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Applications of ion chromatography and capillary ion electrophoresis in the alumina and aluminium industry

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ABSTRACT

Applications of ion chromatography and capillary ion electrophoresis (Waters' trade name: Capillary Ion Analysis) for the determination of anionic solutes in the alumina/aluminium industry are presented. The use of ion chromatography for the determination of chloride and sulfate in alumina refinery liquors and for the analysis of fluoride in hydroxide fused samples from aluminium smelting environs is discussed. The results obtained are compared with traditional wet chemical methods of analysis. Capillary ion electrophoresis, a relatively new separation techniqe which has a different selectivity from ion chromatography, permits very rapid quantitation of oxalate in Bayer liquor, and the results from this methodology are compared to those obtained using capillary gas chromatography. The potential for other applications of these techniques in the alumina/aluminium industry will also be discussed.

INTRODUCTION

The analysis of ionic species is of great importance in alumina (aluminium hydroxide) production, which involves the extraction of alumina from bauxite via the Bayer process, and also in the subsequent electrolytic reduction of the alumina to form aluminium metal. Solutes of interest in these industries include inorganic anions such as fluoride, chloride, sulfate, phosphate and silicate, as well as organic acids such as oxalate, succinate, malonate, and a variety of short-chained carboxylic acids. These anions are typically analyzed by traditional wet chemical or spectroscopic techniques [1] in matrices ranging from process waters to very complex, high ionic strength solutions such as liquors from the Bayer process. Ion chromatography (IC) is now a well accepted analytical technique which is finding increased usage in industrial production management, process control and environmental monitoring, and offers considerable advantages over classical methods of anion analysis in terms of ease of use, speed, precision and accuracy [2]. In this paper, two complex applications of IC in the alumina and aluminium industry are presented; the analysis of chloride and sulfate in Bayer liquors and the determination of fluoride in environmental samples prepared by hydroxide fusion. The IC results are compared to those obtained by classical wet chemical methods [1,3].

Capillary ion electrophoresis (CIE) (Waters' trade name: Capillary Ion Analysis, CIA) is a recently introduced analytical technique for the determination of inorganic and organic anions which results in a different separation selectivity compared to that obtained by conventional anion exchange in ion chromatography. The different selectivity is particularly useful for the analysis of samples containing short-chained carboxylic acids in the presence of inorganic anions [4,5]. There are a number of additional advantages of this approach for the

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determination of anions, including very rapid analysis times, high separation efficiences (> 250 000 theoretical plates have been demonstrated using this approach) and only nanoliter sample volumes are required. The use of CIE for the determination of oxalate in Bayer liquor, certainly the most critical anion analysis in the alumina industry, is discussed; and the results are compred to those obtained by capillary gas chromatography. The possibility for other applications of both IC and CIE in the alumina and aluminium industry will also considered.

EXPERIMENTAL

Ion chromatographic system

The ion chromatograph consisted of a Waters Chromatography Division of Millipore (Milford, MA, USA) Action Analyzer, WISP 712 autoinjector, Model 431 conductivity detector and an 820 Maxima data station. A Waters Reagent Delivery Module (RDM) was added to the system for Solid Phase Reagent (SPR) conductivity detection. Three analytical columns from the Waters IC-Pak range were used: an IC-Pak Anion (50 × 4.6 mm I.D.), an IC-Pak Anion HC (150 × 4.6 mm I.D.) and an IC-Pak Ion Exclusion (300 × 7.8 mm I.D.) column.

Capillary ion electrophoresis system

The capillary electrophoresis instrument used was a Waters Quanta 4000 with a Waters 820 data station. Data were collected at 20 points per second with CIE. The separations were carried out using conventional fused-silica capillaries obtained from Waters. Detection was carried out using indirect photometry at 254 nm.

