

# Determination of Oxalate and Other Anions in Bayer Liquor Using Ion Chromatography

## **INTRODUCTION**

The Bayer Process is used to isolate alumina ( $\text{Al}_2\text{O}_3$ ) from bauxite. In this process, the manufacturer dissolves bauxite in sodium hydroxide to extract the aluminum from other components which are not soluble in sodium hydroxide, mainly oxides.<sup>1</sup> The solution is referred to as Bayer liquor, and the temperature of this process depends on the mineral composition of the bauxite. The next steps precipitate aluminum hydroxide [ $\text{Al}(\text{OH})_3$ ] that is used to form alumina, which is used in the aluminum smelting process. Alumina is formed by placing  $\text{Al}(\text{OH})_3$  crystals in a kiln and driving off the water, a process referred to as calcination.

Many variables determine the success of calcination to form alumina, and one is the size of the  $\text{Al}(\text{OH})_3$  crystals. Large crystals are preferred, and after precipitation only the large crystals are put into the kiln for calcination. Small crystals are returned to the precipitator. Oxalate can interfere with crystal

formation, and therefore a measurement of the oxalate concentration helps predict the success of forming large crystals from a given Bayer liquor.

Ion chromatography (IC) is the method of choice for determining oxalate as well as other organic acids and inorganic anions in Bayer liquor, though the sample's high ionic strength and metal content make it a challenging sample. To address these challenges, a direct injection method was designed using a Reagent-Free™ Ion Chromatography (RFIC™) system with in-line sample cleanup to accurately and reproducibly measure oxalate in Bayer liquor. The online sample preparation removes most of the aluminum so that it does not contaminate either the column or suppressor. The remaining aluminum oxalate retained by the preparation devices is recovered by rinsing with a small volume of sodium fluoride. Fluoride is used to promote ligand exchange with oxalate for aluminum. This online sample preparation method allows an accurate, reproducible, and rugged determination of oxalate in Bayer liquor.

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## **EQUIPMENT**

Dionex ICS-2000 or ICS-3000 RFIC system  
AS40 or AS autosampler  
CIRA 11AXCS Electrolytic Purifier (Troviion, P/N 591218)  
CIRA installation kit (Troviion, P/N 591250)  
PC-100 Pump Controller (Troviion, P/N 590100) consisting of a 2-channel peristaltic pump and 3-way selection valve  
1 L plastic container (P/N 063291)  
4 L plastic container (P/N 063292)  
Chromeleon® 6.8 Chromatography Data System

### **For ICS-2000:**

IonPrep Controller (Troviion, P/N 591320) consisting of a 10-port valve and constant current power supply

### **For ICS-3000:**

AM Automation Manager (P/N 061736) consisting of a 10-port valve and a 3-way valve  
PS-50 Power Controller (Troviion, P/N 590050)

## **REAGENTS AND STANDARDS**

Deionized water (DI), Type I reagent grade, 18 MΩ-cm resistivity.  
Sodium chloride (NaCl)  
Malonic acid [CH<sub>2</sub>(COOH)<sub>2</sub>]  
Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>)  
Sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)  
Sodium fluoride (NaF)  
All compounds should be ACS reagent grade or better from reliable sources.

## **CONDITIONS**

Guard Column: IonPac® AG17, 4 × 50 mm (P/N 055684)  
Analytical Column: IonPac AS17, 4 × 250 mm (P/N 055682)  
Trap Column: IonPac UTAC LP1 (P/N 063079)  
Eluent Source: EGC II KOH cartridge (P/N 058900) with CR-ATC (P/N 060477)

### Eluent Concentration:

Time (min)	KOH conc (mM)
-7.0	6
0.0	6
3.0	6
5.0	14
8.0	14
12.0	30
12.1	50
17.9	50
18.0	6

Flow Rate: 1.0 mL/min  
Inj. Volume: 10 μL  
Temperature: 30 °C  
Pressure: 2100 psi  
Detection: Suppressed conductivity, ASRS® 300 suppressor, external water mode, 124 mA

## PREPARATION OF SOLUTIONS AND STANDARDS

### Eluent Solution

The eluent generator (EG) produces the eluent using the EluGen® EGC II KOH cartridge and deionized water supplied by the pump. The eluent concentration is controlled by Chromeleon software. Because the IonPac AS17 column set does not produce 2000 psi of backpressure, backpressure tubing must be added to achieve the 2100–2200 psi backpressure that will allow the EG degasser to function properly.

