

**A New FTIR Technique for Monitoring the Conditions of Lubricants
Used in Pulp and Paper Mills**

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ABSTRACT

Condition monitoring of paper machine lubricants is a very important tool for the pulp and paper industry as it strives for higher productivity and profitability. In this paper, we introduce a recently developed technology encompassed and integrated in ThermalLube's patented COAT[®] System. This technique is based on FT-IR spectroscopy and designed for rapid analysis of lubricants in real time. It is very effective in determining a wide variety of lubricant condition parameters including soot, oxidation, nitration and moisture. Laboratory test results indicate that this new technique provides a high accuracy and good reproducibility, with significant advantages over the traditional chemical analysis methods, particularly when the lubricants are dark, sooty and thick.

Keywords: Lubricant, FT-IR, Quality Control, COAT[®] System

INTRODUCTION

A myriad of complex components synergistically work together to make up the mammoth papermaking machine. To keep the equipment running smoothly and efficiently, these huge machines consume enormous quantities of lubricants. Lubricants used in the pulp and paper industry include a variety of fluid oils as well as semi-fluid and conventional greases. Both oils and greases may be formulated from mineral or synthetic base stocks. The primary lubrication problem found in pulp and paper mills is the selection, maintenance, and monitoring of all the lubricants in use. The selection and development of the lubricants for paper machines has been discussed in recent publications [1-4]. However, the monitoring and maintenance of the lubricants often proves to be more important, because no matter the type of lubricant being used, contamination is unavoidable [5-9]. Contamination causes changes in the physical and chemical properties of lubricants which result in malfunction or premature failure of components and untold profit loss for the manufacturer. Furthermore, the contamination and disposal of used lubricants from the pulp and paper mill present environmental problems.

Although, significant effort has been made to develop specialty lubricants for pulp and paper machinery, it has faced some challenges. For example, water contamination is an important problem in the wet end of a paper machine where almost every part is run in a moist, humid environment. Water contamination promotes corrosion and stress on gears, bearings, gaskets, and stack rolls, leading to increased maintenance costs and unscheduled downtime [5]. To minimize damages caused by water contamination, continuous monitoring of lubricants is the key. At the dry end of the paper machine, lubricants must overcome different challenges. Paper machine lubricants run relatively hot, i.e., hotter than typical hydraulic oil systems, and for economic reasons, paper mills would like to reduce the frequency of lubricant changeouts. Therefore the oxidation and thermal stability of the lubricants are of critical importance. With the ever-increasing speeds of existing and new paper machines to improve production rates and maintain their competitive edge, oil-lubricated bearing temperatures at the dryer section often exceed 93 °C. This trend, coupled with the paper mills' endeavours to reduce lubricant loss, create a strong need for continuous monitoring of lubricants.

With pulp and paper mills pushing their paper machines to maximum production levels under demanding operating conditions, there is increased attention paid to the performance properties of paper machine lubricants. For maximum productivity and profitability, it is very important for pulp and paper mills to track the lubrication

requirements of specific machinery and establish a regular monitoring and control system. At any paper machine facility, minimizing degradation and water contamination is an everyday concern. A central lubrication monitoring system has recently been applied in a paper mill [10]. Practice shows that whether off-line or on-line, the monitoring and lubricant controlling system has become more and more important. To help address these issues, in this paper, we will introduce a new analytical technique based on FT-IR spectroscopy which will allow for the rapid analysis of lubricants for condition monitoring purposes. This technique provides a powerful tool for mill personnel to monitor the chemical and physical change of lubricants over time so that they may not only decide the exact time for an oil change, but also select the appropriate lubricants for each specific application.

EXPERIMENTS FOR CONDITION MONITORING OF LUBRICANTS

1. Traditional Chemical Analysis

Historically, lubricant testing was accomplished by colour, taste and smell. Modern lubricants analysis technology is collected and analyzed utilizing some relevant standards, such as the standards of the American Society of Testing Materials (ASTM). The total acid number (TAN) is a key parameter for representing a lubricant's condition to provide an early warning of critical contaminants and/or breakdown products forming due to improper maintenance, or contamination and consequently assisting an operator in identifying component failure. The determination of total base number (TBN) is also very important, because almost every lubricant contains some effective performance-enhancing additives, the TBN represents the operating efficiency of the additive package [11 -13]. The determination of the moisture content in the lubricants used in a pulp and paper mill is also important, because, as stated before, the lubricants used are stressed under extreme pressure, high temperature, and high humidity environments. Most methods based on wet chemistry analysis from ASTM are time-consuming, labour-intensive and create disposal problems of substantial amounts of environmentally unfriendly chemicals. More important is that chemical analysis methods such as TAN/TBN are difficult to use when lubricants are dark and sooty.

