Analysis of Acidity in Oil-Based Matrices by Infrared Spectroscopy

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OIL ACIDITY DETERMINATION BY IR SPECTROSCOPY

Abstract

The feasibility of employing a portable variable filter array (VFA) infrared spectrometer equipped with a transmission flow cell to quantitatively analyze edible oils for free fatty acids (FFA) was evaluated. The approach to FFA determination was based on a previously reported FTIR method that involves the extraction of FFAs into methanol containing the base sodium hydrogen cyanamide (NaHNCN), which converts the FFAs to their salts, followed by measurement of the carboxylate absorbance at 1571 cm^{-1} in the spectrum of the methanol phase. The VFA IR spectrometer, which had a relatively weak pulsed IR source, was found to provide insufficient energy for accurate measurement of the carboxylate absorption superimposed on the strong methanol absorption at 1450 cm^{-1}. By changing the extraction solvent to ethanol, good spectra and calibrations having an overall SD of ±0.07% FFA could be obtained. This work in turn led to the investigation of an ethanol solution of NaHNCN as a signal transduction reagent for Acid Number (AN) analysis in mineral-based lubricants, whereby total acidity would be measured by monitoring the decrease of the νC≡N absorption of NaHNCN at 2109 cm^{-1} as a result of the acid/base reaction. The equivalent response of the νC≡N band to strong inorganic acids and oleic acid demonstrated that NaHNCN, a somewhat weaker base than KOH, fully ionizes organic acids. Calibration standards were prepared by direct addition of oleic acid to the NaHNCN/ethanol solution, and a calibration equation for the determination of AN was obtained by a quadratic fit of the concentration data to the FTIR νC≡N absorbance data. The AN values obtained for ethanolic NaHNCN extracts of used oils by the FTIR method correlated well with those produced by titration of these extracts. Comparison between FTIR and titrimetric AN values (obtained by ASTM Standard Method D664-89) for a set of used oils spanning an AN range of 0.3-5 mg KOH/g showed a reasonably good linear relationship (R = 0.985), with the FTIR method generally producing lower values. This tendency was attributed to the presence of weakly acidic species, which would be less extensively ionized by NaHNCN than by KOH. Implementation of the FTIR AN method on an autosampler-equipped spectrometer allowed for the automated analysis of up to 120 pre-prepared samples/h, representing a significant increase in analytical throughput relative to traditional titrimetric procedures. Thus, this research work has led to the development of two practical IR spectroscopic methods, one an economical instrumental means for at-line monitoring of FFA levels in crude and refined edible oils, and the second, an automated instrumental procedure for determining AN in mineral-based lubricants.

Résumé

La praticabilité d'utiliser un spectromètre infrarouge portatif comportant un filtre variable superposé à une barrette de détecteurs (dénommé un spectromètre VFA IR) et équipé d'une cellule d'écoulement de transmission pour analyser quantitativement les huiles de table pour leur teneur en acide gras libre (AGL) a été évaluée. L'approche à la détermination de la teneur en AGL a été basée sur une méthode précédemment élaborée sur un spectromètre infrarouge à transformée de Fourier (IRTF) qui implique l'extraction des AGL dans le méthanol contenant le cyanamide d'hydrogène de sodium, qui convertit les AGL en leurs sels, suivie de la mesure de l'absorbance de carboxylate à 1571 cm^{-1} dans le spectre de la phase de méthanol. L'Énergie fournie par la source pulsée relativement faible du spectromètre VFA IR s'est avérée insuffisante pour la mesure précise de l'absorption de carboxylate superposée à l'absorption forte de méthanol à 1450 cm^{-1}. En changeant le dissolvant d'extraction en éthanol, de bons spectres et des courbes d'étalonnage ayant un écart-type global de ±0.07% AGL ont pu être obtenus. Ce travail a à son tour mené à la recherche sur l'utilisation d'une solution d'éthanol et de NaHNCN comme réactif de transduction de signal pour une analyse de nombre acide (NA) en huiles lubrifiantes à base minérale, par lequel l'acidité totale soit mesurée par la diminution de l'absorption νC≡N du NaHNCN à 2109 cm^{-1} comme résultat de la réaction acide-base. La réponse équivalente de l'absorption νC≡N aux acides inorganiques forts et à l'acide oléique a démontré que le NaHNCN, une base légèrement plus faible que le KOH, ionise entièrement les acides organiques. Des solutions étalons ont été préparées par l'addition directe de l'acide oléique à la solution de NaHNCN/éthanol, et une équation de calibrage pour la détermination de NA a été obtenue par un ajustement quadratique des données de concentration aux données d'absorbance du νC≡N. Des valeurs obtenues pour les extraits éthanoliques de NaHNCN de huiles usées par la méthode IRTF ont concordé avec celles produites par la titration de ces extraits. La comparaison entre des valeurs obtenues par la méthode IRTF et des valeurs titrimétriques (obtenues par méthode standard D664-89 d'ASTM) pour un ensemble d'enjambement de huiles usées a montré un rapport linéaire raisonnablement bon (R = 0.985) pour une gamme de valeurs de 0.3-5 mg KOH/g, avec la méthode IRTF produisant généralement des valeurs plus basses. Cette tendance a été attribuée à la présence des espèces faiblement acides, qui seraient moins intensivement ionisées par NaHNCN que par KOH. Exécution de la méthode IRTF sur un spectromètre équipé d'un auto-échantillonneur a tenu compte de l'analyse automatisée de jusqu'à 120 échantillons/h

préalablement préparés, représentant une croissance significative de débit analytique relative aux procédures titrimétriques traditionnelles. Ainsi, ce travail de recherches a mené à l'élaboration de deux méthodes spectroscopiques d’analyse pratiques, la première, un moyen économique pour l’analyse sur place de la teneur en AGL en brut et huiles de table de raffinage, et la deuxième, une procédure instrumentale automatisée pour déterminer le NA en huiles lubrifiantes à base minérale.

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Contributions of Authors

Chapters 2 and 4 of this thesis are embellished texts of papers that have been accepted for publication. The thesis author was responsible for the concepts, design of the experiments and manuscript preparation. Dr. van de Voort was the thesis supervisor and had direct advisory input into the work as it progressed. Drs Sedman and Gonzalez contributed to resolving some of the software and chemometric issues related to this work, while Mr. Yu, a visiting scholar from China, contributed his knowledge of fats and oils analysis.

List of publications produced from this thesis:

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Application Note:

Li Yue and van de Voort, F.R.

Analysis for Free Fatty Acids (FFAs) in Oils for Biodiesel and Edible Oil Applications Using the InfraSpec (Appendix)

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Chapter 1 Introduction and Literature Review

1.1 Oils

An oil is a substance that is in a viscous liquid state at ambient or slightly warmer temperatures and is both hydrophobic (immiscible with water) and lipophilic (miscible with other oils). This general definition encompasses a wide range of classes of hydrophobic compounds with unrelated chemical structures, properties and uses, including vegetable and other edible oils (Gunstone, 1994) and petrochemical or mineral-based hydrocarbons (Ellinger, 1975). This thesis concerns itself specifically with edible oils (triacylglycerols) and mineral lubricating oils (hydrocarbons) from the standpoint of analyzing them for acidity by Fourier transform infrared (FTIR) spectroscopy.

1.1.1. Edible Oils and Acidity

Fats and oils are recognized as essential nutrients in both human and animal diets (Belitz et al., 2004). They provide the most concentrated source of energy of any foodstuff, supply essential fatty acids which are precursors for important hormones, the prostaglandins, contribute to the feeling of satiety after eating, are carriers for fat-soluble vitamins, and serve to make foods more palatable (Gurr, 1996). Fats and oils are present in varying amounts in many foods, with the principal sources being meats, dairy products, poultry, fish, nuts, and vegetable fats and oils. More importantly, fats and oils extracted from a variety of sources; predominantly plant based, are important commodities that are incorporated into processed foods and used in the oleo-chemical sector. From a chemical standpoint, edible oils are a mixture of triglycerides, which are the esters of glycerol and fatty acids of varying chain lengths and degrees of unsaturation (Belitz et al., 2004). The presence of free fatty acids (FFAs) in edible oils is largely the result of lipolysis, the hydrolysis of ester linkages in the triglyceride molecules by heat, enzymatic or chemical action. The FFA content of a crude oil is indicative of raw material quality and of potential refining losses (Hudson, 1989). In the refining process, the FFAs are removed by adding dilute NaOH and centrifuging out the soap formed. This process has to be carefully controlled to minimize refining losses due to saponification of the oil by excess

NaOH while ensuring that the residual FFA content is within specifications (typically, <0.1% by weight). This makes it imperative that the FFA concentration in the crude oil be determined accurately by at-line or on-line monitoring of this parameter in the refining process to minimize refining losses. Once oil has been refined, subsequent release of FFAs due to lipolysis or oxidation causes a reduction in the smoke point of the oil, representing a fire hazard and a source of air pollution, and can result in off-flavors and accelerate oxidation of the oil. As such, FFA content is a particularly important oil quality parameter associated with frying oils. Another means by which the acidity of oils can change is via the process of oxidation, mediated by a free radical mechanism. This results in the formation of hydroperoxides, which break down to form free fatty acids and other oxidative breakdown products such as aldehydes, ketones and alcohols. Most methods available for FFA analysis are insufficiently sensitive to detect the accumulation of FFA derived from this mechanism until the product is unacceptable organoleptically.

1.1.2 Lubricants and Acidity

A lubricant, commonly a mineral oil, is a substance introduced between two moving surfaces to provide a thin protective film or layer that lessens the friction between the surfaces and reduces wear (Ellinger, 1975). One of the largest applications of lubricants, in the form of motor oil, is to reduce friction and wear of moving components in internal combustion engines, which are used in motor vehicles and power equipment. In addition to lubricating, the lubricant also serves to dissipate heat, solubilize contaminants and minimize corrosion. Typically, lubricants are composed of a mineral base oil, usually a petroleum distillate or petroleum fraction, containing additives, which usually comprise <10% of the formulation (Wills, 1980). In general, these mineral oils are transparent, colorless oils and are composed mainly of alkanes, typically 15 to 40 carbons, and cyclic paraffins. Hydrogenated polyolefins, vegetable oils and/or synthetic esters may also serve as base oils, while silicones, fluorocarbons and many others types are used in specialty applications. Table 1.1 presents a list of the more common lubricant types produced commercially. The present study specifically focuses on simple hydrocarbon- based lubricants, best represented by polyalphaolefins (PAO).

Table 1.1. Oil classification system based on the predominant functional groups which characterize the oil (adapted from van de Voort et al, 2006).

Hydrocarbon based	**Functional groups**
Ground petroleum	CH
Synthetic polyalphaolefins	CH
Alkylated aromatics	CH, $CH_{(aromatic)}$
Monoalkylbenzenes	CH, $CH_{(aromatic)}$
Dialkylbenzenes	CH, $CH_{(aromatic)}$
Ester based	
Carboxylic acid esters	
Dicarboxylic acid esters (diesters)	CH, (O–C=O)
Dimer acid ester	CH, (O–C=O)
Polyols	CH, (O–C=O)
Polyoleates	CH, (O–C=O)
Phthalate	CH, $CH_{(aromatic)}$, (O–C=O)
Trimellitate	CH, $CH_{(aromatic)}$, (O–C=O)
Pyromellitate	CH, $CH_{(aromatic)}$, (O–C=O)
Phosphate esters	
Trialkyl phosphates	CH, O–P=O
Triaryl phosphates	CH, $CH_{(aromatic)}$, O–P=O
Alkyl aryl phosphates	CH, $CH_{(aromatic)}$, O–P=O
Polyalkylene glycols	
Monoalkyl ethers	CH, C–O–C, OH
Diol/triol ethers	CH, C–O–C, OH
Silicone based	
Silicone oils	CH, Si–O–Si
Polysilicone oils (siloxanes)	CH, Si–O–Si
Silicate esters	CH, O–Si=O
Polyphenylethers	CH, $CH_{(aromatic)}$, C–O–C
Polyfluoroalkylethers	CF, C–O–C
Chlorofluorocarbons	CF, CCl
Polymethacrylate/polyalphaolefin co-oligomers	CH, O–C=O

Mineral oil based lubricants usually contain additives, which may include detergents, antioxidants, dispersants, anti-foam additives, pour point depressants, polymer thickeners, etc., all of which serve to maintain or improve the performance of lubricants. These additive packages are proprietary and are usually undefined, complicating the makeup and hence the infrared spectral signatures of lubricants. From this perspective, lubricants can be divided into two categories, those containing base in their additive pack (over-based oils) and those which do not (Robertson, 1984). Over-based oils are usually destined for use in combustion engines and are designed to neutralize strong inorganic acids produced as a result of the combustion process in diesel and gasoline engines as well as engines running on natural gas. When these acids bypass the piston rings as blow-by, they accumulate in the oil sump and, together with organic acids formed by oxidative processes, acidify the oil. High acidity in lubricants can cause the formation of gums and lacquers on metal surfaces, increase viscosity, which impairs oil circulation, and cause corrosion, particularly if moisture is present (Anon, 1995). Oils that do not contain a base additive package are employed in applications in which the acidity accumulating is largely from oxidative processes only, so strong acids are not normally present. Some examples of the types of acids produced in various lubricants and their related applications are listed in Table 1.2.

In oils that do not contain a base additive package, acidity is measured directly as Acid Number (AN), in a manner analogous to the measurement of FFAs. In over-based oils, acidity is measured indirectly because strong acids are neutralized by the base package in the oil. Thus, the Base Number (BN) is determined by titration with acid to measure how much reserve alkalinity is left relative to the starting point (Kauffman, 1998), the decision to change the oil being made when this reserve is close to exhaustion *(*Anon 1994*)*. Both AN and BN are expressed in units of milligrams of KOH per gram of sample, irrespective of whether one is measuring acid or base. In addition to being used to monitor relative changes in acidity or reserve alkalinity in in-service oils over time, AN and BN analyses are also performed to characterize new oils.

Table 1.2. Acids found in lubricants based on their use. (Anon)

Acid Type	Source	Lube Application
Organic	Oil oxidation	All severe lubricant environment
HCl	Freon refrigerant breakdown	Chillers
HF	Freon refrigerant breakdown	Chillers
H_2SO_4	Diesel fuel and water, H_2S contamination, breakdown of anti-wear and extreme-pressure additives	Diesel engines, natural-gas compressors, hydraulic systems
HNO_3	Nitration and nitric oxides	Gas engines, gasoline engines
H_3PO_4	Phosphate ester degradation by-product	Mobile equipment, especially hydraulics

1.2 Standard Methods for Acidity Determination

A commonality associated with the oils discussed above is that acidity is of concern; accumulating in lubricants through oxidation, degradation or blow-by and in edible oils as a result of hydrolysis or oxidation. Standard methods for the determination of acidity in both types of oils are similar, but the test procedures used and the terms in which the results are expressed differ.

1.2.1 Edible Oils

Acidity in edible oils is expressed as %FFA, usually in terms of %oleic acid even though the FFA contributions are in fact variable and dependent on the oil's FA composition (Robards, 1988). FFA content is usually measured by standardized titrimetric methods by dissolving the oil in neutralized ethanol and titrating it with a strong base to a phenolphthalein end point. A number of official methods exist, including those of the AOAC, AOCS and IUPAC, but are effectively the same. The AOAC method (Anon, 1995) provides a procedure by which a standardized end-point color can be established as a reference point for subsequent analyses. The method is generalized but subdivided into expected acidity ranges, with the sample weight changing accordingly (more oil for the determination of lower FFA levels), as the FFA content of edible oils can range from 8% in crude oils down to <0.01% in refined oils. For refined oils, 56.4g is weighed out and added to 50 ml of ethanol and heated to 60-65^{o}C to ensure complete dissolution before titration. The sample is then titrated with 0.1N NaOH to a weak but consistent pink endpoint, established in the reference procedure. The FFA content of the oil is then calculated using the following equation:

$$\% \, FFA_{Oleic} = ((N*V)/ W)*MW \qquad (1)$$

Where: N = normality of the titrant
V= volume of the titrant
W = weight of oil
MW = molecular weight of oleic acid (282.461 g/mol)

This calculation is based on the assumption that FFAs are the only source of acidity in the material being analyzed. The procedure can be automated with an auto-titrator using a potentiometric equivalence point instead of a colorimetric end point, providing not only automation but also overcoming the difficulty of end point detection when dark oils are analyzed. Although relatively simple and straightforward, such methods are tedious and consume substantial amounts of environmentally problematic solvents and reagents.

1.2.2 Lubricants

The acidity sources in lubricants are far more variable than in edible oils. There are not only organic acids arising from oxidation, but if the lubricant is used in a combustion engine, there are also contributions from inorganic acids. In oils that do not contain a base additive package, acidity is measured directly by titration, in a manner analogous to the measurement of FFAs but expressed as Acid Number (AN), in units of mg KOH/g oil, rather than % FFA (oleic acid). The AN of a lubricant is calculated using the following equation:

$$AN = ((N*V)/ W)*MW_{KOH}*1000 \quad (2)$$

Where: N = normality of the titrant
V = volume of the titrant
W = weight of oil
MW_{KOH} = 56.106 g/mol

As mentioned above, in over-based oils, BN serves as an indirect measure of acid accumulation over time (Anon, 1995) and is therefore part of this discussion. Equation (2) is also employed for the calculation of BN, although BN is obviously not determined by KOH titration.

The American Society for Testing and Materials (ASTM) is the body that regulates and sanctions standard methods for lubricant analysis. Table 1.3 lists ASTM methods for AN (D974, D664) and BN determination (D974, D2896/D4739). Like FFA determination in edible oils, these methods are based on colorimetric or potentiometric titration, with the procedure employed being dependent on the oil, its use and its additive package.

Table 1.3. Common ASTM methods for determining acidity in lubricants (Anon,2004).

Method	Designation	Protocol	Indicator/pH	Comments
Acid/Base Number	D974	Colorimetric	*p*-Naphtholbenzein/11.5	
Acid Number	D664	Potentiometric/KOH	pH 4 and 11 endpoints	
Base Number	D4739	Potentiometric/HCl	pH 11 and 4 endpoints	Used oils
Base Number	D2896	Potentiometric/ $HClO_4$	mV	Basic additives

Since the acid types and strengths present in lubricants can vary dramatically, titrimetric AN and BN values are strongly dependent on the titrant used and the analytical procedure. Hence, there are clear warnings in the various ASTM methods that values obtained by different methods are not directly comparable. In this regard, it is instructive to examine the hypothetical titration curves presented in Figure 1.1.

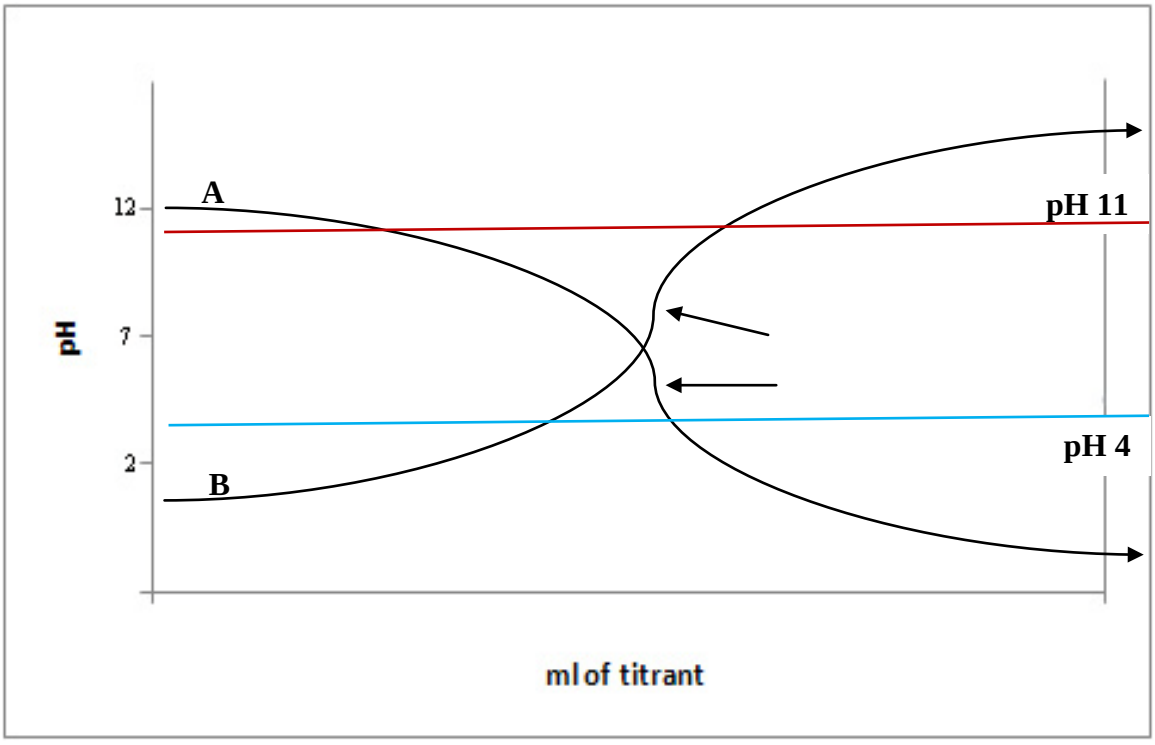

Figure 1.1. Titration curves illustrating the colorimetric end points and potentiometric equivalence points for strong acids and bases.

