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QUANTITATIVE CONDITION MONITORING OF LUBRICATING OILS BY FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

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A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of Doctor of Philosophy

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> > August, 2000

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CONDITION MONITORING OF LUBRICANTS BY FTIR SPECTROSCOPY

ABSTRACT

Three new quantitative Fourier transform infrared (FTIR) spectroscopic methods were developed to measure key lubricant condition monitoring parameters; total acid number (TAN), total base number (TBN), and moisture (H₂O). All methods employ a common sample-handling accessory and are based on the addition of specific reagents designed to react stoichiometrically with target species in oils, with quantification being carried out using differential FTIR spectroscopy. The combined use of a stoichiometric reaction and differential spectroscopy overcomes the need for a reference oil, which has traditionally hindered quantitative analysis of lubricants by FTIR spectroscopy. Potassium hydroxide, trifluoroacetic acid (TFA) and 2,2-dimethoxypropane (DMP) were the stoichiometric reagents used to develop the FTIR TAN, TBN and H₂O methods, respectively. Calibrations were developed using either peak height measurements or partial least squares (PLS) regression and the methods were validated using standard addition techniques, as the ASTM (American Society of Testing and Materials) standard methods were not sufficiently reproducible to make valid comparisons. Validation of the methods indicated that the TAN, TBN and H₂O methods had accuracies of +0.095 mg KOH/g, ±0.5 mg KOH/g and ±32ppm respectively and corresponding reproducibilities of +0.05 mg KOH/g, +0.17 mg KOH/g and +22 ppm. The TAN, TBN and H₂O methods were implemented on a Continuous Oil Analysis and Treatment (COAT[®]) System, integrating instrumentation, software and sample handling so as to provide packaged, user and environmentally friendly analytical methods that are alternatives to conventional ASTM wet chemical methods.

RÉSUMÉ

Trois nouvelles méthodes d'analyse quantitative ont été développées afin de mesurer les paramètres d'importance en référence avec l'évolution de la fonctionnalité des lubrifiants grâce au support de la spectroscopie à infrarouge à transformation de Fourier (FTIR). Celles-ci visant à mesurer l'indice d'acidité (TAN) de basicité (TBN) ainsi que le niveau d'humidité. Toutes ces méthodes font appel à un accessoire de traitement des échantillons conventionnel et sont basées sur l'addition d'un réactif soigneusement sélectionné afin de produire une réaction stochiométrique directement en rapport avec le phénomène étudié qui pourra par la suite être quantifiée à l'aide d'une mesure différentielle obtenue grâce à la spectroscopie à infrarouge à transformation de Fourier. L'utilisation conjointe d'une réaction stochiométrique et d'une mesure différentielle obtenue par l'entremise de la spectroscopie élimine l'obligation d'avoir recours à une huile de référence qui avait dans le passé constitué un obstacle majeur à l'utilisation d'une telle technologie. L'hydroxyde de Potassium, l'acide Trifluoroacétique (TFA) et le 2,2-Dimethoxypropane (DMP) furent utilisés comme produits réactifs dans le cadre de cette recherche pour mesurer à l'aide de la spectroscopie à infrarouge à transformation de Fourier (FTIR) respectivement TAN, TBN et humidité et servir au développement de ces méthodes. Le calibrage fut développé à l'aide d'une mesure des sommets à la longueur d'onde étudiée et/ou à une régression basée sur la moindre partielle des carrés (PLS). Ces méthodes furent ensuite validées grâce à l'utilisation de techniques d'additions standard telles que décrites par l'ASTM (American Society of Testing and Materials). Il fut toutefois noté que le peu de reproductibilité de ces méthodes empêcha d'effectuer une comparaison appropriée. La validation de ces méthodes confirma un niveau d'exactitude de ±0.095mg KOH/g pour TAN, ±0.5 mg KOH/g pour TBN ainsi que ±32ppm pour l'humidité avec une reproductibilité de ±0.05 mg KOH/g, ± 0.17 mg KOH/g et ± 22 ppm. Ces trois méthodes furent par la suite mises en fonction sur un système d'analyse et de traitement continu des huiles (COAT[•]) permettant une intégration de toutes ces fonctions, d'une analyse par logiciel et d'un traitement des échantillons de façon rapide et efficace et par surcroît sans danger pour l'environnement -

définitivement une alternative viable à la méthode chimique traditionnelle prônée par l'ASTM qui utilise un large volume de produits nocifs à l'environnement.

STATEMENT FROM THE THESIS OFFICE

In accordance with the regulations of the Faculty of Graduate Studies and Research of McGill University, the following statement from the Guideline for Thesis Preparation (McGill University, October 1999) is included:

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The thesis must include the following: (1) a table of contents; (2) an abstract in English and French; (3) an introduction which clearly states the rational and objectives of the research; (4) a comprehensive review of the literature (in addition to that covered in the introduction to each chapter); (5) a final conclusion and summary.

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CONTRIBUTIONS OF AUTHORS

The four papers listed below make up Chapters 3-6 of this thesis. The author of this thesis was responsible for the concepts, design of experiments, experimental work, and manuscript preparation. Drs. F. R. van de Voort and A. A. Ismail are thesis supervisor and co-supervisor, respectively, and had direct advisory input into the work as it progressed. Dr. Yaylayan provided advice relative to the chemistry of the reactions and reagents used in Chapters 4 and 5. Mr. A. Brazeau and A. Taghizadeh, respectively, provided facilities and technical assistance relative to the ASTM methods described in Chapter 4 and 5. Mr. D. Pinchuk, Dr. E. Akochi-Koblé and Mr. J. Pinchuk of Thermal-Lube, Inc. provided samples, additives and technical advice related to lubricants integral to this research work.

List of publications reproduced in the thesis:

Dong, J., van de Voort, F.R., Ismail, A.A., Akochi-Koblé, E. and Pinchuk, D., Rapid Determination of the Carboxylic Acid Contribution to the Total Acid Number of Lubricants by Fourier Transform Infrared Spectroscopy, *Lubr. Eng.*, 56(6), 12-20, 2000.

Dong, J., van de Voort, F.R., Yaylayan, V., Ismail, A.A., Pinchuk, D., and Brazeau, A., A New Approach to the Determination of Moisture in Hydrocarbon Lubricating Oils by Mid-FTIR Spectroscopy, *Lubr. Eng.*, in press, 2000.

Dong, J., van de Voort, F.R., Yaylayan, V., Ismail, A.A., Pinchuk, D. and Taghizadeh, A., Determination of Total Base Number (TBN) in Lubricating Oils by Mid-FTIR Spectroscopy, *Lubr. Eng.*, in press, 2000.

Dong, J., Ismail, A.A., van de Voort, F.R., Pinchuk, D., Pinchuk, J. and Akochi-Koblé, E., A Novel Method to Determine TAN, TBN and Moisture Using FTIR Spectroscopy, in 2000 Technology Showcase, JOAP International Conditional Monitoring Conference, Humphrey, G.R., Martin, R.W. and Yarborough, T.A. ed., Mobile, Alabama, 132-141, 2000.

CONTRIBUTIONS TO KNOWLEDGE

- 1. Demonstrated the utility of the technique of differential spectroscopy in conjunction with a chemical reagent as a quantitative basis for lubricant condition monitoring by Fourier transform infrared (FTIR) spectroscopy. The characteristic absorptions of products formed by reacting species of interest in lubricating oils with specific reagents were shown to be clearly discernible by ratioing the spectra recorded after addition of the reagent against the spectrum recorded before reagent addition. By using spectral ratioing to obtain differential spectra, most spectral interferences associated with the base oil and additive package are effectively removed, making quantitative measurement possible without requiring a reference oil.
- 2. Developed a quantitative method of measuring carboxylic acid contribution to the Total Acid Number (TAN) in mineral based lubricants by FTIR spectroscopy.

The method is based on the addition of a KOH/hexanol solution to react with carboxylic acids in oil, indicative of base oil oxidation. The acids are converted into their respective salts and quantification is based on the salt absorbance appearing in the 1603-1560 cm⁻¹ region. The method can replace the standard wet chemical TAN procedure recommended by the American Society of Testing and Materials (ASTM).

3. Developed a quantitative method of measuring Total Base Number (TBN) in mineral based lubricants by FTIR spectroscopy.

The method is based on the addition of trifluoroacetic acid (TFA)/hexanol solution to react with basic constituents in an oil, their depletion being indicative of oxidation of base oil or accumulation of acids formed by combustion. TFA is converted to its salt and quantification is based on salt absorbance at 1673 cm⁻¹. The method can replace the standard wet chemical TBN procedure recommended by the American Society of Testing and Materials (ASTM).

4. Developed a quantitative method for the determination of moisture present in mineral based lubricants by FTIR spectroscopy.

The method is based on the addition of 2,2-dimethoxypropane (DMP) to oils to react with moisture and the measurement of the absorption of the gem-diol formed over the region of 3945-3156 cm⁻¹. The method can replace the Karl-Fischer method recommended by the American Society of Testing and Materials (ASTM).

5. Integrated and implemented the methods developed so as to make them simple and routine to use.

The methods developed were programmed and integrated into a Continuous Oil Analysis and Treatment ($COAT^{\bullet}$) System so that the FTIR methods could be used in a routine manner in an industrial laboratory.

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LIST OF ABBREVIATIONS AND SYMBOLS

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AA	Atomic absorption
AE	Atomic emission
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
BaDNS	Barium dinonylnaphthalene sulfonate
BS	Bright stocks
CLS	Classical least squares
COAT	Continuous Oil Analysis and Treatment
cSt	Centistoke
CV	Coefficient of variation
DMP	2,2-Dimethoxypropane
DTGS	Deuterated triglycine sulphate
EGR	Exhaust gas recirculation
EP	Extreme pressure
ESDC	Engine System Development Center
FFT	Fast Fourier transform
FT	Fourier transform
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HEAR	High erucic acid rapeseed oil
ICP	Inductively coupled plasma
ILS	Inverse leas squares
IR	Infrared
IRE	Internal reflection element
JOAP	Joint Oil Analysis Program
KF	Karl Fischer
KTFA	Potassium trifluoroacetate
LC	Liquid chromatography

MS	Mass spectrometry
NETE	Naval Engineering Test Establishment
NIR	Near infrared
NPO	Naphthene pale oils
PAG	Polyalkylene glycols
PAO	Polyalphaolefin
PCA	Polycyclic aromatics
PCR	Principal component regression
PIBS	Polyisobutylene succinimides
PLS	Partial least squares
ppm	Parts per million
PRESS	Predicted residual error sum of squares
RUL	Remaining useful life
SD	Standard deviation
SNO	Solvent neutral oils
STCUM	Société de Transport de la Communauté Urbaine de Montréal
TAN	Total acid number
TBN	Total base number
ТСР	Tricresyl phosphate
TFA	Trifluoroacetic acid
TGA	Thermal gravimetric analysis
TOST	Turbine Oil Stability Test
UMPIRE	Universal Method Platform for Infra-Red Evaluation
UV	Ultraviolet
VI	Viscosity index
ZDDP/ZDTP	Zinc (dialkyl) dithiophosphate

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CHAPTER 1 GENERAL INTRODUCTION

Lubricating oils, which represent a very significant portion of lubricants in general, are formulated from a range of base oils and chemical additives that serve to lubricate a variety of engines, equipment and machinery. The predominant component, the base oil, provides its lubricating function by forming a fluid layer that separates moving surfaces, and additional functions including removing heat, dispersing wear particles as well as circulating additives to where they are needed. The chemical additives in a base oil function as lubricant stabilizers and/or performance enhancers, e.g., addition of antioxidants improves the base oil's resistance to oxidative degradation. Additives and additive packages, often undefined, complicate the usually simple chemical nature of the base oil. There can often be a wide range of undefined additives present in lubricating oils, which can make them quite complex in their overall chemical makeup.

All lubricating fluids are subject to degradation during service, which gradually leads to a loss of the functionality that the fluids are designed for. Among various processes leading to degradation, reactions with oxygen are very important as the oil may become corrosive and can form insoluble sludges. Additive degradation and/or losses via chemical reactions or physical processes such as evaporation also shorten the useful life of lubricants as can unwanted contaminants such as soot or moisture, all of concern to machinery operators because they can lead to expensive mechanical failures. Additionally, it has been standard practice to change lubricants on an operating time or mileage basis, without consideration of the actual state of the lubricant. Depending on the load or stresses incurred during operation, two identical machines may end up having lubricants in quite different conditions from each other. Thus, it has effectively been argued that the condition of lubricants should be regularly monitored or measured in order to justify procurement and disposal expenses, which are usually high. This has led to the concept of *condition monitoring* and *predictive maintenance* as a means to be more efficient, reduce costs and obtain maximum lubricant service life without sacrificing equipment safety and reliability. Many large commercial enterprises as well as the military have very extensive machinery and equipment inventories for which lubricant changes and disposal are a significant cost of operation. Condition monitoring can be a very effective means of controlling these variable costs as long as there are effective ways of monitoring the condition of the lubricant.

The methods commonly used to monitor oil condition, usually in central or commercial testing laboratories, are largely based on the standard methods of the American Society of Testing and Materials (ASTM). Many of these methods are traditional wet chemical methods that are time consuming and labor intensive and often involve hazardous solvents and reagents. Over the past 10 years, there has been a major effort to develop instrumental methods that allow the condition of an oil to be monitored more readily. A key development in this regard has been the more extensive use of Fourier transform infrared (FTIR) spectroscopy as a condition monitoring tool, an initiative undertaken by the US military under the guise of the Joint Oil Analysis Program (JOAP). FTIR spectroscopy is a major advance over traditional dispersive IR instrumentation in terms of ease of use, versatility of sample handling and software for the managing and interpretation of spectral data. The JOAP protocol is a structured methodology that makes use of characteristic infrared absorptions of the functional groups of constituents in the oil to indicate whether they are present, rising or dropping in relative concentration. In condition monitoring, speed and multiple analytical capabilities are very desirable, and a broad range of constituents can be evaluated simultaneously by FTIR spectroscopy. FTIR is being used extensively for the rapid and routine screening of used lubricants for remaining additives, oxidative degradation of base oils and oil contaminants, however, the results obtained are still qualitative and an extensive lubricant degradation database is required to interpret the meaning of the spectral trends and values output.

Although FTIR spectroscopy has generally been used as a qualitative tool, the McGill IR Group has successfully developed quantitative FTIR analytical methodologies for industrial quality control applications, especially for edible fats and oils. The methods developed are rapid, use minimal or no solvents or reagents and have been designed to replace traditional wet-chemical methods. Thermal-Lube Inc., a Montreal based lubricant manufacturer, recognized that if the quantitative capabilities of FTIR spectroscopy could be applied to lubricants, condition monitoring would become a much more reliable and useful analytical tool. An industrial research partnership between the McGill IR Group and Thermal-Lube led to the development of an automated Continuous Oil Analysis and Treatment (COAT[•]) System that utilizes FTIR spectroscopy and has been successfully used to monitor the depletion of additives in lubricating oils. As experience was gained in working with lubricating oil matrices, it became clear that developing quantitative methods would be problematic because of the undefined nature of the oil due to constituents making up the additive package. Without defining the oil, or at least knowing that the oil formulation would remain consistent, there is no reference point to work from. Because there are so many formulations and even for branded products, formulations can change without notice, the concept of having reference oils on file is considered impractical. It is largely due to these problems that the FTIR based JOAP protocol is a mostly qualitative rather than quantitative procedure. Thus, although oil condition information can be obtained via FTIR, most users still turn to traditional methods to verify or determine a definitive value for specific parameters to make their decision whether or not to change oil.

Recognizing that the qualitative nature of the JOAP FTIR protocol ultimately limits its usefulness, the objective of this research was to develop quantitative FTIR methods which could replace key ASTM chemical methods such as total acid number (TAN), total base number (TBN) and moisture (H_2O). This work draws on experience, concepts and FTIR methodology development work carried out by the McGill IR Group and extends them, particularly the use of stoichiometric reactions in conjunction with the use of differential spectroscopy. The methodologies developed for TAN, TBN and H_2O analyses are described in Chapters 3-5, respectively, with Chapter 6 integrating and summarizing the concepts in relation to their instrumental implementation. The research results presented will demonstrate that generalized quantitative analysis of lubricants is feasible and that with appropriate instrumentation, sample handling and programming, quantitative FTIR spectroscopy should be both practical and beneficial to the lubricant industry.

4

CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION

In relation to industrial machinery, lubricant quality is an essential part in preserving the performance and longevity of equipment. As oil gradually degrades during the service, if not attended to, excessive mechanical wear will occur, leading to permanent and/or costly hardware damage. Typically, used oil may become too dirty and/or viscous to protect a machine, even becoming corrosive, forming harmful sludge and deposits, all of which can cause machine damage. Additives formulated as part of a lubricant for protection of specific functionalities may also deplete as the lubricant deteriorates, leading to impaired performance. Based on extensive investigation and experience, scientists and engineers have noted that certain operating cycles cause specific changes to a lubricant and that each type of lubricant degradation results in damage or loss of performance of specific mechanical components. It became evident that qualitative and quantitative analyses of lubricant physical properties, its organic/inorganic constituents and wear metals could yield worthwhile information. Such analysis provided information on the condition of the oil and the equipment and often provided indication of pending failures of key components such as bearings (Smolenski and Schwartz, 1994). Monitoring the presence of wear metals commonly employs ferrographic techniques and elemental analysis methods such as atomic absorption (AA) or atomic emission (AE) spectroscopy. Condition monitoring can provide supplemental information to indicate the state, effectiveness, and remaining useful life (RUL) of the lubricant based on degradation and contamination analysis (Lukas and Anderson, 1998).

Condition monitoring is defined as a "field of technical activity in which selected physical parameters associated with an operating machine are periodically or continuously sensed, measured and recorded for the interim purpose of reducing, analyzing, comparing and displaying the data and information so obtained and for the ultimate purpose of using this interim result to support decisions related to the operation and maintenance of the machine" (Anonymous). An effective lubricant condition monitoring program commonly employs a variety of tests involving physical and chemical approaches, many of which only provide indirect information on oil condition and/or contamination. More direct and comprehensive information is available via FTIR spectroscopy, the JOAP protocol facilitating its use as a standardized tool for qualitative lubricant condition monitoring. On the other hand, FTIR spectroscopy also has the potential to be used as a quantitative tool, its development being the subject and objective of this thesis. To provide appropriate background, the following sections provide an overview of lubricant technology and review selected analytical methods as well as IR spectroscopy in relation to lubricant condition monitoring.

2.2 LUBRICANT TECHNOLOGY

Lubricant use has a historical record dating back to the beginnings of civilization when natural fats and oils obtained from animal or vegetable sources were used (Dowson, 1979). These oils were first used to lubricate wheels on carts by spreading them on contact moving surfaces to reduce friction. The industrial revolution gave new impetus to lubricant technology as heavy machinery was developed and this led to large-scale production and commercialization of mineral oils in the early 19th century. In the 1930's, lubricant technology advanced significantly when it was recognized that the overall effectiveness of lubricants could be enhanced with the addition of oil soluble "performance additives", thus giving birth to the science of lubricant additive chemistry. Subsequently, various lubricants based on synthetic fluids and vegetable oils have become available on the market, in part because of either their unique lubricating properties or their biodegradability in the environment.

2.2.1 Lubricating Base Oils

The most common base oils currently used for formulating lubricants include mineral oils, synthetic fluids and vegetable oils, with the mineral oils making up the majority of overall base oil production. Depending on the type of application a lubricant is designed for, modern lubricating oils are formulated by mixing base oil(s) with special chemical additive(s) to enhance lubricant performance or stability. Base oils contribute basic lubricant functional properties such as provision of a fluid layer to separate moving surfaces, removing heat and wear particles, and acting as a carrier for additives and keeping them in solution under normal working conditions.

2.2.1.1 Mineral Oils

Mineral (or petroleum) oil was first introduced in the late 18th and early 19th centuries and rapidly overtook natural lubricants as the essential base lubricant fluid for the 20th century. Due to its abundance and reasonable lubricating performance attributes, mineral oils comprises the largest group of liquid lubricants in common use (Dowson, 1979; Durant and Teintze, 1991). Mineral oils are produced by refining crude oil, with each source having particular quality characteristics and properties depending on its makeup and how it is refined. There is no fixed chemistry for mineral oils per se, since they contain varying amounts/ratios of hydrocarbons, including alkanes (paraffins), alkenes (olefins), alicyclics (naphthenes), aromatics, and small amounts of organo-sulfur, -nitrogen and -oxygen species (Prince, 1997; Sequeire, 1994). Figure 2.1 summarizes the general structures of these constituents. The variation in the composition of mineral oils strongly influences their chemical and physical properties, such as viscosity and viscosity index (VI), thermal-oxidative stability, and pour point, all of which are governed by molecular structure. Mineral oils used in the manufacture of lubricants include: solvent neutral oils (SNO), naphthene pale oils (NPO), bright stocks (BS), cylinder oils, and specialty oils (Sequeire, 1994).

In general, mineral oil based lubricants are not necessarily the best lubricants because trace elements, especially sulfur, and unsaturation make them subject to oxidation, causing the formation of sludge and other undesirable compounds. Even so, mineral base oils still dominate lubricant base fluids and have found wide application in most areas of machinery lubrication because of availability, reasonable performance and price. Important attributes of mineral oils include: (i) a wide range of viscosities available



Figure 2.1 Examples of hydrocarbon and non-hydrocarbon constituents commonly present in mineral oils.

for various applications; (ii) relatively low and consistent coefficient of friction and low compressibility; (iii) reasonable effectiveness in dissipating heat; and (iv) low price. Nonmineral based fluids tend to be used in application where special properties are necessary, where petroleum base oils are in short supply or where substitution by natural products is practicable or desirable.

2.2.1.2 Synthetic Fluids

The term synthetic fluids covers a broad range of polymeric compounds and out of over 25 types of synthetic fluids identified by Gunderson and Hart (1962), seven are of primary importance. These include the polyalphaolefins (PAO), polyalkyleneglycols (PAG), phosphate esters, alkylated aromatics, polybutenes (or polyisobutenes, PIB), and two synthetic esters, namely, polyol esters and aliphatic diesters (Brown, et al., 1997). Figure 2.2 presents typical functional group structures found in the more commonly used synthetic base fluids.

Synthetic based lubricants were simultaneously and independently developed in Germany and the United States in the early 1930s (Brown, et al., 1997), with the technology developing extensively during WWII due to the shortages of petroleum products at that time (Shubkin, 1993). It soon became evident that in many applications, synthetic lubricants were superior to mineral oil formulations because they did not contain any of the readily oxidized or sludge forming compounds commonly present in mineral oils. They also have inherent advantages such as lower coefficients of friction and significantly prolonged service life due to molecular structures that are more chemically stable. In addition, they have low pour points (which allows function at very low temperatures); do not readily ignite or burn; withstand radiation; and (iv) do not gas off in a vacuum or space environment (Groshart, 1989). Their main disadvantage is that they are expensive relative to mineral base oils.

Owing to their unique physical and chemical properties, synthetic lubricants have



Phosphate esters

$$OR'$$

$$O=P-OR'$$

$$OR''$$

$$CH_3-(CH-CH_2)_n-CH_2$$

R R

Alkylated aromatics





Diesters



 $\begin{array}{c} O & O \\ \parallel & \parallel \\ RO - C - (CH_2) = C - OR \end{array}$



Polyalkylene glycols

R-(O-CH₂CH₂)_x-CH₂CH₂OH

Figure 2.2 Typical structures or functional groups of selected synthetic fluids.

found wide application in all areas of lubrication, including automobiles, trucks, marine diesels, transmissions, general industrial lubricants, as well as areas where mineral based lubricants are undesirable, such as the aviation and aerospace sectors.

2.2.1.3 Vegetable Oils

Lubricating base oils obtained from vegetable sources (rapeseed, soybean, etc.) are made up predominantly of triacylglycerols or triglycerides, which are triesters of fatty acids and glycerol.



In terms of performance in reducing friction and wear when used as lubricants, vegetable oils are superior to both mineral based and synthetic oils (Hairston, 1994). With increasing awareness of environmental issues, there has been a trend toward making more extensive use of vegetable oil lubricants in environmentally sensitive applications. Another reason for considering vegetable based lubricants is the growing concern about polycyclic aromatics (PCAs) present in mineral oils, considered a potential risk to human health. Vegetable oils are free of PCAs and low in unwanted species such as sulphurcontaining compounds, which are often associated with mineral oils. Aside from direct use as lubricants, vegetable oils have value as a feedstock for the oleochemical industry to produce a wide variety of chemical products which find use in many applications associated with lubrication, either as lubricant additives or for the production of synthetic materials such as ester base fluids (Crawford, et al., 1997).

Vegetable oils that can be used directly as lubricating base oils include soybean, castor, Canola, coconut, palm kernel and industrial high erucic acid rapeseed (HEAR) oils. Among these, HEAR oil is the most promising one, having good adherence properties, a high flashpoint, a high viscosity index, low volatility, good miscibility with other oils as well as excellent stability under shear stress over a wide range of operating temperatures (Kyriakopouls, 1995; Flider, 1995; Cheng, et al., 1991). Commercial utilization of vegetable oils with a predominantly higher degree of monounsaturation for lubrication purposes has also been reported (Gapinski, et al., 1994).

Vegetable oil based lubricants are particularly attractive to environmentally sensitive sectors such as construction, rock and quarry, the forest industry, and the mining industry (Hydrick, 1995). Vegetable oils have found applications in the automotive area (Randles, et al., 1989), tractor transmissions (Saunders, 1995), two-cycle outboard engines (van der Waal and Kenbeek, 1993), hydraulic oils (Sraj, et al., 2000; Legisa, et al., 1997, Cheng, et al., 1991), and as chainsaw lubricants (van der Waal and Kenbeek, 1993). They have not however been completely successful as engine crankcase lubricants and tend to be restricted to a limited number of applications due to their inherently poor oxidative, hydrolytic and thermal stability. At low temperatures they tend to solidify and at high temperatures they deteriorate rapidly. These disadvantages can however, be overcome to some degree by the use of appropriate performance-enhancing additives, such as antioxidants and pour point depressants.

