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Short Communication

Analysis of fluoride, acetate and formate in Bayer liquors by ion chromatography

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Abstract

Fluoride, acetate and formate in Bayer liquors have been separated on an AS5A column by suppressed ion chromatography using a very weak sodium hydroxide eluent before a rapid change in the eluent composition was required to elute the remaining liquor components. Fluoride data for four liquor samples analysed by ion chromatography with conductivity detection correlated well with potentiometric data obtained by a fluoride ion-selective electrode. Acetate and formate were analysed by conductivity and spectrophotometric detection and reasonable agreement was achieved.

1. Introduction

Bauxite used to produce pure alumina in the Bayer process contains quantities of chloride, fluoride, sulfate, phosphate, organic matter and traces of many metals. The organic matter is oxidised progressively to oxalate within the process liquors and this, along with the soluble components, accumulates in the liquors. Many of these components require constant monitoring of the liquors as the purity and yield of the final product may be affected adversely [1].

Currently in the aluminium industry, fluoride is assayed quantitatively using a fluoride ion-selective electrode (ISE). An ionic strength adjustment buffer allows the ISE potential to be correlated directly to concentration rather than to the activity of the analyte by ensuring a constant ionic strength for each solution. These buffers also adjust the sample pH to ca. 5 or 8.5 (depending upon the particular buffer) to eliminate hydroxide ion interference in the fluoride ISE measurements at room temperature. Ionic strength adjustment buffers also contain a complexing agent, although some conjecture exists as to which particular complexing agent should be employed [2]. These reagents complex aluminium and iron(III) in particular, releasing any fluoride bound to these metals [3,4]. The choice of buffer is dependent on the interfering components and the aluminium levels in the sample.

Although the potentiometric procedure is quite reliable, ion chromatography (IC) [5] is a more useful technique because anions such as fluoride, chloride, sulfate and phosphate, as well as organic acids including oxalate and tartrate, can be analysed simultaneously and, after optimal conditions for peak separation have been obtained, with minimal user intervention.

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regarding chloride, phosphate, sulfate and oxalate analysis in Bayer liquors using IC with conductivity detection [6–8], but the chromatographic analysis of fluoride in these liquors has not been reported presumably because of interference from early-eluting organic acids present in the liquor sample. This paper describes the development of an elution program for the separation of fluoride from early-eluting organic acids and the application of this program to the analysis of some Bayer liquors in order to explain the discrepancy in fluoride levels determined by potentiometry and chromatography.

2. Experimental

2.1. Ionic strength adjustment buffers

The following buffers were prepared fresh before use.

Citrate buffer (pH 8.9). Citric acid monohydrate (60 g), sodium citrate dihydrate (210 g), ammonium chloride (53.5 g) and ammonia solution (67 ml) were made up to 1 l in deionised water.

TISAB IV (pH 8.8). Concentrated hydrochloric acid (84 ml), TRIZMA base (Tris; Sigma, St. Louis, MO, USA; 242 g) and sodium tartrate dihydrate (230 g) were made up to 1 l in deionised water.

Modified TISAB IV (pH 8.0). As for TISAB IV above, but 150 ml concentrated hydrochloric acid was added.

All glassware was soaked in caustic detergent (Pyroneg, Diversey) and rinsed thoroughly with deionised water before use. All solutions were prepared using deionised NANOpure water purified on a Sybron/Barnstead filtration system.

2.2. Fluoride standards

A 1000 mg/l fluoride stock solution was prepared from anhydrous sodium fluoride and transferred immediately to a polyethylene container for storage. Fresh standards, 10 mg/l or below, were prepared weekly.

2.3. Sodium hydroxide eluents

A 50% (w/v) stock solution of NaOH was prepared and allowed to stand in a closed polypropylene container for about 48 h until insoluble sodium carbonate had settled. Eluents 200 and 0.75 m*M* sodium hydroxide were prepared daily by adding the necessary volume of 50% (w/v) NaOH stock solution to deoxygenated water. Before starting a series of chromatographic runs, the eluents were sparged with helium for ca. 15 min each day to prevent possible carbonate contamination.

2.4. Samples

Two spent liquors (samples 1 and 2) and two pregnant liquors (samples 3 and 4) were available for analysis.

2.5. Instrumentation

Chromatography was carried out on a Dionex 4500i ion chromatograph fitted with an AS5A column (150 × 5 mm), an AG5A guard column (50 × 5 mm) and an AMMS micromembrane suppressor. IC data were acquired and stored using a WYSE ECM 5400 personal computer and DAPA Chromatography System VI.40 software. Detection of fluoride, formate and acetate was achieved on the Dionex conductivity detector and detection of formate and acetate was performed on a Hewlett-Packard 1050 spectrophotometric detector at 200 nm.