Titration curve A represents a strongly basic component present in an oil titrated with a strong acid and curve B illustrates a strongly acidic component titrated with a strong base. These curves show clear-cut inflection points, which represent the titration end points at which these strongly basic and strongly acidic components have been neutralized. The horizontal lines across the graph at pH 11 and pH 4 are the titrimetric end points considered to delineate weaker acids and bases, which produce pH values ranging from 4 to 11, from strong acids and bases, which produce pH values <4 and >11, respectively. Colorimetric pH indicators changing color around similar pH values are commonly used as titrimetric end points for non-potentiometric titrations (van de Voort et al, 2002). It is clear that when the same sample is titrated using different titrants or different indicators, the values obtained can be completely different. For instance, the two ASTM potentiometric BN methods in Table 1.3 use HCl (pK_a = -4) and $HClO_4$, (pK_a = -7), respectively, as titrant, the latter method being designed specifically to monitor the levels of very weak bases in the additive package that would not be neutralized by HCl (Anon, 2004). Similarly, very weakly acidic substances that may be present in lubricants, such as phenolics, lactones, resins, salts of heavy metals or ammonia, as well as acid salts of polybasic acids and certain additives, are considered the main cause of the non-concurrence between the results obtained by various titrimetric AN methods. In this context, it may be noted that carboxylic acids, common products associated with the oxidative breakdown of lubricants, generally represent the weakest acids in lubricants that are of significance in terms of corrosion and gumming (Frankel, 1980), and, accordingly, any base that is capable of neutralizing these constituents should be a suitable titrant for the determination of acidity in in-service oils.

For both colorimetric and potentiometric AN or BN methods, lubricant samples must be agitated and heated to ~60^{o}C to make sure any sediment is homogeneously suspended in the oil, then cooled and titrated below 30^{o}C. Colorimetric titration is only suitable for colorless and transparent samples, while potentiometric titration overcomes problems of end point detection in dark oils; however, the equivalence point can be very difficult to determine because all used lubricants are multi-acid/base systems, from which one can obtain multiple equivalence points. These and other factors limit the reliability of these

Table 1.4. Repeatability and reproducibility of ASTM AN methods (Anon, 2004)

Standard Method	Repeatability	Reproducibility
ASTM D974	5%	15%
ASTM D664*	11.70%	44%
ASTM D2896*	24%	32%
ASTM D4739*	22%	153%

* Based on used oils

methods as shown in Table 1.4, which lists the reported repeatability and reproducibility of these standard methods.

1.2.3 Summary

The measurement of acidity is a key analysis for the quality assessment of both edible and mineral oils. Traditional titrimetric methods are employed despite the many limitations and problems associated with these methods, largely because there are few other options. The McGill IR Group has worked toward the development of new instrumental methods for the analysis of edible oils and lubricants based on Fourier transform infrared (FTIR) spectroscopy. The research described in this thesis builds on previously developed FTIR methodology for the determination of acidity in edible oils and lubricants, with the objective of providing rapid, accurate FTIR methods as alternatives to the traditional titrimetric methods normally employed for this purpose The subsequent sections provide a brief introduction to FTIR spectroscopy and an overview of the literature relevant to understanding the work carried out.

1.3 Overview of FTIR Analysis of Oils

1.3.1 Basic Infrared Spectroscopy

Infrared (IR) spectroscopy is the study of the interaction between IR radiation and molecules, a quantum mechanical process (Doyle, 1992). This interaction results in the transition of molecules to higher vibrational levels after absorbing quanta of IR radiation. It is well known that electromagnetic radiation carries energy, and its energy content is proportional to its frequency. If any interaction or coupling between the radiation and a molecule occurs, energy transfer will take place. Two requirements must be met if IR

radiation is to be absorbed by a molecule. First, the incident ray must have the same frequency as a fundamental vibrational mode of the molecule and, secondly, this vibrational motion must cause a change in the dipole moment of the molecule. Thus, only frequencies that match the frequency of the skeletal or functional-group vibrations of the molecule can be absorbed. The frequencies of these vibrations depend on many factors, including bond strengths and the atomic masses of the bonded atoms, the spatial interrelationship of the atoms in the molecular unit and the molecular environment. The complexity of molecular vibrations virtually assures that no two different molecules produce identical IR spectra, so that matching the IR spectrum of an unknown with that of a pure compound, a procedure known as fingerprinting, is an unequivocal method of identification. To date, more than 200,000 reference spectra have been recorded and stored for fingerprinting (Li-Chan et al, 2002). In addition, because various functional groups have their own characteristic vibrational frequencies, which are fairly invariant irrespective of the molecule to which the functional group is attached, IR spectroscopy is useful for characterization of substances based on functional group analysis.

Apart from the qualitative aspects of IR analysis considered so far, IR spectroscopy has found a number of applications in quantitative analysis. In this type of IR analysis, one measures the amount of IR radiation absorbed by a functional group that is representative of a molecule or associated with a parameter. Quantitation is based on the Beer-Lambert law, where at a defined frequency (wavenumber) and a constant path length, the absorbance of a functional group is proportional to its molar concentration. Once calibrated and the extinction coefficient determined under defined conditions, the concentration of an unknown sample can be calculated.

Both qualitative and quantitative IR analysis benefited substantial from the advent of Fourier transform infrared (FTIR) spectrometers. Traditionally, IR spectrometers employed a dispersive element (grating or prism) to separate the beam from an IR source into its component wavelengths (Doyle, 1992). These dispersive IR spectrometers have largely been replaced by FTIR spectrometers, which do not have an optical dispersive element such as a prism or grating but instead use interferometry in conjunction with a Fourier transform to obtain a conventional spectrum. Figure 1.2 illustrates a Michelson

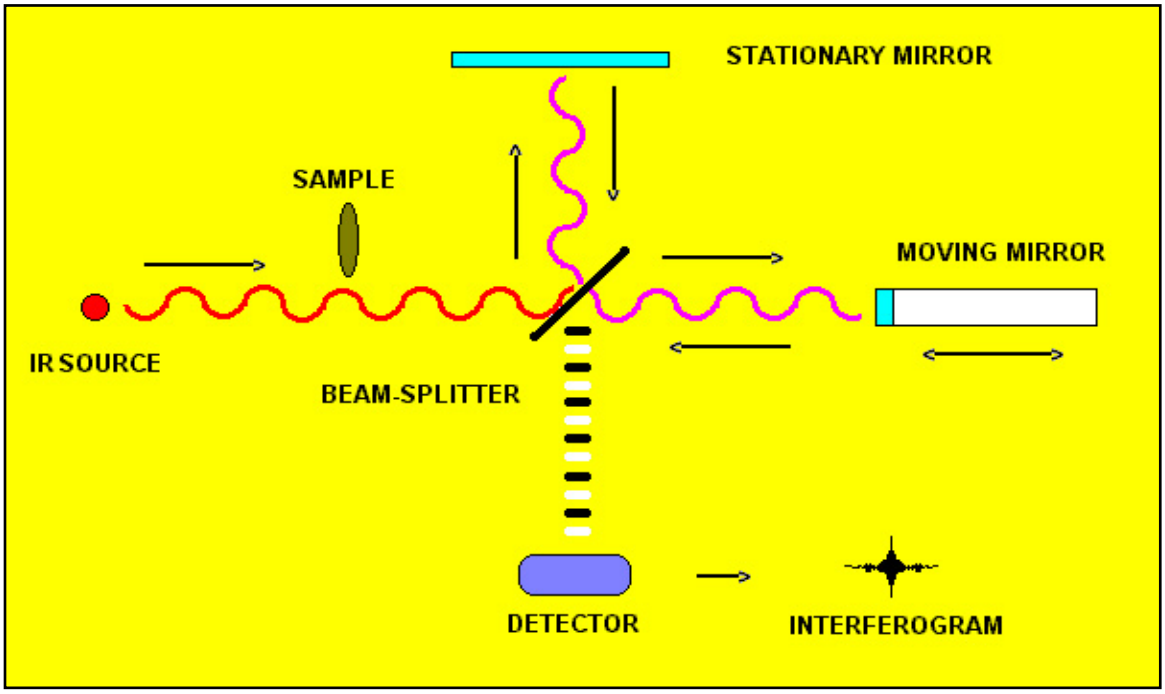

Figure 1.2. Schematic diagram of a Michelson interferometer

interferometer, showing the IR beam passing through a sample placed in front of the source and then reaching the beam splitter, where it is split, with half going to a fixed mirror and half going to a moving mirror. On reflection back to the beam splitter, the two light beams recombine, which will result in constructive or destructive interference, depending on whether they are in-phase or out-of-phase. The detector receives a successive sequence of high and low intensity energy in the time domain, which produces an interferogram. The interferogram is then converted into the frequency domain by a Fourier transform to produce a conventional infrared spectrum. Thus, in an FTIR spectrometer, all wavelengths are measured in a single sweep of the moving mirror. As a consequence, spectra can be obtained very quickly (~1 s) as opposed to a 10-min scan using dispersive instruments (Griffiths & De Haseth, 2007). This also allows for co-addition of scans to obtain better signal-to-noise ratio (S/N) spectra in a much shorter time frame. A second advantage of FTIR spectrometers is that they have no slits to attenuate the infrared beam as in dispersive spectrometers. This provides greater optical throughput. Finally, the frequency scale of the spectrum is very accurately determined by

passing a laser beam (usually HeNe at 632nm) through the interferometer together with the beam from the IR source to track the position of the moving mirror. This means that "mirror-movement averaging" is possible and there is no spectral diffusion. Consequently, co-addition of scans is accurate, and subsequent spectral manipulations such as spectral subtraction can be used with confidence, for example to remove the spectral contribution of a solvent to obtain that of the solute.

One disadvantage of FTIR instruments is that they are single-beam instruments, whereas dispersive instruments usually are double-beam spectrometers (Griffiths & De Haseth, 2007). Thus, separate background measurements are required before analysis of a sample. Assuming there are no appreciable changes in atmospheric conditions throughout the experiment, this does not cause a problem. However, for quantitative work and work where time is a factor, CO_2 and water vapor changes do affect specific regions of the spectrum, and purging of the instrument of CO_2 and water vapor by using either nitrogen or a Balston dryer may be a requirement.

Over the past 20 years, FTIR spectroscopy has evolved to become an important tool for both qualitative and quantitative analysis. This evolution has been due not only to a progressive decrease in the cost of FTIR spectrometers but also to the development of chemometric techniques for the multivariate analysis of FTIR spectral data, which have made it possible to extract much more of the information contained within IR spectra than was possible in the past. However, as these techniques are not relevant to the research presented in this thesis, they will not be discussed further.

1.3.2 FTIR Analysis of Edible Oils

The application of FTIR spectroscopy to edible oil analysis has been an active area of research (van de Voort et al., 2008). Figure 1.3 illustrates a typical spectrum of an edible oil and its associated functional groups. Table 1.5 associates these functional groups with corresponding analytical parameters that they can be related to. Based on the information on oil composition provided by FTIR spectroscopy, it has been possible to develop quantitative FTIR methods for FFA, iodine value (IV) (van de Voort et al., 1992), saponification number (SN) (van de Voort et al., 1992), peroxide value (PV) (Hamilton, 1998), *trans* content (van de Voort et al., 2006), moisture content (H_2O) (van de Voort et

al., 2007), and anisidine value (AV) (Przybylski, 2000). While some of these methods employ a simple univariate (Beer-Lambert law) calibration, most require multivariate calibration approaches, mainly partial-least-squares (PLS) regression using either molecular model systems or process samples (Defernez & Wilson, 1997). Several different types of approaches have been investigated for the determination of FFA content, and these will be considered in detail in Section 1.4.

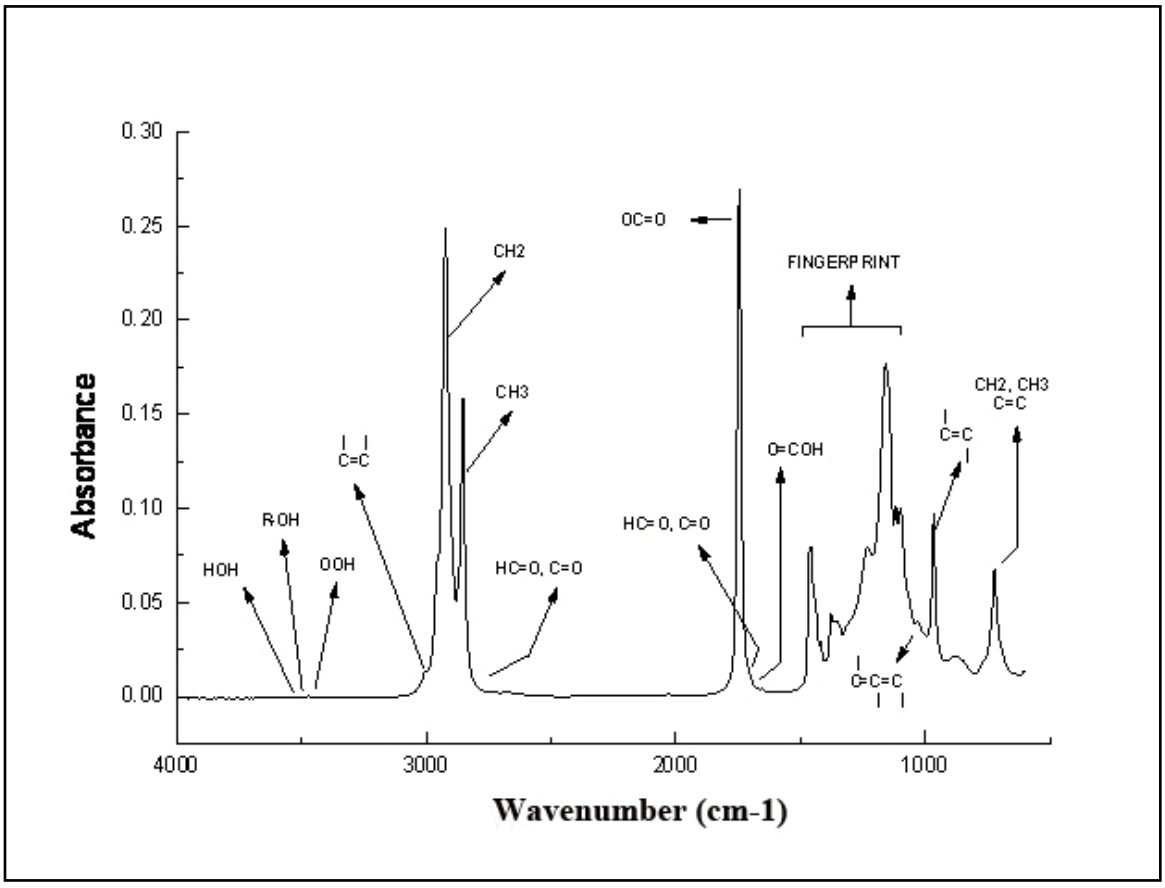

Figure 1.3. The mid-IR spectrum of an edible oil collected on an attenuated total reflectance (ATR) crystal. The functional-group labels indicate absorptions associated with triacylglycerols and minor constituents that may be present in oils.

Table 1.5. Functional groups found in edible oils, the compositional parameters or constituents that they can be related to, and the corresponding quality parameters traditionally measured by chemical methods.

Functional group(s)	**Parameter/constituent**	**Quality parameter**
C=C	Degree of unsaturation	Iodine value
cis-C=C, *trans*-C=C CH, C=C, C=C-C=C	Type of unsaturation	Trans analysis Fatty acid profile (GC)
CH	Chain length	Saponification number
OOH	Hydroperoxides	Peroxide value
HC=O	Carbonyl compounds	Anisidine value
COOH	Carboxylic acids	Free fatty acids
OH	Hydroxyl groups (mono/diglycerides)	Hydroxyl number
OH	Moisture	Moisture content
CH, C=C, O-C=O	Solids content	Solid fat index

1.3.3 FTIR Analysis of Lubricants

FTIR spectroscopy occupies a unique niche in the field of lubricant analysis in the form of condition monitoring (CM) of in-service lubricants (Anon, 2006). The CM protocol, originally developed and standardized by the Joint Oil Analysis Program (JOAP) of the U.S. military as a trending procedure (Toms, 1994), evolved into an ASTM Standard Practice (Anon, 2004). The Practice specifies various peak height/area measurements that serve to track deteriorative changes (soot buildup, nitration, oxidation, sulfation, etc.) in in-service oils over time and is designed to allow decisions as to whether an oil should be changed to be based on clear-cut spectral changes rather than just on time in service. Most major FTIR manufacturers supply instruments specifically configured for CM, which are utilized by centralized laboratories to qualitatively monitor engine oils and other lubricants. These CM systems generally couple an FTIR spectrometer with an autosampler and use a peristaltic pump to alternately push oils and a rinse solvent through a 100-μm flow cell, attaining throughputs of 20-30 samples/h.

By using FTIR spectroscopy to track additive levels in in-service oils in a manner analogous to CM, the McGill IR Group assisted Thermal-Lube Inc. a lubricant formulator, in the development of the COAT® (Continuous Oil Analysis and Treatment) system, which integrated an FTIR spectrometer and automated additive replenishment technology (Ismail et al., 1999), Subsequent collaborative work led to the adaptation of the COAT system for CM as well as the development of quantitative FTIR methods to determine three key quality parameters associated with lubricants, namely, acid number (AN), base number (BN) and moisture (van de Voort et al., 2006).

1.4 FTIR Determination of Acidity in Oils

As discussed above, similar titrimetric procedures are traditionally employed for the determination of acidity in both edible oils and mineral-based lubricants. From both a fundamental and a practical perspective, this commonality does not extend to FTIR analysis for numerous reasons. However, the development of FTIR methods for acidity determination in these two types of matrices, including the research that will be presented in this thesis, has seen much beneficial crossover of concepts and approaches. Owing to this crossover, the developments reviewed in this section will be presented in chronological order rather than being separated into edible oil and lubricant methods.

1.4.1 Direct Measurement of FFA in Edible Oils

Free fatty acids in edible oils are predominantly present as dimers, which have a *vC*=O absorption band at ~1712 cm^{-1}. Although *v*C=O absorptions are very intense, FFAs are present at low levels in edible oils, and accordingly this band is largely overwhelmed in the spectra of edible oils by the *v*C=O absorption of the triacylglycerol ester linkages and shows up only as a weak shoulder. Figure 1.4 illustrates this band overlap, which makes accurate measurement of the intensity of the FFA absorption difficult, especially at the very low levels of FFAs in refined oils (generally <1%). Other factors complicating the direct measurement of FFAs in edible oils are the sensitivity of the FFA *v*C=O band to polarity changes in the system and the deviation from Beer's law owing to the FFA monomer ↔ dimer equilibrium (Ismail et al., 1993). Thus, as discussed later, several indirect methods have been proposed that overcome the above limitations by converting the acid into its salt form, which relocates the band to ~1570 cm^{-1} and avoids self association.

