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Improved analysis of process liquors for the pulp and paper industry by ion chromatography

Steve Utzman

Boise Cascade Research and Development, 4435 N. Channel Avenue, Portland, OR 97217 (USA)

ABSTRACT

In this paper, techniques are presented to overcome interferences from caustic matrices and neighboring ions found in process solutions. Column switching and the use of low-capacity columns to characterize strongly retained analytes are described. Oxalate, sulfide, sulfite, sulfate and thiosulfate are characterized on one set of separator columns. High-capacity cation-exchange resins are shown to be an effective pre-treatment tool for neutralizing a caustic chlorine dioxide scrubbing liquor, enabling baseline resolution of chlorate.

INTRODUCTION

Wood is converted into fibers for papermaking by a number of pulping processes [1,2]. Chemical pulping is a process that dissolves lignin, leaving the cellulose and hemicellulose components of the fibers for papermaking [3]. In the kraft process, wood chips are delignified by digesting at high temperature with a cooking liquor consisting of an aqueous solution of sodium hydroxide and sodium sulfide. The cooking solution is called a white liquor.

The white liquor becomes black after the pulp is digested, due to dissolved and degraded wood constituents. The black liquor is then washed from the pulp and transferred to a storage tank where sodium sulfate is added to make-up for losses of inorganic elements during the digestion. The mixture from the storage tank is evaporated to a solids content of 60–70% and fed to a recovery furnace where the organic components are burned to evolve heat. A molten mass of sodium carbonate and sodium sulfide remain. It contains impurities in small quantities of sodium sulfate, sulfite, and thiosulfate [4]. A green liquor is produced by dissolving the molten mass in water. The mixture is treated with a suspension of calcium hydroxide to convert the sodium carbonate back into sodium hydroxide, thereby producing white liquor for reuse in the cooking process.

Some pulp mills employ the use of an on-site bleach plant to manufacture chlorine dioxide as an additional method of delignifying the pulp. Concerns about chemicals released to the atmosphere from a bleach plant have resulted in the establishment of state and federal programs, limiting the emissions of chlorine and chlorine dioxide. To combat these emissions, studies have shown that white liquor is among the more effective process solutions used as a scrubbing agent [5]. This scrubbing action (by the white liquor) becomes another process that is tied into the recovery liquor cycle. It is also a point in the process where corrosive ions are introduced.

Pulp mill process engineers are very concerned about corrosion, and how efficient the recovery cycle is working. The ion chromatographer plays an important role in monitoring and troubleshooting the process chemistry involved in the recovery cycle.

Corrosion is best understood by focusing on chloride, chlorite and chlorate. Sulfite, sulfate and thiosulfate have already been mentioned as by-products of the recovery process. The presence of oxalate can cause the formation of insoluble salts. The relative abundance of all these anions provide a

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method of monitoring the reduction–oxidation environment at various points in the recovery cycle.

One of the goals of this paper is to present an analysis of anions in pulping and scrubbing solutions, with an emphasis on minimizing system modifications. All too often, the analyst incorporates numerous methods —each developed for a specific family of anions— in an effort to obtain a comprehensive anion characterization. This is often tedious and time-consuming: columns are changed and equilibrated, eluents are modified or replaced, all requiring a period of time to re-equilibrate. The methods presented in this paper will reduce column changes, improve the baseline resolution of chlorate and improve the resolution of oxalate from sulfate using a carbonate eluent.

Previous work has described a fast analysis of sulfite, sulfate and thiosulfate in pulping liquors using column switching [6]. The switching technique was originally designed for white liquors and other process solutions. This paper will expand upon that work to consider the more complex black liquor. Sulfide analysis will also be presented using the same column configuration for oxalate, sulfite, sulfate and thiosulfate analysis. Improved chlorate resolution is achieved through sample matrix neutralization, using a high-capacity cation-exchange resin.