2. The FT-IR Methods

It has been recognized for a long time that infrared spectroscopy is a powerful tool by which many individual functional groups can be identified and quantitatively analyzed due to their absorption at specific wavelengths in the infrared portion of the spectrum. To address the above problem, the IR research group at McGill University and

ThermalLube Inc. developed a rapid, quantitative quality control technology for the analysis of lubricants by Fourier Transform Infrared (FT-IR) spectroscopy.

Measurement Principles

The FT-IR spectra of lubricants are generally extremely complex, exhibiting numerous bands, many of which overlap extensively. Thus, among the wide variety of acidic or basic constituents that may be present in a lubricant, few will give rise to readily identifiable bands in its spectrum, making the direct determination of TAN or TBN from an infra red band measurement difficult. Hence, an indirect approach based on concepts of *signal transduction*, *differential spectroscopy* and *back-titration* is used. The FT-IR methods developed is somewhat similar to the quantitative determination of free fatty acids in edible oils [14, 15]. In the analysis of lubricants, the presence of carboxylic acids is an indicator of oxidation of the hydrocarbons on the lubricants. The moisture content of hydrocarbon-based lubricants is determined by FT-IR spectroscopy by measuring hydrated acetone gem-diol produced when 2,2-dimethoxypropane reacts with water in the lubricants.

Equipment

A schematic diagram of the prototype COAT[®] System is presented in Figure 1. The main components of the COAT[®] System are an FT-IR analyzer, an IR flow cell, a logical fluid transfer pump and a computer running under windows-based COAT[®] System UMPIRE[®] software. The flow-through cell as well as the inlet and outlet lines are maintained at 40°C to facilitate the sample flow. To minimize water vapour and CO₂ interference, the COAT[®] System is continuously purged with dry air. All spectra are collected by co-adding 16 scans at a resolution of 4 cm⁻¹ and a gain of 1.0 and are ratioed against a 16-scan open-beam background spectrum.

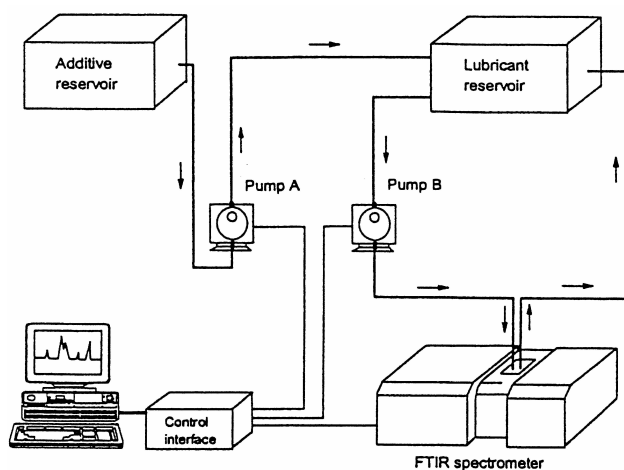


Figure 1. Schematic diagram of the prototype COAT[®] system.

Reagents and Chemicals

Reagent-grade oleic acid, potassium hydroxide, hexyl alcohol (hexanol), trifluoroacetic acid and potassium trifluoroacetate are obtained from Aldrich Chemicals. A stock solution (10% w/w) of KOH is prepared in hexanol. The alcohol is used as a convenient carrier for dispersing KOH in the lubricants. All the other standard reagents required for the chemical analysis are obtained from Fisher Scientific.

A series of fresh and used lubricants with different additive levels, such as SAE 5W30 and SAE 15W40 semisynthetic motor oil are supplied by ThemaLube Inc. Additive-free polyalphaolefin (PAO) base oil and barium dinonylnaphthalene sulfonate (BaDNS) concentrate and its overbased form {BaDNS-xBa(OH)₂} are also supplied by ThemaLube Inc.

