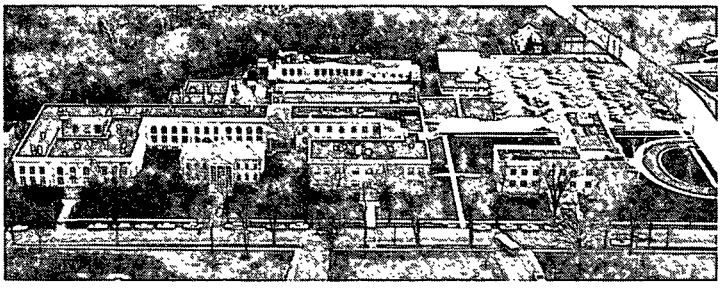
To Bill Fisher



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ANALYSIS OF PULPING LIQUORS BY ION CHROMATOGRAPHY: EVALUATION AND VALIDATION

DWIGHT B. EASTY, MARCIA L. BORCHARDT, AND ARTHUR A. WEBB

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Analysis of pulping liquors by ion chromatography: evaluation and validation

Dwight B. Easty, Marcia L. Borchardt, and Arthur A. Webb
The Institute of Paper Chemistry
P.O. Box 1039, Appleton, Wisconsin 54912, U.S.A.

ABSTRACT

Procedures proposed for ion chromatographic determination of anions in pulping liquors have been evaluated and validated. Sulfoxy anions, sulfide, chloride, and carbonate are determinable in black liquors by ion chromatography (IC). Excellent recoveries have been obtained of known amounts (spikes) of each of the species added to liquors. Satisfactory agreement between IC results and those from wet chemical methods was achieved for sulfate (in another laboratory), thiosulfate, sulfide, chloride, and carbonate. Limiting the utility of IC for sulfide determination is the need for samples to be extensively diluted and protected from oxidation.

INTRODUCTION

Ion chromatography (IC) principles and possible applications in the pulp and paper industry have been outlined in several earlier publications (1-3). It has been anticipated that IC will revolutionize the analysis of pulping liquors. Probable benefits of IC include enhanced accuracy, quicker analyses, and the ability to measure species not formerly determinable.

In 1983, Test Method T 699 pm-83, Analysis of Bleaching and Pulping Liquors by Ion Chromatography, was issued by TAPPI. Contained in that method are the basic instructions for purchasers of dual-column IC instrumentation who are interested in pulping and bleaching liquor analysis. In spite of the information provided by T 699, it is likely that the new user of IC for liquor analysis will require considerable time and effort to develop techniques, judgment, and supporting data before he can generate reliable IC results. The goal of the current research is to develop these types of information in a central laboratory and thereby ease the burden of startup for the individual analyst.

Specific tasks in current work include evaluation of the procedures outlined in TAPPI T 699, development of supplemental techniques necessary for efficient ion chromatography, and validation of results from IC analysis of pulping liquors. Validation is based upon comparison of IC results with those of other accepted methods and recovery of known amounts of materials of interest ("spikes") added to authentic liquors ("spiked samples"). This study emphasizes the application of IC for the determination of anions in kraft black liquor, a most challenging matrix for any analytical method. Also included in this report is an assessment of time demands and operational constraints involved in the use of IC for black liquor analysis.

EXPERIMENTAL

Ion chromatography

Apparatus and reagents are listed in TAPPI T 699 pm-83. Essential details and modifications are described below. The ion chromatograph is a dual-channel Model 2020i equipped with electrolytic conductivity and electrochemical (amperometric) detectors (Dionex Corporation, Sunnyvale, CA, U.S.A.). Sulfoxy anions, chloride, and sulfide were determined on an HPIC AS-3 column, and carbonate was measured on an HPICE AS-3 column. An anion fiber suppressor column was used for sulfoxy anions and chloride; no suppressor is required for sulfide or carbonate. Water was used as eluent for carbonate; the eluent for sulfide was 0.001M Na_2CO_3, 0.01M NaH_2BO_3, 0.0147M ethylene diamine; the eluent for sulfoxy anions and chloride was 0.003M $NaHCO_3$, 0.0024M Na_2CO_3. Completed run times (not including time for preparation of sample and standards and calibration) were for sulfoxy anions and chloride, 40 min; for sulfide, 3-4 min; for carbonate, 15-20 min. Each day that a column was used, eluent was pumped through the column for the following equilibration times in order to obtain a stable base line before running the first sample: HPIC AS-3, 1/2-1 hr; HPICE AS-3, 2 hr. These times are for well maintained columns which are regularly used. Columns which have been stored, regenerated, or which are new require more time to stabilize.