EXPERIMENTAL

Instrumentation

Method development was performed isocratically on a gradient ion chromatograph (Model 4000, Dionex, Sunnyvale, CA, USA). The sample loop size was 50 μl and the eluent flow-rate was 1.0 ml/min. The chromatograph module was equipped with two eight-port slider valves. The first valve is used for injection; the other for column switching to redirect the flow of anions. The column switching, or slider valve is placed in series after the injector valve. The OmniPax-100 guard (50 × 4 mm) and analytical (250 × 4 mm) columns were placed on either side of the switching valve. These columns were used for the separation of oxylate, sulfide, sulfite, sulfate and thiosulfate. AS9-SC guard (50 × 4 mm) and analytical (250 × 4 mm) columns were used to resolve chlorate.

Sulfite, sulfate, thiosulfate and oxalate were resolved using an eluent composed of 1.3 m*M* Na_2CO_3, 6 m*M* NaOH and 1.58 m*M* *p*-cyanophenol. For sulfide, an eluent of 10 m*M* boric acid, 15 m*M* ethylenediamine, 10 m*M* NaOH, 1 m*M* $NaNO_3$ in 2% methanol was used. The chlorate eluent was composed of 2 m*M* Na_2CO_3 and 0.75 m*M* $NaHCO_3$.

Chemical suppression was achieved with an anion micromembrane suppressor (Dionex), using 10 m*M* sulfuric acid regenerant at a flow-rate of 5 ml/min.

Oxalate, chlorate, sulfite, sulfate and thiosulfate were detected by conductivity (Model CDM, Dionex) in the 30 μS range. Sulfide was detected electrochemically using amperometry (Model PAD-2, Dionex), at an applied potential of 0 V. The detector cell is solvent compatible, three-electrode thin-layer design with a silver working electrode and an Ag/AgCl reference electrode. The working electrode was cleaned as needed, with fine polishing compound.

Detector output was directed to a Waters LAC/E interface and 845 workstation. Data processing was performed with Waters ExpertEase chromatography software, version 3.0.

Reagents

Sulfite, sulfate, thiosulfate, oxalate and chlorate standards were prepared from 1000 mg/l stock solutions using analytical-grade EM-Science reagents. The sulfite working standard was prepared in 10% isopropanol to prevent oxidation. The use of formaldehyde as an anti-oxidant was avoided. Formaldehyde will influence the peak height and retention characteristics, based on the amount of formaldehyde added [7,8].

Working sulfide standards were prepared from a 1000 mg/l stock solution containing 1 ml/l anti-oxidant buffer (17.6 g of ascorbic acid, 8 g of 50% NaOH and 1.0 ml of ethylenediamine in 100 ml of water). The stock solution was standardized by potentiometric titration with cadmium nitrate using a sulfide ion-selective electrode.

Working standard solutions of sulfite and sulfide were prepared fresh daily. Degassed, high-purity 18 MΩ cm water was used for all eluent and standard solution preparations.

Dealkalization of white liquor samples was achieved with Duolite C-433 weak-acid cation-ex-

change resin. The resin was pre-wetted and rinsed with high-purity deionized water. The resin slurry was poured into a glass, gravity flow column (30 × 0.9 cm, Spectrum Industries, Los Angeles, CA, USA). The resin bed was washed with 3–5 bed volumes of distilled, deionized water. Sample loading volumes were 5 ml; bed volume was 18.9 ml, with a void volume of 6 ml. Samples collected for chlorate analysis were made at 8 ml, using a 2-ml aliquot. The resin was returned to its fully regenerated form with 1% H_2SO_4. The acid dosage was set at 105% of the resin operating capacity (4 equiv./l).

RESULTS AND DISCUSSION

Fig. 1 is a chromatogram of a diluted black liquor and shows the resolution of oxylate from sulfate. A column-switching technique was used to shorten the analysis time and maximize the resolution of the divalent species. Initially, the switching valve is in the off position, allowing chloride, sulfite, sulfate and oxalate to pass through the guard column and on to the analytical column in less than 3 min. Thiosulfate remains on the guard column. At 3.1 min, the switching valve is activated, redirecting the flow of anions. For the remainder of the analysis, chloride, sulfite, sulfate and oxalate all flow from the analytical column back to the guard column where they elute with thiosulfate. Thiosulfate only passes through the guard column and is eluted after chloride. The time saved by using column switching for thiosulfate analysis is approximately 60% [6]. The reduction in retention time also improved the peak symmetry of this strongly retained analyte.

