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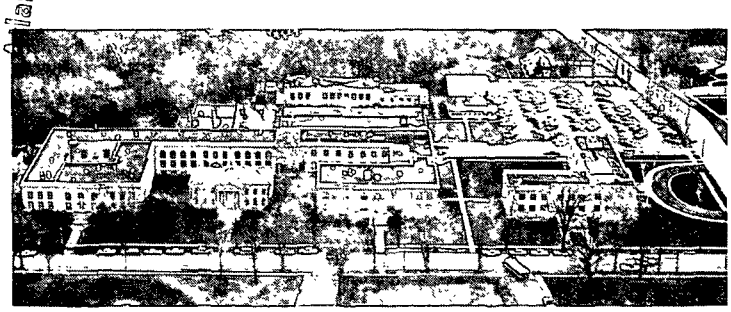

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RECENT PROGRESS IN THE ION CHROMATOGRAPHIC ANALYSIS OF PULPING LIQUORS: DETERMINATION OF SULFIDE AND SULFATE

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RECENT PROGRESS IN THE ION CHROMATOGRAPHIC ANALYSIS OF PULPING LIQUORS: DETERMINATION OF SULFIDE AND SULFATE

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ABSTRACT

An ultraviolet (UV) detector has been evaluated for use in the ion chromatographic determination of sulfide in pulping liquors. Because the UV detector is less sensitive and has a wider range than the amperometric detector, liquors do not need to be diluted as extensively for sulfide measurement. This makes sample preparation easier and reduces oxidative loss of sulfide. Problems in the ion chromatographic determination of sulfate in green liquor have been investigated and resolved. Sulfate can be determined accurately in green liquor if the liquor is diluted with deoxygenated distilled water and immediately injected into the ion chromatograph.

INTRODUCTION

Results of early studies (1-3) suggested that ion chromatography (IC) would revolutionize the determination of anions in pulping and bleaching liquors. An investigation designed to test that premise was initiated at The Institute of Paper Chemistry in 1983. Shortly thereafter, Test Method T 699 pm-83, Analysis of Bleaching and Pulping Liquors by Ion Chromatography, was issued by TAPPI. Although the test method described essential equipment and reagents, the analysis procedure appeared to be based upon limited experience with pulping and bleaching liquors. Consequently, T 699 became the focus of Institute studies on ion chromatography.

The approach taken in this investigation involved evaluation of the procedures in T 699, development of supplemental techniques when necessary, and validation of IC results by spike recovery studies and comparisons with other methods. Limited studies of this type are needed by any laboratory starting work with a new technique or instrument. We felt that an extensive investigation in a central laboratory should ease the startup burden for the individual analyst and enhance the utility of IC for the industry. It was envisioned that findings from this work would be incorporated in an updated version of T 699. The procedure leading to adoption of the revised test method is underway.

Initial results from our investigation indicated that the ion chromatograph, with the electrolytic conductivity detector, could be used to determine most of the common anions in pulping liquors, including sulfite, sulfate, thiosulfate, chloride, and carbonate (4). Sulfide cannot be detected by conductivity; an amperometric detector was recommended for sulfide in T 699. Limitations to the sulfide determination by IC using the amperometric detector were encountered and are reviewed in detail below. Kraft black liquor was used for this work because it tends to be a difficult matrix for any analytical method. We felt that a method that works on black liquor would work on virtually anything. Results of studies at the University of Maine (5) were consistent with those from the Institute. In addition, the Maine workers demonstrated the utility of IC for determining organic acids in black liquor.

The second phase of our investigation was devoted to evaluation of IC for bleach liquor analysis. Determinations of chlorite, chlorate, oxalate, hypochlorite, and chlorine (as hypochlorite) were studied and shown to be feasible (6). The unanticipated ability of IC to determine chlorine dioxide was revealed. It is based on a chlorite response in the ion chromatograph which is proportional to the chlorine dioxide injected. Chlorite originally present in the liquor is measured in a second aliquot of sample from which chlorine dioxide has been removed by sparging.

Problems in the ion chromatographic analysis of pulping liquors, revealed in studies at the Institute and elsewhere, were the subject of the most recent phase of our investigation. An ultraviolet detector for sulfide was evaluated to learn if it was subject to the same limitations as the amperometric detector. Problems in determining sulfate in green liquor, encountered in another laboratory (7), were also studied. Findings from these two investigations, which were needed in order to prepare the T 699 revision, are the subject of this report.

ULTRAVIOLET DETECTION OF SULFIDE

The UV detector was evaluated because of the limitations of the amperometric detector revealed in earlier work (4). Weak black liquor samples had to be diluted 1:10,000 to 1:50,000 to bring their sulfide contents into the optimum range of the amperometric detector, approximately 0.4-1 ppm $S^{=}$. Black liquor samples diluted 1:10,000 with deoxygenated water incurred significant sulfide losses. To combat the oxidative loss, sulfide antioxidant buffer (8) was added at 5 mL/L.

