Analysis of pulping liquors by suppressed ion chromatography

1. Scope

1.1 This method provides procedures for determination of sulfide, sulfite, sulfate, thiosulfate, chloride, and carbonate in white, green, and black liquors and in solidified smelt. In addition, procedures for determining oxalate, lactate, formate, acetate, and propionate in black liquor are provided.

1.2 Concentrations determined by this method are in the mg/L (ppm) range. Liquors containing higher anion concentrations are diluted to the mg/L level before analysis.

2. Summary

2.1 An aliquot of filtered, diluted liquor or dissolved smelt is injected into the ion chromatograph. Eluent is pumped through the chromatograph to carry the sample through the separator column, a suppression device (when needed), and the detector. Separator columns separate anions on the basis of their affinity for exchange sites on the column's resin packing. Weakly dissociated acids are separated by Donnan exclusion. The suppression device (column, fiber, or membrane) chemically lowers the conductivity of the eluent relative to that of the ions of interest when they are to be measured by electrolytic conductivity. The conductivity detector is used for all of the ions except sulfide, which is detected with an ultraviolet photometer. Ions are identified by their retention times compared to those of standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from standards.

3. Significance

3.1 Ion chromatography provides rapid qualitative and quantitative determination of the anions listed in 1.1. This requires a minimum of four chromatographic runs, the longest of which lasts about 40 min.

3.2 The determination of these ions is of importance in monitoring process efficiencies and in controlling corrosion within the process.
4. Definitions

4.1 Suppressed ion chromatography, a form of liquid chromatography in which ionic constituents are separated by ion exchange or Donnan exclusion followed by chemical suppression and conductivity detection.

4.2 Chemical suppression, use of a device (fiber, column, or membrane) which lowers the conductivity by chemically altering the eluent.

NOTE 1: An example of chemical suppression is the conversion of sodium carbonate eluent to carbonic acid by cation-exchange resin in the hydrogen form.

4.3 Ion chromatography exclusion, a form of liquid chromatography in which weak acids are separated by Donnan exclusion.

5. Apparatus

5.1 Ion chromatograph, capable of delivering 0.5-5.0 mL of eluent per minute at a pressure of 1379-8274 kPa (200-1200 psi). The chromatograph should be equipped with an injection valve, high pressure in-line filters for eluents, and the following components. Specific component recommendations and system configurations are given in the Appendix.

5.1.1 Guard column, placed before the separator column to protect the separator from being fouled by particulates, strongly retained anions, or certain organic constituents. The column packing is the same as used in the separator column.

5.1.2 Ion chromatography separator column, column packed with low-capacity pellicular anion exchange resin which has been found to be suitable for resolving the ions of interest.

5.1.3 Ion chromatography exclusion separator column, column packed with high capacity cation exchange resin which has been found to be suitable for resolving weak acids.

5.1.4 Suppressor (for sulfite, sulfate, thiosulfate, chloride, and oxalate), a fiber, column, or membrane capable of cation exchange which converts the eluent and separated anions to their respective acid forms.

5.1.5 Suppressor (for monoprotic organic acids), a fiber or membrane capable of cation exchange which replaces the hydrogen ions of the eluent and of the organic acids with tetrabutylammonium ions.

5.1.6 Silver suppressor column, column packed with a cation exchange resin in the Ag⁺ form capable of removing Cl⁻ from 0.0015 M HCl eluent.

5.1.7 Conductivity detector, low volume, flow-through, temperature-compensated, electrolytic conductivity cell equipped with a meter capable of reading 0-10 mS/m on a linear scale.

5.1.8 Ultraviolet detector, a selectable wavelength, double-beam filter photometer containing a low-volume, flow-through measuring cell. The wavelength is set at 215 nm for sulfide determination.

5.2 Recorder or integrator, compatible with detector outputs.

5.3 Syringe, minimum capacity 2 mL, equipped with a filter holder to permit injection through a membrane filter.

5.4 Membrane filters, 0.22 µm.

5.5 Syringe, capacity approximately 50 mL, to which is attached a glass tube of capacity 10 mL, for withdrawing sample from container of heated heavy black liquor.