2.2.2 Lubricating Oil Additives

Lubricant additives were first used in the 1920s and their routine use in modern lubricants has increased tremendously since then. Today, practically every lubricant contains at least one additive, and some oils contain several different types (Anonymous, 1979; Wills, 1980). Lubricant formulators usually incorporate an additive package containing "performance additives" to improve the chemical and physical properties of an oil. From the standpoint of functionality, lubricant additives can be classified as: antiwear additives, corrosion inhibitors, oxidation inhibitors, viscosity modifiers, pour point depressants, emulsion modifiers, form decomposers, tackiness agents, seal swell agents and dyes. Widely used additives for engine oils usually include dithiophosphates, overbased calcium sulfonates, succinimidic dispersants, and polymer viscosity index improvers (Herdan, 1997). A comprehensive examination of all additives is beyond the scope of this review, however, some of the more critical additives and the associated processes or functional parameters they are designed to control will be discussed.

2.2.2.1 Antioxidants and Oxidation

Antioxidants are probably the most important additives used in lubricating oils because oxidative deterioration plays a major role in oil degradation. The decision of what particular type of antioxidant to use is largely based on knowledge of the oxidative mechanism and the nature of the products predominantly formed. The need for antioxidants is based on the fact that all oils commonly deteriorate over time/use by autoxidation, a free radical chain reaction consisting of three distinct stages (Igarashi, et al., 1996), summarized below:

(a) Initiation:

$$RH \xrightarrow{M^{\#^*}/O_2} R\bullet$$
 [1]

(b) Propagation:

$$R \bullet + O_2 \longrightarrow ROO \bullet$$
 [2]

$$ROO \bullet + RH \longrightarrow ROOH + R \bullet$$
 [3]

(c) Termination:

$$R \bullet + ROO \bullet \longrightarrow ROOR$$
 [5]

The general sequence of events depicted above is prevalent at temperatures below 120°C (Rasberger, 1997). The site of oxygen attack in step [1] is determined by the strength of the C-H bond and the reaction rate is generally slow. Once an alkyl radical has been formed, it reacts irreversibly with oxygen to form an alkyl peroxy radical (step [2]). This reaction is extremely fast while the next step ([3]) in the chain propagation that leads
to the formation of a hydroperoxide and a new alkyl radical is slow. The propagation sequence of steps [2] and [3] continues in a chain reaction until finally the free radicals (R• and ROO•) form stable inactive products through the bimolecular radical-radical termination steps ([4], [5], and [6]). Effectively, each time one alkyl free radical is generated, a large number of hydrocarbon molecules may be oxidized to form hydroperoxides including alkylhydroperoxides (ROOH) and dialkylperoxides (ROOR), with limited formation of alcohols (ROH), aldehydes (RCHO) and ketones (RR'C=O). In addition, cleavage of dihydroperoxides (RCOOH(CH₂)_xCOOHR') formed via intramolecular propagation leads to more complex products, including diketones (RCO(CH₂)_xCOR'), keto-aldehydes (RCO(CH₂)_xCHO), and hydroxyketones (RCH(OH)-(CH₂)_xCOR') (Rasberger, 1997).

Oxidation of hydrocarbons at temperatures >120°C generally proceeds through two phases: a primary oxidation phase which involves the cleavage of hydroperoxides and formation of carboxylic acids (RCO(OH)); and a secondary oxidation phase in which formation of high molecular weight molecules takes place, leading to a bulk viscosity increase. In the primary oxidation phase, initiation and propagation of the radical chain reaction are the same as those under low temperature conditions, but the reaction rate is increased because breakdown of hydroperoxides leads to a proliferation of hydroxy radicals:

ROOH ----- RO• + HO•

Once formed, hydroxy and especially primary alkoxy radicals are so active that they abstract hydrogen atoms of hydrocarbons in a non-selective manner to produce new free radicals. At the same time, intramolecular propagation is a more favorable route of hydrogen abstraction (Jensen, et al., 1979; 1981) in a peroxy radical to produce a hydroperoxide-peroxy radical:

$$\begin{array}{cccc} OO & OOH & OOH \\ & & & & \\ -CH-CH_2-CH_2- & \longrightarrow & -CH-CH_2-CH- & O_2 & & \\ & & & & \\ -CH-CH_2-CH_2- & \longrightarrow & -CH-CH_2-CH- & OOH \\ & & & & \\ & & & & \\ OO & & & \\ \end{array}$$

Starting from this hydroperoxide-peroxy radical, via intramolecular hydrogen abstraction reactions, carboxylic acids are formed according to the following reaction schemes:



Secondary oxidation at high temperature involves polycondensation of the oxygenated products (aldehydes and ketones) formed in the primary oxidation phase, producing high molecular weight intermediates. Further polycondensation and polymerization reactions of these high molecular weight intermediates result in sludge, or varnish-like deposits under thin-film oxidation conditions. More detailed descriptions of the reaction mechanisms have been documented elsewhere (Rasberger, 1997; Igarashi, et al., 1996; Blaine and Savage, 1991a, 1991b, 1992; Hsu, et al., 1983). In summary, oxidation of hydrocarbons at high temperatures (>120°C) leads mainly to the formation of carboxylic acids (RCOOH), esters (ROOR'), and high molecular weight sludge and varnish which are no longer soluble in oil.

Since oil oxidation proceeds via a free radical chain reaction, any agents that will interrupt this reaction will slow or inhibit oxidation. Two general types of oxidation inhibitors are available: (a) radical scavengers that react with initiators, such as peroxy radicals and hydroperoxides, to form inactive components; and (b) hydroperoxide decomposers that decompose hydroperoxides to form less reactive compounds. Common radical scavenging antioxidants include sterically hindered phenols, aromatic amines, and organo-copper antioxidants; while common hydroperoxide decomposers include organosulfur compounds, zinc dialkyl dithiocarbamates, and organophosphorus compounds (GLW Consulting, 1992; Wills, 1980; Al-Malaika et al., 1987). Zinc dithiophosphates (ZDTPs), which have been extensively used as multifunctional additives in providing oxidative, wear, and rust protection, function as antioxidants in a complex interaction involving both hydroperoxide and peroxy radical mechanisms (Rasberger, 1997). Antioxidants are used in almost every lubricant type, including engine oils, turbine oils, hydraulic fluids, and air compressor oils and are critical to ensuring a prolonged operational life for the lubricant.

2.2.2.2 Antiwear Additives

Common antiwear additives are polar materials that adsorb on a metal surface and provide a film that reduces metal-to-metal contact. Important antiwear additives commonly found in lubricating fluids are zinc dithiophosphates (ZDTPs) and tricresyl phosphate (TCP). ZDTPs inhibit surface friction by adsorption of zinc dithiophosphate group on metal surfaces, with the aliphatic chains forming a boundary lubrication film in conjunction with other lubricant components (Powell and Compton, 1993). The structure of the alkyl groups determines the anti-wear potency of the ZDTPs, chain branching and chain length being particularly critical (Bovington, 1997). TCP typically finds use in synthetic polyol ester lubricants. Both ZDTPs and TCP contain a common phosphate functional group but their antiwear mechanisms are different. TCP is believed to provide protection via the formation of reactive films when oxygen, water and other polar impurities are present in the oil as well as providing some anti-rust protection by hydrolysis to produce phosphoric acid (Bovington, 1997).

2.2.2.3 Detergents and Dispersants

Detergents and dispersants are incorporated into a lubricant largely to prevent the formation of harmful carbon and sludge deposits. The terms "detergents" and "dispersants" are sometimes used interchangeably because both additive types keep

insoluble combustion debris and oil oxidation products dispersed within the oil. Technically, detergents are normally utilized to minimize high-temperature engine varnish and lacquer deposits while dispersants are used to control low-temperature engine sludge deposits. Both detergents and dispersants are long chain hydrocarbons with polar ends in which detergents have a polar metal ion, while dispersants (also known as ashless dispersants) utilize oxygen and/or nitrogen for their polarity and do not contain metal ions. According to the hydrocarbon substrate, ashless dispersants are of four general types: succinimides, succinate esters, Mannich types, and high molecular weight amines (Rizvi, 1999).

Detergents can be classified as sulfonates, phenates, salicylates, and phosphates (Colver and Gergel, 1997). In addition to the detergency ability, detergents incorporated with basic functional groups can provide some ability to neutralize acidic constituents. This ability is greatly enhanced by detergents overbased with alkaline earth metal hydroxides or carbonates in the form of micelles (Charter, 1997; Anonymous 1991). In terms of classification, overbased detergents have been casually defined by the amount of base contained in the product, often labeled by its total base number (TBN) or the equivalent amount of potassium hydroxide contained in the material (mg KOH/g of oil). However, solely using TBN to define an overbased detergent is often misleading because two detergents having the same TBN may differ in molecular weight, metal ratio, etc., and not necessarily have similar performance characteristics. Therefore, additional parameters such as metal ratio (the ratio of metal base to substrate), the amount of neutral detergent ('soap' content), the molecular weight of the substrate used, and the amount of sulfur present (when sulfonates are under consideration) more specifically define a detergent. Typical detergents, their basic structures, and TBN range as well as selected specifications are summarized in Table 2.1 (Colyer and Gergel, 1997).

In addition to being used in a range of lubricants including automatic transmission fluids, hydraulic fluids, gear lubricants, and industrial oils, detergents/dispersants have

Parameter	Sulfonates	Phenates	Salicylates	
Basic structures	0 0 R-S-O+M-CO, }M-O− S-R 0 0″			
TBN (mg KOH/g)	0-500	50-400	20-400	
Metal ratio	1-30	0.8-10	1-10	
Soap content (%)	10-45	30-50	10-45	
Metal cation	Ca, Mg, Na, Ba	Ca, Ba, Mg	Ca, Mg	
Molecular weight Sulfonic acid Alkylphenol	375-700	160- 6 00		
Carboxylic acid			250-1000	
Sulfur, %	0.5-4.0	0-4	-	

-

Table 2.1 Basic structure and selected specifications of typical detergents

found extensive application in engine oils. Commercial detergents are generally available diluted in mineral oil and are used in formulating engine oils in amounts ranging from 0.5% up to 30%, resulting in TBN values as high as 100 in marine diesel engine oils (Colyer and Gergel, 1997). Dispersants are a vital component in gasoline engine oils and are also used to advantage in diesel engine oils to suspend harmful soot contaminants.

2.2.2.4 Viscosity Index (VI) Improvers

VI improvers are long chain, high molecular weight polymers that function by increasing the relative viscosity of an oil, being more effective at high temperatures than at low temperatures. Principal VI improvers include methacrylate polymers and copolymers, acrylate polymers, olefin polymers and copolymers, and styrene butadiene copolymers (Stambaugh, 1997; O'Brien, 1983; Wills, 1980). The degree of VI improvement from these materials is a function of the molecular weight distribution of the polymer (Wills, 1980).

2.2.2.5 Vegetable Oil Derivatives

Vegetable oil derivatives have found increasing use as additives in modern lubricants. Soaps of 12-hydroxystearic acid, derived from castor oil, have superb thickening and lubricating properties. Sulphated castor oil is used in a mineral-based lubricant for presizing polyester fibres and thus minimizing abrasion. Ethoxylated castor oil is a hydrophilic emulsifier that has been used in metal-working fluids (Crawford, et al., 1997), while good oxidative stability and antiwear properties of high oleic vegetable oils have been reported (Asadauskas, et al., 1996). Although current use of vegetable oil derivatives as additives is relatively limited, genetic engineering, commercialization of new varieties, new chemical modifications, and environmental and economic trends are likely to increase the variety and supply of vegetable oil lubricants.

2.3 MARKET AND ENVIRONMENTAL IMPACT OF LUBRICANTS

Total world production of crude mineral oil amounts to approximately $3 \times 10^{\circ}$ tons annually. Of this amount, ~1% is used as mineral lubricant base fluids (van der Waal and Kenbeek, 1993), resulting in the production of ~40,000,000 tons of lubricant containing more than 1,200,000 tons of additives being produced annually (Herdan, 1997). The lubricant market is led by engine oils (Figure 2.3), which in turn utilize more than 50% of the additives produced, followed by gear oils, industrial oils, metalworking oils, and others. Statistical data obtained from the European Oil Companies organization, CONCAWE, (CONCAWE, 1985) indicates that of the total of lubricant sold in the EU, ~50% is consumed, 30% successfully disposed of via recycling or used as fuel (Table 2.2), 7% unaccounted for and ~2% deliberately dumped to the environment.

With increasing demand for environmental protection, new legislation is being proposed and enforced to reduce environmental impact of used lubricants. Improved engineering can minimize leaks and spills and there is an increasing reliance on authorized waste disposal specialists to eliminate dumping. Ultimately, however, the problem is that mineral oils do not biodegrade readily (Betton, 1997) and the solution rests in finding new lubricant formulations that are more environmentally friendly or measures that lead to a reduction in oil consumption or disposal. Natural fats and oils in theory can meet the need for biodegradability, however total world production is only 8 x 10⁷ tons, of which only 7% is presently being used for oleochemistry. Even if all natural fats and oils were available for lubricant use, only 19% of the mineral oil market could be displaced (van der Waal and Kenbeek, 1993). Hence, with few realistic alternatives available, any means of reducing overall lubricant consumption, including improved analytical methods which might allow more efficient use of lubricants, become important.

Lubricant condition monitoring is not only a tool for determining lubricant quality and serviceability, but also a means of ensuring maximum lubricant service life without sacrificing performance. In most situations, lubricating oil is periodically replaced with new oil according to the manufacturer's recommendations so as to sustain the reliability of the equipment and components. These maintenance schedules are usually quite conservative (Bijwe, et al., 2000) and replacing oil before the end of its useful life is



Figure 2.3 Lubricating oils' share of the market (Herdan, 1997).

	Tonnes per year (x 10 ³)	%	
Total EU Lubricant Sales	4500	100	
Consumed	2300	50-55	
Recycled	700	15	
Burnt as fuel	750	17	
Unaccounted for	600	13	
Poured down drain deliberately	100	2	

Table 2.2 Total lubricant production in the EU

highly undesirable in terms of cost and waste disposal. As oil condition is a function of operating and environmental conditions as well as maintenance practices, effective condition monitoring techniques tend to be a vital part of obtaining accurate and real-time information about the oil. By employing an appropriate condition monitoring program and establishing the most cost-effective oil change periodicity, drain intervals can be extended, resulting in reduced lubricant consumption and disposal.

2.4 LUBRICANT CONDITION MONITORING

Lubricant condition monitoring methods have evolved within the petroleum industry and its related technical associations. The chemical complexity of formulated lubricating oils containing additives requires that most of the parameters measured in condition monitoring be bulk physical or chemical properties indicative of the average performance of all the molecular types in the oil. The number and type of monitoring analyses performed on an oil sample vary with the type of oil and the type of machine the oil is designed for (Lukas and Anderson, 1998). Some of the routine measurements used for monitoring lubricant quality include: viscosity, total acid number (TAN), total base number (TBN), and contaminants such as water content, fuel dilution, ethylene glycol, and insolubles (Lukas and Anderson, 1998; Smolenski and Schwartz, 1994). The test parameters reviewed herein are those used most frequently and documented as standard procedures in lubricant condition monitoring.

2.4.1 Viscosity

Measuring viscosity is very useful for characterizing a new lubricant as well as following its overall performance while in service. Viscosity is a function of temperature, decreasing with increasing temperature, however, viscosity at a specific temperature may also change as a result of base oil degradation or due to contamination with other materials such as coolant or fuel. Kinematic viscosity expressed in centistokes (cSt, or 10^{-6} m²/s) is usually used to indicate lubricant viscosity, which is determined by the time required for a specified volume of liquid to flow through a pre-calibrated capillary viscometer at a constant temperature. Measurement of kinematic viscosity largely relies

on viscometers suspended in precisely controlled temperature baths at either 40°C or 100°C, or both temperatures as defined in ASTM standard guidelines (D445, 1990), while high temperature, high shear viscosity is determined using ASTM D4683 and D4741 (1990).

As oil viscosity varies with temperature, the most frequently used method for comparing viscosity variation with temperature is by calculation of the viscosity index (VI) based on the measurement of kinematic viscosity at two temperatures (40°C and 100°C) and subsequent comparison with an empirical reference scale as described in ASTM D2270 (1990). The higher the VI, the less affected the viscosity of an oil is by temperature. Semiautomatic and fully automatic viscometers that meet the ASTM D445 standard are commercially available to speed up analyses (Lukas and Anderson, 1998) and viscosity may also be measured on site using oscillating viscometers. The latter are not as accurate as a capillary tube, but sufficiently accurate for condition monitoring with an overall advantage of being of a rugged design, easy to use and rapid (Lukas and Anderson, 1998).

2.4.2 Total Acid Number (TAN)

Total acid number (TAN) is a measure of all the acidic constituents present in an oil, including weakly acidic components of the fresh oil and acids formed during combustion and oil oxidation (Smolenski and Schwartz, 1994). ASTM standard methods (D663, D664 and D974, 1990) for the determination of the TAN of an oil are based on the titration of acidic constituents in an oil with base to a fixed endpoint, the titer being expressed in terms of acid number (mg KOH/g oil). Two versions of the ASTM methods are available differing in their approach to determining the endpoint. In the case of used oils that are opaque and too dark to use a color indicator (ASTM D974, 1990), the TAN endpoint is measured potentiometrically (ASTM D664, 1990). TAN values of new oils tends to be less than 1.0 (Lukas and Anderson 1998; Fuchs, 1997), while TAN of used lubricants vary depending on operation conditions, with high TAN values being indicative of oil oxidation. For most lubricating oils, TAN values will start at relatively

low initial values and gradually increase throughout the service life of the oil. Although TAN generally tracks the progress of oxidation, solely using TAN values can be misleading under certain circumstances. For example, it has been noted that some beneficial additives contribute to TAN (Wurzbach, 1999), thus lubricants containing such additives may initially show a decrease in TAN during the early stages of service due to depletion of the additive.

As TAN is one of the most widely accepted parameters in monitoring the physical state of lubricating oil (Roberton, 1989; Bowman and Stachowiak, 1996), a number of oxygen-uptake tests, such as the Turbine Oil Stability Test (TOST) (ASTM D-943, 1990) designed to measure the oxidative stability of an oil, employ TAN measurements. In addition to various standardized commercial TAN titrators, electrochemical micro-sensor based testers have been developed for in-situ monitoring of oil condition (Wang, et al., 1994; Lee and Wang, 1994) and yield results that correlate well with chemical TAN results.

2.4.3 Total Base Number (TBN)

As opposed to TAN, TBN measures the total alkalinity reserve remaining in a lubricant. Such alkalinity indicates the ability of a lubricant to neutralize corrosive acids that are formed during engine or machinery operation. As noted earlier, lubricant alkalinity is often contributed by basic additives such as overbased detergents; thus, TBN is also a means of monitoring the rate of base consumption, which is related to the rate of buildup of strong acids in the oil. By establishing a normal basic additive depletion rate, TBN can provide an indication as to whether the rate of acid generation is consistent with expectations. Sudden higher rates of base consumption may be indicative of abnormal machinery operation or contamination of the lubricant.

Like TAN analysis, ASTM TBN measurements (D 2896, 1990) are based on acid/base titration but use strong acid (HCl or HClO₄) as the titrant, the results also being expressed in mg KOH/g. Therefore TAN and TBN analyses can usually be performed

with the same equipment without much modification. Currently, several manufacturers market titrators capable of performing automatic TAN and TBN titrations, with autosamplers available, as some titrations require a fair amount of time for the reaction to equilibrate after incremental acid or base addition. Like most traditional wet chemical methods, both TAN and TBN are time consuming and require large amount of organic solvents that are increasingly difficult to dispose of. Among various methods that attempt to avoid titration, one is an indirect TBN measurement based on gas evolution from an acid/base reaction (Ricardo Consulting Engineers, 1984). Wohltjen, et al. (1994) made use of a solid state microchip pressure transducer to monitor CO₂ pressure produced by the reaction of the basic additive in the oil with a mildly acidic reagent. Such approaches simplify TBN measurement, are reasonably accurate and reliable, but tend to be limited to carbonate (CO₃²) containing oils. More recently, Kauffman (1989, 1998) developed a rapid voltammetric technique for determining the TBN of a wide variety of oils and fluids. This technique requires less than 1 ml of oil, a small amount of acetone and ethanol solution, and less than 2 minutes for analysis, and can be performed in vials using inexpensive, portable instruments. TAN and antioxidant levels can also be measured by this technique as well.

2.4.4 Moisture Content

Water is detrimental to the physical and chemical properties of a lubricant. Water generally enters a lubricant through leaks from the cooling system, via condensation or as a combustion byproduct. Water is only slightly soluble in mineral oil (50-80 ppm), increasing to a few hundred ppm in formulated oils (Herguth Laboratory Inc., 1995) depending on the additives present. Water is an undesirable contaminant because it catalyzes oil oxidation and acid formation and reacts with or precipitates additives. If water reacts with ferrous parts, rust and hydrated iron oxide will form, creating solid debris in the oil and pitting metal surfaces. However, in specific instances, maintaining or controlling water content in oil can be equally important. For example, some hydraulic fluids require high levels of water in order to provide acceptable pumping and fire resistance properties, in contrast to transformer oils where moisture must be carefully restricted to trace levels to ensure insulation.

Testing moisture in lubricants involves various physical and chemical methods ranging from simple visual observation and the hot plate "crackle" test for qualitative determination, to sophisticated methods such as Karl Fischer volumetric or coulometric titrations (ASTM D1744, D4928, 1990). The simplest means of moisture determination is by distilling off the water in a lubricant according to ASTM D95 (1990), however, it is time consuming and can only adequately measure concentrations above 1000ppm (Lukas and Anderson, 1998). Karl Fischer (KF) based titrations (ASTM D1744, 1990) are able to analyze much lower moisture contents (50-1000 ppm) and these methods are widely used in well equipped laboratories (Scholz, 1984). The Karl Fischer method is based on a series of stoichiometric reactions involving moisture:

$$CH_{3}OH + SO_{2} + RN \longrightarrow [RNH]SO_{3}CH_{3}$$

$$H_{2}O + I_{2} + [RNH]SO_{3}CH_{3} + 2RN^{1} \longrightarrow [RNH]SO_{4}CH_{3} + 2[RNH]I$$

$$^{1}RN = \text{base like pyridine, imidazole, etc.}$$

$$[7]$$

Various automated titrators based on either volumetric or coulometric measurements are commercially available, facilitating the routine determination of moisture in oils. Volumetric methods are based on determining water content by reacting the oil sample volumetrically with KF reagent to an electrometric end point. Coulometric methods employ a potentiometric end point, determining the complete reaction of water with KF reagent (I_2) electrolytically generated (Hydranal Manual, 1992; Skoog, et al., 1988). The principal advantages of coulometric titrations are lower detection limits (< 10ppm) and the minimization of problems associated with preparation, standardization, and storage of standard solutions (Lukas and Anderson, 1998).

According to the literature, the determination of moisture in base oils without additives is straightforward by KF methods (Hydranal Manual, 1992); however, measuring moisture in lubricants containing additives using either volumetric or coulometric KF autotitrators can be problematic. Table 2.3 presents KF results obtained

	S 1	S2	S 3	S4	S5	S6	S7	Average
Lab A	Trace	0	0	0	0	0	0	0
Lab B	397	203	321	195	106	77	71	196
Lab C	1020	2190	1300	1990	250	280	153	1026
Lab D	143	218	182	193	166	76	130	144
Lab E	1100	2056	921	1525	142	135	44	705
Lab F	800	1200	1001	1300	600	600	400	843
Average	692	987	622	867	211	167	115	NA

Table 2.3 Karl Fischer moisture analytical results obtained for 42 identical oil samples analyzed by six commercial laboratories

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by General Motors for the moisture content for 42 identical oil samples sent to six different commercial laboratories on seven separate occasions (Dong, et al., 2000). The lack of any correspondence between laboratories is indicative of the limitations of the KF method as applied to lubricant analysis. This lack of correspondence may be due to the oxidation of reductive components in oil by iodine (Hydranal Manual, 1992) or the presence of active carbonyl compounds, which can interfere with KF measurement because they continuously react with methanol to form water, causing a vanishing end point and erroneously high water contents (Cedergren and Oradd, 1994). An optional tubular drying oven used to drive the moisture out of a lubricant directly into a KF coulometric cell is recommended to avoid such additive or oxidative product interferences; however, these systems have not been proven to be reliable. In summary, KF determination of moisture in lubricating oils, particularly motor oils, does not appear to be practically reliable (Hydranal Manual, 1992) especially when undefined additives are present, which is generally the case.

Aside from standard ASTM methods, there are few alternate methods available for the analysis of moisture in lubricants. Water has strong characteristic absorptions in the mid-infrared (mid-IR) and is easy to detect in additive free mineral oils at levels of around 1000 ppm (Anonymous, 1995), a point at which water-related problems commonly begin to occur. However, it is generally difficult to quantify water by direct IR measurement in formulated oils because its characteristic absorption band, centered around 3400 cm⁻¹, is broad and overlaps with the absorptions of other OH-containing constituents such as alcohols, hydroperoxides and glycols. As a complement to mid IR, near infrared (NIR) spectroscopy coupled with sophisticated multivariate approaches has been used for moisture measurement in lubricating oils with high additive contents (Blanco, et al., 1998). New methods based on liquid chromatography (LC) and gas chromatography (GC) have been developed for moisture determination in various sample matrixes other than lubricating oils (Chen and Fritz, 1989, 1991; Zhou, et al., 1998); however, their application to lubricating oils has not been assessed.