Polymeric multi-mode columns, like the OMNIPAX columns used in Fig. 1, are ideal for process liquor analysis. They allow ion exchange in a solvent compatible matrix [9]. And most importantly, they can be cleaned with pure solvent, washing off strongly retained hydrophobic compounds (like humic acids) and other contaminants found in process liquors. The manufacturing of the multimode columns (Dionex), requires the use of at least 1% organic solvent to hydrate the hydrophobic regions of the resin.

Poor resolution of oxalate from sulfate was found, using a carbonate eluent with the minimum amount of recommended organic solvent. Resolution was improved (over direct injection) using column switching. However, this technique alone did not supply baseline resolution of these two analytes.

It was found by *eliminating* the organic solvent entirely, complete resolution of oxalate from sulfate was achieved, as shown in Fig. 1. When the solvent was removed, system back-pressure increased by a

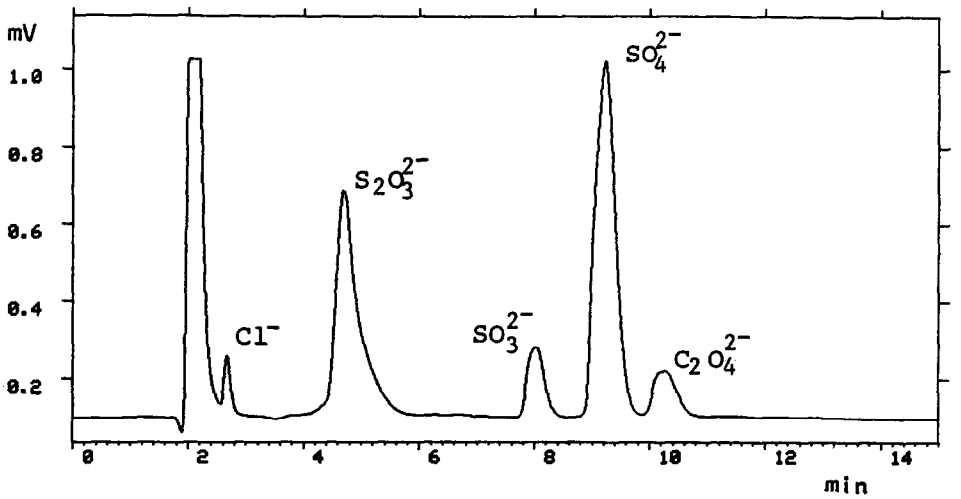

Fig. 1. Chromatogram of a diluted (1:500) black liquor using the column-switching technique. The switching valve was activated at 3.1 min. The eluent was composed of 1.3 m*M* Na_2CO_3, 6 m*M* NaOH and 1.58 m*M* *p*-cyanophenol. All other conditions are described in text.

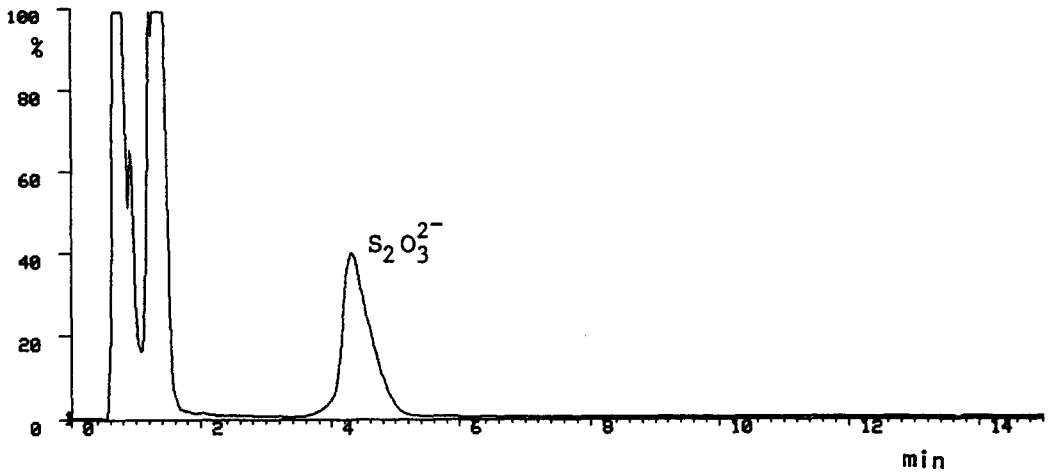

Fig. 2. Chromatogram of the same black liquor sample used in Fig. 1. The column switching method was optimized for thiosulfate by activating the switching valve at 0.3 min. The sample passes only the switching valve and guard column at this activation time. All other conditions the same as in Fig. 1.

