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Analysis of oxalate in Bayer liquors: a comparison of ion chromatography and capillary electrophoresis

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Abstract

The performances of ion chromatography (IC) and capillary electrophoresis (CE) are compared for the quantitative analysis of oxalate in Bayer liquor, an industrial process solution used in the extraction and precipitation of alumina from bauxite. CE has a number of advantages over IC for this particular application. The most important difference between the two techniques was the fact that the selectivity of CE allowed for complete resolution of oxalate from the matrix components in Bayer liquor. However, oxalate results obtained by IC were consistently higher than those for CE due to the presence of chromatographic interferences. Chloride and sulfate could also be determined with oxalate in the same separation using CE, however the simultaneous determination of oxalate, chloride and sulfate in Bayer liquors was not possible by IC due to significant chromatographic interferences. CE gave improved precision for the replicate analysis of oxalate in liquor samples, with an overall average of 1.71% R.S.D., compared to an average of 2.85% R.S.D. when using IC. A further advantage of CE was the fact that it also allowed the simultaneous determination of oxalate, chloride and sulfate in liquor samples which had been stabilised with tartaric acid.

1. Introduction

The Bayer process involves the extraction (and precipitation) of alumina from bauxite using hot sodium hydroxide. The process is cyclic and soluble impurities, mostly organic and inorganic ions, accumulate in the process liquor stream [1]. Of these ions, oxalate is of prime importance as its stability and removal controls refinery productivity [2]. A typical liquor contains approximately 3.5 *M* sodium hydroxide, 0.5 *M* sodium carbonate, 1.0 *M* sodium aluminate [$NaAl(OH_4)$], 0.4 *M* sodium chloride, 0.25 *M* sodium sulfate, 2–3.5 g/l sodium oxalate and 20–30 g/l total organic carbon present as organic acid anions [1]. These amounts vary from refinery to refinery and also depend upon the source of the bauxite. The high ionic strength and pH, coupled with the fact that aluminium hydroxide is insoluble in the pH range of approximately 5–10, makes the routine analysis of oxalate in Bayer liquor a difficult task.

Oxalate is typically analysed in such a matrix using either gas chromatography (GC), after methylation, or ion chromatography (IC). Both techniques suffer significant drawbacks; in terms of either lengthy sample preparation time for GC, or organic acid interferences and short column (and suppressor) lifetime with IC. The selectivity of capillary electrophoresis (CE) appears to be particularly advantageous for the analysis of mixtures of inorganic anions and

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organic acids [3,4] and the feasibility of this technique for the analysis of oxalate in Bayer liquor has been demonstrated previously [1]. In this paper, the performances of IC and CE are compared for the quantitative analysis of oxalate in Bayer liquor. The advantages and disadvantages of both techniques for this particular analysis will be presented. The feasibility of performing simultaneous chloride, sulfate and oxalate analysis, using both IC and CE, will also be discussed.

2. Experimental

2.1. Ion chromatography system

The ion chromatograph consisted of a Waters (Milford, MA, USA) 510 solvent-delivery system, a 717 autosampler, a 431 conductivity detector, a 486 variable-wavelength UV detector operated at 214 nm and a Millennium 2010 chromatography management system. Data were collected at 1 point/s for IC. Two methacrylate-based anion exchangers were used, a Waters IC Pak Anion high-resolution (HR) column (75 × 4.6 mm I.D.) and a Waters IC Pak Anion high-capacity (HC) column (150 × 4.6 mm ID). The borate–gluconate eluent consisted of 1.6 m*M* sodium tetraborate, 7.3 m*M* boric acid, 1.6 m*M* sodium gluconate, 5 g/l glycerin, 120 ml/l acetonitrile and 20 ml/l *n*-butanol at pH 8.5.

2.2. Capillary electrophoresis system

The CE instrument used was a Waters Quanta 4000E with a Millennium 2010 chromatography management system. Data were collected at 10 points/s for CE. The separations were performed on a conventional (60 cm × 75 μm I.D.) fused-silica capillary from Waters. An electrolyte of 5 m*M* chromate with an osmotic flow modifier, Waters CIA-Pak OFM anion-BT, at pH 8.0 was used at an operational voltage of −20 kV. Isomigration mode, value 3, was used for all separations. Detection was carried out using indirect photometry at 254 nm with a time constant of 0.1 s. The capillary and the sample cabinet were maintained at a constant temperature of 25°C.