### 0.1% Sodium Fluoride

Dissolve 1 g of NaF in 1000 mL of deionized water. Place the solution in a 1 L plastic container.

### Standard Solutions

#### Stock Standards

Prepare 1000 mg/L standards for each of the anions and organic acids in DI water. Standards should be prepared from the highest purity compounds available. Table 1 provides the amounts needed to prepare 100 mL of each standard. Concentrated standards are stable for at least one month when stored at 4 °C.

**Table 1. Masses of Compounds Used to Prepare 100 mL of 1000 mg/L Standard**

Standard	Compound	Amount (g)
Chloride	Sodium chloride	0.165
Malonate	Malonic acid	0.102
Sulfate	Sodium sulfate	0.148
Oxalate	Sodium oxalate	0.152

#### Working Standards

Prepare working standards on the day of use from the stock standards. For this experiment, four mixed standards were made for system calibration. The concentrations of those standards are shown in Table 2.

**Table 2. Standard Concentrations for Method Calibration and Calibration Results**

Analyte	Concentration (mg/L)				Results		
	Level 1	Level 2	Level 3	Level 4	% R <sup>2</sup>	Offset	Slope
Chloride	1	5	10	30	100.000	-0.0074	0.2570
Malonate	1	5	10	30	99.975	0.0467	0.0891
Sulfate	1	5	10	30	99.999	0.0368	0.1932
Oxalate	1	5	10	30	99.930	0.0762	0.1143

## SAMPLE PREPARATION

Prediluted (200-fold with deionized water) Bayer liquor samples were kindly provided by a customer.

To remove the high concentration of aluminum from the sample in an automated manner prior to injection, use a CIRA 11AXCS Electrolytic Anion Purifier. The CIRA 11AXCS consists of two depletion chambers where one chamber removes all ions to produce UPW necessary for flushing sample from the loop. The other chamber is used to remove metals, including aluminum, from the sample. To ensure that there is no secondary retention of oxalate in the matrix removing chamber, flush the chamber with 0.1% sodium fluoride to elute any remaining aluminum oxalate.

## SYSTEM PREPARATION AND SETUP

The following steps describe fluidic connections of the 10-port valve on both the IonPrep Controller (ICS-2000 installation) and the Automation Manager (ICS-3000 installation).

1. After installing the columns and suppressor with the suppressor effluent entering the conductivity cell, locate the in-line filter/pressure relief assembly in the CIRA installation kit (P/N 591250). Connect the filter assembly to the CD outlet port and to CIRA 11 AXCS (P/N 591218) port #1.
2. Connect CIRA port #4 to 10-port valve port #1 with an appropriate length of 0.020" i.d. (orange) tubing.
3. Connect CIRA port #2 to 10-port valve port #6 with an appropriate length of 0.020" i.d. (orange) tubing.
4. Connect CIRA port #5 to injection valve port S with an appropriate length of 0.020" i.d. (orange) tubing.
5. Connect 10-port valve port #8 to the 3-way valve outlet port labeled C, located in the rear panel of the PC-100 Pump Controller with an appropriate length of 0.020" i.d. (orange) tubing. Connect the 3-way valve port labeled B to the 1 L plastic container (0.1% NaF solution). Plug port labeled A with a ¼-28 end fitting.