2.4.5 Fuel Dilution

Fuel dilution of lubricants is commonly associated with gasoline or diesel contamination of the lubricant, both of which consist of a wide variety of volatile straight chain and branched aliphatic compounds and aromatic compounds. Fuel in a lubricant at levels > 2% can significantly reduce its viscosity and lubricating efficiency. In addition, high levels of fuel contamination can pose a fire hazard, of particular concern in the shipping industry and naval forces where shipboard testing is desirable (Akochi-Koblé, 1998). Traditional tests usually rely on the measurement of lubricant viscosity (ASTM D445, 1990), determination of flashpoint (ASTM D92, D93, 1990), distillation (ASTM D322, 1990), and/or gas chromatography (ASTM D3524, D3525, 1990). Measuring viscosity and flashpoint can provide rapid detection of fuel dilution problems but the reliability is questionable as non-fuel related factors may interfere. ASTM GC methods using direct injection of a mixture of the oil and internal standards are widely accepted as the most reliable approaches for determining fuel dilution. Although reasonably sensitive $(\pm 0.2-0.3\% \text{ v/v})$, the GC methods are time consuming, prone to interferences from nonfuel, low boiling point components in base oils, and do not provide on-site information. Using GC-mass spectrometry (MS) is more reliable and sensitive (Hiltz and Haggett, 1991), but requires even more sophisticated instrumentation and operator skills. Infrared spectroscopy has been evaluated for fuel dilution analysis and was shown to be effective in terms of reliability, speed of analysis, and amenability to automation (Stuart, et al., 1989; Akochi-Koblé, et al., 1998). More recently, a solid state microsensor based technique for the measurement of fuel dilution has been described (Jarvis, et al., 1994). In general, due to the limitations of the analytical methods available for fuel dilution analysis, a single test is usually considered inadequate to make a reliable determination (Anonymous, 1995).

2.4.6 Insolubles

Aside from metallic hard particles such as shop debris, sand and other wear fragments, the term "oil insolubles" generally applies to contaminants such as thermaloxidative polymerization products, carbonaceous material (soot), micro-organisms, oil/additive/water reaction products, and fragments of elastomers (Herguth Laboratories, 1995). Since these contaminants form part of the sludge that accumulates over time and may plug pipes, orifices and strain pumps, measurement of insolubles is important. In combustion engines, abnormally high levels of insolubles may be due to excessive ring wear or high fuel-to-air ratios or be indicative that the dispersant is no longer performing its intended function (Smolenski and Schwartz, 1994). ASTM D893 (1990) provides a standard method for the determination of pentane and toluene insolubles in used lubricating oils, the pentane insolubles being indicative of total insoluble matter, including combustion soot, dust, and wear particles as well as oil and fuel oxidation products; while the toluene insolubles are considered to represent the inorganic components (Najjar, 1987; Smolenski and Schwartz, 1994).

Membrane filtration and thermogravimetric analysis (TGA) are also used to measure insolubles in used oils (Anonymous, 1995; Lukas and Anderson, 1998). The filtration method requires predilution of the oil with pentane or heptane before filtration and the insolubles are calculated from the weight change in the membrane after filtration and drying. Membranes can be selected according to the pore size to limit the size of the insolubles measured. However, the method is labor intensive and uses highly flammable solvents. The TGA method, which can be automated, incrementally heats a pre-weighed oil sample in a stream of nitrogen to 650°C. After the sample weight has stabilized, it is recorded and subsequently 10% of air into the stream of nitrogen is introduced to oxidize carbon and soot. The air content is gradually increased to 100% and when the sample weight has re-stabilized, the inorganic residual being determined. The primary advantage of TGA is its ability to differentiate combustion formed carbon/soot formed by combustion from non-combustion insolubles in an used oil. Although useful, this technique is rarely employed in routine oil condition monitoring programs because it may take as long as one hour to analyze a sample (Lukas and Anderson, 1998).

2.4.7 Ethylene Glycol

Of all the contaminants that may be present in a lubrication fluid, contamination

of coolant fluids (usually ethylene glycol) represents the greatest hazard to the equipment durability as is can cause rapid sludging and aging of oils (Smolenski and Schwartz, 1994). The presence of glycol can be detected by either colorimetric (ASTM D2982, 1990) or GC determination using a flame ionization detector (ASTM D4291, 1990). In the first method, ethylene glycol is extracted from the oil sample with an acid solution and oxidized to formaldehyde with periodic acid; the formaldehyde is subsequently detected colorimetrically with decolorized fuchsin. The reaction of fuchsin is not specific to the formaldehyde produced from ethylene glycol. Other 1,2-glycols, some oil additives and oxidation products such as aldehydes can interfere with the test, leading to false positives (ASTM D2982, 1990; Smolenski and Schwartz, 1994). The standard GC method is based on extraction of ethylene glycol with water and the analysis is performed directly on the water extracts. More recently, a capillary GC method for indirect analysis of ethylene glycol in diesel engine oils was developed based on derivatization of glycol with a silvlating reagent to produce a trimethylsilyl derivative prior to injection into the non polar GC column (Hiltz, et al., 1992). Newer combined capillary GC/MS systems can accurately determine 10-10,000 ppm of ethylene glycol.

2.4.8 Summary

A good lubricant condition monitoring program usually requires a full spectrum of lubricant analyses, including measurements described above as well as information about wear metals. Thus, a general lubricant laboratory would need an AE spectrometer, viscometers, a FTIR spectrometer, a particle counter, TAN, TBN, and KF titrators, and a ferrograph to provide effective service. The first three items would be considered the minimum, the balance of the equipment required depending on the type of machines being monitored and the types of oil being analyzed (Lukas and Anderson, 1998). As indicated early on in this review, IR spectroscopy has become increasingly important as an analytical tool for lubricants because it is able to provide information about most organics and moisture in oils via the functional group absorptions associated with those constituents. Owing to its ability to deliver rapid, multifunctional qualitative, and potentially, quantitative information, FTIR spectroscopy is being used as a monitoring tool for the evaluation of additives, fluid breakdown products and external contaminants (Blanco, et al, 1998; Powell and Compton, 1993). Since the development of FTIR based methodology is the focus of this study, the following sections will review the basic principles of infrared spectroscopy, instrumentation, sample handling, and chemometrics and the current state of FTIR spectroscopy relevant to lubricant condition monitoring.

2.5 INFRARED SPECTROSCOPY

2.5.1 Introduction

Development of IR spectroscopy began in the early 1900's, but, it was not until the 1930's that prototype infrared instruments were built for industrial laboratories and the theoretical study of spectral information gathered momentum. Commercial instruments based on single-beam designs became available in 1944 and the first doublebeamed infrared spectrophotometer was introduced in 1947. By the 1960's, IR spectroscopy had become the single most powerful analytical tool for exploring the molecular structure of organic materials (Griffiths and de Haseth, 1986). Infrared spectroscopy has evolved extensively in the form of near-IR and mid-IR, the latter being the focus in this work. Until recently, dispersive instruments using gratings and prisms have been the norm, but, these instruments have now been superseded by Fourier transform infrared (FTIR) spectrometers that became available to researchers in the early 1970s (Griffiths and de Haseth, 1986).

FTIR spectroscopy utilizes the complete source spectrum modulated by an interferometer rather than individual wavelengths generated by a grating, and this brings advantages of speed, improved reliability, low operating costs, and better performance attributes, making FTIR spectrometers a significant advance over dispersive type instruments (van de Voort, 1994). In addition to instrumentation, sample handling techniques and accessories have significantly advanced over the past decades to accommodate new applications in a wide variety of areas, including food analysis, polymer and materials science, kinetics, biological and pharmaceutical studies, gas analysis, and electrochemical area, to name but a few (Putzig et al, 1994).

2.5.2 Basics of IR Spectroscopy

Infrared radiation covers a part of the electromagnetic spectrum lying between the visible and microwave regions having wavenumbers ranging from about 12800 to 10 cm^{-1} or (0.78 to $1000\mu\text{m}$). Of greatest practical use in the study of molecular structure is the mid-infrared region extending from 4000 to 400cm^{-1} . The near-IR region (12800-4000 cm⁻¹) is also important, especially for quantitative analysis, with the far-IR region (400-200 cm⁻¹) finding the fewest applications (Silverstein, et al., 1991). Owing to its ability to provide a wealth of information about the structure of a wide range of organic compounds, mid-infrared spectroscopy became a preeminent technique for the identification and verification of chemical constituents (Martin, 1966).

When an organic molecule absorbs mid-infrared radiation, the absorbed radiation is converted into discrete forms of vibrational energy. The frequency (or wavelength) or band position of the absorption is dependent on the relative masses of the atoms, the force constants of the bonds and the geometry of the atoms. Band intensities can be expressed either as transmittance (T) or absorbance (A) and are proportional to the concentration of the molecule (Silverstein, et al., 1991). Bond stretching and bending are two basic types of molecular vibration and only those vibrations resulting in a change in the dipole moment of the molecule are observed in the IR spectrum. The changing electric field produced by the alternating charge distribution accompanying a vibration couples the molecular vibration with the oscillating electric field of the electromagnetic radiation. In addition to the basic vibrations noted above, other absorptions can be observed resulting from overtones and combinations of the fundamental frequencies, which in turn, may complicate band interpretation (Silverstein, et al., 1991).

Identification of organic compounds by IR spectroscopy is based on characteristic absorptions associated with functional groups in the molecule. Although functional groups or structural units have characteristic-vibrations, the precise frequency of functional group absorptions can be influenced by a variety of factors including coupling with the vibrations, hydrogen bonding, electronic effects, bond angles and field effects (Kemp, 1991).

2.5.3 IR Instrumentation

There are two basic types of mid-IR spectrophotometers available, traditional dispersive and newer interferometer based instruments, the latter requiring a Fourier transform (FT) algorithm to convert an interferogram into a conventional transmission/absorption spectrum (Kemp, 1991). A FTIR spectrometer possesses all the characteristics of a conventional IR spectrometer, but has improved speed and sensitivity and unparalleled wavelength precision and accuracy. These factors, as well as decreases in capital and operating costs of these instruments, led to FTIR instruments rapidly displacing dispersive instruments in most laboratories (Borman, 1983).

The core of an FTIR spectrometer is the Michelson interferometer (Figure 2.4), conceived and designed by Michelson in 1891 (Michelson, 1961). The device consists of a moving mirror and a stationary mirror perpendicular to each other, with a beam splitter positioned at 45° between them. The beam splitter can divide a beam of source radiation into two paths, one being transmitted to the stationary mirror and the other being reflected to the moving mirror. When two paths of the beam are reflected back to the beam splitter, they recombine with a path difference known as the retardation (δ) introduced by the moving mirror, producing a constructive/destructive interference pattern as shown in Figure 2.5. If the moving mirror travels at constant velocity, part of the recombined beam that passes to the detector will be observed to vary sinusoidally for any one wavenumber. Thus, the intensity (I) of the beam recorded at the detector is a function of retardation, δ , which is proportional to time *t* because the moving mirror travels at constant velocity *v*. When an infrared beam passes through a sample placed between the beam splitter and the detector (Figure 2.4), fluctuations in the intensity of the energy sensed by the detector at



Figure 2.4 Schematic diagram of a Michelson interferometer.



Figure 2.5 Schematic diagram of the phase of the electromagnetic waves from the fixed mirror (solid line) and movable mirror (broken line) at different values of the optical retardation. (a) Constructive interference at zero path difference; (b) deconstructive interference at a path difference of one-half wavelength; (c) constructive interference at a path difference of one wavelength.

all wavelengths are digitized in real time, $I(\delta)$, to yield an interferogram (Figure 2.6). The interferogram contains all the information related to the absorption of mid-IR wavelengths by the sample but is difficult to interpret. It can however be transformed from the interferogram time domain to the frequency domain so as to produce a conventional IR spectrum via a Fourier transform by using the following relationship:

$$I(\delta) = 0.5 H(\nu) I(\nu) \cos 2\pi \nu \delta$$
[9]

where $H(\bar{\nu})$ is a single wavenumber-dependent coefficient, $I(\bar{\nu})$ is the intensity of the source and $\bar{\nu}$ is the wavenumber of the radiation. The $I(\bar{\nu})$ represents a single-beam interferogram which consists of the emittance profile of the IR source superimposed with the absorption activities of the sample as well as the background absorptions such as absorptions of carbon dioxide and water vapor present in the optical path. In order to obtain an absorption spectrum of the sample $[A(\bar{\nu})]$, the single-beam spectrum of the sample is digitally ratioed against a single-beam spectrum recorded with no sample placed in the beam $[I_0(\bar{\nu})]$ by taking the negative logarithm of the single-beam values:

$$A(v) = -\log[I(v)/I_0(v)]$$
[10]

With the development of the Cooley-Tukey fast Fourier transform (FFT) algorithm in 1964 and widening availability of microcomputers and personal computers, rapid FTIR scanning and computation became practical. Since their introduction, FTIR spectrometers have undergone significant improvement and today have almost completely replaced traditional dispersive instruments (Sedman, 2000).

Owing to the unique design of the interferometer, FTIR instruments have three major advantages over the traditional dispersive designs. The interferometer allows all



Figure 2.6 A typical interferogram recorded by an FTIR spectrometer.

frequencies from the source to reach the detector simultaneously (Fellgett advantage or multiplexing advantage), making it possible to obtain an entire spectrum within 1s or less. FTIR instruments have fewer optical elements and no slits to attenuate radiation, thus they have higher energy throughput (the Jacquinot advantage) that leads to better signalto-noise ratios. Through the use of an internal reference laser, wavelength position of the interferometer is tracked with very high precision and wavelength drifts over time are almost totally eliminated (the Connes advantage).

2.5.4 FTIR Sample Handling

The variability in the nature of a sample's physical/chemical makeup makes sample handling an important part of any FTIR analysis. The selection of appropriate sample handling techniques is a critical issue so as to obtain maximum convenience as well as quality results. The superior optical throughput and signal-to-noise characteristics of modern FTIR spectrometers, together with the good linearity of the commonly employed deuterated triglycine sulfate (DTGS) detector brings increased versatility to selecting sample handling accessories for these instruments. Two sample handling accessories commonly employed for various applications, including lubricant analysis are: transmission cells and attenuated total reflectance (ATR) accessories (Coleman, 1993; Skoog and Leary, 1992; Muller, et al., 1981). In relation to this work, where a customized flow through transmission cell was developed and used, the merits of this accessory are briefly discussed.

2.5.4.1 Transmission cell

Transmission measurements can be made by placing the sample between two infrared transmitting windows separated at a fixed pathlength; the IR beam is passed through the sample, the IR radiation transmitted is measured by the detector. Figure 2.7 (Stuart, B., 1996) illustrates the basic components of a standard demountable FTIR transmission cell commonly used for oil analysis. This design provides substantial flexibility in terms of selection of window materials and allows pathlength variability by



Figure 2.7 A schematic example of a transmission IR cell.

varying the thickness of the spacer. Depending on the sample characteristics and/or wavelength range to be covered, a variety of window materials are available. Table 2.4 summarizes some of the characteristic properties of common infrared window materials available.

Although standard IR cells are useful, they are not necessarily convenient for multi-sample analyses. Flow versions of standard cells are also available, but these are often sealed and invariant. To overcome these limitations, the McGill IR Group developed a specialized IR transmission cell accessory more suited to routine analysis of fats and oils in an industrial setting (Sedman et al., 1997), incorporating the ability to control temperature which is especially beneficial for fats that are semi-solid at room temperature. Figure 2.8 shows a schematic diagram of the transmission sample handling accessory developed. The accessory has sample inlet and outlet lines, a cell block with two heater cartridges and capable of accepting a removable cell insert, all components made of stainless steel. A controller powers the heater cartridges and the thermocouple regulates the temperature via a feedback loop in relation to the desired temperature set on the controller, allowing temperature regulation to within +0.2°C. The cell insert can be easily removed for collecting an open-beam spectrum, and has a spring-loaded faceplate to allow the cell to be dismantled so that the cell windows can be replaced whenever necessary. A three-way valve on the inlet line allows the oil flow through either the cell or a bypass line, to the outlet line emptying into a waste collecting vessel, which in turn is connected to a vacuum line or pump. The purpose of the bypass line is to facilitate line cleanout between samples to be analyzed so that large volumes of often viscous liquid are not all forced through the relatively narrow cell and also to reduce window wear. This accessory has proven to be reliable and practical for the routine analysis of edible fats and oils (Sedman, et al., 1998; Ma, et al., 1997; Dubois, et al., 1996) and was considered suitable for lubricating oils as they have similar physical characteristics as their edible oil counterparts.

Table 2.4 Physical properties of selected infrared window materials

Window material	Transmission range (cm ⁻¹)	Remarks
Sodium Chloride (NaCl)	40,000-625	Hygroscopic, easy to polish
Potassium Chloride (KCl)	40,000-500	Hygroscopic, inexpensive
Potassium Bromide (KBr)	40,000-400	Hygroscopic, inexpensive
Calcium Fluoride (CaF ₂)	66,666-1,100	Water insoluble, do not use with ammonium salts
Barium Fluoride(BaF ₂)	50,000-870	Slightly hygroscopic
Infrared quartz (SiO ₂)	50,000-2,500	Water insoluble
Cesium Bromide (CsBr)	20,000-250	Hygroscopic, fogs easily, easily deformed
Cesium Iodide (CsI)	10,000-200	Hygroscopic
ThalliumBromide-Iodide(DRS-5)	15,385-250	Water insoluble
Silver Chloride (AgCl)	25,000-435	Water insoluble, darkens with UV
Silver Bromide (AgBr)	20,000-285	Water insoluble, darkens with UV
Irtran-2 (ZnS)	10,000-715	Water insoluble, attacked by oxidizing agent
Zinc Selenide (ZnSe)	10,000-555	Water insoluble
Germanium (Ge)	5,000-850	Water Insoluble

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Figure 2.8 Schematic of the heated oil analysis sample handling accessory.

2.6 CHEMOMETRICS

Many instrumental methods, including IR spectroscopy are secondary methods that require calibration of the instrument against a primary method to establish a relationship between the instrumental response and the concentration of the species of interest. The goal of IR quantitative analysis is to develop a calibration equation or a series of equations that can be applied to spectra of unknown samples to accurately predict the concentration of the component(s) of interest. The central premise is that the concentration is related to the spectral data acquired, the simplest univariate form being Beer's law, with more sophisticated multivariate analysis such as classical least-squares (CLS), inverse least-squares (ILS), principal component regression (PCR), and partial least squares (PLS) also being employed. The major advantage of multivariate methods is that they provide mathematical relations that can account for interactions, underlying absorptions, overlapping bands and other factors which may affect the spectra as the concentrations of all components change. In all these calibration approaches, the term least squares regression represents a mathematical technique that calculates coefficients for a calibration equation(s) such that the differences between the known responses and the predicted responses are minimized. Among various multivariate methods, PLS is the most versatile and combines the advantages of CLS and ILS and also improves on PCR, making it the most powerful statistical tool available for quantitative analysis (Haaland and Thomas, 1988).

2.6.1 Beer's Law

Beer's law, an abbreviation of the Bouguer-Beer-Lambert law, serves as the foundation of quantitative spectroscopy and states that the absorbance of a species is proportional to its concentration:

$$A_1 = \varepsilon_1 bc \tag{[11]}$$

Here, A is the spectral absorbance at wavelength λ , ε is the molar absorption coefficient of the absorbing species at this wavelength, b is the pathlength through the sample

containing the species, and c is the concentration of the absorbing species. To apply Beer's law to determine the concentration of the species present in a sample, ε should be determined by measuring the absorbance of a set of calibration standards prepared with known concentration of the compound in question. A calibration plot (or equation) is then produced in which the relationship between absorbance and concentration is established, which is generally linear when interferences such as hydrogen bonding, dimerization, and other intermolecular interactions are minimal.

Calibration based on Beer's law is straightforward and adequate in a simple, single component system dissolved in a non-interacting solvent with negligible spectral interferences. However, such ideal situations are not generally the case in many sample matrixes, particularly in lubricating oils, where various base oils and additive packages may be present, interfering and interacting with each other. To account for such complications, one has to use more sophisticated multivariate calibration techniques.

2.6.2 Classical Least Squares (CLS) -K Matrix

The CLS, also known as K matrix approach, is based on the expression of Beer's law but extended to matrix form to account for the spectral contributions of all absorbing species at a specific wavelength. For example, the two component equations could be

$$\mathbf{A}_{\lambda 1} = \mathbf{K}_{\mathbf{a}\nu\lambda 1} \mathbf{C}_{\mathbf{a}} + \mathbf{K}_{\mathbf{b}\nu\lambda 1} \mathbf{C}_{\mathbf{b}} + \mathbf{E}_{\lambda 1}$$
[12]

$$A_{\lambda 2} = K_{b,\lambda 2} C_{b} + K_{b,\lambda 2} C_{b} + E_{\lambda 2}$$
[13]

In matrix terms, these types of equations can be formulated as:

$$A_{(n,m)} = K_{(n,l)} C_{(l,m)} + E_{(n,m)}$$
[14]

where m is the number of calibration or *training spectra*, n is the number of wavelengths used, l is the number components, and E is the matrix of *residual errors*, being the differences between the least squares fit line and the actual absorbances. Using matrix

algebra, a computer can solve the equations and produce the K matrix of absorption coefficients. The solution gives the best fit least squares line(s) to the data and the equations can then be used to predict the concentrations of unknown samples. CLS can provide significant improvements in precision over methods restricted to a small number of frequencies and allows simultaneous fitting of spectral baselines (Haaland and Easterling, 1980). A major disadvantage of this method is that an equation is required for every component in the mixture and knowledge of all components in a sample is essential for accurate CLS quantitative spectral analysis (Ismail, et al., 1997).

2.6.3 Inverse Least Squares (ILS) - P Matrix

The ILS, also known as P matrix approach, utilizes the inverse of Beer's law and assumes that concentration is a function of absorbance. Thus the matrix expression of the inverse Beer's law model for m calibration standards with spectra of n digitized absorbance values is given by:

$$C_{(l,m)} = P_{(n,l)} A_{(n,m)} + E_{(n,m)}$$
[15]

where A and C are absorbance and concentration, P is the $n \times l$ matrix of the unknown calibration coefficients relating the l component concentrations to the spectral intensities, and E is the error in the concentrations predicted by the least squares fit line. The inverse representation of Beer's law has the significant advantage that even if the concentrations of all the other components in the mixture are not known, the matrix of coefficients (P) can still be correctly calculated. However, it also means that each component requires measurements at different wavelengths and the selected wavelengths must be in a region where the components more or less contribute to the overall spectrum. ILS tends to be a more practical alternative since information about component concentrations in a system is often lacking. One major disadvantage of the ILS method is the dimensional limitation of the matrix equations, restricting it to a small number of frequencies since if the number of frequencies becomes too large, co-linearity and over-fitting problems may become significant and the results can actually become worse (Anonymous, 1998). Therefore, the

full-spectrum advantages gained with the CLS approach are diminished, and this can hinder the application of the ILS method.

2.6.4 Partial Least Squares (PLS)

PLS is a spectral decomposition technique that does not attempt to establish direct relationships between concentration and absorbance at specified wavelengths like CLS and ILS. PLS compresses the raw spectral data obtained for the calibration standards (training set) into a set of orthonormal basis vectors, known as the *loading spectra*, *loading vectors*, *principal components*, or *factors*, which represent the changes in the absorbances at all the wavelengths in the spectra and are then used as the basis for developing a calibration model. To predict unknown samples, the loading spectra are used to reconstruct the spectrum of the unknown. Each of the loading spectra is multiplied by constants derived from regression of the loading vectors against the concentration data for the calibration standards and adding the results together until the new spectrum approximates that of the unknown sample. The constants are known as *scores* that serve as a bridge between spectral absorbance and concentration. Since the same loading spectra produced during calibration development are always used to model the unknowns, the differences between unknowns with different component concentrations are reflected only by differences in the scores.

General steps for the development of a PLS calibration involves: (i) compressing the calibration spectra into a series of mathematical "spectra" (*loading spectra*), (ii) decomposing the spectrum of each calibration standard into a weighted sum of the loading spectra, the spectra containing higher component concentrations usually weighted more than those of low concentrations; and (iii) regressing the weights (*scores*) against the concentration data for the standards. The prediction step reconstructs the spectrum of an unknown from the loading spectra and *scores* and uses the *scores* to predict the concentration of the unknown. Selection of the appropriate number of loading spectra (or factors) is pivotal in producing a robust PLS model and models with too few factors underfit, while those with too many factors overfit and model noise rather than concentration changes. The challenge is to determine the optimum number of loading spectra and to do this validation of PLS calibration models is always necessary, preferably using known standards not included in the calibration set. An alternative means of validation is to carry out a "leave-one-out" cross-validation whereby the calibration is devised n times with n-1 standards in place, and the nth standard is predicted as an unknown.

Repeating this process to obtain n predictions, the Predicted Residual Error Sum of Squares (PRESS) is then computed from the errors of these predictions and plotted as a function of the number of factors included in the calibration model (Figure 2.9) and the appropriate number of factors selected based on the F-test (Haaland and Thomas, 1988). The PRESS values of all smaller factors are compared to that of the minimum PRESS, known as F-ratio, and the number of factors where the F-ratio falls below a predefined significant level is used to determine the optimum number of factors to be included in the PLS model.

