TABULATION

STANDARD-SPECIFIC INTEREST GROUP BALLOT
OFFICIAL TEST METHOD OR STANDARD PRACTICE

DATE: March 30, 2021

TO: Chris Czyryca
Working Group Chairman

DUE DATE: **N/A**

RE: T 699, WI 130802.05 Draft 3 - SARG

Please return report to:

Standards Department
TAPPI
15 Technology Parkway South
Peachtree Corners, GA 30092
standards@tappi.org
FAX: (770) 446-6947

The results of the SSIG ballot of the subject document are as follows:

AFFIRMATIVE 6 NEGATIVE 0 ABSTENTION 3

9 ballots returned = 69% / 100% affirmative; Standard may proceed to SARG.

x No comments received. Standard is being balloted for the SARG.

_____ Copies of comments from the SSIG ballots are attached.

_____ Please review and return this form with recommendations and dispositions of comments and negatives, along with your **MARKED UP COPY** for preparation of the next ballot. **DO NOT RE-TYPE.**

_____ Please indicate whether the method is to be:

_____ re-balloted to the SSIG,

_____ or balloted for the SARG.

RECOMMENDATIONS AND DISPOSITIONS OF COMMENTS AND NEGATIVES:
(MUST be in BLACK or RED ink for reproduction)

The ballot 2 for proposed WITHDRAWAL of this Draft received 6 votes affirmative for withdrawal, three votes for abstention and no negative votes or comments objecting to the withdrawal. This Test Method is now ready to go to the Standards Advisory Review Group (SARG) for final approval of the proposed WITHDRAWAL.

❒ Continuation on attached sheet(s)-PLEASE DO NOT WRITE ON REVERSE

Your completion of this form constitutes the working group chairman's report. Please send copies of your resolution of comments to those SSIG members who made comments. This form and attachments should be returned to the Standards Department.

WORKING GROUP CHAIRMAN _____ _____
Signature Date

T 699 - Draft 2, due Friday, October 30 2020

Voting Summary by Option

Option	*# Votes*
Affirmative for WITHDRAWAL	6
Negative (OBJECTION to withdrawal)	0
Abstention	3
TOTAL VOTES RECEIVED	9

Voting Statistics

Total Members of SSIG	13
Percent return	69%
Votes received	9
Total votes minus abstentions	6
Percent affirmative	100%

Voting Details

Voter Name	**Interest Category**	**Vote**
Zhihua Jiang	Educator	Did not vote
David Carlson	Consultant	Did not vote
Christopher Czyryca	General Interest	Affirmative for withdrawal
Rob Robinson	Supplier - service/general	Affirmative for withdrawal
Jeff Lundeen	Producer	Affirmative for withdrawal
Terry Witkowski	General Interest	Did not vote
Dennis Crawshaw	Producer	Affirmative for withdrawal
Mike Buchanan	General Interest	Did not vote
Benjamin Frank	Producer	Affirmative for withdrawal
Nicholas Riggs	Supplier - equipment	Abstention
Colleen Walker	Educator	Affirmative for withdrawal
Donald Guay	Producer	Abstention
Philip Wells	Supplier - equipment	Abstention

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VOTER SUBJECT COMMENT

Voter Comments Collected During Ballot Voting

Submitter First Name	Submitter Last Name	Comment Category	Section	Page	Line	Subject	Comment	Proposal	Response

No comments were made on this ballot

T 699 - Draft 2, due Friday, October 30 2020

Voting Summary by Voter Interest Category

Interest Category	*Affirmative for WITHDRAWAL*	*Negative (OBJECTION to withdrawal) w/comment*	*Abstention*	*Not Returned*	*Total*	
					Qt.	*%*
Consultant	0	0	0	1	1	7.7%
Educator	1	0	0	1	2	15.4%
General Interest	1	0	0	2	3	23.1%
Producer	3	0	1	0	4	30.8%
Supplier - equipment	0	0	2	0	2	15.4%
Supplier - service/general	1	0	0	0	1	7.7%
Total	6	0	3	4	13	100.0%

WI 130802.05

T 699

DRAFT NO. 2

DATE September 15, 2020

WORKING GROUP CHAIRMAN Christopher Czyryca

SUBJECT CATEGORY Chemical Properties

RELATED METHODS See "Additional Information"

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

(Five-year review of T 699 om-09)

(Proposed WITHDRAWAL of Official Method T 699 om-09)

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.

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,*[1] 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.