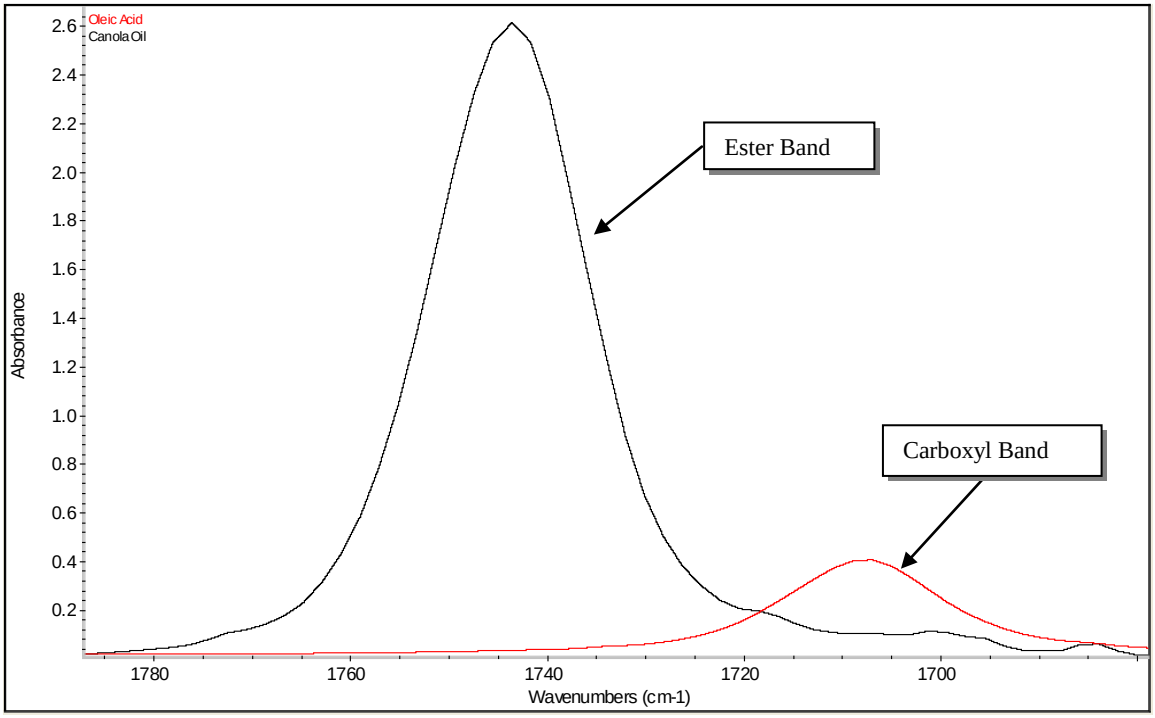

Figure 1.4. The *v*C=O absorption region, illustrating the ester band of triacylglycerols, and the carboxyl band of FFAs.

In 1991, Lanser et al. were the first scientists to use FTIR spectroscopy to determine FFA content in edible oil. Their methodology targeted crude soybean oil, and so a calibration was derived by spiking oleic acid into soybean oil at levels of 0.1–5%. The FTIR spectra of the standards were Fourier self-deconvolved to better resolve the FFA absorption band, and the area of this band in the deconvolved spectra, expressed as a percentage of the total νC=O area, was related to %FFA. The results obtained for samples of crude soybean oils extracted from damaged beans (0.5-2.1% FFA) indicated that the FTIR method tracked the AOCS titrimetric method Ca 5a-40 to within ±0.5% FFA, with the FTIR method being less sensitive. In addition, as the FTIR spectra were acquired by simply placing each sample between two KBr windows, without the use of an internal standard, the accuracy of this method was also limited by the resulting variability in pathlength. In 2001, Verleyen et al. used a fixed-pathlength flow cell to develop calibrations for a variety of oils based on peak height measurements at 1711 cm^{-1} and showed that the calibration equations were strongly oil dependent, largely owing to the band overlap discussed above. They also showed that calibration standards prepared by spiking the oils with oleic acid or lauric acid produced similar calibration equations to those prepared with FFAs obtained by saponifying the oils. Validation studies indicated that the reproducibility of the FTIR method was superior to that of the titrimetric method and that the FTIR data was in good agreement with the titrimetric data when the appropriate oil-specific calibration equation was employed. Biases were observed when the calibration for one oil type was applied to samples of a different oil type, confirming the need for oil-specific calibration equations. The use of partial-least-squares (PLS) regression, a chemometric technique that is often employed to develop calibration models that account for band overlap, was examined by Bertran et al., in two publications in 1992, which dealt with FFA analysis of palm oil and olive oil, respectively. However, in each case, the calibration developed was limited to one oil type and did not lead to generalization of the method.

1.4.2 Indirect Determination of FFAs in Edible Oils

In 1993, Ismail et al. investigated an indirect method for the determination of FFAs in edible oils. This method used a KOH/methanol solution to extract FFAs present in the oil and convert them to their salts, followed by measurement of the carboxylate ion

absorption band at ~1570 cm^{-1}. This approach eliminated spectral interferences from the triacylglycerol νC=O band and thus made it possible to develop an oil-independent calibration utilizing a simple peak height measurement. Subsequently, Cañada et al. developed an automated FTIR-based continuous-flow analysis system capable of analyzing ~40 samples/h using this indirect approach. However, they reported that even within the ~90 s required for analysis in this automated system, some saponification of the oil could occur, which limited the accuracy of the method.

1.4.3 FTIR Determination of Acidity by Signal Transduction

In 2003, van de Voort et al. developed FTIR-based instrumental methods to replace ASTM titrimetric procedures for the determination of acid number (AN) and base number (BN) in mineral and ester-based lubricating oils. The ASTM AN methods are similar to those traditionally employed for the determination of FFA content in edible oils except that they measure not only carboxylic acids but also a variety of other acidic constituents, organic or inorganic, that accumulate in lubricating oils either as a result of oxidation or as combustion by-products. However, from the perspective of FTIR analysis, the fundamental differences in the types of acidic constituents that may be present in lubricants as compared to edible oils required a completely new approach to the determination of acidity. Lubricant analysis was also complicated by much greater matrix variability, owing to the wide range of lubricant formulations on the market and the various contaminants and by-products that develop in in-service oils. Furthermore, lubricants tend to be more viscous than edible oils while the high sample volumes common in the field of lubricant analysis made automation a prerequisite (van de Voort et al., 2008). The approach developed by van de Voort et al. to address these issues was based on a concept termed *signal transduction*, which involved the addition of a basic (for AN determination) or acidic (BN determination) reagent solution to the oil sample followed by measurement of the changes in the spectrum of the reagent solution resulting from its reaction with the acids or bases present in the oil. In this manner, the “signals” from the various types of acids or bases present (some of which are not IR-active, e.g., HCl) were “transduced” into a single IR measurable signal. In addition, the dilution of the sample by the reagent solution minimized matrix effects and reduced sample viscosity.

For AN determinations, potassium phthalimide was used as the signal-transducing reagent while trifluoroacetic acid (TFA) was used in the BN method. These signal-transducing reagents were selected because the corresponding conjugate acid (phthalimide) and conjugate base (trifluoroacetate) have strong and readily measurable absorption bands in the mid-IR spectrum. 1-Propanol, which is the lowest alcohol that is miscible with oils, served as a carrier for the reagents. To eliminate spectral interferences, the AN and BN methods employed a two-step analytical protocol. The oil sample was split into two halves, one half was treated with the propanol solution of the signal-transducing reagent while an equal volume of propanol was added to the other half, and the spectra of the two halves were then recorded and subtracted from each other to produce a differential spectrum. In this manner, the spectral features of the oil were removed and the spectral changes resulting from the acid-base reaction were isolated. This is illustrated in Figure 1.5, which shows the differential spectra obtained for a mineral oil spiked with various amounts of the weak acid 4-nitrophenol (4-NP) and analyzed by the AN method utilizing potassium phthalimide. With increasing AN, there is a progressive increase in the two νC=O bands of phthalimide as well as a split 4-NP band, with the negative component representing the loss of the neutral form while the positive component is due to the formation of the ionized form. In the case of Figure 1.6, showing the differential spectra obtained for a mineral oil spiked with various amounts of the weak base dodecylamine, the only bands observed are associated with the ionization of the signal-transducing reagent, trifluoroacetic acid, as dodecylamine does not exhibit any bands in the portion of the IR spectrum displayed in this figure.

The FTIR AN and BN methods were validated by analyzing a large variety of new and used lubricants and comparing the results with those obtained by standard titrimetric procedures. On an FTIR spectrometer equipped with an autosampler, ~60 samples/h could be analyzed, a good throughput relative to automated titrimetric procedures. This was possible because the oil samples were diluted with propanol, reducing their viscosity and facilitating sample flow. One disadvantage of these methods was the two-step procedure, which doubled the analysis time. However, as described above, this procedure was necessary to compensate for oil spectral interferences.

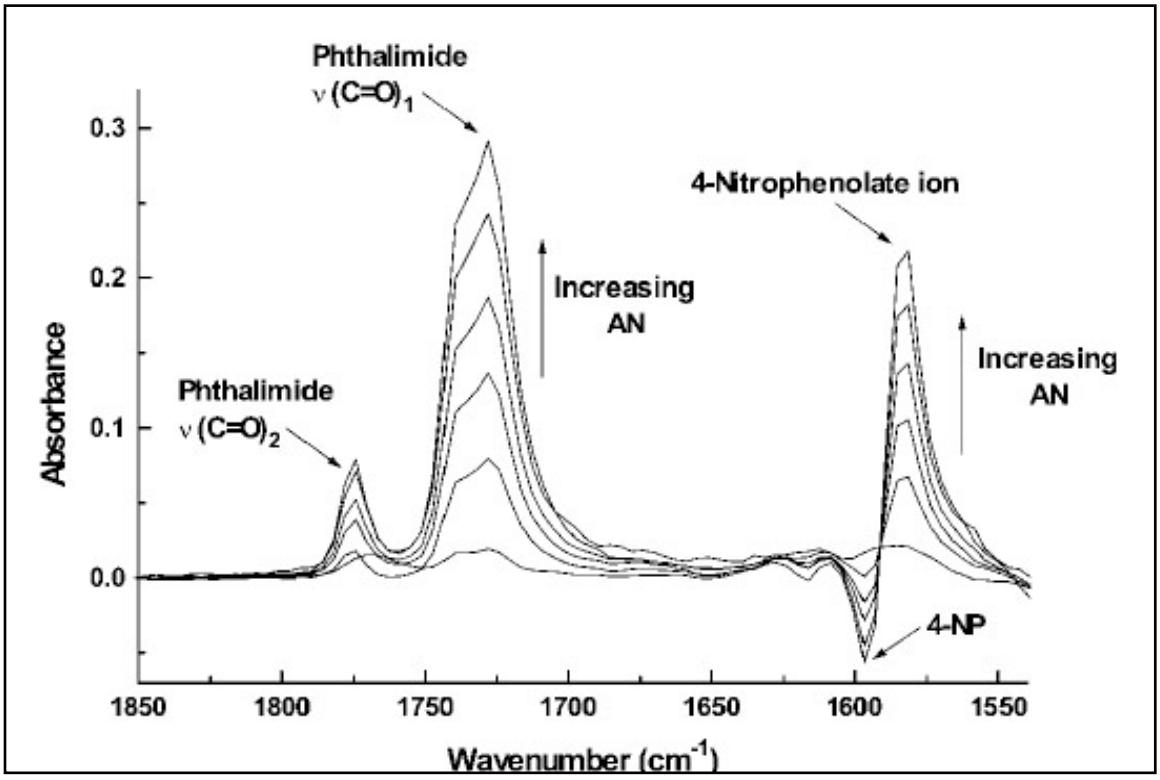

Figure 1.5. Differential spectra obtained for PAO spiked with varying amounts of 4-introphenol (4-NP), representing AN values of 0-5 mg KOH/g oil, and treated with potassium phthalimide as the signal-transducing reagent, illustrating the increase in the phthalimide $\nu(C=O)_1$ (1727 cm^{-1}) and $\nu(C=O)_2$ (1774 cm^{-1}) bands with increasing AN.

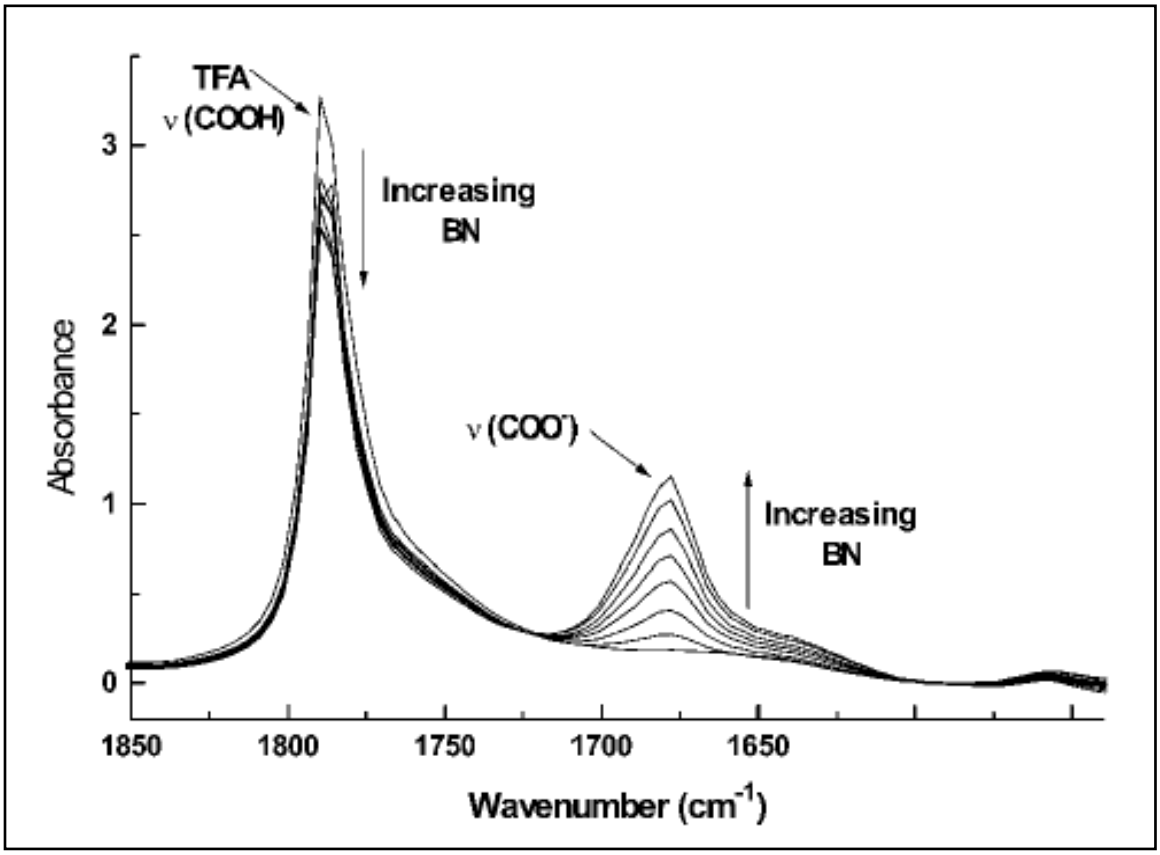

Figure 1.6. Differential spectra generated for a series of samples prepared by spiking PAO with dodecylamine (BN 0–20 mg KOH/g oil), illustrating the relative changes produced in the *v*COOH (1788 cm^{-1}) and *v*COO^- (1679 cm^{-1}) absorptions of the signal-transducing reagent TFA and its anion.

In 2004, Al-Alawi et al. investigated the application of the AN method of van de Voort et al, 2003 to the determination of FFA content in edible oils as an alternative to the indirect method of Ismail et al., 1993. The objective was to overcame the possibility of saponification associated with the strong base (KOH) used in the indirect method by employing a milder base, potassium phthalimide (pK_a = 8.3), to convert FFAs to their salts. Because the phthalimide formed in this reaction has a strong absorption band that overlaps with the carboxylate absorption of the FFA salts, determination of the FFA content was based on signal transduction as in the AN method described above. Although shown to be a very reliable method overall, having an SD < 0.020% over a FFA range of 0-4%, it was not ideal owing to the two-step procedure.

In 2005, Al-Alawi et al. investigated the use of a methanol solution of sodium hydrogen cyanamide (NaHNCN) as a signal transduction reagent in the determination of FFA content in edible oils. NaHNCN, although a stronger base than potassium phthalimide, did not cause any saponification of the oil, while the use of an oil-immiscible solvent (methanol) as the carrier eliminated the need for a two-step procedure to compensate for oil spectral interferences. However, as will be discussed further in Chapter 3 of this thesis, the rapid tautomerization of NaHNCN in methanol to its carbodiimide form (NaNCNH) did not permit its use as a signal transduction reagent. Thus, the determination of FFA content was based on the measurement of the carboxylate band of the FFA salts, making this method a variant of the indirect method of Ismail et al. but overcoming the problem of saponification associated with the latter method. As such, this new method provided a significant improvement in the accuracy and reliability of FFA determination in edible oils.

1.5. Rationale and Objectives of the Research

Over the past two decades, there has been a steady evolution in the analysis of acidity in edible oils and lubricants by FTIR spectroscopy. In the case of edible oils, the methodology in its present form is well suited to central laboratories and high-speed, high-volume analysis, but it is not suited for routine industrial laboratory use due to the cost of the instrumentation. The first objective of the work described in this thesis was to determine if a newly developed, low-cost variable filter array IR spectrometer might be

used to carry out the determination of FFA in edible oils as per the NaHNCN-based method of Al-Alawi et al. (2005). Chapter 2, which is presented in paper format, describes the work carried out and its results. A discovery made during the course of this work that led to the evaluation of the potential use of NaHNCN as a signal transduction reagent is presented in Chapter 3, which serves as a transition to Chapter 4, in which a new FTIR method for AN determination in mineral-based lubricants is described. The overall relevance of this work is summarized in the concluding chapter along with suggestions for future work.

Chapter 2 Determination of FFA in Edible Oils Using a Variable Filter Array (VFA) IR Spectrometer

2.1 Introduction

Although FTIR spectroscopy is a powerful analytical tool, for some applications all of its attendant capabilities may not be required once an analytical method has been developed and is to be implemented. Thus IR instruments with more limited resolution or wavelength range(s) may suffice for some dedicated applications, such as milk analysis (van de Voort et al., 1980, 1992), where simple, fixed-wavelength filter instruments are widely employed. Recent innovations in infrared instrumentation include miniaturization and portability through the combined use of variable filter array (VFA) technology and electronically modulated (pulsed) sources. By interposing a transmission cell (or ATR accessory) between a pulsed IR source and a linear variable filter (LVF) superimposed on a 64-pixel pyroelectric infrared detector array, a simple, compact spectrometer with no moving parts can be produced (Wilks). An LVF is a wedge-shaped interference filter that spatially resolves the IR beam into bands of wavelengths because the filter bandpass varies linearly as a function of the thickness of the filter. With each pulse of the source (1 pulse/s), a "scan" is generated as the different wavelength bands impinge on different pixels of the detector array, and multiple scans can then be co-added to improve the signal-to-noise ratio of the spectrum obtained. Because the pulsed source is cool, since it is not continually on, it can be placed close to the sample accessory and detector, maximizing the energy throughput of this relatively weak IR source, and this allows the instrument to be very small. Figure 2.1 illustrates the VFA instrument used in this study, the Infraspec produced by Wilks Enterprises (South Norwalk, CT), and its specifications are presented in Table 2.1. The Infraspec is controlled by proprietary software running on a Windows platform (Windows 98 or higher) and can be linked to a computer or Personal Data Assistant (PDA) via a USB connector. The system runs on 9 V DC power and the software provides basic capabilities such as setting the number of scans and allows one to display the spectra collected. The LVF in the instrument employed in the present study had a spectral resolution of ~30 cm^{-1} across a wavelength range of 5.5-10.5

microns (1818-952 cm^{-1}). This low-resolution IR spectrometer potentially provides one with the ability to implement pre-established FTIR methods, such as analysis for free fatty acid (FFA) content of fats and oils, on a compact, portable and rugged unit.

The FFA content of triacylglycerol oils (triglycerides) is an important quality or process control variable which strongly affects the utility and value of an oil when used as an edible oil or as feedstock for biodiesel methyl ester production. The FFA content of oils is usually determined by dissolving the oil in alcohol and titrating it with a strong base to a phenolphthalein end point (AOCS, 1989). Although relatively simple and standardized, such titrimetric methods are tedious, consume substantial amounts of solvent and use environmentally problematic reagents, as well as being of limited reliability when dark, crude oils are analyzed. FTIR spectroscopy has been developed as an instrumental means of determining the FFA content of triacylglycerol oils, with a wide range of approaches having been considered. Among these, the most sensitive and versatile is that developed by Al-Alawi et al., 2005, which involves mixing oil with an immiscible solution of methanol containing sodium hydrogen cyanamide. This process extracts the FFAs as well as stoichiometrically converting them to their respective sodium salts; which are then measured in the spectrum of the methanol extract (Figure 2.2) to determine the FFA content from a calibration devised from an oil spiked with known amounts of a pure fatty acid standard.