5.6 Analytical balance, capable of weighing analytical reagents to ± 0.1 mg.

5.7 Oven, capable of drying analytical reagents at 105°C.

5.8 Purging gas, nitrogen gas used to purge oxygen from reagent water.

5.9 Sample container, alkali resistant (polypropylene or glass) container capable of holding at least 250 mL.

Caps for glass bottles must have Teflon liners.

5.10 Glove box or glove bag, for preparation of smelt samples in a nitrogen atmosphere.

5.11 Other glassware: pipets (0.5-10 mL) and volumetric flasks (100-1000 mL).

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1 Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list in the bound set of TAPPI Test Methods, or may be available from the TAPPI Technical Services Department.
6. Reagents

6.1 Purity of water: Reagent grade water conforming to ASTM D 1193, Type II, filtered through a 0.22-µm filter should be used. Water used for dilution of standards and the sample must be deoxygenated by vigorous sparging with nitrogen from a gas dispersion tube for at least 15 min. Water for preparation of eluents and regenerants must be degassed. Alternatively, eluents may be degassed by use of a commercial degassing module employing a helium sparge.

6.2 Eluents

6.2.1 For sulfite, sulfate, thiosulfate, chloride, and oxalate: Dissolve 1.008 g of sodium bicarbonate (3 mM NaHCO₃) and 1.018 g of sodium carbonate (2.4 mM Na₂CO₃) in water and dilute to 4 L with water.

6.2.2 For sulfite, sulfate, thiosulfate, chloride, and oxalate (alternate eluent): Dissolve 0.424 g of sodium carbonate (1.0 mM Na₂CO₃), 0.800 g of sodium hydroxide (5.0 mM NaOH), and 0.381 g of p-cyanophenol (0.8 mM CNC₄H₇NOH) in water and dilute to 4 L with water.

6.2.3 For sulfite, sulfate, thiosulfate, chloride, and oxalate (alternate eluent): Dissolve 0.848 g of sodium carbonate (2.0 mM Na₂CO₃) and 0.252 g of sodium bicarbonate (0.75 mM NaHCO₃) in water and dilute to 4 L with water.

6.2.4 For sulfite, sulfate, thiosulfate, chloride, and oxalate (alternate eluent): Dissolve 1.008 g of sodium bicarbonate (3.0 mM NaHCO₃), 1.018 g of sodium carbonate (2.4 mM Na₂CO₃), and 0.381 g of p-cyanophenol (0.8 mM CNC₄H₇NOH) in water. Add 80 mL of acetonitrile (2% CH₃CN) and dilute to 4 L with water.

6.2.5 For sulfite: Dissolve 0.424 g of sodium carbonate (1.0 mM Na₂CO₃), 1.600 g of sodium hydroxide (10 mM NaOH), 2.473 g of boric acid (10 mM H₃BO₃), and 4.0 mL of ethylenediamine (15 mM NH₂CH₂CH₂NH₂) in water and dilute to 4 L with water.

6.2.6 For sulfite (alternate eluent): Dissolve 0.106 g of sodium carbonate (0.25 mM Na₂CO₃), 0.800 g of sodium hydroxide (5.0 mM NaOH), and 0.4 mL of ethylenediamine (1.5 mM NH₂CH₂CH₂NH₂) in water and dilute to 4 L with water.

6.2.7 For lactate, formate, acetate, and propionate: Dilute 6 mL of 1N HCl to 4 L with water (1.5 mM HCl).

6.2.8 For lactate, formate, acetate, and propionate (alternate eluent recommended for use with fiber and membrane suppressors): Dissolve 0.776 g of octanesulfonic acid [1.0 mM CH₃(CH₂)₇SO₃H] in water and dilute to 4L with water. This solution is available from the vendor of the ion chromatograph.

6.3 Suppressor regenerant solution

6.3.1 For fiber suppressor AFS-1 or membrane suppressor AMMS: Add 2.8 mL of concentrated H₂SO₄ (sp.gr. 1.84) to approximately 600 mL of water. Dilute to 4 L with water.

