. Results

3.1 *Organic partition*

Table 1 presents the TOC analyses of the three solvent-free fractions obtained via the SPE method on the 10 spent liquors, as well as the results from the liquid-liquid extraction method applied to the same liquors. As can be seen in the table, LMW organic fractions represent from 30 to 50% of the TOC.

3.2 *Mass spectrometry analysis of the Bayer organic matter*

3.2.1 *Direct MS/MS analyses of liquid-liquid extracts*

Direct injection (without chromatographic separation) spectra of the ether, ether-n-butanol and n-butanol extracts were recorded for each liquor of the present study. A typical example is presented in Figure 1.

One can see that the three different spectra contain different peaks and also similar peaks but of different intensities. Table 2 lists the 20 major peaks for which an intensity comparison between the three extracts was made. From these relative intensities, a phase coefficient P_i, was calculated as follows:

$$P_i = \frac{1 \times I^{ether} + 2 \times I^{ether\text{-}butanol} + 3 \times I^{butanol}}{I^{ether} + I^{ether\text{-}butanol} + I^{butanol}} \quad [1]$$

where I^{ether}, $I^{ether\text{-}butanol}$ and $I^{butanol}$ are the signal intensity of a mass i in each of the three organic phases. This coefficient, introduced to obtain a numerical data for an observation that is mostly qualitative, represents the affinity of a particular organic for one of those extraction phases. The phase coefficient calculated for an organic compound present in higher amounts in the ether fraction will be close to one, but it will be close to three for an organic compound present in higher amounts in the n-butanol fraction. Then, all the masses reported in Table 2 were analysed by

Table 1 — TOC, HMW/MMW/LMW obtained by solid-phase extraction and mass of organic obtained from three successive liquid-liquid extraction for 10 Bayer plant spent liquors

	TOC	Solid-phase extraction			Liquid-Liquid Extraction			
		HMW	MMW	LMW	Ether	Ether-n-butanol	n-butanol	Total
	gpl	gpl (as C)	gpl (as C)	gpl (as C)	gpl	gpl	gpl	gpl
LT1	4.5	0.01	2.8	1.7	1.3	4.9	2.6	8.8
LT2	5.6	0.03	3.8	1.8	2.2	5.7	3.0	10.9
LT3	6.8	0.15	4.2	2.5	2.8	5.2	2.3	10.3
LT4	8.0	0.02	4.0	4.0	1.6	7.1	4.1	12.8
LT5	10.4	0.02	5.2	5.2	2.1	10.1	5.3	17.5
LT6	13.6	0.09	6.6	6.9	5.9	15.2	6.4	27.5
LT7	19.0	0.09	10.6	8.3	10.0	20.0	10.0	40.0
LT8	22.6	0.13	13.6	8.9	9.0	26.3	17.4	52.7
HT1	11.1	0.11	6.0	5.0	5.6	7.0	3.3	15.9
HT2	29.0	0.30	19.0	9.7	20.3	23.4	10.3	54.0

various MS/MS experiments that involved fragmentation of the molecular ions. These experiments allow the proposition of a list of likely structures to explain the observations. These structures, that are presented in Figure 2, should be viewed as general patterns from which many structural isomers are possible.

For each molecular structures presented in Figure 2, a carbon weight ratio, w_C, is calculated and reported in Figure 2. This ratio represents the proportion of the molecular weight in the form of carbon. For a pure aromatic or aliphatic compound, w_C is typically ≈ 0.9 and decreases as the number of polar functions increases, to reach 0.26 for oxalic acid. From Table 2, it is also notable that P_i is related to w_C. One can see that a compound characterised by a low w_C will have a high P, while aromatic materials that are characterised by a high w_c are mostly found in the ether fraction. From this relation between P and w_C, it is possible to convert the weight of organics found in the three solvent extracted fractions into weight of carbon. It was assumed that w_C was 0.55 for the ether extract (P≈1); 0.45 for the ether-n-butanol extract (P≈2) and 0.4 for the n-butanol extract (P>2). With these values, it is possible to calculate the proportion of the TOC that was extracted from each plant liquor (results not shown). For example, only 60% of the TOC is extracted from HT1 liquor while 95% of the TOC from LT8 is extracted. The difference is attributed to the volatile low molecular acids, which can only be partially extracted.