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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, available as part of the CD or printed set of Standards, or on the TAPPI website general Standards page.

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

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. 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 m*M* $NaHCO_3$) and 1.018 g of sodium carbonate (2.4 m*M* Na_2CO_3) 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 m*M* Na_2CO_3), 0.800 g of sodium hydroxide (5.0 m*M* NaOH), and 0.381 g of *p*-cyanophenol (0.8 m*M* CNC_6H_4OH) 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 m*M* Na_2CO_3) and 0.252 g of sodium bicarbonate (0.75 m*M* $NaHCO_3$) 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 m*M* $NaHCO_3$), 1.018 g of sodium carbonate (2.4 m*M* Na_2CO_3), and 0.381 g of *p*-cyanophenol (0.8 m*M* CNC_6H_4OH) in water. Add 80 mL of acetonitrile (2% CH_3CN) 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 m*M* Na_2CO_3), 1.600 g of sodium hydroxide (10 m*M* NaOH), 2.473 g of boric acid (10 m*M* H_3BO_3), and 4.0 mL of ethylenediamine (15 m*M* $NH_2CH_2CH_2NH_2$) 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 m*M* Na_2CO_3), 0.800 g of sodium hydroxide (5.0 m*M* NaOH), and 0.4 mL of ethylenediamine (1.5 m*M* $NH_2CH_2CH_2NH_2$) in water and dilute to 4 L with water.

6.2.7 *For lactate, formate, acetate, and propionate:* Dilute 6 mL of 1*M* HCl to 4 L with water (1.5 m*M* 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 m*M* $CH_3(CH_2)_7SO_3H$] 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_2SO_4 (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 (0.01*M* $[CH_3(CH_2)_3]_4$ NOH) to 2 L with water.

6.3.3 *For packed-bed suppressor*: Add 112 mL of concentrated H_2SO_4 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_4^{2-}). Dry sodium sulfate (Na_2SO_4) 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_3^{2-}). Dry sodium sulfite (Na_2SO_3) 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 $S_2O_3^{2-}$). Dry sodium thiosulfate ($Na_2S_2O_3$) 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^{2-}). Dissolve 7.5 g sodium sulfide hydrate ($Na_2S \bullet 9H_20$), 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 (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 $C_2O_4^{2-}$). Dry sodium oxalate ($Na_2C_2O_4$) 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.

6.4.7 *Formic, acetic, propionic, and lactic acid solutions* (1000 pm; 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 85% 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_3^{2-}). Dry sodium carbonate (Na_2CO_3) 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 $(NO_3)_2 \bullet 4H_2O$ 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 1mL 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 For each ion to be determined, inject the appropriate working standards to develop a calibration curve. Make sure the standards are in the linear range of the column. Calculate a linear least squares regression line and correlation coefficient for each curve. The R^2 value should be 0.95 or better. If < 0.90, repeat injections. If necessary, remake working standards. Determine the slope and intercept of the calibration curve for use in calculating ion values.

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 TAPPI 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.

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.

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.

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.

8.7 *Immediately after dilution*, inject an aliquot of the liquor through a 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. Calculate the spike recovery %. The recovery should be within 80–120% except for sulfite, where it should be 70–130%. It is recommended that every sample has one or more ions spiked for a check.

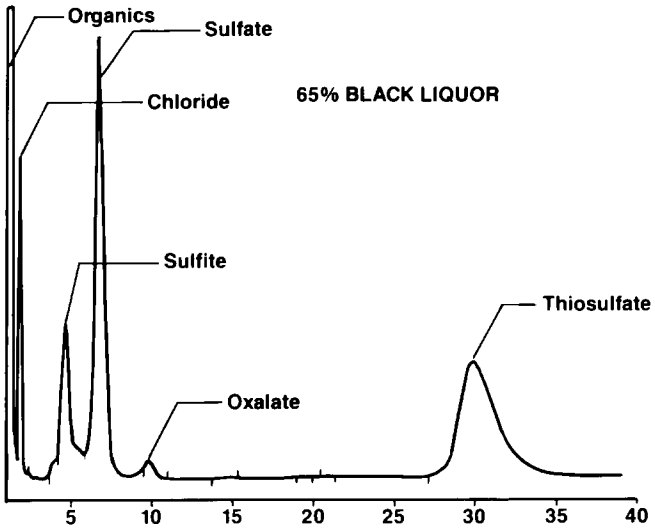

Fig. 1. Ion chromatogram of a black liquor.