Repeated injection of high-sulfide samples caused tarnishing of the silver electrode in the amperometric detector. The electrode then had to be removed and cleaned. Sulfoxy anions and sulfide cannot be determined simultaneously. Because of sensitivity differences between the conductivity and amperometric detectors, a sample dilution appropriate for sulfoxy anions is inappropriate for sulfide, and vice versa. Sulfide antioxidant buffer is not compatible with the conductivity detector.

As indicated in Table 1, the UV detector measures sulfide at higher levels than the amperometric detector. The useful range of the UV detector is about 1-20 ppm. Thus liquor samples do not have to be diluted as extensively. Data in Table 2 indicate that some sulfide was lost with time when black liquor was diluted 1:1000 with deoxygenated water; the loss is less than that incurred with 1:10,000 dilution in earlier work. The sulfide loss was hardly perceptible when millimolar ascorbic acid was added as an antioxidant. Higher ascorbic acid concentrations interfered with the UV measurement of sulfide. If the liquor is analyzed

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immediately after dilution, the antioxidant is not essential.

Table 1 Response of UV detector to sulfide in black liquor

Added Sulfide, mg/L[a]	Indicated Sulfide, mg/L
None	0
5.0	5.0
10.0	10.0
15.0	14.8
20.0	19.6

[a]Added to oxidized black liquor diluted 1:2000.

Table 2 Effect of time on measured sulfide content

Time After Sample Dilution,[a] min	Measured Sulfide, %[b]	
	Without Antioxidant	With Antioxidant[c]
< 1	1.99	2.05
15	1.55	2.05
30	1.25	2.01
45	1.22	1.97
60	1.13	1.97
90	0.99	1.91

[a]1:1000.
[b]Percentage of o.d. liquor solids.
[c]0.001M ascorbic acid.

Results in Table 3 show quantitative recovery of known amounts of sulfide added to black liquor and detected by UV. Sulfide contents of black liquors measured by IC with UV detection and by potentiometric titration with mercuric chloride were in excellent agreement, as indicated by Table 4. We were originally concerned that the organics in black liquor would interfere with the UV measurement, but that did not occur at 215 nm.

Table 3 Recovery of sulfide added to black liquor

Sample	Original, %	Added, %	Total Found, %	Recovery, %
KBL	2.12	1.63	3.75	100
PBL	1.18	0.80	2.01	104
SBL	2.18	1.46	3.63	99

Table 4 Comparison of sulfide determined by ion chromatography and potentiometric titration

Sample	Ion Chromatography[a]	Potentiometric Titration[b]
KBL1	2.12	2.06
KBL2	2.05	2.04
PBl	1.18	1.32
SBL	2.18	2.14
ABL	0.69	0.67
KWBL	0.90	0.88

[a]UV detector. Black liquor samples diluted approx. 1:1000. Values are percentage of o.d. liquor solids.
[b]Titration with $HgCl_2$.

The UV detector and the conductivity detector sense sulfide and sulfoxy anions, respectively, at similar concentrations. Nevertheless, sulfide and sulfoxy anions are not usually determined simultaneously. The preferred eluents for sulfide and sulfoxy anions are different, and ethylenediamine in the sulfide eluent is not removed by the fiber suppressor. A packed bed suppressor column must be used if conductivity measurements are to be made in eluents containing ethylenediamine.

This study has shown that the UV detector provides valid measurements of sulfide in black liquor and, because of its lower sensitivity, represents an improvement over the amperometric detector for sulfide determinations.

DETERMINATION OF SULFATE IN GREEN LIQUORS

A report from another laboratory has shown sulfate values in green liquors measured by IC which were twice as high as those from gravimetric determinations (7). Parigi hypothesized that thiosulfate, sulfite, and other sulfur compounds were oxidized to sulfate when the liquor was diluted 1:1000 with distilled water for analysis by IC. To overcome this problem, he diluted the green liquor 1:1000 with 0.1% hydrochloric acid. The acid would be expected to volatilize sulfide and sulfite and convert thiosulfate to elemental sulfur. Parigi's ion chromatographic analysis of green liquors diluted with acid yielded data which agreed closely with values from gravimetric analysis.

Workers in Finland, studying sulfate in black liquor, obtained results which were contrary to those of Parigi; they found higher sulfate values by gravimetry than by IC (9). Liquors for IC analysis were diluted 1:500 with carbonate/bicarbonate eluent. Sulfate values obtained by IC agreed well with those from potentiometric titration with lead perchlorate using a lead ion-selective electrode.

An investigation was therefore undertaken in this laboratory to determine if dilution with acid is essential for accurate ion chromatographic determination of sulfate in green liquor. Data in Table 5 show the effect of the dilution medium on measured sulfate content. When green liquor was diluted with 0.1% HCl, sulfate values were essentially constant with time. Sulfate values increased gradually following dilution with deoxygenated water. However, if the sample was injected into the ion chromatograph within a half hour after diluting the liquor, results with deoxygenated water and with HCl diluent agreed within 0.1 g/L.

A portion of the same green liquor was diluted with air-saturated water and injected promptly into the ion chromatograph. An elevated sulfate content, 6.85 g/L, suggests that some oxidation had occurred immediately upon dilution.