3.2.2 *LC/MS/MS analyses*

Direct MS/MS analysis allowed the characterisation of compounds present in each liquid-liquid extraction phase. However, for each molecular structure presented in Figure 2, many isomers are possible. The differentiation of these isomers was done by comparing the retention time (r_t) of the standard materials to the detected mass to charge ratios (m/z). This rigorous identification was done by recording chromatograms for different extracts of different types of liquors. An optimisation exercise then allowed the separation of the isomers of each predominant mass. Figure 3 presents two examples of this type of analysis.

In order to attribute the different peaks on the chromatograms, 73 different pure compounds were eluted. These molecules were chosen for their commercial availability and their molecular weights. For all these compounds, the r_t were determined and their w_c were calculated (results not shown). Peak attribution on the liquor chromatograms was then made using this data base. As an example, the single peak on chromatogram A of Figure 3 was attributed to 3-hydroxybenzoic acid. Its isomer, salycilic acid (2-hydroxybenzoic acid) was observed in small amounts in some liquors, while 4-hydroxybenzoic acid was never observed.

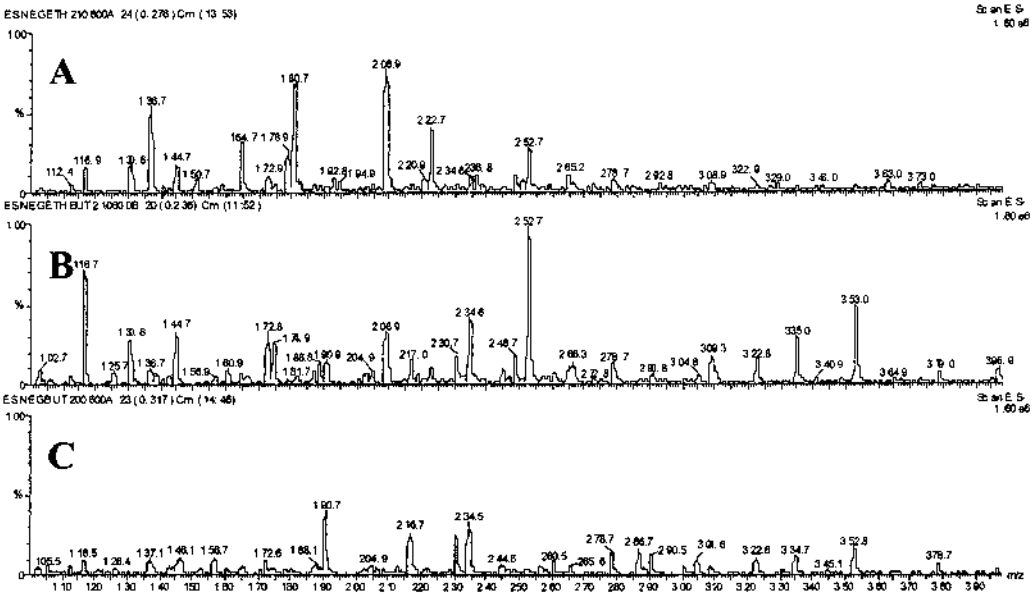

Figure 1 — Mass spectra in "scan" mode for a sample obtained via liquid-liquid extraction:
A) ether, B) ether-n-butanol and C) n-butanol.

Table 2 — Molecular Weight (MW), Carbon Weight Factor (w_c) and Phase Coefficient (P) calculated for the molecular structures presented in Figure 2

Structure	MW u.m.a.	w_C	P	Structure	MW u.m.a.	w_C	P
1	104	0,35	2,0	11	138	0,61	1,0
2	118	0,41	2,0	12	152	0,63	1,0
3	132	0,45	1,8	13	166	0,58	1,3
4	146	0,49	1,6	14	180	0,60	1,0
5	160	0,53	1,0	15	182	0,53	1,0
6	162	0,37	2,3	16	210	0,51	1,4
7	176	0,41	2,3	17	224	0,54	1,3
8	206	0,35	1,8	18	254	0,47	2,0
9	122	0,69	1,0	19	298	0,44	2,4
10	136	0,71	1,0	20	342	0,42	2,5

The many peaks on chromatogram B were only partially attributed. By this extensive identification process, the validity of the proposed structures presented in Figure 2 was confirmed.