This chapter describes the implementation of the cyanamide method on a VFA-IR spectrometer, including modifications made to both the instrument and the method to optimize analytical performance, and evaluates its capability to quantitatively determine FFA content of edible oils relative to that of a FTIR spectrometer.

Figure 2.1. The Infraspec VFA IR spectrometer with transmission flow cell and Luer-Lok needle used to aspirate the sample into the flow cell.

Table 2.1. General specifications of the Wilks Infraspec VFA IR spectrometer.

Characteristic	Specification
Dimensions	5″ × 5″ × 1.5″, 12.7 × 12.7 × 3.8 cm^3
Weight	3.5 lbs., 1.5 kg
PC Interface	RS 232
Power Requirements	9V DC, 2.0 amps
Power Supply	Universal AC/DC converter type
Detectivity D* @ 10 Hz	$1.5\text{-}10^8$ $(cm \cdot Hz)^{0.5}$ /W
Temperature Operating Range	15^oC–60^oC
Humidity	0–98% RH (non-condensing)
Detector Array	64 Pixel linear pyroelectric array
Standard Spectral Ranges	2.5–5 μm (400-2000 cm^{-1}) 5.5–11 μm (1818-910cm^{-1})

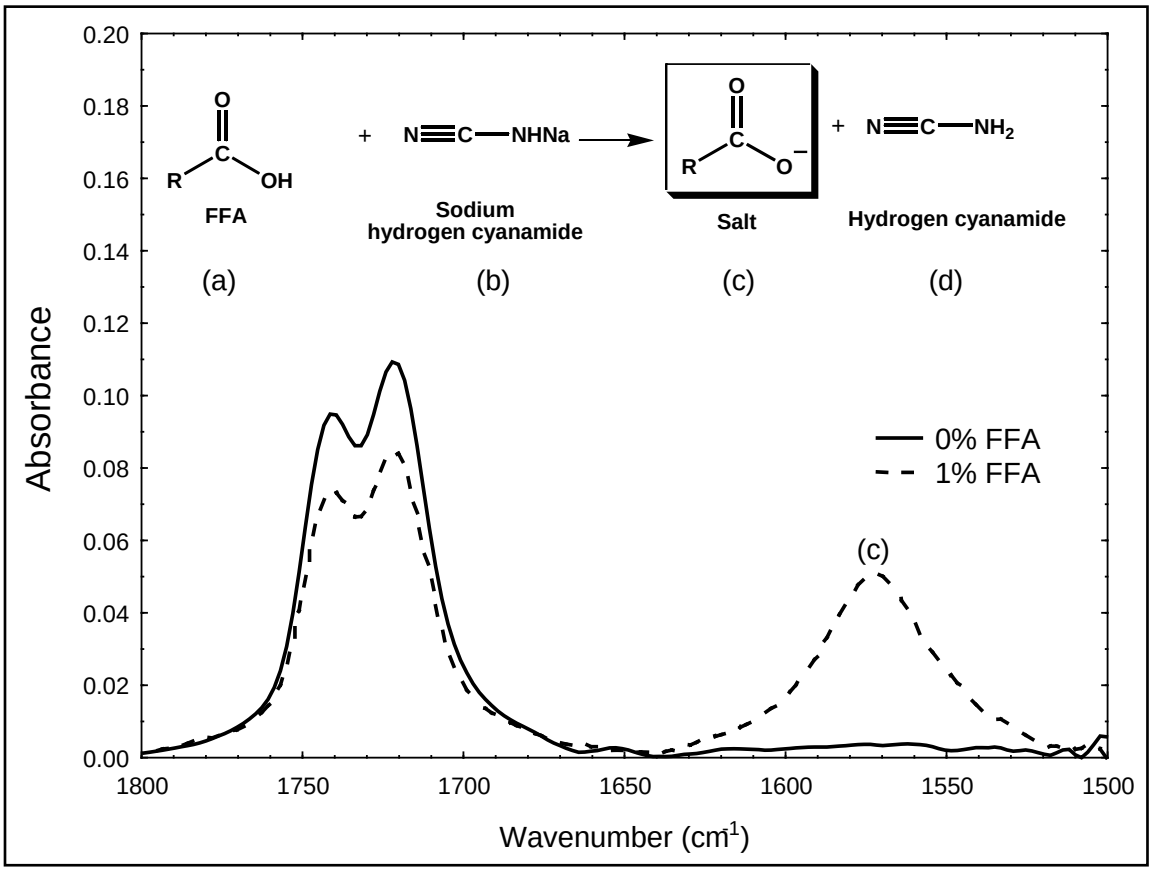

Figure 2.2. The stoichiometric reaction associated with IR analysis of oils for their FFA content and the corresponding spectral changes taking place when carboxylic acids extracted into methanol react with sodium hydrogen cyanamide.

2.2 Materials and Methods

Two extraction solvents were used in this work: reagent-grade methanol and absolute ethanol, both dried over molecular sieves for 24 h prior to use. Reagent-grade oleic acid, used as the fatty acid calibration standard, and sodium hydrogen cyanamide (NaHNCN), also known as sodium carbodiimide, were both obtained from Sigma-Aldrich (St. Louis, MO). Concentrated extraction-reagent solutions were prepared by dissolving NaHNCN in either anhydrous ethanol or methanol at a concentration of ~2 g/l or 9 g/l, respectively. In the case of methanol, the NaHNCN solution was "aged" for a minimum of 4 days to allow the nitrile (C≡N) form to convert to the carbodiimide (C=N=C) form, indicated by the complete disappearance of the nitrile band at ~2100 cm^{-1} (Al-Alawi et al., 2005). Aging was not required for ethanol solutions as this transformation occurs much more slowly (~60 d). Refined edible oils of various types were purchased locally and were used for calibration as well as validation purposes.

2.3 Sample Preparation/Calibration

Details of the cyanamide FFA method have been published elsewhere (Al-Alawi et al., 2005). The analytical protocol used for both calibration standards and unknowns involved mixing oil with selected ratios of extraction-reagent solution, mixing on a vortex mixer for 30 s and then centrifuging the samples for 2 min to separate the layers. The upper solvent layer was aspirated by vacuum into a 100-µm transmission cell and its spectrum recorded. Calibration oils were prepared by running locally purchased, refined, bleached and deodorized (RBD) oils through an activated silica gel column to remove any residual FFAs that may have been present. These oils were gravimetrically spiked (±0.0001 g) with oleic acid to obtain precise levels of added oleic acid over two ranges, 0-1% and 0-5%. These standards were then extracted using the extraction-reagent solution, and the spectra of the extracts were recorded. After ratioing out the spectrum of the extraction-reagent solution, the absorbance at ~1573 cm^{-1} (νCOO^-) was measured relative to a baseline at ~1687 cm^{-1} The absorbance values obtained for the standards were regressed against the % FFA added to generate a standard curve, which was subsequently used to calculate the FFA content of the validation samples. All analyses were run in duplicate.

2.4 Spectroscopic Analysis

For this work a Bomem Work IR (ABB Bomem, Quebec, QC, Canada) was used as the reference instrument to generate conventional FTIR FFA data via the cyanamide method (Al-Alawi et al., 2005). FTIR spectra were recorded at a resolution of 4 cm^{-1} by co-adding 16 scans and were ratioed against the spectrum of the extraction solution as a background and converted to absorbance spectra. The net result of this protocol is that the solvent contributions common to the background and sample spectra are ratioed out, leaving only the spectrum of the constituents extracted from the oil. This basic protocol was also followed for analysis by the Infraspec VFA IR spectrometer (Wilks Enterprises, South Norwalk, CT), with both instruments sharing the same 100-µm CaF_2 flow cell (ICI International Crystal Laboratories, Garfield, NY) equipped with Luer-Lok fittings. The ethanol or methanol extracts were loaded into the cell by aspiration using a stainless steel Luer-Lok needle (Figure 2.1). A two-way valve controlled the loading and emptying of the cell, and a solvent trap was located in the outlet line. Spectral data processing and statistical analysis were carried out using TQ Analyst 7.2 (Thermo Electron Inc.) and Origin.

2.5 Results

2.5.1 VFA-IR Characteristics

The fats and oils sector requires simple, rugged at-line instrumentation capable of analyzing key quality and process control parameters such as FFA content, whether in relation to processing of edible oils or screening of biodiesel feedstocks. The portability (e.g., interfaced to a PDA), ruggedness and simplicity of the VFA IR spectrometer make it particularly suitable for such purposes. However, its low resolution and limited capabilities relative to FTIR spectrometers could compromise its ability to perform quantitative analysis. In the present study, a preliminary assessment of the performance of a VFA IR spectrometer in relation to the methanol-cyanamide procedure for FFA analysis using a 100-µm cell indicated that the system was energy-limited, as “bad pixel” warnings issued by the software were an indication that insufficient energy was reaching the detector in some portion of the spectrum collected. This was not an issue for the FTIR spectrometer, which uses a hot Globar with substantially higher energy output relative to

the cool pulsed source of the VFA IR spectrometer. These warnings were eliminated when the cell pathlength was reduced from 100 to 50 μm, but this resulted in an unacceptable reduction in sensitivity and restricted sample flow. It was found that the energy could be increased sufficiently to allow for use of a 100-μm cell simply by moving the source from its original location, ~5 cm from the cell window, to ~1 cm from the cell window. With the source re-located in this manner, the increased energy throughput was sufficient to eliminate "bad pixel" warnings. The VFA IR spectrometer was subsequently evaluated in terms of signal-to-noise (S/N) performance relative to the FTIR spectrometer by measuring the peak-to-peak noise in spectra obtained by ratioing back-to-back open-beam scans against each other. As can be seen in Table 2.2, the noise level in the VFA IR spectra was ~20× higher than in the FTIR spectra for the same number of co-added scans. Although the noise level progressively decreases as the number of co-added scans increases, it was concluded that for practical purposes, there was little to be gained in S/N beyond 32 co-added scans (corresponding to a spectral acquisition time of ~30 s). Accordingly, this was the setting used in all subsequent experimentation.

2.5.2 FFA Analysis with the Use of NaHNCN/Methanol

The basic principle associated with the determination of the FFA content of an oil by the method investigated in this study is the extraction of the FFAs into methanol and their conversion to their respective salts, which are subsequently measured in the IR spectrum

Table 2.2. Average peak-to-peak noise in milli-absorbance (mAbs) units for the VFA IR and the FTIR spectrometer

Number of co-added scans	Peak-to-peak noise (mAbs)	
	VFA IR	FTIR
8	5.6	0.34
16	3.7	0.21
32	2.4	0.1
64	1.5	0.085
128	1	0.075

of the methanol extract. To assess the feasibility of employing a VFA IR spectrometer for the determination of FFA content at the low levels generally found in process samples (<0.1-1%), standards covering this restricted range were prepared by spiking acid-free Canola oil with known amounts of oleic acid and were then mixed in a 1:1 (w/w) ratio with a methanol solution of NaHNCN (9 g NaHNCN/L). The FTIR and VFA IR spectra of these standards are compared in Figure 2.3. The FTIR spectra illustrate a clear absorption band at ~1571 cm^{-1}, which is due to the νCOO^- absorption of the carboxylate salt produced by the reaction of oleic acid with NaHNCN. In the VFA IR spectra, this band is not resolved from the strong methanol absorption band in this region, owing to the much lower resolution of the VFA IR spectrometer (~30 cm^{-1} vs. 4 cm^{-1}). Relating FFA concentration to the FTIR spectral response measured at 1571 cm^{-1} (relative to a baseline at 2000 cm^{-1}) produced an excellent standard curve (Figure 2.4a). Despite its lower resolution, the VFA IR spectrometer yielded similar quantitative information when the carboxylate response was measured at 1598 cm^{-1} (6.257 μm) relative to a baseline at 1687 cm^{-1} (5.926 μm) (Figure 2.4b). The calibration equations obtained for the FTIR and VFA IR spectrometers are presented below:

$$\%FFA_{(FTIR)} = 0.008 + 5.167*Abs_{(1571/2000\ cm^{-1})} \quad R = 0.998 \quad SD = 0.015 \qquad (3)$$

$$\%FFA_{(VFA\ IR)} = 0.002 + 6.024*Abs_{(1598/1687\ cm^{-1})} \quad R = 0.997 \quad SD = 0.029 \qquad (4)$$

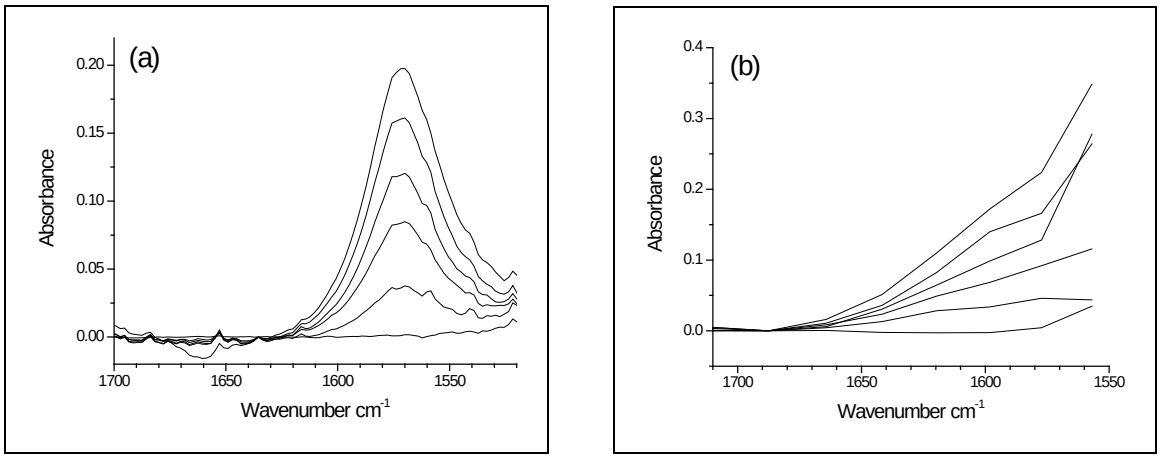

Figure 2.3. Calibration spectra obtained for FFA standards (0-1% oleic acid in Canola oil) using the Bomem FTIR spectrometer (a) and the Infraspec VFA IR spectrometer (b).

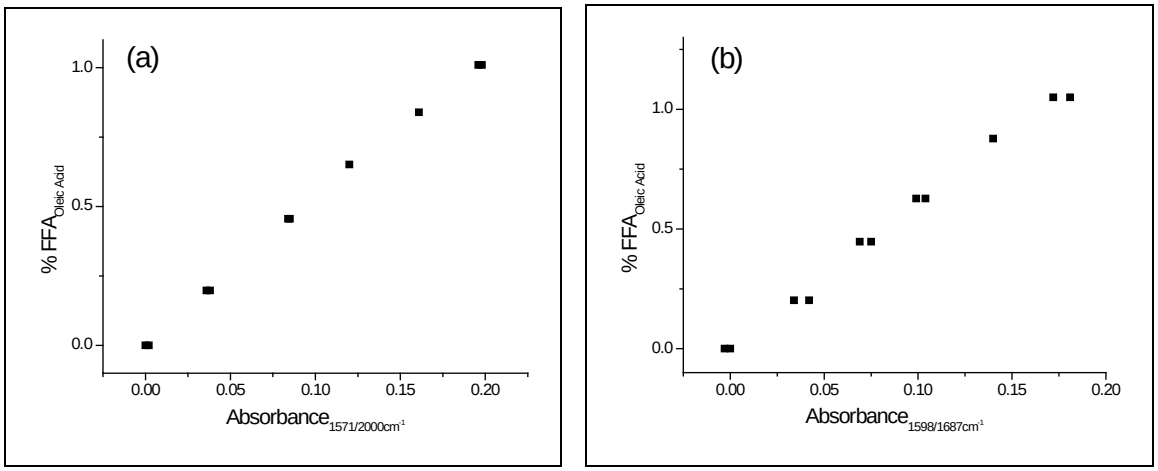

Figure 2.4. Calibration plots of % FFA vs. peak height of the carboxylate absorption for the FTIR (a) and for the VFA IR (b) spectrometer.

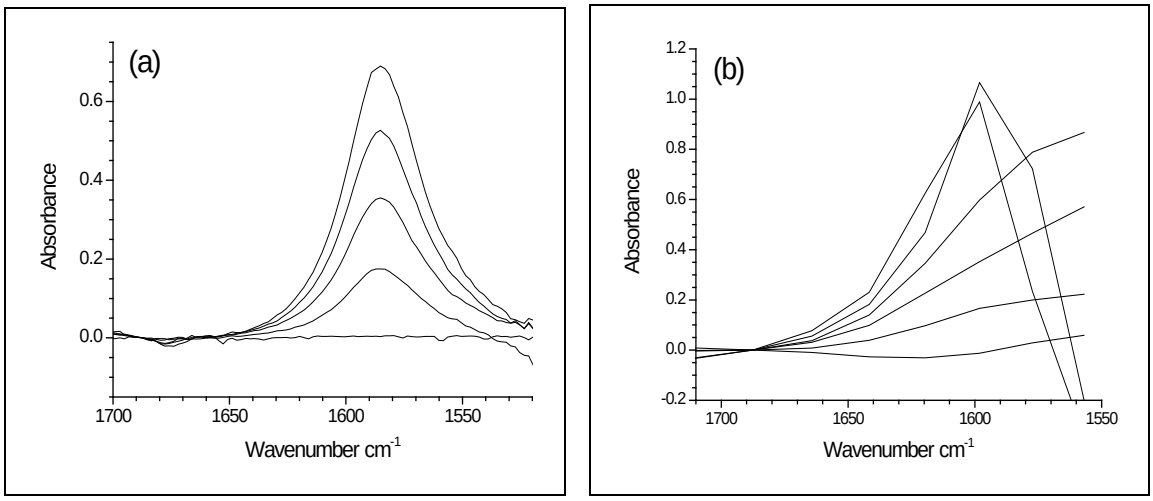

Figure 2.5. Calibration spectra obtained for FFA standards (0-5% oleic acid in Canola oil) using the Bomem FTIR spectrometer (a) and the Infraspec VFA IR spectrometer (b).

Thus, the VFA IR spectrometer is capable of tracking lower levels of added oleic acid quite well, with the SD being about double that of the FTIR (0.030 *vs.* 0.015% FFA). Subsequent work involved assessing the performance of both instruments over an FFA concentration range of 0-5%, performance over this range being essential for the analysis of crude oils and biodiesel samples, where high FFA levels are often encountered. In the FTIR spectra (Figure 2.5), a clear-cut progression in absorbance at 1571 cm^{-1} as the concentration of FFA increases is still observed, while in the case of the VFA IR spectra, the trend previously observed over the 0-1% range is perturbed, with the higher concentration samples in the calibration series producing truncated spectra and "bad pixel" warnings. Calibration based on the same measurements as used for the 0-1% calibration produced the following regression equations:

$$\%FFA_{(FTIR)} = -0.013 + 6.204*Abs_{(1571/1799\ cm^{-1})} \quad R = 0.999 \quad SD = 0.045 \qquad (5)$$

$$\%FFA_{(VFA\ IR)} = 0.267 + 4.305*Abs_{(1598/1687\ cm^{-1})} \quad R = 0.977 \quad SD = 0.402 \qquad (6)$$

As can be seen, there was a clear deterioration of the calibration SD over the 0-5% range for the VFA IR spectrometer relative to the FTIR spectrometer. However, by moving the VFA IR measurement wavelength one data point over to 1620 cm^{-1}, the calibration equation SD improved to a more acceptable value of ±0.107%:

$$\%FFA_{(VFA\ IR)} = 0.21 + 7.93*Abs_{(1620/1687\ cm^{-1})} \quad R = 0.998 \quad SD = 0.107 \qquad (7)$$

It was concluded that the VFA IR spectrometer was again becoming energy limited, specifically at higher FFA levels (>3%) owing to the combined absorption of MeOH and FFAs. Thus, while there was enough residual energy over an FFA range of 0-1% to obtain good quantitative results, at higher FFA concentrations the absorption at 1598 cm^{-1} exceeded the available source energy, taking the absorbance off-scale. Making the measurement at a higher wavenumber compensated somewhat, but with a loss in sensitivity. Since no further energy could be gained by reconfiguring the instrument, other than by shortening the cell pathlength and losing sensitivity, a simple modification of the method was considered, as described in the following section.