6.3.2 For fiber suppressor AFS-2 or membrane suppressor AMMS-ICE: Dilute 12.975 g of 40% tetrabutylammonium hydroxide solution (0.01M [CH₃(CH₂)₄]₄NOH) to 2 L with water.

6.3.3 For packed-bed suppressor: Add 112 mL of concentrated H₂SO₄ to approximately 600 mL of water. (Caution! Heat generated.) Cool and dilute to 4 L with water.

6.4 Master standard solutions: Sulfite standard should be prepared fresh every 1-2 weeks. The sulfide solution should be standardized daily. Other standards should not be retained for longer than one month. All master standard solutions should be made from analytical grade reagents.

6.4.1 Sulfate solution (1000 ppm; 1.00 mL = 1.00 mg SO₄²⁻). Dry sodium sulfate (Na₂SO₄) for 1 h at 105°C and cool in a desiccator. Dissolve 1.479 ± 0.002 g of the dried salt in water and dilute to 1 L with water.

6.4.2 Sulfite solution (1000 ppm; 1.00 mL = 1.00 mg SO₃²⁻). Dry sodium sulfite (Na₂SO₃) for 1 h at 105°C and cool in a desiccator. Dissolve 1.574 ± 0.002 g of the dried salt in formaldehyde master solution (see 6.4.9).

6.4.3 Thiosulfate solution (1000 ppm; 1.00 mL = 1.00 mg S₂O₃²⁻). Dry sodium thiosulfate (Na₂S₂O₃) for 1 h at 105°C and cool in a desiccator. Dissolve 1.410 ± 0.002 g of the dried salt in water and dilute to 1 L with water.

6.4.4 Sulfide solution (1000 ppm; 1.00 mL = 1.00 mg S⁰). Dissolve 7.5 g sodium sulfide hydrate (Na₂S • 9H₂O), 1.8 g ascorbic acid, and 0.4 g sodium hydroxide in water and dilute to 1 L with water. Standardize daily by potentiometric titration with cadmium nitrate using a silver/sulfide ion-selective electrode.

6.4.5 Chloride solution (1000 ppm; 1.00 mL = 1.00 mg Cl⁻). Dry sodium chloride for 1 h at 105°C and cool in a desiccator. Dissolve 1.648 ± 0.002 g of the dry salt in water and dilute to 1 L with water.

6.4.6 Oxalate solution (1000 ppm; 1.00 mL = 1.00 mg C₂O₄²⁻). Dry sodium oxalate (Na₂C₂O₄) for 1 h at 105°C and cool in a desiccator. Dissolve 1.522 ± 0.002 g of the dry salt in water and dilute to 1 L with water.
6.4.7 **Formic, acetic, propionic, and lactic acid solutions** (1000 ppm; 1.00 mL = 1.00 mg of each organic acid). Dissolve 1.000 ± 0.002 g of formic, glacial acetic, and propionic acid in water and dilute to 1 L with water. Dissolve 1.176 ± 0.002 g of lactic acid in water and dilute to 1 L with water.

6.4.8 **Carbonate solution** (1000 ppm; 1.00 mL = 1.00 mg CO\textsubscript{3}\textsuperscript{2-}). Dry sodium carbonate for 1 h at 105°C and cool in a desiccator. Dissolve 1.767 ± 0.002 g of the dried salt in water and dilute to 1 L with water.

6.4.9 **Formaldehyde solution** (1.0 mL/1000 mL). Dilute 1.0 mL of 37-39% formaldehyde into 1000 mL of water.

6.4.10 **Cadmium nitrate solution** (0.100 M). Dissolve 7.710 ± 0.002 g of Cd(NO\textsubscript{3})\textsubscript{2} • 4H\textsubscript{2}O in water and dilute to 250 mL with water.

6.4.11 **Antioxidant buffer** (active ingredient is 1 M ascorbic acid). Dissolve 40 g NaOH, 176 g ascorbic acid, and 10 mL ethylenediamine in water and dilute to 1 L with water.