Reagents and procedures

Water (18 MΩ) purified using a Millipore Milli-Q Water Purification System (Bedford, MA, USA) was used for all solutions. Millitrap H^+ sample preparation cartridges were obtained from Waters and Maxi-clean IC H^+ solid-phase extraction cartridges were obtained from Alltech (Deerfield, IL, USA). Sodium tetraborate [analytical reagent (AR) grade], glycerin [laboratory reagent (LR) grade], tartaric acid (LR), lithium hydroxide (AR) and boric acid (AR) were obtained from Ajax Chemicals (Sydney, Australia), as were the analytical grade sodium salts used for the preparation of all the anion standards. Sodium gluconate (LR) was obtained from Fluka (Buchs, Switzerland). Acetonitrile, methanol and *n*-butanol (HPLC grade) were obtained from Waters. Sodium chromate tetrahydrate was obtained from Aldrich (Milwaukee, WI, USA). Oxalic acid dihydrate [guaranteed reagent (GR) grade] was obtained from Merck (Darmstadt, Germany). The electroosmotic flow modifier, CIA-Pak OFM anion-BT, and Z1-Methyl are proprietary chemicals obtained from Waters. Eluents and electrolytes were prepared daily, filtered and degassed with a Waters solvent clarification kit. Specific operating conditions are provided as captions to the figures.

RESULTS AND DISCUSSION

Analysis of chloride and sulfate in Bayer liquors by ion chromatography

The Bayer process involves the extraction and precipitation of alumina (aluminium hydroxide) from bauxite. The process uses hot sodium hydroxide extraction and is cyclic; hence, soluble impurities accumulate in the process liquor stream. Chloride and sulfate themselves do not exert any detrimental effects upon the Bayer process unless present at extreme concentrations, however, the sodium associated with each anion can cause significant problems with alumina refining chemistry. Increased sodium levels cause decreased stability of oxalate and increased difficulty of oxalate removal from the liquor, increased liquor viscosity and elevated boiling point [1]. Bayer liquor is a very complex matrix which can contain 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 25–30 g/l total organic carbon present as organic acid anions. The high ionic strength and pH, coupled with the fact that aluminium hydroxide is insoluble in the pH range of approximately 5–10, make this a challenging sample for analysis by ion chromatography. The poor solubility of aluminium hydroxide restricts the choice of eluents to those which are of very low pH, very high pH or those which keep the alumina soluble through complex formation. The poor solubility of alumina also complicates the use of suppressed ion chromatography [1] for this analysis as the aluminium hydroxide

can precipitate in the suppressor, reducing both its lifetime and efficiency.

Hydroxide was initially chosen as an eluent with a Waters IC-Pak Anion column and conductivity detection for the determination of chloride and sulfate in Bayer liquor. Apparently well resolved peaks for chloride and sulfate resulted when using this eluent, however the results obtained for the quantitation of sulfate by IC were consistently high compared to those by gravimetric analysis. Dilution of the eluent indicated that sulfate was co-eluting with divalent organic acids, such as succinate and oxalate. A weaker, complexing eluent (borate/gluconate) was then used for the analysis of the same sample. This mobile phase allowed resolution of sulfate from both succinate and oxalate; however, the extreme pH of the sample caused a system peak [6,7] which interfered with the quantitation of chloride. The chromatographic run time was also significantly increased. Tartrate/borate eluents are typically operated in the pH range 3–5 [8] and offer a considerable advantage for this analysis as their use strongly discriminates against the retention of organic acid anions. Both mono- and divalent organic acid anions elute at the void volume with tartrate/borate as a result of the low eluent pH and high boric acid concentration. Hence, this eluent is particularly suited to the analysis of chloride and sulfate in Bayer liquors and also for other samples such as soil and plant extracts. Fig. 1 shows a chromatogram of chloride and sulfate in a Bayer liquor sample using an eluent of 3.0 m*M* tartaric acid, 0.6 *M* boric acid and an IC-Pak Anion HC column with conductivity detection. The sample was diluted 1:1000 with 3 m*M* tartaric acid, filtered through 0.45-μm Millipore Millex durapore filter and passed through a Waters Millitrap cartridge in order to improve the baseline stability [9]. Table I shows comparative data for Bayer liquor analysis by IC and conventional wet chemical methods for 25 replicates of two different samples from each of three refinery sites. The % variation (at 1 σ) for each of the samples is given in brackets in the Table. The precision of the titrimetric method for chloride analysis was approximately 0.90% and the precision of the gravimetric method for sulfate analysis was approximately 2.55% at 1 σ. The results obtained using IC were similar to the conventional methods, with IC showing comparable precision for both chloride and sulfate, better accuracy for chloride (the titrimetric method overestimated chloride by approximately 3%) and the added advantage of significantly improved throughput for these analyses.

