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DEVELOPMENT OF FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY FOR DETERMINING OIL QUALITY

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TABLE OF CONTENT

ABSTRACT

The *on-line* or *at-line* monitoring and treatment of oil quality and the performance of stabilizing additives are particularly important in oil industry in terms of optimizing oil stability and extending its service life. In this work, a rapid Fourier transform near infrared (FT-NIR) spectroscopic peroxide value (PV) method was developed and a prototype Continuous Oil Analysis and Treatment (COAT) system was assessed for monitoring and analytical purposes. High erucic acid rapeseed (HEAR) oil, a principle representative of triglyceride based oils suitable for biodegradable lubricating applications and mineral oil were used to test the methodology developed.

The FT-NIR PV method is based on a well defined stoichiometric reaction of triphenylphospine (TPP) with hydroperoxides to form triphenylphospine oxide (TPPO). A partial least squares (PLS) calibration model for the prediction of PV was developed using the NIR spectral region where TPP and TPPO co-absorb. The resulting calibration was highly linear over the analytical range of 100PV. Validation of the method carried out by comparing the PV of PLS prediction to the results of AOCS iodometric procedures indicated an excellent concurrence between the two methods. By programming the FT-NIR spectrometer, the analytical procedure simply consists of the addition of TPP stock solution to oil sample, mixing, taking its spectrum and predicting PV value. Through selected testing procedures, the prototype COAT system utilizing FTIR spectroscopy, advanced sample handling system designs, and computer programming was proved to be effective in monitoring the oil quality and behavior of antioxidants in real time. This design was demonstrated to be good means of reducing overall cost in machinery.

In terms of practical application, both approaches offer combined advantages of speed, accuracy, low labor cost, automation, and environmental friendliness mainly derived from FTIR spectroscopy, and can serve as convenient means for routine quality control applications in oils and fats industry. Potential application based on the joint usage of the two methods in the obtaining of true value of oil stability was also presented in this text.

RÉSUMÉ

Le contrôle de la qualité, en continu sur la ligne de production ou en parallèle, et l'ajustement de la qualité et de la performance des additifs stabilisants sont particulièrement importants dans l'industrie des huiles afin d'optimiser la stabilité des huiles et accroître leur longévité. Les travaux présentés traitent du développement d'une méthode rapide permettant de déterminer l'indice de peroxyde (PV) par le biais de la spectroscopie infrarouge proche à transformée de Fourier (FT-NIR). De plus, l'évaluation de la performance d'un prototype de système d'Analyse et de Traitement des Huiles en Continu (COAT) a été effectué pour déterminer sa capacité d'analyse de l'huile minérale et de l'huile de canola (HEAR), un triglycéride représentatif des produits utilisés pour la fabrication de lubrifiants biodégradables.

La base de la méthode FT-NIR pour la détermination de l'indice de peroxyde repose sur la réaction stochiométrique de la triphénylphosphine (TPP) avec les hydroperoxydes produisant l'oxyde de triphénylphosphine (TPPO). Un model de calibration utilisant la méthode des moindres carrés partiels pour prédire l'indice de peroxyde a été développé en utilisant la région du spectre infrarouge proche où TPP et TPPO coabsorbent. La calibration produite démontre une très bonne linéarité pour des indices de peroxyde entre 0 et 100. La validation de la méthode a été effectuée en comparant les résultats obtenus par la méthode FT-NIR avec les mesures obtenues selon la méthode officielle de détermination de l'indice de peroxyde de l'AOCS. Une excellente corrélation entre les résultats des deux méthodes a été obtenue. Suite à la programmation du système FT-NIR, la procédure d'analyse a été simplifiée et consiste à ajouter une solution standardisée de TPP à l'échantillon d'huile, mélanger et obtenir le spectre FT-NIR. Le résultat apparait ensuite à l'écran. La performance d'un prototype du système COAT a été mesurée. Ce système utilise la spectroscopie infrarouge moyen à transformée de Fourier et bénéficie d'un design avancé de procédé de manipulation des échantillons et d'une programmation informatique simplifiant son utilisation. Le système s'est montré très efficace pour évaluer la qualité de l'huile et le comportement des antioxydants en temps réel. Le design du système s'est révelé efficace pour reduire le coût total de fabrication.

En terme d'application pratique, les deux approches offrent des avantages combinés de rapidité, précision, faible coût de main-d'oeuvre, automatisation et de faible impact sur l'environnment via une utilisation minime de produits chimiques et solvents. Les systèmes infrarouges se montrent donc pratiques pour le contrôle de la qualité routinier dans les industries de graisses et d'huiles, autant commestibles qu'industrielles. Finalement les applications potentielles basées sur l'utilisation conjointe des deux méthodes pour obtenir la mesure réelle de la stabilité d'une huile sont présentées.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor Dr. F. R. van de Voort, for his support, guidance, encouragement and invaluable advice throughout this research as well as thesis preparation, particularly, for providing me the chance for conducting this research work and the friendly environment for problem discussion and solving. I also wish to thank Dr. A. A. Ismail, Ms. J. Sedman and my colleagues for their academic advice, discussion and support throughout this study. The translation of the abstract in to French by Ms. J. Dubois is gratefully acknowledged.

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Finally, I want to take this opportunity to present my special thanks and gratefulness to my parents and sister, whose support and encouragement have made this work possible.

LIST OF FIGURES

1

INTRODUCTION

Mineral oils are the largest group of liquid lubricants which have been extensively used for a long period and in many areas, such as industrial and agricultural machinery, and wherever mechanical lubrication is required. However, with the increasing concern of environment protection, the current trend in lubrication is more toward those lubricants which offer a high level of performance without harming the environment. Due to the environmental contamination resulting from spillage and disposal of traditional mineral based lubricating fluids, the demand for biodegradable lubricants has been increasing rapidly in recent years, especially in the field of machinery operating near forests, crops and waterways. Information from various sources indicates that the public demand for the use of renewable resources, the threat of global warming and the search for enviro-friendly lubricants has already tipped away from mineral oils and toward biodegradable oils (Saunders, 1995). Current biodegradable lubricants available on the market are commonly based on vegetable (triglyceride based) oils, synthetic esters, or polyethylene glycols. Among these categories, vegetable oils are essentially considered as having the advantage of being a renewable resource lubricant and superior performance in reducing friction and wear over mineral based or synthetic oils (Hairston, 1994). A representative vegetable oil used in lubrication industry is rapeseed oil which is considered as an excellent lubricant owing to its good adherence properties, high flashpoint, high viscosity indices, low volatility, good miscibility with other lubricant base fluids as well as excellent stability under shear stress over a wide range of operating temperature (Kyriakopouls, 1995). A limitation of triglyceride based lubricating oils is their relatively poor oxidative and hydrolytic stability and temperature sensitivity. At low temperatures they tend to solidify and at high temperatures they readily deteriorate. These disadvantages could potentially be overcome by the use of appropriate additives, such as antioxidants, antiwear additives, and corrosion inhibitors.

The monitoring of an oil during their usage or storage is particularly informative in terms of determining oil quality and the performance of additives. A number of analytical methods including standard methods and various procedures are available to the industry, however, most of them more or less suffer from limitations such as time taken for the analysis, the use of environmentally harmful reagents, lack of sensitivity/selectivity, cost of analysis, and lack of automation. The McGill IR Group has worked on the development of Fourier Transform Infrared (FTIR) spectroscopic method, an advanced technique of infrared spectroscopy that has been used for the study of oils and related materials for a number of years (Compton, et al., 1987), to eliminate such problems and concerns to carry out rapid, accurate, and automated analyses directly on neat fats and oils.

In accordance to the overall goal of our research group, this thesis work addresses issues related to the development of a continuous oil analysis and treatment (COAT) system, which was part of an industrial research program carried out in conjunction with Thermal-Lube Inc. in Montreal. In terms of thesis structure, an overview of the triglyceride based fats and oils and the principles of IR/FTIR are presented, subsequent chapters consisting of two papers submitted for publication dealing with the development of a Peroxide Value (PV) method based on a stoichiometric reaction of hydroperoxides in oils and the performance of COAT system for additive tracking and replenishment. A general conclusion and the potential application of the methodology developed were discussed at the end of this thesis.

2

LITERATURE REVIEW

2.1 Introduction in Fats and Oils

Fats and oils are water insoluble, hydrophobic substances which predominantly consist of glyceryl esters of fatty acids. Triglycerides normally represent over 95% (weight) of the composition in food fats and oils derived from oilseed and animal sources. Other components including mono- and diglycerides, free fatty acids, phosphatides, sterols, fatty alcohols, and fat-soluble vitamins etc. are considered as minor components of most fats and oils (ISEO, 1994). Triglycerides are predominantly comprised of fatty acids present in the form of esters of glycerol, which contribute 94~96% of the total weight of the molecule of glyceride. Because of their predominant weight in the glyceride molecules, the physical and chemical properties of triglycerides that are greatly influenced by the kinds, proportions of the component fatty acids and the way they are positioned on the glycerol moiety, directly govern the properties of fats and oils.

Numerous triglyceride based fats and oils are currently available. Of particular interest in this study is the high erucic acid rapeseed (HEAR) oil which belongs to rapeseed categories consisting of high erucic-acid type (20-60%), low erucic-acid type (0-5%) and zero-erucic acid type (Sonntag, 1979a), of which HEAR oil is characterized with some unique and advantageous lubrication properties. An illustration of the selected physical characteristics and fatty acid compositions of HEAR oil obtained from various sources is presented in Table 1. The unique lubrication properties of HEAR oil relative to other vegetable oils are attributed to the relative high concentration of erucic acid, a monounsaturated fatty acid with physical properties such as melting point and titer comparable to oleic acid, while its oxidative stability properties more closely approach those of saturated fatty acids because of its chain length (Flider, 1995). Relatively new

Table 1. Characteristics and fatty acid composition of HEAR Oil from various sources during the period 1948-1977 (Sonntag, 1979a)

Analysis	High Erucic Acid Rapeseed Oil
Fatty Acid (% w.t.)[a]	
14:0	tr.-1.2
16:0	0.6-4.9
16:1	0.1
18:0	0.6-2
18:1	9.6-33.5
18:2	11.4-14.3
18:3	4.7-11.3
20:0	0.5.-0.7
20:1	0.8-13.5
20:4	tr.-0.4
20:5	tr.-0.4
22:0	-
22:1	20.1-59.4
24:0	0.1-1.4
Characteristic[b]	
Specific gravity at 25/25°C	0.906-0.910
Refractive index at 25°C	1.470-1.474
Titer	11.5-15°C
Viscosity (Saybolt Universal at 100°C)	≥210 sec
Flash point, open cup	≥550°F
Iodine number	97-108
Saponification number	170-180

[a] Data based on the commercial and developmental rapeseed oils mainly from Sweden and Canada during the period of 1965-1977.

[b] Data based on the rapeseed oils produced during the period of 1940-1965.

applications for HEAR oil and its derivatives include: (i) being as an excellent functional substitute for diesel oil-based release agents in the manufacture of clay roofing tiles; (ii) used as viscosity enhancers (such as Telomers) for vegetable oil-based lubricants and hydraulic fluids; and (iii) widely used in various applications including drilling muds, metal-working fluids, aluminum billeting and steel casting (Flider, 1995).

Knowing the physical properties of fats and oils is important in applications. For example, many technical applications of fatty products require the viscosity, solubility, melting behavior, or other physical characteristics to be defined or controlled. The physical characteristics of fats and oils are strongly dependent upon internal and external factors which commonly include the length of the carbon chains in fatty acids, the degree of unsaturation, the isomeric forms of the fatty acids, molecular configuration, and processing. In most circumstances, internal factors are always important and dominate the physical behavior of fats and oils. Important measurements of physical properties of fats and oils usually include: viscosity, smoke, fire and flash points, solubility and miscibility, refractive index (n_D), and melting point.

Depending on the stresses encountered and agents they are in contact with, most fats and oils can undergo a variety of reactions, such as hydrolysis, oxidation, polymerization, and isomerization, etc. Fatty acids that contain eight or more carbon atoms are capable of undergoing most of the reactions of the simpler members of the series, such as acetic acid. Unlike most edible materials, fats and oils suffer relatively little spoilage or deterioration from bacterial activity. Most of the damage occurring in fats and oils during storage is the result of atmospheric oxidation, also known as autoxidation (Sonntag, 1979b). The oxidative stability of fats and oils can be significantly improved by adding appropriate antioxidant(s), mostly applied in combination of two or more antioxidants rather than the equivalent amount of a single compound. More detailed information about autoxidation and antioxidation in fats and oils, their mechanisms, functionalities, and most popular detection/determination techniques are provided in the subsequent sections.

2.2 Autoxidation and Antioxidants

2.2.1 Autoxidation

Autoxidation is the most common deteriorative reaction occurring in all fats and oils. The stability of fats and oils in the presence of air or oxygen is considered as an important chemical property in the oil industry.

During oxidation, oxygen reacts with unsaturated fatty acids to form hydroperoxides which are odorless and tasteless substances, being the primary products of autoxidation. Free radical reaction of unsaturated fatty acids which can be described in terms of initiation, propagation, and termination processes has been the most widely accepted main mechanism of the primary steps of oxidation reaction. A generalized scheme of the primary steps in autoxidation is illustrated in Figure 1. As shown, free radicals (R*) react with oxygen to form peroxy free radicals which attack hydrocarbons of fats and oils to form hydroperoxides (ROOH) and new free radicals. As the reaction proceed, free radicals are formed more rapidly and the rate of oxidation increases.

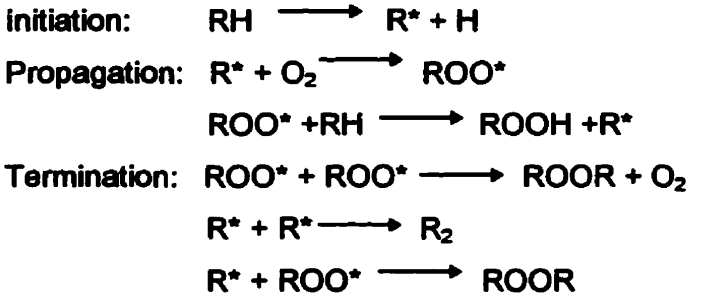


Figure 1 Primary steps in autoxidation reaction (Paquette, et al., 1985a)

Sensory quality of fats and oils is not affected until volatile secondary products are formed mainly from hydroperoxide breakdown. Such secondary products are usually powerful odoriferous compounds, and even in the very small amounts in which they occur will produce strong characteristic rancid-off flavors. Among the resulting products, carbonyl compounds are the main odor carriers in lipid peroxidation. Hydrocarbons, such

as alkanes, alkenes, alkylfurans and alcohols play a lesser role in such aspect. As the formation of secondary products is a complex process and not related to this study, hence its mechanisms will not be discussed in depth. In general, the oxidative products are much more complex than those of other reactions such as hydrolysis. For vegetable based oils, the oxidation products are usually a combination of hydroperoxides, alcohols, and aldehydes. In addition, moisture, hydrocarbons, free fatty acids and esters, lactones, furans and other minor products may also be produced (van de Voort, 1994a). Oxidation reactions occurring at higher temperature may not follow precisely the same routes and mechanisms as reactions at more moderate temperatures, where in the former case, polymerization might predominate (Paquette, et al., 1985b).

By measuring the amount of oxygen absorbed or by determining the amount of peroxides formed in fats and oils, the initiation of oxidation steps can be readily followed. Experimental observation has determined that the course of oxidation consists of two distinct phases as shown in Figure 2. During the initial stage, oxidation proceeds at a relatively slow and uniform rate. After a certain amount of oxidation has occurred, the reaction enters a second stage characterized by rapid oxidation of which the reaction rate is many times greater than that of the initial stage. It has been estimated that the point at which fats and oils began to smell or taste rancid coincides more or less with the beginning or early part of the second stage (Sonntag, 1979b).

Scientific research has revealed that the stability of fats and oils to autoxidation is affected by a number of factors covering both internal and external conditions. The more unsaturated fats and oils are, the greater their susceptibility to oxidative rancidity. Internal factors affecting the rate of oxidation include the distribution, geometry, and number of double bonds in the glyceride chains. Other structural factors which may contribute include: (i) conjugated double bonds being more reactive to autoxidation than nonconjugated; (ii) *cis* acids oxidize more readily than trans isomers; (iii) addition of each reactive methylene group to a structure directly leads to increase in autoxidation rate; (iv)

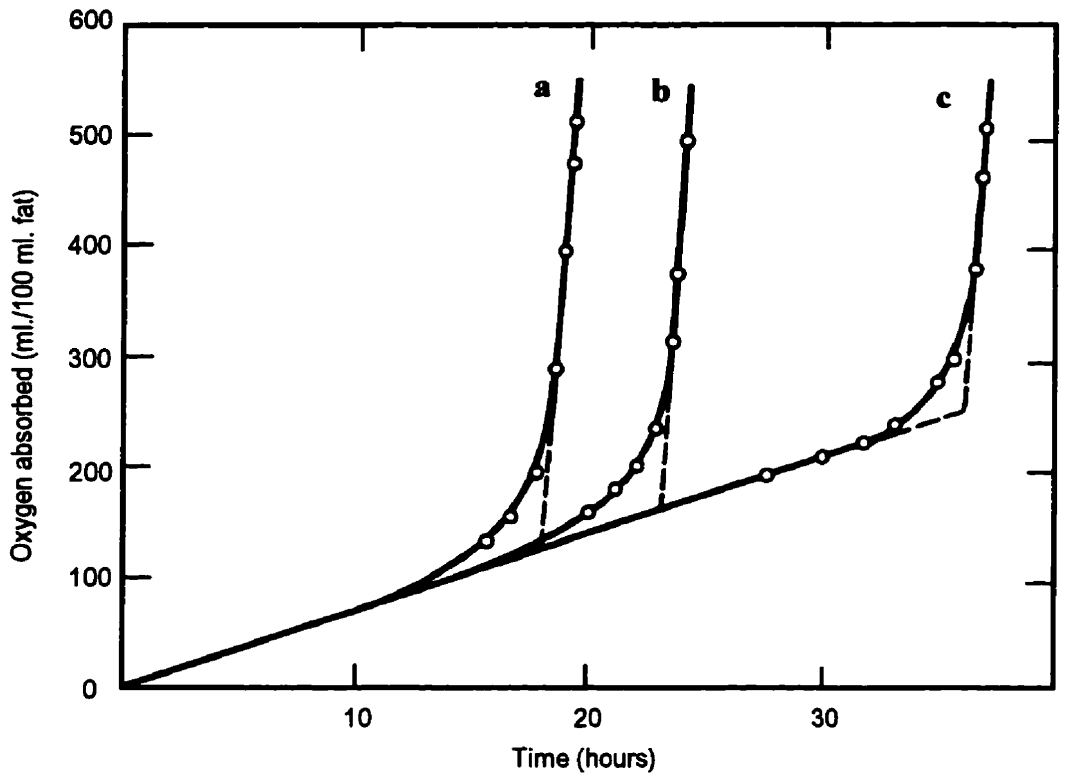


Figure 2. Oxygen uptake at 90°C of (a) corn oil, (b) corn oil plus 0.02% lauryl caffeate, and (c) corn oil plus 0.10% lauryl caffeate (adapted from Sonntag, 1979b).

randomizing the fatty acids in a fat using alkali decreases the rate of autoxidation, and (v) an increase of ratio of unsaturated acyl groups at the 2-position of glyceride increases oxidation stability (Raghuveer and Hammond, 1967). In addition to these internal features, many external factors are also important. Trace of metals, such as iron, copper, and cobalt can catalyze oxidation by enhancing the formation of free radicals or by acting as prime oxidizing agents usually in the highest valence state (Waters, 1971). The presence of water in an oil affects the oxidation reaction and the efficacy is somewhat complex. At low concentrations, water acts much like an antioxidant, whereas at high concentrations it functions as a prooxidant because it can hydrate and solubilize trace metals. Exposure of fats and oils to light, particularly in the ultraviolet or near ultraviolet region will accelerate the oxidation. The presence of heat and prooxidants can also greatly accelerate the rate of oxygen absorbance, thus increase the rate of oxidation. In this case, the accelerating effect of temperature varies more or less with the source and processing history of an oil because natural fats and oils differ in their antioxidants and prooxidant content, and prooxidants are not equally effective over all temperature ranges. It has been estimated that at the temperatures below 60^0C, the rate of oxidation is fairly low with a rate doubling at about every 45^0C rise in temperature, while above 60^0C the doubling interval is about 11^0C (Sonntag, 1979b).