6.5 **Working standard solutions.** From the master standard solutions, prepare working standard solutions of sulfide and sulfite fresh each day that they are used. Prepare other working standard solutions weekly. Concentrations of ions in working standards should be similar to concentrations of ions in diluted liquors, typically less than 20 ppm. Prepare working standards in water; add 0.5 mL of 37% formaldehyde per liter of sulfite working standard and 1 mL of antioxidant buffer per liter of sulfide working standard. Prepare at least three different working standard solutions for each ion to be determined. These solutions will be used to establish the useful linear range of the ion chromatograph for that ion.

7. **Sampling**

7.1 Collect a sample of the liquor of interest, at least 250 mL, filling the bottle completely with no air space. Keep the bottle sealed until just before analysis.

7.2 Alternate method for sampling hot, concentrated black liquor: Add the hot, concentrated black liquor to a preweighed amount of water sufficient to dilute the liquor to 15-20% solids. Fill the void space in the sample bottle with nitrogen, cap immediately, and gently swirl the bottle to mix. Cool and reweigh to obtain the weight of the liquor added.

**NOTE 2:** Storage of the sample under refrigeration has been recommended (1).

7.3 Collect a 100-g or larger smelt sample in a stainless steel ladle. Allow smelt to cool and solidify, transfer to a glass or polypropylene bottle, and store under nitrogen until analyzed.

7.4 Analyze the sample of liquor or smelt as soon as possible after collection, preferably within one week.

8. **Procedure**

8.1 Set up the ion chromatograph according to the manufacturer's instructions. See the Appendix for information concerning possible configurations for instrument set-up. Before the first standard or sample is run, pump eluent through the chromatograph long enough to obtain a stable baseline on the recorder or integrator.

**NOTE 3:** The analyst should be alert for rising back pressure, variable baselines, changes in peak shapes, and poor chromatogram reproducibility. Regular cleaning of the guard column, as recommended by the manufacturer, and replacement of column bed supports will usually eliminate these problems. It is imperative that the liquor sample be filtered through a 0.22-µm membrane and adequately diluted to avoid fouling the columns.

8.2 Inject working standards. Calculate the regression line and the correlation coefficient.

8.3 Withdraw a portion of concentrated black liquor and dilute it to 15-25% solids in the following manner: Heat the heavy black liquor to 70-80°C in a hot water bath and mix thoroughly. Withdraw about 10 mL of the hot liquor into a glass tube connected to a syringe. Expel the liquor into preweighed dilution water in a tared container. Cool and reweigh to obtain the weight of the liquor added. (These weights are used only if one calculates the solids content of the diluted liquor from that of the concentrated liquor. The weights are not needed if one measures the solids content of the diluted liquor as specified in 8.4).

8.4 Warm the diluted liquor which had been stored under refrigeration to room temperature. Mix the liquor thoroughly. Withdraw a portion of black liquor for determination of solids content in accordance with T 650 "Solids Content of Black Liquor." For ion chromatographic analysis, withdraw 0.5-1.0 g of dilute black liquor, weigh accurately, and dilute to about 0.5 g/L total solids with deoxygenated water. This is volume V in the equation used to calculate ion concentration.
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NOTE 4: To avoid oxidation of liquor constituents, handling of the liquor under nitrogen in a glove box has been recommended (1).

NOTE 5: To the diluted sample in which sulfite is to be determined, add 0.5 mL of 37% formaldehyde per liter. If carbonate is to be determined, prepare a separate dilution without added formaldehyde (to avoid formate interference with carbonate).

NOTE 6: To the diluted sample in which sulfide is to be determined, add 1 mL of antioxidant buffer per liter.

NOTE 7: Prior to determining sulfide in a white liquor containing polysulfide (typically indicated by a yellow or orange color), add sufficient sodium sulfite to decompose the polysulfide. The analytical result will be the free sulfide plus the sulfide bound in the polysulfide.

8.5 For analysis of smelt, place the bottle containing the solidified smelt in a nitrogen-filled glove box or bag. Open the bottle in the glove bag, discard the outer layer of the smelt, and crush the remainder to a fine gravel. Weigh the portion for analysis in a closed, nitrogen-filled bottle; this may be done outside the glove bag. The amount of material taken for analysis must be sufficiently large to be representative of the solidified smelt, which often is not homogeneous. Return the portion to the glove bag and dissolve it in deoxygenated water. Analyze like green liquor.

