

Experience and Learning from FT-NIR Installations in North American Pulp Mills for Applications in Digester, Recovery, Recaust, and ClO₂ Generator

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ABSTRACT

Over the past 15 years, a number of mills in North America have installed FT-NIR-based process analyzers in various areas of the mill for process automation and control. Through applications on digesters, recausticizing, recovery, and ClO₂ generators, there has been continuing maturation, improvement in uptime and reliability, and new developments in measurement properties as well as applications. This paper reviews some of these installations and examines the criteria for a successful installation. We will examine an early installation in each of 3 areas of the mill, digester, recaust and ClO₂, and compare those installations with current successful installations.

INTRODUCTION

In the late 1970's, MoDo-Chemetics (Vancouver, BC, Canada) began installing an on-line liquor analyzer as part of a digester control package in North America. The heart of the control system was an automatic black liquor titrator developed by Modo (Sweden). Based on potentiometric titration technique, the analyzer measured the REA (residual effective alkali) value in the cooking liquor to be used as feed-forward information for a Kappa control algorithm. Initially, four digester control systems were sold to mills in Ontario and New Brunswick, Canada and in North Carolina and Alabama. Success at those mills led to more installations throughout North America over the next 20 years.

Early Development of FTIR Analysis for Pulp Mill Liquor Properties

In the early 1990's, Paprican and MoDo-Chemetics began development of a mid-Infrared (MIR) analyzer to replace the on-line titrator.[1] The goal of the project was to develop new measurement methodology using vibrational spectroscopy, which promised to provide more liquor properties than could be offered by titration, to construct a more robust analyzer, and to eliminate the need for reagents.[2] In 1995, a beta site was set up to install an analyzer that would sample liquor from a continuous digester.

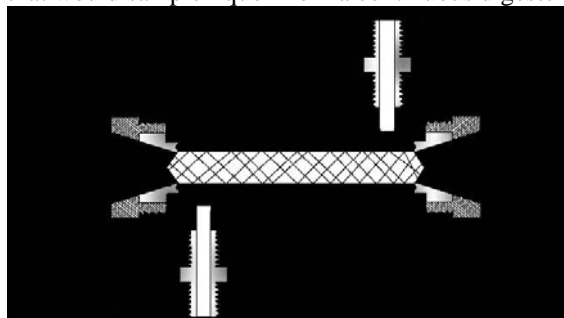


Figure 1: ATR cell containing crystal.

The first prototype mid-IR-based analyzer utilized a cylindrical attenuated total reflectance (ATR) cell (Figure 1). The sampling apparatus consists of a crystal rod around which liquor flowed. Light interacting at the surface of the rod can be analyzed for chemical compositions. ATR crystal of different material, zinc sulphide, zinc selenide, zirconia, and fused silica, were tested immersing the crystal in white liquor and heating to 90 degrees C for 4 hours and showed that zinc sulphide was able to withstand chemical attack. The ATR cell was integrated with a Hartmann and Braun (Bomem) FT-IR spectrometer and packaged in a cabinet for mill testing. Infrared light, at critical angle, passed through the crystal while some of its energy was absorbed by the liquor contacting the surface of the crystal. The resulting light spectrum detected at the other end of the crystal was used to determine the liquor properties. Data was gathered from many samples, models of liquor properties were created, and the results verified by lab analysis.



Figure 2: ATR Cell and FT-IR spectrometer.

The early version of the FT-IR mid-Infrared liquor analyzer did show that it was able to measure cooking liquor residual effective alkali, sodium carbonate, and sodium sulphide. However, the ATR cell and the maintenance of the cylindrical ATR crystal proved to be high maintenance. Over time, the crystal in the sampling chamber would become coated and would need to be removed for cleaning. It was found that unless the crystal was reinserted in exactly the same plane, an offset in results would occur. The model needed to be tweaked each time the crystal was cleaned. In addition, removal and replacement of the ATR crystal was difficult. Furthermore, signal is affected by changes in refractive index.

Development of FT-NIR (Fourier-transform Near Infrared) Analyzers for Pulping Liquor Measurements:

In 1994 to early 1995, Chemetics International and Paprican explored the idea of using NIR transmission measurement technique. Using FT-NIR technique has many advantages over the mid-Infrared FT-IR technique, including: remote analysis using fibre-optic cable connecting the spectrometer and the cell, transmission measurement to simplify sample flow through cell, large pathlength to eliminate potential plugging while increasing sensitivity of measurements, and ability to multiplex several cells into one spectrometer.