2.2.2 Antioxidants

The ubiquitous property of oxygen in attacking lipids requires protecting the oil from deterioration as well as prolonging its life time, a goal that can be achieved by the use of antioxidants. A remarkable characteristic of antioxidants is their high efficiency at relative low concentrations in the oil. So far, no universally accepted mechanism is available to explain how these trace amount of additives are able to exert so powerful influence in retarding autoxidation. There is a general agreement that the antioxidants control oxidation either by a free radical inhibiting mechanism via attacking the hydroperoxides formed in the initial oxidation step or by reducing the rate of chain initiation via a variety of mechanisms such as metal ion deactivation (Gordon, 1990)

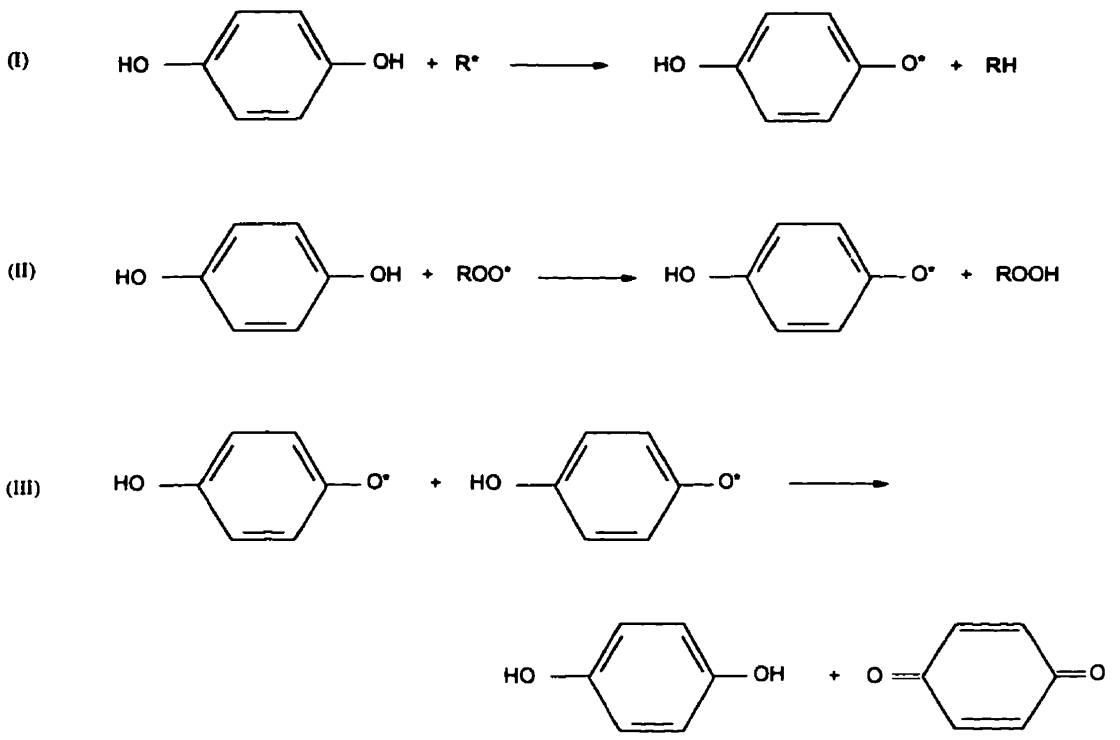
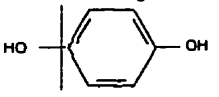


Figure 3. The mechanism for the antioxidation reaction of hydroquinone

R* = free radical

ROO* = oxygenated free radical

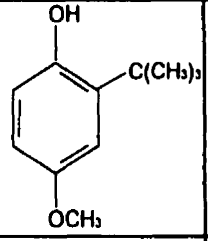
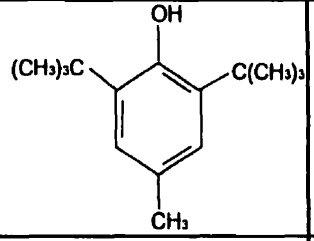
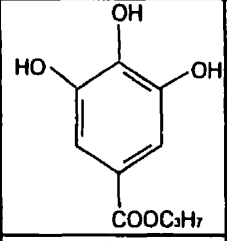
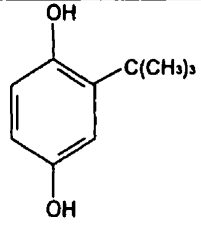
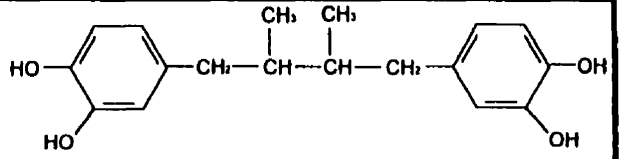
ROOH = primary oxidation product (hydroperoxide)

 = hydroquinone

Each mechanism inhibits oxidation at a different segment of the chain reaction. A typical example of the radical inhibiting reaction of hydroquinone is present in Figure 3. In this example, equations I and II show that the antioxidant supplies hydrogen atoms to terminate both the initiating and propagation steps in the autoxidation chain reaction. The reversed steps are sluggish because energy is required to remove hydrogen atoms from RH and ROOH. If the antioxidant were present before many radicals and chain carriers were produced, the presence even of trace amount of antioxidant would causes a tremendous decrease in the rate of autoxidation. Since the antioxidants are eventually depleted during the induction period, there is a rapid increase in the rate of peroxide formation afterwards. Therefore, to assure the oil quality and the performance of antioxidants as well as other additives, replenishing fresh additives by employing appropriate dosing systems during the usage or storage of fats and oils would be useful. After the end of the induction period, antioxidants have no effect in decreasing autoxidation. Once rapid oxidation is in process, the rate of oxidation in originally protected fats and oils is as rapid as those in unprotected systems. In some cases, decomposed antioxidant may also yield substances which can produce prooxidant effects (Sonntag, 1979b).

The structures, important physical properties, and typical applications of five most common food antioxidants, namely butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ), propyl gallate (PG), and nordihydroguaiaretic acid (NDGA) are listed in Table 2, the first four being the most popular antioxidants for rapeseed oils (Anonymous, 1989b). TBHQ is stable at high temperature and is known to be a very effective antioxidant for vegetable oils whereas BHA and BHT are less effective in this aspect. However, BHA is an effective antioxidant in fried foods and both BHA and BHT perform well in animal fats (Gordon and Kourimska, 1995). Classification of antioxidants varies from source to source, depending on the functionality of the antioxidant and its application. Antioxidants commonly used in edible fats and oils are primary types, functioning as the interrupter of the free radical

Table 2. Selected synthetic antioxidants commonly used in food systems (Robards and Dilli, 1987; Kochhar and Rossell, 1990)

Antioxidant*	BHA	BHT	PG	TBHQ	NDGA
Structure					
Melting point (^{0}C)	48-55	69-70	146-148	126.5-128.5	184-185
solubility (g/100ml) Water Typical fat/oil	 Negligible 30-40	 Negligible 20-30	 0.35 1	 1 5-10	 Negligible 1
Typical applications	Animal fat, cheese spread, biscuits, beef, potato, flakes, stock cubes	Animal fat, walnuts, chewing gum	Vegetable oils, chewing gum	Palm oil, frying oils	N/A

* BHA = butylated hydroxyanisole;
BHT = butylated hydroxytoluene;
PG = propyl gallate;
TBHQ = tertiary butylhydroquinone;
NDGA = Nordihydroguaiaretic acid.

Table 3. Classification of selected food antioxidants (Kochhar and Rossell, 1990)

Group	Functionality	Antioxidants
Primary antioxidants	terminating the free radical chains	BHA, BHT, TBHQ, tocopherols, alkyl gallates, etc.
Secondary antioxidants	decomposing the hydroperoxides into stable end products	dilauryl thiopropionate, thiodipropionic acid, etc.
Oxygen scavengers	removing oxygen	ascorbic acid, ascorbyl palmitate, erythorbic acid and its sodium salt, etc.
Enzymic antioxidants	removing oxygen or highly oxidative species	glucose oxidase, superoxide dismutase, catalase, glutathione perosidase, etc.
Chelating agents	chelating metallic ions	citric acid, amino acids, ethylenediaminetetra-acetic acid (EDTA), etc.

chain reactions in lipid oxidation. A summary of the classification of food antioxidants based on the functionality of the antioxidant are presented in Table 3.

2.3 Monitoring the Oxidation and Antioxidant levels in Fats and Oils

2.3.1. Oxidation

Monitoring the course of oxidation in fats and oils can be achieved by measuring the oxidation products of each steps of oxidation, making use of a number of physical/chemical procedures to determine characteristic products of each steps, such as measuring the loss of unsaturation in initiation stage via Iodine Value (Anonymous, 1989a), determining the hydroperoxides in propagation step through Peroxide Value (Anonymous, 1989a), and observing secondary carbonyl and hydrocarbon compounds such as aldehydes, free fatty acids by Anisidine Value (Anonymous, 1989a), TBA number (Patton et al., 1951 and Patton, 1974), and Free Fatty Acid value (Asakawa and Matsushita, 1976 and Gray, 1992), etc.. Among these methods, the determination of hydroperoxides is crucial since such components are important indicators of the status of an oil in terms of quality and potential shelf life, owing to their being the primary products formed as the autoxidation commences and serving as precursors to the formation of secondary oxidation products (Gray, 1978). The PV method is also extensively used in monitoring the oxidative status of bulk oils in storage and testing the oil stability as well as the efficacy of antioxidant by stability test such as Active Oxygen Method (Anonymous, 1989a).

Peroxide Value

Peroxide Value is defined as milliequivalents of oxygen or millimoles of peroxide per 1000 grams of oils or fats. A number of methods for the determination of PV have been proposed and used, among them AOCS approved (Anonymous, 1989a) iodometric procedures (Cd 8b-90 and Cd 8-53) are probably the most popular official methods used around the world (Dubois, 1995). The ability of these two methods to determine hydroperoxides in fats and oils is through the stoichiometric liberation of molecular iodine from potassium iodide by peroxides in acidic environment, the iodine subsequently

quantitated by titration with sodium thiosulfate, the hydroperoxide concentration known based on the stoichiometry of the two reactions (Anonymous, 1989a) outlined below:

$$ROOH + 2I^- + 2H^+ \longrightarrow I_2 + ROH + H_2O$$
$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

The iodometric method, although highly empirical, is relatively simple, reliable, reasonably sensitive and reproducible and applicable to all normal fats and oils (Anonymous, 1989a). However, most methods suffer from being labor intensive, tedious, consumption of environmental hazardous solvents/reagents, and requirement of specialized knowledge for chemical analysis (Berner, 1987; Matsushita and Asakawa,1979). The accuracy of the results depends on a number of factors, including experimental conditions, standardization of solutions, absorption of iodine at double bonds of unsaturated fatty acids, and the release of iodine from potassium iodide in the presence of oxygen dissolved in the solution to be titrated, the latter two being the principal sources of error (Gray, 1978, 1992; Mehlenbacher, 1960; Robards et al., 1988). Modifications of the original iodometric methods to improve the sensitivity or minimize the errors have been reported, largely addressing the optimization of the conditions of each step such as saturating the sample tube with nitrogen to eliminate the oxygen error (Lea, 1931), replacing the titration step by an automated routine or by electrochemical technique (Fiedler, 1974) to eliminate the uncertainty attributable to the experimenter. Different methods based on spectrophotometry have been reported by Lips and co-workers (Lips, et al., 1943) in their early work of making use of the oxidation of ferrous (II) to ferric iron (III) and the determination of the latter as ferric thiocyanatel; and by Eskin and colleagues (Eskin, et al., 1976) in their approach of reducing hydroperoxide with titanium (III). Time consuming is the major drawback within these alternatives.

Instrumental analyses are of particular value in the hydroperoxides determination. Numerous procedures based on spectrophotometry (St. Angelo, et al., 1975), polarography (Lewis, et al., 1949), refractometry (Ayra, et al., 1969), gas

chromatography (GC), gas chromatography/mass spectrometry (GC/MS) (Frankel, 1979), liquid chromatography (LC) (Frankel, 1962), and infrared spectroscopy (IR) (O'Connor, 1956; van de Voort, et al., 1994b and c) etc. have been described for the qualitative and quantitative determination of hydroperoxides in various lipid systems. A more detailed discussion of these methods has been presented elsewhere (Gray, 1978; Frankel, 1979).

2.3.2. Determination of Antioxidants

Methods for the detection and determination of antioxidants in fats and oils involve a large variety of analytical techniques including AOCS, AOAC, and IUPAC approved standard tests and other physical/chemical procedures, requiring considerable sample preparation such as extraction prior to separation and estimation of individual antioxidants. Table 4 lists some official methods for the identification and quantitative determination of commonly used antioxidants in fats and oils.

Table 4 Official or standard methods for detection and determination of selected food antioxidants (Kochhar and Rossell, 1990)

Component	Method Source	Procedure/technique	Reference
BHA and BHT	IUPAC	Steam distillation/colorimetry/ spectrophotometry	IUPAC, 1987
TBHQ, TBHP, PG, BHA, and BHT	AOAC, AOCS	Extraction/HPLC/ UV detection at 280nm	AOAC, 1984, Anonymous, 1989a

Earlier work on the determination of food antioxidants employed various colorimetric and UV-visible spectrophotometric methods as listed in Table 5, most based on the specific reaction between functional group(s) of antioxidant and chemical reagents to form characteristic colored products that produce absorptions under UV-Vis regions of the electromagnetic spectrum. Due to the lack of selectivity/sensitivity and various limitations of colorimetric and spectrophotometric methods, alternative procedures based on chromatography (paper, TLC, GPC, GLC and HPLC) are becoming more popular in the detection and estimation of most common antioxidants in fats and oils. Among them,

paper (PC) and thin-layer chromatography (TLC) might have been used the most extensively in the past owing to their simplicity and low cost. Particularly, the identification of antioxidants in food systems by TLC is considered to have potential application because of low cost and ability to obtain quantitative results (Robards and Dilli, 1987). A description of the relative merits of PC and TLC for antioxidant analysis have been presented by Seher (1959 and 1960). Selected applications of PC and TLC for food antioxidants are listed in Table 5.

Gas-liquid chromatographic (GLC) methods have been extensively used to determine antioxidants in various food products, such as fats and oils, dairy products, sea foods, meat products, etc., owing to its ability to separate, identify and determine nanogram amounts of complex mixtures simultaneously. Commonly used antioxidants, BHA, BHT and TBHQ exhibit excellent GC separation properties and their determinations may be readily achieved on either polar or non-polar stationary phases. Usually, low stationary phase loadings are used to reduce the retention time since phenolic antioxidants are relatively nonvolatile. Some GC techniques for the determination of antioxidants in fats and oils are compared in Table 5.

High performance liquid chromatography (HPLC) probably is the most powerful chromatographic technique in antioxidant determination compared to pervious approaches because HPLC offers all the advantages of GC and possess great flexibility in choosing mobile phase, stationary phase and detector. Normal phase HPLC has been developed and, however restricted to the analysis of BHT, BHA, and TBHQ (Ansari, 1983; Indyk and Woolard, 1986). Simultaneous determination of nine synthetic antioxidants in oils, lard and shortenings was reported by Page (1979) using reversed phase column (Table 5). Size-exclusion technique has also been used and still holds the promise of direct injection of complex samples with minimal sample pre-treatment (Pokorny, et al., 1972; Doeden, et al., 1979).

In addition to the methods described above, there exists a number of other procedures applicable to the testing of fats and oils which can be very useful in solving specific problems relating to both oil status and performance of additives. Among these, infrared (IR) spectroscopy is probably the most universally applied method among instrumental techniques and has been used for a number of years (Compton, et al., 1987). This technique is particularly useful in routine quality control applications as little or no sample pretreatment is required and both qualitative and quantitative determinations can be readily achieved. The method is capable of identifying oil compositions, additives and their concentration, reaction products, and contamination of oil with organic materials. A further descriptions of infrared spectroscopy, its history, basic theory, instrumentation, and application pertinent to this work is presented in the next chapter.