modest 100 p.s.i. Perhaps in the absence of organic solvent, the *p*-cyanophenol component of the eluent is sufficient to condition the hydrophobic regions of the column. No reduction in column performance was observed in six months of using eluent without organic solvent (in the presence of *p*-cyanophenol), or other separations and cleaning methods requiring high solvent concentrations.

Caution should be exercised when quantifying thiosulfate in the presence of significant levels of nitrate or phosphate, using the column-switching technique. Simultaneous elution was found with all three of these anions using a column-switching time of 3.1 min.

This problem was avoided by directing all the anions through the guard column alone. This was accomplished by advancing the switching time to 0.3 min. This was the minimum time necessary for the sample to clear the switching valve. Fig. 2 is a chromatogram showing the use of the shorter

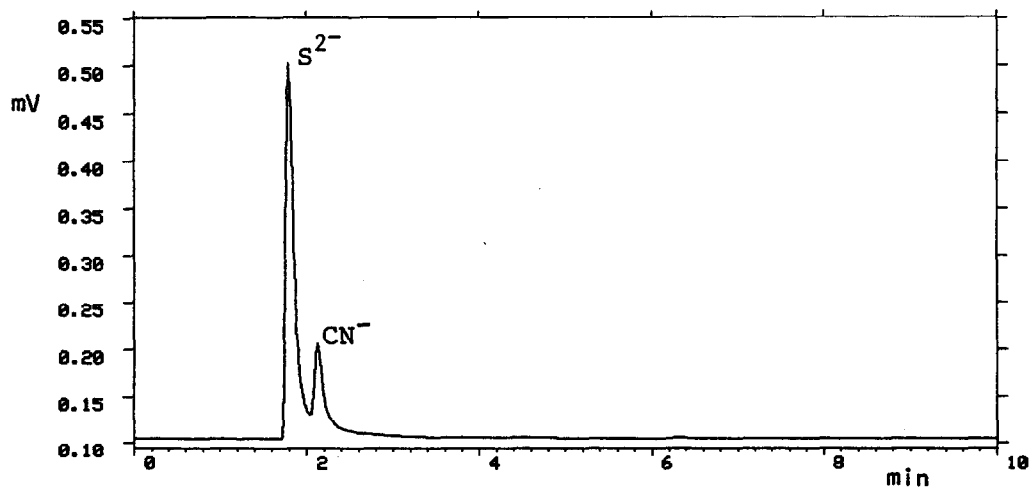

Fig. 3. Chromatogram of a diluted (1:2000) white liquor and a 1 mg/l cyanide spike, direct injection. The spike was added to show the resolution of sulfide from other anions using the PAX-100 columns. An eluent of 10 m*M* boric acid, 15 m*M* ethylenediamine, 10 m*M* NaOH and 1 m*M* $NaNO_3$ in 2% methanol was used.