It was observed that the main factor that explains the chromatographic retention time (r_t) for the 73 different compounds was the carbon weight ratio. A clear linear relation exists between r_t and w_c (results not shown). However, w_c could not explain the difference r_t between isomers that are mainly due to the specific tridimensional structure of these molecules. This relation between r_t and w_c opened the way to preparative chromatography to fractionate Bayer organics. It also explained the separation on the SPE cartridge that is based on polarity. On C18 type SPE cartridges, molecules with high w_c are retained while molecules with low w_c are not retained.

When all the peaks are attributed, a qualitative analysis is possible. Integration of all the peaks present in the ether extract was done for all liquors but also for their corresponding washed hydrate samples. Table 3 reports the mean intensities (relative to phthalic acid) for 13 aromatic compounds with $P<1.5$. The mean intensities were calculated separately for high digestion temperature (HT) and low digestion temperature (LT) plants. A value lower than 1 represents a compound whose peak is smaller than the phthalic one, while it is the opposite for a value higher than 1. A detailed discussion of these results is presented in Section 4.1.

3.2.3 *MS/MS analyses of HMW extract*

The organic residue that is retrieved after acidification of Bayer liquor has always been considered as being composed of humic acids [Lever, G., 1983; Lever, G., 1978]. Analyses of this residue by ultracentrifugation and size-exclusion chromatography have been reported in the literature [Lever, G., 1983; Lever, G., 1978]. These techniques

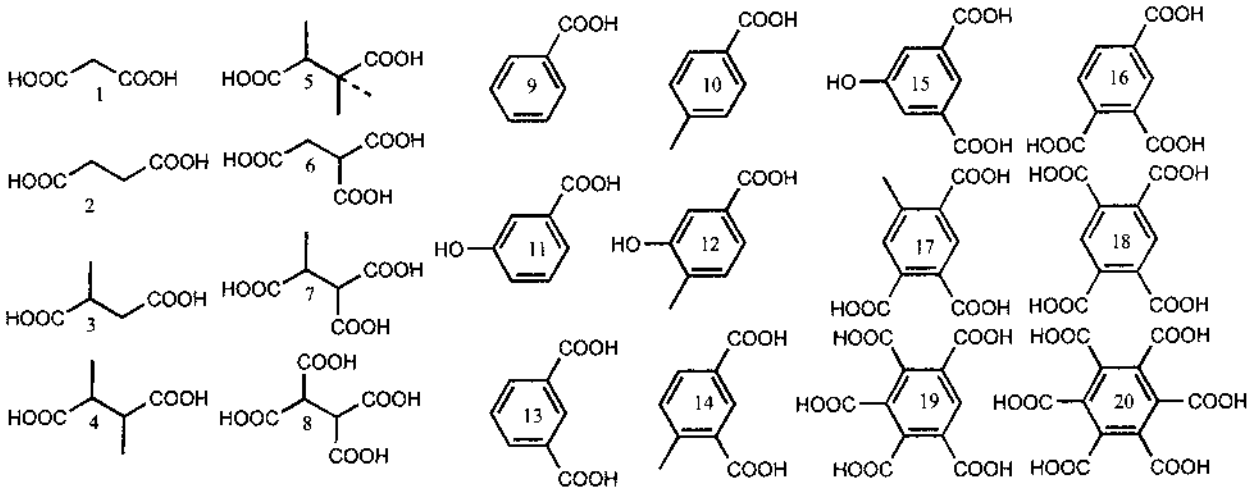

Figure 2 — Proposed structures for the 20 most intense peaks observed in the spectra of Figure 1.