Table 5. Summary of selected methods for the determination of common antioxidants

Reagents/conditions used	*Antioxidant*	*Reference*
Colorimetry		
iron (III) chloride-2,2'-dipyridyl	BHA	Stuckey and Osborne, 1965
Gibb's reagent	BHA	Mahon and Chapman, 1952; Berger, et al., 1960
diazotised sulphanilic acid	BHA	Laszlo and Dugan, 1961
Spectrophotometry(UV)		
Propan-2-ol / 232, 241, 252nm	BHA, PG	Whetsel, et al., 1955
chloroform-methanol/270,290,310nm	BHA	Hansen, et al., 1959
Paper Chromatography (PC)		
aqueous methanol/water as solvent; PMA[a] as detection reagent	BHA, BHT, PG, NDGA	Mitchell, 1957
Acetone - ethyl acetate - water as solvent; PMA as detection reagent	BHA, BHT, PG, NDGA	Dehority, 1959
Thin-layer Chromatography (TLC)		
Light petroleum - benzene -acetic acid and Hexane -acetone - acetic acid as solvent; GB[b] as reagent	BHA, BHT, PG, TBHQ, NDGA	Van Peteghem and Dekeyser, 1981
Benzene then acetonitrile as solvent; GB as reagent	BHA, BHT, PG, NDGA	Sahasrabudhe, 1964
Chloroform /methanol/acetic acid as solvent; GB as reagent	BHA, BHT, PG, NDGA	Seheidt and Conroy, 1966
Hexane as solvent; FC[c] as reagent	BHA, BHT	Phipps, 1973
Gas Liquid Chromatography (GLC)		
3% JXR o Gas Chrom Q as SP[d]	BHT	Stoddard, 1972
10% DC 200 or 10% Carbowax 20M on Gas Chrom Q as SP	BHT, BHA	Hartman and Rose, 1970
10% GE-Versilube F-50 on Gas Chrom Q as SP	BHT, BHA, TBHQ, PG	Wyatt, 1981
10% polymetaphenoxylene on Tenax-GC as SP	BHT, BHA, TBHQ	Min and Schweizer, 1983
High Performance Liquid Chromatography (HPLC)		
SP: LiChrosorb NH_2 MP[e]: hexane/ethanol	TBHQ	Kitada, et al., 1985
SP: Porsail or Rad-Pak cyano MP: Hexan/dichloromethane/acetonitrile	BHT, BHA, TBHQ	Indyk and Woolard, 1986
SP: 5 µm LiChrosorb DIOL MP: Hesane/1,4-dioxane/acetonitrile	BHA, TBHQ, PG, OG, DG, NDGA	Anderson and Van Niekerk, 1987
SP: 10 m LiChrosorb RP-18 MP: (1) 5% acetic acid in water (2) 5% acetic acid in acetonitrile	BHT, BHA, TBHQ, PG, TBHP, NDGA, OG, DG, Ionox-100	Page, 1979 and 1983

[a] PMA = phosphomolybdic acid or ammoniacal phosphomolybdic acid; [b] GB = Gibb's reagent;
[c] FC = Folin-Ciocalteau reagent; [d] SP = stationary phase; [e] MP = mobile phase

2.4 Infrared Spectroscopy

2.4.1. Introduction

Initial attempts at using infrared (IR) spectroscopy as a tool for chemical analysis took place in the early 1900's, however, it was not until the 1930's that appropriate dedicated instrumentation was developed. Prototype infrared instruments were built for industrial laboratories and theoretical exploration of spectral information of small molecules. Commercial instruments based on single-beam designs became available in 1944, and the first double-beamed infrared spectrophotometer was introduced in 1947. Since then, the application of infrared spectroscopy for molecular identification grew rapidly. By the 1960's, infrared spectroscopy had become the single most powerful analytical tool for exploring molecular structure of organic materials (Griffiths and Hasethk, 1986).

Infrared spectroscopy has been developed extensively in many forms, mainly making use of the near or mid infrared portions of the electromagnetic spectrum. Traditional IR spectroscopy makes use of dispersive instruments, using gratings and prisms, and its application have generally been limited to gas samples and materials soluble in IR transparent solvents. An important advance in current IR spectroscopy is the use of Fourier transform infrared (FTIR) techniques which greatly expand the application of IR technology. These techniques have been commercially available to researchers since the early 1970s (Griffiths and Hasethk, 1986). The use of complete source spectrum provided by interferometer rather than individual wavelengths which are generated by grating and/or prisms in conventional IR spectroscopy makes FTIR spectrometers a significant advance over dispersive type instruments (Griffiths and Hasethk, 1986). In addition, modern FTIR spectrometers are characterized as being more reliable, faster, having low operating costs, and better performance attributes, which make them more preferable than dispersive instruments.

2.4.2. Theoretical Basis

Infrared radiation covers that part of the electromagnetic spectrum lying between the visible and microwave regions, i.e. with wavenumbers ranging from about 12800 to 10 cm^{-1} or wavelengths from 0.78 to 1000μm. Of greatest practical use to organic chemists is the mid-infrared region extending from 4000 to 400cm^{-1}, however, a variety of applications have also made use of the near-IR (14290 - 4000 cm^{-1}) and the far-IR regions (700 - 200 cm^{-1}) (Silverstein, et al., 1991).

When infrared radiation of frequencies less than about 100 cm^{-1} is absorbed by an organic molecule, the absorbed portion of radiation is converted into energy of molecular rotation, this absorption resulting in a spectrum consisting of discrete lines. Infrared radiation ranging from about 1000 -100 cm^{-1} absorbed and converted by an organic molecule into vibrational energy will result in vibrational spectra appearing as band rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. The frequency or wavelength of absorption, or band position is dependent on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms. Band intensities which can be expressed either as transmittance (T) or absorbance (A) is proportional to the concentration of the molecule. It is with these vibrational-rotational bands that we shall be concerned (Silverstein, et al., 1991).

There are two basic types of molecular vibrations: stretching and bending. Only those vibrations resulting in an asymmetric change in the dipole moment of the molecule are observed in IR. The change of electric field, produced by the alternating charge distribution accompanying a vibration, couples the molecule vibration with the oscillating electric field of the electromagnetic radiation. In addition to these two fundamental vibrations discussed above, other frequencies can be generated by modulation of the fundamentals such as overtones (multiples of a given frequency) and combination tones (sum of two other vibrations). These two effects will increase the number of bands. A number of other phenomena that will reduce the number of bands was summarised elsewhere (Silverstein, et al., 1991)

The use of infrared spectroscopy to identify an organic compound is based on the appearance of common structural features or functional groups present in the compound. Group frequencies are vibrations that are associated with common structural units which produces consistently characteristic vibrations in the spectrum. Although structural units have their characteristic vibrations, many factors can influence the precise frequency of a molecular vibration. Detailed exploration of these factors is beyond the scope of this study. In general, factors influencing vibrational frequencies may include: coupled interactions, hydrogen bonding, electronic effects, bond angles and field effects (Kemp, 1991).

2.4.3. IR instrumentation

There are two basic types of infrared spectrophotometer, characterized by the manner in which the infrared frequencies are handled. In the first type, infrared light is separated into its individual frequencies by dispersion, using a grating monochromator, whereas in the second type the infrared frequencies are interacted to produce an interference pattern. The first type has had a long history and the second type is relatively new, where individual frequencies and intensities are determined by using Fourier transform as a tool for mathematically analyzing interference (Kemp, 1991).

The original design in the first type of instrument based on a simple prism monochromator is now largely obsolete, with most modern dispersive instruments using gratings as diffraction optics. However, dispersive infrared spectrometers also suffer from some disadvantages, typically including relatively low scanning speed, poor sensitivity and poor wavelength accuracy. A Fourier transform infrared spectrometer based on an entirely different principle possesses all the advantages of a simple IR spectrometer, but with improved speed, sensitivity and unparalleled wavelength precision and accuracy. These factors as well as a decrease in operating cost has popularized Fourier transform instruments, which are rapidly displacing dispersive instruments in most laboratories (Borman, 1983).

2.4.4. FTIR Spectroscopy

Basics

FTIR spectroscopy is based on interferometry, a concept and design originated by Michelson in 1891 (Michelson, 1961). Fig. 4 shows the simplest form of the Michelson

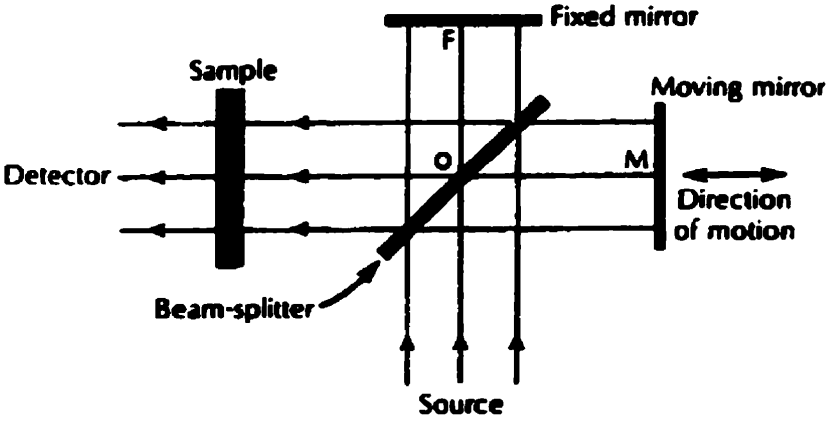


Fig. 4. Schematic diagram of a Michelson interferometer (van de Voort, 1994a)

interferometer. The whole device consists of a moving mirror and a fixed mirror being pendicular to each other, with a beamsplitter positioned at a 45^0 angle between them. The beamsplitter can divide a beam of source radiation into two paths and then recombine the two beams after a path difference has been introduced by the moving mirror. The moving mirror is either moved at a constant velocity or is held at equally spaced points for short fixed intervals and rapidly stepped between these points. The reflected beam strikes the movable mirror and is reflected back toward the beamsplitter, when combined with the transmitted beam after the beamsplitter and reflected from the fixed mirror, a path difference occur. As shown in Fig. 4, the path difference between the beams from fixed and movable mirrors results in a *retardation* (δ), which is equal to 2(OM-OF). The electromagnetic wave pattern and the intensity of the beam passing to the detector depends on the sum of behaviors of the beams reflected from the fixed and movable mirrors, as shown in Figure 5, could be *constructive interferogram* ($I'(\delta)= I(\nu)$, Fig. 5 a and c), resulted from a retardation of zero or λ, or *destructive interferogram* ($I'(\delta)=0$, Fig. 5 b) resulted from a retardation of $1/2\lambda$. As the mirror is moved at constant velocity,

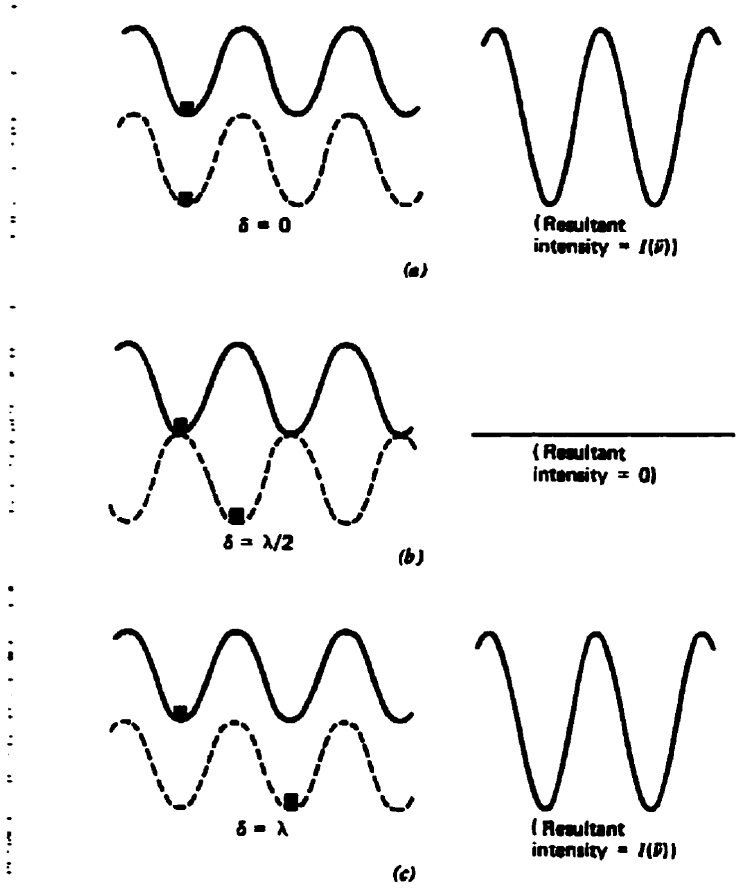


Fig 5. Schematic diagram of the phase of the electromagnetic waves from the fixed mirror (solid line) and movable mirror (broken line) at different values of the optical retardation. (a) Zero path difference; (b) path difference of one-half wavelength; (c) path difference of one wavelength. (Griffiths and Hasethk, 1986)

the signal at the detector will be observed to vary sinusoidally. The intensity of the beam at the detector at any values of δ can be expressed as:

$$I'(\delta) = 0.5\ I(\bar{\nu})\{\ 1 + \mathrm{COS}\ 2\pi\ \bar{\nu}\ \delta\}$$

where $I(\bar{\nu})$ is the intensity of the source and $\bar{\nu}$ is the wavenumber of the radiation. The *interferogram* ($I'(\delta)$) can subsequently be Fourier transformed mathematically by a computer algorithm to produce an IR absorbance spectrum.

FTIR Instruments

Fourier transform spectrometers basically consists of two parts: an optical system using an interferometer and a sophisticated computer for controlling optical components, collecting and storing data, performing signal averaging, carrying out the Fourier transformations and displaying spectra. The heart of commercially available FTIR instruments is the Michelson interferometer which drives the movable mirror and houses beamsplitter discussed in detail below.

To obtain a satisfactory interferograms (and thus satisfactory spectra), the speed of the moving mirror must be constant or its position exactly known at any instant. To accomplish this requirement, in most instruments, an internal reference laser is employed to monitor the position of the moving mirror and control the speed of the mirror-driving system at a constant level. In addition, the planarity of the mirror must also remain constant during its entire sweep of 10 cm or more. Thus, compared to the far-infrared region, the mid- and near-infrared instruments are equipped with more precise and sophisticated driving mechanisms (Skoog and Leary, 1992).

Ideally, the beam splitter is capable of precisely reflecting and transmitting 50% of the source radiation. However, in practice, most transparent materials coated on the beamsplitter can only approximate this ideal. Thin Mylar polymer film is ideal for far-infrared region, whereas, thin films of germanium or silicon deposited on cesium iodide or

bromide, sodium chloride, or potassium bromide beamsplitters are widely used for the mid-infrared region. For the near-infrared region, a film of iron (III) oxide deposited on calcium fluoride is generally used (Skoog and Leary, 1992)..

The infrared sources for Fourier transform instruments are similar to those used for most infrared instruments. For mid-infrared spectrometry, Nernst glowers, Globars, and nichrome coils are commonly used. For the far-infrared region of the spectrum, the use of a high-pressure mercury lamp is preferred. The mercury lamp is mandatory when wavenumbers below 75 cm^{-1} are used. For the wavelength in near-infrared regions of 4000 to 12800 cm^{-1}, an ordinary tungsten filament lamp is the most convenient source.

Infrared detectors can be divided into two types: thermal detectors and quantum detectors. Generally, thermal detectors are not readily adapted to Fourier transform instruments because of their slow response. Triglycine sulfate (TGS) pyroelectric detectors are commonly used for the mid-infrared region. For improved sensitivity and response, as well as high resolution work, liquid-nitrogen-cooled mercury cadmium telluride or indium antimonide photoconductive detectors are commonly employed. (Skoog and Leary, 1992; Griffiths and Hasethk, 1986).

To facilitate specialized applications, FTIR can be used in conjunction with other powerful instrumental techniques. For example, gas chromatography (GC) is an important quantitative technique for the analytical chemist. However, it provides less specificity in identification of eluate. To overcome this drawback, a hybrid instrument incorporating FTIR can be helpful. One such "hyphenated" technique is gas chromatography/Fourier transform infrared (GC-FTIR) spectrometry, first designed by Low and Freeman (1967). In this design, the FTIR spectrometer is used as a detector for the GC. FTIR as a detector is nondestructive and can provide structural information abut GC eluates (Low and Freeman, 1967; Griffiths and Hasethk, 1986). Further developments have brought GC/FTIR/MS systems which are very helpful in the structural identification that is not always possible by infrared spectrometry alone (Wilkins, et al., 1981; Crawford, et al.,

1982). Another chromatographic version of FTIR is high-performance liquid chromatography/ Fourier transform infrared (HPLC/FTIR) spectrometry. Prototype systems have been described by Kizer and colleagues in the 1970s (Kizer, et al., 1977), and applications of this technique have been documented by other authors (Vidrine and Mattson, 1978; Vidrine, 1979; Shafer, et al., 1979).

Applications of FTIR Spectroscopy

Since its introduction, IR technology has been advanced dramatically, particularly with mid and near IR spectroscopy. Mid infrared spectra are usually quite complex and provide a wealth of structural information about a chemical compound, which is related to their physical properties, thus providing a *fingerprint* that is readily able to distinguish one compound from another by differentiating their respective absorption pattern, with the exception of optical isomers. Hence, mid-infrared spectroscopy has been used as a common qualitative technique for the identification and verification of chemical materials for many years (Compton, et al., 1987, Martin, 1966). In addition, mid-IR spectroscopy is also amenable to quantitative analysis by using Beer's law and may be expanded to more complex multicomponent systems using advanced chemometric techniques. In the last several years, the use of near-IR spectroscopy has been greatly expanded, particularly owing to the application of silica core optical fibers which allows remote measurements and near-IR fiber-optic-based instruments and probes are becoming popular for routine laboratory and process analysis (Putzig, et al., 1994). Due to the greater difficulty in interpreting the spectra of near-IR vs. mid-IR spectra, the analysis of NIR spectra usually requires the use of more advanced mathematical modelling techniques using appropriate chemometric methods such as Partial Least Squares (PLS) (Anonymous, 1993). In terms of application, IR spectroscopy has been expanded into various forms for specialized fields and has been applied to a wide range of research areas in the past decades.