Table 6 contains sulfate contents of several green liquors which were diluted and immediately injected into the ion chromatograph. Samples diluted with 0.1% HCl and with deoxygenated water gave comparable results. Thus when samples are injected promptly after dilution, use of 0.1% HCl as diluent does not appear to be necessary.

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Table 5 Effect of dilution medium on sulfate content as function of time after dilution

Time After Dilution, min	Sulfate, g/L; Liquor Diluted with 0.1% HCl	Deox. H_2O
< 1	6.50	6.49
15	6.38	6.46
30	6.45	6.52
45	6.39	6.65
60	6.36	6.55
120	6.41	6.91
180	6.41	7.12
240	6.46	7.22
300	6.46	7.39

Green liquor diluted 1:1250. Sulfate determined by ion chromatography.

Table 6 Sulfate contents of green liquors diluted with 0.1% HCl and with deoxygenated water

Liquor	Sulfate, g/L; Liquor Diluted with 0.1% HCl	Deox. H_2O
1	6.64	6.61
2	5.62	5.66
3	9.55	9.56
4	15.0	14.9
5	9.80	9.80
6	3.46	3.42
7	8.37	8.37
8	0.63	0.63

Liquors were diluted from 1:200 to 1:2000 depending on sulfate content. Samples were injected into the ion chromatograph within 1 min after dilution.

This investigation has provided the basis for the following conclusions regarding determination of sulfate in green liquor: Dilution of samples with 0.1% HCl is effective but not essential. Deoxygenated water may be used for dilution if samples are injected into the ion chromatograph promptly. Dilution water containing dissolved oxygen is not recommended.

EXPERIMENTAL

The ion chromatograph used for this work is a dual-channel Model 2020i equipped with electrolytic conductivity and ultraviolet/visible detectors (Dionex Corporation, Sunnyvale, CA). Sulfide determinations employed a metal-free metal removing column, HPIC-AG3 and HPIC-AS3 columns connected in series, and the UV detector. No suppressor column is required for sulfide. The eluent for sulfide contained 10 mM Na_2CO_3, 10 mM NaOH, 10 mM H_3BO_3, and 15 mM ethylenediamine. Eluent flow rate was 2.0 mL/min. The UV detector wavelength was 215 nm.

Used for sulfate determinations were HPIC-AG3 and HPIC-AS3 columns, an anion fiber suppressor, and the conductivity detector. Eluent was a 3 mM $NaHCO_3$, 2.4 mM Na_2CO_3 at 2.8 mL/min. Distilled water for dilution of samples and standards was deoxygenated by nitrogen sparging.

ACKNOWLEDGMENTS

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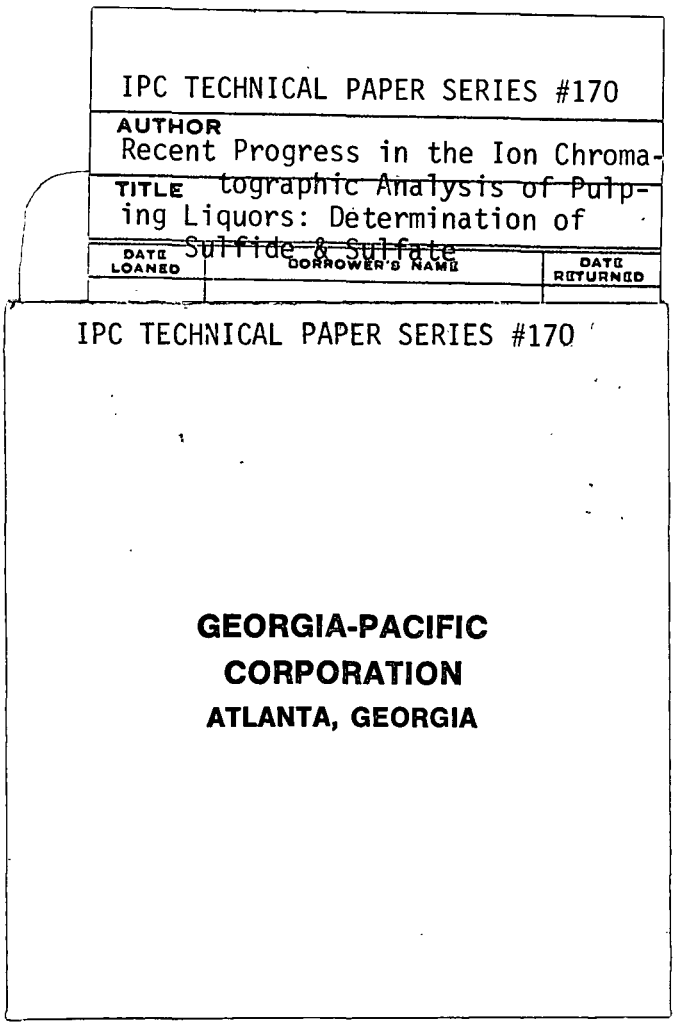
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