Experimental Procedure

Experiments including calibrating and sample analysis are described mainly as the following process [17-19]:

- 1) A portion of the lubricant to be analyzed is used to rinse and load the flow-through transmission cell and its absorbance spectrum is recorded as AS₁.
- 2) From the balance of the lubricant sample, pipette 5 g of lubricant into a 20 ml vial and add the required chemicals using two gravimetrically pre-calibrated re-pipettes. Cap the vial, shake until the reaction has terminated.
- 3) Rinse and load the transmission cell with the reacted sample and record its absorbance spectrum as AS₂, and if necessary, multiply the resulting spectrum by the correction factor.
- 4) Spectrum AS₁ is subtracted from AS₂ to produce a "differential spectrum" as AS₃.

AS₃ is used to predict the TAN, TBN and moisture content of the sample by either peak height or partial least squares in different absorbance spectrum regions, such as at 1565 cm⁻¹, 1672 cm⁻¹ and 3691 cm⁻¹.

3. Advantage of FT-IR Methods

The new FT-IR methods have the potential to provide lubricant analysis laboratories with substantial savings in terms of labour, time, and reagent and disposal costs. These savings come largely from circumventing the slow titration process and large solvent volumes inherent to the ASTM methods, whereas the FT-IR method requires only small volumes of sample and reagent. While these FT-IR methods adhere to the fundamental tenets of the ASTM methods, they vastly improve on accuracy and reproducibility, therefore leading to more uniform inter-laboratory test results. In short, FT-IR spectroscopy provides a viable alternative to titrimetric methods.

VALIDATION AND DISCUSSION

The results of the determination of TAN, TBN, and moisture content in lubricants using FT-IR before and after addition of the anti-oxidant and anti-wear additives are compared with traditional wet-chemical methods and are discussed summarily as follows:

1. Determination of TAN in Lubricants

In terms of tracking lubricant degradation, the main components are carboxylic acids formed as a result of oxidation processes, and these are readily observed and measured by FT-IR spectroscopy, because the carboxylic acid functional group has a strong absorption maximum at 1710 cm^{-1} .

Two acid samples are blended to produce a series of samples that are gravimetrically spiked with the lubricant to produce a series of calibration standards containing known amounts of acid. These standards have TAN values ranging from 1.8-4.7 mg KOH/g, with the COOH contribution to the TAN value ranging from 0.8-4.0 mg KOH/g. The samples are aspirated into the flow-through IR cell. Their absorbance spectrum is recorded, using the COAT[®] System parameters. Variance and correlation spectra are examined to determine the spectral regions where strong absorbance changes correlated with the changes in acid concentration in the calibration set and to determine the optimal regions to use in developing a Partial-Least-Squares calibration model [17].

Figure 2 shows the FT-IR spectra of a series of lubricating oil samples, depicting the absorption band at 1710 cm^{-1} increasing in height and area with acid concentration.

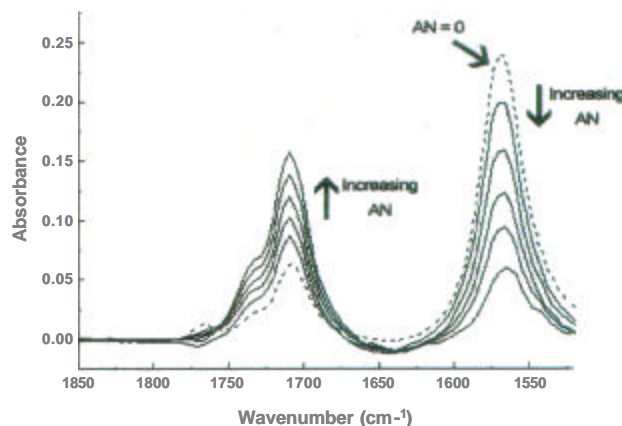


Figure 2. FT-IR spectra of a series of lubricants.

