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**CAUTION:**

This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

# 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 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.

Approved by the Standard-Specific Interest Group for this Test Method

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## 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*,<sup>1</sup> 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  $\text{Ag}^+$  form capable of removing  $\text{Cl}^-$  from 0.0015M 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  $\mu\text{m}$ .

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  $\pm 0.1$  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).

<sup>1</sup>Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list, available as part of the CD or printed set of Standards, or on the TAPPI website general Standards page.

## 6. Reagents

6.1 *Purity of water:* Reagent grade water conforming to ASTM D 1193, Type II, filtered through a 0.22- $\mu$ m 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. This may be achieved 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 NaHCO<sub>3</sub>) and 1.018 g of sodium carbonate (2.4 mM Na<sub>2</sub>CO<sub>3</sub>) in water and dilute to 4 L with water or other concentrations as appropriate for column used.

6.2.2 *For sulfite, sulfate, thiosulfate, chloride, and oxalate (alternate eluent):* Dissolve 0.424 g of sodium carbonate (1.0 mM Na<sub>2</sub>CO<sub>3</sub>), 0.800 g of sodium hydroxide (5.0 mM NaOH), and 0.381 g of *p*-cyanophenol (0.8 mM CNC<sub>6</sub>H<sub>4</sub>OH) in water and dilute to 4 L with water or other concentrations as appropriate for column used.

6.2.3 *For sulfite, sulfate, thiosulfate, chloride, and oxalate (alternate eluent):* Dissolve 0.848 g of sodium carbonate (2.0 mM Na<sub>2</sub>CO<sub>3</sub>) and 0.252 g of sodium bicarbonate (0.75 mM NaHCO<sub>3</sub>) in water and dilute to 4 L with water or other concentrations as appropriate for column used.

6.2.4 *For sulfite, sulfate, thiosulfate, chloride, and oxalate (alternate eluent):* Dissolve 1.008 g of sodium bicarbonate (3.0 mM NaHCO<sub>3</sub>), 1.018 g of sodium carbonate (2.4 mM Na<sub>2</sub>CO<sub>3</sub>), and 0.381 g of *p*-cyanophenol (0.8 mM CNC<sub>6</sub>H<sub>4</sub>OH) in water. Add 80 mL of acetonitrile (2% CH<sub>3</sub>CN) and dilute to 4 L with water or other concentrations as appropriate for column used.

6.2.5 *For sulfide:* Dissolve 0.424 g of sodium carbonate (1.0 mM Na<sub>2</sub>CO<sub>3</sub>), 1.600 g of sodium hydroxide (10 mM NaOH), 2.473 g of boric acid (10 mM H<sub>3</sub>BO<sub>3</sub>), and 4.0 mL of ethylenediamine (15 mM NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) in water and dilute to 4 L with water.

6.2.6 *For sulfide (alternate eluent):* Dissolve 0.106 g of sodium carbonate (0.25 mM Na<sub>2</sub>CO<sub>3</sub>), 0.800 g of sodium hydroxide (5.0 mM NaOH), and 0.4 mL of ethylenediamine (1.5 mM NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) in water and dilute to 4 L with water.

6.2.7 *For lactate, formate, acetate, and propionate:* Dilute 6 mL of 1M 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 CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>SO<sub>3</sub>H] in water and dilute to 4L with water. This solution is available from the vendor of the ion chromatograph.

6.2.9 *For carbonate:* Use deoxygenated water as per 6.1.

### 6.3 Suppressor regenerant solution

6.3.1 *For fiber suppressor AFS-1 or membrane suppressor AMMS:* Add 2.8 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (sp.gr. 1.84) to approximately 600 mL of water. Dilute to 4 L with water. Use the suppressor appropriate to the column used.

6.3.2 *For fiber suppressor AFS-2 or membrane suppressor AMMS-ICE:* Dilute 12.975 g of 40% tetrabutylammonium hydroxide solution (0.01M [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>]<sub>4</sub> NOH) to 2 L with water.

6.3.3 *For packed-bed suppressor:* Add 112 mL of concentrated H<sub>2</sub>SO<sub>4</sub> 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 SO<sub>4</sub><sup>2-</sup>). Dry sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) 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 SO<sub>3</sub><sup>2-</sup>). Dry sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) 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 S<sub>2</sub>O<sub>3</sub><sup>2-</sup>). Dry sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) 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 S<sup>2-</sup>). Dissolve 7.5 g sodium sulfide hydrate (Na<sub>2</sub>S • 9H<sub>2</sub>O), 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<sup>-</sup>). Dry sodium chloride (NaCl) 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 C<sub>2</sub>O<sub>4</sub><sup>2-</sup>). Dry sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) for 1 h at 105°C and cool in a desiccator. Dissolve 1.522 ± 0.002 g of the dried salt in water and dilute to 1 L with water.