For ISE fluoride determinations, an Orion EA-940 expandable ion analyser was used in conjunction with an Orion 94-09 fluoride ISE and an Orion 90-02 double-junction reference electrode. Measurements of pH were made using an Orion research microprocessor Ionalyzer Model 901 digital pH/mV meter in conjunction with an Activon combination pH (glass/calomel) electrode.

2.6. Determination of fluoride by potentiometry

Equal volumes of an ionic strength adjustment buffer and a standard (or sample) were mixed. The potential for each mixture was measured and a calibration curve of potential versus log concentration of fluoride was plotted. Spent liquors and pregnant liquors were diluted to yield fluoride concentrations in the 10-100 mg/l region and to dilute the aluminate concentration, thus reducing possible aluminium interference [4,9].

2.7. Determination of fluoride, formate and acetate by IC

For the determination of fluoride, formate and acetate the calibration graph method was used. Spent liquors were diluted by a factor of at least 1000 and pregnant liquors by a factor of at least 400. Recalibrations were performed regularly; a stable temperature is essential as fluctuations throughout the day affect reproducibility of peak areas.

The IC elution program developed for resolution of fluoride, acetate and formate at a flow-rate of 1 ml/min using two eluents, eluent 1 (0.75 m*M* NaOH) and eluent 2 (200 m*M* NaOH), was as follows: 0–6.0 min, 100% eluent 1; 6.0–6.5 min, linear gradient to eluent 1–eluent 2 (50:50); 6.5–13.5 min, eluent 1–eluent 2 (50:50); 13.5–14.0 min, linear gradient down to 100% eluent 1; 14.0–33.0 min, 100% eluent 1. The initial isocratic conditions (until 6 min) permitted the elution and resolution of fluoride, acetate and formate. The increase in eluent strength beyond 6 min ensured rapid elution of other components of the liquor before the column was re-equilibrated in preparation for the next injection.

Continuous regeneration of the AMMS suppressor was achieved using 20 m*M* sulfuric acid at a flow-rate of ca. 10 ml/min. For these particular samples containing a high aluminium content, it is necessary to flush the AMMS regularly with a strongly acidic reagent (1 *M* HCl) otherwise precipitation of $Al(OH)_3$ may result.

3. Results and discussion

3.1. Determination of fluoride by potentiometry

For the determination of fluoride in Bayer liquors, the currently adopted industrial method of analysis involves the calibration graph method using a fluoride ISE. A high-pH buffer is required in order to decrease potential aluminium interference and to ensure the buffer capacity is sufficiently strong to cater for the highly caustic liquors [9]. Three high-pH buffers examined in this work were a citrate buffer (pH 8.9), TISAB IV (pH 8.8) and modified TISAB IV (pH 8.0).

Nicholson and Duff [4] recommended that a complexing time of at least 20 min and preferably 24 h should be used with TISAB buffers before measurement of the electrode potential in fluoride analysis. They observed an initial rapid potential change due to the release of fluoride arising from complexation of the aluminium, thus supporting the need to delay the measurement for 20 min. In the present work, complexing time dependence studies were carried out on two of the Bayer liquor samples by taking measurements at various intervals from 3 min to 24 h after addition of one of the above buffers. In the case of the citrate buffer, the measured fluoride concentration increased slightly and remained constant after about 2 h. No significant differences in the fluoride concentration were found for the TISAB buffers after 3 min and there seemed to be no improvement in the detection range using the pH 8.0 buffer. All subsequent measurements were taken 5 min after addition of TISAB IV (pH 8.8) buffer.

A calibration plot for a series of standards was found to be linear over the range 10–1000 mg/l fluoride. Recovery studies were conducted by addition of known amounts of fluoride to previously analysed liquor samples and, in all cases, recoveries of 100% were obtained.

3.2. Fluoride by IC

Using 35 m*M* NaOH as eluent, the fluoride peak at ca. 1.3 min in the chromatogram of a dilute liquor sample was found to be relatively unsymmetrical, which suggested that other solutes were co-eluting with fluoride. Furthermore, initial quantitation of the nominated fluoride peak yielded a fluoride concentration at least four times that obtained by potentiometric measurements. Fig. 1 shows a typical chromatogram obtained with an elution program which commences with 0.75 m*M* NaOH to separate three components which co-elute with the eluent used in the preliminary studies above. The elution program includes a rapid change to a stronger eluent to elute more strongly retained components of the liquors and these are observed in Fig. 1 at retention times greater than 8 min.

Small organic acids such as acetic, formic and gluconic are often present in Bayer liquors [1] and these acids are well known to elute very early in IC. The co-elution of these species with fluoride using 35 m*M* NaOH was highly likely. Under the conditions employed in Fig. 1, spiking of the sample suggests that the first peak at 3.8 min is fluoride, the second peak at 5.0 min is acetate and the third peak at 7.2 min is formate. However, further confirmation of these assignments is presented later in the paper.