Figure 3 presents a calibration plot of absorbance values determined at 1565 cm^{-1} vs. the “actual TAN” calculated from the amount of oleic acid added to the TAN value of the oil base stock. The corresponding best-fit linear regression equation obtained over a TAN range of 2.7-6.0 mg KOH/g is:

$$\begin{aligned} \text{TAN} &= 1.32 + 5.02 A \\ R &= 0.999, \text{SD} = 0.068 \end{aligned} \quad (1)$$

where: TAN = Total Acid Number mg KOH/g
 A = Absorbance at 1565 cm^{-1}
 R = Correlation coefficient
 SD = Standard deviation

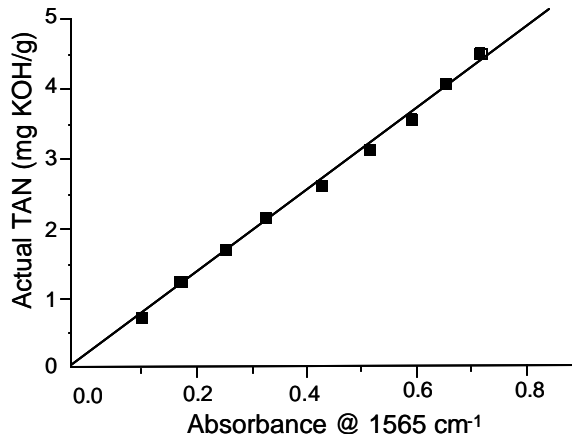


Figure 3. Calibration plot of absorbance values at 1565 cm^{-1} vs. the actual TAN.

The simple peak-height calibration illustrates that FT-IR tracks the change in -COOH quite readily and accurately. As oxidation takes place and the lubricant becomes more oxygenated, the system becomes more polar and the carboxyl groups engage in other forms of hydrogen bonding, which causes band shifts as well as changes in intensity. After some new experiments, the linear regression equation of the FT-IR predictions for several replicates of each sample against the spiked TAN values has yielded the following:

$$\begin{aligned} Y &= 0.071 + 0.93 X \\ R &= 0.996, \text{SD} = 0.044 \end{aligned} \quad (2)$$

where: Y = FT-IR-predicted spiked TAN value
 X = Actual spiked TAN value

2. Determination of TBN in Lubricants

Experiments showed that condition monitoring of performance-enhancing additives in lubricating oil is very important for predictive maintenance and extending equipment life. TBN represents the overall reserve alkalinity contributed to lubricants by additive packages. TBN is determined by spectroscopically measuring the COO- functional group of the salt produced when trifluoroacetic acid (TFA) reacts with basic constituents present in the lubricant. FT-IR quantification is also based on a differential spectrum derived from two lubricant spectra collected separately, one recorded prior to and the other after the addition of a TFA reactant solution, the first spectrum being subtracted from the second.

Several fresh and used lubricants are analyzed by the ASTM potentiometer titration method as well as by the FT-IR method to compare the results. Spectral subtraction is used to eliminate the spectral interference of the lubricant and to identify the spectral changes associated with the formation of the carboxylate anion, its absorbance being used to quantify the acidic constituents.

Figure 4 presents a calibration plot of the absorbance values measured at 1672 cm^{-1} vs. the actual TBN value calculated from the amount of BaDNS concentrate added to the base oil.

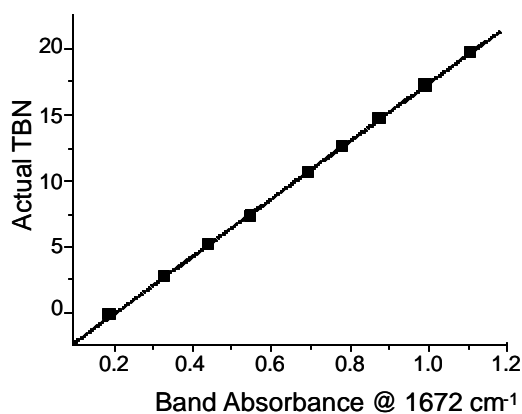


Figure 4. Calibration plot of the absorbance values measured at 1672 cm^{-1} vs. the actual TBN.