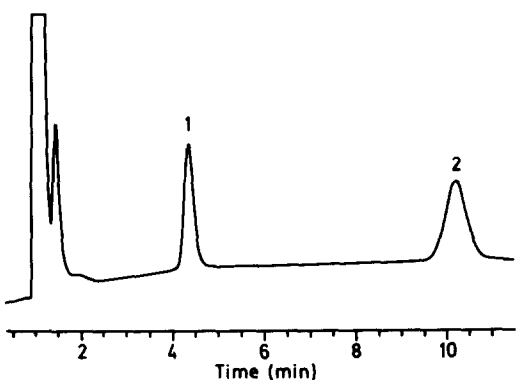

Fig. 1. Chromatogram of a Bayer liquor sample using a tartrate/borate eluent and conductivity detection. Conditions: column, Waters IC-Pak Anion HC; eluent, 3.0 m*M* tartaric acid, 0.6 *M* boric acid adjusted to pH 4.5 with hydroxide; flow-rate, 2.0 ml/min; injection volume, 100 μl; detection, conductivity; sample preparation, 1:1000 dilution with 3 m*M* tartaric acid, filtration through a Millex 0.45-μm durapore filter and passage through a Waters Millitrap H^+ cartridge. Solutes: 1 = chloride (31 ppm); 2 = sulfate (43 ppm).

Analysis of fluoride in aluminium refinery environmental samples by ion chromatography

Fluoride is a component of the electrolyte (cryolite) used in the electrolytic reduction of alumina to aluminium metal and can be released into the atmosphere as a result of the production process. Hence, the determination of fluoride in the environs of aluminium refineries is of great importance, considering the toxicity of this anion to both flora and fauna. Samples from refinery environs (such as water, soil, vegetation and even bones from carrion) are required to be analyzed for fluoride, although as yet no standardized method for sample preparation exists. The two current methods used for sample preparation prior to fluoride analysis are acid leaching or hydroxide fusion. All the samples for this work were prepared by hydroxide fusion prior to analysis by either ion chromatography or an autoanalyzer with on-line distillation and colourimetric determination after reaction with alizarin fluorine blue–lanthanum reagent [3].

Typically, the best ion chromatographic ap-

TABLE I

COMPARATIVE DATA FOR THE ANALYSIS OF CHLORIDE AND SULFATE IN BAYER LIQUORS BY ION CHROMATOGRAPHY AND CONVENTIONAL METHODS

The precision of the titrimetric method for chloride analysis and the gravimetric method for sulfate analysis was approximately 0.90% and 2.55%, respectively.

Sample	Cl (g/l) (% variation)		SO_4 (g/l) (% variation)	
	IC (n = 25)	Titrimetric	IC (n = 25)	Gravimetric
Refinery 1-a	12.9 (1.8)	13.4	23.9 (1.6)	21.4
Refinery 1-b	14.6 (2.1)	15.1	25.7 (2.2)	25.7
Refinery 2-a	14.8 (1.1)	14.5	30.4 (1.8)	30.7
Refinery 2-b	17.2 (2.6)	17.6	35.4 (1.7)	35.9
Refinery 3-a	16.7 (2.1)	17.3	14.8 (2.7)	15.4
Refinery 3-b	18.4 (1.6)	18.6	16.3 (2.7)	17.2

proach for the analysis of fluoride in high ionic strength samples is based on an ion-exclusion separation [10]. A Waters IC-Pak ion-exclusion column was initially used with a camphorsulfonic acid eluent and conductivity detection for the determination of fluoride in the hydroxide fused samples. Fig. 2 shows a chromatogram of fluoride in a forage vegetation sample after being ashed, fused with 1.5 *M* hydroxide, diluted 5× and passed through a 0.45-μm Millex durapore filter. The fluoride peak was well resolved from the large void disturbance despite the direct injection of 0.3 *M* hydroxide into

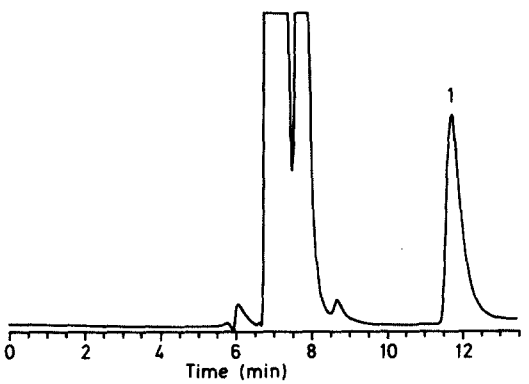

Fig. 2. Chromatogram of a forage vegetation sample using a camphorsulfonic acid eluent and an ion-exclusion separation. Conditions: column, Waters IC-Pak Ion Exclusion; eluent, 2.0 m*M* camphorsulfonic acid; flow-rate, 1.0 ml/min; injection volume, 100 μl; detection, conductivity; sample preparation, ashing, hydroxide fusion, 1:5 dilution with water: Solute: 1 = fluoride (34 ppm).

