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Short communication

Quantitative determination of oxalate in Bayer liquor by capillary zone electrophoresis
A validative study

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Abstract

The applicability of capillary zone electrophoresis (CZE) for the routine determination of oxalate in Bayer liquors was investigated. The effects of electrolyte composition, capillary conditioning, temperature and applied voltage were studied, with the use of temperature control, isomigration mode and an appropriate capillary conditioning regime proving critical in minimising variations in peak migration time. The CZE method, which utilised a chromate-based electrolyte (containing an osmotic flow modifier) and indirect photometry, demonstrated excellent within-batch precision, giving a migration time precision of less than 0.30% R.S.D. and an analysis precision of less than 1.2% R.S.D. The method also demonstrated excellent between-batch precision, with the overall analysis precision, obtained for five alumina refinery samples run over five days, being 2.3, 1.1, 1.7, 1.5 and 1.3% R.S.D., respectively. The between-batch migration time precision for the oxalate peak was 0.89% R.S.D., while the absolute oxalate peak area precision was 2.5% R.S.D. The method within- and between-batch precision values were comparable to those expected from other instrumental separation techniques, demonstrating that CZE can be an appropriate technique for routine analysis, even for complicated sample matrices, such as Bayer liquors.

Keywords: Bayer liquor; oxalate

1. Introduction

Alumina is extracted (and precipitated) from bauxite using hot sodium hydroxide *via* the cyclic Bayer process. Oxalate is the most important of the soluble impurities which accumulate in the process liquor stream, as its stability and removal controls refinery productivity [1]. Bayer liquor contains high levels of hydroxide, carbonate, aluminate, chloride and sulfate (as sodium co-anions), in addition to approximately 2–3.5 g/l of sodium oxalate and 20–30 g/l of total organic carbon, present as organic acid anions [2]. Oxalate is typically analysed in such a matrix using either gas chromatography (GC), after methylation, or ion chromatography (IC). Both techniques have disadvantages; GC requires lengthy sample preparation time, while IC suffers from organic acid interferences and short column (and suppressor) lifetimes [3].

Capillary zone electrophoresis (CZE) is becoming more widely accepted as an alternative separation approach to IC, particularly for the analysis of mixtures of inorganic anions and organic acids [4–7]. The feasibility of using CZE for the analysis of

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inorganic and organic acid components in Bayer liquor has been demonstrated previously [2,7], while the effects of matrix interferences on both IC and CZE analyses of oxalate in Bayer liquor have also been compared [3]. In this paper, the performance of CZE as a tool for the routine quantitation of oxalate in Bayer liquor is evaluated. The effects of operating parameters, such as electrolyte composition, capillary conditioning regime, temperature and applied voltage, were investigated in order to develop a rugged method for routine analysis. A number of liquor samples were run as a batch, with the process being repeated in a randomised sequence for five consecutive days, allowing the calculation of within-batch and between-batch precision data. The overall method precision data are presented, together with the advantages of CZE for this particular analysis.

2. Experimental

2.1. Instrumentation

The capillary electrophoresis instrument used was a Waters (Milford, MA, USA) Quanta 4000E with a Millennium 2010 Chromatography Management System. Data were collected at ten points per s. A polyimide-coated fused-silica capillary (obtained from Waters) measuring 60 cm total length (52 cm effective length)×75 μm I.D. was used throughout. A final electrolyte of 5 m*M* chromate containing an osmotic flow modifier (Waters CIA-Pak OFM anion-BT) at pH 8.0 was used at a negative voltage of 20 kV. Detection was carried out using indirect photometry at 254 nm with a detector time constant of 0.1 s. The capillary and the sample cabinet were maintained at a constant temperature of 25°C.

2.2. Reagents and procedures

Millipore (Bedford, MA, USA) Milli-Q 18 MΩ·cm water was used for the preparation of all electrolytes, samples and standards. Oxalic acid dihydrate (guaranteed-reagent grade) was obtained from Merck (Darmstadt, Germany) and sodium chromate tetrahydrate was obtained from Aldrich (Milwaukee, WI, USA). Electrolytes were prepared daily, filtered through a Millipore 0.45 μm HV filter and degassed in an ultrasonic bath before use. The samples were diluted 1:100 with Milli-Q water prior to hydrostatic injection.