2.5.3 FFA Analysis with the Use of NaHNCN/Ethanol

The effects of a change of the solvent in the reagent solution from methanol to ethanol were assessed as a potential means of overcoming the energy limitations discussed above. Figure 2.6 presents the spectral region of interest in the FTIR spectra of methanol and ethanol in a 25-µm cell, illustrating that ethanol absorbs half as much energy as methanol and should thus provide substantially more residual energy to work with to measure FFA salts in solution. Testing indicated that the solubility of NaHNCN in ethanol was substantially lower than in methanol (~2 g/L vs. ~10 g/L) and that the NaHN-C≡N → NaN=C=NH conversion was much slower (~60 d vs. ~4 d). Despite these differences, the reactivity of NaHNCN toward FFAs was similar in the two solvents. However, as a consequence of the lower solubility of NaHNCN in ethanol, the oil:solvent ratio had to be increased to 1:5 to provide sufficient reagent to convert up to 5% oleic acid to its salt form.

Typical VFA IR calibration spectra covering the range of 0-5% obtained using the ethanol reagent solution are presented in Figure 2.7. As can be seen, there is a substantial improvement in the appearance of the calibration spectra, the energy gain manifesting itself in well-defined spectra, more in line with the FTIR spectra (Figure 2.5), albeit of lower resolution. These spectra yielded the following calibration equation:

$$\%FFA_{VFA\text{-}IR(EtOH\text{-}1:5)} = 0.249 + 22.445*Abs_{1598/1687\ cm^{-1}} \quad R = 0.999 \quad SD = 0.075 \qquad (8)$$

Even though a 1:5 oil:solvent ratio was employed (as compared to 1:1 in the case of the methanol reagent solution), resulting in the measurement of lower concentrations of FFA per unit volume (larger slope in Eq. 8 than in Eq. 6), the calibration SD improved relative to the methanol procedure (± 0.075 vs. 0.107%). Thus, the use of the NaHNCN/ethanol reagent solution allows the VFA IR spectrometer to be used for the analysis of a wider range of FFA contents to within <±0.1%. However, if samples to be analyzed are routinely expected to have FFA contents below <1%, then the original MeOH-based procedure would be a better method in terms of sensitivity and accuracy as the extract is less dilute.

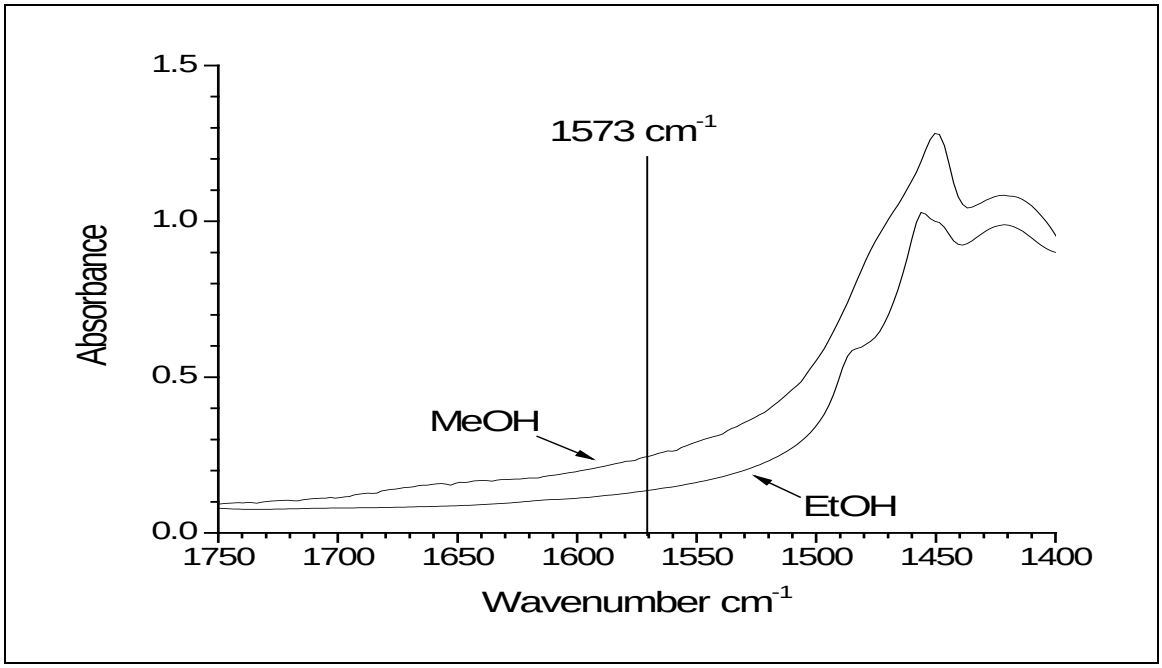

Figure 2.6. Comparative spectra of methanol and ethanol recorded in a 25-μm CaF_2 cell, illustrating their relative absorption profiles in the 1750-1400 cm^{-1} region.

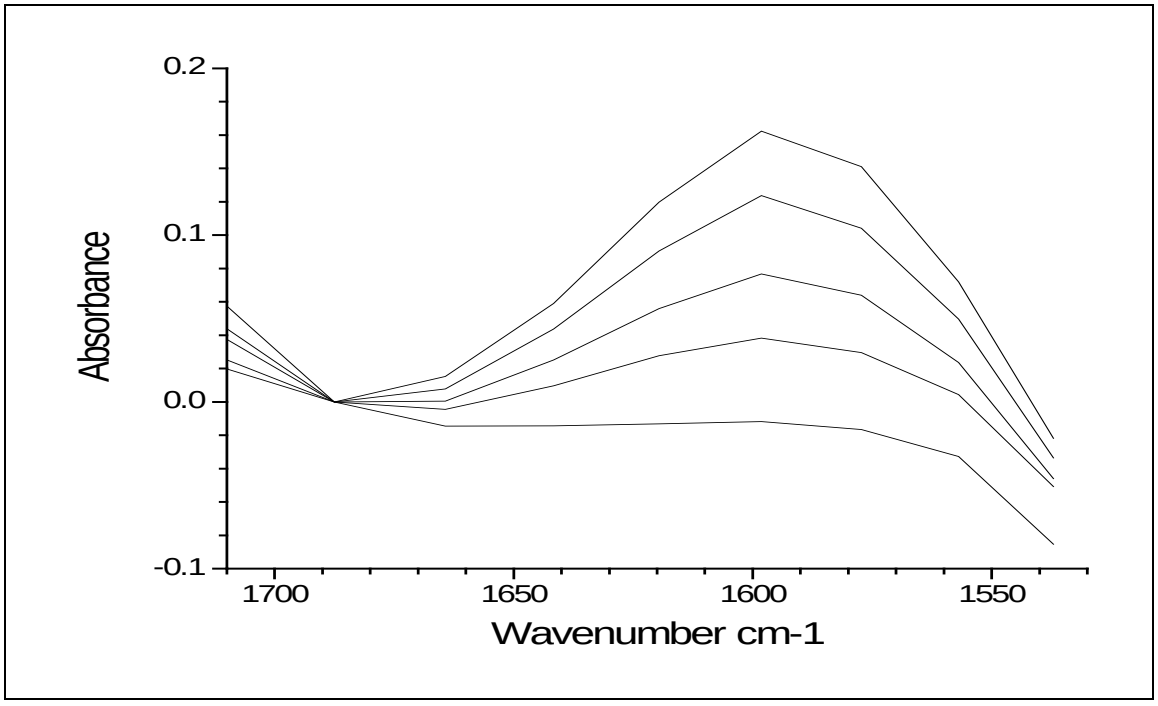

Figure 2.7. Calibration spectra obtained for FFA standards (0-5% oleic acid in Canola oil) after addition of the NaHNCN/ethanol reagent solution in a 1:5 oil:solvent ratio.

2.6 Conclusion

Based on the results of this work, the VFA IR spectrometer is capable of replacing a conventional FTIR spectrometer to analyze for FFA content in oils using the method developed by Al-Alawi et al, 2005. If the method is only to be used to measure low levels of FFA (<1%), no modification of the original method is required; however, the use of ethanol as the extraction solvent in place of methanol allows for the accurate analysis of a wider range of FFA concentrations. Thus, a VFA-IR spectrometer can serve as a portable, dedicated FFA analyzer, providing a simple and economical instrumental means of determining FFA levels in crude and refined edible oils as well as biodiesel feedstocks and, as configured in this study, can readily analyze 20-30 samples/h once the samples have been prepared for analysis.

Chapter 3 Transition - New Opportunity for Total Acidity Determination

In Chapter 2, the use of sodium hydrogen cyanamide as a base in FFA determination was described. This work was based on an FTIR method developed by Al-Alawi et al., 2005, which employed an "aged" methanol solution of this base, in which NaHNC≡N had tautomerized completely to its sodium carbodiimide form (NaN=C=NH). Although the IR spectrum of this "aged" reagent solution has two readily measurable absorption bands in the 1660-1600 cm^{-1} region, there are no significant intensity changes in this region after the reaction with acids (Figure 3.1). As a result, while FFA determination was achieved by measuring the carboxylate (νCOO^-) band of the FFA salts formed by reaction with this reagent solution, it would not be possible to determine total acidity in lubricants, as had been originally conceived by Al Alawi et al., in 2004. As noted in the literature review, acids present in lubricants are far more diverse than those in edible oils. In lubricants, there are not only carboxylic acids produced by oxidation of the oil but also inorganic acids resulting from combustion processes. Although there is no IR band that is representative of all acids, the determination of total acidity can be achieved by a process termed signal transduction. In this process all the acids react stoichiometrically with a base to produce a measurable change in its IR spectrum, with differential spectroscopy being employed to minimize oil matrix effects that could interfere with the IR measurements. Sodium hydrogen cyanamide had been originally considered by Al-Alawi et al., 2005 as a possible "signal transduction reagent" in this context, but its rapid tautomerization in methanol did not permit this approach to be pursued.

As described in Chapter 2, during the course of adapting the FFA methodology of Al-Alawi et al., 2005 for use with a VFA IR spectrometer, the methanol solvent in the reagent solution was replaced by ethanol. This change in solvent was made because the VFA IR spectrometer has very limited energy throughput by comparison with an FTIR spectrometer and methanol proved to be too strongly absorbing under certain circumstances discussed in Chapter 2. It was then noted that the tautomerization of NaHNC≡N to NaN=C=NH (Figure 3.2) is slowed substantially in ethanol relative to methanol (60 days vs. 4 days) (Figure 3.3). This observation opened the door to making use of this base as a signal transduction reagent as originally intended by Al-Alawi et al.

Figure 3.4 illustrates the strong *v*C≡N band of NaHNCN and the much weaker absorption of its conjugate acid, cyanamide (H_2NCN). Because these two bands are well separated and the salt is a much strong absorber, the decrease of its absorbance due to reaction with acids was considered a potential route to determining total acidity. In addition, this total acid information minus the carboxylate signal contribution would provide a measure of the inorganic acid contribution. This is especially important for the measurement of acidity in in-service lubricants as the additional capability of differentiating between organic and inorganic acids could be of diagnostic value. Chapter 4 is a manuscript describing the development and assessment of this approach as applied to the analysis of acidity of mineral-based lubricants.

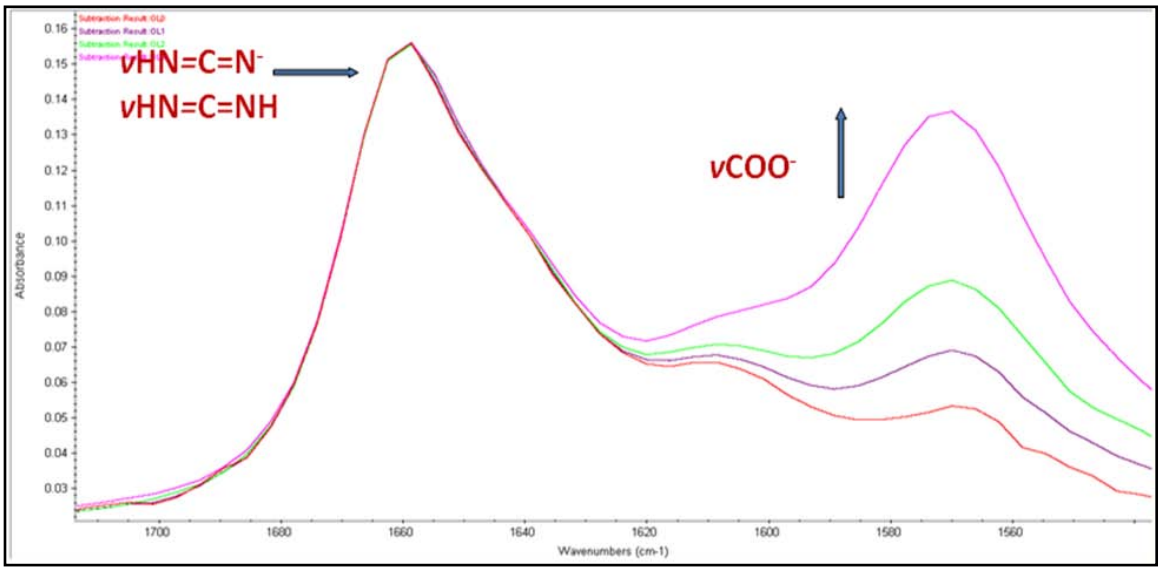

Figure 3.1. Differential spectra obtained after reacting four samples containing different amounts of FFAs with NaN=C=NH solution, illustrating that the absorption of the reagent is not affected by the reaction.

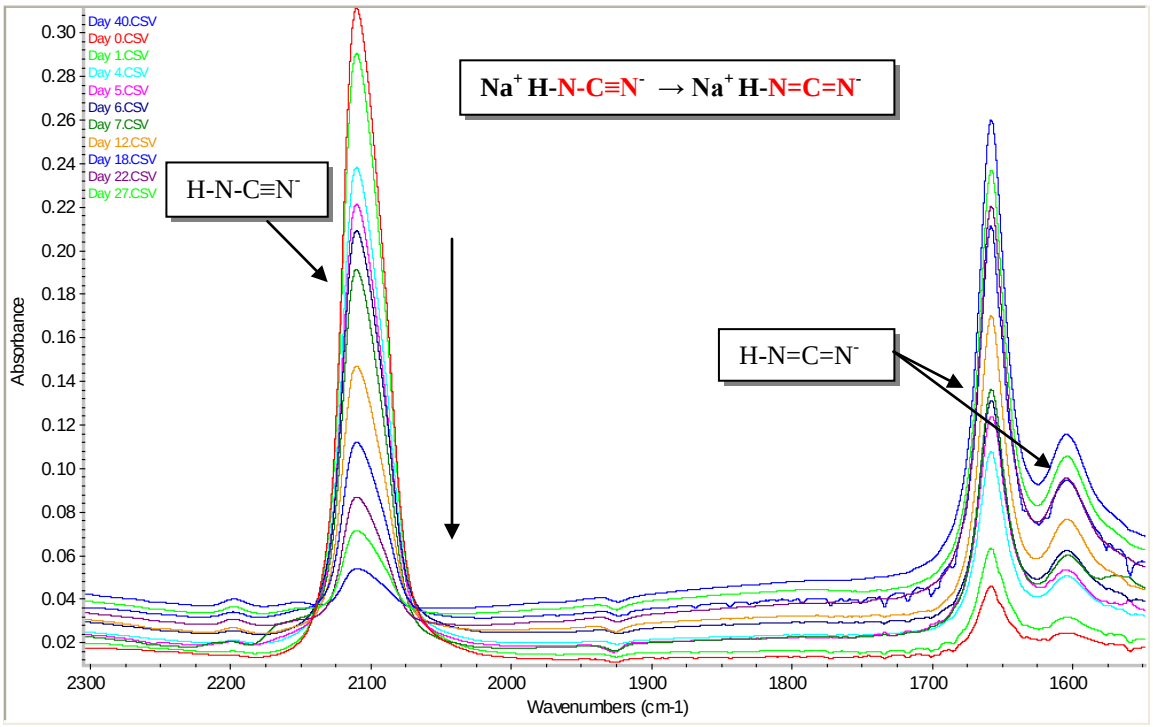

Figure 3.2. Series of differential spectra of NaHNC≡N in ethanol over time, showing the progressive loss of the cyanamide ion and the production of the carbodiimide ion.

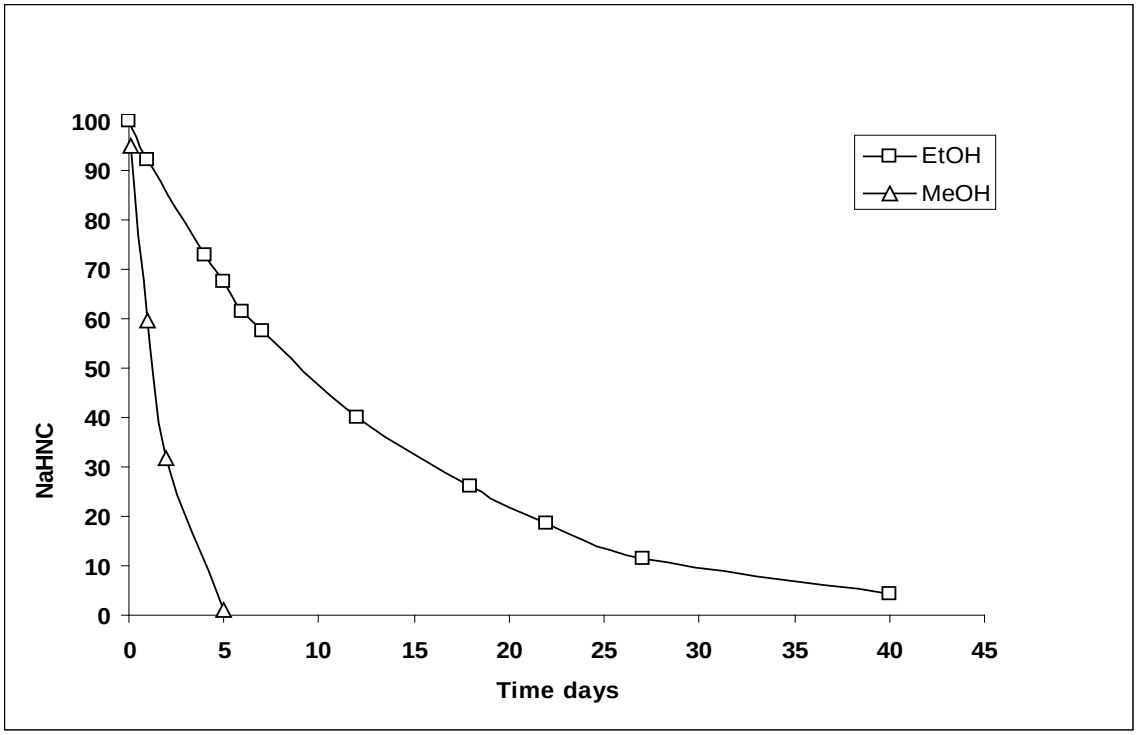

Figure 3.3. Plot of the decrease over time of the νC≡N band (2109 cm^{-1}) in the spectra of freshly prepared solutions of NaHNCN in ethanol and methanol.

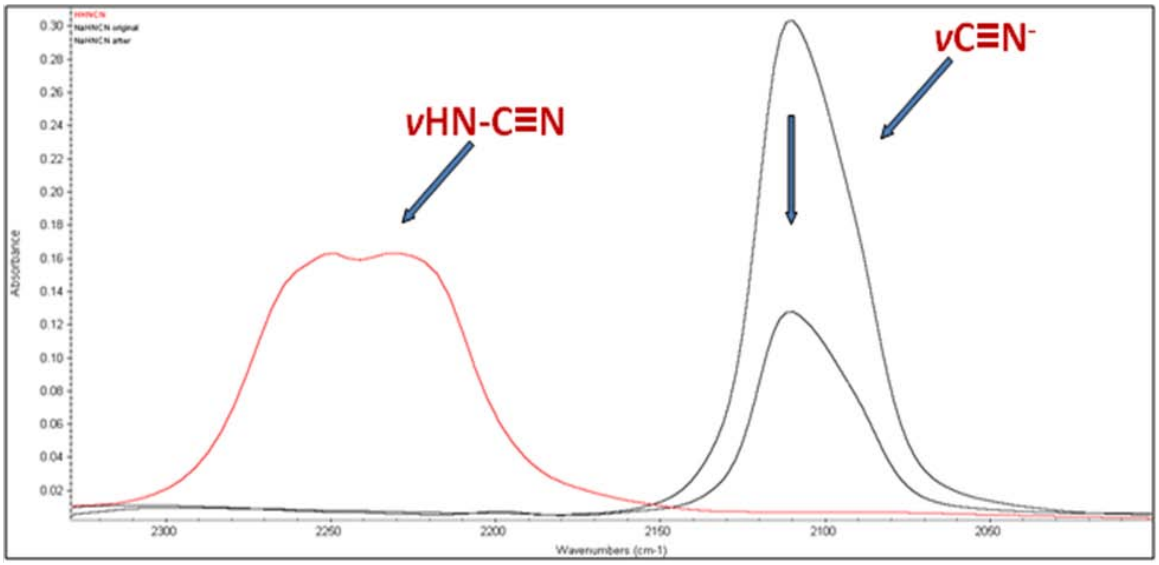

Figure 3.4. *ν*C≡N$^-$ band before and after reaction of NaHNCN with acid; *ν*HN-C≡N band, product of the reaction.