The general advantages of FTIR spectroscopy indicate the potential of this technique as an analytical tool in food system. Food scientists are recognizing the potential of this technology in food and initiating research programs to exploit the

technology (Barnett and Ismail, 1989). In addition, the introduction of attenuated total reflectance (ATR) techniques which can provide better signal-to-noise ratio, multiplexing, higher energy and improved resolution, makes quantitative FTIR analysis to food systems a viable proposition. As a consequence, food applications of FTIR have already covered a variety of food systems, including the analysis of milk, meat, fats and oils, butter and margarine, sweetened condensed milk, sugar and juice, etc. (van de Voort, et al., 1987). Proximate analysis of foods is one area which can benefit from infrared spectroscopy. Food systems are mainly composed of carbohydrates, proteins, fats, and moisture, which can produce characteristic absorption under infrared radiation. A typical example of FTIR application in food system is milk analysis for producer payment, dairy herd recording and quality control (van de Voort, et al., 1987). However, the application of traditional mid-IR spectroscopy to food systems has been limited because of the presence of water, which will generate strong absorptions across the mid-IR spectrum (van de Voort, 1994a). Near-IR spectroscopy is more powerful in the area of food analysis and continues to be widely applied to various food products such as sugar measurement, grain and feed evaluation, protein analysis, and fatty acids content in oils (Putzig, et al., 1994). The applications of near-IR spectroscopy to the field of clinical chemistry and the production of chemicals and polymers have also been reported. Detailed information of such applications could be addressed to the review of infrared spectroscopy by Putzig, et al. (1994). In addition to food products and the systems described above, the applications of FTIR technology to other areas have also been well documented, employing various IR regions (near, mid, and far IR) and instruments. These in general may include molecules and macromolecules studies (Rivera-Gaines, et al., 1991), solid-state materials characterization (Julien and Eddrief, 1992), studies in electrochemistry (Zhu, et al., 1994) and catalyst (Choi and Vannice, 1991), environmental (Brown, 1993; Homenauth and McBride, 1994) and biochemical (Drennen, et al., 1991) applications, and surface technology (Hoffmann, et al., 1992).

During the last decade, a number of studies in fats and oils by FTIR have been carried out. The range of this research is as broad, having covered most aspects of fats

and oils and employed most types of FTIR and combination techniques. Early examination of fatty acids in vegetable oils was carried out by Sebedio and co-workers (Sebedio, et al., 1987) by using GC/FTIR. Similar estimation of free fatty acids by FTIR has also been done by other authors (Lanser, et al., 1991; Ismail, et al., 1993). Brown and Elliott (1987) conducted quantitative analysis of minerals in oil shales by FTIR spectroscopy. A study of microemulsion structure by FTIR was reported by Macdonald et al. (1986). In addition, some work has been carried out on engine oils and their combustion deposits. Using a single cylinder engine, Kim and colleagues analyzed the engine combustion chamber deposits by FTIR and variety of other techniques. They found high-boiling aromatic compounds greatly contribute to deposit formation while olefinic compounds show no significant deposit-forming tendencies. An automated FTIR spectrometer was employed by Powell and Compton (1993) to monitor hydrocarbon-based engine oils. This approach can be very useful for trouble shooting, quality control, and competitive analysis. FTIR technology has also been applied successfully to monitor the performance of additives in lubricating oils (Bucsi, 1990).

Significant work has been carried out on FTIR spectroscopy of edible oils in the Department of Food Science at McGill University as of 1990. The McGill IR group has focused on the development of methodology of FTIR analysis for fats and oils. The group's initial focus into FTIR oil analysis methodology involved the simultaneous determination of iodine value (IV) and saponification number (SN) (van de Voort, et al., 1993). Second method developed was for rapid quantitative determination of free fatty acids in fats and oils (Ismail, et al., 1993). Subsequent work involved fundamental spectroscopic studies of oil oxidation under various conditions. This approach lead to the "development of conceptual framework for FTIR analysis of a variety of oxidative products that commonly are measured by AOCS methods" (van de Voort, et al., 1994b). More recent work include: the determination of peroxide (van de Voort, et al., 1994c) and moisture content of high-fat products (van de Voort, et al., 1993).

2.5 Objectives

Through the efforts of the McGill IR Group, FTIR and attenuated total reflectance (ATR) technology have been successfully applied to the analysis of various food systems such as butter, milk, meats, juices (van de Voort, 1994a) and edible oils (van de Voort, et al., 1994b), indicating that FTIR apparatus, by benefiting from numerous advantages of FTIR spectroscopy, can serve as a powerful and convenient means for routine quality control purposes. Further exploration in this aspect directs our interests in the development of FTIR methodology readily and effectively applicable to oil industry in the detection and determination of oil quality and behavior of performance-enhancing additives that commonly used. In particular, the objectives of this research covers the following considerations:

1. To identify a simple, rapid, and reproducible reaction based on stoichiometric conversion of lipid hydroperoxides, of which the resulting products have characteristic absorption in the mid-IR or near-IR region.

2. To develop a calibration model based on the stoichiometric reaction of hydroperoxides noted in item 1 for the prediction of peroxide value (PV) in oil samples and validate it by the comparison to that of AOCS approved standard methods.

3. To develop a fully integrated, FTIR based continuous oil analysis and treatment system (COAT) for the *on-line* or *at-line* monitoring of oil quality and performance-enhancing additives.

4. To test the performance of COAT system through automated tracking the depletion of and the replenishment of antioxidant added in oils.

3

STOICHIOMETRIC DETERMINATION OF HYDROPEROXIDES IN OILS BY FOURIER TRANSFORM NEAR INFRARED (FT-NIR) SPECTROSCOPY

Abstract

A rapid Fourier transform near-infrared (FT-NIR) spectroscopic method was developed for the quantitative determination of peroxide value (PV) in edible oils based on the stoichiometric reaction of triphenylphosphine (TPP) with hydroperoxides to produce triphenylphosphine oxide (TPPO). Calibration standards were prepared by addition of randomized amounts of TPPO and TPP to peroxide-free high-erucic-acid rapeseed (HEAR) to produce a calibration matrix spanning the concentrations of TPPO and residual TPP that would be present in oils having PV values in the range of 0 to 100 after complete reaction of the hydroperoxides with added TPP. A partial least squares (PLS) calibration model for the prediction of PV was developed using the NIR spectral region from 4710 to 4540 cm^{-1} , where TPP and TPPO both absorb. The resulting calibration was linear with a standard deviation of ± 1.36 PV over the analytical range. Validation of the method was carried out by comparing the PLS-predicted PV of oils spiked with tert-butyl hydroperoxide (TBHP) and those of naturally oxidized HEAR oils to the results obtained using the American Oil Chemists' Society (AOCS) iodometric procedure. The FT-NIR PV method correlated very well (SD = 1.20) with the reference AOCS method for TBHP-spiked oil samples. Similar results were obtained for naturally oxidized HEAR oil, with an SDD_r of ± 1.11 PV being obtained for both methods. In terms of application, the analysis simply consists of the addition of ~0.04 ml of TPP stock solution to 1g of oil, shaking, recording the spectrum and using the PLS calibration to predict the PV value. Based on the simple and rapid stoichiometric reaction and its excellent correspondence to the iodometric method, the FT-NIR method provides a simple and alternative means of PV measurement. The FT-NIR method avoids the solvent and reagent disposal problems associated with the AOCS method and can be readily automated by appropriate programming of the FTIR spectrometer, providing a simple and rapid analytical technique for PV determinations in fats and oils.

3.1 Introduction

The determination of hydroperoxides formed in lipids due to autoxidation, being an important quality indicator for edible oils and useful as a means of assessing the stability of biodegradable lubricants, is crucial in the edible and industrial fats and oils industry. In the presence of oxygen, lipid autoxidation is initiated by a variety of mechanisms, including heat, light, and metal ions, etc., leading to the formation of hydroperoxides (primary oxidation products), which subsequently break down to produce a variety of alcohols and carbonyl compounds (secondary oxidation products) producing the characteristic rancid off flavors (Paquette, et al., 1985 a, b). As hydroperoxides are an important indicator of the oxidative status of an oil, AOCS approved methods are available for their measurement (Anonymous, 1989), the key ones being two iodometric procedures for the determination of peroxide value (PV; Cd 8b-90 and Cd 8-53), differing in the solvent used, chloroform ($CHCl_3$) being discontinued due to environmental concerns. Both methods are based on the stoichiometric conversion of KI to molecular iodine by hydroperoxides in an acidic environment and subsequent titration using standardized sodium thiosulfate to determine the molecular iodine released. Although relatively simple, reasonably sensitive, reliable and reproducible, the iodometric method is labor intensive and tedious and uses large volumes of acidified solvent, considered environmentally problematic. A rapid Fourier transform infrared (FTIR) method for the quantitative determination of PV in vegetable oils without the use of reagents was previously developed by our research group, based on the use of *tert*-butyl hydroperoxide (TBHP) as a calibration standard (van de Voort, et al., 1994c). However, the calibration procedure developed, which employed partial-least-squares (PLS) regression to account for a variety of potentially interfering factors and components, was seen as being too difficult to implement on a routine basis. As a consequence of a substantive study being undertaken in our laboratory on the oxidative stability of biodegradable oil formulations, we were faced with the prospect of carrying out several thousand PV analyses. This prompted a re-assessment of our original approach to PV determination by FTIR spectroscopy and consideration of developing a method which placed less reliance on specialized sample handling accessories and made use of IR instrumentation more suitable

for an industrial setting. From this standpoint, FT-NIR was considered the instrumental approach of choice, specifically the NEMA certified Bomem system, which can operate in relatively hostile environments and which has a simple-to-use vial accessory capable of using low cost glass vials ranging in pathlength from 1 to 10 mm. We also wanted the analysis to be independent of oil variability by basing it on a well-defined stoichiometric reaction which could be readily tracked in the NIR. A detailed mid-IR spectral investigation and chemometric analysis of the reaction of triphenylphosphine (TPP) with hydroperoxides to form triphenylphosphine oxide (TPPO) carried out in our laboratory (Ma, et al., 1996) forms the basis of this work. This paper focuses on the development, implementation and performance of a FT-NIR method using the conversion of TPP to TPPO by hydroperoxides to determine the PV of neat fats and oils.

3.2 Materials and Methods

Instrumentation and Sample Handling

The instrument used in this study was a Bomem FT-NIR spectrometer (Hartmann & Braun MB-Series, Bomem Inc., Quebec) capable of covering the spectral range of 10,000-2000 cm^{-1}, controlled by an IBM compatible 486 DX-66 MHz PC running under Windows based Bomem-Grams/386 (Galactic Industries Co., Salem, NH) software. The sample handling accessory used was a temperature-controllable multi-vial holding block capable of accepting vials of various pathlengths. The vials used in this study were 8 mm (o.d.) transparent glass vials (Kimble Glass Inc., Vineland, NJ), having a volume of ~1 ml (Fig. 6). With the cell holder in the IR beam with a clean empty vial in place, the accessory was aligned to transmit >96% of the incident radiation. For sample analysis, vials were filled with ~0.7-1.0 ml of oil and scanned.

Spectra were recorded by co-adding 128 scans at a resolution of 4 cm^{-1}, using triangular apodization and a gain of 1.0, and ratioed against a 128-scan single-beam background spectrum of a clean empty vial. The spectra collected were subsequently normalized for pathlength, using a customized normalization routine (Bomem Inc.,

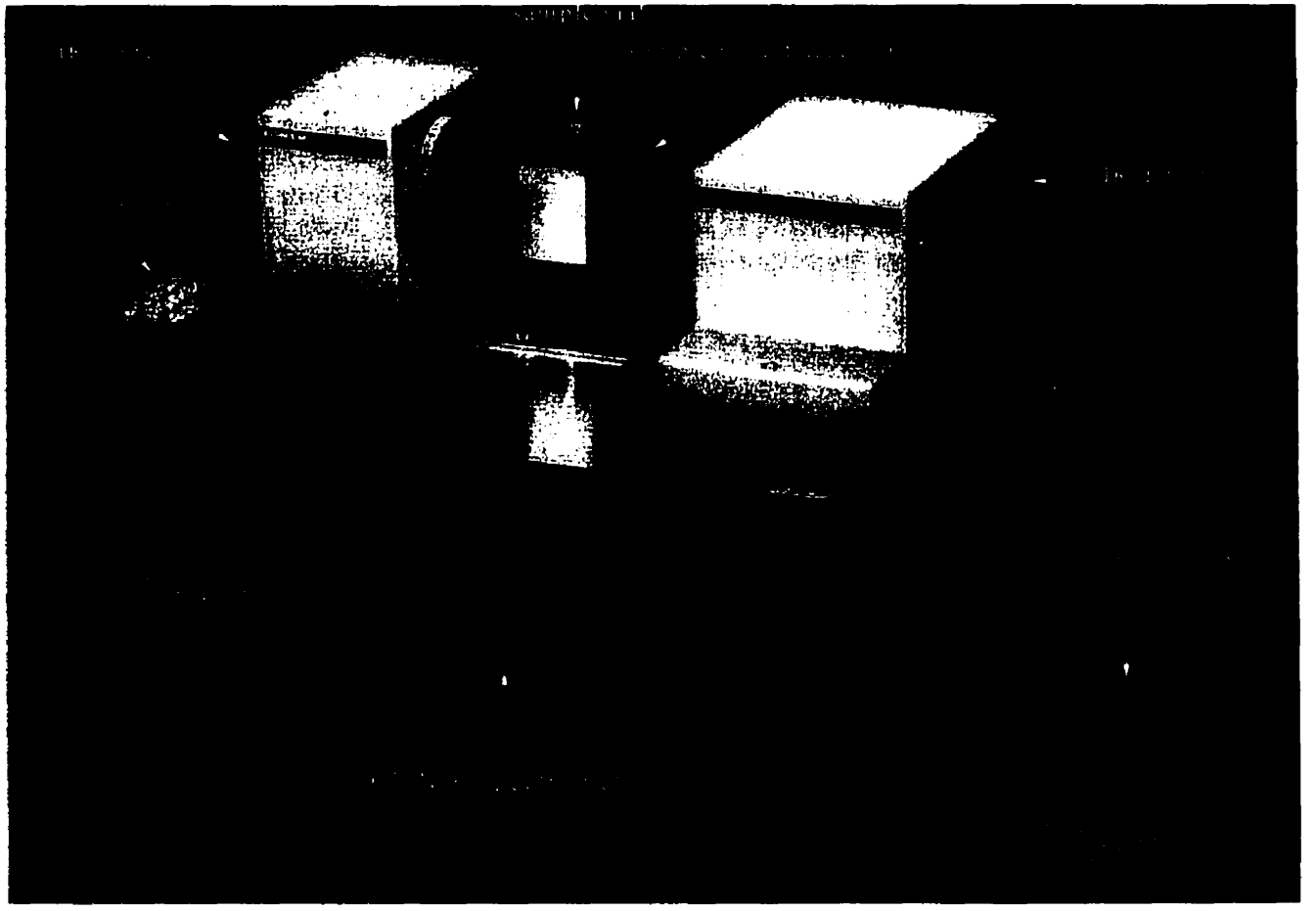


Figure 6. The Bomem MB-Series FT-NIR spectrometer with sample mount accessory placed in the IR beam.

Quebec), scaling on the peak height at 8262 cm^{-1}, referenced to two baseline points at 9200 and 7600 cm^{-1}, the purpose of this procedure being to minimize any spectral variations due to variations in vial diameter.

Reagents

High-erucic acid rapeseed (HEAR) oil, used as the base oil for biodegradable oil formulation studies, was provided by Thermal-Lube Inc. (Montreal, Quebec). The oil was heated at 200°C under vacuum to destroy any hydroperoxides and to remove low molecular weight secondary oxidation products and then passed through a column of activated silica gel to remove any remaining partially polar oxygenated molecules that might be present in the oil. The cleaned HEAR oil was analyzed by the AOCS PV (Anonymous, 1989a) standard method and was determined to have a PV of <0.50. Reagent grade triphenylphosphine (TPP, >99%), triphenylphosphine oxide (TPPO, >99%) and *tert*-butyl hydroperoxide solution (~5.5 M in isooctane; 95% TBHP, 5% H_2O and 5% butanol) were obtained from Aldrich Chemicals (Milwaukee, WI). Separate concentrated stock solutions (40% w/w) of TPP and TPPO were prepared in chloroform, selected as a convenient carrier to allow the uniform dispersion of each reagent in the HEAR oil. The TBHP solution was analyzed by the AOCS method to establish its PV value, and various amounts were added directly to clean HEAR oil as required to obtain oil standards of known hydroperoxide concentration.

Calibration Standards, Calibration and Validation Samples

Calibration standards were prepared by gravimetrically adding known and varying amounts (0-1.5g) of TPPO/chloroform stock solution (40%, w/w) and random amounts (0-1.0g) of TPP/chloroform stock solution (40%, w/w) into 30g of clean HEAR oil. One gram of each standard was transferred to the 8-mm NIR sample vials and scanned using the instrumental parameters described above, with the spectral data stored to disk for subsequent PLS calibration development. The Nicolet Quant-IR® Calibration and Prediction Package (Nicolet Instrument Co., Madison) was used for spectral analysis and

PLS calibration development (Anonymous, 1993). Correlation and variance spectra were examined to determine the regions where most of the spectral changes in the calibration set took place, these regions being explored for calibration development. Each calibration was assessed using the leave-one-out cross validation procedure and optimized in terms of the appropriate number of factors using the predicted residual error sum of squares (PRESS) test. The calibration was considered optimized when the cross validation error was minimized.

Two sets of validation samples were prepared, one consisting of samples of clean HEAR oil spiked with TBHP, a stable hydroperoxide standard, and the other consisting of HEAR oil in which hydroperoxides had been generated by thermally stressing the oil. The TBHP validation sample set was prepared by adding varying amounts of the stock TBHP solution to 30g of clean HEAR to produce samples varying in PV from 0 to 100, while for the thermally stressed oil set, a high-PV HEAR oil (~110 PV) was diluted with clean oil to produce samples covering a range of PV. Additional time-course validation samples were prepared by heating 200g of HEAR oil at 100°C while bubbling oxygen continuously through the oil @ ~3 ml/min to accelerate oxidation. Oxidation and sampling were automatically carried out using the Continuous Oil Analysis and Treatment (COAT) system (Dong, et al., 1996) devised for monitoring additive levels in oils, the oil being collected automatically at selected time intervals in a fraction collector.

Analytical Protocol

The analytical protocol simply consisted of transferring ~ 1 ml of an oil to an 8-mm NIR vial and adding 0.04 ml of the 40% stock TPP/chloroform solution using a precalibrated re-pipette. The amount of TPP added provides a reactant reservoir sufficient to react with the hydroperoxides in samples containing up to an equivalent of 120 PV to produce TPPO. After the TPP reagent has been added, the vial is capped, shaken and is ready for presentation to the FT-NIR spectrometer, where it is scanned and the PV value subsequently predicted by the PLS TPP/TPPO calibration. All the validation samples were also analyzed in parallel by the AOCS PV standard method (Anonymous, 1989) and the

results of both methods were compared. All the analytical samples above were run under the same FTIR operating conditions as the calibration standards.