Distilled water for dilution of samples and standards was deoxygenated by nitrogen sparging. Sulfide antioxidant buffer (SAOB) (4), 5 mL/L, was added to samples and standards for sulfide determination. Stock sulfide standard solution (~ 5 g/L $S^=$) was prepared in 50% SAOB and was standardized daily by potentiometric titration with $Cd(NO_3)_2$. Significant changes in sulfide concentration

were not observed. Working sulfide standards were prepared daily from the stock standard.

Wet chemical methods

Sulfide and thiosulfate were titrated with mercuric chloride using a sulfide ion-selective electrode (5). Prior to titration of thiosulfate, sulfide was removed by addition of $ZnSO_4$ and centrifugation.

Samples for potentiometric determination of chloride were digested with H_2SO_4 and H_2O_2 to remove interfering sulfide.

RESULTS AND DISCUSSION

Preliminary studies

Procedures supplied by the instrument manufacturer originally suggested use of the HPIC AS-4 separator column for analysis of pulping liquors. However, during the attempted analysis of a spent sulfite liquor in this laboratory, severe plugging of the AS-4 column was experienced. Subsequent attempts at running kraft black liquor on another AS-4 column also brought about irreversible plugging. Thus it was concluded that the AS-4 column was not suitable for any spent pulping liquors.

An HPIC AS-3 column, with greater void volume and larger resin particles, was used successfully for analysis of black liquors diluted 1:1000 and filtered through a 0.22-μm filter. As a result of this work, the manufacturer's recommendations were then modified to specify use of the AS-3 column for liquors.

Sulfoxy anions

Sulfoxy anions were determined by ion chromatography in five weak black liquors. Data are summarized in Table I. Values for thiosulfate in the liquors

were also determined by mercuric chloride titration for comparison. With the exception of Sample TBL, black liquor thiosulfate contents determined by IC and by titration exhibited good agreement.

(Table I here)

Satisfactory agreement between sulfate values determined by IC and by titration with lead perchlorate has been reported by Koivuniemi et al. (6). Additional sulfate comparisons were therefore not undertaken.

Table I indicates that sulfite can be determined in black liquor by ion chromatography. Historically, use of the TAPPI T 625 titrimetric procedure in this laboratory has measured little or no sulfite in black liquor samples. This discrepancy was resolved by the findings of Tonsi-Eldakar et al. (7), reported in Table II, which revealed that zinc carbonate, added to remove sulfide prior to titration of sulfite and thiosulfate, also removed sulfite.

(Table II here)

Use of formaldehyde for preserving sulfite standards and liquor samples in which sulfite is to be determined is described in T 699. Without added formaldehyde, sulfite is rapidly oxidized to sulfate. As shown in Table III, sulfite retention times and peak heights varied with formaldehyde concentration. It is therefore essential to have equal amounts of formaldehyde in samples and standards.

(Table III here)

Spike recoveries were used to further demonstrate the value of IC for determining sulfoxy species in black liquors. Results in Table IV, typical of those

in this extensive study, are close to 100%.

(Table IV here)

Data in Table V were obtained in a brief study of the stability of sulfoxy anions. Five separate bottles of a single sample of white (chip chute) liquor were completely filled and remained sealed at room temperature for the indicated storage times. The data show no consistent trend with time of storage; thus these species do not have to be determined immediately after liquor samples arrive in the laboratory as long as bottles remain completely filled and sealed.

(Table V here)

Chloride

The chloride contents of 11 heavy black liquor samples (43-64% solids) were determined by IC at the Institute and by direct potentiometry (chloride ion-selective electrode) in another laboratory. Two of the liquors were also analyzed by potentiometric titration with silver nitrate using chloride and silver/sulfide indicating electrodes. Results of the chloride determinations are shown in Table VI.

(Table VI here)

Considering the difficulties inherent in handling heavy black liquor samples, the agreement between chloride values obtained by the different methods is good. This level of agreement between methods based on entirely different principles supports the validity of IC for determining chloride in black liquors.