Chapter 4 Automated Acid Number Determination in Lubricants by FTIR Spectroscopy

4.1 Introduction

Fourier transform infrared (FTIR) spectroscopy has found extensive application as an automated, qualitative analytical technique for condition monitoring (CM) (van de Voort et al., 2006) of in-service lubricants of machinery, vehicles and equipment. It is based on monitoring changes in the spectral signature of a lubricant at periodic sampling intervals, with the objective of screening lubricant quality so that oils are replaced only when their functionality is clearly compromised. An overview of CM analyses by FTIR has been presented in a recent publication (van de Voort et al., 2004), in which we described a technique termed spectral reconstitution that facilitates a substantial increase in sample throughput (>100 samples/h), and which represents an important advance for centralized laboratories that routinely perform CM analyses on hundreds of samples per day (van de Voort et al., 2004). We have also worked toward enhancing the general utility of FTIR spectroscopy as a tool for lubricant analysis through the development of new, automated *quantitative* methods to assess critical lubricant parameters such as acid number (AN), base number (BN) and moisture content (van de Voort et al., 2003). These FTIR methods help to amortize the investment in CM FTIR instrumentation as well as providing substantive cost reductions and production benefits relative to the slow and reagent-intensive ASTM titrimetric methods traditionally employed for the determination of these quality parameters.

The present study extends our previous work on acidity determination by FTIR spectroscopy by simplifying the procedure and thus increasing sample throughput by a factor of >2, relative to earlier FTIR methodology (van de Voort et al., 2003). AN determinations are important in tracking lubricant quality, as acidity is of concern from the standpoint of oil functionality and is associated with equipment corrosion. Table 1.2 lists the predominant acids that may accumulate in various types of lubricants. In combustion engines, these include organic acids (COOH) produced over time as a result of oxidative processes as well as strong inorganic acids, which may be incorporated into oils as a result of blow-by or due to inherent acidity in fuels. In refrigeration compressor

systems, refrigerant breakdown can lead to the accumulation of HCl or HF in the lubricants used. Given that H^+ itself is not IR-active, a key obstacle to the determination of acidity by FTIR spectroscopy would appear to be the need to measure the specific IR absorptions of each of the acids listed in Table 1.2, which is problematic as monatomic anions (i.e., Cl^-. F^-) do not give rise to IR absorption bands. This obstacle, however, has been surmounted by developing the concept of *signal transduction*, whereby the acids in the sample are reacted with a base whose conjugate acid has a readily measurable IR absorption (van de Voort et al., 2003). In an earlier method developed on the basis of this concept, two spectra are acquired for each sample, one before and one after addition of the base. The first spectrum is subtracted from the second in order to isolate the spectral changes associated with the acid–base reaction and to eliminate spectral interferences arising from the oil matrix by differential spectroscopy (van de Voort et al., 2003). This approach provides an overall measure of all acid contributions, and extensive experience with this approach has indicated that the results track the AN values determined by the ASTM D664-89 potentiometric titration fairly well (Anon, 1994), producing similar trends, but not directly comparable results in terms of absolute magnitude. Approximately 60 samples/h can be analyzed by this method on an FTIR system equipped with an autosampler (van de Voort et al, 2004), a good throughput relative to that of automated titrimetric procedures; however, the requirement of two analyses to obtain a single result is clearly a drawback of this method.

In this chapter, we present a means by which to overcome this limitation through the use of a combined extraction/signal-transduction approach. While having its roots in the previous AN methodology, this approach has also evolved from the development of FTIR methods for the determination of free fatty acid (FFA) content in edible oils. Specifically, "indirect" methods for this analysis, whereby the oil is extracted with a basic methanolic solution to convert the FFAs to their carboxylate salts, which are then quantitated by FTIR spectroscopy, have provided a simple yet effective means of eliminating oil spectral interferences (Ismail et al., 1993). While this methodology should be equally applicable to the determination of organic (i.e., carboxylic) acids in lubricants, the determination of total acidity requires a base that has suitable spectral characteristics for use in signal transduction. Among the bases that have been successfully employed for effecting the

COOH $\rightarrow$ COO^- conversion in FFA analysis, sodium hydrogen cyanamide (NaHN-C≡N) is potentially ideal in this regard, by virtue of its intense and fairly well isolated νC≡N absorption band (Al-Alawi et al., 2005). Although a methanolic solution of this base is unsuitable as a "signal-transducing" reagent for reasons that will be described later in this paper, the use of ethanol as solvent restores the signal-transducing capability of NaHN-C≡N and hence also provides a means of differentiating between organic and inorganic acidic constituents. Thus, this paper describes the determination of acidity in lubricants by extraction/signal transduction using ethanolic NaHN-C≡N.

As a final note at the outset, an issue of terminology merits discussion. Given the potential advantages of replacing traditional titrimetric AN methods by FTIR methods, as outlined above, an important question that arises concerns the extent to which these two types of methods can be expected to concur. In this regard, it may be noted that the ASTM has several official methods for the determination of AN in lubricants that differ in the titrant used, the titration endpoint, and the analytical procedure and hence effectively differ in their "definition" of acidity. Thus, the variable AN contributions of weakly acidic substances that may be present in lubricants, such as phenolics, lactones, resins, salts of heavy metals or ammonia, as well as acid salts of polybasic acids and certain additives, are considered the main cause of the non-concurrence between the results obtained by various titrimetric AN methods. As such, there are clear warnings in the various ASTM AN methods that the values from different methods are in effect not directly comparable. This caveat is equally applicable to FTIR methods based on signal transduction, which effectively mimic titrimetric procedures but use a unique, spectrally active base, such as potassium phthalimide or NaHN-C≡N, whose pK_a in effect determines the spectral "endpoint." As will be seen below, it is our contention that the FTIR method described in the present paper satisfactorily measures all acids of concern from an oil quality or corrosion standpoint and thus serves the same purpose as most AN analyses of in-service lubricants. However, because it is both conceptually and procedurally different from conventional titration procedures, we have accepted a recommendation that the values obtained by this FTIR method be referred to as acid content (AC), reported in the same units as AN (i.e., mg KOH/g oil). Throughout the remainder of this paper, only results obtained by official ASTM AN methods or

equivalent titrimetric procedures are designated as AN values; data obtained by alternative titrimetric methods for the purpose of comparison with FTIR AC results are considered to be AC rather than AN values.

4.2 Materials and Methods

4.2.1 Reagents and Sample Preparation

Sodium hydrogen cyanamide (NaHN-C≡N), also known as sodium carbodiimide, oleic acid, and anhydrous ethanol were obtained from Sigma-Aldrich and were all of reagent grade. The anhydrous ethanol was kept over 3A molecular sieves, 8-12 mesh (also from Sigma-Aldrich). Additive-free mineral oil (P-032) as well as a variety of new and used oils was obtained from Thermal-Lube Inc (Pointe Claire, QC, Canada), a lubricant formulator. The reagent solution employed in the FTIR AC methodology was prepared by dissolving NaHN-C≡N in anhydrous ethanol at a concentration of ~2.5 g/L. The resulting solution was filtered through Whatman #1 filter paper to remove any turbidity resulting from insolubles and was then stored at -18^{o}C (freezer) Sample preparation for FTIR analysis involved weighing 8 g of oil into a 30-mL screw-capped vial and adding 18 mL of the NaHN-C≡N/ethanol reagent solution. After capping, the vials were subjected to 5 min of horizontal shaking on an Eberbach (Ann Arbor, Michigan) reciprocal shaker operated at 4 cycles/s and then left to stand for up to 30 min to allow for complete phase separation prior to FTIR analysis of the upper ethanol layer. For direct FTIR-titrimetric comparisons, the sample preparation/extraction procedures were scaled up to provide sufficient sample for analysis by both techniques.

4.2.2 FTIR Spectroscopy

The instrument used in this study was a COAT (Continuous Oil Analysis and Treatment) FTIR analyzer (Thermal-Lube Inc., Pointe Claire, QC, Canada), which integrates a Bomem WorkIR FTIR spectrometer, an autosampler, and a micro-pump to facilitate automated sample analysis. The instrument was controlled by UMPIRE (Universal Method Platform for Infra Red Evaluation), a proprietary software package developed by Thermal-Lube. The spectrometer was equipped with either a 100- or a 300-µm CaF_2 transmission flow cell, depending on the AC range to be covered (0-5 or 0-2 mg KOH/g

oil, respectively). For method development work, the sample (upper ethanol layer in the sample vial) was manually aspirated into the cell using vacuum. Once the methodology was automated, samples were pumped into the cell automatically from vials loaded into the autosampler rack (Al-Alawi et al., 2006). All spectra were collected by co-addition of 16 scans at a resolution of 4 cm^{-1} and ratioed against an open-beam background spectrum. To correct for displacement effects due to the slight, but variable miscibility of oils with the reagent solution, the spectrum of each sample was multiplied by a displacement correction factor (DCF), determined by dividing the height of the ethanol overtone band at 1925 cm^{-1} in the spectrum of the reagent solution by the height of this band in the spectrum of the sample extract. Following multiplication of the latter spectrum by DCF, the spectrum of the reagent solution was subtracted from it to produce a differential spectrum, from which the AC was determined using the calibration equation devised. In the case of automated analysis, the first two vials in the autosampler tray were reserved for ethanol (used to condition the cell) and the reagent solution, with the spectrum of the latter serving as the reference spectrum employed by the software for the determination of DCF for all samples subsequently analyzed. In both manual and automated modes of analysis, the spectra of the reagent solution and the sample extract(s) were recorded within 2 h after addition of the reagent solution to the sample(s) to minimize errors resulting from the slow conversion of sodium hydrogen cyanamide to its breakdown products.

4.2.3 Calibration

Calibration standards were gravimetrically prepared by adding oleic acid to the NaHN-C≡N/ethanol reagent solution. The concentrations of acid in these calibration standards were converted to “oil” AC values, expressed in units of mg KOH/g oil and calculated on the basis of the sample preparation protocol (18 mL of reagent/8 g oil). Thus, to prepare a calibration standards with an AC equal to *Z* mg KOH/g oil, the amount of oleic acid to be weighed out and added to 18 mL of reagent was calculated as follows:

$$\text{Oleic acid}_{mg} = 8 \times Z \times Mw_{\text{oleic acid}}/Mw_{KOH} = 8 \times Z \times 5.03.$$

The spectra of the calibration standards were collected by co-addition of 16 scans at a resolution of 4 cm^{-1} and ratioed against an open-beam background spectrum. Following subtraction of the spectrum of the reagent solution from the spectra of the standards, the (negative) intensity of the νC≡N band at 2109 cm^{-1} was measured relative to a single-point baseline at 1859 cm^{-1}. A calibration equation was derived by least-squares regression of AC against $Abs_{2109/1859\ cm^{-1}}$ using a quadratic fit.

4.2.4 Assessment and Validation of the Methodology

A preliminary assessment of the methodology involved standard addition of oleic acid to an unformulated base mineral oil, P-032. These spiked oils were analyzed for acid content (AC) by the FTIR analytical protocol described and by potentiometric titration using a Mettler-Toledo DL58 auto-titrator equipped with a DGi114 solvent electrode. To make the FTIR and titrimetric procedures directly comparable, the spiked P-032 oils were extracted with a NaOH/ethanol solution (isomolar with the NaHN-C≡N/ethanol reagent solution) and back-titrated with 0.1 N HCl, the endpoint being determined from the inflection point of the titration curve. A second study entailed extraction of used-oil samples with NaHN-C≡N/ethanol followed by FTIR analysis as well as back-titration of the extracts. For validation, 27 used-oil samples were provided by Hewitt Equipment (Pointe-Claire, QC, Canada) along with their corresponding AN data obtained by potentiometric titration in accordance with ASTM D664-89. This validation set was supplemented with five compressor oils obtained from Thermal-Lube Inc., for which AN values were obtained in our laboratory by extraction with ethanolic NaOH followed by back-titration with HCl as described above.

4.3 Results and Discussion

4.3.1 Principles of the FTIR Acid Content Method

The FTIR method for the determination of acid content in lubricants developed in this work is based on the extraction of the acids present in the lubricant into an ethanolic solution of the base NaHN-C≡N, which serves as a "signal-transducing" reagent. As mentioned at the outset, an analogous signal-transduction approach was developed in our previous work on the determination of AN as well as BN by FTIR spectroscopy (van de Voort et al., 2003), but the lack of an extraction step led to certain drawbacks. In this

earlier methodology, the acid content of an oil was determined by adding a solution of potassium phthalimide in *n*-propanol (the signal-transducing reagent) to the oil and measuring the ν(C=O) absorption of phthalimide produced by the acid-base reaction. To eliminate spectral interferences from the oil, a two-step analytical protocol was required, whereby the oil sample was split into two halves, one half was mixed with the signal-transducing reagent and the other with an equal volume of *n*-propanol, and the spectrum of the latter was subtracted from that of the former to produce a differential spectrum representing the spectral changes associated with the acid-base reaction. The objective of the present work was to simplify the methodology by extracting the acids present in an oil sample into an oil-immiscible signal-transducing reagent, thereby eliminating spectral interferences from the oil rather than compensating for them by differential spectroscopy. Beyond halving the sample preparation and spectral acquisition time, this combined extraction/signal-transduction approach can provide substantial additional gains in sample throughput owing to the reduction in sample viscosity.

In developing this approach, an alternative signal-transducing reagent was sought because phthalimide would undergo partitioning in a two-phase system. Sodium hydrogen cyanamide (NaHN-C≡N) was identified as a potential candidate on the basis of its fairly strong basicity and the suitable IR absorption characteristics of the C≡N functional group. Initial work with this base concerned its use in FTIR methodology for the determination of free fatty acid (FFA) content (effectively AN) in edible oils (triacylglycerols) (Al-Alawi et al., 2006). Because the νC=O absorption of FFAs overlaps with the intense ester νC=O absorption of triacylglycerols, FFAs are more readily quantitated if converted to their carboxylate salts by extraction into alcoholic KOH (Ismail et al., 1993). However, errors due to saponification of triacylglycerols by this strongly basic solution have been reported. Thus, our initial work focused primarily on the use of a methanolic NaHN-C≡N solution as an alternative to alcoholic KOH rather than as a signal-transducing reagent. However, it became evident during this investigation that the latter (but not the former) possibility was precluded by the instability of NaHN-C≡N in methanol, as evidenced by the progressive decrease of its νC≡N band over time, resulting in complete disappearance of this band ~4 days after preparation of the solution, with the concomitant appearance of two new bands at 1650 and 1610 cm^{-1}. These spectral changes are postulated to arise

from tautomerization of NaH-N-C≡N to an unstable carbodiimide (NaN=C=NH) and subsequent reaction of this species with methanol to form methyl isourea (H_2N-$C(OCH_3)$=NH). Although the nature of the basic species present in an "aged" reagent (i.e., a solution that no longer exhibits any νC≡N absorption) remains under investigation, extraction of edible oils with such a solution deprotonates all the FFAs without saponifying triacylglycerols, and hence this "aged" reagent worked well as an alternative to alcoholic KOH for the FTIR determination of FFAs by measurement of their carboxylate salts (Al-Alawi et al., 2006).

Although the above FFA methodology could be used to measure carboxylic acids in mineral and synthetic lubricants, the results would have to be qualified as "oxidative" acidity values (Dong et al., 2000), rather than acid content *per se*, as inorganic acids would not contribute to this form of FTIR-determined acidity. Thus, the concept of employing NaHN-C≡N in FTIR analysis of lubricants had to be abandoned. However, efforts to adapt the FFA methodology for use with a variable-filter-array IR spectrometer (Li et al., 2008) led to the serendipitous discovery that the stability of NaHN-C≡N in ethanol is surprisingly different from that observed in methanol. Although the νC≡N band in the spectrum of an ethanolic NaHN-C≡N solution shows a gradual decrease over time, the rate at which NaHN-C≡N is depleted is much slower than in methanol, taking ~60 days to reach completion. Furthermore, the solution has been found to be indefinitely stable when stored at freezer temperatures. Consequently, the stability of ethanolic NaHN-C≡N is sufficient to warrant its consideration as a signal-transducing reagent for the determination of acidity in lubricants. The principle of this approach is illustrated in Figure 4.1, which shows the strong νC≡N band observed at 2109 cm^{-1} in the spectrum of an ethanolic solution of NaHN-C≡N (Figure 4.1(*a*)) and the shift of this band by >100 cm^{-1} upon formation of cyanamide (H_2N-C≡N) by addition of excess acid to the basic solution (Figure 4.1(*b*)). The differential spectrum obtained by subtraction of Figure 4.1(*a*) from 4.1(*b*) Figure 4.1(*c*), exhibits a well-isolated and easily measurable negative NaHN-C≡N band that represents the amount of base consumed by the acid-base reaction. Thus, the acid content of an oil sample can, in principle, be determined by extraction of the oil with an ethanolic NaHN-C≡N solution of appropriate concentration (dependent on the amount of acid in the oil) followed by measurement of the decrease of the νC≡N band

in the spectrum of this reagent solution resulting from reaction of NaHN-C≡N with the extracted acids.

Another important consideration in relation to the suitability of ethanolic NaHN-C≡N as a reagent for a lubricant FTIR AC analysis is its basicity. As the only pK_b data available for NaHN-C≡N is a value determined in DMSO, we obtained relative pK_b data by titrating isomolar ethanolic solutions of NaHN-C≡N and NaOH with 0.1N HCl. The results indicated that the pK_b values differed by ~1.45 units, with NaHN-C≡N being the weaker base. Thus, in principle, an FTIR AC method using ethanolic NaHN-C≡N as a base should fully measure the weakest acids of concern from an oil quality standpoint, namely, carboxylic acids, as well as all acids stronger than carboxylic acids.