3. Results and discussion

3.1. Preliminary investigations

Having previously established the feasibility of CZE [2], as well as having compared the effects of matrix interferences with both IC and CZE, for the determination of oxalate in Bayer liquor [3], the primary objective of this work was to investigate the performance of CZE for the routine determination of oxalate in samples from an alumina refinery. Five refinery samples were studied, including a synthetic liquor standard (matrix), a control liquor (control), two pregnant liquor samples (liquors 1 and 2) and a run-off lake water sample (lake). A chromate-based electrolyte was used with indirect UV detection, since this combination had previously been shown to generate good peak shape and sensitive detection for high-mobility anions [8,9]. Various separation conditions and electrolyte additives were investigated in order to maximise the precision and ruggedness of the analysis. The within-batch precision values for oxalate concentration, obtained using constant voltage and no temperature control, for electrolytes containing chromate and the osmotic flow modifier, in addition to either calcium, methanol, Waters Z1-Methyl (a protein de-coating reagent) or no additional modifiers, were 2.1, 3.8, 2.2 and 2.3% R.S.D., respectively. Consequently, a relatively simple electrolyte of 5.0 m*M* chromate with 0.5 m*M* CIA-Pak OFM anion-BT at pH 8.0 was used [10], since this gave comparable within-batch precision results to those for the more complicated electrolytes.

The use of an appropriate capillary conditioning regime was found to be critical for attaining reproducible migration times and peak areas. Several combinations of hydroxide, water and chromate electrolyte purges were studied, with an automated capillary conditioning regime of 0.1 *M* sodium hydroxide, followed by water and then electrolyte, for 1.0/1.0/2.0 min, respectively, proving the most appropriate. The manner in which the current and voltage were applied to the capillary also had a significant effect on the reproducibility of the oxalate migration time. The instrument used allowed the

application of either constant voltage, constant current or a patented combination of constant current/voltage termed "isomigration mode", designed to minimise variations in migration time arising from changes in the ionic strength of the sample [11]. The average migration time precision [R.S.D. (%)] for the oxalate peak, obtained from five replicates of a batch of the five samples, was 3.7, 4.4, 2.2, 1.7 and 1.5%, using constant voltage, constant current and isomigration settings of 1, 2 and 3, respectively. The values of 1, 2 and 3 represent the application of a constant current (20 μA) for intervals of 30, 60 and 120 s, respectively, before switching to a constant voltage of −20 kV. An isomigration value of three was used for all further work as this gave the best migration time precision. The capillary and the sample cabinet were maintained at a constant temperature of 25°C to further minimise migration time variations.

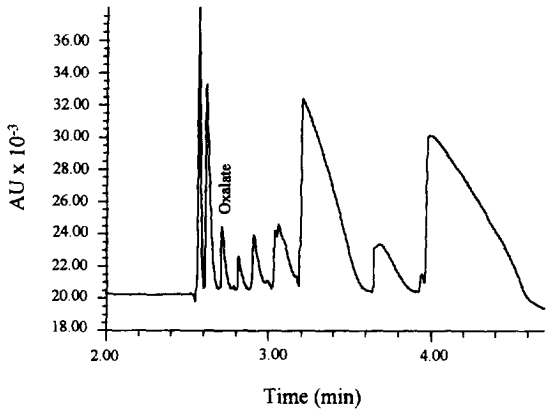

Fig. 1. Representative electropherogram of the Bayer liquor samples. Conditions: capillary, 60 cm×75 μm fused-silica; power supply, negative at 20 kV using an isomigration value of three; electrolyte, 5 m*M* chromate with 0.5 m*M* CIA-Pak OFM anion-BT at pH 8.0; injection, hydrostatic (raised to 10 cm and held for 20 s); detection, indirect UV at 254 nm; sample dilution, 1:100; oxalate concentration, 3.37 g/l in original sample.