First Commercial Digester Application

In 1996, the first commercial installation by MoDo-Chemetics of an on-line version of the FT-NIR analyzer was made on two continuous digesters at a northern Ontario, Canada, pulp mill. Nine liquor sample lines from the two digesters were piped to the FT-NIR analyzer and marshaled together to allow one sample at a time to be drawn into the sampling apparatus (Figure 3). Samples of white liquor, upper and lower circulation black liquor and extraction black liquor were sampled from each digester. A wash circulation sample was also drawn from the “B” digester.



Figure 3: Field sampling lines for digester installation.



Figure 4: FT-NIR Analyzer cabinet of WorkIR

The analyzer cabinet (Figure 4) was split into two compartments with the spectrometer mounted in between. One side housed the piping, valves, and various switches and indicators necessary to trap the liquor sample, and the other

side housed a PC, PLC and electronics. The PC contained CAAP software (Bomem Hartmann and Braun) for operating the spectrometer and performing advanced mathematical routines, and the AB PLC contained ladder logic necessary to route the liquor into the sample cell. The analyzer PC and PLC were connected to the mill's Foxboro DCS where the liquor property results were used in advanced digester control programs. This original system ran satisfactorily until being replaced in 2007.

The use of FT-NIR technology in combination with the proprietary developed fibre-optic flow cell (Figure 6) with large pathlength allowed accurate measurements of cooking liquor REA. Other applications based on the same principle developed quickly and included complete recausticizing liquor chemistry, ClO₂ generator acid and chlorate strength, and dissolving tank raw and clarified green liquors [US Patent 6,339,222.].

Improvement in Sampling Cell Design

A prototype flow through transmission cell was constructed with a fixed pathlength through which NIR light, transmitted by fiber optic cable, would pass. The cell consisted of ¼" fused silica windows which was held in place using Teflon compression o-ring. Liquor resided in the sampling cell while NIR light passed through it and the resulting absorption spectrum, when ratioed to a water background, allowed quantitative analyses of liquor chemical compositions. Figure 5 is an illustration of the Bomem Michelson Interferometer with the transmission cell and detector. Figure 6 shows the first generation transmission flow cell developed by Modo-Chemetics and Paprican. Materials of construction were SS316 and grade 7 Titanium. Flow orifices were a ½" face-seal male connector. The fibre optic connection is standard SMA connectors.

To validate the performance of this new design cell, it was installed in parallel with an existing MoDo-Chemetics on-line liquor titrator that had been measuring white and black liquor REA at a mill for several years.[3] Whenever the on-line titrator was triggered for a liquor sample, the FT-NIR analyzer would sample the same liquor, and a third sample would be tested in the lab. The three sets of REA results were plotted and compared. The FT-NIR analyzer also measured carbonate and sulphide in white liquor, which were validated by comparing to lab tests.

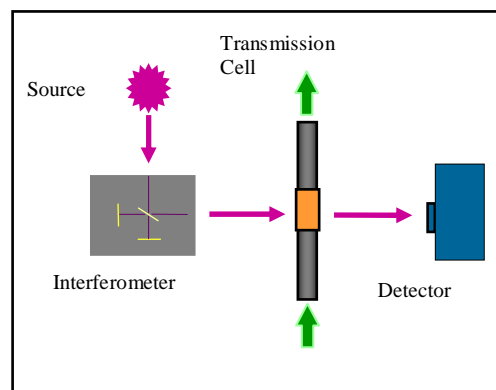


Figure 5: FT-NIR transmission measurement schematic showing spectrometer, cell and detector.

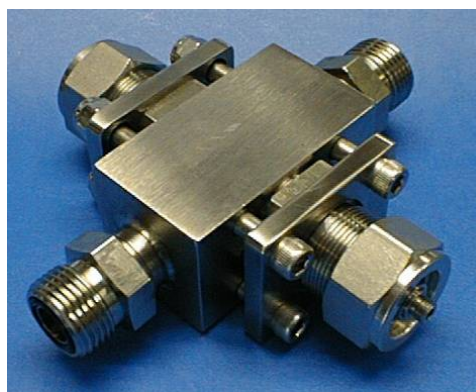


Figure 6: Original fibre-optic coupled transmission cell for FT-NIR Analyzer.

First Commercial ClO₂ Application

In 2000, the first commercial FT-NIR application for measurements of ClO₂ generator acid and chlorate concentration was installed by Kvaerner – Chemetics (formerly Modo-Chemetics). The analyzer consisted of grade 7 Titanium transmission flow cell, was installed at Prince George, BC. By this time, new software had been developed in-house that incorporated all the necessary function to sample, analyze and report the results to various PLC and DCS systems. Models to measure acid and chlorate properties of ClO₂ generators had been developed by Paprican. Also, the WorkIR spectrometer had been replaced by a NetworkIR spectrometer, which allowed for the computer and spectrometer rack to be separated from the sampling system. Necessary spectral information between the spectrometer and the controlling PC was transferred by fiber optic cable.

