

# Troubleshooting of the Kraft Recovery System Using Modern Analytical Tool

V. Janbade Anuradha, M.P. Singh, B. P. Thapliyal, R. M. Mathur and A. G. Kulkarni

Central Pulp and Paper Research Institute, P. O. Box 174, Saharanpur-247001 (U.P.)

With the closure of the recovery cycle, the presence of non-process elements in black liquors have assumed greater significance. Elements that were relatively benign have become potential source of deposit formation & corrosion in partially or completely closed cycles.  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  & oxalates in black liquors contribute to the build-up of dead load in the recovery boilers & lead to deposit problems in the digesters & evaporators while chlorides lower the smelting temperature & cause corrosion problems. It is therefore necessary to incorporate a rapid process-monitoring tool for the analysis of such ions that are detrimental to the recovery operations. Literature has long demonstrated the use of Ion Chromatography for the speedy analysis of Kraft black liquor anions. Despite the several advantages like simplicity of operation, speed and selectivity of analysis offered by ion chromatography, the technique has not been adopted as routine method of analysis. Ion Chromatographic analysis of Kraft black liquor anions was carried out to gain insight into the practical aspects of the technique and to establish it as an alternative to conventional wet chemical analysis that is cumbersome and time consuming. The paper incorporates the optimization studies carried out for the analysis of Kraft black liquor and the drawbacks associated with the ion chromatographic technique.

## INTRODUCTION

A variety of inorganic constituents are introduced into the Kraft process cycle by means of raw material, process water & chemicals. Some of these constituents like chlorides & oxalates find their way into the black liquors that contain varying amount of these species. Poor process efficiency of chemical recovery operations also lead to the accumulation of conversion products of  $\text{Na}_2\text{S}$  like  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$  &  $\text{Na}_2\text{S}_2\text{O}_3$ . The presence of all these compounds in the black liquor contribute to the dead load in the recovery boilers that adversely affect the operation of the recovery boiler and limit its capacity. With recycling of these constituents in the process cycle, there is a build up of various non- process elements & dead load leading to number of potential operational problems.

$\text{Na}_2\text{SO}_4$  concentration influences the precipitation of the burkeite scales in the evaporators. At high black liquor solids,  $\text{Na}_2\text{SO}_3$  precipitates from the liquor along with  $\text{Na}_2\text{CO}_3$  causing scales. These scales reduce the heat transfer area and limit the evaporator capacity. Oxalates are also a potential source of harmful scale deposits. Chlorides and thiosulphates are amongst most corrosive species encountered in the Pulp & Paper Industry. These ions promote corrosion of process equipments under aqueous environment. High chlorides concentration can

also lead to fouling & plugging of recovery boilers. Chlorides have a radical effect on the lowering of the sticky temperature causing massive deposit accumulation. A quick measurement of dead load & corrosive ion concentration in black liquor can help generate timely information for monitoring their build up & troubleshooting kraft recovery operations. The conventional methods for sulphate & chloride measurements are time consuming. Even today determination of  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_3$  & oxalates in black liquors is difficult. Due to the non-availability of rapid analytical procedures these constituents are routinely not monitored by Indian Pulp and Paper mills. Ion Chromatography is a simple & accurate method that can rapidly analyze sulphate, sulphite, thiosulphate & oxalate in Kraft Black Liquors. At Central Pulp & Paper Research Institute, efforts have been made to establish Ion Chromatography as analysis and troubleshooting tool for non-process elements build up and to understand the chemistry of black liquor in detailed manner (1). In this paper results for optimizing inorganic anions analysis of Kraft Black Liquors by Ion Chromatographic method with the objective to establish the technique as an effective process monitoring and troubleshooting tool for kraft recovery operations are presented.

## EXPERIMENTAL

### General Procedure

Inorganic anions of Kraft black liquor were determined by comparison of the sample chromatogram with the chromatogram of working calibration standard by measuring the peak areas. A composite calibration solution was prepared by mixing various ions of interest. The concentration of individual ions was adjusted to give the recommended conductivity range of 0-10 $\mu$ s. The response of chromatographic technique for the determination of individual ions concentration was evaluated by making chromatographic determination of solution containing known concentration of anions.

### Instrumentation

All analysis were carried out on Dionex DX 600 HPIC consisting of GS 50 Gradient Pump, ED50 Electrochemical detector & L-C 25 Chromatography oven. GS 50 gradient pump consists of a pump head that delivers the eluent to the gradient mixer. An injection valve placed after the gradient mixer introduces the sample into the Eluent stream that passes through the guard column, separator column and anion suppressor that are placed in the LC-25 column compartment. ED50 electrochemical detector operates on different modes of detection like conductivity, electrochemical or pulsed amperometric detection.