The fluoride peak in the chromatogram of a liquor sample displays noticeable band broadening compared to that in a standard, but the effect does not extend so prominently to the acetate and formate peaks. One explanation for this discrepancy may be a matrix effect because the standards are prepared in deionised water of pH $\approx$ 5 and the diluted liquor is pH $\approx$ 11. Injection of a standard results in direct adsorption of fluoride and elution with the 0.75 m*M* NaOH eluent (pH $\approx$ 10.8) whereas the pH of a liquor sample is slightly higher than that of the eluent and hence there may be some preliminary elution of fluoride which appears as band broadening. An alternative explanation for the apparent band broadening of the liquor sample is that band compression may be occurring on the column after injection of a standard of low ionic strength but it may be absent in the samples which have high ionic strength.

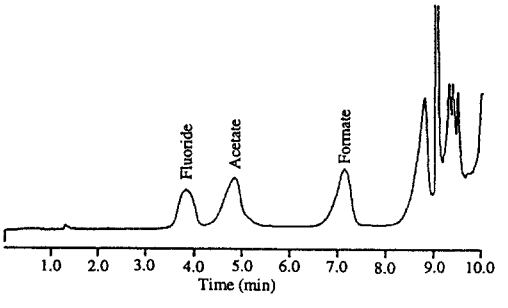

Fig. 1. Ion chromatogram of diluted sample 2 (spent liquor). Elution program as in Experimental section; flow-rate, 1 ml/min; column, Dionex AS5A (150 × 5 mm); guard column, AG5A (50 × 5 mm); sample loop, 25 μl; conductivity detector sensitivity, 100 μS.

Calibration plots of peak area vs. fluoride concentration were more reliable than peak height plots and they were linear over the range 1–4 mg/l fluoride. IC and ISE data for fluoride in four samples are presented in Table 1; the linear regression equation for these data is $y = 0.993x + 4.01$, with $r = 0.999$, which indicates excellent agreement between these two sets of data. The precision of ISE measurements (0.9–1.9%) is slightly better than the IC precision (1.3–3.2%), although the latter is quite acceptable for Bayer liquor analysis [6].

3.3. Determination of acetate and formate by IC

The carboxylate functional groups of carboxylic acids are known to absorb in the low 200 nm region [10,11], as do their conjugate bases COO^-. However, molar absorption coefficients are extremely low and detection of these species at low concentrations would be difficult [10]. UV detection was attempted by connecting a spectrophotometric detector directly to the outlet of the conductivity detector with a minimum length of connection tubing to minimise dispersion. This approach revealed two peaks at similar retention times to those observed for peaks 2 and 3 by conductivity detection and this supports their assignment as acetate and formate. As fluoride does not absorb at 200 nm, the absence of a peak

Table 1
Bayer liquor fluoride concentrations obtained by IC–conductivity detection and ISE potentiometry

Sample	IC		ISE	
	mg/l	R.S.D. (%)	mg/l	R.S.D. (%)
1	920	3.2 ($n = 38$)	930	0.9 ($n = 12$)
2	1550	1.4 ($n = 18$)	1540	0.7 ($n = 13$)
3	180	2.6 ($n = 16$)	180	1.8 ($n = 8$)
4	330	2.1 ($n = 14$)	330	1.8 ($n = 8$)

Chromatographic conditions as in Fig. 1. In potentiometry, electrode potentials were taken 5 min after addition of TISAB IV (pH 8.8) buffer.

Table 2
Acetate and formate in Bayer liquors obtained by IC–conductimetric and spectrophotometric detection

Sample	Acetate (mg/l)		Formate (mg/l)	
	UV	Conductivity	UV	Conductivity
1	18 700	19 600	6400	6300
R.S.D. (%, $n = 17$)	2.7	2.3	3.3	2.7
2	21 000	21 600	7500	6800
R.S.D. (%, $n = 10$)	2.6	2.9	4.1	2.4

Chromatographic conditions as in Fig. 1.

close to 3.8 min is consistent with its assignment as fluoride by conductivity detection.

The calibration plot for acetate was linear over the range 0–20 mg/l using conductivity detection and linear over the range 0–40 mg/l by UV detection. The plot for formate was linear over the range 0–5 mg/l by conductivity detection and linear over the range 0–20 mg/l by UV detection. The IC analytical data for acetate and formate in samples 1 and 2 by UV and conductivity detection appear in Table 2. There is good agreement in the data derived from the two different modes of detection and either of the two detection methods is recommended for the analysis of acetate and/or formate in Bayer liquors.

4. Conclusions

The main development in this paper was the successful analysis of fluoride in Bayer liquors by suppressed IC. An elution program was devised to separate fluoride from acetate and formate. The fluoride data correlated well with ISE measurements and the acetate and formate data showed good agreement with on-line UV spectrophotometric data. ISE studies also revealed TISAB IV as the most appropriate buffer for potentiometric analysis of fluoride in Bayer liquors.

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