

# Instrumental Analytical Methods in Pulp and Paper Field

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*An attempt has been made in this present compilation to highlight the applicability of modern instrumental techniques in the field of Pulp & Paper Industry Basic Theories behind the modern instrumental analysis are discussed and applicability reviewed.*

## Introduction

Frequently some minor quantity of constituents in Pulp or Paper need precise quantitative estimation, which is either beyond the scope of classical analytical techniques or are tedious, time consuming and sometime unreliable. It is increasingly important here, to use such techniques which can yield reliable information and reproducible results within resonable length of time in an economical way.

In pulp and Paper Industry from chipping to finishing of paper varying degree of chemical modification to the total carbohydrate and lignin complex takes place. In order to control and modify pulping, bleaching and other chemical reactions involved in various stages of processing, it is necessary to understand the reaction mechanism involved and to identify the products resulted from such processes at various stages partly or wholly due to change in process, parameters.

Some of the major analytical tools used today in Pulp & Paper research/industry for analytical and process control may be mentioned as Electron microscope, U.V-Vis spectro-

photometer, I.B. Spectrophotometer, A.A. Spectrophotometer, N.M.R. Spectroscope, Selective ion electrode and gas chromatograph.

According to survey (1) jointly conducted by TAPPI-ASTM to obtain data on the relative standing of instrumentation used for chemical analysis in Pulp and Paper Industry, it was revealed that most widely used intrumental techniques were :

Potentiometry (PH) etc.	92%
U.V—VIS Spectroscopy	90%
I.R. Spectroscopy	58%
Others less than	40%

## Electron Microscope:

There are basically two types of electron microscopes, transmission type and scanning type, Transmission type electron microscope is operated by producing a beam of electron from a heating filament, accelerating the beam with a high voltage applied to an anode and then diverting this beam of illuminating electrons onto the specimen, which is then magnified by an objective lens and a projector lense and finally strikes either film held in Camera or a fluorescent screen.

In scanning type microscope, the

surface of solid sample is bombarded with fine probe of electrons generally less than 100A° in diameter. The sample emits secondary electrons and are collected and amplified by the instrument. Since the beam strikes at one point on the sample surface in a raster pattern to generate a picture of the surface sample the picture is displayed on cathod ray tube from which it can be photographed.

There has been considerable use of these methods in Pulp and Paper Field. Bann (2) carried out studies on reprographic papers using electrone microscope and energy expensive X-ray analysis. Later provides a means for critical examination of electrophotographic and dielectric coated paper. The X-Ray data reveal eltro conductive resin penetration and distribution non uniformity in the dielectric film of paper additives and impurities. These techniques used in conjunction with electrical measurement and evaluation of print quality provides a more thorough understanding of the complex process involved in the imaging of reprographic papers.

Electrone microscopy has also been used to study (3) the fibre

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interface of coated paper after separating the coated layer. Determination of particle size of pigment in technical blends by means of small angle X-ray scattering and Indication of Core shell structure in potato starch grain has also been reported (4) SEM studies yield valuable information on identification of solid particles in Viscose, Pitch Particles in cellulose pulp and problems connected with close water system (5). In the field of improvement of functional properties of cellulosic fibre by graft polymerization SEM is extensively used for characterization of graft polymerized surfaces.

#### U.V.—VIS Spectrophotometer :

The near U.V. (200-400 nm) and visible (400-800 nm) regions are concerned with electronic transition and in molecules, these are accompanied by vibrational and rotational charge giving band spectra which can be termed as electronic vibration rotation band.

Molecules or atoms which absorb radiation characteristically may be determined or studied by measurement of light absorbed. Incident radiation is emitted from a suitable source and is passed generally via an optical system which isolate a narrow band of wave length through a homogenous layer of absorbing medium the intensity of the radiation transmitted by the medium is compared with the intensity by allowing each in turn to pass a suitable detector.

Quantitative analysis is based on Beer Lambert Law. The relative strength of absorption band are

expressed in exponential units of absorbance or optical density. The function being directly related to concentration. Absorbency is measured in a spectrophotometer by comparing the intensity of incident radiation with that transmitted by the solution and termed 14 molecular extinction. Coefficient  $\epsilon$  (or absorbency) of the molecule in the given solvent. Graph of  $\epsilon$  against  $\lambda$  (wave length) is termed absorption curve.