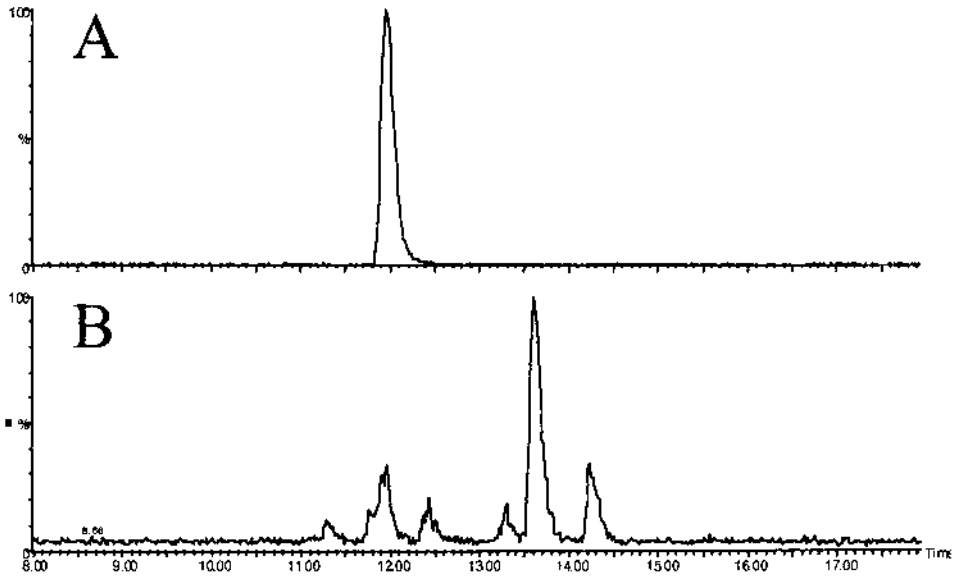

Figure 3 — Chromatograms obtained for an ether extraction for m/z ratio of:
A) 137 a.m.u. (Structure #11) and B) 151 a.m.u. (Structure #12).

separate molecules by size and the results are given in molecular weight after calibration with standard compounds. Mass spectroscopy is much more powerful since the molecular weight (*m/z* ratio) is measured directly, i.e., without a calibration curve. Unfortunately, mass spectroscopy required molecules soluble in organic solvents, which is not the case for humic acids. But HMW compounds obtained from Bayer liquor are soluble in dimethylformamide (DMF) and even in methanol, for a short period of time. This observation is a quick demonstration that HMW are different from humic acids present in soils. Solutions of HMW organics in a mixture of DMF and methanol were introduced, without chromatography separation, in the MS/MS instrument. Figure 4 presents an example of the recorded spectra.

The HMW spectra of all plant liquors were very similar. All the signals were recorded below 1000 a.m.u. from molecular ions that possess many carboxylic functions but only one charge (z = 1). The molecular weight of HMW is very low compared to that reported to date in the literature. All the spectra were composed of a broad envelope and of some specific peaks at 239, 253, 255, 283, 297 a.m.u. Daughter MS/MS experiments have demonstrated, with great assurance, that these masses were from fatty acids made of 15 to 19 carbons, mono-unsaturated and unsaturated chains. Fatty acids are not soluble at acidic pH and are likely to be found in the HMW fractions. They could come from bauxites but they are also degradation products of oils, crystal growth modifiers and anti-foaming agents. They are not really HMW compounds, so they bias the value obtained for this fraction.

3.2.4 *IC/MS analyses*

Oxalate is analysed daily in most plant liquors by IC using a conductivity detector. Unfortunately, this method is not applicable to a wide range of organics in Bayer liquors since many inorganic species interfere. However, a new specific IC method that uses MS detection was developed and a typical chromatogram is presented in Figure 5. Note that with MS detection, the masses that are detected are chosen by the instrument operator.

Quantification of four different compounds for the 10 plant liquors selected for this study was done using IC/MS. These values were as high as 21.3 gpl for sodium acetate in HT2. In Figure 6, the results were reported as percentage of the TOC. Together, the organic compounds presented in this figure represent up to 10 g/L of carbon or between 15 and 40% of the TOC. The oxalate contribution decreases as the TOC increases due its limited solubility in caustic solution (~4-5 gpl). With the notable exception of oxalate, no published study suggesting a particular influence of these organics on precipitation yield, classification performance or hydrate sizing was found.