3.3 Results and Discussion

Analytical Concept

In our previous work on the development of an FTIR-based PV method, quantitation of hydroperoxides was achieved by the measurement of their characteristic OH stretching absorptions @ ~3445 cm^{-1}. This approach was complicated by the large number of potential spectral interferences in this region of the spectrum due to other OH-containing species such as alcohols, free fatty acids, moisture, and monoglycerides. A PLS calibration accounting for these interferences was successfully developed, based on the use of calibration standards prepared by addition of *tert*-butyl hydroperoxide (TBHP) plus random amounts of potentially interfering compounds to zero-PV oils (van de Voort, et al., 1994c). However, the accuracy and sensitivity of this approach are highly dependent on the calibration design, which requires a detailed knowledge of the interfering substances and the magnitude of their influence. Thus, since the compositions of oxidizing oils are rather complex and influenced by a variety of factors, the development of this type of calibration is not a routine matter.

In order to avoid this complex calibration procedure in the development of an FT-NIR method, the possibility of employing a simple stoichiometric reaction as the basis for the determination of PV was considered. One well-characterized reaction is the stoichiometric conversion of triphenylphosphine (TPP) to triphenylphosphine oxide (TPPO) in the presence of hydroperoxides, which has been described by Nakamura and Maeda (1991) in their development of a micro-assay method for lipid hydroperoxide determination in biological samples, using a combination of HPLC and UV detection. When an excess of TPP is present, this reaction is rapid and complete, with hydroperoxides being reduced to their respective alcohols and TPP being converted to TPPO according to the following reaction (Ma, et al., 1996):

$$ROOH + X_3\text{-}P: \longrightarrow X_3\text{-}P{=}O + R\text{-}OH \qquad [1]$$

where X_3-P: is TPP and X_3-P=O is TPPO.

From studies of the FTIR spectra of TPP and TPPO in the mid-IR region (Ma, et al., 1996), it was shown that the three phenyl moieties provide a strong signal and that the binding of oxygen to TPP, forming TPPO, perturbs the phenyl vibrations sufficiently to allow them to be distinguished from those of TPP, allowing TPPO to be quantitated accurately in the presence of TPP through the use of chemometric techniques such as PLS. In order to investigate the possibility of employing the reaction of TPP with hydroperoxides as the basis for an FT-NIR method for PV determination, it was first necessary to evaluate whether TPP and TPPO can be similarly distinguished in the near-IR region of the spectrum.

General Spectroscopy

The spectral characteristics of TPP and TPPO in HEAR oil were investigated by adding each component individually to clean HEAR oil, recording the FT-NIR spectrum of the spiked oil, and ratioing out the spectral contribution of the HEAR oil to produce "differential spectra" (van de Voort, et al., 1994b). Figure 7 illustrates the differential spectra of TPP and TPPO as well as that of a 1:1 mixture of TPP/TPPO over the range 5500-4500 cm^{-1}. TPP gives rise to a series of well-defined bands in the 4714-4500 cm^{-1} region (Fig. 7a) while TPPO produces a similar spectral signature (Fig. 7b), closer inspection revealing that the bands are shifted to longer wavelength. When these two compounds are present together in a 1:1 ratio (Fig. 7c), their bands are extensively overlapped. Under such circumstances, quantitation of the individual components generally requires the use of chemometric techniques such as PLS in order to adequately discriminate the relative amounts of each species present.

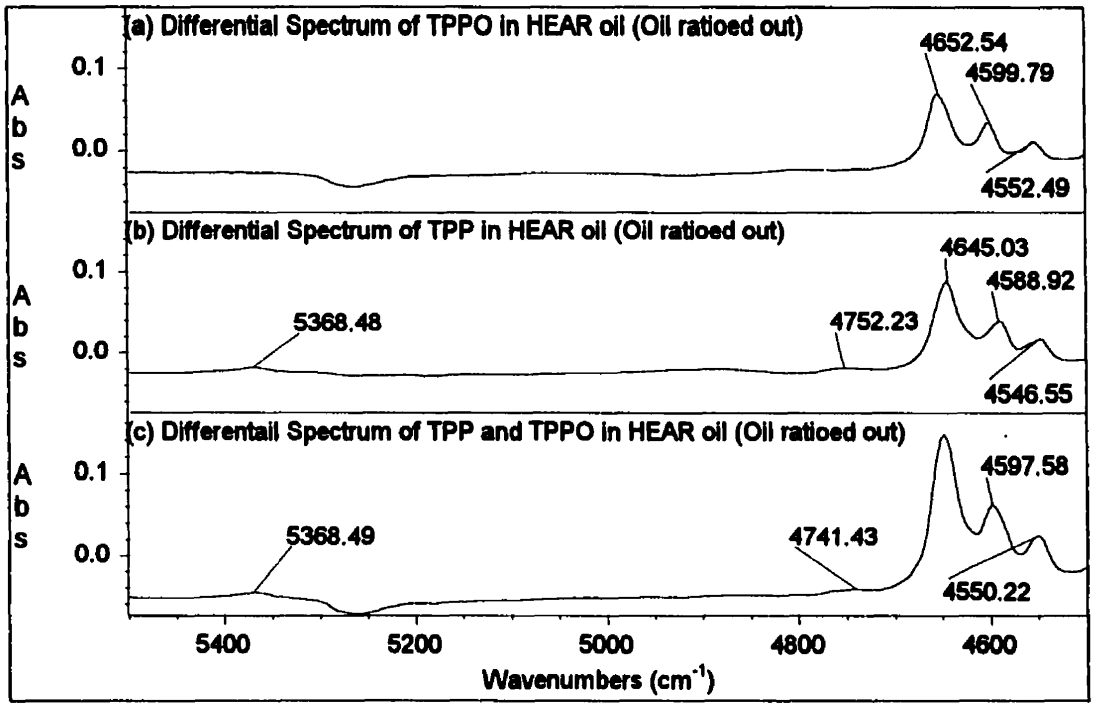


Figure 7. Differential spectra of TPP, TPPO, and a 1:1 TPP/TPPO mixture in HEAR oil after ratioing out the HEAR oil spectral contribution

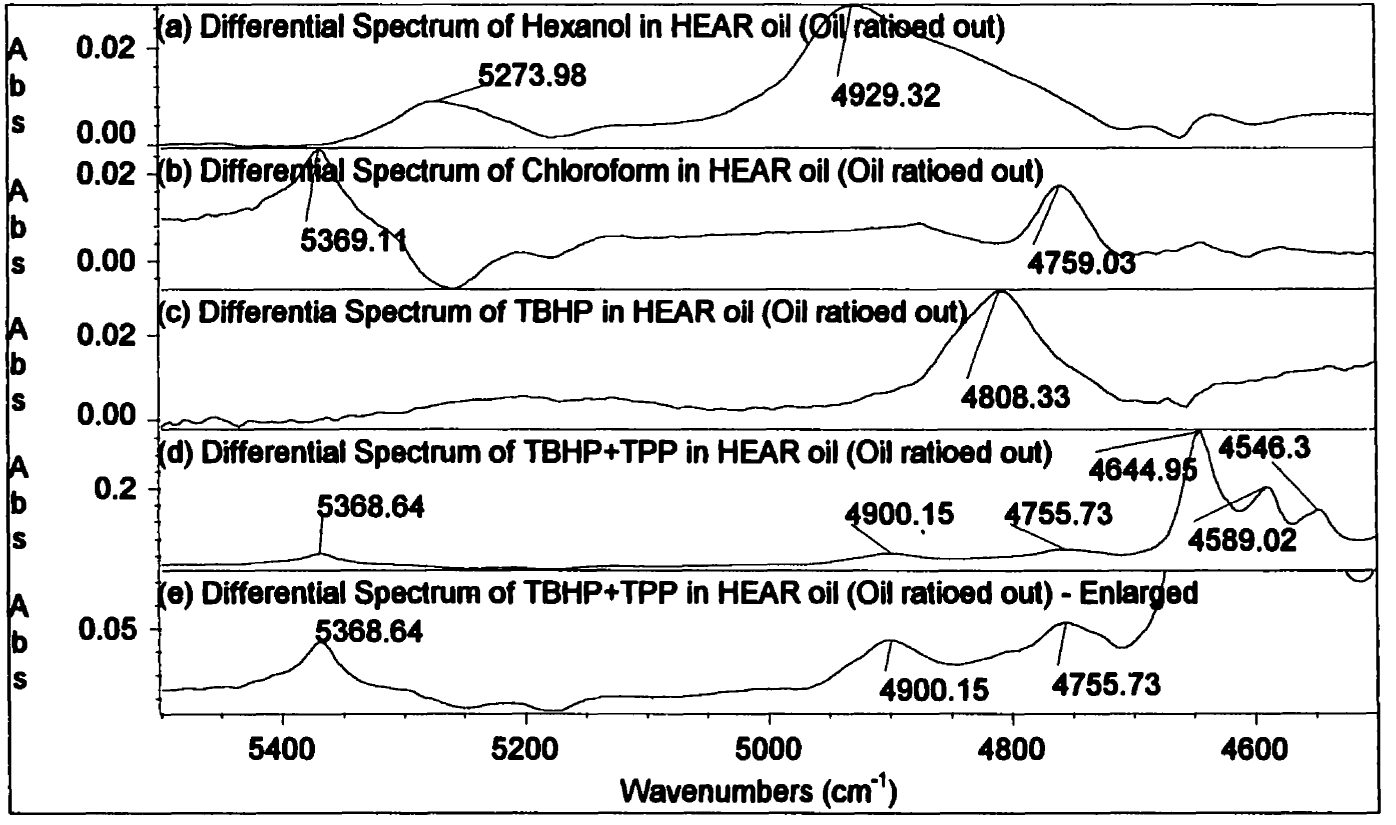


Figure 8. Differential spectra of hexanol, chloroform, TBHP and reacted TBHP and TPP in HEAR oil after ratioing out the HEAR oil spectral contributions.

In terms of measuring the amount of TPPO formed in an oil by the reaction of TPP with hydroperoxides present in the oil, the three main potential sources of interference present are $CHCl_3$ (used as a carrier to facilitate mixing of TPP with the oil), hydroperoxides and the alcohols formed as a result of the reaction. Figure 8a-c illustrate the spectra of HEAR oil spiked with hexanol, spectrally representative of the alcohols that are formed, the solvent $CHCl_3$ used as a carrier, and TBHP, spectrally representative of lipid hydroperoxides formed in oxidizing oil (van de Voort, et al., 1994c). As can be seen, the absorption bands of these components are well removed from the absorption bands of TPP and TPPO. Figure 8e illustrates the NIR spectrum obtained when TBHP is reacted with TPP; this spectrum is magnified in Fig. 8f so that the weaker bands can be more clearly discerned. Comparing Figs. 8e-f to Figs. 8a-c, it is apparent that the TBHP hydroperoxide absorption band at 4808 cm^{-1} (Fig. 8c) is lost upon reaction of TBHP with TPP, and a new band appears at ~4900 cm^{-1} (Fig. 8 e/f), which is due to the alcohol formed by the reaction. Thus, the loss of TBHP and the formation of an alcohol are spectrally evident, although the TPP/TPPO spectrum does not visibly appear to be changed. Although measurement of the loss of hydroperoxide, the formation of alcohol, or a combination of both could potentially be a simple basis for PV determination, the complications introduced by hydrogen bonding, the broadness of the hydroperoxide and alcohol bands, and the possible variability of these bands depending on the nature of the hydroperoxide and alcohol (or other OH-containing species) present make this a difficult proposition. A more convenient means of quantitation is to determine the amount of TPPO formed; however, this approach requires that TPPO can be accurately measured in the presence of TPP using a chemometric approach such as PLS. One of the benefits of this approach is that most of the potentially interfering constituents do not absorb in the spectral region of interest, avoiding many of the problems encountered in our previous PV methodology (van de Voort, et al., 1994c).

Partial Least Squares (PLS) Calibration

Principal components regression (PCR) and partial least squares (PLS) regression are widely employed in quantitative NIR analysis as a basis for calibration because the

extensive band overlap in the near-IR region of the spectrum generally makes it necessary to use statistical analysis techniques to establish correlations between spectral and compositional data. Both calibration approaches are based on the compression of the spectral data for the calibration standards into a set of mathematical "spectra", known as *loading spectra*; the spectrum of each calibration standard is then decomposed into a weighted sum of the loading spectra, and the weights given to each loading spectrum (known as *scores*) are regressed against the concentration data for the standards. Because PLS uses the concentration data for the standards in the compression of the spectral data, fewer loading spectra are required to account for the concentration data than in the PCR approach, making PLS calibration models potentially more robust. When the PLS calibration model obtained is used to predict unknowns, PLS attempts to: (i) reconstruct the spectra of the unknowns from the loading spectra; (ii) use the scores (i.e., the amounts of each loading spectrum employed in reconstructing the spectrum) for prediction; and (iii) use the residual spectra to detect anomalous samples.

Since all the variability that exists in the spectra of the calibration standards is accounted for in calibration development, PLS is considered to be a very powerful tool for the analysis of systems containing multiple components. For the development of a robust PLS calibration model, three essential requirements must be met in the design of the calibration standards: (i) the concentration range of the component(s) of interest in the samples to be analyzed must be adequately spanned; (ii) all interfering components that may be present in the samples to be analyzed must be present; and (iii) there should be no correlation between the concentrations of the interfering components and the component(s) of interest. Thus, in the development of a PLS calibration model for the prediction of the amount of TPPO formed in the reaction between TPP and hydroperoxides, in the presence of residual TPP, it is important that the calibration set devised should be randomized so as to avoid building in any concentration correlations between TPP and TPPO, which would necessarily exist if the standards were prepared by addition of a fixed amount of a TPP stock solution to a set of oils covering a range of PV. Thus, to develop a set of appropriate calibration standards, TPPO was added to 30-g

Table 6. Calibration matrix for partial least squares calibration

Standard #	TPPO (PV)[a]	TPP (PV)
1	0	29.68
2	1.64	79.37
3	2.22	102.36
4	2.49	57.74
5	5.35	11.53
6	9.61	87.46
7	12.04	63.71
8	13.33	40.82
9	19.51	7.11
10	21.37	27.50
11	27.16	63.15
12	32.35	17.73
13	34.75	49.29
14	38.21	33.65
15	47.01	47.55
16	47.23	11.73
17	53.72	24.77
18	58.79	33.86
19	62.75	10.55
20	74.59	22.84
21	78.44	7.56
22	90.82	10.47
23	104.98	2.41

[a]PV = peroxide value; the amounts of TPP (Mw=262.28) and TPPO (Mw=278.29) added in PV-free HEAR oil are expressed in terms of PV units, according to the stoichiometric reaction; i.e., an oil containing 1 PV unit of ROOH as determined using the standard iodometric reaction would require 0.1311g TPP/kg oil, producing 0.1391g TPPO/kg oil.

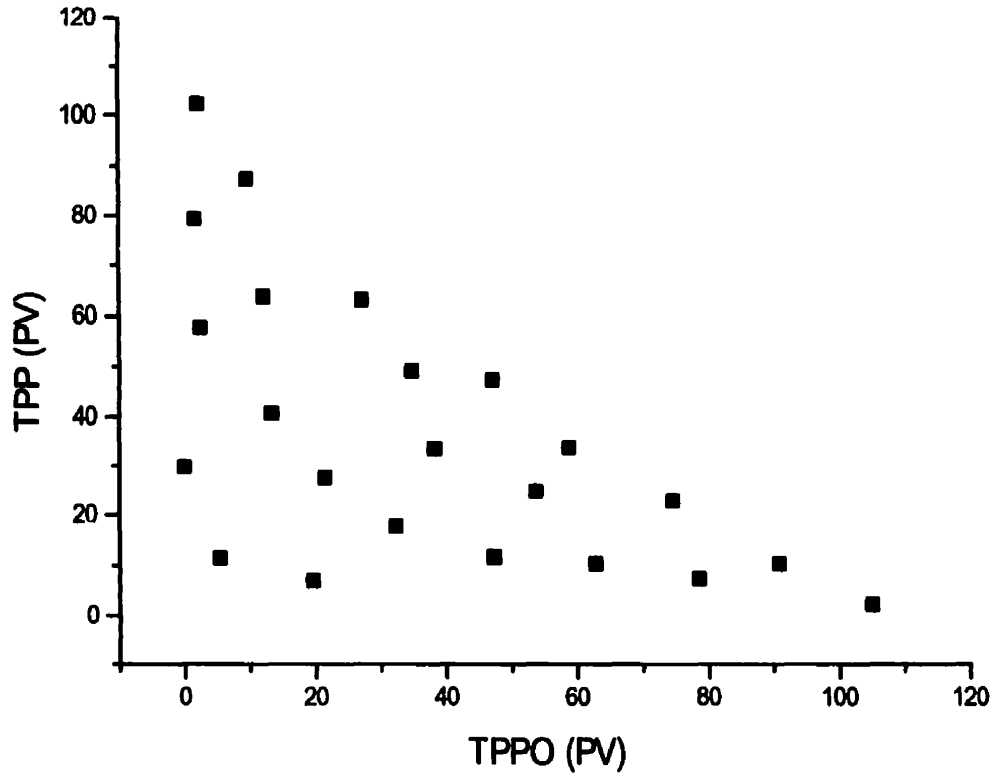


Figure 9. TPP/TPPO composition of PLS calibration standards. The concentrations of TPP and TPPO are expressed in terms of PV units, according to the stoichiometric reaction; i.e., an oil containing 1 PV unit of ROOH as determined using the standard iodometric reaction would require 0.1311g TPP/kg oil, producing 0.1391g TPPO/kg oil.

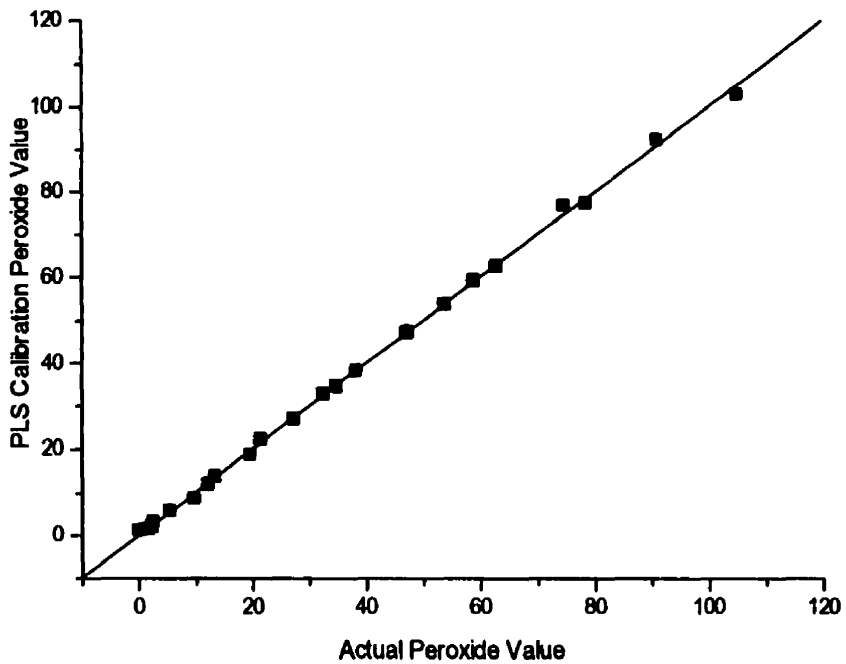


Figure 10. Plot of the predicted peroxide value vs. the actual peroxide value for the 23 calibration standards as derived from the partial least squares calibration (PLS)

samples of clean HEAR oil at concentrations representing the levels of TPPO that would be produced in oils having a PV in the range 0-105 PV, with TPP subsequently added in a random manner in amounts representing the various concentrations of residual TPP that might be present at the completion of the reaction of TPP with hydroperoxides. Table 6 summarized the calibration standard matrix used to develop the PLS calibration, Figure 9 illustrating the matrix in graphical form to better illustrate its randomness and range.