For this first installation, the computer/spectrometer rack was placed some distance away from the sampling cabinet, which was located beneath the generator. ClO₂ solution from the generator would flow through the analyzer until a sample request was made. Then the solution would be drawn up into the sampling cell for analysis. Figure 7 shows this schematic diagram for the ClO₂ generator analyzer. This ClO₂ installation is still in operation today.

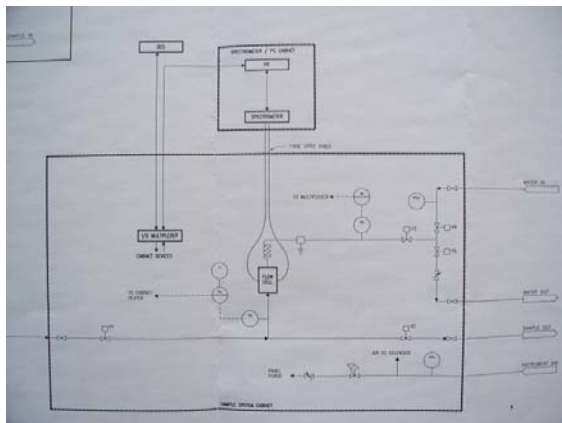


Figure 7: Schematic diagram of ClO₂ generator FT-NIR acid and chlorate analyzer.



Figure 8: Stainless steel enclosure showing Titanium cell and piping of ClO₂ generator acid and chlorate analyzer, still in operation since 2000.

First Commercial Recaust Application

In 2000, an analyzer was installed at a pulp mill in Texas to measure liquor streams from the recaust area. A large cabinet housing 2 separate sample cells was built to accept samples from 8 locations in recaust. One cell path would accept liquor from streams with adequate pressure, and the other cell path included an eductor to assist with sample collection. Recaust streams sampled by this analyzer were green liquor (GL) equalization tank output, GL to slaker, weak wash (WW), #1, #2 and last causticizers, and filtered WL. Although some sample streams were abandoned over the years, this analyzer is still in service today.



Figure 9: Recaust sampling skid showing two flow cells. The FT-NIR recaust analyzer was installed in 2000 and is still operational today.

Current State-of-the Art FT-NIR Liquor Analyzers Incorporating Many Improvements:

Over the past 15 years, we have seen maturation of the technology. NIR spectrometry as process analytical technology has grown in many industries, from pharmaceuticals to food processing to petroleum processing. We have tested and incorporated many of these developments which have led to increase uptime, reliability, and accuracy of the FT-NIR liquor analyzer technology.

Sampling Cell Design

Compared to the ATR cell, the flow-through cell developed in the mid to late 90's was a good improvement. Although this sampling cell design eliminated the initial offset in results, it had its own set of shortcomings. Since the windows protruded into the liquor stream, occasionally a window would shear off because of hydraulic shock. The Teflon o-ring would creep with temperature and leak.. Another problem with this window design was that the fiber optic connection on the ends of the windows had to be optimized each time the cell was removed for cleaning or window replacement. These issues sometimes caused erratic results

Current Design

Sapphire has replaced fused silica as the window material. Sapphire has higher hardness and better chemical resistance than fused silica. In the new cell, the sapphire window is fused to the metal, thus, eliminating leaks. In addition, the new cell design requires no optimization of the fiber optic cable if the windows are cleaned or replaced. Using corner cube reflectors, light from one fibre optic tip is reflected 90 degrees through the cell opening to another corner cube mirror and launched back into the receiving fibre optic cable. In fact, once the sampling cell is installed, there is no further need to adjust the fiber optic cable. The cell block that contains the windows can be easily removed for cleaning and replacement. Also, the windows are flush with the cell block interior, eliminating the possibility of hydraulic shock shearing off the tips of the windows. Several current installations of the analyzer have had the cell in place for at least 2 years without the need to remove the inner block for cleaning or window assembly replacement.



Figure 10: New FT-NIR transmission flow through cell.



Figure 11: New FT-NIR transmission cell showing cell block and window assembly.