4. Discussion

Analytical methods are the foundation of development, improvement or fine-tuning of chemical processes. Particularly in the domain of destruction or removal of organic

Table 3 — Normalised MS intensities of 13 aromatic acids in spent Bayer liquors and for corresponding washed hydrates

	MW	Liquors			Hydrates		A*
		HT	LT	HT/LT	HT	LT	
2-hydroxybenzoic (Salicylic)	138	0.12	0.50	0.24	0.05	0.08	0.29
3-hydroxybenzoic	138	7.07	0.98	7.22	0.02	0.02	0.07
3-methylsalicylic	138	0.00	0.04	0.00	0.01	0.03	0.12
1,2-benzenedicarboxylic (Phthalic)	166	1.00	1.00	1.00	1.00	1.00	1.00
1,3-benzenedicarboxylic (Isophthalic)	166	3.50	1.10	3.19	0.02	0.05	0.07
1,4-benzenedicarboxylic (Terephthalic)	166	1.46	2.55	0.57	0.26	0.77	0.31
1,2-benzenediacetic (Homophthalic)	166	1.27	1.09	1.16	0.07	0.10	0.09
4-hydroxy-1.3-phthalic	182	0.00	0.26	0.00	0.00	0.01	0.02
4-hydroxy-1.2-phthalic	182	0.01	0.17	0.06	0.01	0.01	0.13
5-hydroxy-1.3-phthalic	182	17.12	4.50	3.81	0.05	0.15	0.15
1,2,3-benzenetricarboxylic (hemimellitic)	210	0.01	0.05	0.09	0.00	0.04	0.36
1,2,4-benzenetricarboxylic (Trimellitic)	210	1.06	0.61	1.75	0.01	0.03	0.14
1,3,5-benzenetricarboxylic (Trimesic)	210	1.13	0.56	2.02	0.01	0.01	0.06

*Affinity coefficient calculated according to equation [2]

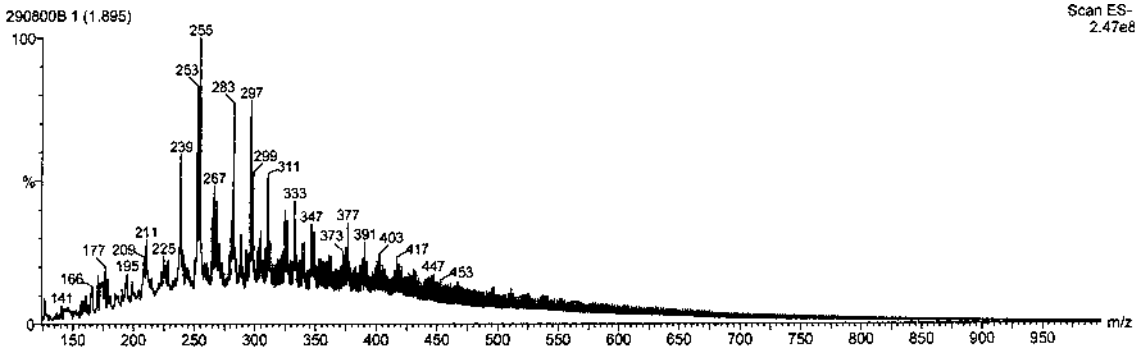

Figure 4 — Mass spectra in “scan” mode for a HMW sample.

materials from Bayer liquors, the need to have new analytical methods is even more important. In the preceding sections, new preparation and analytical methods were presented. These methods are mostly supported by the availability of mass spectrometry to analyse liquids. This technology, that is now widely used in pharmaceutical and environmental sciences, has not been spread to other domains, particularly commercial IC/MS, since it has entered the market only in the last few years. The above results will be discussed from two points of view: the effects of temperature on Bayer liquor organics and the presence of hydrate active organics (HAO). These are only two examples of the application of these methods. These methods were also used to support the evaluation and development of organic destruction and removal processes, but these studies will not be reported here.

4.1 *High temperature digestion (HT) versus low temperature digestion (LT)*

Among the factors that could modify the Bayer liquor organic composition are: temperature, presence of oxidants and caustic concentration. Preliminary tests showed that the effects of varying caustic concentrations between 175 and 300 gpl (as Na_2CO_3), which are the current range within the Bayer industry, seem to have less impact than varying temperatures between 135°C to 260°C (results not shown). Based on the observed molecules in the Bayer liquors, it seems reasonable to think that the degradation is an oxidation process, which makes the effects of increasing oxidant concentration very attractive. However, if the presence of oxidant is important, this will have to be done in addition to an increase in temperature, which is the basis of all the wet oxidation processes that have been proposed until now. If a process like wet oxidation is effective, this means that a refinery based on high digestion temperatures should have an organic composition different than in a low digestion temperature plant. This is the reason why these two types of plants were compared.