2.3. Reagents and procedures

Millipore (Bedford, MA, USA) Milli-Q 18 MΩ water was used for all electrolyte, eluent, sample and standard preparations. Sodium tetraborate, boric acid, sodium chloride, sodium sulfate (analytical-reagent grade) and glycerin (laboratory-reagent grade) were obtained from Ajax (Sydney, Australia). HPLC-grade acetonitrile and *n*-butanol were also obtained from Ajax. Sodium gluconate (laboratory-reagent grade) was obtained from Fluka (Buchs, Switzerland) and oxalic acid dihydrate (guaranteed-reagent grade) was obtained from Merck (Darmstadt, Germany). Sodium chromate tetrahydrate was obtained from Aldrich (Milwaukee, WI, USA). Electrolytes and eluents were prepared daily, filtered through a Millipore 0.45-μm HV filter and degassed in an ultrasonic bath before use. Samples were injected after dilution with Milli-Q water and filtration through a Millipore 0.45-μm Millex HV syringe filter.

3. Results and discussion

Having previously established the feasibility of the determination of oxalate in Bayer liquor by CE [1], the objective of this work was to compare CE results to those obtained by the more commonly used technique of IC. A further objective of the work was to investigate the possibility of performing simultaneous chloride, sulfate and oxalate analysis, using both CE and IC, as the analysis of these two inorganic anions in Bayer liquor is also of importance.

3.1. Ion chromatography

The IC analysis of Bayer liquor is complicated by the high ionic strength and pH of the sample; along with the fact that aluminium hydroxide is insoluble in the pH range of approximately 5–10. This then restricts the choice of eluents to those which are of low pH, high pH or those which

keep alumina soluble through complex formation [2]. Tartrate–borate at pH 4.5 has been used to determine both chloride and sulfate in Bayer liquors; however, this eluent does not permit resolution of organic acid solutes, such as oxalate [1]. Carbonate–hydrogencarbonate with suppressed conductivity detection has previously been used for oxalate analysis in liquors [5], however the main disadvantage of this approach is that alumina has limited solubility in the suppressor, which reduces suppressor efficiency and lifetime [2].

Borate–gluconate is a complexing mobile phase which permits good resolution and sensitivity for chloride, sulfate and oxalate. Fig. 1 shows the chromatograms obtained from a 100-μl injection of a standard solution containing chloride, sulfate and oxalate obtained using a borate–gluconate eluent and the Anion HR column with dual conductivity (a) and direct UV detection at 214 nm (b). Fig. 2 shows chromatograms of a typical Bayer liquor, after 200 × dilution, again using conductivity (a) and direct UV detection (b). The combination of conductivity and direct UV detection, which is widely used for the analysis of complex samples by IC [6], proved useful in order to determine the presence of organic acid interferences in this case. The conductivity chromatogram showed that chloride was not fully resolved from an adjacent unknown peak and that a non-interfering system peak, eluting at approximately 5.5 min, was present under the mobile phase conditions used [7]. The UV chromatogram indicated oxalate was not completely resolved from the other organic acids present in the sample;

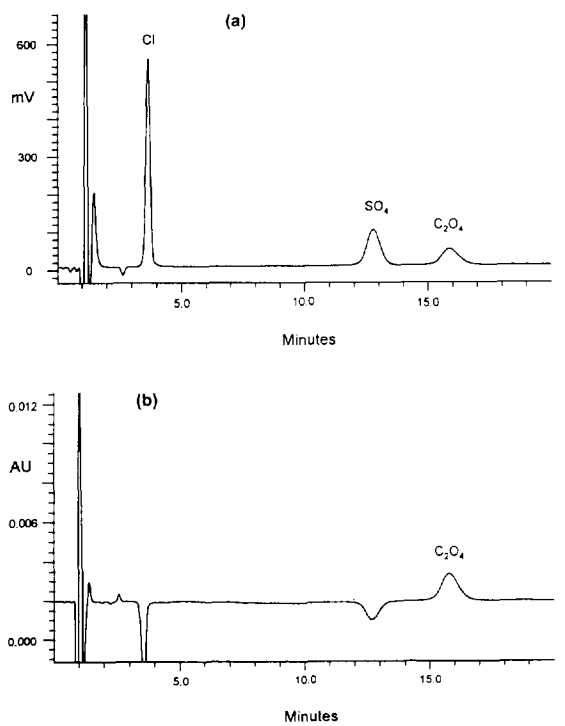

Fig. 1. Chromatogram of chloride, sulfate and oxalate standard obtained using IC with dual conductivity and direct UV detection. Conditions: column, Waters IC Pak Anion HR; eluent, borate–gluconate at 1.0 ml/min; injection volume, 100 μl; detection, conductivity (a) and direct UV detection at 214 nm (b); solutes: chloride (10 ppm), sulfate (8 ppm), oxalate (5 ppm).