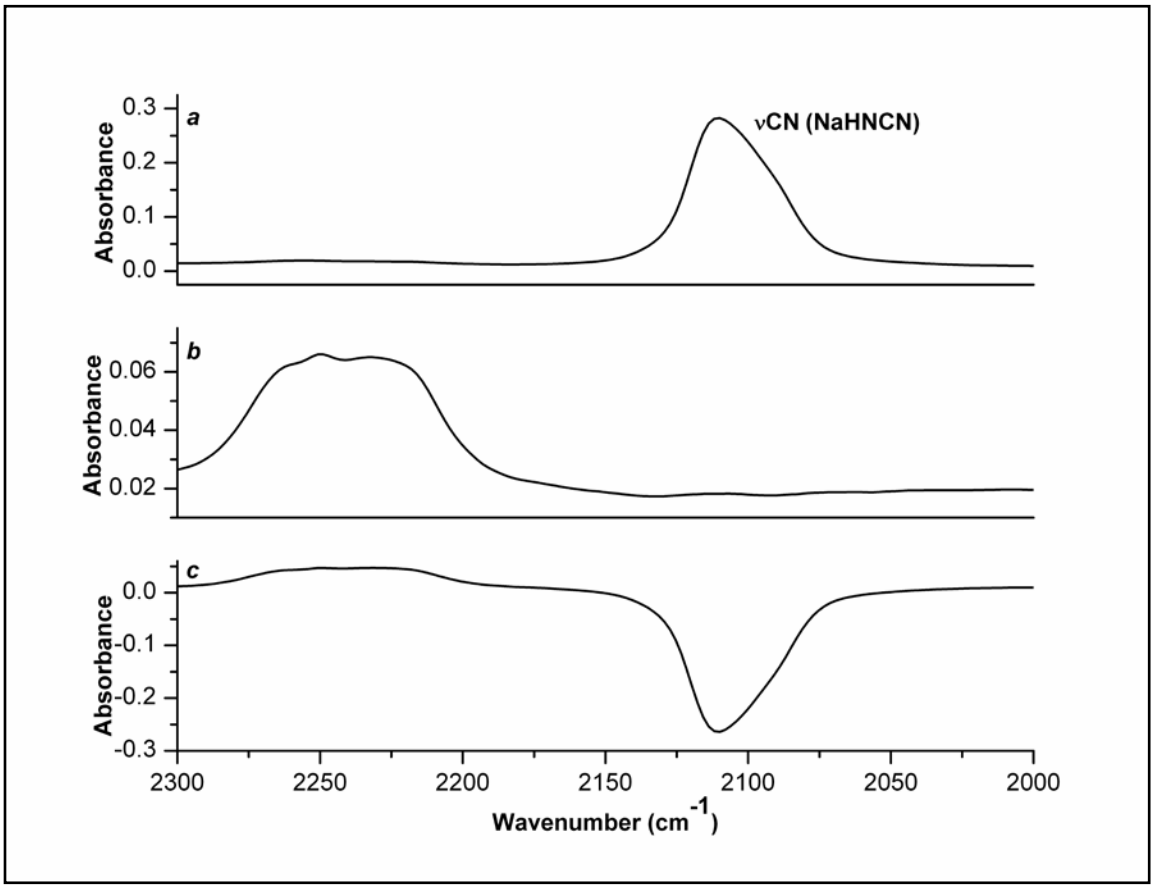

Figure 4.1. The νC≡N band in the FTIR spectrum of NaHN-C≡N in ethanol (*a*) and in the spectrum obtained after addition of excess acid (*b*). The spectrum of ethanol has been subtracted out. The differential spectrum (*c*), produced by subtraction of (*a*) from (*b*), shows the spectral changes associated with the acid-base reaction.

4.3.2 Calibration

The relationship between AC and the intensity of the νC≡N band was established by the quantitative addition of varying amounts of acids to a ~2.5 g/L NaHN-C≡N/ethanol solution. The acids selected were strong inorganic acids (HCl, HNO_3, and H_2SO_4) and oleic acid ($C_{18}H_{35}COOH$) the latter considered representative of organic acids in general. Figure 4.2 illustrates a series of differential spectra obtained by subtracting the spectrum of the reagent solution from the spectra recorded after spiking this solution with varying amounts of oleic acid to produce "oil" AC values in the range of 1-5 mg KOH/g oil. In these spectra, the increasingly negative intensity of the νC≡N band is paralleled by an increase in the intensity of the νCOO^- band of the salt of oleic acid at 1569 cm^{-1}.

Figure 4.3(*a*) presents calibration plots of AC vs. the absolute value of the absorbance at 2109 (νC≡N) and 1569 cm^{-1} (νCOO^-), both measured relative to a single-point baseline at 1859 cm^{-1}. These plots illustrate that the relationship for the νC≡N band is distinctly curvilinear, while that for the νCOO^- band is linear. Data for both these bands were assessed by least-squares regressions using both first- and second-order equations:

$AC_{(2109\ cm^{-1})}$	= 0.27 - 144.71∗Abs	R = -0.999	SD = 0.08	(9)
$AC_{(2109\ cm^{-1})}$	= 0.05 - 174.27∗Abs -716.2∗Abs^2	R = 0.999	SD = 0.02	(10)
$AC_{(1569\ cm^{-1})}$	= 0.20 + 159.72∗Abs	R = 0.999	SD = 0.07	(11)
$AC_{(1569\ cm^{-1})}$	= 0.21 + 157.6 ∗Abs + 56.7∗Abs^2	R = 0.998	SD = 0.08	(12)

As can be seen, for the νC≡N band the quadratic fit (Eqn (10)) results in a fourfold decrease in the regression SD by comparison with the linear fit (Eqn (9)), whereas for the νCOO^- band no improvement is obtained with a quadratic fit. Figure 4.3(*b*) shows that the responses of the νC≡N band upon addition of strong inorganic acids (HCl, HNO_3, and H_2SO_4) to the reagent solution were all similar to those obtained with oleic acid, confirming that NaHN-C≡N/ethanol solution is sufficiently basic to fully ionize the relatively weak organic acid. Combining all the acid responses presented in Figure 4.3(*b*) yielded the following first- and second-order regression relationships:

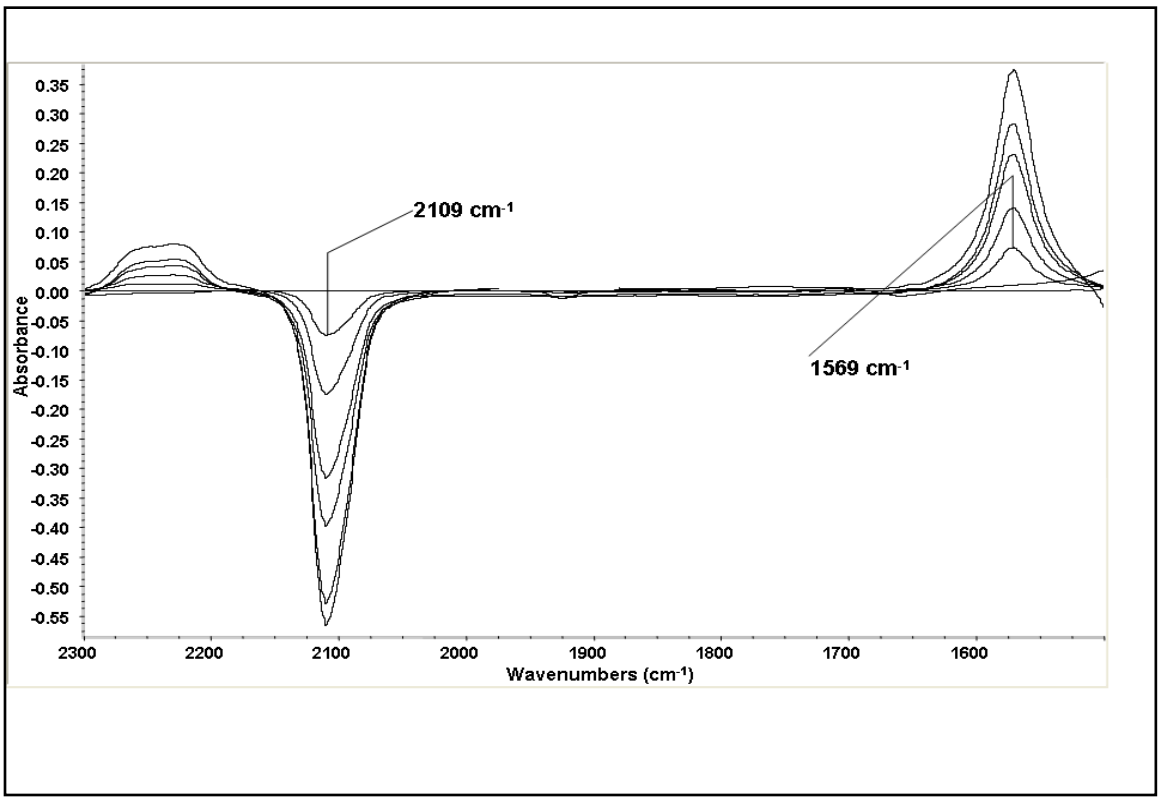

Figure 4.2. Series of differential spectra obtained upon addition of increasing amounts of oleic acid to the NaHNCN/ethanol reagent solution, showing the decrease of the νC≡N band and the growth of the νCOO- band of the oleate salt produced by the acid-base reaction.

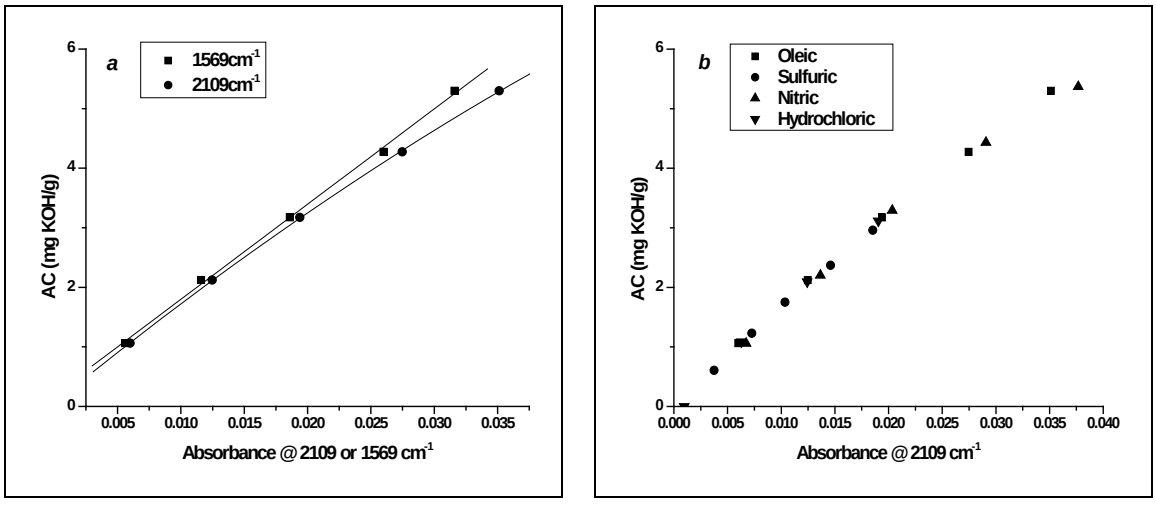

Figure 4.3. (*a*) AC vs. absorbance plots for the νC≡N band at 2109 cm^{-1} and the νCOO$^-$ band at 1569 cm^{-1} in the differential spectra obtained after addition of various amounts of oleic acid to the reagent solution. (*b*) Composite plot of AC vs. absorbance at 2109 cm^{-1} for addition of HCl, H_2SO_4, HNO_3, and oleic acid to the reagent solution. The absorbance values of the νC≡N band have been multiplied by -1 to facilitate comparison of the plots.

$AC_{(All\ Acids)}$ = 0.16 - 146.83*Abs R = -0.996 SD = 0.13 (13)

$AC_{(All\ Acids)}$ = -0.10 -189.09*Abs -1109.7*Abs^2 R = -0.998 SD = 0.06 (14)

The similarity of equations (13) and (14) to equations (9) and (10) indicates that a calibration equation based only on oleic acid standards can serve for the determination of carboxylic acids and all acids stronger than carboxylic acids in lubricants, yielding a value designated as AC. Oleic acid is a convenient standard, being easier to handle than strong acids and readily dissolving in hydrophobic media. In addition, although not explicitly considered in this work, the use of oleic acid as a calibration standard affords a potential means of independently measuring the contributions of organic acids to AC via a calibration based on the νCOO^- band. This additional capability may be of diagnostic value, given the different routes by which inorganic and organic acids accumulate in lubricants as well as their differing effects on oil quality and corrosovity. (see Table 1.2)

In calibrating the FTIR AC method with standards prepared by direct addition of oleic acid to the NaHN-C≡N/ethanol reagent solution, the scaling factor required to adjust the AC values by the oil:reagent-solution ratio employed in the extraction step, standardized at 1:2.25 w/v, is effectively built into the calibration equation. Accordingly, use of this calibration equation not only requires that this standardized ratio be strictly adhered to but also rests on the assumption that the lubricant is completely immiscible with the ethanolic reagent solution into which any acids present in the oil are extracted. This assumption may not be entirely valid and would lead to overestimation of AC because dilution of the ethanol phase by oil will lead to an increase in the (negative) intensity of the νC≡N band in the differential spectrum. Accordingly, it was necessary to devise a means of compensating for the normally slight, but variable, miscibility of oils with the reagent solution. The procedure developed involves the use of the ethanol overtone absorption at 1925 cm^{-1} to measure the extent of dilution of the reagent solution by oil dissolved in it. This band is suitable for this purpose because there are rarely interfering absorptions in this region of the spectrum. Thus, prior to generating the differential spectrum, a displacement correction factor (DCF) is calculated by measuring the ratio of the absorbance at 1925 cm^{-1} in the spectrum of the reagent solution to that in the spectrum of

the sample extract, and the latter spectrum is then multiplied by the DCF. The differential spectrum produced after this step mathematically corresponds to the spectrum that would have been obtained in the absence of any displacement effect, allowing the AC value of the sample to be determined directly from the original calibration equation.

A final consideration in relation to the validity of the calibration is the need to safeguard against the possibility of errors resulting from instability of NaHN-C≡N and its conversion to other products. While the NaHN-C≡N/ethanol reagent solution appears to be stable indefinitely when stored at -18^{o}C, slow conversion does occur at room temperature, resulting in a significant drop in the intensity (~8%) of the νC≡N band within 24 h. A small change in intensity is not of concern *per se* because AC determination is based on the intensity of the νC≡N band in the differential spectrum obtained by subtraction of the spectrum of the reagent solution from that of the sample extract. Thus, provided that these two spectra are collected within a reasonable time (<2 h) after addition of the reagent solution to the sample, the effect of the slow conversion of NaHN-C≡N will be negligible. However, given that a methanolic solution of NaHN-C≡N remains capable of deprotonating carboxylic acid after complete disappearance of the νC≡N band, it is likely that the slow depletion of NaHN-C≡N in ethanol is accompanied by the formation of basic species that will react with acids extracted from the oil and will thus lead to errors in the determination of AC, since the ionization of these acids will not produce any change in the νC≡N band. As such, if the extent of depletion of NaHN-C≡N in the reagent solution becomes significant as measured by spectroscopic changes, then the calibration developed ceases to be valid. Thus, it is important to verify that the spectrum of the reagent solution that is about to be employed for sample analysis matches that of the original zero-AC calibration standard. If the height of the νC≡N band has decreased by >1%, then recalibration with oleic acid is required to account for the altered response of the νC≡N band to changes in AC. Together with storing the reagent solution at -18^{o}C, this technique provides a means by which the reagent solution can be used for extended periods of time. However, the applicability of this recalibration approach beyond a 10% decrease in the height of the νC≡N band has not been tested.

4.3.3 Validation

Table 1.2 indicates that the acids of concern in in-service oils are primarily organic acids associated with the oxidative breakdown of lubricants or ester additives as well as any strong inorganic acids, although, as noted earlier, many other substances that may be present in oils have some acid character and could contribute variably to FTIR AC values on the one hand and titrimetric AN values on the other. Because the acidity of acids weaker than carboxylic acids is generally not significant in terms of contributing to corrosion oil quality and impaired functionality, our initial assessments of the FTIR-based AC methodology were carried out using acid-free P-032 mineral oil spiked with defined but varying amounts of oleic acid, serving as a representative carboxylic acid. Each of these samples was split into two halves, which were then extracted with isomolar solutions of ethanolic NaHN-C≡N and ethanolic NaOH for AC determinations by the FTIR method and by back-titration (inflection endpoint), respectively. In Figure 4.4, the FTIR results obtained using the *ν*C≡N and *ν*COO^- calibration equations (equations (10) and (11), respectively), as well as the titrimetric results are plotted against the actual AC values, calculated from the amounts of oleic acid added to the oil. The corresponding linear regression relationships are presented below:

FTIR $AC_{(2109\ cm^{-1})}$	= 0.08 + 1.028∗AC_{spiked}	R =0.999	SD = 0.07	(15)
FTIR $AC_{(1569\ cm^{-1})}$	= -0.01 + 1.019∗AC_{spiked}	R = 0.999	SD = 0.02	(16)
Titration AC	= 0.17 + 1.047∗AC_{spiked}	R = 0.999	SD = 0.05	(17)

Figure 4.4 graphically illustrates the correspondence between the two sets of FTIR AC measurements as well as between the FTIR and titrimetric results. Furthermore, all three regression equations (Eqns 15-17) have no appreciable intercept and a slope close to unity, indicating that NaHN-C≡N/ethanol as well as NaOH/ethanol completely extracted the oleic acid spiked into the mineral oil and converted it to its carboxylate salt.

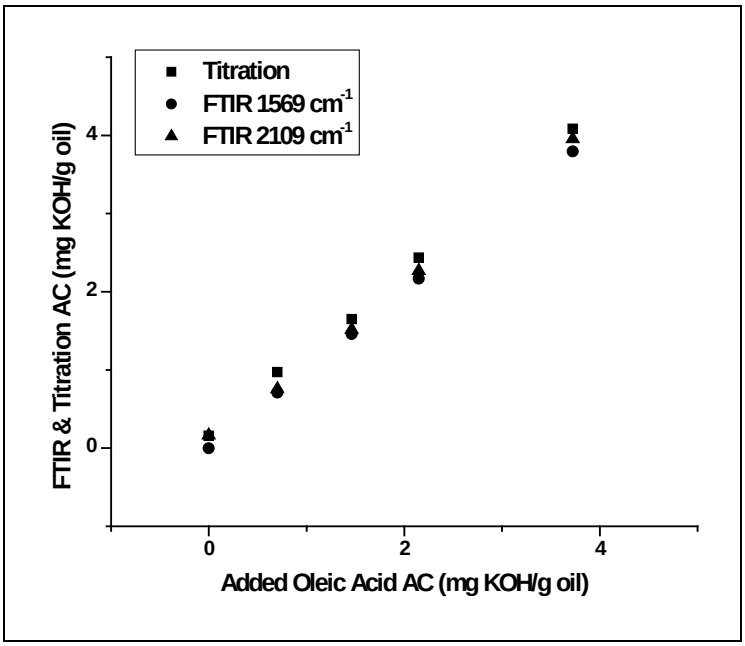

Figure 4.4. Plots of FTIR and titrimetric AC results for a mineral oil spiked with various amounts of oleic acid vs. AC values calculated from the spiked amounts. The FTIR results were obtained from measurements of the νC≡N (2109 cm^{-1}) or the νCOO^- (1569 cm^{-1}) band in the spectra of ethanolic sodium hydrogen cyanamide extracts of the spiked oils, with the use of Eqs. (10) and (11), respectively. The titrimetric data were obtained by extracting the same oils with ethanolic NaOH and back-titrating with HCl.

Having demonstrated that the FTIR AC method can accurately measure all acids as strong as or stronger than carboxylic acids, we undertook validation studies using real lubricants. To assess the repeatability and reproducibility of the method, a set of 22 used engine oils of unknown AC was analyzed in duplicate in a single day and reanalyzed several weeks later. The results indicated that the FTIR analyses were repeatable to within ±0.06 mg KOH/g oil and reproducible to within ±0.19 mg KOH/g oil over an FTIR-determined AC range of 0-~2.5 mg KOH/g oil.

The accuracy of the FTIR method was then assessed by extracting 13 of these used oils with the NaHN-C≡N/ethanol reagent solution, with half of each extract being analyzed by the FTIR method and the other half back-titrated with HCl. Figure 4.5 illustrates the correspondence between the titrimetric results and the FTIR AC results obtained using both the $\nu C{\equiv}N$ and νCOO^- measurements.

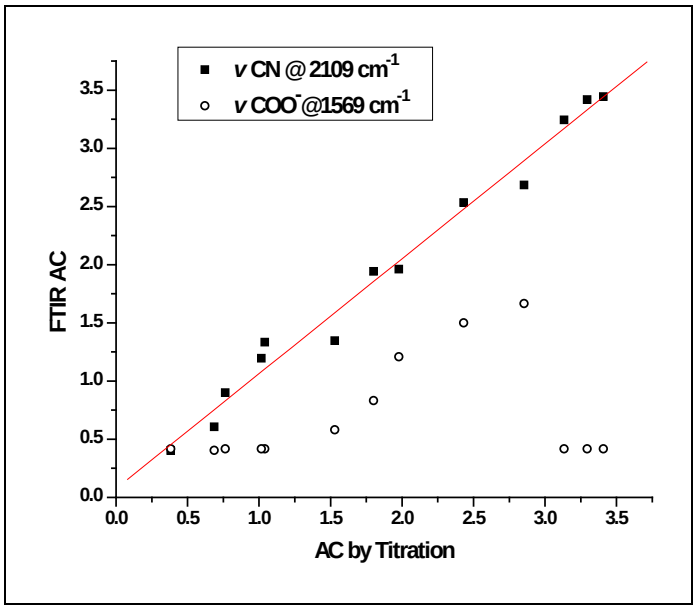

Figure 4.5. AC results obtained for 13 used oils extracted with ethanolic sodium hydrogen cyanamide and measured by HCl back-titration and FTIR analysis. FTIR results based on measurement of the νC≡N band (2109 cm^{-1}) represent the total acidity whereas the 1569 cm^{-1} band is specific to organic acids.