Table 3 reports the relative intensity for 13 aromatic molecules. These values were separated into two columns: the mean values for HT and LT plants. Based on Table 2, these compounds have phase coefficients lower than 1.4, which means that they are more likely extracted by ether. An investigation of the organic compounds present in the ether extract showed that some organics are promoted in HT plants, while the presence of others is favoured in LT plants. This is particularly true for position isomers. In all liquors, molecules that possess adjacent functions (e.g., salicylic and phthalic acids) are present in concentrations lower than their isomers (i.e., 3-hydroxybenzoic and isophthalic acids) in which the functions are non-adjacent. A first conclusion is that Bayer liquor conditions seem to promote molecules with non-adjacent functions. This discrepancy between adjacent and non-adjacent functions is more pronounced in high temperature plants than in low temperature plants, as shown by the ratios HT/LT given in column 5 of Table 3. This ratio shows that salicylic acid, which possesses adjacent functions, is four times more present in LT plants than in HT plants. On the other hand, 3-hydroxybenzoic acid is seven times more present in HT plants than

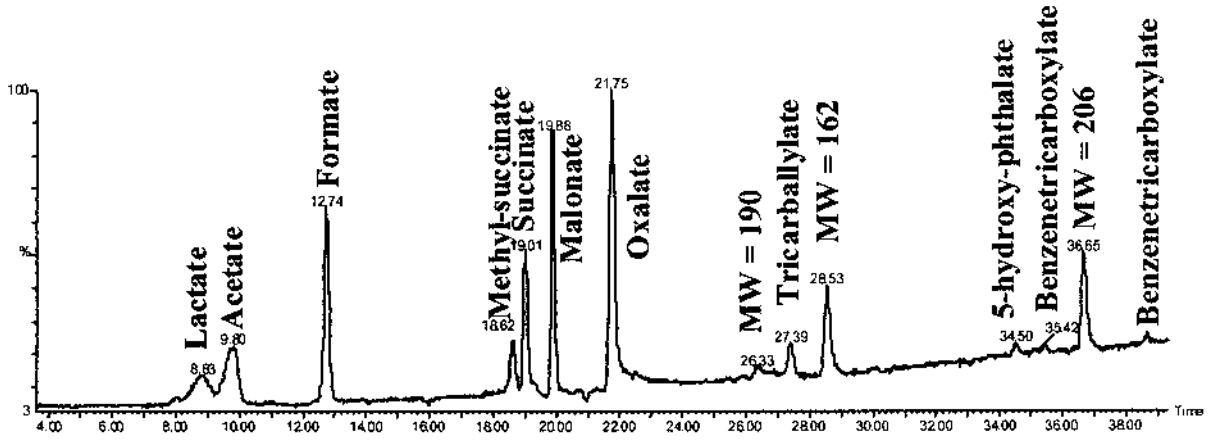

Figure 5 — Ion Chromatograms recorded using a MS detector.

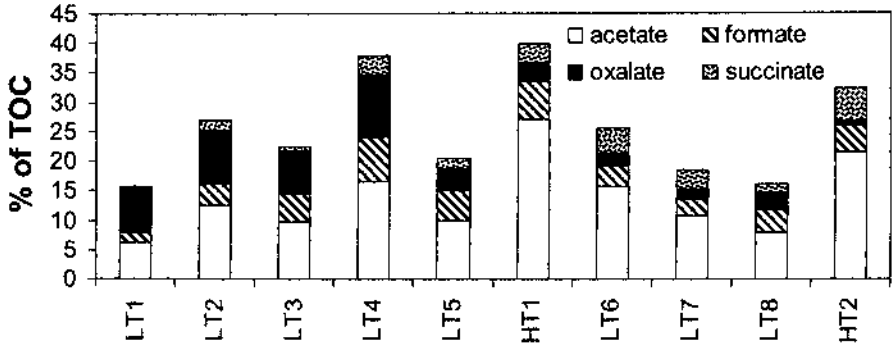

Figure 6 — Contribution of four LMW organics to the TOC of ten Bayer plant spent liquors.

in LT plants. This same observation can be made for every isomer couple. In conclusion, the temperature seems to significantly promote aromatic molecules with non-adjacent functions over molecules with adjacent functions when the digestion temperature is increased.