the chromatographic system. However, a problem occurred with this analysis as a result of the high silica (up to 40% w/w) levels in the soil and plant fusion samples. After approximately 40 sample injections, the fluoride peak response started to decrease and the calibration curve became non-linear. This decreased response was found to occur as a result of silica build-up on the ion-exclusion column. While the column could be regenerated by washing with strong acid then water overnight to restore the fluoride response to that of a new column, this approach was obviously of limited utility.

The next approach studied was to use an ion-exchange separation with conductivity detection, however the 1.5 *M* hydroxide in the fused sample required much larger sample dilutions than was necessary when using an ion-exclusion separation in order to resolve the weakly retained fluoride peak from the large void disturbance. A borate mobile phase was initially used but the large sample dilution meant that the fluoride concentration in the final sample diluent was frequently below the detection limit of this approach. Solid-phase reagent conductivity detection was then investigated as this detection technique has been shown to permit a high degree of sample matrix independence [11,12]. Hydroxide, borate and carbonate/bicarbonate mobile phases are applicable for use with this detection method, with the latter giving the best separation selectivity for this application. The calibration curve obtained using this eluent and detection method was linear in the range of 0.01 to 5 ppm

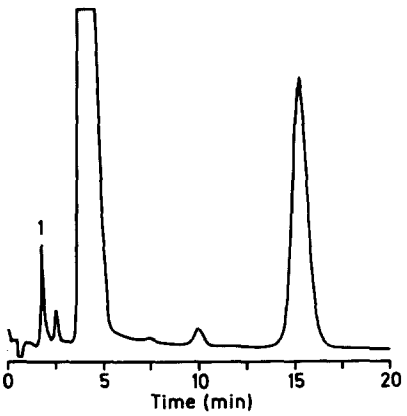

Fig. 3. Chromatogram of a forage vegetation sample using a carbonate/bicarbonate eluent and an ion-exchange separation with solid-phase reagent conductivity detection. Conditions: column, Waters IC-Pak Anion; eluent, 1.2 m*M* carbonate, 1.2 m*M* bicabonate; flow-rate, 1.2 ml/min; injection volume, 100 μl; detection, SPR-conductivity at 0.8 ml/min; sample preparation, ashing, hydroxide fusion, 1:50 dilution with water then 2 ml through a Maxi-clean H^+ cartridge with the first 0.5 ml discarded to waste. Solute: 1 = fluoride (0.4 ppm).

fluoride. A Millitrap H^+ cartridge was used to neutralize the fused sample in order to further decrease the magnitude of the void peak, however the silica in the samples eventually bound to ion-exchange fiber in the cartridge resulting in decreased fluoride recoveries. Maxi-clean H^+ cartridges proved more appropriate for this particular application as they are single use devices, unlike the Millitrap H^+ cartridge; consequently, they did not have problems with silica build-up. Fig. 3 shows a chromatogram of fluoride in a fused forage vegetation sample after a 50× dilution and passage through a Maxi-clean H^+ cartridge using a carbonate/bicarbonate eluent, a Waters IC-Pak Anion column with solid phase reagent conductivity detection. Quantitative recoveries (90–105%) were obtained for samples spiked with fluoride and Table II shows the reproducibility for three vegetation samples, each passed through three separate cartridges. The agreement between the results obtained by ion chromatography and the autoanalyzer method are shown in Table III. The correlation between the two methods was only fair and this probably occured as a result of the two methods performing slightly different analyses. The autoanalyzer, with on-line distillation, determines the "total" fluoride while ion chromatography only determines "free" fluoride in the fused sample, hence some difference between the results is not surprising. Ion chromatography could be expected to give better correlation with the autoanalyzer method if the samples were prepared using an acid leach rather than hydroxide fusion, as the acid leach only extracts free fluoride. The ion chromatographic and autoanalyzer methods showed very good correla-

TABLE II

REPRODUCIBILITY OF FLUORIDE QUANTITATION WITH MAXI-CLEAN IC H^+ SPE CARTRIDGES

Sample No.	Fluoride concentration (ppm after 50× sample dilution)
42	0.211
42	0.213
42	0.239
Average ± R.S.D.[a]	0.221 ± 7.2%
H	0.196
H	0.168
H	0.188
Average ± R.S.D.	0.182 ± 9.7%
56	0.668
56	0.680
56	0.679
Average ± R.S.D.	0.670 ± 1.0%

[a] R.S.D. = relative standard deviation.