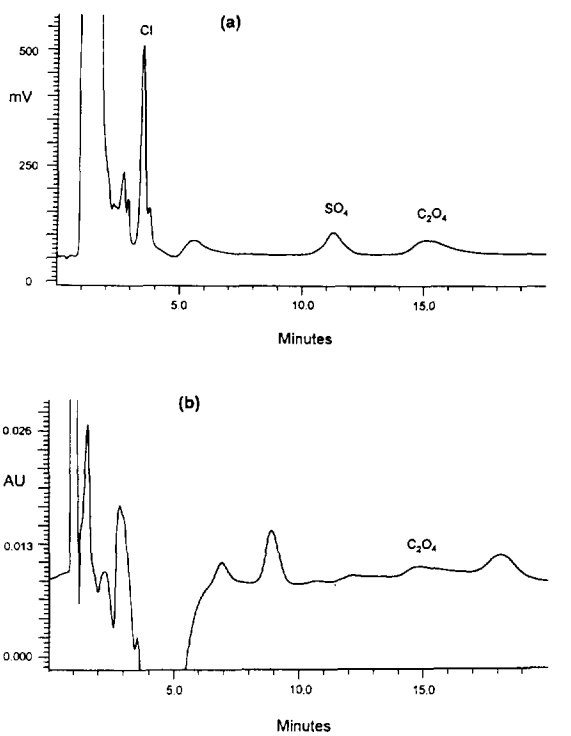

Fig. 2. Chromatogram of a typical Bayer liquor obtained using IC with dual conductivity and direct UV detection. Conditions as for Fig. 1, except: injection volume, 50 μl; sample preparation, 200 × dilution with water; solutes (injected concentrations): chloride (20.6 ppm), sulfate (11.1 ppm), oxalate (15.1 ppm).

however, the total peak area of the interferences was negligible compared to that of oxalate with conductivity detection. The UV detector also showed the (negative) system peak and a number of additional organic acids, including succinic acid at a retention time of approximately 12 min, which co-eluted with the sulfate peak.

Variation of the eluent ionic strength and the use of a higher-capacity column, the IC Pak Anion HC, resulted in increased separation for the oxalate peak and somewhat improved resolution for both the chloride and sulfate peaks, although at the expense of increased chromatographic run time. The addition of up to 20% acetonitrile to the mobile phase also allowed for some minor selectivity changes, however these were not sufficient to completely resolve sulfate and oxalate from the other interferences. Generally, most anion exchangers have very similar selectivity and organic acids, such as succinate and tartrate, typically interfere with divalent inorganic anions, such as sulfate, when using a mobile phase in the pH range of 7–11. Lowering the mobile phase pH results in protonation, hence decreased retention, of the organic acids, although this results in the oxalate quantitation being significantly affected as a result of interference by other organic acids. Consequently, efforts to simultaneously determine chloride, sulfate and oxalate by IC are typically carried out using an anion-exchange separation, with the mobile phase conditions optimised to achieve maximum resolution of oxalate, which is the most important assay. Table 1 shows the results for chloride, sulfate and oxalate (reported conventionally as g/l disodium oxalate) in a number of Bayer liquor samples, obtained using the HC column, a borate–gluconate eluent and conductivity detection.

3.2. Capillary electrophoresis

The selectivity of CE is particularly advantageous for the analysis of oxalate as the ion's electrophoretic mobility is intermediate between the very mobile inorganic anions, such as chloride and sulfate, and the less mobile organic acids, such as tartrate, succinate and acetate, which are present in Bayer liquor. A chromate-based electrolyte was used with indirect UV detection as this combination permits good peak shape and sensitive detection [8]. A variety of separation conditions and electrolyte modifiers, including the addition of calcium, methanol and Z1-Methyl, were investigated in order to optimise the separation and precision of the CE analysis. A relatively simple electrolyte of 5.0 m*M* chromate with 0.5 m*M* CIA-Pak OFM anion-BT at pH 8.0, when used with an automated purge routine of 0.1 *M* sodium hydroxide, water and electrolyte for 1.0/1.0/2.0 min, respectively, proved to be the most appropriate for the determination of chloride, sulfate and oxalate in Bayer liquor samples.