- If using an Automation Manager (AM), the NaF line is connected to the port labeled open on the AM 3-way valve. Plug the port labeled closed with a ¼-28 end fitting.
- Connect 10-port valve port #9 to the peristaltic pump inlet with an appropriate length of 0.020" i.d. (orange) tubing.
  - Install the remaining channel of the peristaltic pump inlet to the 4 L external water reservoir (for ASRS external water mode). Connect the pump outlet line to the rest of the regenerant ports, preferably CR-ATC regen in and out to ASRS regen in.
  - Install a sample loop (10 µL) between ports #2 and #5 of the 10-port valve.
  - Install a 25 µL loop between ports #10 and #7 of the 10-port valve.
  - Install the autosampler lines (in and out) to ports #4 and #3, respectively, of the 10 port valve.
  - Install the concentrator column on the injection valve in place of an injection loop.
  - Now looking at the diagram below, connect the ASRS Regen waste line to CIRA port #3.
  - Install CIRA waste line at port #6.

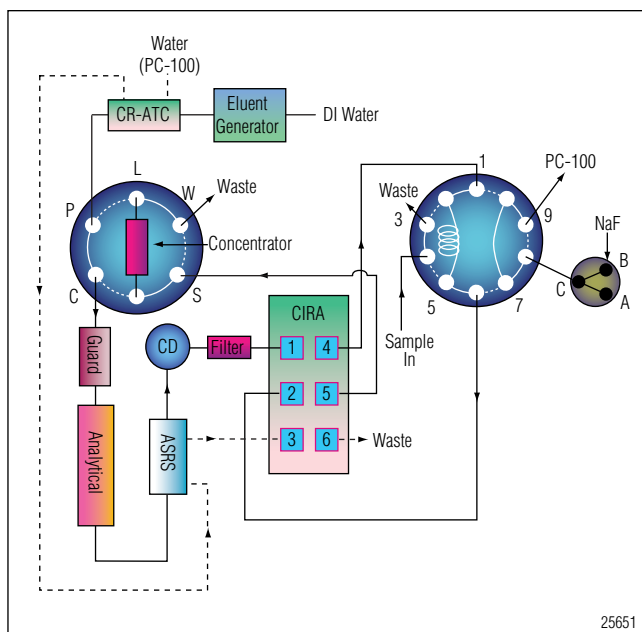


Figure 1. Diagram of the matrix elimination setup.

### ICS-2000—IonPrep Controller and PC-100 Pump Controller

Set power selector located at the rear of the controller to an appropriate voltage (120 V or 240 V). In addition to main power input, connect the 24 V DC power adapter to the IonPrep Controller rear panel. Use appropriate power cord to power up the controller.

The IonPrep Controller supplies a constant current to the CIRA. The IonPrep 10-port valve is used for sample injection and NaF addition.

The PC-100 Pump Controller delivers DI water to regeneration chambers of the CR-ATC, ASRS, and CIRA. The second channel delivers the NaF solution to the IonPrep Controller. The 3-way valve is used for NaF line selection.

#### TTL Connections

Connect TTL1 and TTL2 cables of the IC to IonPrep Valve TTL and Pump Controller Valve TTL located on the rear panels of the two components. If required, use Relay1 and Relay2 of the IC to control CIRA and pump ON/OFF by connecting Relay cables to appropriate TTL/Relay connections at the rear panel of the two components. In normal operation, the CIRA and pump are switched ON and OFF manually.

#### CIRA Power Connection

Locate the CIRA cable in the CIRA Installation Kit. Connect this cable to CIRA and to “CIRA Power Cable” port at the rear of the IonPrep. Use default Medium setting for routine applications. Turn CIRA power ON only when PC-100 Pump flow is on.

### ICS-3000—Automation Manager, PS-50 Power Controller, and PC-100 Pump Controller

Set power selector located at the rear of the PC-100 and PS-50 to an appropriate voltage (120 V or 240 V).

The AM 10-port valve is used for sample injection and NaF addition. The PS-50 supplies a constant current to the CIRA.

The PC-100 Pump Controller delivers DI water to regeneration chambers of the CR-ATC, ASRS, and CIRA. The second channel delivers NaF solution to the AM. The 3-way valve is used for NaF line selection.