PLS possesses many of the full-spectrum advantages of the CLS method and, at the same time, retains the ILS advantage of being able to perform the analysis for one chemical component at a time while avoiding the ILS frequency selection problem. PLS is considered a very powerful tool for the analysis of complex systems, where many potential sources of interference/interaction may be encountered. However, experience with this technique is necessary to understand its benefits and limitations. The PLS method has been successfully applied to quantitative analyses by a variety of techniques including ultraviolet spectrophotometry (Otto and Wegscheider, 1985), near-infrared spectroscopy (Neimanis, et al., 1999; Dong, et al., 1997), chromatography (Montana et al., 2000; Dunn, et al., 1984), and electrochemistry (Donachie, et al., 1999; Otto and Thomas, 1985). This approach has proven to be highly effective and in fact necessary to extract quantitative information from complex spectra such as those obtained from nearinfrared and UV measurements (Lindberg, et al., 1983). With the commercial availability



Figure 2.9 Typical PRESS plot obtained from cross-validation of a PLS calibration.

of PLS software for IR analysis from several FTIR instrument manufacturers and software companies, PLS has become easier to implement and numerous successful applications of this calibration approach have been reported for various mid-FTIR methods (Sedman, et al., 2000; Man and Mirghani, 2000; Ma, et al., 1998; van de Voort, et al, 1994; 1995).

2.7 FTIR LUBRICANT CONDITION MONITORING

Although IR spectroscopic methods for assessing lubricant performance have been available for over 20 years (Anonymous, 1995), acceptance of these techniques as standard methods for lubricant analysis has been rather slow. This is largely due to inertia related to familiarity with the traditional physical and wet chemical procedures as well as the unfamiliarity of FTIR spectroscopy. In the early 1990's, the Joint Oil Analysis Program (JOAP) of the U.S. Department of Defense undertook evaluation of FTIR spectroscopy as a means of determining lubricant condition and contamination. This program began to provide supporting evidence that FTIR analysis had the potential to increase the amount and quality of information normally provided by traditional wet chemical methods routinely practiced for various lubricants (Toms, 1994). As a result, the U.S. Army has adopted FTIR spectroscopy as a general technology to meet advanced lubricant test requirements and has implemented FTIR condition monitoring systems at 12 Army laboratories worldwide (Toms, et al., 1998).

FTIR spectroscopy has been successfully applied to the general analysis of mineral based (Garry, 1992; Powell and Compton, 1993) and synthetic based lubricants (Toms, 1994). It is able to provide information on the relative changes in levels of contaminants such as water, fuel, and ethylene glycol and provide qualitative measures of soot and nitrogen-, oxygen- and sulfur-containing by-products. However, the capability to obtain quantitative information by FTIR spectroscopy can be quite limited, in particular when the base oil and additive package are not defined or referenced, as the spectral contributions of unknown or undefined additives can be problematic in interpreting the spectral data. This is further complicated by the fact that most of the contaminants and
degradation products that are important in condition monitoring develop slowly, in relatively small quantities, and may spectroscopically interfere with each other.

There appear to be two schools of thought in relation to FTIR analysis of lubricants, one suggesting that all analyses be carried out in relation to a sample of the unused oil and the other assuming that an unused reference oil will not necessarily be available. Having a reference oil available is clearly the better option, as one would have a means of determining changes by subtracting the spectrum of the used oil from that of the unused oil and in this circumstance, measurement of both qualitative and quantitative changes are facilitated. In practice, however, given the many suppliers, formulations and formulation changes and substitutions, the availability of suitable reference oil cannot be guaranteed. In addition, suppliers are requested to meet performance specifications rather than formulation specifications; hence, many oils with varying formulations can meet specifications but may be quite different spectroscopically. Oil formulations/additive packages are often changed without notice, but the brand name stays the same. As a result of these realities, both schools of thought have merit, the first in a situation where a few defined oils are used consistently in all equipment; the second in a general oil analysis laboratory receiving many samples of unknown origin for which they may not have a reference oil. Without a reference oil, condition monitoring requires that base parameters of oil degradation be established and that subsequent oils be compared to the general trend to determine whether anything unusual is occurring. With a reference oil, FTIR spectroscopy could be semi-quantitative or quantitative and provide a clearer picture of changes in oil condition.

The JOAP protocol has adopted the "no reference oil" approach as standard procedure, developing a data base of spectral changes over time in relation to specific constituents to determine significant condition changes. Current FTIR applications in the JOAP protocol for the condition monitoring of used lubricants address specific lubricant types, including regular mineral based lubricants (typically engine oils), extreme pressure (EP) fluids (typically mineral based gear or hydraulic fluids) and synthetic polyol ester based lubricants (typically aero related gas turbines oils) (Anonymous 1999). Depending on oil type and the constituents analyzed for, warning levels may vary. Hence to a large degree the JOAP approach is empirical, but it is still a major improvement over simple scheduled oil changes and analysis by wet chemical methods. The subsequent section focuses on the principles of analysis of basic constituents by FTIR spectroscopy for condition monitoring, emphasizing the JOAP protocol.

2.7.1 Water

Although water is a very strong infrared absorber, confident detection can only be made at levels above 0.1% (Anonymous, 1995). Water contamination is readily monitored in mineral based lubricants by measuring the O-H stretching absorption in the 3500-3100 cm⁻¹ region, characterized by broad bands due to hydrogen-bonding (Figure 2.10). Because of band broadening, measurement is usually based on integrated area relative to baseline set at the minima over the range of 4000 to 3680 cm⁻¹. When soot levels in oils are greater than 3%, significant interference with water measurements may occur.

In gear oils and hydraulic fluids that contain EP additives, the infrared response changes and the manner in which water is measured requires adjustment. Figure 2.11 illustrates the typical absorption of water in EP fluids, which is characterized by a general, horizontal baseline offset of the entire infrared spectrum. A non-baseline integrated area from 3400 to 3250 cm⁻¹ is used for water measurement; however, at very high water levels (greater than 2%), a similar hydrogen-bonded OH stretch band as seen in the mineral crankcase oils is observed (Figure 2.10). Soot, dirt and high concentration of infrared scattering particulates will cause a proportionate baseline offset, causing the amount of water present to be overestimated. This measure is workable because typical gearboxes and hydraulic systems do not usually accumulate or contain significant levels of particulates so as to cause significant baseline offsets and tilts.



Figure 2.10 Characteristic water band in mineral based oils (Anonymous, 1999).



Figure 2.11 Water in mineral based EP fluids (Anonymous, 1999).

Figure 2.12 shows water contamination in a synthetic polyol ester based oil, illustrating two bands (3640 and 3550 cm⁻¹) responding to incremental increases in water content, however, only the 3700 to 3595 cm⁻¹ is used for water measurement, the other being used for determination of base stock degradation (Toms and Powell, 1997). Hydroxyl containing degradation products such as hydroperoxides and alcohols, which also absorb in this region, further complicate the situation, while high soot levels (>10% w/w solids) can cause baseline curvature, disrupting quantitation.

In addition to the interferences from soot, water measurement is generally complicated by the presence of additives having polar character, thereby affecting hydrogen bonding. This can result in dramatic changes in both band shape and position as a function of moisture concentration or the additive, making it nearly impossible to obtain accurate quantitative analyses until the moisture content is fairly high in an oil of stable composition.

2.7.2 Carbonyl Oxidation Products

In mineral based oils such as engine crankcase oil as well as EP lubricants, oxidation products have an absorption centered around 1750-1600 cm⁻¹ due to C=O stretching vibrations (Figure 2.13 and 2.14), the exact frequency and band shape depending on the adjacent atoms and interacting constituents. Common components found in used petroleum lubricants that absorb in this region include aldehydes, ketones, carboxylic acids and salts formed by neutralization of the acids. Increased absorption in this region is indicative of base oil oxidation, specifically the formation of carboxylic acids that are traditionally determined by TAN analysis (Toms and Powell, 1997). Various additives such as detergents, dispersants, and antioxidants may complicate measurements in this region (Anonymous, 1999). Using the region of 1750-1600 cm⁻¹ for direct measurement of oxidation products can be problematic in polyol ester based oils or oils containing esters. High levels of esters cause the absorptions of oxidation products (such as carboxylic acids) to be swamped by the ester signal, making measurement



Figure 2.12 Water contamination in polyol ester lubricants (Toms and Powell, 1997).



Figure 2.13 Oxidation and nitration products in mineral crankcase oils (Anonymous, 1999).



Figure 2.14 Oxidation and sulfation products in mineral based oils (Anonymous, 1999).



Figure 2.15 Oxidative breakdown measurements of polyol ester based oils.

difficult or even impossible. In such cases, detection of carboxylic acids can be made in the region between 3595 and 3500 cm⁻¹ (Figure 2.15), where weakly hydrogen-bonded O-H containing species absorb, however, excessive water contamination can cause offsets that lead to overestimation of the amount of acid present.

2.7.3 Nitration and Sulfation Products

Buildup of nitration and sulfation products may become significant in combustion engine oils. Nitration is particularly significant in gasoline engines with exhaust gas recirculation (EGR) and natural gas engines because of the nature of the combustion process (Anonymous, 1995). In diesel engines, sulfation products are produced as a result of sulfur in the fuel, forming sulfates upon combustion and causing the accumulation of these products in the oil. Both nitration and sulfation of lubricants have a significant impact on the oil service life. The products from nitration can lead to the formation of high molecular weight varnishes, sludges and acids, while sulfation products can produce acidic precipitates that react with the base reserve additives in the oil. Standard methods such as TAN, TBN, and viscosity in part measure nitration and sulfation contributions by changes in levels of acid, the loss of base, and the formation of high molecular weight compounds, respectively. IR spectroscopic tracking of nitration and sulfation uses characteristic bands associated with these compounds as illustrated in Figures 2.13 and 2.14. The broad feature around 1630 cm⁻¹ in Figure 2.13 is assigned to nitrate esters in the oils. Sulfur oxidation products generate a broad absorption near 1150 cm⁻¹ (Figure 2.14), assigned to sulfate compounds as well as overlapping absorption of oxidation products. Although the IR bands for both nitration and sulfation products are relatively specific, quantitation by comparison to pure prepared standards tends to be difficult as there are a large variety of nitration and sulfation compounds that can be produced and gradually build up in the oil. High moisture levels can generate erroneous positive values for nitration, and very high (>5%) glycol contamination may interfere with sulfation measurements. As in the case of carbonyl oxidation measurements, various additives can interfere with the determination of nitration and sulfation products.

2.7.4 Coolant Contamination

Coolant (ethylene glycol) contamination in engine crankcase oils is simple to measure by FTIR spectroscopy as ethylene glycol absorbs strongly in the OH stretching region, much like water. However, as glycol and water co-exist as a coolant mixture, it is difficult to differentiate between the two by using the OH stretch measurement. Alternatively, glycol does have some characteristic bands in the "fingerprint" region and can be detected using the distinctive absorbance pattern of its C-O stretch doublet, located in the region of 1080-1040 cm⁻¹ (Figure 2.16). To avoid spectral interferences associated with other compounds, the ASTM quantitative infrared method (ASTM E168, 1992) recommends the use of very narrow, specific baseline points on either side of the band, allowing detection of glycol contamination above 0.1% (Powell and Compton, 1993). More sensitive measurements can be obtained by removal of the spectral contributions of the base oil, additive packages, and other contaminants based on the exact knowledge of the components present.

2.7.5 Fuel Dilution

Fuel dilution of lubricants is important to monitor for, as any leakage of fuel into the lubricant severely impacts on the lubrication efficiency of the oil. Although both gasoline and diesel fuels both consist of a wide variety of straight chain and branched aliphatic compounds, aromatic compounds, and other substituted compounds, they can be differentiated spectroscopically. In gasoline, ortho-substituted aromatic constituents that absorb at 750 cm⁻¹ can be detected, while para-substituted aromatics absorbing at 810 cm⁻¹ characterize diesel (Sadtler, 1993). By examining the spectrum of a lubricant for either of these specific absorptions, fuel dilution in regular and jet engine oils can be estimated by FTIR spectroscopy.

2.7.6 Soot

FTIR spectroscopy can indirectly detect particulates present in a lubricant that scatter IR radiation as a result of similar or greater size than the wavelengths of the



Figure 2.16 Glycol contamination in crankcase oils.



Figure 2.17 Spectra illustrating increasing soot loadings in diesel crankcase oils evidenced as a baseline offset and spectral tilt.

radiation. In used oil, such particulates are predominantly soot particles and other insolubles. However there is no ability to differentiate these or correlate IR results with other standard physical tests such as pentane/benzene insolubles which are related to particle size distribution differences (Garry, 1992). FTIR soot analysis is based on baseline offset measurements produced by Tyndal scattering (Compton, et al., 1987) made at 2000 cm⁻¹ (Figure 2.17). High levels of water contamination (>5% w/w) will interfere with the measurement of soot.

2.7.7 Summary

Table 2.5 provides a guide to wavenumber regions associated with components, additives and contaminants commonly found in new and used lubricants. Through research and the JOAP initiative, it is becoming clear that FTIR spectroscopy can be a powerful tool for lubricant condition monitoring. It can provide a broad assessment of the condition of a lubricant in relation to the constituents listed in Table 2.5. This information can be gathered in a rapid and cost effective manner on a single instrument with minimal sample handling and preparation. On the other hand, FTIR in its present form is still a crude tool as it is not quantitative. As indicated earlier when discussing the JOAP protocol, only trending is possible and even in that circumstance one has to be aware of, and consider potential interferences from additives and contaminants on the measurements made.

If one accepts the argument that reference oil availability is a problem, then quantitative analysis would appear to be out of reach. If reference oils are available, then trending would be more accurate and quantitative analysis could be possible. Even with reference oil availability, interferences are still an issue; however, sophisticated chemometric techniques such as PLS can greatly assist an FTIR spectroscopist in developing workable, robust calibrations. If one can develop quantitative methods rather than qualitative trending methods for key oil condition constituents, then the IR data could be more readily correlated with mechanical performance, corrosion etc. and would

Table 2.5	Band	assignments	used in FT.	R condition	monitoring	of lubricants
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Component	Region (cm ⁻¹)	Assignments	
Additives:			
Hindered phenol	3650	O-H stretch	
Amine antioxidant	3400; 1625	N-H stretch; N-H bending	
ZDDP/TCP	990; 650	P-O-C stretch; P-S stretch (ZDDP only)	
<u>By-product:</u>			
Carbon oxidation products	1750 – 1600	Carbonyl esters, ketones, carboxylic acid	
	3595-3500	For polyol ester based lubricants	
Nitration products	1630	Nitrate esters (Nitro Ox)	
Sulfation products	1150	Sulfate compounds (Sulf Ox)	
Contaminants:			
Water	3500 - 3100	O-H stretch	
Coolant (glycol)	1080, 1040	C-O stretch doublet	
Diesel fuel	810	C-H bending of aromatic ring	
Gasoline fuel	750	C-H bending of aromatic ring	
Soot	2000	Baseline offset	

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become more interpretable. To date, generalized quantitative FTIR methods have not been established for any condition monitoring parameters. The research results presented in the following chapters address the analysis of lubricants from a fundamental perspective so as to develop principles, practices and methods that work toward developing FTIR spectroscopy as a quantitative methodology for condition monitoring.

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CHAPTER 3

DETERMINATION OF THE CARBOXYLIC ACID CONTRIBUTION TO THE TOTAL ACID NUMBER (TAN) OF LUBRICANTS BY FTIR SPECTROSCOPY

3.1 ABSTRACT

A Fourier transform infrared (FTIR) spectroscopic method was developed to rapidly and quantitatively determine the contribution of carboxylic acids to the Total Acid Number (TAN) of lubricating oils. The method is based on measurement of the carboxylic acids present as a result of oil oxidation and employs differential spectra in order to eliminate interferences from other components present in the oil. The analytical procedure consists of splitting the sample into two 5-g portions, adding 0.38 g of 10% (w/w) KOH/hexanol stock solution to one, in order to convert the carboxvlic acids present in the sample to carboxylate anions, and pure hexanol to the other, and then recording the FTIR spectra of both samples in a 410-µm KCl flow-through transmission cell. Differential spectra are obtained by subtracting the oil/hexanol spectrum from the oil/hexanol/KOH spectrum. A partial-least-squares (PLS) calibration was derived from the differential spectra obtained in this manner from oils spiked with oleic acid, which served as a carboxyl group standard. The PLS calibration derived was found to be accurate to within ± 0.095 mg KOH/g over the analytical range of up to 4 mg KOH/g. The predictive capability of the calibration was assessed using standard addition of an additive-free, oxidized base oil to a composite bus oil sample obtained from the Montreal Transit Authority. The calibration performed well, capable of reproducibly following the changes in the added TAN to within ±0.05 mg KOH/g. Bus oil samples taken over time (~17,000 km) were monitored for TAN value as well as antiwear and soot levels by FTIR spectroscopy. The changes in the TAN values, although relatively minor, could be tracked and were found to be directly related to the soot levels and inversely related to the amount of ZDDP antiwear additive present. It was found that the ASTM standard chemical TAN reference methods (titrimetric or potentiometric) were generally problematic in terms of obtaining reliable results, especially when dark, sooty oils were being analyzed. The FTIR method did not suffer from this problem and was found to be simpler as well as more reproducible in the analysis of used oils. The FTIR method, when programmed and automated using a continuous oil analysis and treatment (COAT[•]) system developed in previous work, provides a simple and accurate means of determining carboxylic acid contributions to TAN values and can be combined with other FTIR methods to provide a comprehensive means of monitoring oil quality.

3.2 INTRODUCTION

Routine monitoring of lubricating oils during equipment operation can serve a variety of functions, including: indicating a lubricant's condition for the scheduling of periodic oil changes, providing an early warning of critical contaminants and breakdown products forming due to improper operation or maintenance, and assisting an operator in identifying component failures or adverse operating conditions. The most common analyses carried out to assess lubricant condition include a large variety of measurements, including viscosity, total base number (TBN), and total acid number (TAN). TAN has been considered to be an important indicator of oil quality, specifically in terms of defining oxidative status (Anonymous, 1995; Hsu, et al., 1983). In the presence of oxygen, which is ubiquitous in most lubricating environments, hydrocarbons making up the base oil can react to form carbonyl-containing products (primary oxidation products), which subsequently undergo further oxidation to produce carboxylic acids (secondary oxidation products), resulting in increased TAN values (Zhitova and Polipanov, 1994). In addition, with time and temperature, the oxidation products formed can polymerize, leading to a marked increase in viscosity. If not controlled, these products can eventually precipitate out of the oil as varnishes and sludges, decreasing the efficiency of lubrication and causing excessive wear.

The American Society for Testing and Materials (ASTM) has potentiometricbased (ASTM D664, 1991) and color-indicator-based (ASTM D663; D974, 1991) methods for the determination of the total acid number of an oil. These methods are based on the titration of the acidic constituents in an oil with base (potassium hydroxide, KOH) to a fixed endpoint, the titer being expressed in terms of acid number (mg KOH/g oil). Although relatively simple to carry out, the ASTM procedures can be problematic, as they are time-consuming and labor-intensive and consume substantial amounts of environmentally unfriendly solvents and reagents which are becoming increasingly difficult to dispose of. In addition, the standard titrimetric method is based on a visual endpoint, which is difficult to determine accurately when dark, sooty oils are being analyzed. Theoretically, this can be overcome by using a potentiometric electrode instead; however, measuring pH or electrode potential in a mixed solvent system tends to make this determination somewhat erratic also. Hence, the standard methods available tend to be less than satisfactory and it would be useful to have a more rapid, accurate, and reliable procedure for determining TAN.

It has been recognized for some time that infrared (IR) spectroscopy is a powerful analytical tool in the edible fats and oils industry (van de Voort, 1994). In our laboratories, we have focused on the development of rapid. Fourier transform infrared (FTIR) spectroscopic quality control methods that are environmentally friendly. These methods require little or no sample preparation and are capable of replacing the traditional wet-chemical-based standard procedures (Ma, et al., 1998; Dong, et al., 1997; Dubois, et al. 1996; van de Voort et al., 1996; 1995; 1992; Ismail, et al., 1993). One FTIR method developed which is somewhat similar to a TAN analysis is the quantitative determination of free fatty acids in edible oils (Ismail, et al., 1993). Although lubricating oils and edible oils differ markedly (hydrocarbons vs. triglycerides), the determination of carboxylic acids is a common analytical issue. In the case of edible oils, the presence of carboxylic acids (free fatty acids) is an indicator of triglyceride lipolysis, while in lubricating oils, it is an indicator of oxidation of the hydrocarbons. Using this previously developed methodology as a foundation, we present the development of a new approach to the determination of TAN using FTIR spectroscopy and illustrate how FTIR spectroscopy can be used to accurately measure the contributions of carboxylic acids to TAN values in less than five minutes per sample.

3.3 MATERIALS AND METHODS

3.3.1 Instrumentation and Spectral Acquisition

FTIR spectra were recorded on a COAT[•] system (Thermal-Lube, Pointe-Claire, Quebéc) equipped with a corner-cube interferometer and a flow-through heated transmission cell (Figure 3.1), assembled with KCl windows spaced 410 μ m apart. The instrument was controlled by an IBM-compatible Pentium 150-MHz PC running under Windows-based COAT[•] software. The flow-through cell as well as the inlet and outlet lines were maintained at 40°C (±0.2°C) to facilitate sample flow should the oil viscosity be high. To minimize water vapor and CO₂ interferences, the system was continuously purged with dry air supplied by a Balston dryer (Balston, Lexington, MA). All spectra were collected by co-adding 128 scans at a resolution of 4 cm⁻¹ and a gain of 1.0 and were ratioed against a 128-scan open-beam background spectrum.

3.3.2 Reagents and Oil Samples

For the FTIR analytical development work, reagent-grade oleic acid, potassium hydroxide, and hexyl alcohol (hexanol) were obtained from Aldrich Chemicals (Milwaukee, WI). A stock solution (10% w/w) of KOH was prepared in hexanol, this alcohol being used as a convenient carrier for dispersing KOH in the lubricants to be analyzed. All the standard reagents required for the TAN evaluation (base, indicator, solvents) were obtained from Fisher Scientific (Milwaukee, WI). Base oils and additive packages were provided by Thermal-Lube, Inc. (Montréal, Quebec) and an SAE 15W40 semi-synthetic motor oil was subsequently formulated according to the directions provided by Thermal-Lube. An SAE 5W30 synthetic motor oil, also supplied and formulated by Thermal-Lube, was taken from a vehicle which had been run for 8,000 km. The TAN values of these oils were determined in triplicate using ASTM D974 (1991) and were 1.73 and 2.01 mg KOH/g, respectively. These two oils, differing in their molecular weight and level of contaminants, were mixed in various ratios to make a variable base oil for developing a TAN calibration. Oil samples were also obtained from busses operated by the Société de Transport de la Communauté Urbaine de Montréal



Figure 3.1 Schematic diagram of the heated IR flow cell and the sample handling accessory used to load the oil for spectral analysis.

(STCUM) and used to make a composite sample for validation of the FTIR method by standard addition. A fourth oil, a P-032 mineral base oil, was oxidized in our laboratory by bubbling oxygen through it at elevated temperature so as to develop a high acid number (4.2 mg KOH/g). This oxidized oil was used in the standard addition experiments to validate the FTIR TAN method.

3.3.3 Standards/Spectroscopy

Freshly prepared SAE 15W40 and used SAE 5W30 motor oil were blended in random proportions to produce a series of 10-g samples which were gravimetrically spiked with oleic acid, a commercially available fatty acid, to produce a series of calibration standards containing known amounts of acid. These calibration standards had TAN values ranging from 1.8 to 4.7 mg KOH/g, with the COOH contribution to the TAN value ranging from 0.8 to 4.0 mg KOH/g. Each standard was split into two 5-g samples, placed into glass vials, and to one, 0.38 g of hexanol was added, while to the other, 0.38 g of 10% KOH/hexanol was added. The vials were capped and shaken for 30 seconds. The sample containing the 10% KOH/hexanol solution was aspirated into the flow-through IR cell (Figure 3.1), and its spectrum recorded, using the instrumental parameters described above. Subsequently, the second oil sample, containing only hexanol, was aspirated into the cell and its spectrum also recorded. The latter spectrum (oil/hexanol) was subtracted from the first (oil/KOH/hexanol) to produce a "differential spectrum" (van de Voort, et al., 1994).

3.3.4 Calibration

The differential spectra of all the standards were stored to disk for subsequent spectral analysis and calibration development, carried out using the Nicolet TQAnalyst Calibration and Prediction Software Package (Nicolet Instrument Co., Madison), which includes a partial-least-squares (PLS) routine (Anonymous, 1993). Variance and correlation spectra were examined to determine the spectral regions where absorbance changes correlated most strongly with the changes in oleic acid concentration in the calibration set and to determine the optimal regions to use in developing a PLS calibration model. The calibration was assessed by using the leave-one-out crossvalidation procedure, and the optimum number of spectral factors to be included in the calibration model was selected using the F-statistic obtained from the predicted residual error sum of squares (PRESS) test. The calibration was considered to be optimal when the cross-validation error was minimized.

3.3.5 Validation

To test the efficacy of the PLS calibration model, validation was carried out on a composite sample prepared from used engine oils obtained from the Montréal bus fleet. The composite sample was first analyzed by the FTIR method and its TAN value determined. The bus oil was subsequently spiked with oxidized P-032 base oil to determine whether the FTIR response was proportional to the amount added. This standard addition technique was used due to difficulties in obtaining reproducible results with the reference ASTM methods. All analyses used the standard protocol developed, i.e., splitting the sample, adding 10% KOH/hexanol to one half and only hexanol to the other half, and predicting the TAN value from the differential spectrum obtained.

3.3.6 Monitoring Trial

The FTIR TAN analysis was also used to follow the oxidative changes taking place in the oils obtained from a bus which was monitored periodically over 17,000 km. Aside from the TAN value, the level of the antiwear agent zinc dialkyl dithiophosphate (ZDDP) and the soot content were also quantitated by FTIR spectroscopy to determine whether there was any correlation between these measures and the TAN value. ZDDP was monitored by following the changes in its absorption maximum at 980 cm⁻¹, which is assigned to the stretching of the P-O-C bond. Soot, on the other hand, was measured by determining the difference in the baseline values at 2200 cm⁻¹ and 1817 cm⁻¹, this baseline shift correlating with the relative changes in soot content (Anonymous, 1995).