The use of the purge routine proved to be crucial in attaining reproducible migration times, hence reproducible peak areas and amounts. The manner in which the current and voltage were applied to the separation also had a significant effect on the oxalate migration time reproduci-

Table 1
Oxalate (g/l disodium oxalate), chloride and sulfate (ppm) results for five Bayer liquor samples obtained using IC and CE

Sample[a]	Ion chromatography			Capillary electrophoresis		
	C_2O_4	Cl	SO_4	C_2O_4	Cl	SO_4
431	1.96	3369	1917	1.98	3320	494
432	4.66	1964	1012	4.15	1420	257
433	12.8	780	478	12.5	874	177
434	13.4	339	239	12.9	383	112
435	3.10	434	313	3.33	385	318

IC results obtained using HC column and borate–gluconate eluent.
[a]Bayer liquor samples diluted 200 × prior to analysis.

bility. The CE instrument allowed the application of either constant voltage, constant current or a patented combination of constant current/voltage termed "isomigration mode" [9]. The average migration time variation (% R.S.D.) for the oxalate peak, obtained from five replicates of a set of five liquor samples, was 3.690, 4.352, 2.242, 1.726 and 1.512 using constant-voltage, constant-current and isomigration settings of 1, 2 and 3, respectively. An isomigration value of 3 was used for all further work as this resulted in the least migration time variation. Fig. 3 shows an electropherogram of a 20-s hydrostatic injection of the standard solution containing chloride, sulfate and oxalate, while Fig. 4 shows an electropherogram of the same Bayer liquor sample shown in Fig. 2, again after a 200 × dilution. Table 1 also shows the results for chloride, sulfate and oxalate (reported as g/l disodium oxalate) in five Bayer liquor samples, obtained using the chromate electrolyte and indirect photometric detection at 254 nm.

3.3. Comparison of results

CE and IC can be considered complimentary analytical techniques for the determination of ionic solutes [3]. CE offers the advantages of increased separation efficiency with a selectivity

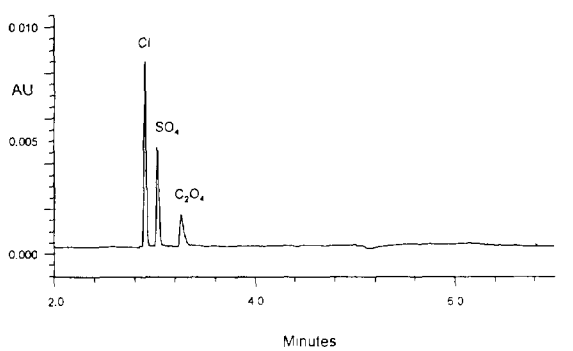

Fig. 3. Electropherogram of chloride, sulfate and oxalate standard obtained using CE with indirect photometric detection. Conditions: capillary, 60 cm × 75 μm fused silica; power supply, negative at 20 kV using isomigration value of 3; electrolyte, 5 m*M* chromate with 0.5 m*M* CIA-Pak OFM anion-BT at pH 8.0; injection, hydrostatic for 20 s; detection, indirect UV at 254 nm; solutes: chloride (10 ppm), sulfate (8 ppm), oxalate (5 ppm).

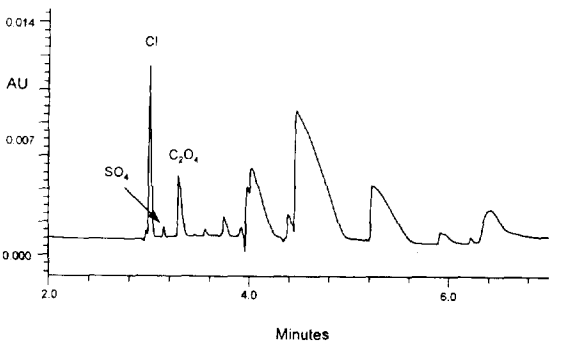

Fig. 4. Chromatogram of a typical Bayer liquor obtained using CE with indirect photometric detection. Conditions as for Fig. 3, except: sample preparation, 200 × dilution with water; solutes (injected concentrations): chloride (14.2 ppm), sulfate (0.8 ppm), oxalate (12.2 ppm).