Software

A major drawback of previous versions of the analyzer control software was that there was a lack of graphical user interface (GUI) between the analyzer and operating or maintenance personnel. The controlling software operated in the background and the only system information available, other than a few alarms, was the analysis results. Granted, there were very few operational problems, but when problems arose, troubleshooting was difficult. We have adopted ABB's proprietary software, FTSW100 software, which is used in over 5000 installations in food, pharmaceuticals and petrochemical areas and is well suited to controlling the analyzer in the pulp and paper industry. The software can be operate in a multitude of formats and can communicate with DCS via Modbus, OPC,

CANOPEN, and other protocols. Diagnostic features can be programmed in to allow for alarms. Parameters can be optimized on the fly.

Property Models and Calibration

The models developed for use with the FT-NIR analyzer are cumulative. That is, each time the system is installed in a mill, spectral and property information from that mill's liquor is used to optimize the property model for each component. Once the analyzer is calibrated for that mill's unique liquor, no further calibration is necessary. The models used in today's analyzers have the advantage of many years of data in the spectral library. Calibration is maintained through automatic reference updates.

Modern FT-NIR Systems

Today's integrated systems consist of a computer/spectrometer rack situated in a clean environment, such as a control room or MCC. Keeping the computer and spectrometer in a stable temperature environment will afford many more years of trouble-free service.

In the field, an enclosure housing the sampling cell is located on a sampling skid along with pipes, valves, switches and other equipment that route the chosen sample through the sample cell. Figures 12-14 illustrate sample skids for the recaust, digester, and ClO₂ generator applications. Each skid can accept liquor from multiple sources, depending upon which area of the pulp mill is being analyzed. For example, a continuous digester may have 5-8 sample points, a recaust may have 3-4, and a ClO₂ generator may have 1-2.



Figure 12: Recausticizing sampling skid.



Figure 13: Digester sampling skid.



Figure 14: CIO₂ generator sampling skid.

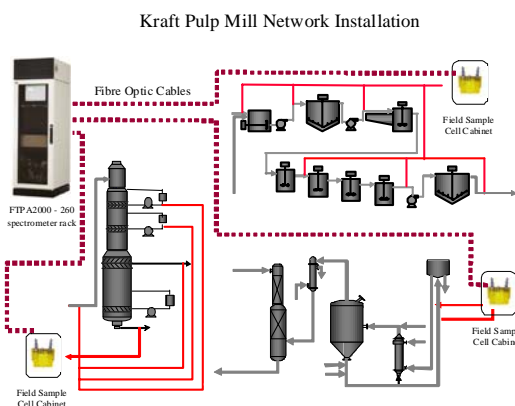


Figure 15: Schematic of a FT-NIR setup with multiple cells for three applications.

Fiber optic cables between the spectrometer and the sampling cells beam infrared light through the trapped liquor sample and back to the spectrometer's detectors. Just as each sampling station can have multiple liquor streams to it, the spectrometer and associated computer are capable of reading information from as many as 8 sampling cells. The liquor residing in each cell is analyzed in turn. The key is to place the computer and spectrometer rack in a location convenient to multiple pulp mill areas. For example an analyzer could service both a digester and a CIO₂ generator, if the computer and spectrometer rack was situated at a convenient distance from both of those areas. Figure 15 shows a schematic of a potential FT-NIR multi-cell application setup.

CONCLUSIONS

FT-NIR technology as process analysers for the pulp and paper industry has matured significantly over the past 15 years. Three main advancements have lead to improved sampling, reliability and accuracy when using FT-NIR analyzers:

1. Sampling
 - Modern sampling cell design allows years of trouble-free sampling
 - Increased light throughput and more sensitive detectors allow for increased spectral intensity
2. Reliability
 - Robust software developed for multiple industries insures reliability and continued support
3. Accuracy
 - Many years of model development using thousands of mill data files has resulted in increased accuracy of chemical property measurement.

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References

1. Carver, J., Kester, M., Roberts, C., Sands, T., "Inroads in Quantitative Analysis and its Role in the Control of Pulping Processes", 1998 Process Control, Electrical and Information Conference, Vancouver, BC.
2. Kester, M., Trung, T., Leclerc, D., and Carver, J., "On-Line Determination of Kraft Liquor Constituents by Fourier-Transform Near Infrared Spectroscopy", Journal of Pulp and Paper Science: Vol. 30 No. 5 May 2004.
3. Trung, T., Betts, S., Pouw, D., Allison, B., Uloth, V., Porter, J., "On-Line Determination of Green Liquor Reduction Efficiency by Fourier-Transform-NIR Spectrometry: Mill Trial Results", 2007 International Chemical Recovery Conference, Quebec City, QC.
4. Allison, B., Wallbacks, L., Trung, T., "Development and Application of Vibrational Spectroscopy for On-Line Process Analysis and Control", 2008 Control Systems/Pan-Pacific Conference, Vancouver, BC.