3.4 RESULTS

3.4.1 Analytical Concept

Infrared spectroscopy is a means by which one can identify and quantitate individual functional groups due to their absorption at specific wavelengths in the infrared portion of the spectrum. In terms of tracking oil degradation, the main components of interest are carboxylic acids, formed as a result of oxidation processes, and these are readily observed and measured by FTIR spectroscopy, as the carboxylic acid functional group (COOH) has a strong absorption maximum at ~ 1710 cm⁻¹. In the standard wet chemical TAN determination, all the acidic components present in the oil that are capable of reacting with the base used as the titrant are measured; these may include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, antioxidants, and/or detergents (ASTM D974, 1991). New, refined base oils are mixtures of hydrocarbons which contain no appreciable levels of acidity. However, depending on the application an oil is destined for, a wide range of additives can be incorporated at relatively low levels and, hence, depending on which additives are present, a fresh oil may have a substantive TAN value which is unrelated to any degradation of the oil. This complicates the use of the TAN value as an indicator of oil condition. For this reason, as well as to simplify the development of an infrared spectroscopic method of analysis, only the contributions of COOH groups to TAN are considered in the present work.

Figure 3.2a illustrates the FTIR spectra of a series of SAE 15W40 samples spiked with increasing levels of oleic acid ($C_{17}H_{33}COOH$), the absorption band at ~1710 cm⁻¹ increasing in height and area with concentration. If excess KOH is added to these same oils using hexanol as a carrier capable of solubilizing KOH as well as dispersing in the oil, the carboxylic acid groups of the oleic acid are converted to their respective salts (COO⁻Na⁻), which have an absorption maximum at ~1565 cm⁻¹ (Figure 3.2b). It is important to note that there is still an appreciable absorption in the 1710-cm⁻¹ region after base addition, which is not due to residual COOH groups, but might be a contribution of one of the additives incorporated into the oil. As noted earlier, a wide variety of additive



Figure 3.2 Overlaid FTIR spectra of 15W40 motor oil spiked with various levels of oleic acid (a), the corresponding spectra recorded after addition of KOH/hexanol (b), and the differential spectra obtained by subtracting the spectra in (a) from those in (b).

packages may be incorporated into lubricants, and the presence of the additives is obviously problematic if their absorption bands should overlap with the bands of analytical interest (COOH or COO⁻Na⁺), as they can confound quantification of the COOH-containing molecules. Based on our experience, it is impractical to develop individual calibrations to account for all potential additive or additive breakdown product interferences.

This dilemma can, however, be overcome through the technique of differential spectroscopy. In this technique, one spectroscopically measures the sample twice, once as is and once after the addition of base, subtracting one spectrum from the other to isolate both the COOH and COO'Na⁺ absorptions. To minimize volumetric displacement effects due to the dilution of the sample with KOH/hexanol, the sample is split and equivalent weights of hexanol and hexanol/KOH are added to each portion, respectively. This leaves only an insignificant displacement effect due to the small amount of KOH present. The two portions of the sample are then scanned back-to-back and the spectra obtained subtracted from each other to obtain the differential spectrum. Figure 3.2c illustrates the differential spectra produced when the same series of samples shown in Figures 3.2a and b are treated in this manner.

In the differential spectra obtained, the COOH band is inverted because the spectrum of the KOH-containing sample is devoid of COOH contributions, while the COO^{Na⁺} band stays positive. The benefit of working with the differential spectrum is that the spectral features observed reflect only the spectral changes introduced by the addition of KOH, which in this case are the loss of COOH groups and the formation of COO^{Na⁺} groups; the KOH itself does not absorb in the region of interest. All other spectral features are canceled out, as they are common to the two samples, and hence the differential spectrum isolates the changes in the component of interest, in this case oleic acid. This approach has the benefit of eliminating any concern as to what additives or breakdown products may be present, as such common features are all eliminated in the differential spectrum, except if the additive/product has a carboxyl group.

3.4.2 Calibration

Having devised a means of isolating the COOH/COO'Na⁺ contributions in the spectrum of an oil, calibration development work was initially carried out using freshly formulated SAE 15W40 motor oil spiked with various amounts of oleic acid. Both peakheight and PLS techniques were investigated as calibration approaches, the peak-height approach being used as an exploratory procedure. Figure 3.3a presents a calibration plot of absorbance values determined @ 1565 cm⁻¹ vs. the "actual TAN" calculated from the amount of oleic acid added and the TAN value of the oil basestock (1.73, as determined by the ASTM titrimetric method). The corresponding best fit linear regression equation obtained over a TAN range of ~1.7-6.0 mg KOH/g was:

TAN = 1.32 + 5.02A R = 0.999 SD = 0.068 [1] Where: TAN = Total Acid Number

> A = Absorbance @ 1565 cm⁻¹ R = Correlation coefficient

SD = Standard deviation

The calibration is linear but has a positive intercept, representing the non-COOH contribution to the TAN value of the oil basestock. This simple peak-height calibration illustrates that FTIR tracks the changes in COOH quite readily and accurately (SD = \pm 0.07).

In this simple model, we do not have the complications of variations in the additive mixture, new products being formed or changing in concentration, soot, changes in viscosity, etc., as would be the case in a used oil taken from the crankcase of an engine. A myriad of undefined changes can take place under these conditions, and one of the issues of concern here is the polarity of the oil, which affects the hydrogen bonding of the carboxyl groups. Aliphatic carboxylic acids naturally hydrogen bond, and the absorption



Figure 3.3a Plot of TAN determined using the ASTM D974 vs. absorbance @1565 cm⁻¹ for nine 15W40 calibration standards spiked with known amounts of oleic acid.



Figure 3.3b. Plot of PLS-predicted TAN vs. the TAN calculated from the amount of oleic acid spiked into the 26 randomized mixtures of freshly formulated 15W40 oil and used 5W30 crankcase oil.

Standard	15W40 (g)	5W30 (g)	Oleic Acid (g)	Carboxyl TAN
1	0.23243	9.8692	0.00237	1.60473
2	9.25493	0.8048	0.00327	0.78856
3	8.47358	1.5578	0.00422	0.87736
4	8.97987	1.0364	0.00603	0.86497
5	8.26660	1.7081	0.00700	0.94757
6	2.71972	7.3849	0.00828	1.49066
7	9.40820	0.6696	0.00910	0.88973
8	8.95474	1.1744	0.01216	0.99438
9	2.20062	7.8285	0.01488	1.66721
10	3.31385	6.7217	0.01825	1.63004
11	8.80353	1.2873	0.02127	1.18354
12	3.77610	6.2197	0.02420	1.70384
13	5.47883	4.6559	0.03007	1.6597
14	2.3273	7.7831	0.03510	2.04618
15	8.44376	1.5896	0.04014	1.58313
16	5.29759	5.1523	0.04811	2.01075
17	8.96248	1.0470	0.05652	1.85489
18	1.98549	7.9841	0.06341	2.6374
19	6.20110	3.6440	0.07160	2.41658
20	8.93959	1.0092	0.08241	2.3649
21	7.27558	2.6386	0.09192	2.7082
22	5.52264	4.3749	0.10466	3.12186
23	3.37698	6.7832	0.11882	3.54495
24	7.86788	2.1361	0.13252	3.42614
25	4.25128	5.6112	0.14352	4.00226
26	9.02951	1.0962	0.15539	3.73184

Table 3.1 PLS calibration of matrix formulation showing proportions of used and fresh oil blended, the amount of oleic acid added and the final calculated TAN value based on the carboxylic acid contributions

observed at ~1710 cm⁻¹ is actually the absorption of the dimer. As oxidation takes place and the oil becomes more oxygenated, the system becomes more polar and the carboxyl groups can engage in other forms of hydrogen bonding, causing band shifts as well as changes in intensity (Ismail, et al., 1993). Given that the polarity as well as the mixture of compounds present in used oils is likely to be variable, a simple peak-height calibration is very limiting. For this type of situation, PLS is a more powerful chemometric technique (Dubois, 1996; van de Voort, et al., 1995) allowing one to correlate spectral changes to changes in the concentration of the component of interest, while simultaneously accounting for spectral variability due to interfering components as well as any spectral perturbations such as hydrogen bonding.

To develop more realistic standards with the type of variability likely to be encountered in real samples, a used 5W30 oil from the crankcase of a vehicle run for 8,000 km was mixed with fresh 15W40 oil in randomized proportions to produce a series of 26 oils varying in their chemical composition. These blends were designed to simulate the effects of variations in the amounts of oil oxidative products, changes in additive composition and breakdown products, as well as variations in the average chain length of the oil. Various amounts of oleic acid were added to the 26 used/fresh oil blends to produce a set of calibration standards with oleic acid concentrations ranging from ~0 to 2%. The TAN values of the used and the fresh base oil were determined by the ASTM titrimetric method to be 2.01 and 1.73 mg KOH/g, respectively. The carboxylic acid contributions to these TAN values were then estimated by developing a peak-height calibration equation for each of these oils by following the procedure used to obtain Eq. [1] and subtracting the intercept from the chemical TAN value; the values obtained were 0.65 mg KOH/g for the fresh oil and 1.58 mg KOH/g for the used oil. The TAN values for the calibration standards were then calculated from their oleic acid concentrations and the carboxylic acid contributions determined for the two base oils; these TAN values (due to COOH only) values spanned the range of 0-4 mg KOH/g. Table 3.1 shows the randomized design of the calibration standard matrix; in order to develop a robust and functional PLS calibration model for the prediction of TAN from used oils, such
randomization is an essential element to avoid building in any correlations between oil characteristics and the TAN value.

The differential spectra of these calibration standards were obtained as described above and input into the Nicolet TOAnalyst[®] package along with their corresponding calculated TAN values. After extensive optimization, guided by the PRESS test (Anonymous, 1993) and minimizing the cross-validation error, a PLS calibration model for the prediction of TAN was obtained using the 1603-1560 cm⁻¹ spectral region. referenced to a single-point baseline at 1603 cm⁻¹. A plot of the predictions obtained for the calibration standards using the two-factor PLS calibration developed is presented in Figure 3.3b. Linear regression of these data produced a correlation coefficient of 0.997 and an SD of \pm 0.072 mg KOH/g; the leave-one-out cross-validation SD, which is indicative of the expected operational accuracy of the calibration, was $\sim \pm 0.095$ mg KOH/g. Although this calibration has approximately double the SD of the simple peakheight calibration obtained for a single oil spiked with oleic acid (Eq. 1), it is able to account for a wide variety of factors which would otherwise confound the predictions. To underline this point, a peak-height calibration developed using the oil blends was evidently worse, the correlation coefficient and SD obtained being 0.987 and 0.153 mg KOH/g, respectively.

3.4.3 Validation

Validation of the FTIR TAN method was first attempted by thermally stressing and bubbling air through freshly prepared 15W40 oil; however, after 500 hours of thermal stress, no measurable oxidation had occurred because of the efficiency of the antioxidants present. Alternatively, it was decided to measure the TAN values of bus oil samples from the Montreal Transit Authority. However, these samples were also problematic as they were exceedingly dark, and reliable TAN values could not be obtained using the standard ASTM method because the endpoint was indeterminate. Attempts to use the potentiometric approach also gave very erratic results, inadequate to

Table 3.2 FTIR predictions for the TAN contributions arising from the addition of oxidized P-032 base oil having a defined TAN value to varying and known amounts of used bus oil^a

Sample	1	2	3	4
TAN Added ^b	0.43	0.85	1.32	1.71
FTIR 1	0.45	0.86	1.33	1.65
FTIR 2	0.49	0.85	1.35	1.66
FTIR 3	0.49	0.82	1.33	1.71
FTIR 4	0.49	0.90	1.30	1.62
FTIR 5	0.41	0.87	1.16	1.61
FTIR 6	0.48	0.86	1.29	1.71
Mean FTIR	0.47	0.86	1.30	1.66
SD	0.034	0.027	0.069	0.044

*FTIR-predicted value of added TAN is determined by:

[FTIR-predicted TAN of sample] - [FTIR-predicted TAN of bus oil]*(wt. of bus oil/total wt of sample).

"TAN added is determined by: [(wt.(g) of oxidized P-032 added)*(4.2 mg KOH/g)]/total wt of sample (g)



Figure 3.4 A plot of FTIR-predicted TAN contributed by oxidized P-032 oil added gravimetrically to a composite bus oil sample vs. actual TAN added.

provide good reference values by which the performance of the FTIR method could be assessed. Because of these limitations, we resorted to standard addition, using an antioxidant-free P-032 base oil which had been aerated and thermally stressed, by which it developed a high TAN value (4.2 mg KOH/g, as determined by the ASTM titrimetric method). The objective here was to determine whether the FTIR TAN method would respond quantitatively to the standardized addition of known amounts of the oxidized oil. The acid-containing P-032 base oil was serially spiked into a composite bus oil sample at four concentrations, and the FTIR TAN analysis was repeated six times at each concentration as well as on the unspiked bus oil. For each analysis, the sample was split, the two portions were treated with KOH/hexanol and hexanol, respectively, and scanned, and the resulting differential spectrum was quantitated using the PLS calibration developed. The contribution of the P-032 to the FTIR-predicted TAN for each sample was obtained by subtracting the contribution of the bus oil, determined using the mean PLS-predicted TAN value for six replicates of the unspiked bus oil and the weight fraction of the bus oil in the sample. The results obtained are presented in Table 3.2 and are plotted in Figure 3.4. Linear regression of the FTIR predictions for the six replicates of each sample against the spiked TAN values yielded the following equation:

Y = 0.071 + 0.93X SD = 0.044 R = 0.996 n = 24 [2] Where: Y = FTIR-predicted spiked TAN value X = Actual spiked TAN value

From these data it can be concluded that the FTIR TAN predictions are highly reproducible and that the FTIR method responds proportionately to the changes in TAN introduced by standard addition, having an overall standard deviation of ± 0.044 TAN units. The FTIR-predicted TAN values for these samples cannot be compared with the true chemical TAN values as the latter could not be obtained by either the titrimetric or the potentiometric ASTM method due to the indeterminate nature of the endpoint when analyzing these samples. This is even the case under relatively ideal circumstances, when oils are low in soot and transparent. To better illustrate this, a slightly darkened SAE

15W40 oil was serially spiked with oleic acid and its TAN determined by the FTIR and ASTM titrimetric methods. It was found that, over the same TAN range as in Eq. [1], the reproducibility of the FTIR method was ± 0.047 mg KOH/g, which matches that in the equation, whereas that of the ASTM method was significantly poorer (± 0.23 mg KOH/g). When clear oils were analyzed, however, the reproducibility of the ASTM method (± 0.050 mg KOH/g) was comparable to that of the FTIR method.

In general, we can conclude that the FTIR method is more reproducible than the ASTM method and responds linearly to TAN changes. Thus, although the overall accuracy of the FTIR method is indeterminate as the primary reference method is less reproducible in its own right than the secondary method being developed, we can infer that the FTIR method is also more accurate than the ASTM method in measuring TAN, with the stipulation that the FTIR method only measures the contributions of carboxylic acid constituents to TAN.

3.4.4 Oil Monitoring

Having established that the FTIR method tracks changes in TAN in a linear manner, the calibration was transferred to a $COAT^{\bullet}$ system which had been designed and used for *on-line* or *at-line* monitoring of oil quality and additive levels (Dong, et al., 1997a). Oil samples were periodically collected from the crankcase of a city bus over a three-month period, spanning ~17,000 km. TAN levels, as well as soot content and the levels of one antiwear additive (ZDDP), were monitored by FTIR spectroscopy as a function of the odometer reading (time). Table 3.3 presents the data obtained for TAN, soot, and the antiwear additive (ZDDP). The amounts of ZDDP and the soot content are expressed in terms of percentage remaining relative to new oil (100%) and the absorbance value obtained by subtracting the absorbance at 1817 cm⁻¹ from that at 2200 cm⁻¹.

Figure 3.5 plots the data tabulated in Table 3.3, but normalized to range from 0 to 1 for each variable so as to allow a comparison of the three parameters measured on a

Km	FTIR TAN	ZDDP (% Remaining)	Soot Content (Abs.)
<u>0</u> <i>a</i>	2.227	74.68	0.074
2,459	2.281	59.36	0.143
3,074	2.385	49.57	0.172
5,021	2.349	50.64	0.196
9,428 ^b	2.431	54.47	0.130
10,657	2.450	53.62	0.158
12,451 ^b	2.342	72.98	0.070
13,783	2.372	72.55	0.088
15,730	2.439	59.79	0.125
17,882	2.427	47.66	0.180

Table 3.3 FTIR TAN values, antiwear levels, and soot content of oil samples collected from the crankcase of a Montréal city bus monitored over 17,000 km

^aFresh oil was not added at the beginning of the monitoring period (designated as 0 km).

^bOil was topped off in the interval between collection of this sample and the previous sample.



Figure 3.5 A normalized plot of the relative changes occurring in TAN, the level of antiwear additive, and soot content in bus crankcase oil as a function of kilometers (time).

common scale. In terms of the TAN changes, the significance of the difference between some of the measured changes is questionable, as the total change in TAN is only 0.28mg KOH/g from one extreme to the other, while the reproducibility of the analysis is on the order of ± 0.045 mg KOH/g. Substantive changes in TAN would not be expected unless the antioxidant in the oil were exhausted. On the other hand, the TAN changes and trends do make sense relative to what one would expect to happen as a function of time (oxidation) and oil addition (dilution). The TAN value rises with time until the oil is topped up, drops, and then rises again until 5 liters of oil were added, upon which the same cycle begins to repeat itself. These results lend credence to the overall impression that the FTIR TAN analysis is quite sensitive and is able to distinguish relatively small changes, on the order of 0.05 TAN mg KOH/g.

In terms of the antiwear additive, its trend tends to be opposite to the TAN trend, the levels dropping fairly rapidly, then staying relatively constant until the 5-liter oil addition, after which the same pattern begins to repeat itself. Soot, on the other hand, tends to follow the TAN trend, rising with time and dropping when the crankcase oil is diluted with new oil. These data indicate that in this case ZDDP and soot levels are complementary and probably more sensitive indicators of oil deterioration, correlating inversely and directly, respectively, with the trends observed in TAN value. A plot of the normalized ZDDP values against (1-normalized soot content) values (Figure 3.6) illustrates that these parameters are strongly related to each other (R = 0.957); however, similar relationships cannot be derived relative to TAN, as its values are discontinuous.

3.5 DISCUSSION

The FTIR analytical approach provides a versatile means of analyzing lubricating oils, the objective in this work being to develop a method for the determination of TAN. The FTIR TAN method developed is designed to complement the Continuous Oil Analysis and Treatment (COAT[•]) system developed jointly by the McGill IR Group and Thermal-Lube Inc. for on-line or at-line monitoring of oil quality and additive



Figure 3.6 A plot of normalized values of the change in the level of antiwear additive vs. values of (1 - normalized soot content), illustrating their inverse relationship.

performance (Dong, et al., 1997a). The system has proven to be effective in performing real-time monitoring of lubricating oils and can provide early warning of oil degradation or the need for additive replenishment. The FTIR TAN PLS calibration is a very general one, covering a wide range of TAN values (0-4 mg KOH/g); furthermore, because it is based on differential spectra obtained by measuring the sample twice, once with hexanol added (no KOH) and once with KOH/hexanol added, it has the important benefit of being directly applicable to any oil. The method is both sensitive and reproducible (± 0.044 mg KOH/g) and could be made even more sensitive by expanding the pathlength of the cell.

The method developed can be readily automated by programming the FTIR spectrometer to perform the spectral data collection, spectral subtraction, and quantitation by applying the PLS calibration, the TAN values being output to the screen and/or a spreadsheet file. This type of automation is standard for most of the methods we have developed (Ma, et al., 1998; Dong, et al., 1997; Dubois, et al, 1996; van de Voort et al., 1996; 1995; 1992; Ismail, et al., 1993), and with the FTIR spectrometer programmed, the operator need not have any training to carry out the analysis other than to follow the menu-driven prompts provided by the computer which drives the spectrometer. Sample preparation is straightforward, consisting only of splitting the sample into two 5-g portions and delivering ~0.38 g of KOH/hexanol stock solution by repipette into one sample and ~0.38 g of hexanol into the other. The two samples are mixed for 30 seconds on a vortex mixer, aspirated into the IR cell, and scanned for one minute. When the two scans are completed, spectral data is automatically processed to present the final TAN value, the total analysis time being ~5 min/sample.

In the analysis of oils containing non-COOH acidic components (e.g., nitrogen- or sulfur-based additives), the FTIR values obtained will not match the TAN values provided by the standard ASTM method, as the FTIR method devised only measures COOH groups. As such, it may be necessary in the future to qualify the analysis by using a term such as Carboxyl Value (CV) rather than TAN. On the other hand, in the case of monitoring the relative changes in, TAN with time in used oils, the FTIR results should

largely parallel the chemical TAN results. It is the changes in TAN, rather than the absolute values, which are important in oil monitoring as the initial TAN values differ widely in formulated oils. On this basis, we conclude that we are in effect measuring TAN and that FTIR spectroscopy provides an excellent alternative to the standard methods.

3.6 CONCLUSION

This work has demonstrated that FTIR spectroscopy can be used for the determination of TAN values in mineral oils. The analytical principle is similar to that of the standard ASTM methods; however, acid detection is more selective and the measurement more reproducible. In particular, the reproducibility of the FTIR approach is not affected by the color of the oil, making it applicable to severely darkened oils that are problematic in the ASTM titrimetric method. The FTIR method also has the benefit of minimizing solvent/reagent use and disposal. In its automated form, this new method could significantly reduce analytical time and labor requirements, making it suitable for routine quality control and monitoring applications in the lubricant sector.

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BRIDGE

In Chapter 3 the ASTM TAN reagent system was modified and utilized so that the TAN measurement could be effectively performed on FTIR spectroscopy. To be quantitatively successful, the stoichiometric reaction was combined with differential spectroscopy to minimize spectral effects of formulation variability between oils that would affect quantitation. Such ability to eliminate spectral matrix variability is crucial to generalizing the method as well as allowing the component specific reaction to be accentuated. Chapter 4 extends this concept to a related measure, total base number (TBN). In contrast to TAN, which measures acidic constituent, the ASTM TBN method measures the reserve of basic constituents in oils usually formulated for engines, particularly diesel engines running fuels with higher level of sulphur. High sulphur containing fuels contribute acidic products from fuel combustion, and the basic constituents neutralize the acids formed over time. TBN analyses are used to track the remaining base in the oil, being indicative of the rate of oil acidification.

CHAPTER 4

DETERMINATION OF TOTAL BASE NUMBER (TBN) IN LUBRICATING OILS BY MID-FTIR SPECTROSCOPY

4.1 ABSTRACT

A Fourier transform infrared (FTIR) spectroscopic method was developed to rapidly and quantitatively determine the Total Base Number (TBN) of hydrocarbon lubricating oils by spectroscopically measuring the COO⁻ functional group of the salt produced when trifluoroacetic acid (TFA) reacts with basic constituents present in an oil. FTIR quantification was based on a differential spectrum derived from two oil 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. The analytical protocol consisted of splitting the sample, scanning the spectrum of one portion, and adding 0.500 g of the second portion to 5.00 ml of TFA reactant solution and then recording its spectrum. A peak height calibration was developed from the differential spectra obtained by the standard addition of barium dinonylnaphthalene sulfonate (BaDNS) concentrate to additive-free polyalphaolefin (PAO) base oil. The calibration devised covered a TBN range of 0-20 mg KOH/g and was found to be applicable to a wide range of additive-formulated mineral oils. The FTIR method tracked ASTM potentiometric analyses quite well. Validation with various new and used oils indicated that the IR calibration performed well in terms of reproducibility (+0.17 mg KOH/g) and had an accuracy of ~±0.20 mg KOH/g based on standard addition. The FTIR method was used to track the TBN of bus oil samples taken over time, the TBN trending well with maintenance log data. Since the TFA/base reaction is rapid, complete and stoichiometric. the FTIR method was found to be very robust and capable of reliably monitoring relatively small changes in TBN. The method is simple to execute and avoids the environmentally unfriendly solvents associated with the ASTM wet chemical methods. Implemented with appropriate software, the determination of TBN by FTIR spectroscopy would be a simple and convenient procedure, useful for routine condition monitoring and a significant improvement over the methods presently available.

4.2 INTRODUCTION

Documented evidence has shown that condition monitoring of performanceenhancing additives in lubricating oils is an important activity for predictive maintenance and that equipment life is prolonged when optimum levels of additives are maintained (Robertson, 1984). Among the routine tests carried out to monitor the condition of lubricants is the measurement of total base number (TBN), which represents the overall alkalinity contributed to an oil by the additive package. TBN has been widely recognized by both oil formulators and engine manufacturers as a key determinant of oil quality, particularly for diesel engine oils (Herguth, 1992). Because diesel fuel tends to contain relatively high levels of sulfides, internal combustion of the fuel results in the production of a variety of sulfur derivatives, including sulfuric acid. In addition, nitrogen- and nitrogen/oxygen-containing acids accumulate in the oil from blow-by (O'Brien, 1984), and these acidic products result in metal corrosion if not controlled. In order to protect engines from the deleterious effects of these acidic components, diesel engine oil must be provided with an adequate level of acid-neutralizing basic materials which can buffer a substantial amount of acid buildup.

Depending on the quality of the fuel, formulated TBN values of new diesel engine oils can reach up to 80 mg KOH/g if high-sulfur fuels are being used (Wills, 1980). Modern diesel engine lubricants derive most of their alkalinity from overbased detergents such as sulfonates/phenates/salicylates of calcium, magnesium, sodium or barium. Dispersants are also a common secondary source of basic compounds (Sharma and Chawla, 1988), usually nitrogenous constituents contained in polyisobutylene succinimides (PIBS) which can also contribute some alkalinity. In addition to detergents and dispersants, some antiwear additives also contribute basic properties and play a role in acid neutralization (Kauffman, 1998). In marine diesel applications, overbased calcium carbonate detergent additives, with base numbers ranging from 250-400, predominate (Carter, 1997).