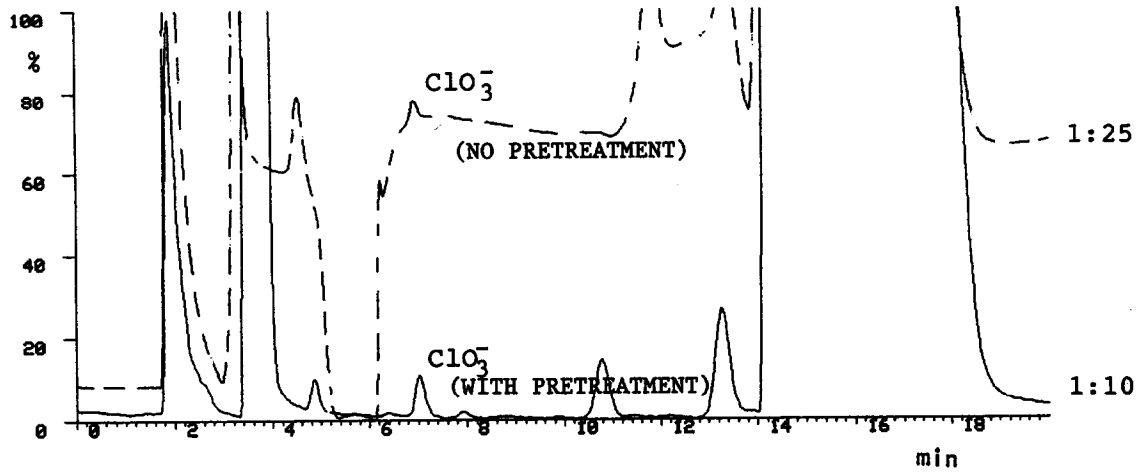

Fig. 4. Chromatograms of diluted white liquors showing the dealkalization of the sample matrix by pretreating the diluted sample with cation-exchange resin. The upper chromatogram is a diluted (1:25) white liquor with no pretreatment. The lower chromatogram is the same sample, diluted 1:10, after pretreatment with Duolite C-433 cation-exchange resin. Conditions for chlorate analysis were: Dionex AS9-SC guard and analytical columns, with an eluent of 2 m*M* Na_2CO_3 and 0.75 m*M* $NaHCO_3$. Injection volume was 50 μl. Chlorate was detected by conductivity in the 30 μS range.

switching time, with the same diluted black liquor used in Fig. 1. The chromatogram in Fig. 2 shows thiosulfate eluting in less than 5 min, with good peak symmetry. One of the simultaneously eluting anions in Fig. 1, nitrate, is now eluted much earlier with the weakly retained anions and does not interfere. It was found that a low-capacity guard column cannot resolve thiosulfate from phosphate. However, black liquors (the most complex process solution) contain low levels of phosphate, and errors from contamination are minimal.

In an effort to reduce system modifications, columns used for oxylate, sulfite, sulfate and thiosulfate determinations were also tested for sulfide analysis. A linear calibration plot for sulfide was obtained using these columns. Fig. 3 is a chromatogram of a diluted white liquor, showing the resolution of sulfide from a 1 mg/l cyanide spike. The OMNI-PAX multi-mode columns are not optimized for weakly retained analytes such as sulfide. The added cyanide spike was included to demonstrate the resolving power of these columns for weakly retained species, under the conditions described. Fortunately, a column with more selectivity for weakly retained anions is not necessary for sulfide analysis in process liquors. Large dilutions (*i.e.* 1:2000) are necessary to bring sulfide concentrations within the working range of the electrochemical cell. Hence, all possible contaminants are eliminated by dilution.

Chlorate analysis in caustic white liquors was improved with sample dealkalization. Fig. 4 shows chromatograms of a white liquor diluted 1:25 without pretreatment, and the same liquor sample at 1:10, treated with ion-exchange resin. When alkaline earth metals are removed by the resin, hydroxide levels are also reduced. This pretreatment process has a great effect on improving the baseline stability of a conductivity detector. Little to no baseline upset was observed in the more concentrated sample. The weak-acid resin, with a capacity of 4 equiv./l, neutralized the pH 14 liquors to pH 5. This process had little if any effect on chlorate stability: recoveries were between 94 and 104%. Chlorate is a stable analyte, resisting degradation from reductions in pH [10].

Attempting to neutralize caustic liquor samples more concentrated than 1:10 generated visible amounts of dangerous hydrogen sulfide in the pretreatment column resin. This was due to the acidification of sulfide and polysulfide species present in the sample. During the neutralization of the more concentrated samples, air pockets formed and channeling occurred. This is not a problem for low

level chlorate determinations in scrubbing liquors. At a 1:10 dilution, chlorate levels were found to be at or above 0.5 mg/l.

CONCLUSIONS

Previous work has demonstrated the effectiveness of column switching in reducing the analysis time of white liquors and dilute recirculated process solutions. A more complete characterization of process liquors is now achieved. Oxalate and sulfide can be characterized using the same multi-phase columns used for sulfite, sulfate and thiosulfate analysis. Low levels of chlorate can be determined in chlorine dioxide scrubbing liquors via pre-treatment with cation-exchange resin.

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