The best-fit linear regression equation obtained over a TBN range of 0-20 mg KOH/g is:

$$\begin{aligned} \text{TBN} &= -4.35 + 21.44 A \\ R &= 0.9998, \text{ SD} = 0.160 \end{aligned} \quad (3)$$

where: TBN = Total Base Number
A = (Absorbance at 1672 cm^{-1}) – (Absorbance at 2110 cm^{-1})

Various fresh and used lubricants, including additive-free zero-TBN base oil, and a number of locomotive diesel engine oils with various viscosity and additive package compositions are analyzed for TBN by the ASTM method as well as by the FT-IR Method. Figure 5 illustrates the relationship between the TBN values obtained by the two methods. After changing the proportionality constant, a new linear regression equation relating the FT-IR and ASTM TBN data is forced through the origin, yielding the following equation:

$$\begin{aligned} \text{FT-IR TBN} &= 1.024 \text{ ASTM TBN} \\ R &= 0.97, \text{ SD} = 1.55 \end{aligned} \quad (4)$$

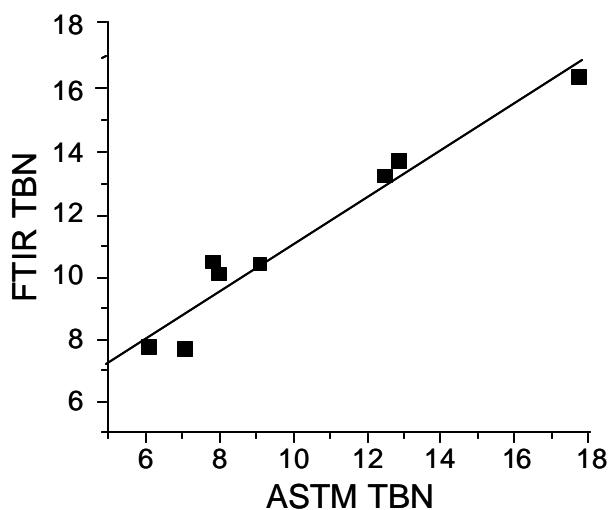


Figure 5. Relationship between TBN values obtained by two methods.

3. Determination of Moisture Content of Lubricants

After having developed the technology of determination of TAN and TBN, the McGill IR group and ThermoLube Inc. begin to research the feasibility of determining moisture in hydrocarbon lubricating oils by FT-IR Spectroscopy [20].

The determination of moisture in lubricants is based on the measurement of hydrated acetone gem-diol produced when 2,2-dimethoxypropane (DMP) reacts with water present in the lubricant under neutral or basic conditions. The gem-diol is quantified from a differential spectrum derived from two lubricant spectra collected separately, one taken prior to the addition of DMP and the other 30 minutes after DMP addition. Peak height calibrations are developed by standard addition of water to commercial hydrocarbon based lubricants that are also sampled for calibration development by

partial least squares (PLS) regression. The DMP/water reaction is determined as the basis for calculation of moisture in lubricants by FT-IR spectroscopy, using various lubricants including various commercial fresh and used lubricants.

The overall reaction involves one mole of 2,2-dimethoxypropane reacting with water in the presence of acid, the DMP being converted into one mole of acetone and two moles of methanol, as follows:



Figure 6 illustrates a series of overlaid differential spectra obtained using the standardized analytical protocol, covering the 3800-3300 cm^{-1} region for PAO samples spiked with increasing amounts of distilled water. These spectra illustrate that both the gem-diol (3690 cm^{-1}) and methanol (3500 cm^{-1}) peak heights increase as a function of water content in the lubricant.

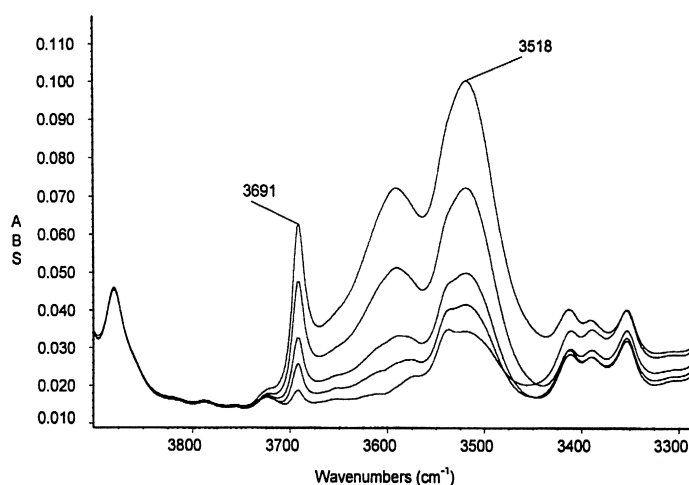


Figure 6. A series of overlaid differential spectra for PAQ samples.