8.6 Withdraw an aliquot of white or green liquor by pipet and dilute 1:1000 with deoxygenated water. Prepare additional dilutions as needed to bring the concentrations of the ions of interest into the useful linear range of the ion chromatograph. Sample responses must be within the range of standards used to prepare the calibration curves.

8.7 Immediately after dilution, inject an aliquot of the liquor through a 0.22-μm membrane filter into the sample loop of the ion chromatograph. Record the ion chromatogram. Figure 1 shows an ion chromatogram of an authentic black liquor.

8.8 Each day that an ion is determined, prepare and analyze at least one aliquot of sample to which is added a known amount of that ion (called a "spiked sample"). The amount of added ion should be similar to that originally found in the aliquot, and the total response of the spiked sample should not exceed the calibration line.

9. Calculations

9.1 Identify ions in the sample by comparison of sample chromatograms with chromatograms of working standards. Measure peak heights or areas. Refer the peak height or area for the ion(s) of interest to the appropriate calibration curves to determine the ion concentration in the diluted liquor in mg/L. Alternatively, determine the concentration of the ion of interest by direct proportion from its response and the response of a working standard of similar concentration. If a single standard is used and its response differs from a previously made calibration curve, remake the calibration curve.

9.2 Calculate the concentrations of the ions of interest in the liquors or smelt as follows:
**Black liquors and smelt samples:**

Ion concentration, % of liquor solids or solidified smelt = \( \frac{AVD(100)}{W} \)

**Green and white liquors:**

Ion concentration, g/L = \( \frac{AVD}{1000P} \)

where

\( A \) = concentration of ion in solution injected into the ion chromatograph, mg/L

\( V \) = volume of initial dilution of green, white, or weak black liquor or smelt, L

\( D \) = dilution factor for subsequent dilution(s)

\( W \) = moisture-free weight of portion of dilute black liquor or of solidified smelt taken for ion chromatographic analysis, mg

\( P \) = volume of initial aliquot of green or white liquor, L

9.3 Calculate the percentage recovery of ions added to spiked samples as follows:

Spike recovery, % = 100 \( \frac{(T-B)}{S} \)

\( T \) = total amount of the ion measured in the spiked sample

\( B \) = background amount of ion originally found in the sample

\( S \) = known amount of ion ("spike") added to sample

10. **Report**

10.1 For black liquors and smelts, report results as the ions determined or calculated as their sodium salts, to the nearest 0.1% of dry liquor solids or of solidified smelt.

10.2 For green and white liquors, report results as the ions determined or calculated as their sodium salts, to the nearest 0.1 g/L of liquor.

11. **Precision**

11.1 For the maximum expected difference between two test results, each of which is based upon a single determination:

11.1.1 Repeatability (within a laboratory) = see Table 1;

**Table 1.** Repeatability values for ion chromatographic analysis of pulping liquors\(^1\)

<table>
<thead>
<tr>
<th></th>
<th>Carbonate</th>
<th>Sulfate</th>
<th>Chloride</th>
<th>Sulfite</th>
<th>Thiosulfate</th>
<th>Sulfide</th>
<th>Organic acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor</td>
<td>10</td>
<td>12</td>
<td>15</td>
<td>30</td>
<td>16</td>
<td>N.A.(^2)</td>
<td>15</td>
</tr>
<tr>
<td>Green liquor</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>25</td>
<td>7</td>
<td>N.A.</td>
<td>...</td>
</tr>
<tr>
<td>White liquor</td>
<td>12</td>
<td>10</td>
<td>12</td>
<td>30</td>
<td>15</td>
<td>N.A.</td>
<td>...</td>
</tr>
<tr>
<td>Smelt</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>...</td>
</tr>
</tbody>
</table>

\(^1\)Repeatability expressed as percentage of mean.