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 = AVD (100) / W

Green and white liquors:

Ion concentration, g/L = 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 (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. These values are based on replicate determinations at The Institute of Paper Science and Technology.

Table 1. Repeatability values for ion chromatographic analysis of pulping liquors[1]

	Carbonate	*Sulfate*	*Chloride*	*Sulfite*	*Thiosulfate*	*Sulfide*	*Organic acids*
Black liquor	10	12	15	30	16	N.A.[2]	15
Green liquor	15	10	10	25	7	N.A.	...
White liquor	12	10	12	30	15	N.A.	...
Smelt	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	...

[1]Repeatability expressed as percentage of mean.

[2]N.A. = not available

11.1.2 Reproducibility. The estimates of reproducibility shown in Table 2 are based on data from an interlaboratory trial involving six laboratories and five different samples of pulping liquors. The trial was conducted in February 1998 using the T 699 om-87 version of this method. Testing is based on one determination per test result and one result per lab, per material.

11.1.3 The above terms are used in accordance with the definitions of these terms in TAPPI T 1206 "Precision Statement for Test Methods."

Table 2. Reproducibility - ion concentration measurements

Pulping Liquor	*Chloride* *mean* *% R* *# included*	*Sulfate* *mean* *% R* *# included*	*Thiosulfate* *mean* *% R* *# included*
Heavy black liquor	1.57 g/L 10.2% 3	17.70 g/L 22.1% 3	0.94 g/L 38.2% 3
Weak black liquor	1.53 g/L 51.9% 3	11.21 g/L 30.2% 3	8.94 g/L 55.8% 3
White liquor	1.433 g/L 30.4% 4	9.69 g/L 18.0% 4	4.42 g/L 36.8% 4
Oxidized white liquor	1.72g/L 51.4% 4	31.38 g/L 21.0% 4	11.36 g/L 22.2% 4
Green liquor	1.22 g/L 54.4% 4	10.29 g/L 6.7% 4	4.34 g/L 37.9% 4

Sulfite, oxalate, sulfide and carbonate concentrations were also measured during this interlaboratory study, however, there were not sufficient data to generate precision statistics.

Repeatability and reproducibility are estimates of the maximum difference (at 95%) which should be expected when comparing test results for materials similar to those described above under similar test conditions. These estimates may not be valid for different materials or testing conditions.

12. Keywords

White liquors, Green liquors, Black liquors, Smelt, Sulfides, Sulfites, Sulfates, Thiosulfates, Chlorides, Carbonates, Oxalates, Lactates, Formates, Acetates, Propionates, Ion chromatography, Liquors, Chromatography

13. Additional information

13.1 Effective date of issue: to be assigned.

13.2 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.

13.3 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.

13.4 This method was revised in 1999. A reproducibility statement was also added. The 2009 version included editorial changes and deletion of the reference to an autoclave in Section 6.1.

References

1. Krishnagopalan, J., Hill, M., and Fricke, A.L., "Chromatographic Analysis of Kraft Liquor Anions," *Tappi* **68** (9): 108 (1985).
2. Easty, D.B., Borchardt, M.L., and Webb, A.A., "Analysis of Pulping Liquors by Ion Chromatography: Evaluation and Validation," *Paperi Puu* **67** (9): 501 (1985).
3. Easty, D.B., and Johnson, J.E., "Recent Progress in Ion Chromatographic Analysis of Pulping Liquors: Determination of Sulfide and Sulfate," *Tappi* **70** (3): 109 (1987).

Appendix A

A.1 Columns, eluents, flow rates, detectors, and suppressor used for different analyses are summarized in Table 3. Alternate configurations and operating conditions are shown in Tables 4, 5 and 6 contain typical retention times with different columns and eluents. Please note that there are many newer columns and suppressors which will provide better, sharper, and quicker analyses.