Sulfide

Values for sulfide in two black liquors determined by IC and by potentiometric titration with Hg^{++} and Cd^{++} titrants are shown in Table VII. The data

show some between-method variation, but no trend is evident other than a possible decrease in sulfide content with sample age. These results and the spike recovery values in Table VIII indicate that sulfide can be measured in black liquor by IC.

(Table VII and VIII here)

Although black liquor sulfide measurements are possible by IC, special techniques are necessary to ensure the success of the determination. The principal objectives of the special techniques are (a) operation at a sulfide concentration within the linear range of the electrochemical detector, and (b) avoiding loss of sulfide from samples and standards.

Weak black liquor samples had to be diluted from 1:10,000 to 1:50,000 to bring their sulfide contents into the optimum range of the detector, approximately 0.4-1 ppm $S^{=}$. Samples with a sulfide concentration below 0.4 ppm did not generate a sufficient electrode response, as shown in Table IX. Ten injections of a standard solution containing 3.7 ppm $S^{=}$ tarnished the electrode significantly. Thus, the electrochemical detector can accommodate occasional high-sulfide samples, but persistent overloading of the detector will lead to excessive downtime for electrode cleaning.

(Table IX here)

Liquors are normally diluted about 1:1000 for determination of sulfoxy anions. A liquor having enough thiosulfate to be measured by electrolytic conductivity at that dilution will usually contain sufficient sulfide to foul the electrochemical detector. Therefore, simultaneous determination of sulfide and sulfoxy anions in black liquors does not appear to be realistic.

Black liquor samples diluted 1:10,000 with deoxygenated water incurred significant sulfide losses, as indicated in Table X. When the deoxygenated water contained 5 mL/L of sulfide antioxidant buffer (SAOB) (4), the sulfide losses were prevented. The incompatibility of SAOB with the conductivity detector is an additional reason why sulfide and sulfoxy anions cannot be measured simultaneously.

(Table X here)

Thiosulfate increases due to oxidative loss of sulfide have not been observed. It is speculated that sulfide is not oxidized as readily in the more concentrated solutions (1:1000 dilution) in which thiosulfate is determined.

Operations necessary to start sulfide determinations include preparation of SAOB, stock sulfide, dilute standards, and dilute samples; standardization of stock sulfide; equilibration of column and stabilization of detector; and finally running of standards and samples. These procedures require a minimum of 4-6 hours before the first sample is run. Thus, while IC is useful for large numbers of determinations, it would not appear to be the method of choice for measuring sulfide in one or two samples.

Carbonate

Data in Table XI indicate that the IC and CO_2 evolution (TAPPI Test Method T 624) techniques yielded carbonate contents of black liquors which were generally in agreement. Recoveries of carbonate spikes added to four black liquors ranged from 94 to 103%. Determination of carbonate by IC is a valuable technique because of the great time saving compared with the CO_2 evolution method.

(Table XI here)

Comments on operation and maintenance of the ion chromatograph

Ion chromatography can be most efficiently performed by an analyst who has become well acquainted with the instrument's operation and maintenance. The analyst should be alert for rising back pressure, variable base lines, changes in peak shapes, and poor chromatograph reproducibility. Regular cleaning of the guard column and replacement of column bed supports will usually eliminate these problems. It is imperative that liquor samples be filtered and adequately diluted to avoid fouling the columns and the electrochemical detector.

For efficient determination of a wide variety of ionic species, a dual-channel IC has been found to be essential. Although it permits concurrent determinations, the second channel has been of greatest value for column and detector conditioning and stabilization without inhibiting productive use of the first channel.

CONCLUSIONS

Ion chromatography is a valuable technique for determining sulfoxy anions, chloride, and carbonate in black liquors. Although sulfide can also be determined in black liquors by IC, special techniques must be employed to ensure success. Samples must be extensively diluted to avoid fouling of the detector and to operate in the detector's limited linear range. In addition, an antioxidant must be added to samples and standards to prevent loss of sulfide. IC would not normally be the method of choice for determining sulfide in a small number of samples.

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Table I. Determination of sulfoxy anions in black liquor.

	Ion Chromatography			Titration
Sample	Sulfite, %	Sulfate, %	Thiosulfate, %	Thiosulfate, %
314	0.06	2.2	4.1	4.1
TBL	0.60	1.3	2.0	3.1
31-8	0.05	1.0	3.4	3.4
31-10	0.33	1.0	2.1	2.5
31-31	0.72	1.0	1.6	1.7

Results expressed as percentage of o.d. liquor solids.
Values are means of from two to six replicate determinations.