Using this global calibration matrix, a PLS calibration was developed and optimized using the 4710-4540 cm^{-1} spectral region referenced to a single-point baseline at 4710 cm^{-1}. The optimization of the wavelength region, baseline selection, and number of factors used in the calibration was guided by the PRESS test (Anonymous, 1993) and minimization of the cross validation error. Figure 10 illustrates the calibration plot obtained from the PLS calibration model in terms of predicted vs. actual PV for the 23 standards, having an overall mean error of 1.00 PV and a standard deviation of 1.36 PV. The "leave one out" cross validation procedure, designed as a preliminary test of the accuracy of the calibration, produces an overall mean error of 1.20 PV.

Validation

Figure 11 presents an overlaid plot of duplicate FT-NIR results for serially diluted oxidized HEAR oil samples, the duplicates having an SD of 0.633. Similar reproducibility was obtained for the TBHP-spiked samples (SD = 0.875 PV). Figure 12 presents a plot of the means of the duplicate PV determinations using the iodometric method (IOPV) plotted against the corresponding means of the FT-NIR predictions for duplicate analyses of the TBHP-spiked samples (FT-NIRPV). The plot is highly linear, and the regression equation for the line was:

$$\text{FT-NIRPV} = -0.075 + 0.994\ \text{IOPV} \quad SD=1.20 \quad r=0.9994 \qquad [2]$$

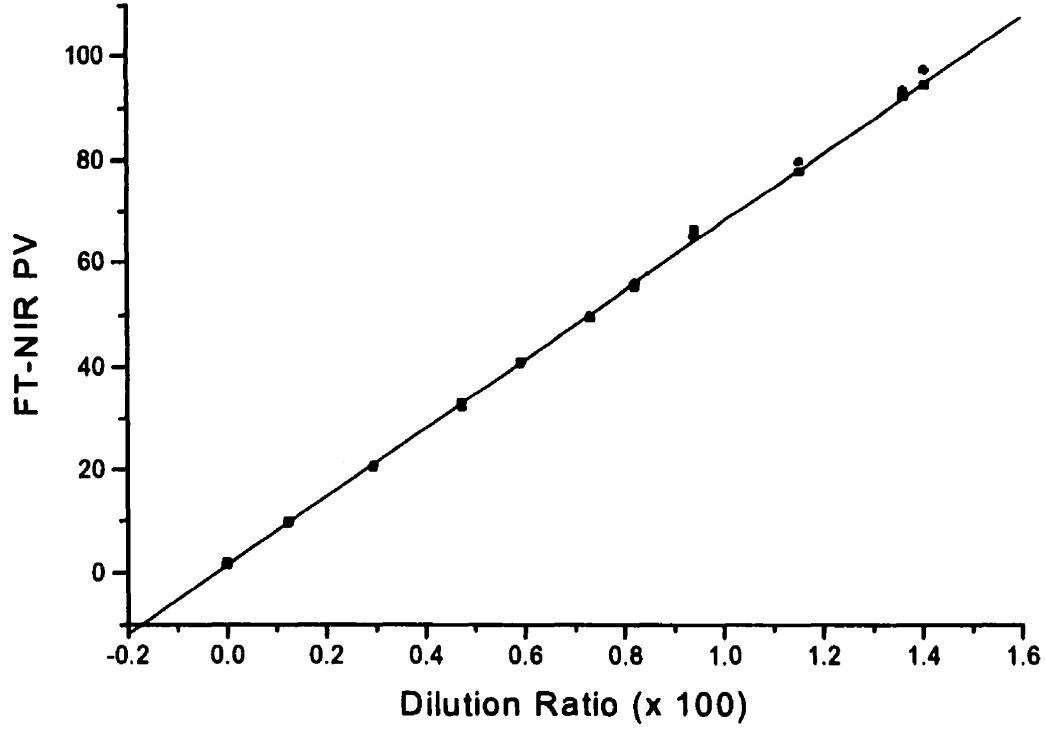


Figure 11. Plot of FT-NIR PV data obtained as a high PV HEAR oil is proportionally diluted with a clean HEAR oil

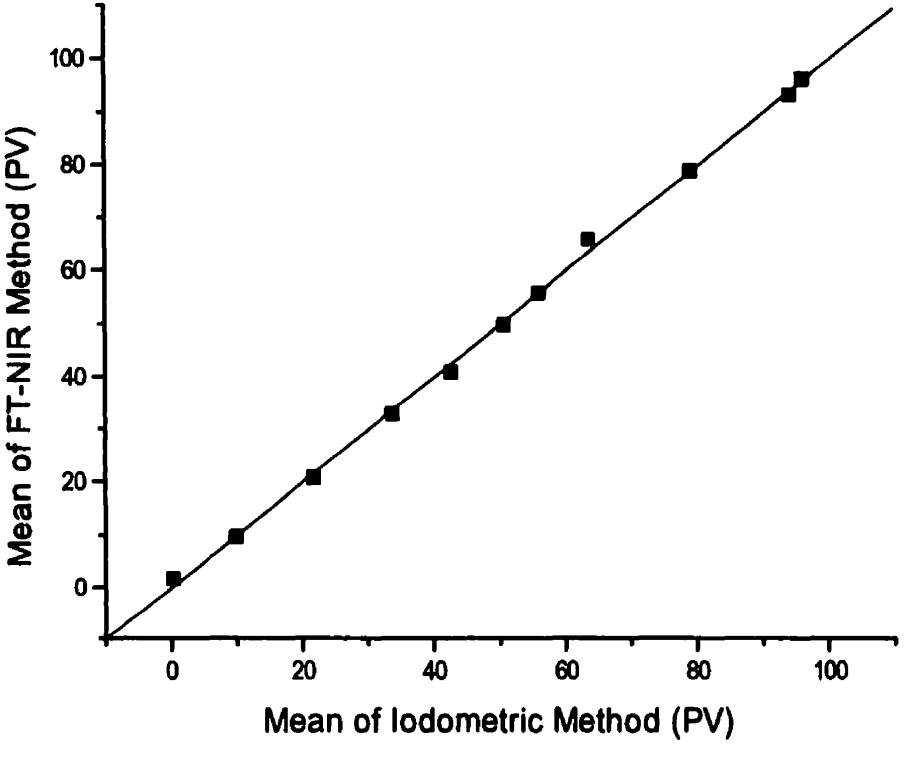


Figure 12. Plot of the mean FT-NIR PV values vs. the mean iodometric PV values for TBHP spiked HEAR oils

Table 7. Reproducibility and accuracy data for PV determinations by the FT-NIR and iodometric methods for oxidized and TBHP-spiked HEAR oils.

Methods →	FT-NIR Method		Iodometric Method	
Statistic ↓	Thermally Stressed HEAR Oil	TBHP Spiked HEAR Oil	Thermally Stressed HEAR Oil	TBHP Spiked HEAR Oil
MD_r	±0.543	±0.400	±0.359	±0.007
SDD_r	±1.109	±1.245	±1.118	±0.941
CV_r	1.69%	2.50%	1.71%	1.88%
MD_a	-1.279	-0.381	NA[a]	NA
SDD_a	±1.085	±1.379	NA	NA
CV_a	1.66%	2.76%	NA	NA

[a] Not applicable

effectively indicating that there is a 1:1 correspondence between the FT-NIR predictions and the standard iodometric method, similar results being obtained for the oxidized HEAR oil dilutions. Further comparisons of the two methods in terms of mean differences (MD), standard deviation of the differences (SDD) and coefficient of variation (CV) for reproducibility (r) of duplicate analyses are summarized in Table 7, as well as the accuracy (a) of the secondary FTIR method relative to the primary iodometric method (Youden, 1967). There is little to differentiate the performance of the two methods, although there is a somewhat larger negative bias in terms of accuracy for the oxidized HEAR oil relative to that of the TBHP spiked samples when compared to the iodometric method. This may be due to the ability of KI to react with both hydroperoxides and peroxides, while TPP may not be as effective in that regard (Ma, et al., 1996). The NIR calibration developed is a general one, designed for carrying out active oxygen method (AOM) monitoring of biodegradable oil undergoing thermal stress, and as such covers a relatively large PV range. In terms of performance, a calibration covering a smaller range, more ideal for edible oil analysis, would likely perform somewhat better and be more sensitive if the calibration were devised over an narrower range, i.e. 0-15 PV.

Monitoring Oil Oxidation

As noted above, the McGill IR group is working on the development of a continuous oil analysis and treatment (COAT) system designed to monitor oils and additive levels in biodegradable lubricants on-line (Dong, et al., 1996). In its present configuration, the COAT system is equipped with a mid-IR spectrometer and as such could not be used directly for FT-NIR PV analysis; however, the system was used to carry out the continuous oxidation and automated sampling of the oil, passing the sample through the spectrometer to a fraction collector. Samples of HEAR oil undergoing thermal stress were collected over time and reacted with TPP and scanned in a FT-NIR spectrometer to simulate the results one might obtain during time-course monitoring of PV, effectively producing an AOM plot. The FT-NIR predictions obtained from the time course of thermally stressed HEAR oil are compared to the results obtained from the

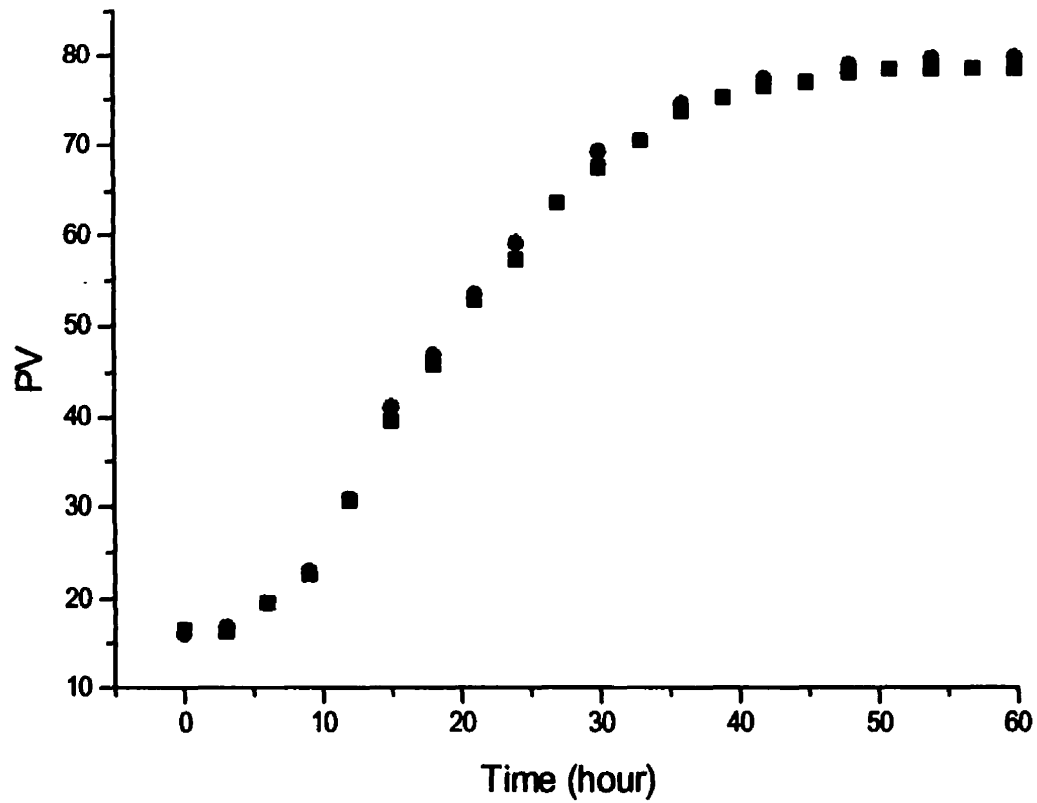


Fig 13. Real-time AOM plot of HEAR oil under forced thermal/oxidation conditions comparing FT-NIR (■) and iodometric (●) PV results

iodometric analyses of the same samples in Figure 13, again illustrating an excellent concurrence between the two methods.

3.4 Conclusion

As noted in our previous work, the methodology developed in this study can readily be automated by programming the FT-NIR spectrometer to carry out spectral data collection, processing, and data output presentation. In its simplest form the PV method entails only adding ~0.04 ml of TPP/chloroform stock solution, using a re-pipette, to 1 ml of oil in an 8-mm glass vial, mixing, scanning and predicting the PV value using the PLS calibration derived. For most applications, the vial-based, at-line approach is simple, rapid and convenient. This study demonstrates the overall efficacy of FT-NIR spectroscopy as a means of rapidly and accurately determining PV of industrial and edible triglyceride-based oils using the stoichiometric conversion of TPP to TPPO in the presence of hydroperoxides. The FT-NIR method is also a significant improvement over most chemical approaches in terms of avoiding solvent/reagent disposal problems and would reduce manpower requirements in routine quality control applications.

As one of the key objectives of our industrial research mandate was the evaluation of the COAT system in its mid-IR configuration, the subsequent work carried out focuses on the performance of the COAT system in its operational and performance characteristics for additive replenishment and control (see Chapter 4).

3.5 Acknowledgments

This chapter is based on the manuscript entitled "Stoichiometric Determination of Hydroperoxides in Oils by Fourier Transform Near Infrared (FT-NIR) Spectroscopy" which has been submitted for publication. The contribution of co-authors to this manuscript, namely, Ma, K.M., van de Voort, F.R. and Ismail, A.A. is gratefully acknowledged.

4

A CONTINUOUS OIL ANALYSIS AND TREATMENT (COAT) SYSTEM FOR THE MONITORING OF OIL QUALITY AND PERFORMANCE OF ADDITIVES

Abstract

A prototype of a fully integrated Continuous Oil Analysis and Treatment (COAT) system based on Fourier transform infrared (FTIR) technology was developed to perform real-time monitoring of lubricant quality and automatic additive replenishment. The system mainly consists of an FTIR spectrometer, an infrared (IR) flow cell, a logical pump and valve system, and a programmed computer controlling the fully automatic operation of the whole system. The performance of the system was tested with mineral-based and high-erucic acid rapeseed (HEAR) oil under accelerated oxidation conditions. It was demonstrated that the system is capable of monitoring oil quality and tracking the depletion of additives in real time and that its automatic additive replenishment function provides a means of reducing lubricant consumption and replacement. The system is also environmentally friendly as condition monitoring is performed without the use of chemical reagents or solvents and the frequency of waste oil disposal can be reduced substantially.

4.1 Introduction

Established oil testing procedures have proven that proper monitoring and regular oil changes are critical factors in extending the service lifetime of machinery. In addition, as lubricant disposal costs have recently come up to, if not surpassed, initial lubricant costs, oil analysis and maintenance has gained importance as a cost-effective tool for reducing lubricant disposal. However, traditional oil analysis methods can prove ineffective if improper oil sampling methods are employed or samples are taken too late to initiate corrective action. The optimum benefit in terms of extending both equipment and lubricant life could be derived from automated *on-line* oil analysis, allowing for continuous monitoring of lubricant performance and degradation or *at-line* monitoring for intermittent verification. Furthermore, *on-line* oil analysis may be combined with automated dosing with corrective performance additives (such as antioxidants, antiwear reagents, extreme pressure additives, polymers, etc.) as they become depleted to further extend lubricant life.

The availability of a simple, rapid and efficient method for the evaluation of lubricants would also be beneficial in the development of lubricant formulations, especially in relation to extending lubricant stability and serviceability. In industrial applications, oxidative stability, which can be significantly enhanced by adding appropriate antioxidants, is the most common variable of concern in terms of the chemical properties of a lubricant (Klaus and Tewksbury, 1983). Conventional methods for measuring oxidative stability involve inducing oxidation by heating the oil and/or by forcing air or oxygen through it and subsequently carrying out chemical analyses of the oxygen-containing products formed (Baker, 1984). Such procedures, however, have several practical disadvantages, including: (i) the requirement for time-consuming analyses; (ii) use of environmentally hazardous solvents and reagents; (iii) lack of amenability to automation; and (iv) inability to provide *on-line* oxidation information.

The potential benefits of using infrared (IR) technology for the analysis of oil degradation products and key contaminants in oils were demonstrated some years ago (Powell and Compton, 1993), and IR oil analysis methods have been applied in a large number of industries, including engine, vehicle, and heavy equipment manufacturing and in lubricant production (Anonymous). The utility of IR spectroscopy in oil analysis is due to the suitability of this technique for (i) the quantitative measurement of the levels of additives such as antioxidants, antiwear agents, etc.; (ii) the monitoring of the formation of by-products of oil or additive degradation; and (iii) the detection of external contaminants, such as water and glycols (Powell and Compton, 1993). However, in the past, the application of IR oil analysis for routine monitoring of lubricant oils was fairly limited, largely owing to the slow sample turnaround time of traditional dispersive IR instruments (Anonymous). However, since the early 1970s, the development of Fourier transform infrared (FTIR) spectrometers, together with advances in data analysis software, has made it possible to reduce analysis times to 1-2 min per sample. The superior speed of FTIR instruments is primarily due to the multiplexing advantage which results from their use of interferometry rather than dispersive technology. Other advantages of FTIR systems over dispersive instruments include superior signal-to-noise characteristics, higher energy throughput, excellent wavenumber reproducibility and accuracy, extensive and precise spectral manipulation capability, plus advanced chemometric software to handle calibration development (Griffiths and Haseth, 1986). In addition, the speed, reliability, and low operating costs of modern FTIR spectrometers plus their capabilities for automated operation make them highly suitable for real-time, on-line monitoring applications.