#### TTL Connections

Connect TTL2 cables of the IC to the Pump Controller Valve TTL located on the rear panel of the controller. If required, use Relay1 and Relay2 of the IC to control CIRA and pump ON/OFF by connecting Relay

cables to appropriate TTL/Relay connections on the rear panel of the PS-50 and PC-100. In normal operation, the CIRA and pump are switched ON and OFF manually.

### CIRA Power Connection

Locate the CIRA cable in the CIRA Installation Kit. Connect this cable to CIRA and to “CIRA Power Cable” port at the rear of the PS-50. Use the default Medium setting for routine applications. Turn CIRA power ON only when PC-100 Pump flow is on.

### Fluidic Flow

The ASRS effluent from the CD outlet flows into CIRA port #1 and through port #4 where all ions are removed [ultrapure water (UPW) is produced]. In “A” position (10 port), the purified effluent flows through the 10-port valve ports #1, #10, #7, and #6, respectively. Sample or standard solution is loaded at this time. The purified effluent continues to flow into the CIRA and the injection valve (Inject position) and out to waste. The matrix elimination begins when the 10-port and injection valves switch to B and load positions, respectively. The purified effluent from port #1 is diverted to ports #2, #5, and #6 where the sample is flushed. The sample band flows into CIRA port #2 and through #5 where all metals are removed. The anions continue with the flow from the CIRA to the concentrator column. During this time, the 3-way valve switches to the B position, which allows the NaF solution to flow into the 25  $\mu$ L loop. After 1.0 min of sample flush, the 10-port valve returns to the A position where NaF starts to flow into CIRA ports #2 and #5. Typically, 3–5 mL is required to completely flush the sample to the concentrator column. The analysis starts immediately after the injection valve switches to the inject position.

### Valve Control Program

Time (min)	TTL1 (10-port)	TTL2 (3-way)	Injection (6-port)
-7.0*	5 V (A)	5 V (A)	Inject
-6.0	—	—	Load
-5.0	0 V (B)	0 V (B)	—
-4.0	5 V (A)	5 V (A)	—
0.0	—	—	Inject

\*sample loading must be completed

## RESULTS AND DISCUSSION

### Separation

To keep analysis times short, the IonPac AS17, a lower capacity anion-exchange column, was chosen to separate oxalate from sulfate, malonate, chloride, and other anions. Figure 2 shows a separation of four concentration levels of a mixed standard of chloride, malonate, sulfate, and oxalate. The large early eluting peak is fluoride, from the subsequent injection of 0.1% sodium fluoride during the matrix elimination. If the separation of less retained organic acids such as acetate and formate is required, a longer separation can be performed using an IonPac AS19 while omitting the addition of the sodium fluoride. The AS19 separation was developed by a customer who also uses a carbonate removal device (CRD 200) in their method to simplify the quantification of some of the anions. There is also a published report of using an IonPac AS11-HC column to separate formate, acetate, propionate, oxalate, succinate, glutarate, fluoride, chloride, and sulfate in Bayer liquor.<sup>1</sup>

### Sample Analysis

Prior to sample analysis the system was calibrated with the standards in Table 2. Calibration results are shown in the same table. The results showed good linearity for each ion in the chosen concentration range.

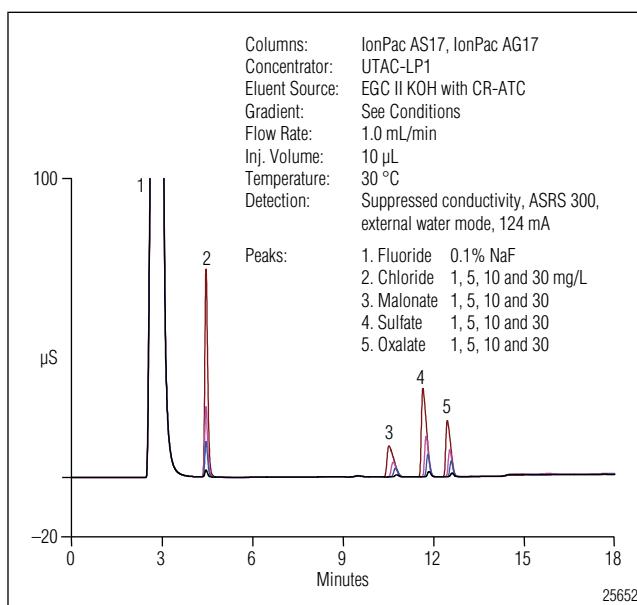


Figure 2. Overlay of chromatograms of the blank and four standards at concentrations of 1, 5, 10, and 30 mg/L.