3.2. Routine analysis

The protocol adopted for routine analysis involved running two oxalate standards (2.51 and 5.13 g/l of sodium oxalate) at the beginning and end of each batch of samples, with all four points and zero (origin) being used to generate the calibration curve. The sample batch consisted of the five sample types run five times each. Both the standards and samples were diluted 1:100 with Milli-Q water, prior to hydrostatic injection for 20 s. The process was repeated for five consecutive days, with the samples being run in a randomised sequence over the five days. A representative electropherogram for the liquor 1 sample is given in Fig. 1, which shows oxalate well resolved from the sample matrix components. Other peaks were not specifically identified, except that previous studies indicated that the first two peaks resulted from chloride and sulfate, respectively. The same automated data processing method was used to integrate and quantitate the oxalate peak in all the sample types, which was highly desirable in a method intended for routine analysis. Calibration curves generated using peak areas over the five days all showed correlation coefficients of $r^2>0.999$.

The CZE results obtained for all the samples demonstrated excellent within-batch precision, primarily as a result of the combination of temperature control, isomigration mode and an appropriate capillary conditioning regime. The within-batch precision data for oxalate migration time (and the mean values) for each of the five samples obtained over five days are summarised in Table 1. All the samples showed a within-batch migration time precision of less than 0.3% R.S.D. The within-batch precision data for the measured oxalate concentration (and the mean values) for each of the five samples obtained over five days are summarised in Table 2, with all the samples showing a within-batch precision of less than 1.2% R.S.D. The between-batch precision data for migration time, peak area, peak height and measured oxalate concentration for the five samples obtained over five days are summarised in Table 3. All five samples gave an overall precision for measured oxalate concentration of less than 2.5% R.S.D., which is comparable to values expected from other instrumental separation techniques, such as HPLC or GC [12].

4. Conclusions

CZE appears to be an appropriate technique for the routine determination of oxalate in Bayer liquors and similar alumina refinery samples. The CZE method can be fully automated, requires only a relatively simple electrolyte, has low operating and

Table 1
Within-batch precision for oxalate migration time for each of the five samples [RSD (%)]

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Overall
Matrix	0.29	0.08	0.10	0.14	0.06	0.13
Control	0.18	0.07	0.08	0.09	0.08	0.10
Liquor 1	0.11	0.01	0.04	0.06	0.10	0.06
Liquor 2	0.09	0.05	0.14	0.05	0.01	0.07
Lake	0.12	0.10	0.08	0.10	0.07	0.11

Table 2
Within-batch precision for oxalate concentration for each of the five samples [RSD (%)]

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Overall
Matrix	1.11	1.09	1.20	0.60	0.92	0.98
Control	0.53	0.63	0.52	0.37	0.60	0.53
Liquor 1	0.73	0.73	0.92	0.79	0.94	0.82
Liquor 2	0.70	0.66	0.60	0.82	0.41	0.64
Lake	0.50	0.43	0.24	0.54	0.31	0.40

Table 3
Between-batch precision values for each of the five samples [RSD (%)]

Sample	Migration time	Peak area	Peak height	Measured oxalate concentration
Matrix	0.78	2.61	5.12	2.29
Control	0.70	1.80	1.71	1.14
Liquor 1	0.99	2.00	1.52	1.71
Liquor 2	1.01	2.51	1.82	1.53
Lake	0.97	2.89	2.47	1.26

consumable costs and the sample turn-around time is less than 10 min. The use of temperature control, isomigration mode and an appropriate capillary conditioning regime were critical to the success of the method, in terms of minimising variation in migration times. The average within-batch precision values for oxalate migration time were less than 0.13% R.S.D. for all samples, whilst the average within-batch precision values for oxalate concentration were less than 0.98% R.S.D. for all samples. The CZE method also demonstrated excellent between-batch precision data for migration time, peak area, peak height and oxalate concentration, generating precision values comparable to those expected from other instrumental separation techniques.

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