which differs from IC. This selectivity proved to be particularly advantageous for the determination of oxalate, chloride and sulfate in Bayer liquors as all three peaks of interest were completely resolved from the matrix components. However, IC permits more stable retention times which subsequently makes automated peak identification and quantitation less prone to error. The absolute magnitude of the signal generated by IC was also significantly greater than that for CE, as shown by a comparison of the *y* axis scales for Fig. 1a and Fig. 3. As a result, detection limits obtained by IC are typically an order of magnitude lower than for CE.

Table 1 indicates that the results obtained for oxalate by IC using conductivity detection correlated reasonably well to those obtained using CE, not as well for chloride and very poorly for sulfate. Chloride accuracy was compromised by the adjacent unknown peak in IC, while sulfate co-eluted with succinate under all the chromatographic conditions investigated, leading to appreciably higher values than those obtained using CE. Table 1 also shows that the oxalate results obtained using CE were typically lower than the IC results, indicating the effect of the chromatographic interference which occurred with IC.

The precision of both techniques was then compared by analysing five liquor samples, obtained from a different site, five times each using both IC and CE. The results are shown in Table 2. Once again, the IC results were consistently

Table 2
Oxalate (g/l disodium oxalate) precision results (% R.S.D.) obtained from five replicate injections of Bayer liquor samples using IC and CE

Sample[a]	IC		CE	
	C_2O_4	R.S.D. (%)	C_2O_4	R.S.D. (%)
Liquor 1	1.78	3.13	1.62	0.97
Liquor 2	1.99	2.86	1.78	1.06
Liquor 6	2.49	2.33	2.29	1.78
Liquor 7	3.32	2.71	3.09	2.97
Liquor 8	4.61	3.13	3.72	1.76

IC results obtained using HR column and borate–gluconate eluent.
[a]Bayer liquor samples diluted 200 × prior to analysis.

higher than those obtained by CE, indicating the effect of the chromatographic interference with oxalate. Attempts to increase the separation of oxalate from the interferences by using an eluent of 1.2 m*M* carbonate–1.2 m*M* hydrogencarbonate with the HR column proved to be unsuccessful as the oxalate results were still consistently high. The CE gave improved precision, with an overall average of 1.71% R.S.D., compared to an overall average of 2.85% R.S.D. for IC. The precision of the IC results were perhaps not as good as would be expected for conventional HPLC, largely due to the difficulties associated with integrating the poorly shaped oxalate peak.

Perhaps the final advantage of CE for this analysis is the fact that the technique is also equally able to determine oxalate (plus chloride and sulfate) in "stabilised" liquor samples. Bayer liquors are frequently stabilised by the addition of ca. 3 m*M* tartaric acid [1]; however, this leads to a large peak which completely masks sulfate and significantly interferes with oxalate when using IC. All three solutes are completely resolved in the tartrate-stabilised liquor samples using CE.

4. Conclusions

The determination of oxalate in Bayer liquors appears to one of the few ion analysis applications where CE is clearly preferable to IC. Oxalate results obtained by IC were consistently higher than those for CE due to the presence of minor chromatographic interferences. The chloride and (particularly) sulfate results obtained by IC were subject to more severe chromatographic interferences, hence the simultaneous determination of oxalate, chloride and sulfate in Bayer liquors was not possible when using an anion-exchange separation with a borate–gluconate eluent and conductivity detection. Chloride and sulfate can be accurately determined in Bayer liquors by IC using a tartrate–boric acid eluent which discriminates against organic acid retention; however, this eluent does not permit oxalate analysis. Alternatively, the different selectivity of CE allowed for complete resolution of chloride, sulfate and oxalate from the matrix components in Bayer liquor using a relatively simple electrolyte, in a run time of less than 6 min. The electrophoretic technique gave improved precision for oxalate, with an overall average of 1.71% R.S.D., compared to an average of 2.85% R.S.D. for IC. A further advantage of CE is that it also allows the simultaneous determination of all three anions in tartaric acid-stabilised liquor samples.

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