To test the method we analyzed 12 Bayer liquor samples provided by a customer. Table 3 shows the sample analysis results. The customer confirmed that the results in Table 3 were accurate. The chromatogram in Figure 3, an overlay of three injections of sample #1, and the results of those injections, presented in Table 4, show the method's precision. The customer that uses the IonPac AS19 separation with the sample preparation method in this application note, but without the co-injection of 0.1% sodium fluoride, has found the method to be accurate and rugged, with replacement of neither column nor suppressor in over 6 months of sample analysis.

**Table 3. Bayer Liquor Sample Analysis Results (mg/L)**

Sample Name	Chloride	Malonate	Sulfate	Oxalate
Sample #1	34.47	11.93	44.84	16.77
Sample #2	29.87	9.35	73.48	11.88
Sample #3	34.80	12.14	45.37	16.77
Sample #4	47.10	10.70	63.05	12.26
Sample #5	29.64	16.19	108.72	21.15
Sample #6	32.38	10.09	80.28	19.13
Sample #7	32.47	16.47	114.21	27.40
Sample #8	34.68	12.08	45.55	16.57
Sample #9	3.63	n.a.	8.55	3.05
Sample #10	6.31	1.88	15.48	2.10
Sample #11	n.a.	9.80	86.34	23.30
Sample #12	33.20	11.92	47.25	17.09

**Table 4. Reproducibility for Three Injections of Sample #1 (RSD)**

Analyte	Retention Time	Amount	Height	Plate (EP)
Chloride	0.074	0.680	0.754	0.102
Malonate	0.161	0.667	0.068	1.727
Sulfate	0.116	0.782	0.301	1.469
Oxalate	0.093	0.611	0.275	0.959

## CONCLUSION

This application note describes an accurate and rugged method using an RFIC system with online sample preparation to determine oxalate and other ions in Bayer liquor. This method can be very useful for aluminum producers in determining the potential success of a given Bayer liquor for forming large  $Al(OH)_3$  crystals prior to calcination.

## REFERENCES

- 1) Xiao, J. B. *J. of the Chilean Chem. Soc.* **2006**, 51 (3), 964-967.

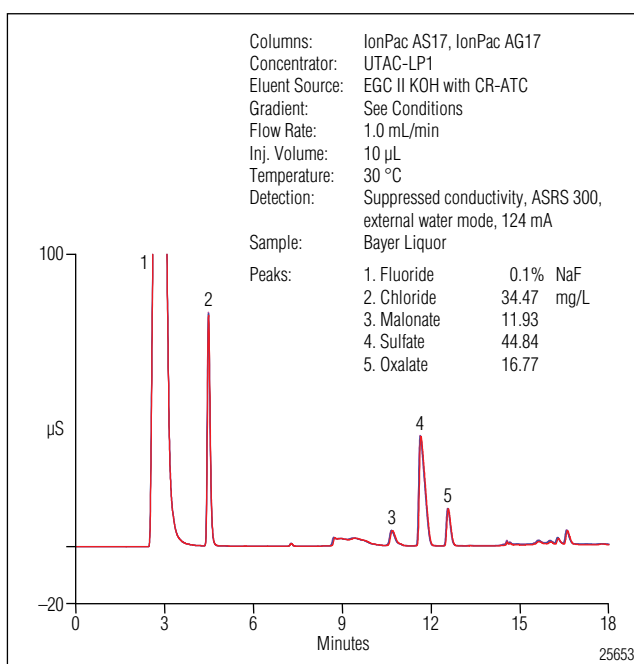


Figure 3. Overlay of three consecutive runs of sample #1.

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