TBN Analysis

Since the TBN value of an oil will gradually drop over time as an engine is operated, routine and on-site testing for TBN can provide useful information about serviceability of the oil and an early warning of developing corrosion problems. Existing methods for TBN determination can be classified into two major categories: (a) the American Society for Testing and Materials (ASTM) approved standard primary chemical methods (ASTM D2896; D974, 1995) and (b) secondary TBN instruments/meters based on simple, rapid voltammetric measurements or pressure sensing technologies (Kauffman, 1998; Wohltjen, et al., 1994). The ASTM standard methods are based on the titration of all the basic constituents in an oil with standardized acid (HCl or HClO₄) to a fixed endpoint, the titer, however, being expressed in terms of base number (mg KOH/g oil). As is often the case with solvent-based titrimetric methods, such methods are fine in theory, but problematic in practice. Aside from the timeconsuming and labor-intensive nature of the analysis itself, a major drawback is the need for substantial volumes of organic solvents and corrosive reagents that are hazardous and difficult to dispose of. Beyond these issues are other disadvantages such as poor sensitivity at low TBNs and difficulty in determining visual endpoints in sooty oils. Even with automated potentiometric titration versions of the ASTM methods, the analysis is still time-consuming and cumbersome.

Secondary methods have been developed to circumvent these problems and simplify TBN measurement. One approach is a device developed by Wohltjen et al. (1994) which measures the pressure generated by CO₂ released when oils containing overbased CaCO₃ detergents are acidified. This analytical approach is largely restricted to marine engine oils, commonly formulated with CaCO₃, but will not respond to other basic constituents. A more promising approach is the voltammetric method described by Kauffman (1998), which appears to be suitable for the analysis of both TBN and TAN. With this method, voltammetric plots of oils dissolved in selected solvents are obtained before and after acid or base addition, the voltammogram peak height differential correlating with the ASTM TAN and TBN measurements, respectively. One drawback is that the method appears to be affected by a number of variables and, as such, one needs to

be familiar with the formulation of the oils being analyzed, especially the antioxidants and their types, as these influence the results substantially. TBN is obviously an important oil condition parameter to monitor, but an unambiguous, rapid, practical and reliable means of measuring this parameter is still lacking.

Infrared Spectroscopy

Infrared spectroscopy has always had a place in lubricant analysis to characterize various constituents qualitatively. With the advent of Fourier transform infrared (FTIR) spectroscopy, the possibility of developing quantitative methods of lubricant analysis has been facilitated (Anonymous, 1995; Powell and Compton, 1993). This is because of the inherent computing power of FTIR instruments, advances in sample handling techniques, and the availability of new chemometric methods to facilitate quantitative analysis. A tentative, but important step forward has been the establishment of standard practices for condition monitoring of lubricants by FTIR spectroscopy by the Joint Oil Analysis Program of the U.S. Department of Defense. In 1997, Thermal-Lube Inc., a Canadian lubricant formulator, approached the McGill IR Group to consider adapting FTIR analysis techniques originally developed for the edible oil sector (van de Voort, 1994) to lubricants and assist in the development of an FTIR-based Continuous Oil Analysis and Treatment (COAT[•]) system designed to monitor antioxidant and additive levels in oils (Dong, et al., 1997). In subsequent work, an FTIR method for the determination of total acid number (TAN) in mineral-based lubricants (Dong, et al., 2000) was developed. This method is based on the use of differential FTIR spectroscopy to measure carboxylate anion formation (COO) upon addition of KOH to oils in which carboxylic acids are present as a result of oxidation. In effect, the FTIR TAN method mimics the acid/base ASTM TAN procedure but is much more rapid and accurate. Reagent-based FTIR analyses of this type have great promise as a means of developing a variety of new methods for analyzing important lubricant parameters. In this paper we build on our developing knowledge of lubricant chemistry and further exploit the spectroscopic aspects of acid/base reactions to develop a general FTIR-based TBN method suitable for mineral lubricants.

4.3 MATERIALS AND METHODS

4.3.1 Instrumentation

The instrument used in this study was a COAT[•] (Thermal-Lube, Pointe-Claire, Quebec) system consisting of an FTIR spectrometer equipped with an automated sample handling accessory (Figure 4.1). A Balston dryer (Balston, Lexington, MA) was used to continually purge the optical compartment of the spectrometer in order to minimize water vapor and CO₂ interferences. The sample handling accessory consists of a micro-pump and a demountable 410- μ m CaF₂ transmission flow cell equipped with a bypass; the unit is mounted on a slide rail in the optical compartment so as to allow an open-beam background spectrum to be acquired without disrupting the purging of the optical compartment. The spectrometer was controlled by an IBM-compatible Pentium 150-MHz PC running under proprietary Windows-based UMPIRE[•] (Universal Method Platform for InfraRed Evaluation, Thermal-Lube, Pointe-Claire, Quebec) software. All spectra were collected by co-adding 16 scans at a resolution of 4 cm⁻¹ and a gain of 1.0 and were subsequently ratioed against a 16-scan open-beam background spectrum to produce absorbance spectra.

4.3.2 Reagents and Oils

All reagents used for methodology development were obtained from Aldrich Chemicals (Milwaukee, WI). These included reagent-grade trifluoroacetic acid (TFA, 99+%), potassium trifluoroacetate (KTFA, 98%), and hexyl alcohol (98%). Additive-free polyalphaolefin (PAO) base oil and barium dinonylnaphthalene sulfonate (BaDNS) concentrate and its overbased form [BaDNS-xBa(OH)₂, King Industries, CT] were supplied by Thermal Lube Inc. (Pointe-Claire, PQ). Various oils, including new and used diesel engine oils, were obtained from Naval Engineering Test Establishment (NETE, LaSalle, PQ) and Engine System Development Center Inc. (ESDC, Lachine, PQ). A 1.9% (v/v) TFA reactant solution was prepared by mixing 28 ml of TFA/hexanol stock solution



Figure 4.1 Schematic diagram illustrating the key components of the IR oil analysis accessory designed by Dwight Analytical (Toronto, ON).

(14%, v/v) with 172 ml of additive-free PAO base oil. This solution, which is stable for extended periods of time at room temperature, must be prepared at least 12 h prior to use to allow TFA dimers to dissociate.

4.3.3 Calibration /Analytical Protocol

Calibration standards with TBN values of 0-20 mg KOH/g were prepared by gravimetrically adding BaDNS concentrate (TBN = 47.78) to additive-free PAO base oil. Each standard was thoroughly mixed on a vortex mixer and then sonicated (2-3 h) to ensure uniform dispersion of the base. For FTIR analysis, ~10 ml of oil is required and a standardized analytical protocol, outlined below, was developed and followed for both calibration standards and samples to be analyzed.

- (a) Using ~ 5 ml of oil, rinse and load the flow cell (Figure 4.1), scan the spectrum of the oil, and store the absorbance spectrum (AS₁).
- (b) Using two gravimetrically pre-calibrated volumetric re-pipettes, accurately dispense, into a 20-ml vial, 5.00 g of the TFA/hexanol reactant solution and 0.500 g of the oil sample. Cap the vial, shake the mixture for ~20 sec and allow to stand for ~2 min to allow any gas released to disperse.
- (c) Rinse and load the flow cell with the reacted sample prepared in step (b) and record its absorbance spectrum (AS_2) .
- (d) Subtract spectrum AS1 from spectrum AS_2 with a scaling factor of 0.111, corresponding to the factor by which the oil sample was diluted in step (b), to produce a "differential spectrum" AS_3 .
- (e) If a calibration is being developed, the AS3 peak height values measured at 1672 cm⁻¹, referenced to 2110 cm⁻¹, for each of the calibration standards are regressed against their known TBN values to produce a calibration equation.
- (f) AS3 is used for sample quantitation if the system is already calibrated. The peak height measured at 1672 cm⁻¹, referenced to 2110 cm⁻¹, is processed through the linear regression calibration derived in step (e).

4.3.4 Validation of the FTIR TBN Calibration

Several approaches were used to validate the FTIR method. To evaluate reproducibility, three engine oils were selected and analyzed in duplicate on three

different days. Selected diesel engine oils made available by ESDC were analyzed by the ASTM potentiometric method as well as by the FTIR method to obtain a relative measure of accuracy. Accuracy was also evaluated by standard addition, where various levels of another basic detergent, overbased BaDNS, were added to new engine oils. In addition to the tests described above, FTIR TBN analyses were also carried out on oils periodically taken from the crankcase of a city bus over 17,000 km of service.

4.4 RESULTS

4.4.1 Spectroscopy of TFA/base reactions in PAO base oil

In the calibration of an FTIR method for TAN determination, we modeled carboxylic acid oxidation end products accumulating in an oil by addition of oleic acid to fresh base oil (Dong, et al., 2000). FTIR analysis of used oils consisted of recording the spectra of an oil sample before and after the addition of KOH, the KOH transforming all the organic acids present in the oil into their carboxylate anion form. Spectral subtraction was used to eliminate the spectral features of the oil and magnify the spectral changes associated with formation of the carboxylate anion, its absorbance being used to quantify the acidic constituents. Similar concepts were used in developing the FTIR TBN method. Owing to the electron-withdrawing inductive effect of the fluorine atoms on the carbon adjacent to the carboxyl group, trifluoroacetic acid is a very strong organic acid that dissociates completely in aqueous media (Roberts and Caserio, 1965). As a consequence, TFA is able to react completely with most basic constituents normally present in oils, including sulfonates, phenates, and salicylates as well as their overbased forms, to produce their respective TFA salts:

$$F_3C-C-OH + R_1M \longrightarrow F_3C-C-OM^+ + R_1H$$

$$\begin{array}{c} O \\ 0 \\ 2(x+1) F_3 C - C - OH + R_2 M - (M_2 CO_3) x \longrightarrow 2(x+1) F_3 C - C - OM^+ + R_2 H + x H_2 O + x CO_2 \end{array}$$



Figure 4.2 Differential spectra of TFA and KTFA in PAO. (a) TFA/hexanol solution added to PAO with the spectral contributions of PAO and hexanol subtracted out; (b) KTFA/hexanol solution added to PAO with the spectral contributions of PAO and hexanol subtracted out; and (c) TFA/hexanol solution added to PAO containing BaDNS with the spectral contributions of PAO and hexanol subtracted out.

 R_1M represents neutral sulfonates, phenates, and salicylates, whereas $R_2M-(M_2CO_3)_x$ represents overbased carbonate detergents. Because the end product in all cases is a TFA salt, FTIR measurement of the TFA anion should provide a means of measuring TBN.

Figure 4.2a and b present the differential spectra of TFA/hexanol in PAO base oil and KTFA/hexanol in PAO, respectively, after the PAO and hexanol contributions have been subtracted out. Hexanol, which is used as a carrier to assist in dispersing TFA and its potassium salt in the base oil, does not absorb in the region of interest. In Figure 4.2a the sharp band at 1790 cm⁻¹ is due to the C=O stretching vibration of the -COOH functional group of TFA, shifted to somewhat higher frequencies than the normal range of 1730-1680 cm⁻¹ associated with long-chain carboxylic acids (van de Voort, et al., 1994), owing to the inductive effect of the fluorine atoms. The spectrum of the potassium salt of TFA dissolved in PAO (Figure 4.2b) exhibits a strong band at 1672 cm⁻¹ due to the carboxylate anion (COO⁻), again shifted to a higher frequency than that (1656 cm⁻¹) normally associated with long-chain carboxylic acid salts (Dong, et al., 2000). The intensities of the 1790 and 1672 cm⁻¹ bands are proportional to the concentrations of their respective TFA forms. Figure 4.2c illustrates the differential spectrum obtained when the spectrum of PAO oil containing BaDNS is subtracted from the spectrum of the same oil to which a small amount of TFA/hexanol has been added. Some of the TFA is converted to a salt [(F₃CCOO⁻)₂Ba²⁺] by the TFA/BaDNS reaction, producing a band at 1673 cm⁻¹ corresponding to that illustrated in Figure 4.2b for F₃CCOO^{*}K⁺. Based on the stoichiometry of the acid/base reaction, the amount of TFA salt formed should be directly proportional to the concentration of BaDNS in the oil. As such, the method effectively mimics the acid/base reaction on which the ASTM TBN method is based but uses the strong infrared band produced by formation of the TFA salt to measure the basic constituents present in the oil.



Figure 4.3 Calibration plot of actual TBN added to PAO vs. the peak height of the TFA salt measured at 1672 cm^{-1} relative to a single-point baseline at 2110 cm^{-1} .

4.4.2 Calibration

In principle, a calibration could be devised simply by adding known amounts of KTFA to additive-free PAO base oil and using the characteristic band of the TFA anion at 1672 cm⁻¹ as a means of quantitating TBN based on the TFA/base reaction stoichiometry. In practice, this approach is impractical because even when hexanol is used as a carrier, the solubility of KTFA is too low to span a workable concentration range. This solubility limitation can be overcome by preparing PAO standards containing BaDNS and adding a constant excess of TFA/hexanol to produce the TFA salt *in situ*. Each calibration standard was processed according to the "analytical/calibration protocol" described above and the differential spectra thus obtained were used for calibration development. Figure 4.3 presents a calibration plot of the absorbance values measured at 1672 cm⁻¹ referenced to a single baseline point at 2110 cm⁻¹ vs. the actual TBN value calculated from the amount of BaDNS concentrate added to the base oil. The resulting best-fit linear regression equation obtained over a TBN range of 0-20 mg KOH/g was:

$$TBN = -4.35 + 21.44A \qquad SD = 0.160 \qquad R = 0.9998 \qquad [1]$$

Where: TBN = Total Base Number

- A = (Absorbance at 1672 cm⁻¹) (Absorbance at 2110 cm⁻¹)
- R = Correlation coefficient
- SD = Standard deviation

The highly linear response of absorbance at 1672 cm⁻¹ to changes in TBN is indicative that the acid/base reaction proceeds to completion with the expected stoichiometry over the TBN range spanned by the calibration standards (0-20 mg KOH/g). The regression SD of 0.16 mg KOH/g represents a coefficient of variation (CV) of <2% over the analytical range.

4.4.3 Validation

A new automotive engine oil, a used diesel bus engine oil, and a used diesel locomotive engine oil, each undefined in terms of additives, were analyzed 6 times, twice

FTIR Replicate	TBN Oil A ^t	TBN Oil B ²	TBN Oil C ³	
la	9.59	7.27	5.28	
1b	9.67	7.14	5.13	
2a	9.80	7.27	5.32	
2b	9.71	7.40	5.36	
3a	9.90	7.33	5.19	
3b	9.65	7.14	5.26	
Mean	9.73	7.25	5.27	
SD	<u>+0.10</u>	<u>+0.12</u>	<u>+0.10</u>	
CV	1.03%	1.66%	1.90%	

Table 4.1 FTIR TBN predictions obtained for three engine oils from duplicate analyses on three days

1. A = Used locomotive diesel engine oil provided by ESDC

 B = New automotive engine oil
C = Used bus diesel engine oil provide by the Société de Transport de la Communauté Urbaine de Montréal



Figure 4.4 A plot of the FTIR-determined TBN values for various oils vs. ASTM autotitration potentiometric results.

per day over three days, by the FTIR TBN method. Table 4.1 summarizes the results obtained for the replicates and their corresponding statistics. The data indicates that the method provides consistent results over time, with an overall SD of the order of <0.20 mg KOH/g. The SD could be reduced somewhat (<0.10 mg KOH/g) if all sample and reagent manipulations were carried out gravimetrically rather than volumetrically; however, the benefit of this reduction in the SD was considered insignificant relative to the additional manipulations introduced by weighing.

Various new and used oils, including additive-free zero-TBN base oil, diesel engine break-in oil, and a number of locomotive diesel engine oils varying in viscosity and additive package composition, were analyzed for TBN by the ASTM D-2896 potentiometric titrimetric method (ASTM D2896, 1995) using HCl as the titrant, as well as by the FTIR TBN method. Figure 4.4 illustrates the relationship between the TBN values obtained by the two methods, the linear regression equation obtained being:

FTIR TBN =
$$3.57 + 0.7374$$
 ASTM TBN $R = 0.97$ $SD = 0.77$ [2]

Clearly, the two methods track each other; however, the proportionality constant obtained (0.74) is substantially less than the ideal value of 1.0 and the SD relative to the ASTM reference method is $\sim \pm 0.80$ mg KOH/g. This comparison indicates that both methods measure the basic components in the oil, but that their responses differ to some degree. On the other hand, standard addition of Ba(OH)₂ overbased BaDNS to SAE W50 diesel engine oil produced a linear 1:1 relationship, as indicated by the following regression equation:

$$\Delta FTIR TBN = -0.2 + 0.97(\Delta TBN)$$
 R = 0.998 SD = 0.20 [3]

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Figure 4.5 A plot of the relative changes occurring in TBN values of a bus crankcase oil as a function of bus mileage and service.

On the basis of standard addition, the regression SD indicates that the accuracy of the FTIR method is around ± 0.20 mg KOH/g.

4.4.4 TBN Condition Monitoring

The FTIR TBN method was standardized and the analytical protocol implemented on a COAT[®] FTIR system using a newly developed software package [Universal Method Platform for InfraRed Evaluation (UMPIRE[®])], which guides the operator through the analytical protocol, automatically performs all the required spectral manipulations and calculations, and outputs the analytical results, in this case, TBN values. Oil samples collected from the crankcase of a city bus serviced periodically over a three-month (~17,000 km) period were analyzed for TBN. Figure 4.5 illustrates the results obtained as a function of mileage relative to the service record. The highlighted areas indicate two points where significant changes in TBN occur, the TBN value dropping off with time while the bus was in operation and then increasing when 5 liters of fresh oil were added. The overall change in TBN spans ~0.9 mg KOH/g, well in excess of the sensitivity of the FTIR method. Similar trends were also observed in the relative soot levels of the oil as measured by the standard IR protocol (SAE 841373).

4.5 DISCUSSION

The ASTM standard chemical titrimetric or potentiometric methods make use of strong inorganic acids (HCl or HClO₄) to react completely with the basic constituents in an oil (ASTM D2896; D974, 1995). The FTIR TBN method effectively does the same thing using a strong organic acid, TFA, which provides an infrared signal that is readily measured. The FTIR TFA/base reaction clearly is stoichiometric and very reproducible. The power of the method lies in the use of differential spectroscopy, which allows the potential spectral interferences associated with undefined additive packages or oil breakdown products to be eliminated. This benefit is obtained at the expense of having to collect two spectra rather than one; however, the drawback of having to perform this extra step is outweighed by being able to use a single calibration for a wide range of oils, rather than having to develop oil-specific calibrations.

It is clear that the FTIR method tracks the results obtained by the ASTM potentiometric method, but the results from the two methods are not exactly the same. In the ASTM procedure, small additions of acid are required, each having to come to equilibrium (stabilize) before the titration can continue. Even with an autotitrator, a continuum of titer values are required to determine the endpoint by extrapolation. In contrast, the FTIR procedure uses excess TFA and the reaction is rapidly driven to completion. This difference between the ASTM and IR approaches may account for some of the differences in the results obtained. The FTIR TBN method is very reproducible, even using our simplified protocol (no weighing), and is also quite accurate as determined by standard addition. The method is capable of analyzing a relatively broad range of TBN values (0-20mg KOH/g) and is applicable to mineral-based oils. For higher TBN oils, the sample can be diluted with a zero-TBN base oil prior to spectral analysis, and thus the upper limit of the analytical range open-ended. Our experience indicates that the analytical performance of the FTIR method is not adversely affected by dark or sooty oils, which are definitely problematic with indicator-based methods. Because the amount of reagent (TFA/hexanol) used for each FTIR analysis is minimal, the FTIR method reduces the volume of waste disposal.

4.6 CONCLUSION

Compared to the ASTM standard methods, the FTIR method for the determination of TBN is simple, versatile, and eminently suited to condition monitoring. Sample preparation is simple and straightforward, consisting only of delivering 0.50 g of sample by re-pipette into 5.00 ml of TFA/hexanol reagent, loading the infrared cell, and scanning the spectrum; the total analysis time is ~3-5 min per sample. Automation of the analysis is facilitated by implementing the analytical protocol via the UMPIRE software, which automatically performs the required spectral manipulations and quantitation by applying the appropriate calibration, with the analytical results output to the computer monitor or printer in a spreadsheet or control chart. The TBN method developed in this study is complementary to the FTIR TAN method developed earlier, and two methods

can be implemented with a common instrumental/cell configuration. To date, these two new FTIR methods are all limited to conventional hydrocarbon-based lubricating oils; however, it is likely that their application can be broadened to other oil classes (i.e., synthetic esters, polyglycols, silicones, etc.) with appropriate further investigation.

4.7 ACKNOWLEDGEMENTS

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BRIDGE

In Chapter 4, a FTIR TBN method was developed for the measurement of base reserve in oils. In this case, the ASTM reagents HCl and HClO₄ could not be employed as they lack IR suitable absorptions and trifluoroacetic acid (TFA) was employed as a replacement. TFA was shown to be an adequately strong organic acid to react with the basic constituents normally used to formulate diesel oils and upon reaction to form IR active TFA salts that could be quantified. The approach to the analysis is somewhat different from the TAN method in that the reagent is the dominant constituent rather than the oil and that spectral ratioing was carried out in a different fashion. The development of the TBN method indicates that the concepts and principles initially formulated for the TAN method have a fair degree of flexibility and potentially provide a generalized means of quantification of other constituents if appropriate reagents can be found.

Besides TAN and TBN, moisture is a key condition monitoring variable in lubricating oils as it is a catalyst for corrosion, promotes additive deterioration and negatively affects overall lubricant functionality. It is also one of the most problematic analyses, largely due to matrix effects and additive interferences which affect the ASTM Karl Fischer methods that have been routinely practised. Chapter 5 investigates the FTIR reagent/differential spectroscopy concept in relation to the quantitative determination of moisture in lubricants.

CHAPTER 5 A NEW APPROACH TO THE DETERMINATION OF MOISTURE IN HYDROCARBON LUBRICATING OILS BY MID-FTIR SPECTROSCOPY

5.1 ABSTRACT

The moisture content of hydrocarbon based lubricating oils was determined by FTIR spectroscopy by measuring hydrated acetone gem-diol produced when 2.2dimethoxypropane (DMP) reacts with water present in the oil under neutral or basic conditions. The gem-diol was quantified from a differential spectrum derived from two oil spectra collected separately, one taken prior to the addition of DMP and the other 30 min after DMP addition. Peak height calibrations were developed by standard addition of water commercial hydrocarbon based lubricating oils which were also pooled for calibration development by partial least squares (PLS) regression. The peak height calibrations performed well (± 22 ppm), but were oil formulation dependent, while the calibration allowed all the oil formulations to be analyzed for using a single calibration with little loss in predictive accuracy (\pm 32 ppm) over a range of 0-1200 ppm. Attempts to compare the FTIR results to Karl Fischer (KF) methods were problematic with additive-containing oils and highlighted the superior quantification capabilities of the FTIR DMP method. For multiple analyses, with the FTIR programmed and automated, the analytical time is reduced and should provide convenient and reliable means of determining moisture in hydrocarbon based oils.

5.2 INTRODUCTION

The McGill IR Group has specialized in the development of rapid quantitative quality control methods for the analysis of edible fats and oils, lubricants and food products by Fourier transform infrared (FTIR) spectroscopy. The methods developed feature minimal sample preparation and are designed to replace environmentally unfriendly wet-chemical methods. One of the most elusive methods has been a generalized FTIR method for the analysis of moisture. Although moisture analysis by both mid- (Anonymous, 1992; Powell and Compton, 1993) and near- (Blanco, et al., 1998) infrared (IR) spectroscopy has been well documented as a simple, sensitive and accurate means of determining moisture, this is only the case in some rather specific and relatively ideal circumstances. Water absorbs strongly in the IR portion of the spectrum due to its O-H stretching and bending vibrations, however, its quantitation is frequently complicated by spectral interferences from other OH containing constituents such as alcohols, phenols and hydroperoxides and confounded further by hydrogen bonding effects. In new and used oils, many additives, breakdown products and contaminants containing OH groups are commonly present, making quantitation of moisture difficult, especially at lower (<0.1%) moisture levels (Anonymous, 1995).

Alternative approaches to the direct IR determination of moisture in oils are the extraction of the moisture into a suitable dry solvent (van de Voort, et al., 1994) or reaction of the water with an appropriate reagent followed by IR quantitation of the reaction product(s). Attempts to use absolute methanol to extract water from mineral oils proved unworkable. Monitoring the products of stoichiometric reactions is an alternative technique which has been successfully applied to the determination of carboxylic acids and total base number (TBN) (Dong, et al.,2000a; b) in mineral oils. This approach was originally used to determine moisture in solvents (Critchfield and Bishop, 1961), by reacting 2,2-dimethoxypropane (DMP) with water under acidic conditions to produce acetone, thereafter measured by IR spectroscopy at 5.87 μ m (1703 cm⁻¹). The limit of detection of this method was ~0.05% (500ppm). The limit of detection was subsequently improved (~15 ppm) through the use of capillary gas chromatography (Dix, et al., 1989) and in combination with an alternative reagent, triethyl orthoformate (Chen and Fritz, 1991). Both of these GC methods are considered broadly applicable to the analysis of traces of moisture in a wide range of solvent systems.

This paper examines the DMP/water reaction as the basis for quantitation of moisture in lubricants by FTIR spectroscopy. The feasibility of this approach to the determination of moisture was investigated sequentially in carbon tetrachloride (CCl₄), poly- α -olefins (PAO) five commercial hydrocarbon lubricants and used oils, the

analytical protocols and calibration development process detailed to illustrate the general concepts of the method.