Figure 7 shows a representative absorbance plot for the gem-diol measured relative to a single point baseline at 3691 cm^{-1} as a function of added water. The best-fit linear regression equation is as follows:

$$[\text{H}_2\text{O}] = -118.6 + 44884 A \quad (6)$$

$R = 0.998, \text{SD} = 9.88$

where: $[\text{H}_2\text{O}]$ = Actual water, ppm
 A = Absorbance at 3690 cm^{-1} /baseline at 3705 cm^{-1}

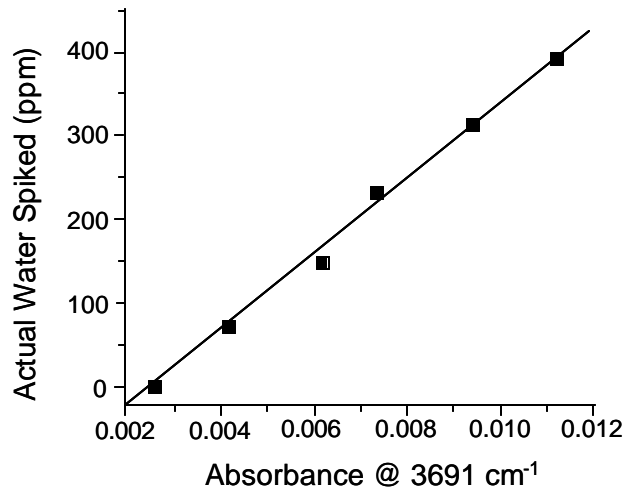


Figure 7. A representative absorbance as a function of added water.

Figure 8 illustrates the plot of the optimal PLS calibration devised after extensive study and optimization of regions that correlated with the moisture contents. The regression equation for the validation plot is as follows:

$$\text{FT-IR } [\text{H}_2\text{O}] = 3.93 + 0.994 \text{ H}_2\text{O} \quad (7)$$

R = 0.997, SD = 34.1 ppm

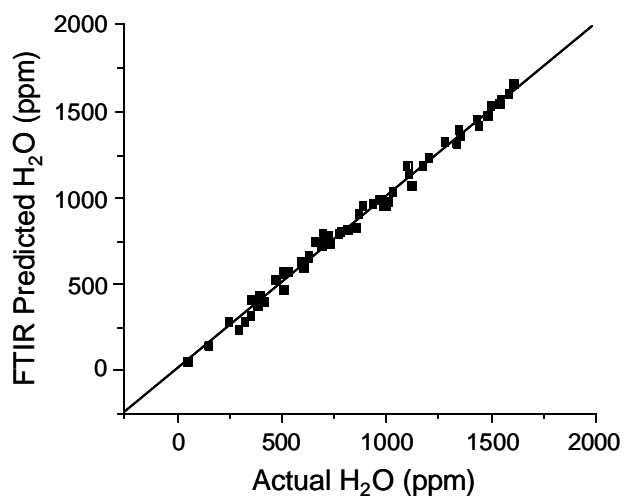


Figure 8. Amount of water measured by FT-IR vs. actual moisture content.

These results indicate that the optimized PLS calibration is capable of predicting the moisture content of any of the lubricants using individual peak height calibrations with a high degree of accuracy.

SUMMARY

1. The research work demonstrated that FT-IR spectroscopy is an excellent method for determining the quality of the lubricants, including TAN, TBN, and moisture content. Measurements are not affected by the colour or the condition of the lubricant itself as it is referenced against itself.
2. The COAT[®] System based on FT-IR can be used for determining the total acid number, total base number and moisture content in the various lubricants. Using Thermal-Lube's newly developed UMPIRE[®] software package, it will guide the operator through the analytical protocol, and automatically perform all required spectral manipulation and calculation outputs of the analysis.
3. The analytical results can be used for monitoring and controlling the quality of lubricants and for determining the time and quantity of addition of additives for extending lubricant life.
4. This new analysis also has the benefit of minimizing the use and disposal of solvents and reagents, rendering this method more environmentally friendly.

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