There has been quite frequent use of U.V. Spectroscopy for detection and estimation in Pulp and allied Industry. Determination of zinc dimethyl dithio carbonate in treated paper was carried out (6). In viscose industry quantitative estimation of Xanthate Bye product and total sulphur in viscose was reported (7, 8). These technique help studying wood chromophores (9), and based on later principal quantitative estimation of lignin were carried out (10, 11). For analytical control in sulphite pulping process (absorbency at 280 and 205 nm was suggested (12, 13) as a reliable method for evaluation of degree of cooking.

Extensive research work (14-17) carried out by different researchers confirmed the applicability of U.V.—IR Spectrophotometry for estimation of structural characteristics of lignin.

Visible methods are well established and are being extensively used for determination of various trace elements. In Pulp & Paper Industry it can be used for routine analysis of water and waste water (18).

#### Infrared Spectrophotometer

The Infrared region of the electromagnetic spectrum lies between the visible region and the submillimeter, or micro wave region and extends from approximately 0.78 to 300 microns. It is of scientific importance because molecular vibration and rotation occur in this frequency range. Analysis of infrared spectra provides basic information on molecular structure in terms of geometry and interionic forces and distances, but the widest industrial application is probably the use of vibrational spectra for qualitative and quantitative analysis. Each molecule is characterised by a unique set of vibrational absorptions which serve as a set of identifying "finger prints" and the depth of absorption bands serves as a measure of the number of molecules present. Sample size requirements range from milligram for routine studies to as little as a fraction of microgram when special accessories are used in conjunction with the basic spectrophotometer.

In pulp & paper field IR Spectry finds considerable application. O'Conner studied crystallinity of cellulose and cellulose derivatives (19), completeness of methylation of alpha-cellulose was determined and reported (20) by determining absence of hydroxy peak on fully methylated alpha-cellulose.

Effect of temperature on I.R. Spectra of lignin & lignin compounds was carried by Halkyn and Nakano (21). Pearl and Co-workers identified (22) Tri-o-methyl d-glucose by I.R. Spectra. Bolker & Terashima (23) identified lignin-carbohy-

drate bonds using I.R. Spectroscopy. Determination of phenolic acid group in bark of slush pine, (24) delignification studies of *E. regnens* by Michelle (25) and indentification of oil and grease spots (26) for Pulp and Paper are some of the noteworthy contributions of I.R. Spectry.

#### Atomic absorption Spectrophotometer

A new technique developed by Walsh and Co-Workers (1955-57) is based on specific absorption of light by the unexcited atoms and is hence termed atomic absorption spectrophotometry. In this method the flame is irradiated with a beam of monochromatic light the wave length of which is matched to that of a resonance line of the unexcited atom. As a result of absorption, an electronic transition occur for the ground state to the appropriate excited level. The unabsorbed radiation transmitted by the flame is passed through a monochromator or narrow band filter to eliminate back ground radiation from the flame and the source, and its intensity is measured by means of a suitable photometric system. Measurements are made of the incident and transmitted intensities and results are expressed in transmittance or absorbance units as in conventional absorptiometry. The Beer-Lambert law is observed over a limited concentration range and a plot of absorbance against concentration is generally linear at low concentration and curved at higher ones.

Application of AAS to Pulp & Paper Field is not very old. Rapid determination of metals in

wood pulps using AAS with graphite furnace was reported (27). These determination seem increasingly important when functional properties of paper restrict the presence of certain metals even to the extent of traces. For example Iron & Copper in butter wrapping, Iron in refrographic papers, chloride for base paper for aluminium foil etc. etc. Determination of total inorganic mercury in water and waste water (28, 29) and determination of lead in confectionary wrappers by AAS has been reported (30). AAS Methods have been widely adopted as standard methods for analysis of water and wastes (18).

#### NMR Spectroscope

The magnetic properties of the atomic nucleus were referred to in connection with magnetic and spin quantum Number. Any isotope possessing a spin other than zero shows magnetic properties as a result of angular motion in an orbit. If an external stationary magnetic field is applied the axis of orbit rotate about the same direction of the field. The procession may only be studied by applying a second alternating field of variable frequency, when the constant and varying field have particular combination of field strength for one and the frequency for the other. The procession of nucleus synchronizes exactly with the frequency the applied field and energy is absorbed by the nucleus. It is then re-emitted as electromagnetic induction and is detected by means of coil tuned to frequency of the applied field. Since the latter is usually on

radio frequency region, the signal is handled by radio receiving equipment. The process is termed as Nuclear Magnetic Resonance (NMR) Spectroscopy.