5.3 MATERIALS AND METHODS

5.3.1 Instrumentation

A Continuous Oil Analysis and Treatment (COAT[•], Thermal-Lube, Pointe-Claire, Quebec) system, consisting of an FTIR spectrometer equipped with an oil sample handling accessory manufactured by Dwight Analytical (Mississauga, Ont.) was employed in this work (Figure 5.1). Using vacuum, the 520μ m CaF₂ transmission flow cell was easily loaded and emptied with oil via a two-way valve. The instrument was controlled by an IBM-compatible Pentium 150-MHz PC running under Windows-based COAT[•] software. A Balston dryer (Balston, Lexington, MA) was used to purge the optical compartment of the COAT system to minimize water vapor and CO₂ interferences. All spectra were collected by co-adding 16 scans at a resolution of 4 cm⁻¹ and a gain of 1.0 and were subsequently ratioed against a 16-scan open-beam background spectrum to produce absorbance spectra.

Two commercial Karl Fischer (KF) titrators were employed to carry out the ASTM primary reference method (D1744, 1991) for moisture determination of oil samples and standards. One instrument was a Mettler Toledo[®] DL36 coulometric autotitrator, equipped with a double-pin platinum electrode (Mettler Toledo, Switzerland), charged with AquaStar[®] Coulomat AK & CK (Crescent Chemical Co., NY) reagent solutions containing chloroform and imidazole, respectively, suitable for the coulometric determination of water in the presence of ketones and aldehydes. The other instrument was a Mettler Toledo[®] DL18 volumetric autotitrator, equipped with dual platinum pin electrode for voltammetric measurement. This system was charged with Hydranal[®] Composite-5 reactant (Riedel-de Haen Chemicals, Germany). All samples were analyzed by direct injection without prior treatment.


Figure 5.1 Schematic diagram of the flow transmission cell assembly inserted into the spectrometer sample compartment. Oil is aspirated into the cell via the spigot by vacuum, controlled by the valve on the arm.

5.3.2 Reagents and Oils

Molecular sieves (4A, 1/8-inch beads) and reagent-grade 2,2-dimethoxypropane (DMP, 98%) were obtained from Aldrich Chemicals (Milwaukee, WI). These were dried for at least 12h at 120°C prior to use and the DMP solution was always stored over the activated sieves for at least 72h prior to use. The oils used in this study included poly- α olefin (PAO) base oil, five branded commercial lubricants (Oils A-E) and a blended used oil. The oils used to make the used oil blend were obtained from the crankcases of vehicles operated for at least 6,000 km. All the oils used as standards were kept over molecular sieves for a minimum of 72h to remove as much moisture as possible.

5.3.3 Calibration Standards/Analytical Protocol

Calibration standards (up to 1200 ppm) were prepared gravimetrically by adding distilled water to the oils. For PAO, hexylamine (0.06% w/w) was used as a dispersing agent to assist in the distribution of added moisture in the oil. The oils containing additives (A-E) and the used oil blend had sufficient polarity to incorporate water without requiring a dispersant. Prior to FTIR or KF analysis, all samples and standards were sonicated to ensure uniform dispersion of the moisture added.

The following analytical protocol was developed to facilitate FTIR spectroscopy, analysis and quantitation of moisture:

(a) A portion of the oil to be analyzed is used to rinse and load the flow-through transmission cell (Figure 5.1) and its absorbance spectrum (AS_1) is recorded.

(b) From the balance of the oil sample, pipette 5g of oil into a 20-ml plastic vial and add 1g of the DMP using two gravimetrically precalibrated re-pipettes. Cap the vial, shake for 30 seconds and react for 30 min.

(c) Rinse and load the transmission cell with the reacted sample and record its absorbance spectrum (AS_2) and multiply the resulting spectrum by a correction factor of 0.833.

(d) Spectrum AS_1 is subtracted from AS_2 to produce a "differential spectrum", AS_3 , which represents only DMP and its reaction products, the spectral contributions of the base oil having been subtracted out.

(e) AS_3 is used to predict the moisture content of the sample or standard by either peak height or partial least squares (PLS) calibrations.

5.3.4 Spectroscopy and Calibration

The DMP/H₂O reaction was first investigated in CCl₄ to study the dynamics of the reaction, followed by studies in PAO and then in lubricating oils. Peak height and PLS regression approaches were investigated as procedures for measuring the moisture content in individual and combined oil matrices, respectively. For PLS calibration development, correlation and variance spectra were examined to determine the regions where spectral changes correlated most strongly with the changes in moisture content. The PLS calibration was optimized using the leave-one-out cross-validation procedure and the appropriate number of spectral factors selected using the F-statistic from the predicted residual error sum of squares (PRESS) test. The calibration was considered to be optimal when the cross-validation error was minimized.

5.3.5 Validation

To test the efficacy of the calibrations, validation was carried out on selected engine oils to which varying amounts of water had been added. These samples were analyzed by the standard FTIR analytical protocol described above in steps (a)-(e), as well as by KF titration. KF titrations were carried out using both volumetric and coulometric methods using reagents, equipment and procedures recommended for the analysis of water in lubricating oils (Anonymous, 1992).

5.4 RESULTS

5.4.1 Spectroscopy of DMP/H₂O in CCl4

The overall reaction under investigation (Figure 5.2) involves one mole of 2,2dimethoxypropane (DMP) reacting with water in the presence of acid, the DMP being



Figure 5.2 Overall reaction of DMP with water under acidic conditions, producing one mole of acetone and two moles of methanol.



Figure 5.3 Differential spectra of DMP and its reaction products. (a) dry DMP added to dry CCl₄ with the spectral contributions of CCl₄ subtracted out; (b) dry DMP added to moist CCl₄ with the spectral contributions of CCl₄ subtracted out; (c) same as (b), but with both the CCl₄ and DMP spectral contributions subtracted out.

converted into one mole of acetone and two moles of methanol. The DMP/H₂O reaction was initially studied in CCl₄ without acid present and monitoring the spectral changes occurring as a function of time. Figure 5.3a-c shows three differential spectra illustrating the changes taking place in the hydroxyl region of the mid-IR portion of the spectrum when DMP is added to dry or moist CCl₄. Figure 5.3a is the spectrum of dry DMP added to dry CCl₄ with the spectral contribution of CCl₄ subtracted out. Figure 5.3b is the spectrum of dry DMP added to moist CCl₄, again with the CCl₄ spectral contribution subtracted out, while Figure 5.3c represents the same conditions as Figure 5.3b, but with both the CCl₄ and DMP spectral contributions ratioed out. Figure 5.3c shows two strong bands, one at 3690 cm⁻¹ and the other at 3500 cm⁻¹, with a diffuse, broad shoulder in between.

These spectral changes are typical of the DMP/H₂O reaction without acid present the 3500 cm⁻¹ band confirmed to be due to methanol. The 3690 cm⁻¹ band was postulated to be a hemi-acetal and/or the hydrated acetone gem-diol produced by the reaction. Under non-acidic conditions, no carbonyl band indicative of acetone formation (1700-1760 cm⁻¹) was observed. However, when methylsulfonic acid was added, an intense carbonyl band appeared at 1720 cm⁻¹, indicative of acetone formation and the band at 3690 cm⁻¹ disappeared. In subsequent experimentation, when excess acetone was added to moist CCl₄ in the presence of acid, without DMP present, the 3690 cm⁻¹ band appeared, indicative of the gem-diol since methanol would not be produced under these conditions. Subsequent addition of methanol to this mixture resulted in the appearance of a new band at 3640 cm⁻¹, tentatively attributed to the formation of the hemi-acetal, but could not be confirmed as this frequency also coincides with the absorption of non-hydrogen bonded methanol. The 3640 cm⁻¹ absorption is not present in DMP treated samples, so it would appear that neither non-hydrogen bonded methanol nor hemi-acetal is not present at significant levels. Based on extensive spectral investigation of the reactions and a review



Figure 5.4 Summary of DMP reactions with water in CCl_4 . DMP = [1], hemi-acetal = [2], Gem-diol = [3] and acetone = [4].

of the commonly postulated mechanisms for acetal/water reactions (Fessenden & Fessenden, 1986), the DMP/H₂O reactions are summarized in Figure 5.4.

The reaction can proceed by two distinct pathways depending on whether acid is present or not for catalysis. Without acid, DMP [1] initially reacts with water to form a hemi-acetal intermediate [2] plus one molecule of methanol, the hemi-acetal in turn reacting with a second molecule of water to produce the acetone hydrate or gem-diol [3] plus a second molecule of methanol. The reaction cannot proceed further without acid and the system comes to equilibrium in terms of participating species (H₂O, DMP, gemdiol, hemi-acetal and methanol). If a relatively strong acid is added, the reaction is catalyzed by H⁻ to continue on to produce acetone and water from the gem-diol. Here the equilibrium strongly favors acetone, consuming water, DMP, the hemi-acetal and the gem-diol until water is exhausted. The water molecule released along with acetone rereacts with DMP (assuming DMP is in excess) and is ultimately consumed, resulting in the net production of only acetone and methanol as end products of the acid-catalyzed reaction.

This preliminary spectroscopic study of the DMP/H₂O reaction, under acidic and non-acidic conditions in CCl₄, indicated that the amounts of both acetone and the gemdiol/methanol intermediates produced were proportional to added moisture. If these reactions were to proceed in a similar manner in hydrocarbon oils, then either version of the DMP reaction could potentially serve as a means of determining moisture in lubricating oils. From a practical standpoint, however, the acid-catalyzed DMP reaction would be limited to oils devoid of basic constituents in their additive package, which is not generally the situation. In this case such constituents, when acidified, could produce water, which would confound quantitation. The DMP reaction without acid does not suffer from this problem, however, it results in a complex equilibrium of molecular species rather than being driven to produce a single measurable component. In general, reactions at equilibrium may be used for quantitation if the K_w is known, which is not the



Figure 5.5 Overall reaction of water with excess DMP [1] with no acid present. The dominant equilibrium products are the gem-diol [3] and methanol.

case in this situation. However, if the equilibrium is shifted to one side by an excess of one component, such as DMP, then one has in effect a largely unidirectional reaction as per Figure 5.5, that could be used for quantitation. Subsequent experimentation focused on the further investigation of the DMP/H₂O reaction under non-acidic conditions in a model hydrocarbon oil to determine whether quantitative analysis was possible by adding excess DMP.

5.4.2 Spectroscopy of DMP/H₂O in PAO

Lubricating oils come in many forms, not only in terms of the base oil, but also from the standpoint of the additive packages incorporated to provide specific functionalities. To simplify the study of moisture analysis with DMP under non-acidic conditions, dry, additive-free, PAO base oil was examined as the analytical test matrix. Dispersing water directly in PAO is very difficult, if not impossible, given its extreme hydrophobicity. To assist in dispersing moisture in PAO, a small amount of hexylamine was added to the bulk oil so that up to 1000 ppm water could be uniformly dispersed in solution, facilitated by sonication.

It was found that the reactions and equilibrium behavior observed in CCl₄ also occurred in PAO. The peak heights of the gem-diol and methanol bands produced when a fixed amount of excess DMP was added to water spiked PAO samples were found to be directly proportional to moisture added. However, the proportionality constant varied with the total amount of DMP added, even at levels well in excess of the maximum moisture content on a molar basis. After an extensive investigation of DMP/PAO ratios (1:10 to 1:1) for a fixed series of moisture levels in the PAO, it was found that the optimal spectral response at 3690 cm⁻¹ and 3500 cm⁻¹ was obtained when a 1:5 (w/w) DMP/PAO ratio was used. This optimal DMP/PAO ratio drives the reaction as far as possible toward the formation of the gem-diol/methanol products while minimizing the concurrent dilution effects of adding more DMP. Even though the reaction comes to a complex equilibrium involving four species, ultimately concentrations of the gem-diol



Figure 5.6 Differential spectra of a series of PAO oil samples spiked with increasing amounts of water to which DMP has been added in a 1:5 ratio.

and methanol are proportional to the moisture content under standardized conditions (i.e., a fixed DMP/PAO ratio), attesting to the validity of the overall reaction (Figure 5.5).

Based on this information, a standardized sample preparation protocol and scanning routine was developed to facilitate calibration development and sample analysis (Materials and Methods, steps a-e). The spectral multiplication factor of 0.833 used in step (c) is designed to correct for the density and dilution effects on the oil by DMP addition, so that the spectral contributions of the oil are accurately subtracted out and do not appear in the resulting differential spectrum. Figure 5.6 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. Both the gem-diol and methanol responses were linear and Figure 5.7 illustrates a representative absorbance plot for the gem-diol measured relative to a single point baseline at 3709 cm⁻¹ as a function of added water, the best fit linear regression equation being:

$$[H_2O] = -118.6 + 44884A$$
 $R = 0.998$ $SD = 9.88$ [1]

Where:

[H₂O] = ppm water added to PAO
A = Abs @ 3691 cm⁻¹/baseseline @3705 cm⁻¹
R = Correlation coefficient
SD = Standard deviation

The plot is linear, having a regression SD of <10 ppm, while the negative intercept of -118 ppm implies that there is residual moisture in the oil or that moisture was carried in with the hexylamine dispersant added. The inverse of the slope indicates that one would need to be able to measure spectral differences of ~ 0.02 mAbs units to detect a 1 ppm difference in water content. Under optimal purge conditions, the S/N for the instrument



Figure 5.7 Plot of ppm water added to PAO vs. the peak height of the gem-diol measured at 3691 cm⁻¹ measured relative to a single point baseline at 3709 cm⁻¹.

was determined to be ~0.25mAbs, peak-to-peak, representing ~10 ppm H_2O , in line with the regression SD obtained for the PAO calibration. Good water vapor purging is essential for quantitative work over the 3800-3300 cm⁻¹ region, as superimposition of water vapor variability on the sample spectral signature causes significant fluctuations in the calculated results.

5.4.3 DMP/H₂O in Lubricating Oils

Based on the results obtained with PAO, a series of commercial hydrocarbon lubricating oils (A-E) were evaluated in a similar manner after first drying them over molecular sieves. These oils all contained additive packages of various types to which up to 1600 ppm of water could be added without visual evidence of physical separation. Gravimetric standard addition was again used to produce a series of standards which were treated using 1:5 DMP/oil and the methanol and gem-diol peak heights measured in the differential FTIR spectra of each oil series. For these oils, the spectral linearity of the 3500 cm⁻¹ methanol band relative to the amount of water added was lost, but that of the 3691 cm⁻¹ diol band was retained. The loss of the linearity at 3500 cm⁻¹ was attributed to hydrogen bonding interactions of methanol with the polar moieties of the additives in these oils, shifting the peak maximum and affecting the overall band shape and width. In contrast, the gem-diol band was unaffected in terms of band position or shape, although its response (slope) varied somewhat with each oil. Table 5.1 summarizes the linear regression equations, moisture ranges investigated as well as regression statistics obtained for the gem-diol band for each oil type. Every oil has a somewhat different slope and all exhibited negative intercepts, implying that they contained residual water even after being stored over molecular sieves prior to water addition. The regressions are all highly linear (r>0.997) and all have SD's of <30 ppm, averaging \pm 22 ppm overall. This data indicates that for any particular oil type, largely defined by its viscosity and the manufacturer's additive package, one can develop a satisfactory peak height calibration based solely on measuring the gem-diol formed, even in used oils. The equations also indicate that the gem-diol peak height calibration is oil specific and that individualized calibrations would

Oil Type/Mix ¹	H ₂ O Regression Equation		R	SD
	(ppm)			(ppm)
Poly- α -olefin (Synthetic)	0-400	$[H_2O] = -118 + 44884A$	0.998	10
Oil A (Semi-synthetic)	0-850	[H ₂ O]= -369 + 57071A	0.998	20
Oil B (Conventional)	0-1200	$[H_2O] = -370 + 60891A$	0.998	28
Oil C (Conventional)	0-1200	[H ₂ O]= -409 + 50587A	0.999	20
Oil D (Conventional)	0-1200	[H ₂ O]= -525 + 48329A	0.998	27
Oil E (Conventional)	0-1200	[H ₂ O]= -359 + 36564A	0.999	22
Used Oil (Conventional/Synthetic)	0-1200	$[H_2O] = -64 + 62698A$	0.998	26

Table 5.1 Linear regression equations, correlation coefficients and standard deviations obtained for a variety of hydrocarbon oils by plotting the ppm water added to the oil against the peak height of the gem-diol formed in the differential spectrum collected

¹ All oils are hydrocarbon based, conventional oils are mineral oils, while composites are blends of synthetic and conventional oils.

be required for each oil type to be analyzed. This slope sensitivity is likely related to polarity differences in the oils, which in turn tend to be determined by the composition of the additive package.

5.4.4 PLS and Lubricating Oils

Although moisture analysis of lubricating oils appears possible using oil specific calibrations, the necessity of having to develop a multitude of distinct calibrations is not very convenient, nor practical. Multivariate chemometric approaches to calibration are a means by which more generalized calibrations may be devised even when substantial variability exists in the sample matrix to be analyzed (Adams, 1995). Among the oil samples being considered, the main sources of variability other than the component of interest (water), are additive package composition, the grade of the base oil (conventional, semi-synthetic or synthetic hydrocarbon) and the inter-component interactions (i.e., hydrogen bonding). PLS regression is a sophisticated chemometric tool that has been successfully applied to develop robust calibrations for complex interacting systems (Haaland and Thomas, 1988). Given enough information, PLS can distinguish and mathematically reduce systematic and random spectral contributions not directly associated with the spectral information correlating with the component of interest. The application of PLS was studied by pooling all of the spectra and relating each spectrum to its respective ppm of added water to which was added the intercept value (ppm) obtained by linear regression for the oil set (Table 5.1). Figure 5.8 illustrates the plot of the optimal PLS calibration devised after extensive study and optimization of regions that correlated with the moisture content. The regression equation for the validation plot was:

FTIR
$$[H_2O] = 3.93 + 0.994 H_2O$$
 r = 0.997 SD = 34.1 ppm [2]

These results indicate that the optimized PLS calibration is capable of predicting the moisture content of any of the seven oils listed in Table 5.1 to within \pm 34 ppm, only slightly higher than the average SD of ~22 ppm obtained using the individual peak height



Figure 5.8 Cross validation plot of the ppm water predicted by FTIR spectroscopy using the composite oil PLS calibration vs. the total moisture present in the samples.

calibrations. The PLS calibration, encompassing 3945-3156 cm⁻¹ and referenced to a single point baseline at 3764 cm⁻¹, includes the spectral contributions of the gem-diol, hemi-acetal and methanol absorptions. Restricting PLS to only the gem-diol spectral region did not work well as PLS requires information about all three component spectral contributions to be able to eliminate the confounding effects of the additives and component interactions. Attempts to drop the intercept contributions from the added water values also caused the PLS calibration to deteriorate markedly, providing indirect proof that the intercept values were not artifacts, but represented actual amounts of water already present in the oils.

In theory, PLS should also be able to calibrate on the unsubtracted spectra, rather than the differential spectra, stripping out the spectral contributions of the base oil and its respective additive packages without significant deterioration in quantitation. In practice, however, this was not found to work, apparently because our data set was too small to model the calibration adequately, most of the factors being used by PLS to strip out spectral variability of the oils and additive packages, leaving little information on which to model water. Hence it would appear that spectral subtraction is required, in effect to pre-process the data so that PLS is presented with more relevant spectral information to work with.

5.4.5 Karl Fischer (KF) Comparison

It was our intent to validate the FTIR calibrations and predictions for the oil samples against KF titration results. KF titrations were carried out on all the samples and standards, however, it became clear that the determination of moisture in commercial hydrocarbon lubricating oils by KF was not a trivial analytical exercise. Other than for PAO, neither the volumetric or potentiometric versions of the KF method, nor the use of specially formulated reagents (Anonymous, 1992), resulted in meaningful data being obtained for water spiked, branded oils containing additives. Only the PAO samples using hexylamine as a moisture carrier provided some semblance of tracking water spiked oil,



Figure 5.9 Plot of ppm water added to PAO vs. the ppm water determined by the volumetric (\bullet) and coulometric (\blacksquare) Karl Fischer methods.

the volumetric and potentiometric KF method results being compared in Figure 5.9. Both methods do track added moisture, however, their relative responses are quite different from each other as indicated by their respective regression equations:

 $KF_{v}[H_{2}O] = 130 + 0.46 H_{2}O$ r = 0.99 SD = 22 ppm [3] $KF_{p}[H_{2}O] = 7 + 0.80 H_{2}O$ r = 0.97 SD = 58 ppm [4]

Where: $KF_v = Volumetric KF$ $KF_p = Coulometric KF$ $H_2O = ppm water$

Both slopes are significantly less than 1.0, particularly in the case of the volumetric method, with the regression SD for the two methods averaging out to ~40 ppm. The poor KF PAO results and the inability to obtain sensible moisture data for the branded lubricants illustrate the problematic nature of the KF titration as applied to lubricants. Hence, rather than serving as a means of validating the FTIR method as originally intended, the KF analyses serve more to highlight the ability of FTIR to analyze samples which could not be analyzed by KF. These problems, as well as other limitations specific to the KF analysis of moisture in oils, have been summarized elsewhere (Anonymous, 1992).

5.5 DISCUSSION

This study has illustrated that DMP readily reacts with water, to produce three reaction products in equilibrium, a gem-diol, hemi-acetal and methanol under standardized reaction conditions (no acid, 1:5 DMP/oil ratio and 30 min reaction time). Via differential spectroscopy oil specific calibrations can be devised based on the linear regression of the gem-diol peak height vs. added water, the intercept providing an extrapolated value for any residual water in the base oil. A more generalized PLS calibration may be devised by pooling the differential water-spiked spectra of each oil type and relating it to the total water content (ppm added + ppm intercept).

At this point in time, only calibrations for mineral oils, synthetic hydrocarbon and their mixtures have been investigated. The feasibility of using the DMP approach for determining moisture in synthetic esters or other base oil classes (i.e., polyalkylene glycols, polybutenes and silicones) needs further investigation. Used hydrocarbon oil blends were also examined and successfully analyzed, however, the total acid number (TAN) of these oils was not known. The analysis of used oils could be problematic as the accumulated acidic compounds could serve to catalyze the reaction to produce acetone rather than coming to the desired multicomponent equilibrium. If accumulated acids are shown to be problematic, quantitation based on acetone will need to be examined.

Assuming the generalized PLS calibration developed is representative of the type of results obtainable for hydrocarbon oils, one can basically determine moisture contents in such oils to within \pm 35 ppm. Increasing the path length to 1cm, reducing the resolution to 16 cm⁻¹ and/or increasing the scans are means by which one could potentially reduce the variability of the analysis down to 10-15 ppm. The main drawback of the FTIR method is the need to scan the sample twice and the reaction time of 30 minutes after DMP has been added. The time drawback becomes minimal when multiple sample analyses are carried out. Typically it takes ~1h to prepare 15 samples and scan them twice with the 30 minute interval included, effectively requiring ~4 min per sample. This type of throughput can readily be attained on the COAT[•] (Dong, et al., 1997) analytical platform with the method programmed so that all the spectral manipulations and data processing are automated and the moisture content is output directly in ppm H₂O.

5.6 CONCLUSION

In summary, this work has demonstrated that FTIR spectroscopy in conjunction with DMP reagent can be used for the accurate determination of moisture in hydrocarbon lubricating oils containing additives. The method is clearly superior in this regard to the conventional KF direct titrimetric method for oils containing additives. The main advantages include reduced operating costs, the elimination of the hazards associated with KF reagents as well as minimizing solvent/reagent use and disposal. In its automated form, the FTIR DMP method could significantly reduce analytical time and labor requirements as well as providing reliable moisture content data, making it suitable for routine quality control and monitoring applications in the lubricant industry.

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BRIDGE

Chapters 3-5 describe in detail the concepts and methodology used to develop three new FTIR based methods for the analysis of TAN, TBN and H_2O , respectively. As such, they are rather specific and academic in their outlook and do not take into consideration the perspective of their implementation. As this research program progressed, the methods developed were being implemented as analytical packages to facilitate their use in an industrial setting. It was also necessary to provide an overview of these methods from a more practical context so that analysts in the field of tribology could grasp the general benefits, limitations and features of the methods developed. Chapter 6 presents an overview of the methods developed from such perspective, this paper having been presented at the annual Joint Oil Analysis Program (JOAP) conference held in Alabama in June 2000 and published in the conference proceedings. The purpose of this Chapter is to summarize the basic concepts, explain the potential benefits and bring into perspective the benefits of hardware and software integration so as to facilitate automation of the methods.

CHAPTER 6 DETERMINATION OF TAN, TBN AND MOISTURE IN LUBRICATING OILS BY A CONTINUOUS OIL ANALYSIS AND TREATMENT (COAT[®]) SYSTEM

6.1 ABSTRACT

Recently, three new Continuous Oil Analysis and Treatment (COAT[•]) analytical methodologies, total acid number (TAN), total base number (TBN) and moisture (H_2O), have been developed and implemented. These methods, employing a common sample handling/cell configuration, are based on the addition of reagents designed to react stoichiometrically with target species in oil, which are then quantitated by FTIR spectroscopy. The overall performance of these innovative FTIR methods has been demonstrated to be superior to the standard ASTM methods and their integration into Thermal-Lube's proprietary UMPIRE[•] software standardizes the procedures, making them rapid, simple, and routine to carry out. The methods require minimal amounts of sample and reagent and are substantially more environmentally friendly than methods currently in use. The COAT[•] System implemented with these methods should be of particular interest to commercial and industrial QC laboratories routinely analyzing for TAN, TBN and H₂O in volume.