### Method & Materials Employed

Inorganic anions analysis of black liquor was carried out using Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> eluent using suppressed conductivity detection. Dionex ASRS Ultra was used for suppression of background conductivity. Dionex Ion Pac AS-12 Analytical column was used along with AS 12 guard column for the separation of chloride, sulphite, sulphate, oxalate & thiosulphate ions. All eluents were prepared using ultra pure grade chemicals and diluted with de-ionized water and filtered through 0.45 $\mu$  nylon membrane filters before use.

### Sample Preparation

For the purpose of study kraft black liquor was collected from a hard wood based mill. After withdrawing

portions for solid determination black liquor was refrigerated for subsequent analysis. Prior to the analysis, black liquor sample were diluted to appropriate solids concentration using de-ionized water and filtered through 0.45 $\mu$ m nylon filters. To stabilize sulphite & thiosulphate ions antioxidant reagents were added to the samples.

## RESULT & DISCUSSION

For establishing ion chromatography as a standard process monitoring and troubleshooting technique for kraft recovery operations various steps such as optimization of test conditions, preservation of anions, setting ranges of detection limits of different anions (sample dilution) and validation of chromatographic analysis were carried out. Results of the above optimization analysis conducted for hardwood kraft black liquor sample collected from a mill are given below.

### Optimization of Eluent Strength & Flow rate

For ion exchange mechanism the two most important variables are the ionic strength & the flow rate of the mobile phase. By changing the variables, it is possible to alter the retention times of the ions and thus the total run time. With an objective to reduce the overall run time, standard solution containing chloride, sulphite, sulphate, oxalate & thiosulphate ions were analyzed using varying strength of Na<sub>2</sub>CO<sub>3</sub> & NaHCO<sub>3</sub> eluent. After conducting a series of trials with different eluent strength and flow rates it was possible to optimize the eluent strength of 2.7 mM Na<sub>2</sub>CO<sub>3</sub> and 2.3 mM NaHCO<sub>3</sub>. This exercise helped us to reduce the run time from 35 minutes (2) to less than 20 minutes without compromising on the resolution of the chromatogram. Fig. 1 depicts the chromatogram obtained for separation of the anions under optimized condition of eluent strength and flow rate.

### Preparation of Calibration Standard

Use of calibration standard containing appropriate concentration of ions is important for the simultaneous quantification of all desired ions as even small

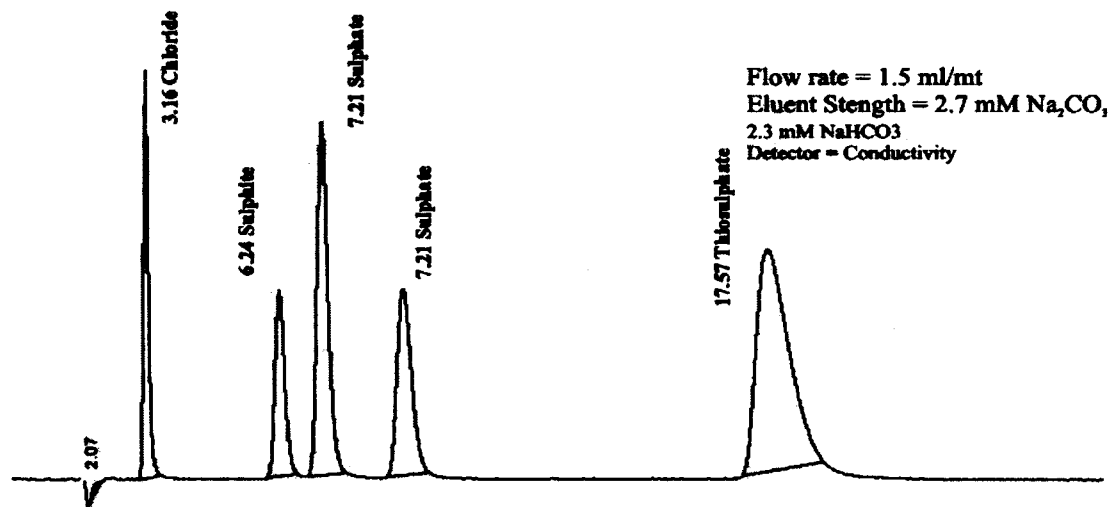


Fig. 1 : Ion Chromatogram of Standard Test Solution Under Optimized Conditions

Table 1 : Data for Conductivity & Retention times for Standard Calibration Solution.

Ion	Concentration (ppm)	Retention Time (in minutes)	Conductivity (in $\mu$ s)
Chloride	10	3.16	10.9
Sulphite	25	6.24	5.0
Sulphate	25	7.21	9.1
Oxalate	25	9.01	4.8
Thiosulphate	90	17.57	5.7

disagreements between calibration standard and sample ion concentration can alter the retention times making quantification difficult. A calibration standard containing 10,25,25,25 and 90 ppm of chloride, sulphite, sulphate, oxalate, thiosulphate ions respectively was found suitable for quantification of these ions in black liquors. The retention time & conductivity of the individual ions with an eluent of 2.7mM  $\text{Na}_2\text{CO}_3$  and 2.3 mM  $\text{NaHCO}_3$  and flow rate of 1.5 ml/minutes is given in the Table 1.

#### Selection of Antioxidising Reagents

For preservation of the liquor samples in which sulphite & thiosulphate have to be determined, antioxidantising

agent like glycerol (3) & formaldehyde (4) have to be added prior to analysis. Without addition of these antioxidantising reagents, oxidizable sulphur species of sulphite & thiosulphate are rapidly oxidized to sulphate leading to erroneous results. For every ml of undiluted black liquor used, 1 ml of glycerol was added and 1.0 ml of 37-41 % formaldehyde / liter was added to the diluted black liquor samples.

Fig. 2 shows the typical chromatogram for the Black Liquor using formaldehyde. It was observed that the chromatogram obtained for the black liquor using formaldehyde was similar to the one obtained with glycerol Fig 5. The close agreement of concentration

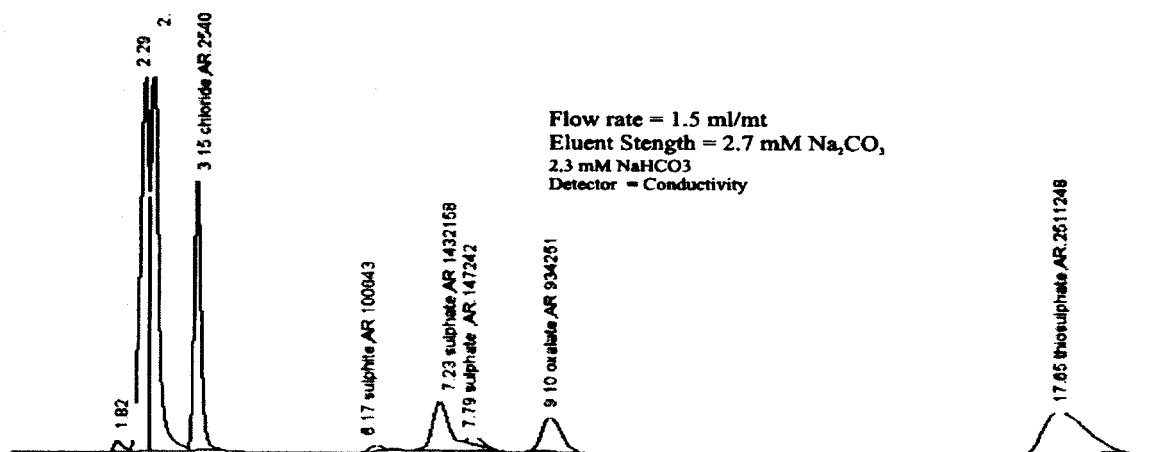


Fig. 2 : Ion Chromatogram of Black Liquor using Formaldehyde

Table 2 : Concentration of Different Anions Determined With & Without Antioxidizing Agent

Ion	Concentration in B.L. without Glycerol or Formaldehyde	Concentration B. L. with Glycerol (ppm)	Concentration in Black Liquor with Formaldehyde (ppm)
Chloride	ND*	28.4	28.9
Sulphite	ND*	3.8	3.14
Sulphate	ND*	21.6	21.4
Oxalate	ND*	21.2	20.18
Thiosulphate	ND*	70.0	71.0

\* Could not be determine due to large variations in measured values

Table 3 : Recovery rates for measurement of different ions by Ion Chromatography

Ion	% Recovery of measured concentration
Chloride	100%
Sulphite	95-100%
Sulphate	98-100%
Oxalate	99-100%
Thiosulphate	96-100%

values obtained for the different ions also established the suitability of both glycerol & formaldehyde as antioxidising agent for black liquor analysis. Table 2 presents the results of addition of formaldehyde & glycerol in the black liquor sample.

### Optimizing Sample Dilution

For inorganic ion analysis black liquor solids reported in the literature are in the range of approximately about 0.5 g/l. At this concentration reasonable sized peaks are expected in the 3-10  $\mu$ S scale and is considered suitable for all the desired ions (5). Fig-3 shows the chromatogram obtained for black liquor sample at 0.5 g/l dilution and 0-10  $\mu$ S range. In this detection range, the baseline drifted constantly due to increased detection sensitivity. Peak obtained for sulphite ion was also very small decreasing the accuracy of the reading. Fig 4

shows the chromatogram obtained at the same dilution but in the 0-50  $\mu$ S range. Stable baseline was achieved but the peak for sulphite ion disappeared completely. Optimization of the sample with different dilutions revealed that reasonable sized peaks can be obtained for all the five ions i.e. chloride, sulphate, sulphite, oxalate & thiosulphate with black liquor diluted to approximately 2.5 g/l solids in the 0-50 or 100  $\mu$ S range. Fig.5 shows the chromatogram obtained for black liquor at 2.44 g/l solids. Determination of black liquor ions at approximately 2.5 g/l solids also eliminated the need for extensive sample dilution.

### Validation of Chromatographic Measurements

In order to validate the results of Ion Chromatographic measurements chromatographic runs were first made on aqueous solution containing known concentration of the desired ions. Recovery rates for measurement of individual ions, as determined on the basis of ion concentration present in the test solution, are given in the Table 3

Test conducted at CPPRI revealed excellent recovery rates for chloride, oxalate & sulphate ions. Close agreement between the added and measured ion concentration were observed in case of sulphite and thiosulphate.

### Determination of dead load in Kraft Black Liquor

Chromatographic analysis of kraft Black liquor was performed under optimized conditions of eluent

Table 4 : Concentration of different ions in Kraft Black Liquor at 2.5 g/l solid and 0-100  $\mu$ S detection range

Ion	Percentage on Basis of Black Liquor Solid (Ion Chromatography)	Percentage on Basis of Black Liquor Solid (Conventional Method)
Chloride	1.1	1.0
Sulphite	0.15	ND
Sulphate	0.86	0.8
Oxalate	0.86	ND
Thiosulphate	2.86	ND

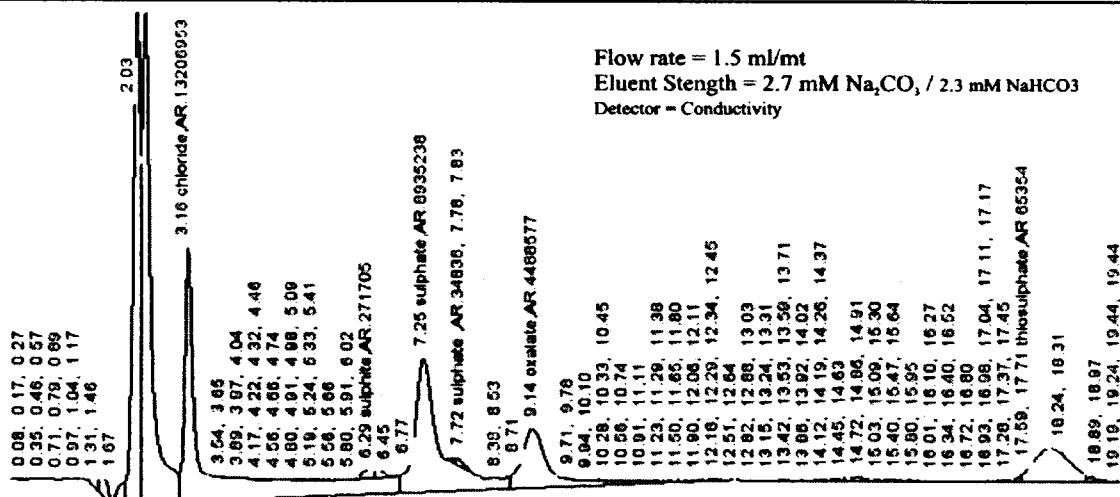


Fig. 3 : Ion Chromatogram of Kraft Black Liquor at 0.5g/l solids & detection range 0-10 $\mu$ s