TABLE III

COMPARATIVE DATA FOR THE ANALYSIS OF FLUORIDE IN VEGETATION AND WATER BY ION CHROMATOGRAPHY AND AUTOANALYZER

Sample		Ion chromatography (ppm fluoride)	Autoanalyzer (ppm fluoride)
Vegetation	1	244	210
	2	253	250
	3	177	185
	4	321	395
	5	78	75
Water	1	0.07	<0.1
	2	3.5	3.6
	3	3.4	3.6
	4	0.4	0.4
	5	0.9	0.8

tion for water samples, where the fluoride was only present as the free anion.

Analysis of oxalate in Bayer liquors by capillary ion electrophoresis

Capillary ion electrophoresis is a relatively new separation technique which utilizes narrow diameter capillaries (typically polyimide-coated, 25–100 μm fused silica) to separate ionic solutes according to their mobility under the influence of an applied potential (usually 10–30 kV). The separation of inorganic anions and low-molecular-weight organic acids by capillary ion electrophoresis (also termed Capillary Ion Analysis) offers a totally different separation selectivity compared to that obtained using conventional anion exchange in ion chromatography [4]. The selectivity of CIE is particularly advantageous for the determination of oxalate in Bayer liquors, which, as discussed previously, are a strongly alkaline matrix containing very high levels of both inorganic anions and organic acids. The mobility of oxalate is intermediate between the very mobile inorganic anions in the sample, such as chloride and sulfate, and the less mobile organic acids, such as succinate and acetate, hence the peak is well resolved from the other components in Bayer liquor.

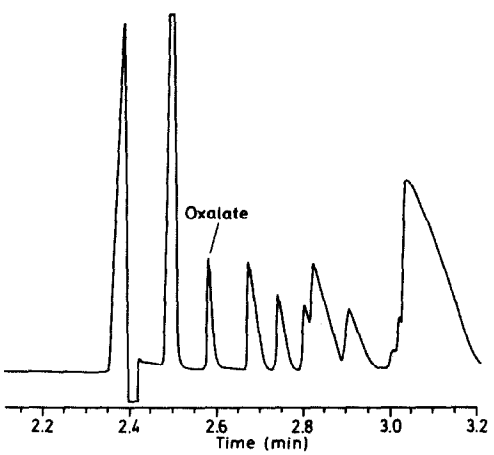

Fig. 4. Electropherogram of oxalate in a Bayer liquor sample obtained by CIE using optimized conditions. Conditions: capillary, 60 cm × 75 μm I.D. fused silica; power supply, negative at 20 kV; electrolyte, 5 m*M* chromate, 2.5 m*M* CIA-Pak OFM anion-BT, 5% (v/v) methanol, 1.0 *M* Z1-Methyl at pH 10.5; injection, hydrostatic for 45 s; detection, indirect UV at 254 nm; sample preparation, 1:200 dilution with water. Solute: oxalate (approximately 10 ppm).

A variety of different conditions, such as capillary diameter and length, electrolyte composition, running voltage, sample dilution and injection time were investigated in order to optimize the analysis of oxalate by CIE. The use of a 60 cm × 50 μm I.D. capillary gave better resolution of oxalate from the other peaks in the sample matrix than did a 60 cm × 75 μm I.D. capillary, however the response for the oxalate peak was less and the area precision was poor compared to that obtained when using the 75-μm capillary. The use of 100 cm x 75 μm I.D. capillary gave improved resolution when compared to a 60-cm capillary, although run times were significantly longer with a 100-cm capillary. The electrolyte used for the analysis of high-mobility anions in CIE typically contains 5 m*M* chromate and 0.5 m*M* CIA-Pak OFM anion-BT at a pH of 8.0 [4], however adjusting the electrolyte pH to 10.5 and adding 5% methanol and 1.0 *M* Z1-Methyl (a zwitterionic reagent used to prevent the adsorption of charged macromolecules to the capillary wall) improved the baseline noise and reproducibility of the oxalate analysis. Fig. 4 shows an electropherogram of oxalate in a Bayer liquor sample obtained by CIE using the optimized conditions. The two large peaks migrating before oxalate are chloride and sulfate, respectively, while the later migrating peaks are organic acids such as tartrate, succinate and acetate. This separation demonstrates several advantages of CIE in comparison to IC. CIE is a very matrix independent technique, *e.g.*, cations do not participate in the separation since they travel in the opposite direction to the anions and neutral solutes are carried along by the electroosmotic flow and have appreciably longer migration times than ionic solutes. The neutral solutes and late migrating anionic species can simply be purged from the capillary once the desired separation is obtained and so no "void" peak appears in the electropherogram. The high pH of the sample did not create any problems as hydroxide is the most mobile anion and migrates well resolved from all other ionic solutes, which is not the case for most ion chromatographic separations. No sample pretreatment other than dilution in water was necessary and the run time was less than 5 min. Between samples, the capillary can be purged with hydroxide, water and then electrolyte to re-