Table II. Effect of zinc carbonate added to a standard solution containing sulfite and thiosulfate.

$ZnCO_3$, mL/250 mL	Na_2SO_3, g/L	$Na_2S_2O_3$, g/L
0	0.86	4.61
1	0.56	4.71
10	0.34	4.65
30	0.19	4.55
60	0.08	4.71

Zinc carbonate addition and sulfite and thiosulfate determinations were performed according to TAPPI T 624 os-68.
Initial solution concentrations: 0.9 g/L Na_2SO_3 and 4.6 g/L $Na_2S_2O_3$.

Table III. Sulfite response in presence of formaldehyde.

HCHO, % x 10^3	Retention Time, min	Peak Height, mm	Peak Area
0.04-0.7	4.14	120	2323
4	4.08	114	2501
7	4.05	107	2469
15	3.98	101	2333
37	3.85	90	2232
370	2.89	68	2639

Table IV. Recovery of sulfoxy species added to black liquor.

Ion	Original, %[a]	Added, %[a]	Total Found, %[a]	Recovery, %
Sulfite	0.33	0.59	0.94	102
			0.89	97
Sulfate	0.98	1.18	2.13	99
			2.13	99
Thiosulfate	2.13	1.78	3.97	102
			3.91	100

[a]Percentage of o.d. liquor solids.

Table V. Determination of sulfoxy species after varied storage time.[a]

Storage Time, hr	Na_2SO_3	$Na_2S_2O_3$	Na_2SO_4
3	4.9	5.1	5.3
24	6.8	5.8	5.0
48	4.1	4.7	4.1
96	7.0	5.7	5.2
120	8.4	5.7	5.2

[a]Results in g/L of indicated compound.

Table VI. Chloride in black liquor.[a]

Sample	Ion Chromatography	Direct Potentiometry	Potentiometric Titration	
			Cl Electrode	Ag/S Electrode
Unoxidized, 6/24	0.68	0.57		
Unoxidized, 7/12	0.65	0.70	0.60	0.61
10 & 11 Feed, 6/24	0.69	0.66		
10 & 11 Feed, 7/4	0.66	0.50	0.61	0.62
10 Mix tank, 6/24	0.92	0.94		
10 Mix tank, 6/28	0.95	0.89		
11 Mix tank, 6/24	0.92	0.73		
11 Mix tank, 7/5	0.88	1.08		
A[b], 6/13-16	0.46	0.41		
B[b], 6/20-25	0.53	0.41		
C[b], 6/20-26	0.39	0.42		

[a]All values expressed as percentage of o.d. liquor solids.
[b]Purchased waste liquors.

Table VII. Sulfide in black liquor, %.

Method	Sample			
	TBL		31-31	
IC	1.71	8/18/83	1.28	8/18/83
	1.74		1.34	
	1.62			
$HgCl_2$ titration	1.62	8/15/83	1.70	8/15/83
	1.60			
	1.56	8/16/83		
	1.55			
$Cd(NO_3)_2$ titration	1.41	8/21/83	1.32	8/21/83

Results expressed as percentage of o.d. liquor solids.

Table VIII. Recovery of sulfide added to black liquor.

Sample	Original, %	Added, %	Total Found, %	Recovery, %
TBL	1.68	0.34	2.08	103
			2.05	101
31-31	1.31	0.42	1.75	101
			1.79	103

Table IX. Response of electrochemical detector to low sulfide concentrations.

Added Sulfide, mg/L[a]	Indicated Sulfide, mg/L
None	< 0.05
0.1	< 0.05
0.2	0.07
0.3	0.16
0.4	0.42

[a]Added to oxidized black liquor diluted 1:10,000.

Table X. Effect of time on measured sulfide content.

Time After Sample Dilution, min	Measured Sulfide, %[a]	
	Without SAOB	With SAOB
0	1.51	1.62
18	1.07	1.60
45	0.53	1.62

[a]Percentage of o.d. liquor solids.

Table XI. Carbonate in black liquor samples.[a]

Sample	IC	CO_2 Evolution
314	5.7	5.7, 5.7
31-8	5.0, 5.1	4.8, 4.6
31-10	4.7, 4.8	4.4, 4.4
HTBL1	6.7	7.1
HTBL2	6.3	6.2

[a]Percentages as $CO_3^=$ in o.d. liquor solids.