The impact of temperature seems to not only promote specific isomers, but also seems to completely change the organic distribution. The ether fraction of HT plants represents 37% of the solvent extractable organics, while this fraction is between 12 to 27% in LT plants, as shown in Table 1. This fraction contains mostly aromatic molecules, with only one to three carboxyl groups. This fact could be explained by a possible decarboxylation of poly-substituted aromatics in high temperature digestion plant liquors. Table 3 shows that very stable molecules, such as 1,3-dicarboxilic acid and 1,3,5-tricarbioxilic acids, are highly promoted in HT plants.

IC/MS results reported in Figure 6 indicated a very high proportion of sodium acetate in each liquor considering their TOC content. This high concentration has also been noted in liquors that have been treated by wet oxidation processes (results not shown). It therefore seems that acetate is a common degradation product that is stable in hot caustic media. The other low molecular weight organics do not seem to be affected by temperature.

4.2 *Alditols, polyols and other hydrate active organics (HAO)*

Much effort has been exerted over the years to find which molecules interact with alumina hydrate and inhibit or lower precipitation yields. The usual approach to this kind of study is to measure the yield or the kinetics of hydrate precipitation. In these experiments, a known amount of supposed poison is added to the liquor. A series of molecules has been studied in this way [Armstrong, L., 1993; Coyne et al., 1994; Owen et al., 1999; Rossiter et al., 1999; Alamdari et al., 1993]. Among these molecules, alditols, polyols and humic acids have been identified as HAO. However, to our knowledge, polyols and alditols have never been detected in Bayer liquors. In the case of humic acids, Section 3.2.3 showed that HMW organics are far away from the concept of humic acids found in soils. Among alditols and polyols that have been identified as poison compounds for the precipitation, there are molecules such as sodium gluconate, sodium tartrate, sodium citrate, mannitol and sodium 3,4-dihydroxybenzoate, etc. With the exception of 3,4-dihydroxybenzoate, all these molecules have a low w_c. They are all very polar and most of them are insoluble in ether. They are soluble in water but their solubility is higher in alcohol. Therefore, they should be extracted by n-butanol in their acid form.

All these molecules emitted signals in MS/MS spectroscopy (results not shown). However, they were not observed in any of the Bayer liquors. It is also possible to dilute acidified Bayer liquors in methanol and inject this solution directly into the mass spectrometer. Even though this method gives a poor signal due to the presence of a lot of inorganic salt, it is possible to perform a qualitative analysis. Again, these poisons were not observed.

4.3 *HAO's present in Bayer liquors*

Another approach to define HAO's is proposed here. This approach is based on the assumption that a molecule with high affinity for hydrate will be entrained in the precipitation process and should therefore be present in hydrate samples. Even if this hypothesis is applicable to all organics, only the ether soluble organics were investigated in this study. Therefore, other compounds, like sodium oxalate, were not included as part of this study, even if they are known to interact with hydrate. In order to identify the HAO, hydrate organics were compared with liquor organics of the same plant. The comparison of 13 aromatic molecules extracted by ether from 10 Bayer plants is reported in Table 3. As previously discussed, due to temperature stability, molecules with non-adjacent functions are favoured in Bayer liquors. *However, completely opposite trends are found for hydrates.* These observations led to the definition of a HAO scale to classify the organics relatively to their affinity towards the hydrate. This affinity coefficient is defined as:

$$A^i = \frac{I_H^i}{I_L^i} \qquad [2]$$

where I_H is the intensity of a molecule "i" in the hydrate (ideally the true concentration), while I_L is the intensity of the same molecule in the liquor. Affinity coefficients have been calculated and are reported in column 8 of Table 3 for the 13 studied aromatic acids. Phthalic acid has the highest affinity for the hydrate, followed by hemimellitic and salicylic acids, all three of which are molecules with adjacent functions. Overall, organic molecules seem to be partitioned according to their hydrate affinity, leaving mainly, in spent Bayer solution, the soluble inactive species.

5. Conclusions

This paper dealt with the development of state-of-the-art analytical tools to further the analysis of Bayer organics, taking full advantage of the latest technology in liquid-liquid and solid-liquid extractions coupled to ion chromatography-tandem mass spectrometry for the analysis of organics in complex liquid samples.