Its application in the field of Pulp and Paper is generally extended to investigation connected with lignin. Lenze (31) examined structure of ten lignin preparations and compared with NMR Spectry through qualitative and quantitative determination of proton distribution. Initial exploratory examination with high temperature spectra and use of time averaging technique indicate that these are potentially useful methods for investigations of lignin preparations. Hyoe Halkeyama & Nakano (32) studied lignin in solid state. The NMR absorption of dioxane lignin, thio lignin and calcium lignin sulphorate all prepared from softwood were studied.

#### Selective Ion Electrode

A new electro-analytical approach known as selective Ion Electrode method based on chemistry of glass and crystal and on specificity of various ions by synthetic and natural organic complexing agent has been developed recently and widely accepted for direct and rapid determination of various ions in different substances. S.I. Electrodes response directly to the activity of given ion even in complex solution, when a large excess of other ions are also present. Electrode response in terms of voltage is easily measured with a precision pH meter.

In Ion Selective electrode—prin-

ciple involved in the measurement is very much akin to that of pH electrode and electrical current is carried through the membrane by a single ion species. The potential of the electro-chemical cell created by selective ion electrode and a reference electrode into a simple solution is sum of a number of individual potentials.

$$E_{\text{Cell}} = E^{\circ} + E_M + E_J$$

$E^{\circ}$  is a constant which includes the internal potential of the two electrodes and the asymmetric potential of the membrane.  $E_M$  is the potential across the membrane &  $E_J$  is the liquid junction potential.

Because of its versatility, ease, accuracy and interference free response, it is being widely employed in various analysis in pulp and paper industry. Boczkowski (33) reported the use of lead ion electrode for determination of sulphur in pulp and paper mill process streams and highlighted the capability of analysis of liquors having upto 0.1 ppm sulphur level. Determination of sulphur in alkaline pulping liquor is also possible to carry out using sulfide ion electrode (34). Sodium sulphide content in black liquor can be measured as sulfide ion or by direct measurement as hydrogen sulphide following acidification & stripping  $\text{Na}_2\text{S}$  monitoring following black liquor oxidation is important for process control to warn of upset condition for feed control with oxygen system and as an indicator of hydrogen sulphide emission following direct contact evaporation. Direct in-situ sodium sulfide

measurement can employ oxidation, reduction, Silver—Silver-sulfide and sulfide ion electrode (35).

Determination of sodium in black and green liquor often poses problems by titrometric methods. Use of S.I. Electrode for the purpose has been reported by Swasey (36) and Lenz & Co-workers (37).

These technique can be successfully applied for accurate and rapid determination of chloride, sulfate, Nitrate, Ammonia, Sodium, Potassium, Calcium, Magnesium and hardness of water and waste water and some of them have been widely adopted as standard methods (18).

#### Gas Chromatograph

It is a physical method for separating components in a mixture. A gaseous mobile phase percolates through the stationary phase (solid in gas solid chromatography and liquid distributed over the surface of solid support in gas liquid chromatography) packed in a column.

The basic process responsible for separation by gas liquid chromatography is partition. Amongst various separation techniques elution method is more common. A sample is injected, into the stream of carrier gas as "Plug" of vapour, which is swept into the head of packed column. Separation of components that comprise the sample results from difference in multiple force by which the column materials tend to retain each of the components. Whatever the nature of retention is, absorption solubility, chemical

bonding, polarity or molecular filtration, the column retains some component longer than others, and emerging out of the column in the inverse order of their retention by the column material.

Most frequent use of G.L.C. recorded for determination of carbohydrates in wood pulp (38) by hydrolysing them with sulphuric acid. Adam & Co-workers (39) separated Silylated derivative of disaccharide mixture, and separation of complex mixture of carbohydrates & cyclitols by converting them to additol acetate and separating them for their estimation has also been reported by Tham and Coworkers (40). These techniques were applied for separation of uronic acid also (41). A gas chromatographic technique has been developed for identifying the pyrolysis products and for determining D.S. of number of cellulose ethers and esters (42).

Other mentionable application are, quantitative determination of tripropyl butoxide in insect repellent paper (43), a rapid method of sampling and analyzing kraft gases for hydrocarbon sulfide (44), determination of no. and amount of low molecular weight stream volatile compounds present in the spent sulfite liquor (45) and improved methylation technique for analysis of lignin degradation product (46).

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