At present, a number of FTIR analyzers dedicated to used oil analysis are commercially available. However, the potential demand for practical automatic oil analysis and treatment systems which can serve as a tool for dynamic on-site acquisition and

adjustment of lubricant conditions has not been addressed. Fundamental work directed toward the development of a fully integrated Continuous Oil Analysis and Treatment (COAT) system has been undertaken by the McGill IR group based on principles adopted from previous work on edible oil analysis using FTIR spectroscopy (van de Voort, et al., 1992; 1994a-c; Ismail, et al., 1993) and incorporating automated sampling techniques. The purpose of this paper is to demonstrate the efficacy of a prototype COAT system in following antioxidant depletion and replenishment in mineral oil and antioxidant loss in high-erucic acid rapeseed (HEAR) oil under forced oxidation.

4.2 Instrumentation

General Considerations in System Design

The general requirements for FTIR-based oil analysis systems have been outlined by Powell and Compton (1993). For the purpose of designing an automated monitoring system, a number of additional requirements need to be considered. The system must be suitable for *on-line* or *at-line* operation, operate reliably for extended, continuous periods, and be capable of extensive data collection and processing. In addition, it may require multitasking capability to allow for simultaneous control of multiple lubricating units. The system must be able to process the spectral data obtained from the FTIR spectrometer in real time, provide rapid on-site information about lubricant quality and performance of additives, and automatically interpret the analytical results to allow a variety of actions to be taken; i.e., (i) if the analytical values fall within pre-established boundaries, no corrective action is taken; (ii) if the analytical values indicate significant depletion of a specific target additive, the correct additive treatment is automatically selected and pumped into the main system until the additive is determined to be replenished; and (iii) if the analytical values indicate that the lubricant is contaminated with a foreign substance, the fluid is automatically removed from the main circulating system via a diversion line for secondary treatment until the fluid is determined to be "clean".

System Configuration and Operation

A schematic diagram of the prototype COAT system is presented in Fig. 14. The main components of the system are an FTIR spectrometer, an IR flow cell, a logical pump and valve system, and a computer. The FTIR instrument used was a Nicolet Impact 400 FTIR spectrometer (Madison, WI), interfaced to an IBM compatible 486/DX 33 MHz PC operating under Windows-based software. To minimize water vapor and CO_2 interferences, the FTIR spectrometer and sample compartment were purged with dry air produced by a Balston air dryer (Balston, Lexington, MA). The sample handling system consists of an IR flow cell located in the sample compartment of the FTIR spectrometer, transfer lines, and computer-controlled pumps and valves (York Fluid Controls LTD., Brampton, Ont.). The cell assembly (Fig. 15) uses two KCl windows separated by a Teflon spacer, providing a pathlength of 200 μm, allowing a spectral range from 4000 cm^{-1} to 500 cm^{-1} to be measured. Two in-line filters (300 μm and 50 μm) were placed in series along the cell input line to prevent clogging of the cell by any particulates that may be present in the oil.

The system runs under a program written in Visual Basic (Microsoft Co.), which controls the spectrometer running under Nicolet Omnic 2.0 software via dynamic data exchange routines provided with the Nicolet Macros\Pro utility. In the oil monitoring mode, pump B is activated at prespecified intervals to divert oil from the lubricant reservoir to the IR cell in the flow pattern shown in Fig. 14. Spectral acquisition is then triggered, and the data analyzed by preprogrammed routines for the determination of levels of oxidation products and additives. In the additive replenishment mode, pump A is activated to deliver fresh additive from the appropriate additive reservoir to the lubricant reservoir until the additive level falls within the prescribed range.

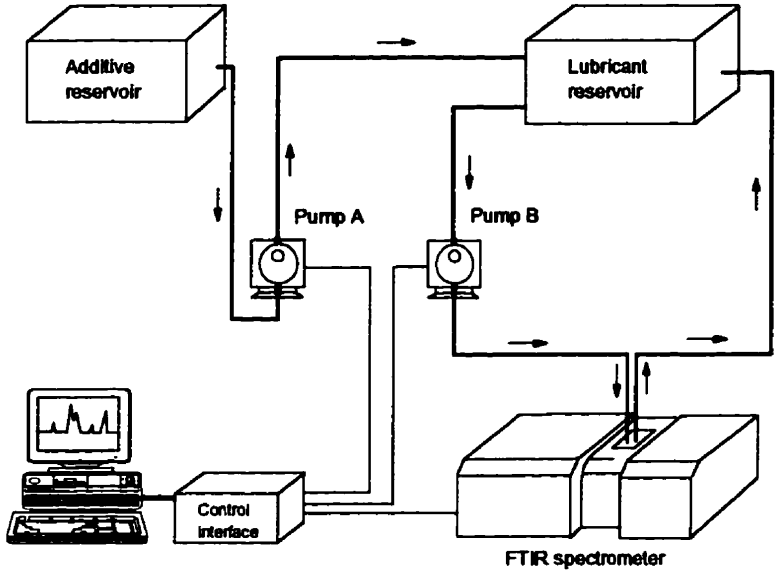


Figure 14. A schematic diagram of the COAT System and flow pattern

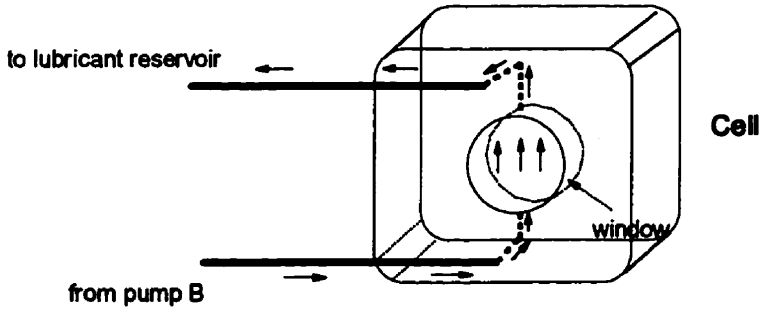


Figure 15. A schematic diagram of the cell and flow pattern

4.3 Materials and Experimental Procedures

Two basic oxidation experiments were carried out to test the system, one involving HEAR oil and a second using mineral oil. Initial experiments were conducted with pure HEAR oil for the purpose of monitoring the oxidation process in the absence of antioxidant. In subsequent experiments, an antioxidant was added to the HEAR oil, and both the oxidation process and the depletion of antioxidant were followed. For the mineral oil experiments, oil containing antioxidant was thermally stressed, the antioxidant level monitored, and the replenishment function of the COAT system tested.

Materials

Antioxidant/antiwear additive C-125, HEAR oil and base mineral oil free of additives were obtained from Thermal-Lube Inc. (Montreal, Canada). Food-grade butylated hydroxyanisole (BHA) and *tert*-butylhydroquinone (TBHQ) were obtained from Nutritional Biochemicals (Cleveland, OH) and Eastman Chemical Company (Kingsport, TN), respectively. A programmable block heater (model 36200, Cole-Parmer Instrument Co., Chicago, IL) was used to maintain the oils at $100 \pm 0.5°$ C, with an Erlenmeyer flask substituting for the lubricant reservoir (Fig. 14) to allow the samples to undergo thermal and oxidative stress.

Experimental Procedures

In the first set of experiments, 200 g of HEAR oil was heated in the flask at 100°C and dry air was bubbled continuously through the oil @ ~3 ml/min to accelerate oxidation. Every 3 h, oil in the flask was pumped through the IR cell, circulating in the flow pattern shown in Figure 15 for 6 min in order to flush out the previous sample. The FTIR spectrum of the oil was then collected by co-adding 128 scans at a resolution of 4 cm^{-1}, using triangular apodization and a gain of 1.0. Each spectrum was subsequently ratioed against the spectrum recorded at t = 0 to produce "differential spectra." The purpose of this ratioing procedure is to eliminate invariant spectral features, allowing the spectral changes taking place in the oil to be clearly seen (van de Voort, et al., 1994b). In the second set of experiments, antioxidants (BHA and TBHQ) were added to the HEAR

oil at levels of ~0.5%, representative of antioxidant levels in typical hydraulic lubricant formulations. These spiked oils were subjected to the same conditions as the unspiked HEAR oil, and monitoring was performed as described above. In addition, tracking of the antioxidant levels was performed by measuring the absorbances of their characteristic infrared bands as a function of time.

In another set of experiments designed to assess the efficacy of automatic additive replenishment, a mineral oil spiked with an antioxidant/antiwear additive (C-125) at a level of 0.5% was subjected to the same conditions as described above and monitored for over 3 weeks. During this run, the COAT system was operated in the automatic additive replenishment mode, such that when the additive level dropped below 90% of a specified target value, a pump (pump A in Figure 14) was automatically activated to deliver additive to the lubricant reservoir until the concentration of the additive, as predicted from the FTIR spectrum of the lubricant circulating through the IR cell, was within 90-110% of the target level.

4.4 Results and Discussion

General Spectroscopy - HEAR Oil

A major limitation of vegetable oil-based lubricants is their relatively poor oxidative stability in comparison to that of mineral-based lubricants. Thus, the development of formulations with enhanced stability, through the use of appropriate additives, may allow the range of application of vegetable oil-based lubricants to be extended significantly. In the development and testing of such formulations, the ability to continuously monitor their oxidative stability by FTIR spectroscopy would be highly beneficial.

Established IR methods for the measurement of oxidation products in mineral oils are not directly applicable to vegetable oils, as their oxidative degradation occurs by entirely different chemical pathways. The oxidation products of vegetable oils usually include hydroperoxides, alcohols, and aldehydes. Moisture, hydrocarbons, free fatty acids

and esters, lactones, furans and other minor products may also be produced (van de Voort, et al., 1994b). The infrared spectrum of HEAR oil is shown in Figure 16a, and the spectrum of the same oil having undergone forced oxidation for 48 hours is presented in Figure 16b. In this spectrum, however, it is difficult to detect the oxidation products by simple inspection. Upon ratioing this spectrum against that of the clean HEAR oil, the spectral features of oxidation products become distinguishable as illustrated in Figure 16c. In this spectrum, the absorption bands between 3800 cm^{-1} and 3100 cm^{-1} are due to the OH stretching vibrations of hydroperoxides, water and alcohols (van de Voort, et al., 1994b). The peaks at 1726 cm^{-1} and 1640 cm^{-1} are associated with the formation of aldehydes as the oxidation proceeds, while the peaks in the region between 1000 and 900 cm^{-1} are due to the C=C-H bending vibrations of *trans* double bonds, which are present in both hydroperoxides and aldehydes formed in the oxidative process (van de Voort, et al., 1994b). By monitoring the differential spectrum over time, it is possible to dynamically follow the spectral changes associated with the process of oxidation.

HEAR oil spiked with 1% (by weight) BHA exhibits a spectrum similar to that shown in Figure 16a, and the spectral features of the antioxidant are difficult to discern. However, the differential spectrum (Figure 16d) obtained by ratioing the spectrum of the BHA-spiked oil against that of the unspiked oil shows a strong and sharp band at 1506 cm^{-1} which is due to a ring vibration of the aromatic functional group of BHA. The strength and uniqueness of this band provides a sensitive means for the quantitation of this antioxidant in HEAR oil. Similarly, TBHQ can be readily quantitated in HEAR oil by measurement of its absorption band at 1506 cm^{-1}. The band at 3480 cm^{-1} in Figure 16d is due to the OH stretching vibration of BHA, but the use of the intensity of this band as a measure of antioxidant concentration in HEAR oil is problematic because OH-containing species formed during the course of oxidation of HEAR oil, such as hydroperoxides, alcohol, and water, will also exhibit bands in this region (see Fig. 16c) that interfere with the quantitation of the antioxidant.

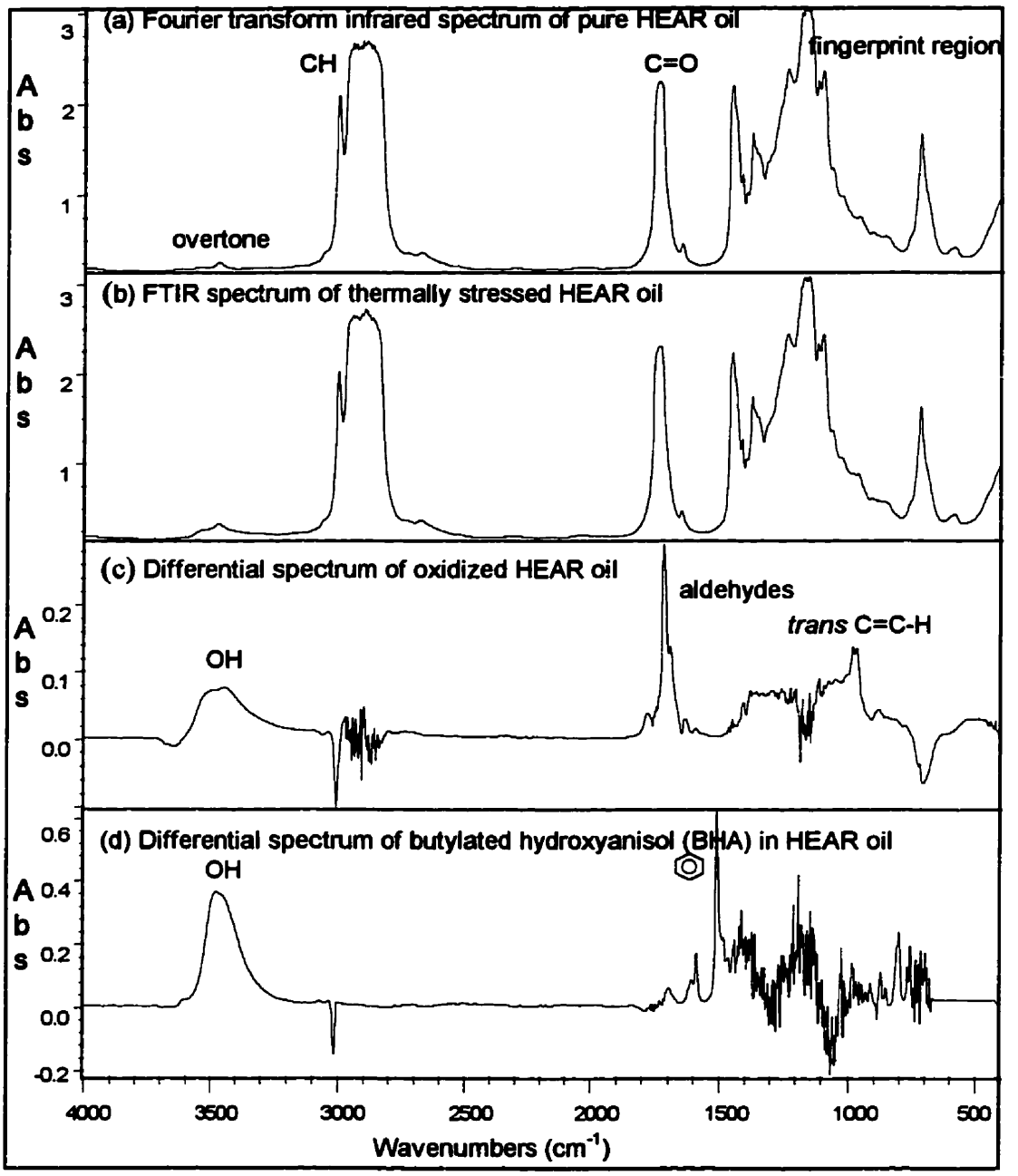


Figure 16. (a) Fourier transform infrared spectrum of pure HEAR oil; (b) pure HEAR oil heated at 100°C with dry air bubbled through @ ~3ml/min for 48 hours; (c) the differential spectrum obtained by ratioing b against a; and (d) differential spectrum obtained by ratioing the HEAR oil spiked with 1% (w.t.) BHA against that of the pure HEAR oil

Real-Time Monitoring Plot of TBHQ in HEAR Oil

The unique feature of the COAT system is its ability to carry out real-time monitoring of lubricant composition, providing rapid and continuous information on lubricant quality and additive performance. By using the FTIR ratio method, the COAT system was programmed to monitor the appearance of oxidation products and the depletion of antioxidant in the lubricating oil as a function of time as oxidation proceeds. Figure 17 is an overlaid time plot illustrating changes in the intensity of the 1506-cm^{-1} band in the spectrum of HEAR oil spiked with 0.5% (by weight) TBHQ as a function of time during heating at 100°C with dry air bubbled through the oil @ ~3 ml/min. Spectra were recorded at 3-hour intervals and ratioed against that of the unspiked HEAR oil. To obtain a graphical representation of the relative changes in the antioxidant level during the course of oxidation, the COAT system was programmed to measure the peak height of the band at 1506 cm^{-1} in each spectrum using the dual-wavelength peak height method (baseline point set at 1493 cm^{-1}), and the values were subsequently normalized with respect to the maximum absorbance value at that wavelength (A_v/A_v^{max}) and plotted against time to produce a real-time plot that represents the depletion of antioxidant during the course of oxidation as illustrated in Figure 18. From this plot, it is simple to monitor the depletion of the antioxidant as a function of time. Under the thermal/oxidation conditions employed in this study, the concentration of TBHQ decreased linearly and 70% of the antioxidant was consumed within 60 hours of forced oxidation.