\(^2\)N.A. = not available

11.1.2 Reproducibility (between laboratories) = not available;

11.1.3 Comparability (between materials) = not available; in accordance with the definitions of these terms in TAPPI T 1206 "Precision Statement for Test Methods." These values are based on replicate determinations at The Institute of Paper Chemistry.

12. **Additional information**

12.1 Effective date of issue: July 30, 1987.
12.2 In this method as originally issued, as a portion of T 699 pm-83, sulfide was determined using an electrochemical (amperometric) detector. Since that time, reservations regarding use of the electrochemical detector have been revealed (1-2), and use of the ultraviolet detector for sulfide has been investigated (3). Thus, in this revision the UV detector is used for sulfide, and methods have been added for determining organic acids and carbonate and for the analysis of smelt. Repeatability data for individual ions in black, green, and white liquors have also been added.

12.3 Procedures described in this test method should also be valid for other industry process streams, such as paper machine white waters and spent sulfite liquor.

References


Appendix A

A.1 Columns, eluents, flow rates, detectors, and suppressor used for different analyses are summarized in Table 2. Alternate configurations and operating conditions are shown in Table 3. Tables 4 and 5 contain typical retention times with different columns and eluents.

Table 2. Ion chromatograph configurations and operating conditions

<table>
<thead>
<tr>
<th>Substance determined</th>
<th>Eluent</th>
<th>Flow rate, mL/min</th>
<th>Guard column</th>
<th>Separator column</th>
<th>Suppressor</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite, sulfate, thiosulfate, chloride, oxalate</td>
<td>3 mM NaHCO₃ +2.4 mM Na₂CO₃</td>
<td>2.3</td>
<td>4 x 50 mm (HPIC-AG3)</td>
<td>4 x 250 mm (HPIC-AS3*)</td>
<td>Fiber (AFS-1) or membrane (AMMS)</td>
<td>Conductivity</td>
</tr>
<tr>
<td></td>
<td>+10 mM NaOH</td>
<td>0.8</td>
<td>None</td>
<td>9 x 250 mm (HPICE-AS1)</td>
<td>Fiber (AFS-2) or membrane (AMMS-ICE)</td>
<td>Conductivity</td>
</tr>
<tr>
<td></td>
<td>+10 mM H₂BO₃</td>
<td>0.8</td>
<td>None</td>
<td>9 x 250 mm (HPICE-AS3) or 9 x 250 mm (HPICE-AS1)</td>
<td>None</td>
<td>Conductivity</td>
</tr>
<tr>
<td></td>
<td>+15 mM ethylene-diamine</td>
<td>0.8</td>
<td>None</td>
<td>9 x 140 mm (HPICE-AS3) or 9 x 250 mm (HPICE-AS1)</td>
<td>None</td>
<td>Conductivity</td>
</tr>
</tbody>
</table>

*AS4 columns should not be used for analysis of spent liquors; the columns will become irreversibly plugged.
### Table 3. Alternate ion chromatograph configurations and operating conditions

<table>
<thead>
<tr>
<th>Substance determined</th>
<th>Eluent</th>
<th>Flow rate, mL/min</th>
<th>Guard column</th>
<th>Separator column</th>
<th>Suppressor</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfite, sulfate, thiosulfate, chloride, oxalate</td>
<td>1.0 mM Na₂CO₃ + 5.0 mM NaOH + 0.8 mM p-cyano-phenol</td>
<td>1.6</td>
<td>(HPIC-AG4)</td>
<td>(HPIC-AS5)</td>
<td>Fiber (AFS-1) or membrane (AMMS)</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Sulfite, sulfate, thiosulfate, chloride, oxalate</td>
<td>0.75 mM NaHCO₃ + 2.0 mM Na₂CO₃</td>
<td>2.0</td>
<td>HPIC-AG4A</td>
<td>HPIC-AS4A</td>
<td>Fiber (AFS-1) or membrane (AMMS)</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Sulfite, sulfate, thiosulfate, chloride, oxalate</td>
<td>3.0 mM NaHCO₃ + 0.8 mM p-cyano-phenol + 2% CH₃CN</td>
<td>1.8</td>
<td>HPIC-AG4</td>
<td>HPIC-AS5</td>
<td>Fiber (AFS-1) or membrane (AMMS)</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Sulfide</td>
<td>0.25 mM Na₂CO₃ + 5.0 mM NaOH + 1.5 mM ethylenediamine</td>
<td>2.0</td>
<td>Metal-free or metal removing column</td>
<td>HPIC-AS3 or HPIC-AG3 or HPIC-AG4A or HPIC-AG5</td>
<td>None</td>
<td>UV at 215 nm</td>
</tr>
<tr>
<td>Organic acids</td>
<td>1 mM octane-sulfonic acid</td>
<td>0.8</td>
<td>None</td>
<td>HPICE-AS1</td>
<td>Fiber (AFS-2) or membrane (AMMS-ICE)</td>
<td>Conductivity</td>
</tr>
</tbody>
</table>