Table 3. Ion chromatograph configurations and operating conditions

Substance determined	*Eluent*	*Flow rate, mL/min*	*Guard column*	*Separator column*	*Suppressor*	*Detector*
Sulfite sulfate, thiosulfate, chloride, oxalate	3 m*M* $NaHCO_3$ +2.4 m*M* Na_2CO_3	2.3	4 × 50 mm (HPIC-AG3)	4 × 250 mm (HPIC-AS3*)	Fiber (AFS-1) or membrane (AMMS) or 6 × 60 mm or 9 ×10 mm	Conductivity
Sulfide	1.0 m*M* Na_2CO_3 +10 m*M* NaOH +10 m*M* H_3BO_3 +15 m*M* ethylene-diamine	2.0	Metal-free metal removing column + 4 × 50 mm (HPIC-AG3)	4 × 250 mm (HPIC-AS3*)	None	UV at 215 nm
Organic acids	1 m*M* HCl	0.8	None	9 × 250 mm (HPICE-AS1)	Fiber (AFS-2) or membrane (AMMS-ICE) or 4 ×280 mm (Ag+ form)	Conductivity
Carbonate	Water	0.8	None	9 ×140 mm (HPICE-AS3) or 9 ×250 mm (HPICE-AS1)	None	Conductivity

*AS4 columns should not be used for analysis of spent liquors; the columns will become irreversibly plugged.

Table 4. Alternate ion chromatograph configurations and operating conditions

Substance determined	*Eluent*	*Flow rate, mL/min*	*Guard column*	*Separator column*	*Suppressor*	*Detector*
Sulfite sulfate, thiosulfate, chloride, oxalate	1.0 m*M* Na_2CO_3 +5.0 m*M* NaOH +0.8 m*M* *p*-cyano-phenol	1.6	(HPIC-AG4)	(HPIC-AS5)	Fiber (AFS-1) or membrane (AMMS)	Conductivity
Sulfite, sulfate thiosulfate, chloride, oxalate	0.75 m*M* $NaHCO_3$ +2.0 m*M* Na_2CO_3	2.0	HPIC-AG4A	HPIC-AS4A	Fiber (AFS-1) or membrane (AMMS)	Conductivity
Sulfite, sulfate, thiosulfate, chloride, oxalate	3.0 m*M* $NaHCO_3$ +2.4 m*M* Na_2CO_3 +0.8 m*M* *p*-cyano-phenol +2% CH_3CN	1.8	HPIC-AG4	HPIC-AS5	Fiber (AFS-1) or membrane (AMMS)	Conductivity
Sulfide	0.25 m*M* Na_2CO_3 +5.0 m*M* NaOH +1.5 m*M* ethylene-diamine	2.0	Metal-free metal removing column + HPIC-AG3 or HPIC-AG4A or HPIC-AG5	HPIC-AS3 or HPIC-AS4A or HPIC-AS5	None	UV at 215 nm
Organic acids	1 m*M* octane-sulfonic acid	0.8	None	HPICE-AS1	Fiber (AFS-2) or membrane (AMMS-ICE)	Conductivity

Table 5. Some typical retention times: chloride, oxalate, sulfoxy anions

Guard column	*Separator column*	*Eluent*	*Flow rate, mL/min*	*Retention time, min**				
				Chloride	*Sulfite*	*Sulfate*	*Oxalate*	*Thiosulfate*
HPIC-AG3	HPIC-AS3	3.0 m*M* $NaHCO_3$ +2.4 m*M* Na_2CO_3	2.3	2.0	5.7	8.6	12.0	40.9
HPIC-AG4A	HPIC-AS4A	2.0 m*M* Na_2CO_3 +0.75 m*M* $NaHCO_3$	2.0	1.8	6.1	7.8	9.8	27.4
HPIC-AG4	HPIC-AS5	1.0 m*M* Na_2CO_3 +5.0 m*M* NaOH +0.8 m*M* *p*-cyano-phenol	1.6	1.8	5.8	6.9	8.1	29.6
HPIC-AG4	HPIC-AS5	3.0 m*M* $NaHCO_3$ +2.4 m*M* Na_2CO_3 +0.8 m*M* *p*-cyano-phenol +2% CH_3CN	1.8	1.6	5.5	6.1	6.9	26.0

*Approximate times with new columns. Retention times decrease with column use.

Table 6. Some typical retention times: sulfide, carbonate, organic acids

Separator column	*Suppressor*	*Eluent*	*Flow rate, mL/min*	*Retention time, min*					
				Sulfide	*Carbonate*	*Lactic acid*	*Formic acid*	*Acetic acid*	*Propionic acid*
HPIC-AS3	None	1.0 m*M* Na_2CO_3 +10 m*M* NaOH +10 m*M* H_3BO_3 +15 m*M* ethylene-diamine	2.0	1	X	X	X	X	X
HPICE-AS3	None	Water	0.8	X	10.5	X	X	X	X
HPICE-AS1	Fiber (AFS-2)	1 m*M* HCl	0.8	X	X	12.2	13	14.5	17.3

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department. ■