The fractionated liquid-liquid extraction showed that the extractable organics were partitioned into three fractions based on molecular polarity. Formate, acetate, oxalate, and succinate making up the low molecular weight organic fraction, represent up to 45% of the total organic carbon in liquors. With the solid-phase extraction method that allows partition of the organics without the use of organic solvent, a carbon mass balance calculation is now possible. A comparison of the organic content of spent liquors from 10 different plants showed that the highest acetate concentrations are found in liquors from high temperature plants and that high digestion temperature plants produce a lower proportion of molecules with a high affinity for hydrate. Among the chemical compounds present in high quantities in the liquor, phthalic acid is the molecule with the highest affinity for hydrate. It was also shown that molecules with a high affinity for hydrate have two adjacent functions (acid or alcohol). However, the nature of the chemical compounds present on aluminium hydrate differs little, regardless of the organic composition of the plant liquor or the digestion temperature.

The availability of these new characterisation tools, that can yield more informative data than the proven but limited TOC and IC analyses, makes it now possible to accurately assess the impact of HAO on precipitation yield and to better evaluate processes for organic destruction and removal.

Acknowledgement

This study was realised with the help of a postdoctoral fellowship awarded to Dr. Frédéric Picard by the Natural Science and Engineering Research Council of Canada.

References

Alamdari, A., Raper, J.A. and Wainwright, M.S., (1993), Poisoning of the Precipitation of Alumina Trihydrate by Mannitol, Light Metals, 1993, 143–149.

Armstrong, L., (1993), Bound Soda Incorporation During Hydrate Precipitation, Proceedings of the Alumina Quality Workshop, 1993, 282–292.

Bird, R.D., Vance, H.R. and Fuhrman, C., (1983), The Effect of Four Common Bayer Liquor Impurities on Alumina Solubility, Light Metals, 1983, 65–82.

Coyne, J.F., Wainwright, M.S., Cant, N.W. and Grocott, S.C., (1994), Adsorption of Hydroxy Organic Compounds on Alumina Trihydrate, Light Metals, 1994, 39–45.

Guthrie, J.D., The, P.J. & Imbrogno, W.D., (1984), Characterization of Organics in Bayer Liquor, Light Metals, 1984, 127–146.

Lever, G., (1978), Identification of Organics in Bayer Liquor, Light Metals, 1978, 71–83.

Lever, G., (1983), Some Aspects of the Chemistry of Bauxite Organic Matter on the Bayer Process: The Sodium Oxalate-humate Interaction, "Travaux de l'ICSOBA", vol. 13, 1983, 335–347.

Owen, A., Watling, H.R., van Bronswick, W. and Yu, Z.S., (1999), Poisons, Polyols and Precipitation, Proceedings of the Alumina Quality Workshop, 1999, 163–169.

Power, G.P., (1991), The Impact and Control of Organic Compounds in the Extraction of Alumina from Bauxite, Proceedings of the Extractive Metallurgy Conference, 1991, 337–345.

Rossiter, D.S., Illievski, D. and Parkinson, G.M., (1999), Sodium Gluconate Poisoning of Primary and Secondary Nucleation of Gibbsite from Synthetic Bayer Liquor, Proceedings of the Alumina Quality Workshop, 1999.

Roumeliotis, P., Unger, K.K., Kudermann, G. and Winkhaus, G., (1982), HPLC of Carboxylic Acids in Sodium Aluminate Liquors from the Bayer Process, Chromatographia, 15, 1982, 107-116.

Solymár, K., Gimpel-Kazár, M. and Molnár, E., (1996), Determination and Evaluation of Organic Balances of Alumina Refineries, Light Metals, 1996, 29–35.

Stevenson, F.J., (1994), Humus Chemistry, 2nd Edition, John Wiley and Son, Inc., New York, 1994, 496 p.

Susic, M. and Armstrong, L.G., (1990), High Performance Liquid Chromatographic Determination of Humic acid in Sodium Aluminate Solution, Journal of Chromatography, 502, 1990, 443-446.

Verghese, K.I., (1987), The impact of Impurities on the Bayer Process, Light Metals 1987, 42–46.

Wilson, M.A., Farquharson, G.J., Tippett, J.M., Quezada, R.A. and Armstrong, L., (1998), Aluminophilicity of the Humic Degradation Product 5-hydroxybenzene-1,3-dicarboxylic acid, Ind. Eng. Chem. Res., 37, 1998, 2410–2415.