Automatic Additive Replenishment by COAT System

For the assessment of the performance of the COAT system in the additive replenishment mode, mineral oil was chosen as a more conventional system for study. An FTIR calibration was developed for the prediction of the level of additive C-125 in mineral oil by adding various known amounts of this additive to mineral oil and measuring the intensity of its characteristic infrared absorption band at 3650 cm^{-1} using the dual-wavelength peak height method (baseline point set at 3760 cm^{-1}). The calibration equation derived was incorporated into the COAT system software, allowing the spectral data

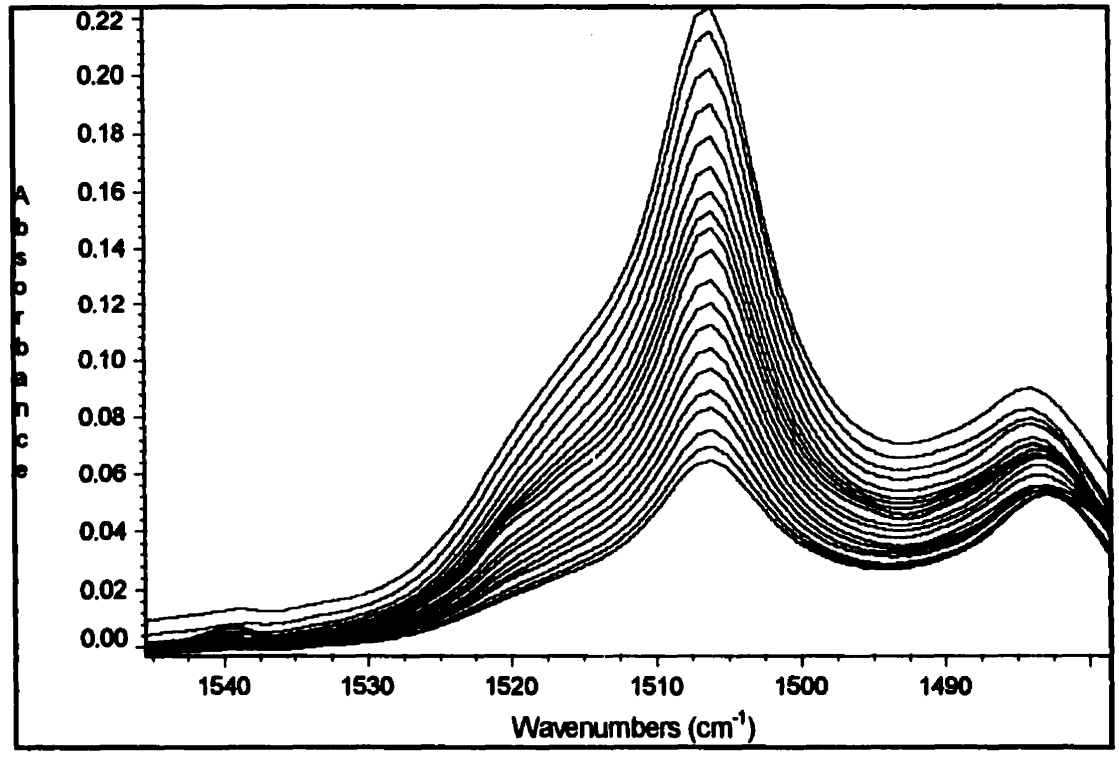


Figure 17. Spectral overlay plot illustrating changes at 1508 cm^{-1} of 0.5% (w.t) TBHQ spiked in HEAR oil heated at 100°C and bubbled with dry air @ ~ 3ml/min as a function of time. The overlaid spectra were collected at 3 hour intervals and have been ratioed against the spectrum of the clean HEAR oil.

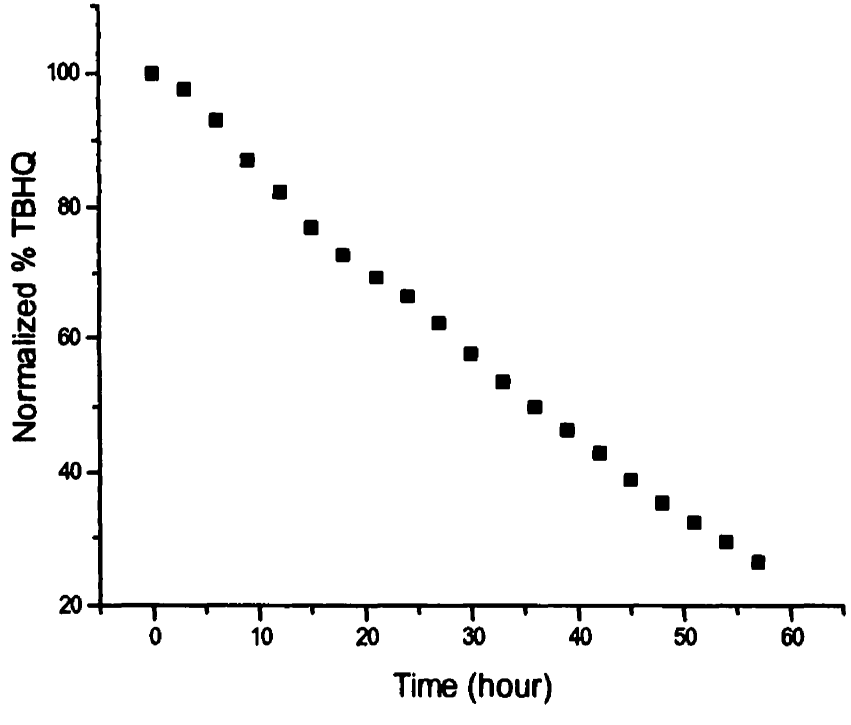


Figure 18. Real-time depletion plot of 0.5% (w.t.) TBHQ spiked in HEAR oil heated at 100°C with dry air bubbled through @ ~ 3 ml/min.

obtained during real-time monitoring of mineral oil containing C-125 (0.5% by weight) under thermal/oxidation conditions to be used to predict additive concentration directly.

A typical real-time plot of additive concentration from a run in the additive replenishment mode is presented in Figure 19, illustrating that the COAT system responded appropriately to the depletion of C-125 over time and maintained the additive level within the specified limits. Furthermore, analysis of the FTIR spectral data collected during this test showed no evidence of oxidation of the base oil, validating the hypothesis that automatic additive replenishment is effective in extending the lifetime of the oil. This was confirmed by total acid number and viscosity measurements on these samples. It was also noted that although there was some discoloration of the oil due to the breakdown of the antioxidant, this had no influence on the stability of the oil.

4.5 Conclusion

A prototype COAT system has been developed to perform the monitoring and treatment of lubricating oils in real time. By providing dynamic information on oil degradation and additive depletion over time and automatically replenishing additives as required, the COAT system affords a means of enhancing lubricant stability, which in turn can substantially reduce overall costs by reducing downtime and extending drain intervals of lubricating fluids. The resulting reduction in lubricant consumption and hence disposal of waste oil is also beneficial from an environmental perspective; in addition, the COAT system itself is environmentally friendly as no solvents or reagents are required. As such, the COAT system can play an important role in monitoring of machinery operated in environmentally sensitive areas such as forests, agricultural areas, and near waterways, where consumption and disposal of oil are of particular concern.

4.6 Acknowledgments

This chapter is based on the manuscript entitled "A Continuous Oil Analysis and Treatment (COAT) System for the Monitoring of Oil Quality and Performance of Additives" which has been submitted for publication. The contribution of co-authors to

this manuscript, namely, van de Voort, F.R., Ismail, A.A. and Pinchuck D. is gratefully acknowledged.

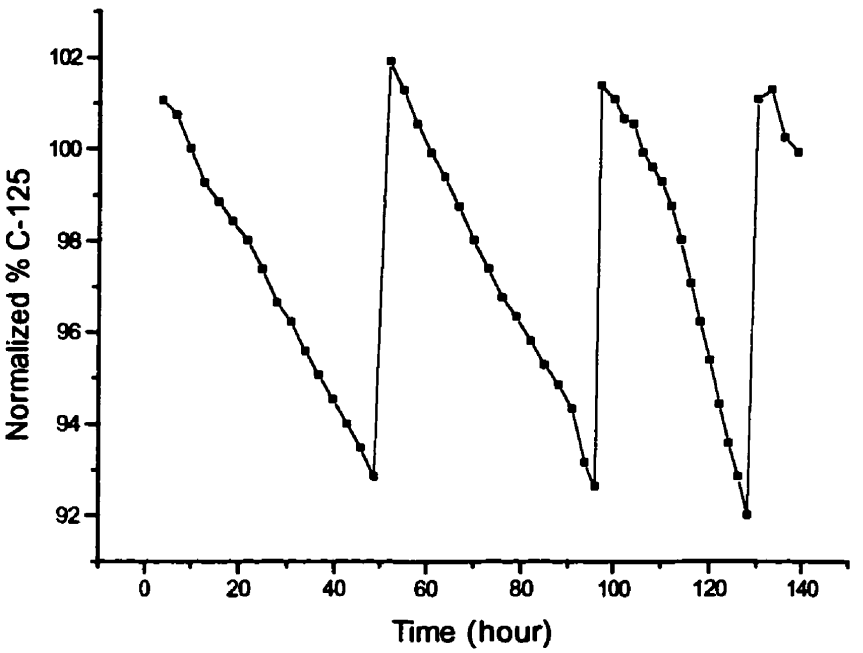


Figure 19. Real-time replenishment plot of C-125 added in mineral base oil heated at 100°C with dry air bubbled through @ ~3 ml/min.

5

GENERAL DISCUSSION AND CONCLUSION

Although infrared spectroscopy has been an analytical important tool in the edible and lubricating oils sectors, the advent of FTIR spectroscopy has opened up a wide range of new possibilities, specifically in the areas of monitoring oil quality and quantitative analyses for specific components. As part of the mandate of the McGill IR Group, which focuses on the application and development of FTIR methods, this work involved two distinct aspects, the development of a FT-NIR method for the determination of PV of vegetable oil based lubricants as well as the assessment of the newly developed COAT system for the continuous monitoring of antioxidant levels in vegetable oil lubricants. The unifying theme of this research is the determination of oil quality through the use of FTIR spectroscopy in general, the work involving the use of two distinct FTIR instrumental techniques (mid and NIR). Both concepts are novel and serve to demonstrate the power of FTIR spectroscopy as a rapid analysis tool in this case applied to biodegradable lubricants.

Peroxide Value (PV) Determination

In the first phase of this work, consideration was given to the development of a FT-NIR method for the analysis of PV in biodegradable oils. The formation of hydroperoxides in triglyceride based oils are the first signs of oxidative deterioration and are highly correlated with a reduction in their overall performance characteristics. The AOCS standard chemical method for PV determination, based on the stoichiometric conversion of KI to I_2, is both tedious and time consuming as well as environmentally unfriendly, however, to date no effective methods have been developed which challenge its analytical predominance. The stoichiometric conversion of TPP to TPPO by hydroperoxides is another well characterized reaction, which has commonly been used for the structural analysis of hydroperoxides (Graff, et al., 1979) and has more recently used

by Nakamura and Maeda (1991) for the development of a sensitive method (1PV in 10 mg lipid) for the determination of PV in biological samples. Although the use of this stoichiometric reaction is not novel per se, linking it with FTIR spectroscopy as a means of determining PV is. Although not discussed in this thesis, the fundamental aspects associated with the development of a mid-IR TPP/TPPO were carried out in conjunction with Ma et al. (1996). This method works very well, however, the mid-IR has a variety of limitations, specifically the lack of ruggedness of the instrumentation for use in an industrial setting as well as restrictions in sample handling. The mid-IR method developed is restricted to the use of water susceptible KCl cell window materials as well as being limited to cell pathlengths of <100 μm. In contrast, FT-NIR, as exemplified by the instrument supplied by Bomem, is NIMA certified and was equipped with a simple, disposable glass vial sample handling accessory. This feature was considered important for convenient at-site sampling and analysis, obviating the substantially more complex and expensive mid-IR sample handling accessory.

In order to develop and implement a FT-NIR method for biodegradable lubricants, a number of modifications were required. The key difference was the chemometric approach required, as in the mid-IR, TPPO has a single unique absorption band at 540 cm^{-1}, distinct from TPP. This allows one to calibrate directly on TPPO using a simple Beer's law approach, while in the NIR, such a unique band does not exist and TPP and TPPO phenyl absorptions overlap spectrally. As a result, the calibration approach in the NIR required the use of advanced chemometrics (PLS) to allow the TPPO formed by the reaction with hydroperoxides to be quantitated in the presence of the TPP. In developing a FT-NIR approach to PV determination, selection of solvent able to provide optimum miscibility for both TPP and TPPO was crucial since a good carrier not only eliminates various errors introduced by the addition of organic solvents that might be highly evaporative, but also can effectively disperse TPP in oil, thus shorten reaction time. In the fundamental study of TPP/TPPO reaction by mid-IR (Ma, et al., 1996), hexanol was selected as a convenient carrier in which TPP and TPPO could be dissolved at concentration adequate for the determination of PV values up to 15. However, for this

work, which requires the analysis of PV values >100, the use of hexanol as carrier is somewhat problematic because the concentrations required were much greater and one had to resort to keeping the solution warm to obtain adequate concentrations for delivery, which was not practical. In addition, it was found that hexanol interfered with the alcohol bands produced from TPP/hydroperoxides reaction. To address these problems, among a variety of solvents, chloroform was determined to be an ideal carrier, effectively solubilizing both TPP and TPPO, allowing the concentrations of TPP and TPPO chloroform solution to be as high as 50% (w/w) at room temperature. In this study, a level of 40% (w/w) for both stock solutions was chosen, offering sufficient reactant reservoir and good solution stability. With chloroform as a carrier, TPP can be uniformly dispersed in the oil and rapidly reacts with hydroperoxides. Time course studies by Nakamura and Maeda (1991) indicated that under the conditions they specified, 95% of the methyl 13-hydroperoxides were reacted with TPP within 5 minutes, using our procedure, the reaction was 99% complete within 2 minutes, providing for rapid and consistent analytical turnaround.

The main benefit of the FT-NIR approach to PV determinations is that the methodology can be automated if the instrument is programmed, delivering a simple numerical result. Beyond obtaining a single PV value, the method has been developed with the active oxygen method (AOM) in mind, covering a wide range of PV values and can be used to track the stability of an oil under various oxidative stress conditions. Because the method is stoichiometrically based, like the AOCS method, the FT-NIR approach can also be considered as primary method as opposed to a secondary method. Theoretically, AOCS standard PV method is applicable to PV measurement ranging from ~0.2-150. From a practical standpoint, however, the lower limit of sensitivity is ~1PV as the endpoint of the reaction indicated by the starch becomes difficult to judge accurately when below this level and analysis of a wide range is difficult unless one has some ideas of the PV value to allow an appropriate concentration of thiosulphate to be used. This aspect is not of concern in the IR method and if calibrated over a smaller range, the calibration devised would likely outperform AOCS iodometric method in terms of reproducibility,

particularly at low PV values (< 1). This in addition to the analysis of gross PV changes, it is likely that this method would serve well in quality control analysis of edible oils, where a PV range of 0-15 is commonly encountered. As the NIR method is traced back to a gravimetric base and involves a straightforward, rapid, reproducible stoichiometric reaction it has many of the hallmarks of a well founded analytical method. Considering the speed of analysis, cost of labor, disposal of reagents, and a number of variables and manipulation errors associated with the iodometric method, a robust FT-NIR TPP/TPPO method would appear to be an excellent candidate to replace the traditional AOCS PV method. In its present state, the FT-NIR method consists of computer program for automated spectral data collection, processing, and data interpretation and the analytical procedure consist of manually pipeting a TPP/$CHCl_3$ mixture into the oil, mixing, scanning, and reading the PV value obtained from PLS prediction. Further developments can be envisioned to fully automatize the analysis. One which was tested was to prepare a column loaded with TPP and allowing the oil to flow through it to the spectrometer via the column. In this design, the solubilization of TPP in the oil (albeit minimal) leads to excessive consumption of TPP, which is a major drawback associated with this design. It may be possible overcome by using appropriate stationary materials to bind TPP that reduces its solubility in the oil. A preferred alternatives is to make use of a TPP stock solution reservoir, a reaction compartment maintained at elevated temperature and through the use of dosing pumps the TPP stock solution is delivered into the reaction compartment to meet oil diverted from sample source, mixed and subsequently diverted to FTIR spectrometer for scanning and data processing. These elements are beyond the scope of this work and can be considered as potential future developments.

Antioxidant Monitoring

The second part of this work involved the assessment of a prototype continuous oil analysis system. The COAT system was developed as a generalized multifunctional mid-FTIR analysis system which could be used for monitoring oil quality on a continuous, on-site or at-site basis. Although not available for this study, the original design instrumentation has now evolved into a mobile unit and the spectrometer mounted on the

system is a combined mid/NIR Bomem FTIR spectrometer. The prototype was the forerunner of this system and designed for monitoring stationary systems such as bulk lubricant reservoirs, while the new system is designed for analyzing multiple units in various locations. The purpose of the prototype system was to determine if the system could be used to monitor critical oil parameters and control replenishment of antioxidants or additives to increase oil life and reduce waste and disposal. Although there were many potential additives and/or parameters which could be monitored, monitoring antioxidant levels in HEAR oil undergoing thermal stress was chosen in line with a research program being undertaken by the McGill IR group on biodegradable lubricants, which are very susceptible to autoxidation. In addition and for comparison, mineral oil was also tested. At the time this work was being carried out, only the mid-FTIR configuration was available and basic spectroscopic work was carried out to determine the fundamental wavelengths at which the two antioxidants used could be quantitated and the appropriate calibrations developed. In this case, the monitoring was carried out using differential spectra, which allow one to monitor only the changes taking place with time. A substantial amount of effort went into the programming of the system so that the instrument would automatically allow the pumps to deliver the appropriate amount of antioxidant when it was replenishing. As such, most of the work has focused on the spectroscopic aspects, however, much of the additional work associated with making the programming is outside the scope of this thesis. The prototype COAT system demonstrated the ability to monitoring and treat both triglyceride and mineral oil lubricants in real time, providing a convenient and efficient means by which oils can be extended. As noted earlier, the basic design of this unit is more suited for bulk oil analysis, a typical example being paper making machine lubricants used in newsprint manufacture. In this situation, a typical tank holds 30,000 litters of specialty oil for machinery worth several millions of dollars. When an oil change is required, the down time is worth about $20,000/h and its disposal problematic. This is an extreme, but real example where the combination of monitoring and extending the life of an oil becomes financially worthwhile. One does not have to go to such extremes, another example is the oil changes required by city bus fleets. Montreal uses about one million litters of oils per year, which if extended

by routing monitoring (using a mobile unit), would pay the city back in less than one year in disposal and new oil savings. This preliminary antioxidant monitoring and replenishment study has served to prove that the basic concept of an FTIR monitoring system works effectively. The results have led to the development of a portable unit which is being considered for quality control use by a major Asian lubricant formulator. The concept is not restricted to mid-FTIR and in terms of future work can also be developed for FT-NIR where appropriate. Further development of the COAT system for a variety of other applications, including the capability to dynamically detect contaminants such as water and glycol infiltration in lubricant systems from external sources are examples of other applications. Depending on the degree of sophistication desired, one can automatically divert flow from an operating unit to auxiliary devices for further processing, such as filtering, drying, centrifuging, retention, disposal, etc. Once again these concepts are beyond the scope of this thesis, but provide an inference that this technology has many applications in both biodegradable and mineral oil lubricants.

In summary, this work has focused more on basic spectroscopy, especially in the development of a new FT-NIR PV method in the first instance, the second phase of the work directed more towards exploring the on- and at-line potential of FTIR spectroscopy. Both are interrelated, as it is the basic spectroscopic work which underpins the applications and subsequent automation. There is ample evidence that FTIR spectroscopy in general can meet a wide range of analytical needs in the lubricant sector, both for biodegradable oils as well as traditional mineral based oils. This research, undertaken under the umbrella of the McGill IR group, has provided me with an opportunity to make a small contribution towards illustrating that FTIR spectroscopy can be used as a practical and useful quality control and monitoring tool in the lubrication sector and possibly contribute to the development of biodegradable lubricants and a reduction of mineral oil disposal.

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