6.2 INTRODUCTION

Routine monitoring of lubricant status plays an important role in the predictive maintenance of equipment (Robertson, 1984). Although commercial analyzers are available for some key analyses, the ability to analyze for total acid number (TAN), total base number (TBN) and moisture (H_2O) using a single instrument is not available. Fourier transform infrared (FTIR) spectroscopy has the potential to deliver multifunctional quantitative analytical capabilities, and the protocol developed by the Joint Oil Analysis Program (JOAP) of the U.S. Department of Defense to track a variety of changes in lubricant status over time has been an important step forward in FTIR analysis of lubricants. However, the JOAP protocol does not provide absolute quantitation of individual constituents, which has so far eluded implementation even

though the chemometric tools required have been available for some time. One of the main impediments to absolute quantitation is the variability in oil formulations, making it necessary in most cases to have available or identify an appropriate reference oil. Although highly accurate quantitation can be achieved when a reference oil is available, the reality is that often this requirement is impractical to meet. The methods described in this paper do not suffer from this limitation because they effectively employ the sample to be analyzed as its own reference. Based on this novel concept, three new analytical methods have been developed and implemented on a Continuous Oil Analysis and Treatment (COAT[®]) System. In this work we have specifically addressed the determination of TAN, TBN and H_2O , in recognition of the critical nature of these analyses in oil condition monitoring. This paper provides an overview of the analytical concept as well as the performance characteristics of these new methods.

6.3 INSTRUMENTATION/SOFTWARE

The COAT[®] System (Dong, et al., 1997; Akochi-Koblé, et al., 1998) consists of a ruggedized FTIR spectrometer, an associated PC loaded with proprietary Windows NT[®]based Universal Method Platform for Infra-Red Evaluation (UMPIRE[®]) software to drive the system as well as an automated sample handling accessory (Figure 6.1). The accessory consists of a micro-pump and a demountable transmission flow cell equipped with a by-pass, mounted on a slide rail within the optical compartment so as to allow an open-beam background spectrum to be acquired without removing the cell. The cell insert itself is simple to remove and exchange with other inserts, allowing one to switch pathlengths or window materials. The whole accessory can be heated and maintained at a specified temperature, an important consideration when working with viscous oils or greases.

Although the hardware elements are important, it is the software which is the key to the analytical flexibility of the COAT^{\bullet} System. The UMPIRE^{\bullet} software written using Microsoft^{\bullet} Visual BasicTM has been developed to facilitate implementation of oil analysis methods, whether based on new or well-established concepts. This software platform



Figure 6.1 Schematic diagram illustrating the key components of the COAT[®] System sampling accessory.

TAN @finaral-based fluic
Cinese (ASTA
TUN (Mineral-based fluid)
Weiter Chinesel based the

Figure 6.2 Method selection menu and output screen for various analyses including TAN, TBN, and moisture as implemented by UMPIRE[®].

allows one to define all the operating conditions, spectral collection settings, data processing, and output required for a particular method, in effect converting a generalpurpose FTIR spectrometer into a dedicated analyzer. As such, UMPIRE^{\circ} automates all aspects of an analysis and has been used to implement the established JOAP protocol, as well as the new TAN, TBN and H₂O methods. One can toggle between methods, in effect dedicating the system to a particular analysis (Figure 6.2).

6.4 METHODOLOGY AND ANALYTICAL CONCEPTS

Although the COAT^{\bullet} System is pre-programmed and capable of determining TAN, TBN or H₂O in lubricants, each analysis is a distinct procedure, using different reagents and protocols. As such, when multiple samples are to be run, the most practical approach is to analyze all the samples for one of these components before moving onto the next type of analysis. Approximately 30 ml of oil is required for each analysis. The three FTIR methods that have been developed all have a common, generalized procedural basis:

- (a) Select the analytical method from the method screen;
- (b) Rinse and load the cell with the oil to be analyzed and collect its spectrum;
- (c) Gravimetrically dispense the oil into a vial and add a reagent;
- (d) Cap, shake and allow to react;
- (e) Rinse and load the cell with the reacted sample and collect the spectrum;
- (f) UMPIRE[®] calculates the analytical result;
- (g) Repeat step (b-f).

These manipulations are minimal and straightforward, and the UMPIRE[®] software provides menu-driven prompts to guide the operator through the specific protocol associated with each method. In terms of calibration of the methods, it is important to recognize that generalized calibrations are provided for each method; the UMPIRE[®] software also provides the capability for refinement or development of new calibrations. In terms of analytical methodology, there are some unifying principles that are common to the three new methods developed, and these can be exemplified by examining the approach used in the determination of TAN. The titrimetric (ASTM D-974) and potentiometric (ASTM D-664) TAN methods provide an estimate of the total acidcontributing constituents present in an oil, primarily carboxylic acids, which are formed as lubricants oxidize. The carboxyl functional group (COOH) of these acids absorbs strongly in the infrared spectrum and can be quantitated fairly readily. However, there are often other carbonyl-containing additives in an oil formulation, which can spectrally interfere with the quantitative measurement of COOH content. Generally, considering the undefined additive packages used in oils and the variety of breakdown products that can form over time, lubricants are relatively complex and largely undefined chemical systems. It is this lack of chemical definition that is the cause of many analytical woes in the lubricant field. It is also one of the key problems facing quantitative FTIR analysis of lubricants, but fortunately there are ways of compensating for this problem, one of them being the application of differential spectroscopy in conjunction with the use of reagents that react stoichiometrically with the constituent of interest. This solution to the problem is illustrated in Figure 6.3 in relation to the determination of TAN and explained below to illustrate the basic concepts used in the new COAT[®] methodology.

Figure 6.3a presents a series of FTIR spectra of an oil to which various amounts of a carboxylic acid have been added, but could just as well represent the spectra of an oil undergoing oxidation. The main band is the absorption of the COOH functional group, and the intensity of this band could be used to estimate the TAN value, once an appropriate calibration equation has been derived. When a reagent is added to these oils (Figure 6.3b), the COOH functional group is converted to a salt (COO'X⁺), and a new band appears at lower frequency. The loss of the original COOH band reveals a previously unseen underlying absorption band, which is probably due to an additive present in the oil. This band is constant in this sample oil formulation, but this would not be the case in the real-world analytical situation. As a consequence, absolute quantitation based on direct COOH absorption band measurements in oils having variable



Figure 6.3 FTIR spectra of carboxylic acid and its salt. (a) Overlaid FTIR spectra of a motor oil spiked with various levels of a carboxylic acid, (b) the corresponding spectra recorded after addition of TAN reagent, and (c) the differential spectra obtained by subtracting the spectra in (a) from those in (b).

formulations is compromised. This problem is not necessarily solved by measuring the $COO^{-}X^{+}$ absorption band produced by addition of the reagent, as there may be underlying interfering absorptions due to additives or decomposition products in that portion of the spectrum also.

The solution to these complications is to collect the spectrum of the sample twice, once before reagent addition and once after reagent addition, and then subtract one spectrum from the other to obtain a differential spectrum. Figure 6.3c illustrates the differential spectra obtained by subtracting each of the spectra in Figure 6.3a from the corresponding spectrum in Figure 6.3b. The differential spectral series illustrates the loss of the COOH group as negative absorbance valleys and the formation of the COO'X' groups as absorbance peaks. Note that the overall baseline is level and that the absorption observed in Figure 6.3b at the same position as the COOH absorption and attributed to an additive in the oil is not present in the differential spectra. This is because the spectral features of this undefined constituent, as well as all spectral features of the oil that are unaffected by the addition of the reagent, are cancelled out when the differential spectrum is generated. The only spectral features left after reagent addition and spectral subtraction are spectral changes related specifically to TAN. Hence, in general terms, the process of addition of a reagent that reacts stoichiometrically with a particular constituent of the oil and spectral subtraction to generate a differential spectrum that reflects only the spectral changes resulting from this reaction provides an unambiguous means of quantitating the constituent in question. Use of this protocol circumvents the problem of undefined chemical variability affecting quantitation. As such, the necessity for a reference oil is eliminated because the sample prior to reagent addition effectively serves as a reference. Although the specifics (reagent and protocol) differ for each of the TAN, TBN and H₂O methods, these three methods all employ similar principles.

6.5 METHODOLOGY EVALUATION

Initially, it was our intent to analyze representative oil samples using the appropriate ASTM method and compare the COAT[®] results to the values obtained. To

gain experience with the ASTM TAN, TBN and H₂O methods and a sense of their relative analytical performance characteristics, we used standard addition of acid, base and water to a variety of oils. This approach was, however, found to be problematic, as even such model oil samples were difficult to analyze accurately by the ASTM methods. Both the titrimetric TAN (ASTM D-974) and potentiometric TAN (ASTM D-664) and TBN (ASTM D-2896) methods were troublesome and, depending on the oil formulation, proved to be fairly inaccurate, especially when dark or used oils were analyzed, since visual endpoints were largely indeterminate and potentiometric measurements tended to be erratic in these cases. Samples were also sent out to a laboratory specializing in lubricant analyses, and the TAN and TBN results obtained did not match or even track our gravimetric standard-addition values. Attempts to measure added moisture by the Karl Fischer (KF) method (ASTM D-1744) using volumetric or coulometric autotitrators were not confidence-inspiring either, both techniques being partially successful for only one of several oil matrices evaluated. Our KF problems were minor compared to the data presented in Table 6.1, showing the KF results obtained by General Motors for the moisture content for 42 identical oil samples sent to six different commercial laboratories on seven separate occasions. Our overall conclusion from working with the ASTM TAN, TBN and KF methods was that they were much too unreliable to serve as a basis for evaluating the analytical performance of the FTIR methods being evaluated. As such, we were largely forced to rely on gravimetric standard addition techniques to provide reference values and base the assessment of the COAT[®] method on its ability to track controlled changes in the constituent of interest.

6.5.1 COAT[®] System Methods I — TAN

As used oils with defined, but variable TAN values are not readily available, the tracking accuracy of the COAT[®]-FTIR TAN method was assessed by simple gravimetric addition of a thermally oxidized base oil, high in TAN, to a composite used bus oil sample. The TAN of the clear, oxidized base oil was determined by the ASTM D-974 method. Because the ASTM method did not yield reproducible values for the used bus oil, its TAN was determined by FTIR spectroscopy. The FTIR TAN values obtained from

	S1	S2	S 3	S4	S5	S6	S7	Average
Lab A	Trace	0	0	0	0	0	0	0
Lab B	397	203	321	195	106	77	71	196
Lab C	1020	2190	1300	1 990	250	280	153	1026
Lab D	143	218	182	193	166	76	130	144
Lab E	1100	2056	921	1525	142	135	44	705
Lab F	800	1200	1001	1300	600	600	400	843
Average	692	987	622	867	211	167	115	NA

Table 6.1 Karl Fischer moisture analytical results obtained for 42 identical oil samples analyzed by six commercial laboratories

Table 6.2 Replicate TAN predictions obtained by the COAT[®]-FTIR method for a composite bus oil spiked with different amounts of oxidized P-032 base oil having an ASTM TAN value of 4.7 mg KOH/g

ASTM TAN Added	0.00	0.12	0.53	0.91	1.27
(mg KOH/g)					
FTIR TAN	1.90	2.01	2.40	2.79	3.10
FTIR TAN	1.90	2.01	2.48	2.84	3.18
FTIR TAN	1.97	2.10	2.50	2.78	3.10
FTIR TAN	1.95	2.01	2.41	2.90	3.25
FTIR TAN	1.88	2.02	2.45	2.80	3.22
FTIR TAN	1.90	2.06	2.42	2.85	3.24
Mean	1.91	2.04	2.44	2.83	3.18
SD	0.039	0.038	0.039	0.046	0.067

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six replicate analyses of the oxidized base oil and of the bus oil samples to which the high-TAN oil was added are presented in Table 6.2. Linear regression of FTIR TAN vs. ASTM TAN (added) yielded the following equation:

FTIR TAN =
$$1.89 + 0.96$$
 ASTM TAN R = 0.997 SD = 0.045 [1]

This data indicates that there is a linear relationship between TAN added and the $COAT^{\bullet}$ -FTIR response, the FTIR method having an overall accuracy and reproducibility on the order of ± 0.05 mg KOH/g.

6.5.2 COAT[®] System Methods II --- TBN

The assessment of the COAT^{\bullet}-FTIR TBN method involved analyzing a fresh automotive engine oil, a used diesel bus engine oil, and a used diesel locomotive engine oil, each undefined in terms of additive composition. Each of these samples was analyzed 6 times, twice per day over three days. Table 6.3 summarizes the results obtained for these replicates and their corresponding statistics. These results provide an indication of the reproducibility of the TBN analysis in varying oil systems, the SD being slightly higher than obtained for the TAN method (~ 0.11 vs. 0.05 mg KOH/g). This slight increase in variability is likely due to the additional variables of varying oil formulations as well as repeating the analysis on different days.

Subsequently, various new and used oils, including an additive-free zero-TBN base oil and a number of diesel locomotive engine oils varying in viscosity and additive package composition, were analyzed for TBN by the ASTM D-2896 potentiometric method and the results compared to those of the FTIR TBN method (Figure 6.4).

It is clear from Figure 4 that the two TBN methods track each other and both measure basic components in the oil, but that their relative responses differ as illustrated by the regression equation derived for the data shown in the plot:

FTIR	TBN Locomotive	TBN Automotive	TBN Used Bus Diesel
Replicate	Oil (mg KOH/g)	Oil (mg KOH/g)	Oil (mg KOH/g)
la	9.59	7.27	5.28
1b	9.67	7.14	5.13
2a	9.80	7.27	5.32
2b	9.71	7.40	5.36
3a	9.90	7.33	5.19
3b	9.65	7.14	5.26
Mean	9.73	7.25	5.27
SD	<u>+0.10</u>	+0.12	<u>+0.10</u>

Table 6.3 FTIR TBN predictions obtained for three engine oils from duplicate analyses on three days



Figure 6.4 A plot of the FTIR TBN results vs. the ASTM TBN data for a variety of oils.

Subsequent experimentation, which involved the gravimetric addition of a $Ba(OH)_2$ overbased detergent to SAE W50 diesel engine oil, produced a 1:1 linear relationship between TBN added and FTIR response, with a regression SD of ±0.20 mg KOH/g.

6.5.3 COAT^e System Methods III — H₂O

The COAT[•]-FTIR H_2O method was evaluated using a series of commercial hydrocarbon lubricating oils first dried over molecular sieves and then spiked with known and increasing amounts of distilled water. In the methodology development process, it was noted that the FTIR analytical response was somewhat oil formulation dependent. This dependence was minimized through the development of a broadly based partial-least-squares (PLS) calibration, which increased the general applicability of the method, with the sacrifice of some accuracy. The overall predictive capability of the FTIR H_2O method for seven oil formulations, including an addivie-free polyalphaolefin (PAO), gravimetrically spiked with water, is presented in Eq. 3.

FTIR
$$[H_2O] = 3.93 + 0.994 * Added [H_2O] R = 0.997 SD = 34.1 ppm [3]$$

These results indicate that the COAT[•] method is capable of predicting the moisture content of mineral oils to $\sim \pm 34$ ppm. For comparison, Figure 6.5 presents the results of two of the more successful ASTM Karl Fischer analyses (the PAO) of a series of samples prepared by standard addition. The linear regression equations for these volumetric (v) and coulometric (c) KF analyses, respectively, were:

KFv =
$$130 + 0.46 H_2O$$
 R = 0.99 SD = 22 ppm [4]
KFc = 7 + 0.80 H₂O R = 0.97 SD = 50 ppm [5]


Figure 6.5 A plot of the volumetric and potentiometric KF results obtained for a set of oils vs. ppm water spiked into the oils.

These relatively good results, which were not the norm, illustrate a substantially different response for the two KF methods, neither having a slope very close to the expected value of 1.0. The FTIR method does not suffer from these problems, and its reproducibility is in line with that obtained using the KF method, although even better results can be obtained if the system is calibrated for a specific oil type rather than using the generalized calibration.

6.6 DISCUSSION/CONCLUSION

The development of FTIR methods for the determination of TAN, TBN and H_2O and their implementation on the COAT[®] System represents the first real quantitative analytical thrust in the lubricant sector to facilitate multiple analyses on a single instrument. The accuracy and reproducibility of these new methods have been shown to be excellent through standard addition techniques. Attempting to work with the standard ASTM methods on the assumption that the data obtained from these methods could readily be used as reference values for evaluation of the FTIR methods under development was found to be a generally frustrating exercise. It has become clear from our experience that these methods leave a lot to be desired in terms of sensitivity and reproducibility and are largely ill suited to the accurate analysis of such complex and variable matrices as lubricants can be. It is not that the principles of the ASTM methods are not sound, but rather that the reliability of these methods is limited by the wide variability encountered in commercial lubricants in terms of the constituents present, resulting in a multitude of interferences of a chemical, optical or potentiometric nature.

The new COAT[®] analyses that have been developed overcome one of the main stumbling blocks to quantitative FTIR analysis of lubricants — the need to have on hand a reference oil whose composition is a close match to that of the sample. Implementation of these new methods is facilitated by the UMPIRE[®] software, which makes it possible for the operator to simply follow the menu-driven instructions, add reagents and record the results. Each analysis requires only small amounts of reagent, reducing operating costs and minimizing disposal issues associated with the ASTM methods. When large sample volumes or throughput are a consideration, the COAT[•] System would significantly reduce analytical time and labor requirements, making it suitable for both routine quality control and monitoring applications in the lubricant industry as well as a useful unit for commercial analytical laboratories.

6.7 REFERENCES

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CHAPTER 7 GENERAL CONCLUSION

The research described in this thesis was undertaken with the intent to develop quantitative FTIR methods that would address key analyses associated with lubricant condition monitoring. Prior to undertaking this research, the McGill IR Group had focused on the development of quantitative FTIR analytical methods for the analyses of edible oils. Thermal-Lube, a Montréal lubricant formulation company, inquired whether the analytical concepts and methodologies that had been developed for edible oil analysis could be transferable and applicable to lubricant analysis and formulation control. Subsequently, a formal University/Industry research collaboration was entered into, and the research reported in this thesis was undertaken in the framework of that collaboration.

Although FTIR spectroscopy has become an important qualitative analytical tool for lubricant monitoring over the past decade, its quantitative use has been severely restricted, largely due to the complex and variable composition of the additive packages added to base oils. In edible oils, matrix variability is relatively limited because the product analyzed is predominantly composed of triglycerides with few additives present, usually antioxidants at low levels. This is not the case for lubricants, and it became clear early in this work that formulation variability was the major impediment to obtaining quantitative data using conventional analytical approaches. This problem was overcome through the use of specific reagents that react stoichiometrically with the constituents of interest to form products that have distinct and quantifiable IR bands, in conjunction with the use of differential spectroscopy to isolate these bands by eliminating the spectral contributions of the constituents of the oil. Although the use of a reference oil is an alternative approach to overcoming compositional variability, in practice, a suitable reference oil of known or consistent formulation is often not available. The application of the reagent/differential spectroscopy approach to quantification was initially developed for TAN analysis and was extended with modifications to TBN and moisture analyses, demonstrating the general applicability of this approach.

FTIR Methods

TAN analysis was selected as the initial FTIR method to be developed (Chapter 3), as TAN is one of the key condition monitoring parameters associated with a wide range of lubricants. Many of the basic principles of the reagent/differential spectroscopy approach were worked out with the TAN method, such as how best to deliver the reagent and monitor and quantify bands related to the constituent of interest. The FTIR TAN method was developed along the lines of the ASTM procedure, using KOH to convert acids to their salts. In simple systems such as PAO spiked with a fatty acid, the spectral changes observed upon reaction with KOH were relatively straightforward, and quantitation could be achieved by simple peak height measurement. Although more complex spectral behavior was observed for commercial oils with additive packages. largely because of the effects of hydrogen bonding on the absorption bands of the acids and their salts, accurate quantitation could be achieved by using PLS regression. Calibrations covering a TAN range of 0-4 mg KOH/g were developed by spiking oleic acid into randomly mixed low ester commercial oils and were able to predict the TAN values of validation samples to within +0.1 mg KOH/g. Analysis of used oils indicated that the FTIR method responded to the addition of acid and was able to track TAN in used motor oils. Because this method measures only carboxylic acid accumulation as opposed to total acidity, the TAN value obtained is not identical to that measured by the ASTM titrimetric method.

Whereas TAN analysis is applied to various lubricants, including used gasoline engine oils, in which increases in TAN are largely indicative that the oil has undergone oxidation, TBN is more commonly used for assessing diesel engine lubricants, in which acids are predominantly formed as fuel combustion by-products. Hence, diesel oils are formulated with substantial reservoirs of basic additives to neutralize the acids produced by combustion. A significant reduction in TBN is indicative of the accumulation of acids, regardless of their source. Chapter 4 considered the development of a TBN method, using concepts and principles established in the development of the TAN method. For the FTIR TBN method, trifluoroacetic acid (TFA) was used as a reagent to react with basic constituents in the oil to form IR-absorbing TFA salts, which were then quantified. Compared to the TAN method, the TBN method is less affected by the sample matrix because it uses a larger proportion of reagent solution (5.0 ml/0.5 g of sample). This allowed a relatively simple calibration to be developed with an additive-free PAO base oil using a simple peak-height approach. A calibration model covering a TBN range of 0-20 mg KOH/g was developed and was shown to be applicable to a wide range of mineral oils, based on the excellent reproducibility (±0.17 mg KOH/g) and accuracy (±0.20 mg KOH/g) obtained employing standard addition. Although not part of the results presented, subsequent analysis of blind diesel engine oil samples provided by Caterpillar Inc. indicated that the FTIR TBN method tracked the ASTM TBN results very well.

The third and last method investigated was the quantitative analysis of moisture in lubricating oils (Chapter 5). As in the other methods, a stoichiometric reaction was required which would produce IR quantifiable bands. After extensive investigation and testing of reagents and solvent systems, 2,2-dimethoxypropane (DMP) was determined to be a potentially suitable reagent. DMP was shown to react with water to form a gem-diol that exhibits a distinctive absorption band around 3700 cm⁻¹, a region where few mineral oil constituents absorb. The calibrations developed were shown to be oil dependent, but for a particular oil system/formulation, a simple peak height calibration was able to measure moisture to within ± 22 ppm. For the more general case, a PLS calibration is required and a good calibration was obtained by pooling oils, yielding a predictive accuracy of ~ ± 32 ppm over an analytical range of 0-1200 ppm moisture. Compared to the standard Karl Fischer method, FTIR moisture analysis was demonstrated to be superior in terms of repeatability and accuracy as well as more practical and reliable.

Implementation of the Methods

Although industry continues to rely largely on the traditional ASTM methods for routine analysis of lubricants, there definitely is a growing interest in the use of instrumental methods. This reflects a desire to replace cumbersome wet chemical methods and the growing environmental concerns associated with the disposal of organic

solvents and reagents associated with their use. Chapters 3-5 described three new FTIR methods that measure key parameters associated with lubricant condition monitoring. However, unless this methodology is packaged so that it becomes relatively straightforward to implement, it is unlikely to be accepted by potential users in industry in the near future. The industry is well aware of qualitative FTIR spectroscopy and its benefits but has been slow to adopt it, and quantitative FTIR methods introduce many additional complexities and unfamiliar elements. Chapter 6 attempts to summarize much of the work carried out in Chapters 3-5 from a perspective that addresses the requirements of lubricant technologists and engineers. More importantly, it presents the Continuous Oil Analysis and Treatment (COAT[®]) system on which these methods have been implemented. Powered by the proprietary UMPIRE[®] software and equipped with a flow cell accessory, the COAT^e system can run the three quantitative methods described in this thesis as well as standardized JOAP qualitative FTIR methods. The operating software provides appropriate instructions and prompts for the method chosen and also allows the input of supplemental information such as sample ID/description and operator name. Calibration update routines have also been developed that compensate for cell pathlength changes, maintain calibration stability, and allow calibrations to be transferred between instruments. Another important issue addressed in Chapter 6, but also relevant to Chapters 3-5, is the reliability of the ASTM standard methods. The ASTM methods are largely unworkable in many situations, especially in the analysis of used, formulated oils. Since FTIR spectroscopy is a secondary method, it is usually calibrated against a wellestablished and reproducible primary reference method. We have learned that the ASTM methods do not qualify as primary methods per se and wanted to make that clear to users, should they attempt to make comparisons between ASTM and FTIR results.

Limitations

Chapter 6 indicates that quantitative FTIR analysis methodology can be packaged, standardized, and automated; however, much depends on the development of suitable calibrations. The ideal, of course, is to have calibrations and methods that will handle all oils, under all circumstances. Based on our experience, that is not likely, as lubricants

comprise a wide variety of base stocks, ranging from mineral oils to a variety of synthetics. The methods developed in this study are presently only applicable to mineral based oils. For example, in the case of the TAN method, the analysis of a mineral oil/ester blend would be problematic because both the strong ester absorption band in close proximity to the carboxylic acid absorption band and attack of the ester by the KOH reagent employed in this method could compromise quantification. Hence, some type of categorization of oils based on the type of formulation would be helpful to allow methodology development to proceed in an organized fashion. On this basis, it may be possible to develop generalized methods for oil category types, where one would have one TAN method (calibration) for a turbine oil and another for a hydraulic oil. Clearly, this level of sophistication is still far off, but, in principle, such oil-specific methodologies could be developed.

Conclusion

The TAN, TBN and H₂O methods described in this thesis represent the first truly quantitative FTIR methods developed for lubricant analysis. By comparison with existing qualitative FTIR methods, the implementation of such quantitative methods would provide a better data base from which to develop cause and effect relationships between lubricant condition and equipment or component failure. Through the use of a reagent-based/differential spectroscopy approach, these new methods effectively overcome most interferences associated with an undefined sample matrix. They also require minimal amounts of solvents and reagents, resulting in dramatic reductions in chemical waste by comparison with the standard ASTM methods. Implemented on the COAT[®] system, these methods also provide a significant reduction in analytical time and labor and are suitable for routine quality control and monitoring applications in the lubricant industry as well as commercial laboratories. The methods that have been developed are presently limited to mineral based lubricants, but it is the author's belief that the door is now open to further developments in the field of quantitative FTIR spectroscopy in the lubricant sector and that others will further develop this new field of endeavor.