### Table 4. Some typical retention times: chloride, oxalate, sulfoxyl anions

<table>
<thead>
<tr>
<th>Guard column</th>
<th>Separator column</th>
<th>Eluent</th>
<th>Flow rate, mL/min</th>
<th>Chloride</th>
<th>Sulfite</th>
<th>Sulfate</th>
<th>Oxalate</th>
<th>Thiosulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPIC-AG3</td>
<td>HPIC-AS3</td>
<td>3.0 mM NaHCO₃ + 2.4 mM Na₂CO₃</td>
<td>2.3</td>
<td>2.0</td>
<td>5.7</td>
<td>8.6</td>
<td>12.0</td>
<td>40.9</td>
</tr>
<tr>
<td>HPIC-AG4A</td>
<td>HPIC-AS4A</td>
<td>2.0 mM Na₂CO₃ + 0.75 mM NaHCO₃</td>
<td>2.0</td>
<td>1.8</td>
<td>6.1</td>
<td>7.8</td>
<td>9.8</td>
<td>27.4</td>
</tr>
<tr>
<td>HPIC-AG4</td>
<td>HPIC-AS5</td>
<td>1.0 mM Na₂CO₃ + 5.0 mM NaOH + 0.8 mM p-cyano-phenol</td>
<td>1.6</td>
<td>1.8</td>
<td>5.8</td>
<td>6.9</td>
<td>8.1</td>
<td>29.6</td>
</tr>
<tr>
<td>HPIC-AG4</td>
<td>HPIC-AS5</td>
<td>3.0 mM NaHCO₃ + 2.4 mM Na₂CO₃ + 0.8 mM p-cyano-phenol + 2% CH₃CN</td>
<td>1.8</td>
<td>1.6</td>
<td>5.5</td>
<td>6.1</td>
<td>6.9</td>
<td>26.0</td>
</tr>
</tbody>
</table>

*Approximate times with new columns. Retention times decrease with column use.
Table 5. Some typical retention times: sulfide, carbonate, organic acids

<table>
<thead>
<tr>
<th>Separator column</th>
<th>Suppressor</th>
<th>Eluent</th>
<th>Flow rate, mL/min</th>
<th>Retention time, min</th>
<th>Sulfide</th>
<th>Carbonate</th>
<th>Lactic acid</th>
<th>Formic acid</th>
<th>Acetic acid</th>
<th>Propionic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPIC-AS3</td>
<td>None</td>
<td>1.0 mM Na₂CO₃</td>
<td>2.0</td>
<td>1</td>
<td>—</td>
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<tr>
<td></td>
<td></td>
<td>+10 mM NaOH</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>+15 mM H₂BO₃</td>
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<tr>
<td></td>
<td></td>
<td>+15 mM ethylene-diamine</td>
<td></td>
<td></td>
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<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>HPICE-AS3</td>
<td>None</td>
<td>Water</td>
<td>0.8</td>
<td>—</td>
<td>10.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>HPICE-AS1</td>
<td>Fiber (AFS-2)</td>
<td>1 mM HCl</td>
<td>0.8</td>
<td>—</td>
<td>—</td>
<td>12.2</td>
<td>13</td>
<td>14.5</td>
<td>17.3</td>
<td>—</td>
</tr>
</tbody>
</table>

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator.