Ion Chromatography - The Technique and its Applications in Pulp and Paper Industry

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

Key words : Chromatography, Analysis, Laboratory

Pulp and Paper Industry is a chemical process industry that incorporates several unit operations like pulping, bleaching, and chemical recovery. Evaluation and optimization of individual unit operation can ensure, cost effective production of quality product with minimum environmental impact. Different analytical procedures both chemical and instrumental are employed to derive useful information on process efficiency, optimum processing condition and product quality during pulping & bleaching operations. Instrumental methods are considered as a reliable quality control and process optimization tool in the Pulp & Paper Industry. Ion chromatography is one of the most versatile & useful techniques that has found several applications for chemical analysis in Pulp & Paper Industry. Evaluation of Pulp & process liquors at various stages of manufacturing can be useful in providing additional information that can help understand pulping, bleaching, and recovery operations and may form the basis for efficiency improvement and process control. This paper presents an overview of applications of this analytical technique in pulp & paper industry along with basic principle, instrumentation and methodology involved.

INTRODUCTION

Chromatography is physico-chemical process by which components of a mixture can be separated. Coupled with new sensitive detectors chromatography has developed into a useful analytical technique for identification & quantification of compounds for a liquid or homogenous gas phase. Chromatographic separation is based on the differential affinities of the compounds of interest for the mobile and stationary phases. Depending upon the physical nature of the phases chromatographic techniques are divided into Liquid-Solid Chromatography (LSC), Gas-Liquid Chromatography (GLC), SFC (Supercritical Fluid Chromatography) etc. Ion chromatography is a type of Liquid-Solid Chromatography where the stationary phase consist of a solid used to conduct ion exchange & mobile phase is an aqueous ionic medium. Compatibility of Ion Chromatography with different modes of detection makes it a versatile technique used for separation of not just inorganic ions also all organic species that are polar. The greatest utility of Ion Chromatographic technique lies in the analysis of anions for which there are no rapid analytical methods available. On account of its uniqueness the technique has been found suitable for analysis of pulp & process liquors in the paper industry. The paper highlights the basics of this analytical method and possible applications for process and quality control during manufacturing.

Ion Chromatography - The Technique

A mixture of ionic species when injected into the stream of mobile phase, migrate through the separating column containing ion-exchange resin. Depending upon the interaction of the individual ions with the ionic sites, ions are retained on the column for different lengths of time & elute as discrete bands. The separated ions are then measured by different modes of detection.

Basic Principle

Separation of the ionic species can be brought about by simple ionic interaction or by Donnan exclusion. Figure 1 illustrates the ion exchange mechanism for separation of Cl^- and SO^{4--} ions using NaOH eluent. SO^{4--} has greater affinity for the separator resin than Cl^- thus the Cl^- moves forward and the SO^{4--} lags behind causing their separation (1).

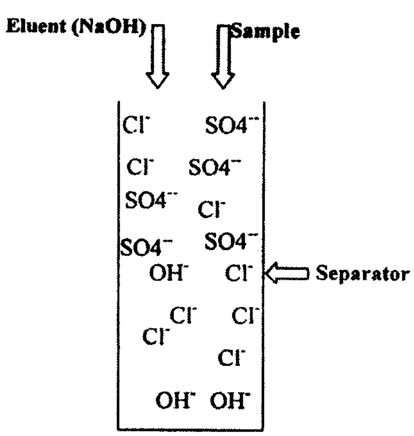

Figure 1. Schematic of Ion Exchange Mechanism

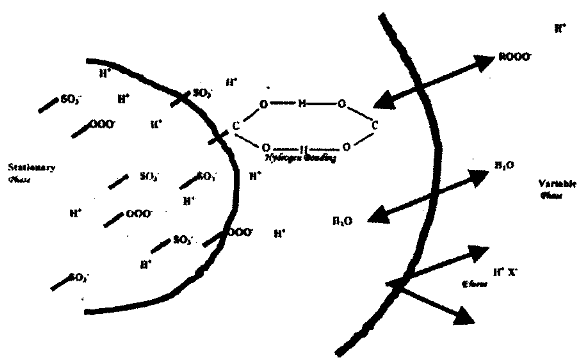

Figure 2. Schematic Representation of Ion Exclusion Mechanism

Figure 2 illustrates the ion exclusion mechanism for the separation of low molecular weight aliphatic organic acids. The hydrolyzed sulphonated surface of the stationary membrane behaves as a negative charged boundary called Donnan membrane which is permeable only to natural molecules. In contrast totally dissociated inorganic acids like dilute hydrochloric acid can not permeate the membrane due to electrostatic repulsion & are totally excluded from the stationary phase (2).

Ion Detection - Three major forms of detection are generally used in conjunction with ion chromatography, which are

Conductivity Detector - This detector is based on the measurement of the magnitude of electrical current carried by dissolved ions in an electric field.

DC Amperometric Detection - Based on the measurement of current resulting from oxidation or reduction (electrolysis) of analyte molecules at the surface of an electrode.

Integrated & Pulsed Amperometric Detectors - It is similar to DC amperometry where the molecules are oxidized or reduced at the surface of an electrode. Current is however measured by integration during a portion of a repeating potential vs time waveform.

The detectors are chosen depending on the type of

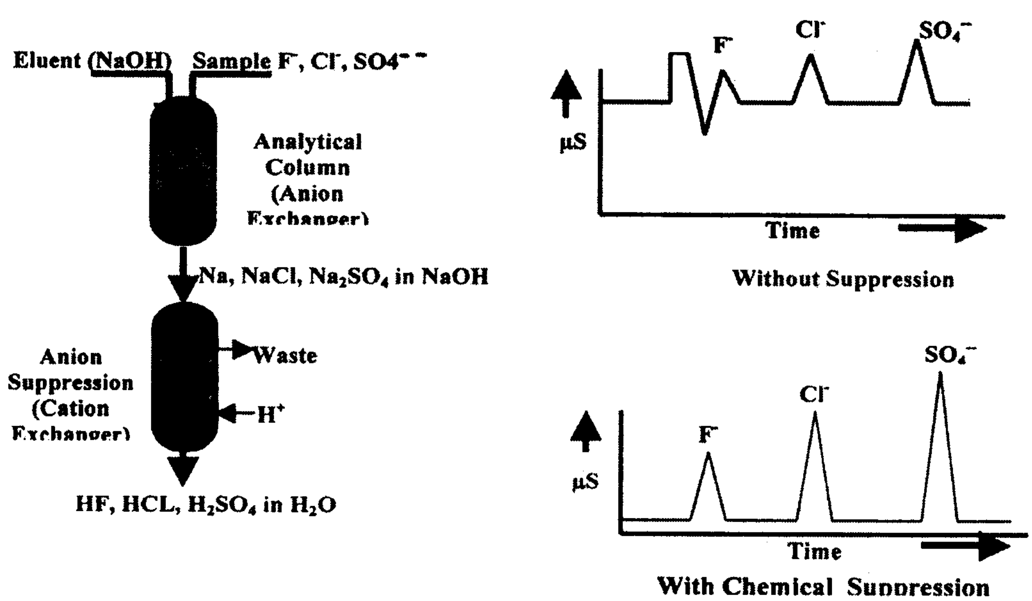

Figure 3. Effect of Chemical Suppression

With Chemical Suppression

application, selectivity & sensitivity of analysis.

Chemical Suppression

A conductivity detector operates by measuring the conductivity of the ions in solution. Problem is faced in measuring the conductivity of the analyte when both the samples & the eluent reach the detector after flowing out of the separate column. The mobile phase contains ions that create a background conductivity making it difficult to measure the conductivity due to the analyte ions. This problem is greatly reduced by introducing a chemical suppressor after the analytical column & before the detector so that the background conductivity is reduced to a low level by converting the mobile phase ions to neutral form. This also enhances the conductance of the analytes. Figure 3 demonstrates the effect of suppression. (4).

Basic Instrumentation

Figure 4 depicts the basic instrumentation for a Chromatograph. The primary head pumps the selected mobile phase into the secondary head that delivers eluent to the pressure transducer that measures the system pressure. A gradient mixer is installed between the pressure transducer and the injection value that ensures that eluent and sample are mixed thoroughly. The sample is injected into the eluent flow path and is carried into the guard & separator column. It then passes through the suppression column before flowing into the detector. The guard column is placed prior to the separator column to prevent sample contaminants to reach the separator column and thus prolongs the life of the separator column.

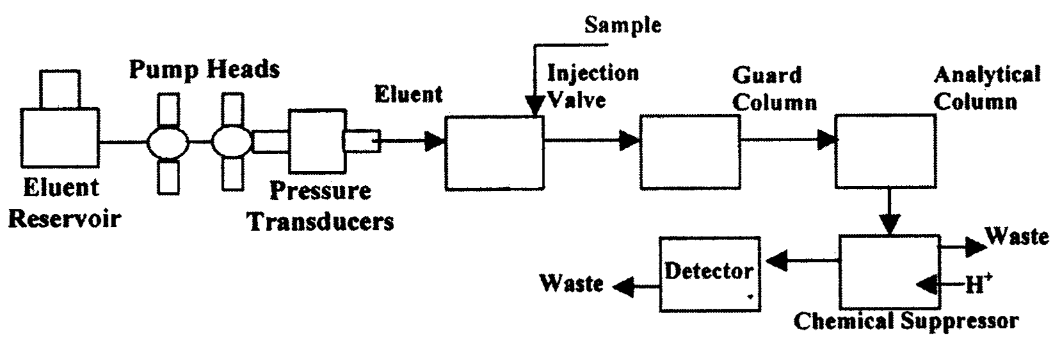

Figure 4. Schematic Illustration of an Ion Chromatograph

When analyte ions, F^-, Cl^- & SO^{4--} elute out of the analyte column they are still in the NaOH eluent that is fully ionized and has high conductivity. The chromatogram that results thus looks like Figure (3a). When a suppressor is used the sodium ions of the eluent are replaced by the hydronium ion. Thus when the analytes leave the suppressor they are in a water solution that has very low conductivity (2).

Eluent Suppression consists of an ion exchange column or membrane. For anion analysis, the eluent suppressor supplies H^+ to neutralize the anions, which retains or removes the Na^+ ion present in the mobile phase, which is often NaOH or $NaHCO_3$(3).

Ion chromatography system using chemical suppressors are referred to as suppressed ion chromatography. System having no suppression of conductivity is classified as Single Ion Chromatography (SIC). Columns of Single Ion Chromatography are silica based ion exchange, reverse phase or polystyrene di-vinyl benzene copolymer columns

Methodology

Identification & Calibration

Identification & quantification of ions is carried out by comparing their retention times and peak heights (or areas) with those of the standards. Calibration standards are prepared with high purity salts. In order to prevent the overloading of the column the standard dilutions are adjusted in such way that the conductivity of the individual ions lie between the range 0-10 µs.

Sample Preparation

Sample preparation is a simple procedure in most of the cases. It involves dilution & filtration before being injected into chromatograph. Dilution step is necessary to bring the concentration of the analyte in the concentration range of the standards.

Applications

Ion Chromatography is an effective analytical tool that has gained wide spread acceptance in the determination of a variety of samples relevant to the pulp and paper industry. Some of the major applications of ion chromatography along with sample preparation methods and detection techniques are summarized below.

Analysis of Kraft Black Liquors

The determination of common inorganic & organic anions in Kraft black liquors is one of the most important applications of Ion Chromatography. Routinely the TAPPI test method T 625 ts 64 is employed for the determination of Na_2SO_4, Na_2S, $Na_2S_2O_3$ & Na_2CO_3 in Kraft liquors. This method is elaborate & takes several days to complete the analysis. The TAPPI test method also does not include any procedure for the determination of organics acids in the black liquors. With Ion chromatography, a number of useful ions both organic and inorganic can be determined with ease in a short span of time. The TAPPI test method T699 om 00 provides procedures for the determination of organic and inorganic ions in white, green, black liquors and solidified smelt samples.

Inorganic Anions Analysis

Figure 5 depicts the chromatographic analysis of a typical Kraft black liquor. Separation of anions like chloride, sulphate, sulphite, oxalate & thiosulphate is brought about by ion exchange mechanism that depends upon ionic size, ionic charge, individual ion concentration & ionic composition of mobile phase. Using appropriate ion exchange column all the ions can simultaneously be determined in single run in about 30 minutes using $Na_2CO_3/NaHCO_3$ eluent and conductivity detector. A small quantity of antioxidant is added to the black liquor sample prior to analysis to retard the oxidation of

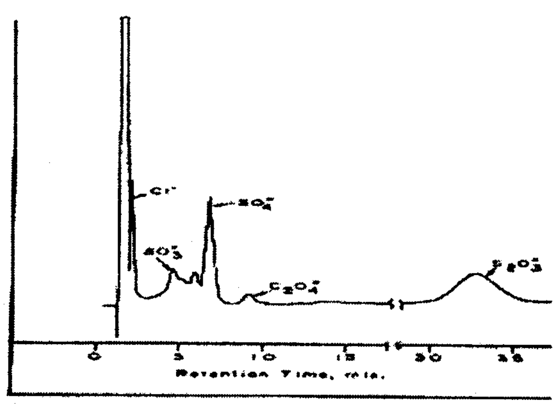

Figure 5. Determination of Inorganic Anion in Kraft Black Liquor

oxidization sulphur species(5). Separate run is required for the determination of sulphide ion that is detected only by the electrochemical detector. Inorganic anions analysis of Kraft Black Liquor and a similar analysis of green liquor is extremely useful for process monitoring & optimization of Kraft recovery operations.

Organic Acids Analysis

Organic acids are separated using Ion Exclusion Chromatography that is based on the principle of Donnan exclusion & ion exclusion. Ion exclusion depends on the pKa values of organic acids and its ionic size[5]. Using appropriate ion-exclusion column, formates, acetates, lactates and propionates can be determined in a single run in less than 30 minutes. The determination of organic acids is carried out using mild minerals acids as eluents and conductivity detectors. Quantification of organic acids can be use in the optimization of pulping conditions.

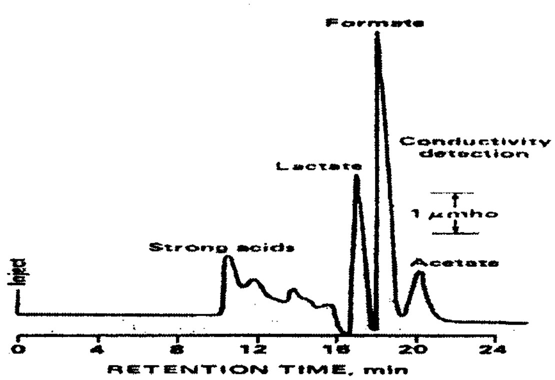

Figure 6. Chromatographic Separation of Organics Acids

ICE is also used for identification & quantification of carbonates presents in kraft-smelt samples dissolved in de-ionized water.

Determination of Wood, Wood pulp Carbohydrates

Traditionally wood pulp carbohydrates are analyzed by the TAPPI test method no T249 cm-00. The procedure provided by the TAPPI method involves elaborate sample preparation and is tedious & time consuming. Samples are required to be hydrolyzed, derivatized & then extracted in methylene chloride before been analyzed by Gas Chromatography. The application of Ion chromatography to the determination of pulp Carbohydrates overcomes the drawbacks of the traditional method. Sample preparation is simple and consists of directly injecting the hydrolyzed wood pulp extract in the

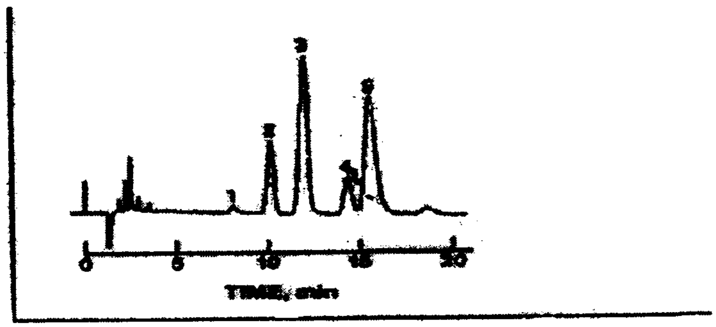

Figure 7. Chromatographic Separation of Organics Acids

Ion Chromatograph for determination of Arabinose, Galactose, Glucose, Xylose and Mannose.

As carbohydrates are weak acids, they are best separated by anion-exchange using hydroxide eluents and electrochemical detection(6). The advantage of using anions exchanges is that selectivity can be altered by changing the eluents composition. The most versatile system for carbohydrates analysis incorporates pulsed amperometric detection with NaOH eluent containing sodium acetate diluents as the pusher ion. The pusher ion concentration is an important variable that affects the overall retention times.

Quantification of wood & wood pulp carbohydrates can play significant role in optimization of process conditions and pulp properties.

Analysis of Pulping & Bleaching Liquors

Ion Chromatography offers significantly easy methods for the analysis of pulping & bleaching liquors. The TAPPI test method T699 om-00 incorporates the suppressed ion chromatographic technique for the analysis of pulping liquors. In a typical Kraft white liquor, sulphate, chloride, sulphite, thiosulphate can simultaneously be determined using conductivity detector, Sulphide present in the Kraft white liquor is determined in a separate run using simple electrochemical detector or UV photometer.

The TAPPI test method no. T700 om-93 also utilizes ion chromatography for analysis of bleaching liquors. Ion chromatography is convenient methods for monitoring relatively unstable chlorine species in bleach liquors. Figure 8 illustrates the chromatographic analysis of bleach liquor. Chloride and Chlorate are determined using Na_2CO_3 eluent with conductivity detectors. Hypochlorite is determined by employing Electrochemical detector. The pulping and bleaching ions-sulphide and hypo chlorite are too weakly ionized to be detected by conductivity detector.

Advantages and Drawbacks

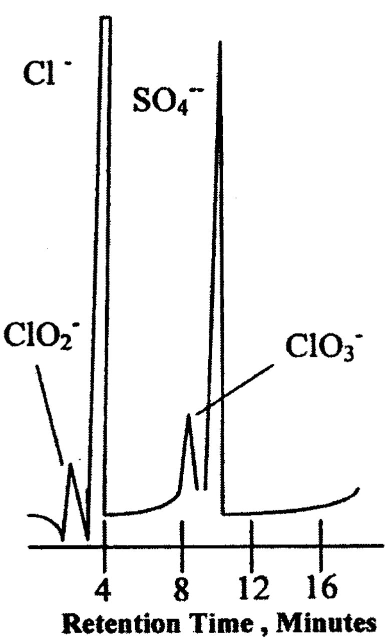

Figure 8. Chromatographic Analysis of Bleach Liquor

Ion Chromatography is a versatile analytical technique that offers several advantages and only a few drawbacks. The technique is simple and easy to use & does not involve elaborate sample preparation. Improved selectively & sensitivity can be achieved by proper choice of columns and detectors making it possible to accurately analyze complex samples. Given the speed of the analysis, large number of samples can be analyzed in short span. One of the few drawbacks of the techniques is that the suppressor columns need to be regenerated periodically.

CONCLUSION

The pulp & paper industry has long relied upon the wet-chemical procedure for analyzing its samples. These procedures suffer from several drawbacks like poor sensitivity & selectivity and tedious & elaborate sample preparation. Ion chromatography is a powerful, fast & versatile technique that overcomes the drawbacks of the traditional test procedures and has proved as an effective alternative to the traditional methods for process monitoring & research. Ion chromatography when applied to mill studies can be extremely useful in trouble shooting & pulp mill, bleach plant & recovery boiler optimization programs.

REFERENCES

1. Ion Chromatography provides useful analysis of the chemistry of pulping & bleaching liquor G. O. Franklin. Tappi J.V.65 No. 5.
2. Dionex HPIC - Product Manual and Trouble shooting Guide.
3. Scimedia - Ion Chromatography.
4. Analysis of Corrosive anions in Paper industry Process Waters by Single Ion Chromatography; Desmond E. Richardson and Ian J. Jewell Appita V. 38 No. 2.
5. Chromatographic Analysis of Kraft Liquor anions Jaya Krishanagapalan, Moriquita Hill and Arthur L. Fricke Tappi J. V. 68 No.9.
6. Determination of Carbohydrates using pulsed amperometric detector combined with anion exchange separators. William T. Edwards, Christopher A. Pohl & Richard Rubin. Tappi J. June 1987.
7. Analysis of bleaching liquors by suppressed ion chromatograph. Tappi test method T 700 om-93.
8. Analysis of pulping liquors by suppressed ion chromatography Tappi test method T 699 om-00.
9. Carbohydrates composition of Extractives free wood & wood pulp by Gas Liquid Chromatograph. Tappi Test Method T 249 cm-00.