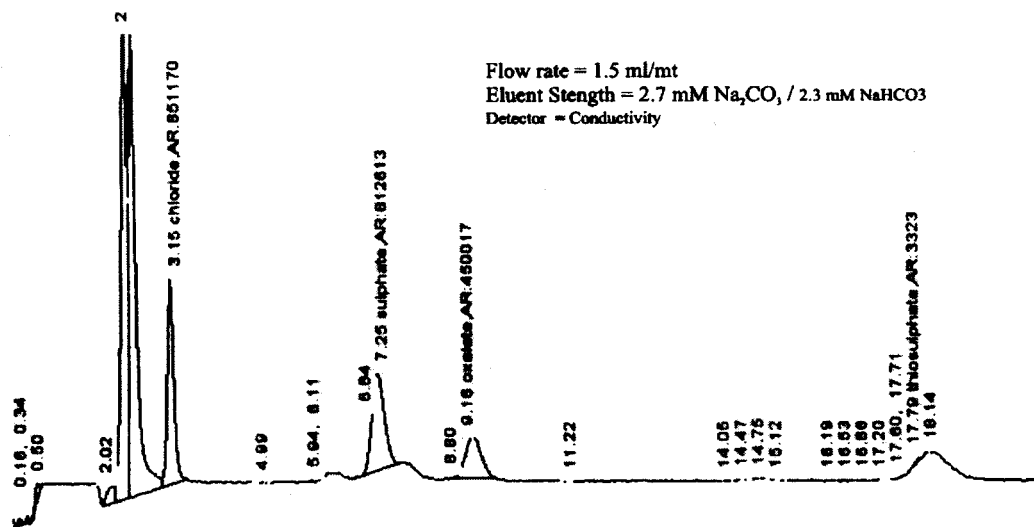


Fig. 4 : Ion Chromatogram of Kraft Black Liquor at 0.5 g/l solids & detection range 0-50  $\mu$ s

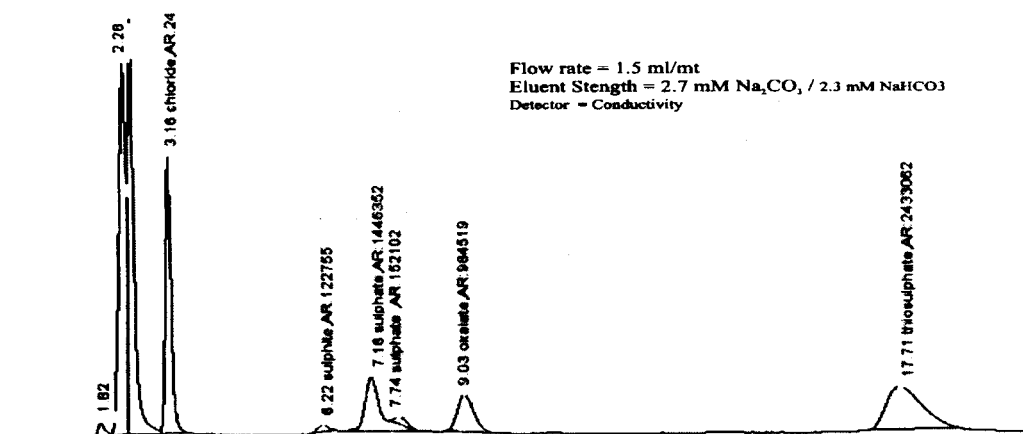


Fig. 5 : Ion Chromatogram of Kraft Black Liquor at 2.5 g/l solids & detection range 0-100 $\mu$ s

strength & sample dilution. The result of the analysis along with the values of chloride and sulphate determined by the conventional titrimetric & gravimetric methods is given in the Table 4. It was observed that the values of chloride & sulphate were in the expected ranges and there is a close agreement between the values determined by chromatographic & conventional procedures. The result also show that sulphite is present only in small quantities but oxalates, sulphates & thiosulphates are present in significant amounts in kraft black liquors. It is therefore necessary to determine the dead load components in kraft liquors to monitor their build up in process cycle.

#### CONCLUSION

Ion chromatography is a valuable tool for the efficient determination of chlorides, sulphites, sulphates, oxalates & thiosulphates in black liquors. In the absence of a quick analytical procedure, even today oxalates are routinely not monitored in black liquors. With growing importance attached to determination of oxalates for monitoring scale depositions, Ion chromatography will prove to be a useful technique. Given the ease with which all the sulphy compounds can individually be

quantified in the black liquors, the technique can lead to a quick understanding of chemical recovery operations and thus prove to be an effective process monitoring and trouble shooting tool.

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