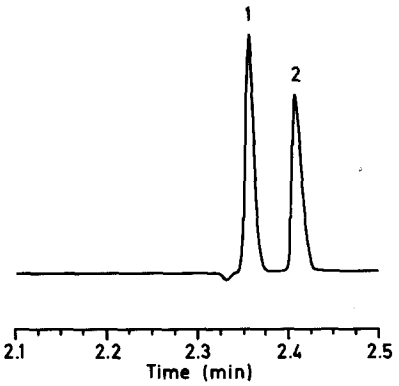

Fig. 5. Electrophetogram of chloride and sulfate in Bayer liquor obtained by CIE using standard conditions. Conditions as for Fig. 4 except: electrolyte, 5 m*M* chromate, 0.5 m*M* CIA-Pak OFM anion-BT; injection, hydrostatic for 30 s; sample preparation, 1:100 dilution with water. Solute: 1 = chloride, 2 = sulfate.

move any solutes which may adhere to the charged capillary walls ensuring a reproducible capillary surface, hence stable migration times.

The best results obtained for the replicate analysis of oxalate in a typical Bayer liquor sample were 2.87 g/l (at 0.38% R.S.D.) and 2.92 g/l (at 0.30% R.S.D.) using external and standard addition calibration respectively; compared to 2.70 g/l (at 0.74% R.S.D.) by capillary gas chromatographic analysis for the same sample. The batch precision is more typically in the order of 1% R.S.D. and present investigations centre upon determining the long term precision of the CIE method for oxalate analysis and the determination of other species in the liquor. Fig. 5 shows an electropherogram, obtained using the standard CIE conditions for the analysis of high mobility anions (chloride and sulfate) in a Bayer liquor sample. The precision for this analysis by CIE is very similar to that obtained by IC, however the run time is less than 3 min compared to 12 min when using ion chromatography.

CONCLUSIONS

Both ion chromatography and capillary ion electrophoresis offer practical, alternative analytical methods for the analysis of chloride, sulfate and oxalate in alumina refinery liquors. Ion chromatography shows comparable precision (*ca.* 2% for chloride and 3% for sulfate at one σ) to titrimetric and gravimetric methods for the analysis of chloride and sulfate respectively in Bayer liquors, with better accuracy for chloride and significantly improved throughput for these analyses. The selectivity of capillary ion electrophoresis is particularly appropriate for the determination of oxalate in Bayer liquor. Optimization of conditions such as capillary dimensions, electrolyte composition, running voltage, sample injection and dilution permit a within batch precision of less than 1% R.S.D. for oxalate in Bayer liquor. The results obtained by CIE showed reasonable agreement to those obtained by the significantly more complex and time consuming derivatization capillary gas chromatographic method. The combination of an ion-exchange separation, carbonate/bicarbonate eluent with solid phase reagent conductivity detection and sample clean-up using a Maxi-clean IC H^+ cartridge allows the ion chromatographic determination of fluoride in hydroxide fused soil and plant samples from aluminium refinery environs. The results obtained by ion chromatography showed only fair agreement to those from an autoanalyzer, although ion chromatography could be expected to give very similar results to the autoanalyzer method if the samples were prepared using the more conventional approach of acid leaching rather than hydroxide fusion. Both ion chromatography and capillary ion electrophoresis show great potential for further applications in the aluminium/alumina industries and future work involves determining the long term precision of the oxalate analysis and the quantitation of other species, such as chloride, sulfate, fluoride and additional organic acids in Bayer liquors by CIE.

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