It is clear that the νC≡N measurement tracks the titrimetric data well, as shown by the following regression equation:

$$AC_{FTIR} = -0.07 + 1.013 * AC_{titration} \qquad SD = 0.14 \qquad R = 0.991 \qquad (18)$$

On the other hand, the νCOO^- measurement does not provide correct AC values, indicating that acids other than carboxylic acids are present in this set of samples; in fact, several of the samples with the highest titrimetric AC values did not exhibit any νCOO^- absorption at all. However, this measurement may be useful diagnostically as it allows the carboxylic acids produced by oil degradation (e.g., oxidation, ester breakdown processes) to be differentiated from other sources of acidity in oils (e.g., combustion blow-by).

Although Equation 18 demonstrates that the FTIR and titration results concur when the base employed in both methods is NaHN-C≡N, it does not necessarily imply concurrence with ASTM titrimetric data obtained using KOH, a stronger base. Thus, a second

experiment was carried out by analyzing 27 used-oil samples independently pre-analyzed by a commercial laboratory using ASTM D664-89. Figure 4.6(*a*) presents a plot of the FTIR data vs. the commercial laboratory results for this series, which yielded the following linear regression equation:

$$AC_{FTIR} = 0.035 + 0.767 * AN_{titration} \qquad SD = 0.11 \qquad R = 0.622 \qquad (19)$$

Overall, the FTIR-determined AC is ~25% lower than the AN determined by titration, indicating that these samples contain some weakly acidic substances that are more reactive with KOH than with NaHN-C≡N. The relationship appears quite poor from a correlational standpoint (R = 0.62), largely owing to the narrow AN range spanned by these samples. Thus, in Figure 4.6(*b*), these data are combined with those obtained for five compressor oils spanning a much broader AN range, for which the titrimetric data were obtained in our laboratory by extracting the oils with ethanolic NaOH and back-titrating the extracts with HCl.

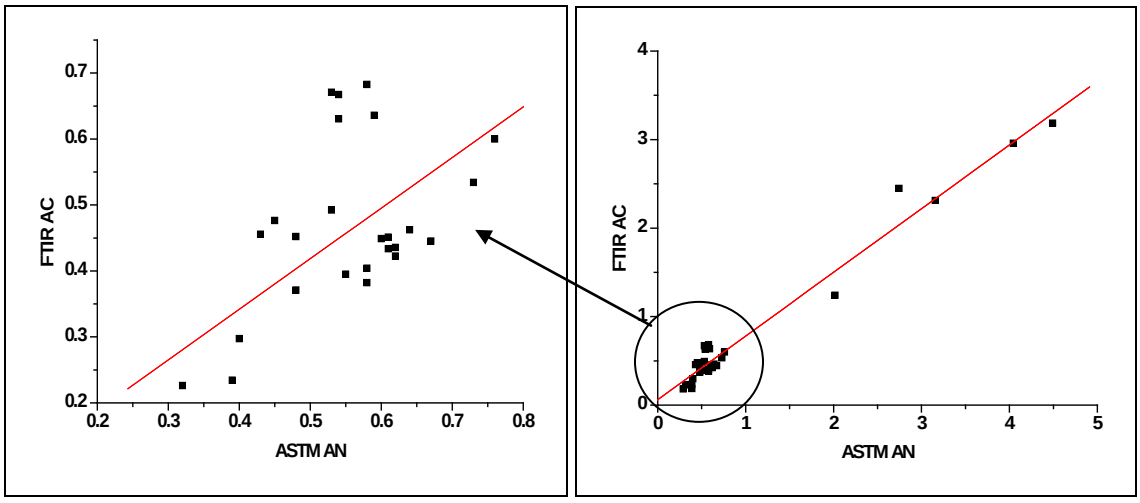

Figure 4.6. (*a*) Plot of FTIR AC results for 27 used oils vs. AN data obtained in a commercial analytical laboratory by ASTM D664-89 potentiometric titration. (*b*) Combined plot for the 27 used-oil samples and 5 additional compressor oil samples spanning a broader AN range.

Linear regression of the data for this enlarged sample set yielded the following relationship:

$$AC_{FTIR} = 0.060 + 0.718 * AN_{titration} \qquad SD = 0.14 \qquad R = 0.985 \qquad (20)$$

Although the SD of the new relationship is slightly greater, there is a substantial drop in the coefficient of variation (from ~12% to ~3%), simply owing to the broadening of the AN range. Given that the FTIR and titrimetric procedures are completely different and use two different bases, their results are surprisingly well correlated. Clearly, more extensive validation studies will be required with a much wider variety of oils before any definitive conclusions can be reached as to the overall performance of this FTIR method relative to titrimetric ASTM methods. Even if there is a reasonable correlation, it is best to clearly differentiate these measures (AC as opposed to AN). In this context, it is our contention that only organic and stronger acids are of concern from an oil quality or corrosion standpoint, and thus for in-service oils AC values will be just as meaningful as (or possibly more meaningful than) AN values obtained by established ASTM methods using stronger bases.

4.3.4 Potential Benefits of the FTIR AC Method

FTIR AC determination is similar in principle to the ASTM titrimetric AN methods but very different in procedure, and, as such, its advantages are manifold. These include simplicity, a traceable and defined calibration, no issues of variable and poorly defined endpoints to contend with, as well as economic and environmental benefits associated with the very substantive reduction in consumables and waste oil/solvent disposal. In its automated form, implemented on a COAT (Continuous Oil Analysis and Treatment) system, as described in Materials and Methods, the software controlled system has the capability to analyze ~120 pre-extracted samples per hour, a very substantive speed advantage over any automated titrimetric AN systems currently available. In this context, most lubricant analysis laboratories already have automated or semi-automated FTIR systems dedicated to qualitative condition monitoring of lubricants, the utility of which can be enhanced by implementation of the FTIR AC analysis. In addition, the functional-group information inherent to the AC method allows differentiation between organic and

other acids contributing to the acidity of lubricants, data that may be of additional diagnostic value.

4.4 Conclusion

The objective of this study has been to lay the groundwork for a simple and readily automatable FTIR-based procedure for determining AC of lubricating oils. Based on the results of this development study, the indications are that this AC method could be a viable alternative to titration-based AN determinations, producing accurate and reproducible results that are comparable within the method and which roughly correlate with ASTM titrimetric methods. However, careful and extensive validation work will be required to solidify this conclusion, bearing in mind that comparison of the results from different AN methods is problematic in its own right as the magnitude of the values is strongly method-dependent. For these reasons as well as its ability to differentiate between organic acid and inorganic acid contributions, the FTIR measure has been designated AC so as to avoid its confusion with the various ASTM titrimetric AN methods.

Chapter 5 Conclusion and Future Work

The research presented in this thesis focused on the determination of acidity in oil-based matrices by IR spectroscopy through the use of the reagent sodium hydrogen cyanamide. The use of a methanolic solution of this reagent for the extraction and deprotonation of FFAs in edible oils followed by measurement of the IR absorption of the carboxylate salts formed by FTIR spectroscopy was first reported by Al-Alawi et al., 2005. Chapter 2 presented the implementation of this method on a VFA IR spectrometer. The objective of this work was to determine whether this low-cost, low-resolution instrument could provide quantitative results comparable to those with a FTIR spectrometer. Although the low energy throughput of the VFA IR spectrometer was initially problematic, moving the source closer to the detector and modifying the method by changing the solvent in the reagent solution from methanol to ethanol ultimately yielded adequate quantitative accuracy. This work provides the basis for a lower cost instrumental method for the determination of FFAs in edible oils. These results were disseminated as a research note and subsequently as a full paper in the Journal of the American Oil Chemists' Society. As noted in Chapter 3, switching the solvent to ethanol also provided a means of stabilizing NaHNCN and thus opened up the opportunity of using this base as a signal transduction reagent for the determination of total acidity in lubricants by FTIR spectroscopy. A detailed investigation of this approach, focusing on mineral-based oils, was presented in Chapter 4, in the form of a paper accepted for publication in the Journal of ASTM International.

Based on the development work carried out to date, the indications are that a VFA IR spectrometer is a viable tool for instrumentally determining FFA content in edible oils and possibly biodiesel feedstocks while the FTIR method for the measurement of total acidity in lubricants could be a viable alternative to titration-based ASTM AN determinations. However, careful and extensive validation work will be required to solidify and confirm this conclusion. In addition, the capability of the FTIR method to provide two measures of acidity in lubricants, i.e., total acidity and organic acidity, with inorganic acidity being obtained by difference, may be examined further, specifically in

oils where oxidative processes are dominant and where this additional capability may be of diagnostic value.

The work described in Chapter 4 also lays the foundation for further simplification and generalization of the methodology developed. In this work, calibration standards were prepared simply by spiking oleic acid directly into the ethanolic reagent solution, and the calibration was based on absorbance differences between the acid-spiked solutions and the acid-free reagent solution. As such, the analysis becomes independent of the initial NaHNCN concentration. Furthermore, if the acid contents of these standards are expressed as mg KOH/ml, the acid content of an oil sample (in units of mg KOH/g oil) can be obtained simply by dividing the result obtained from the calibration equation by the weight of the sample. In work to date, this calibration approach has been found to work well for mineral oils; however, if there is any significant miscibility of the oil with the reagent solution, such as in the case of ester-based oils, then the calibration standards, which simulate the situation where the oil sample is completely immiscible with this solution, are no longer representative of the samples being analyzed. Such a situation would normally be addressed by developing a separate calibration for each oil matrix, but this would limit the universality and general utility of the methodology. As discussed in Chapter 4, an ethanol overtone band was employed to correct the spectra recorded in this study for any slight miscibility of the oils analyzed with ethanol. This points to a means by which matrix-dependent dilution effects might be compensated for, which could be tested using standard addition to specific ethanol-miscible product types, e.g., biodiesel and phosphate esters. If this concept proves workable, it may be possible to develop a universal calibration and methodology for the analysis of acidity in a wide range of samples, from mineral oils (totally immiscible) to biodiesel (totally miscible).

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Appendix:

Application Note: Analysis for Free Fatty Acids (FFAs) in Oils for Biodiesel and Edible Oil Applications Using the InfraSpec VFA IR Spectrometer

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Introduction

Fats and oils from a large variety of sources are widely employed by the food industry and serve as feedstock for the rapidly developing biodiesel sector. Free fatty acids (FFAs), present in the crude oils, are detrimental to oil quality and functionality, and accordingly FFA content is an important parameter in edible oil refining and biodiesel production. In addition, FFAs are formed during prolonged frying operations and are a key determinant of frying oil quality. For all these reasons, simple, rapid and reliable means of determining FFA content are required. To meet this need, analytical methods for the determination of FFAs by FTIR spectroscopy have been developed as alternatives to the traditional time-consuming titration procedures. However, since the purchase of an FTIR spectrometer for the purpose of implementing a single analytical method is unlikely to be cost-effective, a simple, low-cost variable filter array (VFA) IR spectrometer is better suited for dedicated applications of this type, provided that it offers the requisite analytical performance. This application note describes methodology for the rapid and accurate determination of FFAs in oils using the Wilks Enterprise InfraSpec VFA-IR spectrometer.

Characteristics of the InfraSpec

The InfraSpec is a miniature IR spectrometer that operates in either the ATR or the transmission mode. Because it is based on variable filter array technology, it has no moving parts. It utilizes a cool electronically modulated (pulsed) source and a pyroelectric detector, and a spectrum is generated with each source pulse. Consecutively collected spectra are co-added automatically to increase the S/N ratio. The spectrometer module is readily linked to a computer or PDA via a USB connector and comes with

dedicated software to drive the system and process spectral data. Some key instrument specifications are listed below.

Dimensions	5″×5″×1.5″
Weight	3.5 lbs
PC Interface	RS 232
Power	9V DC, 2.0 amps
Power supply	AC/DC converter
Detector array	64-pixel pyroelectric
Spectral ranges	2.5-5 μm, 5.5-11 μm

The InfraSpec spectrometer employed in the present work was configured to cover the wavelength range of 5.5-11 μm (~1800-900 cm^{-1}) at a spectral resolution on the order of 30 cm^{-1}. To obtain optimal analytical performance for FFA determinations and facilitate sample throughput, we equipped it with a 100-μm CaF_2 transmission flow cell (Figure 1). Because the source is cool, the cell could be positioned very close to the source to maximize energy throughput.

Figure 1. The Wilks Enterprise InfraSpec VFA-IR spectrometer.

Methodology

The ability of the InfraSpec to determine FFAs in oils was evaluated by implementing the novel FTIR methodology described in ref. (1). The basic procedure involves the extraction of FFAs from the oil into methanol containing sodium hydrogen cyanamide and their stoichiometric conversion to sodium salts:

$$NaHNCN + R\text{-}COOH \rightarrow R\text{-}COO^{-}Na^{+} + H_2NCN$$

IR quantitation is based on measurement of the strong $\nu(COO^{-})$ absorption at ~1570 cm^{-1} relative to a suitable baseline, and a calibration equation relating this measurement to FFA content (expressed as % oleic acid) is devised using standards prepared by gravimetrically spiking known amounts of oleic acid into an FFA-free oil. In both calibration and sample analysis procedures, 6.5 ml of the methanol reagent is added to 5 g of oil in a 20-ml vial; after shaking on a vortex mixer for 30 sec, the phases are allowed to separate, and the methanol layer is analyzed in a 100-µm transmission cell.

This FTIR procedure is considered one of the most specific, sensitive and versatile methods for FFA analysis. To adapt this methodology to the InfraSpec, ethanol was substituted for methanol so as to obtain more energy in the measurement region. The ethanol extracts were loaded into the cell by aspiration, using a stainless steel needle (Figure 1). A valve controlled the loading and emptying of the cell, and a solvent trap was located in the outlet line. The InfraSpec was evaluated under a variety of scanning regimes as well as various source positions; the optimal conditions were 32 co-added scans, with the source placed within 1 cm of the cell window.

For comparative purposes, the InfraSpec was run side-by-side with a FTIR spectrometer (WorkIR, ABB Bomem), sharing the same cell and cell loading assembly. The FTIR spectra were collected at a resolution of 4 cm^{-1} by co-adding 16 scans and were ratioed against a background spectrum collected with the ethanol reagent solution in the cell to eliminate its contributions from the spectra of the samples.

Results

Figure 2a presents typical differential spectra obtained by FTIR spectroscopy for oils spiked with oleic acid and treated with the ethanol/sodium hydrogen cyanamide reagent. Figure 2b illustrates the resulting standard curve covering the range of 0-5% added oleic acid, the regression equation obtained being:

$$\%FFA = -0.001 + 0.06204*Abs_{(1571/1799\ cm^{-1})} \quad SD = 0.045\ R^2 = 0.999 \qquad [1]$$

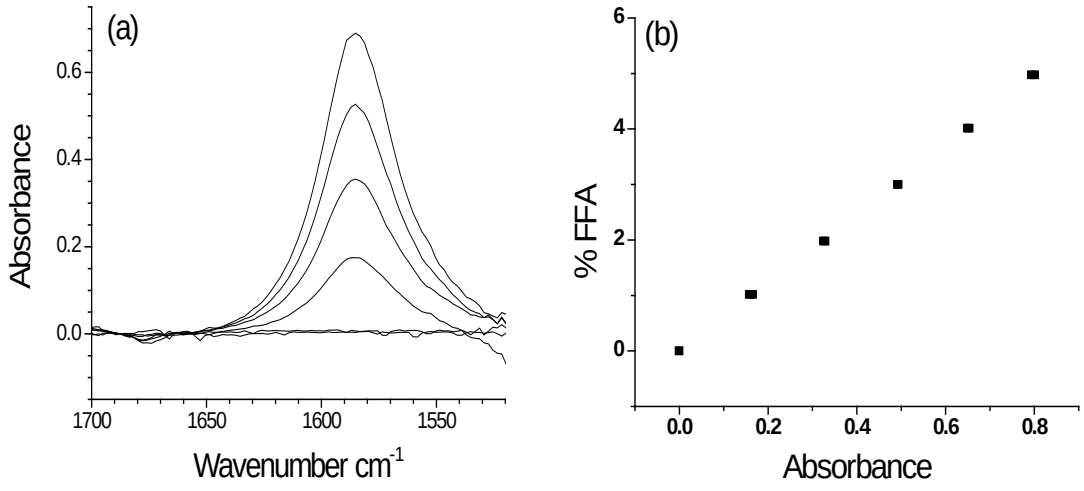

Figure 2. Calibration spectra (a) and calibration standard curve (b) obtained by FTIR spectroscopy.

The corresponding spectra obtained by using the InfraSpec are shown in Figure 3a. The bands in these spectra are much broader owing to the much lower spectral resolution (~30 cm^{-1} vs. 4 cm^{-1} for the FTIR spectra). Despite the limited resolution, good quantitative data can still extracted as indicated by Figure 3b and its resultant regression equation:

$$\%FFA = 0.249 + 22.445*Abs_{(1600/1687cm^{-1})} \quad SD = 0.075\ R^2 = 0.998 \qquad [2]$$

As noted above, it was determined that in a 100-μm cell, methanol absorbed much of the available energy in the spectral region of interest, whereas the lower absorptivity of ethanol resulted in a substantive increase in the amount of residual energy to work with in measuring the FFA signal. This issue arises because the InfraSpec's pulsed IR source is substantially weaker than the FTIR spectrometer's Globar source. On the other hand, when a lower range of FFA concentrations (0-1%) was examined, this effect was not evident as a result of the lower FFA absorption, and excellent regression SDs were obtained with both the methanol reagent and the ethanol reagent (Table 1).

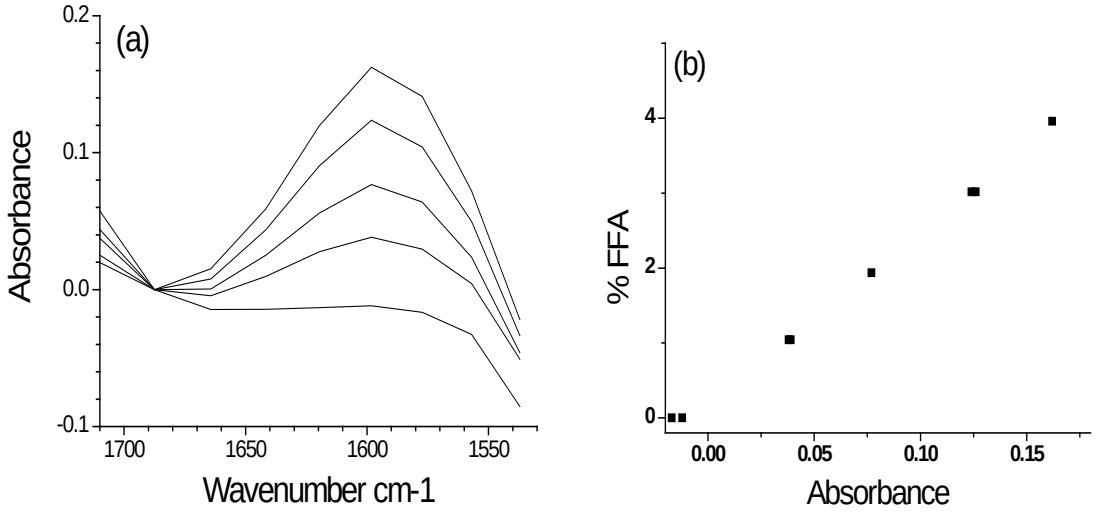

Figure 3. Calibration spectra (a) and calibration standard curve (b) obtained using the InfraSpec.

Table 1. Regression statistics

	FFA 0-1%[a]		FFA 0-5%[b]	
	R^2	SD	R^2	SD
InfraSpec	0.997	0.029	0.998	0.075
FTIR	0.998	0.015	0.999	0.045

.[a]Methanol reagent. [b]Ethanol reagent.

Conclusion

Based on the results of this assessment, the InfraSpec is capable of replacing a conventional FTIR spectrometer to analyze for FFA content in oils using the method developed by Al Alawi et al (1), but modified to use ethanol as the extraction solvent. As such, it can be used as a dedicated analyzer, providing a simple and economical instrumental means by which to monitor FFA levels in crude and refined edible oils and in biodiesel feedstocks. In a flow cell configuration, one can readily analyze 20-30 samples/hr once the samples have been prepared for analysis.

References

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